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Proftest SYKE

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

Helsinki 2020
Finnish Environment Institute

REPORTS OF THE FINNISH ENVIRONMENT INSTITUTE 18 | 2020
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 978-952-11-5165-1 (pbk.)
ISBN 978-952-11-5166-8 (PDF)
ISSN 1796-1718 (print)
ISSN 1796-1726 (Online)

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Publisher and financier of publication: Finnish Environment Institute (SYKE)
Latokartanonkaari 11, FI-00790 Helsinki, Finland, Phone +358 295 251 000, syke.fi.

Year of issue: 2020

SYKE

ABSTRACT

Interlaboratory Proficiency Test 02/2020

Proftest SYKE carried out proficiency test (PT) for analysis of alkalinity, conductivity, nutrients and pH in natural waters in February 2020. In total, there were 31 participants in the PT.

Either the calculated concentration or the robust mean or the median of the reported results was used as the assigned value for the measurands. The overall performance of the participants was evaluated by using z scores. In this proficiency test 89 % of the results evaluated with z scores were satisfactory when total deviation of 0.2 pH units for pH values and 5–25 % for the other determinations was accepted from the assigned value.

Warm thanks to all the participants in this proficiency test!

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

TIIVISTELMÄ

Laboratorioiden välinen pätevyyskoe 02/2020

Proftest SYKE järjesti helmikuussa 2020 pätevyyskokeen luonnonvesiä analysoiville laboratorioille. Pätevyyskokeessa määritettiin alkaliniteetti, pH, ravinteet ja sähkönjohtavuus. Pätevyyskokeessa oli yhteensä 31 osallistujaa.

Testisuureen vertailuarvona käytettiin laskennallista pitoisuutta tai osallistujatulosten robustia keskiarvoa tai niiden mediaania. Osallistujien pätevyyden arviointi tehtiin z-arvojen perusteella. Koko tulosaineistossa oli z-arvoilla arvioituna 89 % hyväksyttäviä tuloksia, kun vertailuarvosta sallittiin pH-määrityksissä 0,2 pH-yksikön ja muissa määrityksissä 5-25 %:n poikkeama.

Kiitos pätevyyskokeen osallistujille!

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

SAMMANDRAG

Provningsjämförelse 02/2020

Under februari 2020 genomförde Proftest SYKE en provningsjämförelse, som omfattade bestämningen av alkalinitet, näringsämnen, pH och ledningsförmåga i naturvatten. Denna jämförelse hade totalt 31 deltagarna.

Som referensvärde av analytens koncentration användes det teoretiska värdet eller robust medelvärdet eller medianen av deltagarnas resultat. Resultaten värderades med hjälp av z-värden. I denna jämförelse 89 % av resultaten var tillfredsställande. Resultatet var tillfredsställande, om det deviera mindre än 0,2 pH enhet eller 5–25 % från referensvärdet.

Ett varmt tack till alla deltagarna i testet!

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

CONTENTS

1 Introduction

Proftest SYKE carried out proficiency test (PT) for analysis of alkalinity, conductivity, nutrients (N_{NH4}, $N_{NO2+NO3}$, N_{tot}, P_{PO4}, $P_{PO4,\ dissolved}$, P_{tot}, $P_{tot,\ dissolved}$) and pH in natural waters in February 2020 (NW 02/2020). In the PT the results of laboratories providing measurements of the swimming pool waters were evaluated.

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 standard ISO/IEC 17043 [1] and applying ISO 13528 [2] and IUPAC Technical report [3]. Proftest SYKE is accredited by the Finnish Accreditation Service as a proficiency testing provider (PT01, ISO/IEC 17043, www.finas.fi/sites/en). The organizing of this proficiency test is included in the accreditation scope of Proftest SYKE.

2 Organizing the proficiency test

2.1 Responsibilities

Organizer
Proftest SYKE, Finnish Environment Institute (SYKE), Laboratory Centre
Mustialankatu 3, FI-00790 Helsinki, Finland
Phone: +358 295 251 000, Email: proftest@environment.fi

The responsibilities in organizing the proficiency test

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

Analytical expert Mika Sarkkinen (SYKE)

2.2 Participants

In total 31 laboratories participated in this proficiency test (Appendix 1), 25 from Finland and 6 from abroad. 81 % of the participants reported that they have accredited quality management system based on ISO/IEC 17025 and 6 % have quality management system according to ISO 9000 series. Altogether 84 % 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 26 (SYKE, Oulu) in the result tables.

2.3 Samples and delivery

Three types of samples were delivered to the participants: synthetic samples and brackish as well as lake water samples for analysis of alkalinity, conductivity, N_{NH4}, $N_{NO2+NO3}$, N_{tot}, P_{PO4}, $P_{PO4,\ dissolved}$, P_{tot}, $P_{tot,\ dissolved}$, 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 Prolabo. The synthetic samples A1A, A1N and A1P for alkalinity, ammonium nitrogen (N_{NH4}), sum of nitrate and 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. Lake water sample was collected from Lake Bodom, Espoo. The sample preparation is described in detail in the Appendix 2.

The samples were delivered on 10 February 2020 to the participants abroad and on 11 February 2020 to the national participants. The samples arrived to the participants mainly on 12 February 2020. One participant (5) received the samples on 13 February 2020.

The samples were requested to be measured as follows:

alkalinity	13 February 2020
pH, conductivity	13 February 2020
N_{NH4}, $N_{NO2+NO3}$, P_{PO4}, $P_{PO4,\ dissolved}$	13 February 2020
N_{tot}, P_{tot}, $P_{tot,\ dissolved}$	latest on 24 February 2020

The results were requested to be reported latest on 27 February 2020 and the participants delivered the results mainly accordingly. One participant delivered the results on 28 February 2020. The preliminary results were delivered to the participants via ProftestWEB and email on 6 March 2020.

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 analysing 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 results, the concentration of N_{NH4} in sample could have decreased in sample N3N, if the temperature increased to 20 °C during sample transport and storage. Based on the reported temperatures of the control sample, they were mainly < 13 °C, one participant reported slightly higher arrival temperature (13.6 °C). Further, within the reported results there was no indication of temperature related decreased concentrations for the sample N3N. Thus, the sample was regarded stable under the sample distribution conditions. According to the test, other samples were considered stable.

2.5 Feedback from the proficiency test

The feedback from the proficiency test is shown in Appendix 5. The comments from the participants mainly dealt with the delivery problems. The comment from the provider focused on e.g. the missing sample arrival documents and replicate results. All the feedback from the proficiency test is valuable and is exploited when improving the activities.

2.6 Processing the data

2.6.1 Pretesting the data

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

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

More information about the statistical handling of the data is available from the Guide for participant [5].

2.6.2 Assigned values

The NIST traceable calculated values were used as the assigned values for the synthetic samples of alkalinity, N_{tot}, P_{PO4}, and P_{tot}. For the other samples and measurands the robust mean or the median (N3A: Alkalinity) of the results reported by the participants was used as the assigned value. Detailed information of the assigned values, their expanded uncertainties and reliability are shown in Appendix 6.

The assigned values based on the robust mean or the 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 values was statistically tested [2, 3].

For the calculated assigned values, the expanded uncertainty (k=2) was estimated by using standard uncertainties associated with individual operations involved in the preparation of the sample. The main sources of the uncertainty were the purity of the stock compounds and the calibration of the flasks. When the robust mean or the median was used as the assigned value, the uncertainty was calculated using the robust standard deviation or the standard deviation [2, 5].

The uncertainty of the calculated assigned values was ≤ 1.3 % (at the 95 % confidence level). 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 8.9 % (Appendix 6). **After reporting the preliminary results no changes have been done for the assigned values.**

2.6.3 Proficiency assessment procedure

The standard deviation for proficiency assessment was estimated based on the measurand concentration, the results of homogeneity and stability tests, the uncertainty of the assigned value, and the long-term variation in the former proficiency tests. The standard deviation for proficiency assessment (2 × s_{pt} at the 95 % confidence level) was set for pH measurements to 0.2 pH units and for the other measurements from 5 % to 25 % depending on the measurands. **After reporting the preliminary results no changes have been done for the standard deviations of the proficiency assessment values.**

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

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

In the following case, the criterion for the reliability of the assigned value was not met and, therefore, the evaluation of the performance is weakened in this proficiency test:

Sample	Measurement
B2N	N_{NH4}

3 Results and conclusions

3.1 Results

The summary of the results is presented in Table 1. The terms in the results tables are explained in the Appendix 7. The results and the performance of each participant are presented in Appendix 8 and the reported results with their expanded uncertainties (k=2) 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 0.9 to 14.6 % (Table 1). The robust standard deviation was lower than 5 % for half of the results and lower than 10 % for 89 % of the results (Table 1). The robust standard deviations were approximately in the same range as in the previous similar proficiency test NW 03/2018, where the deviations varied from 0.6 % to 17.6 % [5].

Table 1. The summary of the results in the proficiency test NW 02/2020.

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	0.16	0.16	0.17	0.16	0.02	10.5	7.5	21	67
	B2A	mmol/l	1.39	1.38	1.39	1.39	0.05	3.3	7.5	20	95
	N3A	mmol/l	0.49	0.49	0.49	0.49	0.02	4.0	7.5	21	86
Conductivity 25	A1J	mS/m	9.95	9.94	9.95	9.93	0.16	1.6	5	24	92
	B2H	mS/m	873	872	873	871	11	1.3	5	22	100
	N3H	mS/m	13.0	13.0	13.0	13.0	0.2	1.8	5	25	88
N_{NH4}	A1N	µg/l	20.6	20.7	20.6	20.7	1.7	8.4	20	22	79
	B2N	µg/l	32.8	32.9	32.8	31.4	4.8	14.6	25	20	84
	N3N	µg/l	202	202	202	201	13	6.6	20	21	95
$N_{NO2+NO3}$	A1N	µg/l	185	185	185	186	6	3.2	8	19	82
	B2N	µg/l	161	160	161	160	14	8.4	15	20	89
	N3N	µg/l	164	163	164	164	11	6.6	15	18	100
N_{tot}	A1N	µg/l	249	257	258	260	16	6.4	15	21	89
	B2N	µg/l	440	440	440	438	33	7.4	20	20	89
	N3N	µg/l	751	747	751	749	27	3.6	15	21	89
pH	A1H		7.27	7.27	7.27	7.28	0.06	0.9	2.7	26	100
	B2H		7.84	7.84	7.84	7.86	0.10	1.2	2.6	25	100
	N3H		7.34	7.33	7.34	7.34	0.08	1.1	2.7	26	96
P_{PO4}	A1P	µg/l	9.95	9.83	10.38	9.90	1.38	13.3	10	21	68
	B2P	µg/l	27.5	27.5	27.5	27.4	1.0	3.8	15	19	89
	N3P	µg/l	27.3	27.3	27.3	27.0	1.2	4.5	10	19	94
$P_{PO4, dissolved}$	B4P	µg/l	27.5	27.4	27.5	27.6	1.5	5.5	15	18	94
	N5P	µg/l	26.2	26.3	26.2	26.2	1.1	4.0	10	17	87
P_{tot}	A1P	µg/l	19.8	19.5	19.6	19.4	1.1	5.8	15	22	89
	B2P	µg/l	33.6	33.1	33.6	33.3	2.5	7.4	15	21	84
	N3P	µg/l	44.0	43.8	44.0	43.5	2.4	5.4	15	21	95
$P_{tot, dissolved}$	B4P	µg/l	30.9	30.9	30.9	30.9	1.6	5.1	15	18	88
	N5P	µg/l	33.1	33.1	33.1	33.1	1.4	4.3	15	17	80

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

In this PT the participants were requested to report replicate results for nutrient measurements. The results of the replicate measurements based on the ANOVA statistical handling are presented in Table 2. The estimation of the robustness of the methods could be done by the ratio s_b/s_w, which should not exceed 3 for robust methods. The robustness criterion was fulfilled for 37 % of the tested measurements (Table 2).

Table 2. The summary of repeatability based on replicate measurements (ANOVA statistics).

Measurand	Sample	Unit	Assigned value	Mean	s_w	s_b	s_t	s_w%	s_b%	s_t%	s_b/s_w
N_{NH4}	A1N	µg/l	20.6	20.7	0.534	1.84	1.91	2.6	8.9	9.3	3.4
	B2N	µg/l	32.8	32.9	0.735	4.31	4.37	2.2	13	13	5.9
	N3N	µg/l	202	202	4.38	12.6	13.4	2.2	6.2	6.6	2.9
$N_{NO2+NO3}$	A1N	µg/l	185	185	1.86	6.50	6.77	1.0	3.5	3.7	3.5
	B2N	µg/l	161	160	1.52	13.3	13.4	0.95	8.3	8.4	8.7
	N3N	µg/l	164	163	1.18	10.6	10.7	0.72	6.5	6.5	9.0
N_{tot}	A1N	µg/l	249	257	3.56	17.8	18.2	1.4	6.9	7.1	5.0
	B2N	µg/l	440	440	5.41	36.7	37.1	1.2	8.3	8.4	6.8
	N3N	µg/l	751	747	5.68	33.0	33.5	0.75	4.4	4.4	5.8
P_{PO4}	A1P	µg/l	9.95	9.83	0.316	1.72	1.75	3.0	16	16	5.4
	B2P	µg/l	27.5	27.5	0.293	0.994	1.04	1.1	3.6	3.8	3.4
	N3P	µg/l	27.3	27.3	0.480	1.11	1.21	1.8	4.1	4.4	2.3
$P_{PO4, dissolved}$	B4P	µg/l	27.5	27.4	0.283	1.56	1.59	1.0	5.7	5.8	5.5
	N5P	µg/l	26.2	26.3	0.380	1.09	1.16	1.4	4.2	4.4	2.9
P_{tot}	A1P	µg/l	19.8	19.5	0.651	1.57	1.70	3.3	8.0	8.6	2.4
	B2P	µg/l	33.6	33.1	0.909	2.57	2.72	2.7	7.6	8.1	2.8
	N3P	µg/l	44.0	43.8	0.574	2.76	2.82	1.3	6.2	6.4	4.8
$P_{tot, dissolved}$	B4P	µg/l	30.9	30.9	0.696	1.35	1.52	2.3	4.4	4.9	1.9
	N5P	µg/l	33.1	33.1	0.652	1.17	1.34	2.0	3.5	4.0	1.8

Ass.val.: assigned value; s_w**:** repeatability standard error; s_b**:** between participants standard error; s_t: reproducibility standard error.

3.2 Analytical methods

The participants could use different analytical methods for the measurements in the PT. The reported results grouped by used analytical methods are shown in Appendix 12. The statistical comparison of the analytical methods was possible for the data where the number of the results was ≥ 5.

Alkalinity

Total alkalinity was measured using titration with two or more end points by 11-13 participants, depending on the sample type. Only from four to six participants reported alkalinity results based on one end point titration (ISO 9963-1 or SFS 3005) depending on the sample type (Appendix 12). Five participants reported the use of other methods. These were e.g. ISO 9963-2 as well as Gran alkalinity method with multiple point titration in pH range 3.6.-3.0. There were no statistically 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 five participants from six gained z score above 2 for the synthetic sample A1A (Appendix 12).

Conductivity
Conductivity was measured by all participants according to the standard method EN 27888 (Appendix 12).

Ammonium nitrogen N_{NH4}
Most participants (7-10, depending on the sample) determined ammonium nitrogen using the automatic standard method EN ISO 11732 and 2-3 participants used the corresponding manual method SFS 3032. Depending on the sample, one or two participants used the spectrophotometric salicylate method modified for Aquachem technique and 6-7 participants used some other method, for example fluorometric method (CFA) or tube method (Appendix 12). No statistically significant differences were observed between the used methods.

Sum of nitrate and nitrite nitrogen $N_{NO2+NO3}$
Participants determined sum of nitrate and nitrite nitrogen mostly using the standard method EN ISO 13395 (13 participants). Both the standard method EN ISO 10304 and the sulfanilamide spectrophotometric method after hydrazine reduction modified for Aquachem technique were used by 1 participant (Appendix 12). Other methods were used by 3 participants, for example IC method. No statistically significant differences were observed between the used methods.

Total nitrogen N_{tot}
Most participants (10-11) determined total nitrogen according to the standard method EN ISO 11905. One participant used tube method while 7 participants used some other method, for example based on standards ISO 29441 or EN 12260 (Appendix 12). No statistically significant differences were observed between the used methods.

pH
Half of the participants (11-12, depending on the sample) measured pH using universal electrode and half (13-14, depending on the sample) used an electrode for low ionic waters. A specific other electrode was used by one participant (Appendix 12). No statistically significant differences were observed between the used methods.

Phosphate phosphorus P_{PO4}
Phosphate phosphorus was determined using the standard method EN ISO 15681 (Automatic (CFA, FIA) ammonium molybdate method) by 7-8 participants. The withdrawn Finnish standard method 3025 was used by 3-4 participants. The ammonium molybdate spectrophotometric method modified for Aquachem technique was used by 1-2 the participants and 5-6 participants used the standard method EN ISO 6878 (manual spectrophotometric method, Appendix 12). No statistically significant differences were observed between the used methods.

Total phosphorus P_{tot}
Total phosphorus was measured using the automatic ammonium molybdate method (EN ISO 15681) by nine participants and the manual ammonium molybdate method (EN ISO 6878) was used by 3-5 participants, depending on the sample). The withdrawn standard method SFS 3026 was used by 3-4 participants. Ammonium molybdate method modified for Aquachem technique was used by 1-2 participants depending on the sample and one participant used ICP-AES (Appendix 12). No statistically significant differences were observed between the used methods.

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

The used analytical methods for dissolved phosphorus compounds were almost the same than for the non-filtered samples (Appendix 12). Based on visual evaluation, EN ISO 6878 gave higher results for dissolved total phosphorus determination than the other used methods (Appendix 12).

3.3 Uncertainties of the results

Altogether 94 % of the participants reported the expanded uncertainties (k=2) with their results for at least some of their results (Table 3, Appendix 13). The range of the reported uncertainties varied between the measurands and the sample types.

Several approaches were used for estimating the measurement uncertainty (Appendix 13). The most used approach was based on using the internal quality control data in the estimation, also method validation data was used (Appendix 13). Up to eight participants used MUkit measurement uncertainty software for the estimation of their uncertainties [6]. The free software is available on the webpage: www.syke.fi/envical/en. Generally, the used approach for estimating measurement uncertainty did not make definite impact on the uncertainty estimates.

Table 3. The ranges of the reported expanded uncertainties by participants as percent (k=2, U_i%) and quality criterion for natural waters published by Finnish Environment Institute [7].

Sample type / Measurand	Synthetic sample, U_i%	Brackish water, U_i%	Lake water, U_i%	Recommendation, U% [7]
Alkalinity	5 – 25	2.1 – 20	5 – 25	20
Conductivity 25	1 – 8	1 – 11	2 – 11	5
N_{NH4}	10 – 35	10 – 22	6 – 22	15
$N_{NO2+NO3}$	6 – 22	6 – 22	6 – 17	15
N_{tot}	6 – 23	6 – 22	6 – 23	15
pH	0.12 – 5	0.04 – 5	0.2 – 5	0.2 pH units
P_{PO4}	10 – 29	10 – 22	10 – 22	15
$P_{PO4,\ dissolved}$	–	8 – 22	8 – 22	15
P_{tot}	11 – 35	8 – 35	8 – 35	15
$P_{tot,\ dissolved}$	–	8 – 35	8 – 35	15

In order to promote the enhancement of environmental measurements' quality standards and traceability, the national quality recommendations for the data entered into the water quality registers have been published in Finland [7]. The recommendations for measurement uncertainties for the tested measurands in natural waters vary from 5 % to 20 % (for pH measurement 0.2 pH units, see Table 3). In this proficiency test some of participants had their measurement uncertainties within these limits, while some did not achieve them. Within the optimal measuring range, the expanded measurement uncertainty (k=2) should typically be 20 – 40 %. Close to the limit of quantification the relative measurement uncertainty is higher. Further, the expanded uncertainties below 5% could commonly be considered unrealistic

uncertainty value for routine laboratories. Harmonization of the uncertainty estimation approaches should be continued.

4 Evaluation of the results

The performance evaluation of the participants was based on the z scores, which were calculated using the assigned values and the standard deviation for proficiency 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, 89 % of the results were satisfactory when total deviation of 0.2 pH units and for the other measurement 5–25 % from the assigned values were accepted. Altogether 84 % of participants used accredited analytical methods at least for a part of the measurands. The summary of the performance evaluation and comparison to the previous performance is presented in Table 4. In the previous similar PT, Proftest SYKE NW 03/2018, the performance was satisfactory for 85 % of the participant results when total deviation of 0.2 pH units (for pH) and 5–20 % (for the other measurands) was accepted [5]. Further, the measurands here were partly same than in PT Proftest SYKE NW 02/2019, and thus the performance is partly compared also against those results [8].

Table 4. Summary of the performance evaluation in the proficiency test NW 02/2020.

Measurand	2 x s_{pt}%	Satisfactory results, %	Remarks
Alkalinity	7.5	83	In the PT NW 03/18 92 % of the results were satisfactory [5].
Conductivity 25	5	93	Good performance. In the PTs NW 03/18 88 % and NW 02/19 79 % (here deviation of 5-8 % from the assigned value was accepted) of the results were satisfactory [5, 8].
N_{NH4}	20-25	86	The evaluation for the sample B2N in only approximate due to high variation of the results. In the PT NW 03/18 73 % of the results were satisfactory when deviation of 15-25 % from the assigned value was accepted [5]. In the PT NW 02/19 87 % of the results were satisfactory when deviation of 20 % from the assigned value was accepted [8].
$N_{NO2+NO3}$	8-15	90	Good performance. In the PTs NW 03/18 and NW 02/19 the performance was satisfactory for 84 % (here deviation of 10 % from the assigned value was accepted) and 88 % of the results, respectively [5, 8].
N_{tot}	15-20	89	In the PTs NW 03/18 and NW 02/19 the performance was satisfactory for 85 % of the results [5, 8]. In 2018 the deviation of 10-15 % from the assigned value was accepted.
pH	0.2 pH units	99	Excellent performance. In the PTs NW 03/18 and NW 02/19 the performance was satisfactory for 94 % and 95 % of the results, respectively [5, 8].
P_{PO4}	10-15	84	In the PTs NW 03/18 and NW 02/19 the performance was satisfactory for 84 % and 83 % of the results, respectively [5, 8].
$P_{PO4,\ dissolved}$	10-15	91	Good performance. In the PT NW 03/18 90 % of the results were satisfactory when deviation of 15–20 % from the assigned value was accepted [5].
P_{tot}	15	89	In the PTs NW 03/18 and NW 02/19 the performance was satisfactory for 84 % and 89 % of the results when deviation of 10-15 % from the assigned value was accepted [5, 8].
$P_{tot,\ dissolved}$	15	84	In the PT NW 03/18 69 % of the results were satisfactory when deviation of 15–20 % from the assigned value was accepted [5].

5 Summary

Proftest SYKE carried out proficiency test (PT) for analysis of alkalinity, conductivity, nutrients (N_{NH4}, $N_{NO2+NO3}$, N_{tot}, P_{PO4}, $P_{PO4,\ dissolved}$, P_{tot}, $P_{tot,\ dissolved}$), and pH in natural waters in February 2020 (NW 02/2020). Three types of samples were delivered to the participants: synthetic samples as well as brackish and lake water samples. In total, 31 laboratories participated in this proficiency test (Appendix 1).

The calculated concentration (NIST traceable) or the robust mean or the median of the results reported results by the participants was used as the assigned value for the measurands (Appendix 6). The uncertainties of the assigned values were estimated at the 95 % confidence level (k=2) and they were ≤ 1.3 % for the calculated values and 0.4–8.9 % for the other assigned values (Appendix 6).

The performance evaluation was based on the z scores. In total, 89 % of the reported results were satisfactory when the total deviation of 0.2 pH units for pH values and 5–25 % for the other measurands was accepted from the assigned value at the 95 % confidence level. Altogether 84 % of the participants used accredited analytical methods at least for a part of the measurements and 91 % of those results were satisfactory.

6 Summary in Finnish

Proftest SYKE järjesti luonnonvesiä analysoiville laboratorioille pätevyyskokeen helmikuussa 2020 (NW 02/2020). Pätevyyskokeessa määritettiin alkaliniteetti, ravinteet (N_{NH4}, $N_{NO2+NO3}$, N_{tot}, P_{PO4}, $P_{PO4,\ dissolved}$, P_{tot}, $P_{tot,\ dissolved}$), pH ja sähkönjohtavuus synteettisestä näytteestä sekä rannikko- ja järvivesinäytteistä. Pätevyyskokeeseen osallistui yhteensä 31 laboratoriota.

Testisuureen vertailuarvona käytettiin laskennallista pitoisuutta (synteettinen näyte, NIST jäljitettävä), osallistujien tulosten robustia keskiarvoa tai mediaania. Osallistujien pätevyyden arviointi tehtiin z-arvojen avulla. Koko tulosaineistossa oli z-arvoilla arvioituna 89 % hyväksyttäviä tuloksia, kun vertailuarvosta sallittiin pH-määrityksissä 0,2 pH-yksikön ja muissa määrityksissä 5–25 %:n poikkeama.

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APPENDIX 1: Participants in the proficiency test

Country	Participant
Estonia	Estonian Marine Institute University of Tartu
Finland	Eurofins Ahma Oy Seinäjoki Eurofins Ahma Oy, Rovaniemi Eurofins Environment Testing Finland Oy, Lahti HSY Käyttölaboratorio Pitkäkoski Helsinki HY, Tvärminnen eläintieteellinen asema, Hanko HY/Ympäristötieteidenlaitos/Almalab KVVY Tutkimus Oy, Tampere KVVY-Botnialab, Vaasa Kymen Ympäristölaboratorio Oy Lounais-Suomen vesi- ja ympäristötutkimus Oy, Turku Luonnonvarakeskus, Viikki B2-laboratorio LUVYLab Oy Ab 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 SeiLab Oy Haapaveden toimipiste SGS Finland Oy, Kotka SYKE Oulun toimipaikka SYKE/Merikeskus Yara Suomi Oy, Uusikaupunki ÅMHM laboratoriet, Jomala, Åland
Germany	Eurofins Umwelt Ost GmbH, Niederlassung Freiberg
Sweden	Nyköpings kommun / Vattenlaboratoriet Stockholm University, ACES Stockholm University, Department of Ecology, Environment and Plant Sciences Umeå Marine Sciences Centre

APPENDIX 2: Sample preparation

Measurand	Sample	Initial concentration	Added compound (Producer) Addition	Assigned value
Alkalinity [mmol/l]	A1A	-	Na_2CO_3 (Merck) 0.16	0.16
	B2A	1.41	-	1.39
	N3A	0.50	-	0.49
Conductivity γ_{25} [µS/cm]	A1J	-	KCl (Merck) 8.26	9.95
	B2H	905	-	873
	N3H	12.8	-	13.0
N_{NH4} [µg/l]	A1N	-	NH_4Cl (Merck) 19.3	20.6
	B2N	7	18	32.8
	N3N	9	42	202
$N_{NO2+NO3}$ [µg/l]	A1N	-	$NaNO_3$ (Merck) 180	185
	B2N	127	-	161
	N3N	143	-	164
N_{tot} [µg/l]	A1N	-	$NaNO_3$ 180 NH_4Cl 19.3 Na_2-EDTA (Merck) 50.6	249
	B2N	439	18	440
	N3N	901	42	751
pH pH unit	A1H	-	Buffer solution pH 7 (BDH Prolabo)	7.27
	B2H	7.8	-	7.84
	N3H	7.3	-	7.34
P_{PO4} [µg/l]	A1P	-	KH_2PO_4 (Merck) 10	9.95
	B2P	25.3	-	27.5
	N3P	6.1	8.8	27.3
$P_{PO4,\ dissolved}$	B4P	24.3	-	27.5
	N5P	3.2	-	26.2
P_{tot} [µg/l]	A1P	-	KH_2PO_4 10 $C_3H_7Na_2O_6P$ (Merck) 10.4	19.8
	B2P	34.1	-	33.6
	N3P	69.5	-	44.0
$P_{tot,\ dissolved}$	B4P	30.6	-	30.9
	N5P	4.9	-	33.1

First letter of the sample code indicates the sample matrix:

A = Synthetic sample

B = Brackish water

N = Lake water

APPENDIX 3: Homogeneity of the samples

Homogeneity was tested as duplicate measurement of selected measurands from four to eight samples of each sample type.

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 in a sub sample
s_{sam} = between-sample deviation, standard deviation of the results between sub samples

$c = F1 \times s_{all}^2 + F2 \times s_{anal}^2$, where
$s_{all}^2 = (0.3 \times s_{pt})^2$

F1 and F2 are constants of F distribution derived from the standard statistical tables for the tested number of samples [2, 3].

Measurand / Sample	Concentration [µg/l] [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	$s_{sam}^2 < c$?
Alkalinity / B2A	1.39	4	3.75	0.05	0.002	0.04	Yes	0	0.0006	Yes
Alkalinity / N3A	0.50	4	3.75	0.02	0.003	0.14	Yes	0	0.0001	Yes
N_{NH4} / B2N	29.1	6	12.5	3.64	0.23	0.06	Yes	1.91	2.73	Yes
N_{NH4} / N3N	194	6	10	19.4	2.33	0.12	Yes	11.5	84.4	Yes
N_{tot} / B2N	483	6	10	48.3	3.22	0.07	Yes	16.2	482	Yes
N_{tot} / N3N	809	6	7.5	60.6	7.75	0.13	Yes	99.5	835	Yes
pH / B2H	7.83	8	1.3	0.10	0.01	0.11	Yes	0.0006	0.002	Yes
pH / N3H	7.35	8	1.35	0.10	0.02	0.22	Yes	0.0006	0.002	Yes
P_{tot} / B2P	32.7	8	7.5	2.45	0.41	0.17	Yes	0.03	1.49	Yes
P_{tot} / N3P	43.8	8	7.5	3.29	0.97	0.30	Yes	0	3.74	Yes

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

APPENDIX 4: Stability of the samples

The samples were delivered on 11 or 12 February 2020 and they arrived to the participants mainly on 12 February 2020. The samples were requested to be measured as follows:

alkalinity	13 February 2020
pH, conductivity	13 February 2020
N_{NH4}, $N_{NO2+NO3}$, P_{PO4}, $P_{PO4,\ dissolved}$	13 February 2020
N_{tot}, P_{tot}, $P_{tot,\ dissolved}$	latest on 24 February 2020

Stability of pH, N_{NH4} and P_{PO4} was tested by analyzing the samples stored at the temperatures 4 °C and 20 °C.

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

N_{NH4}

Sample	Result [µg/l]		Sample	Result [µg/l]		Sample	Result [µg/l]	
Date	13.2. (20 °C)	13.2. (4 °C)	Date	13.2. (20 °C)	13.2. (4 °C)	Date	13.2. (20 °C)	13.2. (4 °C)
A1N	19.6	19.6	**B2N**	27.1	27.4	**N3N**	166	189
D	0.037		D	0.297		D	22.7	
$0.3 \times s_{pt}$	0.618		$0.3 \times s_{pt}$	1.230		$0.3 \times s_{pt}$	6.06	
	D <0.3 × s_{pt}? Yes			**D <0.3 × s_{pt}? Yes**			**D <0.3 × s_{pt}? No**	

pH

Sample	Result		Sample	Result		Sample	Result	
Date	13.2. (20 °C)	13.2. (4 °C)	Date	13.2. (20 °C)	13.2. (4 °C)	Date	13.2. (20 °C)	13.2. (4 °C)
A1H	7.21	7.23	**B2H**	7.84	7.87	**N3H**	7.33	7.36
D	0.018		D	0.033		D	0.025	
$0.3 \times s_{pt}$	0.03		$0.3 \times s_{pt}$	0.03		$0.3 \times s_{pt}$	0.03	
	D <0.3 × s_{pt}? Yes			**D <0.3 × s_{pt}? No** [1)]			**D <0.3 × s_{pt}? Yes**	

[1)] The difference is within the analytical error

P_{PO4}

Sample	Result [µg/l]		Sample	Result [µg/l]		Sample	Result [µg/l]	
Date	13.2. (20 °C)	13.2. (4 °C)	Date	13.2. (20 °C)	13.2. (4 °C)	Date	13.2. (20 °C)	13.2. (4 °C)
A1P	9.53	9.45	**B2P**	26.7	27.0	**N3P**	26.8	26.7
D	0.080		D	0.292		D	0.150	
$0.3 \times s_{pt}$	0.149		$0.3 \times s_{pt}$	0.619		$0.3 \times s_{pt}$	0.410	
	D <0.3 × s_{pt}? Yes			**D <0.3 × s_{pt}? Yes**			**D <0.3 × s_{pt}? Yes**	

Conclusion: According to the test results, the concentration of N_{NH4} in sample N3N could decrease if the temperature increased up to 20 °C during the sample transport and storage. Based on the reported arrival temperatures of the samples (see also Chapter 2.3), the maximum arrival temperature was 13.6 °C. Further, within the reported results there was no indication of temperature related decreased concentrations for the sample N3N. The other observed difference is within the analytical error. Overall, the samples were considered stable in the sample distribution conditions.

APPENDIX 5: Feedback from the proficiency test

FEEDBACK FROM THE PARTICIPANTS

Participant	Comments on technical excecution	Action / Proftest SYKE
5	The participant received the samples with one day delay.	Due to internal error, the samples were not delivered according to the foreseen schedule. The provider apologizes this and will pay more attention to this in future.
22	The participant informed that they didn't received the samples.	The provider delivered the sample package with the correct address, but the package had been delivered and accepted to wrong destination. Thus, the participant received the samples one day after the estimated delivery day.
23	Bottle of sample B2H had leaked.	The provider will pay more attention to careful closing of the bottles.
Several	The participants informed that they could not register via ProftestWEB	Unfortunately, there was an error in registration form. The error was fixed rapidly, and the participants were informed.

FEEDBACK TO THE PARTICIPANTS

Participant	Comments
1, 12, 15, 19, 20, 21, 28, 30	The participants did not return the sample arrival document to the provider. Therefore, the information of the sample arrival temperature was not available from all the participants. The participants should follow up the instructions of the provider.
2, 13, 19, 26	The participant reported only one result instead of requested replicate results for one or more nutrient samples/measurands. Therefore, the performance evaluation is not done for these results.
5, 7, 11, 18, 21, 22, 31	For one or more measurands and/or samples the variance of participant's replicate results was significantly higher than the variance of the other participants, i.e. those results were Cochran outliers. The provider recommends the participants to re-validate their accepted deviation of replicate measurements.
8, 12, 13, 17, 20, 23, 29	Varying information for the expanded uncertainty (Ui%) for pH. Some participants reported the absolute value only as additional information and the actual Ui% was blank and some filled absolute value was filled for Ui%. The provider advises the participants to follow the given instruction. For calculation of the performance evaluation the 0.2 pH unit is converted into relative value.
19	Participant's limit of quantification for N_{tot} and P_{PO4} and P_{tot} in natural waters are quite high (< 1000 µg/l N_{tot} and < 50 µg/l P_{PO4} and P_{tot}). The provider recommends to re-validate the limit of quantification.
28	The participant delivered their results after the given dead line. The provider accepted the delayed results but recommends the participant to pay more attention to the given schedule.

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	0.16	0.00	0.2	Calculated value	0.03
	B2A	mmol/l	1.39	0.03	1.9	Robust mean	0.25
	N3A	mmol/l	0.49	0.01	1.7	Median	0.23
Conductivity 25	A1J	mS/m	9.95	0.08	0.8	Robust mean	0.16
	B2H	mS/m	873	6	0.7	Robust mean	0.14
	N3H	mS/m	13.0	0.1	0.9	Robust mean	0.18
N_{NH4}	A1N	µg/l	20.6	1.2	5.6	Robust mean	0.28
	B2N	µg/l	32.8	2.9	8.9	Robust mean	0.36
	N3N	µg/l	202	8	3.9	Robust mean	0.20
$N_{NO2+NO3}$	A1N	µg/l	185	4	2.1	Robust mean	0.26
	B2N	µg/l	161	8	5.1	Robust mean	0.34
	N3N	µg/l	164	7	4.1	Robust mean	0.27
N_{tot}	A1N	µg/l	249	3	1.2	Calculated value	0.08
	B2N	µg/l	440	20	4.5	Robust mean	0.23
	N3N	µg/l	751	17	2.3	Robust mean	0.15
pH	A1H		7.27	0.03	0.4	Robust mean	0.15
	B2H		7.84	0.05	0.6	Robust mean	0.23
	N3H		7.34	0.04	0.6	Robust mean	0.22
P_{PO4}	A1P	µg/l	9.95	0.12	1.2	Calculated value	0.12
	B2P	µg/l	27.5	0.7	2.4	Robust mean	0.16
	N3P	µg/l	27.3	0.8	2.8	Robust mean	0.28
$P_{PO4, dissolved}$	B4P	µg/l	27.5	1.0	3.5	Robust mean	0.23
	N5P	µg/l	26.2	0.7	2.7	Robust mean	0.27
P_{tot}	A1P	µg/l	19.8	0.3	1.3	Calculated value	0.09
	B2P	µg/l	33.6	1.5	4.4	Robust mean	0.29
	N3P	µg/l	44.0	1.4	3.1	Robust mean	0.21
$P_{tot, dissolved}$	B4P	µg/l	30.9	1.1	3.4	Robust mean	0.23
	N5P	µg/l	33.1	1.0	3.1	Robust mean	0.21

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

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

APPENDIX 7: Terms in the results tables

Results of each participant

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

Summary on the z scores

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

Robust analysis

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

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

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

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

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

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

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

APPENDIX 8: Results of each participant

Participant 1												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Alkalinity	mmol/l	A1A		0.33	0.16	7,5	0.16	0.16	0.16	0.01	4.2	15
	mmol/l	B2A		-0.77	1.39	7,5	1.35	1.39	1.38	0.04	3.0	19
	mmol/l	N3A		-0.33	0.49	7,5	0.48	0.49	0.49	0.02	3.7	19
Conductivity 25	mS/m	A1J		0.00	9.95	5	9.95	9.93	9.94	0.14	1.4	23
	mS/m	B2H		-0.23	873	5	868	871	872	12	1.3	22
	mS/m	N3H		0.31	13.0	5	13.1	13.0	13.0	0.2	1.5	24
N_{NH4}	µg/l	A1N		-0.36	20.6	20	19.9	20.7	20.7	1.9	9.1	14
	µg/l	B2N		-0.54	32.8	25	30.6	31.4	32.9	4.3	13.2	17
	µg/l	N3N		-0.35	202	20	195	201	202	13	6.4	18
$N_{NO2+NO3}$	µg/l	A1N		0.47	185	8	189	186	185	7	3.6	15
	µg/l	B2N		0.33	161	15	165	160	160	13	8.3	17
	µg/l	N3N		0.41	164	15	169	164	163	11	6.5	16
N_{tot}	µg/l	A1N		0.64	249	15	261	260	257	18	7.0	17
	µg/l	B2N		-0.08	440	20	437	438	440	37	8.4	17
	µg/l	N3N		-0.28	751	15	736	749	747	25	3.3	16
pH		A1H		-0.10	7.27	2,7	7.26	7.28	7.27	0.06	0.9	26
		B2H		0.29	7.84	2,6	7.87	7.86	7.84	0.09	1.1	25
		N3H		0.20	7.34	2,7	7.36	7.34	7.33	0.08	1.1	26
P_{PO4}	µg/l	A1P		0.20	9.95	10	10.05	9.90	9.83	0.59	6.1	15
	µg/l	B2P		0.41	27.5	15	28.4	27.4	27.5	1.0	3.7	16
	µg/l	N3P		0.18	27.3	10	27.6	27.0	27.3	1.2	4.2	16
$P_{PO4,\ dissolved}$	µg/l	B4P		0.44	27.5	15	28.4	27.6	27.4	1.6	5.7	15
	µg/l	N5P		0.00	26.2	10	26.2	26.2	26.3	1.1	4.3	14
P_{tot}	µg/l	A1P		-0.64	19.8	15	18.9	19.4	19.5	0.8	4.0	16
	µg/l	B2P		-1.01	33.6	15	31.1	33.3	33.1	1.9	5.7	18
	µg/l	N3P		-0.06	44.0	15	43.8	43.5	43.8	2.2	5.0	19
$P_{tot,\ dissolved}$	µg/l	B4P		-0.52	30.9	15	29.7	30.9	30.9	1.4	4.7	14
	µg/l	N5P		-0.87	33.1	15	31.0	33.1	33.1	1.3	3.8	12

Participant 2												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Alkalinity	mmol/l	A1A		0.33	0.16	7,5	0.16	0.16	0.16	0.01	4.2	15
	mmol/l	B2A		0.19	1.39	7,5	1.40	1.39	1.38	0.04	3.0	19
	mmol/l	N3A		0.54	0.49	7,5	0.50	0.49	0.49	0.02	3.7	19
Conductivity 25	mS/m	A1J		2.21	9.95	5	10.50	9.93	9.94	0.14	1.4	23
	mS/m	B2H		-0.32	873	5	866	871	872	12	1.3	22
	mS/m	N3H		0.92	13.0	5	13.3	13.0	13.0	0.2	1.5	24
N_{NH4}	µg/l	A1N			20.6	20	*19,93**	20.7	20.7	1.9	9.1	14
	µg/l	B2N			32.8	25	*31,2**	31.4	32.9	4.3	13.2	17
	µg/l	N3N			202	20	*191**	201	202	13	6.4	18
$N_{NO2+NO3}$	µg/l	A1N			185	8	*228**	186	185	7	3.6	15
	µg/l	B2N			161	15	*203**	160	160	13	8.3	17
	µg/l	N3N			164	15	*195**	164	163	11	6.5	16
N_{tot}	µg/l	A1N			249	15	*297**	260	257	18	7.0	17
	µg/l	B2N			440	20	*606**	438	440	37	8.4	17
	µg/l	N3N			751	15	*855**	749	747	25	3.3	16

Participant 2												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
pH		A1H		0.31	7.27	2,7	7.30	7.28	7.27	0.06	0.9	26
		B2H		1.57	7.84	2,6	8.00	7.86	7.84	0.09	1.1	25
		N3H		-0.40	7.34	2,7	7.30	7.34	7.33	0.08	1.1	26
P_{PO4}	µg/l	A1P			9.95	10	*10,7**	9.90	9.83	0.59	6.1	15
	µg/l	B2P			27.5	15	*28,0**	27.4	27.5	1.0	3.7	16
	µg/l	N3P			27.3	10	*27,3**	27.0	27.3	1.2	4.2	16
$P_{PO4,\ dissolved}$	µg/l	B4P			27.5	15	*27,4**	27.6	27.4	1.6	5.7	15
	µg/l	N5P			26.2	10	*27,3**	26.2	26.3	1.1	4.3	14
P_{tot}	µg/l	A1P			19.8	15	*18,2**	19.4	19.5	0.8	4.0	16
	µg/l	B2P			33.6	15	*34,2**	33.3	33.1	1.9	5.7	18
	µg/l	N3P			44.0	15	*40,0**	43.5	43.8	2.2	5.0	19
$P_{tot,\ dissolved}$	µg/l	B4P			30.9	15	*29,3**	30.9	30.9	1.4	4.7	14
	µg/l	N5P			33.1	15	*36,0**	33.1	33.1	1.3	3.8	12

** Participant did not report the requested replicate result*

Participant 3												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Alkalinity	mmol/l	A1A		6.00	0.16	7,5	0.20	0.16	0.16	0.01	4.2	15
	mmol/l	N3A		2.18	0.49	7,5	0.53	0.49	0.49	0.02	3.7	19
Conductivity 25	mS/m	A1J		12.66	9.95	5	13.10	9.93	9.94	0.14	1.4	23
	mS/m	N3H		-9.23	13.0	5	10.0	13.0	13.0	0.2	1.5	24
N_{NH4}	µg/l	A1N		-0.12	20.6	20	20.4	20.7	20.7	1.9	9.1	14
	µg/l	N3N		-9.00	202	20	20	201	202	13	6.4	18
N_{tot}	µg/l	A1N		-7.98	249	15	100	260	257	18	7.0	17
	µg/l	N3N		-4.46	751	15	500	749	747	25	3.3	16
pH		A1H		0.10	7.27	2,7	7.28	7.28	7.27	0.06	0.9	26
		N3H		-2.22	7.34	2,7	7.12	7.34	7.33	0.08	1.1	26
P_{PO4}	µg/l	A1P		5.93	9.95	10	12.90	9.90	9.83	0.59	6.1	15
	µg/l	N3P		3.85	27.3	10	32.6	27.0	27.3	1.2	4.2	16
$P_{PO4,\ dissolved}$	µg/l	N5P		4.05	26.2	10	31.5	26.2	26.3	1.1	4.3	14
P_{tot}	µg/l	A1P		1.78	19.8	15	22.5	19.4	19.5	0.8	4.0	16
	µg/l	N3P		1.47	44.0	15	48.9	43.5	43.8	2.2	5.0	19
$P_{tot,\ dissolved}$	µg/l	N5P		3.14	33.1	15	40.9	33.1	33.1	1.3	3.8	12

Participant 4												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Alkalinity	mmol/l	A1A		1.17	0.16	7,5	0.17	0.16	0.16	0.01	4.2	15
	mmol/l	B2A		-0.96	1.39	7,5	1.34	1.39	1.38	0.04	3.0	19
	mmol/l	N3A		-0.22	0.49	7,5	0.49	0.49	0.49	0.02	3.7	19
Conductivity 25	mS/m	A1J		0.04	9.95	5	9.96	9.93	9.94	0.14	1.4	23
	mS/m	B2H		0.14	873	5	876	871	872	12	1.3	22
	mS/m	N3H		0.00	13.0	5	13.0	13.0	13.0	0.2	1.5	24
N_{NH4}	µg/l	A1N		0.05	20.6	20	20.7	20.7	20.7	1.9	9.1	14
	µg/l	B2N		-0.38	32.8	25	31.3	31.4	32.9	4.3	13.2	17
	µg/l	N3N		-0.27	202	20	197	201	202	13	6.4	18
$N_{NO2+NO3}$	µg/l	A1N		3.04	185	8	208	186	185	7	3.6	15
	µg/l	B2N		1.20	161	15	176	160	160	13	8.3	17
	µg/l	N3N		1.34	164	15	181	164	163	11	6.5	16

Participant 4												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
N_{tot}	µg/l	A1N		2.20	249	15	290	260	257	18	7.0	17
	µg/l	B2N		1.10	440	20	489	438	440	37	8.4	17
	µg/l	N3N		1.55	751	15	839	749	747	25	3.3	16
pH		A1H		0.20	7.27	2,7	7.29	7.28	7.27	0.06	0.9	26
		B2H		0.78	7.84	2,6	7.92	7.86	7.84	0.09	1.1	25
		N3H		0.50	7.34	2,7	7.39	7.34	7.33	0.08	1.1	26
P_{PO4}	µg/l	A1P		-0.01	9.95	10	9.95	9.90	9.83	0.59	6.1	15
	µg/l	B2P		0.07	27.5	15	27.7	27.4	27.5	1.0	3.7	16
	µg/l	N3P		-0.73	27.3	10	26.3	27.0	27.3	1.2	4.2	16
$P_{PO4,\ dissolved}$	µg/l	B4P		0.46	27.5	15	28.5	27.6	27.4	1.6	5.7	15
	µg/l	N5P		0.27	26.2	10	26.6	26.2	26.3	1.1	4.3	14
P_{tot}	µg/l	A1P		-0.61	19.8	15	18.9	19.4	19.5	0.8	4.0	16
	µg/l	B2P		-0.22	33.6	15	33.1	33.3	33.1	1.9	5.7	18
	µg/l	N3P		-0.71	44.0	15	41.7	43.5	43.8	2.2	5.0	19
$P_{tot,\ dissolved}$	µg/l	B4P		0.02	30.9	15	31.0	30.9	30.9	1.4	4.7	14
	µg/l	N5P		-0.18	33.1	15	32.7	33.1	33.1	1.3	3.8	12

Participant 5												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Alkalinity	mmol/l	A1A		6.67	0.16	7,5	0.20	0.16	0.16	0.01	4.2	15
	mmol/l	B2A		0.96	1.39	7,5	1.44	1.39	1.38	0.04	3.0	19
	mmol/l	N3A		2.72	0.49	7,5	0.54	0.49	0.49	0.02	3.7	19
Conductivity 25	mS/m	A1J		-0.12	9.95	5	9.92	9.93	9.94	0.14	1.4	23
	mS/m	B2H		0.32	873	5	880	871	872	12	1.3	22
	mS/m	N3H		0.09	13.0	5	13.0	13.0	13.0	0.2	1.5	24
N_{NH4}	µg/l	A1N		0.49	20.6	20	21.6	20.7	20.7	1.9	9.1	14
	µg/l	B2N		-0.29	32.8	25	31.6	31.4	32.9	4.3	13.2	17
	µg/l	N3N		0.02	202	20	203	201	202	13	6.4	18
$N_{NO2+NO3}$	µg/l	A1N		0.21	185	8	187	186	185	7	3.6	15
	µg/l	B2N		1.56	161	15	180	160	160	13	8.3	17
	µg/l	N3N		-0.25	164	15	161	164	163	11	6.5	16
N_{tot}	µg/l	A1N		0.60	249	15	260	260	257	18	7.0	17
	µg/l	B2N		0.46	440	20	460	438	440	37	8.4	17
	µg/l	N3N		0.54	751	15	782	749	747	25	3.3	16
pH		A1H		0.31	7.27	2,7	7.30	7.28	7.27	0.06	0.9	26
		B2H		0.29	7.84	2,6	7.87	7.86	7.84	0.09	1.1	25
		N3H		-0.20	7.34	2,7	7.32	7.34	7.33	0.08	1.1	26
P_{PO4}	µg/l	A1P		-2.71	9.95	10	8.60	9.90	9.83	0.59	6.1	15
	µg/l	B2P		-0.39	27.5	15	26.7	27.4	27.5	1.0	3.7	16
	µg/l	N3P		0.73	27.3	10	28.3	27.0	27.3	1.2	4.2	16
$P_{PO4,\ dissolved}$	µg/l	B4P		-0.27	27.5	15	27.0	27.6	27.4	1.6	5.7	15
	µg/l	N5P		-1.18	26.2	10	24.7	26.2	26.3	1.1	4.3	14
P_{tot}	µg/l	A1P		-1.04	19.8	15	18.3	19.4	19.5	0.8	4.0	16
	µg/l	B2P		-0.20	33.6	15	33.1	33.3	33.1	1.9	5.7	18
	µg/l	N3P		-0.17	44.0	15	43.5	43.5	43.8	2.2	5.0	19
$P_{tot,\ dissolved}$	µg/l	B4P		-0.09	30.9	15	30.7	30.9	30.9	1.4	4.7	14
	µg/l	N5P		-0.75	33.1	15	31.3	33.1	33.1	1.3	3.8	12

Participant 6												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Alkalinity	mmol/l	A1A		-0.50	0.16	7,5	0.16	0.16	0.16	0.01	4.2	15
	mmol/l	B2A		-0.38	1.39	7,5	1.37	1.39	1.38	0.04	3.0	19
	mmol/l	N3A		-0.22	0.49	7,5	0.49	0.49	0.49	0.02	3.7	19
Conductivity 25	mS/m	A1J		0.12	9.95	5	9.98	9.93	9.94	0.14	1.4	23
	mS/m	B2H		0.09	873	5	875	871	872	12	1.3	22
	mS/m	N3H		0.31	13.0	5	13.1	13.0	13.0	0.2	1.5	24
N_{NH4}	µg/l	A1N		1.65	20.6	20	24.0	20.7	20.7	1.9	9.1	14
	µg/l	B2N		2.00	32.8	25	41.0	31.4	32.9	4.3	13.2	17
	µg/l	N3N		0.94	202	20	221	201	202	13	6.4	18
$N_{NO2+NO3}$	µg/l	A1N		3.11	185	8	208	186	185	7	3.6	15
	µg/l	B2N		1.74	161	15	182	160	160	13	8.3	17
	µg/l	N3N		1.18	164	15	179	164	163	11	6.5	16
N_{tot}	µg/l	A1N		1.47	249	15	277	260	257	18	7.0	17
	µg/l	B2N		2.02	440	20	529	438	440	37	8.4	17
	µg/l	N3N		-0.04	751	15	749	749	747	25	3.3	16
pH		A1H		-0.71	7.27	2,7	7.20	7.28	7.27	0.06	0.9	26
		B2H		0.00	7.84	2,6	7.84	7.86	7.84	0.09	1.1	25
		N3H		-0.20	7.34	2,7	7.32	7.34	7.33	0.08	1.1	26
P_{PO4}	µg/l	A1P		0.50	9.95	10	10.20	9.90	9.83	0.59	6.1	15
	µg/l	B2P		0.68	27.5	15	28.9	27.4	27.5	1.0	3.7	16
	µg/l	N3P		0.44	27.3	10	27.9	27.0	27.3	1.2	4.2	16
$P_{PO4,\ dissolved}$	µg/l	B4P		0.56	27.5	15	28.7	27.6	27.4	1.6	5.7	15
	µg/l	N5P		0.00	26.2	10	26.2	26.2	26.3	1.1	4.3	14
P_{tot}	µg/l	A1P		2.26	19.8	15	23.2	19.4	19.5	0.8	4.0	16
	µg/l	B2P		-1.67	33.6	15	29.4	33.3	33.1	1.9	5.7	18
	µg/l	N3P		-0.24	44.0	15	43.2	43.5	43.8	2.2	5.0	19
$P_{tot,\ dissolved}$	µg/l	B4P		-1.19	30.9	15	28.2	30.9	30.9	1.4	4.7	14
	µg/l	N5P		0.06	33.1	15	33.3	33.1	33.1	1.3	3.8	12

Participant 7												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Alkalinity	mmol/l	A1A		6.00	0.16	7,5	0.20	0.16	0.16	0.01	4.2	15
	mmol/l	B2A		0.77	1.39	7,5	1.43	1.39	1.38	0.04	3.0	19
Conductivity 25	mS/m	A1J		0.60	9.95	5	10.10	9.93	9.94	0.14	1.4	23
	mS/m	B2H		0.12	873	5	876	871	872	12	1.3	22
N_{NH4}	µg/l	A1N		1.80	20.6	20	24.3	20.7	20.7	1.9	9.1	14
	µg/l	B2N		1.71	32.8	25	39.8	31.4	32.9	4.3	13.2	17
$N_{NO2+NO3}$	µg/l	A1N		-0.34	185	8	183	186	185	7	3.6	15
	µg/l	B2N		-2.73	161	15	128	160	160	13	8.3	17
pH		A1H		0.51	7.27	2,7	7.32	7.28	7.27	0.06	0.9	26
		B2H		0.78	7.84	2,6	7.92	7.86	7.84	0.09	1.1	25
P_{PO4}	µg/l	A1P		7.14	9.95	10	13.50	9.90	9.83	0.59	6.1	15
	µg/l	B2P		3.15	27.5	15	34.0	27.4	27.5	1.0	3.7	16
$P_{PO4,\ dissolved}$	µg/l	B4P		2.91	27.5	15	33.5	27.6	27.4	1.6	5.7	15
P_{tot}	µg/l	A1P		0.77	19.8	15	21.0	19.4	19.5	0.8	4.0	16
	µg/l	B2P		2.22	33.6	15	39.2	33.3	33.1	1.9	5.7	18
$P_{tot,\ dissolved}$	µg/l	B4P		17.76	30.9	15	72.1	30.9	30.9	1.4	4.7	14

Participant 8												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Conductivity 25	mS/m	A1J		-0.48	9.95	5	9.83	9.93	9.94	0.14	1.4	23
	mS/m	B2H		-0.09	873	5	871	871	872	12	1.3	22
	mS/m	N3H		0.00	13.0	5	13.0	13.0	13.0	0.2	1.5	24
pH		A1H		0.61	7.27	2,7	7.33	7.28	7.27	0.06	0.9	26
		B2H		0.49	7.84	2,6	7.89	7.86	7.84	0.09	1.1	25
		N3H		0.30	7.34	2,7	7.37	7.34	7.33	0.08	1.1	26

Participant 9												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Conductivity 25	mS/m	A1J		0.08	9.95	5	9.97	9.93	9.94	0.14	1.4	23
	mS/m	B2H		1.01	873	5	895	871	872	12	1.3	22
	mS/m	N3H		0.00	13.0	5	13.0	13.0	13.0	0.2	1.5	24
N_{tot}	µg/l	A1N		-1.94	249	15	213	260	257	18	7.0	17
	µg/l	B2N		-0.33	440	20	426	438	440	37	8.4	17
	µg/l	N3N		0.03	751	15	753	749	747	25	3.3	16
pH		A1H		1.12	7.27	2,7	7.38	7.28	7.27	0.06	0.9	26
		B2H		0.29	7.84	2,6	7.87	7.86	7.84	0.09	1.1	25
		N3H		-0.81	7.34	2,7	7.26	7.34	7.33	0.08	1.1	26
P_{tot}	µg/l	A1P		0.13	19.8	15	20.0	19.4	19.5	0.8	4.0	16
	µg/l	B2P		0.16	33.6	15	34.0	33.3	33.1	1.9	5.7	18
	µg/l	N3P		0.30	44.0	15	45.0	43.5	43.8	2.2	5.0	19

Participant 10												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Alkalinity	mmol/l	A1A		5.83	0.16	7,5	0.20	0.16	0.16	0.01	4.2	15
	mmol/l	N3A		1.80	0.49	7,5	0.52	0.49	0.49	0.02	3.7	19
Conductivity 25	mS/m	A1J		-0.20	9.95	5	9.90	9.93	9.94	0.14	1.4	23
	mS/m	N3H		-0.03	13.0	5	13.0	13.0	13.0	0.2	1.5	24
N_{NH4}	µg/l	A1N		7.48	20.6	20	36.0	20.7	20.7	1.9	9.1	14
	µg/l	N3N		1.06	202	20	224	201	202	13	6.4	18
pH		A1H		0.71	7.27	2,7	7.34	7.28	7.27	0.06	0.9	26
		N3H		-0.10	7.34	2,7	7.33	7.34	7.33	0.08	1.1	26

Participant 11												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Alkalinity	mmol/l	A1A		3.50	0.16	7,5	0.18	0.16	0.16	0.01	4.2	15
	mmol/l	B2A		0.38	1.39	7,5	1.41	1.39	1.38	0.04	3.0	19
	mmol/l	N3A		1.80	0.49	7,5	0.52	0.49	0.49	0.02	3.7	19
Conductivity 25	mS/m	A1J		1.01	9.95	5	10.20	9.93	9.94	0.14	1.4	23
	mS/m	B2H		0.18	873	5	877	871	872	12	1.3	22
	mS/m	N3H		3.69	13.0	5	14.2	13.0	13.0	0.2	1.5	24
N_{NH4}	µg/l	A1N		1.63	20.6	20	24.0	20.7	20.7	1.9	9.1	14
	µg/l	B2N		1.66	32.8	25	39.6	31.4	32.9	4.3	13.2	17
	µg/l	N3N		-1.11	202	20	180	201	202	13	6.4	18
$N_{NO2+NO3}$	µg/l	A1N		1.08	185	8	193	186	185	7	3.6	15
	µg/l	B2N		0.66	161	15	169	160	160	13	8.3	17
	µg/l	N3N		0.77	164	15	174	164	163	11	6.5	16

Participant 11												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
N_{tot}	µg/l	A1N		1.31	249	15	274	260	257	18	7.0	17
	µg/l	B2N		-0.15	440	20	434	438	440	37	8.4	17
	µg/l	N3N		-0.43	751	15	727	749	747	25	3.3	16
pH		A1H		0.31	7.27	2,7	7.30	7.28	7.27	0.06	0.9	26
		B2H		1.18	7.84	2,6	7.96	7.86	7.84	0.09	1.1	25
		N3H		1.21	7.34	2,7	7.46	7.34	7.33	0.08	1.1	26
P_{PO4}	µg/l	A1P		-0.97	9.95	10	9.47	9.90	9.83	0.59	6.1	15
	µg/l	B2P		0.00	27.5	15	27.5	27.4	27.5	1.0	3.7	16
	µg/l	N3P		0.15	27.3	10	27.5	27.0	27.3	1.2	4.2	16
$P_{PO4,\ dissolved}$	µg/l	B4P		-0.36	27.5	15	26.8	27.6	27.4	1.6	5.7	15
	µg/l	N5P		-0.15	26.2	10	26.0	26.2	26.3	1.1	4.3	14
P_{tot}	µg/l	A1P		-0.20	19.8	15	19.5	19.4	19.5	0.8	4.0	16
	µg/l	B2P		0.22	33.6	15	34.2	33.3	33.1	1.9	5.7	18
	µg/l	N3P		0.26	44.0	15	44.9	43.5	43.8	2.2	5.0	19
$P_{tot,\ dissolved}$	µg/l	B4P		0.47	30.9	15	32.0	30.9	30.9	1.4	4.7	14
	µg/l	N5P		0.34	33.1	15	34.0	33.1	33.1	1.3	3.8	12

Participant 12												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Alkalinity	mmol/l	B2A		0.56	1.39	7,5	1.42	1.39	1.38	0.04	3.0	19
pH		B2H		-1.57	7.84	2,6	7.68	7.86	7.84	0.09	1.1	25

Participant 13												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Alkalinity	mmol/l	A1A		0.33	0.16	7,5	0.16	0.16	0.16	0.01	4.2	15
	mmol/l	B2A		-1.15	1.39	7,5	1.33	1.39	1.38	0.04	3.0	19
	mmol/l	N3A		-0.87	0.49	7,5	0.47	0.49	0.49	0.02	3.7	19
Conductivity 25	mS/m	A1J		-0.60	9.95	5	9.80	9.93	9.94	0.14	1.4	23
	mS/m	B2H		-0.50	873	5	862	871	872	12	1.3	22
	mS/m	N3H		-0.95	13.0	5	12.7	13.0	13.0	0.2	1.5	24
N_{NH4}	µg/l	A1N			20.6	20	*21,8**	20.7	20.7	1.9	9.1	14
	µg/l	B2N		0.10	32.8	25	33.2	31.4	32.9	4.3	13.2	17
	µg/l	N3N		-0.50	202	20	192	201	202	13	6.4	18
$N_{NO2+NO3}$	µg/l	A1N		0.14	185	8	186	186	185	7	3.6	15
	µg/l	B2N		-0.21	161	15	159	160	160	13	8.3	17
	µg/l	N3N		0.00	164	15	164	164	163	11	6.5	16
N_{tot}	µg/l	A1N		0.67	249	15	262	260	257	18	7.0	17
	µg/l	B2N		-0.78	440	20	406	438	440	37	8.4	17
	µg/l	N3N		-0.37	751	15	730	749	747	25	3.3	16
pH		A1H		0.10	7.27	2,7	7.28	7.28	7.27	0.06	0.9	26
		B2H		0.20	7.84	2,6	7.86	7.86	7.84	0.09	1.1	25
		N3H		0.30	7.34	2,7	7.37	7.34	7.33	0.08	1.1	26
P_{PO4}	µg/l	A1P		0.80	9.95	10	10.35	9.90	9.83	0.59	6.1	15
	µg/l	B2P		0.82	27.5	15	29.2	27.4	27.5	1.0	3.7	16
	µg/l	N3P		1.06	27.3	10	28.8	27.0	27.3	1.2	4.2	16
$P_{PO4,\ dissolved}$	µg/l	B4P		0.63	27.5	15	28.8	27.6	27.4	1.6	5.7	15
	µg/l	N5P		0.57	26.2	10	27.0	26.2	26.3	1.1	4.3	14

Participant 13												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
P_{tot}	µg/l	A1P		-0.34	19.8	15	19.3	19.4	19.5	0.8	4.0	16
	µg/l	B2P		0.20	33.6	15	34.1	33.3	33.1	1.9	5.7	18
	µg/l	N3P		-0.06	44.0	15	43.8	43.5	43.8	2.2	5.0	19
$P_{tot, dissolved}$	µg/l	B4P		0.28	30.9	15	31.6	30.9	30.9	1.4	4.7	14
	µg/l	N5P		0.68	33.1	15	34.8	33.1	33.1	1.3	3.8	12

** Participant did not report the requested replicate result*

Participant 14												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Alkalinity	mmol/l	A1A		0.67	0.16	7,5	0.16	0.16	0.16	0.01	4.2	15
	mmol/l	N3A		-0.27	0.49	7,5	0.49	0.49	0.49	0.02	3.7	19
Conductivity 25	mS/m	A1J		-0.20	9.95	5	9.90	9.93	9.94	0.14	1.4	23
	mS/m	N3H		-0.62	13.0	5	12.8	13.0	13.0	0.2	1.5	24
pH		A1H		0.51	7.27	2,7	7.32	7.28	7.27	0.06	0.9	26
		N3H		-0.91	7.34	2,7	7.25	7.34	7.33	0.08	1.1	26

Participant 15												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Alkalinity	mmol/l	A1A		-0.83	0.16	7,5	0.16	0.16	0.16	0.01	4.2	15
	mmol/l	B2A		-0.77	1.39	7,5	1.35	1.39	1.38	0.04	3.0	19
	mmol/l	N3A		-0.27	0.49	7,5	0.49	0.49	0.49	0.02	3.7	19
Conductivity 25	mS/m	A1J		-0.44	9.95	5	9.84	9.93	9.94	0.14	1.4	23
	mS/m	B2H		0.08	873	5	875	871	872	12	1.3	22
	mS/m	N3H		2.77	13.0	5	13.9	13.0	13.0	0.2	1.5	24
N_{NH4}	µg/l	A1N		0.39	20.6	20	21.4	20.7	20.7	1.9	9.1	14
	µg/l	B2N		-0.38	32.8	25	31.2	31.4	32.9	4.3	13.2	17
	µg/l	N3N		0.23	202	20	207	201	202	13	6.4	18
$N_{NO2+NO3}$	µg/l	A1N		0.76	185	8	191	186	185	7	3.6	15
	µg/l	B2N		-0.05	161	15	160	160	160	13	8.3	17
	µg/l	N3N		0.25	164	15	167	164	163	11	6.5	16
N_{tot}	µg/l	A1N		0.81	249	15	264	260	257	18	7.0	17
	µg/l	B2N		0.12	440	20	445	438	440	37	8.4	17
	µg/l	N3N		0.30	751	15	768	749	747	25	3.3	16
pH		A1H		0.51	7.27	2,7	7.32	7.28	7.27	0.06	0.9	26
		B2H		0.69	7.84	2,6	7.91	7.86	7.84	0.09	1.1	25
		N3H		0.91	7.34	2,7	7.43	7.34	7.33	0.08	1.1	26
P_{PO4}	µg/l	A1P		-1.22	9.95	10	9.35	9.90	9.83	0.59	6.1	15
	µg/l	B2P		-0.50	27.5	15	26.5	27.4	27.5	1.0	3.7	16
	µg/l	N3P		-0.26	27.3	10	27.0	27.0	27.3	1.2	4.2	16
$P_{PO4, dissolved}$	µg/l	B4P		-1.88	27.5	15	23.6	27.6	27.4	1.6	5.7	15
	µg/l	N5P		0.40	26.2	10	26.7	26.2	26.3	1.1	4.3	14
P_{tot}	µg/l	A1P		-0.14	19.8	15	19.6	19.4	19.5	0.8	4.0	16
	µg/l	B2P		0.27	33.6	15	34.3	33.3	33.1	1.9	5.7	18
	µg/l	N3P		-0.48	44.0	15	42.4	43.5	43.8	2.2	5.0	19
$P_{tot, dissolved}$	µg/l	B4P		0.50	30.9	15	32.1	30.9	30.9	1.4	4.7	14
	µg/l	N5P		-0.29	33.1	15	32.4	33.1	33.1	1.3	3.8	12

Participant 16												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Alkalinity	mmol/l	A1A		6.33	0.16	7,5	0.20	0.16	0.16	0.01	4.2	15
	mmol/l	B2A		0.77	1.39	7,5	1.43	1.39	1.38	0.04	3.0	19
	mmol/l	N3A		2.61	0.49	7,5	0.54	0.49	0.49	0.02	3.7	19
Conductivity 25	mS/m	A1J		-0.16	9.95	5	9.91	9.93	9.94	0.14	1.4	23
	mS/m	B2H		-1.24	873	5	846	871	872	12	1.3	22
	mS/m	N3H		0.00	13.0	5	13.0	13.0	13.0	0.2	1.5	24
N_{NH4}	µg/l	A1N		-1.24	20.6	20	18.1	20.7	20.7	1.9	9.1	14
	µg/l	B2N		0.54	32.8	25	35.0	31.4	32.9	4.3	13.2	17
	µg/l	N3N		0.25	202	20	207	201	202	13	6.4	18
$N_{NO2+NO3}$	µg/l	A1N		1.15	185	8	194	186	185	7	3.6	15
	µg/l	B2N		0.54	161	15	168	160	160	13	8.3	17
	µg/l	N3N		0.57	164	15	171	164	163	11	6.5	16
N_{tot}	µg/l	A1N		0.13	249	15	252	260	257	18	7.0	17
	µg/l	B2N		-0.90	440	20	401	438	440	37	8.4	17
	µg/l	N3N		-0.44	751	15	726	749	747	25	3.3	16
pH		A1H		-1.43	7.27	2,7	7.13	7.28	7.27	0.06	0.9	26
		B2H		-0.98	7.84	2,6	7.74	7.86	7.84	0.09	1.1	25
		N3H		-0.10	7.34	2,7	7.33	7.34	7.33	0.08	1.1	26
P_{PO4}	µg/l	A1P		-0.10	9.95	10	9.90	9.90	9.83	0.59	6.1	15
	µg/l	B2P		0.32	27.5	15	28.2	27.4	27.5	1.0	3.7	16
	µg/l	N3P		1.79	27.3	10	29.8	27.0	27.3	1.2	4.2	16
$P_{PO4,\ dissolved}$	µg/l	B4P		0.70	27.5	15	29.0	27.6	27.4	1.6	5.7	15
	µg/l	N5P		1.11	26.2	10	27.7	26.2	26.3	1.1	4.3	14
P_{tot}	µg/l	A1P		0.34	19.8	15	20.3	19.4	19.5	0.8	4.0	16
	µg/l	B2P		-0.56	33.6	15	32.2	33.3	33.1	1.9	5.7	18
	µg/l	N3P		-0.35	44.0	15	42.9	43.5	43.8	2.2	5.0	19
$P_{tot,\ dissolved}$	µg/l	B4P		0.00	30.9	15	30.9	30.9	30.9	1.4	4.7	14
	µg/l	N5P		-0.08	33.1	15	32.9	33.1	33.1	1.3	3.8	12

Participant 17												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Alkalinity	mmol/l	B2A		-0.19	1.39	7,5	1.38	1.39	1.38	0.04	3.0	19
	mmol/l	N3A		-0.16	0.49	7,5	0.49	0.49	0.49	0.02	3.7	19
Conductivity 25	mS/m	B2H		-0.37	873	5	865	871	872	12	1.3	22
	mS/m	N3H		0.31	13.0	5	13.1	13.0	13.0	0.2	1.5	24
N_{NH4}	µg/l	B2N		1.02	32.8	25	37.0	31.4	32.9	4.3	13.2	17
	µg/l	N3N		-0.45	202	20	193	201	202	13	6.4	18
$N_{NO2+NO3}$	µg/l	B2N		-0.41	161	15	156	160	160	13	8.3	17
	µg/l	N3N		-0.33	164	15	160	164	163	11	6.5	16
N_{tot}	µg/l	B2N		0.45	440	20	460	438	440	37	8.4	17
	µg/l	N3N		-0.16	751	15	742	749	747	25	3.3	16
pH		B2H		0.39	7.84	2,6	7.88	7.86	7.84	0.09	1.1	25
		N3H		0.00	7.34	2,7	7.34	7.34	7.33	0.08	1.1	26
P_{tot}	µg/l	B2P		1.39	33.6	15	37.1	33.3	33.1	1.9	5.7	18
	µg/l	N3P		1.06	44.0	15	47.5	43.5	43.8	2.2	5.0	19

Participant 18												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Alkalinity	mmol/l	A1A		0.33	0.16	7,5	0.16	0.16	0.16	0.01	4.2	15
	mmol/l	N3A		0.33	0.49	7,5	0.50	0.49	0.49	0.02	3.7	19
Conductivity 25	mS/m	A1J		0.20	9.95	5	10.00	9.93	9.94	0.14	1.4	23
	mS/m	N3H		-0.31	13.0	5	12.9	13.0	13.0	0.2	1.5	24
N_{NH4}	µg/l	A1N		5.05	20.6	20	31.0	20.7	20.7	1.9	9.1	14
	µg/l	N3N		-0.64	202	20	189	201	202	13	6.4	18
$N_{NO2+NO3}$	µg/l	A1N		0.07	185	8	186	186	185	7	3.6	15
	µg/l	N3N		-0.41	164	15	159	164	163	11	6.5	16
N_{tot}	µg/l	A1N		-0.43	249	15	241	260	257	18	7.0	17
	µg/l	N3N		0.13	751	15	759	749	747	25	3.3	16
pH		A1H		-1.32	7.27	2,7	7.14	7.28	7.27	0.06	0.9	26
		N3H		-1.01	7.34	2,7	7.24	7.34	7.33	0.08	1.1	26
P_{PO4}	µg/l	A1P		2.41	9.95	10	11.15	9.90	9.83	0.59	6.1	15
	µg/l	N3P		1.28	27.3	10	29.1	27.0	27.3	1.2	4.2	16
$P_{PO4,\ dissolved}$	µg/l	N5P		2.14	26.2	10	29.0	26.2	26.3	1.1	4.3	14
P_{tot}	µg/l	A1P		-0.40	19.8	15	19.2	19.4	19.5	0.8	4.0	16
	µg/l	N3P		0.05	44.0	15	44.2	43.5	43.8	2.2	5.0	19
$P_{tot,\ dissolved}$	µg/l	N5P		4.61	33.1	15	44.6	33.1	33.1	1.3	3.8	12

Participant 19												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Alkalinity	mmol/l	A1A		0.50	0.16	7,5	0.16	0.16	0.16	0.01	4.2	15
	mmol/l	N3A		0.05	0.49	7,5	0.49	0.49	0.49	0.02	3.7	19
Conductivity 25	mS/m	A1J		0.60	9.95	5	10.10	9.93	9.94	0.14	1.4	23
	mS/m	N3H		0.62	13.0	5	13.2	13.0	13.0	0.2	1.5	24
N_{NH4}	µg/l	A1N			20.6	20	*31,1**	20.7	20.7	1.9	9.1	14
	µg/l	N3N			202	20	*297**	201	202	13	6.4	18
N_{tot}	µg/l	A1N			249	15	*<1000*	260	257	18	7.0	17
	µg/l	N3N			751	15	*<1000*	749	747	25	3.3	16
pH		A1H		-0.41	7.27	2,7	7.23	7.28	7.27	0.06	0.9	26
		N3H		-0.20	7.34	2,7	7.32	7.34	7.33	0.08	1.1	26
P_{PO4}	µg/l	A1P			9.95	10	*<50*	9.90	9.83	0.59	6.1	15
	µg/l	N3P			27.3	10	*<50*	27.0	27.3	1.2	4.2	16
P_{tot}	µg/l	A1P			19.8	15	*<50*	19.4	19.5	0.8	4.0	16
	µg/l	N3P			44.0	15	*<50*	43.5	43.8	2.2	5.0	19

** Participant did not report the requested replicate result*

Participant 20												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
pH		A1H		-0.39	7.27	2,7	7.23	7.28	7.27	0.06	0.9	26
		B2H		-1.40	7.84	2,6	7.70	7.86	7.84	0.09	1.1	25
		N3H		-1.06	7.34	2,7	7.24	7.34	7.33	0.08	1.1	26

Participant 21												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Alkalinity	mmol/l	A1A		1.00	0.16	7,5	0.17	0.16	0.16	0.01	4.2	15
	mmol/l	B2A		-0.96	1.39	7,5	1.34	1.39	1.38	0.04	3.0	19
	mmol/l	N3A		-0.54	0.49	7,5	0.48	0.49	0.49	0.02	3.7	19
Conductivity 25	mS/m	A1J		1.01	9.95	5	10.20	9.93	9.94	0.14	1.4	23
	mS/m	B2H		1.65	873	5	909	871	872	12	1.3	22
	mS/m	N3H		0.92	13.0	5	13.3	13.0	13.0	0.2	1.5	24
N_{NH4}	µg/l	A1N		-0.22	20.6	20	20.2	20.7	20.7	1.9	9.1	14
	µg/l	B2N		-1.26	32.8	25	27.7	31.4	32.9	4.3	13.2	17
	µg/l	N3N		-0.15	202	20	199	201	202	13	6.4	18
$N_{NO2+NO3}$	µg/l	A1N		-0.34	185	8	183	186	185	7	3.6	15
	µg/l	B2N		-0.21	161	15	159	160	160	13	8.3	17
	µg/l	N3N		-0.20	164	15	162	164	163	11	6.5	16
N_{tot}	µg/l	A1N		-0.19	249	15	246	260	257	18	7.0	17
	µg/l	B2N		-0.90	440	20	401	438	440	37	8.4	17
	µg/l	N3N		0.03	751	15	753	749	747	25	3.3	16
pH		A1H		-0.10	7.27	2,7	7.26	7.28	7.27	0.06	0.9	26
		B2H		-0.10	7.84	2,6	7.83	7.86	7.84	0.09	1.1	25
		N3H		-0.81	7.34	2,7	7.26	7.34	7.33	0.08	1.1	26
P_{PO4}	µg/l	A1P		0.50	9.95	10	10.20	9.90	9.83	0.59	6.1	15
	µg/l	B2P		0.29	27.5	15	28.1	27.4	27.5	1.0	3.7	16
	µg/l	N3P		-0.51	27.3	10	26.6	27.0	27.3	1.2	4.2	16
$P_{PO4,\ dissolved}$	µg/l	B4P		0.05	27.5	15	27.6	27.6	27.4	1.6	5.7	15
	µg/l	N5P		-0.65	26.2	10	25.4	26.2	26.3	1.1	4.3	14
P_{tot}	µg/l	A1P		0.47	19.8	15	20.5	19.4	19.5	0.8	4.0	16
	µg/l	B2P		-0.08	33.6	15	33.4	33.3	33.1	1.9	5.7	18
	µg/l	N3P		-0.39	44.0	15	42.7	43.5	43.8	2.2	5.0	19
$P_{tot,\ dissolved}$	µg/l	B4P		0.32	30.9	15	31.7	30.9	30.9	1.4	4.7	14
	µg/l	N5P		0.26	33.1	15	33.8	33.1	33.1	1.3	3.8	12

Participant 22												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Conductivity 25	mS/m	A1J		-0.48	9.95	5	9.83	9.93	9.94	0.14	1.4	23
	mS/m	B2H		0.05	873	5	874	871	872	12	1.3	22
	mS/m	N3H		-0.31	13.0	5	12.9	13.0	13.0	0.2	1.5	24
N_{NH4}	µg/l	A1N		4.81	20.6	20	30.5	20.7	20.7	1.9	9.1	14
	µg/l	B2N		19.32	32.8	25	112.0	31.4	32.9	4.3	13.2	17
	µg/l	N3N		1.36	202	20	230	201	202	13	6.4	18
$N_{NO2+NO3}$	µg/l	A1N		-0.68	185	8	180	186	185	7	3.6	15
	µg/l	B2N		-0.37	161	15	157	160	160	13	8.3	17
	µg/l	N3N		-0.89	164	15	153	164	163	11	6.5	16
N_{tot}	µg/l	A1N		-0.51	249	15	240	260	257	18	7.0	17
	µg/l	B2N		-0.05	440	20	438	438	440	37	8.4	17
	µg/l	N3N		0.19	751	15	762	749	747	25	3.3	16
pH		A1H		0.00	7.27	2,7	7.27	7.28	7.27	0.06	0.9	26
		B2H		0.39	7.84	2,6	7.88	7.86	7.84	0.09	1.1	25
		N3H		0.71	7.34	2,7	7.41	7.34	7.33	0.08	1.1	26
P_{PO4}	µg/l	A1P		-0.66	9.95	10	9.62	9.90	9.83	0.59	6.1	15
	µg/l	B2P		-0.12	27.5	15	27.3	27.4	27.5	1.0	3.7	16
	µg/l	N3P		-0.33	27.3	10	26.9	27.0	27.3	1.2	4.2	16

Participant 22												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
P_{tot}	µg/l	A1P		0.57	19.8	15	20.7	19.4	19.5	0.8	4.0	16
	µg/l	B2P		0.69	33.6	15	35.4	33.3	33.1	1.9	5.7	18
	µg/l	N3P		0.83	44.0	15	46.8	43.5	43.8	2.2	5.0	19

Participant 23												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Alkalinity	mmol/l	B2A		0.06	1.39	7,5	1.39	1.39	1.38	0.04	3.0	19
pH		B2H		0.10	7.84	2,6	7.85	7.86	7.84	0.09	1.1	25

Participant 24												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Alkalinity	mmol/l	B2A		0.08	1.39	7,5	1.39	1.39	1.38	0.04	3.0	19
	mmol/l	N3A		-0.15	0.49	7,5	0.49	0.49	0.49	0.02	3.7	19
Conductivity 25	mS/m	B2H		-0.27	873	5	867	871	872	12	1.3	22
	mS/m	N3H		-0.31	13.0	5	12.9	13.0	13.0	0.2	1.5	24
pH		B2H		-1.08	7.84	2,6	7.73	7.86	7.84	0.09	1.1	25
		N3H		0.20	7.34	2,7	7.36	7.34	7.33	0.08	1.1	26

Participant 25												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
N_{NH4}	µg/l	A1N		0.12	20.6	20	20.9	20.7	20.7	1.9	9.1	14
	µg/l	B2N		-0.73	32.8	25	29.8	31.4	32.9	4.3	13.2	17
$N_{NO2+NO3}$	µg/l	A1N		-0.93	185	8	178	186	185	7	3.6	15
	µg/l	B2N		-0.90	161	15	150	160	160	13	8.3	17
N_{tot}	µg/l	A1N		0.58	249	15	260	260	257	18	7.0	17
	µg/l	B2N		0.45	440	20	460	438	440	37	8.4	17
pH		A1H		0.82	7.27	2,7	7.35	7.28	7.27	0.06	0.9	26
		B2H		-0.59	7.84	2,6	7.78	7.86	7.84	0.09	1.1	25
P_{PO4}	µg/l	A1P		0.71	9.95	10	10.31	9.90	9.83	0.59	6.1	15
	µg/l	B2P		0.41	27.5	15	28.3	27.4	27.5	1.0	3.7	16
$P_{PO4,\ dissolved}$	µg/l	B4P		0.43	27.5	15	28.4	27.6	27.4	1.6	5.7	15
P_{tot}	µg/l	A1P		-0.25	19.8	15	19.4	19.4	19.5	0.8	4.0	16
	µg/l	B2P		-0.21	33.6	15	33.1	33.3	33.1	1.9	5.7	18
$P_{tot,\ dissolved}$	µg/l	B4P		0.98	30.9	15	33.2	30.9	30.9	1.4	4.7	14

Participant 26												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Alkalinity	mmol/l	A1A		1.00	0.16	7,5	0.17	0.16	0.16	0.01	4.2	15
	mmol/l	B2A		0.19	1.39	7,5	1.40	1.39	1.38	0.04	3.0	19
	mmol/l	N3A		0.71	0.49	7,5	0.50	0.49	0.49	0.02	3.7	19
Conductivity 25	mS/m	A1J		-1.01	9.95	5	9.70	9.93	9.94	0.14	1.4	23
	mS/m	B2H		0.92	873	5	893	871	872	12	1.3	22
	mS/m	N3H		-0.92	13.0	5	12.7	13.0	13.0	0.2	1.5	24
N_{NH4}	µg/l	A1N		-0.46	20.6	20	19.7	20.7	20.7	1.9	9.1	14
	µg/l	B2N		-1.76	32.8	25	25.6	31.4	32.9	4.3	13.2	17
	µg/l	N3N		-0.67	202	20	189	201	202	13	6.4	18
$N_{NO2+NO3}$	µg/l	A1N			185	8	*189**	186	185	7	3.6	15
	µg/l	B2N			161	15	*165**	160	160	13	8.3	17
	µg/l	N3N			164	15	*167**	164	163	11	6.5	16

Participant 26												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
N_{tot}	µg/l	A1N			249	15	*270**	260	257	18	7.0	17
	µg/l	B2N			440	20	*483**	438	440	37	8.4	17
	µg/l	N3N			751	15	*822**	749	747	25	3.3	16
pH		A1H		-0.71	7.27	2,7	7.20	7.28	7.27	0.06	0.9	26
		B2H		0.59	7.84	2,6	7.90	7.86	7.84	0.09	1.1	25
		N3H		0.61	7.34	2,7	7.40	7.34	7.33	0.08	1.1	26
P_{PO4}	µg/l	A1P		-1.01	9.95	10	9.45	9.90	9.83	0.59	6.1	15
	µg/l	B2P		-0.34	27.5	15	26.8	27.4	27.5	1.0	3.7	16
	µg/l	N3P		-0.44	27.3	10	26.7	27.0	27.3	1.2	4.2	16
$P_{PO4,\ dissolved}$	µg/l	B4P			27.5	15	*26,2**	27.6	27.4	1.6	5.7	15
	µg/l	N5P			26.2	10	*24,7**	26.2	26.3	1.1	4.3	14
P_{tot}	µg/l	A1P			19.8	15	*18,7**	19.4	19.5	0.8	4.0	16
	µg/l	B2P			33.6	15	*32,3**	33.3	33.1	1.9	5.7	18
	µg/l	N3P		-0.55	44.0	15	42.2	43.5	43.8	2.2	5.0	19
$P_{tot,\ dissolved}$	µg/l	B4P			30.9	15	*31,3**	30.9	30.9	1.4	4.7	14
	µg/l	N5P			33.1	15	*37,3**	33.1	33.1	1.3	3.8	12

** Participant did not report the requested replicate result*

Participant 27												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Alkalinity	mmol/l	A1A		-1.50	0.16	7,5	0.15	0.16	0.16	0.01	4.2	15
	mmol/l	B2A		-1.73	1.39	7,5	1.30	1.39	1.38	0.04	3.0	19
	mmol/l	N3A		-1.31	0.49	7,5	0.47	0.49	0.49	0.02	3.7	19
Conductivity 25	mS/m	A1J		-0.04	9.95	5	9.94	9.93	9.94	0.14	1.4	23
	mS/m	B2H		-0.41	873	5	864	871	872	12	1.3	22
	mS/m	N3H		0.00	13.0	5	13.0	13.0	13.0	0.2	1.5	24
N_{NH4}	µg/l	A1N		0.07	20.6	20	20.8	20.7	20.7	1.9	9.1	14
	µg/l	B2N		-0.37	32.8	25	31.3	31.4	32.9	4.3	13.2	17
	µg/l	N3N		-0.10	202	20	200	201	202	13	6.4	18
$N_{NO2+NO3}$	µg/l	A1N		-2.36	185	8	168	186	185	7	3.6	15
	µg/l	B2N		-2.57	161	15	130	160	160	13	8.3	17
	µg/l	N3N		-1.42	164	15	147	164	163	11	6.5	16
N_{tot}	µg/l	A1N		0.72	249	15	263	260	257	18	7.0	17
	µg/l	B2N		0.34	440	20	455	438	440	37	8.4	17
	µg/l	N3N		0.73	751	15	792	749	747	25	3.3	16
pH		A1H		-0.31	7.27	2,7	7.24	7.28	7.27	0.06	0.9	26
		B2H		-1.28	7.84	2,6	7.71	7.86	7.84	0.09	1.1	25
		N3H		-1.31	7.34	2,7	7.21	7.34	7.33	0.08	1.1	26
P_{PO4}	µg/l	A1P		-1.05	9.95	10	9.43	9.90	9.83	0.59	6.1	15
	µg/l	B2P		-0.22	27.5	15	27.1	27.4	27.5	1.0	3.7	16
	µg/l	N3P		-0.22	27.3	10	27.0	27.0	27.3	1.2	4.2	16
$P_{PO4,\ dissolved}$	µg/l	B4P		-0.22	27.5	15	27.1	27.6	27.4	1.6	5.7	15
	µg/l	N5P		-0.42	26.2	10	25.7	26.2	26.3	1.1	4.3	14
P_{tot}	µg/l	A1P		-0.47	19.8	15	19.1	19.4	19.5	0.8	4.0	16
	µg/l	B2P		-0.04	33.6	15	33.5	33.3	33.1	1.9	5.7	18
	µg/l	N3P		-0.17	44.0	15	43.5	43.5	43.8	2.2	5.0	19
$P_{tot,\ dissolved}$	µg/l	B4P		0.67	30.9	15	32.5	30.9	30.9	1.4	4.7	14
	µg/l	N5P		0.50	33.1	15	34.4	33.1	33.1	1.3	3.8	12

Participant 28												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Alkalinity	mmol/l	A1A		0.67	0.16	7,5	0.16	0.16	0.16	0.01	4.2	15
	mmol/l	B2A		-0.38	1.39	7,5	1.37	1.39	1.38	0.04	3.0	19
	mmol/l	N3A		0.05	0.49	7,5	0.49	0.49	0.49	0.02	3.7	19
Conductivity 25	mS/m	A1J		-0.80	9.95	5	9.75	9.93	9.94	0.14	1.4	23
	mS/m	B2H		1.01	873	5	895	871	872	12	1.3	22
	mS/m	N3H		-1.29	13.0	5	12.6	13.0	13.0	0.2	1.5	24
N_{NH4}	µg/l	A1N		0.15	20.6	20	20.9	20.7	20.7	1.9	9.1	14
	µg/l	B2N		-0.90	32.8	25	29.1	31.4	32.9	4.3	13.2	17
	µg/l	N3N		0.05	202	20	203	201	202	13	6.4	18
$N_{NO2+NO3}$	µg/l	A1N		0.00	185	8	185	186	185	7	3.6	15
	µg/l	B2N		0.00	161	15	161	160	160	13	8.3	17
	µg/l	N3N		0.04	164	15	165	164	163	11	6.5	16
N_{tot}	µg/l	A1N		0.19	249	15	253	260	257	18	7.0	17
	µg/l	B2N		-1.67	440	20	367	438	440	37	8.4	17
	µg/l	N3N		-1.07	751	15	691	749	747	25	3.3	16
pH		A1H		0.51	7.27	2,7	7.32	7.28	7.27	0.06	0.9	26
		B2H		-1.77	7.84	2,6	7.66	7.86	7.84	0.09	1.1	25
		N3H		1.01	7.34	2,7	7.44	7.34	7.33	0.08	1.1	26
P_{PO4}	µg/l	A1P		-1.01	9.95	10	9.45	9.90	9.83	0.59	6.1	15
	µg/l	B2P		-0.36	27.5	15	26.8	27.4	27.5	1.0	3.7	16
	µg/l	N3P		-0.73	27.3	10	26.3	27.0	27.3	1.2	4.2	16
$P_{PO4, dissolved}$	µg/l	B4P		-0.61	27.5	15	26.3	27.6	27.4	1.6	5.7	15
	µg/l	N5P		-0.92	26.2	10	25.0	26.2	26.3	1.1	4.3	14
P_{tot}	µg/l	A1P		-0.29	19.8	15	19.4	19.4	19.5	0.8	4.0	16
	µg/l	B2P		-1.13	33.6	15	30.8	33.3	33.1	1.9	5.7	18
	µg/l	N3P		-1.32	44.0	15	39.7	43.5	43.8	2.2	5.0	19
$P_{tot, dissolved}$	µg/l	B4P		-0.93	30.9	15	28.8	30.9	30.9	1.4	4.7	14
	µg/l	N5P		-0.28	33.1	15	32.4	33.1	33.1	1.3	3.8	12

Participant 29												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Alkalinity	mmol/l	A1A		-22.92	0.16	7,5	0.02	0.16	0.16	0.01	4.2	15
	mmol/l	B2A		-26.15	1.39	7,5	0.03	1.39	1.38	0.04	3.0	19
Conductivity 25	mS/m	A1J		0.60	9.95	5	10.10	9.93	9.94	0.14	1.4	23
	mS/m	B2H		-0.23	873	5	868	871	872	12	1.3	22
N_{NH4}	µg/l	A1N		3.13	20.6	20	27.1	20.7	20.7	1.9	9.1	14
	µg/l	B2N		-0.34	32.8	25	31.4	31.4	32.9	4.3	13.2	17
$N_{NO2+NO3}$	µg/l	A1N		0.54	185	8	189	186	185	7	3.6	15
	µg/l	B2N		0.20	161	15	163	160	160	13	8.3	17
N_{tot}	µg/l	A1N		1.48	249	15	277	260	257	18	7.0	17
	µg/l	B2N		0.17	440	20	447	438	440	37	8.4	17
pH		A1H		-0.92	7.27	2,7	7.18	7.28	7.27	0.06	0.9	26
P_{PO4}	µg/l	A1P		10.89	9.95	10	15.37	9.90	9.83	0.59	6.1	15
	µg/l	B2P		2.03	27.5	15	31.7	27.4	27.5	1.0	3.7	16
$P_{PO4,\ dissolved}$	µg/l	B4P		0.97	27.5	15	29.5	27.6	27.4	1.6	5.7	15
P_{tot}	µg/l	A1P		-2.98	19.8	15	15.4	19.4	19.5	0.8	4.0	16
	µg/l	B2P		5.45	33.6	15	47.3	33.3	33.1	1.9	5.7	18
$P_{tot,\ dissolved}$	µg/l	B4P		-0.60	30.9	15	29.5	30.9	30.9	1.4	4.7	14

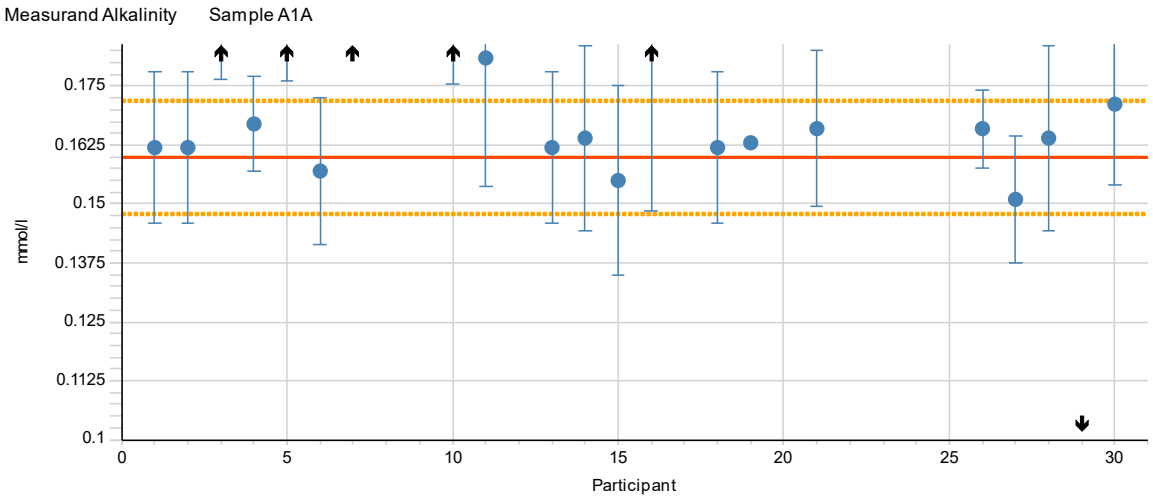
Participant 30												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Alkalinity	mmol/l	A1A		1.87	0.16	7,5	0.17	0.16	0.16	0.01	4.2	15
	mmol/l	B2A		1.31	1.39	7,5	1.46	1.39	1.38	0.04	3.0	19
	mmol/l	N3A		1.89	0.49	7,5	0.52	0.49	0.49	0.02	3.7	19
Conductivity 25	mS/m	A1J		-0.68	9.95	5	9.78	9.93	9.94	0.14	1.4	23
	mS/m	B2H		-0.29	873	5	867	871	872	12	1.3	22
	mS/m	N3H		-0.74	13.0	5	12.8	13.0	13.0	0.2	1.5	24
N_{NH4}	µg/l	A1N		-1.75	20.6	20	17.0	20.7	20.7	1.9	9.1	14
	µg/l	B2N		0.14	32.8	25	33.4	31.4	32.9	4.3	13.2	17
	µg/l	N3N		0.23	202	20	207	201	202	13	6.4	18
$N_{NO2+NO3}$	µg/l	A1N		-0.73	185	8	180	186	185	7	3.6	15
	µg/l	B2N		-1.67	161	15	141	160	160	13	8.3	17
	µg/l	N3N		-1.92	164	15	140	164	163	11	6.5	16
N_{tot}	µg/l	A1N		-0.39	249	15	242	260	257	18	7.0	17
	µg/l	B2N		-0.07	440	20	437	438	440	37	8.4	17
	µg/l	N3N		-0.28	751	15	735	749	747	25	3.3	16
pH		A1H		-0.38	7.27	2,7	7.23	7.28	7.27	0.06	0.9	26
		B2H		0.17	7.84	2,6	7.86	7.86	7.84	0.09	1.1	25
		N3H		0.31	7.34	2,7	7.37	7.34	7.33	0.08	1.1	26
P_{PO4}	µg/l	A1P		5.32	9.95	10	12.60	9.90	9.83	0.59	6.1	15
	µg/l	B2P		-0.36	27.5	15	26.8	27.4	27.5	1.0	3.7	16
	µg/l	N3P		-0.68	27.3	10	26.4	27.0	27.3	1.2	4.2	16
$P_{PO4,\ dissolved}$	µg/l	B4P		-0.50	27.5	15	26.5	27.6	27.4	1.6	5.7	15
	µg/l	N5P		-0.55	26.2	10	25.5	26.2	26.3	1.1	4.3	14
P_{tot}	µg/l	A1P		-0.97	19.8	15	18.4	19.4	19.5	0.8	4.0	16
	µg/l	B2P		-1.01	33.6	15	31.1	33.3	33.1	1.9	5.7	18
	µg/l	N3P		-0.62	44.0	15	42.0	43.5	43.8	2.2	5.0	19
$P_{tot,\ dissolved}$	µg/l	B4P		-0.22	30.9	15	30.4	30.9	30.9	1.4	4.7	14
	µg/l	N5P		0.63	33.1	15	34.7	33.1	33.1	1.3	3.8	12

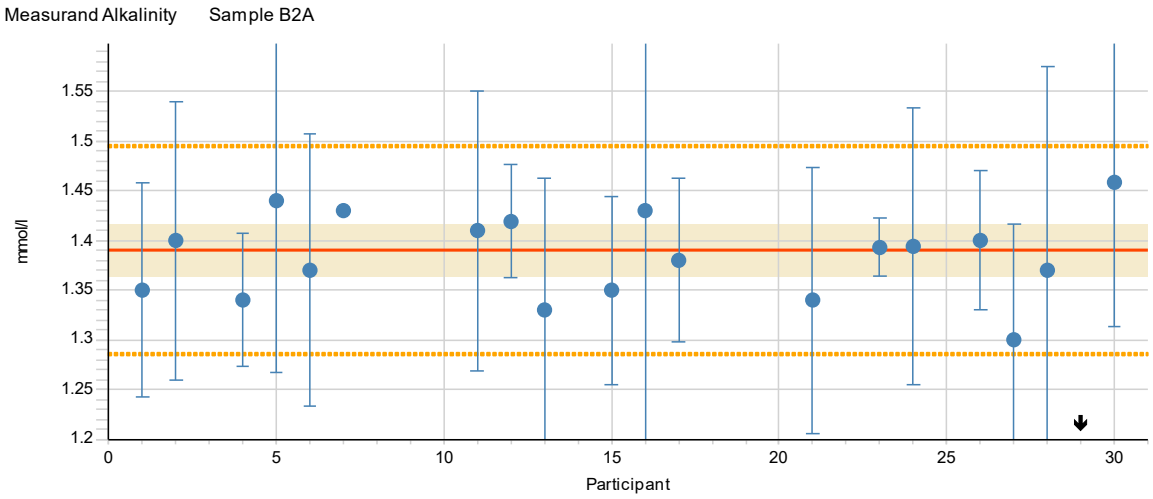
Participant 31												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Conductivity 25	mS/m	B2H		-0.46	873	5	863	871	872	12	1.3	22
	mS/m	N3H		0.62	13.0	5	13.2	13.0	13.0	0.2	1.5	24
N_{NH4}	µg/l	B2N		9.68	32.8	25	72.5	31.4	32.9	4.3	13.2	17
	µg/l	N3N		0.51	202	20	212	201	202	13	6.4	18
$N_{NO2+NO3}$	µg/l	B2N		-1.14	161	15	147	160	160	13	8.3	17
	µg/l	N3N		0.02	164	15	164	164	163	11	6.5	16
N_{tot}	µg/l	B2N		-5.01	440	20	220	438	440	37	8.4	17
	µg/l	N3N		-6.65	751	15	377	749	747	25	3.3	16
pH		B2H		-0.20	7.84	2,6	7.82	7.86	7.84	0.09	1.1	25
		N3H		1.11	7.34	2,7	7.45	7.34	7.33	0.08	1.1	26
P_{PO4}	µg/l	B2P		-1.07	27.5	15	25.3	27.4	27.5	1.0	3.7	16
	µg/l	N3P		-1.36	27.3	10	25.5	27.0	27.3	1.2	4.2	16
$P_{PO4,\ dissolved}$	µg/l	B4P		-1.02	27.5	15	25.4	27.6	27.4	1.6	5.7	15
	µg/l	N5P		0.34	26.2	10	26.7	26.2	26.3	1.1	4.3	14
P_{tot}	µg/l	B2P		2.18	33.6	15	39.1	33.3	33.1	1.9	5.7	18
	µg/l	N3P		2.29	44.0	15	51.6	43.5	43.8	2.2	5.0	19
$P_{tot,\ dissolved}$	µg/l	B4P		6.08	30.9	15	45.0	30.9	30.9	1.4	4.7	14
	µg/l	N5P		5.84	33.1	15	47.6	33.1	33.1	1.3	3.8	12

APPENDIX 9: Results of participants and their uncertainties

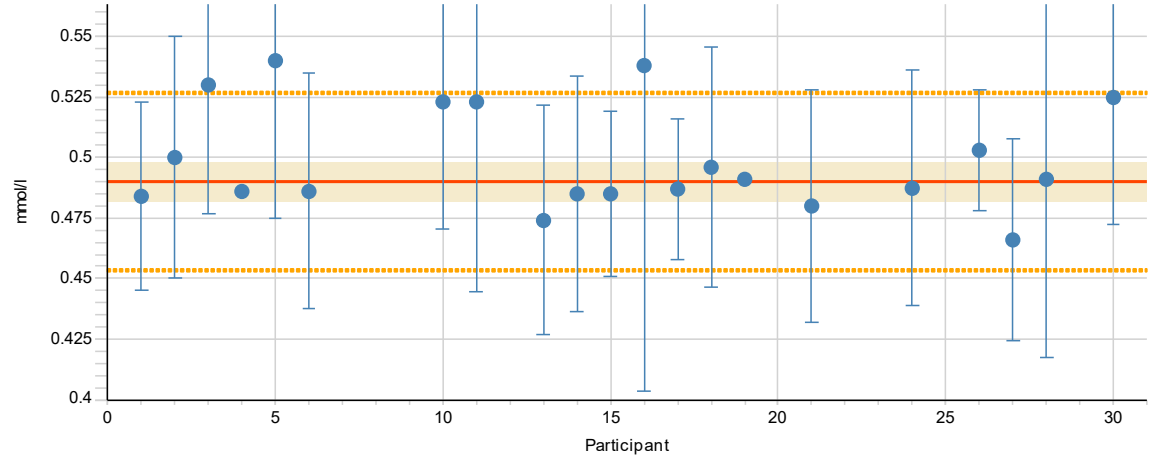
In figures:

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

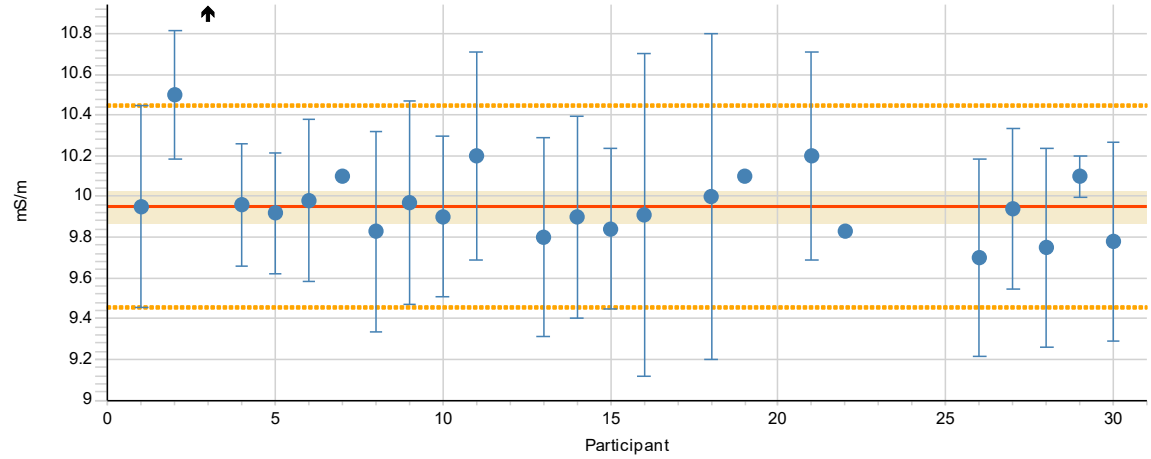




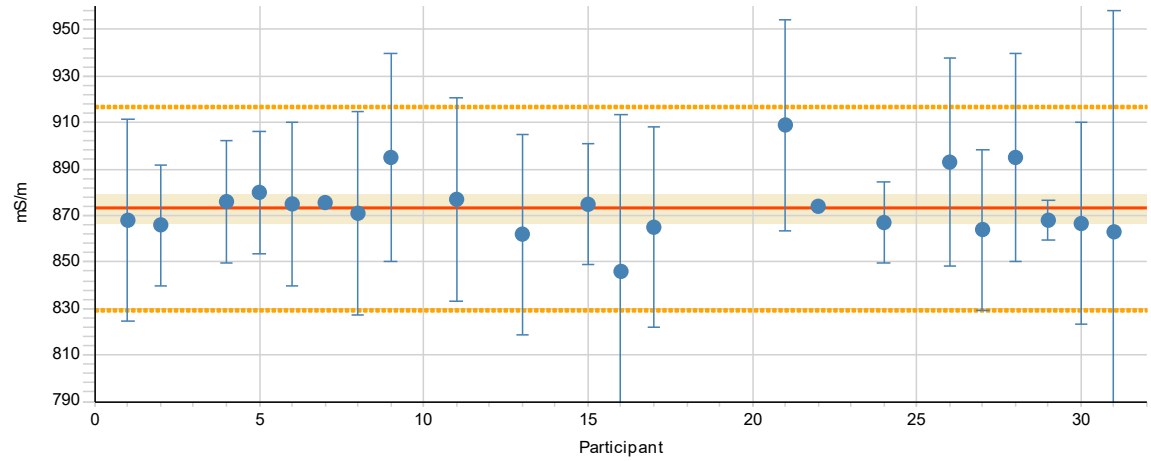
Measurand Alkalinity Sample N3A



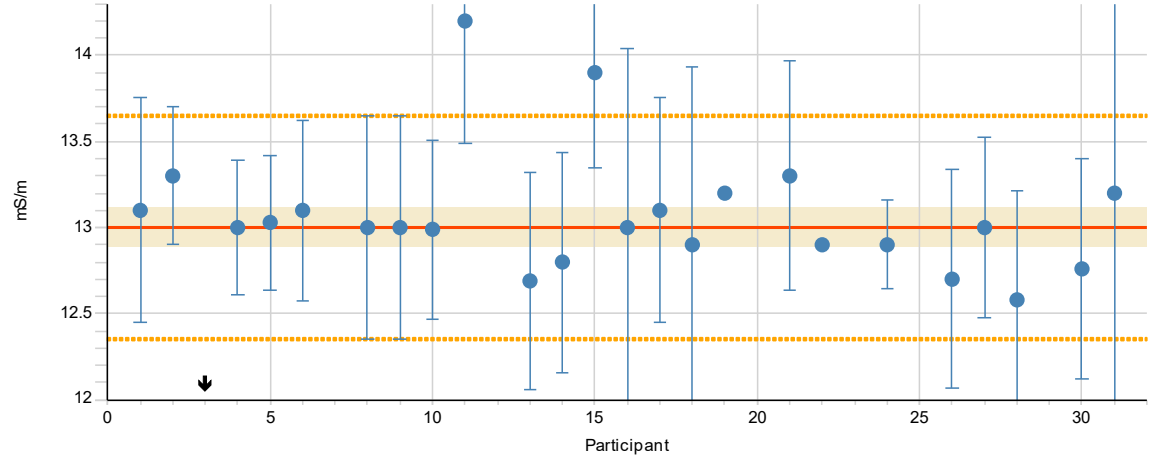
Measurand Conductivity 25 Sample A1J



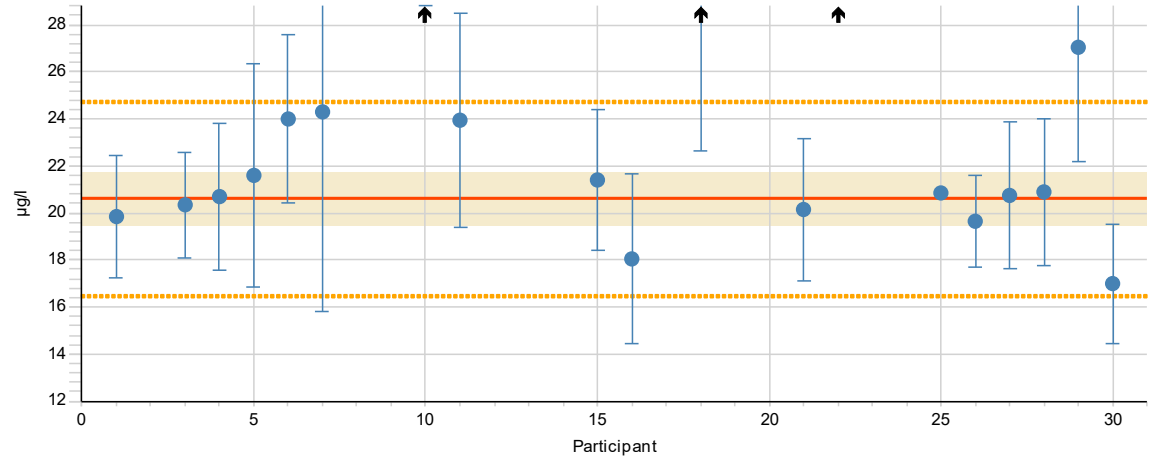
Measurand Conductivity 25 Sample B2H



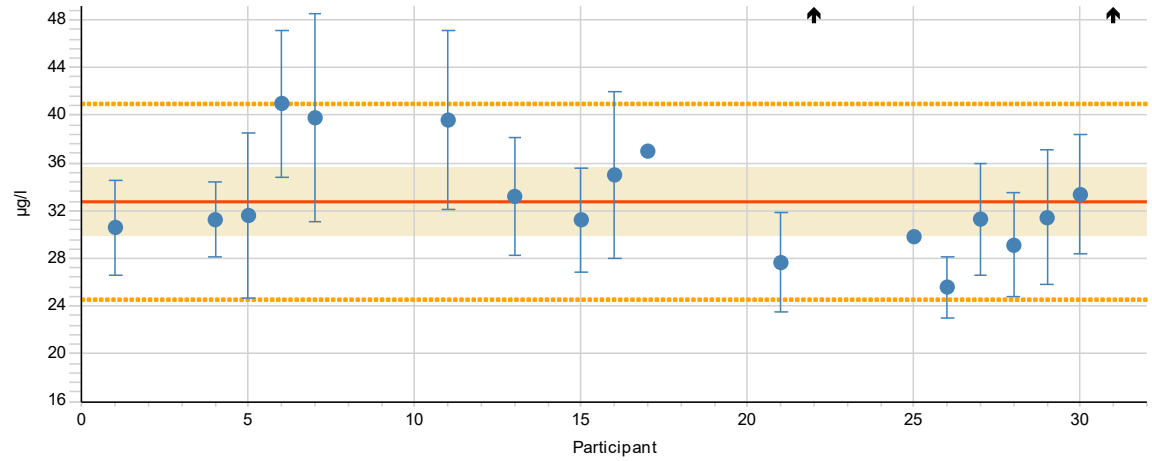
Measurand Conductivity 25 Sample N3H

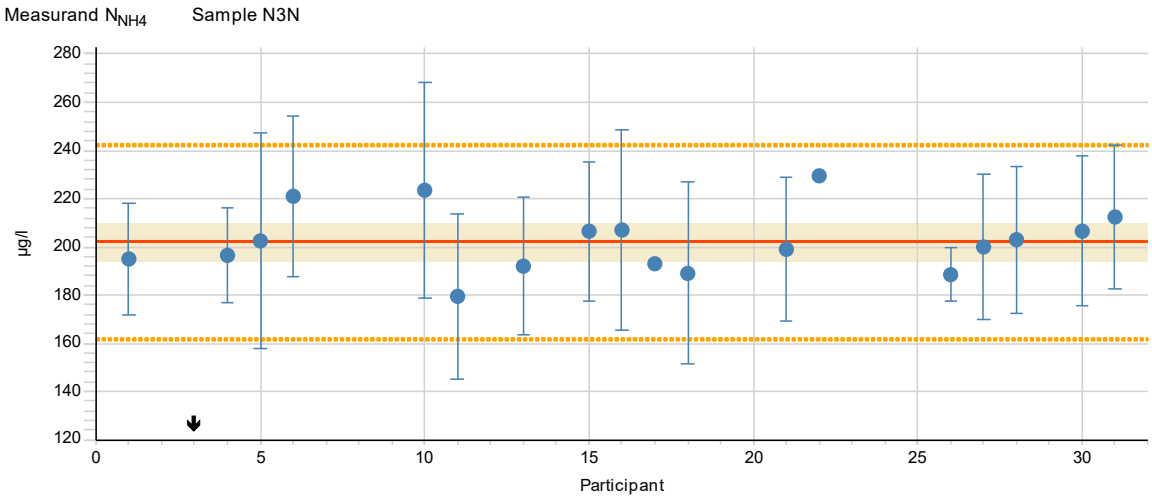


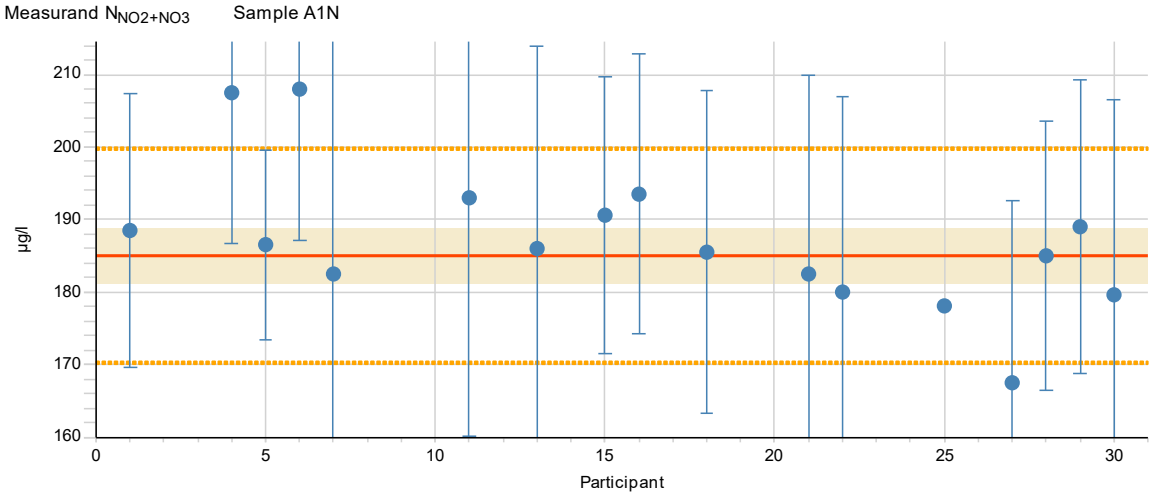
Measurand N_{NH4} Sample A1N

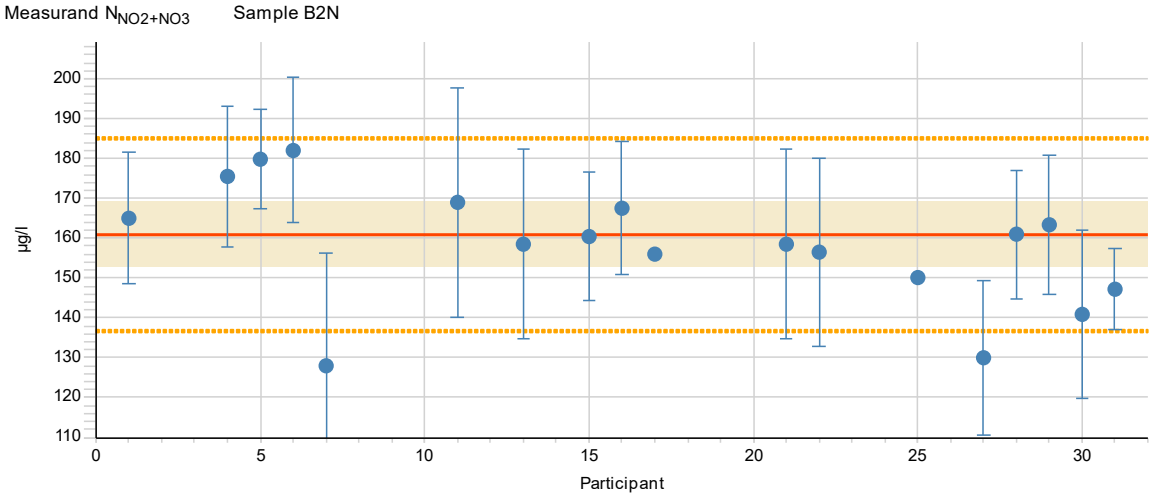


Measurand N_{NH4} Sample B2N

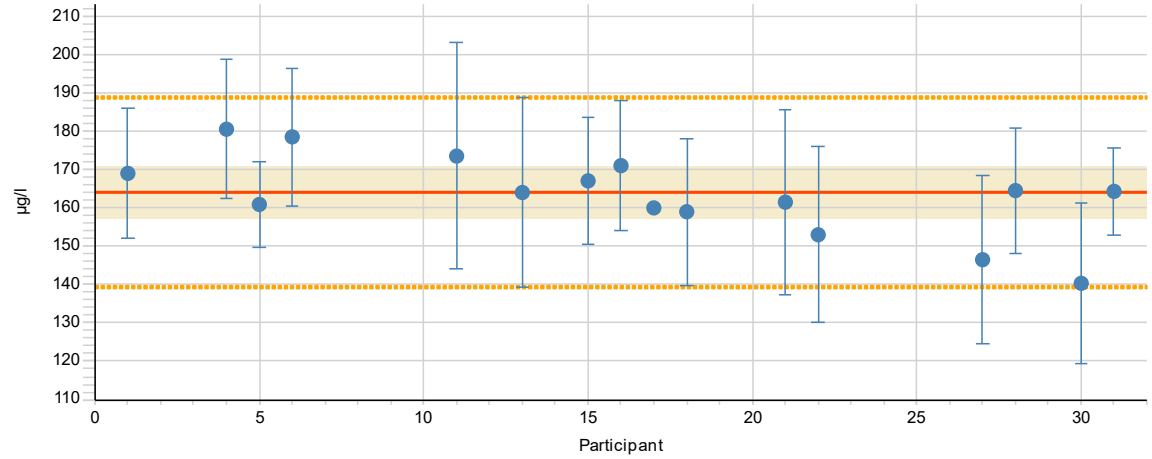



Measurand N_{NH4} Sample N3N
µg/l
280
260
240
220
200
180
160
140
120
0
5
10
15
20
25
30
Participant

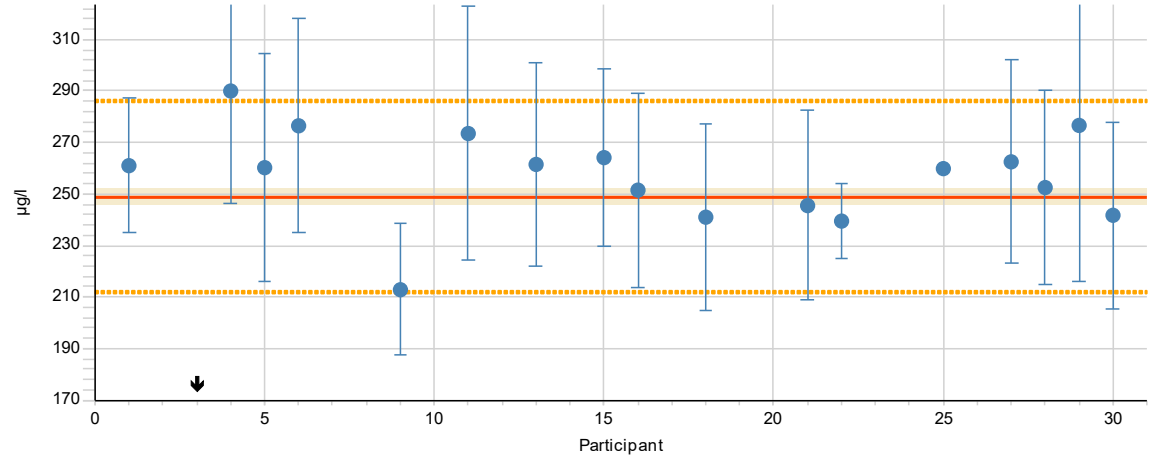

Measurand $N_{NO2+NO3}$ Sample A1N
µg/l
210
200
190
180
170
160
0
5
10
15
20
25
30
Participant


Measurand $N_{NO2+NO3}$ Sample B2N
µg/l
200
190
180
170
160
150
140
130
120
110
0
5
10
15
20
25
30
Participant

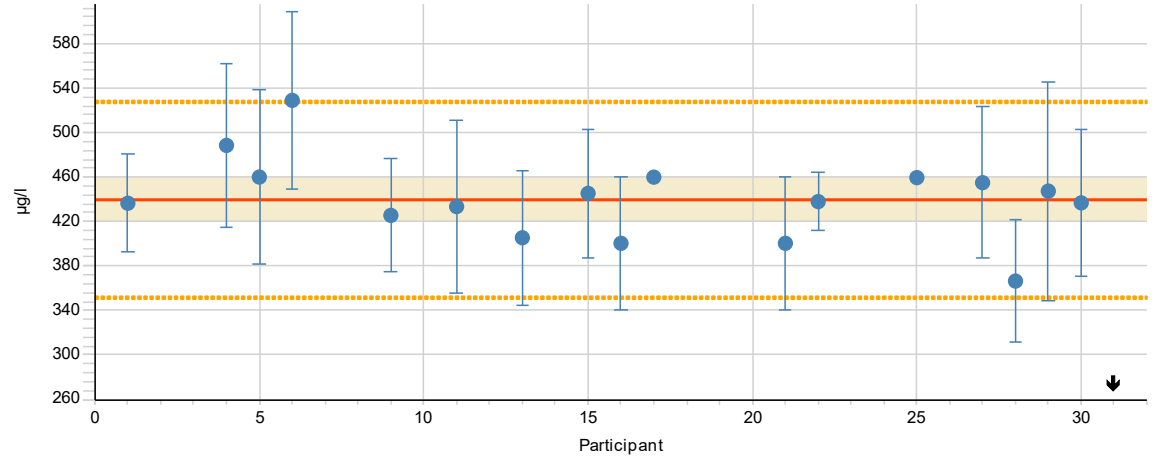
Measurand $N_{NO2+NO3}$ Sample N3N



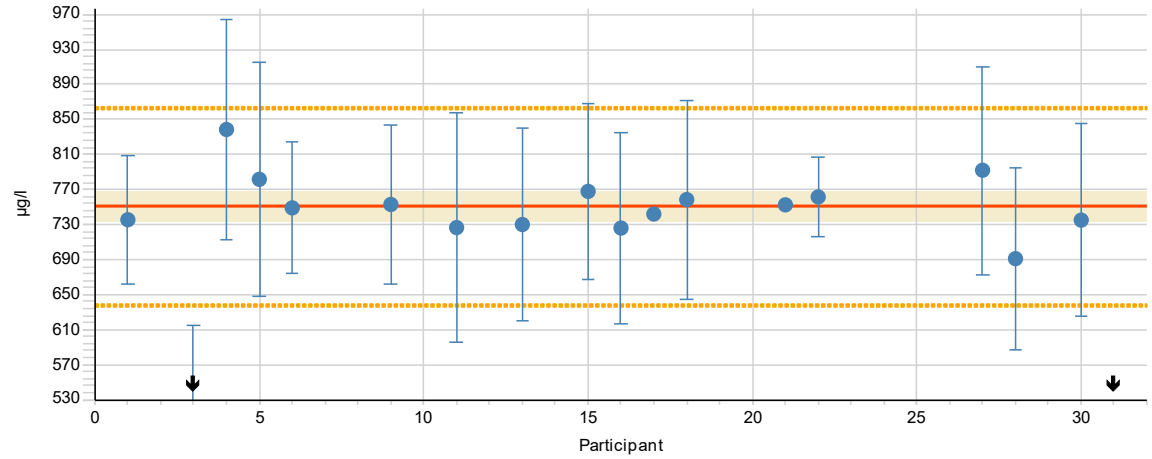
Measurand N_{tot} Sample A1N



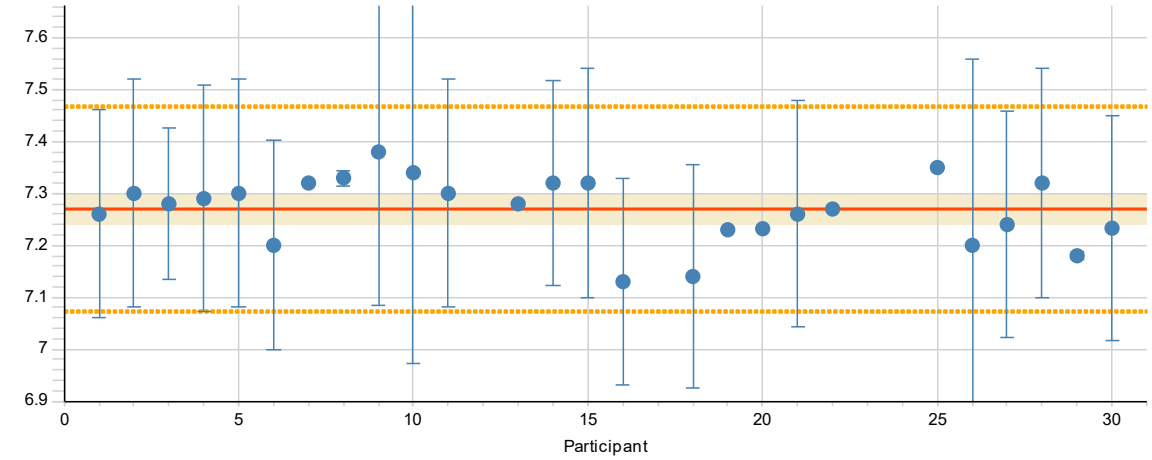
Measurand N_{tot} Sample B2N



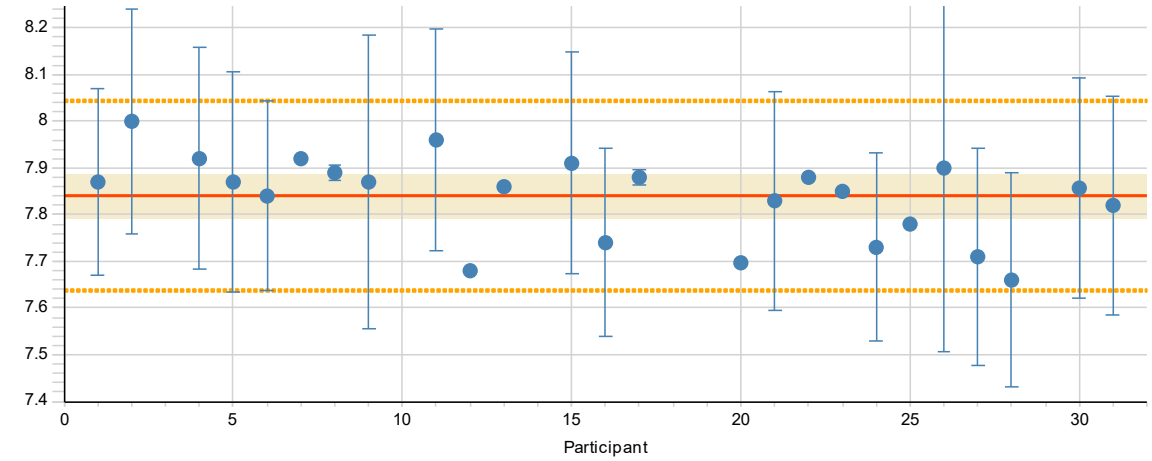
Measurand N_{tot} Sample N3N



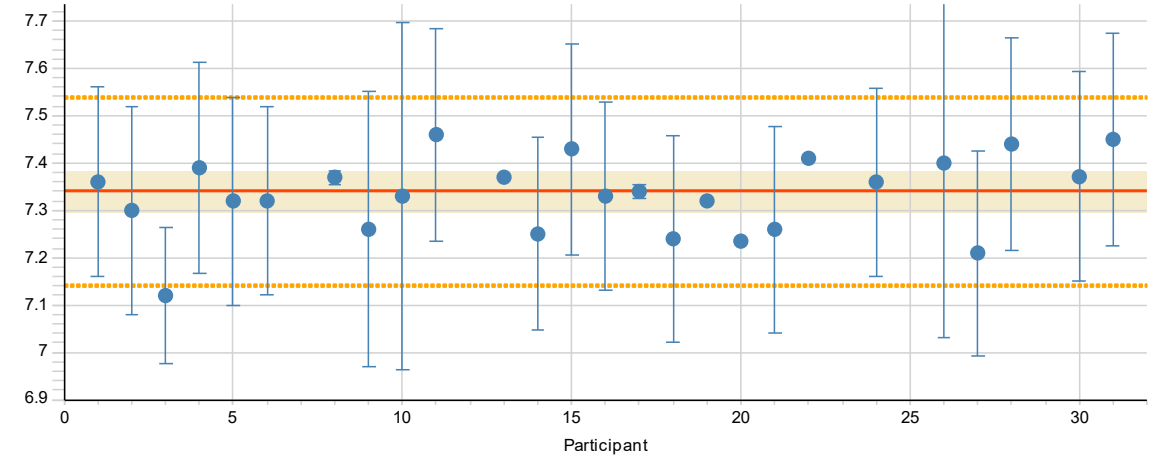
Measurand pH Sample A1H



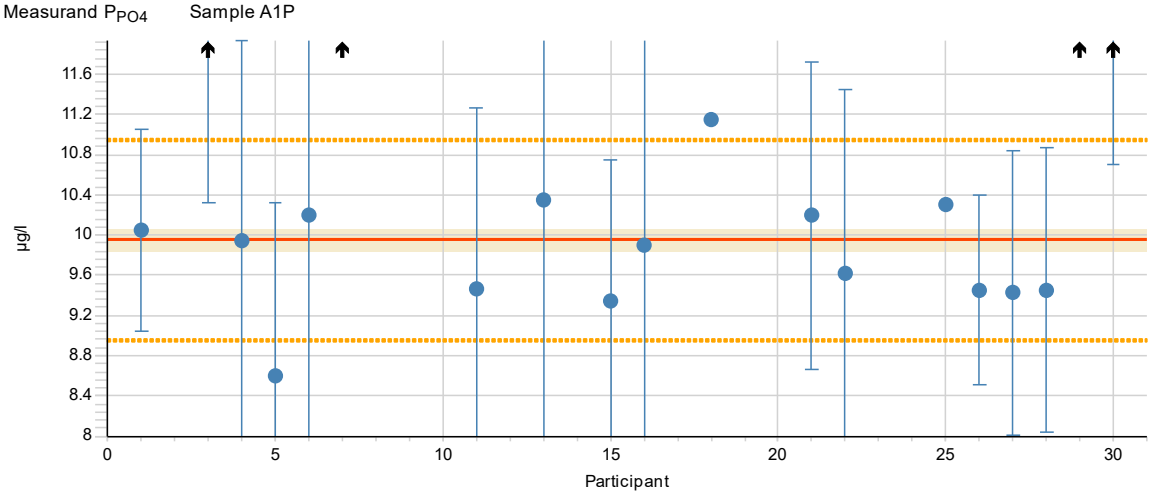
Measurand pH Sample B2H



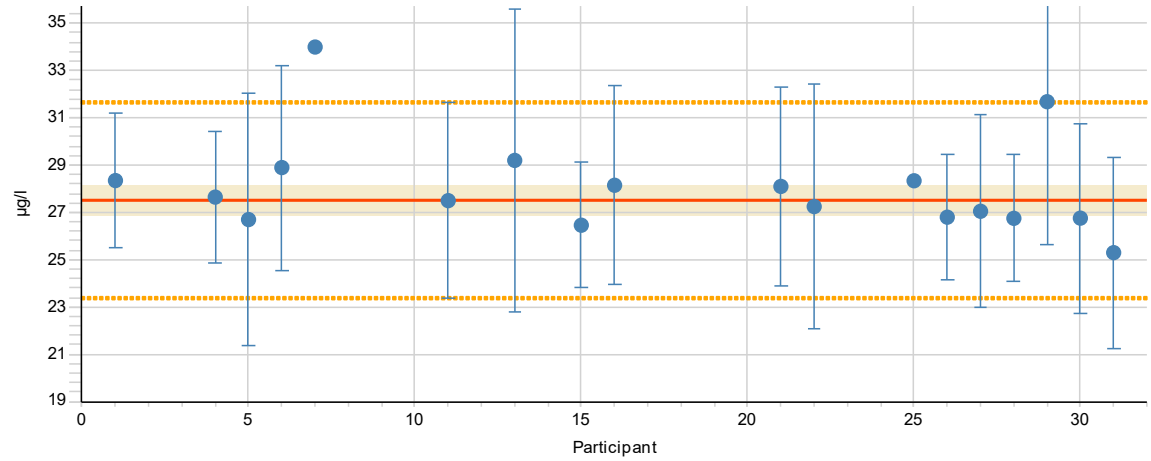
Measurand pH Sample N3H

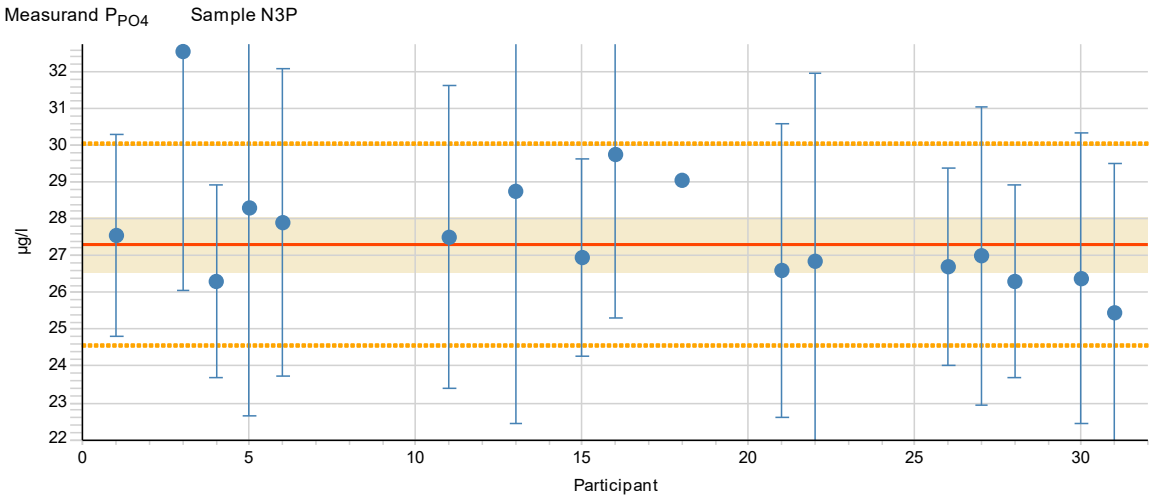


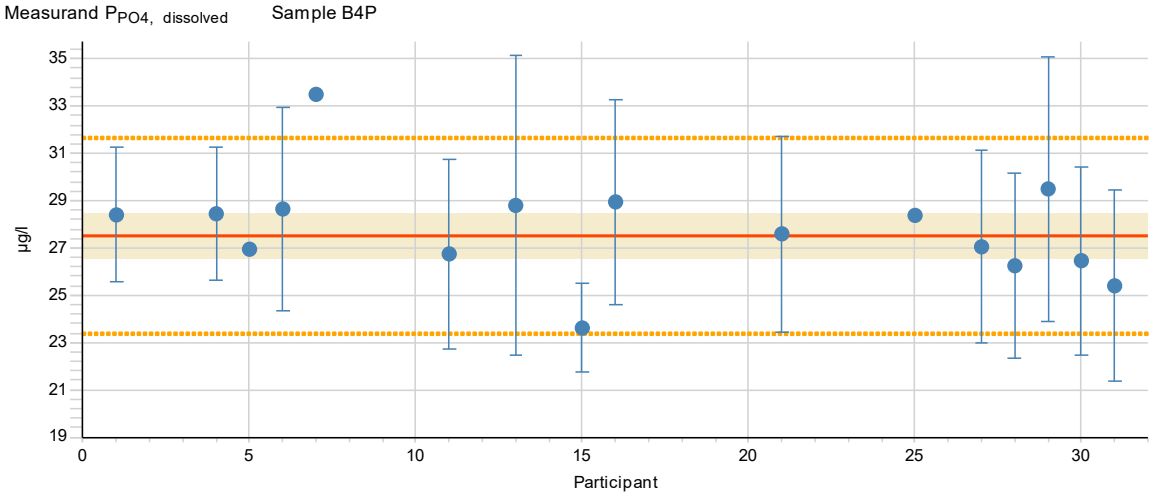
Measurand P_{PO4} Sample A1P

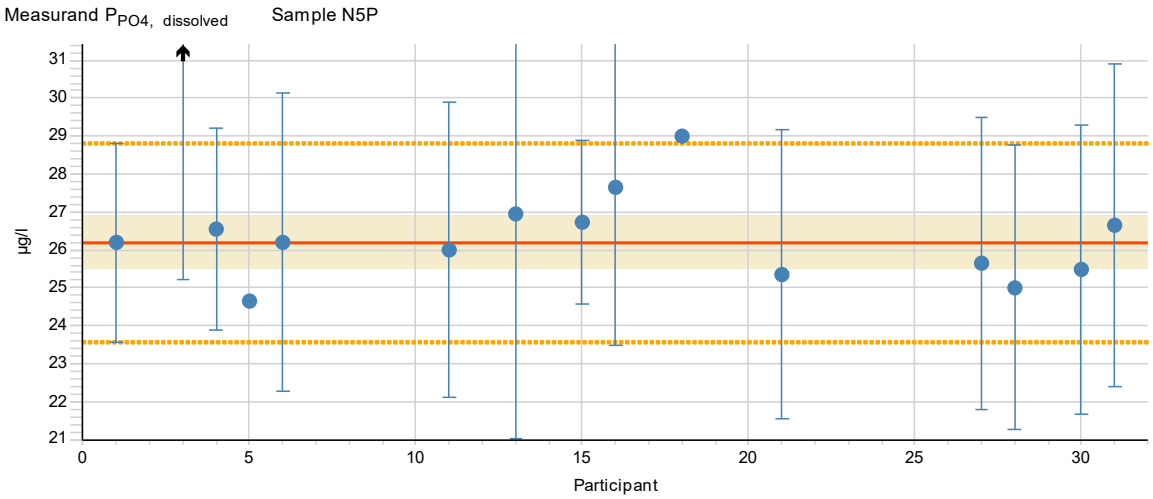


Measurand P_{PO4} Sample B2P

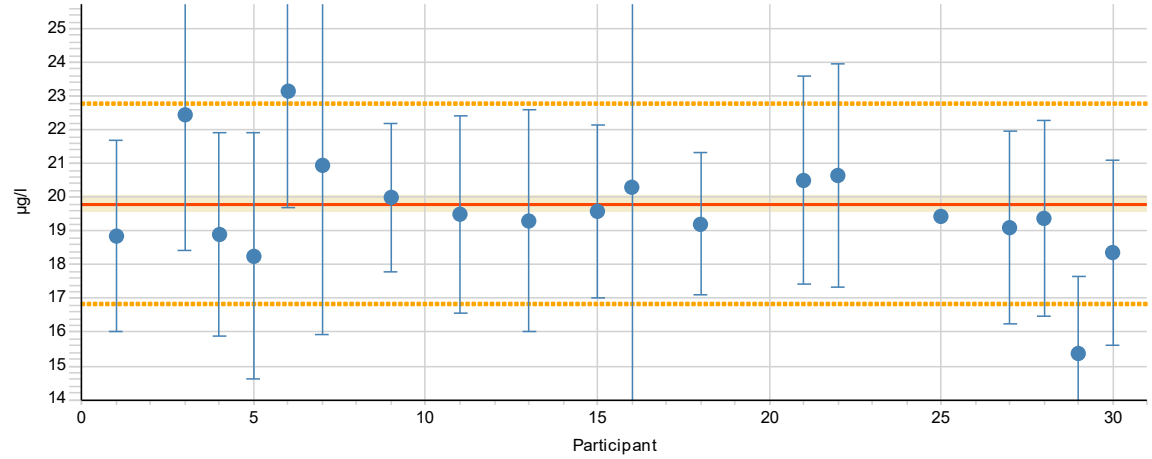



Measurand P_{PO4} Sample N3P
µg/l
Participant

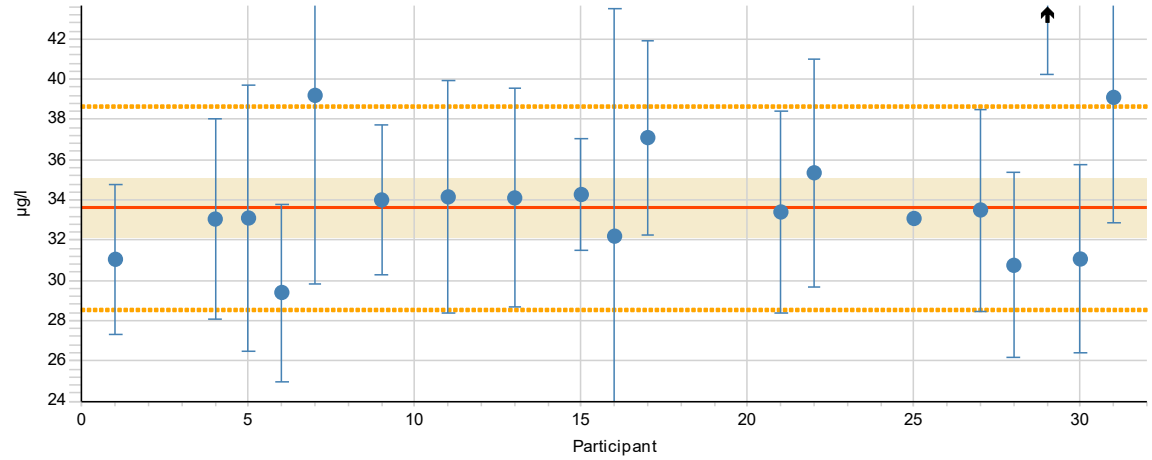

Measurand $P_{PO4,\ dissolved}$ Sample B4P
µg/l
Participant


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

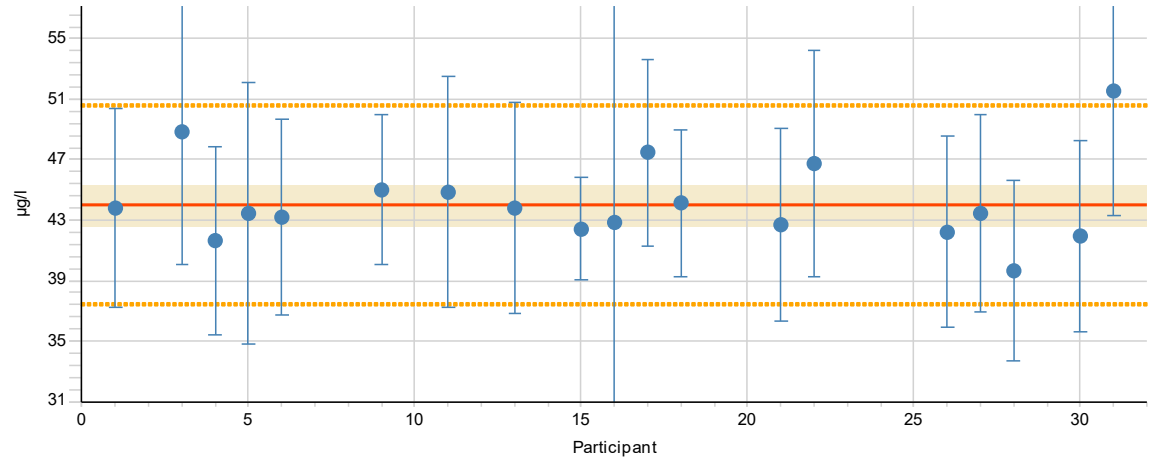
Measurand P_{tot} Sample A1P

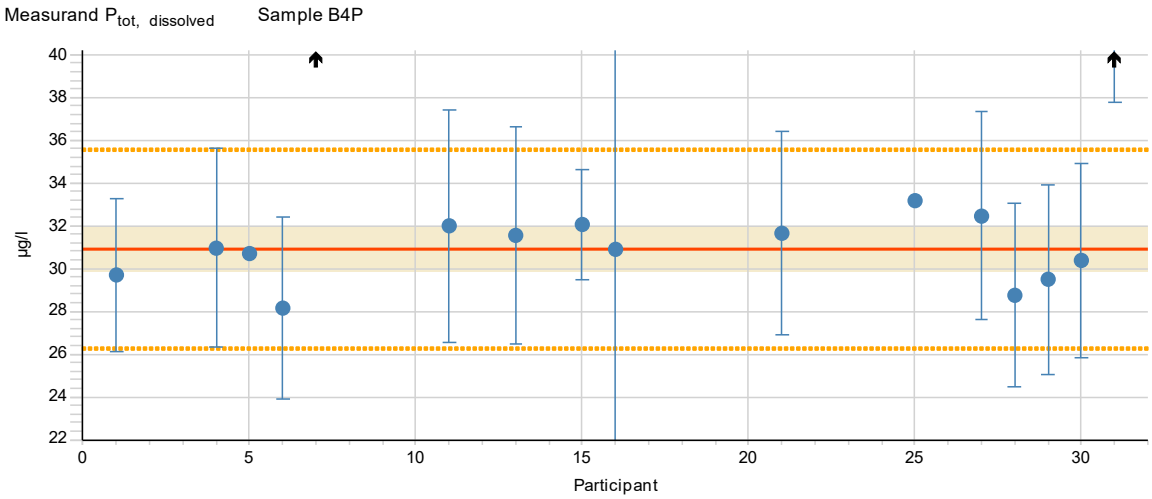


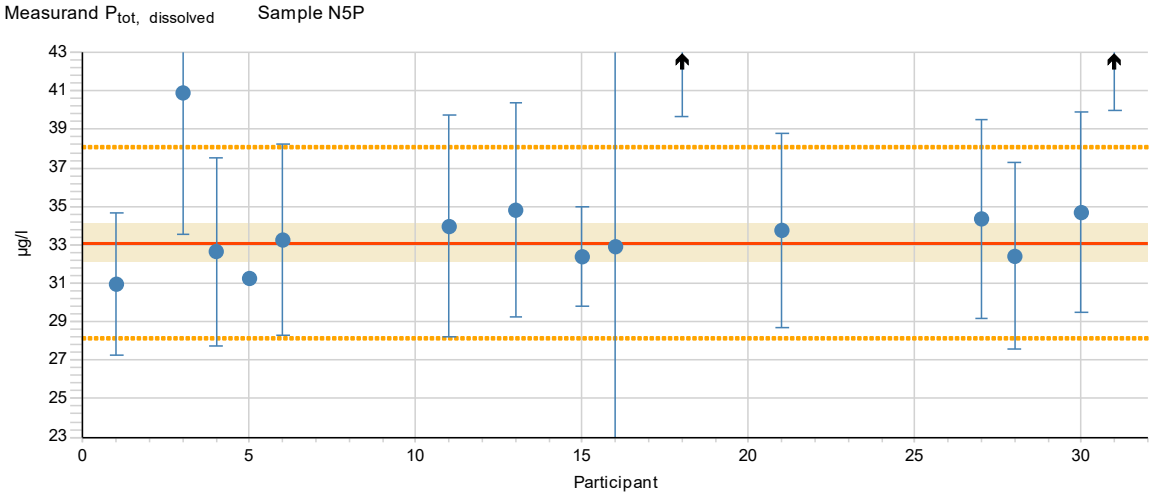
Measurand P_{tot} Sample B2P



Measurand P_{tot} Sample N3P




Measurand $P_{tot,\ dissolved}$
Sample B4P
µg/l
40
38
36
34
32
30
28
26
24
22
0
5
10
15
20
25
30
Participant


Measurand $P_{tot,\ dissolved}$
Sample N5P
µg/l
43
41
39
37
35
33
31
29
27
25
23
0
5
10
15
20
25
30
Participant

APPENDIX 10: Summary of the z scores

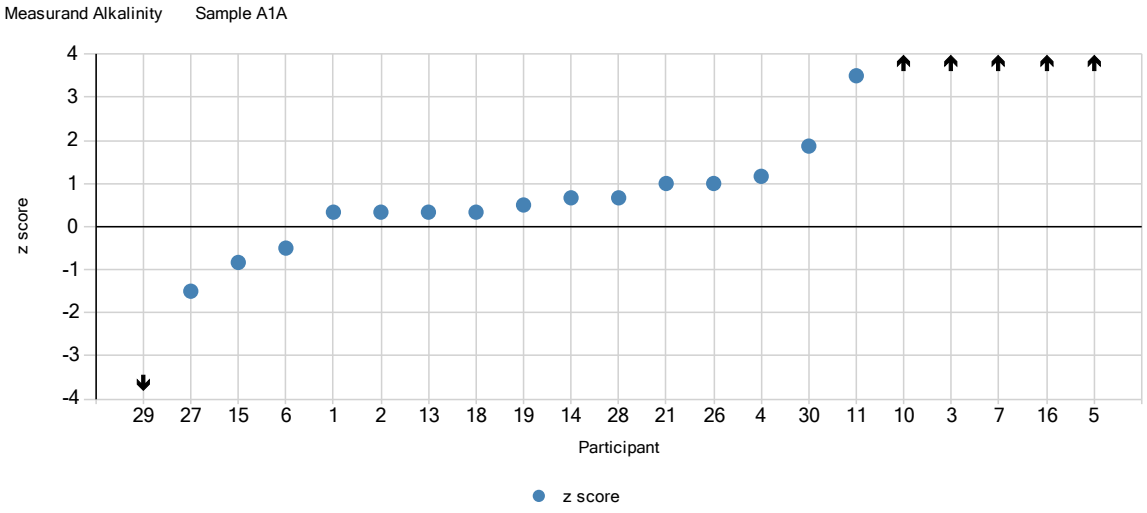
Measurand	Sample	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	%
Alkalinity	A1A	S	S	U	S	U	S	U	.	.	U	U	.	S	S	S	U	.	S	S	.	S	.	.	66.7
	B2A	S	S	.	S	S	S	S	.	.	.	S	S	S	.	S	S	S	.	.	.	S	.	S	95.0
	N3A	S	S	Q	S	Q	S	.	.	.	S	S	.	S	S	S	Q	S	S	S	.	S	.	.	85.7
Conductivity 25	A1J	S	Q	U	S	S	S	S	S	S	S	S	.	S	S	S	S	.	S	S	.	S	S	.	91.7
	B2H	S	S	.	S	S	S	S	S	S	.	S	.	S	.	S	S	S	.	.	.	S	S	.	100
	N3H	S	S	u	S	S	S	.	S	S	S	U	.	S	S	Q	S	S	S	S	.	S	S	.	88.0
N_{NH4}	A1N	S	.	S	S	S	S	S	.	.	U	S	.	.	.	S	S	.	U	.	.	S	U	.	78.9
	B2N	S	.	.	S	S	Q	S	.	.	.	S	.	S	.	S	S	S	.	.	.	S	U	.	84.2
	N3N	S	.	u	S	S	S	.	.	.	S	S	.	S	.	S	S	S	S	.	.	S	S	.	94.7
$N_{NO2+NO3}$	A1N	S	.	.	U	S	U	S	.	.	.	S	.	S	.	S	S	.	S	.	.	S	S	.	82.4
	B2N	S	.	.	S	S	S	q	.	.	.	S	.	S	.	S	S	S	.	.	.	S	S	.	88.9
	N3N	S	.	.	S	S	S	.	.	.	.	S	.	S	.	S	S	S	S	.	.	S	S	.	100
N_{tot}	A1N	S	.	u	Q	S	S	.	.	S	.	S	.	S	.	S	S	.	S	.	.	S	S	.	88.9
	B2N	S	.	.	S	S	Q	.	.	S	.	S	.	S	.	S	S	S	.	.	.	S	S	.	88.9
	N3N	S	.	u	S	S	S	.	.	S	.	S	.	S	.	S	S	S	S	.	.	S	S	.	88.9
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	q	S	S	S	.	S	S	S	S	.	S	S	S	S	S	S	S	S	S	S	.	96.2
P_{PO4}	A1P	S	.	U	S	q	S	U	.	.	.	S	.	S	.	S	S	.	Q	.	.	S	S	.	68.4
	B2P	S	.	.	S	S	S	U	.	.	.	S	.	S	.	S	S	.	.	.	.	S	S	.	88.9
	N3P	S	.	U	S	S	S	.	.	.	.	S	.	S	.	S	S	.	S	.	.	S	S	.	94.1
$P_{PO4,\ dissolved}$	B4P	S	.	.	S	S	S	Q	.	.	.	S	.	S	.	S	S	.	.	.	.	S	.	.	93.8
	N5P	S	.	U	S	S	S	.	.	.	.	S	.	S	.	S	S	.	Q	.	.	S	.	.	86.7
P_{tot}	A1P	S	.	S	S	S	Q	S	.	S	.	S	.	S	.	S	S	.	S	.	.	S	S	.	89.5
	B2P	S	.	.	S	S	S	Q	.	S	.	S	.	S	.	S	S	S	.	.	.	S	S	.	84.2
	N3P	S	.	S	S	S	S	.	.	S	.	S	.	S	.	S	S	S	S	.	.	S	S	.	94.7
$P_{tot,\ dissolved}$	B4P	S	.	.	S	S	S	U	.	.	.	S	.	S	.	S	S	.	.	.	.	S	.	.	87.5
	N5P	S	.	U	S	S	S	.	.	.	.	S	.	S	.	S	S	.	U	.	.	S	.	.	80.0
%		100	89	25	93	89	86	56	100	100	75	93	100	100	100	96	93	100	78	100	100	100	90	100	
accredited		28	9	13	28	24	28		6		8	27	2	27	6	27	28	14	15		3	27		2	

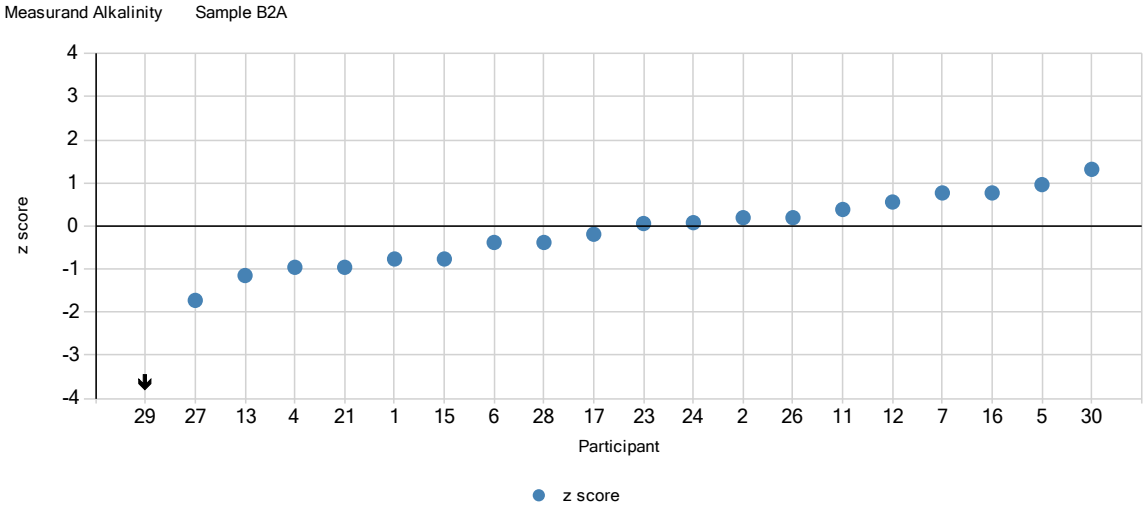
Measurand	Sample	24	25	26	27	28	29	30	31		%
Alkalinity	A1A	.	.	**S**	*S*	**S**	*u*	**S**	.		66.7
	B2A	**S**	.	**S**	*S*	**S**	u	**S**	.		95.0
	N3A	**S**	.	**S**	*S*	**S**	.	**S**	.		85.7
Conductivity 25	A1J	.	.	**S**	**S**	**S**	S	**S**	.		91.7
	B2H	S	.	**S**	**S**	**S**	S	**S**	**S**		100
	N3H	**S**	.	**S**	**S**	**S**	.	S	**S**		88.0
N_{NH4}	A1N	.	*S*	**S**	**S**	**S**	U	**S**	.		78.9
	B2N	.	*S*	**S**	**S**	**S**	**S**	**S**	**U**		84.2
	N3N	.	.	**S**	**S**	**S**	.	**S**	**S**		94.7
$N_{NO2+NO3}$	A1N	.	*S*	.	**q**	**S**	**S**	**S**	.		82.4
	B2N	.	*S*	.	**q**	**S**	**S**	**S**	**S**		88.9
	N3N	.	.	.	**S**	**S**	.	**S**	**S**		100
N_{tot}	A1N	.	S	.	**S**	**S**	**S**	**S**	.		88.9
	B2N	.	*S*	.	**S**	**S**	**S**	**S**	*u*		88.9
	N3N	.	.	.	**S**	**S**	.	**S**	*u*		88.9
pH	A1H	.	*S*	**S**	**S**	**S**	**S**	**S**	.		100
	B2H	**S**	*S*	**S**	**S**	**S**	.	**S**	**S**		100
	N3H	**S**	.	**S**	**S**	**S**	.	**S**	**S**		96.2
P_{PO4}	A1P	.	*S*	**S**	**S**	**S**	**U**	**U**	.		68.4
	B2P	.	*S*	**S**	**S**	**S**	**Q**	**S**	**S**		88.9
	N3P	.	.	**S**	**S**	**S**	.	**S**	**S**		94.1
$P_{PO4, dissolved}$	B4P	.	*S*	.	**S**	**S**	**S**	**S**	**S**		93.8
	N5P	.	.	.	**S**	**S**	.	**S**	**S**		86.7
P_{tot}	A1P	.	S	.	**S**	**S**	**q**	**S**	.		89.5
	B2P	.	*S*	.	**S**	**S**	**U**	**S**	**Q**		84.2
	N3P	.	.	**S**	**S**	**S**	.	**S**	**Q**		94.7
$P_{tot, dissolved}$	B4P	.	*S*	.	**S**	**S**	**S**	**S**	**U**		87.5
	N5P	.	.	.	**S**	**S**	.	**S**	**U**		80.0
%		100	100	100	93	100	59	96	61		
accredited		5		16	25	28	12	27	16		

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 - unknown
% - percentage of satisfactory results

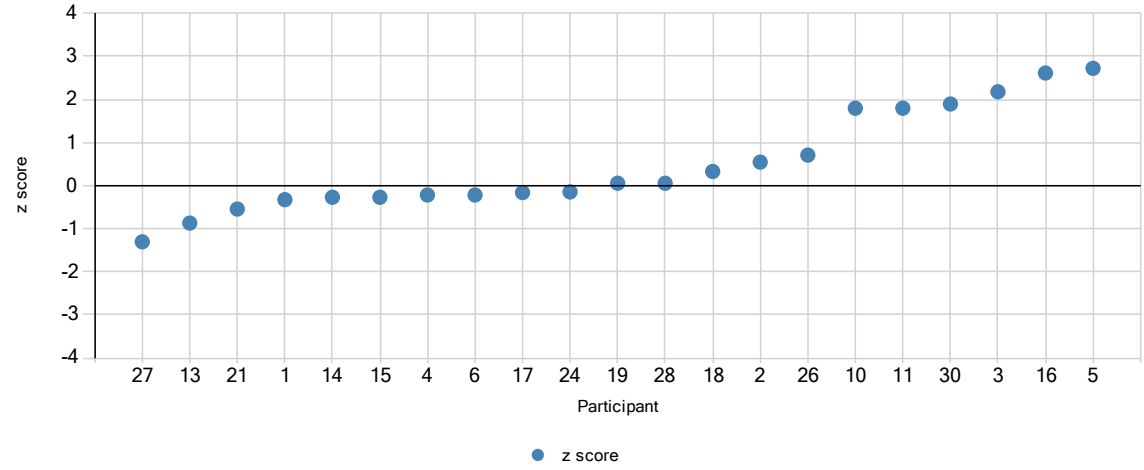
Totally satisfactory, % in all: 89 % in accredited: 91 % in non-accredited: 78

APPENDIX 11: z scores in ascending order

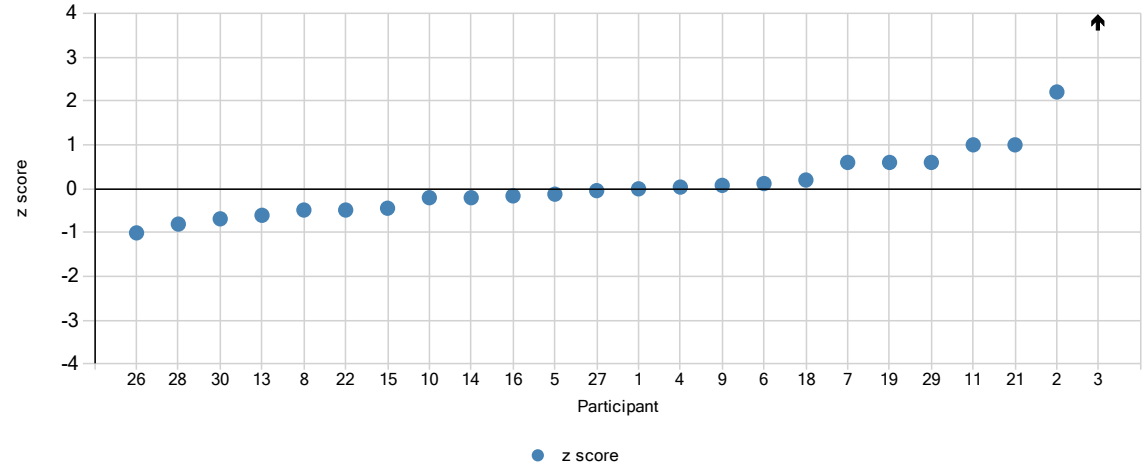




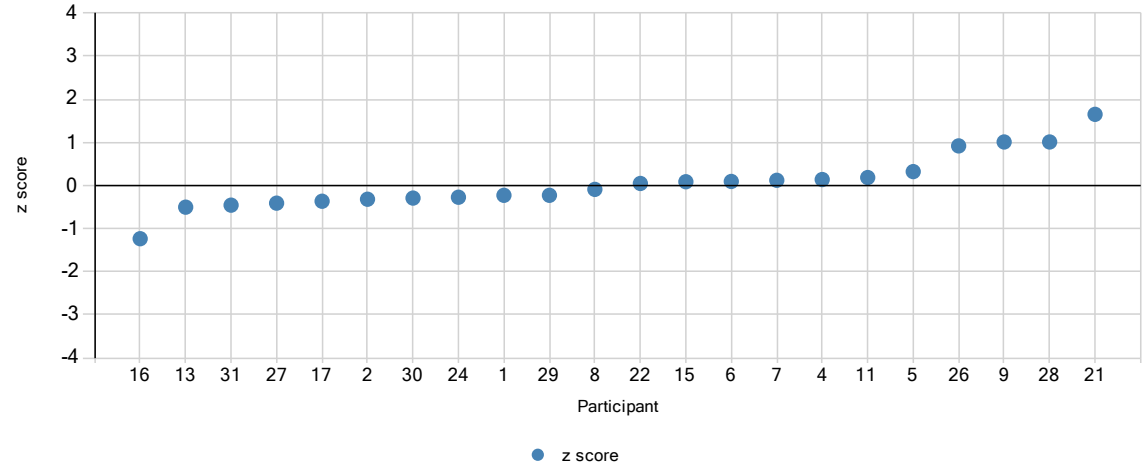
Measurand Alkalinity Sample N3A



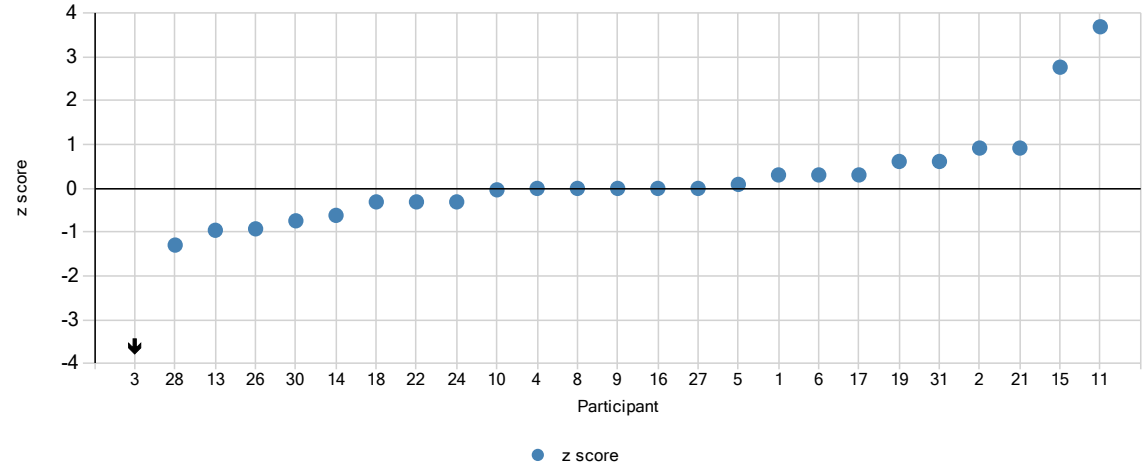
Measurand Conductivity 25 Sample A1J



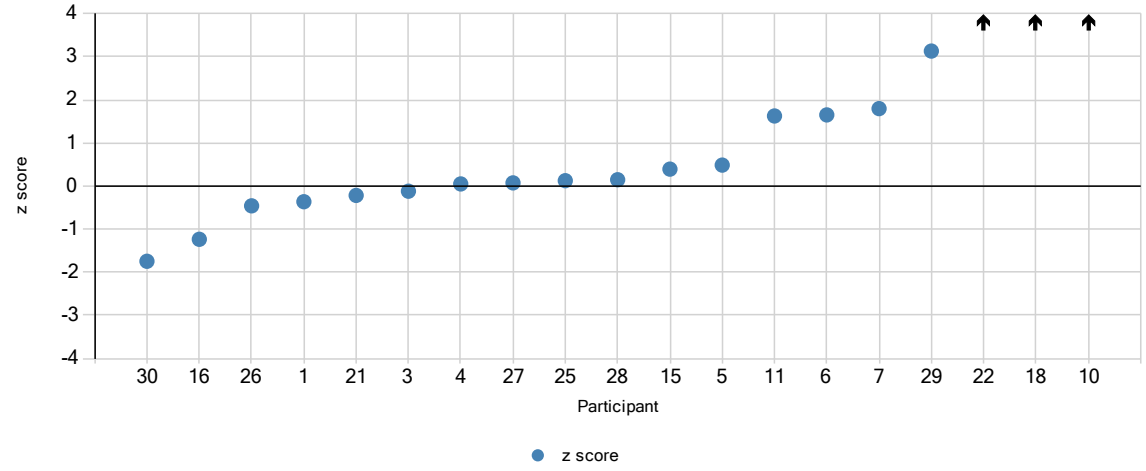
Measurand Conductivity 25 Sample B2H



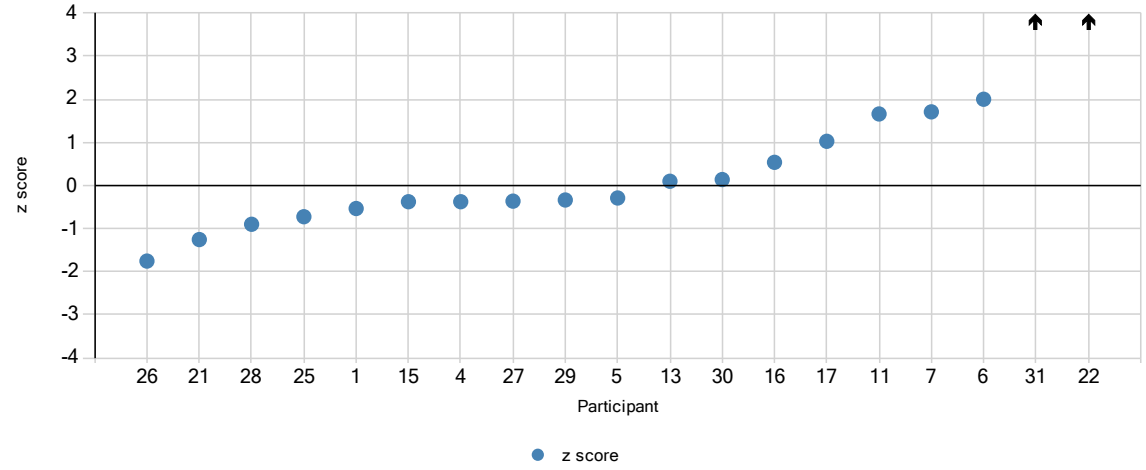
Measurand Conductivity 25 Sample N3H



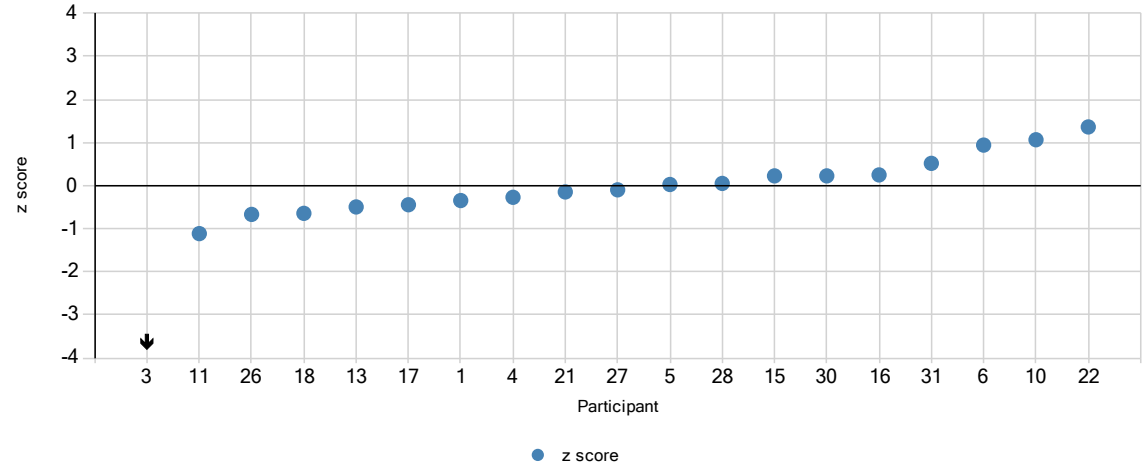
Measurand N_{NH4} Sample A1N



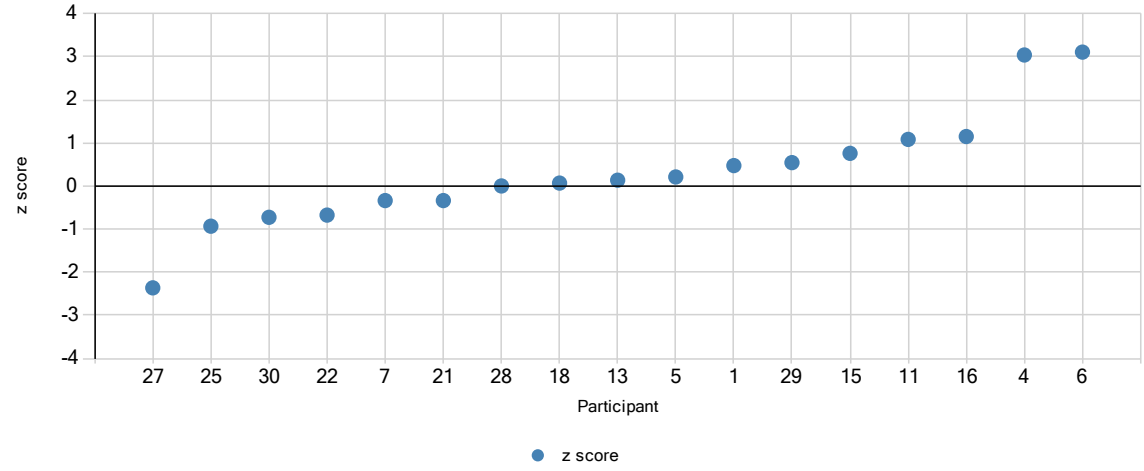
Measurand N_{NH4} Sample B2N



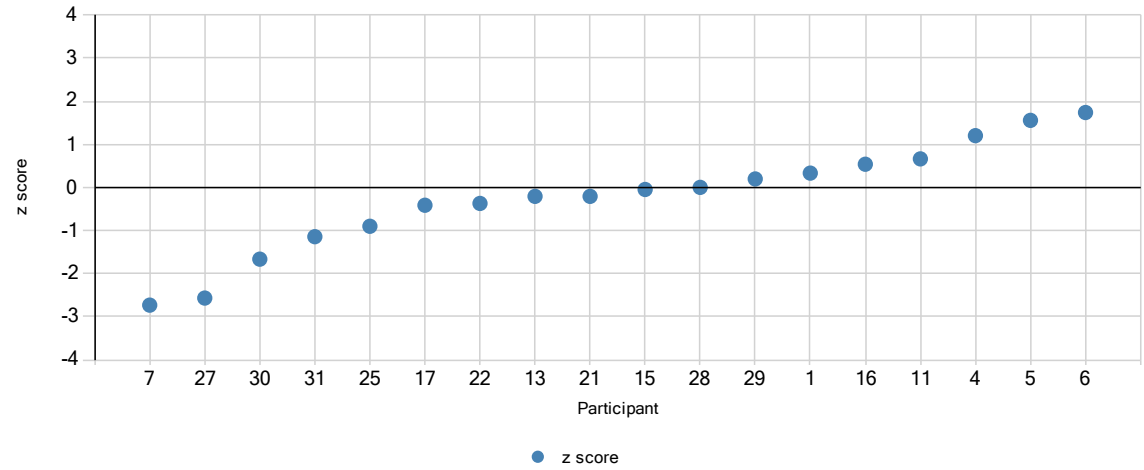
Measurand N_{NH4} Sample N3N



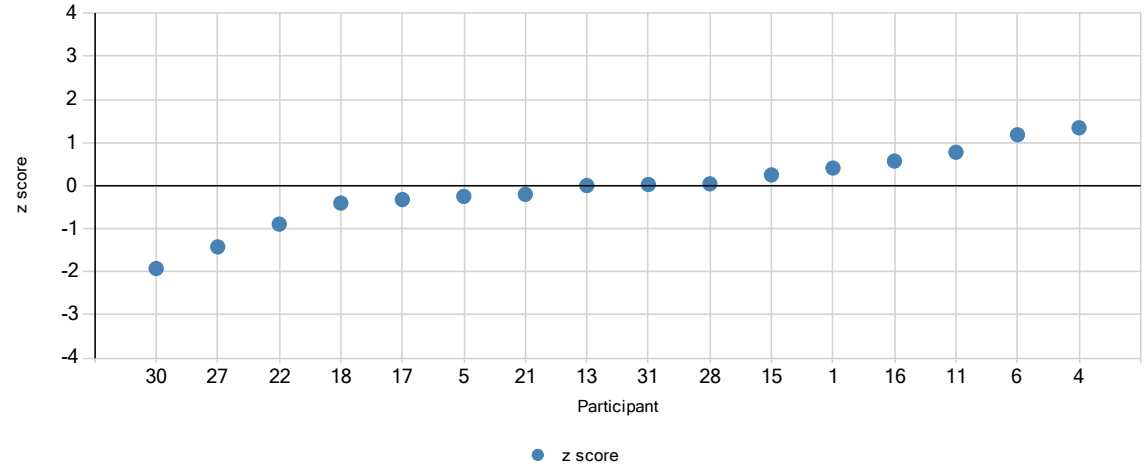
Measurand $N_{NO2+NO3}$ Sample A1N



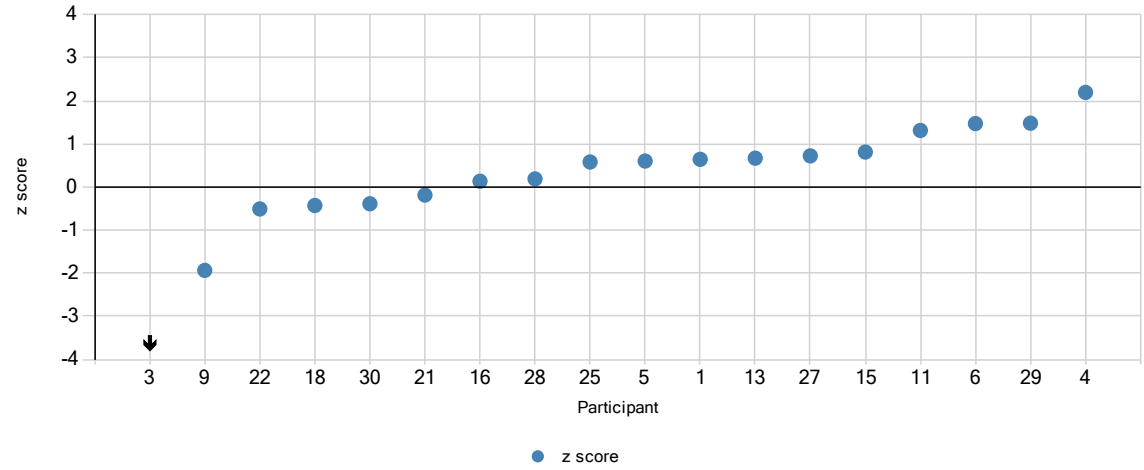
Measurand $N_{NO2+NO3}$ Sample B2N



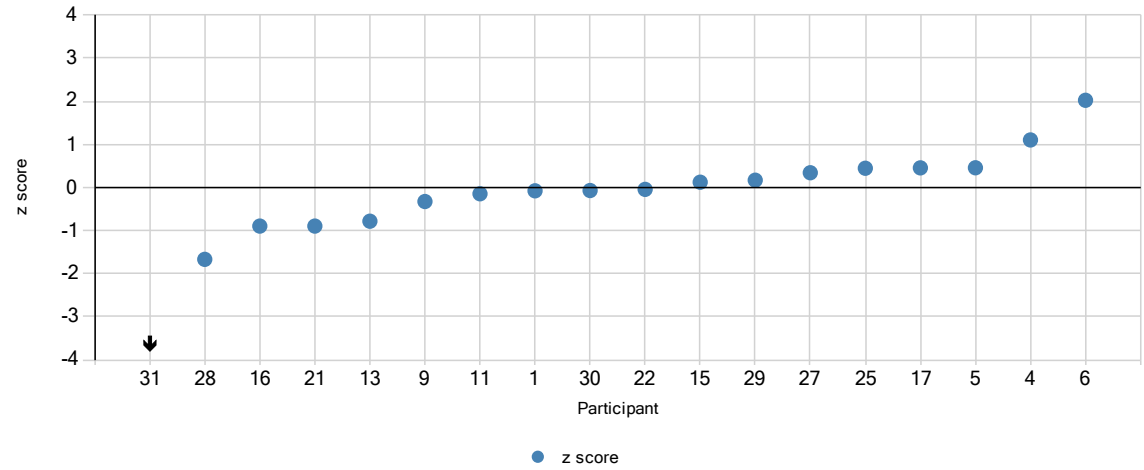
Measurand $N_{NO2+NO3}$ Sample N3N



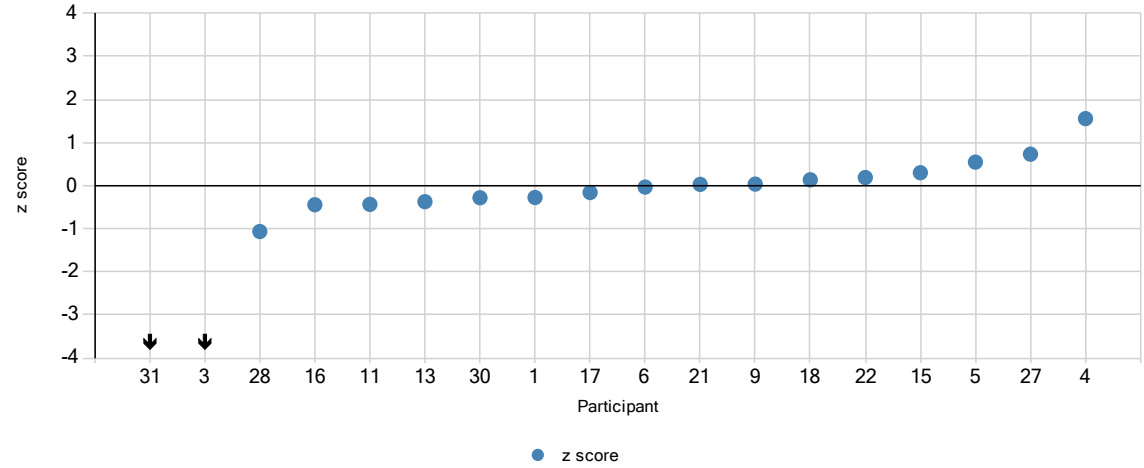
Measurand N_{tot} Sample A1N



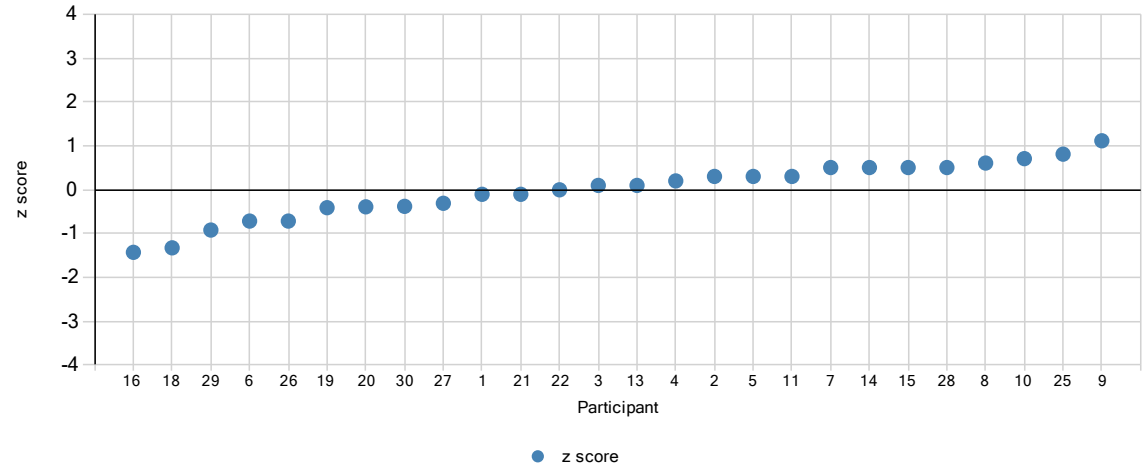
Measurand N_{tot} Sample B2N



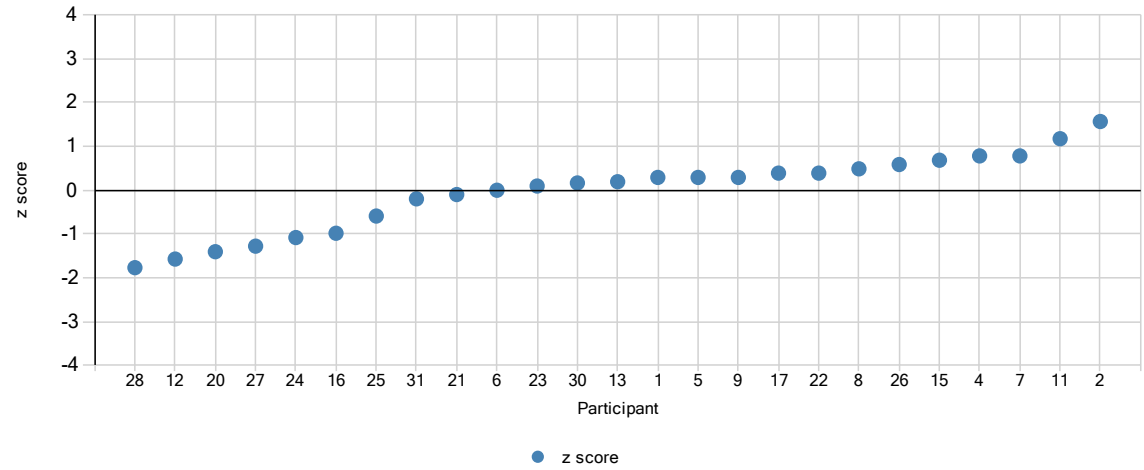
Measurand N_{tot} Sample N3N



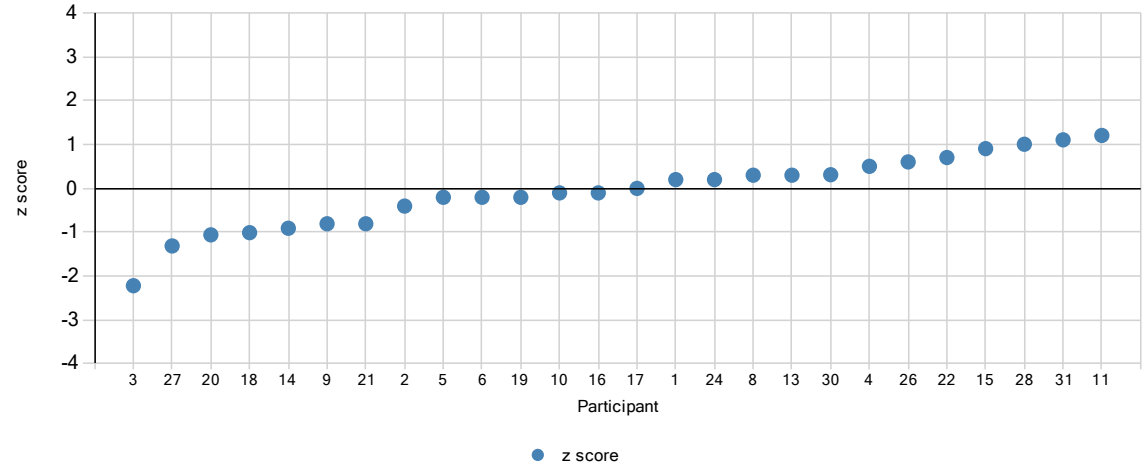
Measurand pH Sample A1H



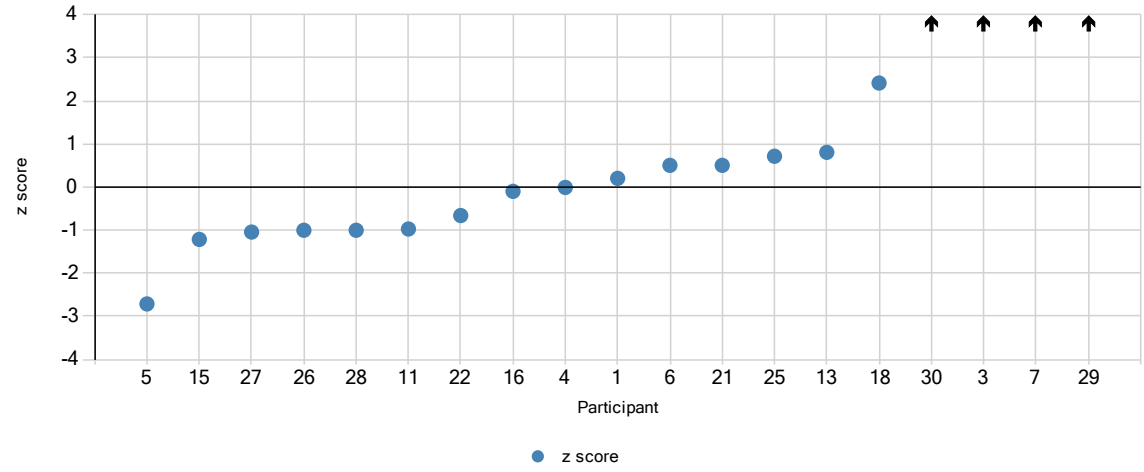
Measurand pH Sample B2H



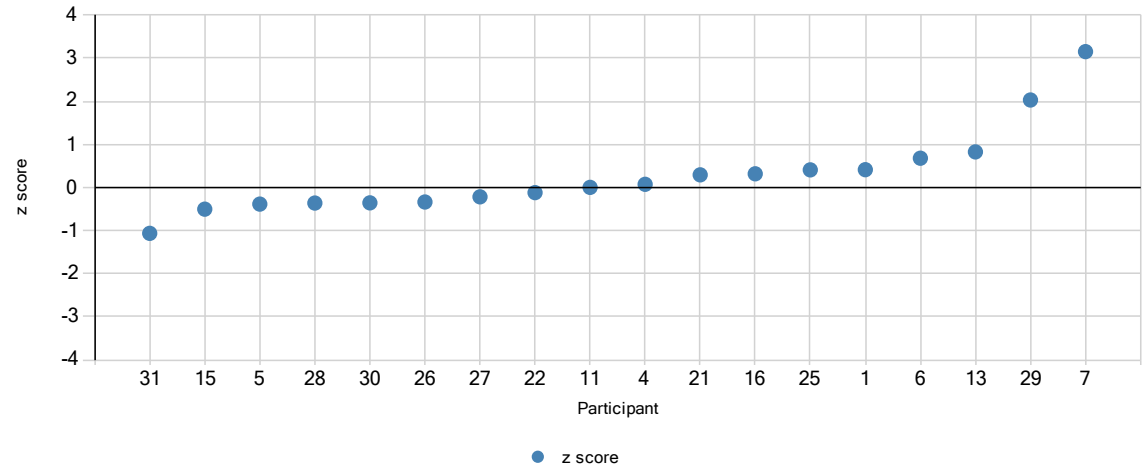
Measurand pH Sample N3H



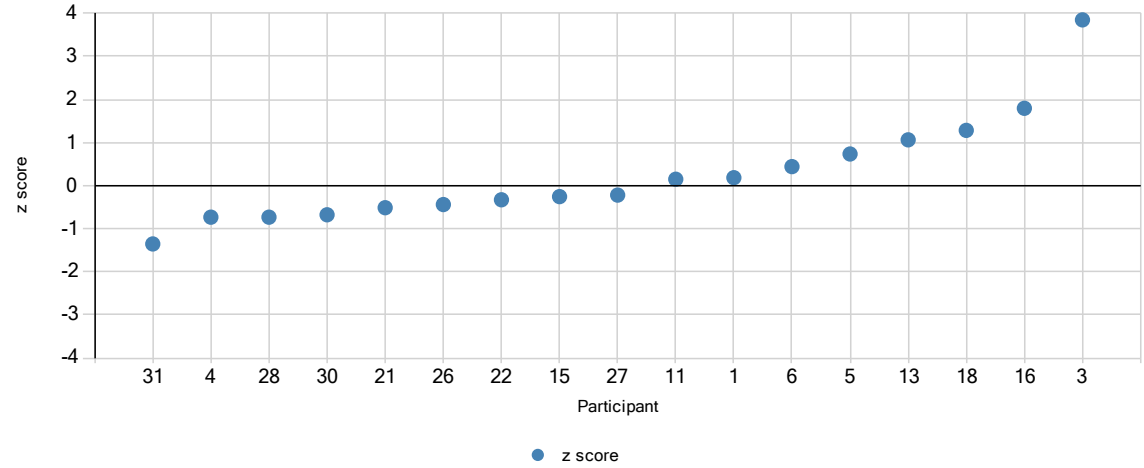
Measurand P_{PO4} Sample A1P



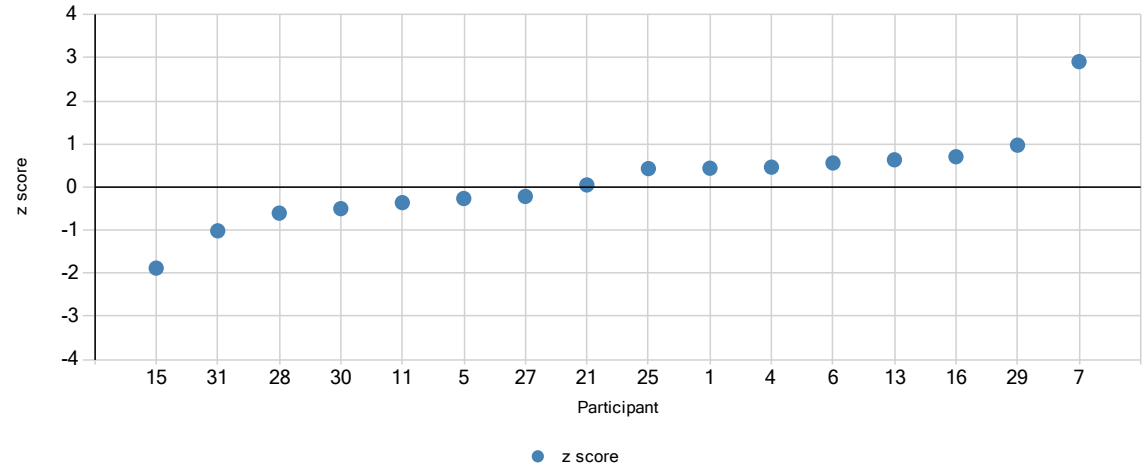
Measurand P_{PO4} Sample B2P



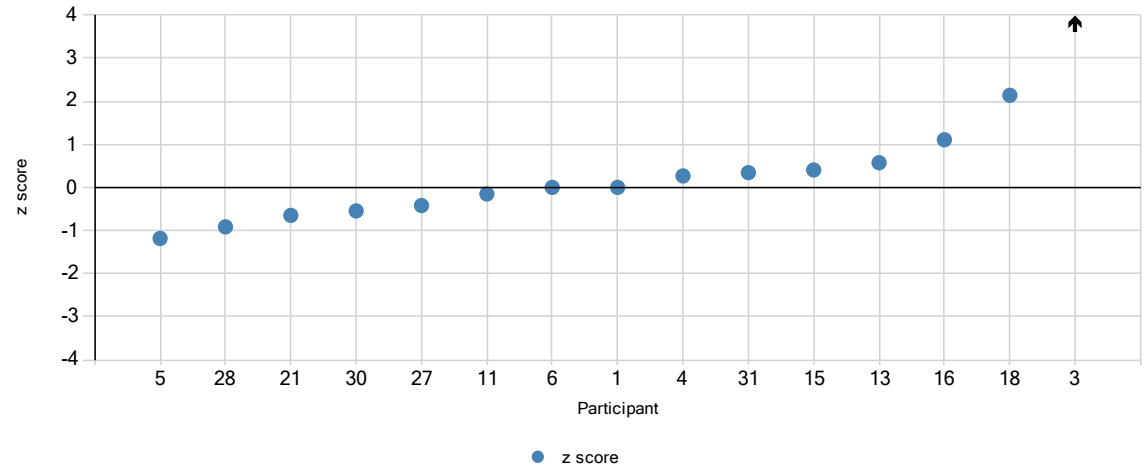
Measurand P_{PO4} Sample N3P



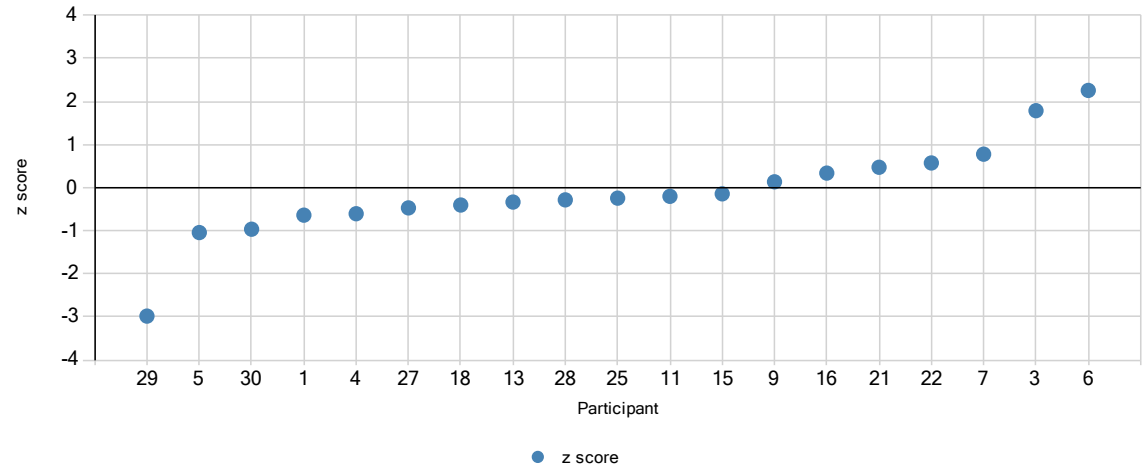
Measurand $P_{PO4,\ dissolved}$ Sample B4P



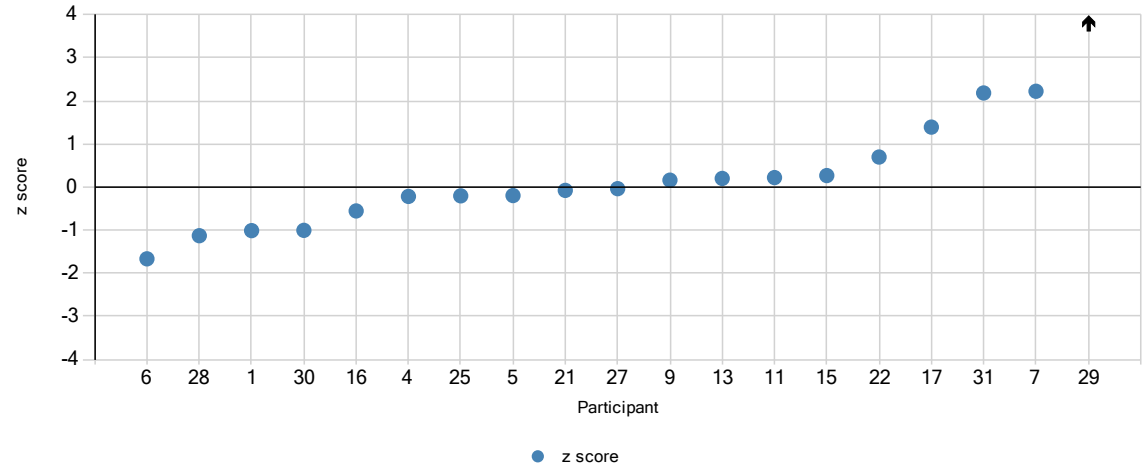
Measurand $P_{PO4,\ dissolved}$ Sample N5P



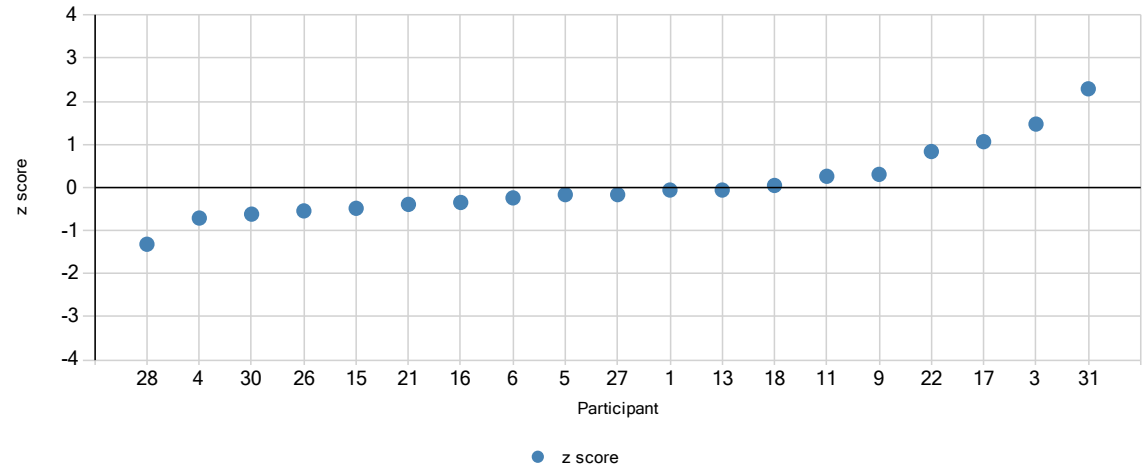
Measurand P_{tot} Sample A1P

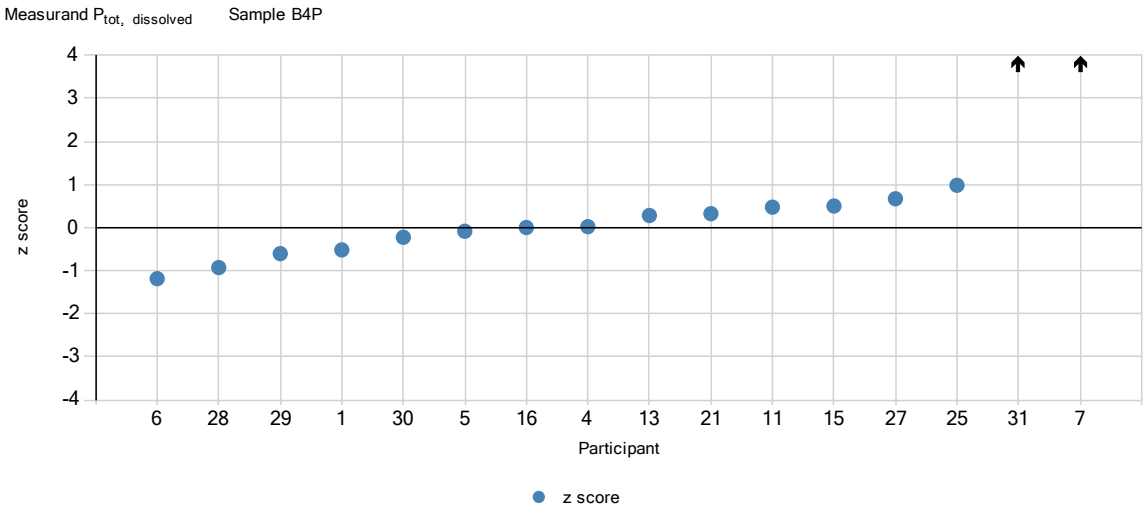


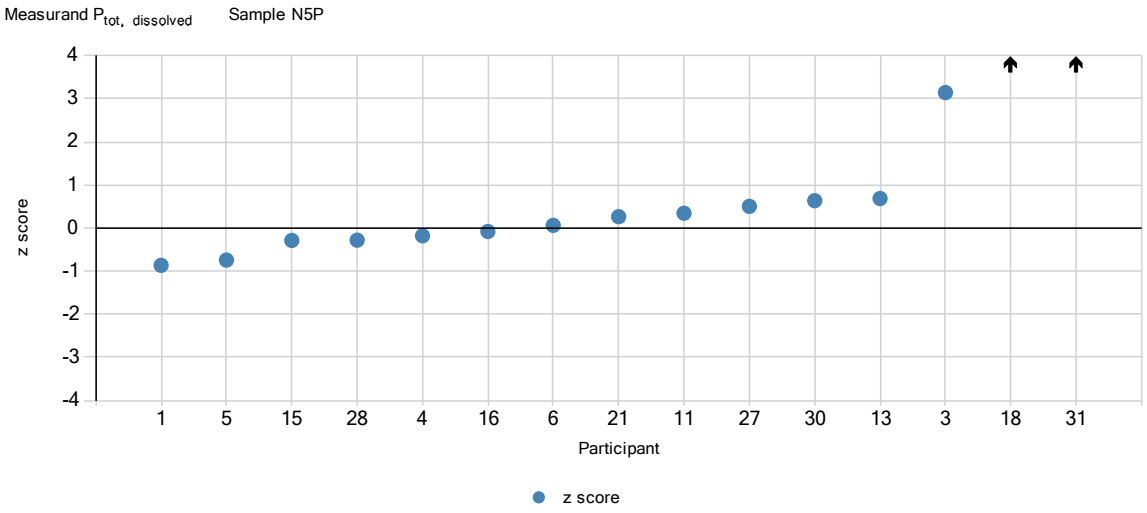
Measurand P_{tot} Sample B2P



Measurand P_{tot} Sample N3P

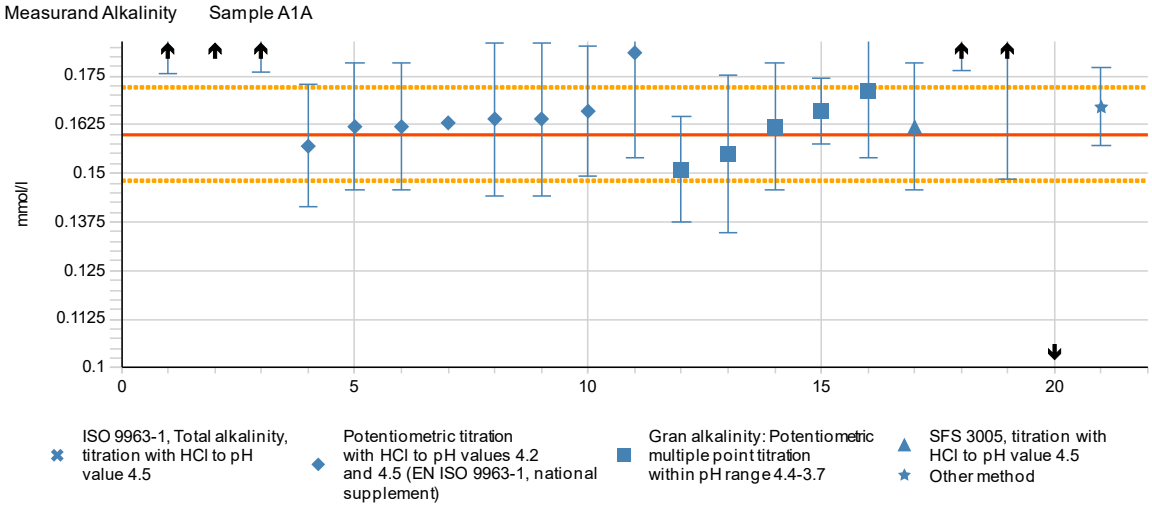


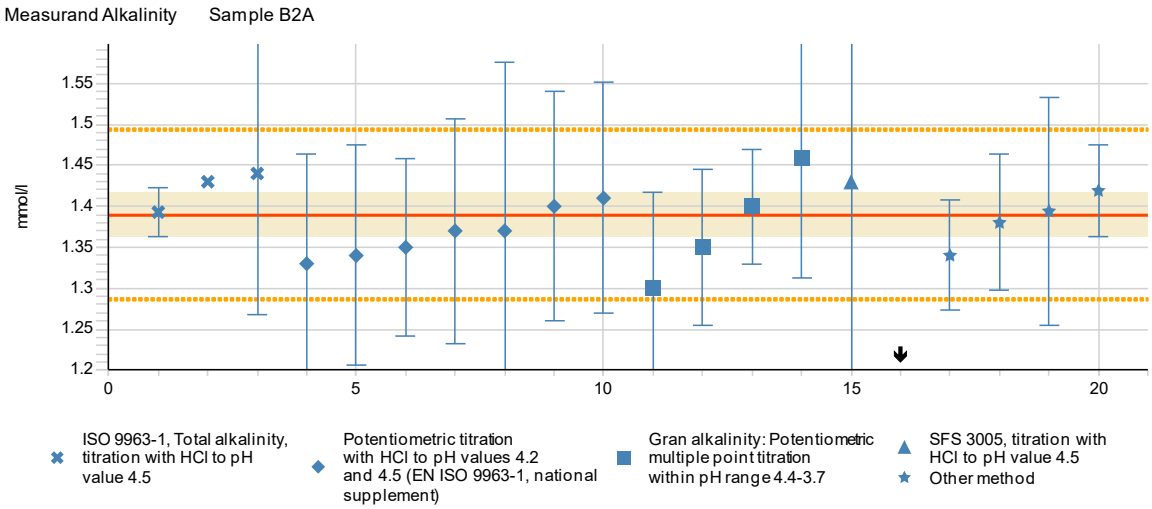

Measurand $P_{tot,\ dissolved}$ Sample B4P
z score
4
3
2
1
0
-1
-2
-3
-4
6 28 29 1 30 5 16 4 13 21 11 15 27 25 31 7
Participant
z score


Measurand $P_{tot,\ dissolved}$ Sample N5P
z score
4
3
2
1
0
-1
-2
-3
-4
1 5 15 28 4 16 6 21 11 27 30 13 3 18 31
Participant
z score

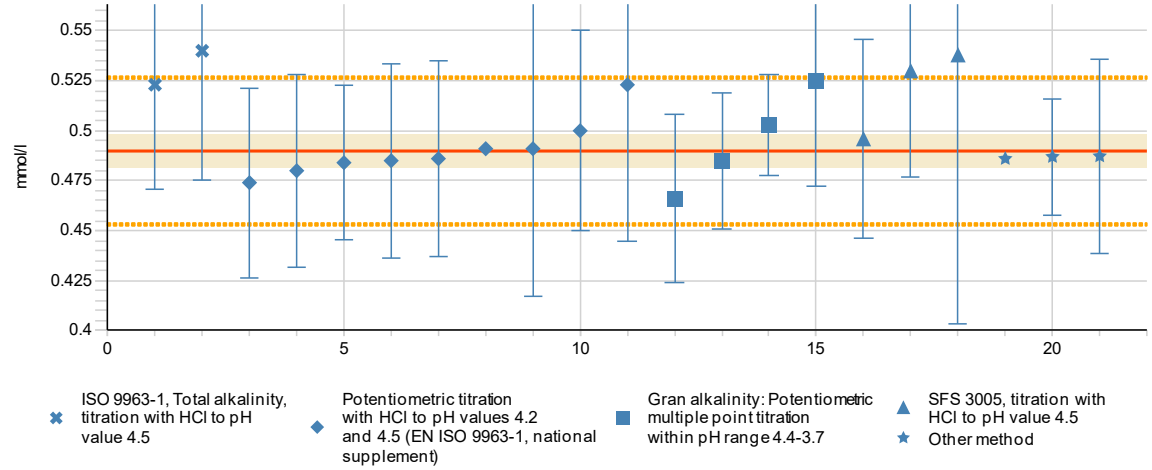
APPENDIX 12: Results grouped according to the methods

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

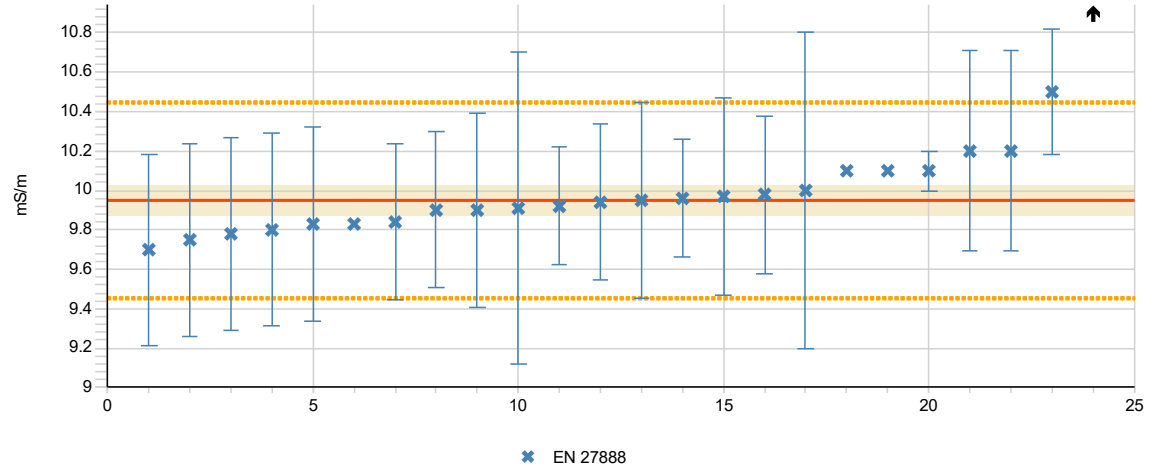




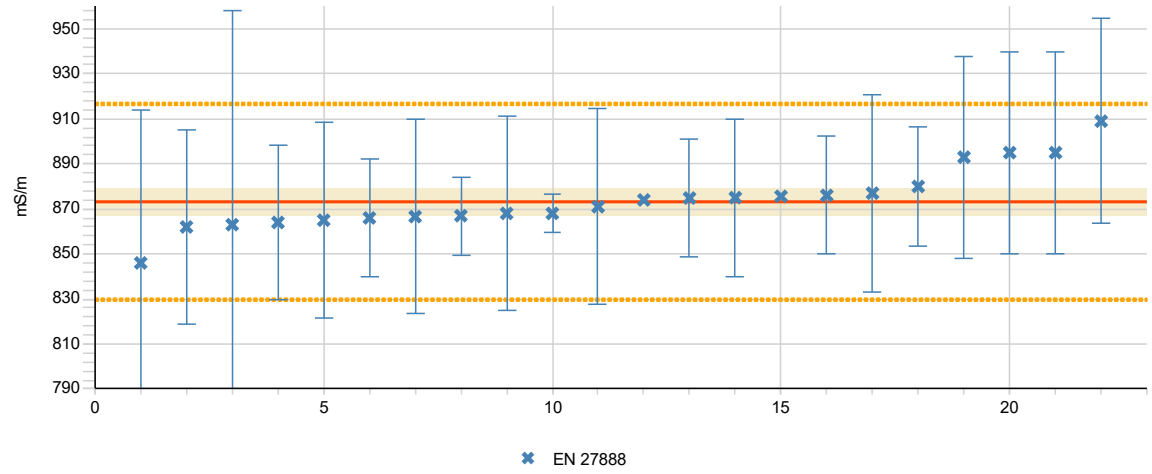
Measurand Alkalinity Sample N3A



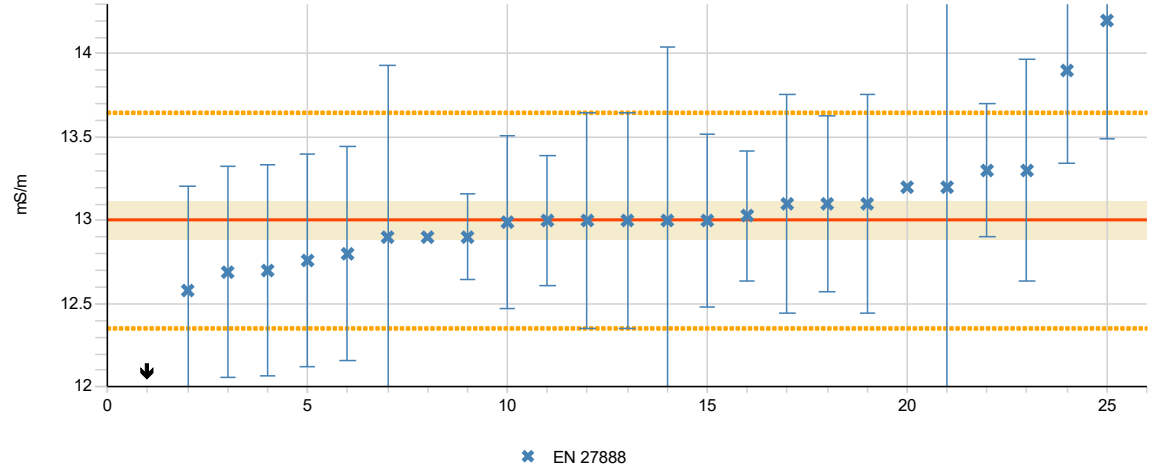
Measurand Conductivity 25 Sample A1J



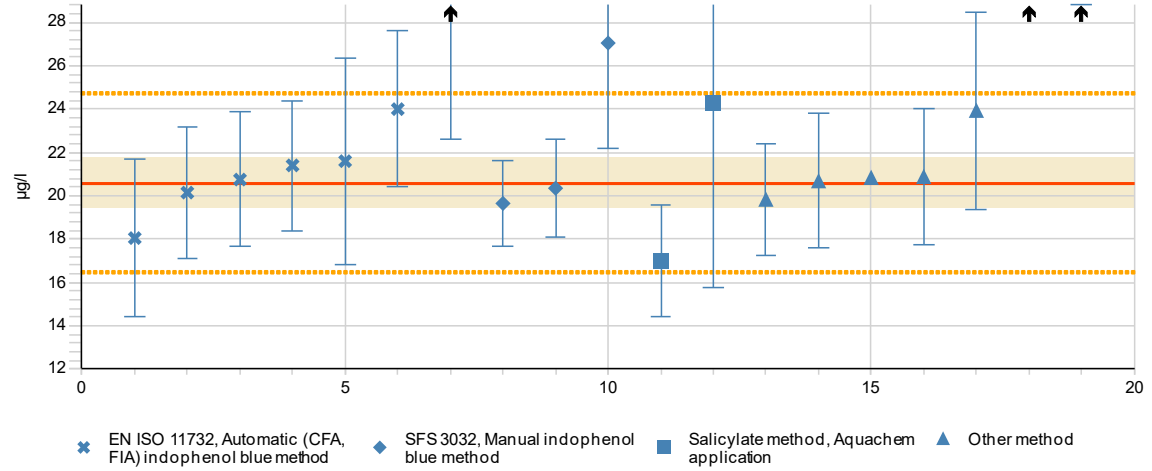
Measurand Conductivity 25 Sample B2H



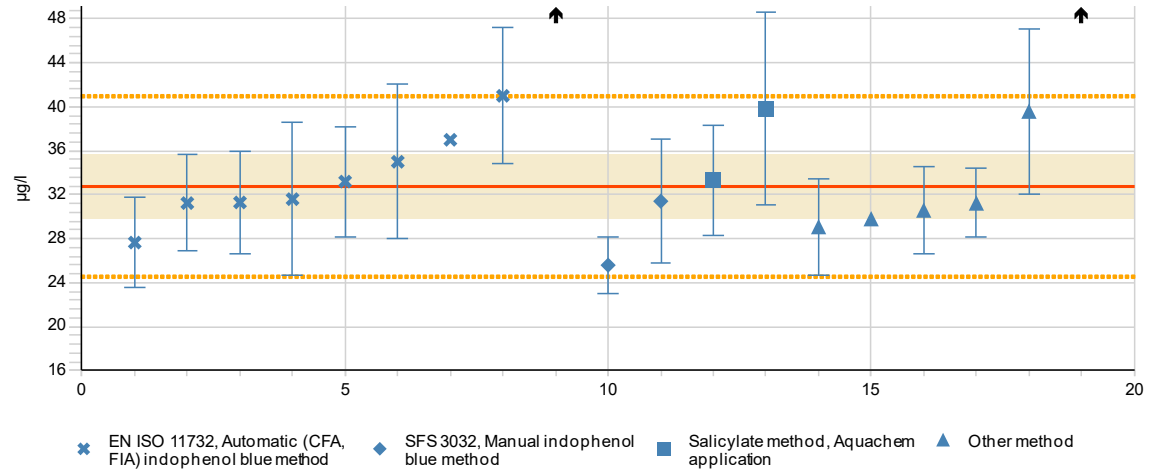
Measurand Conductivity 25 Sample N3H



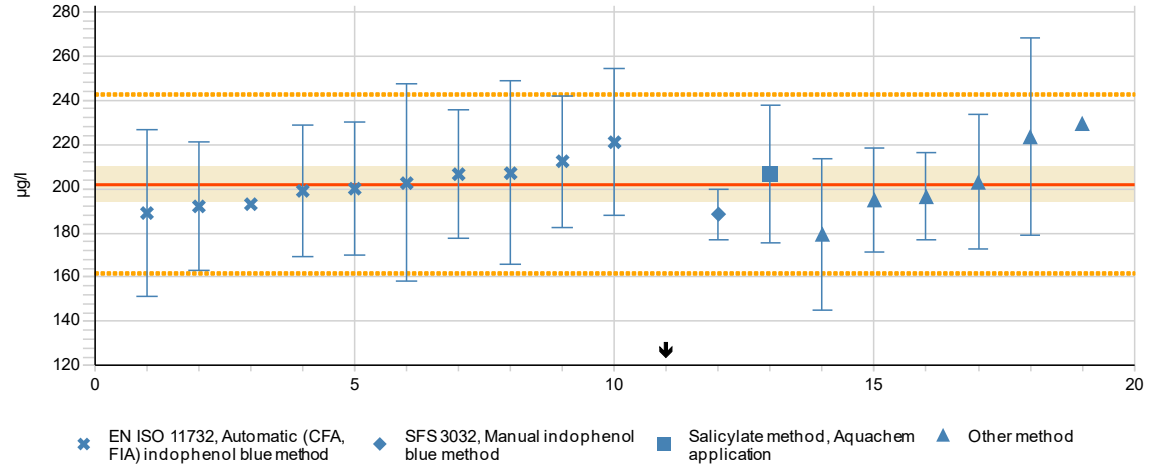
Measurand N_{NH4} Sample A1N



Measurand N_{NH4} Sample B2N

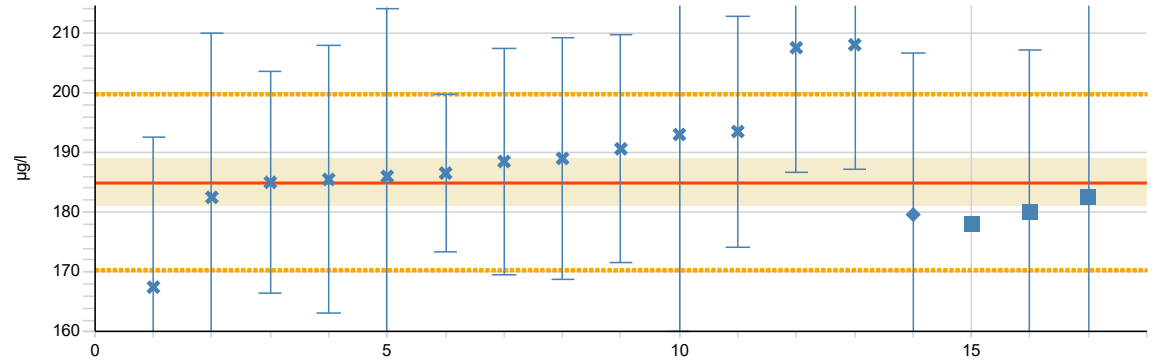


Measurand N_{NH4} Sample N3N



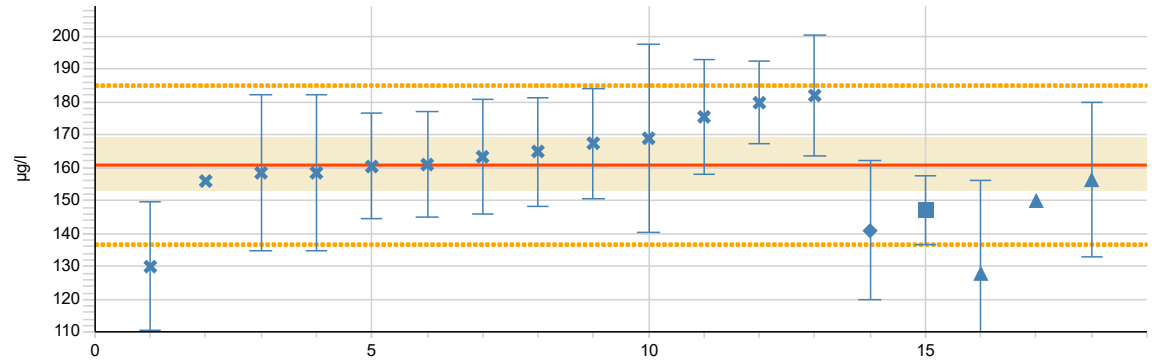
EN ISO 11732, Automatic (CFA, FIA) indophenol blue method
SFS 3032, Manual indophenol blue method
Salicylate method, Aquachem application
Other method

Measurand $N_{NO2+NO3}$ Sample A1N



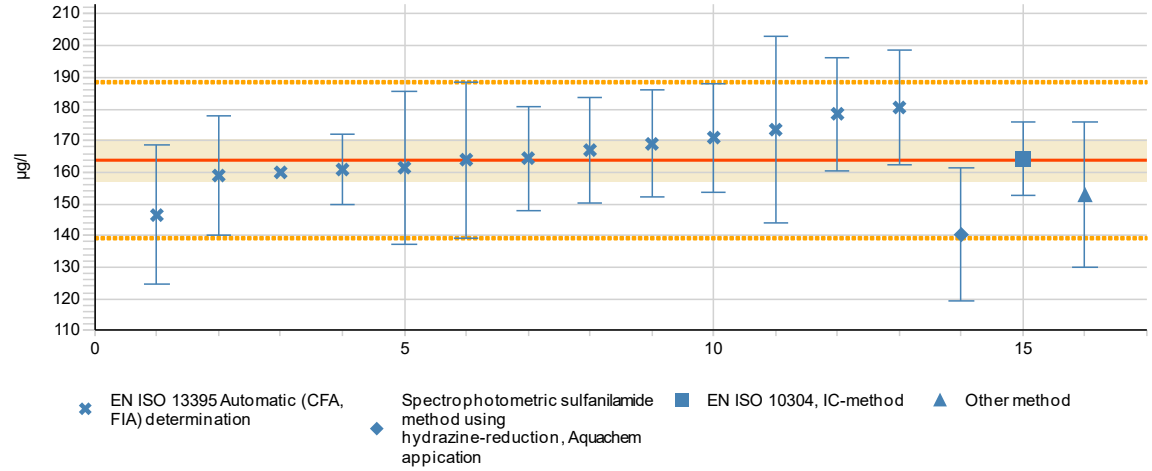
EN ISO 13395 Automatic (CFA, FIA) determination
Spectrophotometric sulfanilamide method using hydrazine-reduction, Aquachem appication
Other method

Measurand $N_{NO2+NO3}$ Sample B2N



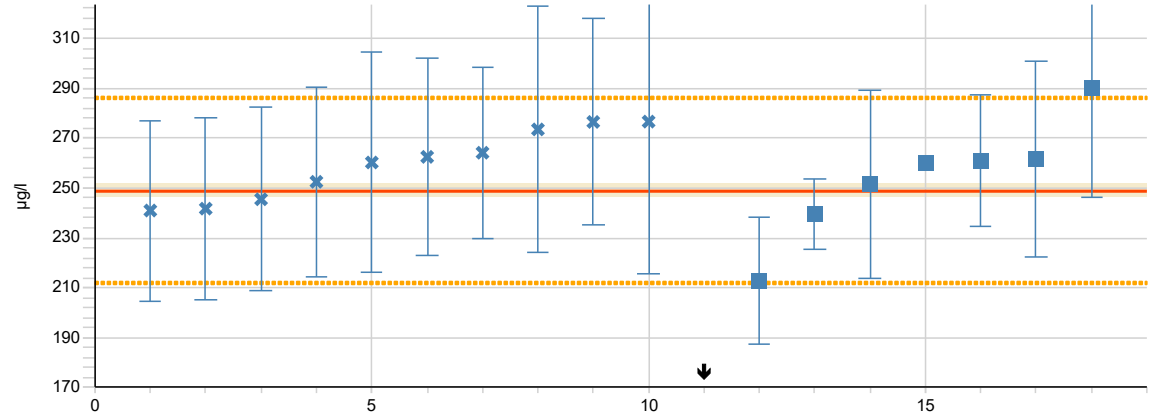
EN ISO 13395 Automatic (CFA, FIA) determination
Spectrophotometric sulfanilamide method using hydrazine-reduction, Aquachem appication
EN ISO 10304, IC-method
Other method

Measurand $N_{NO2+NO3}$ Sample N3N



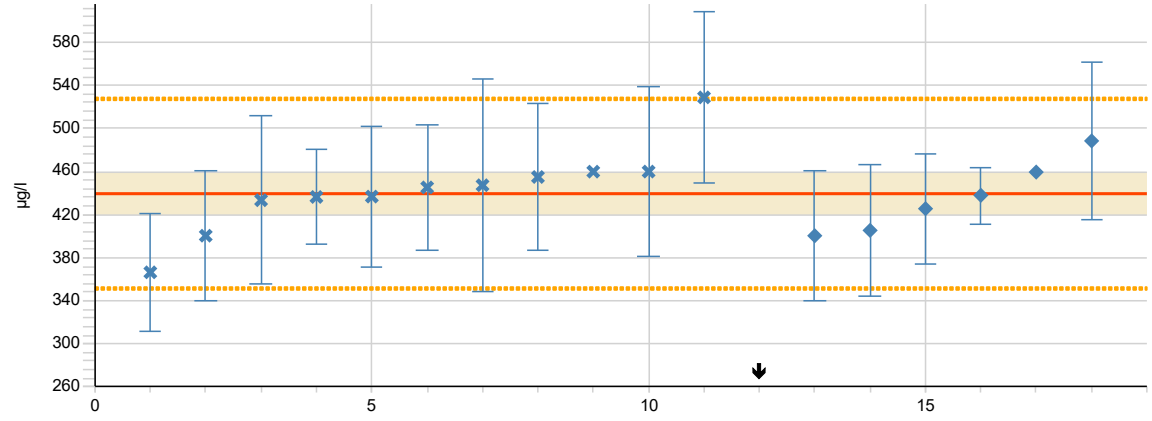
EN ISO 13395 Automatic (CFA, FIA) determination
Spectrophotometric sulfanilamide method using hydrazine-reduction, Aquachem appication
EN ISO 10304, IC-method
Other method

Measurand N_{tot} Sample A1N



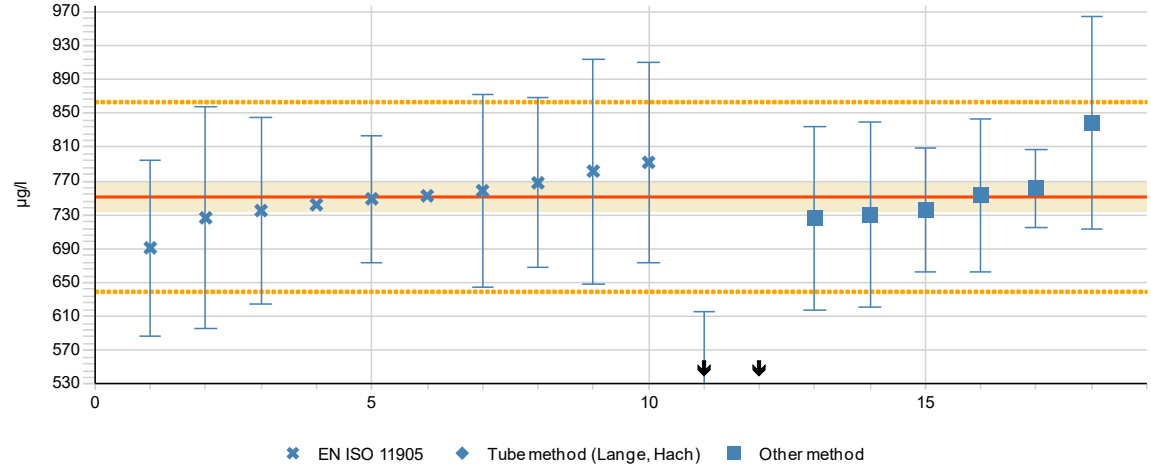
EN ISO 11905
Tube method (Lange, Hach)
Other method

Measurand N_{tot} Sample B2N

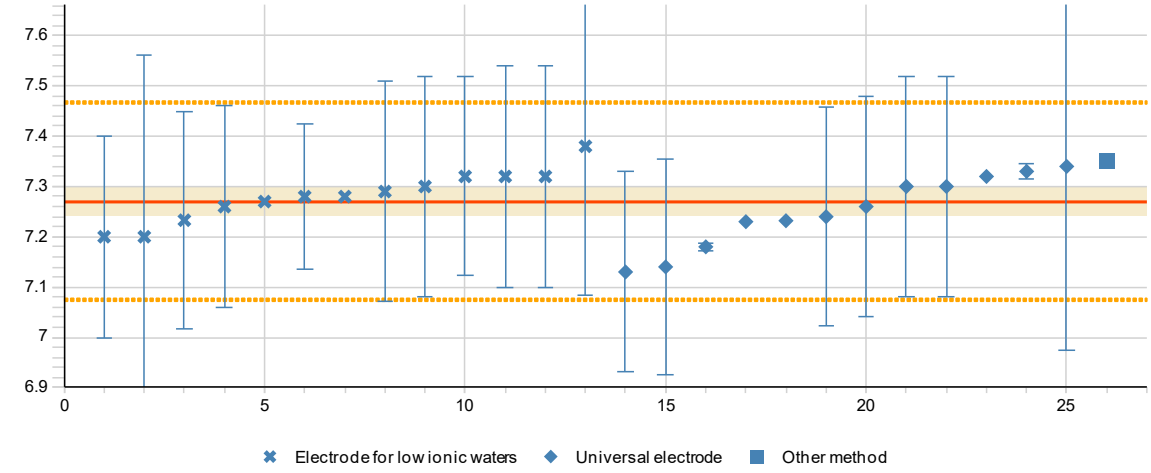


EN ISO 11905
Other method

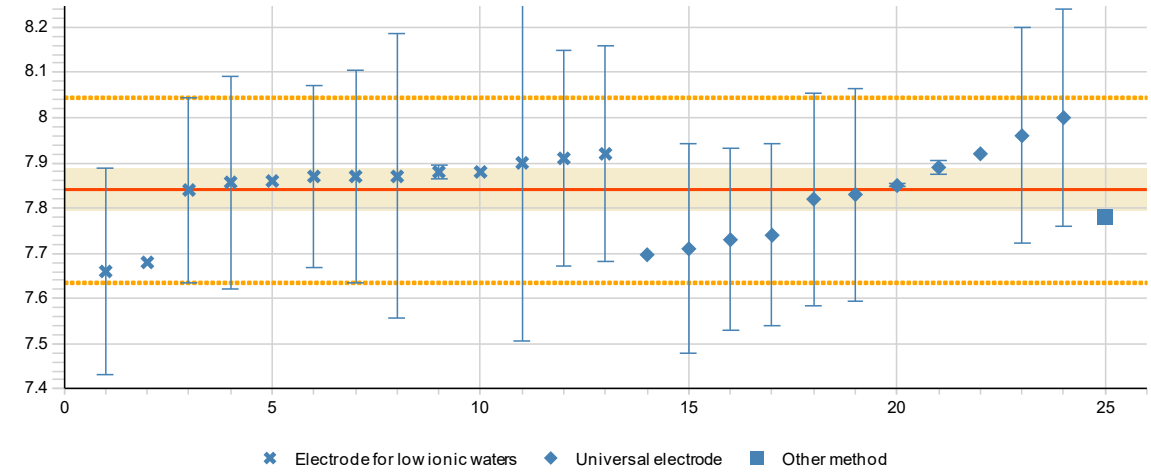
Measurand N_{tot} Sample N3N



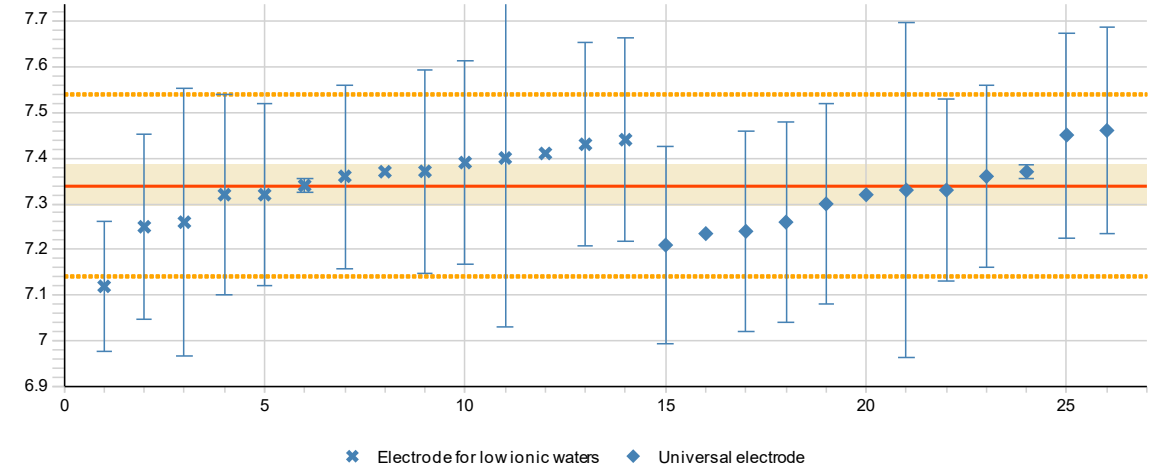
Measurand pH Sample A1H



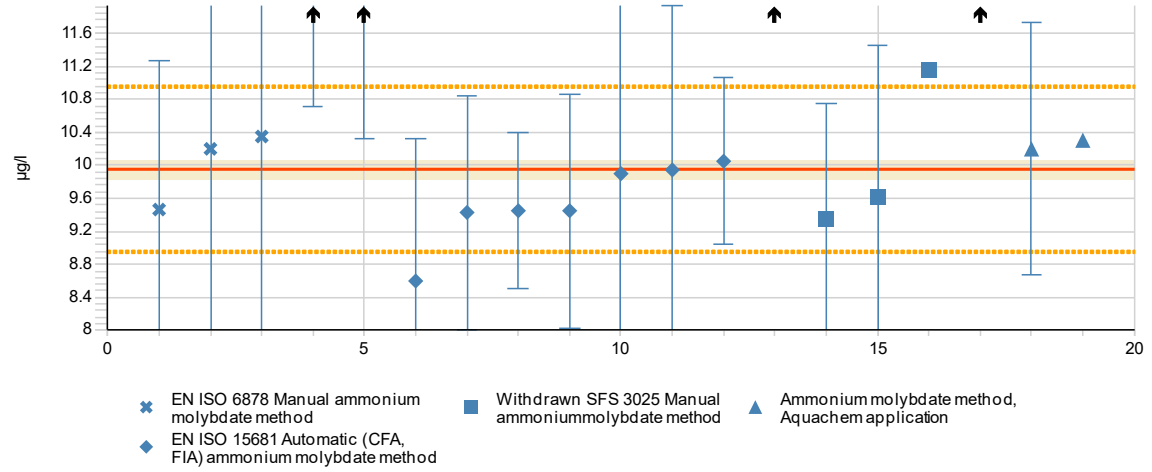
Measurand pH Sample B2H



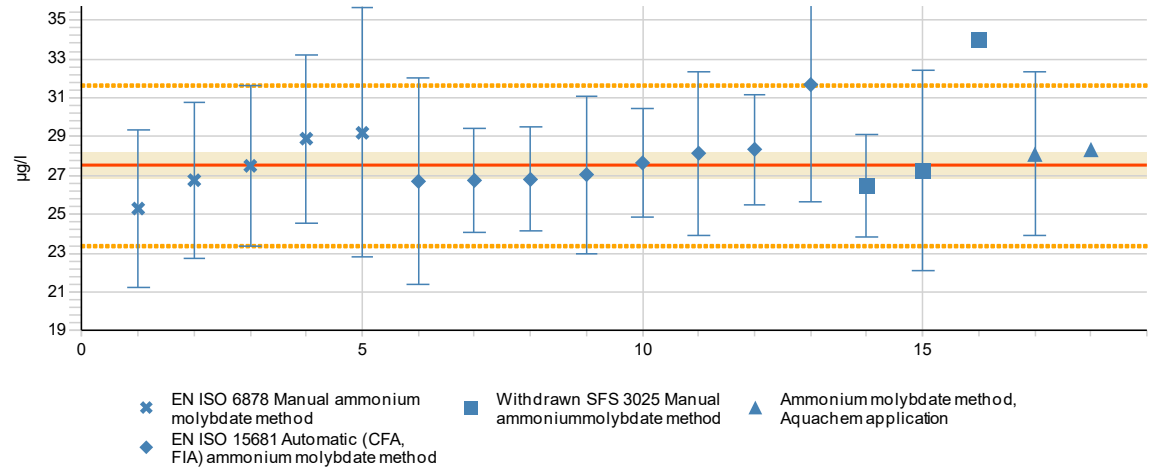
Measurand pH Sample N3H

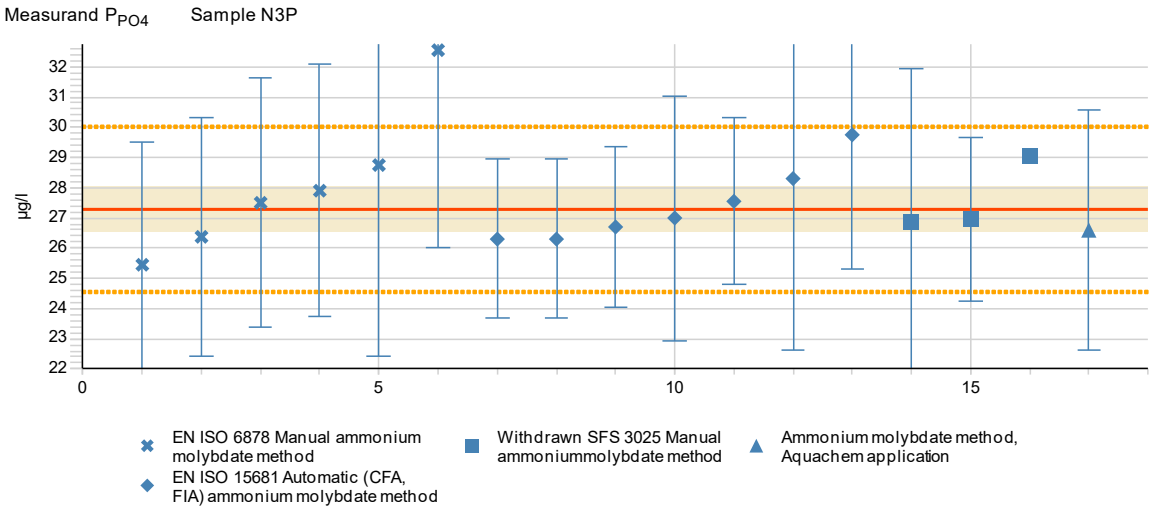


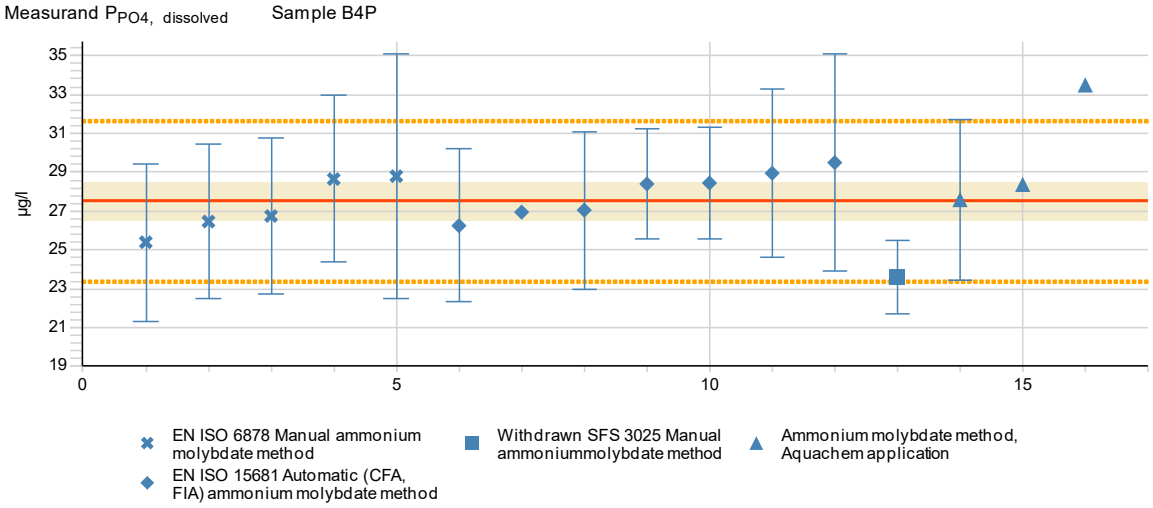
Measurand P_{PO4} Sample A1P

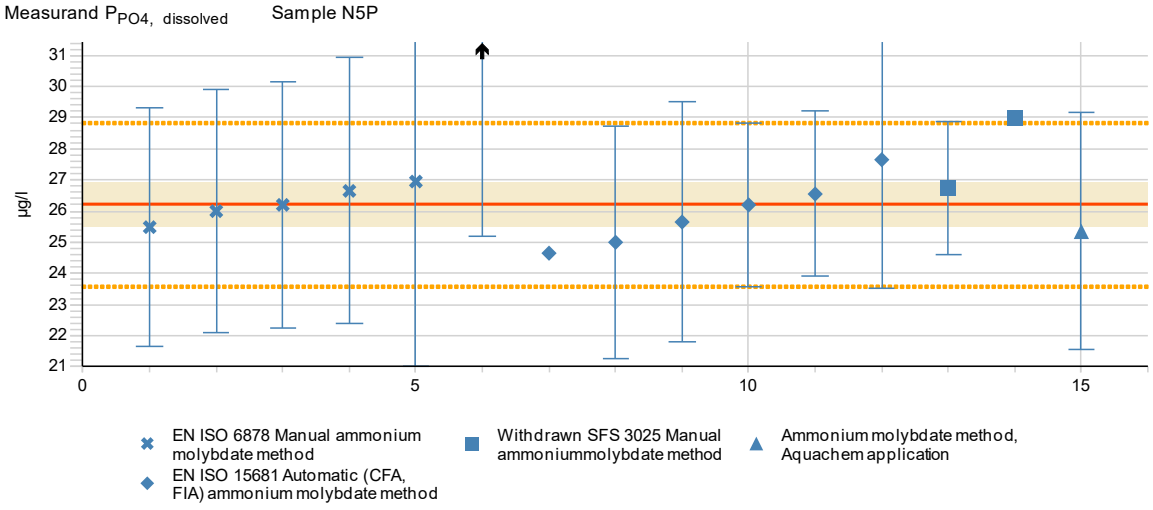


Measurand P_{PO4} Sample B2P

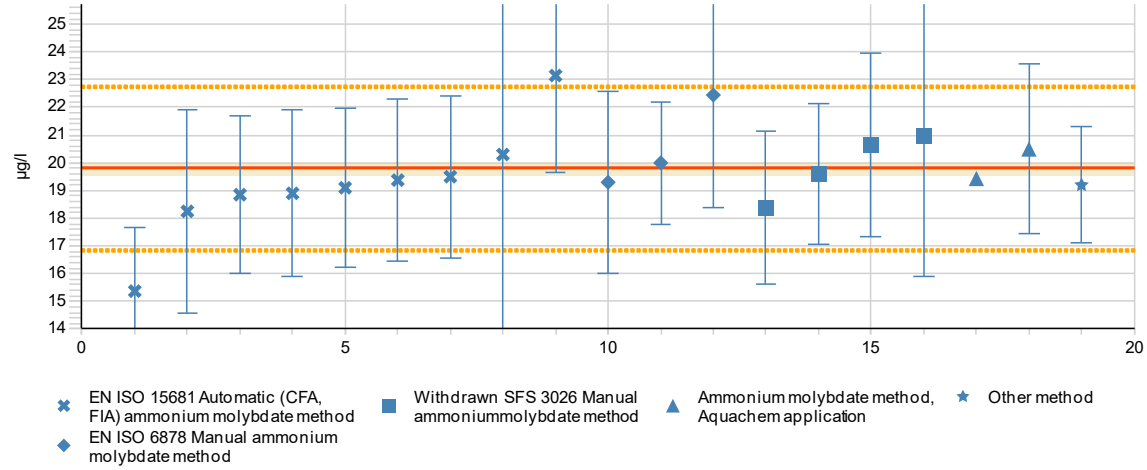



Measurand P_{PO4} Sample N3P
µg/l
32
31
30
29
28
27
26
25
24
23
22
0
5
10
15
EN ISO 6878 Manual ammonium molybdate method
EN ISO 15681 Automatic (CFA, FIA) ammonium molybdate method
Withdrawn SFS 3025 Manual ammoniummolybdate method
Ammonium molybdate method, Aquachem application


Measurand $P_{PO4,\ dissolved}$ Sample B4P
µg/l
35
33
31
29
27
25
23
21
19
0
5
10
15
EN ISO 6878 Manual ammonium molybdate method
EN ISO 15681 Automatic (CFA, FIA) ammonium molybdate method
Withdrawn SFS 3025 Manual ammoniummolybdate method
Ammonium molybdate method, Aquachem application

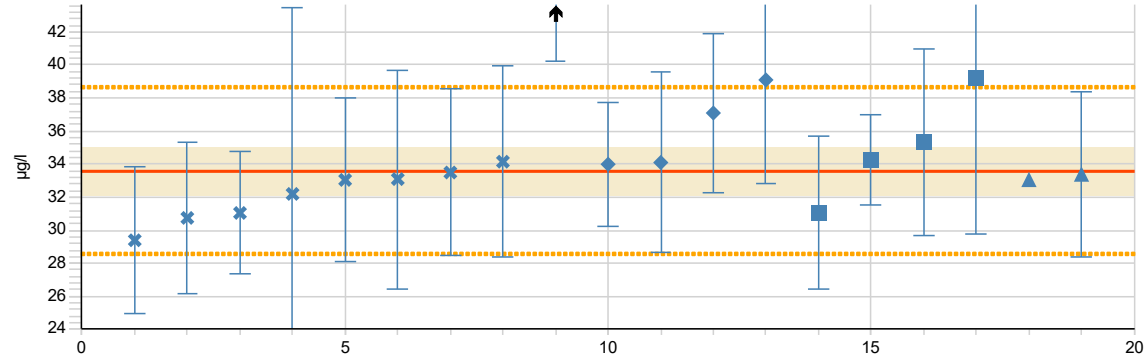

Measurand $P_{PO4,\ dissolved}$ Sample N5P
µg/l
31
30
29
28
27
26
25
24
23
22
21
0
5
10
15
EN ISO 6878 Manual ammonium molybdate method
EN ISO 15681 Automatic (CFA, FIA) ammonium molybdate method
Withdrawn SFS 3025 Manual ammoniummolybdate method
Ammonium molybdate method, Aquachem application

Measurand P_{tot} Sample A1P



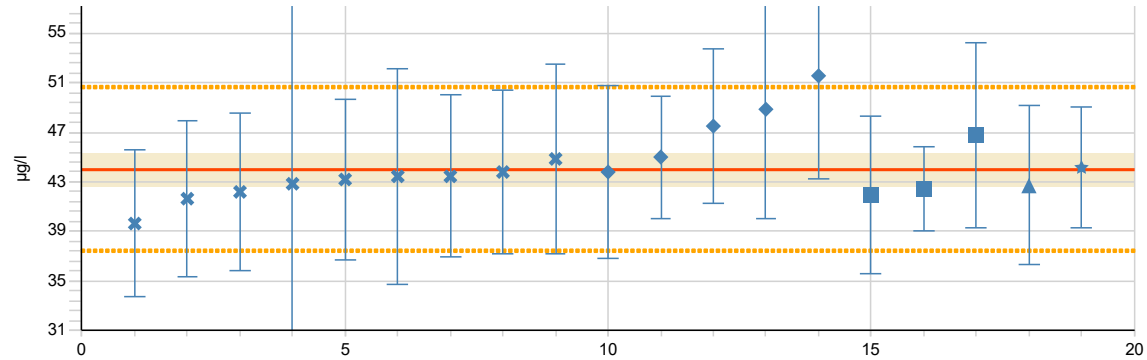
EN ISO 15681 Automatic (CFA, FIA) ammonium molybdate method
Withdrawn SFS 3026 Manual ammoniummolybdate method
Ammonium molybdate method, Aquachem application
Other method
EN ISO 6878 Manual ammonium molybdate method

Measurand P_{tot} Sample B2P

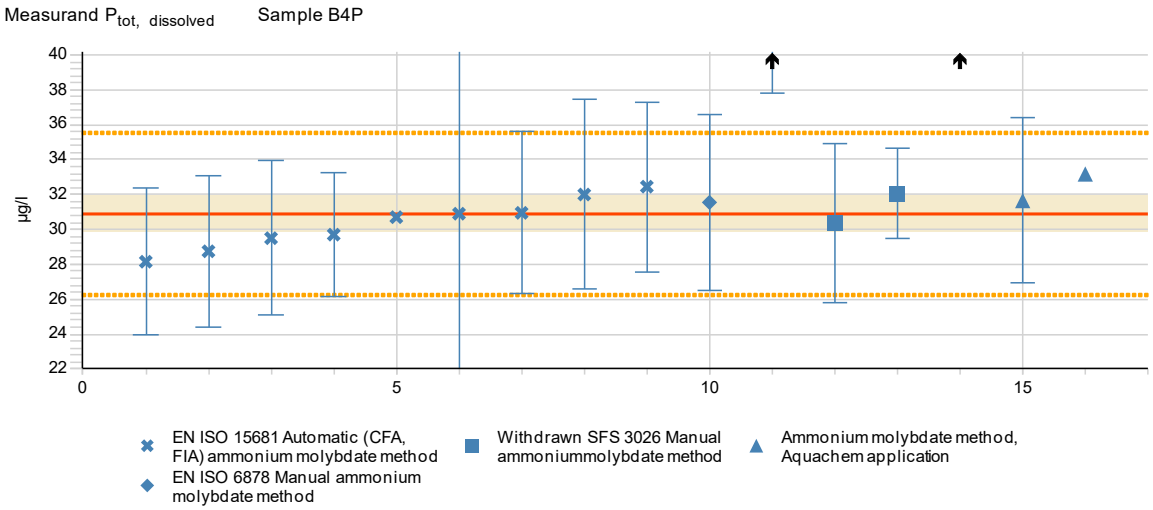


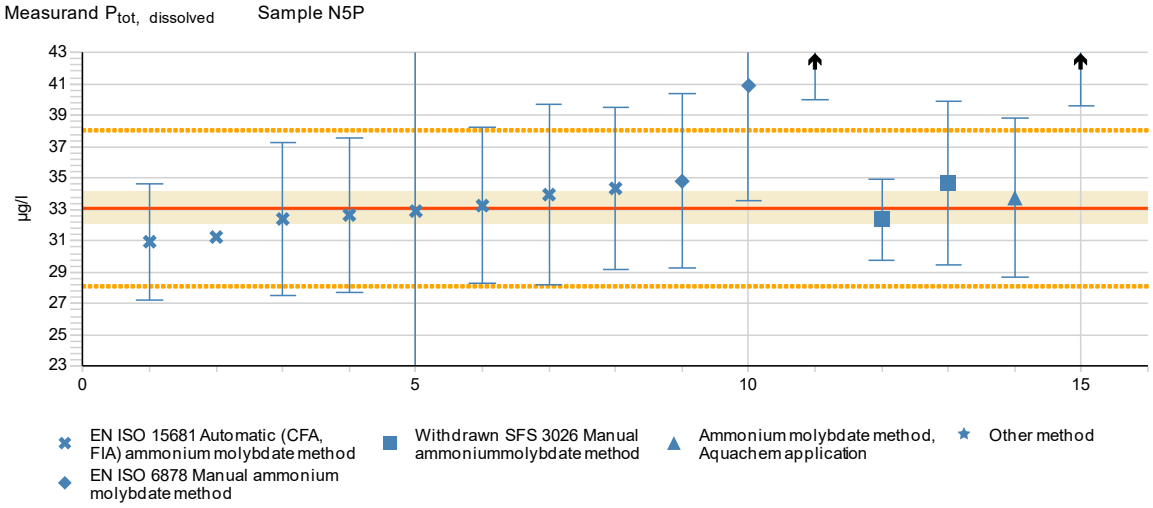
EN ISO 15681 Automatic (CFA, FIA) ammonium molybdate method
Withdrawn SFS 3026 Manual ammoniummolybdate method
Ammonium molybdate method, Aquachem application
EN ISO 6878 Manual ammonium molybdate method

Measurand P_{tot} Sample N3P



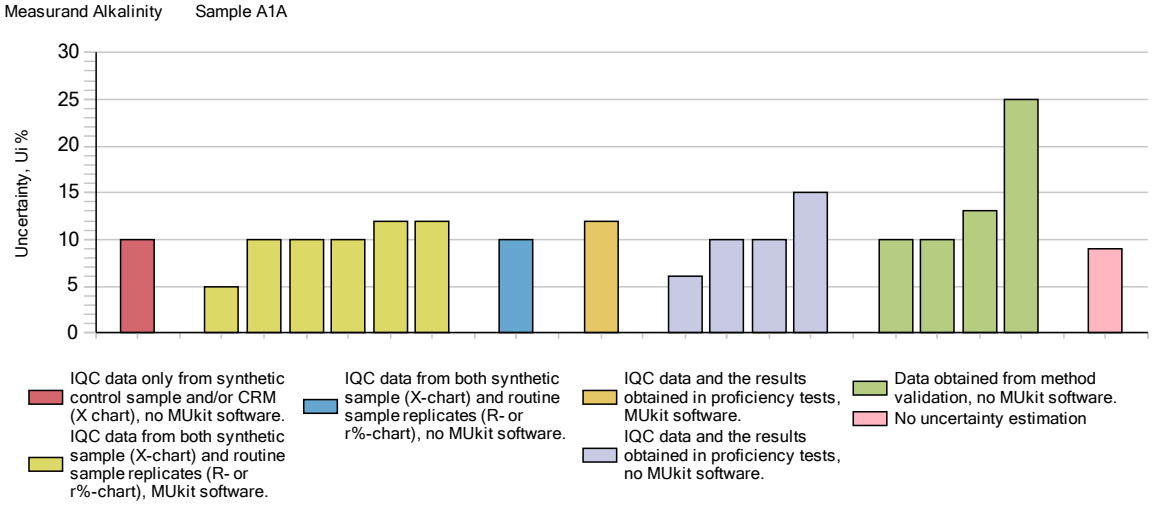
EN ISO 15681 Automatic (CFA, FIA) ammonium molybdate method
Withdrawn SFS 3026 Manual ammoniummolybdate method
Ammonium molybdate method, Aquachem application
Other method
EN ISO 6878 Manual ammonium molybdate method

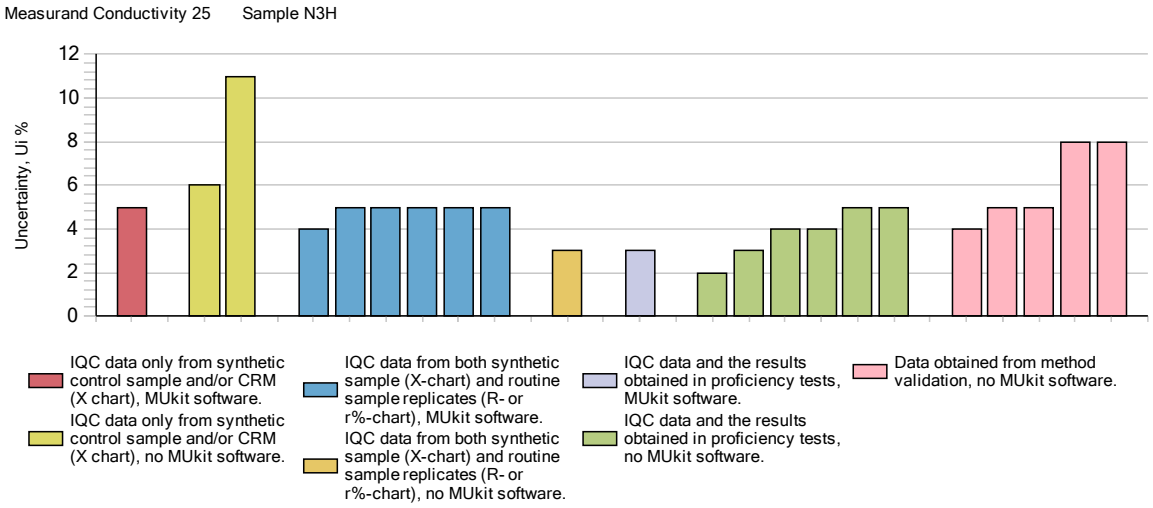

Measurand P tot, dissolved
Sample B4P
µg/l
40
38
36
34
32
30
28
26
24
22
0
5
10
15
EN ISO 15681 Automatic (CFA, FIA) ammonium molybdate method
Withdrawn SFS 3026 Manual ammoniummolybdate method
Ammonium molybdate method, Aquachem application
EN ISO 6878 Manual ammonium molybdate method


Measurand P tot, dissolved
Sample N5P
µg/l
43
41
39
37
35
33
31
29
27
25
23
0
5
10
15
EN ISO 15681 Automatic (CFA, FIA) ammonium molybdate method
Withdrawn SFS 3026 Manual ammoniummolybdate method
Ammonium molybdate method, Aquachem application
Other method
EN ISO 6878 Manual ammonium molybdate method

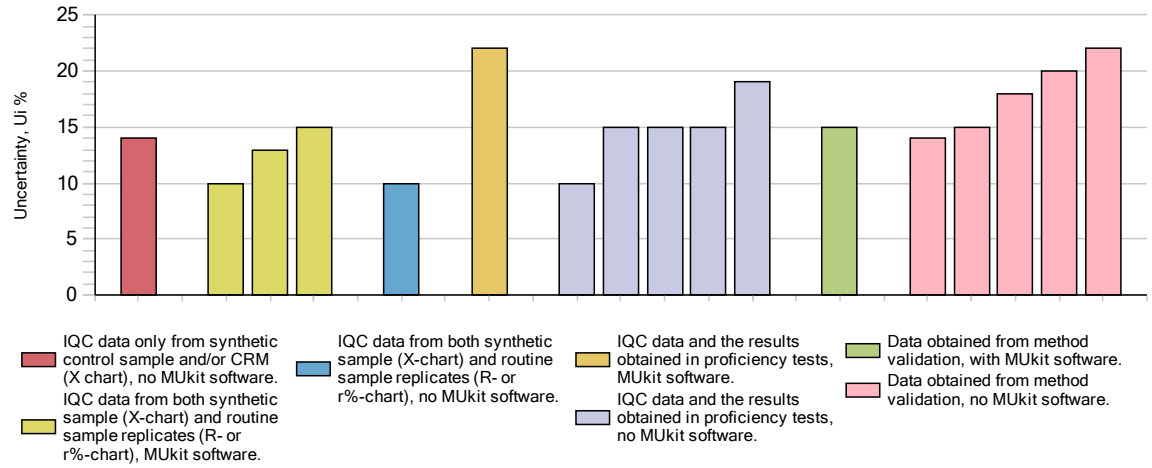
APPENDIX 13: Examples of measurement uncertainties reported by the participants

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 [8, 9].



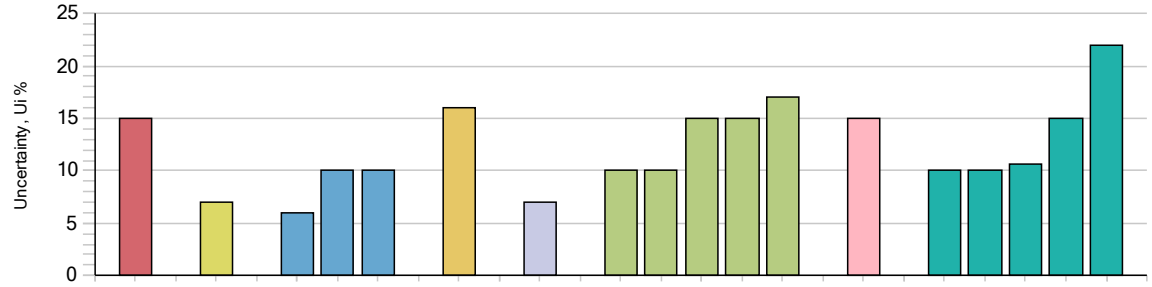


Measurand N_{NH4} Sample B2N



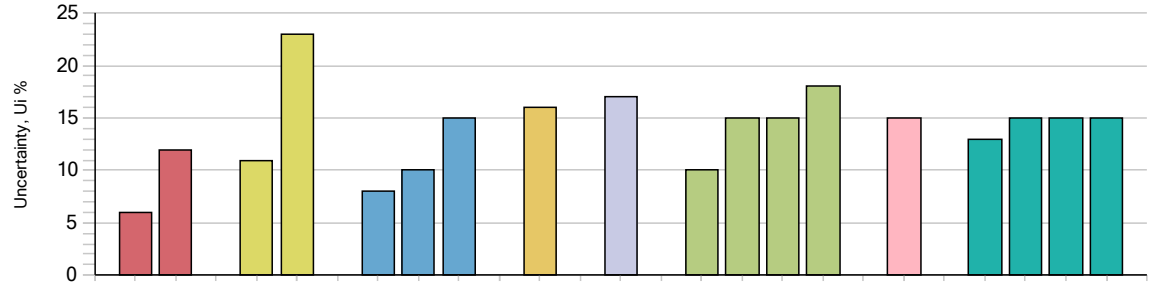
IQC data only from synthetic control sample and/or CRM (X chart), no MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), no MUkit software.
IQC data and the results obtained in proficiency tests, MUkit software.
Data obtained from method validation,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

Measurand $N_{NO2+NO3}$ Sample B2N



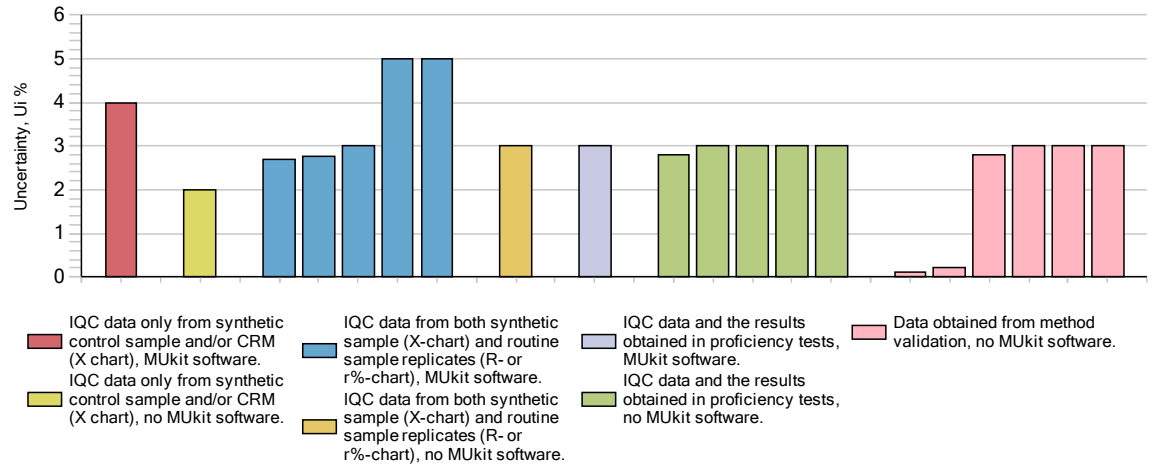
IQC data only from synthetic control sample and/or CRM (X chart), MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.
IQC data and the results obtained in proficiency tests, MUkit software.
Data obtained from method validation,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

Measurand N_{tot} Sample N3N

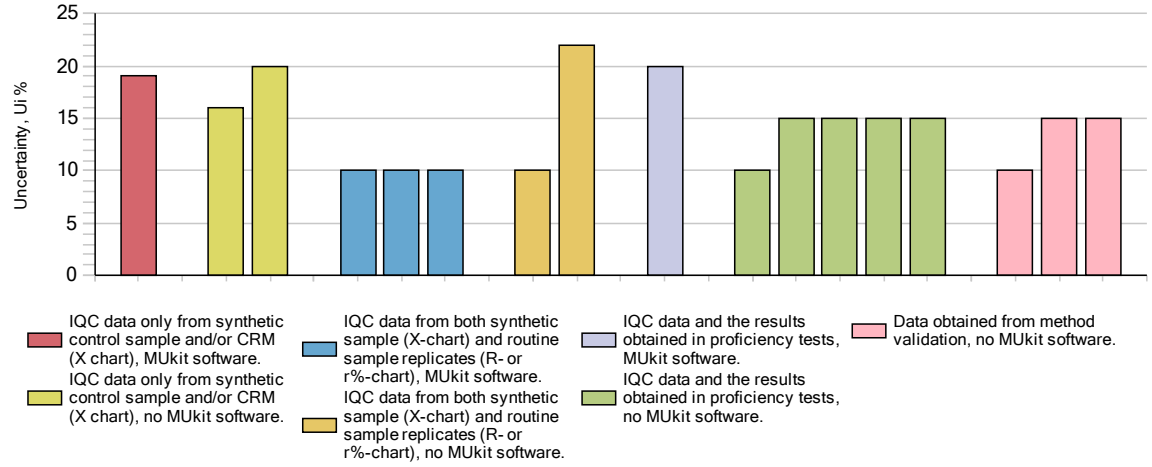


IQC data only from synthetic control sample and/or CRM (X chart), MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.
IQC data and the results obtained in proficiency tests, MUkit software.
Data obtained from method validation,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

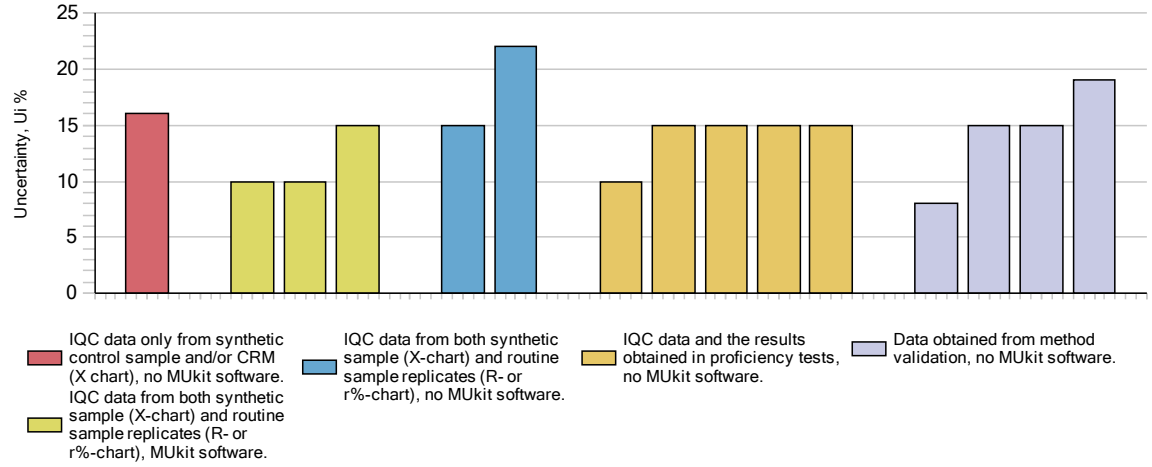
Measurand pH Sample A1H

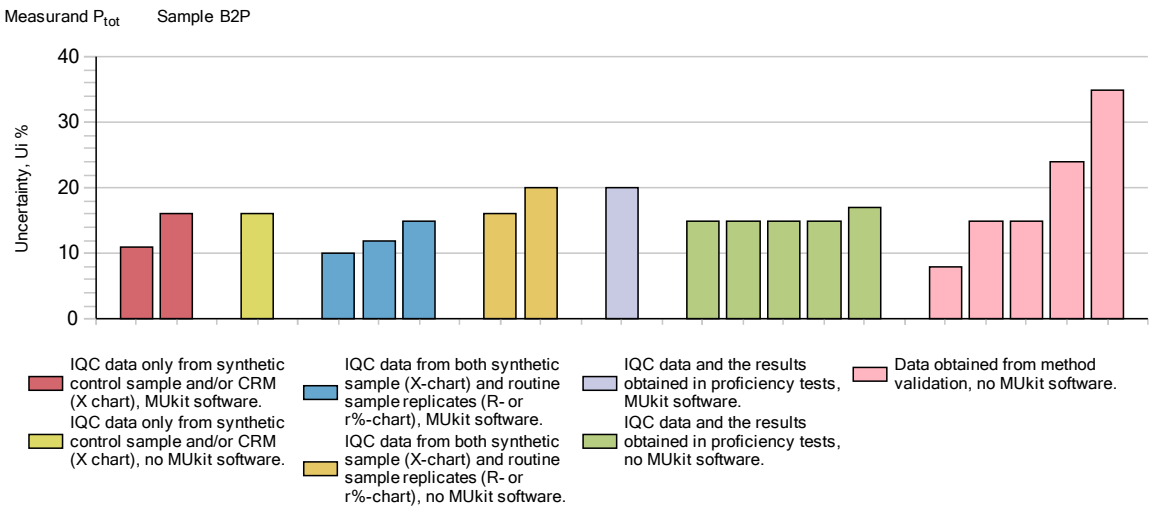


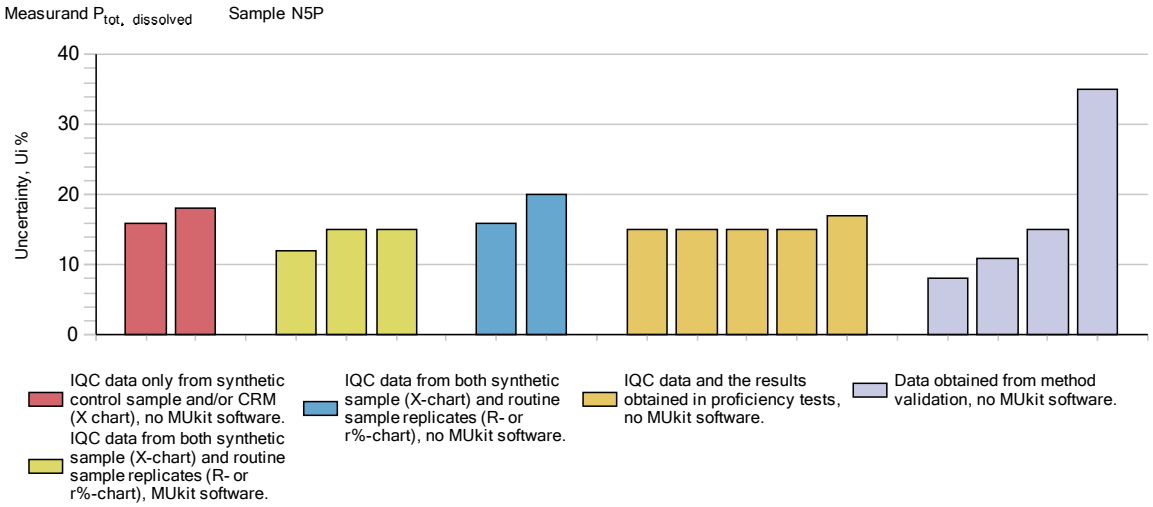
Measurand P_{PO4} Sample N3P



Measurand $P_{PO4,\ dissolved}$ Sample B4P




Measurand P_{tot}
Sample B2P
Uncertainty, Ui %
40
30
20
10
0
IQC data only from synthetic control sample and/or CRM (X chart), MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.
IQC data and the results obtained in proficiency tests, MUkit software.
Data obtained from method validation, no MUkit software.
IQC data only from synthetic control sample and/or CRM (X chart), no MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), no MUkit software.
IQC data and the results obtained in proficiency tests, no MUkit software.


Measurand $P_{tot,\ dissolved}$
Sample N5P
Uncertainty, Ui %
40
30
20
10
0
IQC data only from synthetic control sample and/or CRM (X chart), no MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), no MUkit software.
IQC data and the results obtained in proficiency tests, no MUkit software.
Data obtained from method validation, no MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.

INTERLABORATORY PROFICIENCY TEST 02/2020

FINNISH ENVIRONMENT INSTITUTE

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ISBN 978-952-11-5165-1 (pbk.)
ISBN 978-952-11-5166-8 (PDF)
ISSN 1796-1718 (print)
ISSN 1796-1726 (Online)