REPORTS OF THE FINNISH ENVIRONMENT INSTITUTE 38 | 2020

Interlaboratory Proficiency Test 06/2020

Chlorophyll *a*, oxygen, salinity, SiO_2, TIC and TOC in natural waters

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ABSTRACT

Interlaboratory Proficiency Test 06/2020

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 2020 (NW 06/2020). In total, 27 participants joined in the proficiency test.

Either the calculated concentration or the robust mean, the mean or the median 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 results measured by the salinometry was used as the assigned value. The performance of the participants was evaluated by using z scores. In this proficiency test 85 % of the results were satisfactory, when deviation 3.5–30 % 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

Laboratorioiden välinen pätevyyskoe 06/2020

Proftest SYKE järjesti luonnonvesiä analysoiville laboratorioille pätevyyskokeen toukokuussa 2020. Määritettävinä testisuureina olivat happi, klorofylli *a*, saliniteetti, SiO_2, TIC ja TOC joki- ja murtovedestä. Pätevyyskokeessa oli yhteensä 27 osallistujaa.

Testisuureen vertailuarvona käytettiin joko laskennallista pitoisuutta tai osallistujien tulosten robustia keskiarvoa, keskiarvoa tai mediaania. Saliniteetin synteettiselle näytteelle käytettiin vertailuarvona salinometrimääritysten keskiarvoa. Tulosten arviointi tehtiin z-arvojen perusteella, jolloin määrityksissä sallittiin 3,5–30 %:n poikkeama vertailuarvosta. Koko aineistossa hyväksyttäviä tuloksia oli 85 %.

Kiitos pätevyyskokeen osallistujille!

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

SAMMANDRAG

Provningsjämförelse 06/2020

Under maj 2020 genomförde Proftest SYKE en provningsjämförelse, som omfattade bestämningen av klorofyll *a*, oxygen, salinitet, silikat (SiO_2), TIC och TOC i naturvatten. Proven sändes ut till 27 laboratorier.

Som referensvärde av analytens koncentration användes antingen det teoretiska värdet eller robust medelvärdet, medelvärdet eller median av deltagarnas resultat. Medelvärdet av salinometer resultaten användes som det referensvärdet av salthalten i det syntetiska provet. Resultaten värderades med hjälp av z-värden. I jämförelsen var 85 % av alla resultaten tillfredsställande, när 3,5–30 % totalavvikelsen från referensvärdet accepterades.

Ett varmt tack till alla deltagarna i testet!

Nyckelord: vattenanalyser, klorofyll *a*, oxygen, salinitet, SiO_2, TIC, TOC, provningsjämförelse, vatten- och miljölaboratorier

CONTENTS

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 2020 (NW 06/2020). 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]. The 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 the 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

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

Analytical expert

Mika Sarkkinen (SYKE)	chlorophyll *a*, oxygen, SiO_2, TIC, TOC
Olga Kovru (SYKE)	salinity

2.2 Participants

In total 27 laboratories participated in this proficiency test, 22 participants were from Finland, and five participants from abroad (Appendix 1). Altogether 81 % 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 6 (SYKE, Oulu) in the result tables.

2.3 Samples and delivery

Three types of samples were delivered to the participants; synthetic, river water and brackish water samples for analysis of chlorophyll *a*, oxygen, salinity, SiO_2, TIC, and TOC. The synthetic samples 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 offshore Kirkkonummi, Finland and the river water was collected from the River Mustionjoki, Finland. The sample preparation is described in details in the Appendix 2.

The samples were delivered on 4 May 2020 to the participants abroad and on 5 May 2020 to the national participants. The samples arrived to the participants mainly on 6 May 2020.

The samples were requested to be measured as follows:

chlorophyll *a*, oxygen, TIC	7 May 2020
SiO_2, TOC, salinity	latest on 22 May 2020

The results were requested to be reported at the latest on 25 May. The preliminary results were delivered to the participants via email on 29 May 2020.

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 studies is shown in Appendix 3. According to the homogeneity test results, all samples were considered homogenous.

The stability of the samples was tested by measuring chlorophyll *a*, 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 stability test all the samples, except the sample B2K for chlorophyll *a* and N3O for O_2, were considered stable. More detailed information of stability studies is shown in Appendix 4.

The temperature control sample was placed into the sample package and the temperature was requested to be measured immediately after opening the package. The temperature of control sample was ≤ 15 °C for all the participants who reported this information. The temperature of the control sample should be measured preferably shortly after the arrival of the sample package, especially when the package is not stored in refrigerator. The possible influences to the measurand concentrations due to the changes of the sample temperature were taken into account in the evaluation of results.

2.5 Feedback from the proficiency test

The feedback from the proficiency test is shown in Appendix 5. The comments from the participants mainly dealt with sample volumes and participants' reporting errors. The comments from the provider mainly dealt with the missing sample arrival documents. All the feedback is valuable and is exploited when improving the activities.

2.6 Processing the data

2.6.1 Pretesting the data

The normality of the data was tested by the Kolmogorov-Smirnov test. The outliers were rejected according to the Grubbs or Hampel test before calculating the mean. The results, which differed more than s_{rob} × 5 or 50 % from the robust mean, were rejected before the statistical results handling. If the result 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 assigned values and their uncertainties are presented in Appendix 6. The NIST traceable calculated concentrations 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 results measured by the salinometry was used as the assigned value. For the other samples and measurands the robust mean, the mean (SiO_2: N3P, TIC: A1T, TOC: B2C) or the median (SiO_2: B2P, TIC: N3T, TOC: N3C) of the results reported by the participants was used as the assigned value.

For the calculated assigned values the expanded uncertainty (k=2) was estimated using standard uncertainties associated with individual operations involved in the preparation of the sample. The main individual source of the uncertainty was the uncertainty of the concentration in the stock solution.

The uncertainty of the assigned value for the synthetic sample of salinity was calculated from the standard deviation of the used results of participants [4]. When the robust mean, the mean or the median was used as the assigned value, the expanded uncertainty of the assigned value was

calculated using the robust standard deviation or the standard deviation, respectively [2, 4]. The assigned values based on the robust mean, the 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 value was statistically tested [2, 3].

The expanded uncertainty of the calculated assigned value was 0.6 % for both SiO_2 and TOC. In this final report the uncertainty of assigned value of SiO_2 in the sample A1P has changed from 1.1 % (in the preliminary result report) to 0.6 % due to re-evaluation of the results. This change had only a minimal effect to some zeta values (reported only in the preliminary result report). When using the mean of the participant results from the salinometry method as the assigned value, the expanded uncertainties of the assigned values was 0.3 %. When using the robust mean, the mean or the median of the participant results as the assigned value, the expanded uncertainties of the assigned values varied between 1.0 % and 9.3 %. (Appendix 6)

After reporting the preliminary results no other changes have been done for the assigned values.

2.6.3 Proficiency assessment procedure

The standard deviation for proficiency assessment was estimated on the basis of the measurand concentration, the results of homogeneity and stability tests, the uncertainty of the assigned value, and the long-term variation in the former proficiency tests. The standard deviation for the proficiency assessment ($2\times s_{pt}$ at the 95 % confidence level) was set to 3.5–30 % depending on the sample and measurand. **After reporting the preliminary results no changes have been done for the standard deviations of the proficiency assessment values.**

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

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 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) are presented in Appendix 9. The summary of the z scores is shown in Appendix 10 and z scores in the ascending order in Appendix 11.

The robust standard deviations of the results varied from 1.4 to 15.8 % (Table 1). The robust standard deviation was lower than 5 % for 33 % of the results and lower than 10 % for 87 % of the results (Table 1). The robust standard deviations were approximately in the same range as in the previous similar proficiency test NW 06/2018, where the deviations varied from 2.1 % to 21 % [5].

Table 1. The summary of the results in the proficiency test NW 06/2020.

Measurand	Sample	Unit	Assigned value	Mean	Rob. mean	Median	s_{rob}	s_{rob} %	2 x s_{pt} %	n_{all}	Acc z %
Chlorophyll *a*	A1K	abs/cm	0.22	0.22	0.22	0.22	<0.01	2.1	10	16	100
	B2K	µg/l	6.05	6.00	6.05	6.15	0.87	14.4	30	16	88
	N3K	µg/l	16.0	16.0	16.0	16.0	1.4	8.7	20	16	94
O_2	B2O	mg/l	10.8	10.8	10.8	10.9	0.5	4.9	8	20	85
	N3O	mg/l	11.7	11.7	11.7	11.9	0.6	4.7	8	17	88
Salinity	A1S	PSU	1.65	1.63	1.63	1.64	0.09	5.4	5	12	58
	B2S	PSU	5.98	5.98	5.98	5.98	0.08	1.4	3.5	13	92
SiO_2	A1P	mg/l	8.56	8.27	8.27	8.12	0.63	7.7	10	12	75
	B2P	mg/l	1.39	1.40	1.40	1.39	0.13	9.2	15	12	75
	N3P	mg/l	3.95	3.95	4.25	3.85	0.67	15.8	15	11	55
TIC	A1T	mg/l	2.05	2.05	2.05	2.05	0.12	6.1	15	8	100
	N3T	mg/l	6.51	6.58	6.56	6.51	0.34	5.2	15	8	100
TOC	A1C	mg/l	1.46	1.63	1.68	1.61	0.15	9.1	15	12	67
	B2C	mg/l	5.00	5.00	4.99	4.94	0.23	4.6	15	12	100
	N3C	mg/l	8.16	8.04	8.04	8.16	0.49	6.1	10	12	100

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 $|z| \leq 2$.

3.2 Analytical methods

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

Chlorophyll *a*

Most of the participants (14) determined chlorophyll *a* by spectrophotometry using e.g. the standard methods SFS 5772 and ISO 10260. Two participants used fluorometric determination for the chlorophyll *a* measurements (Appendix 12). Due to the low number of the results, the statistical comparison of the used methods was not possible. Either based on the visual evaluation, no clear differences between the results were noticed.

Oxygen O_2

Depending on the sample, 14–15 participants determined oxygen with the standard method EN 25813, whereas three to five participants used a method based on the withdrawn standard SFS 3040 (Appendix 12). No statistical difference between the methods were observed.

Salinity

Three participants determined salinity using salinometry and eight to nine participants used conductivity meter depending on the sample. Due to the low number of the results, the statistical comparison was not possible. Based on the visual evaluation, somewhat higher variation was observed between the results analyzed with the conductivity meter than between those analyzed with the salinometry (Appendix 12).

SiO_2

Depending on the sample five to six participants used automatic (CFA, FIA) molybdosilicate spectrophotometric method, one participant determined SiO_2 by manual molybdosilicate spectrophotometric method, two participants used ICP-OES or ICP-AES technique and three participants used other methods. Due to the low number of the results, the statistical comparison was not possible, but based on the graphical evaluation, no clear differences between the results were noticed (Appendix 12).

TIC

Four participants measured TIC as carbon dioxide originating only from carbonates and hydrogen carbonates. Four participants measured TIC as carbon dioxide originating from elemental carbon, carbon dioxide, carbon monoxide, cyanide, cyanate, and thiocyanate. According to the graphical evaluation no differences between the methods were observed (Appendix 12).

TOC

Most of the participants (11) measured TOC using the NPOC-method where inorganic carbon is removed prior total carbon measurement. One participant quantified TOC as the calculated difference of total and inorganic carbon. According to the graphical evaluation no clear differences between the methods were observed (Appendix 12).

3.3 Uncertainties of the results

At maximum 94 % (15 participants) of the participants reported the expanded uncertainties (k=2) with their results for at least some of their results (Table 2, Appendix 9). The range of the reported uncertainties varied between the measurements and the sample types.

Several approaches were used for estimating the measurement uncertainty (Appendix 13). The most used approach was based on the internal quality control (IQC) data from synthetic and routine sample replicates and the IQC data with proficiency test results [6]. MUkit measurement uncertainty software for the estimation of the uncertainties was used by at maximum five participants for some measurands and samples (Appendix 13) [7]. The free software is available in the webpage: www.syke.fi/envical/en [6, 7]. Generally, the used approach for estimating measurement uncertainty did not make definite impact on the uncertainty estimates.

In order to promote the enhancement of environmental measurements' quality standards and traceability, the national quality recommendations for data entered into the water quality registers have been published in Finland [8]. The recommendations for measurement uncertainties for tested measurands in natural waters vary from 2 % to 20 %. 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 values for routine laboratories. Obviously, for salinity the minimum uncertainty has reported as absolute value, not relative as requested. Nevertheless, harmonization of the uncertainties estimation should be continued.

Table 2. The ranges of the reported expanded uncertainties by participants (U_i, %) and quality criterion for natural water [8].

Measurand	**Synthetic sample**	**Brackish water**	**River water**	**Recommendation [8]** (Concentration area)
Chlorophyll *a*	10–20	10–23	10–22	±20 % (>2 µg/l)
O_2	-	1–15	5–15	±10 % (>2 mg/l)
Salinity	1–11	0.06–11	–	±2 % (salinometry) ±10 % (others) (> 1 ‰ or PSU)
SiO_2	3–25	3–**50**	3–25	10 % (>0.20 mg/l)
TIC	10–25	–	10–15	–
TOC	5–25	5–25	5–25	±15 % (>2.5 mg/l)

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 score was interpreted as follows:

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

In total, 85 % of the results were satisfactory when total deviation of 3.5–30 % from the assigned value was accepted (Appendix 10). Altogether 81 % of the participants used accredited analytical methods at least for a part of the measurements and 85 % of their results were satisfactory. The summary of the performance evaluation and comparison to the previous performance is presented in Table 3. In the previous similar proficiency test NW 06/2018, the performance was satisfactory for 82 % of the results [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 [9].

Table 3. Summary of the performance evaluation in the proficiency test NW 06/2020.

Measurand	$2 \times s_{pt}$, %	Satisfactory results, %	Assessment
Chlorophyll *a*	10–30	94	Good performance. For the sample B2K some indication of decreased stability was observed. In the NW 06/2018 the performance was satisfactory for 84 % of the results and in the NW 02/2019 for 85 % of the results when deviation of 10-20 % from the assigned value was accepted [5, 9].
O_2	8	87	For the sample N3O some indication of decreased stability was observed. In the NW 06/2018 the performance was satisfactory for 91 % of the results [5].
Salinity	3.5–5	75	Difficulties in measurement of the sample A1S as only 58 % of the results were satisfactory. In the NW 06/2018 the performance was satisfactory for 69 % of the results [5].
SiO_2	10–15	68	Difficulties in the measurements of the samples, < 80 % satisfactory results. For the sample N3P only 55 % of the results were satisfactory. In the NW 06/2018 68 % of the results were satisfactory when deviation of 10 from the assigned value was accepted [5].
TIC	15	100	Excellent performance. In the NW 06/2018 95 % of the results were satisfactory [5].
TOC	10–15	89	Difficulties in measurement of the sample A1C as only 67 % of the results were satisfactory. For the samples B2C and N3C the performance was very good. In the NW 06/2018 86 % of the results were satisfactory [5].

Possible influences of temperature changes during the sample transport

According to the stability test all samples were regarded stable, with the exception of the sample B2K for chlorophyll *a* and N3O for O_2. For these samples and measurands some indication of decreased stability was observed, i.e. the concentrations might have slightly changed if the sample temperature increased. However, all reported arrival temperatures were ≤ 15 °C and no correlation between the performance of the participants and elevated temperatures was observed. Thus, the samples were regarded stable under the sample distribution conditions.

5 Summary

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 2020 (NW 06/2020). In total, 27 laboratories participated in this PT.

Either the calculated concentration or the robust mean, the mean or the median of the results reported by the participants was chosen to be the assigned value for the measurand. For the synthetic sample of salinity (A1S) the mean of the results measured by the salinometry was used as the assigned value. The expanded uncertainty for the assigned value was estimated at the 95 % confidence level and it was 0.6 % for the calculated assigned values and for the other assigned values it was between 0.3–9.3 %.

The evaluation of the performance was based on the z scores, which were calculated using the standard deviation for proficiency assessment at 95 % confidence level. In this proficiency test 85 % of the data was regarded to be satisfactory when the result was accepted to deviate from the assigned value 3.5–30 %.

6 Summary in Finnish

Proftest SYKE järjesti luonnonvesiä analysoiville laboratorioille pätevyyskokeen toukokuussa 2020 (NW 06/2020). Pätevyyskokeessa määritettiin happi, klorofylli *a*, saliniteetti, silikaatti (SiO_2), TIC ja TOC synteettisistä näytteistä, jokivedestä ja murtovedestä. Pätevyyskokeeseen osallistui yhteensä 27 laboratoriota.

Testisuureen vertailuarvona käytettiin joko laskennallista pitoisuutta tai osallistujien tulosten robustia keskiarvoa, keskiarvoa tai mediaania. Saliniteetin synteettiselle näytteelle (A1S) käytettiin vertailuarvona salinometrimääritysten keskiarvoa. Vertailuarvolle laskettiin epävarmuus 95 % luottamusvälillä. Vertailuarvon laajennettu epävarmuus oli 0,6 % käytettäessä laskennallista pitoisuutta vertailuarvona ja muilla välillä 0,3–9,3 %.

Pätevyyden arviointi tehtiin z-arvon avulla ja tulosten sallittiin poiketa vertailuarvosta 3,5–30 %. Koko aineistossa hyväksyttäviä tuloksia oli 85 %.

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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
	KVVY Tutkimus Oy, Tampere
	KVVY-Botnialab, Vaasa
	Kymen Ympäristölaboratorio Oy
	Lounais-Suomen vesi- ja ympäristötutkimus Oy, Turku
	MetropoliLab Oy
	Saimaan Vesi- ja Ympäristötutkimus Oy, Lappeenranta
	Savo-Karjalan Ympäristötutkimus Oy, Joensuu
	Savo-Karjalan Ympäristötutkimus Oy, Kuopio
	SeiLab Oy Haapaveden toimipiste
	SeiLab Oy Seinäjoen toimipiste
	SGS Finland Oy, Kotka
	SYKE Oulun toimipaikka
	SYKE/Merikeskus
	Tampereen Vesi/Viemärilaitoksen laboratorio
	ÅMHM laboratoriet, Jomala, Åland
Lithuania	Environment Research Department, Environmental Protection Agency
Sweden	Medins Havs och Vattenkonsulter AB
	Oceanografiska Laboratoriet, SMHI, Västra Frölunda
	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 4 mg (Sigma)/ 1.6 litres of ethanol	0.22
	B2K	5.2	grown green algae 4.6	6.05
	N3K	1.1	grown green algae 15.2	16.0
Oxygen [mg/l]	B2O	11.1	-	10.8
	N3O	11.9	-	11.7
Salinity [PSU]	A1S	-	Standard seawater (IAPSO) 1.61	1.65
	B2S	5.96	-	5.98
SiO_2 [mg/l]	A1P	-	SiO_2 (Merck CertiPUR)* 8.56	8.56
	B2P	1.4	-	1.39
	N3P	4.0	-	3.95
TIC [mg/l]	A1T	-	Na_2CO_3-$NaHCO_3$ (Merck) 1.45	2.05
	N3T	6.99	-	6.51
TOC [mg/l]	A1C	-	$C_8H_5KO_4$ (Merck CertiPUR)* 1.45	1.46
	B2C	5.6	-	5.00
	N3C	8.6	-	8.16

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

APPENDIX 3: Homogeneity of the samples

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 constant 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	6.53	6	15	0.98	0.22	0.23	Yes	0.02	0.27	Yes
a-chlorophyll/N3K	17.0	6	10	1.70	0.54	0.32	Yes	0.04	1.06	Yes
Oxygen/B2O	10.2	6	4	0.41	0.04	0.09	Yes	0.02	0.04	Yes
Oxygen/N3O	11.3	6	4	0.45	0.02	0.05	Yes	0.007	0.05	Yes
Salinity/B2S	5.95	4	1.75	0.10	0	0	Yes	0	0.003	Yes
SiO_2/B2P	1.30	3	7.5	0.10	0	0	Yes	0.0006	0.003	Yes
SiO_2/N3P	3.65	4	7.5	0.27	0.02	0.06	Yes	0.0004	0.02	Yes
TIC/N3T	6.26	4	7.5	0.47	0.007	0.01	Yes	0	0.05	Yes
TOC/B2C HCl	4.98	4	7.5	0.37	0.03	0.07	Yes	0.0002	0.03	Yes
TOC/N3C HCl	8.28	4	5	0.41	0.03	0.08	Yes	0.001	0.04	Yes

Conclusion: The criteria were fulfilled for the tested measurands and the samples were regarded as homogenous.

APPENDIX 4: Stability of the samples

The samples were delivered on 4 or 5 May 2020 and they arrived to the participants mainly on 6 May 2020. The samples were requested to be analysed as follows:

chlorophyll *a*, oxygen, TIC	7 May 2020
salinity, SiO_2, TOC	latest on 22 May 2020

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	7.5. (20 °C)	7.5. (4 °C)	Date	7.5. (20 °C)	7.5. (4 °C)	Date	7.5. (20 °C)	7.5. (4 °C)
A1K	0.216	0.218	**B2K**	5.28	5.92	**N3K**	15.3	16.1
D	0.002		D	0.63		D	0.79	
$0.3 \times s_{pt}$	0.003		$0.3 \times s_{pt}$	0.27		$0.3 \times s_{pt}$	0.48	
	$D < 0.3 \times s_{pt}$? Yes			**$D < 0.3 \times s_{pt}$? No**			**$D < 0.3 \times s_{pt}$? No[1)]**	

Oxygen

Sample	**Result** [mg/l]		**Sample**	**Result** [mg/l]	
Date	7.5. (20 °C)	7.5. (4 °C)	Date	7.5. (20 °C)	7.5. (4 °C)
B2O	10.94	10.79	**N3O**	12.22	11.51
D	0.15		D	0.71	
$0.3 \times s_{pt}$	0.13		$0.3 \times s_{pt}$	0.14	
	$D < 0.3 \times s_{pt}$? No[1)]			**$D < 0.3 \times s_{pt}$? No**	

TIC

Sample	**Result** [mg/l]		**Sample**	**Result** [mg/l]	
Date	7.5. (20 °C)	7.5. (4 °C)	Date	7.5. (20 °C)	7.5. (4 °C)
A1T	1.924	1.926	**N3T**	6.263	6.286
D	0.003		D	0.02	
$0.3 \times s_{pt}$	0.05		$0.3 \times s_{pt}$	0.15	
	$D < 0.3 \times s_{pt}$? Yes			**$D < 0.3 \times s_{pt}$? Yes**	

[1)] The difference is within the analytical error

Conclusion:
According to the test results, the concentration of chlorophyll *a* might have slightly decreased in the sample B2K and O_2 slightly increased in the sample N3O, if the sample temperature increased during the sample distribution. Stability criterion was fulfilled for the other samples, thus samples could mostly be regarded stable.

APPENDIX 5: Feedback from the proficiency test

FEEDBACK FROM THE PARTICIPANTS

Participant	Comments on technical excecution	Action / Proftest SYKE
All	The preservation for TOC samples was missing from the registration form.	The provider apologized the missing information and participants were asked about preservation by email. The given information was inserted into the registration form.
1	Participant reported some air bubbles in the oxygen sample. Paper in the package was wet.	The air bubbles are formed due to the temperature differences between the sample preparation and storage. The oxygen is fixed in the sample and according to the provider's experience small air bubbles do not have any effect on the result. There has been moisture on the surface of the bottles due to condensation.
3	Participant asked information about the volume of added reagents for oxygen samples.	The total amount of added reagents is 3 ml/sample. The samples have been prepared according to the standard SFS-EN 25813.
14	Participant wished that the sample volume for TIC would be larger than 20 ml.	The participant can order several samples, if they need higher sample volume.
26	Participant asked information about the volume of the oxygen sample. Also, the participant asked about the comparability of the results if different volumes are used in the calculations of oxygen analysis.	Participants should measure the volume of the sample if the whole sample is used in the analysis. The volume of the sample bottle is about 115–120 ml. However, the difference between the results which have calculated using volume 100 ml and those which have calculated using volume 120 ml is only about 0.5 %. The organizing laboratory uses the average volume of 115 ml.

Participant	Comments to the results	Action / Proftest SYKE
1	Participant pointed out the high distribution between the participants' results for oxygen.	This year there was slightly higher variation between the participants' results for oxygen in the brackish water sample than in the previous similar proficiency test. However, the homogeneity and stability tests showed that the samples were homogenous and stable for oxygen in the brackish water sample.
10	Participant informed that they were reported their SiO_2 results as per Si. The corrected results were: A1P 8.68 mg/l B2P 1.44 mg/l N3P 4.09 mg/l	The reported results for SiO_2 were outliers in the statistical treatment, and thus did not affect the performance evaluation. If the participant's results have been reported correctly, the results would have been satisfactory. The participant can re-calculate the z scores according to the Guide for participants [4].

FEEDBACK TO THE PARTICIPANTS

Participant	Comments
4, 9, 11, 12, 28	The participants did not return the sample arrival document to the provider. Thus, their information of the sample arrival temperature was missing as well. The participants should follow up the instructions of the provider.
11, 26	The measurement uncertainty should be reported with the results obtained by accredited method.
26	Participant reported Ui for oxygen sample in mg/l unit. The request was to report relative U_i %. The provider advises the participants to follow the given instruction.

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	0.22	<0.01	1.3	Robust mean	0.13
	B2K	µg/l	6.05	0.56	9.3	Robust mean	0.31
	N3K	µg/l	16.0	0.9	5.6	Robust mean	0.28
O_2	B2O	mg/l	10.8	0.3	2.8	Robust mean	0.35
	N3O	mg/l	11.7	0.4	3.0	Robust mean	0.38
Salinity	A1S	PSU	1.65	0.01	0.3	Mean of salinometry	0.07
	B2S	PSU	5.98	0.06	1.0	Robust mean	0.29
SiO_2	A1P	mg/l	8.56	0.05	0.6	Calculated value	0.06
	B2P	mg/l	1.39	0.08	5.4	Median	0.36
	N3P	mg/l	3.95	0.20	5.1	Mean	0.34
TIC	A1T	mg/l	2.05	0.08	3.8	Mean	0.25
	N3T	mg/l	6.51	0.25	3.8	Median	0.25
TOC	A1C	mg/l	1.46	0.01	0.6	Calculated value	0.04
	B2C	mg/l	5.00	0.13	2.6	Mean	0.17
	N3C	mg/l	8.16	0.25	3.1	Median	0.31

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 ($-2 \le z \le 2$)
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 ($z \ge 3$), positive error, the result deviates more than 3 × s_{pt} from the assigned value
u – unsatisfactory ($z \le -3$), negative error, the result deviates more than 3 × s_{pt} from the assigned value

Robust analysis

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

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

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

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

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

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

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

APPENDIX 8: Results of each participant

Participant 1												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
O_2	mg/l	B2O		2.38	10.8	8	11.8	10.9	10.8	0.5	4.7	19
Salinity	PSU	B2S		-0.29	5.98	3.5	5.95	5.98	5.98	0.08	1.3	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}
SiO_2	mg/l	A1P		-1.66	8.56	10	7.85	8.12	8.27	0.41	4.9	9
	mg/l	B2P		-2.01	1.39	15	1.18	1.39	1.40	0.11	8.1	9
	mg/l	N3P		7.66	3.95	15	6.22	3.85	3.95	0.25	6.3	6

Participant 3												
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		-0.60	10.8	8	10.5	10.9	10.8	0.5	4.7	19
Salinity	PSU	A1S		0.19	1.65	5	1.66	1.64	1.63	0.08	4.8	12
	PSU	B2S		-0.31	5.98	3.5	5.95	5.98	5.98	0.08	1.3	12
SiO_2	mg/l	A1P		0.05	8.56	10	8.58	8.12	8.27	0.41	4.9	9
	mg/l	B2P		0.67	1.39	15	1.46	1.39	1.40	0.11	8.1	9

Participant 4												
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		-0.82	0.22	10	0.21	0.22	0.22	0.00	1.7	16
	µg/l	B2K		0.85	6.05	30	6.82	6.15	6.00	0.91	15.1	15
	µg/l	N3K		1.06	16.0	20	17.7	16.0	16.0	1.2	7.7	15
O_2	mg/l	B2O		1.16	10.8	8	11.3	10.9	10.8	0.5	4.7	19
	mg/l	N3O		1.28	11.7	8	12.3	11.9	11.7	0.5	4.2	15
Salinity	PSU	A1S		2.18	1.65	5	1.74	1.64	1.63	0.08	4.8	12
	PSU	B2S		6.50	5.98	3.5	6.66	5.98	5.98	0.08	1.3	12
SiO_2	mg/l	A1P		0.30	8.56	10	8.69	8.12	8.27	0.41	4.9	9
	mg/l	B2P		-0.10	1.39	15	1.38	1.39	1.40	0.11	8.1	9
	mg/l	N3P		0.74	3.95	15	4.17	3.85	3.95	0.25	6.3	6
TIC	mg/l	A1T		0.46	2.05	15	2.12	2.05	2.05	0.11	5.4	8
	mg/l	N3T		-0.18	6.51	15	6.42	6.51	6.58	0.35	5.4	8
TOC	mg/l	A1C		3.01	1.46	15	1.79	1.61	1.63	0.09	5.7	10
	mg/l	B2C		1.09	5.00	15	5.41	4.94	5.00	0.23	4.5	12
	mg/l	N3C		-0.12	8.16	10	8.11	8.16	8.04	0.44	5.4	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}
TIC	mg/l	A1T		-0.78	2.05	15	1.93	2.05	2.05	0.11	5.4	8
	mg/l	N3T		-0.74	6.51	15	6.15	6.51	6.58	0.35	5.4	8
TOC	mg/l	A1C		1.10	1.46	15	1.58	1.61	1.63	0.09	5.7	10
	mg/l	B2C		-0.35	5.00	15	4.87	4.94	5.00	0.23	4.5	12
	mg/l	N3C		-1.84	8.16	10	7.41	8.16	8.04	0.44	5.4	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}**
Chlorophyll *a*	abs/cm	A1K		0.00	0.22	10	0.22	0.22	0.22	0.00	1.7	16
	µg/l	B2K		-0.39	6.05	30	5.70	6.15	6.00	0.91	15.1	15
	µg/l	N3K		0.00	16.0	20	16.0	16.0	16.0	1.2	7.7	15
O_2	mg/l	B2O		0.23	10.8	8	10.9	10.9	10.8	0.5	4.7	19
	mg/l	N3O		-0.21	11.7	8	11.6	11.9	11.7	0.5	4.2	15
SiO_2	mg/l	A1P		-0.84	8.56	10	8.20	8.12	8.27	0.41	4.9	9
	mg/l	B2P		0.10	1.39	15	1.40	1.39	1.40	0.11	8.1	9
	mg/l	N3P		-0.17	3.95	15	3.90	3.85	3.95	0.25	6.3	6
TIC	mg/l	A1T		-0.98	2.05	15	1.90	2.05	2.05	0.11	5.4	8
	mg/l	N3T		-0.43	6.51	15	6.30	6.51	6.58	0.35	5.4	8
TOC	mg/l	A1C		0.27	1.46	15	1.49	1.61	1.63	0.09	5.7	10
	mg/l	B2C		-0.21	5.00	15	4.92	4.94	5.00	0.23	4.5	12
	mg/l	N3C		0.32	8.16	10	8.29	8.16	8.04	0.44	5.4	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}**
Chlorophyll *a*	abs/cm	A1K		0.09	0.22	10	0.22	0.22	0.22	0.00	1.7	16
	µg/l	B2K		-1.32	6.05	30	4.85	6.15	6.00	0.91	15.1	15
	µg/l	N3K		-0.53	16.0	20	15.2	16.0	16.0	1.2	7.7	15

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*	abs/cm	A1K		0.36	0.22	10	0.22	0.22	0.22	0.00	1.7	16
	µg/l	B2K		-0.48	6.05	30	5.61	6.15	6.00	0.91	15.1	15
	µg/l	N3K		-0.68	16.0	20	14.9	16.0	16.0	1.2	7.7	15
O_2	mg/l	B2O		-1.34	10.8	8	10.2	10.9	10.8	0.5	4.7	19
	mg/l	N3O		-1.75	11.7	8	10.9	11.9	11.7	0.5	4.2	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		0.18	0.22	10	0.22	0.22	0.22	0.00	1.7	16
	µg/l	B2K		-0.94	6.05	30	5.20	6.15	6.00	0.91	15.1	15
	µg/l	N3K		-0.56	16.0	20	15.1	16.0	16.0	1.2	7.7	15
Salinity	PSU	A1S		-3.64	1.65	5	1.50	1.64	1.63	0.08	4.8	12
	PSU	B2S		0.19	5.98	3.5	6.00	5.98	5.98	0.08	1.3	12

Participant 10												
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		0.73	0.22	10	0.23	0.22	0.22	0.00	1.7	16
	µg/l	B2K		-4.57	6.05	30	1.90	6.15	6.00	0.91	15.1	15
	µg/l	N3K		-6.69	16.0	20	5.3	16.0	16.0	1.2	7.7	15
O_2	mg/l	B2O		4.00	10.8	8	12.5	10.9	10.8	0.5	4.7	19
	mg/l	N3O		0.56	11.7	8	12.0	11.9	11.7	0.5	4.2	15
Salinity	PSU	A1S		-0.02	1.65	5	1.65	1.64	1.63	0.08	4.8	12
SiO_2	mg/l	A1P		-10.51	8.56	10	4.06	8.12	8.27	0.41	4.9	9
	mg/l	B2P		-6.91	1.39	15	0.67	1.39	1.40	0.11	8.1	9
	mg/l	N3P		-6.89	3.95	15	1.91	3.85	3.95	0.25	6.3	6

Participant 11												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Chlorophyll *a*	abs/cm	A1K		-0.36	0.22	10	0.22	0.22	0.22	0.00	1.7	16
	µg/l	B2K		1.60	6.05	30	7.50	6.15	6.00	0.91	15.1	15
	µg/l	N3K		0.71	16.0	20	17.1	16.0	16.0	1.2	7.7	15
O_2	mg/l	B2O		-1.41	10.8	8	10.2	10.9	10.8	0.5	4.7	19
	mg/l	N3O		5.45	11.7	8	14.3	11.9	11.7	0.5	4.2	15
Salinity	PSU	A1S		0.48	1.65	5	1.67	1.64	1.63	0.08	4.8	12
	PSU	B2S		0.38	5.98	3.5	6.02	5.98	5.98	0.08	1.3	12
SiO_2	mg/l	A1P		1.10	8.56	10	9.03	8.12	8.27	0.41	4.9	9
	mg/l	B2P		1.44	1.39	15	1.54	1.39	1.40	0.11	8.1	9
	mg/l	N3P		1.32	3.95	15	4.34	3.85	3.95	0.25	6.3	6
TIC	mg/l	A1T		1.17	2.05	15	2.23	2.05	2.05	0.11	5.4	8
	mg/l	N3T		1.56	6.51	15	7.27	6.51	6.58	0.35	5.4	8
TOC	mg/l	A1C		1.28	1.46	15	1.60	1.61	1.63	0.09	5.7	10
	mg/l	B2C		-0.45	5.00	15	4.83	4.94	5.00	0.23	4.5	12
	mg/l	N3C		0.00	8.16	10	8.16	8.16	8.04	0.44	5.4	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}**
Chlorophyll *a*	abs/cm	A1K		0.09	0.22	10	0.22	0.22	0.22	0.00	1.7	16
	µg/l	B2K		0.40	6.05	30	6.41	6.15	6.00	0.91	15.1	15
	µg/l	N3K		0.94	16.0	20	17.5	16.0	16.0	1.2	7.7	15
O_2	mg/l	B2O		-1.39	10.8	8	10.2	10.9	10.8	0.5	4.7	19
	mg/l	N3O		-1.62	11.7	8	10.9	11.9	11.7	0.5	4.2	15
Salinity	PSU	A1S		-2.42	1.65	5	1.55	1.64	1.63	0.08	4.8	12
	PSU	B2S		1.24	5.98	3.5	6.11	5.98	5.98	0.08	1.3	12
SiO_2	mg/l	A1P		-1.38	8.56	10	7.97	8.12	8.27	0.41	4.9	9
	mg/l	B2P		-1.63	1.39	15	1.22	1.39	1.40	0.11	8.1	9
	mg/l	N3P		-0.61	3.95	15	3.77	3.85	3.95	0.25	6.3	6
TIC	mg/l	A1T		-0.20	2.05	15	2.02	2.05	2.05	0.11	5.4	8
	mg/l	N3T		0.16	6.51	15	6.59	6.51	6.58	0.35	5.4	8
TOC	mg/l	A1C		1.37	1.46	15	1.61	1.61	1.63	0.09	5.7	10
	mg/l	B2C		-0.08	5.00	15	4.97	4.94	5.00	0.23	4.5	12
	mg/l	N3C		-1.64	8.16	10	7.49	8.16	8.04	0.44	5.4	12

Participant 13												
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		0.93	10.8	8	11.2	10.9	10.8	0.5	4.7	19
	mg/l	N3O		1.28	11.7	8	12.3	11.9	11.7	0.5	4.2	15
TOC	mg/l	A1C		1.28	1.46	15	1.60	1.61	1.63	0.09	5.7	10
	mg/l	B2C		-0.13	5.00	15	4.95	4.94	5.00	0.23	4.5	12
	mg/l	N3C		0.00	8.16	10	8.16	8.16	8.04	0.44	5.4	12

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		-1.18	0.22	10	0.21	0.22	0.22	0.00	1.7	16
	µg/l	B2K		0.11	6.05	30	6.15	6.15	6.00	0.91	15.1	15
	µg/l	N3K		-0.94	16.0	20	14.5	16.0	16.0	1.2	7.7	15
O_2	mg/l	B2O		-0.93	10.8	8	10.4	10.9	10.8	0.5	4.7	19
	mg/l	N3O		-0.21	11.7	8	11.6	11.9	11.7	0.5	4.2	15
Salinity	PSU	A1S		0.00	1.65	5	1.65	1.64	1.63	0.08	4.8	12
	PSU	B2S		-0.29	5.98	3.5	5.95	5.98	5.98	0.08	1.3	12
SiO_2	mg/l	A1P		-4.93	8.56	10	6.45	8.12	8.27	0.41	4.9	9
	mg/l	B2P		1.82	1.39	15	1.58	1.39	1.40	0.11	8.1	9
	mg/l	N3P		5.03	3.95	15	5.44	3.85	3.95	0.25	6.3	6
TIC	mg/l	A1T		-0.39	2.05	15	1.99	2.05	2.05	0.11	5.4	8
	mg/l	N3T		-0.18	6.51	15	6.42	6.51	6.58	0.35	5.4	8
TOC	mg/l	A1C		6.85	1.46	15	2.21	1.61	1.63	0.09	5.7	10
	mg/l	B2C		-0.93	5.00	15	4.65	4.94	5.00	0.23	4.5	12
	mg/l	N3C		-1.25	8.16	10	7.65	8.16	8.04	0.44	5.4	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}**
O_2	mg/l	B2O		-0.79	10.8	8	10.5	10.9	10.8	0.5	4.7	19
SiO_2	mg/l	B2P		0.00	1.39	15	1.39	1.39	1.40	0.11	8.1	9
TOC	mg/l	B2C		-0.29	5.00	15	4.89	4.94	5.00	0.23	4.5	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}**
Chlorophyll *a*	abs/cm	A1K		0.00	0.22	10	0.22	0.22	0.22	0.00	1.7	16
	µg/l	B2K		0.64	6.05	30	6.63	6.15	6.00	0.91	15.1	15
	µg/l	N3K		0.75	16.0	20	17.2	16.0	16.0	1.2	7.7	15
O_2	mg/l	B2O		-1.16	10.8	8	10.3	10.9	10.8	0.5	4.7	19
	mg/l	N3O		-1.50	11.7	8	11.0	11.9	11.7	0.5	4.2	15
Salinity	PSU	A1S		-1.45	1.65	5	1.59	1.64	1.63	0.08	4.8	12
	PSU	B2S		0.96	5.98	3.5	6.08	5.98	5.98	0.08	1.3	12

Participant 18												
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		1.16	10.8	8	11.3	10.9	10.8	0.5	4.7	19
	mg/l	N3O		0.85	11.7	8	12.1	11.9	11.7	0.5	4.2	15

Participant 19												
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	N3O		0.66	11.7	8	12.0	11.9	11.7	0.5	4.2	15
TOC	mg/l	A1C		4.02	1.46	15	1.90	1.61	1.63	0.09	5.7	10
	mg/l	N3C		0.98	8.16	10	8.56	8.16	8.04	0.44	5.4	12

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		-0.05	0.22	10	0.22	0.22	0.22	0.00	1.7	16
	µg/l	B2K		-2.37	6.05	30	3.90	6.15	6.00	0.91	15.1	15
	µg/l	N3K		-0.69	16.0	20	14.9	16.0	16.0	1.2	7.7	15
O_2	mg/l	B2O		-0.09	10.8	8	10.8	10.9	10.8	0.5	4.7	19
	mg/l	N3O		-4.79	11.7	8	9.5	11.9	11.7	0.5	4.2	15
Salinity	PSU	A1S		-1.07	1.65	5	1.61	1.64	1.63	0.08	4.8	12
	PSU	B2S		0.46	5.98	3.5	6.03	5.98	5.98	0.08	1.3	12
SiO_2	mg/l	A1P		-1.14	8.56	10	8.07	8.12	8.27	0.41	4.9	9
	mg/l	B2P		-0.58	1.39	15	1.33	1.39	1.40	0.11	8.1	9
	mg/l	N3P		-0.74	3.95	15	3.73	3.85	3.95	0.25	6.3	6
TIC	mg/l	A1T		0.46	2.05	15	2.12	2.05	2.05	0.11	5.4	8
	mg/l	N3T		0.72	6.51	15	6.86	6.51	6.58	0.35	5.4	8
TOC	mg/l	A1C		2.92	1.46	15	1.78	1.61	1.63	0.09	5.7	10
	mg/l	B2C		0.45	5.00	15	5.17	4.94	5.00	0.23	4.5	12
	mg/l	N3C		0.66	8.16	10	8.43	8.16	8.04	0.44	5.4	12

Participant 21												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Chlorophyll *a*	abs/cm	A1K		0.18	0.22	10	0.22	0.22	0.22	0.00	1.7	16
	µg/l	B2K		0.62	6.05	30	6.61	6.15	6.00	0.91	15.1	15
	µg/l	N3K		-1.34	16.0	20	13.9	16.0	16.0	1.2	7.7	15
O_2	mg/l	B2O		-0.74	10.8	8	10.5	10.9	10.8	0.5	4.7	19
	mg/l	N3O		-0.88	11.7	8	11.3	11.9	11.7	0.5	4.2	15
Salinity	PSU	A1S		-3.15	1.65	5	1.52	1.64	1.63	0.08	4.8	12
	PSU	B2S		-0.38	5.98	3.5	5.94	5.98	5.98	0.08	1.3	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}**
Chlorophyll *a*	abs/cm	A1K		-1.55	0.22	10	0.20	0.22	0.22	0.00	1.7	16
	µg/l	B2K		0.69	6.05	30	6.68	6.15	6.00	0.91	15.1	15
	µg/l	N3K		0.63	16.0	20	17.0	16.0	16.0	1.2	7.7	15
O_2	mg/l	B2O		0.46	10.8	8	11.0	10.9	10.8	0.5	4.7	19
	mg/l	N3O		0.00	11.7	8	11.7	11.9	11.7	0.5	4.2	15
Salinity	PSU	A1S		2.42	1.65	5	1.75	1.64	1.63	0.08	4.8	12
	PSU	B2S		0.29	5.98	3.5	6.01	5.98	5.98	0.08	1.3	12
SiO_2	mg/l	A1P		5.00	8.56	10	10.70	8.12	8.27	0.41	4.9	9
	mg/l	B2P		4.32	1.39	15	1.84	1.39	1.40	0.11	8.1	9
	mg/l	N3P		3.65	3.95	15	5.03	3.85	3.95	0.25	6.3	6

Participant 23												
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		0.17	0.22	10	0.22	0.22	0.22	0.00	1.7	16
	µg/l	B2K		0.43	6.05	30	6.44	6.15	6.00	0.91	15.1	15
	µg/l	N3K		0.50	16.0	20	16.8	16.0	16.0	1.2	7.7	15
O_2	mg/l	B2O		0.30	10.8	8	10.9	10.9	10.8	0.5	4.7	19
	mg/l	N3O		0.47	11.7	8	11.9	11.9	11.7	0.5	4.2	15
SiO_2	mg/l	A1P		-1.03	8.56	10	8.12	8.12	8.27	0.41	4.9	9
	mg/l	N3P		8.54	3.95	15	6.48	3.85	3.95	0.25	6.3	6

Participant 24												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Chlorophyll *a*	abs/cm	A1K		0.00	0.22	10	0.22	0.22	0.22	0.00	1.7	16
	µg/l	B2K		-0.72	6.05	30	5.40	6.15	6.00	0.91	15.1	15
	µg/l	N3K		-0.51	16.0	20	15.2	16.0	16.0	1.2	7.7	15
O_2	mg/l	B2O		0.25	10.8	8	10.9	10.9	10.8	0.5	4.7	19
	mg/l	N3O		0.98	11.7	8	12.2	11.9	11.7	0.5	4.2	15
TOC	mg/l	A1C		1.95	1.46	15	1.67	1.61	1.63	0.09	5.7	10
	mg/l	B2C		0.14	5.00	15	5.05	4.94	5.00	0.23	4.5	12
	mg/l	N3C		0.79	8.16	10	8.48	8.16	8.04	0.44	5.4	12

Participant 25												
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		-0.86	5.98	3.5	5.89	5.98	5.98	0.08	1.3	12

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		2.41	10.8	8	11.8	10.9	10.8	0.5	4.7	19
TOC	mg/l	B2C		1.09	5.00	15	5.41	4.94	5.00	0.23	4.5	12

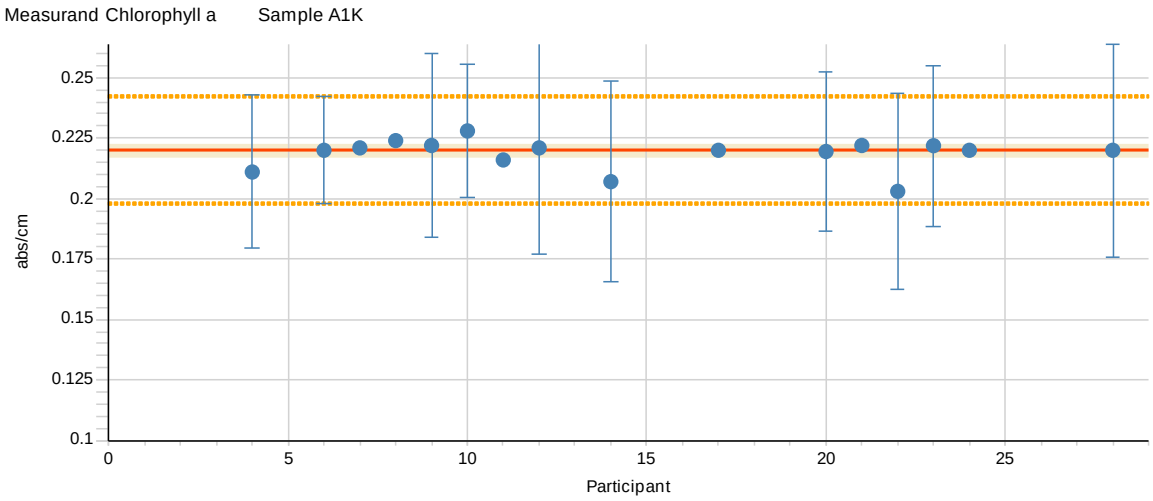
Participant 27												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
TOC	mg/l	A1C		1.46	1.46	15	1.62	1.61	1.63	0.09	5.7	10
	mg/l	N3C		0.37	8.16	10	8.31	8.16	8.04	0.44	5.4	12

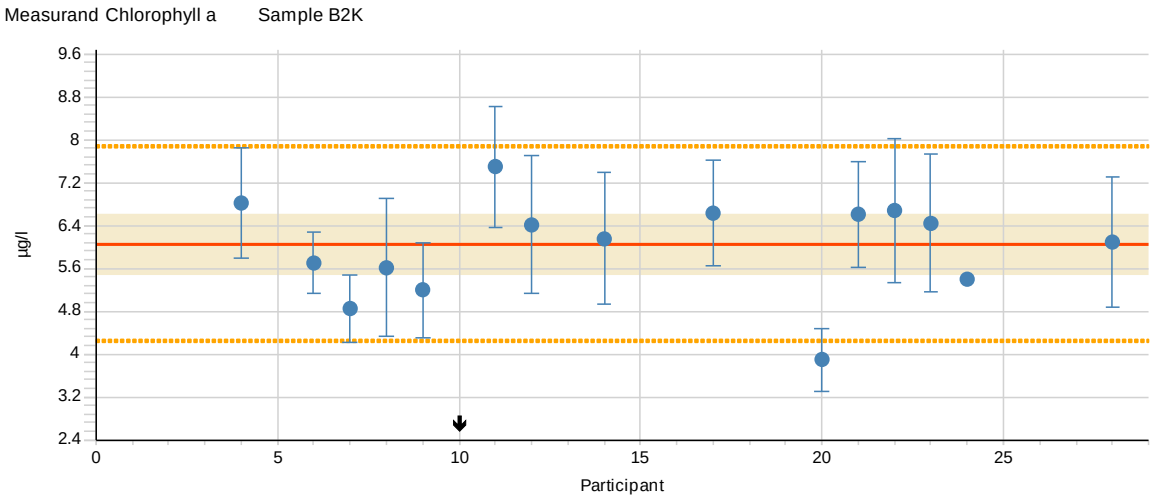
Participant 28												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Chlorophyll *a*	abs/cm	A1K		0.00	0.22	10	0.22	0.22	0.22	0.00	1.7	16
	µg/l	B2K		0.04	6.05	30	6.09	6.15	6.00	0.91	15.1	15
	µg/l	N3K		0.25	16.0	20	16.4	16.0	16.0	1.2	7.7	15
O_2	mg/l	B2O		0.69	10.8	8	11.1	10.9	10.8	0.5	4.7	19
	mg/l	N3O		0.64	11.7	8	12.0	11.9	11.7	0.5	4.2	15
Salinity	PSU	A1S		-0.24	1.65	5	1.64	1.64	1.63	0.08	4.8	12
	PSU	B2S		-1.34	5.98	3.5	5.84	5.98	5.98	0.08	1.3	12
SiO_2	mg/l	A1P		-1.54	8.56	10	7.90	8.12	8.27	0.41	4.9	9
	mg/l	B2P		-0.86	1.39	15	1.30	1.39	1.40	0.11	8.1	9
	mg/l	N3P		-0.51	3.95	15	3.80	3.85	3.95	0.25	6.3	6
TIC	mg/l	A1T		0.20	2.05	15	2.08	2.05	2.05	0.11	5.4	8
	mg/l	N3T		0.31	6.51	15	6.66	6.51	6.58	0.35	5.4	8
TOC	mg/l	A1C		1.10	1.46	15	1.58	1.61	1.63	0.09	5.7	10
	mg/l	B2C		-0.21	5.00	15	4.92	4.94	5.00	0.23	4.5	12
	mg/l	N3C		-1.94	8.16	10	7.37	8.16	8.04	0.44	5.4	12

APPENDIX 9: Results of participants and their uncertainties

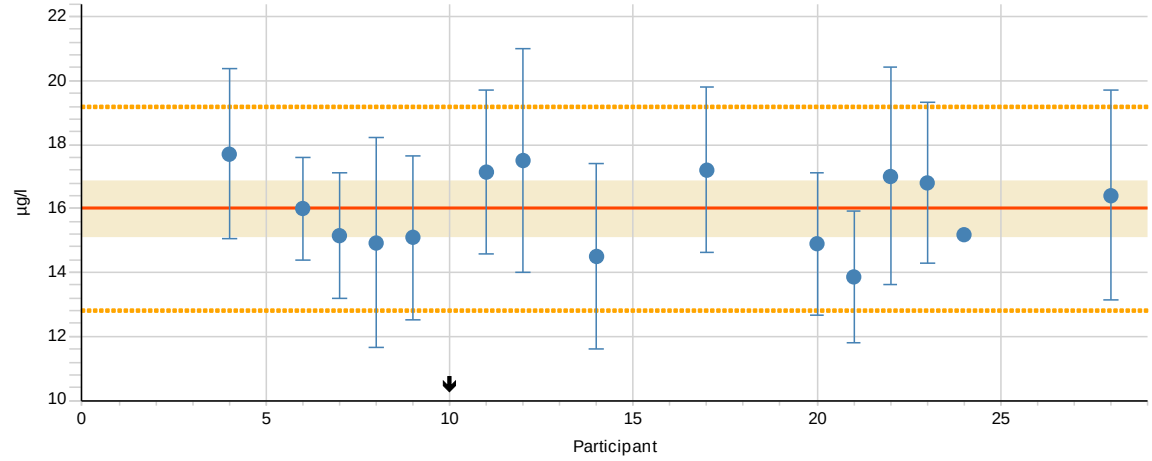
In figures:

- 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.

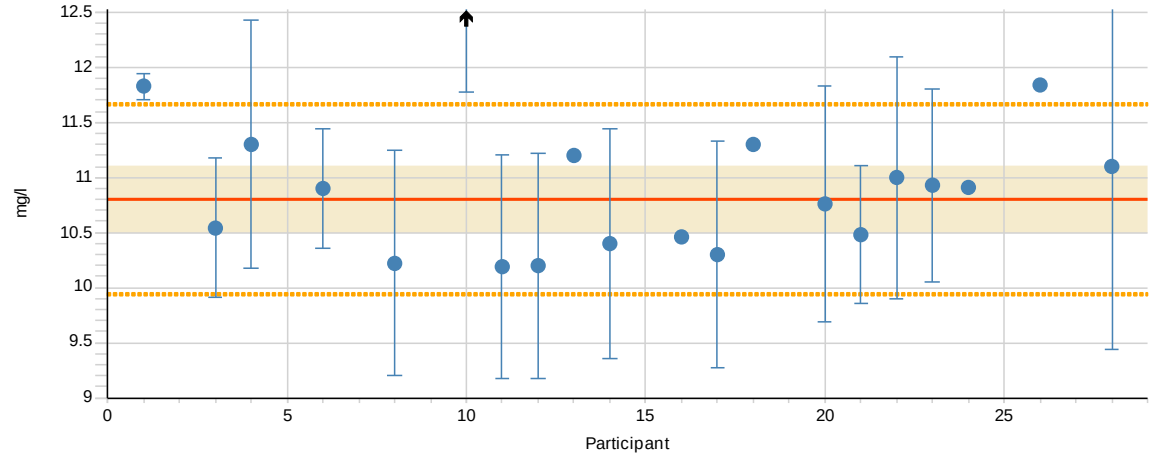




Measurand Chlorophyll a Sample N3K



Measurand O_2 Sample B2O



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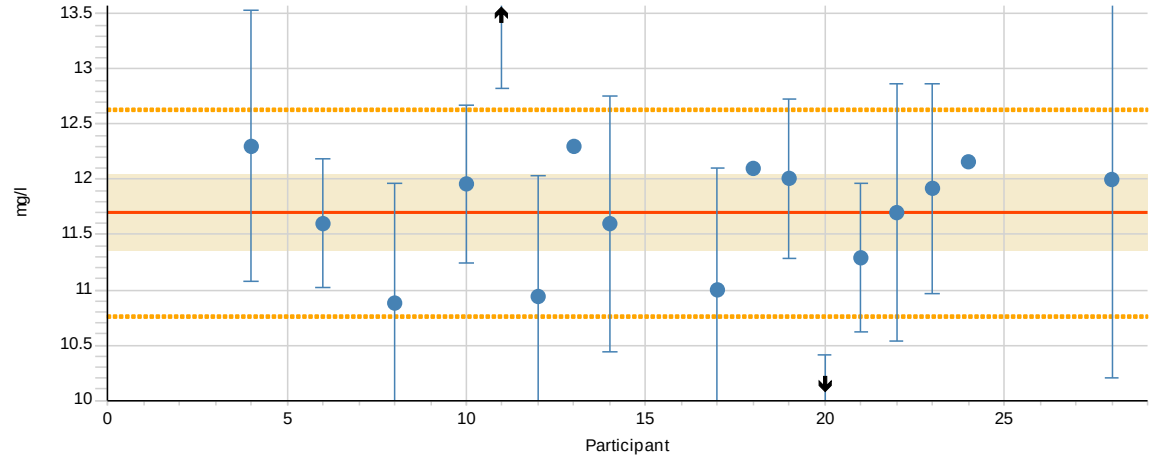
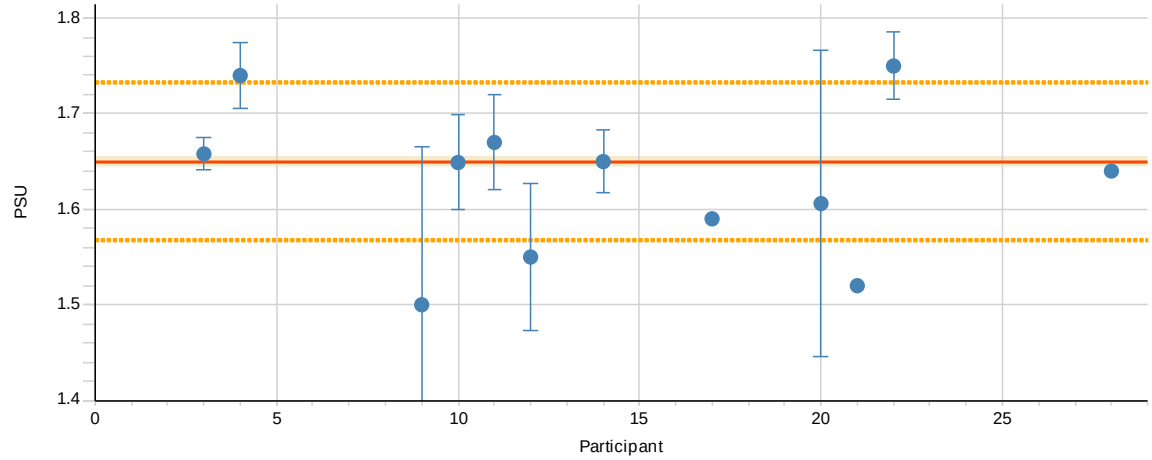
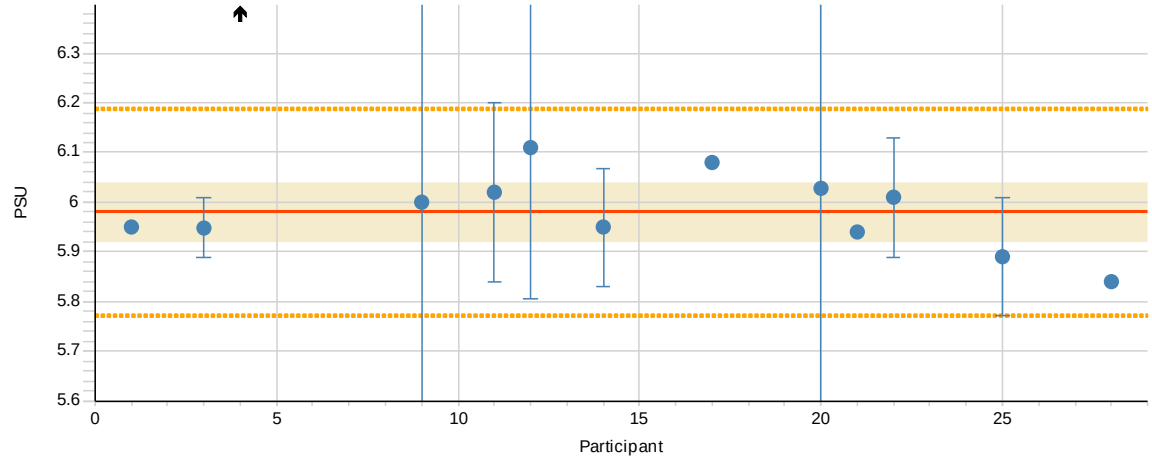


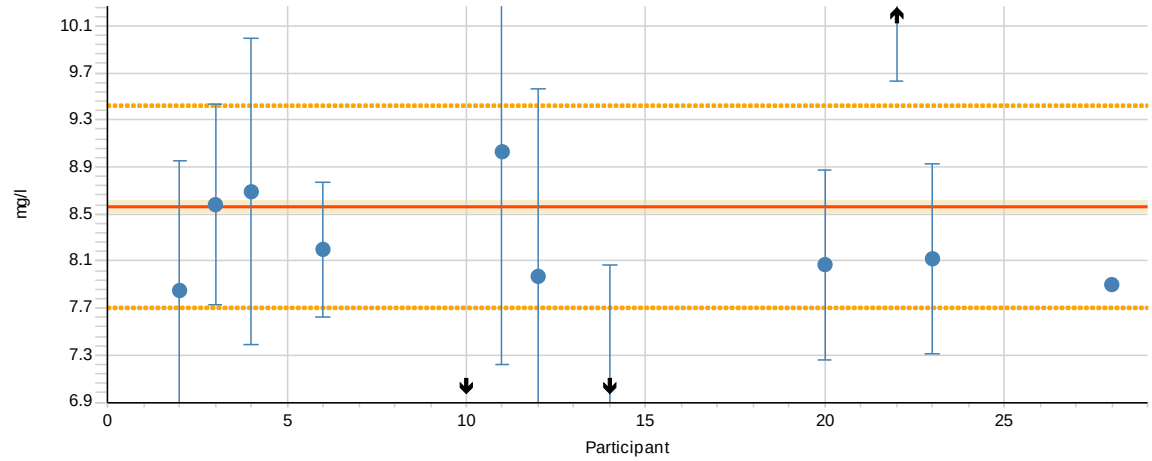
Measurand Salinity Sample A1S



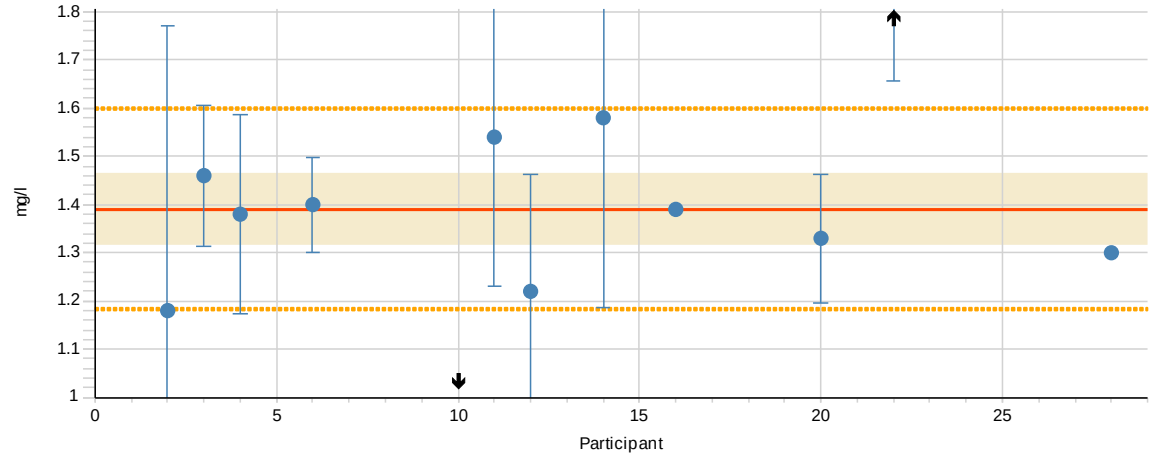
Measurand Salinity Sample B2S



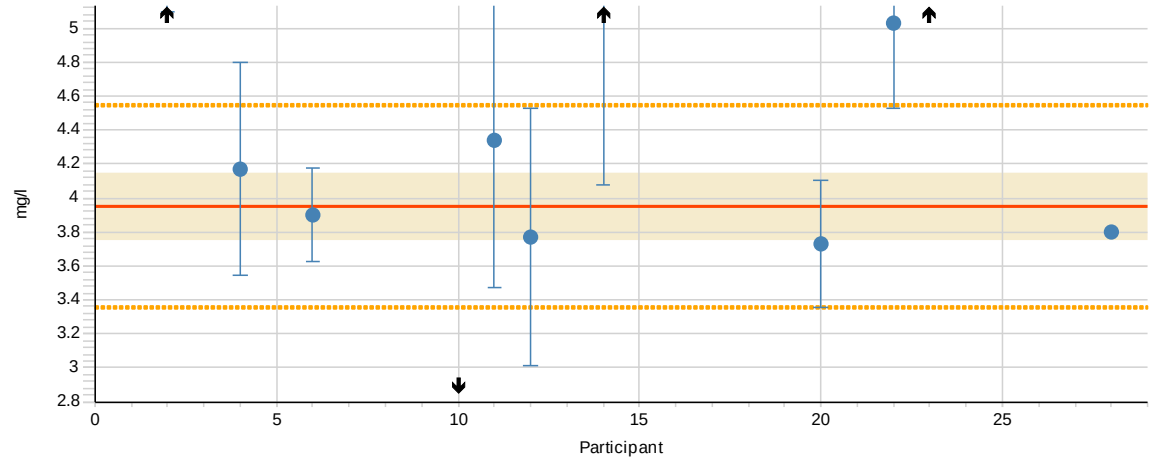
Measurand SiO_2 Sample A1P



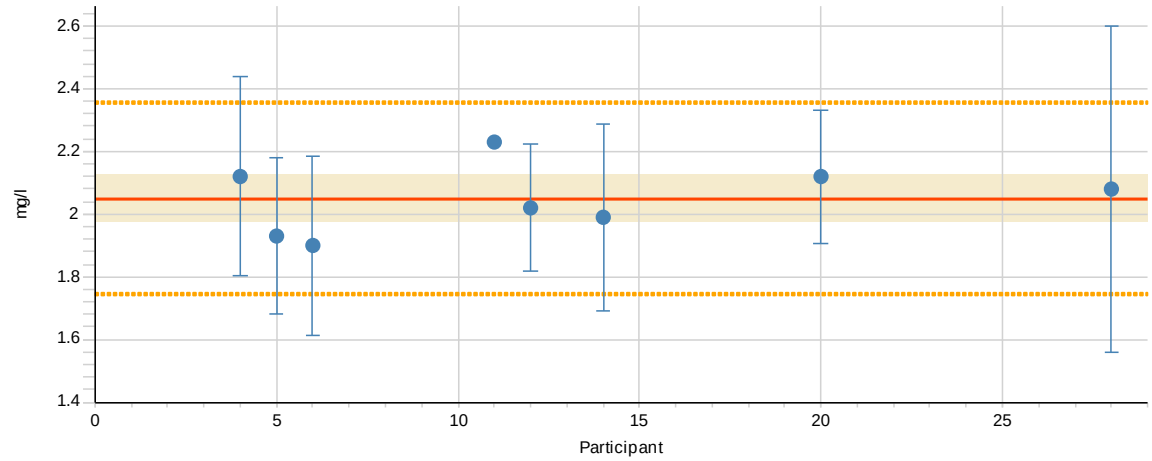
Measurand SiO_2 Sample B2P



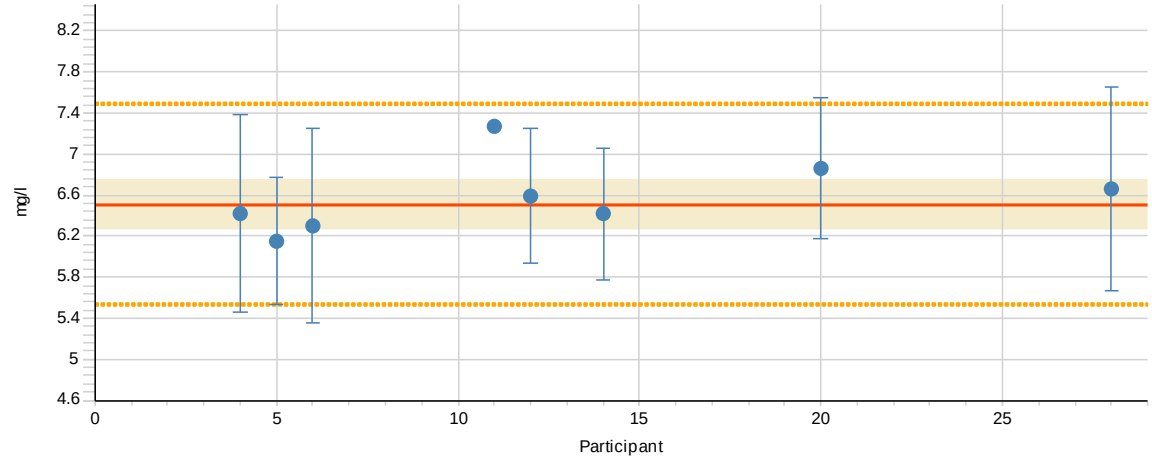
Measurand SiO_2 Sample N3P



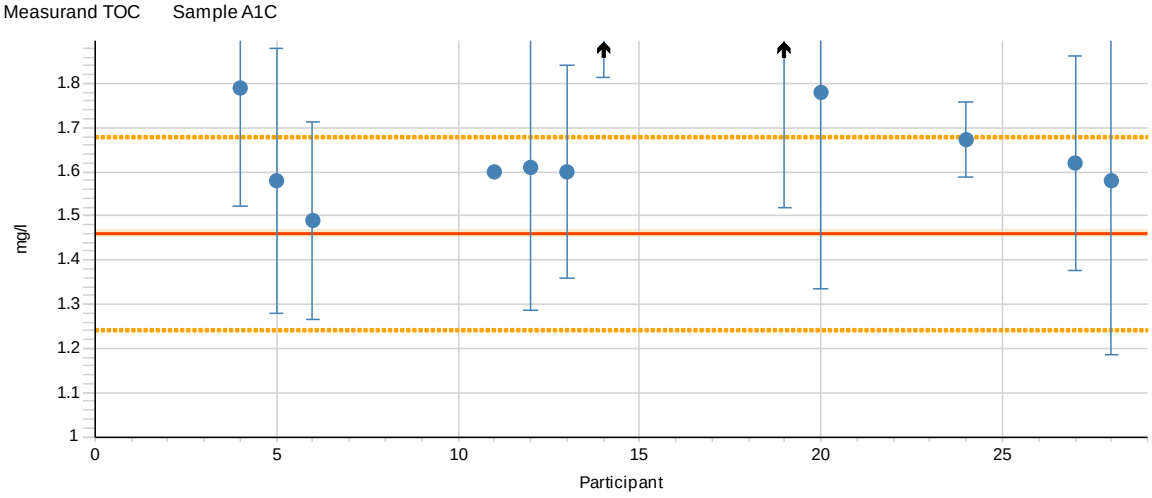
Measurand TIC Sample A1T



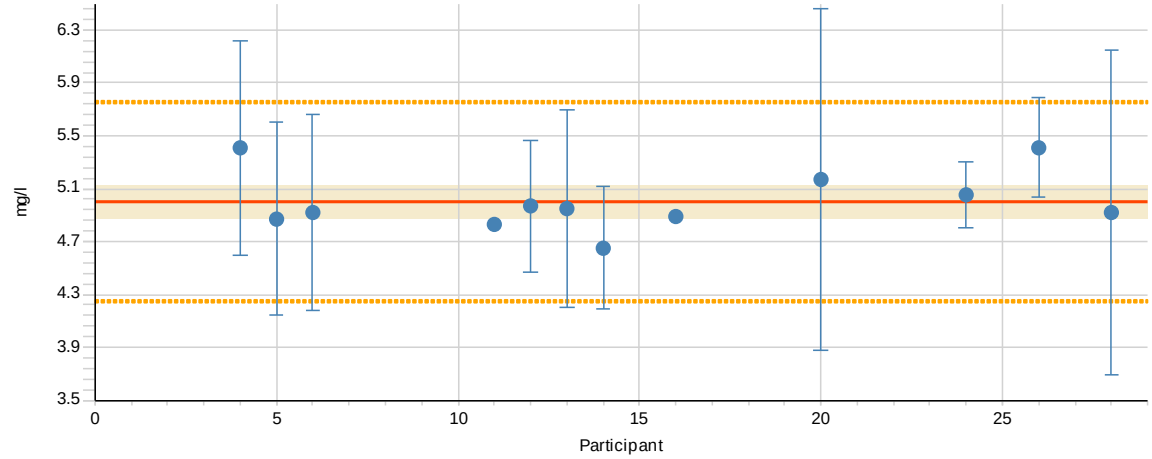
Measurand TIC Sample N3T

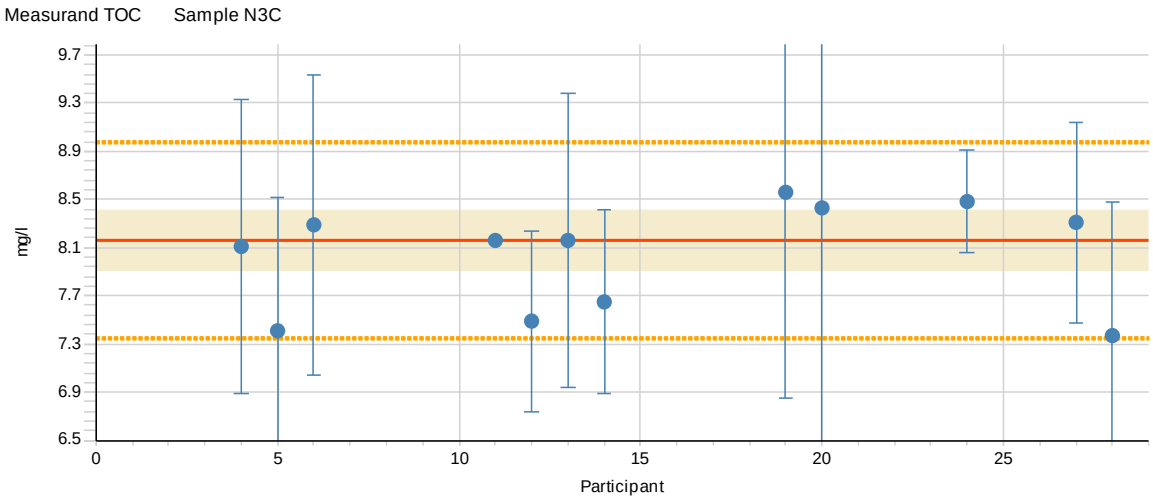


Measurand TOC Sample A1C



Measurand TOC Sample B2C




Measurand TOC
Sample N3C
9.7
9.3
8.9
8.5
8.1
7.7
7.3
6.9
6.5
mg/l
0
5
10
15
20
25
Participant

APPENDIX 10: Summary of the z scores

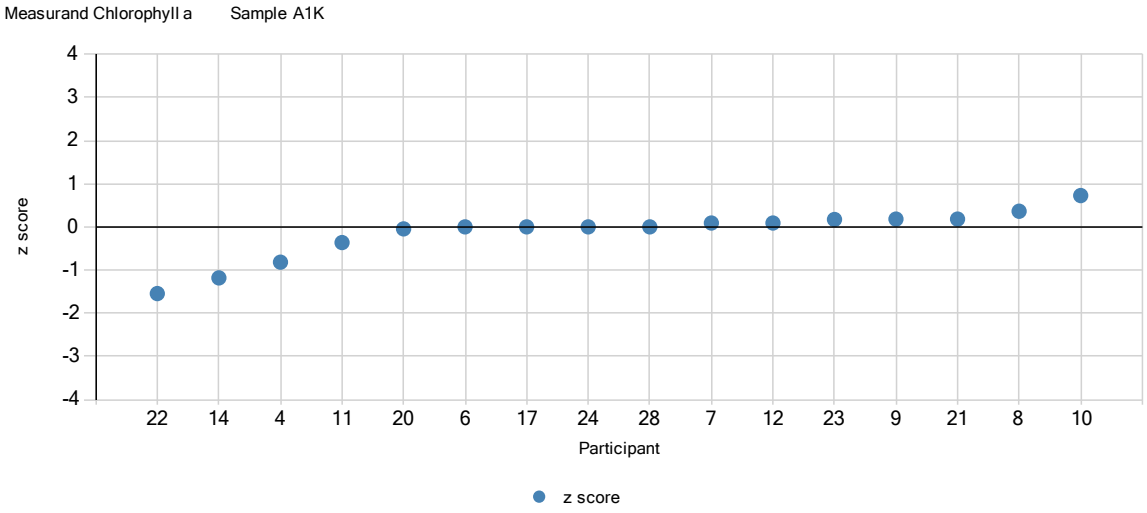
Measurand	Sample	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	%
Chlorophyll *a*	A1K	.	.	.	**S**	.	*S*	*S*	*S*	**S**	**S**	**S**	**S**	.	**S**	.	.	*S*	.	.	**S**	*S*	**S**	**S**	100
	B2K	.	.	.	**S**	.	*S*	*S*	*S*	**S**	**u**	**S**	**S**	.	**S**	.	.	**S**	.	.	**q**	**S**	**S**	**S**	87.5
	N3K	.	.	.	**S**	.	*S*	*S*	*S*	**S**	**u**	**S**	**S**	.	**S**	.	.	**S**	.	.	**S**	**S**	**S**	**S**	93.8
O_2	B2O	**Q**	.	**S**	**S**	.	**S**	.	**S**	.	**U**	**S**	**S**	*S*	**S**	.	*S*	**S**	*S*	.	**S**	**S**	**S**	**S**	85.0
	N3O	.	.	.	**S**	.	**S**	.	**S**	.	**S**	**U**	**S**	*S*	**S**	.	.	**S**	*S*	**S**	**u**	**S**	**S**	**S**	88.2
Salinity	A1S	.	.	**S**	**Q**	.	.	.	.	**u**	**S**	*S*	**q**	.	**S**	.	.	*S*	.	.	**S**	*u*	*Q*	.	58.3
	B2S	**S**	.	**S**	**U**	.	.	.	.	**S**	.	*S*	**S**	.	**S**	.	.	*S*	.	.	**S**	*S*	*S*	.	92.3
SiO_2	A1P	.	*S*	**S**	**S**	.	**S**	.	.	.	**u**	**S**	**S**	.	**u**	.	.	.	.	.	**S**	.	*U*	*S*	75.0
	B2P	.	*q*	**S**	**S**	.	**S**	.	.	.	**u**	**S**	**S**	.	**S**	.	*S*	.	.	.	**S**	.	*U*	.	75.0
	N3P	.	*U*	.	**S**	.	**S**	.	.	.	**u**	**S**	**S**	.	**U**	.	.	.	.	.	**S**	.	*U*	*U*	54.5
TIC	A1T	.	.	.	**S**	**S**	**S**	.	.	.	.	*S*	**S**	.	**S**	.	.	.	.	.	**S**	.	.	.	100
	N3T	.	.	.	**S**	**S**	**S**	.	.	.	.	*S*	**S**	.	**S**	.	.	.	.	.	**S**	.	.	.	100
TOC	A1C	.	.	.	**U**	**S**	**S**	.	.	.	.	**S**	**S**	**S**	**U**	.	.	.	.	**U**	**Q**	.	.	.	66.7
	B2C	.	.	.	**S**	**S**	**S**	.	.	.	.	*S*	**S**	*S*	**S**	.	*S*	.	.	.	**S**	.	.	.	100
	N3C	.	.	.	**S**	**S**	**S**	.	.	.	.	*S*	**S**	*S*	**S**	.	.	.	.	**S**	**S**	.	.	.	100
%		50	33	100	80	100	100	100	100	80	33	93	93	100	80		100	100	100	67	80	86	60	86	
accredited		2		5	15	5	10		2	5	9	9	15	1	15			4		3	15	4	5	5	

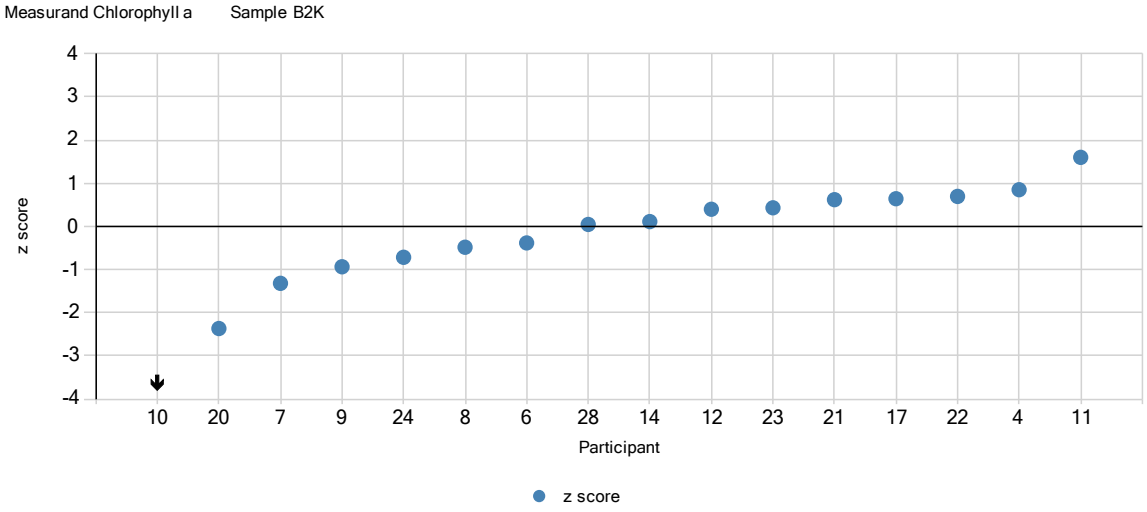
Measurand	Sample	24	25	26	27	28	%
Chlorophyll *a*	A1K	*S*	.	.	.	**S**	100
	B2K	*S*	.	.	.	**S**	87.5
	N3K	*S*	.	.	.	**S**	93.8
O_2	B2O	*S*	.	**Q**	.	**S**	85.0
	N3O	*S*	.	.	.	**S**	88.2
Salinity	A1S	.	.	.	.	*S*	58.3
	B2S	.	**S**	.	.	*S*	92.3
SiO_2	A1P	.	.	.	.	*S*	75.0
	B2P	.	.	.	.	*S*	75.0
	N3P	.	.	.	.	*S*	54.5
TIC	A1T	.	.	.	.	**S**	100
	N3T	.	.	.	.	**S**	100
TOC	A1C	*S*	.	.	**S**	**S**	66.7
	B2C	*S*	.	**S**	.	**S**	100
	N3C	*S*	.	.	**S**	**S**	100
%		100	100	50	100	100	
accredited			1	2	2	10	

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

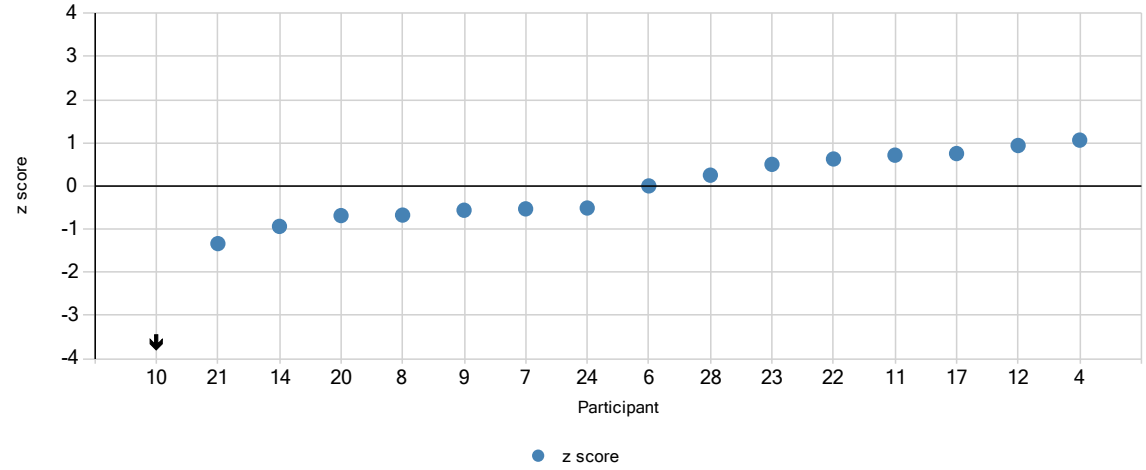
Totally satisfactory, % in all: 85 % in accredited: 85 % in non-accredited: 85

APPENDIX 11: z scores in ascending order

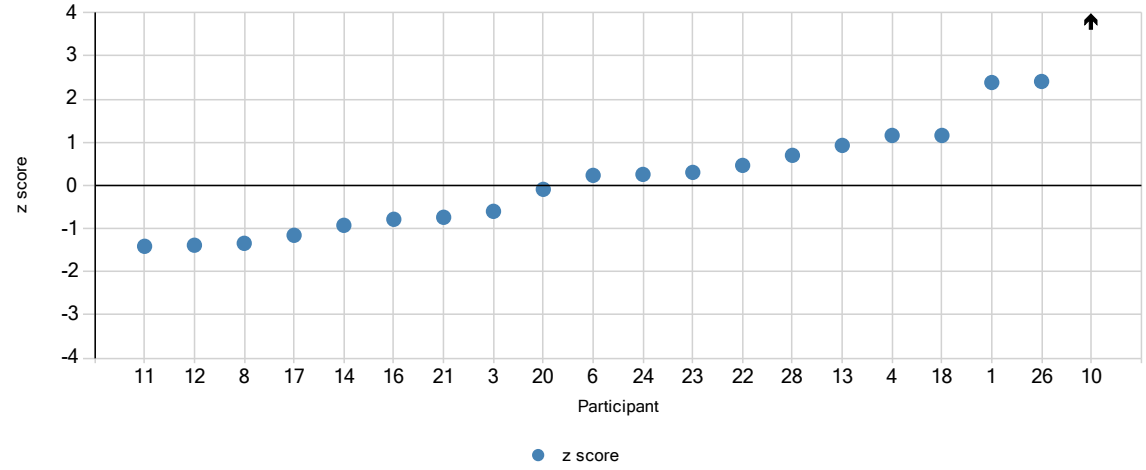




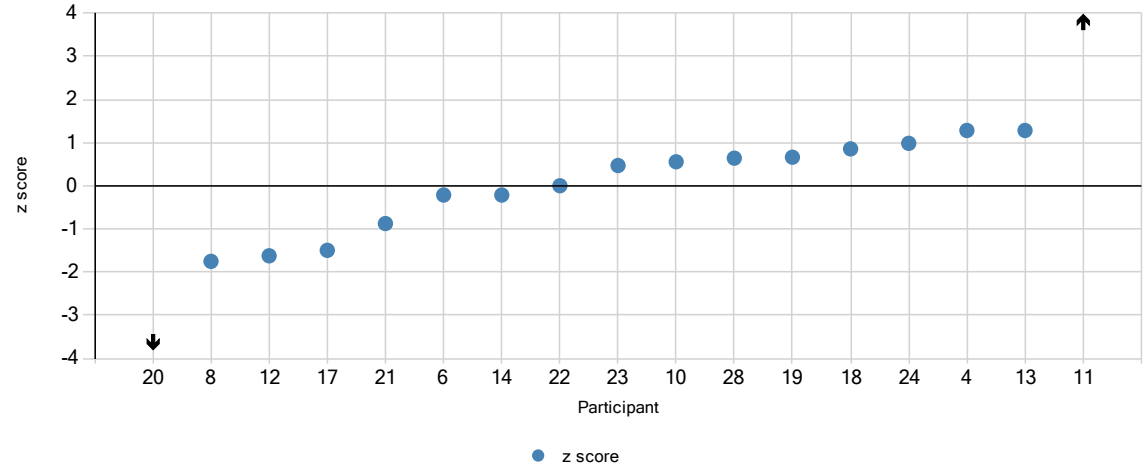
Measurand Chlorophyll a Sample N3K



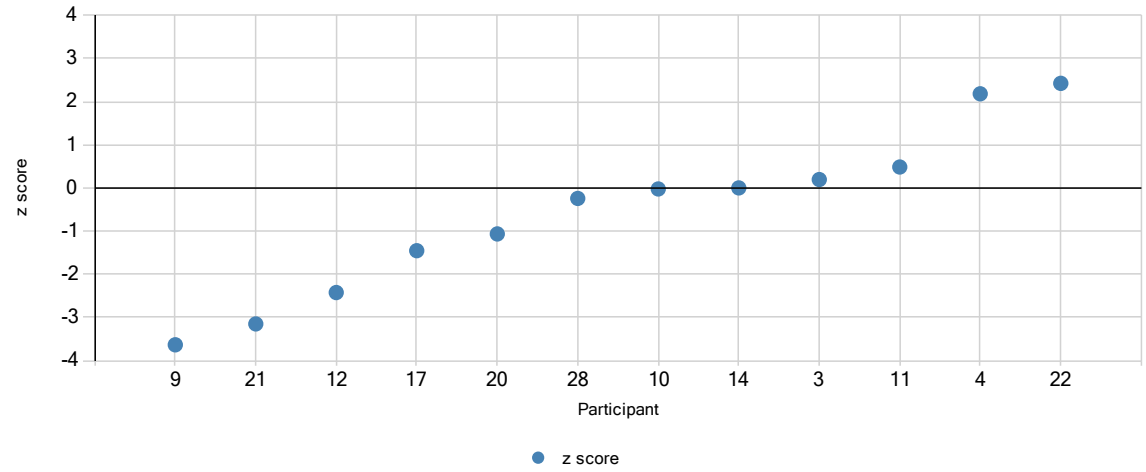
Measurand O_2 Sample B2O



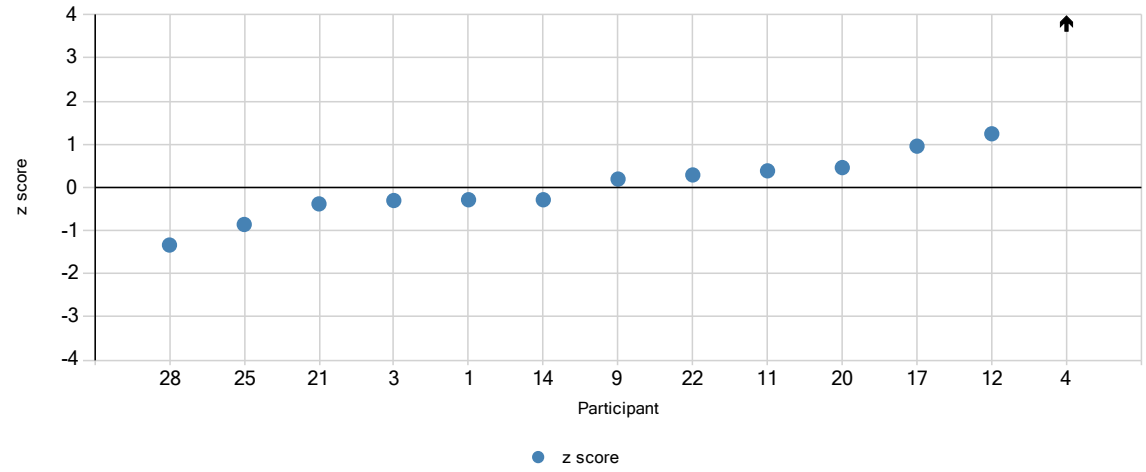
Measurand O_2 Sample N3O



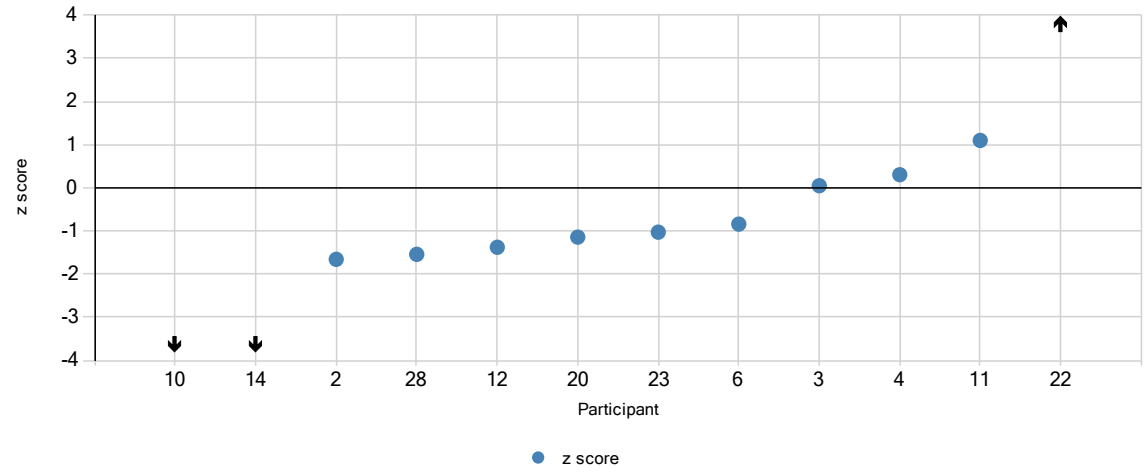
Measurand Salinity Sample A1S



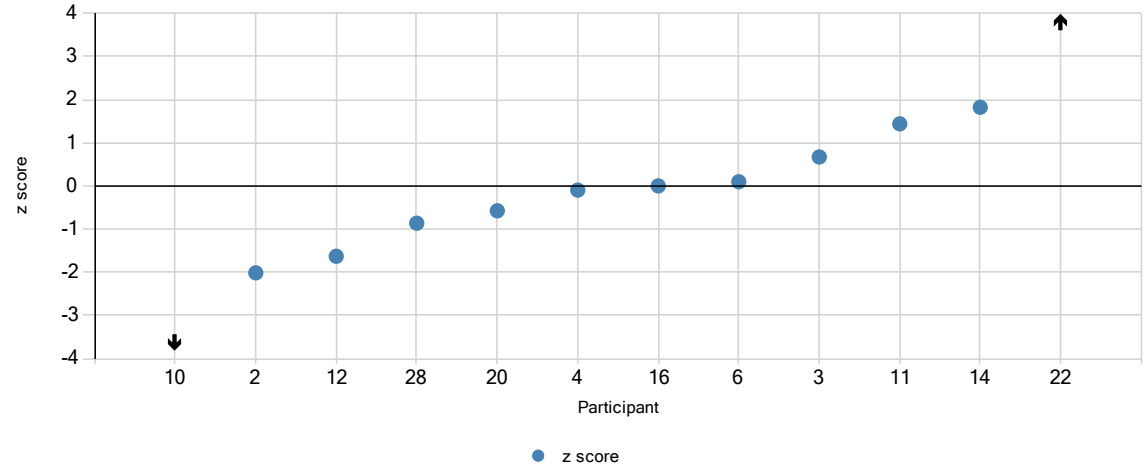
Measurand Salinity Sample B2S



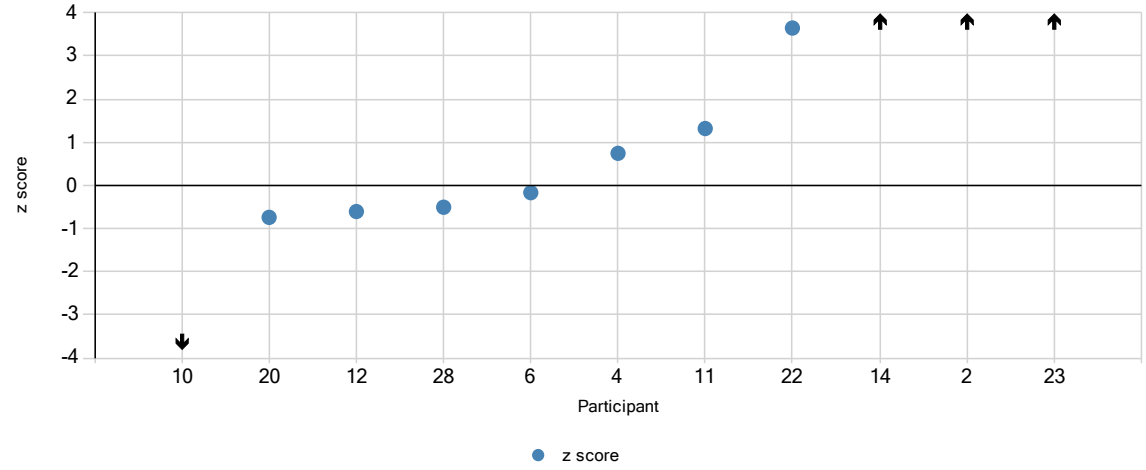
Measurand SiO_2 Sample A1P



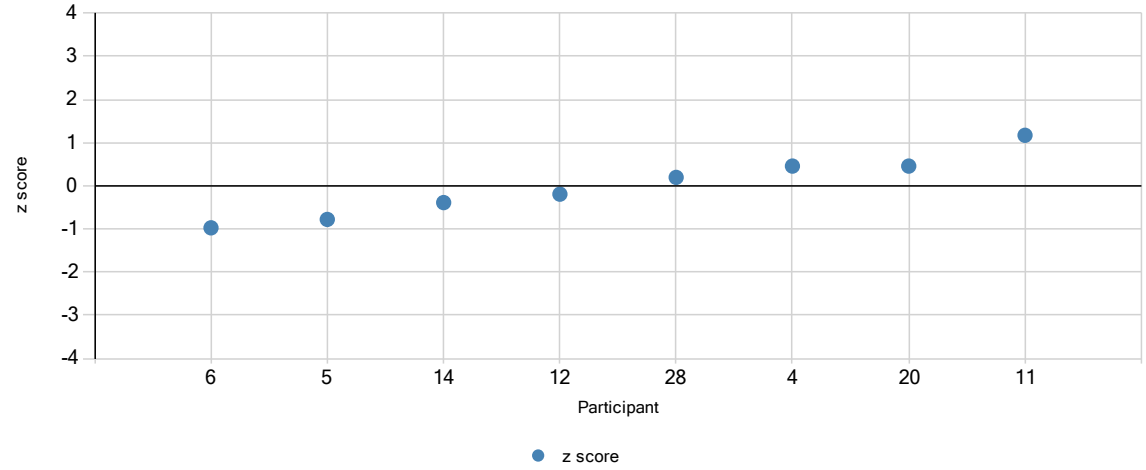
Measurand SiO_2 Sample B2P

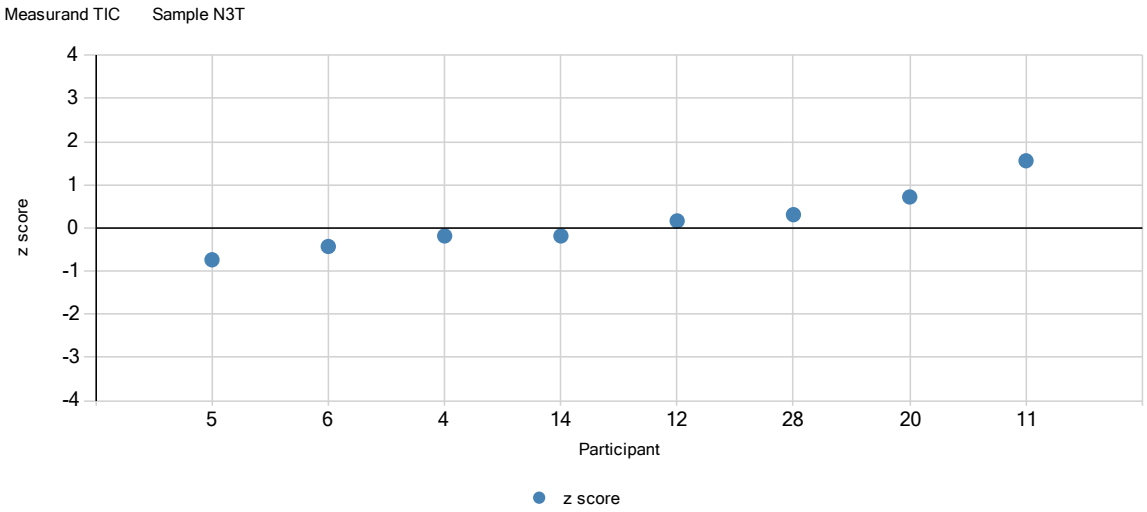


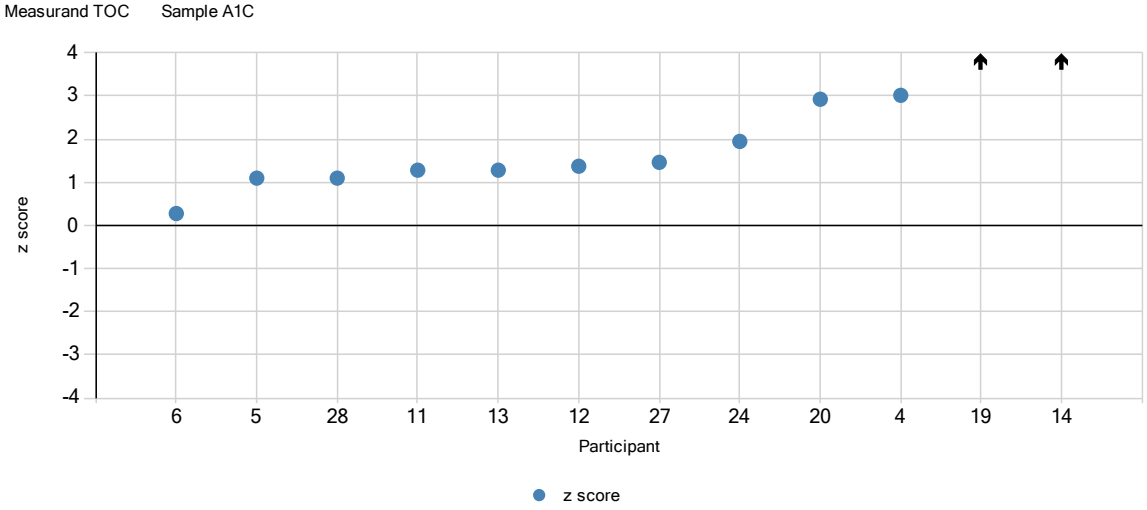
Measurand SiO_2 Sample N3P

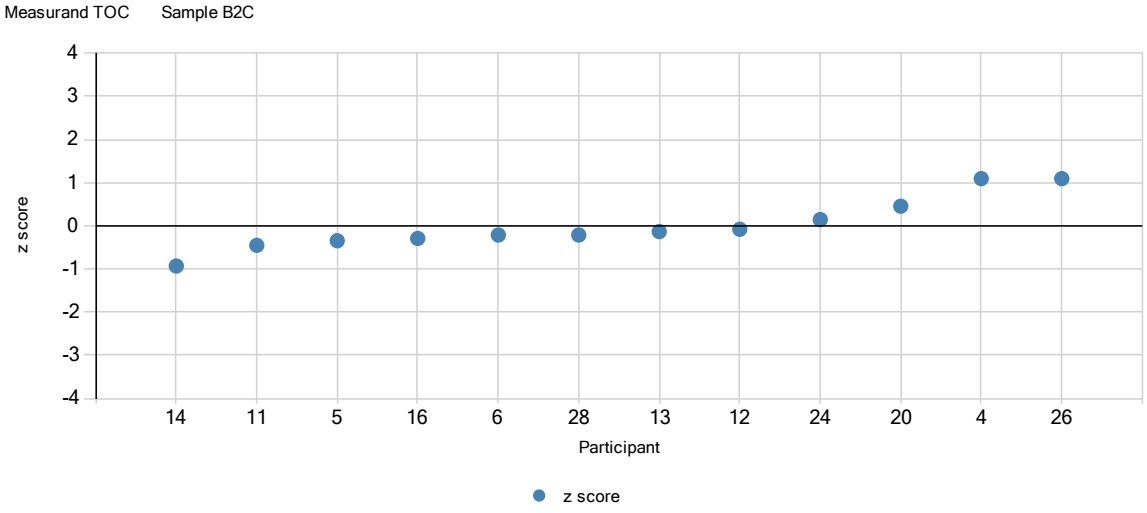


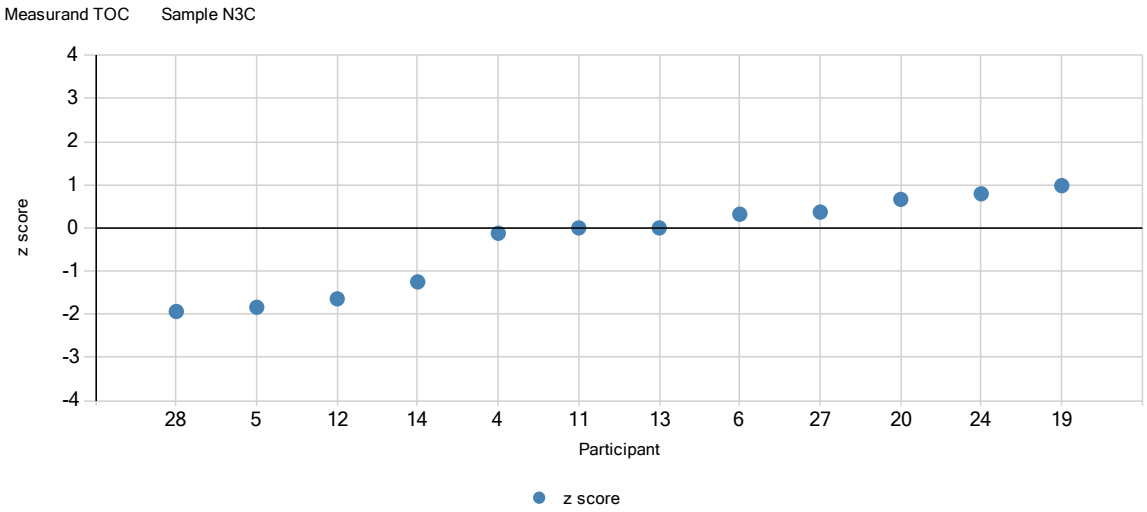
Measurand TIC Sample A1T




Measurand TIC Sample N3T
z score
4
3
2
1
0
-1
-2
-3
-4
5
6
4
14
12
28
20
11
Participant
z score

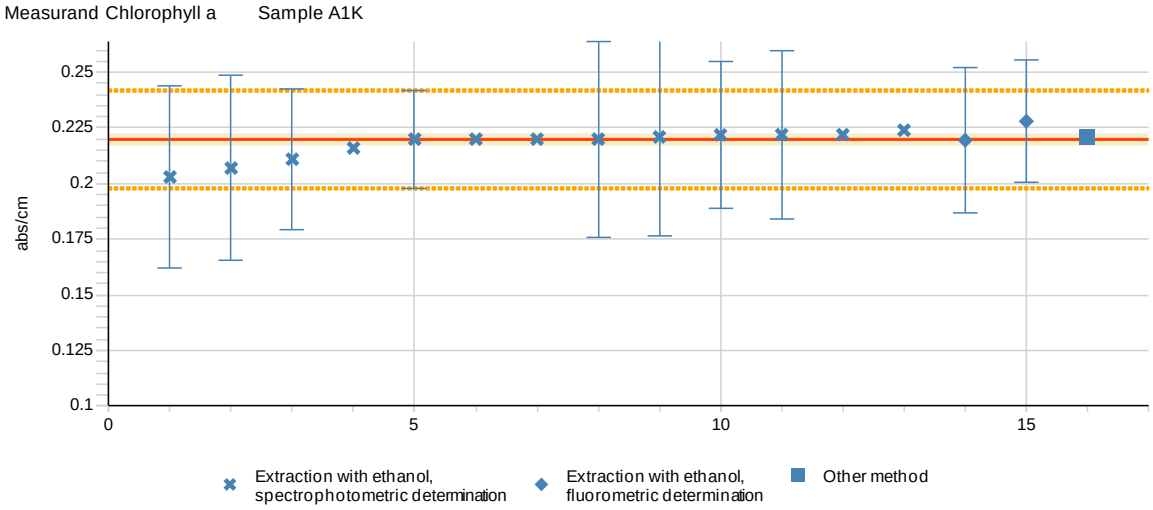

Measurand TOC Sample A1C
z score
4
3
2
1
0
-1
-2
-3
-4
6
5
28
11
13
12
27
24
20
4
19
14
Participant
z score

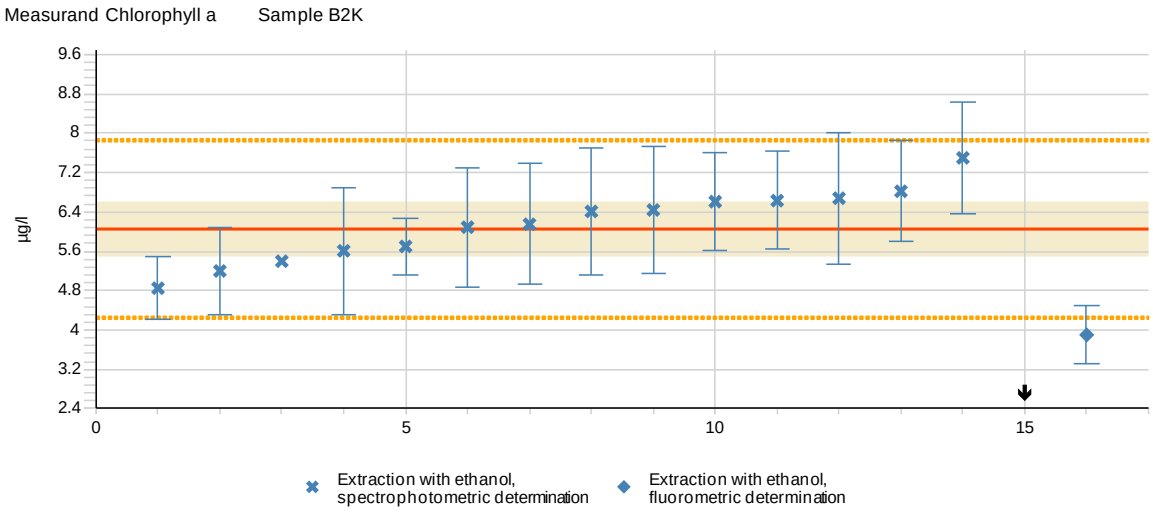

Measurand TOC Sample B2C
z score
4
3
2
1
0
-1
-2
-3
-4
14
11
5
16
6
28
13
12
24
20
4
26
Participant
z score


Measurand TOC
Sample N3C
z score
4
3
2
1
0
-1
-2
-3
-4
28
5
12
14
4
11
13
6
27
20
24
19
Participant
z score

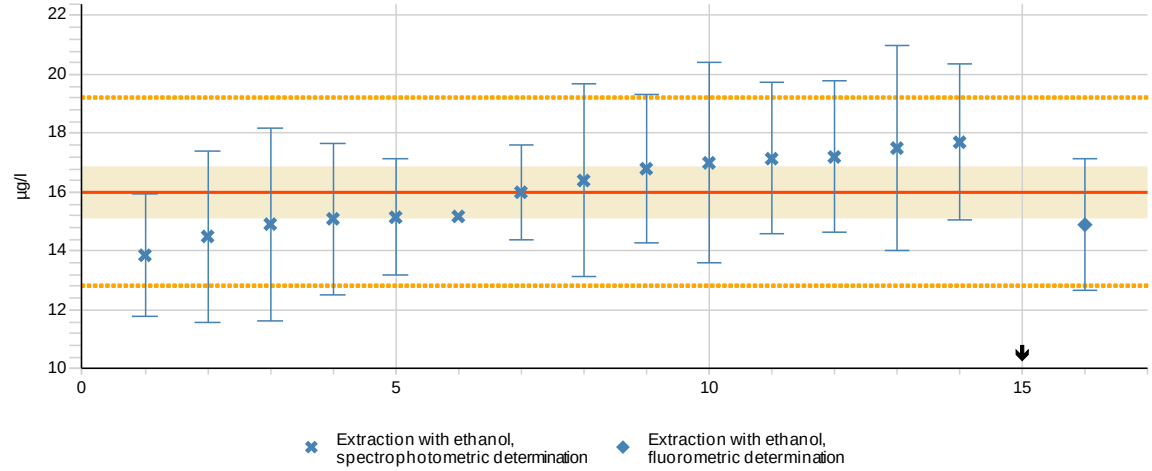
APPENDIX 12: Results grouped according to the methods

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

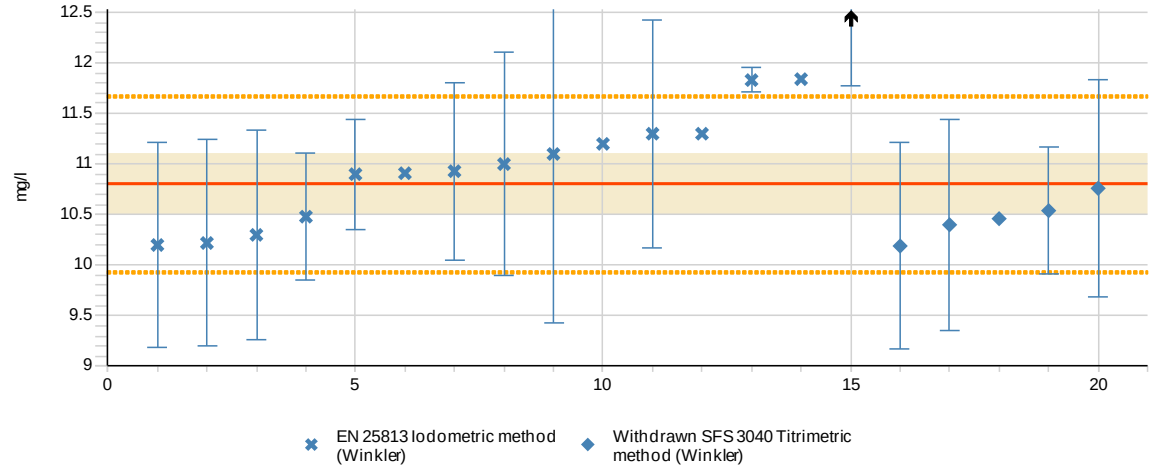




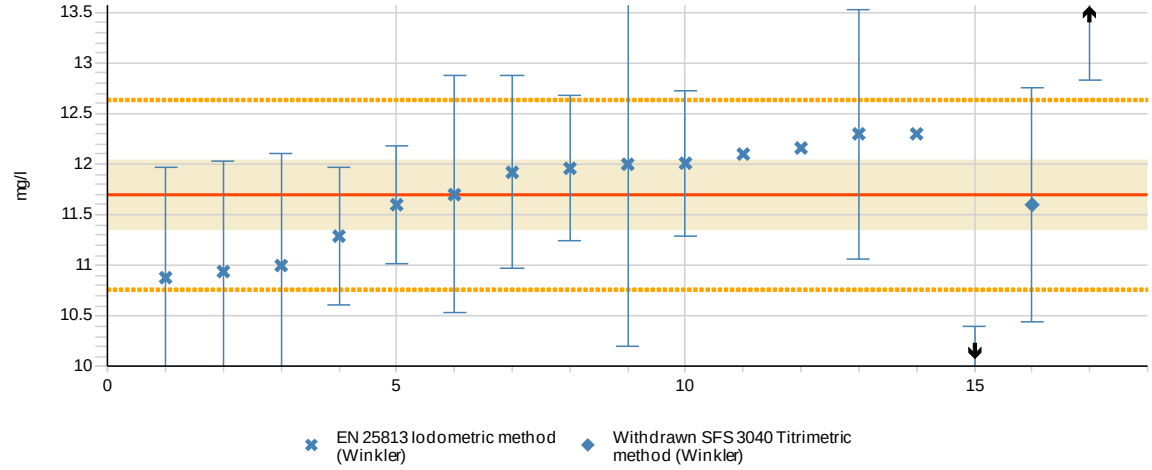
Measurand Chlorophyll a Sample N3K



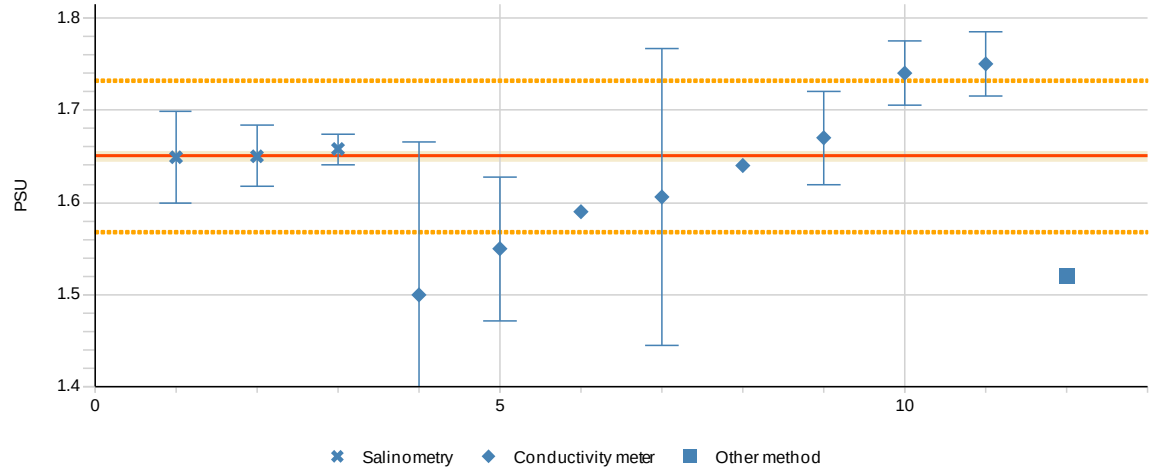
Measurand O_2 Sample B2O



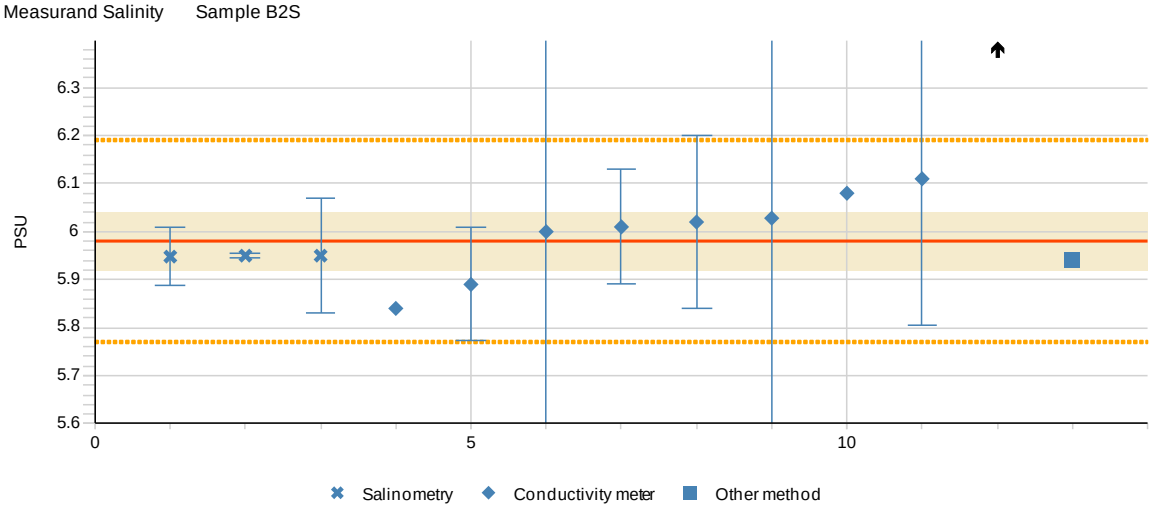
Measurand O_2 Sample N3O



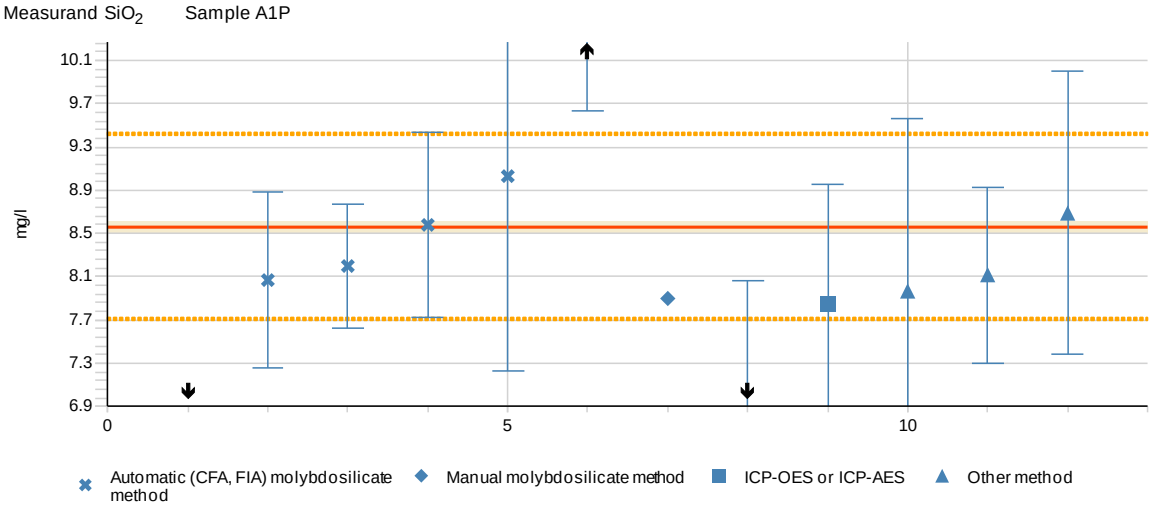
Measurand Salinity Sample A1S



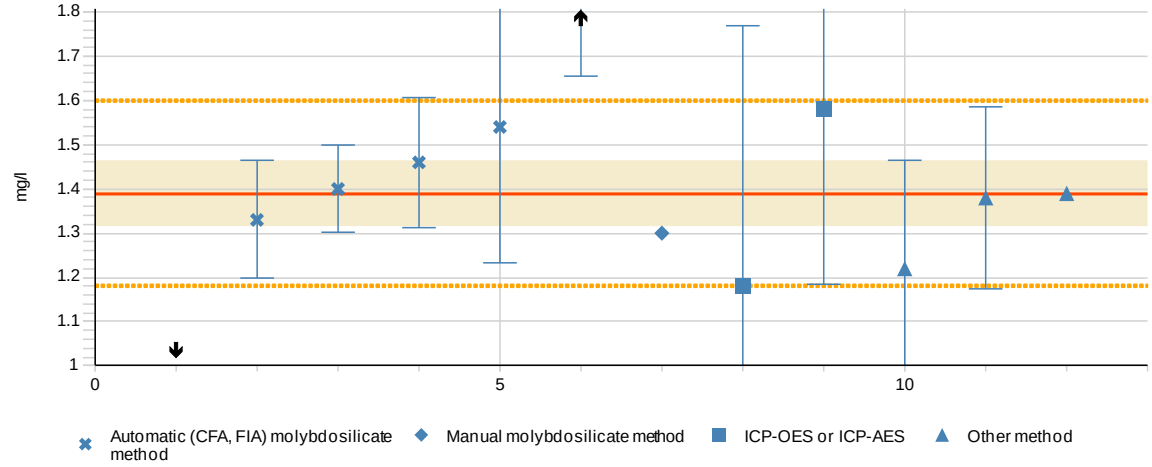
Measurand Salinity Sample B2S



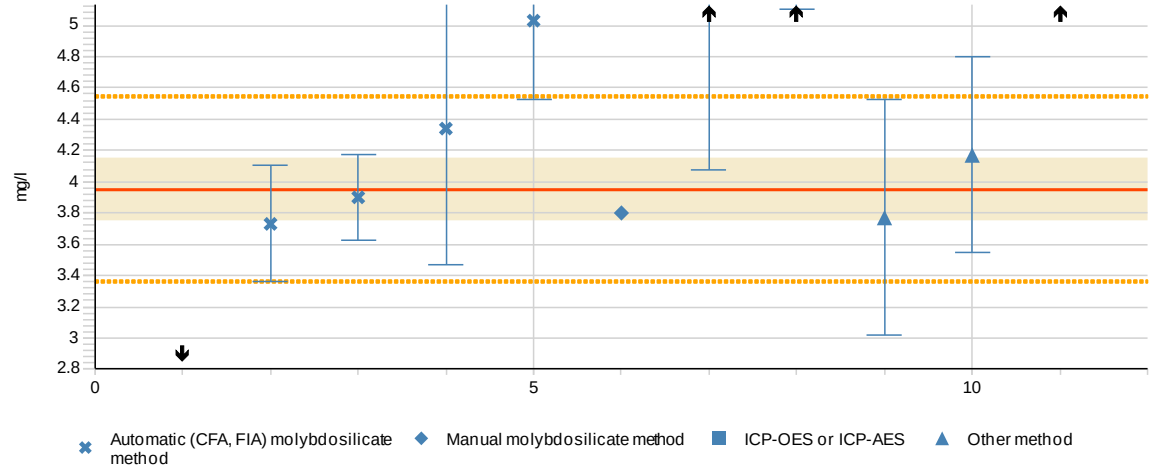
Measurand SiO_2 Sample A1P



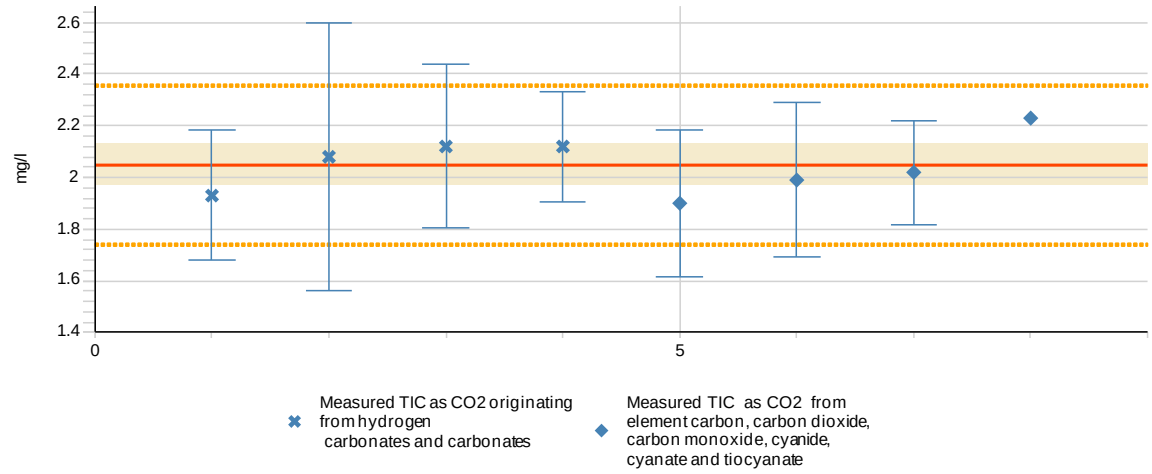
Measurand SiO_2 Sample B2P



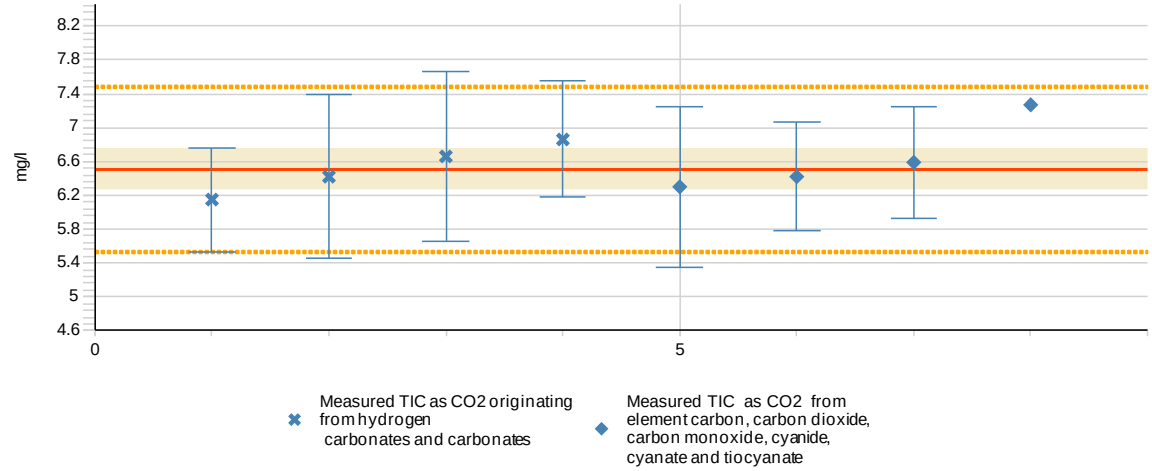
Measurand SiO_2 Sample N3P



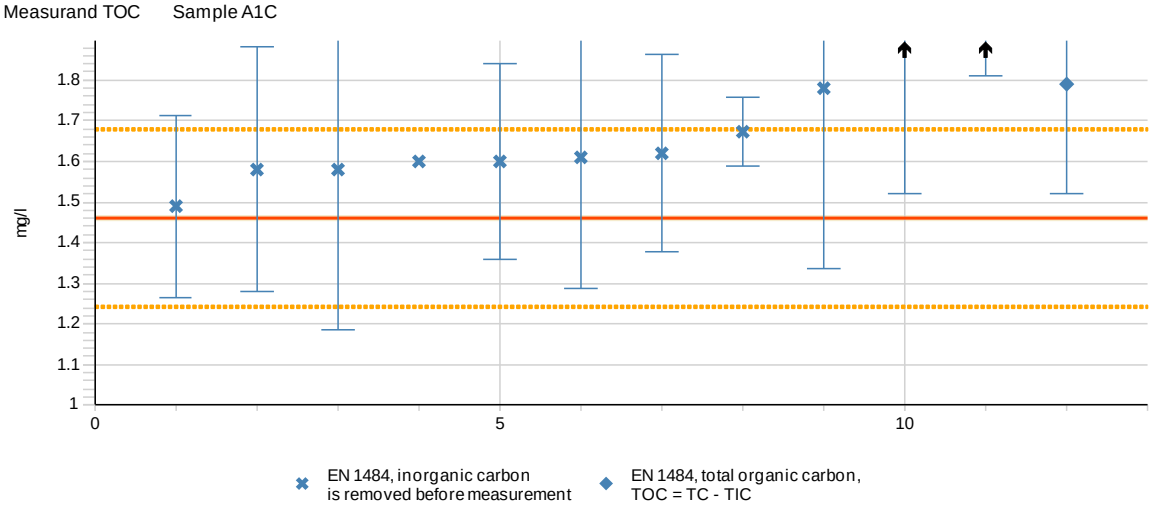
Measurand TIC Sample A1T



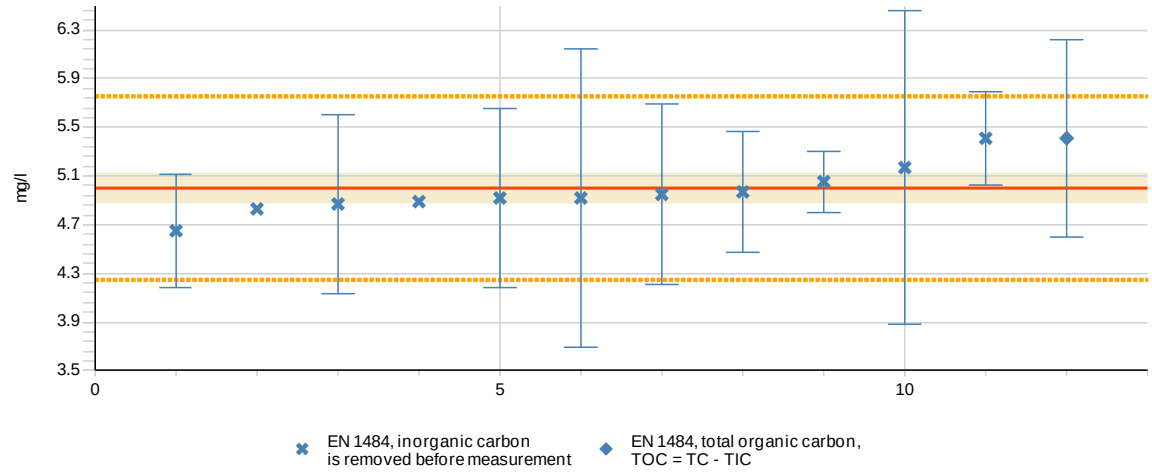
Measurand TIC Sample N3T

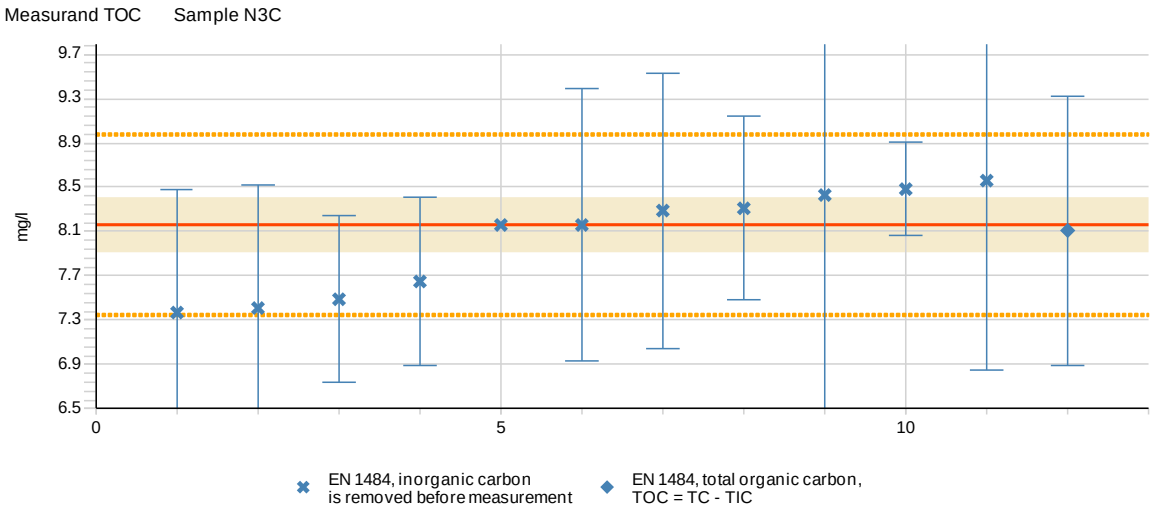


Measurand TOC Sample A1C



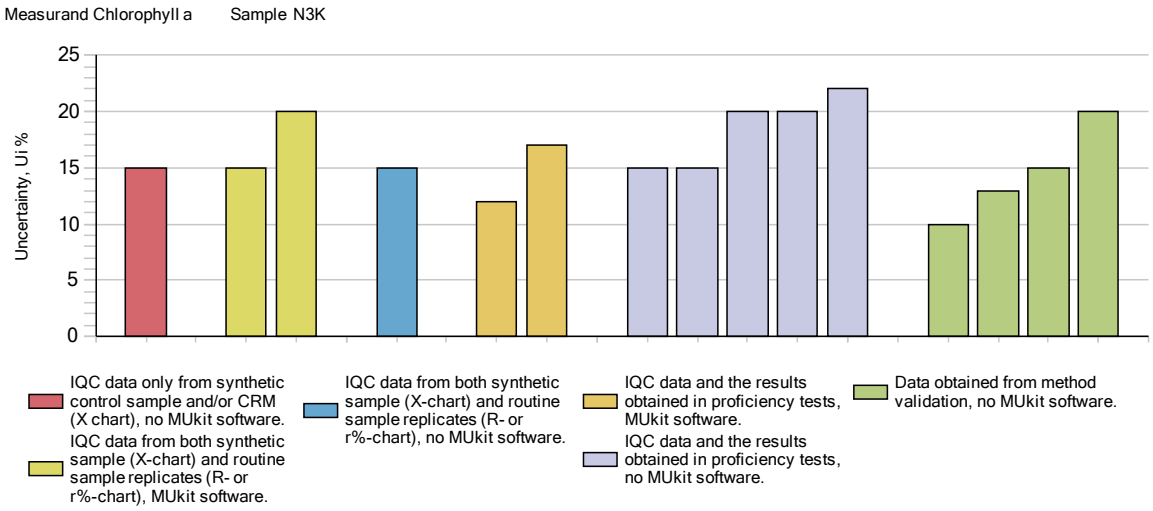
Measurand TOC Sample B2C

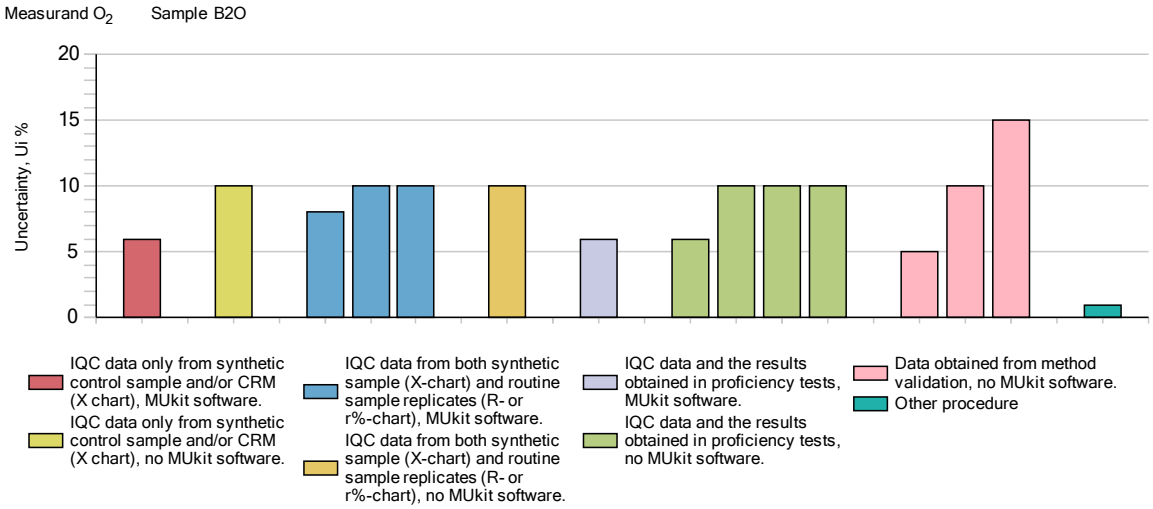



Measurand TOC
Sample N3C
mg/l
9.7
9.3
8.9
8.5
8.1
7.7
7.3
6.9
6.5
0
5
10
EN 1484, inorganic carbon is removed before measurement
EN 1484, total organic carbon, TOC = TC - TIC

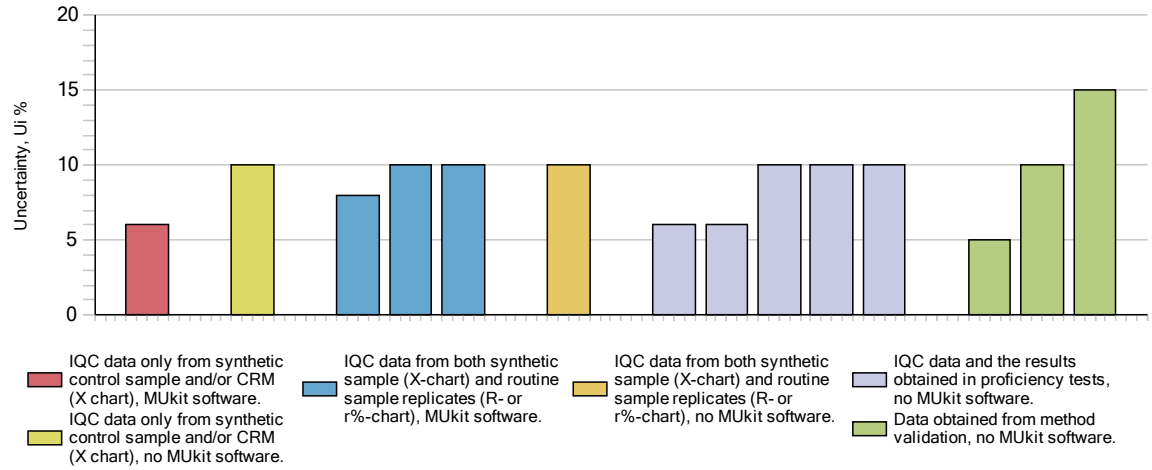
APPENDIX 13: Examples of measurement uncertainties reported by the participants

In figures, the presented expanded measurement uncertainties are grouped according to the method of 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 [6, 7].

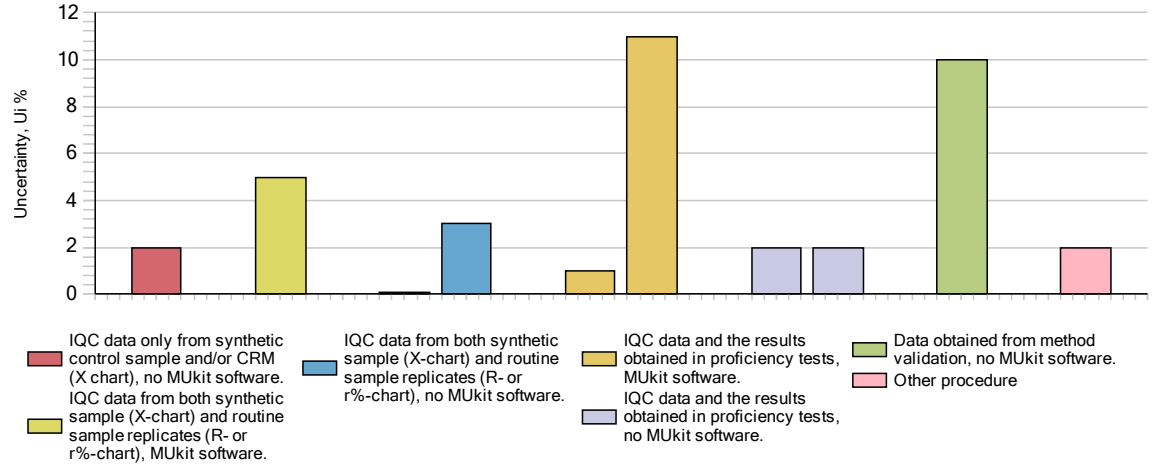




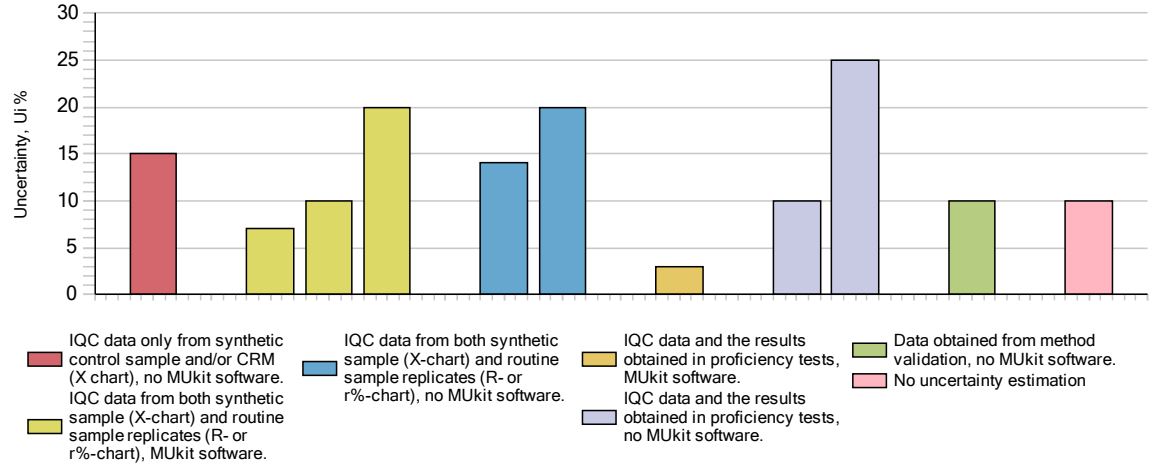
Measurand O_2 Sample N3O



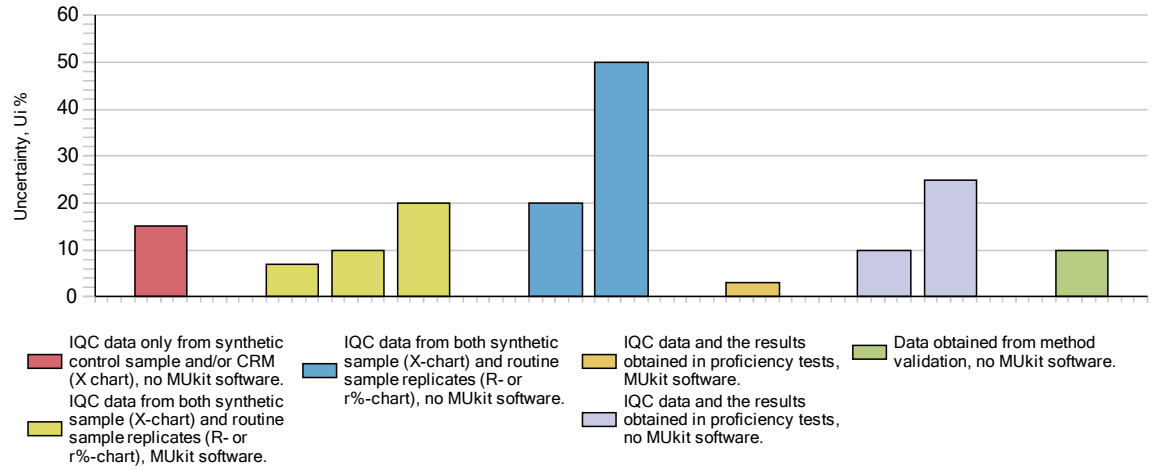
Measurand Salinity Sample B2S



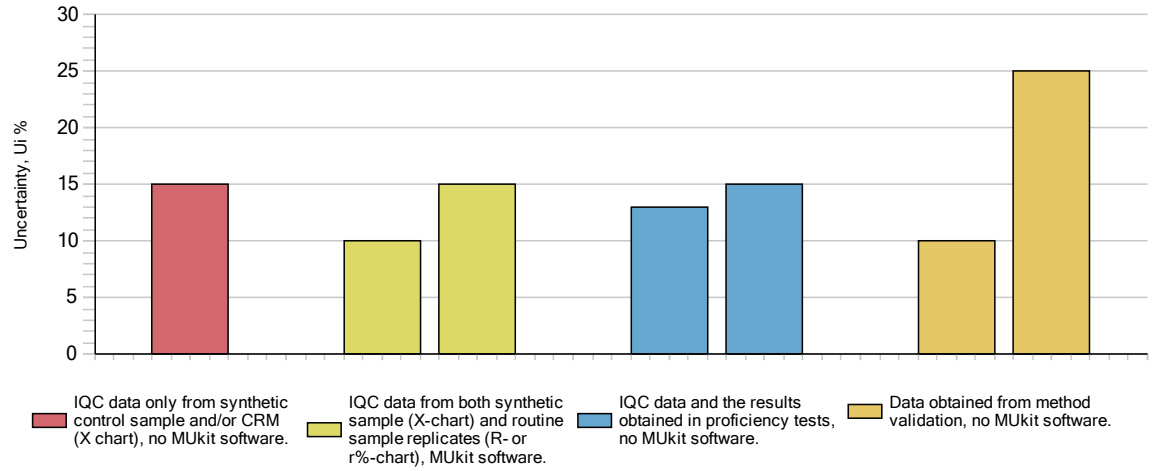
Measurand SiO_2 Sample A1P



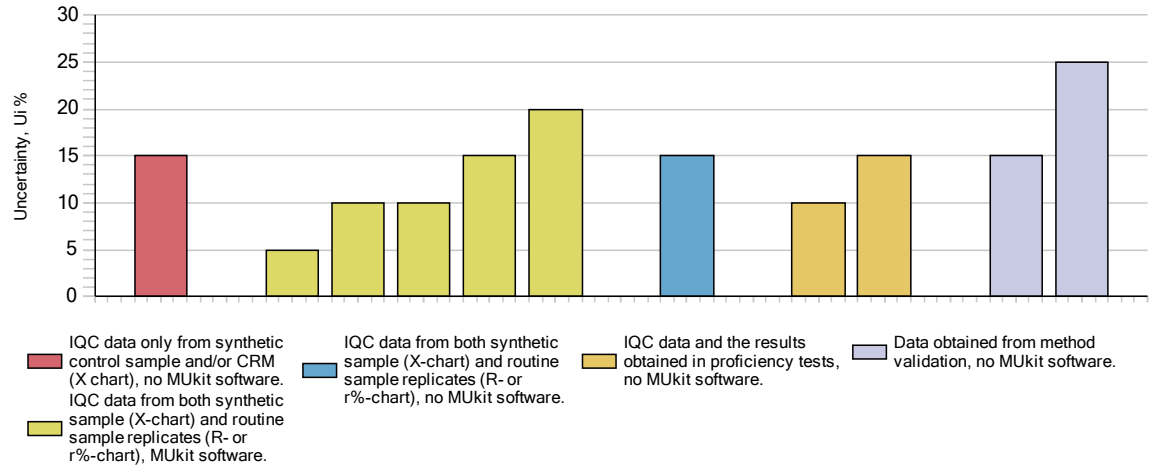
Measurand SiO_2 Sample B2P



Measurand TIC Sample A1T



Measurand TOC Sample N3C



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