REPORTS OF THE FINNISH ENVIRONMENT INSTITUTE 25 | 2018

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## Soil improver maturity test

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## ABSTRACT

**Interlaboratory comparison 15/2018**

Evira and Proftest SYKE carried out this interlaboratory comparison in May 2018 for assessing phytotoxicity, chemical composition and maturity of green waste and sewage sludge compost samples. In total 11 participants took part. Participants measured altogether 14 measurands, which are used for determining composition, phytotoxicity, stability and maturity of soil improvers, caused for instance by ammonia, ethylene oxide or short chain fatty acids. The mean of the results reported by the participants was chosen to be the assigned value for the measurands. The performance of the participants was evaluated by using z scores. In this interlaboratory comparison, 96 % of the results were satisfactory when deviation of 1 pH units and 25–80 % (for other measurands) from the assigned value was accepted. According to the results, many participants have good practices and manage these analyses well. Some participants still need more experience. More detailed guidance on procedures that may affect the results is needed.



Warm thanks to all the participants of this interlaboratory comparison!

**Keywords:** interlaboratory comparison, proficiency test, soil improver, phytotoxicity, carbon dioxide production, maturity assessment.



## TIIVISTELMÄ

**Laboratorioiden välinen vertailumittaus 15/2018**

Evira toteutti yhdessä Proftest SYKEn kanssa maanparannusaineen kypsyysastetta, fytotoksisuutta sekä kemiallista koostumusta koskevan vertailumittauksen toukokuussa 2018. Vertailumittaukseen osallistui yhteensä 11 osallistujaa. Osallistujat analysoivat viherjätekomposti- ja lietekompostinäytteistä yhteensä 14 testisuuretta, joita käytetään maanparannusaineiden koostumuksen, fytotoksisuuden, stabiilisuuden sekä kypsyyden arvioinnissa. Testisuureen vertailuarvona käytettiin osallistujien tulosten keskiarvoa. Osallistujien menestymistä arvioitiin z-arvon perusteella. Kaikkiaan 96 % tuloksista oli hyväksyttäviä, kun pH-määrityksessä sallittiin 1 pH-yksikön ja muissa määrityksissä 25–80 %:n poikkeama vertailuarvosta. Osallistujat hallitsivat kyseiset määritykset pääasiassa hyvin. Käytäntöjen harmonisointia tulisi jatkaa koulutusta tarjoamalla ja päivittämällä nykyisiä ohjeita sellaisilla yksityiskohdilla, jotka voivat vaikuttaa tuloksiin.



Kiitos kaikille vertailumittaukseen osallistujille!

**Avainsanat:** pätevyyskoe, maanparannusaine, fytotoksisuus, hiilidioksidin tuotto, kypsyysaste



## SAMMANDRAG

**Provningsjämförelse 15/2018**

Livsmedelssäkerhetsverket Evira genomförde tillsammans med Finlands miljö central (SYKE) i maj 2018 en provningsjämförelse om jordförbättringsmedels fytotoxiska verkan, kemiska sammasättning och mognadsgraden i två jordförbättringsmaterial. Totalt elva laboratorier deltog i provningjämförelsen. Som referensvärde av analytens koncentration användes medelvärdet av deltagarnas resultat. Resultaten värderades med hjälp av z-värden. Resultatet var tillfredsställande, om det avvek mindre än 1 pH enhet eller 25–80 % från referensvårdet. z-värden beräknades inte för kväveresultaten, $CO_2$ produktion, rotlängd eller Rottegrad-test (Tmax). I denna jämförelse var 96 % av alla resultaten tillfredsställande. På basen av resultaten har många av laboratorierna goda rutiner fast en del av laboratorierna behöver mera erfarenhet.



Ett varmt tack till alla deltagarna i testen!

**Nyckelord:** provningjämförelse, fytotoxicitet, koldioxid production, mognadsgraden av kompost, syreförbrukning

CONTENTS

# 1 Introduction

The Finnish Food Safety Authority (Evira) and Proftest SYKE carried out this interlaboratory comparison (ILC, SIM 15/2018) in May 2018 for determining the quality of two soil improver samples. The performed analyses were: germination and root growth of cress, $NO_3$-N/$NH_4$-N ratio, self-heating and $CO_2$-production. In addition, chemical parameters like dry weight, pH, electrical conductivity, bulk density and organic matter content of samples were measured. These tests are used for determining composition, phytotoxicity, stability and maturity of soil improvers which can be caused for instance by ammonia, ethylene oxide or short chain fatty acids.

The interlaboratory comparison was carried out in accordance with the international standard ISO/IEC 17043 [1], and applying standard 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). This interlaboratory comparison has not been carried out under the accreditation scope of the Proftest/SYKE.

# 2 Organizing the interlaboratory comparison

## 2.1 Responsibilities

| | |
|---|---|
| Organizing laboratory: | Finnish Food Safety Authority Evira<br>Mustialankatu 3, 00790 Helsinki, Finland<br>Contact persons: Liisa Maunuksela, responsible organizer in this ILC, liisa.maunuksela@evira.fi, mobile +358 400 256 097 and Aija Pelkonen, aija.pelkonen@evira.fi, mobile +358 40 593 9278 |
| Co-operation partner: | Katarina Björklöf, coordinator, Proftest SYKE, Finnish Environment Institute (SYKE), Laboratory Centre, katarina.bjorklof@environment.fi, mobile + 358 400 148 596.<br>proftest@environment.fi |

## 2.2 Participants

In this interlaboratory comparison, a total of 11 participants took part, from which eight were from Finland and three from abroad (Table 1). The organizer has code number ten in the result tables. The organizer and participant numbers 4, 6, 7, 11 and 12 were accredited for at least some of the parameters tested.

Table 1. Participants in the interlaboratory comparison SIM 15/2018.

| Country | Participant |
|---|---|
| Finland | Eurofins Viljavuuspalvelu, Mikkeli |
| | Finnish Food Safety Authority, Evira, Organizing laboratory |
| | Finnish Food Safety Authority, Evira |
| | Hortilab Ab Oy |
| | Labtium Oy, Jyväskylä |
| | MetropoliLab Oy |
| | Natural Resources Institute Finland (Luke) |
| | SYNLAB Analytics & Services Finland Oy |
| France | Aurea AgroSciences |
| Germany | LUFA Nord-West, Institut für Boden und Umwelt |
| | Weihenstephan-Triesdorf University of Applied Sciences |

## 2.3 Samples and delivery

This comparison included two soil improver samples: Green waste compost S1 and sewage sludge compost S2. Sample volume was 3 or 6 liters, depending if the laboratory performed the self-heating test. Samples were sieved and moistened to the approximate optimum moisture content by the organizing laboratory ([4] and the fist test). The samples were delivered on 15 May 2018 and participants received the samples by 18 May.

The samples were requested to be homogenized before measurements, testing done as soon as possible and results submitted by 11 June 2018. The preliminary results were delivered to the participants on 26 June 2018.

The following results were submitted according to the normal procedures by the participants:

| Measurand | Abbreviation | Reference |
|---|---|---|
| Average germination ratio (petri dish test using cress, EN 16086-2) | AGR | [5] |
| Bulk density (EN 13040) | Bulk density | [4] |
| $CO_2$-production/bottle (closed bottle test) | $CO_2$-prod/bottle | [6] |
| $CO_2$-production rate (closed bottle test) | $CO_2$-prod rate | [6] |
| Electrical conductivity (EN 13038) | Cond. 25 | [7] |
| Dry matter content (EN 13040) | Dry matter | [4] |
| $N\text{-}NH_4$ (EN 13652, annex B) | $N_{NH3}$ | [8] |
| $N\text{-}NO_3$ (EN 13652, annex B) | $N_{NO3}$ | [8] |
| $N\text{-}NO_3/N\text{-}NH_4$ –ratio (EN 13652, annex B) | $N(_{NO3}/_{NH4})$ | [6], [8] |
| Organic matter content (EN 13039) | Org matter | [9] |
| pH (EN 13037) | pH | [10] |
| Plant root index (petri dish test using cress, EN 16086-2) | RI | [5] |
| Plant root length (petri dish test using cress, EN 16086-2) | Root length | [5] |
| Self-heating test, Rottegrad test (EN 16087-2) | $T_{max}$ | [11] |

Table 2. Results of the homogeneity testing of SIM 15/2018.

| Measurand | Unit | Sample | n | Homogeneity test results | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | Mean | s | CV% | Max | Min | Difference |
| Bulk density (EN 13040) | g/l | S1 | 4 | 645 | 46 | 7 % | 678 | 576 | 102 |
| | | S2 | 4 | 624 | 10 | 2 % | 638 | 616 | 22 |
| $CO_2$-production/bottle (closed bottle test) | mg $CO_2$/g | S1 | 5 | 0.36 | 0.1 | 28 % | 0.4 | 0.2 | 0.2 |
| | | S2 | below detection limit | | | | | | |
| Dry matter content (EN 13040) | % | S1 | 6 | 45 | 0.2 | 0.4 % | 45 | 44.5 | 0.5 |
| | | S2 | 6 | 46 | 0.2 | 0.4 % | 46.1 | 45.7 | 0.4 |
| Organic matter content (EN 13039) | % (w/w) | S1 | 6 | 33 | 0.6 | 2 % | 33.4 | 32 | 1.4 |
| | | S2 | 6 | 44 | 0.6 | 1.4 % | 45 | 44 | 1 |
| Plant root length (EN 16086-2) | mm | S1 | 6 | 367 | 32 | 9 % | 401 | 399 | 2 |
| | | S2 | 6 | 244 | 18 | 7 % | 260 | 221 | 39 |

## 2.4 Homogeneity and stability studies

Samples S1 and S2 for homogeneity test were collected on 16.4.2018 from the same location and similar piles as the comparison test samples using the same sampling scheme on both

sampling occasions. Homogeneity testing was performed from sieved (10 mm) five parallel samples with two or three analytical parallels per sample. Homogeneity was tested using guidelines from IUPAC technical report [3].

The homogeneity of the samples was tested by analyzing bulk density, $CO_2$-production rate, dry matter weight, organic matter content and plant root length (Table 2). According to the homogeneity test results, all samples were considered homogenous for the standard deviation for this interlaboratory comparison used.

## 2.5 Feedback from the interlaboratory comparison

The feedback from the participants of the interlaboratory comparison is shown in Table 3 and feedback from the provider to the participants in Table 4. The comments from the participants dealt with their reporting errors of the samples. The provider does not correct the results after delivering the preliminary results. The comments from the provider are focused on detection limits, reporting of uncertainties and on reporting units. All the feedback is valuable and is exploited when improving the procedures for the future.

Table 3. Feedback from the participants.

| Participant | Comments on technical excecution | Action / Proftest |
|---|---|---|
| 3 | The Tmax results were possibly reported in the wrong order due to unclear labeling. | The results of this measurands were not evaluated due to low number of results. The results were removed from the statistical treatment. |
| 3, 6 | $NO_3$-N measurement: differences in calculation Wrong calculation for the N-$NO_3$/N-$NH_4$ –ratio. | The provider does not correct the results after delivering the preliminary results. In Finland ratio is calculated according to Itävaara et. al. 2006. Because the used formula for ratio calculation was not reported, provider was unable to make conclusion about reliability of the results (3.2.2). |
| 5 | The conductivity results were reported in wrong unit. The correct results are 30 mS/m and 310 mS/m. | The provider does not correct the results after delivering the preliminary results. The results were treated as outliers and not included in the statistical treatment. All results would have been satisfactory if they had been reported in the correct unit. The participant can re-calculate the z scores according to the Guide for participants [12]. |
| 11 | Sample S2 was not diluted accordingly to standard procedures in the petri dish test. | The result was treated as an outlier and was not included in the statistics. |
| 3, 6, 10, 12 | The root length result was reported in the wrong unit (cm instead of mm). | The results were asked to be reported in mm. In the standard EN 16086-2, it is not clearly stated in which unit (cm or mm) the root length should be measured. |

Table 4. Feedback to the participants.

| Participant | Comment |
|---|---|
| 1, 6, 10, 12 | Measurement uncertainty should be reported, if the method is accredited. |
| 11 | Measurement uncertainty should not be expressed with decimals. |
| 5, 6, 10, 11, 12 | Not acceptable to report the results in another unit than requested. More care should be taken when reporting results. |

## 2.6 Processing the data

### 2.6.1 Pretesting the data

The results which differed from the data more than $s_{rob} \times 5$ or 50 % from the robust mean and erroneously reported results (e.g. wrong unit) were rejected before the statistical results handling. 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. If the result has been reported as below detection limit, it has not been included in the statistical calculations. More information about the statistical handling of the data is available from the Guide for participant [12].

### 2.6.2 Assigned values

The means of the participants' results were used as the assigned values for all the measurements (Table 4, Appendix 2). The mean is not a metrological traceable assigned value. Because it was not possible to have metrological traceable assigned values, the means of the results of the participants were the best available values to be used as the assigned values.

The uncertainty of the assigned value was calculated using the standard deviation [2]. The uncertainties of the assigned values were between 0.8 and 31 % (Appendix 1).

The reliability of assigned values was tested according to the criterion $u_{pt} / s_{pt} \leq 0.3$, where $u_{pt}$ is the standard uncertainty of the assigned value (the expanded uncertainty of the assigned value ($U_{pt}$) divided by 2) and $s_{pt}$ is the standard deviation for proficiency assessment [3]. This criterion was fulfilled in most cases and the assigned values were considered reliable (Appendix 1). In the following two cases, the criteria for the reliability of the assigned value were not met and, therefore, the evaluations of the performances are reduced in this proficiency test:

| Sample | Measurement |
|---|---|
| S1 | Conductivity |
| S2 | AGR |

**The assigned value for conductivity measurement in sample S1 results has been changed** from 26.1 mS/m to 26.4 mS/m after reporting the preliminary results. **This change did not affect the performance assessment of the participants** (Table 5, Appendix 6).

### 2.6.3 Standard deviation for proficiency assessment and z score

The standard deviation for proficiency assessment for bulk density, organic matter dry weight, pH and conductivity was set according to The Finnish Decree of the Ministry of Agriculture and Forestry on Fertilizer Products 24/11, attachment III [13]. Other standard deviations for proficiency assessment were estimated on the basis of the measurand concentration, the results of homogeneity and the uncertainty of the assigned value. The standard deviation for the proficiency assessment ($2 \times s_{pt}$ at the 95 % confidence level) was set to 25–80 % and for pH 1 pH-unit.

The reliability of the standard deviation and the corresponding z score was estimated by comparing the deviation for proficiency assessment ($s_{pt}$) with the standard deviation of the reported results (s) [3]. The criterion $s / s_{pt} < 1.2$ was fulfilled. After reporting of the preliminary results no changes have been done for the standard deviations for proficiency assessment.

In the following cases evaluation of performances were not done:

| Measurand | Reason for no evaluation |
|---|---|
| N-$NO_3$ (EN 13652, annex B) | Results in two clusters. More info needed for explanation of methods used. |
| N-$NH_4$ (EN 13652, annex B) | Large s (20-130%) of the participant results. |
| N-$NO_3$/N-$NH_4$ –ratio | Results depend on above mentioned facts. |
| $CO_2$-production/bottle (closed bottle test) | Large s (20-90%) of the participant results. |
| $CO_2$-production rate (closed bottle test) | Large s (70-100%) of the participant results due to variability of covariants ($CO_2$-production/bottle, dry matter and organic matter). |
| Plant root length (EN 16086-2) | Results reported in wrong unit in most cases (cm instead of mm). |
| Self-heating test, Rottegrad test (EN 16087-2) | Few data (n=5). |

# 3 Results

The summary of the results of the interlaboratory comparison is shown in Table 5. The terms used in the results tables are presented in Appendix 2. The results and the performance of each participant are presented in Appendix 3 and participants results graphically with their expanded uncertainties (k=2) in Appendix 4. The summaries of the z scores are shown in Appendix 5. In Appendix 6, the z scores are shown in ascending order. The results grouped according to methods are reported in Appendix 7, and approaches used for estimating of measurement uncertainty are presented in Appendix 8.

The evaluation of the participants was based on the z scores, which were calculated using the assigned values and the standard deviations for proficiency assessment (Appendix 2). The z scores were interpreted as follows:

| Criteria | Performance |
|---|---|
| $\|z\| \leq 2$ | Satisfactory |
| $2 < \|z\| < 3$ | Questionable |
| $\|z\| \geq 3$ | Unsatisfactory |

In total, 95 % of the results were satisfactory when deviations of 25–80 % and 1 pH-unit from the assigned values were accepted. Altogether 50 % of the participants used accredited analytical methods at least for a part of the measurands and 100 % of their results were satisfactory.

Table 5. The summary of the results in the interlaboratory comparison SIM 15/2018.

| Measurand | Sample | Unit | Assigned value | Mean | Rob. mean | Median | $s_{rob}$ | $s_{rob}$ % | 2 x $s_{pt}$ % | n (all) | Acc z % |
|---|---|---|---|---|---|---|---|---|---|---|---|
| AGR | S1 | % | 99.3 | 99.3 | 95.2 | 100.0 | 8.2 | 8.6 | 50 | 7 | 86 |
| | S2 | % | 74.6 | 74.6 | | 85.0 | | | 50 | 7 | 86 |
| Bulk density | S1 | g/l | 675 | 675 | 680 | 675 | 29 | 4.2 | 25 | 11 | 100 |
| | S2 | g/l | 627 | 627 | 644 | 628 | 35 | 5.5 | 25 | 11 | 100 |
| $CO_2$ prod/bottle | S1 | % | 0.37 | 0.37 | | 0.36 | | | - | 5 | - |
| | S2 | % | 0.15 | 0.15 | | 0.20 | | | - | 5 | - |
| $CO_2$ prod rate | S1 | mg CO2-C/g VS/d | 1.0 | 1.0 | | 0.8 | | | - | 7 | - |
| | S2 | mg CO2-C/g VS/d | 0.3 | 0.3 | | 0.3 | | | - | 7 | - |
| Cond 25 | S1 | mS/m | 26.4 | 26.4 | 28.3 | 28.0 | 4.9 | 17.2 | 50 | 11 | 91 |
| | S2 | mS/m | 270 | 270 | 268 | 272 | 25 | 9.4 | 50 | 11 | 82 |
| Dry matter | S1 | % | 43.9 | 43.9 | 43.8 | 43.6 | 1.1 | 2.4 | 25 | 11 | 100 |
| | S2 | % | 42.8 | 42.8 | 43.3 | 43.3 | 1.0 | 2.2 | 25 | 11 | 100 |
| $N_{NH4}$ | S1 | mg/l | 1.5 | 1.5 | | 0.5 | | | - | 10 | - |
| | S2 | mg/l | 20.5 | 20.5 | 20.5 | 20.8 | 5.4 | 26.4 | - | 10 | - |
| $N_{NO3}$ | S1 | mg/l | | 66.6 | 50.0 | 67.0 | 31.1 | 62.3 | - | 11 | - |
| | S2 | mg/l | | 440 | 440 | 587 | 327 | 74 | - | 11 | - |
| $N_{(NO3/NH4)}$ | S1 | | | 39.7 | | 49.0 | | | - | 6 | - |
| | S2 | | | 19.9 | | 25.6 | | | - | 6 | - |
| Org matter | S1 | % (w/w) | 32.0 | 32.0 | 32.2 | 32.4 | 3.9 | 12.1 | 25 | 11 | 100 |
| | S2 | % (w/w) | 43.7 | 43.7 | 44.1 | 44.3 | 1.9 | 4.2 | 25 | 11 | 100 |
| pH | S1 | | 7.8 | 7.83 | 7.83 | 7.82 | 0.20 | 2.6 | 6.5 | 11 | 100 |
| | S2 | | 5.9 | 5.93 | 5.95 | 5.92 | 0.18 | 3.0 | 8.5 | 11 | 91 |
| RI | S1 | % | 101 | 101 | 99 | 100 | 33 | 33.0 | 80 | 7 | 100 |
| | S2 | % | 70.4 | 70.5 | | 73.4 | | | 80 | 7 | 86 |
| Rooth length | S1 | mm | | 32.9 | | 35.0 | | | - | 7 | - |
| | S2 | mm | | 16.3 | 16.3 | 2.6 | 21.7 | 133 | - | 7 | - |
| $T_{max}$ | S1 | C | | 20.7 | | 20.0 | | | - | 5 | - |
| | S2 | C | | 21.2 | | 21.0 | | | - | 5 | - |

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

## 3.1 Important observations of the analytical methods

All the participants received the samples in time so that participants were able to start sample analysis within a week from sample arrival. In addition, samples stayed cool during sample delivery and therefore we can assume that sample maturation didn't occur prior to testing.
Heterogeneity and consistency is challenging for this type of samples; especially sample S2 had some smeary properties and small lumps which might have an effect on the results. However, homogeneity studies showed that sample S2 was homogenous for the standard deviation used in this study.

### 3.1.1 Dry matter and organic matter content

All the participants performed the analysis using the gravimetric methods based on EN standard 13040. Temperature ranged from 60 °C to 105 °C for dry matter analysis and from 450 °C to 550 °C for organic matter analysis.

### 3.1.2 $NO_3$-N, $NH_4$-N and $NO_3$-N /$NH_4$-N-ratio

In this interlaboratory comparison there were big differences between the $NO_3$-N participant's results. The results could be grouped in two different groups (Appendix 7). Reasons for the differences in $NO_3$-N results can be explained at least partly by differences in methodology/technique used. However, the main reason for the difference seems to be that some of the participants reported the results as nitrate and not nitrate-N ($NO_3$-N). In order to get the nitrate-N result, the nitrate result should be multiplied by factor 0.226 (N/$NO_3$ ratio). Probably the high nitrate results should all be corrected this way before calculating the $NO_3$-N/$NH_4$-N.
Reasons for the deviation in $NH_4$-N results may be differences in the equipment used for the measurement (listed in [8]) and probably also time of analysis. Since ammonium evaporates easily, concentration of ammonium will be higher when sample is analyzed immediately after sample arrival. Also the detection limit for $NH_4$ measurement differed in the laboratories from <1 mg/l (participant 1) to <100 mg/l (participant 13).

In general, soil improver samples are considered stable when the $NO_3$-N/$NH_4$-N-ratio is over 1. With ratios between 0.5–1.0 sample is still maturing [6]. However, it is not uncommon to get considerate differences in $NO_3$-$NH_4$- ratio results. Especially $NH_4$-N results usually differ a lot when measured from this type of matrices. In addition, there were errors in the calculation of the ratio (e.g. instead of ratio, the sum of $NO_3$-N and $NH_4$ was calculated). For calculation of the $NO_3$-$NH_4$-ratio, this formula should be used:

(N-$NO_3$) mg/l x M ($NH_4$) / (N-$NH_4$) mg/l x M ($NO_3$) → (N-$NO_3$) mg/l x 18 /(N-$NH_4$) mg/l x 62 [6].

### 3.1.3 $CO_2$- evolution rate

Analysis of sample $CO_2$-production was performed mainly using the same principle method (Appendix 7, VTT closed bottle test, [6]) but with different equipment. Also incubation time and temperature varied (Table 6). In addition to sample heterogeneity, factors such as equipment used (flask volume, septum type and machinery for measurement) has an effect on the result. Two participants (8 and 13) reported clearly higher $CO_2$-evaluation rates for sample S1 than other participants (even though the $CO_2$-production of this sample was in the same range with others). Reason for this might be that different formulas were used for result calculation. All participants reported slightly higher $CO_2$-production and $CO_2$-evolution rates for sample S1 than S2.

For this type of soil improver samples, $CO_2$ –evolution of approximately 1.0 mg $CO_2$-C/g VS/d would be expected [14]. In this interlaboratory comparison, the mean $CO_2$ –evolution was 1.0 mg $CO_2$-C/g VS/d for sample S1 and 0.3 mg $CO_2$-C/g VS/d for sample S2 (Table 5). In general, soil improver samples are considered stable when $CO_2$-evolution rate is < 3 mg $CO_2$-C/g VS/d. All participants reported slightly higher $CO_2$-production and $CO_2$-evolution rates for sample S1 than S2. This is in accordance with the rate stated in the product data sheet provided by the manufacturer for these samples, although measurements in this ILC for both samples were generally lower than in the product data sheet. Moisture content and temperature also

Table 6. Summary of $CO_2$ -production analysis by the participants.

| Participant no | Method | Equipment | Flask volume (ml) | Incubation time (h) and temperature (°C) |
|---|---|---|---|---|
| 4 | | RAE tube | 500 | 24 / 37 |
| 8 | Closed bottle VTT 2351 | PBI Dansensor CheckMate3 | 610 | 24 / 27 |
| 10 | Closed bottle VTT 2351 | CheckMate 9900 | 613 | 48 / 37 |
| 11 | Closed bottle, NaOH trap | | | 72 / 28 |
| 12 | Closed bottle VTT 2351 | CheckMate 9900 | 613 | 48 / 37 |
| 13 | Gas chromatography | Dräger tubes CH25101 | 612 | 24 / 37 |

have a major effect on biological activity of materials and therefore method optimization is critical. We recommend that harmonization of this test protocol should be continued.

### 3.1.4 Plant response

All participants that reported background data, used the standard method EN 16086-2, Petri dish using cress [5] (Appendix 7) and incubated samples for 72 h at room temperature (Table 7). However, there was variation in the control material used (Table 7), and this probably had some impact also on the data variation.

In the plant response/petri dish method, average germination rate (AGR) results between the participants were comparable, except for one participant for sample S1 (participant 8) and three participants for S2 (participants 6, 8 and 11). Low germination result (13 %) from participant 11 results from using undiluted sample for the test. Electric conductivity of sample S2 was ca. 270 mS/m, so this explains the germination inhibition.

Root length measurement (RLP) results could be grouped into two groups (with three and four participants in each group, Appendix 7). The main reason for the very low RLP measurements for four participants (6, 10, 11 and 12) was that root length measurement was reported in cm instead of mm. Therefore the results from all participants varied from 3.5 mm to 37 mm (S1) and 0 mm to 45 mm (S2). In addition, participant 11 didn't dilute sample S2 so they couldn't measure any root growth and also root index (RI) was 0. Also for the other laboratories, dilution ratio of sample S2 varied some (in most cases it was ca. 20 %) and this definitely accounts for the larger variation of RLP results for sample S2. Some differences in root measurement may have been caused also by uncertainty in the measurement of seedling root (Figure 1). Especially with short roots or mainly only shoot growth it may not always be clear what to measure.

Table 7. Summary of plant response measurements reported by the participants.

| Participant No | Control material | Incubation temperature °C) and time (h) |
|---|---|---|
| 3 | Sphagnum peat | |
| 4 | Limed growing media (watered 0,1 % nutrient solution) | 21 / 72 |
| 8 | Filter paper | Room temperature (ca. 20) / 72 h |
| 10 | Growing media | 22.5 / 72 |
| 12 | Growing media | 22.5 / 72 h |

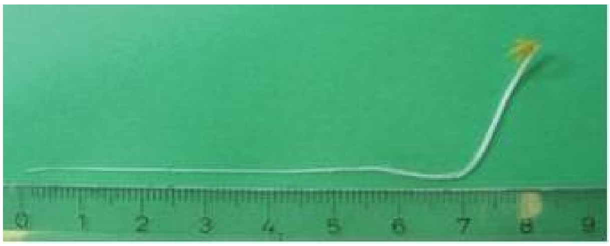

Figure 1. Measurement of root length of germinated cress seed.

According to the product data sheet provided by the manufacturer, the RI of S1 should be ca. 79 % and S2 ca. 91 % (when diluted so that EC< 80 mS/m). Average RI results in this interlaboratory comparison test (when the data with wrong unit was removed) were 73 % for S1 and 77 % for S2, respectively. If the root length measurement results would have been reported in the correct unit, the results from this interlaboratory comparison test would have been more comparable than the results from the previous interlaboratory comparison (Table 8 and [15]).

It seems that the instructions described in standard procedures are not sufficiently detailed (e.g. regarding dilution and root measurement) and therefore allow for subjective opinions. Further harmonization is recommended e.g. by training courses.

Table 8. Root length measurements after measurement unit correction (mm).

| Participant No | RLP Sample S1 | RLP Sample S2 |
|---|---|---|
| 3 | 35 | 45 |
| 4 | 27 | 26 |
| 6 | 57 | 60 |
| 8 | 37 | 37 |
| 10 | 36 | 23 |
| 11 | 53 | 0 |
| 12 | 35 | 26 |

### 3.1.5 Self-heating test

Only five participants performed the self-heating test (Rottegrad, [11], Appendix 7). In addition, from these participants, one participant (3) possibly had the results in wrong order due to unclear labeling of the sample vessels. In general, there were no clear differences in the results between the laboratories (except for participant 3) or between the two samples. According to [6] and the standard [11], both soil improver samples were classified as mature.

## 3.2 Uncertainties of the results

Participants 3, 4, 5, 7, 8, 11 and 13 reported the expanded uncertainties (*k*=2) of the reported results at least for some of their results (Appendix 8). Reporting of the measurement uncertainties is required by accredited laboratories. In this interlaboratory comparison, participants 1, 6, 10 and 12 reported results as accredited without reporting the measurement uncertainties. The range of the reported uncertainties was generally on a good level (Table 9). One participant (11) reported the expanded uncertainties with the precision of one decimal. Measurement uncertainties always are estimations. The values of the expanded uncertainties ($U_i$) should be related to the accuracy of the reported results. Most commonly $U_i$ is expressed as whole numbers without decimals.

Several approaches were used for estimating the measurement uncertainty (Appendix 8). The most used approach was based on method validation data [16]. One participant (4) used MUkit measurement uncertainty software for the estimation of the uncertainties (Appendix 8) [17]. The free software is available in the webpage: www.syke.fi/envical/en. The used approach for estimating measurement uncertainty did not make definite impact on the uncertainty estimates.

It was interesting to notice that the uncertainties for calculated results like RI (root index) and $CO_2$-production, which depend on other measured independent results, were not higher than for the single independent results.

Table 9. The range of the expanded measurement uncertainties ($k$=2, $U_i$%) reported by the participants.

| Measurand | S1 ($U_i$%) | S2 ($U_i$%) |
|---|---|---|
| AGR | 20 | 20 |
| Bulk density | 5-10 | 5-10 |
| $CO_2$-prod/bottle | 30 | 30 |
| $CO_2$-prod rate | 30 | 30 |
| Cond. 25 | 1-10 | 1-10 |
| Dry matter | 3-12 | 3-12 |
| $N_{NH3}$ | 11-20 | 5-10 |
| $N_{NO3}$ | 5-20 | 20 |
| $N(_{NO3}/_{NH4})$ | 20 | 20 |
| Org matter | 5-20 | 5-20 |
| pH | 2-5 | 2-5 |
| RI | 20 | 20 |
| Root length | 20 | 20 |
| $T_{max}$ | - | - |

# 4 Evaluation of the results

In the previous similar interlaboratory comparison on soil improver maturity in 2012, the performance was satisfactory for 91 % of the evaluated results when deviation 4–80 % from the assigned value was accepted [15]. However in the previous test, mainly biological analysis were performed and therefore high result deviation could be expected in that comparison. In total, in this interlaboratory comparison, the results of seven of 11 participants were all satisfactory (Appendix 5). This indicates that many participants have good practices and manage these analyses well but some participants still need more experience.

# 5 Conclusions on maturity testing

Compost quality cannot be determined by using a single test; several tests have to be used in order to analyze the degradation phase of the compost, e.g. the stability level. In addition, the phytotoxicity of the compost also has to be analyzed [6]. In this interlaboratory comparison, participants were able to perform four different analysis for determining sample quality/maturity (Table 10). However, in addition to the organizing laboratory, only participant 11 performed all four tests and/or calculated the results. Four participating laboratories performed three of the maturity tests. Several laboratories didn't report the $NO_3$-N/$NH_4$-N ratio, even though they measured sample nitrate-N and ammonium-N concentrations.

Since these tests are used for soil improver maturity and stability assessment, a conclusion of sample maturity according to laboratory results is depicted in Table 10. Criteria for soil improver maturity in Finnish legislation are: $CO_2$-evolution, <3 mg $CO_2$-C/gVS/d and root length index, > 80% [13]. In addition, soil improver maturity may be assessed by determining $NO_3$-N/$NH_4$-N ratio (> 1).These criteria are also valid if soil improver is used as raw material in growing media products.

In contrast to results from our previous interlaboratory comparison [15], stability and root growth test results showed a clear relationship for sample S1. High electrical conductivity and lack of sample dilution and/or errors in result calculation resulted in lower RI results for S2. However, as stated in our previous report [15], the Finnish legislation (root index, RI > 80 %) is too strict due to changes in the standard procedure (incubation time) which causes bigger differences in relation to the control. If criteria > 70 % would be used and errors in dilution and calculation removed, only result from participant 4 would have been just under this criteria (69 %) for sample S2.

According to these criteria, both samples were considered mature and stable by all the labs (n=6) that performed at least three of these maturity tests.

We thank all participants for taking part in this interlaboratory comparison test and are happy to receive feedback and requests concerning the next round.

Table 10. Maturity assessment of analyzed samples based on mean values of participants' (n=6) results.

| Sample | $CO_2$-evolution (<3 mg $CO_2$-C/gVS/d)* | RI (> 80%)* | Self-heating (20-40°C)** | $NO_3$-N/$NH_4$-N (>1)** |
|---|---|---|---|---|
| S1 | YES | YES (71%) | YES | YES (83%) |
| S2 | YES | YES (29%) | YES | YES |

*according to Finnish Act on Fertilizer Products [19]
**according [5]

# 6 Summary

The Finnish Food Safety Authority (Evira) and Proftest SYKE carried out this interlaboratory comparison test (SIM 15/2018) in May 2018 for determining the quality of two soil improver samples: Green waste compost S1 and sewage sludge compost S2. In total 11 laboratories participated, from which eight were from Finland. The performed analyses were: Germination and root growth of cress, $NO_3$-N/$NH_4$ ratio, self-heating and $CO_2$-production. In addition, chemical parameters like dry weight, pH, electrical conductivity, bulk density and organic matter content of samples were measured. These tests are used for determining composition, phytotoxicity, stability and maturity of soil improvers.

The means of the reported results by the participants were used as the assigned values for measurements. The evaluation of performance was based on the z scores which were calculated using the standard deviation for proficiency assessment. z scores were not calculated for nitrogen measurements, $CO_2$-production, root length index and self-heating test.
According to the results many participants have good practices and manage these analyses well. Other participants still need more experience. In total, 96 % of the results were satisfactory when the deviations of 25–80 % and 1 pH-unit from the assigned values were accepted.
Results for grouping of the nitrogen results is in addition to methodological and technical differences due partly to errors in the reporting unit. Similar observations were made for plant root length measurements (RLP). Several different formulas for calculating nitrogen ratios were used. In addition, it seems that the instructions described in the standard procedures are not sufficiently detailed. Further harmonization is recommended e.g. by training courses and updating existing method description to harmonize procedures that affect the results.

# 7 Summary in Finnish

Evira toteutti yhdessä Proftest SYKEn kanssa maanparannusaineiden kypsyysastetta, fytotoksisuutta sekä kemiallista koostumusta koskevan vertailukokeen toukokuussa 2018. Lisäksi vertailukokeessa mitattiin kemiallisia testisuureita, kuten kuivapainoa, pH, sähkönjohtavuutta sekä näytteiden orgaanisen aineen pitoisuutta. Vertailumittaukseen osallistui yhteensä 11 laboratoriota, joista kahdeksan oli Suomesta. Laboratoriot analysoivat viherjätekomposti- ja lietekompostinäytteistä yhteensä 14 testisuuretta, joita käytetään maanparannusaineiden koostumuksen ja laadun. Mittaussuureen vertailuarvona käytettiin osallistujien ilmoittamien tulosten keskiarvoa. Laboratorioiden pätevyyden arviointi tehtiin z-arvon avulla. Tavoitehajonta määritettiin vertailukokeen hajonnan perusteella. z-arvoja ei laskettu typpituloksille, $CO_2$-tuotolle, juuren pituusindeksille eikä Rottegrad-testille.

Tulosten perusteella kierrokseen osallistujat hallitsevat kyseiset määritykset pääasiassa hyvin, vaikka jotkut laboratoriot tarvitsevat enemmän kokemusta tietyissä analyyseissä. Kaikkiaan 96 % tuloksista oli hyväksyttäviä, kun tavoitehajonta oli 25 - 80 % tai 1 pH-yksikköä tavoitearvosta.

Typpitulosten ryhmittymien kahdeksi eri ryhmäksi johtui todennäköisesti menetelmällisten ja teknisten erojen lisäksi tulosten ilmoittamisesta väärässä yksikössä. Vastaavia havaintoja tehtiin juuren pituustuloksissa. Tulosten perusteella todettiin, että on tarvetta tarkempaan ohjeistukseen tuloksiin vaikuttavien menettelyiden, kuten tulosten ilmoittamistavan sekä laskentakaavojen käytön suhteen. Käytäntöjen harmonisointia tulisi jatkaa koulutusta tarjoamalla ja päivittämällä nykyisiä ohjeita sellaisilla yksityiskohdilla, jotka voivat vaikuttaa tuloksiin.

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# APPENDIX 1: Evaluation of the assigned values and their uncertainties

| Measurand | Sample | Unit | Assigned value | $U_{pt}$ | $U_{pt}$, % | Evaluation method of assigned value | $u_{pt}/s_{pt}$ |
|---|---|---|---|---|---|---|---|
| AGR | S1 | % | 99.3 | 1.3 | 1.3 | Mean | 0.03 |
| | S2 | % | 74.6 | 23 | 31 | Mean | 0.62 |
| Bulk density | S1 | g/l | 675 | 7 | 1.0 | Mean | 0.04 |
| | S2 | g/l | 627 | 5 | 0.8 | Mean | 0.03 |
| $CO_2$ prod/bottle | S1 | % | 0.37 | 0.07 | 20 | Mean | |
| | S2 | % | 0.15 | 0.13 | 80 | Mean | |
| $CO_2$ prod rate | S1 | mg CO2-C/g VS/d | 1.0 | 0.6 | 55 | Mean | |
| | S2 | mg CO2-C/g VS/d | 0.3 | 0.2 | 80 | Mean | |
| Cond 25 | S1 | mS/m | 26.4 | 5.6 | 21 | Mean | 0.43 |
| | S2 | mS/m | 270 | 19 | 7 | Mean | 0.14 |
| Dry matter | S1 | % | 43.9 | 0.6 | 1 | Mean | 0.06 |
| | S2 | % | 42.8 | 1.4 | 3 | Mean | 0.13 |
| $N_{NH4}$ | S1 | mg/l | 1.5 | 1.6 | 110 | Mean | |
| | S2 | mg/l | 20.5 | 3.6 | 18 | Mean | |
| Org matter | S1 | % (w/w) | 32.0 | 2.2 | 6.9 | Mean | 0.28 |
| | S2 | % (w/w) | 43.7 | 1.5 | 3.4 | Mean | 0.14 |
| pH | S1 | | 7.8 | 0.11 | 1.4 | Mean | 0.21 |
| | S2 | | 5.9 | 0.09 | 1.5 | Mean | 0.18 |
| RI | S1 | % | 101 | 25 | 24 | Mean | 0.30 |
| | S2 | % | 70.4 | 16 | 23 | Mean | 0.29 |

$U_{pt}$ = 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 2: Terms in the results tables

**Results of each participant**

| | |
|---|---|
| **Measurand** | The tested parameter |
| **Sample** | The code of the sample |
| **z score** | Calculated as follows:<br>$z = (x_i - x_{pt})/s_{pt}$, where<br>$x_i$ = the result of the individual participant<br>$x_{pt}$ = the assigned value<br>$s_{pt}$ = 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 |
| **Participants'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 $x_i$ ($i = 1, 2, \ldots, p$)
$s^*$ = 1.483 × median of $|x_i - x^*|$ ($i = 1, 2, \ldots, p$)

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

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

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

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

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

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

# APPENDIX 3: Results of each participant

| Participant 1 | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Measurand | Unit | Sample | -3 0 3 | z score | Assigned value | 2×$s_{pt}$ % | Participant's result | Md | Mean | sd | sd % | n (stat) |
| Bulk density | g/l | S1 | | 0.06 | 675 | 25 | 680 | 675 | 675 | 9 | 1.4 | 8 |
| | g/l | S2 | | 0.68 | 627 | 25 | 680 | 628 | 627 | 7 | 1.1 | 8 |
| $CO_2$ prod rate | mg CO2-C/g VS/d | S1 | | | 1.0 | | *<0,2* | 0.8 | 1.0 | 0.7 | 67.6 | 6 |
| | mg CO2-C/g VS/d | S2 | | | 0.3 | | *<0,2* | 0.3 | 0.3 | 0.3 | 98.4 | 6 |
| Cond 25 | mS/m | S1 | | 0.80 | 29.1 | 50 | 34.9 | 28.1 | 29.1 | 3.7 | 12.9 | 10 |
| | mS/m | S2 | | -3.48 | 270 | 50 | 35 | 272 | 270 | 28 | 10.3 | 9 |
| Dry matter | % | S1 | | -0.15 | 43.9 | 25 | 43.1 | 43.6 | 43.9 | 1.0 | 2.4 | 11 |
| | % | S2 | | 0.06 | 42.8 | 25 | 43.1 | 43.3 | 42.8 | 2.3 | 5.4 | 11 |
| $N_{NH4}$ | mg/l | S1 | | | 1.5 | | *< 1* | 0.5 | 1.5 | 2.0 | 134.2 | 6 |
| | mg/l | S2 | | | 20.5 | | *< 1* | 20.8 | 20.5 | 4.8 | 23.3 | 7 |
| $N_{NO3}$ | mg/l | S1 | | | | | 67.0 | 67.0 | 66.6 | 7.5 | 11.2 | 7 |
| | mg/l | S2 | | | | | 67 | 587 | 440 | 288 | 65.5 | 10 |
| Org matter | % (w/w) | S1 | | 1.40 | 32.0 | 25 | 37.6 | 32.4 | 32.0 | 3.7 | 11.5 | 11 |
| | % (w/w) | S2 | | -1.12 | 43.7 | 25 | 37.6 | 44.3 | 43.7 | 2.4 | 5.6 | 11 |
| pH | | S1 | | -0.39 | 7.8 | 6,5 | 7.70 | 7.82 | 7.83 | 0.18 | 2.3 | 11 |
| | | S2 | | 7.18 | 5.9 | 8,5 | 7.70 | 5.92 | 5.93 | 0.14 | 2.3 | 10 |

| Participant 3 | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Measurand | Unit | Sample | -3 0 3 | z score | Assigned value | 2×$s_{pt}$ % | Participant's result | Md | Mean | sd | sd % | n (stat) |
| AGR | % | S1 | | -0.50 | 99.3 | 50 | 87.0 | 100.0 | 99.3 | 1.5 | 1.5 | 5 |
| | % | S2 | | 0.45 | 74.6 | 50 | 83.0 | 85.0 | 74.6 | 28.5 | 38.2 | 6 |
| Bulk density | g/l | S1 | | 0.00 | 675 | 25 | 675 | 675 | 675 | 9 | 1.4 | 8 |
| | g/l | S2 | | 0.10 | 627 | 25 | 635 | 628 | 627 | 7 | 1.1 | 8 |
| Cond 25 | mS/m | S1 | | 0.67 | 29.1 | 50 | 34.0 | 28.1 | 29.1 | 3.7 | 12.9 | 10 |
| | mS/m | S2 | | 0.12 | 270 | 50 | 278 | 272 | 270 | 28 | 10.3 | 9 |
| Dry matter | % | S1 | | -0.16 | 43.9 | 25 | 43.0 | 43.6 | 43.9 | 1.0 | 2.4 | 11 |
| | % | S2 | | 0.19 | 42.8 | 25 | 43.8 | 43.3 | 42.8 | 2.3 | 5.4 | 11 |
| $N_{NH4}$ | mg/l | S1 | | | 1.5 | | 0.0 | 0.5 | 1.5 | 2.0 | 134.2 | 6 |
| | mg/l | S2 | | | 20.5 | | 17.0 | 20.8 | 20.5 | 4.8 | 23.3 | 7 |
| $N_{NO3}$ | mg/l | S1 | | | | | 64.0 | 67.0 | 66.6 | 7.5 | 11.2 | 7 |
| | mg/l | S2 | | | | | 619 | 587 | 440 | 288 | 65.5 | 10 |
| $N_{(NO3/NH4)}$ | | S1 | | | | | 64.0 | 49.0 | 39.7 | 37.6 | 94.7 | 5 |
| | | S2 | | | | | 636.0 | 25.7 | 19.9 | 17.4 | 87.8 | 5 |
| Org matter | % (w/w) | S1 | | 0.95 | 32.0 | 25 | 35.8 | 32.4 | 32.0 | 3.7 | 11.5 | 11 |
| | % (w/w) | S2 | | 0.46 | 43.7 | 25 | 46.2 | 44.3 | 43.7 | 2.4 | 5.6 | 11 |
| pH | | S1 | | -0.39 | 7.8 | 6,5 | 7.70 | 7.82 | 7.83 | 0.18 | 2.3 | 11 |
| | | S2 | | -0.40 | 5.9 | 8,5 | 5.80 | 5.92 | 5.93 | 0.14 | 2.3 | 10 |
| RI | % | S1 | | -0.84 | 101 | 80 | 67 | 100 | 101 | 32 | 32.1 | 7 |
| | % | S2 | | 0.63 | 70.4 | 80 | 88.0 | 73.4 | 70.5 | 19.9 | 28.2 | 6 |
| Rooth length | mm | S1 | | | | | 35 | 35 | 32.87 | 5.518 | 16.8 | 3 |
| | mm | S2 | | | | | 45 | 2.61 | 16.34 | 19.13 | 117.1 | 7 |
| $T_{max}$ | °C | S1 | | | | | 34.8 | 20 | 20.73 | 1.517 | 7.3 | 4 |
| | °C | S2 | | | | | 29.8 | 21.05 | 21.2 | 1.494 | 7.0 | 4 |

| Participant 4 | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Measurand | Unit | Sample | -3 0 3 | z score | Assigned value | $2 \times s_{pt}$ % | Participant's result | Md | Mean | sd | sd % | n (stat) |
| AGR | % | S1 | | 0.03 | 99.3 | 50 | 100.0 | 100.0 | 99.3 | 1.5 | 1.5 | 5 |
| | % | S2 | | 0.66 | 74.6 | 50 | 87.0 | 85.0 | 74.6 | 28.5 | 38.2 | 6 |
| Bulk density | g/l | S1 | | -0.08 | 675 | 25 | 668 | 675 | 675 | 9 | 1.4 | 8 |
| | g/l | S2 | | -0.17 | 627 | 25 | 614 | 628 | 627 | 7 | 1.1 | 8 |
| $CO_2$ prod/bottle | % | S1 | | | 0.37 | | 0.50 | 0.36 | 0.37 | 0.08 | 22.3 | 5 |
| | % | S2 | | | 0.15 | | 0.30 | 0.20 | 0.15 | 0.14 | 94.3 | 5 |
| $CO_2$ prod rate | mg CO2-C/g VS/d | S1 | | | 1.0 | | 1.0 | 0.8 | 1.0 | 0.7 | 67.6 | 6 |
| | mg CO2-C/g VS/d | S2 | | | 0.3 | | 0.5 | 0.3 | 0.3 | 0.3 | 98.4 | 6 |
| Cond 25 | mS/m | S1 | | -0.81 | 29.1 | 50 | 23.2 | 28.1 | 29.1 | 3.7 | 12.9 | 10 |
| | mS/m | S2 | | -0.48 | 270 | 50 | 238 | 272 | 270 | 28 | 10.3 | 9 |
| Dry matter | % | S1 | | -0.05 | 43.9 | 25 | 43.6 | 43.6 | 43.9 | 1.0 | 2.4 | 11 |
| | % | S2 | | 0.06 | 42.8 | 25 | 43.1 | 43.3 | 42.8 | 2.3 | 5.4 | 11 |
| $N_{NH4}$ | mg/l | S1 | | | 1.5 | | <5 | 0.5 | 1.5 | 2.0 | 134.2 | 6 |
| | mg/l | S2 | | | 20.5 | | 16.0 | 20.8 | 20.5 | 4.8 | 23.3 | 7 |
| $N_{NO3}$ | mg/l | S1 | | | | | 67.0 | 67.0 | 66.6 | 7.5 | 11.2 | 7 |
| | mg/l | S2 | | | | | 642 | 587 | 440 | 288 | 65.5 | 10 |
| Org matter | % (w/w) | S1 | | 0.43 | 32.0 | 25 | 33.7 | 32.4 | 32.0 | 3.7 | 11.5 | 11 |
| | % (w/w) | S2 | | 0.07 | 43.7 | 25 | 44.1 | 44.3 | 43.7 | 2.4 | 5.6 | 11 |
| pH | | S1 | | 1.18 | 7.8 | 6,5 | 8.10 | 7.82 | 7.83 | 0.18 | 2.3 | 11 |
| | | S2 | | 0.80 | 5.9 | 8,5 | 6.10 | 5.92 | 5.93 | 0.14 | 2.3 | 10 |
| RI | % | S1 | | -0.74 | 101 | 80 | 71 | 100 | 101 | 32 | 32.1 | 7 |
| | % | S2 | | -0.05 | 70.4 | 80 | 69.0 | 73.4 | 70.5 | 19.9 | 28.2 | 6 |
| Rooth length | mm | S1 | | | | | 26.6 | 35 | 32.87 | 5.518 | 16.8 | 3 |
| | mm | S2 | | | | | 25.9 | 2.61 | 16.34 | 19.13 | 117.1 | 7 |
| $T_{max}$ | °C | S1 | | | | | 23 | 20 | 20.73 | 1.517 | 7.3 | 4 |
| | °C | S2 | | | | | 22.9 | 21.05 | 21.2 | 1.494 | 7.0 | 4 |

| Participant 5 | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Measurand | Unit | Sample | -3 0 3 | z score | Assigned value | $2 \times s_{pt}$ % | Participant's result | Md | Mean | sd | sd % | n (stat) |
| Bulk density | g/l | S1 | | 1.13 | 675 | 25 | 771 | 675 | 675 | 9 | 1.4 | 8 |
| | g/l | S2 | | 1.04 | 627 | 25 | 708 | 628 | 627 | 7 | 1.1 | 8 |
| Cond 25 | mS/m | S1 | | -3.96 | 29.1 | 50 | 0.3 | 28.1 | 29.1 | 3.7 | 12.9 | 10 |
| | mS/m | S2 | | -3.95 | 270 | 50 | 3 | 272 | 270 | 28 | 10.3 | 9 |
| Dry matter | % | S1 | | -0.34 | 43.9 | 25 | 42.0 | 43.6 | 43.9 | 1.0 | 2.4 | 11 |
| | % | S2 | | -0.12 | 42.8 | 25 | 42.2 | 43.3 | 42.8 | 2.3 | 5.4 | 11 |
| $N_{NH4}$ | mg/l | S1 | | | 1.5 | | 0.2 | 0.5 | 1.5 | 2.0 | 134.2 | 6 |
| | mg/l | S2 | | | 20.5 | | 20.8 | 20.8 | 20.5 | 4.8 | 23.3 | 7 |
| $N_{NO3}$ | mg/l | S1 | | | | | 66.5 | 67.0 | 66.6 | 7.5 | 11.2 | 7 |
| | mg/l | S2 | | | | | 684 | 587 | 440 | 288 | 65.5 | 10 |
| $N_{(NO3/NH4)}$ | | S1 | | | | | 295.5 | 49.0 | 39.7 | 37.6 | 94.7 | 5 |
| | | S2 | | | | | 32.9 | 25.7 | 19.9 | 17.4 | 87.8 | 5 |
| Org matter | % (w/w) | S1 | | 0.83 | 32.0 | 25 | 35.3 | 32.4 | 32.0 | 3.7 | 11.5 | 11 |
| | % (w/w) | S2 | | 0.35 | 43.7 | 25 | 45.6 | 44.3 | 43.7 | 2.4 | 5.6 | 11 |
| pH | | S1 | | -1.07 | 7.8 | 6,5 | 7.53 | 7.82 | 7.83 | 0.18 | 2.3 | 11 |
| | | S2 | | -0.48 | 5.9 | 8,5 | 5.78 | 5.92 | 5.93 | 0.14 | 2.3 | 10 |

| Participant 6 | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Measurand | Unit | Sample | -3 0 3 | z score | Assigned value | $2\times s_{pt}$ % | Participant's result | Md | Mean | sd | sd % | n (stat) |
| AGR | % | S1 | | 0.03 | 99.3 | 50 | 100.0 | 100.0 | 99.3 | 1.5 | 1.5 | 5 |
| | % | S2 | | -1.86 | 74.6 | 50 | 40.0 | 85.0 | 74.6 | 28.5 | 38.2 | 6 |
| Bulk density | g/l | S1 | | -0.20 | 675 | 25 | 658 | 675 | 675 | 9 | 1.4 | 8 |
| | g/l | S2 | | -0.05 | 627 | 25 | 623 | 628 | 627 | 7 | 1.1 | 8 |
| Cond 25 | mS/m | S1 | | -0.43 | 29.1 | 50 | 26.0 | 28.1 | 29.1 | 3.7 | 12.9 | 10 |
| | mS/m | S2 | | -0.07 | 270 | 50 | 265 | 272 | 270 | 28 | 10.3 | 9 |
| Dry matter | % | S1 | | 0.35 | 43.9 | 25 | 45.8 | 43.6 | 43.9 | 1.0 | 2.4 | 11 |
| | % | S2 | | 0.32 | 42.8 | 25 | 44.5 | 43.3 | 42.8 | 2.3 | 5.4 | 11 |
| $N_{NH4}$ | mg/l | S1 | | | 1.5 | | <5 | 0.5 | 1.5 | 2.0 | 134.2 | 6 |
| | mg/l | S2 | | | 20.5 | | 15.0 | 20.8 | 20.5 | 4.8 | 23.3 | 7 |
| $N_{NO3}$ | mg/l | S1 | | | | | 67.0 | 67.0 | 66.6 | 7.5 | 11.2 | 7 |
| | mg/l | S2 | | | | | 650 | 587 | 440 | 288 | 65.5 | 10 |
| Org matter | % (w/w) | S1 | | -0.38 | 32.0 | 25 | 30.5 | 32.4 | 32.0 | 3.7 | 11.5 | 11 |
| | % (w/w) | S2 | | -0.18 | 43.7 | 25 | 42.7 | 44.3 | 43.7 | 2.4 | 5.6 | 11 |
| pH | | S1 | | 0.79 | 7.8 | 6,5 | 8.00 | 7.82 | 7.83 | 0.18 | 2.3 | 11 |
| | | S2 | | 0.00 | 5.9 | 8,5 | 5.90 | 5.92 | 5.93 | 0.14 | 2.3 | 10 |
| RI | % | S1 | | 0.10 | 101 | 80 | 105 | 100 | 101 | 32 | 32.1 | 7 |
| | % | S2 | | -1.33 | 70.4 | 80 | 33.0 | 73.4 | 70.5 | 19.9 | 28.2 | 6 |
| Rooth length | mm | S1 | | | | | 5.7 | 35 | 32.87 | 5.518 | 16.8 | 3 |
| | mm | S2 | | | | | 1.8 | 2.61 | 16.34 | 19.13 | 117.1 | 7 |

| Participant 7 | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Measurand | Unit | Sample | -3 0 3 | z score | Assigned value | $2\times s_{pt}$ % | Participant's result | Md | Mean | sd | sd % | n (stat) |
| Bulk density | g/l | S1 | | 0.89 | 675 | 25 | 750 | 675 | 675 | 9 | 1.4 | 8 |
| | g/l | S2 | | 1.76 | 627 | 25 | 765 | 628 | 627 | 7 | 1.1 | 8 |
| Cond 25 | mS/m | S1 | | 0.47 | 29.1 | 50 | 32.5 | 28.1 | 29.1 | 3.7 | 12.9 | 10 |
| | mS/m | S2 | | 0.87 | 270 | 50 | 329 | 272 | 270 | 28 | 10.3 | 9 |
| Dry matter | % | S1 | | 0.18 | 43.9 | 25 | 44.9 | 43.6 | 43.9 | 1.0 | 2.4 | 11 |
| | % | S2 | | -1.25 | 42.8 | 25 | 36.1 | 43.3 | 42.8 | 2.3 | 5.4 | 11 |
| $N_{NO3}$ | mg/l | S1 | | | | | 80.0 | 67.0 | 66.6 | 7.5 | 11.2 | 7 |
| | mg/l | S2 | | | | | 800 | 587 | 440 | 288 | 65.5 | 10 |
| Org matter | % (w/w) | S1 | | -0.95 | 32.0 | 25 | 28.2 | 32.4 | 32.0 | 3.7 | 11.5 | 11 |
| | % (w/w) | S2 | | -0.27 | 43.7 | 25 | 42.2 | 44.3 | 43.7 | 2.4 | 5.6 | 11 |
| pH | | S1 | | -0.39 | 7.8 | 6,5 | 7.70 | 7.82 | 7.83 | 0.18 | 2.3 | 11 |
| | | S2 | | 1.20 | 5.9 | 8,5 | 6.20 | 5.92 | 5.93 | 0.14 | 2.3 | 10 |

| Participant 8 | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Measurand | Unit | Sample | -3 0 3 | z score | Assigned value | $2\times s_{pt}$ % | Participant's result | Md | Mean | sd | sd % | n (stat) |
| AGR | % | S1 | | -2.38 | 99.3 | 50 | 40.2 | 100.0 | 99.3 | 1.5 | 1.5 | 5 |
| | % | S2 | | -1.97 | 74.6 | 50 | 37.8 | 85.0 | 74.6 | 28.5 | 38.2 | 6 |
| Bulk density | g/l | S1 | | 0.11 | 675 | 25 | 684 | 675 | 675 | 9 | 1.4 | 8 |
| | g/l | S2 | | 0.05 | 627 | 25 | 631 | 628 | 627 | 7 | 1.1 | 8 |
| $CO_2$ prod/bottle | % | S1 | | | 0.37 | | 0.40 | 0.36 | 0.37 | 0.08 | 22.3 | 5 |
| | % | S2 | | | 0.15 | | 0.20 | 0.20 | 0.15 | 0.14 | 94.3 | 5 |
| $CO_2$ prod rate | mg CO2-C/g VS/d | S1 | | | 1.0 | | 1.7 | 0.8 | 1.0 | 0.7 | 67.6 | 6 |
| | mg CO2-C/g VS/d | S2 | | | 0.3 | | 0.6 | 0.3 | 0.3 | 0.3 | 98.4 | 6 |
| Cond 25 | mS/m | S1 | | -0.14 | 29.1 | 50 | 28.1 | 28.1 | 29.1 | 3.7 | 12.9 | 10 |
| | mS/m | S2 | | 0.03 | 270 | 50 | 272 | 272 | 270 | 28 | 10.3 | 9 |

| Participant 8 | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Measurand | Unit | Sample | -3 0 3 | z score | Assigned value | $2 \times s_{pt}$ % | Participant's result | Md | Mean | sd | sd % | n (stat) |
| Dry matter | % | S1 | | 0.07 | 43.9 | 25 | 44.3 | 43.6 | 43.9 | 1.0 | 2.4 | 11 |
| | % | S2 | | 0.11 | 42.8 | 25 | 43.4 | 43.3 | 42.8 | 2.3 | 5.4 | 11 |
| $N_{NH4}$ | mg/l | S1 | | | 1.5 | | 0.7 | 0.5 | 1.5 | 2.0 | 134.2 | 6 |
| | mg/l | S2 | | | 20.5 | | 21.6 | 20.8 | 20.5 | 4.8 | 23.3 | 7 |
| $N_{NO3}$ | mg/l | S1 | | | | | 54.5 | 67.0 | 66.6 | 7.5 | 11.2 | 7 |
| | mg/l | S2 | | | | | 554 | 587 | 440 | 288 | 65.5 | 10 |
| $N(_{NO3}/_{NH4})$ | | S1 | | | | | 83.9 | 49.0 | 39.7 | 37.6 | 94.7 | 5 |
| | | S2 | | | | | 25.7 | 25.7 | 19.9 | 17.4 | 87.8 | 5 |
| Org matter | % (w/w) | S1 | | -0.03 | 32.0 | 25 | 31.9 | 32.4 | 32.0 | 3.7 | 11.5 | 11 |
| | % (w/w) | S2 | | 0.40 | 43.7 | 25 | 45.9 | 44.3 | 43.7 | 2.4 | 5.6 | 11 |
| pH | | S1 | | 0.08 | 7.8 | 6,5 | 7.82 | 7.82 | 7.83 | 0.18 | 2.3 | 11 |
| | | S2 | | -0.24 | 5.9 | 8,5 | 5.84 | 5.92 | 5.93 | 0.14 | 2.3 | 10 |
| RI | % | S1 | | -0.47 | 101 | 80 | 82 | 100 | 101 | 32 | 32.1 | 7 |
| | % | S2 | | 0.08 | 70.4 | 80 | 72.7 | 73.4 | 70.5 | 19.9 | 28.2 | 6 |
| Rooth length | mm | S1 | | | | | 37 | 35 | 32.87 | 5.518 | 16.8 | 3 |
| | mm | S2 | | | | | 36.8 | 2.61 | 16.34 | 19.13 | 117.1 | 7 |

| Participant 10 | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Measurand | Unit | Sample | -3 0 3 | z score | Assigned value | $2 \times s_{pt}$ % | Participant's result | Md | Mean | sd | sd % | n (stat) |
| AGR | % | S1 | | 0.03 | 99.3 | 50 | 100.0 | 100.0 | 99.3 | 1.5 | 1.5 | 5 |
| | % | S2 | | 1.36 | 74.6 | 50 | 100.0 | 85.0 | 74.6 | 28.5 | 38.2 | 6 |
| Bulk density | g/l | S1 | | -0.68 | 675 | 25 | 618 | 675 | 675 | 9 | 1.4 | 8 |
| | g/l | S2 | | -0.07 | 627 | 25 | 622 | 628 | 627 | 7 | 1.1 | 8 |
| $CO_2$ prod/bottle | % | S1 | | | 0.37 | | 0.30 | 0.36 | 0.37 | 0.08 | 22.3 | 5 |
| | % | S2 | | | 0.15 | | 0.00 | 0.20 | 0.15 | 0.14 | 94.3 | 5 |
| $CO_2$ prod rate | mg CO2-C/g VS/d | S1 | | | 1.0 | | 0.6 | 0.8 | 1.0 | 0.7 | 67.6 | 6 |
| | mg CO2-C/g VS/d | S2 | | | 0.3 | | 0.0 | 0.3 | 0.3 | 0.3 | 98.4 | 6 |
| Cond 25 | mS/m | S1 | | -0.37 | 29.1 | 50 | 26.4 | 28.1 | 29.1 | 3.7 | 12.9 | 10 |
| | mS/m | S2 | | 0.18 | 270 | 50 | 282 | 272 | 270 | 28 | 10.3 | 9 |
| Dry matter | % | S1 | | -0.07 | 43.9 | 25 | 43.5 | 43.6 | 43.9 | 1.0 | 2.4 | 11 |
| | % | S2 | | 0.06 | 42.8 | 25 | 43.1 | 43.3 | 42.8 | 2.3 | 5.4 | 11 |
| $N_{NH4}$ | mg/l | S1 | | | 1.5 | | 5.0 | 0.5 | 1.5 | 2.0 | 134.2 | 6 |
| | mg/l | S2 | | | 20.5 | | 26.3 | 20.8 | 20.5 | 4.8 | 23.3 | 7 |
| $N_{NO3}$ | mg/l | S1 | | | | | 9.3 | 67.0 | 66.6 | 7.5 | 11.2 | 7 |
| | mg/l | S2 | | | | | 120 | 587 | 440 | 288 | 65.5 | 10 |
| $N(_{NO3}/_{NH4})$ | | S1 | | | | | 0.5 | 49.0 | 39.7 | 37.6 | 94.7 | 5 |
| | | S2 | | | | | 1.3 | 25.7 | 19.9 | 17.4 | 87.8 | 5 |
| Org matter | % (w/w) | S1 | | 0.20 | 32.0 | 25 | 32.8 | 32.4 | 32.0 | 3.7 | 11.5 | 11 |
| | % (w/w) | S2 | | 0.16 | 43.7 | 25 | 44.6 | 44.3 | 43.7 | 2.4 | 5.6 | 11 |
| pH | | S1 | | 0.71 | 7.8 | 6,5 | 7.98 | 7.82 | 7.83 | 0.18 | 2.3 | 11 |
| | | S2 | | 0.28 | 5.9 | 8,5 | 5.97 | 5.92 | 5.93 | 0.14 | 2.3 | 10 |
| RI | % | S1 | | 0.47 | 101 | 80 | 120 | 100 | 101 | 32 | 32.1 | 7 |
| | % | S2 | | 0.13 | 70.4 | 80 | 74.0 | 73.4 | 70.5 | 19.9 | 28.2 | 6 |
| Rooth length | mm | S1 | | | | | 3.59 | 35 | 32.87 | 5.518 | 16.8 | 3 |
| | mm | S2 | | | | | 2.27 | 2.61 | 16.34 | 19.13 | 117.1 | 7 |
| $T_{max}$ | °C | S1 | | | | | 20 | 20 | 20.73 | 1.517 | 7.3 | 4 |
| | °C | S2 | | | | | 20.1 | 21.05 | 21.2 | 1.494 | 7.0 | 4 |

| Participant 11 | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Measurand | Unit | Sample | -3 0 3 | z score | Assigned value | $2 \times s_{pt}$ % | Participant's result | Md | Mean | sd | sd % | n (stat) |
| AGR | % | S1 | | -0.10 | 99.3 | 50 | 96.7 | 100.0 | 99.3 | 1.5 | 1.5 | 5 |
| | % | S2 | | -3.29 | 74.6 | 50 | 13.3 | 85.0 | 74.6 | 28.5 | 38.2 | 6 |
| Bulk density | g/l | S1 | | 0.15 | 675 | 25 | 688 | 675 | 675 | 9 | 1.4 | 8 |
| | g/l | S2 | | 0.03 | 627 | 25 | 630 | 628 | 627 | 7 | 1.1 | 8 |
| $CO_2$ prod rate | mg CO2-C/g VS/d | S1 | | | 1.0 | | 0.2 | 0.8 | 1.0 | 0.7 | 67.6 | 6 |
| | mg CO2-C/g VS/d | S2 | | | 0.3 | | 0.1 | 0.3 | 0.3 | 0.3 | 98.4 | 6 |
| Cond 25 | mS/m | S1 | | -0.21 | 29.1 | 50 | 27.6 | 28.1 | 29.1 | 3.7 | 12.9 | 10 |
| | mS/m | S2 | | -0.55 | 270 | 50 | 233 | 272 | 270 | 28 | 10.3 | 9 |
| Dry matter | % | S1 | | -0.05 | 43.9 | 25 | 43.6 | 43.6 | 43.9 | 1.0 | 2.4 | 11 |
| | % | S2 | | 0.13 | 42.8 | 25 | 43.5 | 43.3 | 42.8 | 2.3 | 5.4 | 11 |
| $N_{NH4}$ | mg/l | S1 | | | 1.5 | | 0.3 | 0.5 | 1.5 | 2.0 | 134.2 | 6 |
| | mg/l | S2 | | | 20.5 | | 3.7 | 20.8 | 20.5 | 4.8 | 23.3 | 7 |
| $N_{NO3}$ | mg/l | S1 | | | | | 13.5 | 67.0 | 66.6 | 7.5 | 11.2 | 7 |
| | mg/l | S2 | | | | | 138 | 587 | 440 | 288 | 65.5 | 10 |
| $N(_{NO3}/_{NH4})$ | | S1 | | | | | 49.0 | 49.0 | 39.7 | 37.6 | 94.7 | 5 |
| | | S2 | | | | | 38.0 | 25.7 | 19.9 | 17.4 | 87.8 | 5 |
| Org matter | % (w/w) | S1 | | -0.72 | 32.0 | 25 | 29.1 | 32.4 | 32.0 | 3.7 | 11.5 | 11 |
| | % (w/w) | S2 | | -0.18 | 43.7 | 25 | 42.7 | 44.3 | 43.7 | 2.4 | 5.6 | 11 |
| pH | | S1 | | 0.16 | 7.8 | 6,5 | 7.84 | 7.82 | 7.83 | 0.18 | 2.3 | 11 |
| | | S2 | | 0.20 | 5.9 | 8,5 | 5.95 | 5.92 | 5.93 | 0.14 | 2.3 | 10 |
| RI | % | S1 | | -0.02 | 101 | 80 | 100 | 100 | 101 | 32 | 32.1 | 7 |
| | % | S2 | | -2.50 | 70.4 | 80 | 0.0 | 73.4 | 70.5 | 19.9 | 28.2 | 6 |
| Rooth length | mm | S1 | | | | | 5.3 | 35 | 32.87 | 5.518 | 16.8 | 3 |
| | mm | S2 | | | | | 0 | 2.61 | 16.34 | 19.13 | 117.1 | 7 |
| $T_{max}$ | °C | S1 | | | | | 20 | 20 | 20.73 | 1.517 | 7.3 | 4 |
| | °C | S2 | | | | | 22 | 21.05 | 21.2 | 1.494 | 7.0 | 4 |

| Participant 12 | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Measurand | Unit | Sample | -3 0 3 | z score | Assigned value | $2 \times s_{pt}$ % | Participant's result | Md | Mean | sd | sd % | n (stat) |
| AGR | % | S1 | | 0.03 | 99.3 | 50 | 100.0 | 100.0 | 99.3 | 1.5 | 1.5 | 5 |
| | % | S2 | | 1.36 | 74.6 | 50 | 100.0 | 85.0 | 74.6 | 28.5 | 38.2 | 6 |
| Bulk density | g/l | S1 | | -0.02 | 675 | 25 | 673 | 675 | 675 | 9 | 1.4 | 8 |
| | g/l | S2 | | 0.01 | 627 | 25 | 627 | 628 | 627 | 7 | 1.1 | 8 |
| $CO_2$ prod/bottle | % | S1 | | | 0.37 | | 0.30 | 0.36 | 0.37 | 0.08 | 22.3 | 5 |
| | % | S2 | | | 0.15 | | 0.00 | 0.20 | 0.15 | 0.14 | 94.3 | 5 |
| $CO_2$ prod rate | mg CO2-C/g VS/d | S1 | | | 1.0 | | 0.6 | 0.8 | 1.0 | 0.7 | 67.6 | 6 |
| | mg CO2-C/g VS/d | S2 | | | 0.3 | | 0.0 | 0.3 | 0.3 | 0.3 | 98.4 | 6 |
| Cond 25 | mS/m | S1 | | 0.11 | 29.1 | 50 | 29.9 | 28.1 | 29.1 | 3.7 | 12.9 | 10 |
| | mS/m | S2 | | 0.07 | 270 | 50 | 275 | 272 | 270 | 28 | 10.3 | 9 |
| Dry matter | % | S1 | | -0.02 | 43.9 | 25 | 43.8 | 43.6 | 43.9 | 1.0 | 2.4 | 11 |
| | % | S2 | | 0.09 | 42.8 | 25 | 43.3 | 43.3 | 42.8 | 2.3 | 5.4 | 11 |
| $N_{NH4}$ | mg/l | S1 | | | 1.5 | | 2.9 | 0.5 | 1.5 | 2.0 | 134.2 | 6 |
| | mg/l | S2 | | | 20.5 | | 26.7 | 20.8 | 20.5 | 4.8 | 23.3 | 7 |
| $N_{NO3}$ | mg/l | S1 | | | | | 10.9 | 67.0 | 66.6 | 7.5 | 11.2 | 7 |
| | mg/l | S2 | | | | | 130 | 587 | 440 | 288 | 65.5 | 10 |
| $N(_{NO3}/_{NH4})$ | | S1 | | | | | 1.1 | 49.0 | 39.7 | 37.6 | 94.7 | 5 |
| | | S2 | | | | | 1.4 | 25.7 | 19.9 | 17.4 | 87.8 | 5 |

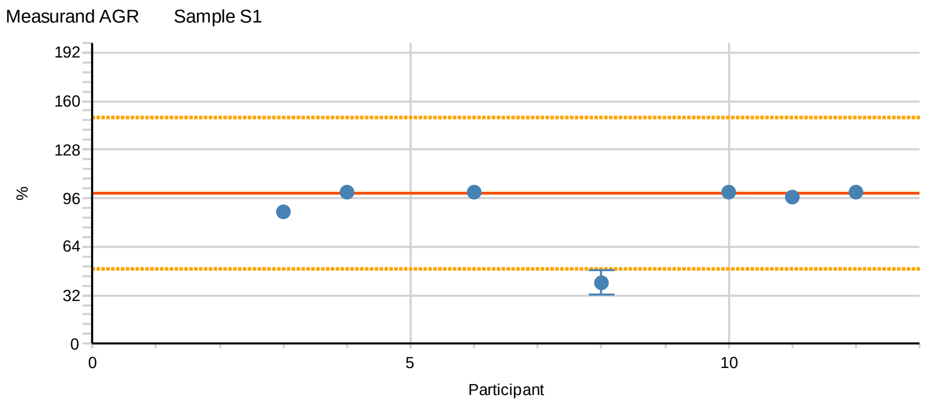
| Participant 12 | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Measurand | Unit | Sample | -3 0 3 | z score | Assigned value | 2×$s_{pt}$ % | Participant's result | Md | Mean | sd | sd % | n (stat) |
| Org matter | % (w/w) | S1 | | 0.10 | 32.0 | 25 | 32.4 | 32.4 | 32.0 | 3.7 | 11.5 | 11 |
| | % (w/w) | S2 | | 0.11 | 43.7 | 25 | 44.3 | 44.3 | 43.7 | 2.4 | 5.6 | 11 |
| pH | | S1 | | 0.91 | 7.8 | 6,5 | 8.03 | 7.82 | 7.83 | 0.18 | 2.3 | 11 |
| | | S2 | | 0.12 | 5.9 | 8,5 | 5.93 | 5.92 | 5.93 | 0.14 | 2.3 | 10 |
| RI | % | S1 | | 1.46 | 101 | 80 | 160 | 100 | 101 | 32 | 32.1 | 7 |
| | % | S2 | | 0.55 | 70.4 | 80 | 86.0 | 73.4 | 70.5 | 19.9 | 28.2 | 6 |
| Rooth length | mm | S1 | | | | | 3.5 | 35 | 32.87 | 5.518 | 16.8 | 3 |
| | mm | S2 | | | | | 2.61 | 2.61 | 16.34 | 19.13 | 117.1 | 7 |
| $T_{max}$ | °C | S1 | | | | | 19.9 | 20 | 20.73 | 1.517 | 7.3 | 4 |
| | °C | S2 | | | | | 19.8 | 21.05 | 21.2 | 1.494 | 7.0 | 4 |

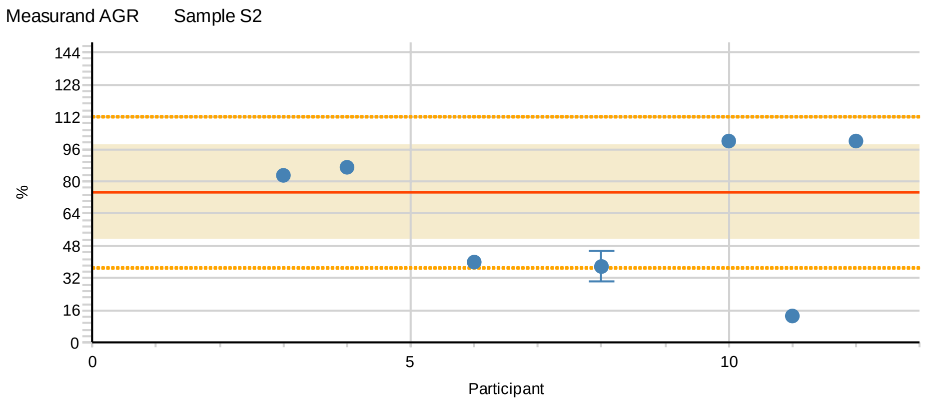
| Participant 13 | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Measurand | Unit | Sample | -3 0 3 | z score | Assigned value | 2×$s_{pt}$ % | Participant's result | Md | Mean | sd | sd % | n (stat) |
| Bulk density | g/l | S1 | | -0.01 | 675 | 25 | 674 | 675 | 675 | 9 | 1.4 | 8 |
| | g/l | S2 | | 0.05 | 627 | 25 | 631 | 628 | 627 | 7 | 1.1 | 8 |
| $CO_2$ prod/bottle | % | S1 | | | 0.37 | | 0.36 | 0.36 | 0.37 | 0.08 | 22.3 | 5 |
| | % | S2 | | | 0.15 | | 0.25 | 0.20 | 0.15 | 0.14 | 94.3 | 5 |
| $CO_2$ prod rate | mg CO2-C/g VS/d | S1 | | | 1.0 | | 2.0 | 0.8 | 1.0 | 0.7 | 67.6 | 6 |
| | mg CO2-C/g VS/d | S2 | | | 0.3 | | 0.8 | 0.3 | 0.3 | 0.3 | 98.4 | 6 |
| Cond 25 | mS/m | S1 | | -0.15 | 29.1 | 50 | 28.0 | 28.1 | 29.1 | 3.7 | 12.9 | 10 |
| | mS/m | S2 | | -0.15 | 270 | 50 | 260 | 272 | 270 | 28 | 10.3 | 9 |
| Dry matter | % | S1 | | 0.16 | 43.9 | 25 | 44.8 | 43.6 | 43.9 | 1.0 | 2.4 | 11 |
| | % | S2 | | 0.36 | 42.8 | 25 | 44.7 | 43.3 | 42.8 | 2.3 | 5.4 | 11 |
| $N_{NH4}$ | mg/l | S1 | | | 1.5 | | *<100* | 0.5 | 1.5 | 2.0 | 134.2 | 6 |
| | mg/l | S2 | | | 20.5 | | *<100* | 20.8 | 20.5 | 4.8 | 23.3 | 7 |
| $N_{NO3}$ | mg/l | S1 | | | | | *<100* | 67.0 | 66.6 | 7.5 | 11.2 | 7 |
| | mg/l | S2 | | | | | *<100* | 587 | 440 | 288 | 65.5 | 10 |
| Org matter | % (w/w) | S1 | | -1.78 | 32.0 | 25 | 24.9 | 32.4 | 32.0 | 3.7 | 11.5 | 11 |
| | % (w/w) | S2 | | 0.29 | 43.7 | 25 | 45.3 | 44.3 | 43.7 | 2.4 | 5.6 | 11 |
| pH | | S1 | | -0.39 | 7.8 | 6,5 | 7.70 | 7.82 | 7.83 | 0.18 | 2.3 | 11 |
| | | S2 | | -0.40 | 5.9 | 8,5 | 5.80 | 5.92 | 5.93 | 0.14 | 2.3 | 10 |

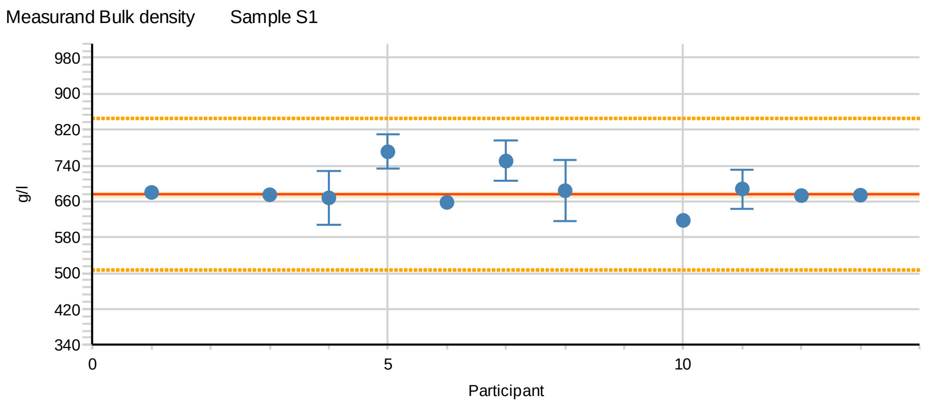
# APPENDIX 4: Results of participants and their uncertainties

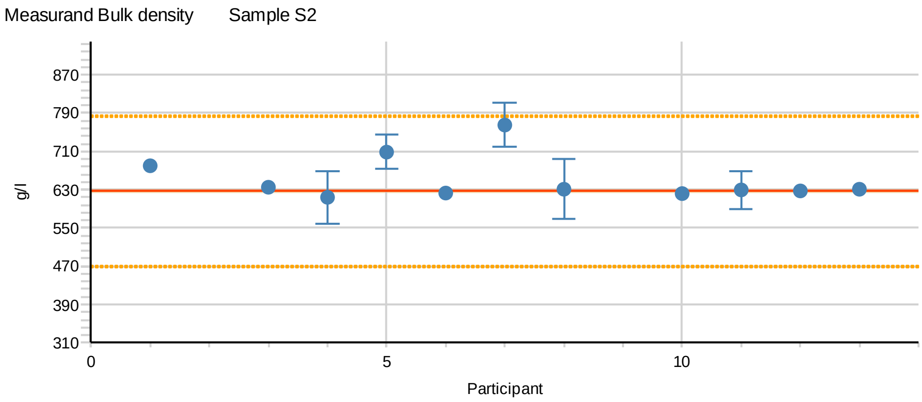
In figures:

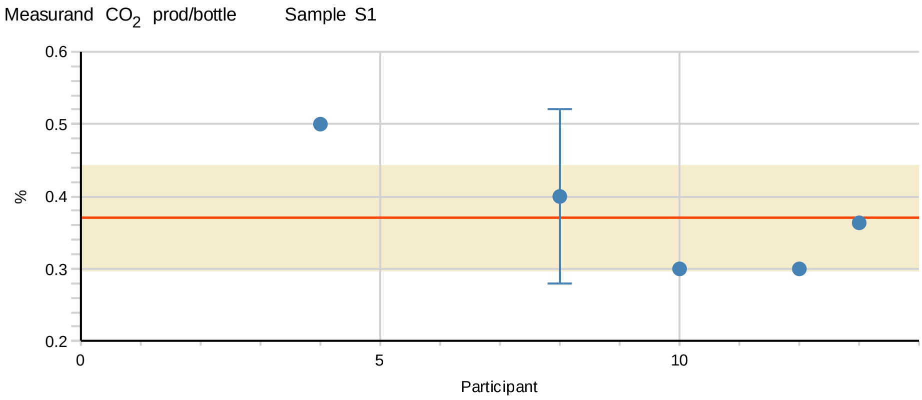
- The dashed lines describe the standard deviation for the proficiency assessment, the red solid line shows the assigned value, the shaded area describes the expanded measurement uncertainty of the assigned value, and the arrow describes the value outside the scale.

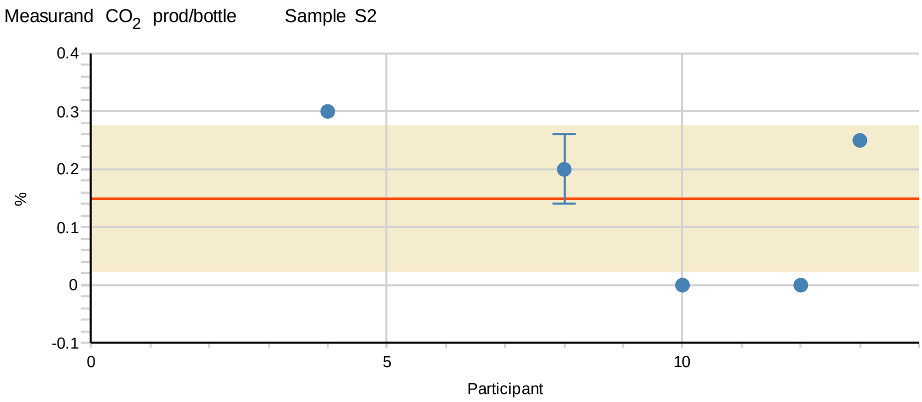


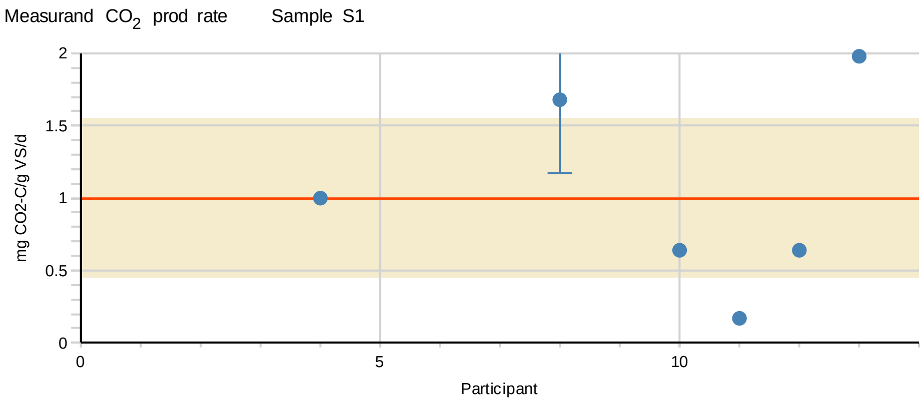



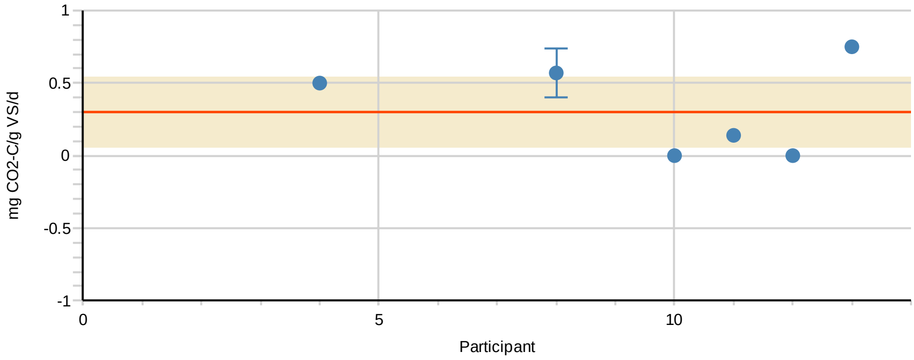

Measurand Bulk density
Sample S2
g/l
870
790
710
630
550
470
390
310
0
5
10
Participant


Measurand $CO_2$ prod/bottle
Sample S1
%
0.6
0.5
0.4
0.3
0.2
0
5
10
Participant

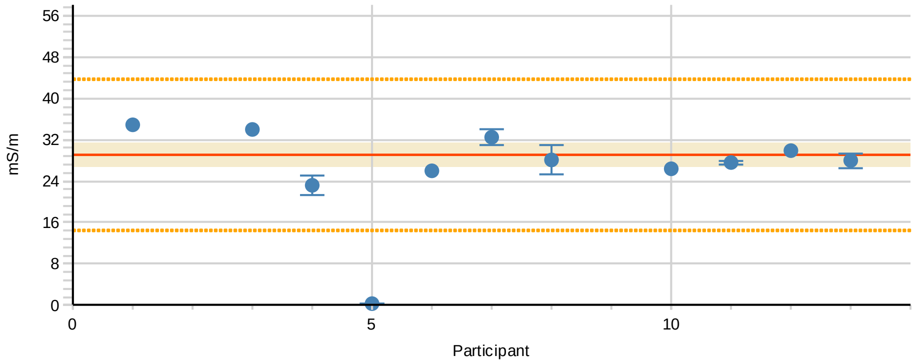

Measurand $CO_2$ prod/bottle
Sample S2
%
0.4
0.3
0.2
0.1
0
-0.1
0
5
10
Participant


Measurand $CO_2$ prod rate
Sample S1
mg CO2-C/g VS/d
2
1.5
1
0.5
0
0
5
10
Participant

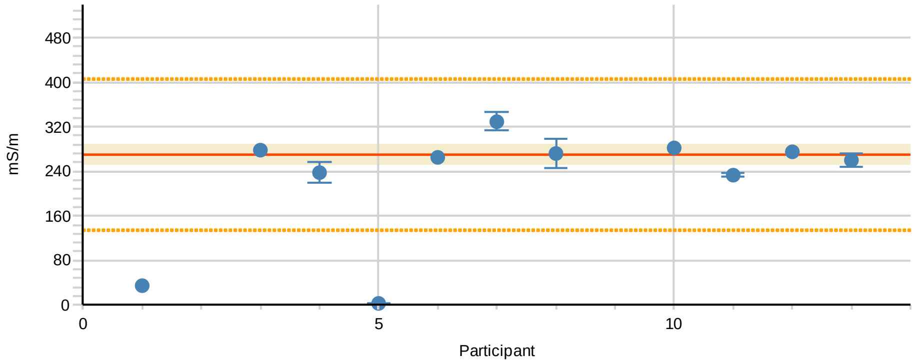
Measurand $CO_2$ prod rate Sample S2



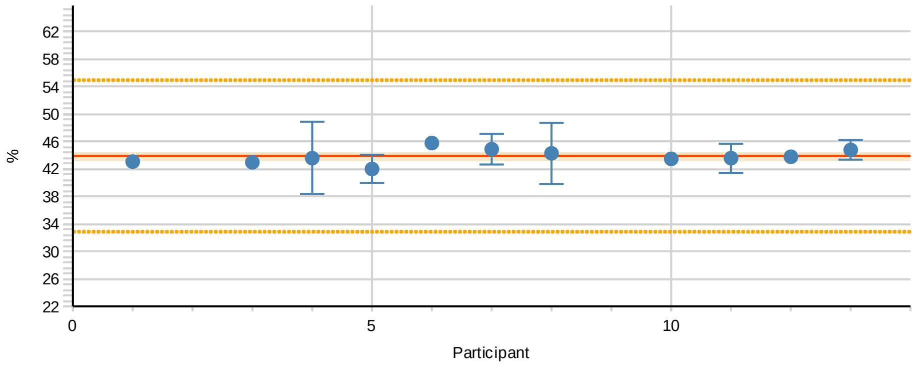

Measurand Cond 25 Sample S1



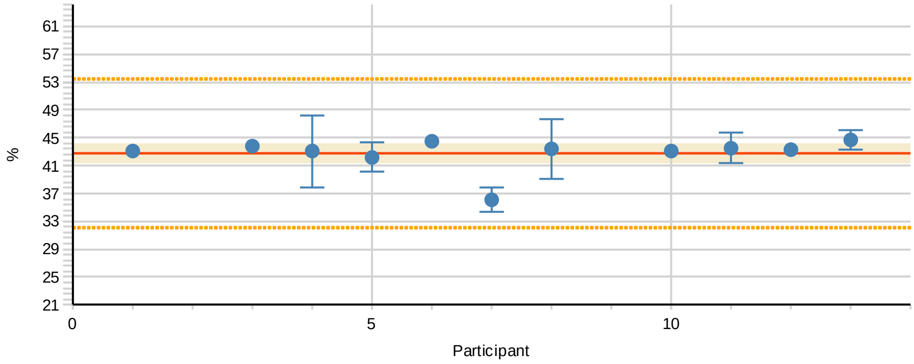

Measurand Cond 25 Sample S2



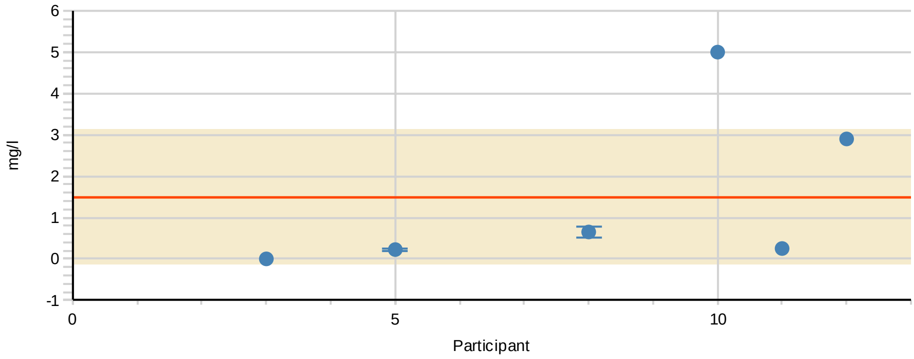

Measurand Dry matter Sample S1



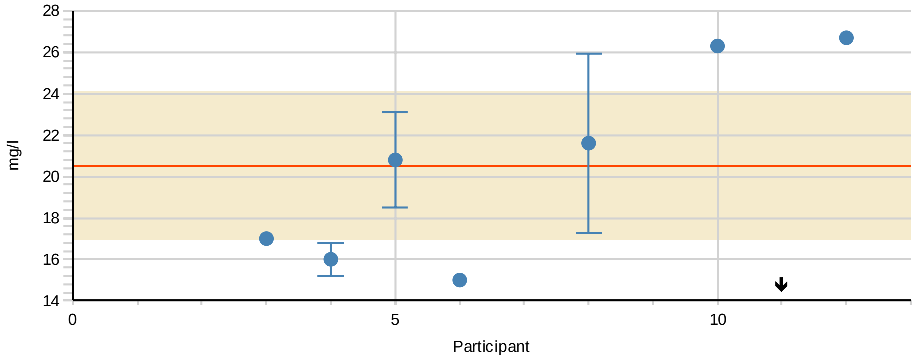
Measurand Dry matter Sample S2



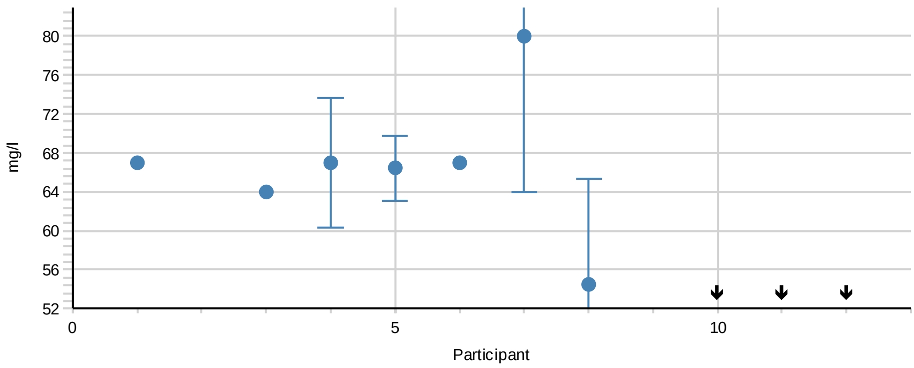

Measurand $N_{NH4}$ Sample S1



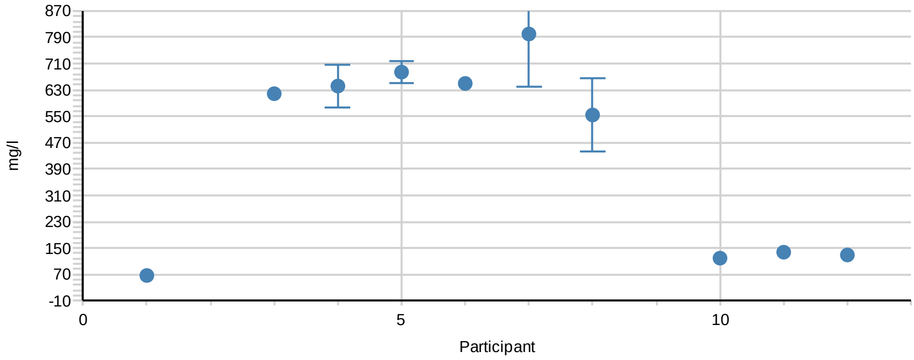

Measurand $N_{NH4}$ Sample S2



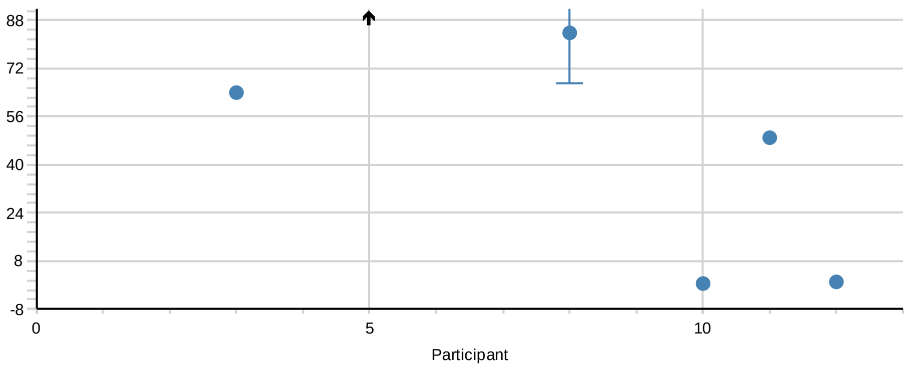

Measurand $N_{NO3}$ Sample S1



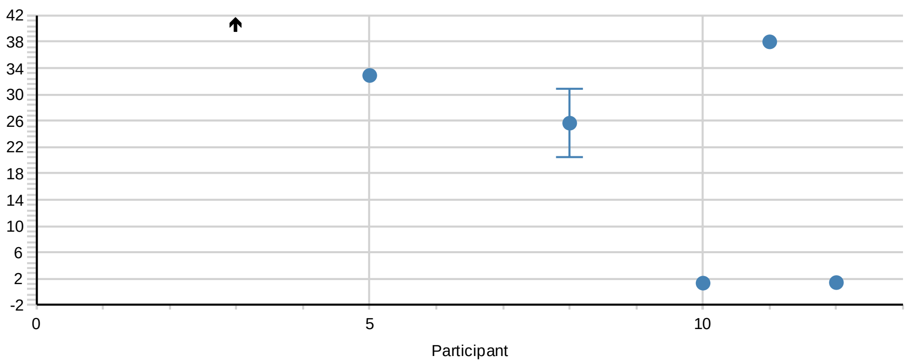
Measurand $N_{NO3}$ Sample S2



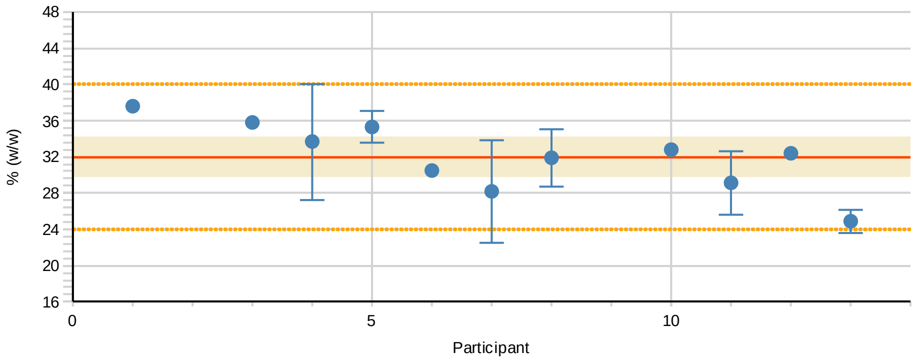

Measurand $N_{(NO3/NH4)}$ Sample S1



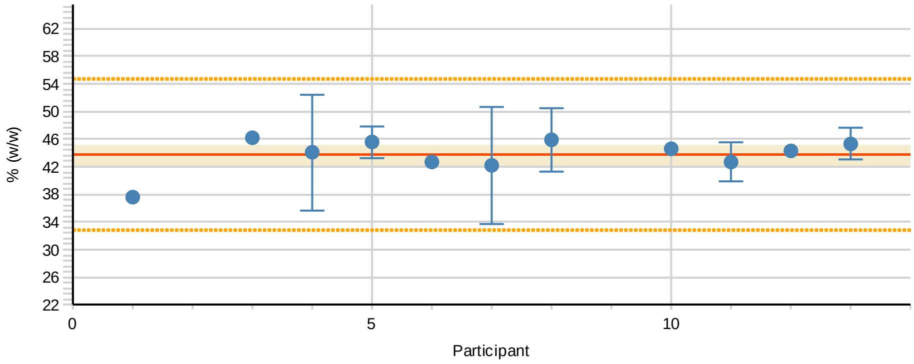

Measurand $N_{(NO3/NH4)}$ Sample S2



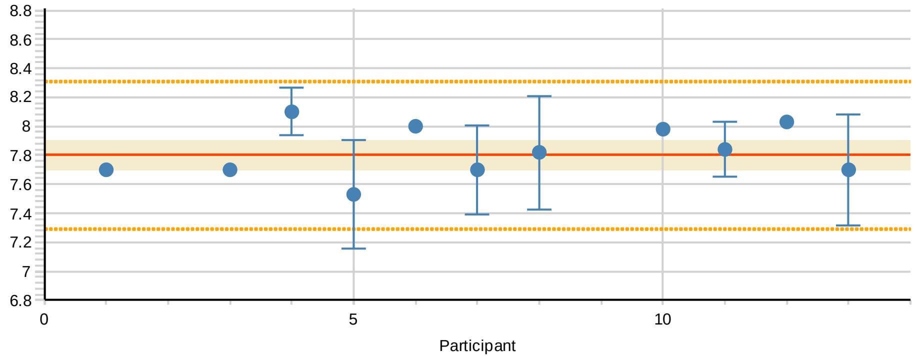

Measurand Org matter Sample S1



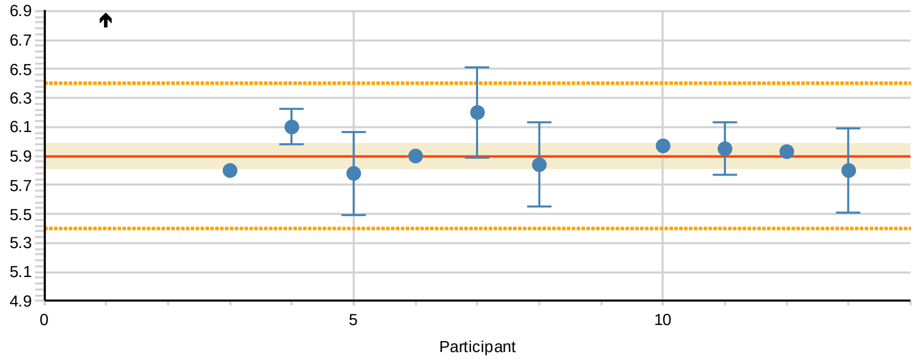
Measurand Org matter Sample S2



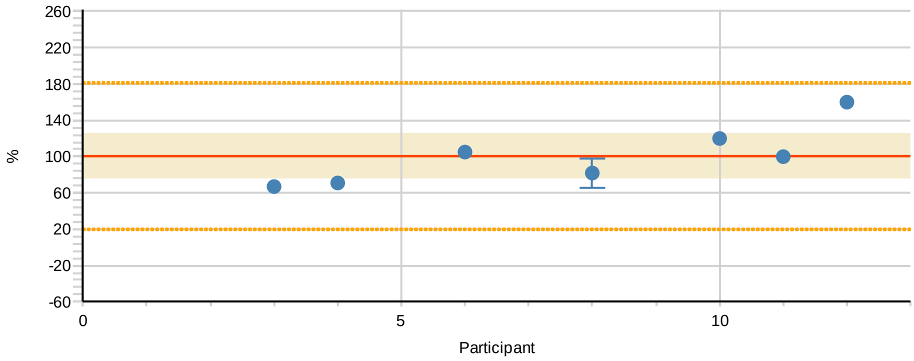

Measurand pH Sample S1



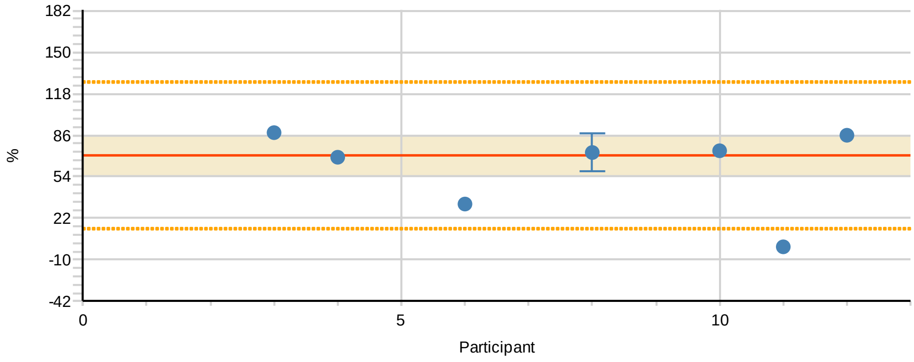

Measurand pH Sample S2



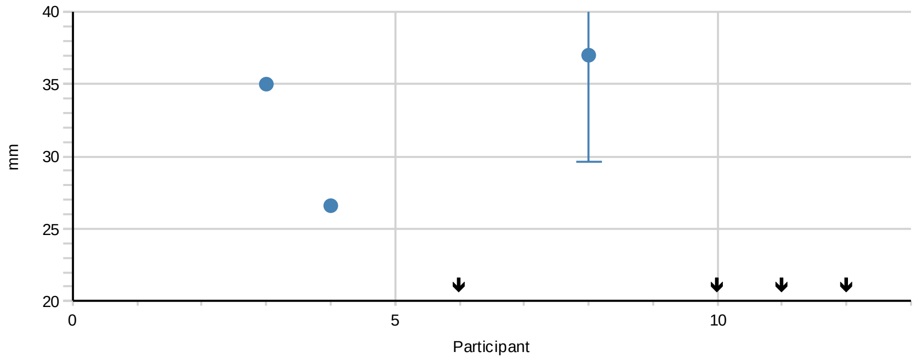

Measurand RI Sample S1



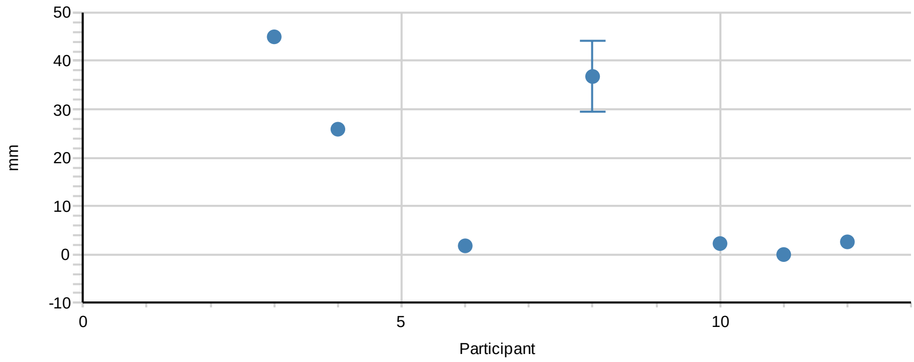
Measurand RI Sample S2



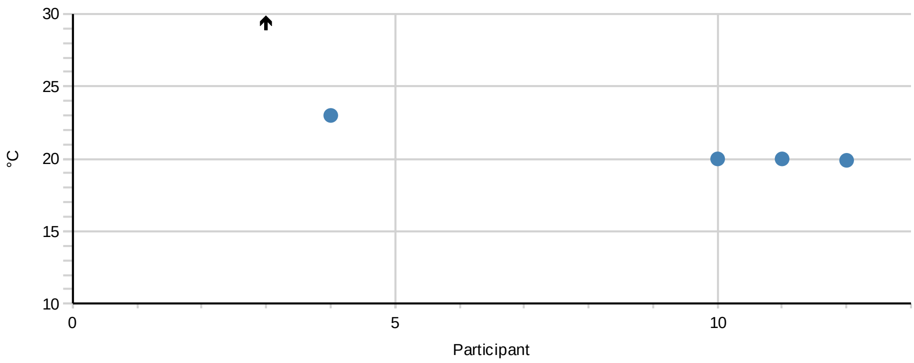

Measurand Rooth length Sample S1

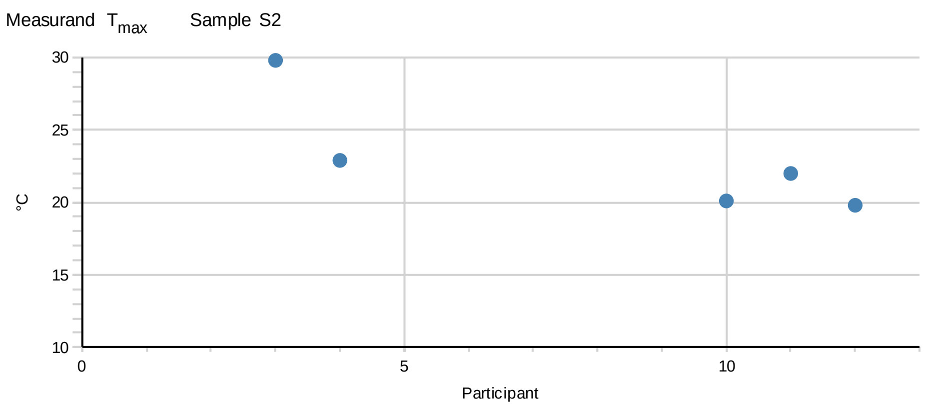



Measurand Rooth length Sample S2




Measurand $T_{max}$ Sample S1




Measurand $T_{max}$ Sample S2
°C
30
25
20
15
10
0
5
10
Participant

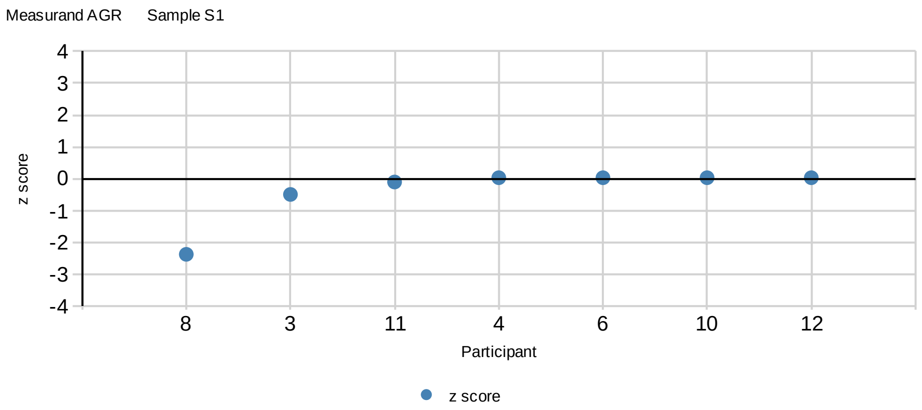
# APPENDIX 5: Summary of the z scores

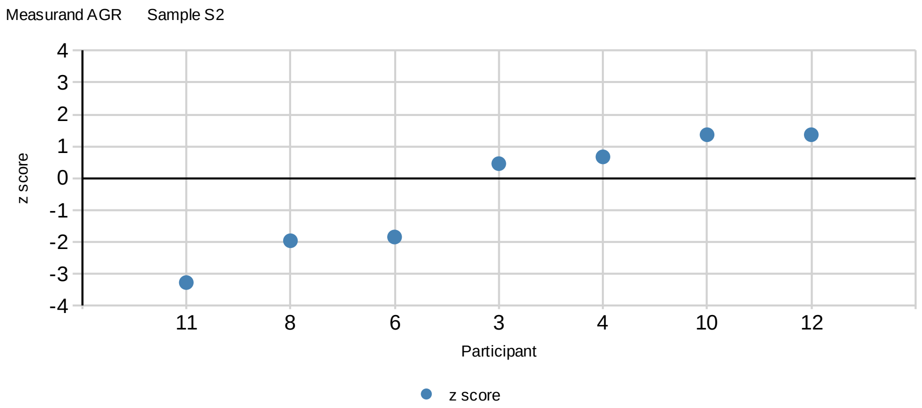
| Measurand | Sample | 1 | 3 | 4 | 5 | 6 | 7 | 8 | 10 | 11 | 12 | 13 | % |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| AGR | S1 | . | S | S | . | S | . | q | S | S | S | . | 85.7 |
| | S2 | . | S | S | . | S | . | S | S | u | S | . | 85.7 |
| Bulk density | S1 | S | S | S | S | S | S | S | S | S | S | S | 100 |
| | S2 | S | S | S | S | S | S | S | S | S | S | S | 100 |
| Cond 25 | S1 | S | S | S | u | S | S | S | S | S | S | S | 90.9 |
| | S2 | u | S | S | u | S | S | S | S | S | S | S | 81.8 |
| Dry matter | S1 | S | S | S | S | S | S | S | S | S | S | S | 100 |
| | S2 | S | S | S | S | S | S | S | S | S | S | S | 100 |
| Org matter | S1 | S | S | S | S | S | S | S | S | S | S | S | 100 |
| | S2 | S | S | S | S | S | S | S | S | S | S | S | 100 |
| pH | S1 | S | S | S | S | S | S | S | S | S | S | S | 100 |
| | S2 | U | S | S | S | S | S | S | S | S | S | S | 90.9 |
| RI | S1 | . | S | S | . | S | . | S | S | S | S | . | 100 |
| | S2 | . | S | S | . | S | . | S | S | q | S | . | 85.7 |
| % | | 80 | 100 | 100 | 80 | 100 | 100 | 93 | 100 | 86 | 100 | 100 | |
| accredited | | 2 | | 10 | | 10 | 10 | | 10 | 10 | 10 | | |

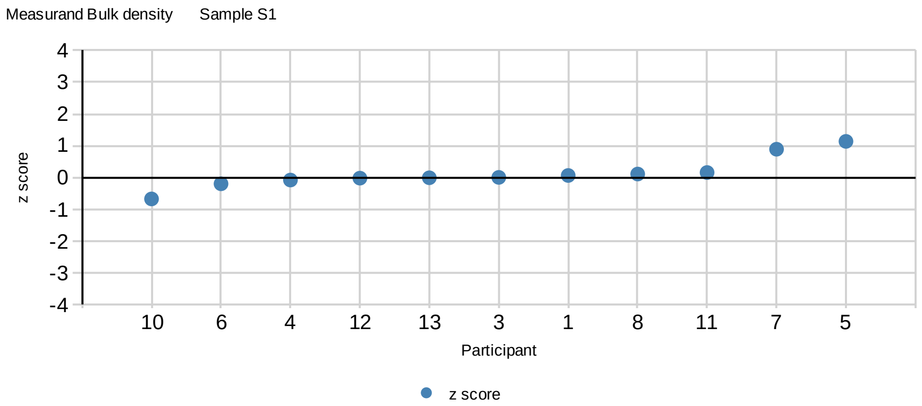
**S - satisfactory (-2 ≤ z ≤ 2), Q - questionable (2 < z < 3), q - questionable (-3 < z < -2),**
**U - unsatisfactory (z ≥ 3), and u - unsatisfactory (z ≤ -3), respectively**
**bold - accredited, italics - non-accredited, normal - other**
**% - percentage of satisfactory results**

Totally satisfactory, % in all: 95 % in accredited: 100 % in non-accredited: 91

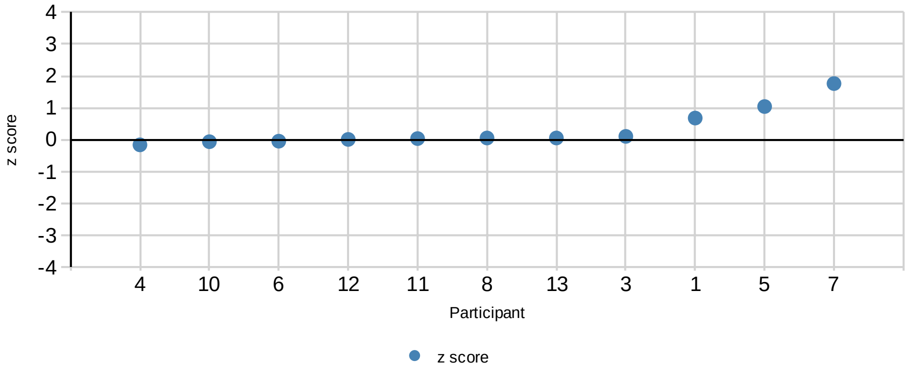
# APPENDIX 6: z scores in ascending order



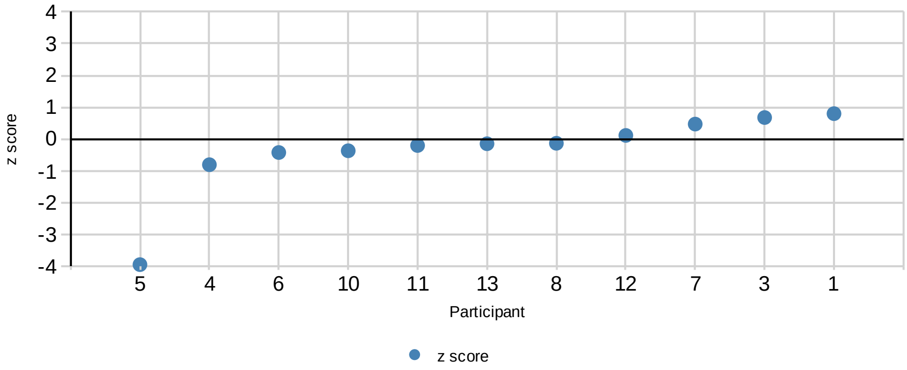



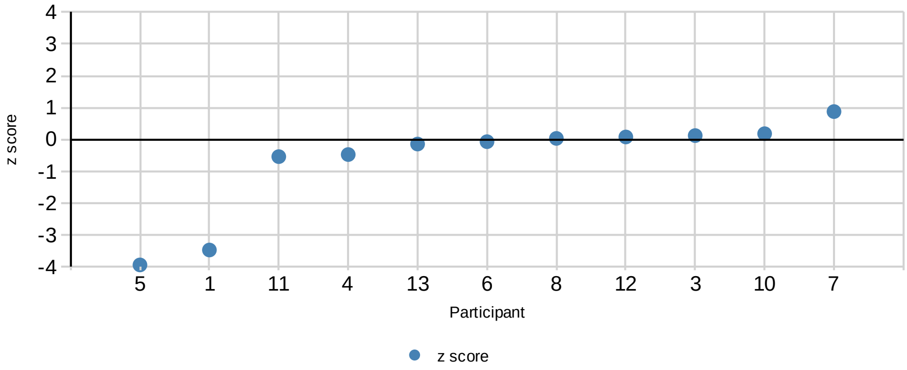
Measurand Bulk density Sample S2



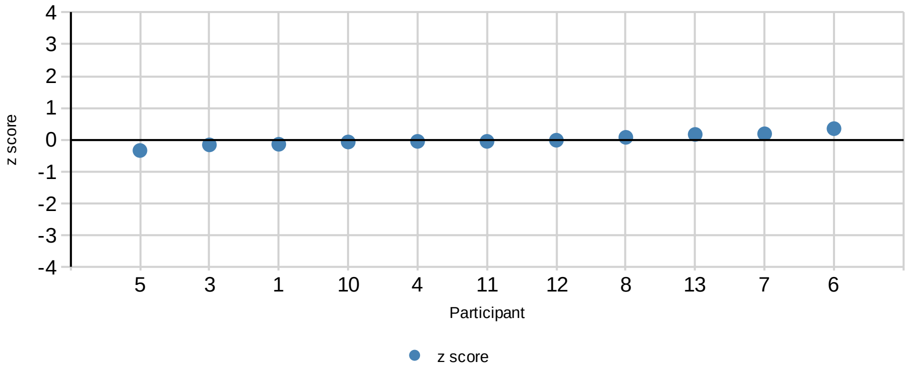

Measurand Cond 25 Sample S1

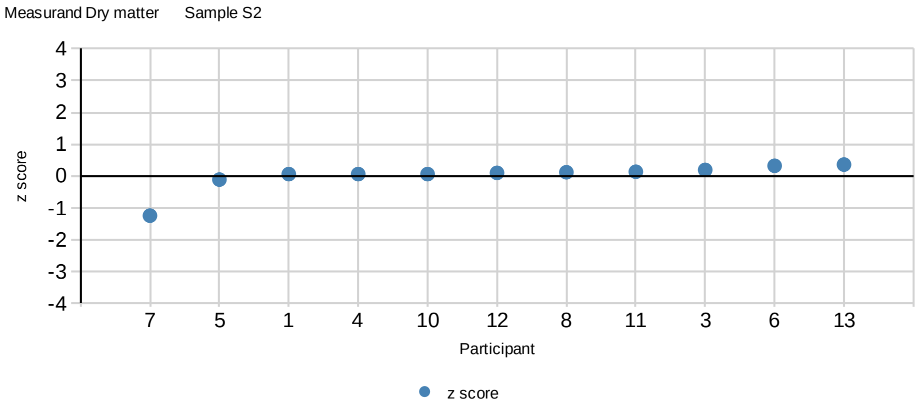


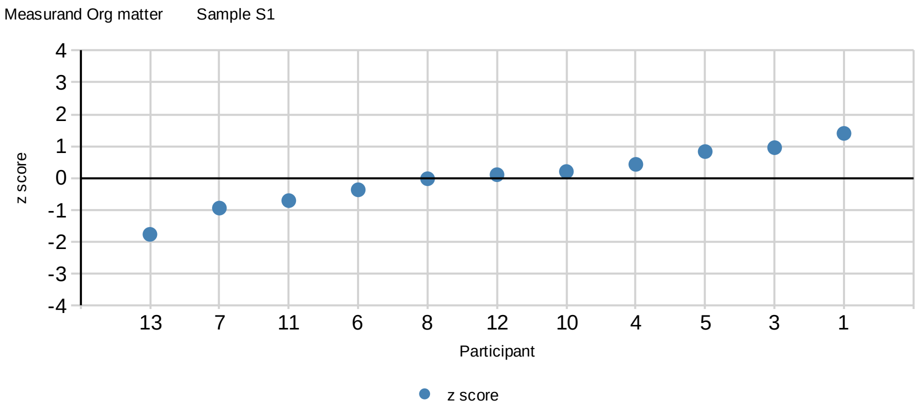

Measurand Cond 25 Sample S2

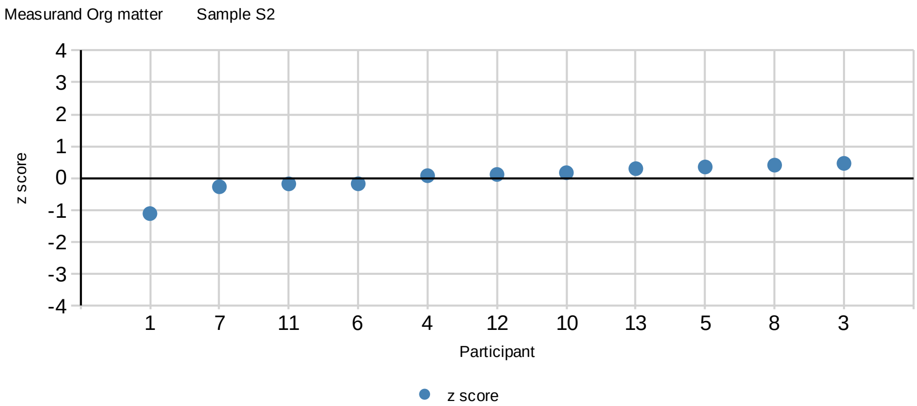


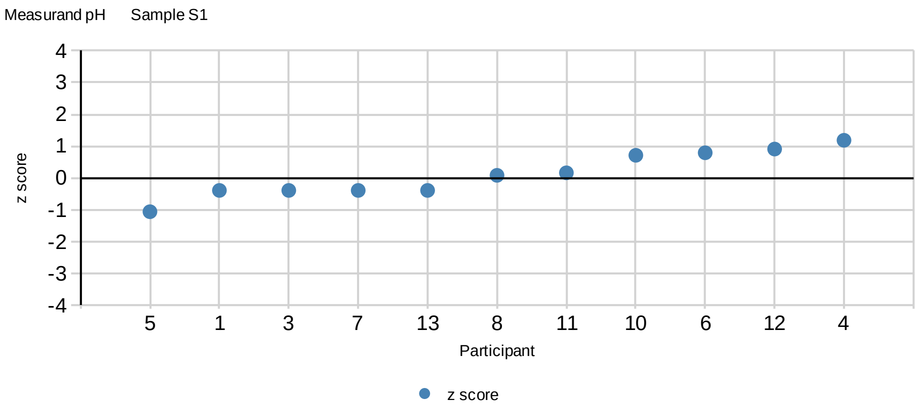

Measurand Dry matter Sample S1



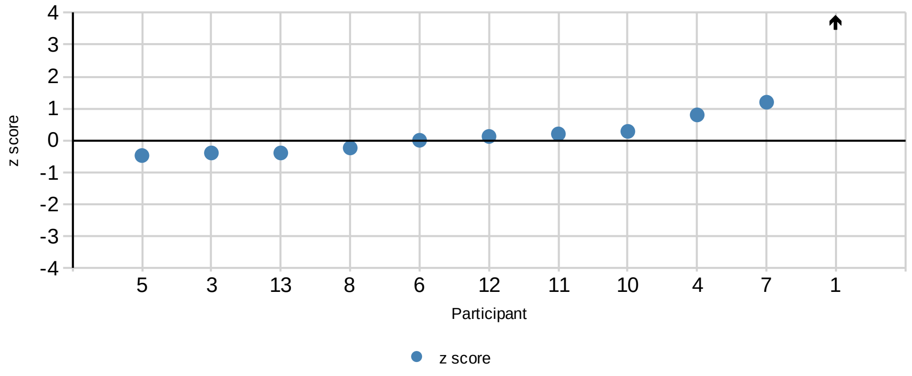

Measurand Dry matter
Sample S2
z score
4
3
2
1
0
-1
-2
-3
-4
7
5
1
4
10
12
8
11
3
6
13
Participant
z score


Measurand Org matter
Sample S1
z score
4
3
2
1
0
-1
-2
-3
-4
13
7
11
6
8
12
10
4
5
3
1
Participant
z score

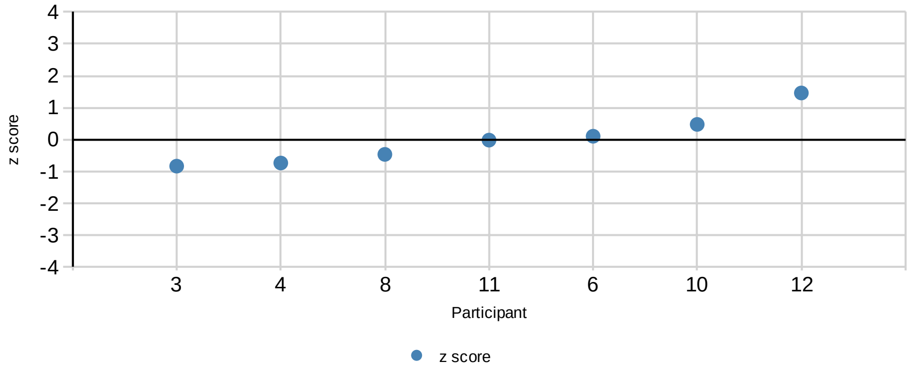

Measurand Org matter
Sample S2
z score
4
3
2
1
0
-1
-2
-3
-4
1
7
11
6
4
12
10
13
5
8
3
Participant
z score


Measurand pH
Sample S1
z score
4
3
2
1
0
-1
-2
-3
-4
5
1
3
7
13
8
11
10
6
12
4
Participant
z score

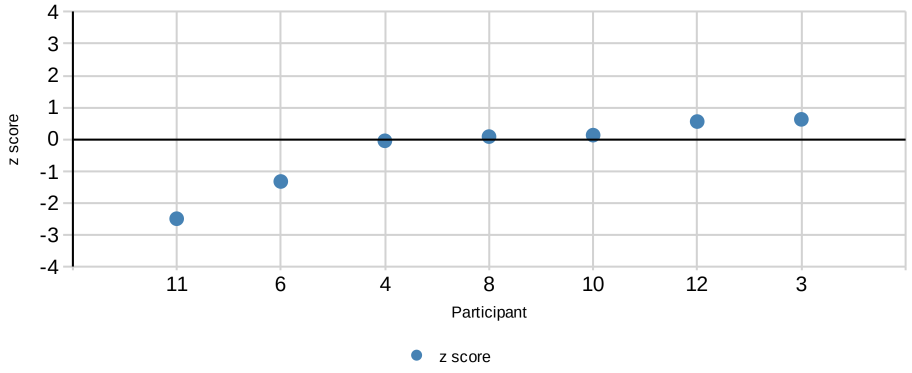
Measurand pH Sample S2




Measurand RI Sample S1

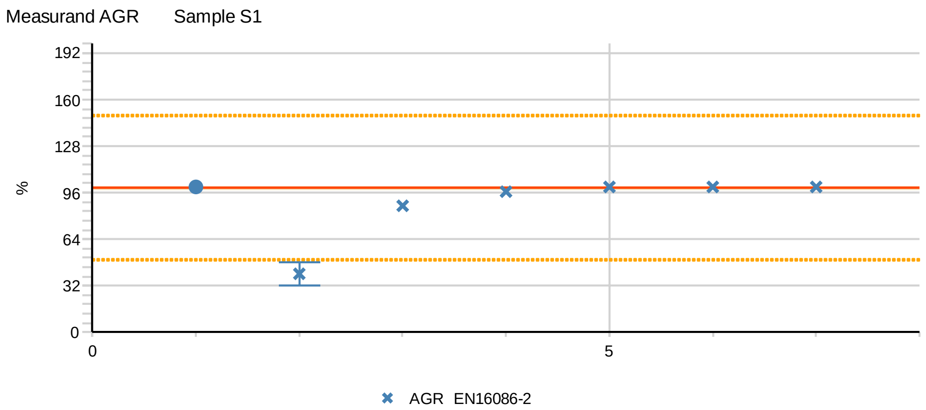


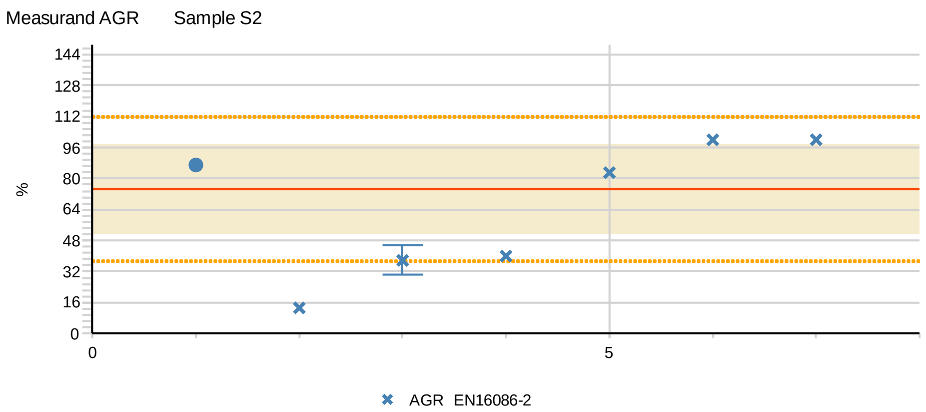

Measurand RI Sample S2

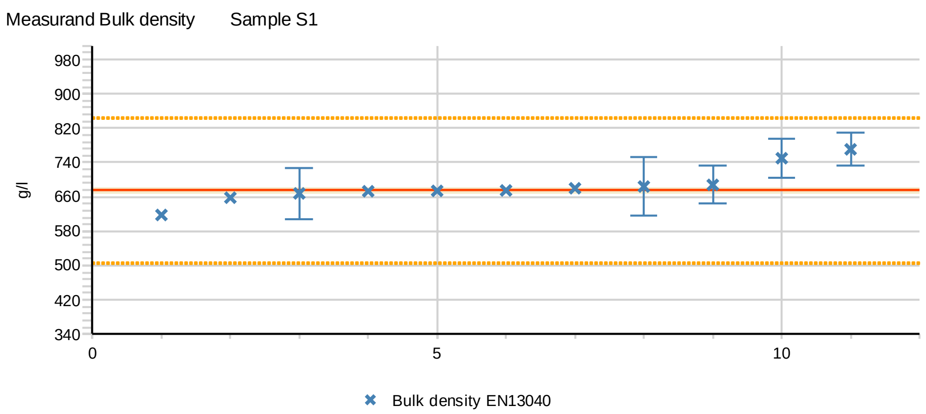


# APPENDIX 7: Results grouped according to the methods

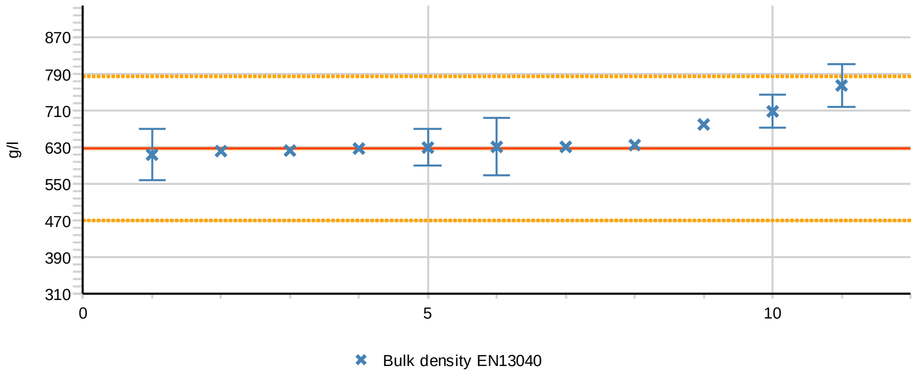
The explanations for the figures are described in the Appendix 4.



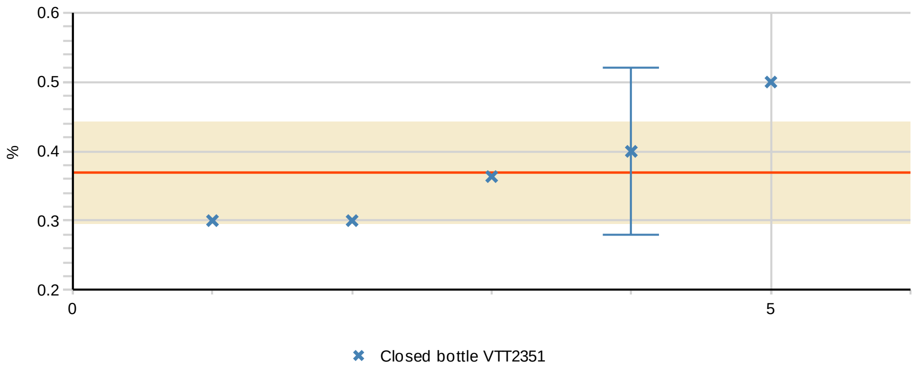



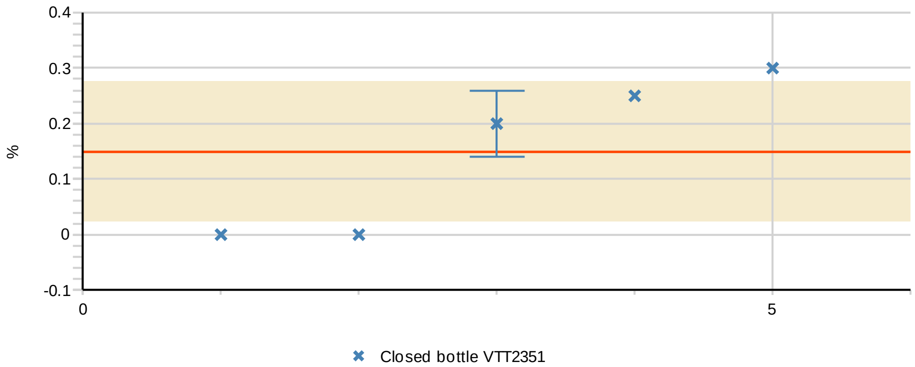
Measurand Bulk density  Sample S2



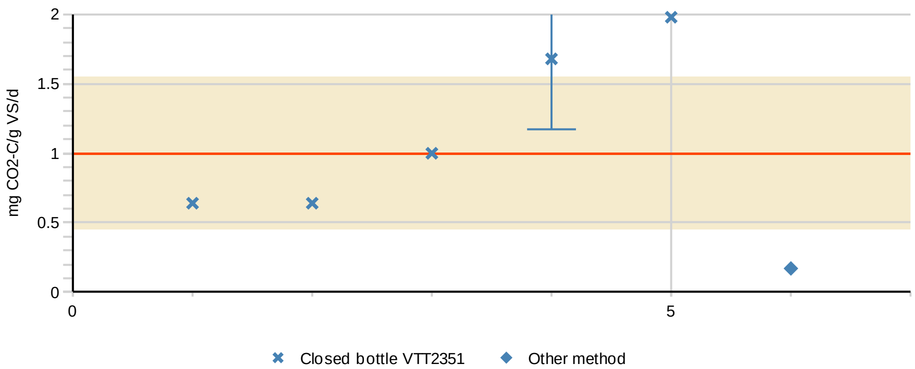

Measurand $CO_2$ prod/bottle  Sample S1



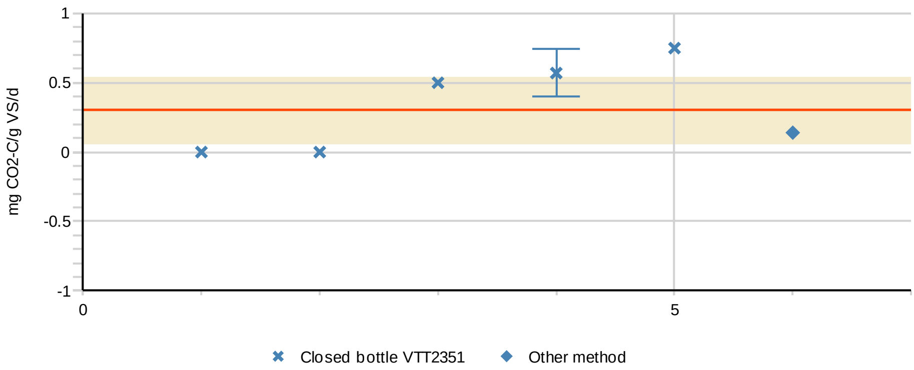

Measurand $CO_2$ prod/bottle  Sample S2



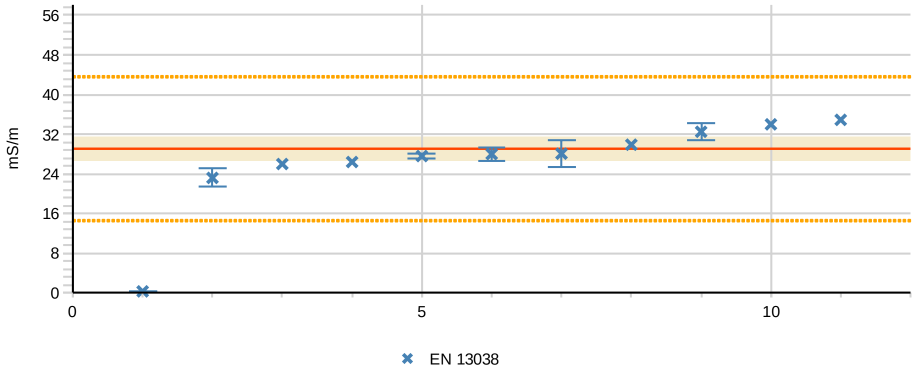

Measurand $CO_2$ prod rate  Sample S1



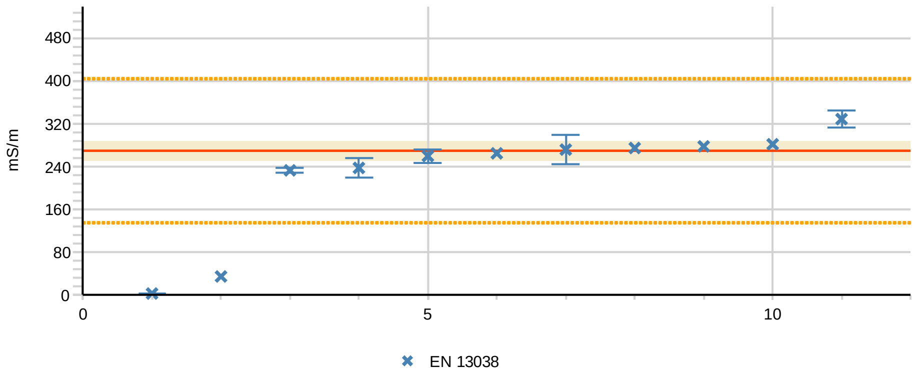
Measurand $CO_2$ prod rate Sample S2



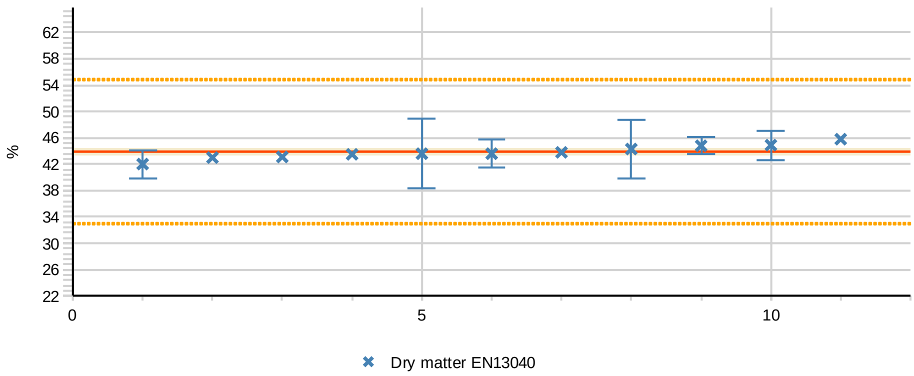

Measurand Cond 25 Sample S1



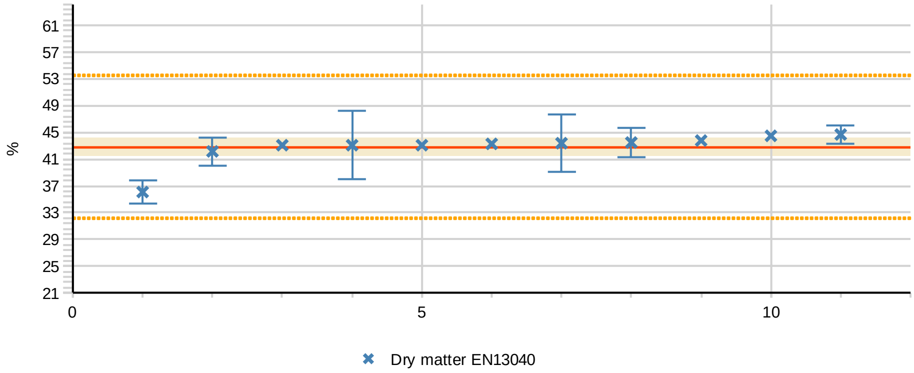

Measurand Cond 25 Sample S2



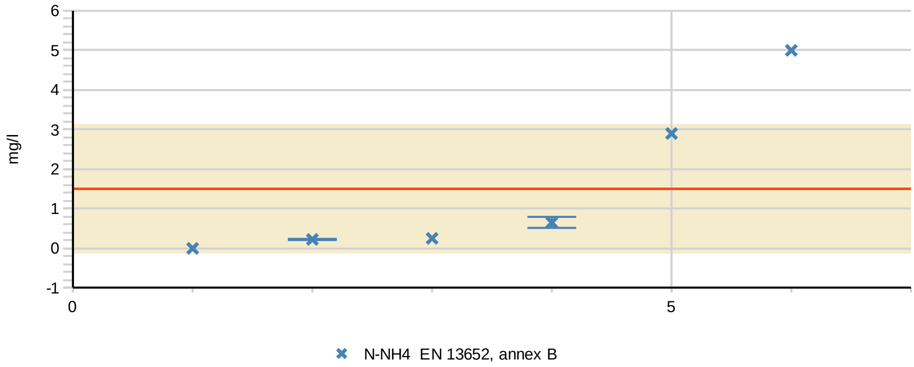

Measurand Dry matter Sample S1



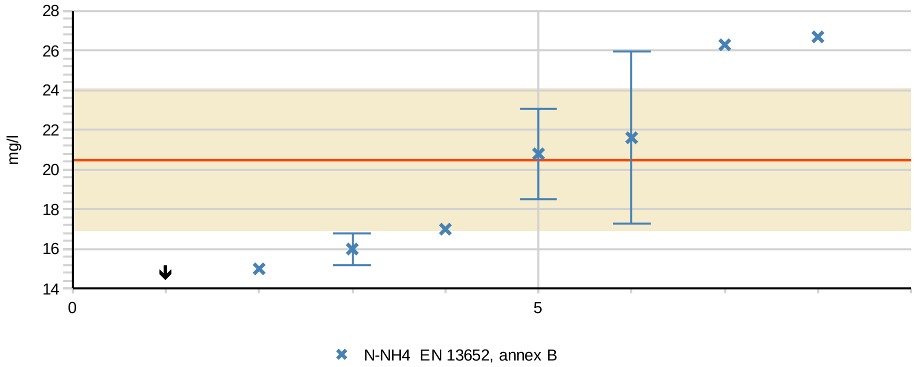
Measurand Dry matter Sample S2



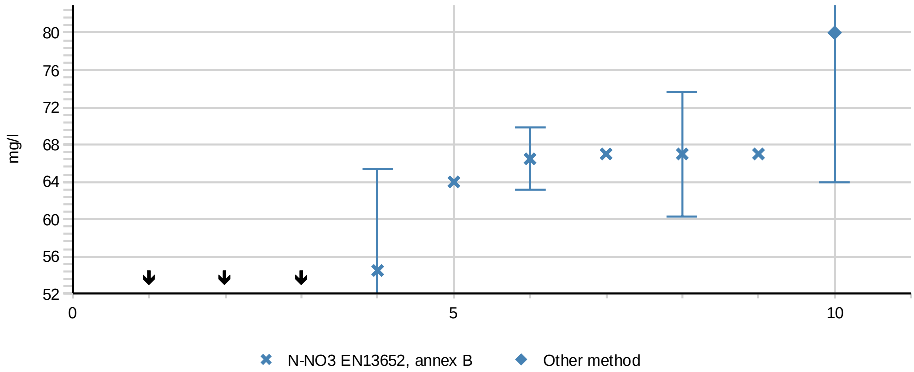

Measurand $N_{NH4}$ Sample S1



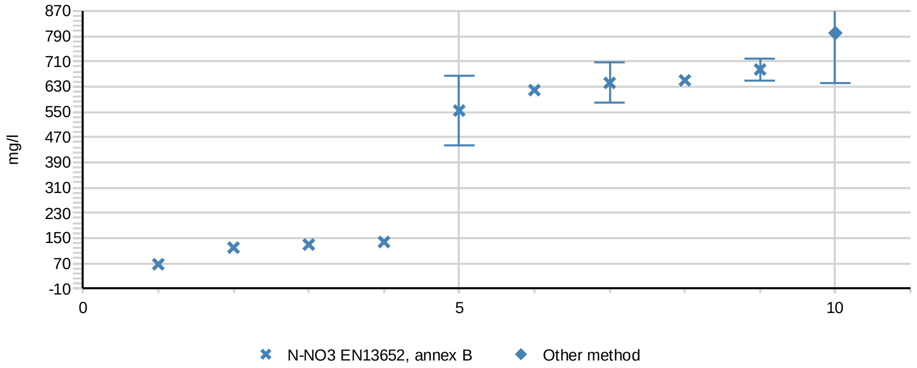

Measurand $N_{NH4}$ Sample S2



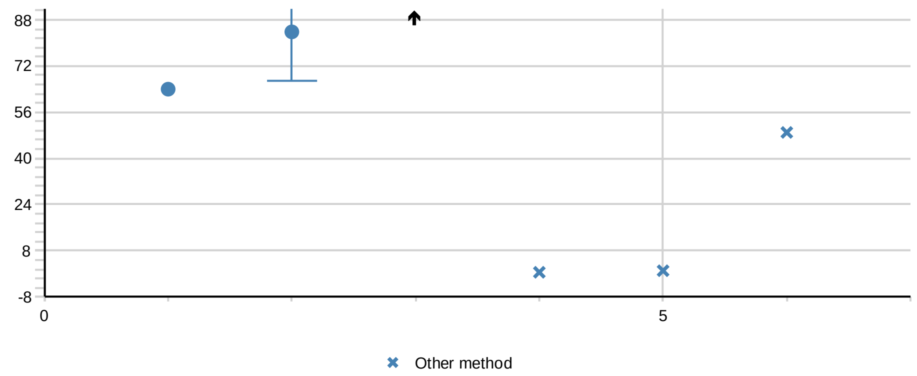

Measurand $N_{NO3}$ Sample S1



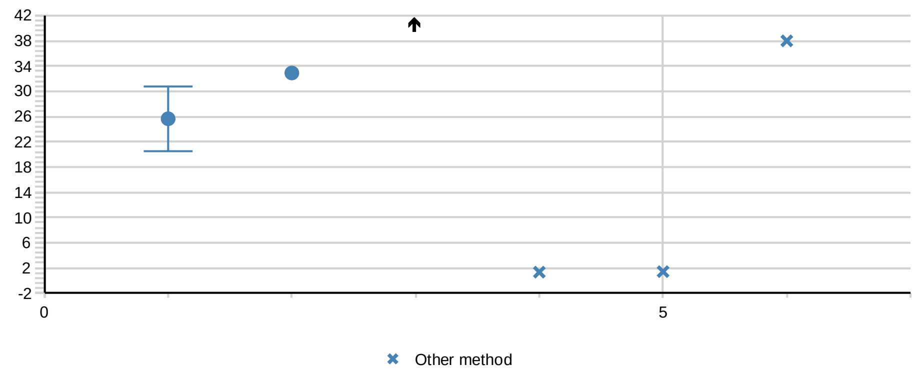
Measurand $N_{NO3}$ Sample S2



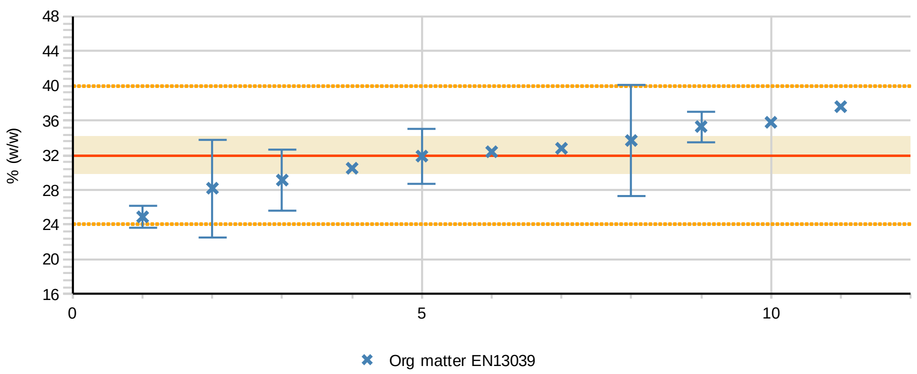

Measurand $N_{(NO3/NH4)}$ Sample S1



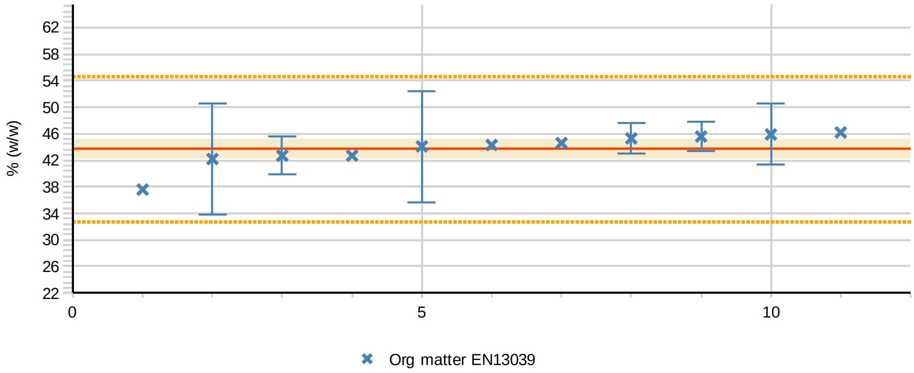

Measurand $N_{(NO3/NH4)}$ Sample S2



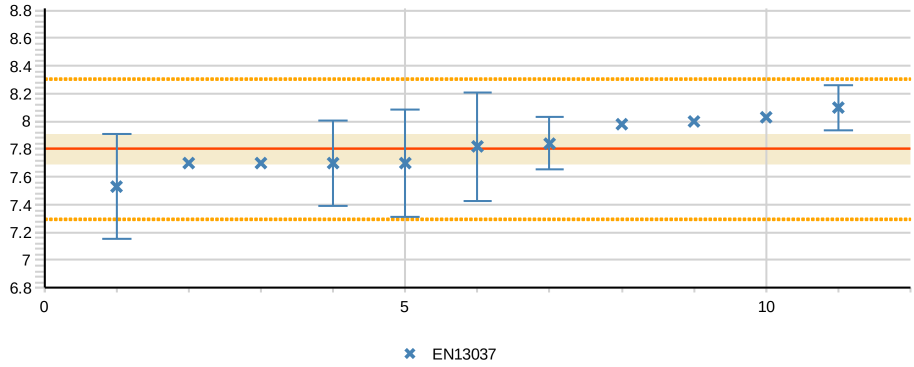

Measurand Org matter Sample S1



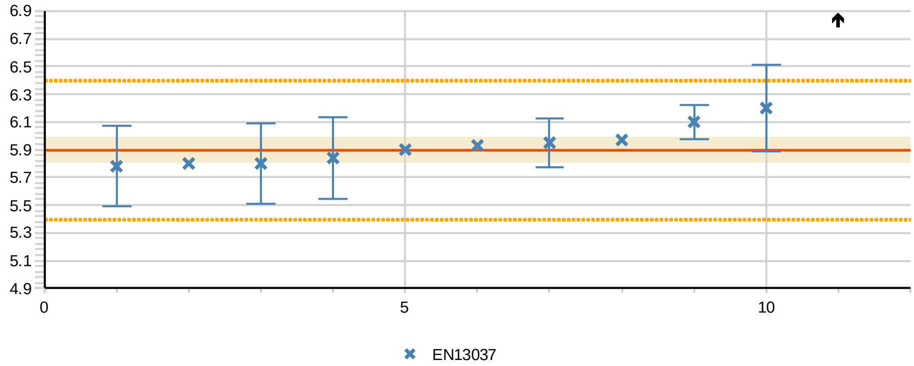
Measurand Org matter      Sample S2



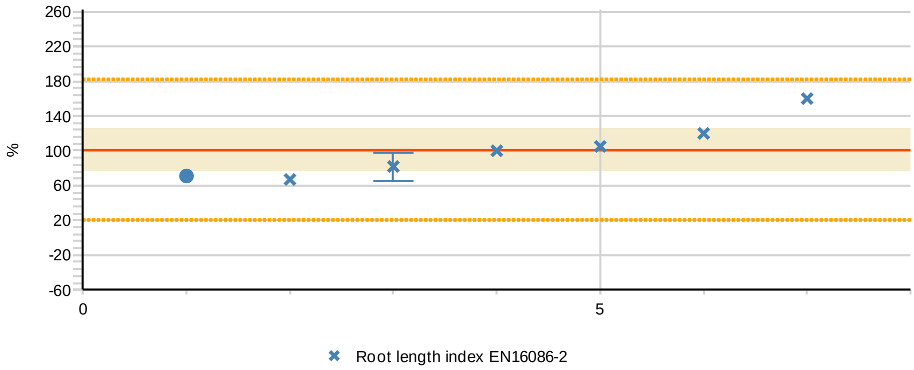

Measurand pH      Sample S1



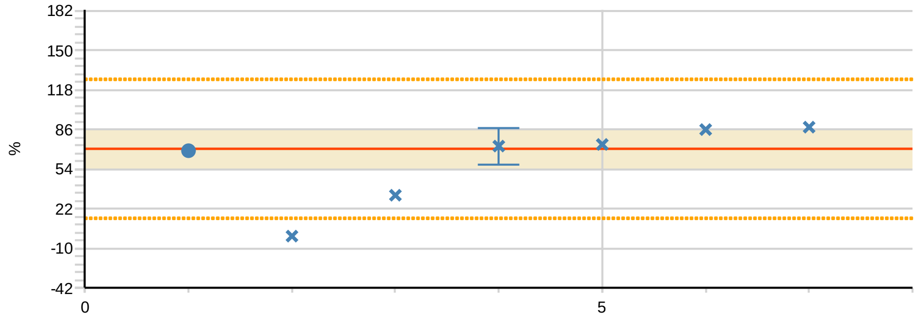

Measurand pH      Sample S2




Measurand RI      Sample S1

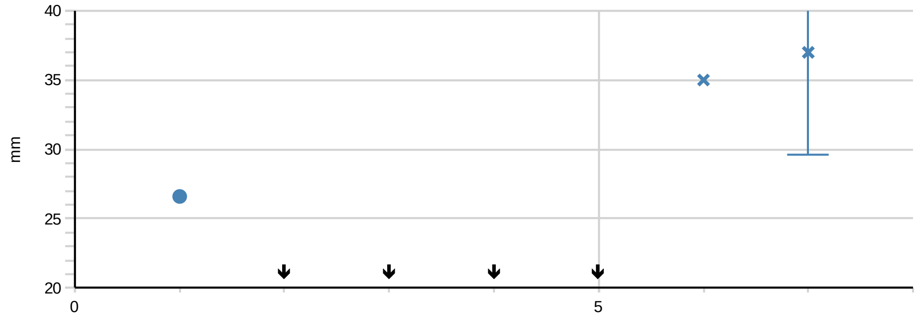


Measurand RI Sample S2



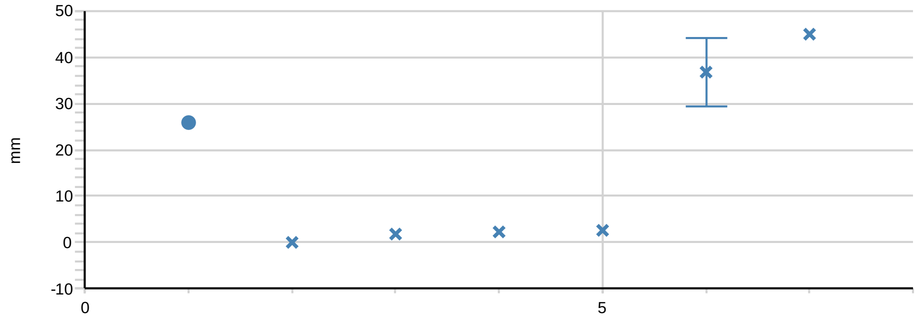

Root length index EN16086-2

Measurand Rooth length Sample S1



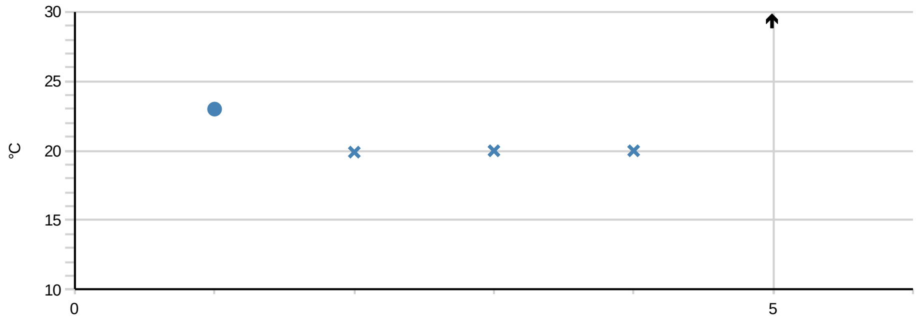

Rooth length mm EN16086-2

Measurand Rooth length Sample S2

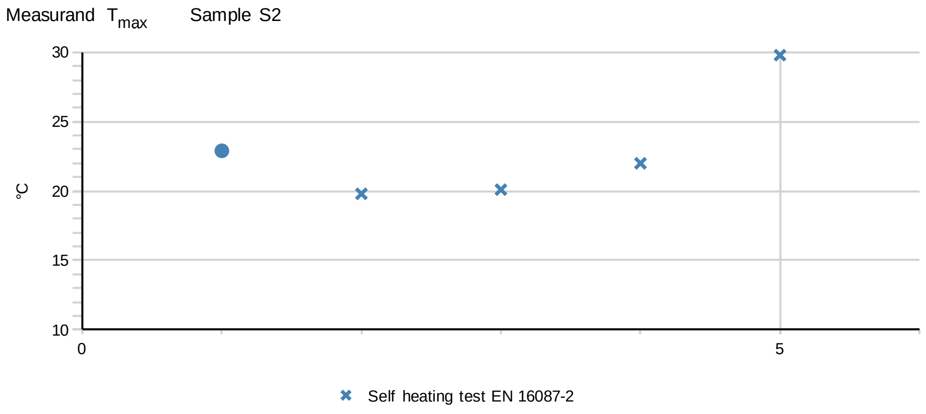



Rooth length mm EN16086-2

Measurand $T_{max}$ Sample S1

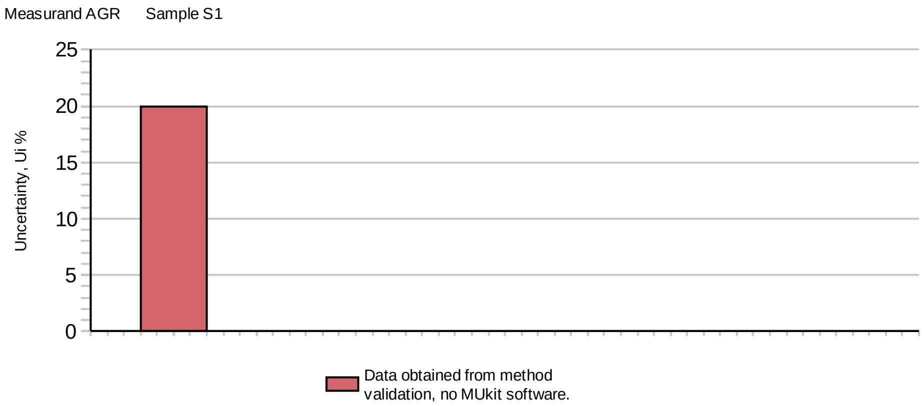


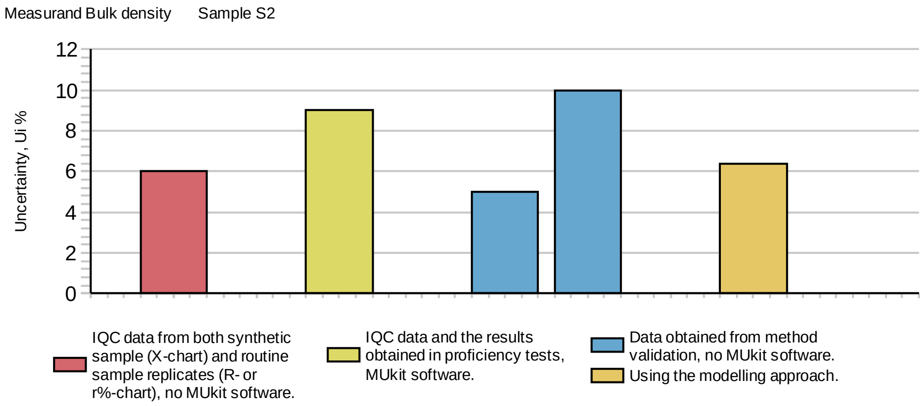

Self heating test EN 16087-2

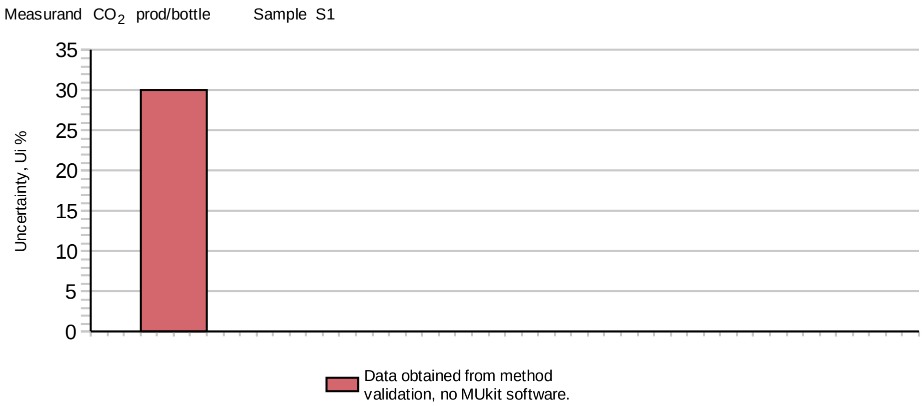

Measurand T max Sample S2
30
25
20
15
10
°C
0
5
Self heating test EN 16087-2

## APPENDIX 8: Estimation of the measurement uncertainties reported by the participants

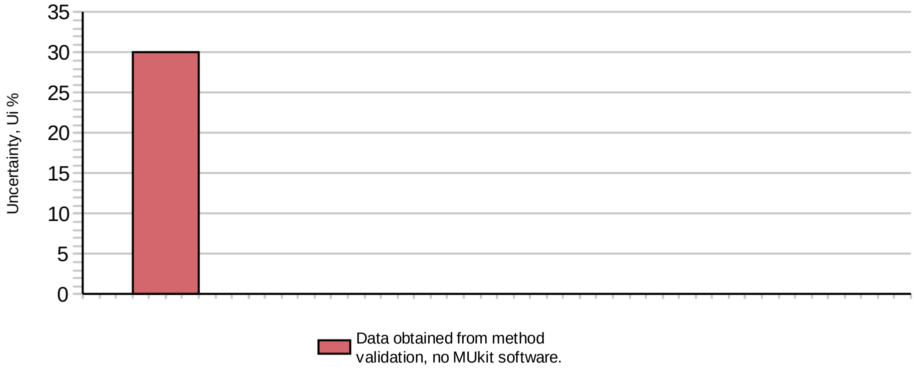
In figures, the presented expanded measurement uncertainties are grouped according to the method of estimation at 95 % confidence level (*k*=2). The expanded uncertainties were estimated mainly by using the internal quality control (IQC) data. The used procedures in figures below are distinguished e.g. between using or not using the MUkit software for uncertainty estimation [16, 17] or using a modelling approach based [18, 19].



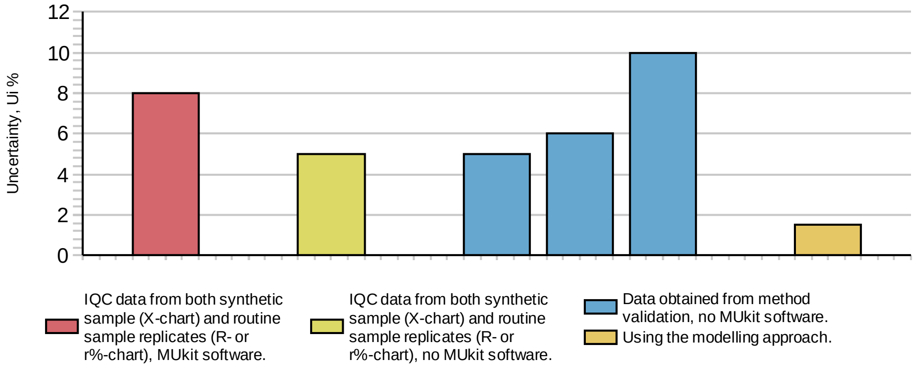



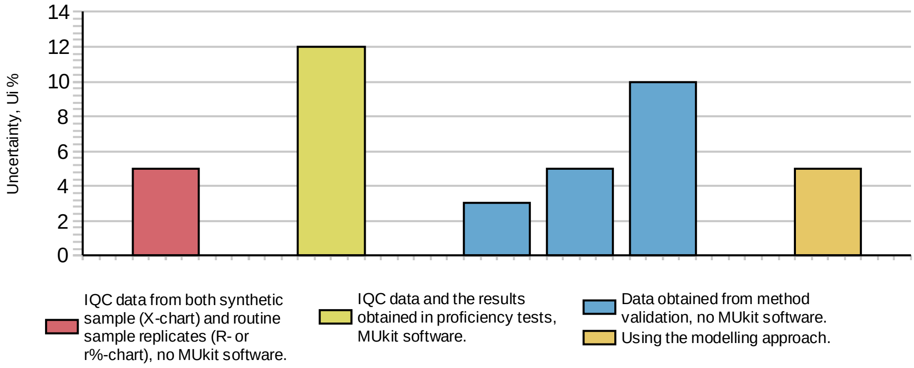
Measurand $CO_2$ prod rate Sample S2



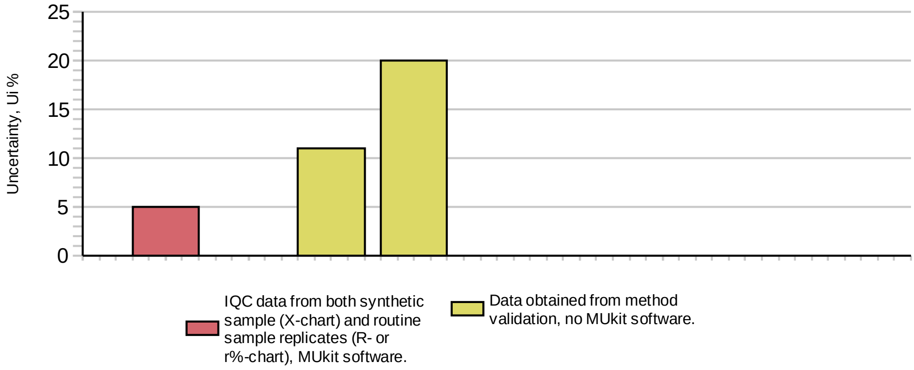

Measurand Cond 25 Sample S1



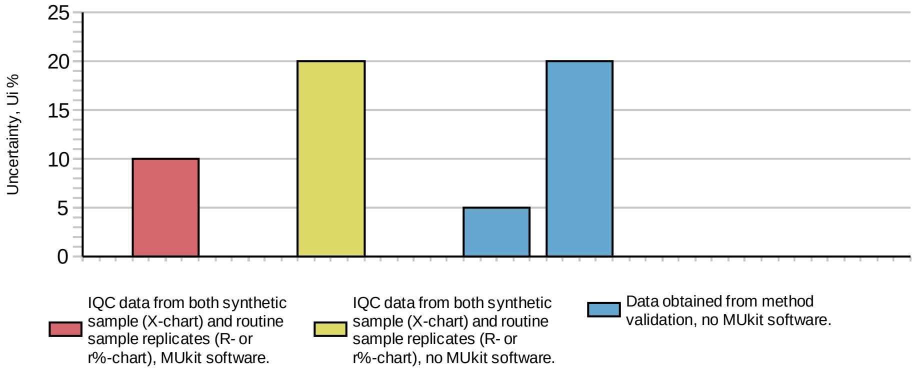

Measurand Dry matter Sample S2



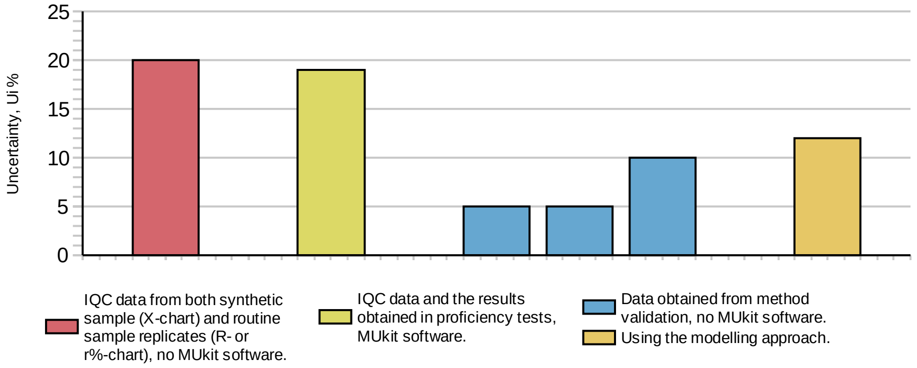

Measurand $N_{NH4}$ Sample S1



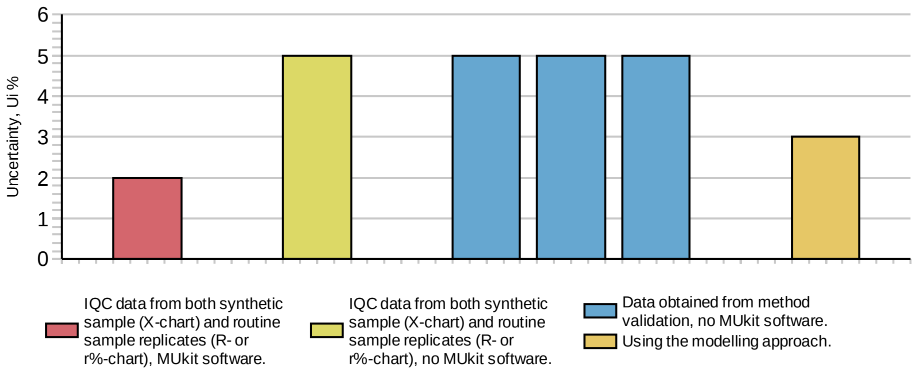
Measurand $N_{NO3}$ Sample S1



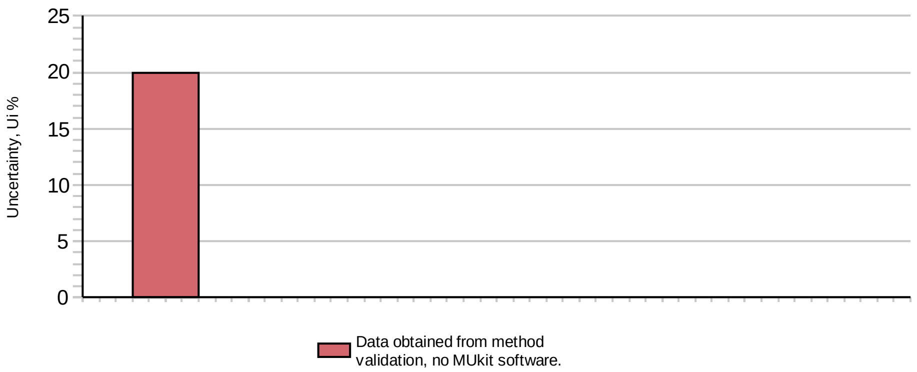

Measurand Org matter Sample S1




Measurand pH Sample S2




Measurand RI Sample S1



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