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Finnish Environment Institute

SUOMEN YMPÄRISTÖKESKUKSEN RAPORTTEJA
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CONTENT

APPENDICES

1 INTRODUCTION

Evira carried out this proficiency test for determining the effect of soil improvers on germination and root growth of cress, sample CO_2-production or oxygen uptake and dry weight and organic matter content. These tests are used for determining phytotoxicity and aerobic biological activity i.e. maturity-level of soil improvers. The proficiency test was carried out in accordance with the international guidelines ISO/IEC 17043 (ISO, 2010), ISO 13528 (ISO, 2005) and IUPAC Technical report (Thompson et al., 2006).

2 ORGANIZING THE PROFICIENCY TEST

2.1 Responsibilities

This proficiency test was planned and arranged by senior researcher Liisa Maunuksela and laboratory assistant Leena Kaarla at the Finnish Food Safety Authority Evira in collaboration with Proftest at Finnish Environment Institute (SYKE), where the expert on proficiency testing was Katarina Björklöf. Proftest SYKE has been accredited by the Finnish Accreditation Service as a proficiency testing provider (PT01, ISO/IEC 17043, www.finas.fi). The field of the present test is not included in the accreditation scope. The homogeneity testing of the samples as well as the statistical treatment, including calculation of z-scores of the data set, was done by Proftest. Further, the layout of the report was done by Markku Ilmakunnas (SYKE).

2.2 Participants

In this proficiency test in total 11 laboratories participated, from which six were from Finland and five from other European countries (Table 1). The organizer has code number three (analyses performed at the target date 19.11.2012) and four (analyses performed 5 days prior, 14.11.2012) in the result tables. Only the organizer and participant number 10 were accredited.

Table 1. Participants in the proficiency test.

Austria	Laboratory Austrian Agency for Health and Food safety, Vienna
Germany	LUFA Nord-West, Oldenburg
Germany	University of Applied Science Weihenstephan-Triesdorf, Freising
Ireland	Bord na Móna, Kildare
Finland	Metropolilab Oy, Helsinki
	Viljavuuspalvelu Oy, Mikkeli
	Maa- ja elintarviketalouden tutkimuskeskus MTT, Jokioinen
	Teknologian tutkimuskeskus VTT, Espoo
	Novalab Oy, Karkkila
	Elintarviketurvallisuusvirasto Evira, Helsinki (two analysis on separate dates)
France	SAS Laboratoire, Ardon

2.3 Samples, analytes and schedule

Used sample codes on the result sheet were as follows:

S1 Soil improver
S2 Soil improver + peat

Samples were collected 13.11.2012 from a composting site in southern Finland established in April 2012. Samples were pretreated and the laboratory compacted bulk density measured according to EN 13040 by the organizer with the exception that sieving was done with a 10 mm sieve. The degree of wetting affects the magnitude of biological activity (Llewelyn, 2005) and therefore samples were moistened to the approximate optimum moisture content according to the “fist test” (FCQAO, 1994) before sending them to the participants. In addition, sample S2 was diluted with peat-based growing media (1:1). Measurements of pH and electrical conductivity from samples were measured according to standards EN 13037, (2011) and EN 13038, (2011).

For sample S1 pH was 6.5 and for sample S2 7.1. Conductivity was 105.6 mS/m for sample S1 and 72.1 mS/m for sample S2.

The sample amount sent to participants was 800 g. Fresh samples were delivered by cool storage to the participants 13-14.11.2012 and were therefore requested to be stored at 2-8 ℃ before testing. Samples were requested to be homogenated before measurements and testing required to be done as soon as possible, preferably starting 19-20.11.2012. The results were requested to be reported no later than 19.12.2012.

The following measurements were reported.

- DW: dry matter content (%)
- Org: organic matter content (%)
- CO_2: CO_2-production/bottle (%)
- CO_2: CO_2-evolution rate (mg CO_2-C/g VS/d), calculated result correcting CO_2-evolution rates with dry weight and organic matter content
- Oc: oxygen consumption (mmol O_2/kg OM)
- OUR: oxygen uptake rate (mmol O_2 x kg^{-1} x OM x $hour^{-1}$)
- AGR: plant response, average germination rate (%)
- RI: plant response, root length index (%)
- GR: germination rate (%)
- RLP: root length, per plant (mm)

2.4 Homogeneity studies

Samples N1 and N2 for homogeneity test were collected on 7.9.2012 from the same location and similar piles as the proficiency test samples using the same sampling scheme on both sampling occasions. Homogeneity testing was performed for humidity, organic matter, CO_2 production and root length using two different pretreatments (sieving 5 mm and 10 mm) and five parallel samples with two or three analytical parallels per sample (Table 2). Homogeneity was tested using guidelines from IUPAC technical report (Thompson et al. 2006).

The objective of the homogeneity study was to establish the heterogeneity of the samples used in this proficiency test. This information has to be taken into account when setting the criteria for evaluations of performance. Samples could be considered homogenous for humidity and organic matter allowing 1.5- 2.8 % deviation, but deviations of 22-60 % was required for the homogeneity criteria for CO_2 production and root length (RLP) to be fulfilled. This reflects natural heterogeneity of biological processes in these organic samples.

Table 2. Results from the homogeneity testing of samples N1 and N2.

Sample	Matrice	Parameter	Mean value	Sp %	Sp	S_{an}	S_{an}/Sp	Is $S_{an}/sp<0.5$?	S_{sam}	S_{sam}^2	c	Is $S_{sam}^2<c$?
N1	5 mm	Humidity, %	71,27	1,50	1,07	0,408	0,382	Yes	0,560	0,313	0,523	Yes
		Organic matter, %	57,96	2,25	1,30	0,303	0,232	Yes	0,175	0,031	0,539	Yes
		CO_2 production (48 h), mg CO_2-C/g VS /d	1,06	35	0,37	0,181	0,487	Yes	0,104	0,011	0,070	Yes
		Rooth length (RLP), mm	0,38	46	0,17	0,086	0,496	Yes	0,032	0,001	0,016	Yes
	10 mm	Humidity, %	69,43	1,50	1,04	0,141	0,136	Yes	0,507	0,257	0,288	Yes
		Organic matter, %	58,06	2,25	1,31	0,243	0,186	Yes	0,244	0,059	0,442	Yes
		CO_2 production (48 h), mg CO_2-C/g VS /d	0,89	38	0,34	0,169	0,499	Yes	0,098	0,010	0,060	Yes
		Rooth length (RLP), mm	0,38	60	0,23	0,081	0,357	Yes	0,137	0,019	0,019	Yes
N2	5 mm	Humidity, %	73,24	1,50	1,10	0,468	0,426	Yes	0,280	0,078	0,546	Yes
		Organic matter, %	62,11	2,25	1,40	0,229	0,164	Yes	0,143	0,020	0,491	Yes
		CO_2 production (48 h), mg CO_2-C/g VS /d	1,10	59	0,65	0,320	0,494	Yes	0,185	0,034	0,217	Yes
		Rooth length (RLP), mm	1,62	24	0,39	0,189	0,488	Yes	0,158	0,025	0,077	Yes
	10 mm	Humidity, %	69,95	2,80	1,96	0,953	0,487	Yes	0,726	0,527	1,945	Yes
		Organic matter, %	62,43	2,25	1,40	0,641	0,456	Yes	0,370	0,137	0,930	Yes
		CO_2 production (48 h), mg CO_2-C/g VS /d	1,16	22	0,25	0,124	0,487	Yes	0,125	0,016	0,034	Yes
		Rooth length (RLP), mm	1,58	26	0,41	0,205	0,499	Yes	0,118	0,014	0,092	Yes

s_p = Assigned standard deviation for homogeneity test, (total standard deviation divided by 2)
s_p% = Assigned standard deviation for homogeneity as percent, (total standard deviation divided by 2)
s_{an} = analytical deviation, mean standard deviation of results in a sub sample
s_{sam} = sampling deviation, standard deviation of results between sub samples
c = F1•sall2 + F2•sa2

where:
sall2 = (0.3•st)2
F1 = 2.21 when the number of sub samples is 6, F2 = 1.69 when the number of sub samples is 6
F1 = 1.88 when the number of sub samples is 10, F2 = 1.01 when the number of sub samples is 10

2.5 Feedback about the proficiency test

The participants did not comment on the arrangements or the evaluation procedures. Many of the reported results had to be corrected after sending of the results. The following corrections were made: correction of units (laboratory 7), missing data (laboratories 9 and 12) and results reported reversed results for the two samples (laboratory 10). The organizers strongly recommend that results should be carefully reported to ensure good customer service.

2.6 Processing of the data

Results were treated according to international ISO-guidelines (ISO, 2005). Before the statistical treatment, the data was tested according to the Kolmogorov-Smirnov normality test and the outliers were rejected according to the Hampel test for calculation of the mean value (H in the results sheets).

2.6.1 Assigned values and their uncertainties

The robust mean was used as the assigned value for measurements of the sample (Table 3, Appendix 5). The robust mean is not a metrological traceable assigned value. Because it was not possible to have a metrological traceable assigned value, the consensus mean was the best available value to use for the assigned values. Before the robust calculation of the reference value, some outliers were rejected in case that the results deviated from the robust mean more than 50 % or in case that the result was reported erroneously (e.g. wrong unit). If the result was reported < DL (detection limit), it has not been included in calculation of the reference value (H in the results sheets). The uncertainties of the assigned values were 1.8 % and 1.3 % for organic matter contents in the samples S1 and S2 respectively and 2.2 % for dry weight measurements (Appendix 5). For other parameters, the uncertainties of the assigned values were 4.3 % - 37 %. The reliability criterion **$u/s_p \leq 0.3$** was not fully met because the u/s_p was between 0.35-0.43 (Appendix 5) which is indicated by the high uncertainty of the assigned value.

2.6.2 Standard deviation for proficiency assessment and z score

The performance evaluation of each participant was carried out by using z scores (Appendix 4). The target values for the total standard deviations for each analyte (Table 2, 2*target SD %), used in the calculation of the z score of the target value, were estimated directly from the total SD_r % of the data set. The reliability criterion, $\mathbf{s_{rob} < 1.2 *} s_p$ was met in all cases except for RLP in sample S2 (Appendix 5). Therefore the evaluation of performance is only indicative for RLP measurements in sample S2.

z scores were not calculated for CO_2 (S2), CO_2 production per bottle (samples S1 and S2), and root length index (RI; S1) due to high standard deviation of the data set for these analytes. For oxygen consumption (Oc) and oxygen uptake rate (OUR) z scores were not calculated due to small data set (n=2). For control materials z scores are not appropriate to calculate because the results are not comparable, due to differences in control material.

3 RESULTS AND CONCLUSIONS

3.1 Results of the proficiency test

The summary of the results is presented in Table 3. Explanations to terms used in the result tables are presented in Appendix 1. The results of participants are presented graphically in Appendix 2 and the reported results of each participant in Appendix 3. A summary of z-scores are presented in Appendix 4 and the evaluation of assigned values and their uncertainties are presented in Appendix 5.

Table 3. Summary of the results in the proficiency test.

Analyte	Sample	Unit	Ass. val.	Mean	Mean rob.	Md	SD rob	SD rob, %	Num. of labs	2*Targ SD%	Ac-cepted z-val%
AGR	S1	%	95,5	95.04	95.51	97.00	5.64	5,9	9	15	89
	S2	%	95,9	95.86	95.86	96.70	4.98	5,2	9	12	100
CO2	S1		1,17	1.07	1.17	1.08	0.43	36,4	8	80	88
	S2		1,13	1.13	1.13	1.05	0.68	59,7	8		
CO2-prod/bottle	S1	%		0.49	0.49	0.50	0.27	55,6	5		
	S2	%		0.78	0.78	0.70	0.13	16,6	5		
DW	S1	%	26,3	25.92	26.26	26.00	0.78	3	12	6	100
	S2	%	29,8	29.76	29.80	29.89	0.91	3,1	12	7	92
GR	S1	%	94,6	94.29	94.59	95.00	6.10	6,4	8	15	88
	S2	%	94,6	100.00	94.58	100.00	5.32	5,6	8	12	100
GR control	S1/S	%		97.04	97.04	100.00	3.23	3,3	8		
Oc	S1			904.12	904.12	879.90	38.83	4,3	2		
	S2			501.17	501.17	509.68	176.10	35,1	2		
org	S1	%	60,5	60.91	60.76	60.34	1.47	2,4	12	6	100
	S2	%	67,4	67.28	67.45	67.53	1.13	1,7	12	4	92
OUR	S1			7.99	7.99	5.24	4.42	55,3	2		
	S2			4.65	4.14	3.95	0.81	19,6	2		
RI	S1	%		37.15	34.63	38.00	30.48	88	9		
	S2	%	67,3	66.72	67.30	64.40	20.72	30,8	9	50	89
RLP	S1	mm	18,1	19.38	18.14	19.40	6.60	36,4	9	80	67
	S2	mm	32,6	32.73	32.59	33.10	8.29	25,4	9	40	89
RLP control	S1/S	mm		47.60	50.07	46.10	12.92	25,8	9		

Ass. Val.- assigned value; Mean- mean value; Mean rob-robust mean; Md- median value; SD rob - the robust standard deviation; SD rob % - robust standard deviation as percent; Num of Labs - number of participants; 2*Targ. SD% - total standard deviation for proficiency assessment at 95 % confidence level, ($2*s_p$); Accepted z-val% - satisfactory z scores: the results (%), where $< z \pm 2$.

The results for some parameters were requested to be reported as triplicate (Table 4). The repeatability of the results (sw%) were often below 10 % but slightly higher for RLP and were highest for CO_2 production per bottle (sample S1 = 22 % and sample S2 = 31%) and for oxygen consumption (sample S2 = 23 %). These levels are acceptable considering the sample heterogeneity. In a similar study the mean repeatability for compost samples producing 1.3 -10.34 mg CO_2/g/VS/day was 2.0 mg CO_2/g/VS/ (Llewelyn, 2005). For a compost sample producing 1.3 mg CO_2/g/VS/day the repeatability was 1.7 mg CO_2/g/VS/day (Llewelyn, 2005). For chemical analyses the reproducibility between laboratories (sb%) are typically about 2-3 times higher than the repeatability which was the case for dry weight and organic matter content results. Sb% values were similar or even less for some measurements (CO_2-production, GR, Oc, RLP for S2) but for CO_2-evolution rate, oxygen uptake rate (OUR) and RLP for S1 and control, the sb% values were 5-14 times higher than the repeatability values.

Table 4. Summary of repeatability on the basis of triplicate determinations (ANOVA statistics).

Analyte	Sample	Unit	Ass. val.	Mean	Md	sw	sb	st	sw %	sb %	st %	2*Targ SD %	Num of labs	Ac-cepted. z-val %
CO2	S1		1,17	1,067	1,075	0,1099	0,5061	0,5179	10	47	49	80	8	88
	S2		1,13	1,131	1,055	0,1016	0,5928	0,6014	9	52	53		8	
CO2-prod/bottle	S1	%		0,5143	0,5	0,1122	0,2061	0,2347	22	40	46		5	
	S2	%		0,775	0,75	0,2415	0	0,2415	31	0	31		5	
DW	S1	%	26,3	25,99	26	0,1917	0,3016	0,3573	0,74	1,2	1,4	6	12	75
	S2	%	29,8	29,83	29,89	0,3935	0,815	0,9051	1,3	2,7	3	7	12	92
GR	S1	%	94,6	94,29	100	5,774	4,987	7,629	6,1	5,3	8,1	15	8	88
	S2	%	94,6	100	100	0	0	0	0	0	0	12	8	38
GR control	S1/S	%		97,04	100	5,401	0	5,401	5,6	0	5,6		8	
Oc	S1			899,3	879,9	29,72	28,37	41,09	3,3	3,2	4,6		2	
	S2			523,1	509,7	121,4	134,1	180,8	23	26	35		2	
org	S1	%	60,5	60,6	60,26	0,4555	1,105	1,195	0,75	1,8	2	6	12	75
	S2	%	67,4	67,21	67,34	0,915	0,6057	1,097	1,4	0,9	1,6	4	12	83
OUR	S1			7,443	5,238	0,2858	3,894	3,904	3,8	52	52		2	
	S2				4,65								2	
RLP	S1	mm	18,1	19,38	19,4	2,493	18,07	18,24	13	93	94	80	9	67
	S2	mm	32,6	32,73	33,1	3,518	7,295	8,099	11	22	25	40	9	89
RLP control	S1/S	mm		47,6	46,1	3,832	10,77	11,43	8,1	23	24		9	

Ass. val. - assigned value, Md - median, sw - repeatability standard error, sb - standard error between laboratories, st - reproducibility standard error

3.2 Analytical methods

Six laboratories analyzed the samples on the requested date 19-20.11.2012 and laboratory 7 a couple of days later due to sample shipment delay. Laboratory number 11 analyzed the samples after ca. two weeks and laboratory number 10 measured organic and dry matter contents immediately after sample arrival and the biological analysis after ca. two weeks.

3.2.1. Dry matter and organic matter content

All the laboratories performed the analysis using the gravimetric methods based on EN standards 13040 and 13039. Temperature ranged from 60°C to 105°C for dry matter analysis and from 450°C to 550°C for organic matter analysis.

3.2.2. CO_2- evolution rate

Description of analysis performed by the laboratories is combined in Table 5.

Table 5. Summary of CO_2-production analysis in the laboratories.

Lab No	Method	Equipment	Flask volume (ml) and septum type	Incubation time and temperature
2	Closed bottle VTT 2351*	Oxybaby V	600-622, silicon	24 h/37°C
3,4	Closed bottle VTT 2351	Checkmate 9900	500, rubber	48 h/37°C
5	Closed bottle VTT 2351	CheckPointII	500	24 h/37°C
6	Gas chromatograph	HP 6890	600, rubber	6 h/37°C
8	Closed bottle VTT 2351	Dräger tubes	612, silicon	24 h/37°C
10	Closed bottle, NaOH trap	TOC meter	500	72 h/28°C
12	Closed bottle VTT 2351	Servoflex MiniFoodpack 5200	500, rubber	24 h/37°C

*Itävaara et al. 2006, 2010

3.2.3 Oxygen uptake rate

Only two labs performed the OUR test, both according to EN standard 16087-1. Number of replicates was two or three and the incubation temperature used was 20°C or 30°C. No clear conclusion can be drawn from these results due to low participation.

3.2.4 Plant response

Description of analysis is combined in Table 6. All laboratories used the standard method EN 16086-2 and vegetable cress seeds with germination capacity of > 90%. Total number of seeds ranged from 30 to 90/sample. All laboratories incubated samples for 72 h.

Table 6. Summary of plant response analysis in the laboratories.

Lab No	Control material	Incubation temperature (°C)
1	Sphagnum peat (pH 5.5-6) + water soluble fertilizer + trace elements	25
3,4	Filter paper Whatman 598	25
5	Filter paper Whatman 598	22
6	Limed peat	20
7	Peat H3-H5 (+ PG mix + ground limestone)	30
9	Limed and fertilized peat	25
10	Sphagnum peat	21
11	Sphagnum peat	25

4 EVALUTION OF PERFORMANCE

The evaluation of the participants was based on z scores, which were calculated using the estimated target values for the total deviation. **The z scores shall be 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, 91 % of the results were satisfactory when target deviations between 4-80 % of the assigned values were accepted (Table 3). The results of eight participants were all satisfactory (z-values between -2 and 2). Please note that the evaluations of the following analytes are indicative only due to very high target standard deviations (40-80 %, Table 3):

- CO_2 (S1)
- RI (S2)
- RLP (S1, S2)

After reporting the preliminary results in January 2013, results from four laboratories were corrected (e.g. change of unit; cm, mm) and data was supplemented for organic matter contents and dry matters. These changes are reflected in the following evaluations: org, DW, AGR (S1), R1 (S1, S2) and RLP (S1, S2).

5 IMPORTANT ASPECTS FROM THE PROFICIENCY TEST

CO_2-production. Analysis of sample CO_2-production was performed mainly using the same principle method but with different equipment and incubation times (Table 5). The results were clearly different for the CO_2 measurement and the CO_2-evolution rates between different laboratories. This was true especially for sample S2. In addition to sample heterogeneity, factors such as equipment used (flask volume, septum type and machinery for measurement) probably had an effect on the result.

For this type of soil improver samples, CO_2 –evolution of approximately 1.0 mg CO_2-C/g VS/d would be expected (Itävaara et al., 2010). Here, the mean CO_2 –evolution of the proficiency tests was 1.17 mg CO_2-C/g VS/d for S1 and 1.13 mg CO_2-C/g VS/d for S2. Results from laboratory 2 (and 6) were considerably lower. Laboratory 6 used gas chromatography for CO_2 production which may explain the difference compared to other laboratories. The reason for exceptionally low result for laboratory number 2 remains unclear. All laboratories except one reported slightly higher CO_2-production and CO_2-evolution rates for sample S2 than S1. This can be due to the addition of peat into sample S2, which may have activated microbial respiration rates. It should be taken into account that the quality of peat used for dilution of soil improvers during testing can affect the results. Moisture content and temperature also 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.

Oxygen uptake rate. Only two laboratories analyzed oxygen uptake rate and there was some difference in the oxygen consumption measurements, probably resulting from sample heterogeneity. In addition, incoherency was found between the OUR results of sample S2, perhaps due to calculation error in the laboratory. Correlation between the measurement of oxygen uptake and CO_2 evolution has been shown earlier (Itävaara et al., 2006).

Plant response. In the plant response/petri dish method, germination rate (AGR) results between the laboratories were comparable except for one laboratory for sample S1. Root length measurements (RLP) however and therefore also root index (RI) calculated from these measurements varied from 3 mm to 62 mm (RI: 5,4 to 103) for S1 and 20 mm to 46 mm (RI: 31 to 77) for S2.

Controls, incubation temperature and the amount of seeds used varied between the laboratories (Table 6) but this doesn't explain the big differences between root length measurement data, especially for sample S1 (laboratories 7 and 11). Differences in root measurement may have been caused by uncertainty in the measurement of seedling root (Figure 1), especially with short roots or mainly only shoot growth it may have not always been clear what to measure. Also sample maturation may have occurred prior to testing, since laboratory 11 performed the analysis two weeks after the recommended date. It seems the instructions described in the standard procedure are not sufficiently detailed and therefore allow for subjective opinions. Further harmonization is needed e.g. by training courses.

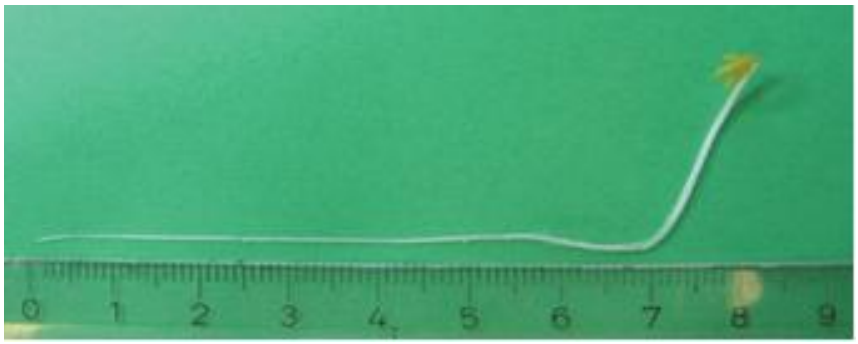

Figure 1. Measurement of root length of germinated cress seed.

Except for laboratories 7 and 11, sample S2 gave better cress root growth results than sample S1. This is in accordance with previous studies where peat has been shown to stimulate cress root growth (Maunuksela et al., 2012). Laboratories 3 and 5, using inert filter paper as control, had RI variation between 23 and 38 (S1) and 54 and 68 (S2). Root length (RLP) of control seedlings on filter paper varied from 36 mm to 65 mm between the laboratories, so probably also seed quality, incubation temperature and filter paper moisture had an effect on the results.

Maturity assessment. 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 7. Stability and root growth test results showed no clear relationships. Criteria for soil improver maturity in Finnish legislation are: CO_2-evolution, <3 mg CO_2-C/gVS/d and root length index, > 80%. According to Wood et al. (2009), very stable (biowaste and green waste) compost is classified as <5 mg CO_2-C/gVS/d CO_2-evolution and <5 mmol O_2/kg VS/h O_2 evolution rates. Stabilities of <6 mg CO_2/g VS/day are desirable for growing media purposes or for any applications where self-heating would be a problem. According to these three criteria, sample S2 was considered mature and stable by only two laboratories, sample S1 by none.

The current maturity criteria for soil improvers in 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. The criteria will be updated.

Table 7. Maturity assessment of analyzed samples

Sample	**CO_2- (< 3 mg CO_2--C/g VS/d)****	**OUR (<5 mmol O2/kg VS/h)***	**RI > 80%****
S1	YES	NO lab 11 =5,24 lab 9 =10,75	NO (labs 1,3,4,5,6,7,9,10) YES (labs 11)
S2	YES	YES lab 9 =4,65 lab 11 = 3.64	YES (labs 1,6) NO (labs 3,4,5,7,9,10, 11)

*according to Wood et al., 2009

**according to Finnish Act on Fertilizer Products

6 CONCLUSIONS

This proficiency test was in our knowledge the first proficiency test performed after the interlaboratory test performed in 2009 in relation to validation of the standard (EN 16086-2, 2011). Sample dispatch time, humidity of the samples and storage temperature are known to affect the results. Therefore the samples used in our test were pretreated by sieving and wetting to the same moisture content and consequently the samples analysed were more homogenous than in earlier intercalibrations. The deviations of the results in this test are thus smaller and evaluation of competence was possible for some of the analytes.

It seems many laboratories have good experience of these methods even though they have been standardized only recently. In some of the participating laboratories all methods were not routinely in use, and we appreciate their participation in these tests despite of this. Proficiency test provide important feedback on laboratory analytics and will help all participants to further improve their performance.

The analyses used in this proficiency test are used for determining soil improver maturity and stability. Stability and plant response test results showed no clear relationships, which complicate the interpretation of results when several test are performed on the same material. Similar conclusions have been made in other studies (Wood et al., 2009).

The diversity of biological processes in soil improver samples is a challenge for this type of proficiency tests as it is difficult to separate deviations caused by methodological reasons and natural diversity of the samples. This has been considered during performance evaluation by using wide target standard deviations. In future rounds of proficiency tests also pretreatment practices, like wetting of the samples, would be interesting to take into account. This will increase standard deviations further.

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

7 SUMMARY

Evira and Proftest SYKE carried out this proficiency test in November-December 2012 for sample phytotoxicity and aerobic biological activity by determining the effect of soil improver samples on germination and root growth of cress, sample CO_2-production or oxygen uptake and sample dry weight and organic matter content. In total 11 laboratories took part in this test.

Sample material was soil improver (S1) and soil improver and peat based growing medium (S2). Standard methods were used to determinate the properties from the samples, except for CO_2 evolution rate analysis for which no standard exist.

The robust 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 CO_2 (S2), CO_2 production per bottle, and root length index (RI; S1), oxygen consumption (Oc) and oxygen uptake rate (OUR). In total, 91 % of the results were satisfactory when the deviations of 4-80 % from the as-signed values were accepted. It seems further guidance in some of the methods is needed.

Results for aerobic biological activity and plant response (phytotoxicity) showed no clear relationships, which complicate the interpretation of results when several test are performed on the same material.

According to the results many laboratories have good practices and manage these analyses well. Other laboratories still need more experience. In future rounds of proficiency tests also pretreatment practices will be taken into account.

8 YHTEENVETO

Evira toteutti yhdessä Proftest SYKEn kanssa maanparannusaineiden fytotoksisuutta ja aerobista biologista aktiivisuuta (stabiilisuutta) koskevan vertailukokeen marras-joulukuussa 2012. Vertailukokeen kahdesta näytteestä tutkittiin krassin itävyys ja juuren kasvu, hiilidioksidintuotto tai hapen kulutus sekä näytteiden kuivapaino ja orgaanisen aineen määrä. Pätevyyskokeeseen osallistui yhteensä 11 laboratoriota.

Näytemateriaalina käytettiin maanparannusainetta (S1) ja maanparannusaineen ja turpeen sekoitusta (S2). Laboratoriot käyttivät standardimenetelmiä näytteiden ominaisuuksien tutkimiseen paitsi hiilidioksidituoton määrityksessä, missä standardit puuttuvat kyseiselle matriisille.

Mittaussuureen vertailuarvona käytettiin osallistujien ilmoittamien tulosten robustia keskiarvoa. Laboratorioiden pätevyyden arviointi tehtiin z-arvon avulla. Tavoitehajonta määritettiin pätevyyskokeen hajonnan perusteella. z-arvoja ei määritetty hiilidioksidille (S2), hiilidioksidituotto per pullo tai juurenpituus-indeksille (RI; S1), hapen kulutukselle (Oc) tai hapen sitoutumisnopeudelle (OUR). Kaikkiaan 91 % tuloksista oli hyväksyttäviä, kun tavoitehajonta oli of 4-80 % tavoite-arvosta. Kahdeksalla laboratoriolla oli kaikki tulokset hyväksyttäviä.

Aerobista biologista aktiivisuutta määrittävien testien ja kasvivastetta määrittävien testien tulokset eivät antaneet selvää korrelaatiota, mikä vaikeutti tulosten tulkintaa.

Tulosten perusteella kierrokseen osallistuvat laboratoriot hallitsevat kyseiset analyysit pääasiassa hyvin vaikka jotkut laboratoriot tarvitsevat enemmän kokemusta tietyissä analyyseissä. Tulevissa pätevyyskokeissa tullaan huomioimaan myös laboratorioiden suorittama näytteen esikäsittelyprosessi.

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TERMS IN THE RESULT TABLES

Results of each participants

Sample	the code of the sample
z-Graphics	z score - the graphical presentation
z value	calculated as follows: $z = (x_i - X)/s_p$, where x_i = the result of the individual laboratory X = the reference value (*the assigned value*) s_p = the target value of the standard deviation for proficiency assessment
Outl test OK	yes - the result passed the outlier test H = Hampel test (a test for the mean value) In addition, in robust statistics some results deviating from the original robust mean have been rejected
Assigned value	the reference value
2* Targ SD %	the target value of total standard deviation for proficiency assessment (s_p) at the 95 % confidence level, equal $2 \cdot s_p$
Lab's result	the result reported by the participant (the mean value of the replicates)
Md.	Median
Mean	Mean
SD	Standard deviation
SD%	Standard deviation, %
Passed	The results passed the outlier test
Outl. failed	The results not passed the outlier test
Missing	i.e. < DL
Num of labs	the total number of the participants

Summary on the z scores

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

Robust analysis

X^* = median of x_i (i = 1, 2,…p)
s^* = 1.483 median of $|x_i - x^*|$ (i = 1, 2,…p)

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

$x_i^* = x^* - \varphi$ if $x_i < x^* - \varphi$
$x_i^* = x^* + \varphi$ if $x_i > x^* + \varphi$
$x_i^* = x_i$ otherwise

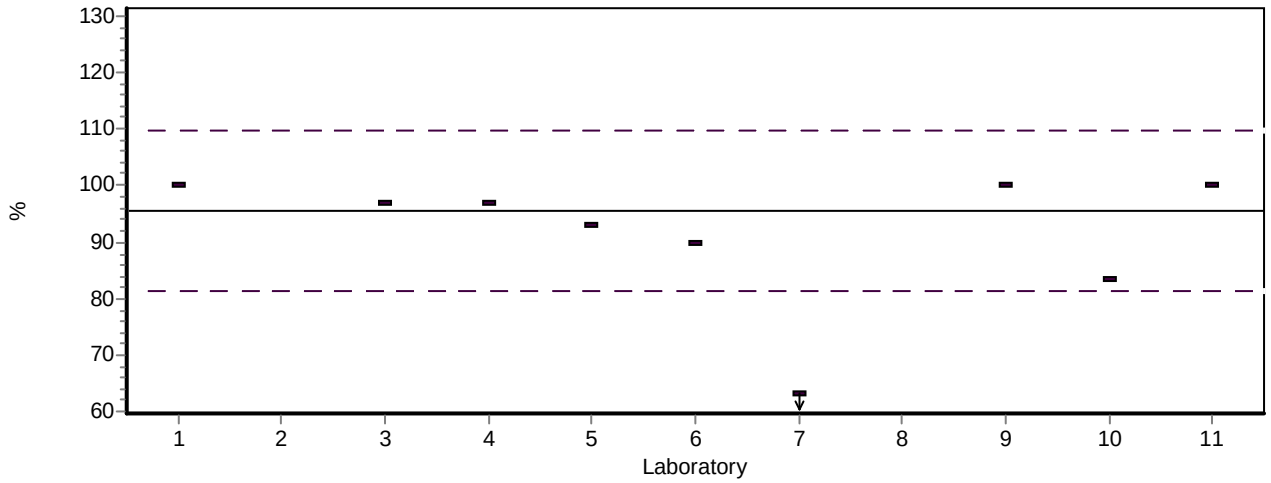
The robust estimates x^* and s^* can be derived by an iterative calculation, i.e. by updating the values of x^* and s^* several times, until the process convergences.

Ref: Statistical methods for use in proficiency testing by inter laboratory comparisons, Annex C [3].

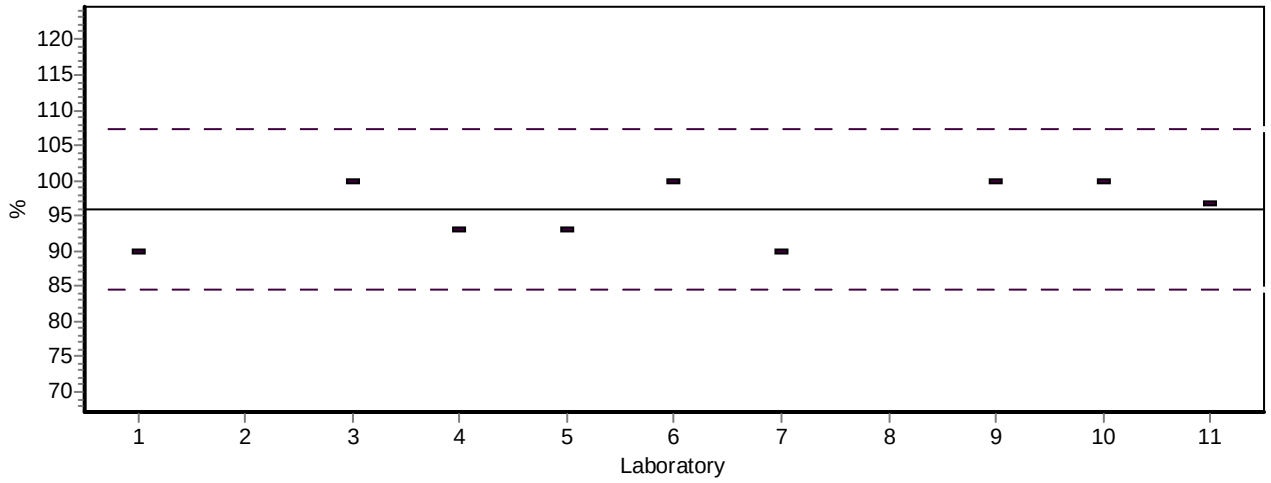
LIITE 2. LABORATORIOIDEN TULOKSET GRAAFISESTI

APPENDIX 2. *RESULTS OF PARTICIPANTS PRESENTED GRAPHICALLY*

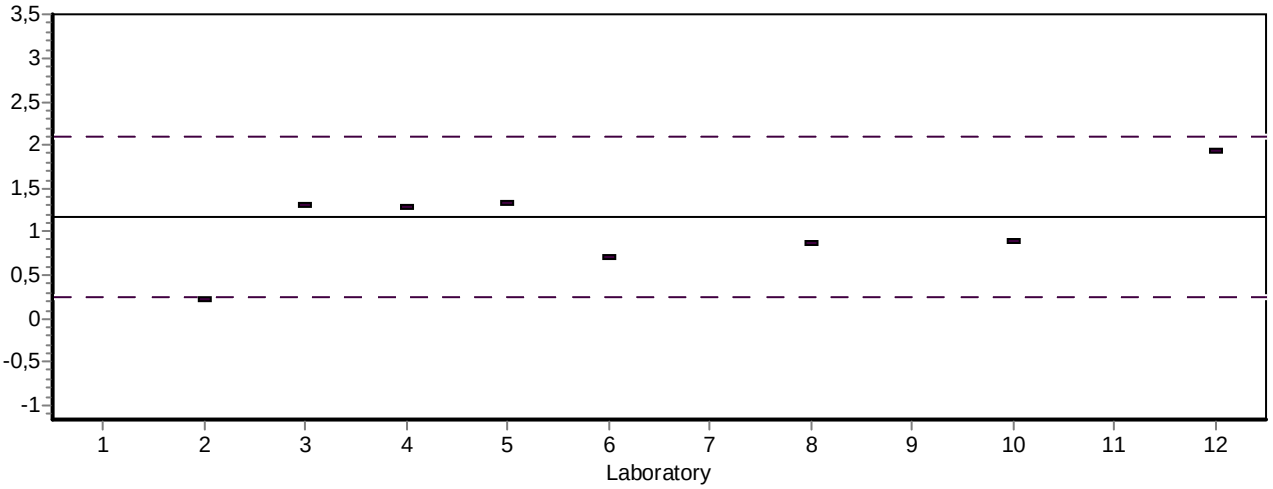
Analyytti *(Analyte)* **AGR** Näyte *(Sample)* S1



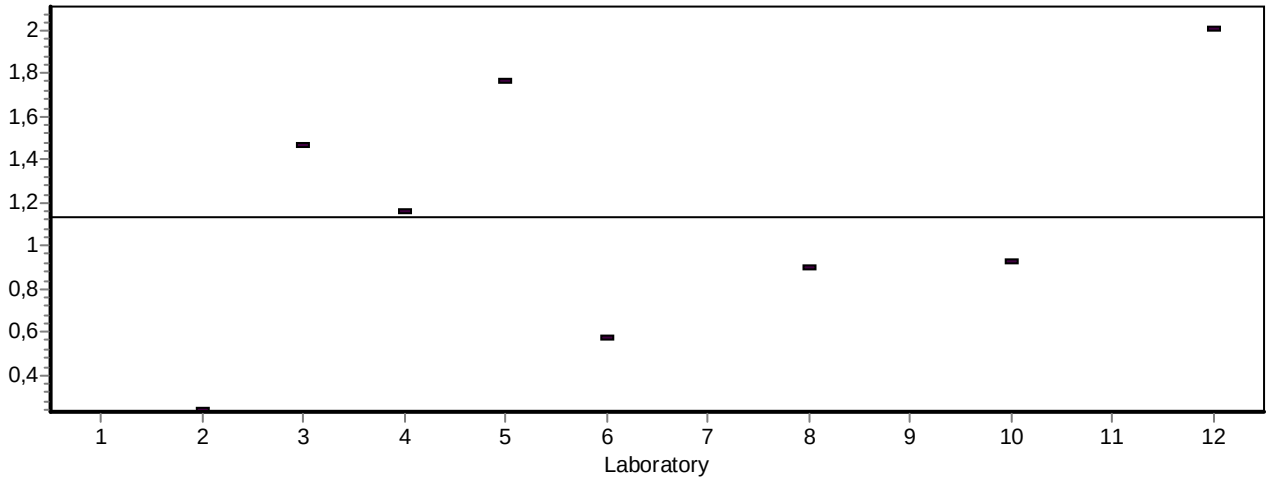
Analyytti *(Analyte)* **AGR** Näyte *(Sample)* S2



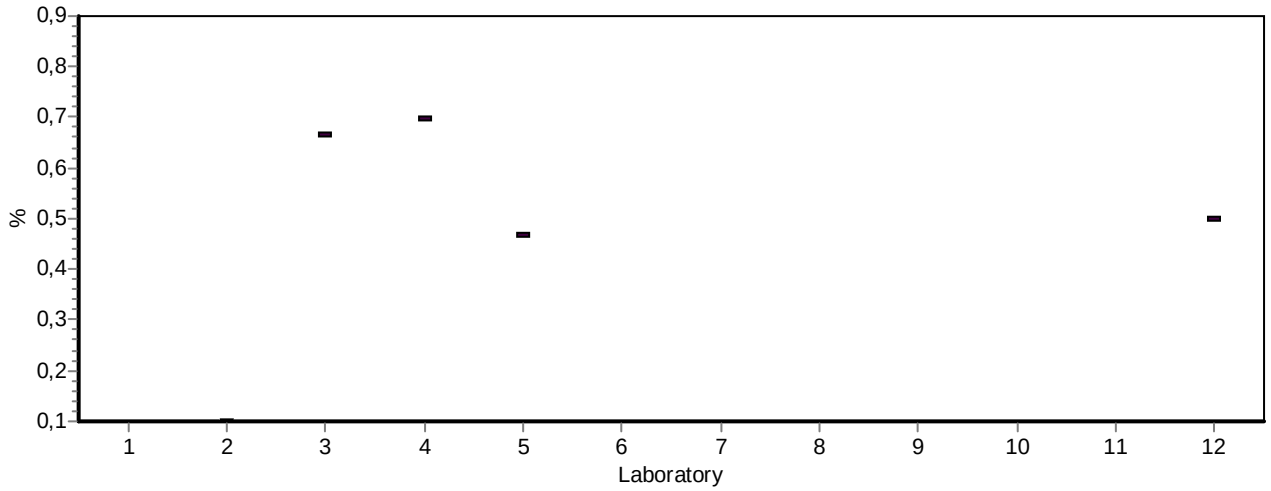
Analyytti *(Analyte)* **CO2** Näyte *(Sample)* S1



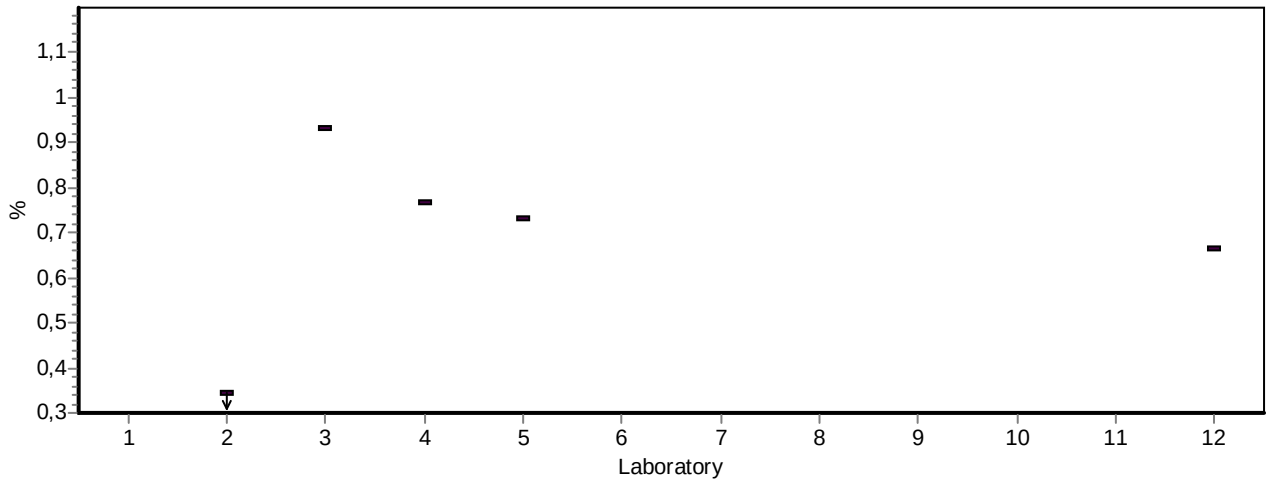
Analyytti *(Analyte)* **CO2** Näyte *(Sample)* S2



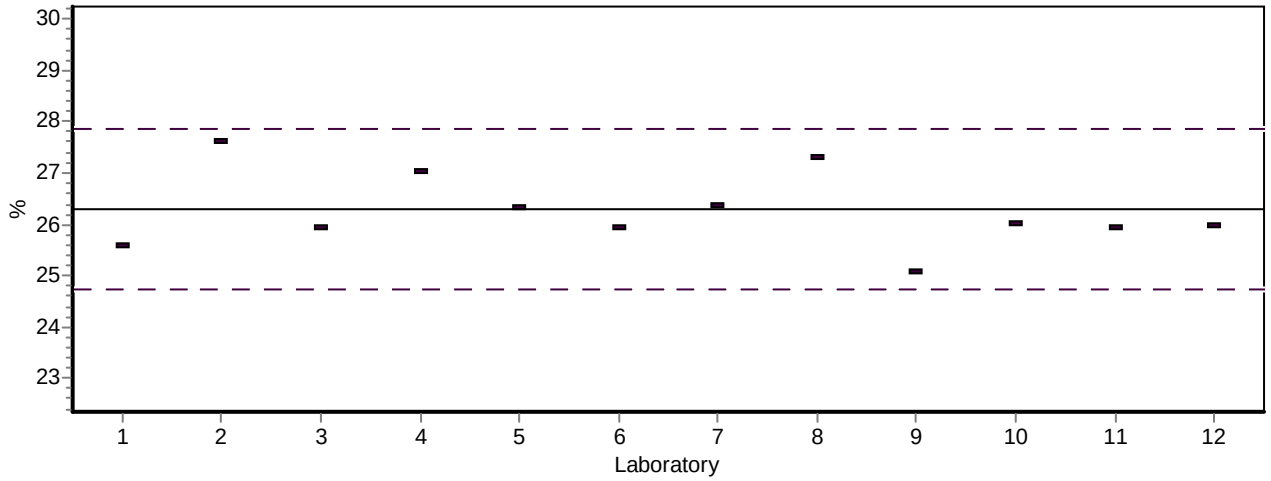
Analyytti *(Analyte)* **CO2-** Näyte *(Sample)* S1



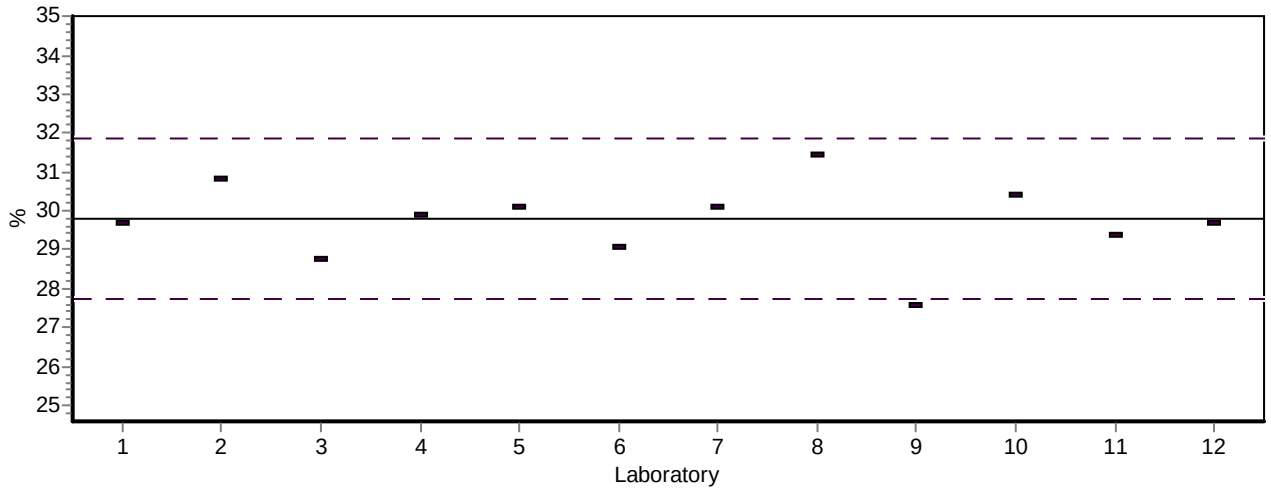
Analyytti *(Analyte)* **CO2-** Näyte *(Sample)* S2



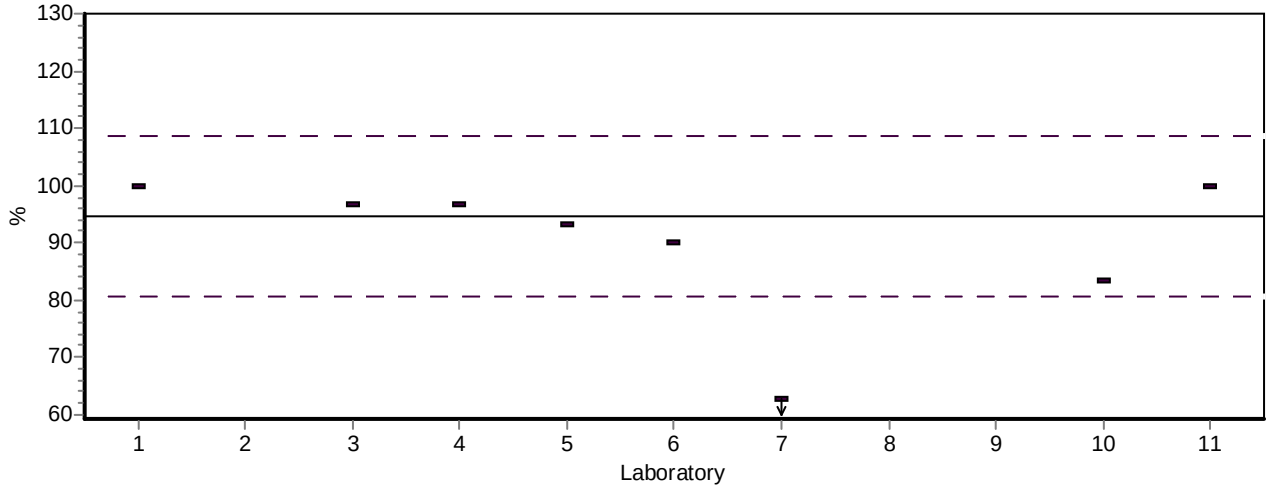
Analyytti *(Analyte)* **DW** Näyte *(Sample)* S1



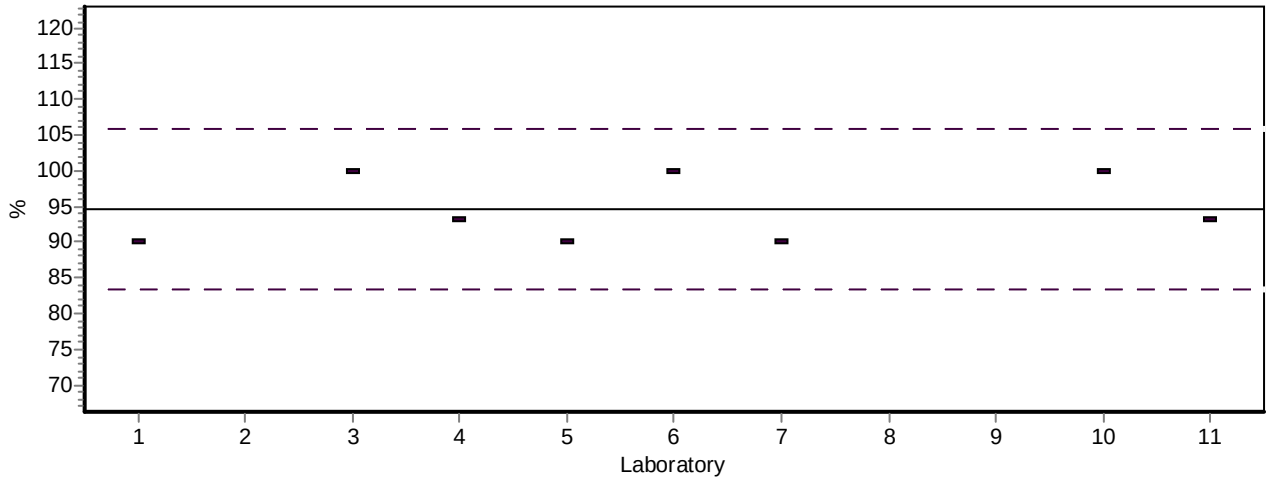
Analyytti *(Analyte)* **DW** Näyte *(Sample)* S2



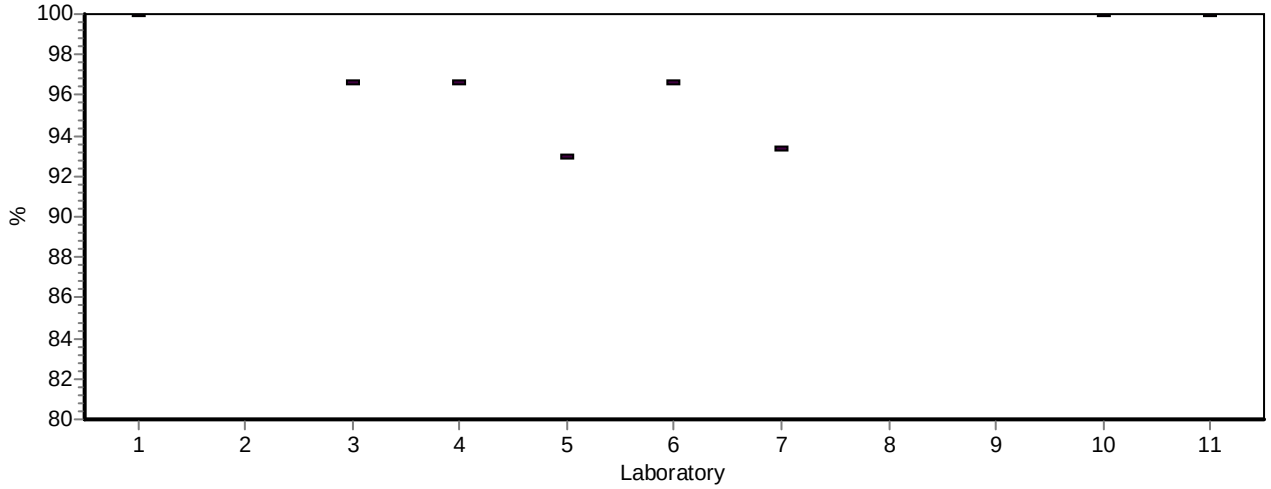
Analyytti *(Analyte)* **GR** Näyte *(Sample)* S1



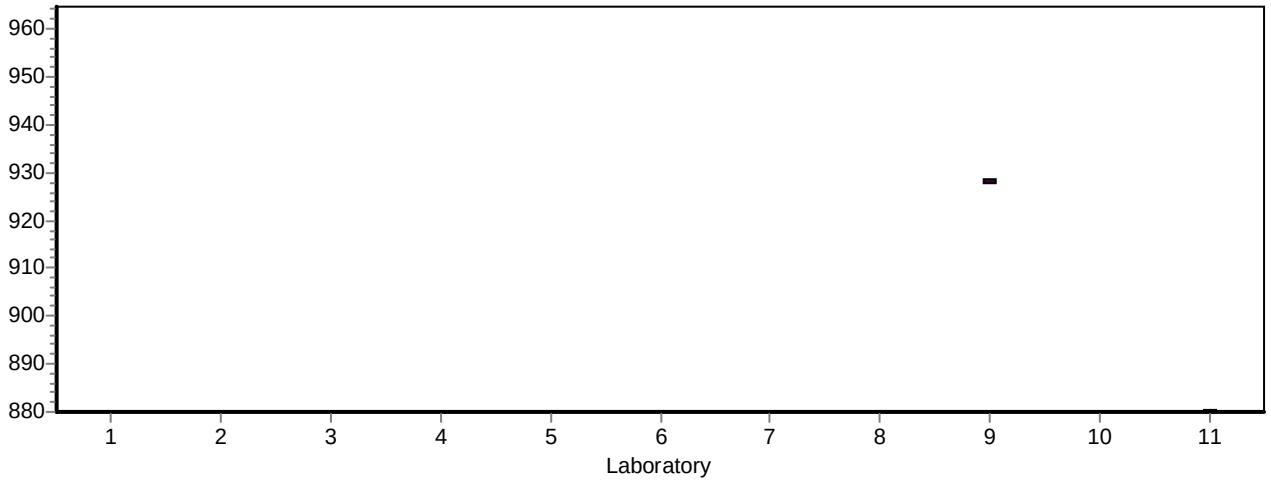
Analyytti *(Analyte)* **GR** Näyte *(Sample)* S2



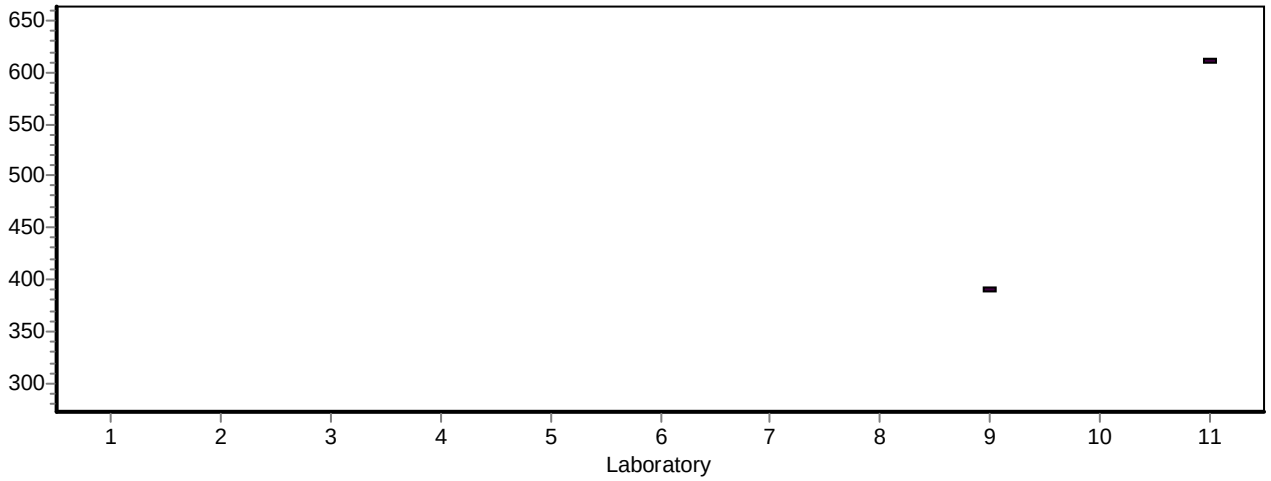
Analyytti *(Analyte)* **GR control** Näyte *(Sample)* S1/S



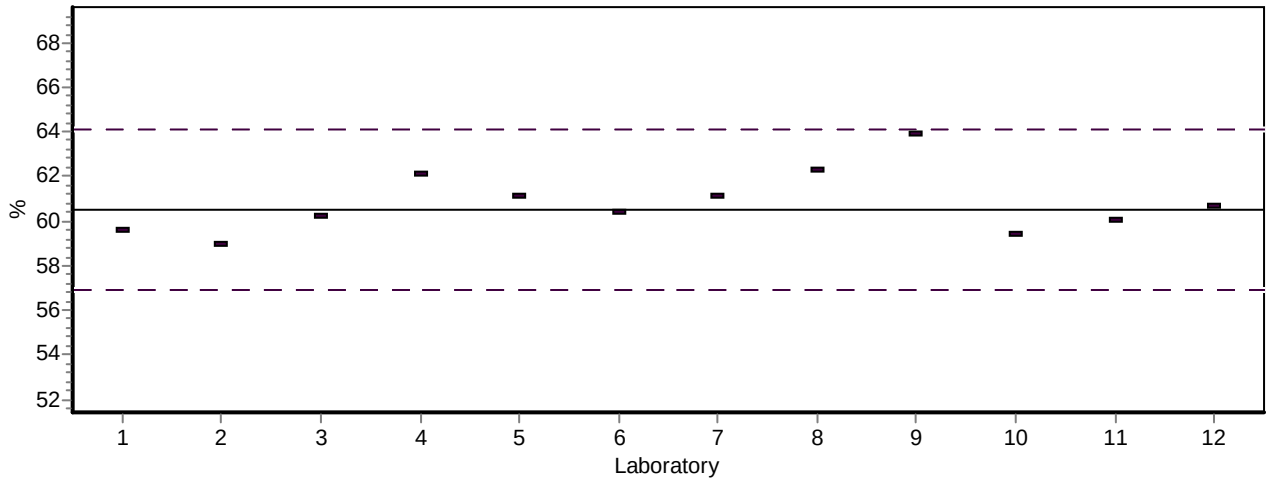
Analyytti *(Analyte)* **Oc** Näyte *(Sample)* S1



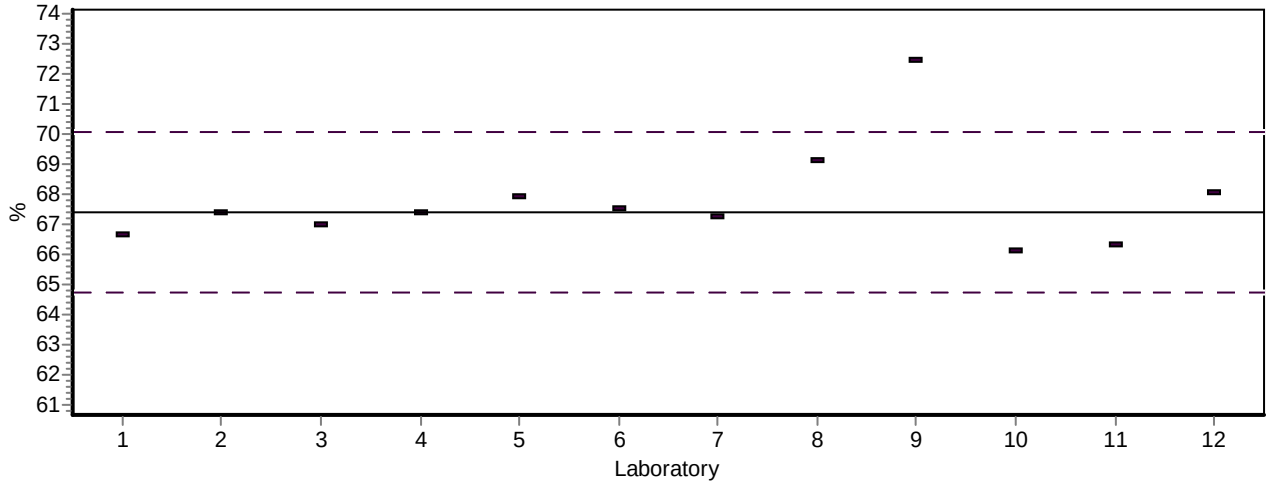
Analyytti *(Analyte)* **Oc** Näyte *(Sample)* S2



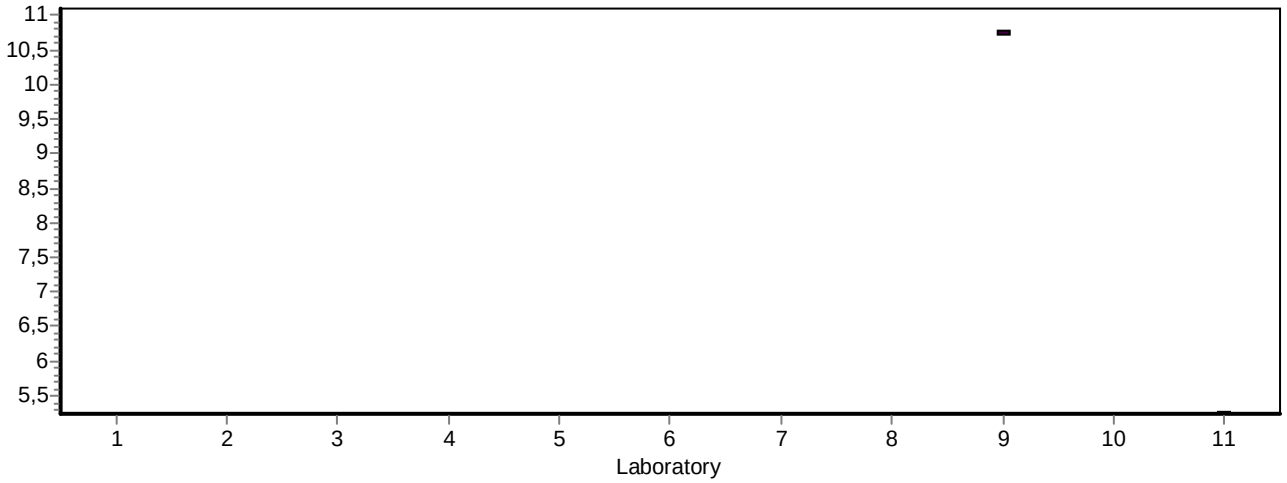
Analyytti *(Analyte)* **org** Näyte *(Sample)* S1



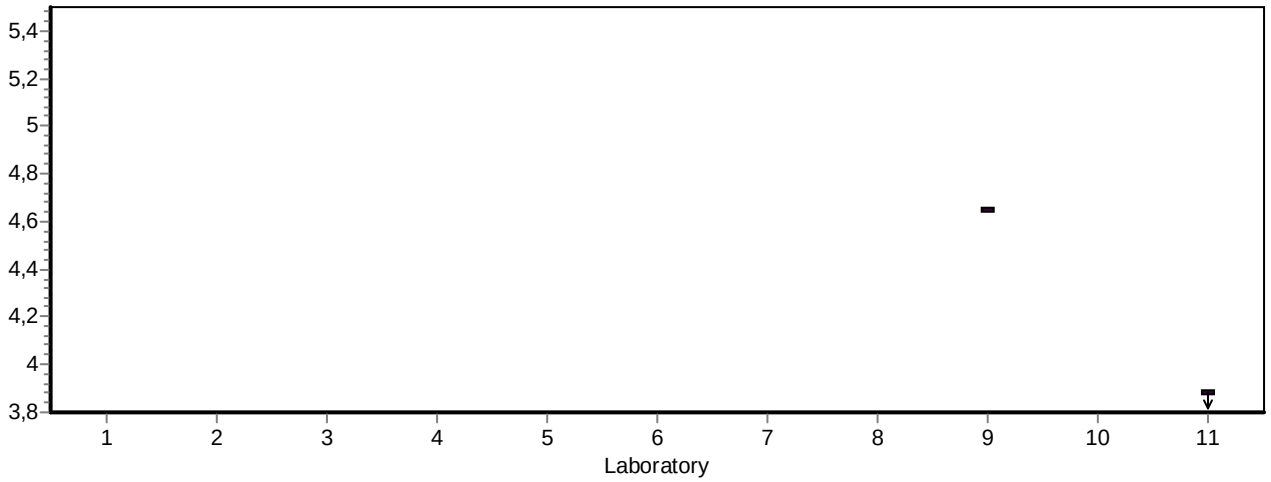
Analyytti *(Analyte)* **org** Näyte *(Sample)* S2



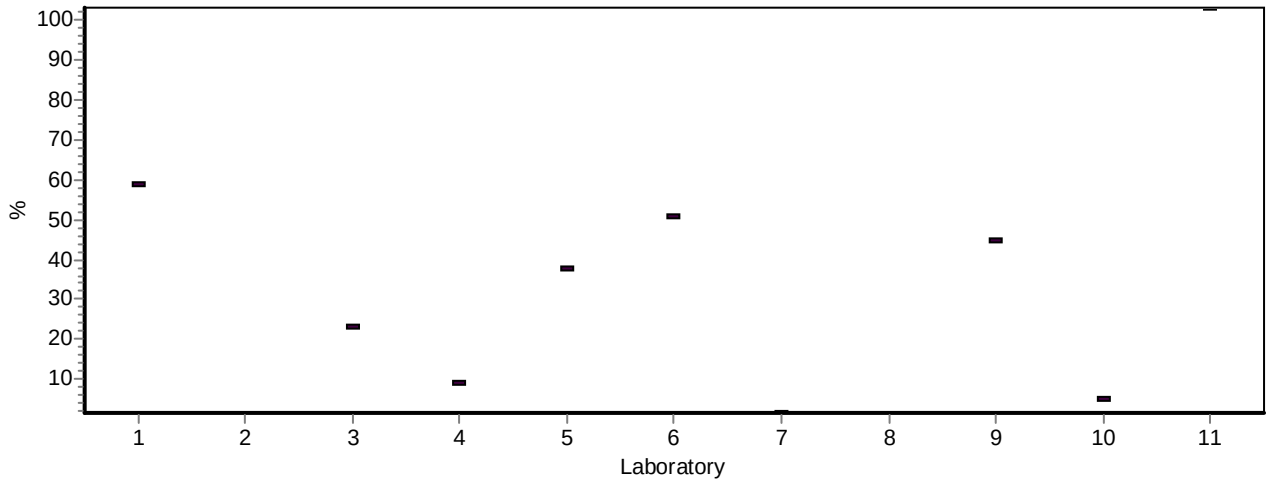
Analyytti *(Analyte)* **OUR** Näyte *(Sample)* S1



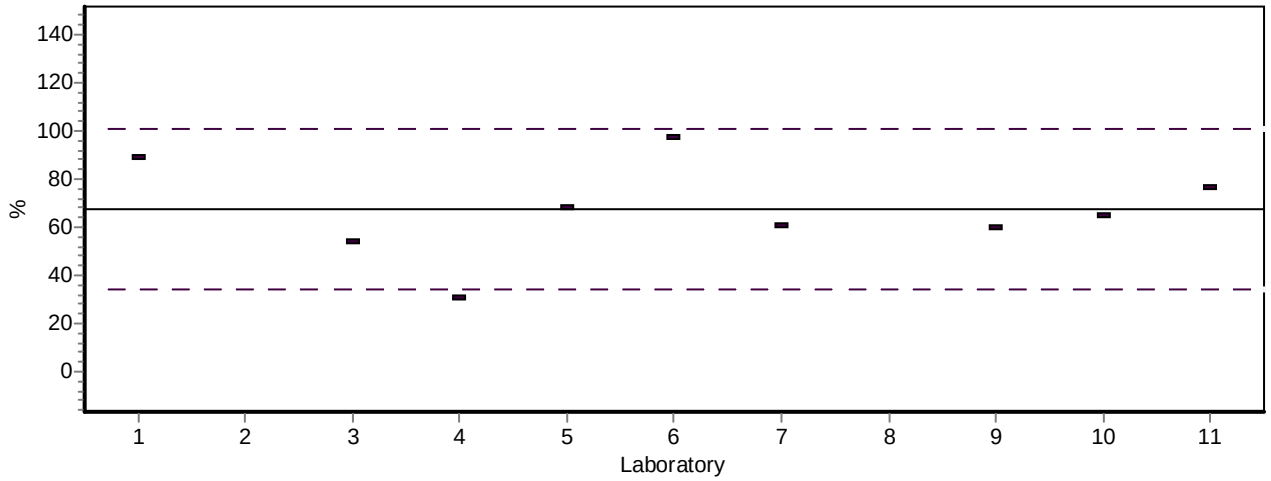
Analyytti *(Analyte)* **OUR** Näyte *(Sample)* S2



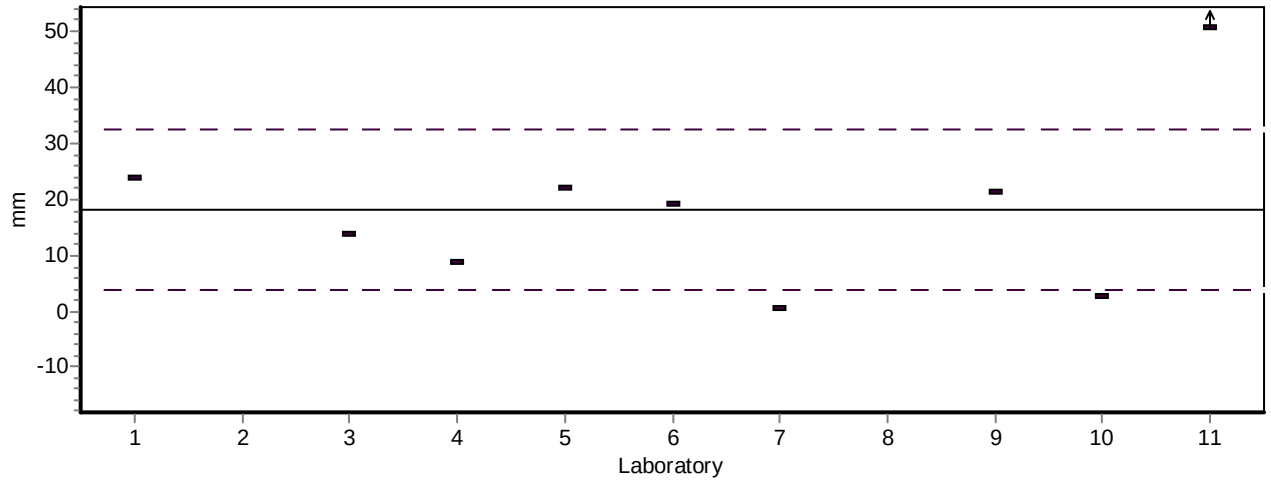
Analyytti *(Analyte)* **RI** Näyte *(Sample)* S1



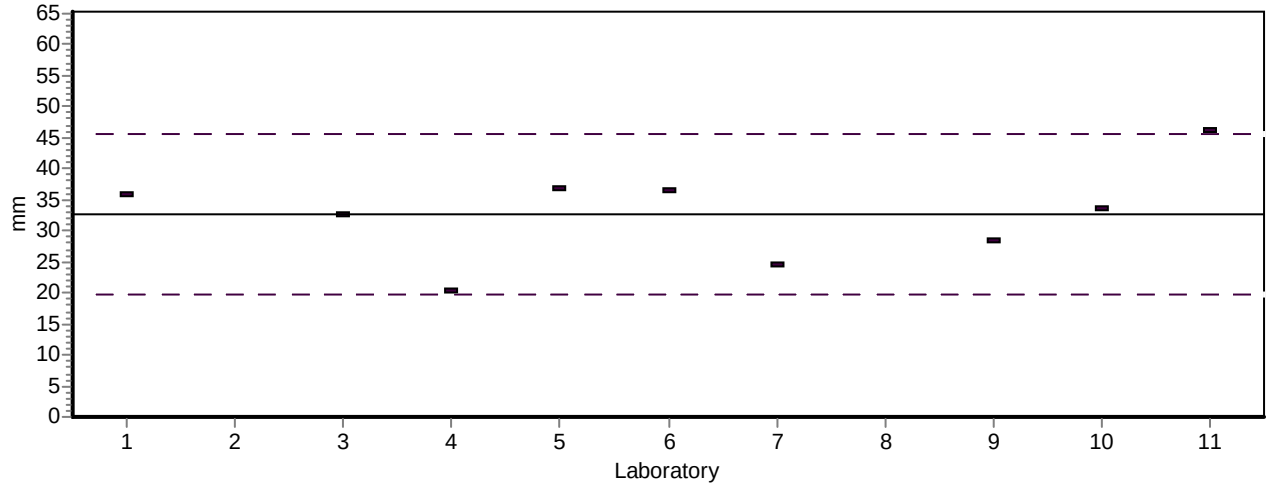
Analyytti *(Analyte)* **RI** Näyte *(Sample)* S2



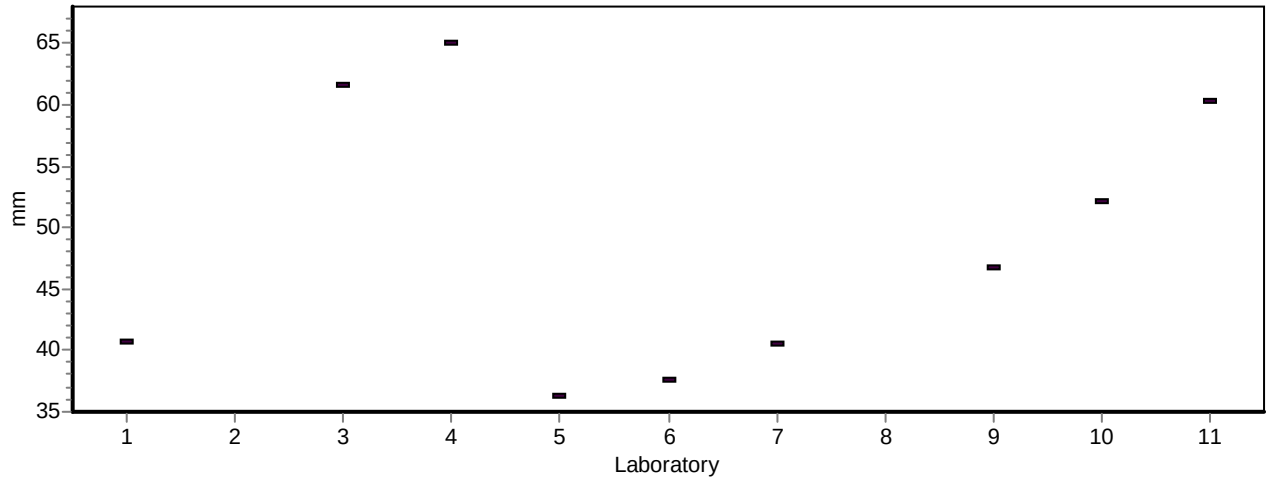
Analyytti *(Analyte)* **RLP** Näyte *(Sample)* S1



Analyytti *(Analyte)* **RLP** Näyte *(Sample)* S2



Analyytti *(Analyte)* **RLP control** Näyte *(Sample)* S1/S



LIITE 3. LABORATORIOKOHTAISET TULOKSET

APPENDIX 3. *Results of each participant*

Analyte	Unit	Sample	z-Graphics -3 -2 -1 0 +1 +2 +3	Z- value	Outl test OK	Assig-ned value	2* Targ SD%	Lab's result	Md.	Mean	SD	SD%	Pas-sed	Outl. fai-led	Mis-sing	Num of labs
Laboratory 1																
AGR	%	S1		0,628	yes	95,5	15	100	97	95,04	5,963	6,3	8	1	0	9
	%	S2		-1,025	yes	95,9	12	90	96,7	95,86	4,392	4,6	9	0	0	9
DW	%	S1		-0,887	yes	26,3	6	25,6	26	25,99	0,3467	1,3	9	3	0	12
	%	S2		-0,096	yes	29,8	7	29,7	29,89	29,83	0,8831	3	12	0	0	12
GR	%	S1		0,761	yes	94,6	15	100	100	94,29	7,464	7,9	7	1	0	8
	%	S2		-0,810	H	94,6	12	90	100	100	0	0	3	5	0	8
GR control	%	S1/S			yes			100	100	97,04	5,262	5,4	8	0	0	8
org	%	S1		-0,514	yes	60,5	6	59,57	60,26	60,6	1,154	1,9	9	3	0	12
	%	S2		-0,569	yes	67,4	4	66,63	67,34	67,21	1,086	1,6	10	2	0	12
RI	%	S1			yes			58,6	38	37,15	32,22	86,7	9	0	0	9
	%	S2		1,266	yes	67,3	50	88,6	64,4	66,72	19,43	29,1	9	0	0	9
RLP	mm	S1		0,815	yes	18,1	80	24	19,4	19,38	17,54	90,5	9	0	0	9
	mm	S2		0,470	yes	32,6	40	35,67	33,1	32,73	7,842	23,9	9	0	0	9
RLP control	mm	S1/S			yes			40,67	46,1	47,6	10,98	23,0	8	1	0	9
Laboratory 2																
CO2		S1		-2,016	yes	1,17	80	0,2267	1,075	1,067	0,496	46,4	8	0	0	8
		S2			yes	1,13		0,24	1,055	1,131	0,5754	50,8	8	0	0	8
CO2-	%	S1			yes			0,1	0,5	0,5143	0,2214	43,0	5	0	0	5
	%	S2			H			0,1	0,75	0,775	0,2301	29,6	4	1	0	5
DW	%	S1		1,673	H	26,3	6	27,62	26	25,99	0,3467	1,3	9	3	0	12
	%	S2		0,983	yes	29,8	7	30,83	29,89	29,83	0,8831	3	12	0	0	12
org	%	S1		-0,821	C	60,5	6	59,01	60,26	60,6	1,154	1,9	9	3	0	12
	%	S2		0,015	yes	67,4	4	67,42	67,34	67,21	1,086	1,6	10	2	0	12
Laboratory 3																
AGR	%	S1		0,209	yes	95,5	15	97	97	95,04	5,963	6,3	8	1	0	9
	%	S2		0,713	yes	95,9	12	100	96,7	95,86	4,392	4,6	9	0	0	9
CO2		S1		0,278	yes	1,17	80	1,3	1,075	1,067	0,496	46,4	8	0	0	8
		S2			yes	1,13		1,467	1,055	1,131	0,5754	50,8	8	0	0	8
CO2-	%	S1			yes			0,6667	0,5	0,5143	0,2214	43,0	5	0	0	5
	%	S2			yes			0,9333	0,75	0,775	0,2301	29,6	4	1	0	5
DW	%	S1		-0,439	yes	26,3	6	25,95	26	25,99	0,3467	1,3	9	3	0	12
	%	S2		-0,972	yes	29,8	7	28,79	29,89	29,83	0,8831	3	12	0	0	12
GR	%	S1		0,291	yes	94,6	15	96,67	100	94,29	7,464	7,9	7	1	0	8
	%	S2		0,951	yes	94,6	12	100	100	100	0	0	3	5	0	8
GR control	%	S1/S			yes			96,67	100	97,04	5,262	5,4	8	0	0	8
org	%	S1		-0,162	yes	60,5	6	60,21	60,26	60,6	1,154	1,9	9	3	0	12
	%	S2		-0,319	yes	67,4	4	66,97	67,34	67,21	1,086	1,6	10	2	0	12
RI	%	S1			yes			23	38	37,15	32,22	86,7	9	0	0	9
	%	S2		-0,790	yes	67,3	50	54	64,4	66,72	19,43	29,1	9	0	0	9
RLP	mm	S1		-0,612	yes	18,1	80	13,67	19,4	19,38	17,54	90,5	9	0	0	9
	mm	S2		0,010	yes	32,6	40	32,67	33,1	32,73	7,842	23,9	9	0	0	9
RLP control	mm	S1/S			yes			61,67	46,1	47,6	10,98	23,0	8	1	0	9
Laboratory 4																
AGR	%	S1		0,209	yes	95,5	15	97	97	95,04	5,963	6,3	8	1	0	9
	%	S2		-0,504	yes	95,9	12	93	96,7	95,86	4,392	4,6	9	0	0	9
CO2		S1		0,228	yes	1,17	80	1,277	1,075	1,067	0,496	46,4	8	0	0	8
		S2			yes	1,13		1,16	1,055	1,131	0,5754	50,8	8	0	0	8
CO2-	%	S1			yes			0,7	0,5	0,5143	0,2214	43,0	5	0	0	5
	%	S2			yes			0,7667	0,75	0,775	0,2301	29,6	4	1	0	5
DW	%	S1		0,934	H	26,3	6	27,04	26	25,99	0,3467	1,3	9	3	0	12
	%	S2		0,112	yes	29,8	7	29,92	29,89	29,83	0,8831	3	12	0	0	12
GR	%	S1		0,291	yes	94,6	15	96,67	100	94,29	7,464	7,9	7	1	0	8
	%	S2		-0,223	H	94,6	12	93,33	100	100	0	0	3	5	0	8
GR control	%	S1/S			yes			96,67	100	97,04	5,262	5,4	8	0	0	8
org	%	S1		0,909	H	60,5	6	62,15	60,26	60,6	1,154	1,9	9	3	0	12
	%	S2		-0,010	yes	67,4	4	67,39	67,34	67,21	1,086	1,6	10	2	0	12
RI	%	S1			yes			9	38	37,15	32,22	86,7	9	0	0	9
	%	S2		-2,158	yes	67,3	50	31	64,4	66,72	19,43	29,1	9	0	0	9
RLP	mm	S1		-1,303	yes	18,1	80	8,667	19,4	19,38	17,54	90,5	9	0	0	9
	mm	S2		-1,881	yes	32,6	40	20,33	33,1	32,73	7,842	23,9	9	0	0	9
RLP control	mm	S1/S			yes			65	46,1	47,6	10,98	23,0	8	1	0	9

Outlier test failed: C - Cohcran, G1 - Grubbs(1-outlier algorithm), G2 - Grubbs(2-outliers algorithm), H - Hampel, M - manual

Analyte	Unit	Sample	z-Graphics -3 -2 -1 0 +1 +2 +3	Z- value	Outl test OK	Assig-ned value	2* Targ SD%	Lab's result	Md.	Mean	SD	SD%	Pas-sed	Outl. fai-led	Mis-sing	Num of labs
Laboratory 5																
AGR	%	S1		-0,349	yes	95,5	15	93	97	95,04	5,963	6,3	8	1	0	9
	%	S2		-0,504	yes	95,9	12	93	96,7	95,86	4,392	4,6	9	0	0	9
CO2		S1		0,349	yes	1,17	80	1,333	1,075	1,067	0,496	46,4	8	0	0	8
		S2			yes	1,13		1,767	1,055	1,131	0,5754	50,8	8	0	0	8
CO2-	%	S1			yes			0,4667	0,5	0,5143	0,2214	43,0	5	0	0	5
	%	S2			yes			0,7333	0,75	0,775	0,2301	29,6	4	1	0	5
DW	%	S1		0,042	yes	26,3	6	26,33	26	25,99	0,3467	1,3	9	3	0	12
	%	S2		0,288	yes	29,8	7	30,1	29,89	29,83	0,8831	3	12	0	0	12
GR	%	S1		-0,178	yes	94,6	15	93,33	100	94,29	7,464	7,9	7	1	0	8
	%	S2		-0,810	H	94,6	12	90	100	100	0	0	3	5	0	8
GR control	%	S1/S			yes			93	100	97,04	5,262	5,4	8	0	0	8
org	%	S1		0,349	yes	60,5	6	61,13	60,26	60,6	1,154	1,9	9	3	0	12
	%	S2		0,420	yes	67,4	4	67,97	67,34	67,21	1,086	1,6	10	2	0	12
RI	%	S1			yes			38	38	37,15	32,22	86,7	9	0	0	9
	%	S2		0,042	yes	67,3	50	68	64,4	66,72	19,43	29,1	9	0	0	9
RLP	mm	S1		0,539	yes	18,1	80	22	19,4	19,38	17,54	90,5	9	0	0	9
	mm	S2		0,624	yes	32,6	40	36,67	33,1	32,73	7,842	23,9	9	0	0	9
RLP control	mm	S1/S			yes			36,33	46,1	47,6	10,98	23,0	8	1	0	9
Laboratory 6																
AGR	%	S1		-0,768	yes	95,5	15	90	97	95,04	5,963	6,3	8	1	0	9
	%	S2		0,713	yes	95,9	12	100	96,7	95,86	4,392	4,6	9	0	0	9
CO2		S1		-0,997	yes	1,17	80	0,7033	1,075	1,067	0,496	46,4	8	0	0	8
		S2			yes	1,13		0,5767	1,055	1,131	0,5754	50,8	8	0	0	8
DW	%	S1		-0,452	yes	26,3	6	25,94	26	25,99	0,3467	1,3	9	3	0	12
	%	S2		-0,710	yes	29,8	7	29,06	29,89	29,83	0,8831	3	12	0	0	12
GR	%	S1		-0,648	yes	94,6	15	90	100	94,29	7,464	7,9	7	1	0	8
	%	S2		0,951	yes	94,6	12	100	100	100	0	0	3	5	0	8
GR control	%	S1/S			yes			96,67	100	97,04	5,262	5,4	8	0	0	8
org	%	S1		-0,026	yes	60,5	6	60,45	60,26	60,6	1,154	1,9	9	3	0	12
	%	S2		0,111	yes	67,4	4	67,55	67,34	67,21	1,086	1,6	10	2	0	12
RI	%	S1			yes			51	38	37,15	32,22	86,7	9	0	0	9
	%	S2		1,765	yes	67,3	50	97	64,4	66,72	19,43	29,1	9	0	0	9
RLP	mm	S1		0,170	yes	18,1	80	19,33	19,4	19,38	17,54	90,5	9	0	0	9
	mm	S2		0,573	yes	32,6	40	36,33	33,1	32,73	7,842	23,9	9	0	0	9
RLP control	mm	S1/S			yes			37,67	46,1	47,6	10,98	23,0	8	1	0	9
Laboratory 7																
AGR	%	S1		-12,400	H	95,5	15	6,7	97	95,04	5,963	6,3	8	1	0	9
	%	S2		-1,025	yes	95,9	12	90	96,7	95,86	4,392	4,6	9	0	0	9
DW	%	S1		0,085	yes	26,3	6	26,37	26	25,99	0,3467	1,3	9	3	0	12
	%	S2		0,320	yes	29,8	7	30,13	29,89	29,83	0,8831	3	12	0	0	12
GR	%	S1		-12,390	H	94,6	15	6,667	100	94,29	7,464	7,9	7	1	0	8
	%	S2		-0,810	H	94,6	12	90	100	100	0	0	3	5	0	8
GR control	%	S1/S			yes			93,33	100	97,04	5,262	5,4	8	0	0	8
org	%	S1		0,367	yes	60,5	6	61,17	60,26	60,6	1,154	1,9	9	3	0	12
	%	S2		-0,124	yes	67,4	4	67,23	67,34	67,21	1,086	1,6	10	2	0	12
RI	%	S1			yes			1,65	38	37,15	32,22	86,7	9	0	0	9
	%	S2		-0,392	yes	67,3	50	60,7	64,4	66,72	19,43	29,1	9	0	0	9
RLP	mm	S1		-2,408	yes	18,1	80	0,6667	19,4	19,38	17,54	90,5	9	0	0	9
	mm	S2		-1,232	yes	32,6	40	24,57	33,1	32,73	7,842	23,9	9	0	0	9
RLP control	mm	S1/S			yes			40,5	46,1	47,6	10,98	23,0	8	1	0	9
Laboratory 8																
CO2		S1		-0,659	yes	1,17	80	0,8617	1,075	1,067	0,496	46,4	8	0	0	8
		S2			yes	1,13		0,8993	1,055	1,131	0,5754	50,8	8	0	0	8
DW	%	S1		1,267	H	26,3	6	27,3	26	25,99	0,3467	1,3	9	3	0	12
	%	S2		1,582	yes	29,8	7	31,45	29,89	29,83	0,8831	3	12	0	0	12
org	%	S1		0,992	yes	60,5	6	62,3	60,26	60,6	1,154	1,9	9	3	0	12
	%	S2		1,298	yes	67,4	4	69,15	67,34	67,21	1,086	1,6	10	2	0	12

Outlier test failed: C - Cohcran, G1 - Grubbs(1-outlier algorithm), G2 - Grubbs(2-outliers algorithm), H - Hampel, M - manual

Analyte	Unit	Sample	z-Graphics -3 -2 -1 0 +1 +2 +3	Z- value	Outl test OK	Assig-ned value	2* Targ SD%	Lab's result	Md.	Mean	SD	SD%	Pas-sed	Outl. fai-led	Mis-sing	Num of labs
Laboratory 9																
AGR	%	S1		0,628	yes	95,5	15	100	97	95,04	5,963	6,3	8	1	0	9
	%	S2		0,713	yes	95,9	12	100	96,7	95,86	4,392	4,6	9	0	0	9
DW	%	S1		-1,521	yes	26,3	6	25,1	26	25,99	0,3467	1,3	9	3	0	12
	%	S2		-2,109	yes	29,8	7	27,6	29,89	29,83	0,8831	3	12	0	0	12
Oc		S1			yes			928,3	879,9	899,3	36,96	4,1	2	0	0	2
		S2			yes			391,4	509,7	523,1	159,7	30,5	2	0	0	2
org	%	S1		1,873	yes	60,5	6	63,9	60,26	60,6	1,154	1,9	9	3	0	12
	%	S2		3,783	H	67,4	4	72,5	67,34	67,21	1,086	1,6	10	2	0	12
OUR		S1			yes			10,75	5,238	7,443	3,029	40,7	2	0	0	2
		S2			yes			4,65	4,65	4,65	1,202	25,8	1	1	0	2
RI	%	S1			yes			44,7	38	37,15	32,22	86,7	9	0	0	9
	%	S2		-0,428	yes	67,3	50	60,1	64,4	66,72	19,43	29,1	9	0	0	9
RLP	mm	S1		0,424	yes	18,1	80	21,17	19,4	19,38	17,54	90,5	9	0	0	9
	mm	S2		-0,634	yes	32,6	40	28,47	33,1	32,73	7,842	23,9	9	0	0	9
RLP control	mm	S1/S			yes			46,77	46,1	47,6	10,98	23,0	8	1	0	9
Laboratory 10																
AGR	%	S1		-1,703	yes	95,5	15	83,3	97	95,04	5,963	6,3	8	1	0	9
	%	S2		0,713	yes	95,9	12	100	96,7	95,86	4,392	4,6	9	0	0	9
CO2		S1		-0,570	yes	1,17	80	0,9033	1,075	1,067	0,496	46,4	8	0	0	8
		S2			yes	1,13		0,9317	1,055	1,131	0,5754	50,8	8	0	0	8
DW	%	S1		-0,330	yes	26,3	6	26,04	26	25,99	0,3467	1,3	9	3	0	12
	%	S2		0,579	yes	29,8	7	30,4	29,89	29,83	0,8831	3	12	0	0	12
GR	%	S1		-1,588	yes	94,6	15	83,33	100	94,29	7,464	7,9	7	1	0	8
	%	S2		0,951	yes	94,6	12	100	100	100	0	0	3	5	0	8
GR control	%	S1/S			yes			100	100	97,04	5,262	5,4	8	0	0	8
org	%	S1		-0,612	yes	60,5	6	59,39	60,26	60,6	1,154	1,9	9	3	0	12
	%	S2		-0,937	yes	67,4	4	66,14	67,34	67,21	1,086	1,6	10	2	0	12
RI	%	S1			yes			5,4	38	37,15	32,22	86,7	9	0	0	9
	%	S2		-0,172	yes	67,3	50	64,4	64,4	66,72	19,43	29,1	9	0	0	9
RLP	mm	S1		-2,113	yes	18,1	80	2,8	19,4	19,38	17,54	90,5	9	0	0	9
	mm	S2		0,153	yes	32,6	40	33,6	33,1	32,73	7,842	23,9	9	0	0	9
RLP control	mm	S1/S			yes			52,17	46,1	47,6	10,98	23,0	8	1	0	9
Laboratory 11																
AGR	%	S1		0,628	yes	95,5	15	100	97	95,04	5,963	6,3	8	1	0	9
	%	S2		0,139	yes	95,9	12	96,7	96,7	95,86	4,392	4,6	9	0	0	9
DW	%	S1		-0,425	yes	26,3	6	25,96	26	25,99	0,3467	1,3	9	3	0	12
	%	S2		-0,393	yes	29,8	7	29,39	29,89	29,83	0,8831	3	12	0	0	12
GR	%	S1		0,761	yes	94,6	15	100	100	94,29	7,464	7,9	7	1	0	8
	%	S2		-0,223	H	94,6	12	93,33	100	100	0	0	3	5	0	8
GR control	%	S1/S			yes			100	100	97,04	5,262	5,4	8	0	0	8
Oc		S1			yes			879,9	879,9	899,3	36,96	4,1	2	0	0	2
		S2			yes			611	509,7	523,1	159,7	30,5	2	0	0	2
org	%	S1		-0,246	yes	60,5	6	60,05	60,26	60,6	1,154	1,9	9	3	0	12
	%	S2		-0,799	yes	67,4	4	66,32	67,34	67,21	1,086	1,6	10	2	0	12
OUR		S1			yes			5,238	5,238	7,443	3,029	40,7	2	0	0	2
		S2			H			3,637	4,65	4,65	1,202	25,8	1	1	0	2
RI	%	S1			yes			103,0	38	37,15	32,22	86,7	9	0	0	9
	%	S2		0,559	yes	67,3	50	76,7	64,4	66,72	19,43	29,1	9	0	0	9
RLP	mm	S1		6,077	yes	18,1	80	62,1	19,4	19,38	17,54	90,5	9	0	0	9
	mm	S2		2,091	yes	32,6	40	46,23	33,1	32,73	7,842	23,9	9	0	0	9
RLP control	mm	S1/S			C			60,3	46,1	47,6	10,98	23,0	8	1	0	9
Laboratory 12																
CO2		S1		1,624	yes	1,17	80	1,93	1,075	1,067	0,496	46,4	8	0	0	8
		S2			yes	1,13		2,009	1,055	1,131	0,5754	50,8	8	0	0	8
CO2-	%	S1			yes			0,5	0,5	0,5143	0,2214	43,0	5	0	0	5
	%	S2			yes			0,6667	0,75	0,775	0,2301	29,6	4	1	0	5
DW	%	S1		-0,380	yes	26,3	6	26,0	26	25,99	0,3467	1,3	9	3	0	12
	%	S2		-0,096	yes	29,8	7	29,7	29,89	29,83	0,8831	3	12	0	0	12
org	%	S1		0,110	H	60,5	6	60,7	60,26	60,6	1,154	1,9	9	3	0	12
	%	S2		0,519	H	67,4	4	68,1	67,34	67,21	1,086	1,6	10	2	0	12

Outlier test failed: C - Cohcran, G1 - Grubbs(1-outlier algorithm), G2 - Grubbs(2-outliers algorithm), H - Hampel, M - manual

LIITE 4. YHTEENVETO z - ARVOISTA

APPENDIX 4.SUMMARY OF z SCORES

Analyte	Sample\Lab	1	2	3	4	5	6	7	8	9	10	11	12	%
AGR	S1	S	.	S	S	S	S	u	.	S	S	S	.	89
	S2	S	.	S	S	S	S	S	.	S	S	S	.	100
CO2	S1	.	q	S	S	S	S	.	S	.	S	.	S	88
	S2	.	.	.	.	.	.	.	.	.	.	.	.	
CO2-prod/bottle	S1	.	.	.	.	.	.	.	.	.	.	.	.	
	S2	.	.	.	.	.	.	.	.	.	.	.	.	
DW		.	.	.	.	.	.	.	.	.	.	.	.	
	S1	S	S	S	S	S	S	S	S	S	S	S	S	100
	S2	S	S	S	S	S	S	S	S	q	S	S	S	92
GR	S1	S	.	S	S	S	S	u	.	.	S	S	.	88
	S2	S	.	S	S	S	S	S	.	.	S	S	.	100
GR control	S1/S	.	.	.	.	.	.	.	.	.	.	.	.	
Oc	S1	.	.	.	.	.	.	.	.	.	.	.	.	
	S2	.	.	.	.	.	.	.	.	.	.	.	.	
org		.	.	.	.	.	.	.	.	.	.	.	.	
	S1	S	S	S	S	S	S	S	S	S	S	S	S	100
	S2	S	S	S	S	S	S	S	S	U	S	S	S	92
OUR	S1	.	.	.	.	.	.	.	.	.	.	.	.	
	S2	.	.	.	.	.	.	.	.	.	.	.	.	
RI	S1	.	.	.	.	.	.	.	.	.	.	.	.	
	S2	S	.	S	q	S	S	S	.	S	S	S	.	89
RLP	S1	S	.	S	S	S	S	q	.	S	q	U	.	67
	S2	S	.	S	S	S	S	S	.	S	S	Q	.	89
RLP control	S1/S	.	.	.	.	.	.	.	.	.	.	.	.	
%		100	80	100	92	100	100	73	100	78	92	82	100	
Accredited				yes	yes						yes			

S - satisfactory ($-2 \leq z \leq 2$), Q - questionable ($2 < z < 3$), q - questionable ($-3 < z < -2$),
U - unsatisfactory ($z \geq 3$), u - unsatisfactory ($z \leq -3$)

%* - percentage of satisfactory results

Totally satisfactory, % In all: 91 In accredited: 94 In non-accredited: 90

EVALUATION OF ASSIGNED VALUE AND THEIR UNCERTAINTIES

All assigned values and their uncertainties were calculated using robust statistics. **The reliability of the assigned value** was tested according to the criterion:

$u/s_p \leq 0.3$, where

u is the standard uncertainty of the assigned value
(the expanded uncertainty of the assigned value (U) divided by 2) and
s_p the standard deviation for proficiency assessment
(total standard deviation divided by 2).

The assigned values used in this comparison test **cannot be considered reliable according** to this criterion.

The reliability of the **target value for the total deviation** and the reliability of the corresponding z score were estimated by comparing the deviation for proficiency assessment (s_p) with the robust standard deviation of the reported results (s_{rob}). The criterion $s_{rob} < 1.2^* s_p$ **was fulfilled for all evaluations except RLP (S1).**

Measurement	Sample	Assigned value	Sd_{rob}	U %	Sp	u/s_p	Is Sd_{rob}< 1.2 Sp?
AGR	S1	95,5	5,6	5,2	7,163	0,35	Yes
	S2	95,9	5,0	4,3	5,754	**0,36**	Yes
CO2	S1	1,17	0,4	34,4	0,468	**0,43**	Yes
DW	S1	26,3	0,8	2,2	0,789	**0,36**	Yes
	S2	29,8	0,9	2,2	1,043	0,32	Yes
GR	S1	94,6	6,1	6,1	8,306	**0,41**	Yes
	S2	94,6	5,3	5,0	5,528	**0,41**	Yes
org.	S1	60,5	1,5	1,8	1,815	0,31	Yes
	S2	67,4	1,1	1,3	1,348	0,32	Yes
R1	S2	67,3	20,7	25,6	21,873	0,39	Yes
RLP	S1	18,1	6,6	37,2	6,52	**0,47**	Yes
	S2	32,6	8,3	22,5	6,52	**0,56**	**No**

Documentation page

Publisher	Finnish Environment Institute (SYKE)	Date May 2013
Author(s)	Liisa Maunuksela, Katarina Björklöf, Leena Kaarla, Mirja Kartio and Mirja Leivuori	
Title of publication	Proficiency Test on soil improver maturity tests	
Parts of publication/ other project publications	The publication is available only in the internet www.syke.fi/publications.	
Abstract	Evira and Proftest SYKE carried out this proficiency test in November-December 2012 for sample phytotoxicity and aerobic biological activity by determining the effect of soil improver samples on germination and root growth of cress, sample CO_2-production or oxygen uptake and sample dry weight and organic matter content. In total 11 laboratories took part in this test. Sample material was soil improver (S1) and soil improver and peat based growing medium (S2). Standard methods were used to determinate the properties from the samples, except for CO_2 evolution rate analysis for which no standard exist. The robust 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 CO_2 (S2), CO_2 production per bottle, and root length index (RI; S1), oxygen consumption (Oc) and oxygen uptake rate (OUR). In total, 91 % of the results were satisfactory when the deviations of 4-80 % from the as-signed values were accepted. It seems further guidance in some of the methods is needed. According to the results many laboratories have good practices and manage these analyses well. Other laboratories still need more experience. In future rounds of proficiency tests also pretreatment practices will be taken into account.	
Keywords	proficiency test, soil inprovers, phytotoxicity, carbon dioxide production, compost, maturity assessment, oxygen uptake rate	
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Tekijä(t)	Liisa Maunuksela, Katarina Björklöf, Leena Kaarla, Mirja Kartio ja Mirja Leivuori	
Julkaisun nimi	Proficiency Test on soil improver maturity tests	
Julkaisun osat/ muut saman projektin tuottamat julkaisut	Julkaisu on saatavana vain internetistä. www.syke.fi/julkaisut	
Tiivistelmä	Evira toteutti yhdessä Proftest SYKEn kanssa maanparannusaineiden fytotoksisuutta ja aerobista biologista aktiivisuuta (stabiilisuutta) koskevan vertailukokeen marras-joulukuussa 2012. Vertailukokeen kahdesta näytteestä tutkittiin krassin itävyys ja juuren kasvu, hiilidioksidintuotto tai hapen kulutus sekä näytteiden kuivapaino ja orgaanisen aineen määrä. Pätevyyskokeeseen osallistui yhteensä 11 laboratoriota. Näytemateriaalina käytettiin maanparannusainetta (S1) ja maanparannusaineen ja turpeen sekoitusta (S2). Laboratoriot käyttivät standardimenetelmiä näytteiden ominaisuuksien tutkimiseen paitsi hiilidioksidituoton määrityksessä, missä standardit puuttuvat kyseiselle matriisille. Mittaussuureen vertailuarvona käytettiin osallistujien ilmoittamien tulosten robustia keskiarvoa. Laboratorioiden pätevyyden arviointi tehtiin z-arvon avulla. Tavoitehajonta määritettiin pätevyyskokeen hajonnan perusteella. z-arvoja ei määritetty hiilidioksidille (S2), hiilidioksidituotto per pullo tai juurenpituus-indeksille (RI; S1), hapen kulutukselle (Oc) tai hapen sitoutumisnopeudelle (OUR). Kaikkiaan 91 % tuloksista oli hyväksyttäviä, kun tavoitehajonta oli of 4-80 % tavoitearvosta. Kahdeksalla laboratoriolla oli kaikki tulokset hyväksyttäviä. Tulosten perusteella kierrokseen osallistuvat laboratoriot hallitsevat kyseiset analyysit pääasiassa hyvin vaikka jotkut laboratoriot tarvitsevat enemmän kokemusta tietyissä analyyseissä. Tulevissa pätevyyskokeissa tullaan huomioimaan myös laboratorioiden suorittama näytteen esikäsittelyprosessi.	
Asiasanat	pätevyyskoe, maanparannusaine, fytotoksisuus, hiilidioksidin tuotto, komposti, kypsyysaste, hapen kulutus	
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Presentationsblad

Utgivare	Finlands Miljöcentral (SYKE)	Datum Maj 2013
Författare	Liisa Maunuksela, Katarina Björklöf, Leena Kaarla, Mirja Kartio och Mirja Leivuori	
Publikationens titel	Proficiency Test on soil improver maturity tests	
Publikationens delar/ andra publikationer inom samma projekt	Publikationen finns tillgänglig på internet www.syke.fi/pyblikationer	
Sammandrag	Livsmedelssäkerhetsverket Evira genomförde tillsammans med Finlands miljö central (SYKE) i november 2012 en kompetensprövning om jordförbättringsmedels fytotoxiska verkan och aerobiska biologiska aktivitet (stabilitet). Från komptensprövningens två prov undersöktes krassens groning och rotens längd under tillväxt i proverna, provernas koldioxidförbrukning och syreförbrukning samt torrvikten och mängden organiskt material i proverna. Totalt elva laboratorier deltog i komptensprövningen. Provmaterialet bestod av jordförbättringsmedel (S1) och en blandning av jordförbättringsmedel och torv (S2). Laboratorierna använde standardiserade undersökningsmetoder utom för produktion av koldioxid, för vilken det inte finns någon standard för denna matris. Som det åsatta värdet användes det robusta medelvärdet av deltagarnas resultat. Laboratoriernas kompetens bedömdes med z-värden. Det beräknade värdet för standardavvikelsen för det åsatta värdet beräknades från deltagarnas robusta standardavvikelse. z-värden beräknades inte för koldioxid (S2), koldioxid per flaska eller index-värdet för rotens längd (RI, S1), syreförbrukningen (Oc) eller bindningshastigheten för syre (OUR). Total var 91 % av resultaten goda när 4-80% avvikelse från det åsatta värdet godkändes. Åtta laboratorier hade alla resultaten goda. På basen av resultaten har många av laboratorierna goda rutiner fast en del av laboratorierna behöver mera erfarenhet. I kommande kompetensprövningar kommer också provernas förbehandlingar beaktas.	
Nyckelord	kompetensprövning, fytotoxicitet, koldioxid production, kompost, mognadsgraden av kompost, syreförbrukning	
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