Reports of the Finnish Environment Institute 36 | 2022

Proficiency Test 06/2022

Natural water analyses II

Päivi Grönroos, Mirja Leivuori, Teemu Näykki, Olga Kovru, Jaana Kolehmainen, Keijo Tervonen, Sari Lanteri, Ritva Väisänen and Markku Ilmakunnas

PROF TEST SYKE

Finnish Environment Institute

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

Reports of the Finnish Environment Institute 36 | 2022
Finnish Environment Institute
Laboratory Centre

Authors: Päivi Grönroos, Mirja Leivuori, Teemu Näykki, Olga Kovru, Jaana Kolehmainen, Keijo Tervonen, Sari Lanteri, Ritva Väisänen and Markku Ilmakunnas

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

Layout: Markku Ilmakunnas
Cover photo: Adobe Stock

The publication is available in the internet (pdf): syke.fi/publications | helda.helsinki.fi/syke

ISBN 978-952-11-5512-3 (PDF)
ISSN 1796-1726 (online)

Year of issue: 2022

Abstract

Proficiency Test 06/2022: Natural water analyses II
Proftest SYKE carried out the proficiency test for the determination of chlorophyll *a*, oxygen, salinity, SiO_2, TIC, and TOC in natural waters in May 2022. In total, 28 participants joined in the proficiency test. Either the calculated concentration or the robust mean or the mean of the results reported by the participants was chosen to be the assigned value for the measurands. For the synthetic sample of salinity, the mean of the participants' and the homogeneity test results measured by the salinometer was used as the assigned value. The performance of the participants was evaluated by using z scores. In this proficiency test 88 % of the results were satisfactory, when deviation 3.5–20 % from the assigned value was accepted. Warm thanks to all the participants in this proficiency test!

Keywords: water analysis, chlorophyll *a*, oxygen, salinity, SiO_2, TIC, TOC, water and environmental laboratories, proficiency test, interlaboratory comparison

Tiivistelmä

Pätevyyskoe 06/2022: Luonnonvesianalyysit II
Proftest SYKE järjesti luonnonvesiä analysoiville laboratorioille pätevyyskokeen toukokuussa 2022. Määritettävinä testisuureina olivat happi, klorofylli *a*, saliniteetti, SiO_2, TIC ja TOC synteettisestä näytteestä sekä murto- ja jokivedestä. Pätevyyskokeessa oli yhteensä 28 osallistujaa. Testisuureen vertailuarvona käytettiin joko laskennallista pitoisuutta tai osallistujien tulosten robustia keskiarvoa tai keskiarvoa. Saliniteetin synteettiselle näytteelle käytettiin vertailuarvona salinometrimääritysten osallistujatulosten ja homogeenisuustestauksen tulosten keskiarvoa. Tulosten arviointi tehtiin z-arvojen perusteella, jolloin määrityksissä sallittiin 3,5–20 %:n poikkeama vertailuarvosta. Koko aineistossa hyväksyttäviä tuloksia oli 88 %. Kiitos pätevyyskokeen osallistujille!

Avainsanat: vesianalyysi, happi, klorofylli *a*, saliniteetti, SiO_2, TIC, TOC, vesi- ja ympäristölaboratoriot, pätevyyskoe, laboratorioiden välinen vertailumittaus

Sammandrag

Kompetensprövning 06/2022: Naturvattenanalyser II
Under maj 2022 genomförde Proftest SYKE en kompetensprövning, som omfattade bestämningen av klorofyll *a*, oxygen, salinitet, SiO_2, TIC och TOC i naturvatten. Denna kompetensprövning hade totalt 28 deltagarna. Som referensvärde av analytens koncentration användes antingen det teoretiska värdet, robust medelvärdet eller medelvärdet av deltagarnas resultat. Resultaten värderades med hjälp av z-värden. I denna kompetensprövning var 88 % av resultaten värderades med z-värden acceptabla. Resultatet var acceptabel, om det devierade mindre än 3,5–20 % från referensvärdet. Ett varmt tack till alla deltagarna i testet!

Nyckelord: vattenanalyser, klorofyll *a*, oxygen, salinitet, SiO_2, TIC, TOC, kompetensprövning, vatten- och miljölaboratorier, jämförelse mellan laboratorier

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1 Introduction

Proftest SYKE carried out the proficiency test (PT) for analysis of chlorophyll *a*, oxygen, salinity, SiO_2, TIC, and TOC in brackish and river waters in May 2022 (NW 06/2022). In the PT the results of Finnish laboratories providing environmental data for Finnish environmental authorities were evaluated. Additionally, other water and environmental laboratories were welcomed in the proficiency test.

Finnish Environment Institute (SYKE) is appointed National Reference Laboratory in the environmental sector in Finland. The duties of the reference laboratory include providing interlaboratory proficiency tests and other comparisons for analytical laboratories and other producers of environmental information. This proficiency test has been carried out under the scope of the SYKE reference laboratory and it provides an external quality evaluation between laboratory results, and mutual comparability of analytical reliability. The proficiency test was carried out in accordance with the international 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@syke.fi*

The responsibilities in organizing the proficiency test

Päivi Grönroos	coordinator
Mirja Leivuori	substitute for coordinator
Keijo Tervonen	technical assistance
Markku Ilmakunnas	technical assistance
Sari Lanteri	technical assistance
Ritva Väisänen	technical assistance
Analytical experts	Teemu Näykki, SYKE (chlorophyll *a*, oxygen, SiO_2, TOC, TIC) Jaana Kolehmainen, SYKE (In the expert orientation: chlorophyll *a*, oxygen, SiO_2, TOC, TIC) Olga Kovru, SYKE (salinity)
Expert laboratory	SYKE, Oulu (T003, www.finas.fi/sites/en)

2.2 Participants

In total 28 laboratories participated in this PT (Appendix 1), 21 from Finland and 7 from abroad. 79 % of the participants reported that they have accredited quality management system based on ISO/IEC 17025. Altogether 89 % of the participants used accredited analytical methods at least for a part of the measurements. For this PT, the expert laboratory has code 19 in the result tables.

2.3 Samples and delivery

Three types of samples were delivered to the participants: synthetic, brackish and river water samples.

The synthetic samples for SiO_2 and TOC measurements (A1C and A1P) were prepared from the NIST traceable certified reference materials (Merck Certipur).

When preparing the samples, the purity of the used sample vessels was controlled. The randomly chosen sample vessels for salinity, SiO_2, TIC, and TOC measurements were filled with deionized water. The purity of the sample vessels was controlled after three days by analyzing conductivity, TIC, and TOC. According to the test results all used vessels fulfilled the purity requirements.

The brackish water was collected from Ruukinranta, Espoo, Finland and the river water was collected from the river Mustionjoki, Finland. The sample preparation is described in detail in the Appendix 2.

The samples were delivered on 9 May 2022 to the participants abroad and mainly on 10 March 2022 to the national participants. The samples arrived to most of the participants on 11 May 2022 and to all the participants at the latest on 13 May 2022.

The samples were to be measured as follows:

oxygen, chlorophyll *a*, TIC	12 May 2022
salinity, SiO_2, TOC	at the latest on 20 May 2022

The results were to be reported at the latest on 23 May 2022. Participants delivered the results mainly accordingly, two participants delivered the results on 24 May 2022. The preliminary results report was delivered to the participants via ProftestWEB and email on 1 June 2022.

2.4 Homogeneity and stability studies

The homogeneity of the samples was tested by analyzing chlorophyll *a*, oxygen, salinity, SiO_2, TIC, and TOC. More detailed information of homogeneity test 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 chlorophyll *a*, oxygen, and TIC from the samples stored at the room temperature for one day. The measurement values were checked against the results of the samples stored at 4 °C. According to the test all samples were considered as stable (Appendix 4). Based on the stability test the possible increase of the sample temperature during the transportation did not affect the performance of the participants.

The temperature control sample was placed into the sample package and the temperature was requested to be measured immediately after opening the package. The reported temperature of the control sample was mainly ≤ 14 °C, two participants reported higher temperature. Based on the stability test the possible increase of the sample temperature during the transportation did not affect the performance of the participants.

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 bubbles in the oxygen sample and delayed sample delivery. The comments from the provider focused on the missing sample arrival information and the measurement uncertainty reporting. 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 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 detection limit, it has not been included in the statistical calculations.

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

2.6.2 Assigned values

The NIST traceable calculated values were used as the assigned values for the synthetic samples of SiO_2 and TOC. For the synthetic sample of salinity (A1S) the mean of the participants' and the homogeneity test results measured by the salinometer was used as the assigned value. For the other samples and measurands the robust mean or the mean (Salinity: B2S, SiO_2: B2P ja N3P, TIC: A1T ja N3T, TOC: B2C, $n_{stat}<12$) of the results reported by the participants was used as the assigned value. Detailed information of the assigned values, their uncertainties and reliability is shown in Appendix 6.

The assigned values based on the robust mean or the mean 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 evaluated by using standard uncertainties associated with individual operations involved in the preparation of the sample. The main individual source of the uncertainty was the purity of the stock compound. When the robust mean or the mean was used as the assigned value, the uncertainty was calculated using the robust standard deviation or the standard deviation, respectively [2, 4].

The expanded uncertainty of the calculated assigned value was 0.8 % for SiO_2 and 1.2 % for TOC. The expanded measurement uncertainties reported for the salinometer determinations (2 % for all measurements) were used as the uncertainty of the assigned value for the synthetic sample of salinity. When using the robust mean or the mean of the participant results as the assigned value, the expanded

uncertainties of the assigned values varied between 0.9 % and 8.4 %. (Appendix 6). **After reporting the preliminary results report no changes have been done for the assigned values.**

2.6.3 Proficiency assessment procedure

The results of this proficiency test were evaluated with the z scores. 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 ($2 \times s_{pt}$ at the 95 % confidence level) was set to 3.5–20 % depending on the measurand. **After reporting the preliminary results report no changes have been done for the standard deviations of the proficiency assessment values.**

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

The reliability 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 (the criterion) [3]. The uniformity criterion s_{rob} (or s) / $s_{pt} \leq 1.2$ was fulfilled.

In the following cases, 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
N3P	SiO_2
N3C	TOC

3 Results and conclusions

3.1 Results

The summary of the results is presented in Table 1. The terms in the results table are explained in 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) are presented in Appendix 9. The summary of the z scores is shown in Appendix 10 and z scores in the ascending order in Appendix 11.

The robust standard deviations of the results varied from 0.9 to 9 % (Table 1). The robust standard deviation was lower than 5 % for 50 % of the results and lower than 10 % for 93 % of the results. The highest standard deviation (10 %) was for SiO_2 in the river water sample (N3P). The robust standard deviations were approximately in the same range as in the previous similar proficiency test NW 06/2020, where the deviations varied from 1.4 % to 16 % [5].

Table 1. The summary of the results in the proficiency test NW 06/2022.

Measurand	Sample	Unit	Assigned value	Mean	Rob. mean	Median	s_{rob} / *s*	s_{rob} % / *s* %	2 x s_{pt} %	n_{all}	Acc z %
Chlorophyll *a*	A1K	abs/cm	0.11	0.11	0.11	0.11	<0.01	1.5	10	16	100
	B2K	µg/l	14.9	14.9	14.9	15.1	1.0	6.5	15	16	88
	N3K	µg/l	21.8	22.0	21.8	22.1	1.4	6.3	15	17	82
O_2	B2O	mg/l	11.5	11.4	11.5	11.5	0.4	3.1	8	18	94
	N3O	mg/l	9.66	9.66	9.66	9.67	0.32	3.4	8	15	93
Salinity	A1S	PSU	1.41	1.38	1.38	1.40	0.08	5.8	5	9	44
	B2S	PSU	3.02	3.02	3.02	3.03	0.05	1.7	3.5	10	100
SiO_2	A1P	mg/l	1.64	1.61	1.61	1.62	0.08	4.8	10	11	91
	B2P	mg/l	6.35	6.35	6.36	6.35	0.30	4.6	10	10	90
	N3P	mg/l	4.12	4.12	-	4.06	*0.42*	*10*	20	9	67
TIC	A1T	mg/l	2.14	2.14	2.14	2.15	0.18	8.4	15	7	100
	N3T	mg/l	7.95	7.95	7.92	7.88	0.41	5.1	15	7	100
TOC	A1C	mg/l	2.05	2.24	2.24	2.24	0.21	9.2	15	14	71
	B2C	mg/l	5.84	5.84	5.83	5.78	0.18	3.0	10	11	91
	N3C	mg/l	8.41	8.44	8.41	8.29	0.43	5.2	10	14	93

Rob. mean: the robust mean, s_{rob}: the robust standard deviation, *s: the standard deviation,* s_{rob} %: the robust standard deviation as percent, *s %: the 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 $|z| \leq 2$.

3.2 Analytical methods

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

Chlorophyll *a*

Most of the participants (14–15, depending on the sample) determined chlorophyll *a* by spectrophotometry using e.g. the standard methods SFS 5772 and ISO 10260. One participant used fluorometric determination (extraction with ethanol) and one participant used other method (photometry, extraction with methanol) for the chlorophyll *a* measurements (Appendix 12).

Oxygen O_2

Depending on the sample, 11–13 participants determined oxygen with the standard method EN 25813, whereas 3–4 participants (depending on the sample) used a method based on the withdrawn standard SFS 3040. One participant used other method (potentiometric titration). Based on the visual evaluation no clear differences between the methods were observed (Appendix 12).

Salinity

Two participants determined salinity using salinometer and 7–8 participants (depending on the sample) used conductivity meter. (Appendix 12).

SiO_2

Depending on the sample, 4–5 participants used automatic (CFA, FIA) molybdosilicate spectrophotometric method, one participant determined SiO_2 by manual molybdosilicate spectrophotometric method, 2–3 participants (depending on the sample) used ICP-OES or ICP-AES technique, and two participants used other methods (Appendix 12).

TIC

Five participants measured TIC as carbon dioxide originating from elemental carbon, carbon dioxide, carbon monoxide, cyanide, cyanate, and thiocyanate. Two participants measured TIC as carbon dioxide originating only from carbonates and hydrogen carbonates (Appendix 12).

TOC

Most of the participants (8–10, depending on the sample) measured TOC using the NPOC-method where inorganic carbon is removed prior total carbon measurement. Depending on the sample, 3–4 participant quantified TOC as the calculated difference of total and inorganic carbon. Based on the visual evaluation no clear differences between the methods were observed (Appendix 12).

3.3 Uncertainties of the results

Together with their results, the participants were to report the expanded measurement uncertainties (k=2) as percentage. Altogether 86 % of the participants reported the measurement uncertainty with at least some of their results (Table 2, Appendix 9). The range of the reported uncertainties varied between the measurements and the sample types.

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 [6]. The recommendations for measurement uncertainties for the tested measurands in natural waters vary from 2 % to 20 %. In this PT some of participants had their measurement uncertainties within these limits, while some did not achieve them.

The most used approach to evaluate the measurement uncertainty was based on using the internal quality control data (synthetic sample and/or routine sample replicates, Appendix 13). Other approaches were using the internal quality control data and the results obtained from proficiency tests as well as evaluation using method validation data. Depending on the sample and measurand, up to five participants used MUkit measurement uncertainty software for the evaluation of their uncertainties, which is available on the webpage: www.syke.fi/envical/en [7, 8]. Generally, the used approach for evaluating the measurement uncertainty did not make definite impact on the uncertainty evaluations. Nearly all the participants reported the measurement uncertainty for their results obtained with accredited methods.

Table 2. The ranges of the reported expanded uncertainties (k=2, U_i%) by participants as percent and quality criteria for natural waters [6].

Measurand	Synthetic sample, %	Brackish water, %	River water, %	Recommendation [6] (Concentration area)
Chlorophyll *a*	10 – 20	10 – 20	10 – 20	±20 % (>2 µg/l)
O_2	-	5 – 22	5 – 22	±10 % (>2 mg/l)
Salinity	2 – 15	2 – 15	–	±2 % (salinometer) ±10 % (others) (> 1 ‰ or PSU)
SiO_2	7 – **68**	7 – 25	7 – 25	10 % (>0.20 mg/l)
TIC	10 – 25	–	10 – 25	–
TOC	5 – 42	10 – 25	5 – 25	±15 % (>2.5 mg/l)

In table with bold the values of expanded measurement uncertainty over 50 %.

Within the optimal measuring range, the expanded measurement uncertainty (k=2) should typically be 10–20 %. Close to the limit of quantification the relative measurement uncertainty is higher. Further, the expanded uncertainties below 5 % could commonly be considered unrealistic uncertainty values for routine laboratories. In this PT participants reported more realistic expanded measurement uncertainties than in the previous similar PT 06/2020 [5]. Nevertheless, harmonization of the uncertainty estimation should be continued.

4 Evaluation of the results

The performance evaluation of the participants was based on the z scores, which were calculated using the assigned values and the standard deviation for 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, 88 % of the results were satisfactory when total deviation of 3.5–20 % from the assigned values were accepted. Altogether 89 % of the 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 3. In the previous similar PT, NW 06/2020, the performance was satisfactory for 85 % of the participant results, when deviation of 10–30 % from the assigned value was accepted. [5]. Further, the measurands here were partly same than in PT NW 02/2021, and thus the performance is partly compared also against those results [9].

Table 3. Summary of the performance evaluation in the proficiency test NW 06/2022.

Measurand	2 x s_{pt}%	Satisfactory results, %	Remarks
Chlorophyll *a*	10–15	90	Good performance. In the NW 06/2020 the performance was satisfactory for 94 % of the results when deviation of 10–30 % from the assigned value was accepted and in the NW 02/2021 the performance was satisfactory for 91 % of the results [5, 9].
O_2	8	84	In the NW 06/2020 the performance was satisfactory for 87 % of the results [5].
Salinity	3.5–5	72	Difficulties in measurement of the sample A1S as only 44 % of the results were satisfactory. Excellent performance for the sample B2S (100 %). In the NW 06/2020 the performance was satisfactory for 75 % of the results [5].
SiO_2	10–20	83	The performance evaluation for the sample N3P only approximate. For the sample N3P only 67 % of the results were satisfactory. In the NW 06/2020 68 % of the results were satisfactory when deviation of 10–15 from the assigned value was accepted [5].
TIC	15	100	Excellent performance. In the NW 06/2020 100 % of the results were satisfactory [5].
TOC	10–15	85	The performance evaluation for the sample N3C only approximate. Difficulties in measurement of the sample A1C as only 71 % of the results were satisfactory. For the samples B2C and N3C the performance was good (> 90 %). In the NW 06/2020 89 % of the results were satisfactory [5].

5 Summary

Proftest SYKE carried out the proficiency test (PT) for analysis of chlorophyll *a*, oxygen, salinity, SiO_2, TIC, and TOC in May 2022 (NW 06/2022). Three types of samples were delivered to the participants: synthetic, brackish, and river water samples. In total, 28 laboratories participated in this proficiency test.

The calculated concentration (NIST traceable) or the robust mean or the mean of the results reported by the participants was used as the assigned value for the measurand. For the synthetic sample of salinity (A1S) the mean of the participants' and the homogeneity test results measured by the salinometer was used as the assigned value. The expanded uncertainty for the assigned value was estimated at the 95 % confidence level and it was 0.8–1.2 % for the calculated assigned values and for the other assigned values it was between 0.9–8.4 %.

The performance evaluation was based on the z scores. In total, 88 % of the results were satisfactory when total deviation of 3.5–20 % from the assigned values were accepted from the assigned value at the 95 % confidence level. Altogether 89 % of the participants reported to used accredited analytical methods at least for a part of the measurands and 88 % of those results were satisfactory.

6 Summary in Finnish

Proftest SYKE järjesti luonnonvesiä analysoiville laboratorioille pätevyyskokeen toukokuussa 2022 (NW 06/2022). Määritettävinä testisuureina olivat happi, klorofylli *a*, saliniteetti, SiO_2, TIC ja TOC synteettisestä näytteestä sekä murto- ja jokivedestä. Pätevyyskokeeseen osallistui yhteensä 28 laboratoriota.

Testisuureen vertailuarvona käytettiin laskennallista pitoisuutta (synteettinen näyte, NIST jäljitettävä), tai osallistujien tulosten robustia keskiarvoa tai keskiarvoa. Saliniteetin synteettiselle näytteelle (A1S) käytettiin vertailuarvona salinometrimääritysten osallistujatulosten ja homogeenisuustestauksen tulosten keskiarvoa. Laskennallisen vertailuarvon laajennettu epävarmuus (95 %:n luottamusväli) oli 0,8–1,2 %. Osallistujatulosten robustin keskiarvon tai keskiarvon avulla laskettujen vertailuarvojen laajennettu epävarmuus oli 0,9–8.4 %

Osallistujien pätevyyden arviointi tehtiin z-arvojen avulla. Koko tulosaineistossa oli z-arvoilla arvioituna 88 % hyväksyttäviä tuloksia, kun tulosten sallittiin vaihdella 3.5–20 % vertailuarvosta. Osallistujista 89 % käytti ainakin joissakin määrityksissä akkreditoituja analyysimenetelmiä ja näistä tuloksista 88 % oli hyväksyttäviä.

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Appendix 1. Participants in the proficiency test

Country	Participant
Finland	Eurofins Ahma Oy Seinäjoki
	Eurofins Ahma Oy, Oulu
	Eurofins Ahma Oy, Rovaniemi
	Eurofins Environment Testing Finland Oy, Lahti
	Hortilab Ab Oy
	HSY Käyttölaboratorio Pitkäkoski Helsinki
	HY, Tvärminnen eläintieteellinen asema, Hanko
	Kymen Ympäristölaboratorio Oy
	Lounais-Suomen vesi- ja ympäristötutkimus Oy, Turku
	Luonnonvarakeskus, Viikki B2-laboratorio
	LUVYLab Oy Ab
	MetropoliLab Oy
	Saimaan Vesi- ja Ympäristötutkimus Oy, Lappeenranta
	Savo-Karjalan Ympäristötutkimus Oy, Joensuu
	Savo-Karjalan Ympäristötutkimus Oy, Kuopio
	SGS Analytics Finland Oy
	SGS Finland Oy, Kotka
	SYKE Oulun toimipaikka
	SYKE/Merikeskus
	Tampereen Vesi/Viemärilaitoksen laboratorio
	ÅMHM laboratoriet, Jomala, Åland
Lithuania	Marine Research Institute, Klaipeda University
Norway	VestfoldLAB AS
Sweden	Medins Havs och Vattenkonsulter AB
	Oceanografiska Laboratoriet, SMHI, Västra Frölunda
	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
Chlorophyll *a* [abs/cm] [µg/l]	A1K	-	Chlorophyll *a* 2 mg (Sigma) / 1.5 litres of ethanol	0.11
	B2K	0.3	grown green algae 12.6	14.9
	N3K	0.3	grown green algae 20.2	21.8
Oxygen [mg/l]	B2O	11.2	-	11.5
	N3O	10.2	-	9.66
Salinity [PSU]	A1S	-	Standard seawater (IAPSO) 1.37	1.41
	B2S	3.19	-	3.02
SiO_2 [mg/l]	A1P	-	SiO_2 (Merck) 1.64	1.64
	B2P	6.03	-	6.35
	N3P	3.94	-	4.12
TIC [mg/l]	A1T	-	Na_2CO_3-$NaHCO_3$ (Merck) 1.70	2.14
	N3T	7.42	-	7.95
TOC [mg/l]	A1C	-	$C_8H_5KO_4$ (Merck) 2.05	2.05
	B2C	6.69	-	5.84
	N3C	9.55	-	8.41

First letter of the sample code indicates the sample matrix
A = Synthetic sample
B = Brackish water
N= Natural water (river water)

Appendix 3. Homogeneity of the samples

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

Criteria for homogeneity:

$s_{anal}/s_{pt}<0.5$ 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 samples
s_{sam} = between-sample deviation, standard deviation of the results between sub samples

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

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

Measurand/Sample	Concentration [µg/l] [mg/l] [PSU]	n	s_{pt} %	s_p	s_a	s_a/s_p	$s_a/s_p<0,5$?	s_{sam}^2	c	$s_{sam}^2<c$?
a-chlorophyll/B2K	16.2	6	7.5	1.22	0.42	0.35	Yes	0	0.59	Yes
a-chlorophyll/N3K	23.3	6	7.5	1.74	0.45	0.26	Yes	0	0.94	Yes
Oxygen/B2O	11.2	6	4	0.45	0.03	0.07	Yes	0.005	0.04	Yes
Oxygen/N3O	9.64	6	4	0.39	0.05	0.14	Yes	0.03	0.03	Yes
Salinity/B2S	3.03	4	1.75	0.05	0.0002	0.003	Yes	0	0.0007	Yes
SiO_2/B2P	6.36	4	5	0.32	0.01	0.05	Yes	0.001	0.02	Yes
SiO_2/N3P	3.98	4	10	0.40	0.02	0.05	Yes	0	0.04	Yes
TIC/N3T	7.66	4	7.5	0.57	0.02	0.04	Yes	0.001	0.08	Yes
TOC/B2C HCl	5.75	4	5	0.29	0.03	0.10	Yes	0	0.02	Yes
TOC/N3C HCl	9.05	4	5	0.45	0.03	0.06	Yes	0.003	0.05	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 9 or 10 May 2022 and they arrived to the participants mainly on 11 May 2022. The samples were to be analysed as follows:

chlorophyll *a*, oxygen, TIC	12 May 2022
salinity, SiO_2, TOC	at the latest on 20 May 2022

Stability of chlorophyll *a*, oxygen, and TIC samples was tested by analyzing the samples stored at the temperatures 4 and 20 ºC.

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

Chlorophyll *a*

Sample	**Result** [abs/cm]		**Sample**	**Result** [µg/l]		**Sample**	**Result** [µg/l]	
Date	12.5. (20 ºC)	12.5. (4 ºC)	Date	12.5. (20 ºC)	12.5. (4 ºC)	Date	12.5. (20 ºC)	12.5. (4 ºC)
A1K	0.1092	0.1108	**B2K**	14.708	15.432	**N3K**	22.081	22.835
D	0.0016		D	0.724		D	0.754	
$0.3 \times s_{pt}$	0.0017		$0.3 \times s_{pt}$	0.335		$0.3 \times s_{pt}$	0.491	
D < 0.3 × s_{pt}? Yes			**D < 0.3 × s_{pt}? No** [1)]			**D < 0.3 × s_{pt}? No** [1)]		

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

Oxygen

Sample	**Result** [mg/l]		**Sample**	**Result** [mg/l]	
Date *Pvm.*	12.5. (20 ºC)	12.5. (4 ºC)	Date *Pvm.*	12.5. (20 ºC)	12.5. (4 ºC)
B2O	11.55	11.52	**N3O**	10.02	9.89
D	0.03		D	0.13	
$0.3 \times s_{pt}$	0.14		$0.3 \times s_{pt}$	0.12	
D < 0.3 × s_{pt}? Yes			**D < 0.3 × s_{pt}? No** [1)]		

[1)] The difference is within the analytical error

TIC

Sample	**Result** [mg/l]		**Sample**	**Result** [mg/l]	
Date *Pvm.*	12.5. (20 ºC)	12.5. (4 ºC)	Date *Pvm.*	12.5. (20 ºC)	12.5. (4 ºC)
A1T	2.191	2.169	**N3T**	7.723	7.839
D	0.02		D	0.12	
$0.3 \times s_{pt}$	0.05		$0.3 \times s_{pt}$	0.18	
D < 0.3 × s_{pt}? Yes			**D < 0.3 × s_{pt}? Yes**		

Conclusion: The observed differences are within the analytical error, thus all criteria for stability were fulfilled and the samples could be considered stable.

Appendix 5. Feedback from the proficiency test

Feedback from the participants

Participant	Comments on technical excecution	Action / Proftest SYKE
7	The participant could not measure the arrival temperature due to the missing temperature control sample.	The organizer apologizes and will be more careful in the future.
10, 16, 23	The participants reported some air bubbles in the oxygen samples.	The air bubbles are formed due to the temperature differences between the sample preparation and storage. The oxygen is fixed in the samples and according to the provider's experience small air bubbles do not have any effect on the results.
13	The participant received the samples within one day after the estimated delivery day.	The used distributor (Posti/TNT) did not deliver the samples according to the agreed schedule.
26	The participant received the samples within two days after the estimated delivery day.	

Feedback to the participants

Participant	Comments
2, 8, 9, 14, 15, 17, 24, 25, 27	The participants did not return the sample arrival information to the provider. Thus, their information of the sample arrival temperature missed as well. The participants should follow the instructions of the provider.
24, 26, 27	The measurement uncertainty should be reported with the results obtained by accredited method.

Appendix 6. Evaluation of the assigned values and their uncertainties

Measurand	Sample	Unit	Assigned value	U_{pt}	U_{pt}, %	Evaluation method of assigned value	u_{pt}/s_{pt}
Chlorophyll *a*	A1K	abs/cm	0.11	<0.01	0.9	Robust mean	0.09
	B2K	µg/l	14.9	0.6	4.3	Robust mean	0.29
	N3K	µg/l	21.8	0.9	4.1	Robust mean	0.27
O_2	B2O	mg/l	11.5	0.2	1.8	Robust mean	0.23
	N3O	mg/l	9.66	0.21	2.2	Robust mean	0.28
Salinity	A1S	PSU	1.41	0.03	2.0	Mean of salinometer determinations	0.40
	B2S	PSU	3.02	0.03	1.0	Mean	0.29
SiO_2	A1P	mg/l	1.64	0.01	0.8	Calculated value	0.08
	B2P	mg/l	6.35	0.19	3.0	Mean	0.30
	N3P	mg/l	4.12	0.35	8.4	Mean	0.42
TIC	A1T	mg/l	2.14	0.12	5.6	Mean	0.37
	N3T	mg/l	7.95	0.32	4.0	Mean	0.27
TOC	A1C	mg/l	2.05	0.02	1.2	Calculated value	0.08
	B2C	mg/l	5.84	0.11	1.9	Mean	0.19
	N3C	mg/l	8.41	0.29	3.5	Robust mean	0.35

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.

Appendix 7. Terms in the results tables

The information could be applied according to the PT.

Measurand The tested parameter

Sample The code of the sample

Assigned value The value attributed to a particular property of a proficiency test item

Participant's result The result reported by the participant (when replicate results are reported, the mean value)

2 × s_{pt} % The standard deviation for proficiency assessment (s_{pt}) at the 95 % confidence level

z score Used for the participant's performance evaluation in the PT.
Calculated with formula:

$$z = (x_i - x_{pt})/s_{pt}, \text{ where}$$

x_i = the result of the individual participant
x_{pt} = the assigned value
s_{pt} = the standard deviation for proficiency assessment

Interpretation of the z scores

$\lvert z \rvert \leq 2$	Satisfactory
$2 < \lvert z \rvert < 3$	Questionable (warning signal), the result deviates more than 2 × s_{pt} from the assigned value.
$\lvert z \rvert \geq 3$	Unsatisfactory (action signal), the result deviates more than 3 × s_{pt} from the assigned value.

E_n score Error, normalized – Used to evaluate the difference between the assigned value and participant's result within their claimed expanded uncertainty. Calculated with formula:

$$(E_n)_i = \frac{x_i - x_{pt}}{\sqrt{U_i^2 + U_{pt}^2}}, \text{ where}$$

U_i = the expanded uncertainty of a participant's result
U_{pt} = the expanded uncertainty of the assigned value

Interpretation of the E_n scores

$\lvert E_n \rvert \leq 1.0$	Satisfactory, should be taken as an indicator of successful performance when the uncertainties are valid.
$\lvert E_n \rvert > 1.0$	Unsatisfactory (action signal), could indicate a need to review the uncertainty estimates, or to correct a measurement issue.

Md Median

s Standard deviation

s % Standard deviation, %

n_{stat} Number of results in statistical processing

More information of the statistical calculations in international standards ISO/IEC 17043 and ISO 13528 as well as in Proftest SYKE Guide for participants [1, 2, 4].

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}
SiO_2	mg/l	A1P		-0.98	1.64	10	1.56	1.62	1.61	0.07	4.2	10
	mg/l	B2P		0.00	6.35	10	6.35	6.35	6.35	0.29	4.6	9
	mg/l	N3P		3.18	4.12	20	5.43	4.06	4.12	0.42	10.3	6

Participant 2												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
TIC	mg/l	A1T		-0.44	2.14	15	2.07	2.15	2.14	0.16	7.4	7
	mg/l	N3T		-0.39	7.95	15	7.72	7.88	7.95	0.42	5.3	7
TOC	mg/l	A1C		0.98	2.05	15	2.20	2.24	2.24	0.19	8.4	14
	mg/l	B2C		-0.41	5.84	10	5.72	5.78	5.84	0.17	2.9	10
	mg/l	N3C		-1.00	8.41	10	7.99	8.29	8.44	0.45	5.3	14

Participant 3												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Salinity	PSU	B2S		-0.87	3.02	3,5	2.97	3.03	3.02	0.05	1.5	10

Participant 4												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
O_2	mg/l	B2O		-0.28	11.5	8	11.4	11.5	11.4	0.3	2.6	18
	mg/l	N3O		-0.36	9.66	8	9.52	9.67	9.66	0.29	3.0	14
Salinity	PSU	A1S		0.00	1.41	5	1.41	1.40	1.38	0.07	5.2	8
	PSU	B2S		0.19	3.02	3,5	3.03	3.03	3.02	0.05	1.5	10
SiO_2	mg/l	A1P		0.37	1.64	10	1.67	1.62	1.61	0.07	4.2	10
	mg/l	B2P		0.60	6.35	10	6.54	6.35	6.35	0.29	4.6	9

Participant 5												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Chlorophyll *a*	abs/cm	A1K		-0.18	0.11	10	0.11	0.11	0.11	0.00	0.9	16
	µg/l	B2K		1.88	14.9	15	17.0	15.1	14.9	1.0	6.9	14
	µg/l	N3K		0.43	21.8	15	22.5	22.1	22.0	1.2	5.4	15
O_2	mg/l	B2O		-1.09	11.5	8	11.0	11.5	11.4	0.3	2.6	18
	mg/l	N3O		-1.19	9.66	8	9.20	9.67	9.66	0.29	3.0	14
SiO_2	mg/l	A1P		0.37	1.64	10	1.67	1.62	1.61	0.07	4.2	10
	mg/l	B2P		0.00	6.35	10	6.35	6.35	6.35	0.29	4.6	9
	mg/l	N3P		-0.19	4.12	20	4.04	4.06	4.12	0.42	10.3	6
TIC	mg/l	A1T		1.62	2.14	15	2.40	2.15	2.14	0.16	7.4	7
	mg/l	N3T		1.33	7.95	15	8.74	7.88	7.95	0.42	5.3	7
TOC	mg/l	A1C		-1.04	2.05	15	1.89	2.24	2.24	0.19	8.4	14
	mg/l	B2C		-0.55	5.84	10	5.68	5.78	5.84	0.17	2.9	10
	mg/l	N3C		-0.81	8.41	10	8.07	8.29	8.44	0.45	5.3	14

Participant 6												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Chlorophyll *a*	abs/cm	A1K		-0.09	0.11	10	0.11	0.11	0.11	0.00	0.9	16
	µg/l	N3K		0.88	21.8	15	23.2	22.1	22.0	1.2	5.4	15
TOC	mg/l	A1C		1.50	2.05	15	2.28	2.24	2.24	0.19	8.4	14
	mg/l	N3C		1.33	8.41	10	8.97	8.29	8.44	0.45	5.3	14

Participant 7												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
TOC	mg/l	A1C		1.82	2.05	15	2.33	2.24	2.24	0.19	8.4	14
	mg/l	N3C		0.78	8.41	10	8.74	8.29	8.44	0.45	5.3	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}
Chlorophyll *a*	µg/l	B2K		-3.63	14.9	15	10.8	15.1	14.9	1.0	6.9	14
	µg/l	N3K		-3.40	21.8	15	16.2	22.1	22.0	1.2	5.4	15

Participant 9												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Chlorophyll *a*	abs/cm	A1K		0.00	0.11	10	0.11	0.11	0.11	0.00	0.9	16
	µg/l	B2K		-0.18	14.9	15	14.7	15.1	14.9	1.0	6.9	14
	µg/l	N3K		-0.18	21.8	15	21.5	22.1	22.0	1.2	5.4	15
O_2	mg/l	B2O		2.39	11.5	8	12.6	11.5	11.4	0.3	2.6	18
	mg/l	N3O		0.70	9.66	8	9.93	9.67	9.66	0.29	3.0	14
Salinity	PSU	A1S		33.48	1.41	5	2.59	1.40	1.38	0.07	5.2	8
	PSU	B2S		-1.14	3.02	3,5	2.96	3.03	3.02	0.05	1.5	10
SiO_2	mg/l	A1P		-1.59	1.64	10	1.51	1.62	1.61	0.07	4.2	10
	mg/l	B2P		-0.98	6.35	10	6.04	6.35	6.35	0.29	4.6	9
	mg/l	N3P		-1.02	4.12	20	3.70	4.06	4.12	0.42	10.3	6
TIC	mg/l	A1T		-0.69	2.14	15	2.03	2.15	2.14	0.16	7.4	7
	mg/l	N3T		0.17	7.95	15	8.05	7.88	7.95	0.42	5.3	7
TOC	mg/l	A1C		0.98	2.05	15	2.20	2.24	2.24	0.19	8.4	14
	mg/l	B2C		-0.45	5.84	10	5.71	5.78	5.84	0.17	2.9	10
	mg/l	N3C		-1.17	8.41	10	7.92	8.29	8.44	0.45	5.3	14

Participant 10												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
O_2	mg/l	B2O		-0.26	11.5	8	11.4	11.5	11.4	0.3	2.6	18

Participant 11												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
TOC	mg/l	A1C		1.50	2.05	15	2.28	2.24	2.24	0.19	8.4	14
	mg/l	B2C		1.13	5.84	10	6.17	5.78	5.84	0.17	2.9	10
	mg/l	N3C		1.26	8.41	10	8.94	8.29	8.44	0.45	5.3	14

Participant 12												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Chlorophyll *a*	abs/cm	A1K		-0.36	0.11	10	0.11	0.11	0.11	0.00	0.9	16
	µg/l	B2K		0.47	14.9	15	15.4	15.1	14.9	1.0	6.9	14
	µg/l	N3K		1.38	21.8	15	24.1	22.1	22.0	1.2	5.4	15
O_2	mg/l	B2O		-1.33	11.5	8	10.9	11.5	11.4	0.3	2.6	18
	mg/l	N3O		-0.68	9.66	8	9.40	9.67	9.66	0.29	3.0	14
Salinity	PSU	A1S		2.47	1.41	5	1.50	1.40	1.38	0.07	5.2	8
	PSU	B2S		1.42	3.02	3,5	3.10	3.03	3.02	0.05	1.5	10

Participant 13												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Chlorophyll *a*	abs/cm	A1K		-0.11	0.11	10	0.11	0.11	0.11	0.00	0.9	16
	µg/l	B2K		-0.98	14.9	15	13.8	15.1	14.9	1.0	6.9	14
	µg/l	N3K		-1.41	21.8	15	19.5	22.1	22.0	1.2	5.4	15
Salinity	PSU	A1S		-0.28	1.41	5	1.40	1.40	1.38	0.07	5.2	8
	PSU	B2S		-0.38	3.02	3,5	3.00	3.03	3.02	0.05	1.5	10

Participant 14												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Chlorophyll *a*	abs/cm	A1K		-0.09	0.11	10	0.11	0.11	0.11	0.00	0.9	16
	µg/l	B2K		0.30	14.9	15	15.2	15.1	14.9	1.0	6.9	14
	µg/l	N3K		0.20	21.8	15	22.1	22.1	22.0	1.2	5.4	15
O_2	mg/l	B2O		-0.10	11.5	8	11.5	11.5	11.4	0.3	2.6	18
	mg/l	N3O		-0.35	9.66	8	9.53	9.67	9.66	0.29	3.0	14
Salinity	PSU	A1S		-3.60	1.41	5	1.28	1.40	1.38	0.07	5.2	8
	PSU	B2S		0.79	3.02	3,5	3.06	3.03	3.02	0.05	1.5	10

Participant 15												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Chlorophyll *a*	abs/cm	A1K		-0.09	0.11	10	0.11	0.11	0.11	0.00	0.9	16
	µg/l	B2K		0.09	14.9	15	15.0	15.1	14.9	1.0	6.9	14
	µg/l	N3K		0.12	21.8	15	22.0	22.1	22.0	1.2	5.4	15
O_2	mg/l	B2O		0.87	11.5	8	11.9	11.5	11.4	0.3	2.6	18
	mg/l	N3O		1.14	9.66	8	10.10	9.67	9.66	0.29	3.0	14
Salinity	PSU	A1S		-0.14	1.41	5	1.41	1.40	1.38	0.07	5.2	8
	PSU	B2S		-0.95	3.02	3,5	2.97	3.03	3.02	0.05	1.5	10
SiO_2	mg/l	A1P		0.12	1.64	10	1.65	1.62	1.61	0.07	4.2	10
	mg/l	B2P		0.31	6.35	10	6.45	6.35	6.35	0.29	4.6	9
	mg/l	N3P		0.02	4.12	20	4.13	4.06	4.12	0.42	10.3	6
TIC	mg/l	A1T		-1.50	2.14	15	1.90	2.15	2.14	0.16	7.4	7
	mg/l	N3T		-0.12	7.95	15	7.88	7.88	7.95	0.42	5.3	7
TOC	mg/l	A1C		0.46	2.05	15	2.12	2.24	2.24	0.19	8.4	14
	mg/l	B2C		-0.24	5.84	10	5.77	5.78	5.84	0.17	2.9	10
	mg/l	N3C		0.43	8.41	10	8.59	8.29	8.44	0.45	5.3	14

Participant 16												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Chlorophyll *a*	abs/cm	A1K		-0.18	0.11	10	0.11	0.11	0.11	0.00	0.9	16
	µg/l	B2K		-1.07	14.9	15	13.7	15.1	14.9	1.0	6.9	14
	µg/l	N3K		-0.06	21.8	15	21.7	22.1	22.0	1.2	5.4	15
O_2	mg/l	B2O		0.22	11.5	8	11.6	11.5	11.4	0.3	2.6	18
	mg/l	N3O		0.36	9.66	8	9.80	9.67	9.66	0.29	3.0	14

Participant 17												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Chlorophyll *a*	abs/cm	A1K		-0.18	0.11	10	0.11	0.11	0.11	0.00	0.9	16
	µg/l	B2K		-1.83	14.9	15	12.9	15.1	14.9	1.0	6.9	14
	µg/l	N3K		-2.82	21.8	15	17.2	22.1	22.0	1.2	5.4	15
O_2	mg/l	B2O		-0.22	11.5	8	11.4	11.5	11.4	0.3	2.6	18
	mg/l	N3O		0.10	9.66	8	9.70	9.67	9.66	0.29	3.0	14
TOC	mg/l	A1C		2.28	2.05	15	2.40	2.24	2.24	0.19	8.4	14
	mg/l	B2C		-0.21	5.84	10	5.78	5.78	5.84	0.17	2.9	10
	mg/l	N3C		-0.59	8.41	10	8.16	8.29	8.44	0.45	5.3	14

Participant 18												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Chlorophyll *a*	abs/cm	A1K		0.27	0.11	10	0.11	0.11	0.11	0.00	0.9	16
	µg/l	B2K		0.45	14.9	15	15.4	15.1	14.9	1.0	6.9	14
	µg/l	N3K		-0.18	21.8	15	21.5	22.1	22.0	1.2	5.4	15
O_2	mg/l	B2O		-1.26	11.5	8	10.9	11.5	11.4	0.3	2.6	18
	mg/l	N3O		-1.35	9.66	8	9.14	9.67	9.66	0.29	3.0	14
Salinity	PSU	A1S		-3.12	1.41	5	1.30	1.40	1.38	0.07	5.2	8
	PSU	B2S		0.95	3.02	3,5	3.07	3.03	3.02	0.05	1.5	10

Participant 19												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Chlorophyll *a*	abs/cm	A1K		-0.09	0.11	10	0.11	0.11	0.11	0.00	0.9	16
	µg/l	B2K		0.43	14.9	15	15.4	15.1	14.9	1.0	6.9	14
	µg/l	N3K		0.66	21.8	15	22.9	22.1	22.0	1.2	5.4	15
O_2	mg/l	B2O		0.24	11.5	8	11.6	11.5	11.4	0.3	2.6	18
	mg/l	N3O		0.72	9.66	8	9.94	9.67	9.66	0.29	3.0	14
SiO_2	mg/l	A1P		-0.20	1.64	10	1.62	1.62	1.61	0.07	4.2	10
	mg/l	B2P		0.76	6.35	10	6.59	6.35	6.35	0.29	4.6	9
	mg/l	N3P		-0.08	4.12	20	4.09	4.06	4.12	0.42	10.3	6
TIC	mg/l	A1T		0.06	2.14	15	2.15	2.15	2.14	0.16	7.4	7
	mg/l	N3T		-0.20	7.95	15	7.83	7.88	7.95	0.42	5.3	7
TOC	mg/l	A1C		3.17	2.05	15	2.54	2.24	2.24	0.19	8.4	14
	mg/l	B2C		0.64	5.84	10	6.03	5.78	5.84	0.17	2.9	10
	mg/l	N3C		2.56	8.41	10	9.49	8.29	8.44	0.45	5.3	14

Participant 20												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Chlorophyll *a*	abs/cm	A1K		0.71	0.11	10	0.11	0.11	0.11	0.00	0.9	16
	µg/l	B2K		0.72	14.9	15	15.7	15.1	14.9	1.0	6.9	14
	µg/l	N3K		0.37	21.8	15	22.4	22.1	22.0	1.2	5.4	15
O_2	mg/l	B2O		-0.11	11.5	8	11.5	11.5	11.4	0.3	2.6	18
	mg/l	N3O		-0.08	9.66	8	9.63	9.67	9.66	0.29	3.0	14
SiO_2	mg/l	A1P		-0.73	1.64	10	1.58	1.62	1.61	0.07	4.2	10
	mg/l	N3P		2.67	4.12	20	5.22	4.06	4.12	0.42	10.3	6

Participant 21												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Chlorophyll *a*	abs/cm	A1K		-1.27	0.11	10	0.10	0.11	0.11	0.00	0.9	16
	µg/l	B2K		-0.63	14.9	15	14.2	15.1	14.9	1.0	6.9	14
	µg/l	N3K		-0.80	21.8	15	20.5	22.1	22.0	1.2	5.4	15
O_2	mg/l	B2O		-0.43	11.5	8	11.3	11.5	11.4	0.3	2.6	18
	mg/l	N3O		0.88	9.66	8	10.00	9.67	9.66	0.29	3.0	14
Salinity	PSU	A1S		0.00	1.41	5	1.41	1.40	1.38	0.07	5.2	8
	PSU	B2S		0.19	3.02	3,5	3.03	3.03	3.02	0.05	1.5	10
SiO_2	mg/l	A1P		-3.29	1.64	10	1.37	1.62	1.61	0.07	4.2	10
	mg/l	B2P		-1.76	6.35	10	5.79	6.35	6.35	0.29	4.6	9
	mg/l	N3P		1.94	4.12	20	4.92	4.06	4.12	0.42	10.3	6
TIC	mg/l	A1T		0.44	2.14	15	2.21	2.15	2.14	0.16	7.4	7
	mg/l	N3T		0.22	7.95	15	8.08	7.88	7.95	0.42	5.3	7
TOC	mg/l	A1C		2.80	2.05	15	2.48	2.24	2.24	0.19	8.4	14
	mg/l	B2C		-4.18	5.84	10	4.62	5.78	5.84	0.17	2.9	10
	mg/l	N3C		-0.14	8.41	10	8.35	8.29	8.44	0.45	5.3	14

Participant 22												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
O_2	mg/l	B2O		0.00	11.5	8	11.5	11.5	11.4	0.3	2.6	18
	mg/l	N3O		0.28	9.66	8	9.77	9.67	9.66	0.29	3.0	14
TOC	mg/l	A1C		0.91	2.05	15	2.19	2.24	2.24	0.19	8.4	14
	mg/l	B2C		0.38	5.84	10	5.95	5.78	5.84	0.17	2.9	10
	mg/l	N3C		-0.19	8.41	10	8.33	8.29	8.44	0.45	5.3	14

Participant 23												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
O_2	mg/l	B2O		0.96	11.5	8	11.9	11.5	11.4	0.3	2.6	18
SiO_2	mg/l	A1P		0.98	1.64	10	1.72	1.62	1.61	0.07	4.2	10
	mg/l	B2P		1.23	6.35	10	6.74	6.35	6.35	0.29	4.6	9
TOC	mg/l	A1C		-0.07	2.05	15	2.04	2.24	2.24	0.19	8.4	14
	mg/l	B2C		-0.68	5.84	10	5.64	5.78	5.84	0.17	2.9	10

Participant 24												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
TOC	mg/l	A1C		-0.49	2.05	15	1.98	2.24	2.24	0.19	8.4	14
	mg/l	N3C		-0.59	8.41	10	8.16	8.29	8.44	0.45	5.3	14

Participant 25												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Chlorophyll *a*	abs/cm	A1K		0.20	0.11	10	0.11	0.11	0.11	0.00	0.9	16
	µg/l	B2K		0.54	14.9	15	15.5	15.1	14.9	1.0	6.9	14
	µg/l	N3K		0.61	21.8	15	22.8	22.1	22.0	1.2	5.4	15
O_2	mg/l	B2O		-0.46	11.5	8	11.3	11.5	11.4	0.3	2.6	18
	mg/l	N3O		-0.31	9.66	8	9.54	9.67	9.66	0.29	3.0	14
Salinity	PSU	A1S		-2.41	1.41	5	1.33	1.40	1.38	0.07	5.2	8
	PSU	B2S		0.02	3.02	3,5	3.02	3.03	3.02	0.05	1.5	10
SiO_2	mg/l	A1P		-1.43	1.64	10	1.52	1.62	1.61	0.07	4.2	10
	mg/l	B2P		-0.23	6.35	10	6.28	6.35	6.35	0.29	4.6	9
	mg/l	N3P		-0.65	4.12	20	3.85	4.06	4.12	0.42	10.3	6
TIC	mg/l	A1T		0.33	2.14	15	2.19	2.15	2.14	0.16	7.4	7
	mg/l	N3T		-0.97	7.95	15	7.37	7.88	7.95	0.42	5.3	7
TOC	mg/l	A1C		2.20	2.05	15	2.39	2.24	2.24	0.19	8.4	14
	mg/l	B2C		0.23	5.84	10	5.91	5.78	5.84	0.17	2.9	10
	mg/l	N3C		-0.37	8.41	10	8.25	8.29	8.44	0.45	5.3	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}**
O_2	mg/l	B2O		0.17	11.5	8	11.6	11.5	11.4	0.3	2.6	18
TOC	mg/l	N3C		-0.59	8.41	10	8.16	8.29	8.44	0.45	5.3	14

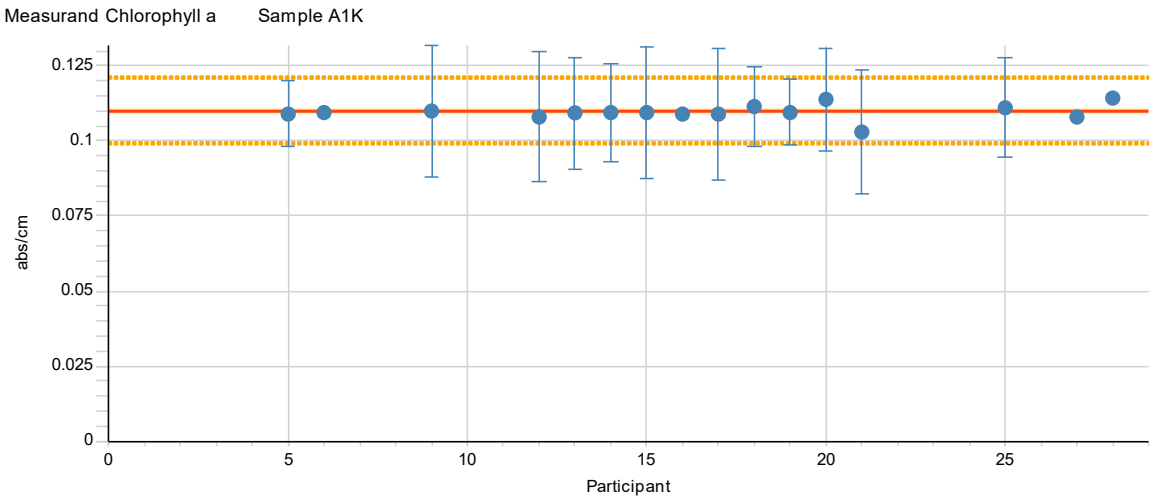
Participant 27												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Chlorophyll *a*	abs/cm	A1K		-0.36	0.11	10	0.11	0.11	0.11	0.00	0.9	16
	µg/l	B2K		-11.31	14.9	15	2.3	15.1	14.9	1.0	6.9	14
	µg/l	N3K		-11.25	21.8	15	3.4	22.1	22.0	1.2	5.4	15
O_2	mg/l	B2O		0.50	11.5	8	11.7	11.5	11.4	0.3	2.6	18
	mg/l	N3O		10.14	9.66	8	13.58	9.67	9.66	0.29	3.0	14
SiO_2	mg/l	A1P		-0.37	1.64	10	1.61	1.62	1.61	0.07	4.2	10
	mg/l	B2P		-7.28	6.35	10	4.04	6.35	6.35	0.29	4.6	9
	mg/l	N3P		5.51	4.12	20	6.39	4.06	4.12	0.42	10.3	6

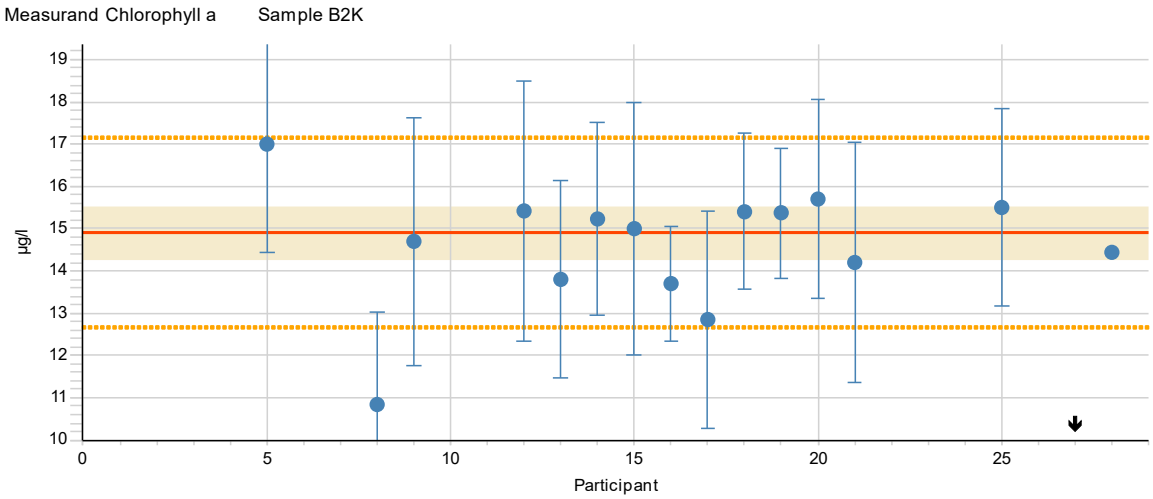
Participant 28												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Chlorophyll *a*	abs/cm	A1K		0.78	0.11	10	0.11	0.11	0.11	0.00	0.9	16
	µg/l	B2K		-0.41	14.9	15	14.4	15.1	14.9	1.0	6.9	14
	µg/l	N3K		-0.59	21.8	15	20.8	22.1	22.0	1.2	5.4	15

Appendix 9. Results of participants and their uncertainties

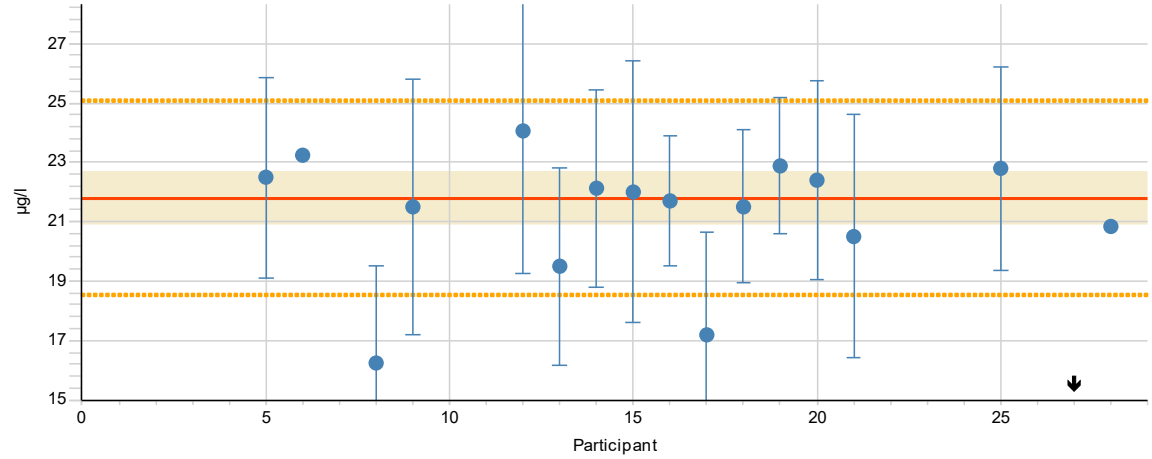
In figures:

- 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.

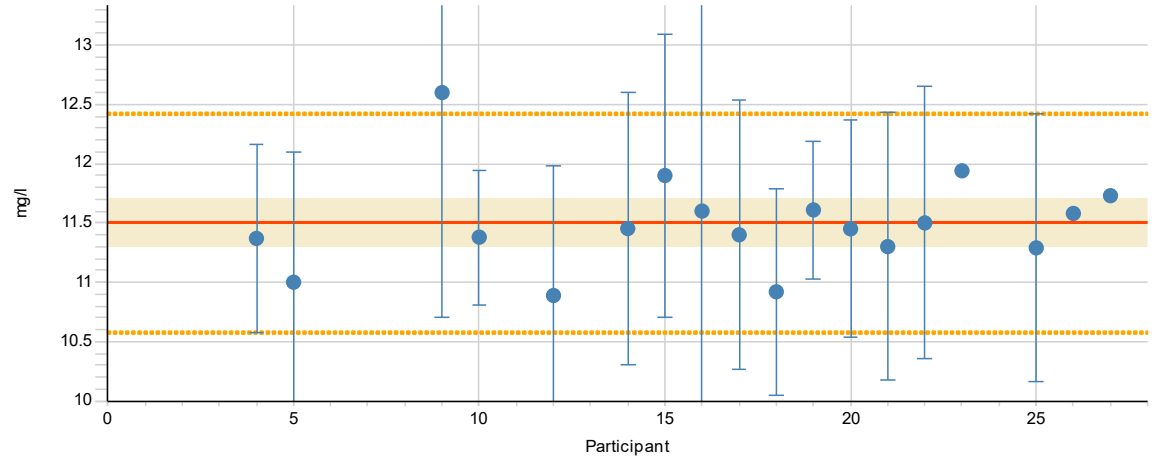




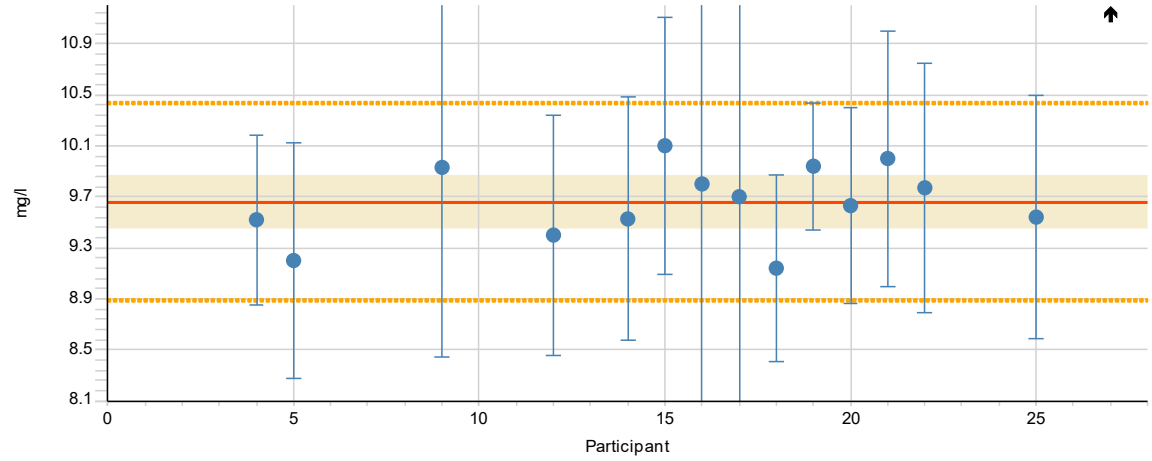
Measurand Chlorophyll a Sample N3K



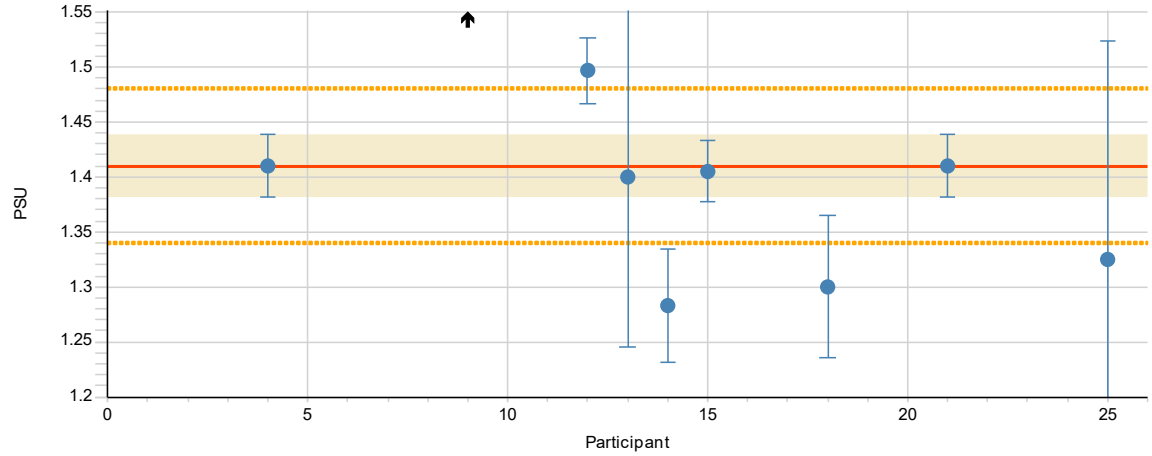
Measurand O_2 Sample B2O



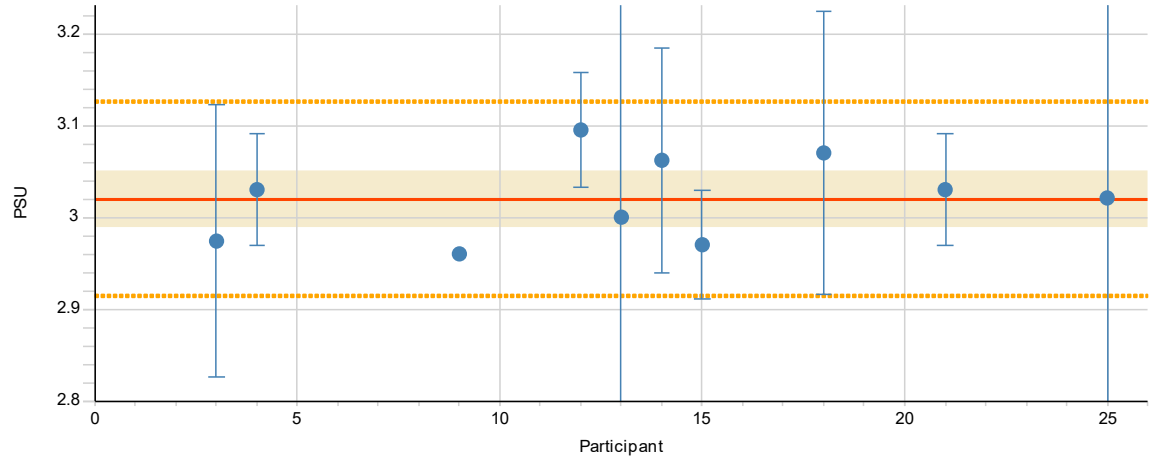
Measurand O_2 Sample N3O



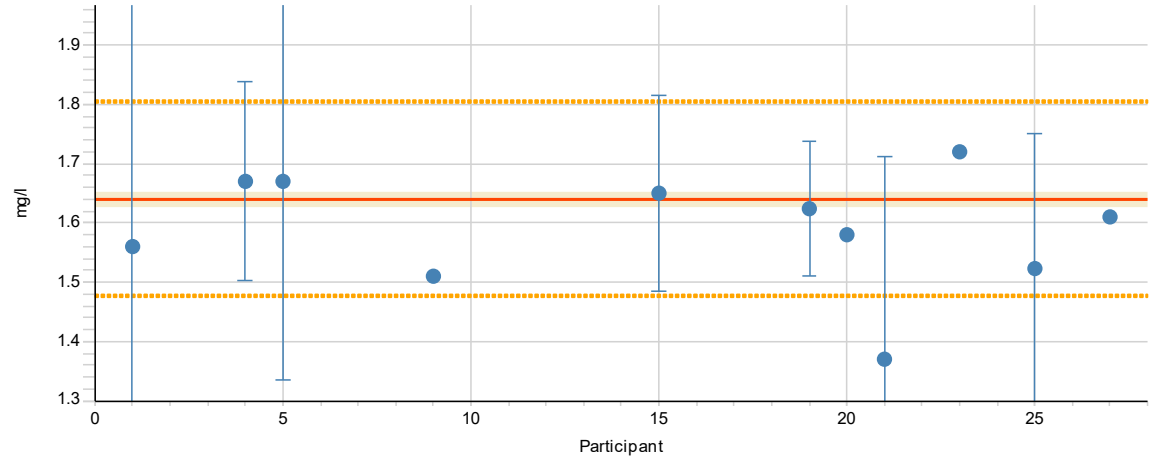
Measurand Salinity Sample A1S



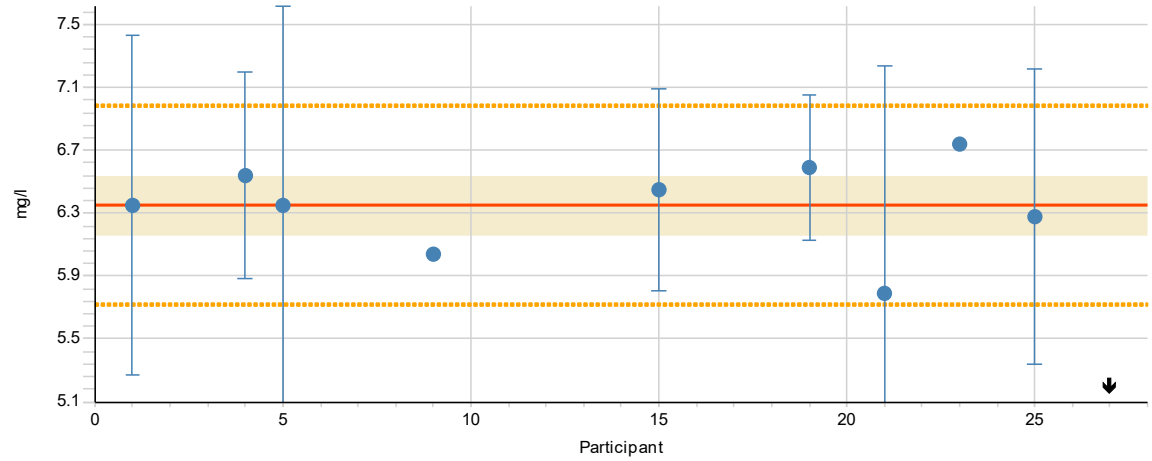
Measurand Salinity Sample B2S



Measurand SiO_2 Sample A1P



Measurand SiO_2 Sample B2P



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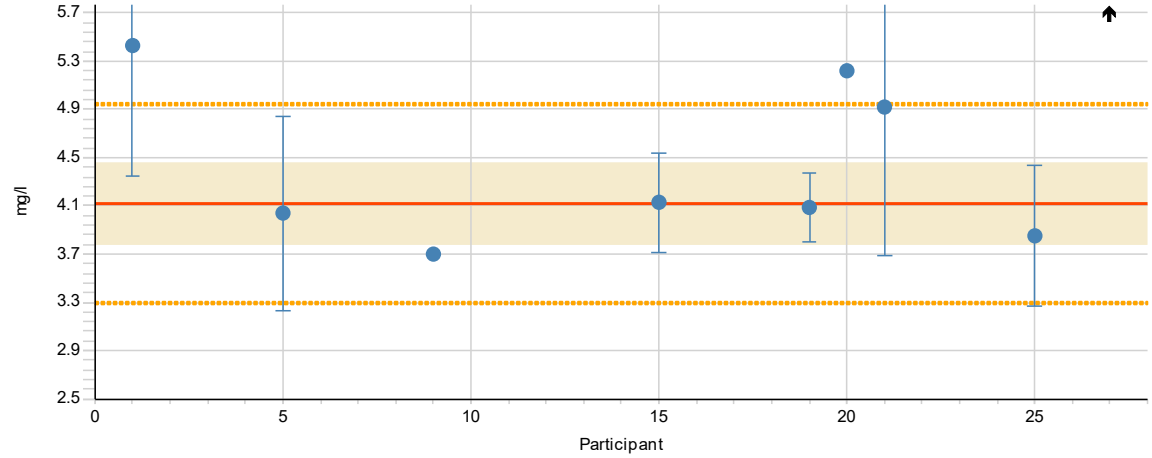
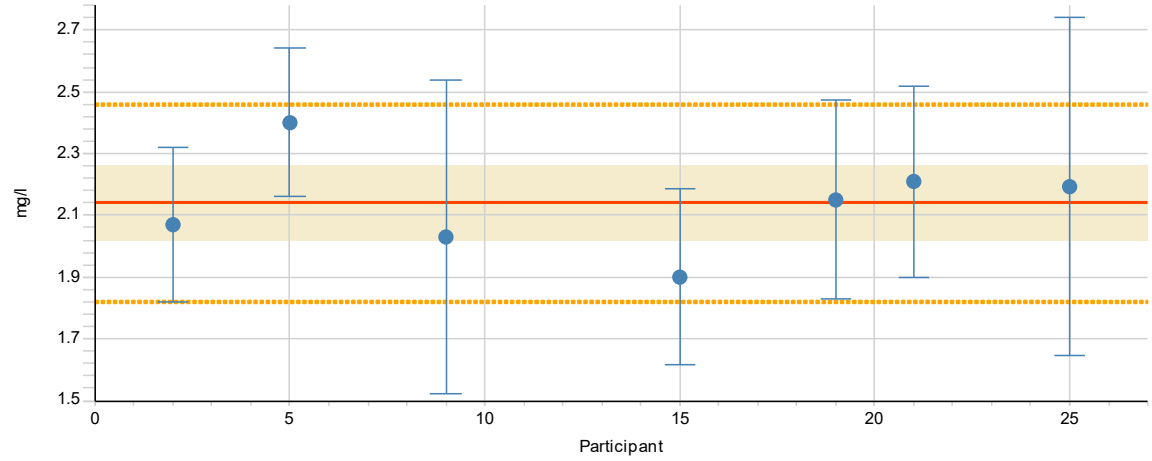
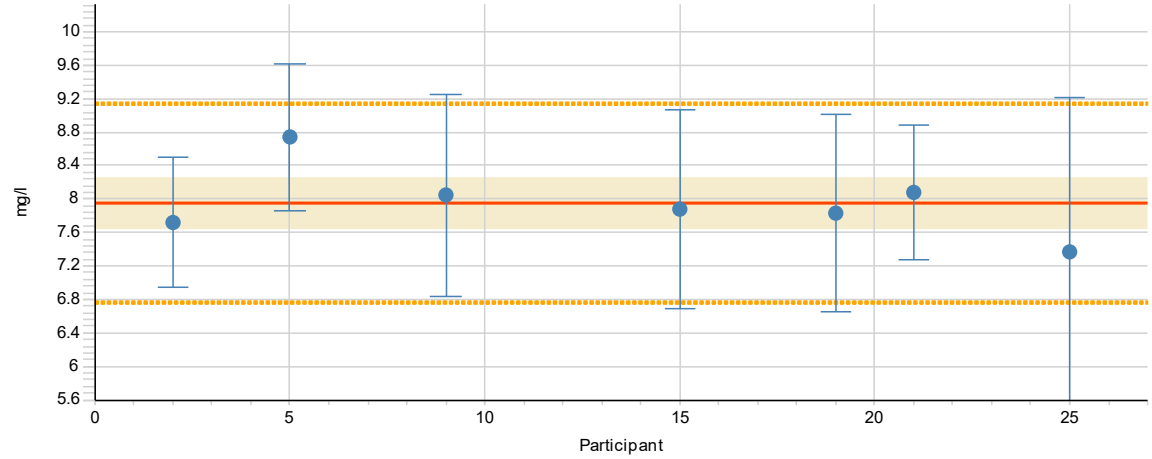


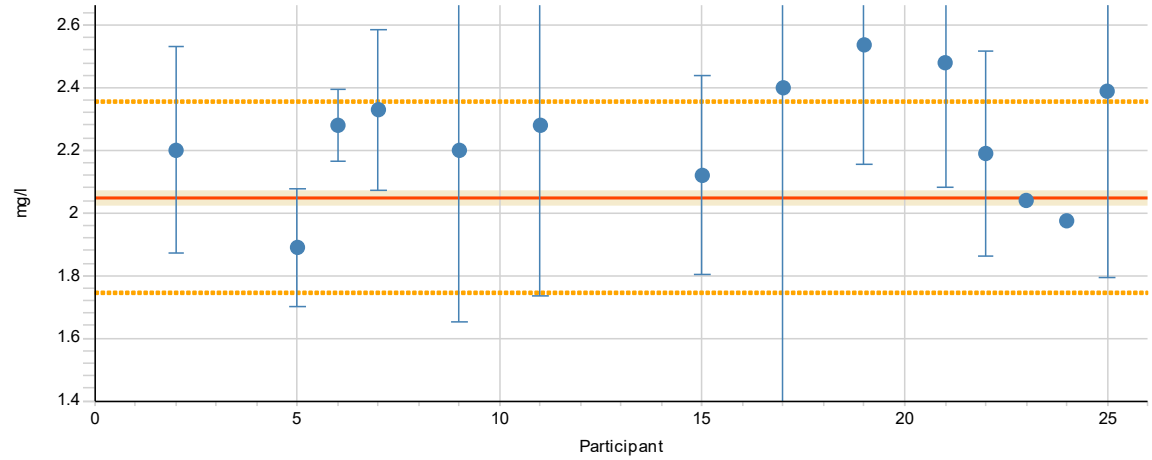
Measurand TIC Sample A1T



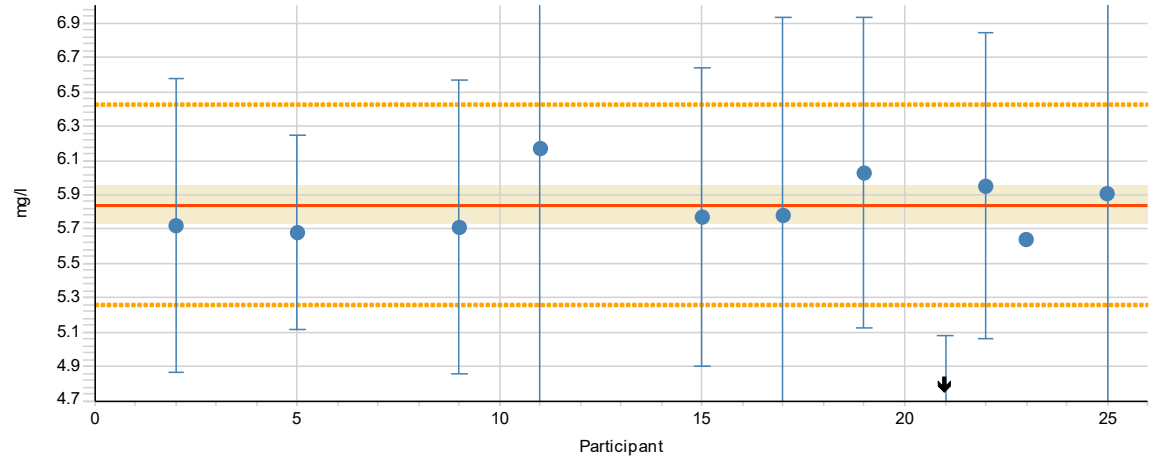
Measurand TIC Sample N3T

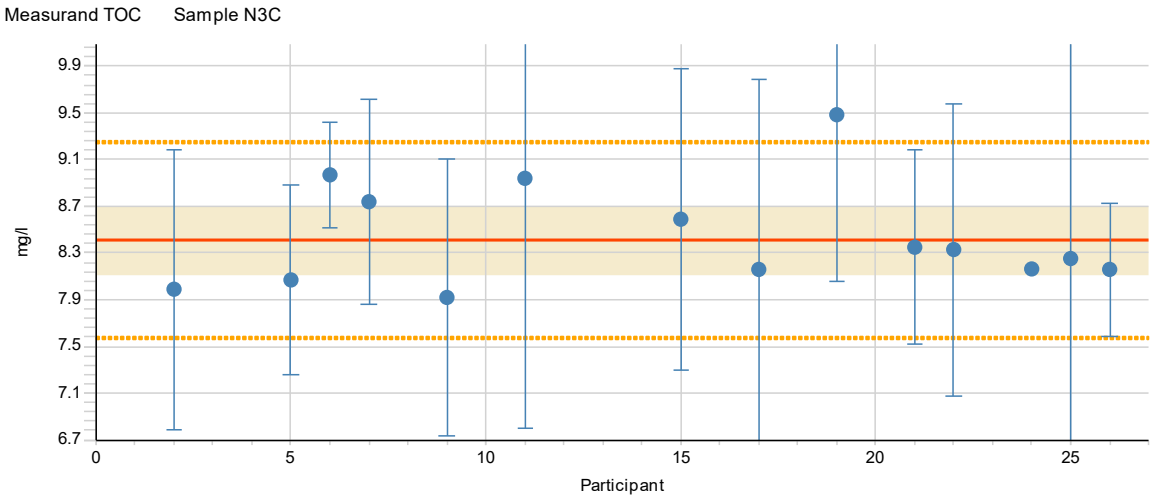


Measurand TOC Sample A1C



Measurand TOC Sample B2C




Measurand TOC
Sample N3C
9.9
9.5
9.1
8.7
8.3
7.9
7.5
7.1
6.7
mg/l
0
5
10
15
20
25
Participant

Appendix 10. Summary of the z scores

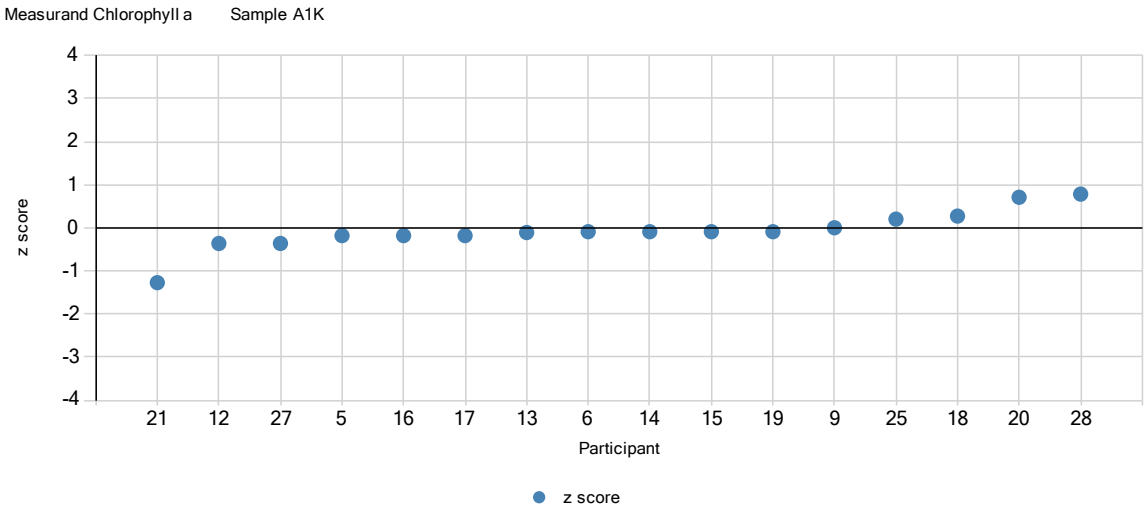
Measurand	Sample	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	%
Chlorophyll *a*	A1K	.	.	.	.	**S**	*S*	.	.	**S**	.	.	**S**	**S**	**S**	**S**	*S*	**S**	**S**	*S*	**S**	**S**	.	.	100
	B2K	.	.	.	.	**S**	.	.	**u**	**S**	.	.	**S**	**S**	**S**	**S**	*S*	**S**	**S**	*S*	**S**	**S**	.	.	87.5
	N3K	.	.	.	.	**S**	*S*	.	**u**	**S**	.	.	**S**	**S**	**S**	**S**	*S*	**q**	**S**	*S*	**S**	**S**	.	.	82.4
O_2	B2O	.	.	.	**S**	**S**	.	.	.	**Q**	**S**	.	**S**	.	**S**	**S**	**S**	*S*	**S**	**S**	**S**	**S**	**S**	*S*	94.4
	N3O	.	.	.	**S**	**S**	.	.	.	**S**	.	.	**S**	.	**S**	**S**	**S**	*S*	**S**	**S**	**S**	**S**	**S**	.	93.3
Salinity	A1S	.	.	.	**S**	.	.	.	.	*U*	.	.	*Q*	**S**	*u*	**S**	.	.	*u*	.	.	**S**	.	.	44.4
	B2S	.	.	**S**	**S**	.	.	.	.	*S*	.	.	*S*	**S**	*S*	**S**	.	.	*S*	.	.	**S**	.	.	100
SiO_2	A1P	*S*	.	.	**S**	**S**	.	.	.	*S*	.	.	.	.	.	**S**	.	.	.	**S**	*S*	**u**	.	*S*	90.9
	B2P	*S*	.	.	**S**	S	.	.	.	*S*	.	.	.	.	.	**S**	.	.	.	**S**	.	**S**	.	*S*	90.0
	N3P	*U*	.	.	.	**S**	.	.	.	*S*	.	.	.	.	.	**S**	.	.	.	**S**	*Q*	**S**	.	.	66.7
TIC	A1T	.	**S**	.	.	*S*	.	.	.	**S**	.	.	.	.	.	**S**	.	.	.	**S**	.	**S**	.	.	100
	N3T	.	**S**	.	.	*S*	.	.	.	**S**	.	.	.	.	.	**S**	.	.	.	**S**	.	**S**	.	.	100
TOC	A1C	.	**S**	.	.	**S**	*S*	**S**	.	**S**	.	**S**	.	.	.	**S**	.	**Q**	.	**U**	.	**Q**	**S**	*S*	71.4
	B2C	.	**S**	.	.	**S**	.	.	.	**S**	.	**S**	.	.	.	**S**	.	**S**	.	**S**	.	**u**	**S**	*S*	90.9
	N3C	.	**S**	.	.	**S**	*S*	**S**	.	**S**	.	**S**	.	.	.	**S**	.	**S**	.	**Q**	.	**S**	**S**	.	92.9
%		67	100	100	100	100	100	100	0	87	100	100	86	100	86	100	100	75	86	85	86	80	100	100	
accredited			5	1	6	10		2	2	10	1	3	5	5	5	15	2	6	5	10	5	15	5		

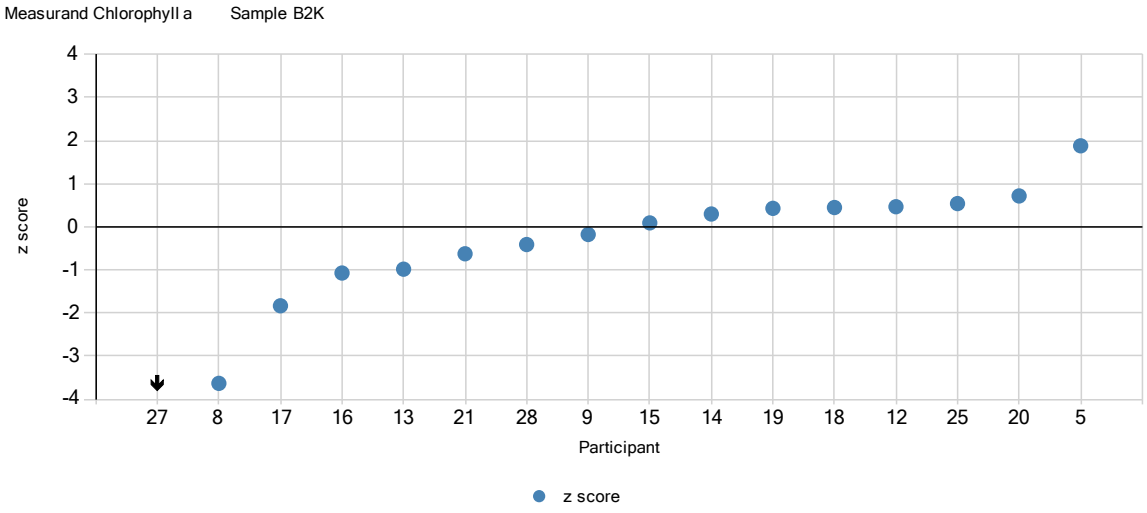
Measurand	Sample	24	25	26	27	28	%
Chlorophyll *a*	A1K	.	**S**	.	**S**	*S*	100
	B2K	.	**S**	.	**u**	*S*	87.5
	N3K	.	**S**	.	**u**	*S*	82.4
O_2	B2O	.	**S**	**S**	**S**	.	94.4
	N3O	.	**S**	.	**U**	.	93.3
Salinity	A1S	.	**q**	.	.	.	44.4
	B2S	.	**S**	.	.	.	100
SiO_2	A1P	.	**S**	.	**S**	.	90.9
	B2P	.	**S**	.	**u**	.	90.0
	N3P	.	**S**	.	**U**	.	66.7
TIC	A1T	.	**S**	.	.	.	100
	N3T	.	**S**	.	.	.	100
TOC	A1C	**S**	**Q**	.	.	.	71.4
	B2C	.	**S**	.	.	.	90.9
	N3C	**S**	**S**	**S**	.	.	92.9
%		100	87	100	38	100	
accredited		2	15	2	8		

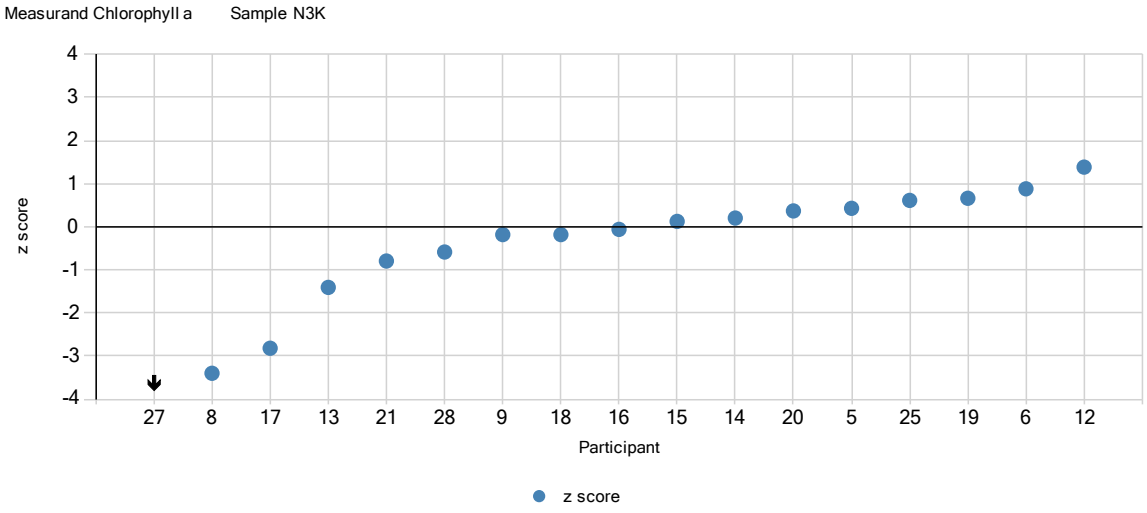
S - satisfactory ($-2 \leq z \leq 2$), Q - questionable ($2 < z < 3$), q - questionable ($-3 < z < -2$),
U - unsatisfactory ($z \geq 3$), and u - unsatisfactory ($z \leq -3$), respectively
bold - accredited, italics - non-accredited, normal - unknown
% - percentage of satisfactory results

Satisfactory results, in total %: 88 in accredited %: 88 in non-accredited %: 84

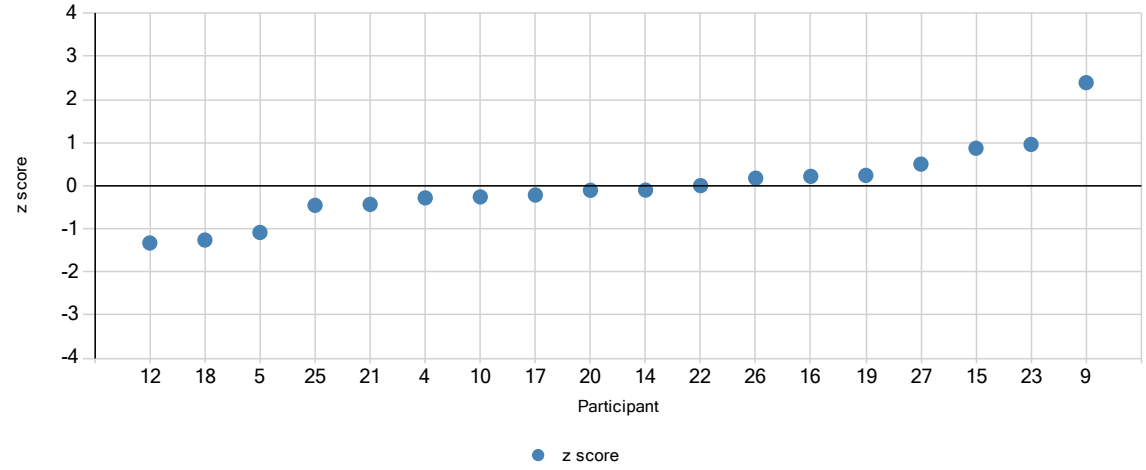
Appendix 11. z scores in ascending order



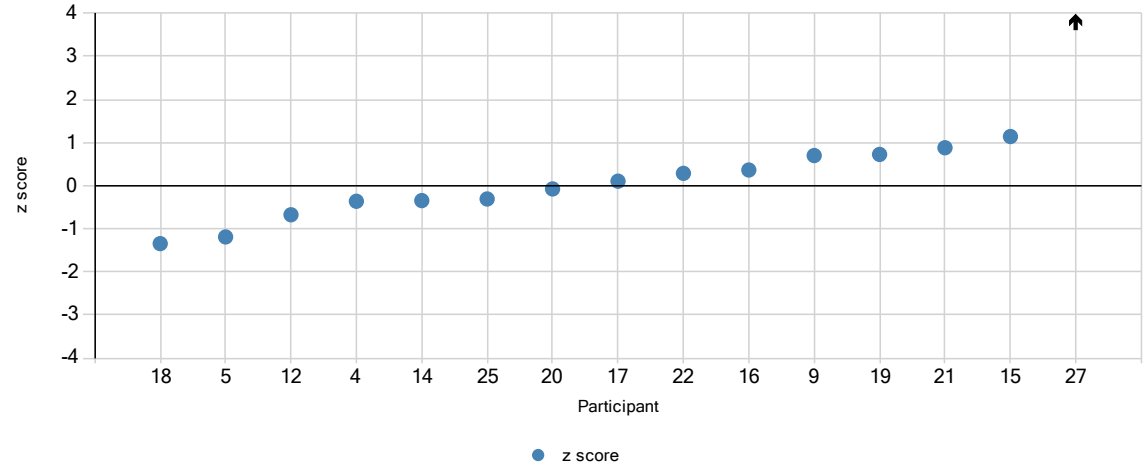




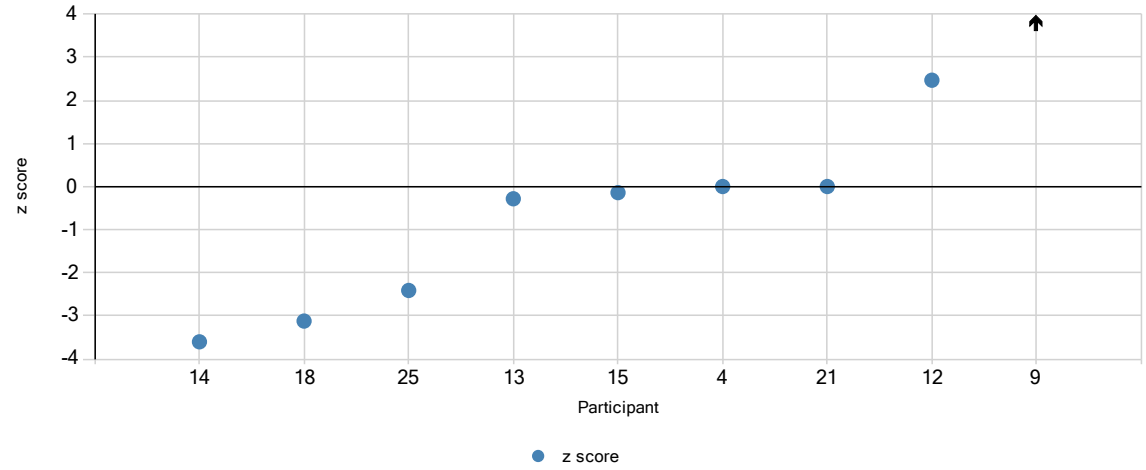
Measurand O_2 Sample B2O



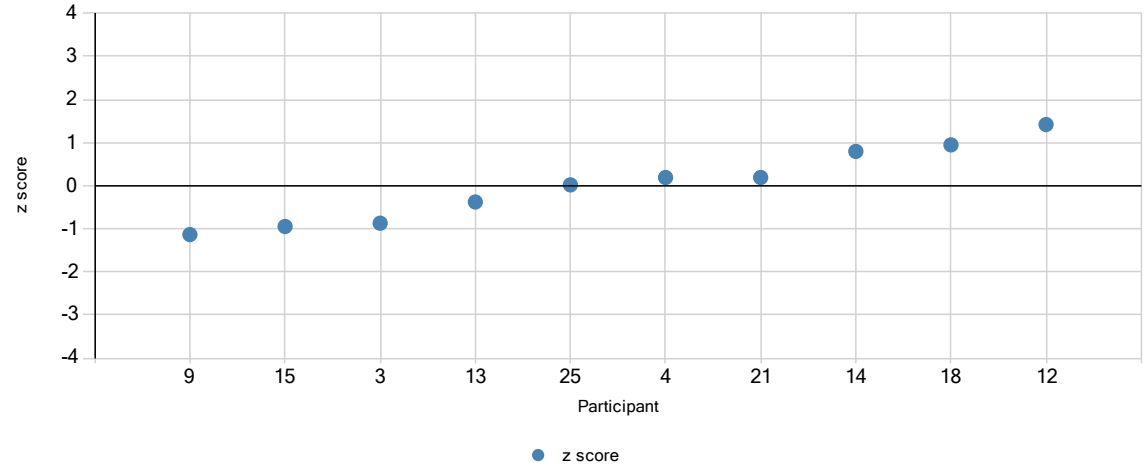
Measurand O_2 Sample N3O



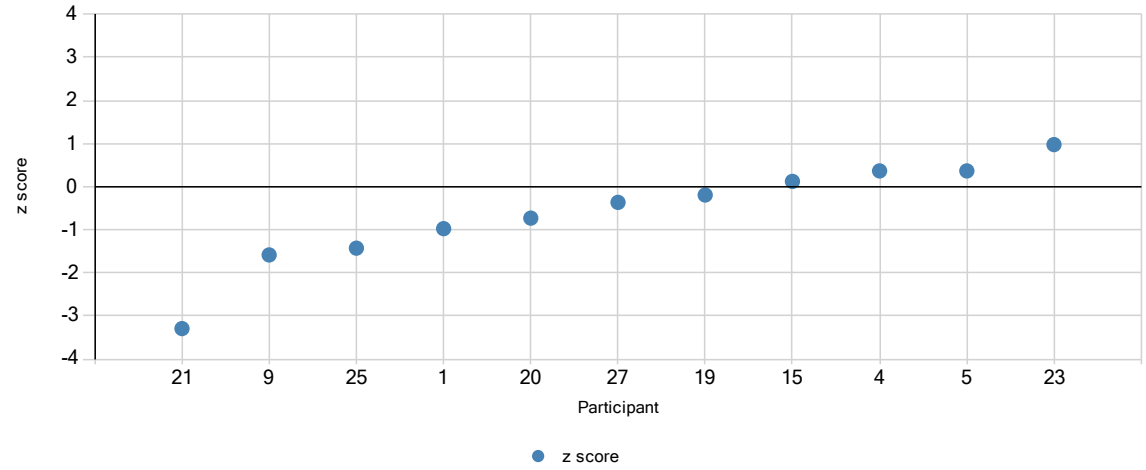
Measurand Salinity Sample A1S



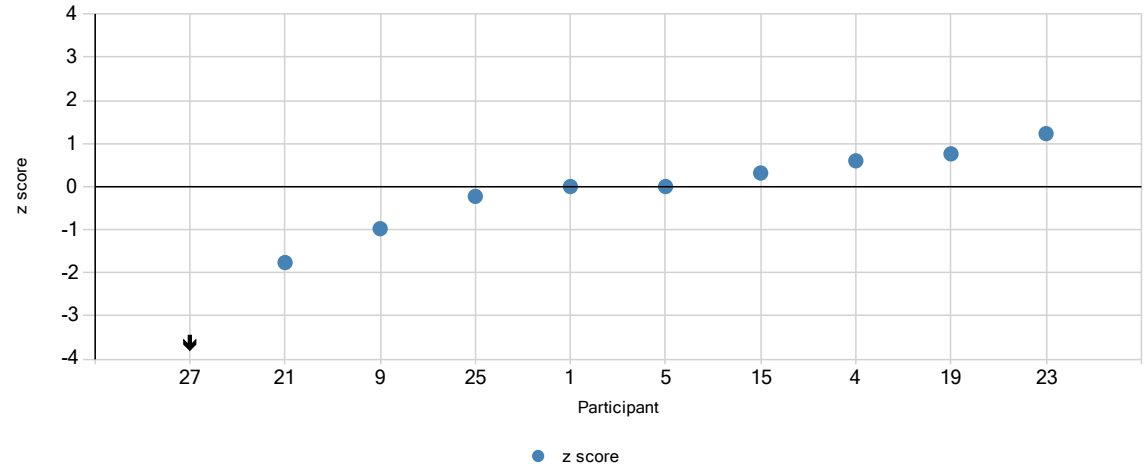
Measurand Salinity Sample B2S



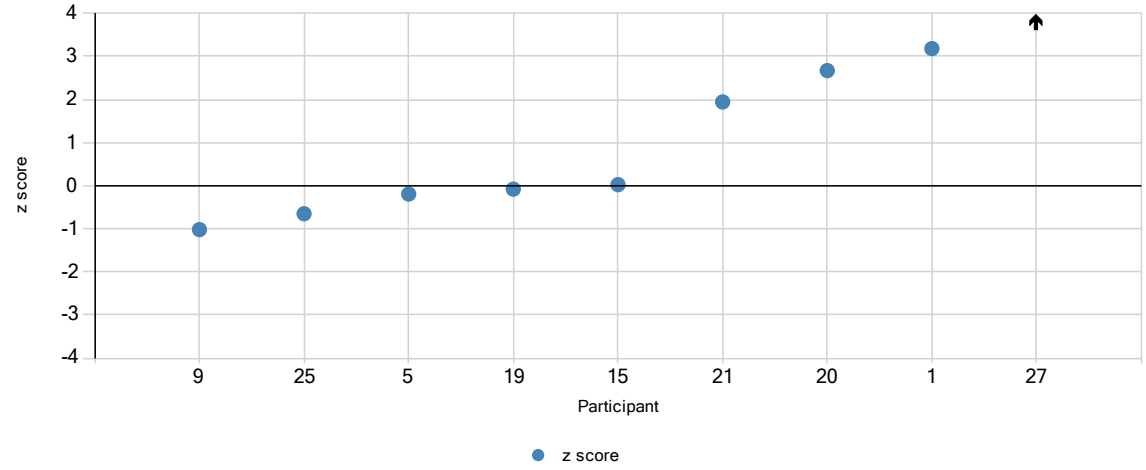
Measurand SiO_2 Sample A1P



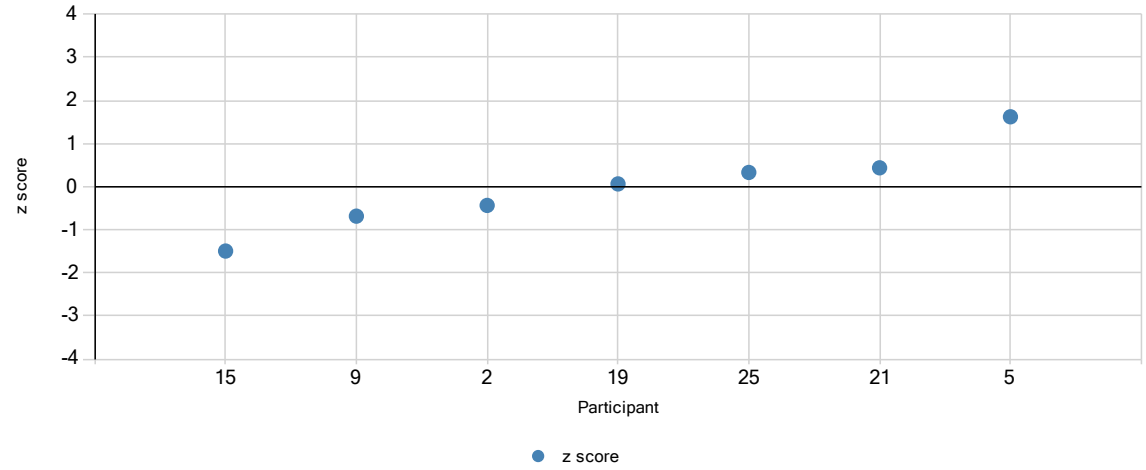
Measurand SiO_2 Sample B2P



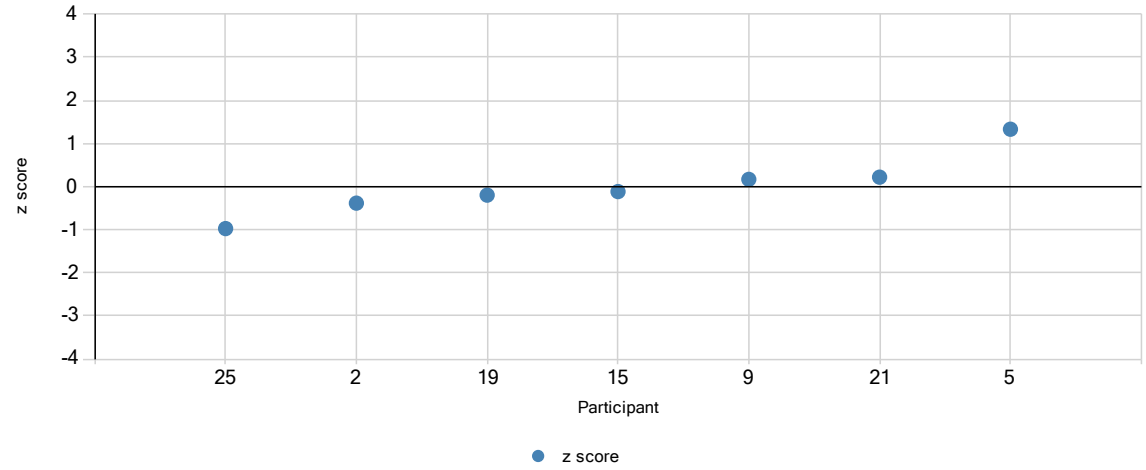
Measurand SiO_2 Sample N3P

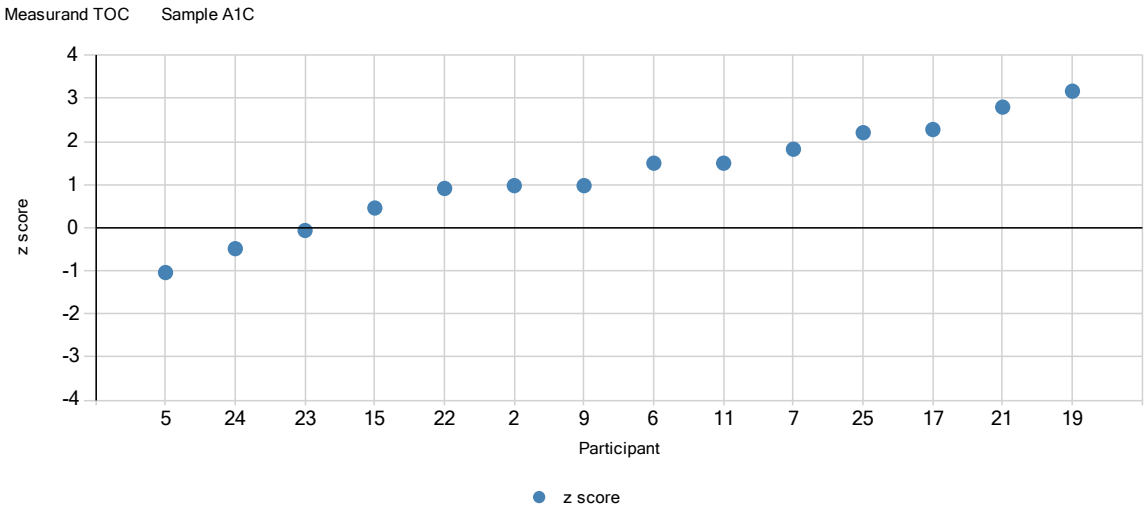


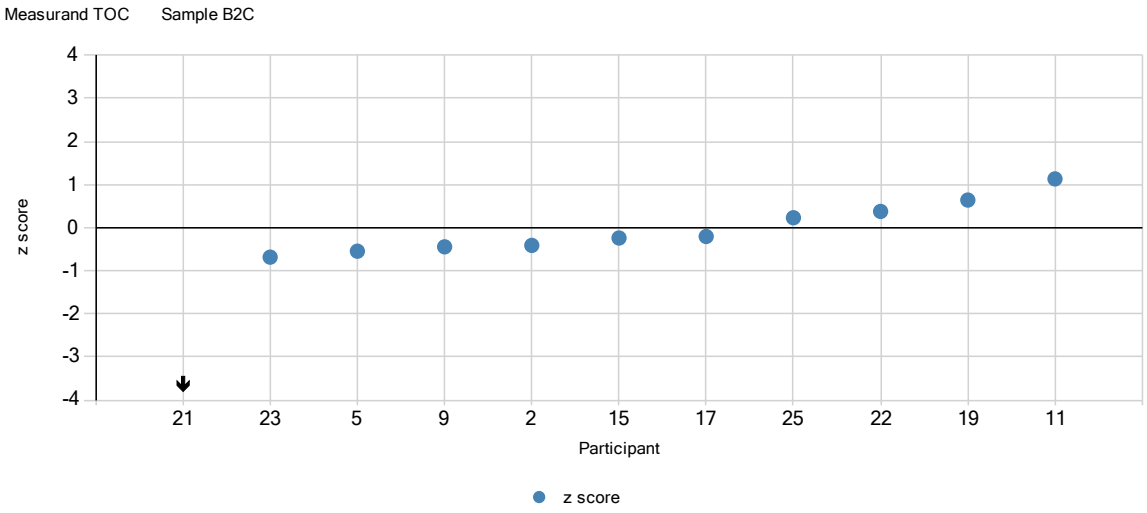
Measurand TIC Sample A1T

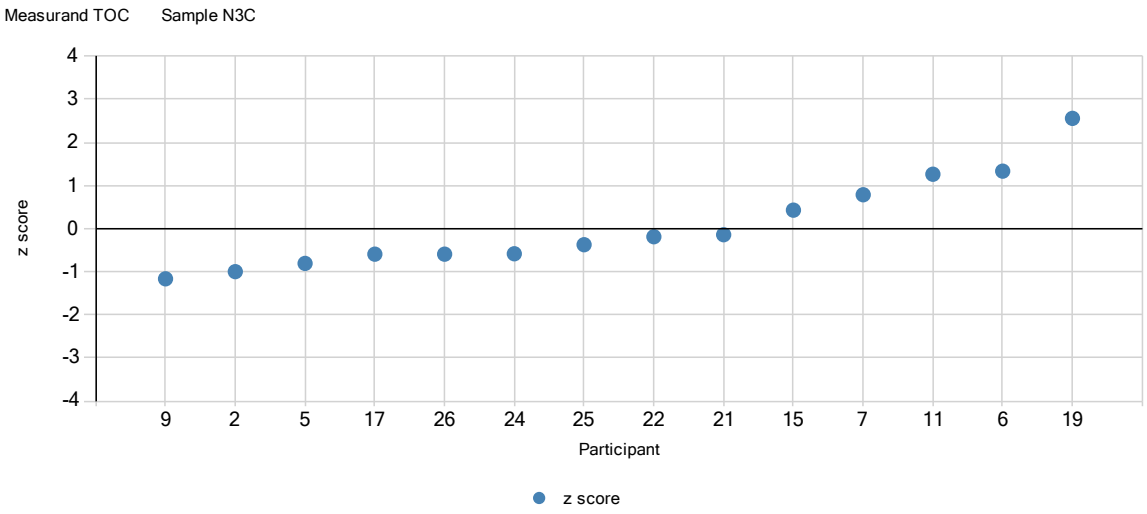


Measurand TIC Sample N3T



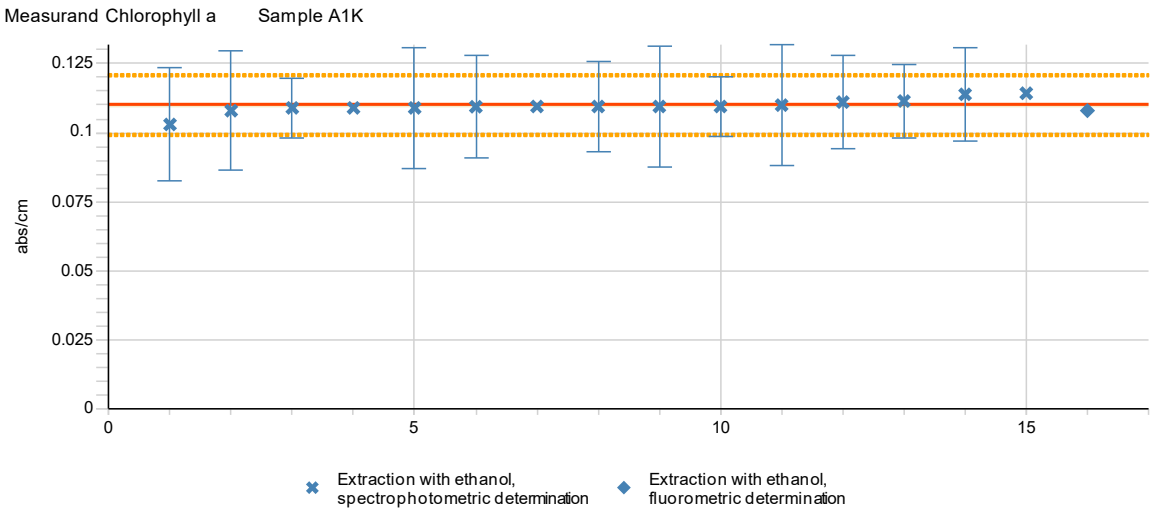

Measurand TOC Sample A1C
z score
4
3
2
1
0
-1
-2
-3
-4
5 24 23 15 22 2 9 6 11 7 25 17 21 19
Participant
z score

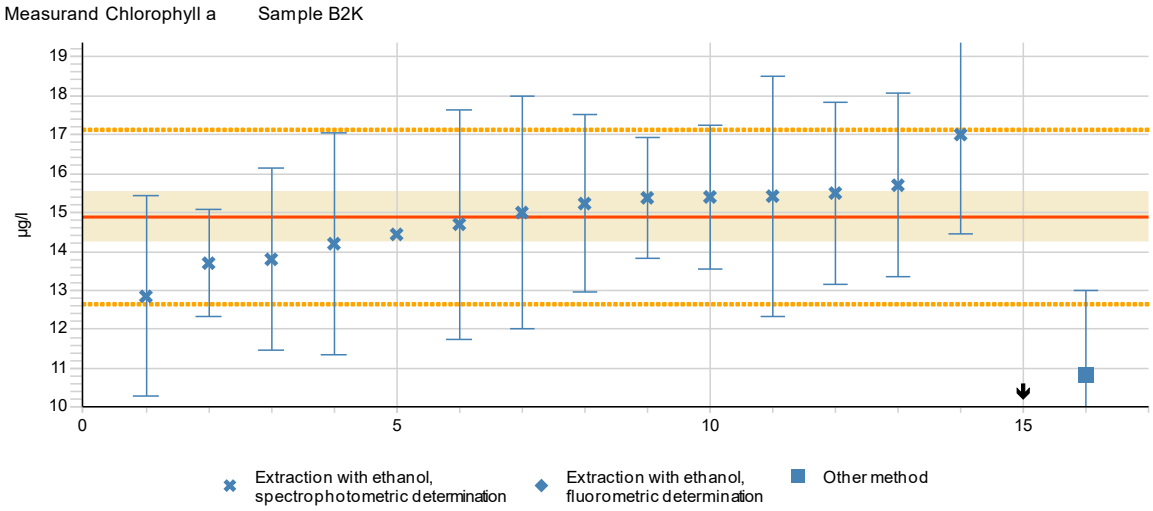

Measurand TOC Sample B2C
z score
4
3
2
1
0
-1
-2
-3
-4
21 23 5 9 2 15 17 25 22 19 11
Participant
z score


Measurand TOC Sample N3C
z score
4
3
2
1
0
-1
-2
-3
-4
9 2 5 17 26 24 25 22 21 15 7 11 6 19
Participant
z score

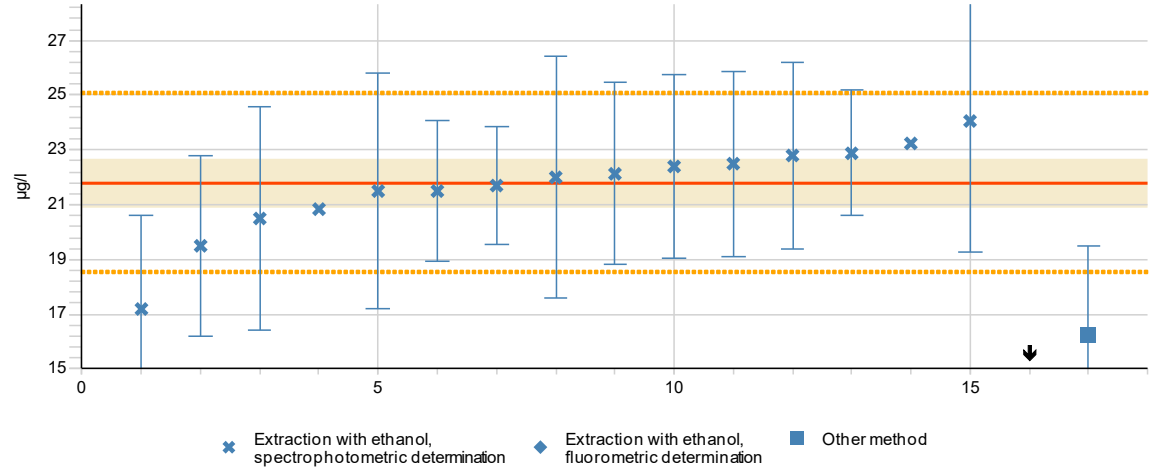
Appendix 12. Results grouped according to the methods

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

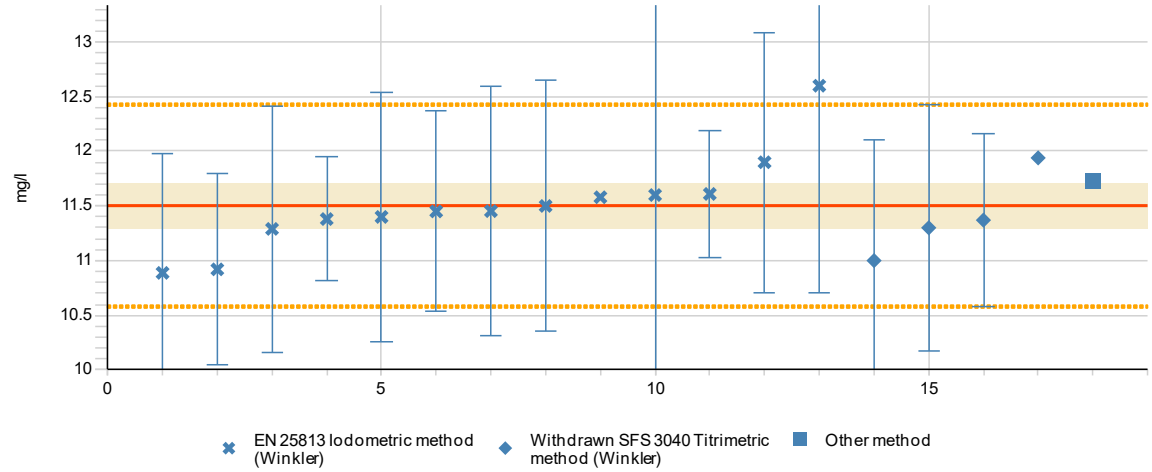




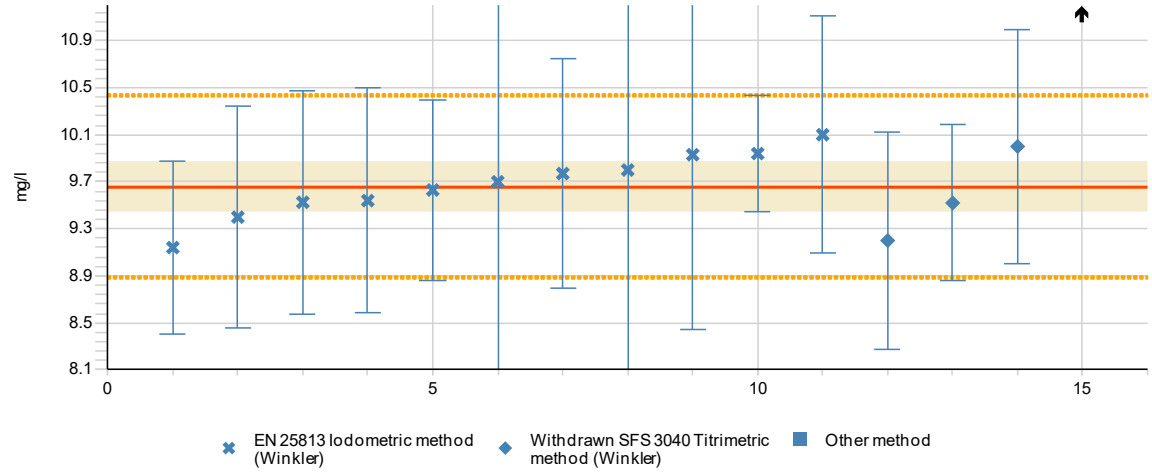
Measurand Chlorophyll a Sample N3K



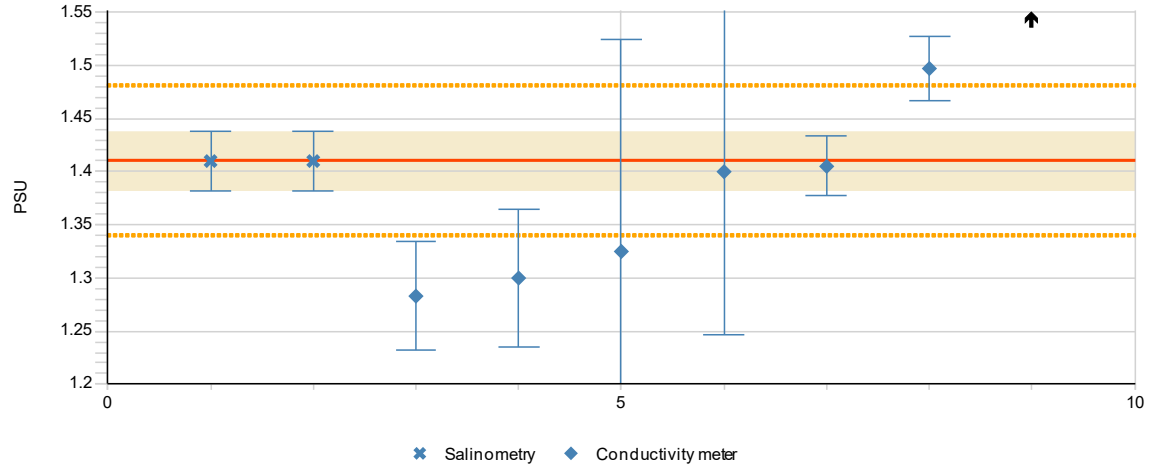
Measurand O_2 Sample B2O



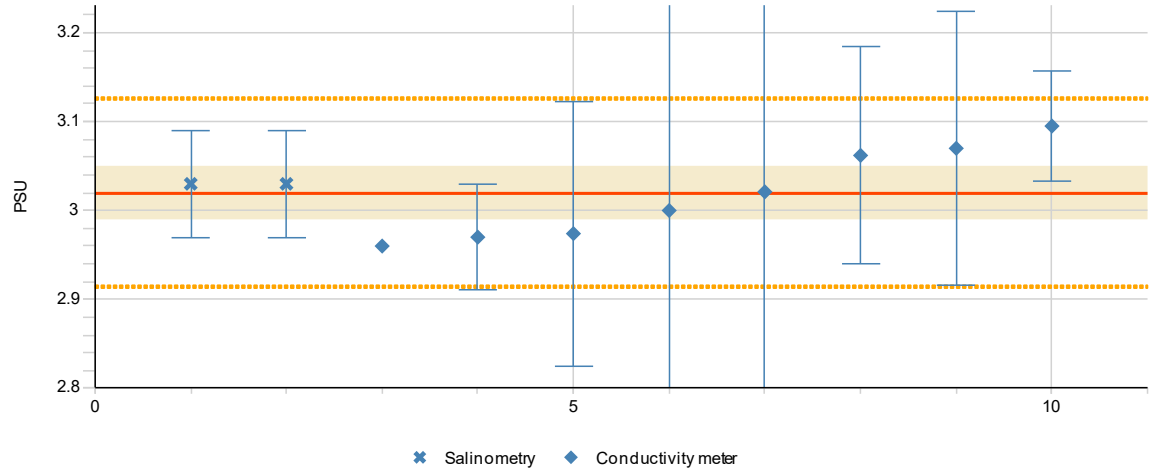
Measurand O_2 Sample N3O



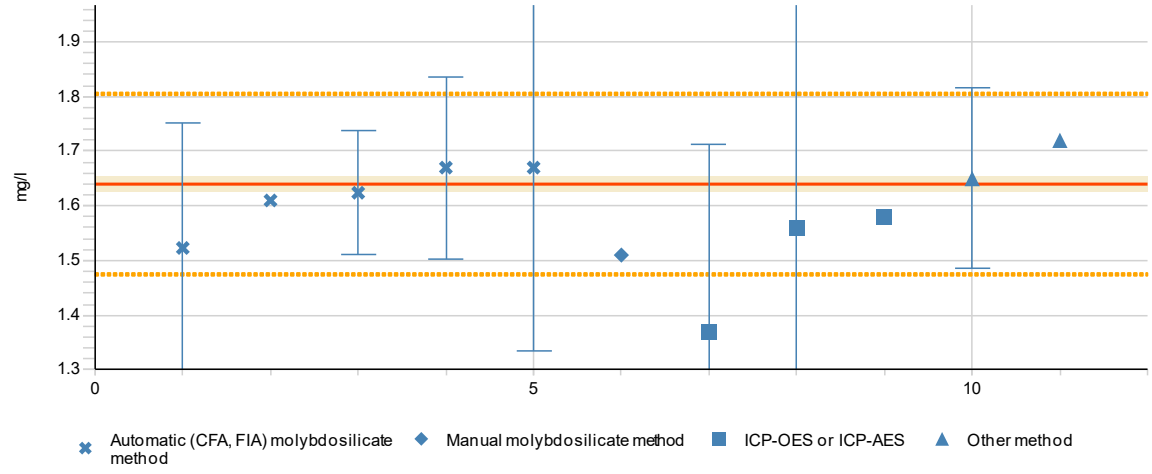
Measurand Salinity Sample A1S



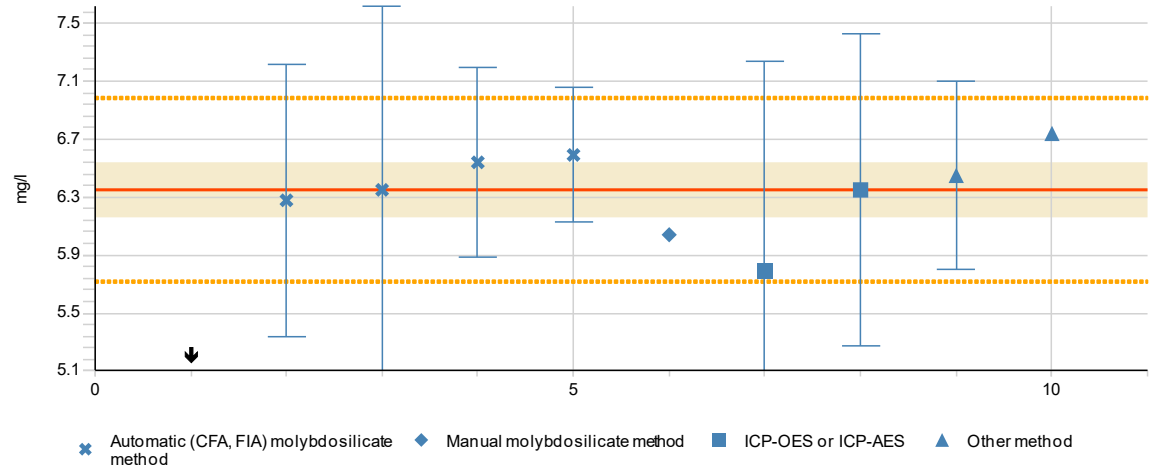
Measurand Salinity Sample B2S



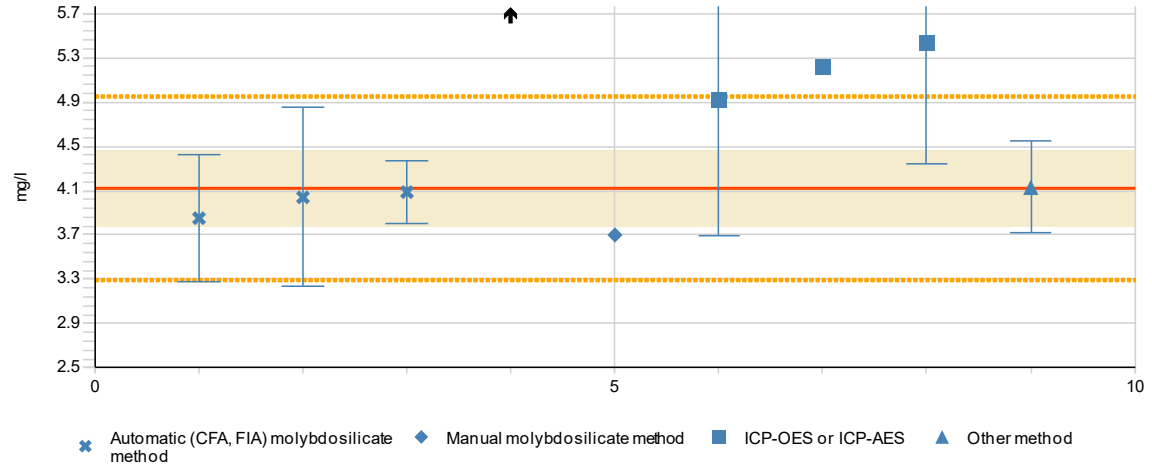
Measurand SiO_2 Sample A1P



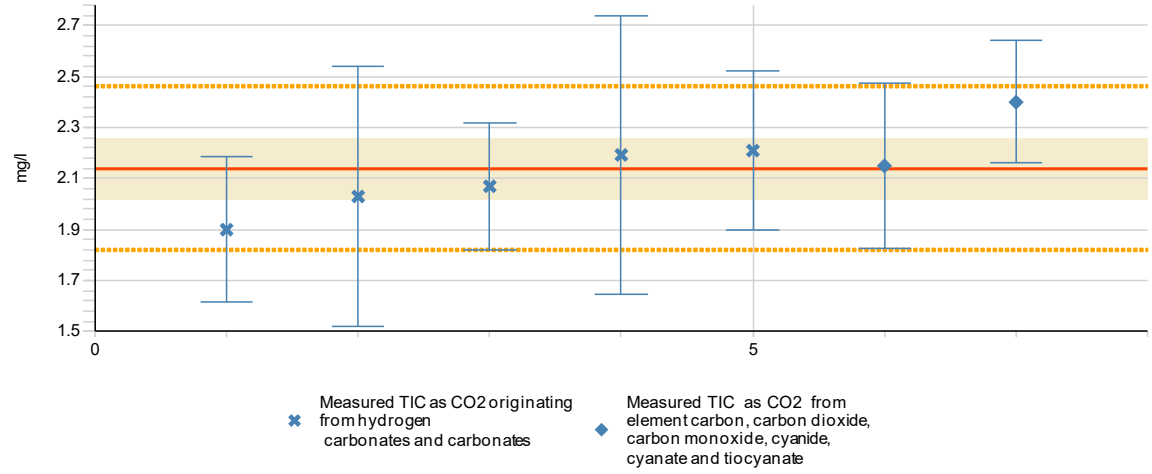
Measurand SiO_2 Sample B2P



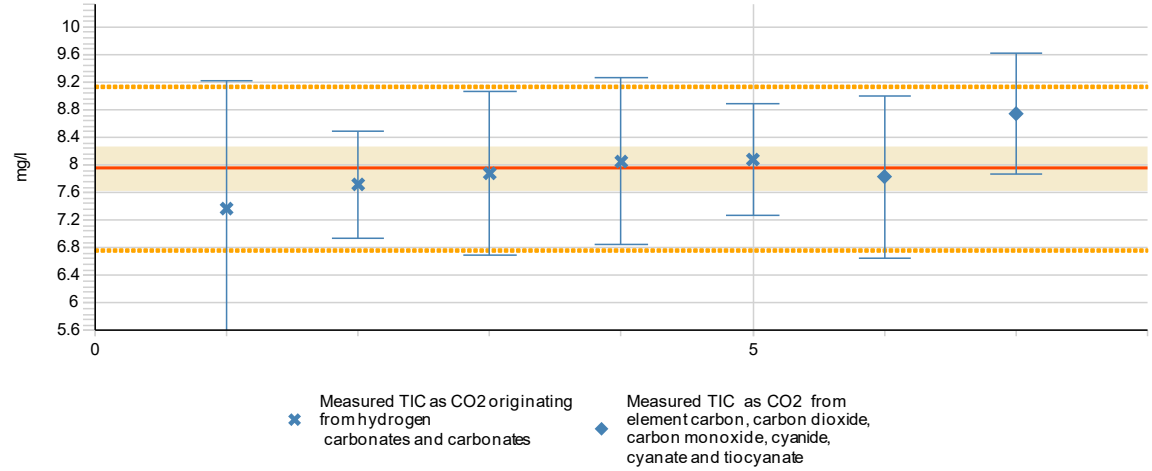
Measurand SiO_2 Sample N3P



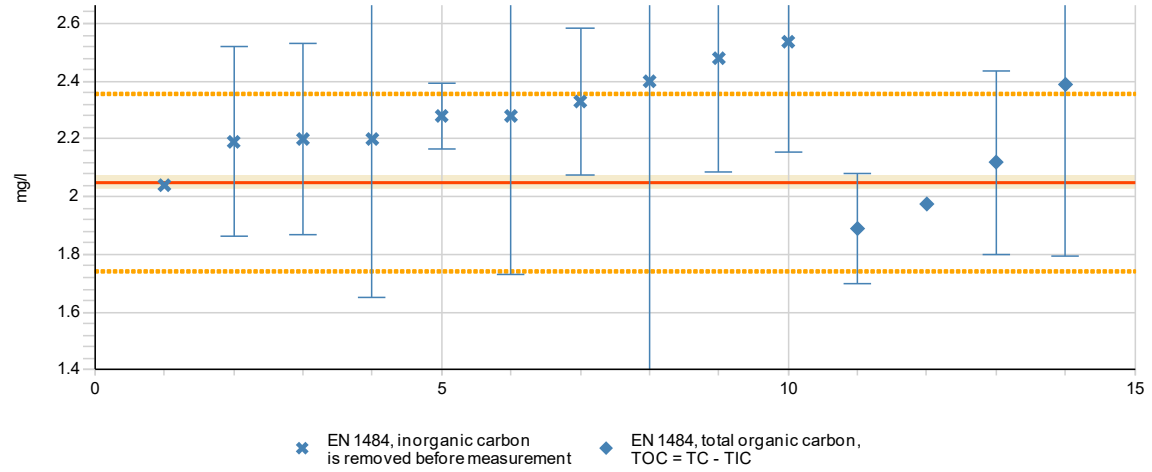
Measurand TIC Sample A1T



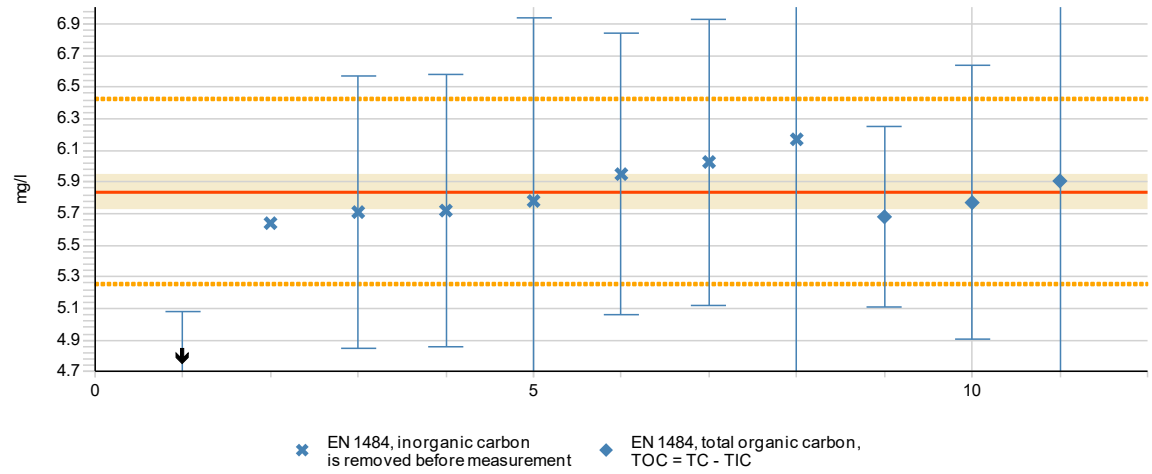
Measurand TIC Sample N3T

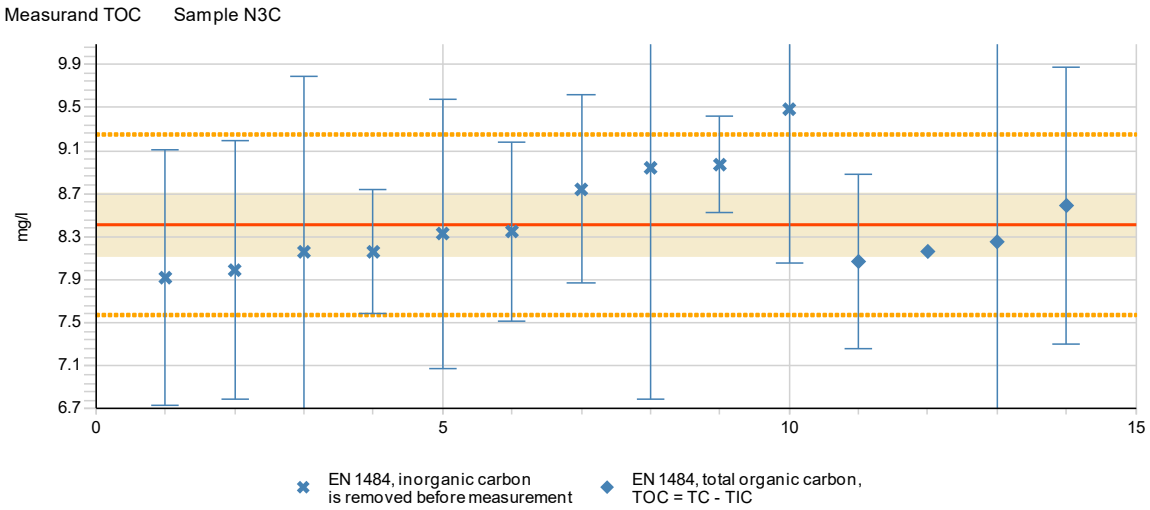


Measurand TOC Sample A1C



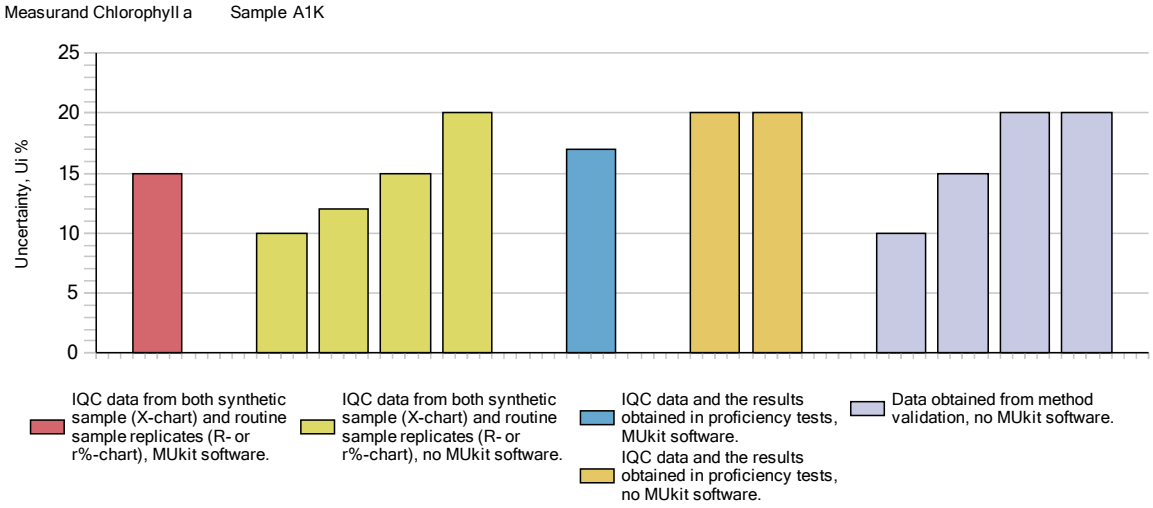
Measurand TOC Sample B2C

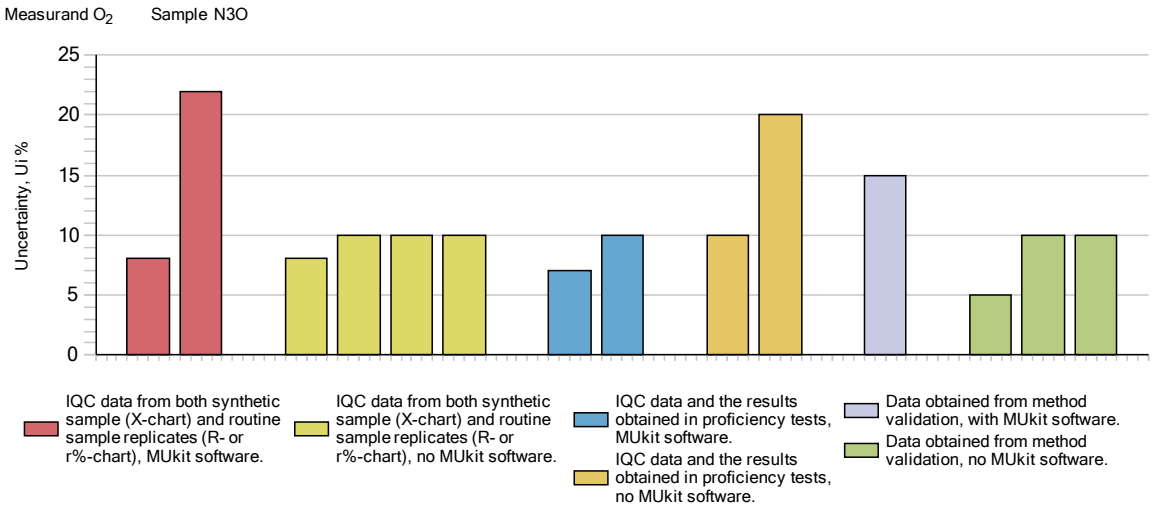



Measurand TOC
Sample N3C
mg/l
9.9
9.5
9.1
8.7
8.3
7.9
7.5
7.1
6.7
0
5
10
15
EN 1484, inorganic carbon is removed before measurement
EN 1484, total organic carbon, TOC = TC - TIC

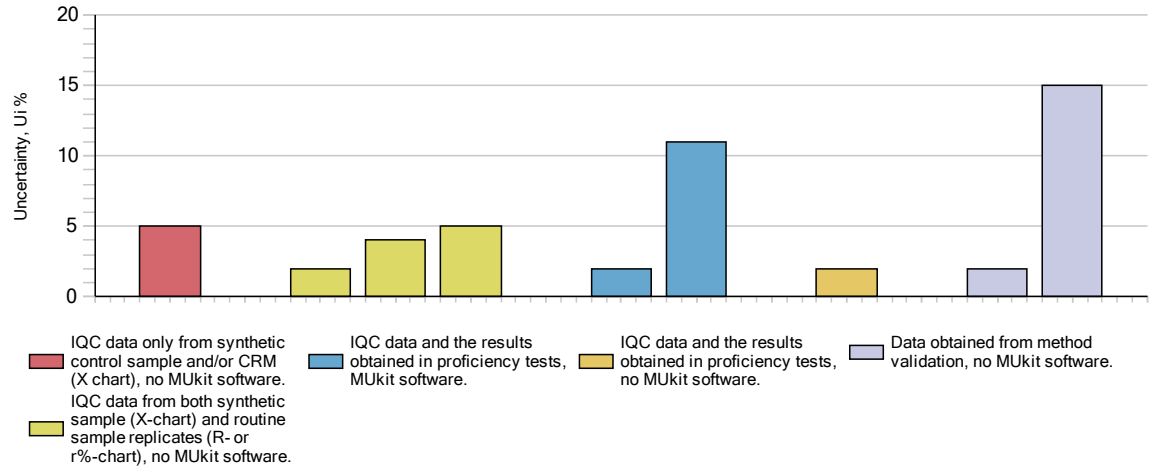
Appendix 13. Examples of measurement uncertainties reported by the participants

In figures, the presented expanded measurement uncertainties are grouped according to the method of evaluation at 95 % confidence level (k=2). The expanded uncertainties were evaluated 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 evaluation [7, 8].

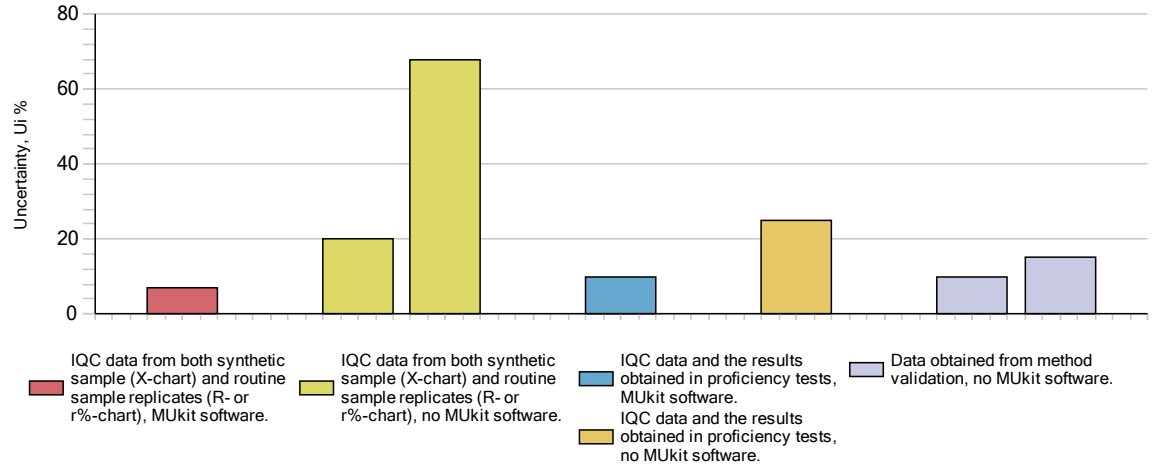




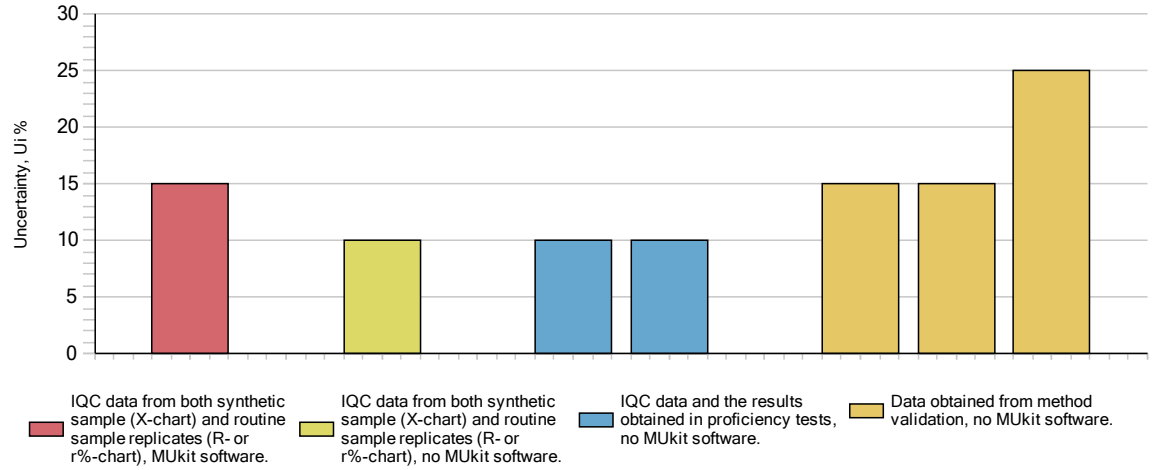
Measurand Salinity Sample B2S

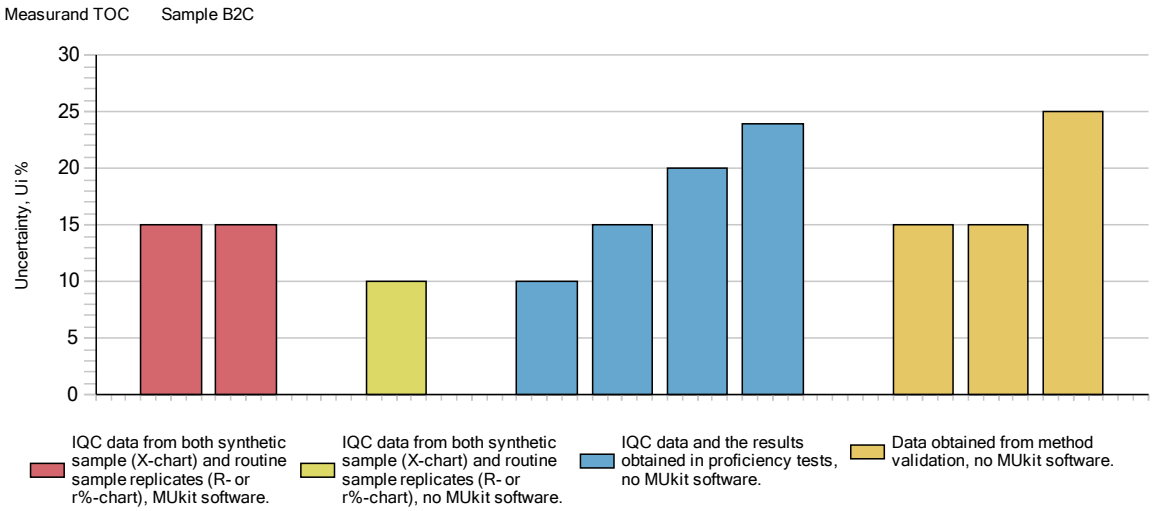


Measurand SiO_2 Sample A1P



Measurand TIC Sample N3T




Measurand TOC
Sample B2C
Uncertainty, Ui %
30
25
20
15
10
5
0
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), no MUkit software.
IQC data and the results obtained in proficiency tests, no MUkit software.
Data obtained from method validation, no MUkit software.

Proficiency Test 06/2022: Natural water analyses II

ISBN 978-952-11-5512-3 (PDF)
ISSN 1796-1726 (online)

Finnish Environment Institute