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Quality Assurance and Quality Control in Forest Soil Analysis: 5th FSCC Interlaboratory Comparison

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LIST OF ABBREVIATIONS

ICP	International Co-operative Programme
FSCC	Forest Soil Co-ordinating Centre
EC	European Commission
EU	European Union
FSEPM	Forest Soil Expert Panel Meeting
QA/QC	Quality assurance – Quality Control
LOI	Loss-On-Ignition
NFC	National Focal Centre
ISO	International Standardisation Organization
$sRepr^2$	Estimation of the reproducibility variance
$sLab^2$	Estimation of the between-laboratory variance
$sRep^2$	Estimation of the repeatability variance
CV	Coefficients of variation
NA	Not Applicable
IQR	Inter quartile range
LOQ	Limit of Quantification

SUMMARY

A total of 48 laboratories reported their results in the 5th FSCC Interlaboratory Comparison 2007. Nine laboratories reported outliers and stragglers for more than 20 % of the total; five based on the between-laboratory variability, and eight laboratories based on the within-laboratory variability. Problem parameters are (1) exchangeable elements, especially Na, Ca, free H^+, Mg, Acidity and Fe, (2) the heavy metals Hg and Cd extracted by Aqua Regia, Extractable Al and Mg, (3) carbon content in sample D with low organic carbon content and (4) the pH determination of a peat sample. In general there are more problems when the concentration of the concerning element is relatively low. Compared to the 4th FSCC interlaboratory comparison in 2005, the coefficients of variation of all groups of analysis have improved or remained at a similar level. The CV of the blind sample B improved by 20% mainly because of a large improvement of the analysis of the Aqua Regia extractable elements.

The application of the data integrity expert rules could have been better. Several laboratories reported data which violated the rules. The rules might need further refinement, especially concerning peat layers e.g. for pH.

1 INTRODUCTION

ICP-Forests of UN-ECE initialised in collaboration with the EC a programme for the assessment and monitoring of air pollution effects on forest ecosystems in Europe. The major objective of the programme was to realise a better understanding of the air pollution processes. The study of the forest soil condition is an important part of this forest monitoring programme.

During the period 1985 – 1998 a first European-wide forest soil survey was carried out (participation of 31 countries). Two intercalibration exercises have been done within the framework of this survey. A **first Intercalibration** exercise, with 22 participating countries, used 4 standard soil samples and aimed at comparing different national analysis methods (Van der Velden and Van Orshoven, 1992). This comparison revealed a high variance between the results obtained by different methods and established the need for harmonisation of the methodologies. Therefore a **second Intercalibration** Exercise (Vanmechelen *et al.,* 1997), with 26 participating laboratories, using 2 soil samples, was conducted in 1993, simultaneously with the analysis of the collected soil samples of the Level I plots. Laboratories using national methods were recommended to analyse the standard soil samples with both national and reference methods, in order to provide a basis for comparison. Once more the existing variance, especially between different methods, asked for the uniform use of reference methods.

In view of a second European wide soil survey, harmonisation and improvement of the analytical techniques was indispensable. In order to assure the quality of the data obtained by soil analysis, the 10th Forest Soil Expert Panel (Warsaw, 2000) decided to proceed to a **third Intercalibration Exercise**. This third ring test (2002-2003) provided insight in the quality of soil analysis results and thus the quality of the future Forest Soil Database. A revision of the ICP Forests Submanual on sampling and analysis of soil' (FSCC, 2003) was a first step in this harmonisation process. All participating countries in the third ring test were requested to use the recently proposed reference methods which are mainly based on ISO-standards. The laboratories improved for the 'easy' parameters such as pH, organic carbon and total nitrogen. However, in the analyses of extractable and exchangeable elements no clear improvements could be demonstrated.

At the onset of the EC Forest Focus demonstration project 'BioSoil', the FSCC proceeded in 2005 with a **fourth Interlaboratory Comparison**. All analyses in the BioSoil project need to be done by laboratories which perform well in the FSCC Intercalibration Exercises. The analytical methods allowed in the fourth interlaboratory comparison and the procedure for the statistical analysis were exactly the same as in the 3rd interlaboratory comparison, allowing to detect possible progress.

The laboratories gained more experience in the reference methods and used more control charts, though the general use of these quality control measures was still limited. Compared to the 3rd Interlaboratory Comparison the coefficients of variation of all the parameters improved except for the total nitrogen which was probably due to the very low nitrogen content of some of the samples. Problem parameters were (1) the heavy metals and S extracted by Aqua Regia, (2) the exchangeable elements, (3) organic carbon in samples with low organic carbon content and (4) the calcium carbonate determinations.

In 2007 FSCC organised this **fifth FSCC Interlaboratory Comparison**. This exercise provides more information on the quality of the laboratory analyses during the period that most of the laboratories are analysing their national BioSoil samples and that the central laboratory is analysing an important subset of these samples. New in this ring test was the use of an on-line registration and data submission system. The analytical laboratory methods are the methods described in the ICP Forests Manual on Sampling and Analysis of Soil (update 2006) and the statistical procedures are the same as in the two previous interlaboratory comparisons.

2 MATERIALS AND METHODS

2.1 Selection of the laboratories

FSCC asked the National Focal Centres (NFC) of ICP Forests to select laboratories for the interlaboratory comparison. Initially 51 laboratories from 29 European countries registered by the 1st of May 2007. 22 of these countries participate in the BioSoil project. The seven other countries (Bulgaria, Croatia, Russian Federation, Serbia, Switzerland and Turkey) participate in the ICP Forests programme but not in BioSoil. Three laboratories (n° 24, 39 and 76) registered, received the test samples, but did not further participate in the ring test. These laboratories will not be mentioned in the further discussion. So a total of **48** laboratories analysed the soil samples and reported their results to FSCC. Their contact persons and addresses are listed in Annex 1.

39 of these laboratories conduct soil analyses in the BioSoil demonstration project following the ICP Forests Manual on Sampling and Analysis of Soil IIIa (FSCC, 2006).

2.2 Sample characterisation

2.2.1 The test samples

Five samples were sent to each of the participating laboratories on the 7th of May 2007. This included 4 mineral soil samples (A, B, C and D) and one forest floor sample (E). The samples were taken under forest conditions in different regions of Europe (Norway, Belgium, Spain, Germany and Sweden).

- **Sample A** is a loamy sand soil sample coming from the iron B horizon of a Cambic Arenosol in Norway. This is the same sample as the aqua regia extracted sample G in the 4th FSCC Interlaboratory Comparison.
- **Sample B** is the FSCC soil reference sample which is a loamy soil sample taken from the 20 - 40 cm layer of a mixed Flemish deciduous forest where Pedunculate oak (*Quercus robur*) and beech (*Fagus sylvatica*) dominate. It is a similar sample as sample B in the 4th FSCC Interlaboratory Comparison, though sampled over a larger area and after a more profound homogenisation.
- **Sample C** is a Spanish calcium carbonate rich soil sample. It is taken from the C horizon between 7 and 29 cm depth.
- **Sample D** is a loamy soil sample from Germany. It is taken at a depth between 40 and 80 cm in the B horizon of a colluvial brown earth. The sample has also been analysed in one of the German ring tests.
- **Sample E** is an acid Swedish peat sample.

Table 1 gives an overview of the properties of the five soil samples, based on the results of the analyses of all participating laboratories in the 5th FSCC Interlaboratory Comparison, making abstraction of the outliers.

Table 1: List of measured parameters with per sample, the mean value and the number of laboratories (N°) on which the values are based after outliers had been excluded

	Sample	A		B		C		D		E	
Parameter	Unit	N°	Mean	N°	Mean	N°	Mean	N°	Mean	N°	Mean
Moisture	%	35	0.9	39	0.7	39	1.7	39	1.2	38	7.5
Particle size clay	%	33	5.2	31	9.6	31	22.6	32	26.0		
Particle size sand	%	31	84.7	32	45.7	34	43.6	31	37.0		
Particle size silt	%	34	10.5	33	43.8	31	34.3	30	37.1		
pHCaCl2		45	4.2	41	3.8	43	7.3	44	4.0	37	2.8
pHH2O		43	4.6	44	4.2	45	7.9	45	4.6	45	4.0
CaCO3	g/kg					39	148.4				
OC	g/kg	38	8.0	41	6.7	40	27.9	32	3.8	38	497.4
Total N	g/kg	39	0.5	42	0.4	37	2.4	43	0.7	42	9.6
Exchangeable Acidity	cmol(+)/kg	32	1.43	29	3.23	8	0.12	32	1.88	26	6.93
Exchangeable Al	cmol(+)/kg	38	1.15	36	2.70	14	0.05	38	1.53	34	0.72
Exchangeable Ca	cmol(+)/kg	26	0.06	28	0.12	34	17.38	28	0.12	36	4.06
Exchangeable Fe	cmol(+)/kg	27	0.02	34	0.11	16	0.01	18	0.01	34	0.21
Exchangeable K	cmol(+)/kg	31	0.03	33	0.07	32	0.69	35	0.20	34	0.21
Exchangeable Mg	cmol(+)/kg	32	0.03	31	0.05	35	0.87	35	0.12	31	3.11
Exchangeable Mn	cmol(+)/kg	35	0.05	35	0.03	19	0.00	37	0.19	33	0.05
Exchangeable Na	cmol(+)/kg	17	0.02	24	0.04	22	0.04	23	0.02	26	0.27
Free H	cmol(+)/kg	13	0.05	23	0.23	5	0.06	17	0.10	25	5.61
Extractable Al	mg/kg	30	14568.0	31	8828.0	28	18281.3	27	25762.7	32	367.5
Extractable Ca	mg/kg	31	1699.1	34	350.7	33	76073.9	33	162.3	32	1081.3
Extractable Cd	mg/kg	21	0.106	15	0.046	21	0.161	18	0.116	22	0.193
Extractable Cr	mg/kg	38	24.6	37	20.7	37	24.1	34	37.2	24	1.4
Extractable Cu	mg/kg	37	11.6	37	4.5	34	13.2	35	12.3	30	1.8
Extractable Fe	mg/kg	32	21360.7	32	11709.2	33	20966.1	33	29367.1	32	397.8
Extractable Hg	mg/kg	12	0.019	14	0.030	11	0.026	12	0.024	10	0.038
Extractable K	mg/kg	32	1479.1	35	1581.2	34	4809.4	34	2414.0	32	114.1
Extractable Mg	mg/kg	30	3414.3	31	1346.0	36	3028.4	36	4200.7	35	500.1
Extractable Mn	mg/kg	38	437.9	37	109.3	37	360.3	34	1106.4	37	17.7
Extractable Na	mg/kg	29	92.4	28	51.8	31	141.4	28	113.3	30	94.3
Extractable Ni	mg/kg	34	18.7	31	4.9	35	17.3	34	58.7	23	1.1
Extractable P	mg/kg	34	688.6	33	101.3	34	428.9	36	279.9	35	182.3
Extractable Pb	mg/kg	38	8.0	38	8.0	34	13.3	36	11.5	34	12.5
Extractable S	mg/kg	26	91.3	24	77.0	25	418.7	25	131.8	25	1131.4
Extractable Zn	mg/kg	36	60.4	39	19.7	39	37.2	38	97.3	32	21.3
Reactive Al	mg/kg	24	2590.0	24	1372.1	25	771.3	24	1725.6	25	229.3
Reactive Fe	mg/kg	25	5637.4	25	2857.9	25	1763.3	24	3781.9	25	305.3
Total Al	mg/kg	10	47642.6	8	27010.0	10	42922.7	10	77065.5	9	666.9
Total Ca	mg/kg	9	8607.7	8	1430.6	10	76593.8	9	1322.2	6	1073.6
Total Fe	mg/kg	10	28129.9	10	13468.2	10	23571.2	10	35844.7	8	443.8
Total K	mg/kg	10	15145.5	10	13761.0	10	15974.9	10	26262.5	7	236.0
Total Mg	mg/kg	10	6818.8	8	1703.2	10	3785.4	9	6443.4	9	516.9
Total Mn	mg/kg	10	629.1	9	145.2	10	396.3	8	1148.0	9	20.0
Total Na	mg/kg	9	11705.3	10	5079.5	7	984.6	8	3303.0	9	147.9

2.2.2 Sample preparation and homogenisation

Samples were dried at 40°C and subsequently sieved on a 2 mm sieve. Then the samples have been homogenised by riffling and divided over 100 subsamples.

Prior to sending the soil samples to the laboratories, the samples were checked for homogeneity. Of each of the five samples (A, B, C, D and E), 8 subsamples were randomly selected and analysed for organic carbon (mineral soil samples by Walkley and Black and the organic sample by LOI) and the non-ferro aqua regia extractable elements. The variation between the subsamples was for most samples and parameters not significantly larger than the variation within the samples and therefore they were considered to be homogeneous. Table 2 gives the variance components for the sample A, C, D and E. The homogeneity of sample B, which is the FSCC reference sample, has been checked during the preparation of the sample and can be consulted in the concerning report. The dot plots of samples A, C, D and E can be consulted in Annex 6 on the attached CD rom.

Table 2: Variance components of the homogeneity tests

Parameter	Units	Sample	N°sub-samples	Gen. mean	St.dev. within sub-samples	St.dev. between sub-samples	General St.dev.	CV	% variation between sub-samples	% variation within sub-samples	
Walkley&Black OM	***%***	***A***	***8***	***1.19***	***0.04***	***0.05***	***0.06***	***5.11***	***62***	***38***	**>**
Walkley&Black OM	%	C	8	4.61	0.30	0.00	0.30	6.59	0	100	OK
Walkley&Black OM	%	D	8	0.62	0.02	0.00	0.02	3.06	1	99	OK
Loss-On-Ignition	%	E	7	99.03	0.02	0.00	0.02	0.02	8	92	OK
Extractable As	ppm	A	8	4.70	0.34	0.00	0.34	7.25	0	100	OK
Extractable As	ppm	C	7	13.03	1.85	0.00	1.85	14.18	0	100	OK
Extractable As	ppm	D	8	11.94	1.17	0.48	1.26	10.56	14	86	OK
Extractable Ca	ppm	A	8	2426.27	562.40	429.52	707.66	29.17	37	63	OK
Extractable Ca	ppm	C	7	74438.48	3967.47	0.00	3967.47	5.33	0	100	OK
Extractable Ca	ppm	D	7	108.29	38.33	8.15	39.19	36.19	4	96	OK
Extractable Ca	ppm	E	8	1038.16	31.61	20.94	37.92	3.65	31	69	OK
Extractable K	ppm	A	8	2382.54	558.59	418.69	698.09	29.30	36	64	OK
Extractable K	ppm	C	7	8146.37	1296.75	0.00	1296.75	15.92	0	100	OK
Extractable K	ppm	D	7	5868.12	1388.12	1048.97	1739.89	29.65	36	64	OK
Extractable K	ppm	E	8	135.83	8.27	4.66	9.49	6.99	24	76	OK
Extractable Mg	ppm	A	8	3131.85	191.41	126.07	229.20	7.32	30	70	OK
Extractable Mg	ppm	C	7	2882.77	204.70	42.46	209.05	7.25	4	96	OK
Extractable Mg	ppm	D	7	4159.14	221.50	37.15	224.59	5.40	3	97	OK
Extractable Mg	ppm	E	8	468.58	11.84	7.45	13.99	2.99	28	72	OK
Extractable Mn	ppm	A	8	548.25	272.76	0.00	272.76	49.75	0	100	OK
Extractable Mn	ppm	C	7	396.00	53.28	0.00	53.28	13.45	0	100	OK
Extractable Mn	ppm	***D***	***8***	***980.85***	***143.68***	***200.75***	***246.87***	***25.17***	***66***	***34***	**>**
Extractable Mn	ppm	E	8	20.28	0.71	0.11	0.72	3.55	2	98	OK
Extractable Na	ppm	***A***	***8***	***78.47***	***16.05***	***17.03***	***23.41***	***29.83***	***53***	***47***	**>**
Extractable Na	ppm	C	7	197.61	50.10	22.91	55.09	27.88	17	83	OK
Extractable Na	ppm	***D***	***7***	***268.87***	***60.92***	***82.13***	***102.26***	***38.03***	***65***	***35***	**>**
Extractable Na	ppm	***E***	***8***	***87.79***	***5.35***	***6.83***	***8.68***	***9.89***	***62***	***38***	**>**
Extractable P	ppm	A	8	706.77	39.54	0.00	39.54	5.59	0	100	OK
Extractable P	ppm	C	7	446.67	40.69	8.06	41.48	9.29	4	96	OK
Extractable P	ppm	D	8	283.67	13.56	7.42	15.46	5.45	23	77	OK
Extractable P	ppm	E	8	200.05	5.76	1.59	5.98	2.99	7	93	OK
Extractable S	ppm	A	8	106.15	9.29	0.00	9.29	8.75	0	100	OK
Extractable S	ppm	C	7	498.39	51.07	23.05	56.03	11.24	17	83	OK
Extractable S	ppm	***D***	***8***	***181.20***	***10.73***	***27.80***	***29.80***	***16.44***	***87***	***13***	**>**
Extractable S	ppm	E	8	1294.23	38.42	25.41	46.07	3.56	30	70	OK

For a few parameters on some samples, the variation between the samples was larger than the variation within the samples (indicated in bold italic in Table 2). The imbalance was never that striking to assume that this is really due to the inherent difference between the subsamples. It may also be due to lab errors or contamination. For example, concerning Na, very high coefficients of variation were found, indicating the limited ability of the laboratory to reproduce neatly its results. For sulphur, there was indeed a significant difference between two subsamples of sample D which can be due to sample heterogeneity.

During the execution period of the interlaboratory comparison, the central laboratory offered their services to conduct additional homogeneity tests. They received of each of the 5 samples, 5 subsamples which were analysed in triplicate for all parameters. These results will be included in an additional report.

2.2.3 Distribution of samples and submission of results

Samples were sent to the participating laboratories on the 7th of May 2007. The data submission deadline was the 1st of September 2007. Several laboratories sent some correction after the deadline which were all included in the database till the 24th of September 2007.

2.3 Soil Analytical Methods

2.3.1 Guidelines for sample analysis

Laboratories were requested to use the methods as described in the revised 'ICP Forests Submanual on Sampling and Analysis of Soil' (FSCC, update 2006). As seen from Table 3, all these methods are based on the ISO-standards. In contrast to the previous interlaboratory comparison, the analysis of total elements was again included in this comparison. However, these parameters are of no immediate relevance for the BioSoil project (where total elements are only optional parameters on Level II plots). Though, many laboratories analysed only a limited set of parameters, while in the BioSoil project they should analyse all mandatory and optional parameters on all Level I plots following the reference methods (see also Table 5).

Table 3: Methods recommended by the manual on soil sampling and analysis

Analysis	Reference Method	Description
Particle Size Distribution	ISO 11277	Pipette method
Soil pH	ISO 10390	Potentiometric pH (volumetric)
Carbonate Content	ISO 10693	Calcimeter
Organic Carbon Content	ISO 10694	Total Organic Carbon by dry combustion
Total Nitrogen Content	ISO 13878 ISO 11261	Elemental analysis by dry combustion Modified Kjeldahl method
Exchangeable Acidity and Free H^+ Acidity Exchangeable Cations	ISO 14254 ISO 11260	Titration or German method Extraction by 0.1 M $BaCl_{2,}$, single extraction
Aqua Regia Extractant Determinations	ISO 11466	Extraction by Aqua Regia
Reactive Fe and Al	ISRIC 1992	Extraction by Acid Oxalate
Total Elements	ISO 14869 ISO 14869	Dissolution with hydrofluoric and perchloric acids Total element analysis by fusion with lithium metaborate

Although the use of the reference methods is mandatory during the BioSoil soil survey, not all the laboratories used these reference methods for all types of analyses. After the 4th FSCC Interlaboratory Comparison, a coding system was suggested. See Annex 2. This system was for the first time used in this 5th FSCC Interlaboratory Comparison. Though, several problems were met and reported by the laboratories.

2.3.1.1 Sieving and milling

The first code asked for the method of sieving and milling (see Annex 2, Table 2.1). Many laboratories answered that they did not have the information on the sieving and milling because the samples were already prepared by FSCC. On the other hand, FSCC clearly informed the laboratories that the samples were sieved at 2 mm and not further milled. Since for certain parameters (e.g. total determinations), further milling is required according to the reference manual, it should have been indicated in the ‘sieving and milling’ field in case the participating laboratory did further mill the sample. A second problem was that the method drop down list of the on-line data submission system contained both the field ‘reference method’ and a field describing this method. For example, the reference method for the analysis of total elements asked for the milling of the sample. So it was not clear whether the laboratory should have indicated a ‘1’ for reference method or a ‘2’ for milling the sample.

2.3.1.2 Removal of compounds

This step is mainly of importance for the texture analysis (see Annex 2, Table 2.2). According to the reference method (ISO 11277) as described in the Manual, the analysis is done on samples where the cementing agents such as organic matter, soluble salts and carbonates are removed. The difficulty with describing the method for 5 samples at the same time, is that the procedure might be different for the different samples. For example, only sample C contained a significant amount of $CaCO_3$ (more than 2% mass fraction), with a $pH(CaCl_2) > 6.0$. Also the drop down system – as it is at the moment- does not allow for multiple selection e.g. combination of removal of organic carbon, the soluble salts, the gypsum and the carbonates (which was the case in Portugal).

2.3.1.3 Pretreatment

See Annex 2, Table 2.3.

2.3.1.4 Determination

See Table 2.4 in Annex 2.

2.3.2 Questionnaire

There was no separate questionnaire. The on-line registration and data submission system does allow so far only the data submission of the laboratory results and information concerning the used methodology.

2.4 Statistical data analysis

2.4.1 General characteristics of data analysis methodology

The statistical data analysis was based on the international standard ISO 5725-2 ‘Accuracy (trueness and precision) of measurement methods and results – part 2: Basic method for determination of repeatability and reproducibility of a standard measurement method’ (ISO, 1994c). Data analysis was done by means of the statistical software package S-plus 7.0 Professional (2005).

This transparent and easily to interpret procedure adds some specific items to the classical procedure:

1. The interpretation of statistics has been facilitated by graphs integrating multiple statistical parameters.
2. The procedure is **iterative.** The presence of very deviant outliers can distort the view of the whole distribution. Multiple outliers can mask each other; by eliminating outliers, new outliers and stragglers may pop up. After outliers are eliminated, the statistical analysis is repeated to study the distributions in order to trace ‘new’ outliers or stragglers. This iterative procedure will continue until no new outliers are found or in this ring test, up to a maximum of seven iterations in this interlaboratory comparison.
3. The procedure allows the comparison of different sources of variance:

$$\boxed{sRepr^2=sLab^2 + sRep^2}$$

where		
	$sRepr^2$	estimation of the **reproducibility variance**
	$sLab^2$	estimation of the **between-laboratory variance**
	$sRep^2$	estimation of the **repeatability (within-laboratory) variance**

The reproducibility (Repr) is a measure of agreement between the results obtained with the same method or identical test or reference material under different conditions (execution by different persons, in different laboratories, with different equipment and at different times). The repeatability (Rep) is a measure of agreement between results obtained with the same method under the same conditions (job done by one person, in the same laboratory, with the same equipment, at the same time or with only a short time interval). The between-laboratory variance is a measure of agreement between the results obtained with the same method or identical test or reference material in different laboratories.

2.4.2 Treatment of reported zero's, detection limits and missing values

"Zero" values: Many laboratories reported "zero's". The chance that these "zero's" are real zero's is very small. A real zero means that the analysed element is not present in the soil sample. This is not easy to detect because each method has its own quantification limit below which the measurement can not be quantified in a reliable way.

A zero value could be accepted for the $CaCO_3$ content in samples A, B, D and E since these samples had a very low pH($CaCl_2$).

"Values below quantification limit": Laboratories have been asked to indicate when the concentration of a certain parameter was below the limit of quantification (LOQ) and to report in such a situation the quantification limit. However, this rule was not always consistently applied by all laboratories. To guarantee consistency throughout the dataset, FSCC did not include the values below the LOQ in the statistical data analysis. So when for a certain laboratory, no statistical evaluation is available for a certain parameter, either the laboratory did not report that parameter, either the reported values were below their LOQ.

"Missing values": Parameters which where not analysed by a certain laboratory have been removed from the dataset for the statistical analysis.

All analyses had to be analysed in triplicate. However some laboratories tried to report certain parameters by only one or two replicates by repeating the same value for the second and/or third observation. These duplicated values have been removed from the dataset (as far as FSCC was informed on this practise). When only one replicate was reported, this observation could not be included in the final evaluation of the inter- and intralaboratory variability for statistical reasons. When two observations have been reported, the parameter was included in the statistical analysis.

2.4.3 Coefficients of variation (CV)

Based on the general mean (Mgen) and the reproducibility variance (sRepr), the coefficient of variation could be calculated. This parameter allows a rough comparison with previous ring tests. The coefficient of variation is defined as:

$$\mathrm{CV} = \frac{\sigma}{\mu}\times 100 = \frac{s\,\mathrm{Re}\,pr}{Mgen}\times 100$$

Where σ = General standard deviation (estimated by the sRepr in the Mandels h/k plot)

μ = General mean (estimated by the Mgen in the Mandels h/k plot)

The CV provides an idea of the average deviation for a certain parameter. As the CV is standardised, it is possible to compare the CV's of the different parameters, and rank the analysed parameters according to their CV.

The CV is thus calculated **based on the cleaned dataset** after outliers have been removed. This CV includes both the within – and between laboratory variability which explains why the CV's in the FSCC Interlaboratory Comparisons are higher compared to ring tests where only the between-laboratory variability is evaluated.

2.5 Research objectives

The aim of the statistical analysis is to investigate three research questions:

1. Which laboratories are performing well and which poorly? These questions will be answered according to the between-laboratory variance (Mandel's h) and according to the within-laboratory variance (Mandel's k).
2. Since the laboratories were assumed to report results obtained under repeatability conditions, it is expected that the variance within the laboratories ($sRep^2$) will be smaller than the variance between de laboratories ($sLab^2$) in the equation:

   $$\boxed{sRepr^2=sLab^2 + sRep^2 \qquad \text{Where :} \qquad sRep^2 < sLab^2}$$

   In other words, we would expect that laboratories will be rather discarded from the laboratory population – and the calculation of the mean and standard deviation - based on the between-laboratory variance and not on the within-laboratory variance.
3. The results of those laboratories that participated in the previous FSCC Interlaboratory Comparison, will be compared for the 4th and 5th FSCC ring test, based on the results of sample B.

3 RESULTS

3.1 Participation

Table 4 provides an overview of the registered and participating laboratories of each country.

Table 4: List of participating countries

Country	Registered	Results	Country	Registered	Results
Austria	1	1	Latvia	1	1
Belgium	2	2	Lithuania	1	1
Bulgaria	1	1	Poland	1	1
Croatia	1	1	Portugal (including Azores)	2	2
Cyprus	1	1	Romania	1	1
Czech Republic	1	1	Russia	3	2
Denmark	1	1	Serbia	1	1
Estonia	2	2	Slovak Republic	1	1
Finland	2	2	Slovenia	1	1
France	1	1	Spain	2	2
Germany	14	13	Sweden	1	1
Greece	1	0	Switzerland	1	1
Hungary	2	2	Turkey	2	2
Ireland	1	1	United Kingdom	1	1
Italy	1	1	**Total**	**51**	**48**

3.2 Statistical data analysis

The data analysis using S-plus produced for each parameter (each analysed element) and each sample (A, B, C, D and E) a total of 7 figures: one dotplot of all reported values, one histogram and one boxplot of the mean of the three reported values, one histogram and one boxplot of the standard deviations, and one Mandel’s h and one Mandel’s k plot. All these graphs are provided in Annex 5 in PPT- presentations and in PDF-files on the attached CD-Rom, and are arranged per parameter group. Below the case of ‘Exchangeable Mg’ in sample C is shown as an example.

3.2.1 Exploratory Data Analysis

The objective of the exploratory data analysis was to ‘explore’ the observations. It allows a visual evaluation of the data and gives an indication of possible outliers. However, based on these exploratory analysis, no observations nor laboratories have actually been excluded from further analysis.

Two sources of variance are investigated: the inter-laboratory variance (between-laboratory variance) and the intra-laboratory variance (within-laboratory variance). Figure 1 and Figure 2 represent the inter-laboratory variance. They indicate the position of each laboratory in the population of all laboratories. Figure 3 and Figure 4 represent the standard deviations of each laboratory. They yield information on the within-laboratory variance. Figure 1 and 3 are histograms, while Figure 2 and 4 are box-plots. The histograms provide a first rough overview of the distribution of all data reported for a certain parameter and sample. The information contained within the histograms is:

- Visual outliers that are very deviant (parameter value and lab N° between parentheses)
- Relative frequencies in each class (in %)
- Density curve (smoothed trend-line)
- N: Number of observations in the histogram
- NA: Not Applicable
- Z: Number of reported zero's (see above)
- E: Number of excluded observations (very deviant outliers) from the presentation in the histogram; separately mentioned for upper and lower limits of distribution. The first number refers to the left side of the diagram, the second number to the right side of the histogram.
- U: Number of used observations in the calculations of a, m and s
- a: average value of the U observations
- m: median value of the U observations
- s: standard deviation of the U observations

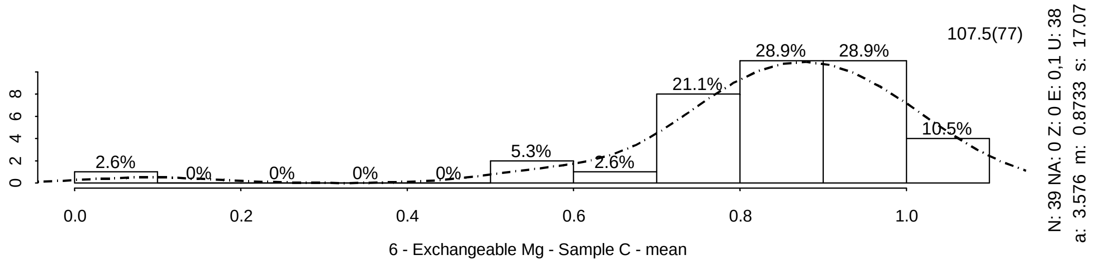

Figure 1: **Histogram showing relative percentages and a rescaled density curve of the mean of 3 replicates of the measured parameter 'Exchangeable Mg' in Sample C.** The units of the X-axis are in cmol(+)/kg soil.

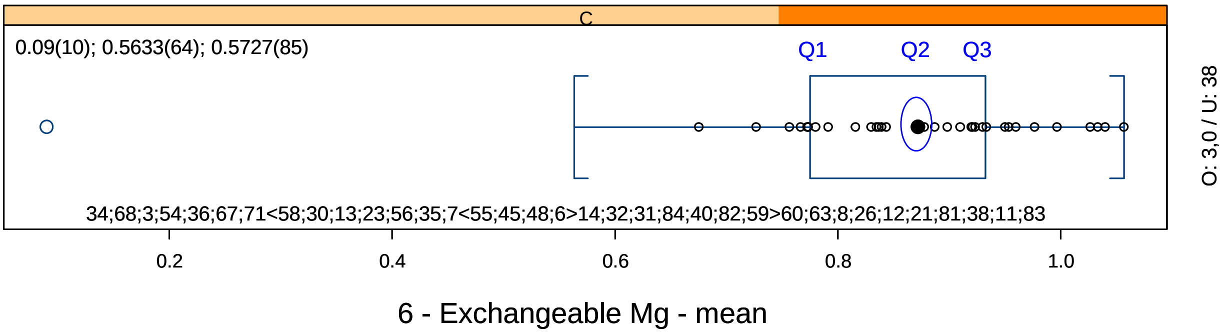

Figure 2: **Box plot of the mean values reported for sample C for the parameter 'Exchangeable Mg'.** The units of the X-axis are in cmol(+)/kg soil.

The information in the box plot starts from the dataset after the first rough cleaning done in the histograms where the very deviant visual outliers have been excluded. In this example of exchangeable Mg in sample C, it means that laboratory N° 77 is not included in the boxplot. The boxplot provides following information:

- Visual outliers (parameter value and lab N° between parentheses). These are placed in the top left and top right corner of the figure. On the right side of the figure ‘O’ indicates the number of outliers excluded from the box plot, respectively on the lower and the higher range of the box-plot. So in this example, three outlying labs have been identified in the box plot on the lower range: Labs N° 10, 64 and 85.
- Percentiles Q1 (25%), Q2 (50% or median) and Q3 (75%)
- U: Number of observations in the box-plot where U=N-E in the histograms.

Laboratories whose observations correspond to the median value, are put between brackets “< >”; observations between Q1 and Q2 are between “< <” and between Q2 and Q3 “> >”.

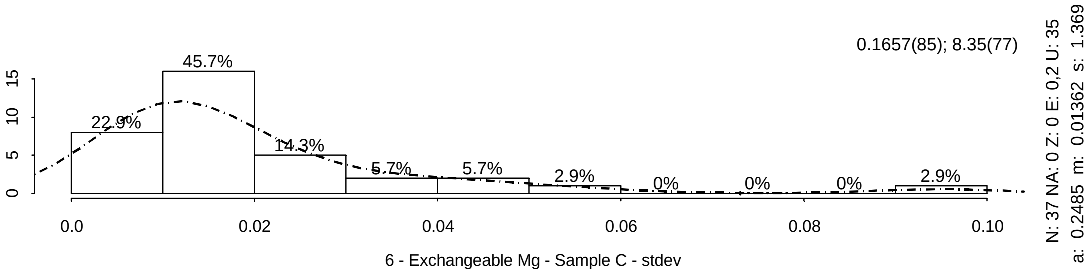

Figure 3: Histogram showing relative percentages and a rescaled density curve of the <u>standard deviation</u> based on 3 replicates of the measured parameter ‘Exchangeable Mg’ on Sample C. The units of the X-axis are in cmol(+)/kg soil.

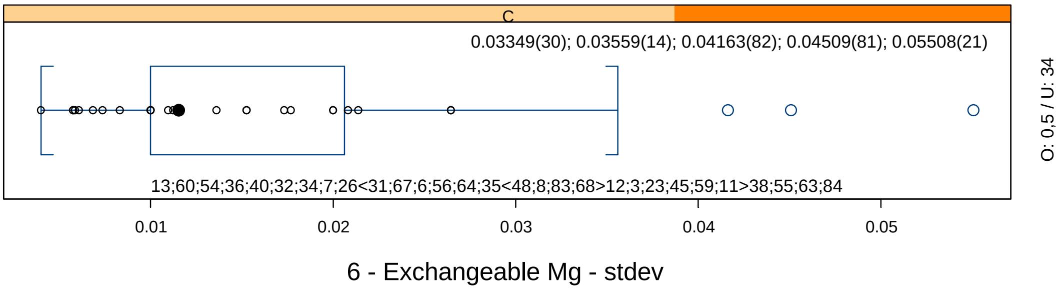

Figure 4: Box plot of the standard deviations for sample C for the parameter ‘Exchangeable Mg’. The units of the X-axis are in cmol(+)/kg soil.

Both histograms and box plots are based on the observations after the ‘very deviant’ outliers have been excluded. ‘Very deviant’ outliers are located more then **3.5 times** beyond the inter-quartile range (IQR). The IQR is defined as the distance from Q1 to Q3. The criterion to exclude observations is thus stronger then the criterion for ‘visual’ outliers as represented in the box-plot (Whiskers are placed at 1.5 * IQR). It is possible that whiskers are placed on a closer distance than 1.5 * IQR from the box-plot, in case there are no observations outside the 1.5 * IQR.

From the text on the right side of Figure 1, can be observed that the histogram is based on results from **N=39** laboratories. None of the reported values, was a “0” (**Z: 0**). One laboratory (laboratory N° 77) is excluded from the histogram, so the results of **U= 38** laboratories are used. Laboratory N°77 reported extremely high exchangeable Mg content (107.55 cmol(+)/kg). The average reported exchangeable Mg content of sample C is **a: 3.576** cmol(+)/kg the median exchangeable Mg content is **m: 0.8733** cmol(+)/kg and standard **deviation s: 17.07** cmol(+)/kg. In order to allow calculations of average, standard deviation and the Mandel’s h and k statistics, data are supposed to have a normal distribution. The shape of the density curve (dotted line) should therefore approach the symmetrical shape of a normal distribution.

Figure 2 shows that the laboratories N° 55, 45, 48 and 6 reported the median value of 0.8733 cmol(+)/kg soil. Laboratories N° 58, 30, 13, 23, 56, 35 and 7 reported values between the first quartile (**Q1**) and the median; laboratories N° 14, 32, 31, 84, 40, 82 and 59 reported values between the median and the third quartile (**Q3**). Laboratories N° 34, 68, 3, 54, 36, 67 and 71 reported values below the first quartile (**Q1**) and laboratories N° 60, 63, 8, 26, 12, 21, 81, 38, 11 and 83 reported values above the third quartile (**Q3**). The laboratories outside the 1.5 * IQR whiskers, are given with their laboratory number and average value above the box plot. Laboratories N° 10, 64 and 85 reported very low Mg contents of 0.09, 0.56 and 0.57 respectively.

Based on the histogram of the means (Figure 1) we would expect that laboratories N°77 will be an outlier in the in-depth statistical analysis for the between laboratory variability. Based on the box plot which is more severe (Figure 2), we see that also laboratories N° 10, 64 and 85 have doubtful results.

Based on the histogram of the standard deviations (Figure 3) we expect that laboratories N° 85 and 77 will be outliers for the within-laboratory variability and based on the more severe box plots, we see that also the within-laboratory variability of the labs N° 30, 14, 82, 81 and 21 is relatively high.

A laboratory can also check its performance compared to the other laboratories by studying the dot plots (Figure 5). Every dot represents a reported value of a specific parameter. The shape of the dot plot follows the sigmoid curve shape of a normal distribution. Laboratories are plotted on the Y-axis, arranged according to the magnitude of the reported values. One laboratory (N°77) reported extremely deviant results for the exchangeable Magnesium content of sample C. The values are given at the top of the graph Laboratory N° 77 reported 99.1, 107.5 and 115.8 cmol(+)/kg soil. Values reported by other laboratories can be read on the X-axis. 80 % of the reported values are located between 0.7 and 1 cmol(+)/kg soil. Again is seen that laboratories N° 10, 64, 85 and 77 tend to be outliers.

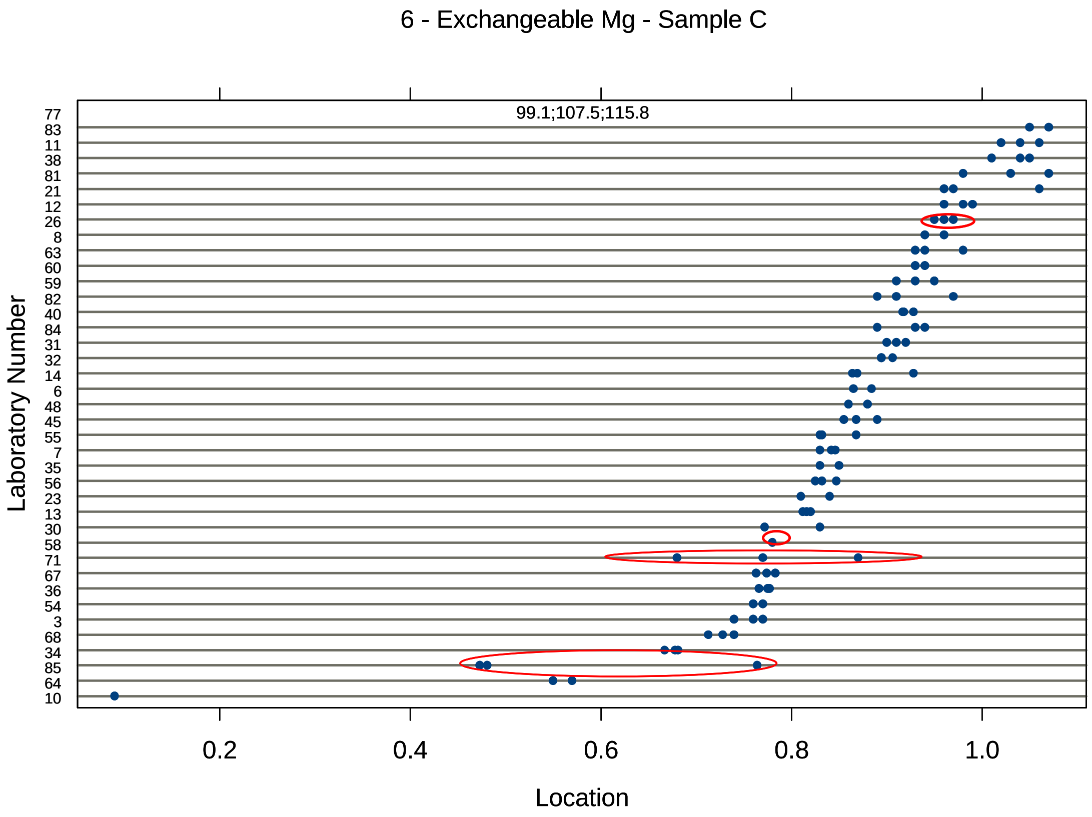

Figure 5: Dot plot of reported values for each laboratory, cumulatively ordered

This figure also tells something about the internal variance within one laboratory. For example, laboratories N° 85 and 71 reported three very different results – represented by 3 dots widely separated from each other – whereas laboratory N° 26 reported 3 very similar results – represented by 3 dots very close to each other. For laboratory N° 58 we see only one dot, which probably are 3 dots on top of each other. We expect that laboratory N° 85 and 71 will have a poor within-laboratory repeatability whereas laboratory N° 26 and 58 will have a very good within-laboratory repeatability.

For layout reasons, the dots of laboratory N° 77 have not been plotted. Their values are so deviant from the median value that showing these dots would completely disturb the figure. Therefore the reported values of laboratory n° 77 have been shown separately on top of the figure.

3.2.2 In-depth statistical data analysis: Mandel's h and Mandel' k statistics

Figure 6 and 7 present an example of Mandel's h and k statistics for the parameter 'Exchangeable Mg' of the test sample C. The Mandel's h statistics test the between-laboratory variance. The Mandel's k statistic is a measure for the within-laboratory variance. The information contained within the two figures is:

- Step x: Iteration number of runs; varies in this interlaboratory comparison from 1 till maximum 7
- Nlab: Number of laboratories after elimination of outliers
- Mgen: General mean after outliers have been excluded
- Fval: tests whether interlaboratory variance $\sigma_L^2 \neq 0$, F test for laboratory effect
- Pval: tests whether interlaboratory variance $\sigma_L^2 \neq 0$, p value of the F test
- sRep^2: estimation of repeatability variance
- sLab^2: estimation of the between-laboratory variance
- sRepr^2: estimation of the reproducibility variance
- CV: coefficient of variation (σ/μ)*100 = sRepr/Mgen*100
- Excluded laboratories: excluded observations that are statistical outliers, mentioning whether it was based on the h or k statistic:
- "h (H) + Laboratory N°": laboratory has been excluded based on the Mandel's h statistics
- "k (K) + Laboratory N°": laboratory which has been excluded based on the Mandel's k statistics
- E: Excluded observations, mentioning whether it was based on the h or k statistics

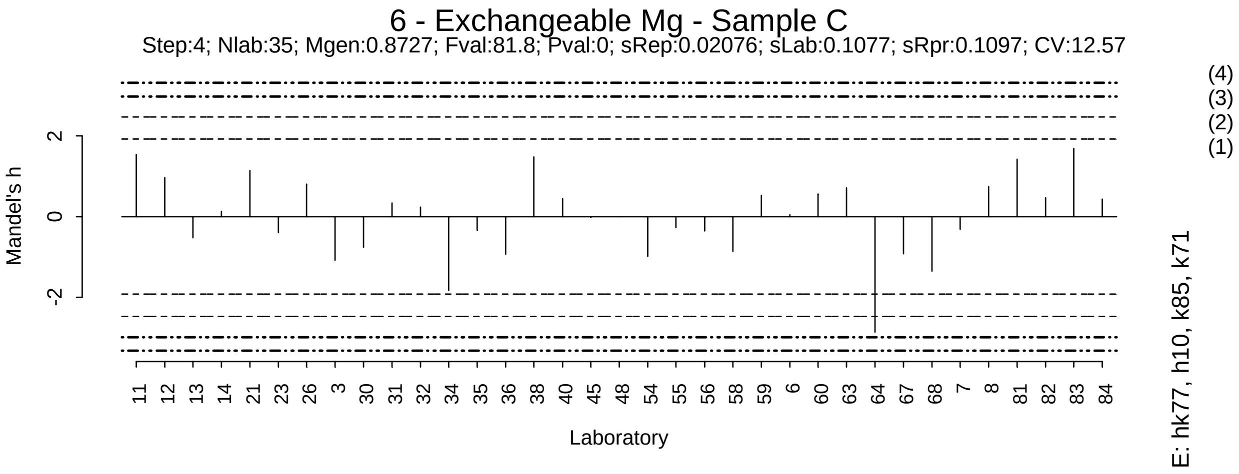

Figure 6: Mandel's h statistic for sample C for the parameter 'Exchangeable Mg'

Laboratory

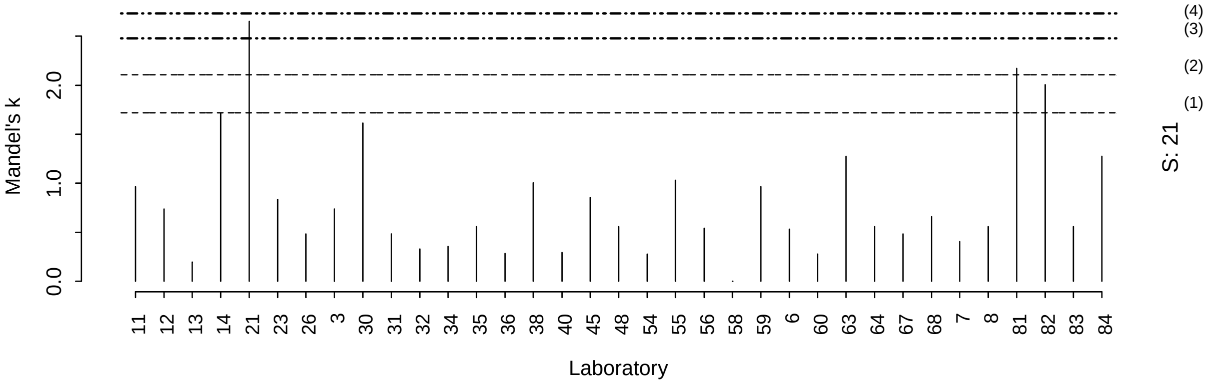

Figure 7: Mandel's k statistics for sample C for the parameter 'Exchangeable Mg'

On both the Mandel's h and k plots, 4 critical levels are indicated. When the critical level is exceeded, the H-null hypothesis "no difference between the mean values" will be rejected.

(1) Critical value where H_0 will be rejected at probability level of 95%

(2) Critical value where H_0 will be rejected at probability level of 99%

(3) Critical value where H_0 will be rejected at probability level of 95% after application of the Bonferroni rule.

(4) Critical value where H_0 will be rejected at probability level of 99% after application of the Bonferroni rule.

Statistical outliers are the observations of which the Mandel's h or k-statistic exceeds the critical value at probability level of 99% after application of the Bonferroni rule. Statistical stragglers are the observations of which the h or k-statistic are situated between the critical values of probability level 95 and 99% after application of the Bonferroni-rule. Figures 6 and 7 form the core of the statistical analysis and contain all necessary information. They usually confirm the expectations after studying Figures 1 till 5.

The Mandel's h statistic of laboratory N° 64 is low, but does not reach critical limit N° (3) (Figure 6). Together with laboratories N° 10 and 85 it forms the tail of the distribution on the lower range (Figure 2). Laboratories N° 77 and 10 have been excluded from the statistical analysis based on the Mandel's h and laboratories N° 77, 85 and 71 based on the Mandel's k statistics (see lower right corner of Figure 6 'E). In the exploratory study, Lab N° 77 was were indeed excluded from the histogram of the menas in Figure 1 and Lab N° 77 and 85 from the histogram of the standard deviations in Figure 3. Lab N° 10 was identified in the box plot of the means. Lab N° 71 (with standard deviation = 0.09504) was included in the histogram (Lab explaining 2.9% of the distribution in the right bar) in the box plot but excluded from the box plot.

From Figure 7 is seen that laboratory N° 21 can be considered a straggler because the Mandel's k value is located between the critical value of the 95% and 99% confidence limits. This was already expected by studying Figures 4 and 5, where the box plot of the standard deviations and the dotplot was given. Observed stragglers are indicated on the right side of the figure behind the symbol 'S'.

Remarks:

1. In this example, no vertical 'line' is seen in the Mandel's k plot for laboratory N° 58. This is because the calculated k values is close or equal to "0". Lab N° 58 reported three identical values. The limit becomes a dot which can disappear in the printed version of the output.
2. Laboratories are excluded through an iterative procedure. A laboratory can, for example, be excluded based on the k statistic in the first step. In that case, it cannot be excluded any more in an subsequent step if it would have been an outlier for the h statistic in a subsequent step after a number of laboratories have been removed and the population composition was altered. A check has been included in the procedure where the excluded laboratory is compared with the laboratories left in the population, in this case, for the h statistic. If the laboratory appears to be an outlier for the h statistics as well, it receives a 'h' (in addition to the 'k') in front of its lab number. A similar procedure is applied when a laboratory is excluded based on the h statistic and checked for the k statistics in a later step (a 'k' in front of the 'h + lab number').
3. Sometimes it happens that, when performing the check in subsequent steps, a laboratory which was an outlier before, suddenly is not an outlier any more. This is possible when many laboratories have been excluded from the population and confidence limits have become wider till the original outlier falls again within the normal population. In that case, the original exclusion is restored, indicated on the right side of the Figures showing the Mandel's h statistics, by the laboratory number, followed by a small 'k' or 'h'.

3.2.3 Laboratory performance based on the number of outliers

The Mandel's h and k plots in Annex 5 visualise the occurrence of outliers and stragglers. The Mandel's h statistics inform about the performance of the laboratory compared to the whole population of laboratories. The Mandel's k statistics provides information on the within-laboratory variance. When a laboratory is excluded from the h or k statistics (defined as an outlier), it is considered as an indicator of poor quality of that laboratory.

Table 5 summarizes the Mandel's h and k plots given in Annex 5. For each laboratory and each analysed parameters a score has been given based on the frequency that a laboratory has been excluded:

(+++): No outlier has been defined for the reported samples, neither for inter - nor intralaboratory variability

(++): Less than or equal to 20% outliers have been identified, either for inter - or for intralaboratory variability

(+): Between 20 and 40% (40% included) outliers have been identified, either for inter - or for intralaboratory variability

(-): Between 40 and 60% (60% included) outliers have been identified, either for inter - or for intralaboratory variability

(--): Between 60 and 80% (80% included) outliers have been identified, either for inter - or for intralaboratory variability

(---): Between 80 and 100% (100% included) outliers have been identified, either for inter - or for intralaboratory variability

Empty cell = not analysed or the measured values were below LOQ

Note that in this table the intra – and interlaboratory variability receive equal weights. So a laboratory that has completely deviant results for the mean of the other laboratories but is relatively good in reproducing its own results can still fall in the 40 till 60% category and receive a (-) evaluation.

Based on the information in this table, the problem parameters for each individual laboratory can be identified. FSCC recommends to consult the more detailed graphs in Annex 5 to study the problem parameters more into detail. In Annex 5 for each sample the reported values are visualized and can easily be compared with the bulk of the data. The detailed statistical output is given in Annex 4.

Most of the laboratories measured a whole set of parameters. So it is interesting to study the frequencies of the exclusion of a laboratory per sample and separately for the between (based on the Mandel's h statistics) and within-laboratory variability (based on the Mandel's k statistics). Figures 8 till 17 compare the performance of the 48 laboratories showing the absolute number of outliers. From the figures, we see that the absolute number of outliers based on the within-laboratory variability is larger than the absolute number of outliers based on the between-laboratory variability. This means that the evaluation in Table 5 is dominated by the within-laboratory variability.

Table 5 can then be compared with the evaluation table of the 4th FSCC Interlaboratory Comparison in 2005 for those laboratories that participated in both comparison exercises. Laboratories N° 77 till 84 participated for the first time in the FSCC Interlaboratory Comparisons. So three of the poor performing laboratories (Lab N° 77, 81 and 82) did not participate in previous FSCC ring tests.

Table 5: Scoring of the laboratories for each individual element

Lab ID	Particle size clay	Particle size sand	Particle size silt	pHCaCl2	pHH2O	CaCO3	OC	Total N	Exchangeable Aci	Exchangeable Al	Exchangeable Ca	Exchangeable Fe	Exchangeable K	Exchangeable Mg	Exchangeable Mn	Exchangeable Na	Free H	Extractable Al	Extractable Ca	Extractable Cd	Extractable Cr
3	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	++	+++
6				+++	+++	+++	+++	+++		+++	+++	+++	+++	+++	+++	+		+++	+++	---	+++
7	+++	+++	+++	+++	+++	+++	+++	+++	++	+++	++	+++	+++	+++	+++	+++		+++	+++	+++	+++
8	+++	+++	+++	+++	+++	+++	++	+++	+++	+++	+++	+++	+++	+++	+++	---	+++	+++	+++	+++	+++
10	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	++	+++	++	+++	+++	+++	---	+++
11	++	+++	+++	+++	+++		+++	+++	+++	+++	+++	+++	+++	+++	+	++		+++	++	+	+++
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40	+++	+++	+++	++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++
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45				+++	+++		+++	+++	+++	+++	+++	+++	+++	+++	+++	+++		+++	+++		+++
48	+++	+++	+++	++	+++	+++	+++	+++		+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+	+++
53	+++	++	+++	+++	+++	+++	++	++													
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55	+++	+++	++	+++	+++			++	+++	+++	+++	+++	+++	+++	+++	+++	+	-	+	--	++
56	+++	+++	+++	+++	+++	+++	+++	+++	+	+++	+++	+++	+++	+++	++	+++	++	+++	+++	---	+
58	+++	+++	+++	+++						+++	+++	+++	+++	+++	+++	+++					
59	+	++	+++	+++	+++	+++	+++	++	++	+++	+	+++	+++	++	+++	+++	+	++	++	++	+++
60	+	+	+	+++	+++	+++	++	+++	+++	+++	+++	++	+++	+++	+++			++	++	+++	++
61	+++	+++	+++	++	+++	+++	++	+++										+++	++	+++	+++
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67	+++	+++	+++	++	+++	+++	+++	+++	+	+++	+	+++	+++	+	+++	-	+++	+++	+++	+++	+++
68				+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	++	+++	+++	+++	+++	-	+++
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79	+++	+++	+++	+++	+++	+++	+++	+++													
80	+++	+++	+++																		
81	+++	+++	+++	++	+++	+++	--	++	+	++	+	--	++	--	++	--	+	-	++		++
82	++	+++	+++	++	+++	+++	++	+		++	+	--	--	++	+++	---		+	+		++
83				++	+++		++		+++	+++	+++	+++	+++	+++	+++			+++	++	+++	+++
84				+++	+++	+++	+++	+++	+++	+++	-		+++	+	+++	-	++	+++	+++	+	+++
85	+++	+	+	++	++	+++	++	+++		+	++	++	+	++	++	-			+++	+++	

(+++): No outlier has been defined for the reported samples, neither for inter - nor intralaboratory variability

(++): Less than or equal to 20% outliers have been identfied, either for inter - or for intralaboratory variability

(+):Between 20 and 40% (40% included) outliers have been identified, either for inter - or for intralaboratory variability

(-): Between 40 and 60% (60% included) outliers have been identified, either for inter - or for intralaboratory variability

(--): Between 60 and 80% (80% included) outliers have been identified, either for inter - or for intralaboratory variability

(---):Between 80 and 100% (100% included) outliers have been identified, either for inter - or for intralaboratory variability

Table 5 (continued): Scoring of the laboratories for each individual element

Lab ID	Extractable Cu	Extractable Fe	Extractable Hg	Extractable K	Extractable Mg	Extractable Mn	Extractable Na	Extractable Ni	Extractable P	Extractable Pb	Extractable S	Extractable Zn	Reactive Al	Reactive Fe	Total Al	Total Ca	Total Fe	Total K	Total Mg	Total Mn	Total Na
3	+++	+++		+++	+++	+++	+++	+++	+++	+++	+++	+++	++	++	+++	+++	++	+++	+++	+++	+
6	+++	++	---	+++	+++	++	+++	+++	+++	++	+++	+++	+++	+++							
7	+++	+++		+++	+++	+++	+++	+++	+++	+++	+++	++	+++	+++	+++	+++	++	+++	+++	+++	+++
8	++	+++		+++	+++	+++		+++	+++	+++	+++	+++	+++	+++							
10	+++	++		+++	+	+++	++	++	+++	+++	++	++	+++	++							
11	++	+++		+++	++	+++	+++	+++	+++	++	++	++	+++	+++							
12	+	+		+	+++	+	++	-		++		+++									
13	+++	+++		+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++
14	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	++	+++	+++	+++	++	+++	+++	++	+++
18	+++							+++	+++	+++		+++									
21																					
23	+++	++	++	++	+++	+++	+++	+++	++	+++		+++									
26	+++	+++		+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++							
30	+++	+++		+++	+++	+++	++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++
31	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++							
32	-	+++		++	+++	+++	++	+++	+++	+++	+++	++	+++	+++	++	+	++	++	+++	++	+++
34	+++	+++	+++	+++	+++	+++	+++	++	++	+++	+++	+++									
35	+++	++	++	++	+++	++	+++	++	+++	+++		+++	+++	++							
36	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++
37	+++	+++		+	+++	+++	++	+++	+++	+++	+++	+++	+++	+++							
38													++	+++							
40	++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	++	+++	+++	+++	+++	+++
42	++					+++				++		++									
45	+++	+++		+++	+++	+++	+++	+++	+++	+++		+++									
48	++	+++	---	+++	+++	++	+++	+++	++	+++	+++	+++	++	+++	++	++	+++	++	++	++	+++
53				++					+												
54	+++	+++		+++	+++	+++	++	+++	+++	+++	+++	+++	+++	+++							
55	++	+++		--	+++	+++	-	++	+++	++	+++	++	+++	+++							
56	---	+++		+++	++	++	--	---	---	---		++	+++	+++							
58																					
59	+++	+++		+++	++	+++	+++	+++	+++	++	+	+++									
60	++	++	+++		++	+++		+++	+++	+		+++									
61	+++	+++	+++	+++	+++	+++	++	++	+++	+++	+++	+++	+++	+++							
62									+												
63	+++	++	++	+++	+++	+++		++	+++	+++	+++	++									
64	+++	++	--	++	++	++	++	+++	+++	+++	++	+++	++	++							
67	+++	+++	--	+++	+++	+++	+++	+++	+++	+++		+++	+	+							
68	+++	+++	++	+++	+++	+++	+++	+++	+++	++		+++	+++	+++							
69	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++									
71	+++					+++		++		+++		++									
77	+++	+		+++	++	++	+++	+++		+++	-	+++									
79																					
80																					
81	+	+		+++	++	++	++	+	+++	++	+++	-									
82	---	++		++	+	++	+++	-		---		---			-	---	+	-	--	---	---
83	+++	+		+++	+	++		+++	++	+++		+++	++	+++							
84	+++	+++	+++	+++	++	+++	+++	+++	++	+++	+++	+++	+++	+++	++	+	+++	+++	++	++	+
85	+++			+++	++	+++			+++	+++		+++									

Empty cells = not analysed or values below the LOQ

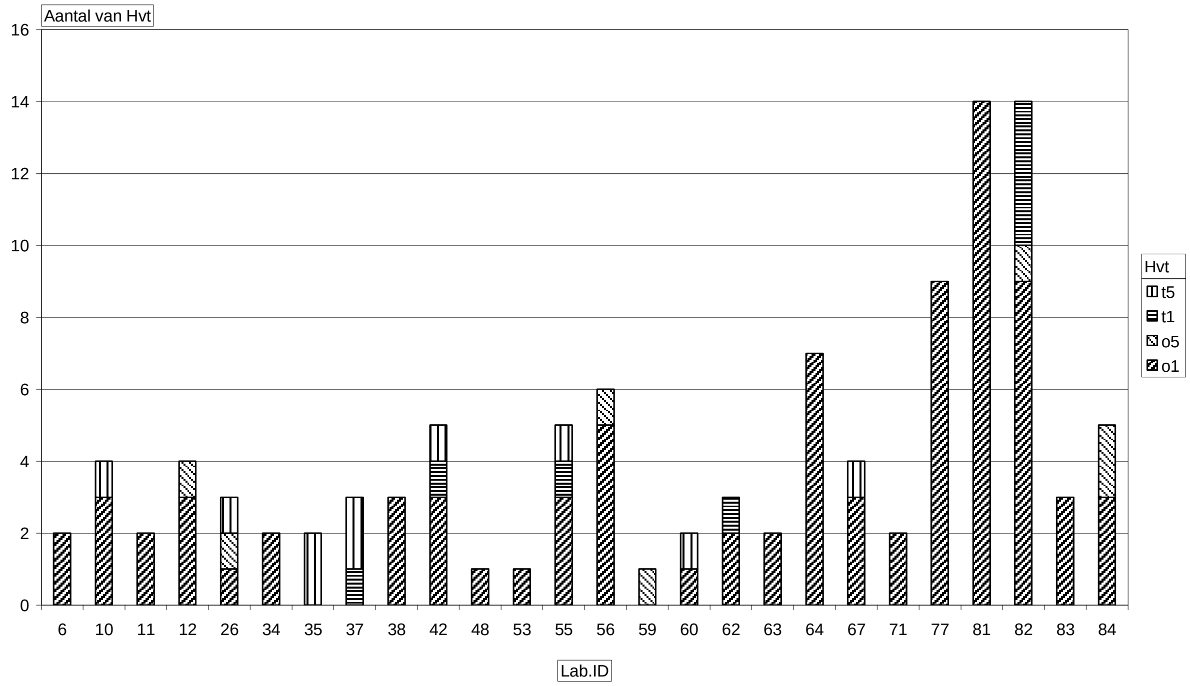


Figure 8: Sample A – Absolute N° of outliers (o1), N° of stragglers (o5) and N° of tail values (t5 and t1) per laboratory for the between-laboratory variability. Laboratories that are not mentioned in this graph did not have any outlier, straggler or tail value.

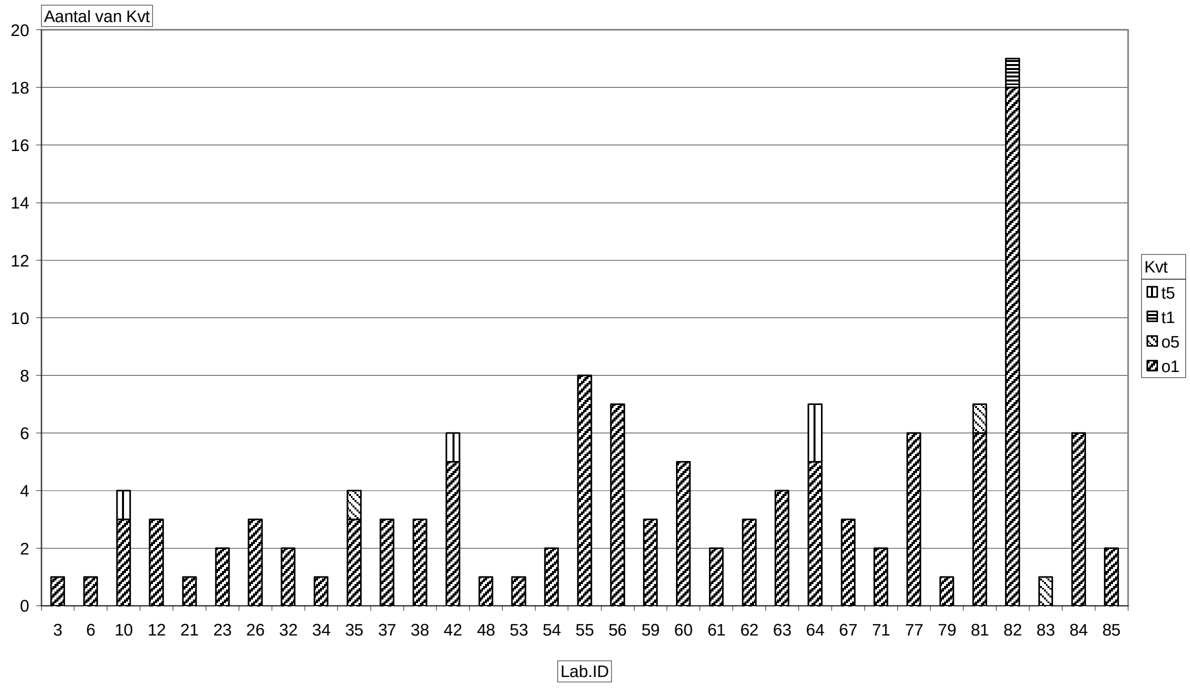


Figure 9: Sample A – Absolute N° of outliers (o1), N° of stragglers (o5) and N° of tail values (t5 and t1)per laboratory for the within-laboratory variability. Laboratories that are not mentioned in this graph did not have any outlier, straggler or tail value.

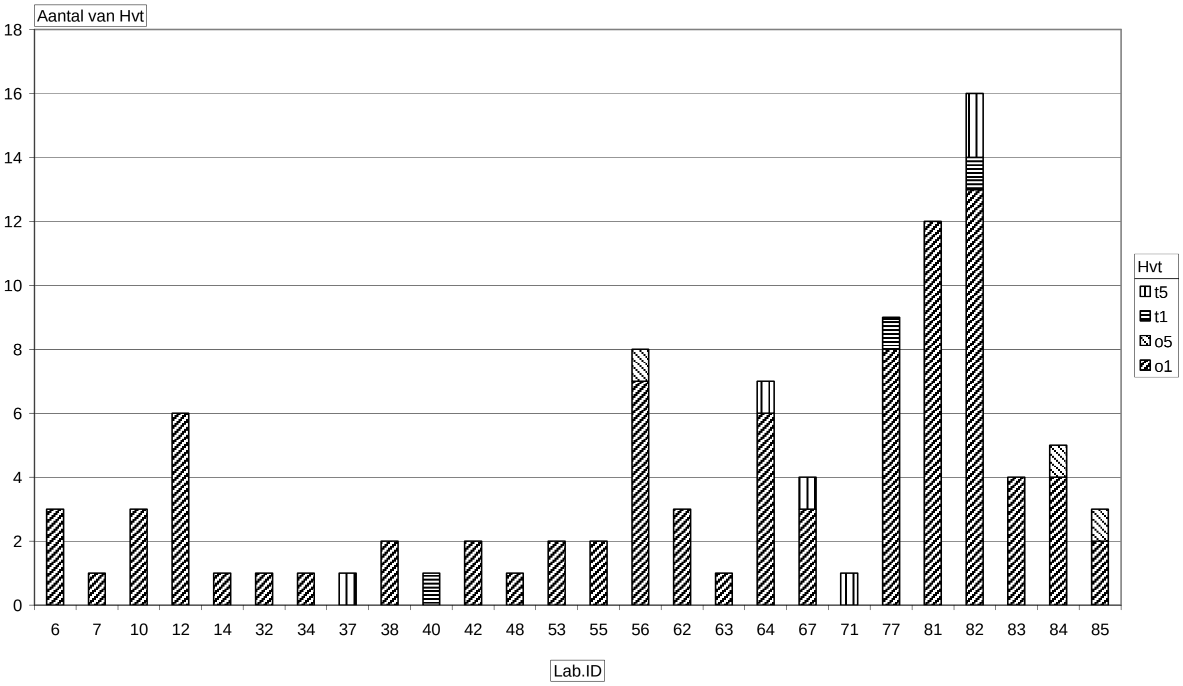


Figure 10: Sample B – Absolute N° of outliers (o1), N° of stragglers (o5) and N° of tail values (t5 and t1) per laboratory for the between-laboratory variability. Laboratories that are not mentioned in this graph did not have any outlier, straggler or tail value.

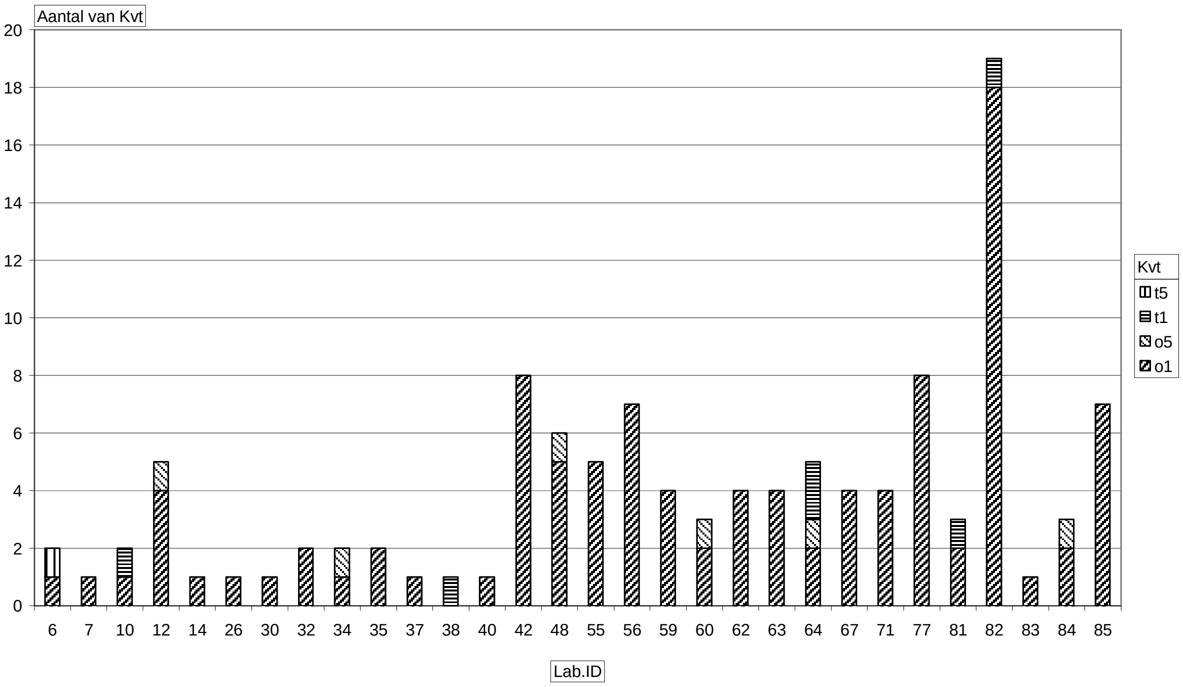


Figure 11: Sample B – Absolute N° of outliers (o1), N° of stragglers (o5) and N° of tail values (t5 and t1) per laboratory for the within-laboratory variability. Laboratories that are not mentioned in this graph did not have any outlier, straggler or tail value.

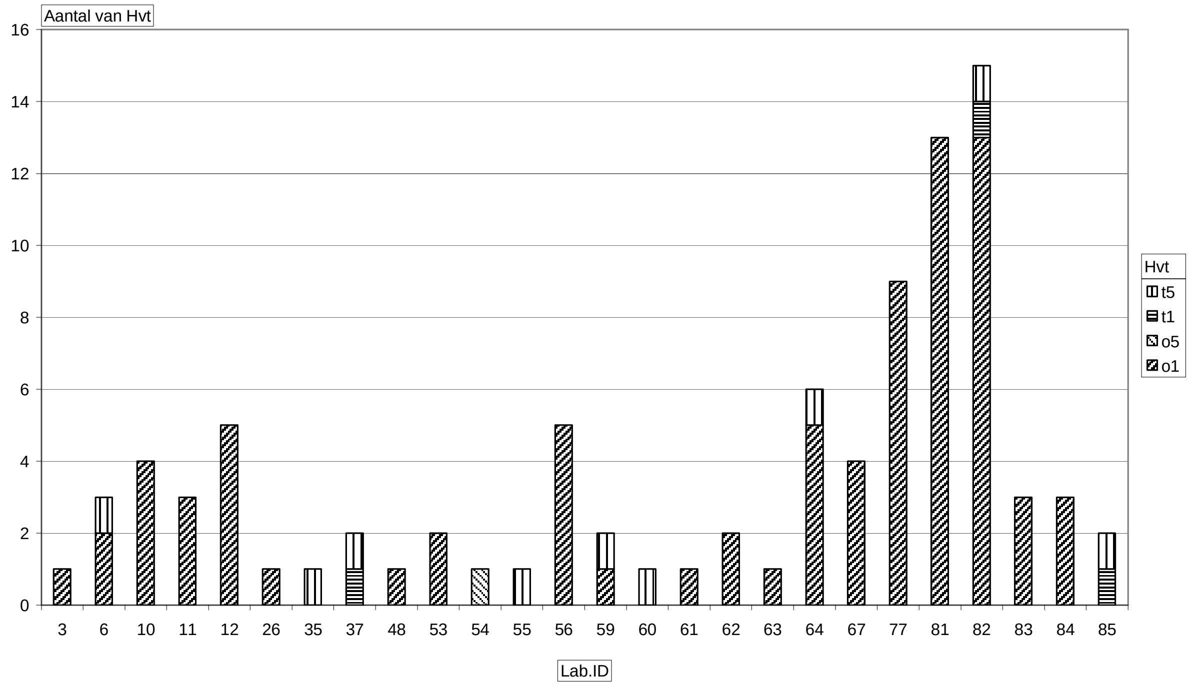


Figure 12: Sample C – Absolute N° of outliers (o1), N° of stragglers (o5) and N° of tail values (t5 and t1) per laboratory for the between-laboratory variability. Laboratories that are not mentioned in this graph did not have any outlier, straggler or tail value.

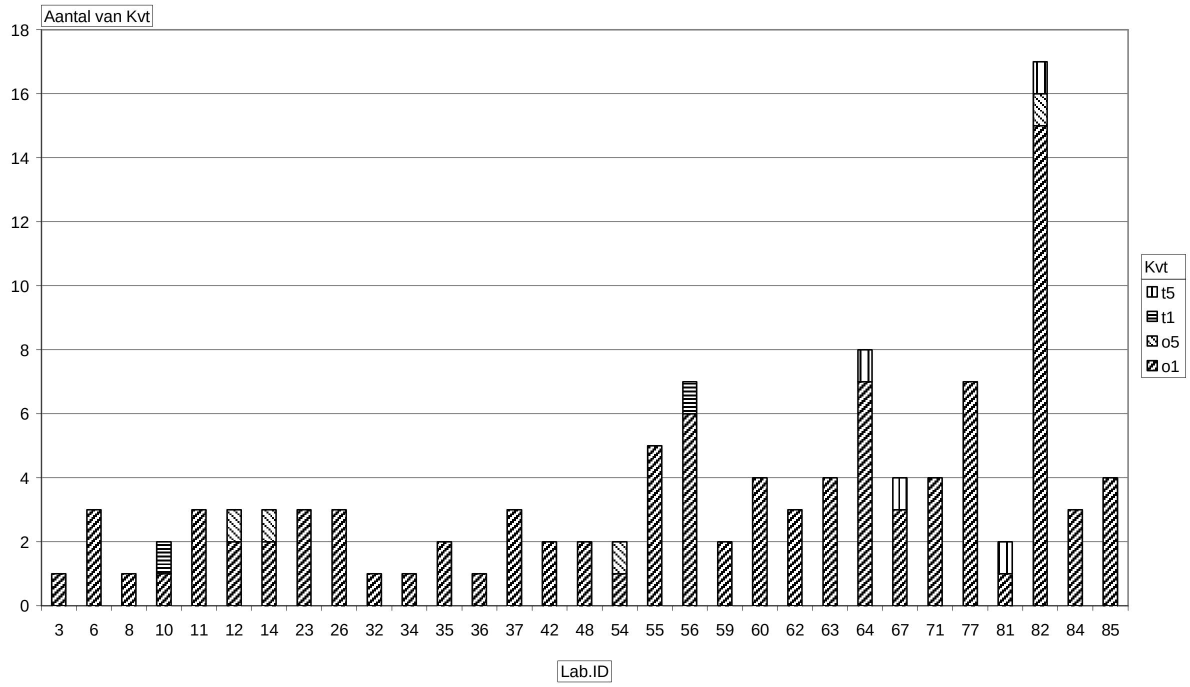


Figure 13: Sample C – Absolute N° of outliers (o1), N° of stragglers (o5) and N° of tail values (t5 and t1) per laboratory for the within-laboratory variability. Laboratories that are not mentioned in this graph did not have any outlier, straggler or tail value.

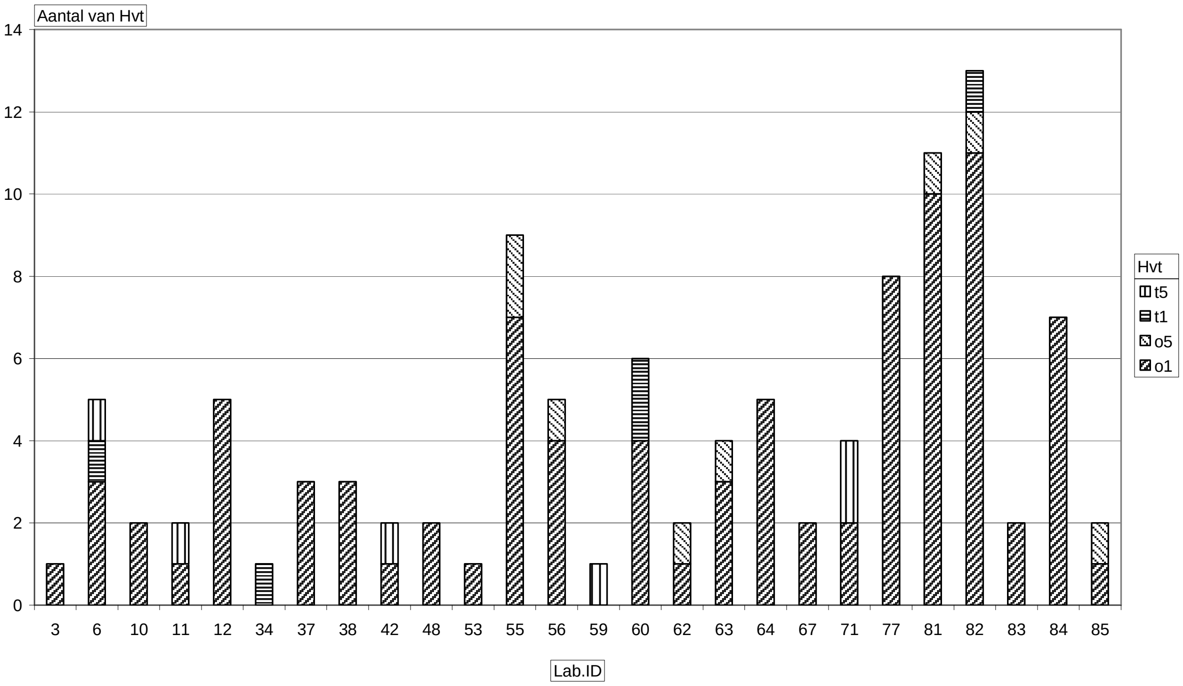


Figure 14: Sample D – Absolute N° of outliers (o1), N° of stragglers (o5) and N° of tail values (t5 and t1) per laboratory for the between-laboratory variability. Laboratories that are not mentioned in this graph did not have any outlier, straggler or tail value.

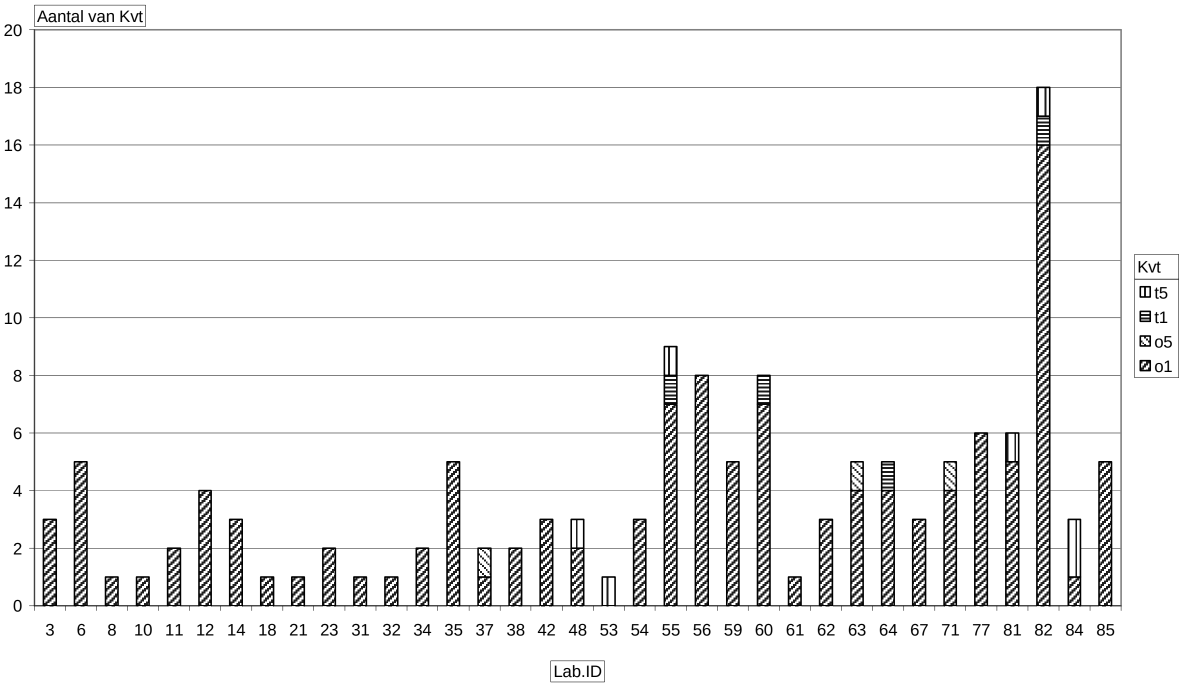


Figure 15: Sample D – Absolute N° of outliers (o1), N° of stragglers (o5) and N° of tail values (t5 and t1) per laboratory for the within-laboratory variability. Laboratories that are not mentioned in this graph did not have any outlier, straggler or tail value.

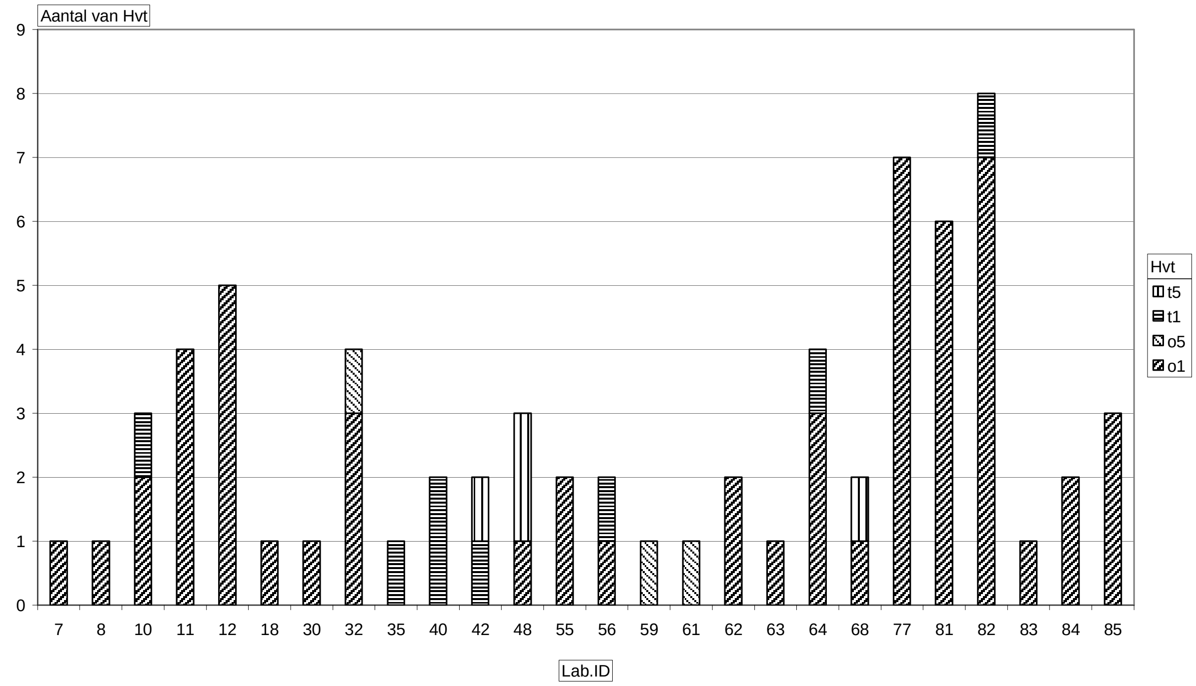


Figure 16: Sample E – Absolute N° of outliers (o1), N° of stragglers (o5) and N° of tail values (t5 and t1) per laboratory for the between-laboratory variability. Laboratories that are not mentioned in this graph did not have any outlier, straggler or tail value.

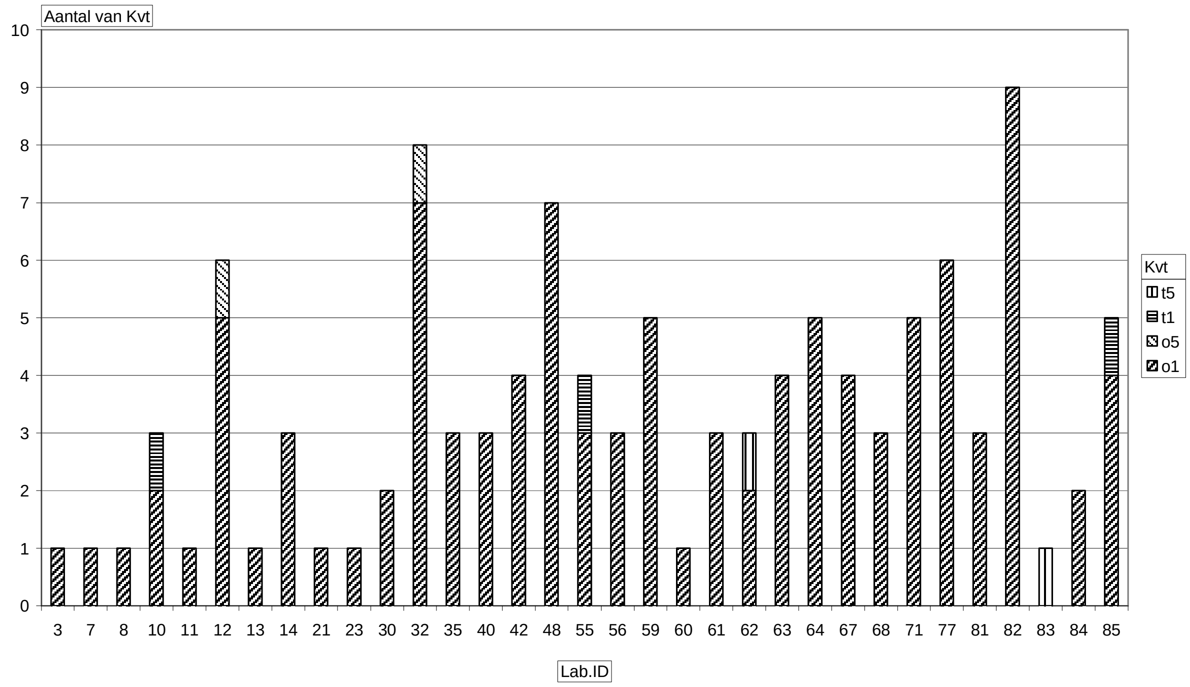


Figure 17: Sample E – Absolute N° of outliers (o1), N° of stragglers (o5) and N° of tail values (t5 and t1) per laboratory for the within-laboratory variability. Laboratories that are not mentioned in this graph did not have any outlier, straggler or tail value.

3.2.4 ‘Percentage of outliers and stragglers’ as a measure of laboratory performance

In order not to discriminate between laboratories which reported many parameters and laboratories which reported only a limited number of parameters, it is interesting to study the percentage of outliers versus the total number of evaluated parameters of each laboratory. Table 6 gives an overview of the total number of evaluated parameters per laboratory and per sample. A parameter was evaluated when at least two replicates were reported above the limit of quantification. The 0 values have not been included.

Table 6: N° evaluated parameters per sample by the individual laboratories

	sample				
Lab.ID	**A**	**B**	**C**	**D**	**E**
3	40	41	37	40	38
6	29	30	30	29	28
7	40	40	40	40	37
8	32	32	28	31	30
10	33	34	33	33	30
11	33	32	30	32	28
12	20	21	21	21	21
13	38	37	37	38	38
14	40	42	38	41	35
18	11	11	11	11	11
21	17	17	14	17	14
23	27	27	27	27	21
26	34	34	34	34	31
30	36	36	36	36	37
31	34	34	32	33	32
32	41	40	38	41	37
34	33	33	32	32	29
35	24	25	24	26	25
36	36	39	39	37	35
37	29	30	27	29	20
38	13	13	12	13	10
40	41	41	41	41	38
42	19	20	13	19	19
45	25	26	23	25	26
48	41	41	38	40	36
53	10	10	11	10	6
54	28	29	27	28	29
55	33	33	33	33	30
56	27	30	26	29	16
58	12	12	9	11	9
59	31	32	28	31	26
60	27	27	27	27	25
61	26	26	27	26	23
62	7	7	8	7	7
63	32	32	30	32	28
64	34	33	34	34	29
67	34	34	35	34	31
68	30	30	28	30	31
69	23	23	24	23	20
71	22	22	19	22	18
77	22	22	22	22	22
79	8	8	9	8	4
80	3	3	3	3	
81	31	31	32	31	19
82	34	34	35	34	24
83	24	23	24	24	22
84	37	37	37	38	36
85	20	23	22	23	20

Most laboratories reported more parameters compared to the previous FSCC Interlaboratory Comparison (except for Labs N° 12, 18, 58, 61, 62 and 69).

The percentage of outliers and stragglers was calculated relative to the number of reported parameters (excluding the moisture content). Figures 18 to 23 give nearly the same information as the previous figures but now expressed as a percentage of the total number of reported parameters.

As was suggested by FSCC at the 12th FSEPM and as is also applied within the Needle/Leaf Interlaboratory Comparsions (Fürst, 2006), we can state that laboratories which have more than 20 % of their results outside the acceptable limits [outliers (o1) + stragglers (o5)], clearly have QA/QC problems and need follow-up.

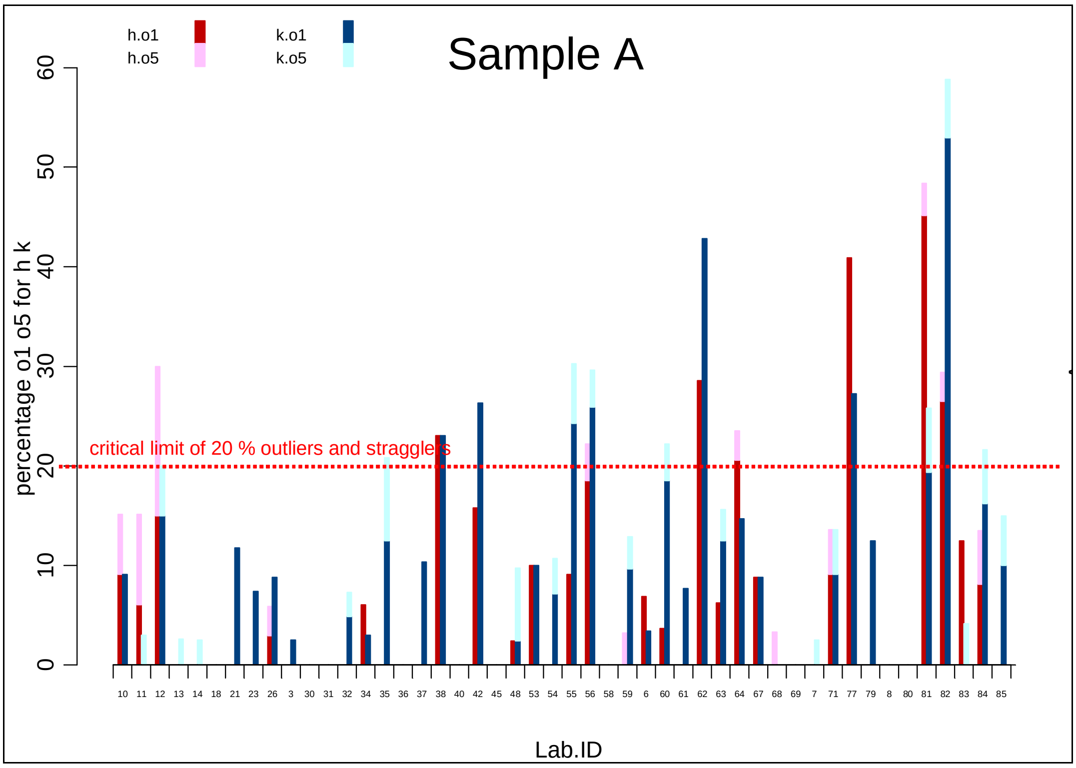


Figure 18: Sample A – Percentage of outliers (o1) and stragglers (o5) per laboratory for the between-laboratory variability (Mandel's h in red) and within-laboratory variability (Mandel's k in blue).

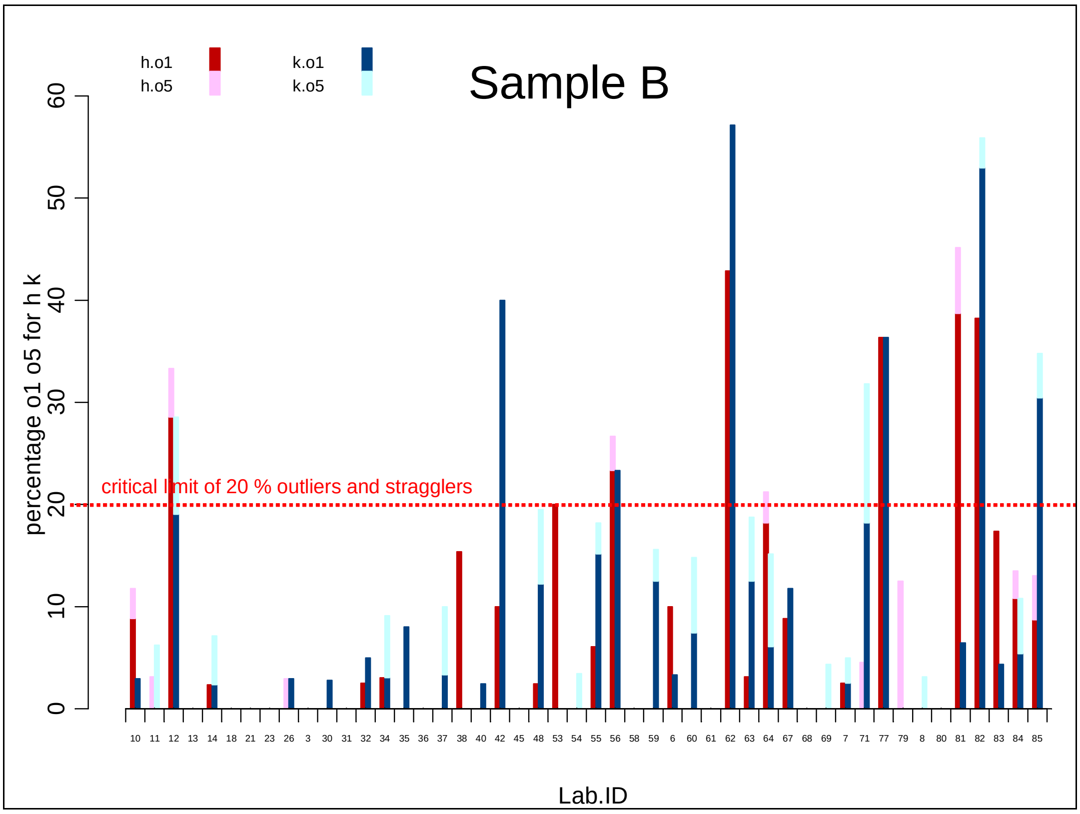


Figure 19: Sample B – Percentage of outliers (o1) and stragglers (o5) per laboratory for the between-laboratory variability (Mandel's h in red) and within-laboratory variability (Mandel's k in blue).

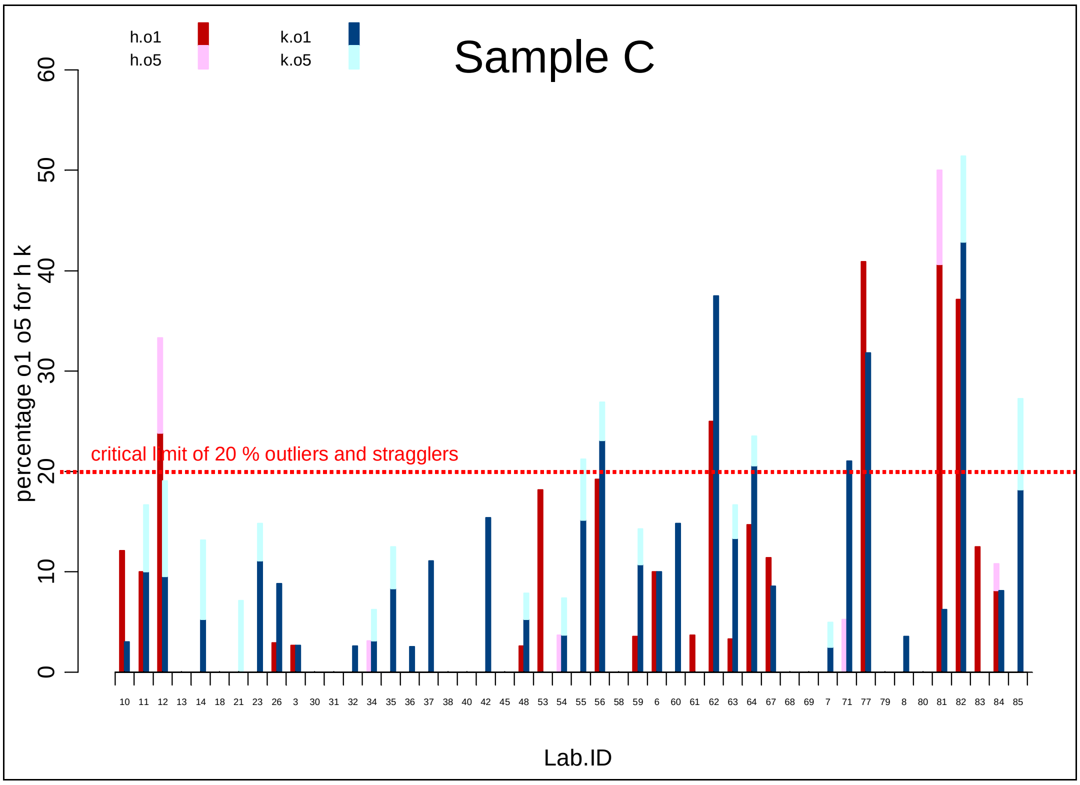


Figure 20: Sample C – Percentage of outliers (o1) and stragglers (o5) per laboratory for the between-laboratory variability (Mandel's h in red) and within-laboratory variability (Mandel's k in blue).

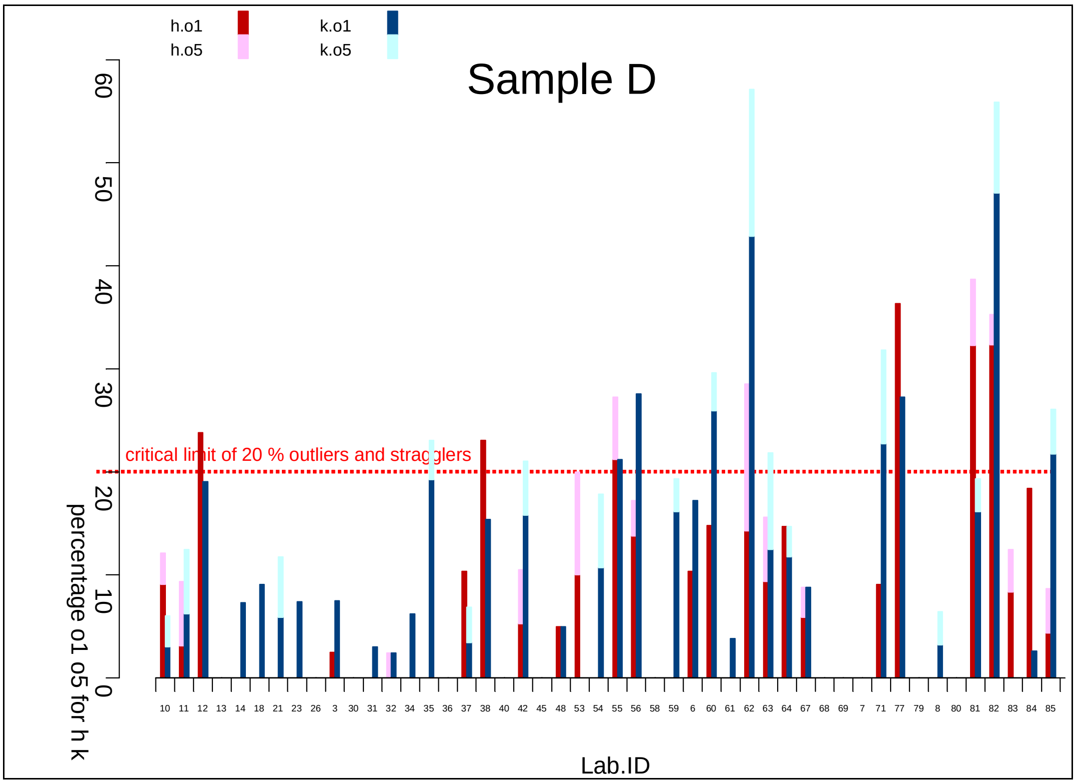


Figure 21: Sample D – Percentage of outliers (o1) and stragglers (o5) per laboratory for the between-laboratory variability (Mandel's h in red) and within-laboratory variability (Mandel's k in blue).

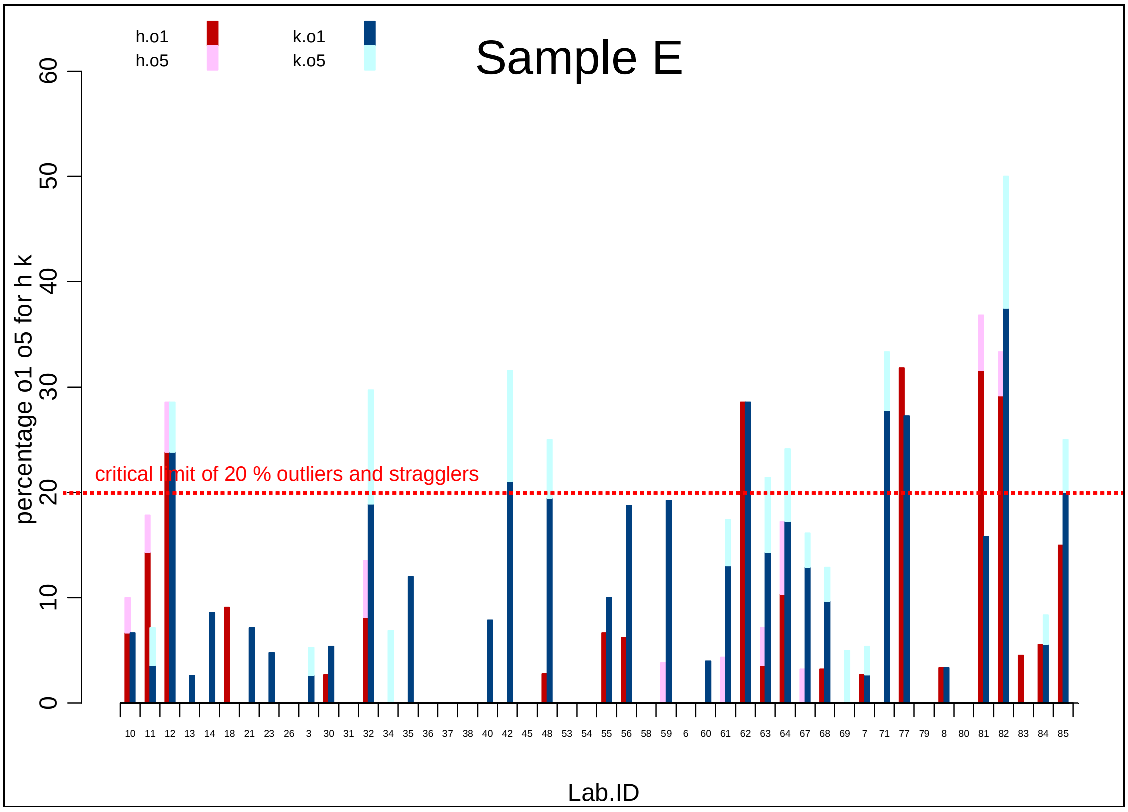


Figure 22: Sample E – Percentage of outliers (o1) and stragglers (o5) per laboratory for the between-laboratory variability (Mandel's h in red) and within-laboratory variability (Mandel's k in blue).

Concerning **Sample A**, 13 laboratories (Labs N° 12, 35, 38, 42, 55, 56, 60, 62, 64, 77, 81, 82 and 84) exceed the critical limit of 20 % outliers and stragglers. Laboratory N° 38, 56, 62, 77, 81 and 82 exceed the limit both for the within – and between-laboratory variability. Lab N° 35, 42, 55, 60 and 84 have been excluded based on their within-laboratory variability. Lab N° 12 and 64 based on their between-laboratory variability.

For **Sample B**, 9 laboratories (Labs N° 12, 42, 56, 62, 64, 71, 77, 81, 82 and 85) exceed the critical limit of 20% outliers and stragglers. Labs N° 12, 56, 62, 77 and 82 exceed the limit both for the within – and between-laboratory variability. Lab N° 42, 71 and 85 only for the within-laboratory variability and Lab N° 64 and 81 only for the between-laboratory variability.

For **Sample C**, 10 laboratories (Labs N° 12, 55, 56, 62, 64, 71, 77, 81, 82 and 85) exceed the critical limit of 20% outliers and stragglers. Labs N° 62, 77 and 82 exceed the limit both for the within – and between-laboratory variability. Lab N° 55, 56, 64, 71 and 85 only for the within-laboratory variability and Lab N° 12 and 81 only for the between-laboratory variability.

For **Sample D**, 14 laboratories (Labs N° 12, 35, 38, 42, 55, 56, 60, 62, 63, 71, 77, 81, 82 and 85) exceed the critical limit of 20% outliers and stragglers. Labs N° 55, 62, 77 and 82 exceeds the limit both for the within – and between-laboratory variability. Labs N° 35, 42, 56, 60, 63, 71 and 85 only for the within-laboratory variability and Labs N° 12, 38 and 81 only for the between-laboratory variability.

For **Sample E**, 12 laboratories (Labs N° 12, 32, 42, 48, 62, 63, 64, 71, 77, 81, 82 and 85) exceed the critical limit of 20% outliers and stragglers. Labs N° 12, 62, 77 and 82 exceed the limit both for the within – and between-laboratory variability. Lab N° 32, 42, 48, 63, 64 and 71 only for the within-laboratory variability and Lab N° 81 only for the between-laboratory variability.

The above figures identify 18 poorly performing laboratories that reported outliers and stragglers for more than 20% of the total number of reported parameters for at least one of the samples. Three laboratories (Lab N° 62, 77 and 82) score badly for all samples based on both the variability within their lab and on the differences with the other labs. Labs N° 12 and 81 fail on all samples concerning the between-laboratory variability. Lab N° 42, 56 and 71 fail for four of the five samples, for the intralaboratory variability. The remaining 10 laboratories (Labs N° 32, 35, 38, 48, 55, 60, 63, 64, 84, 85) failed on 1, 2 or 3 samples either for the within or for the between-laboratory variability.

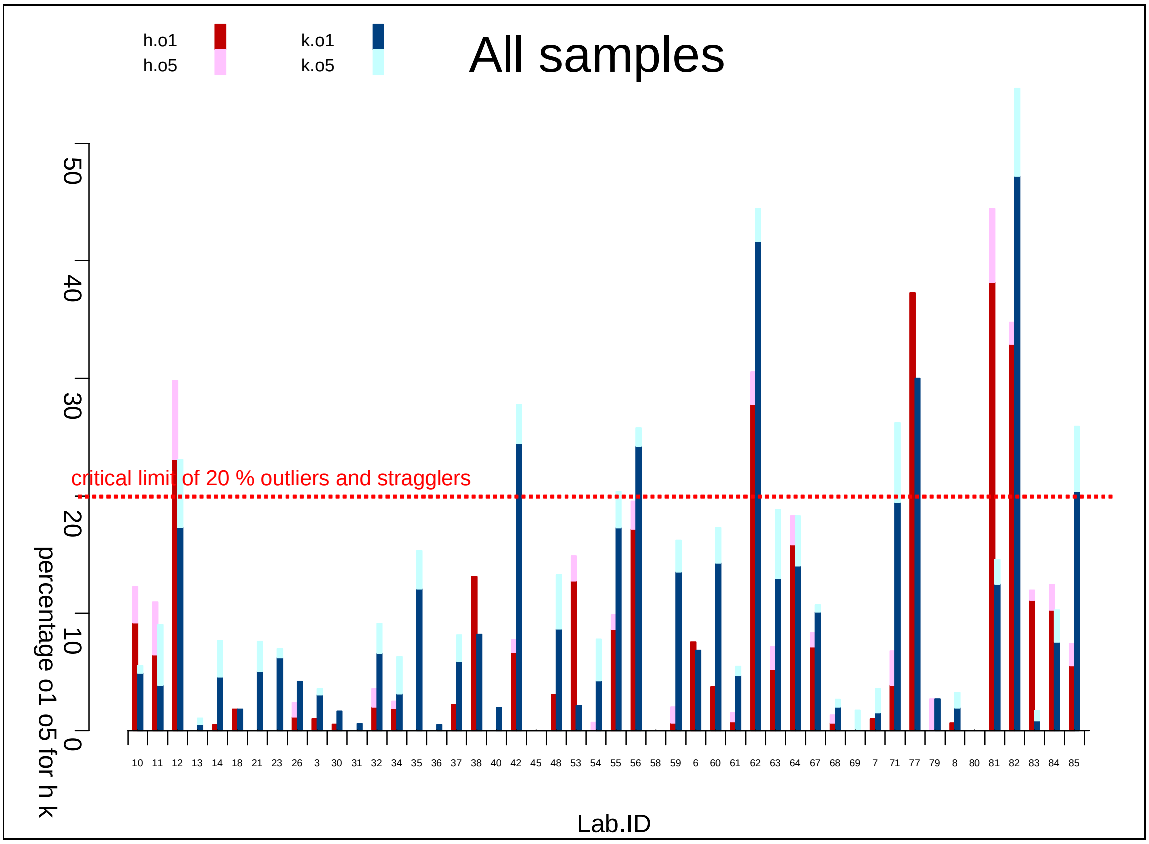
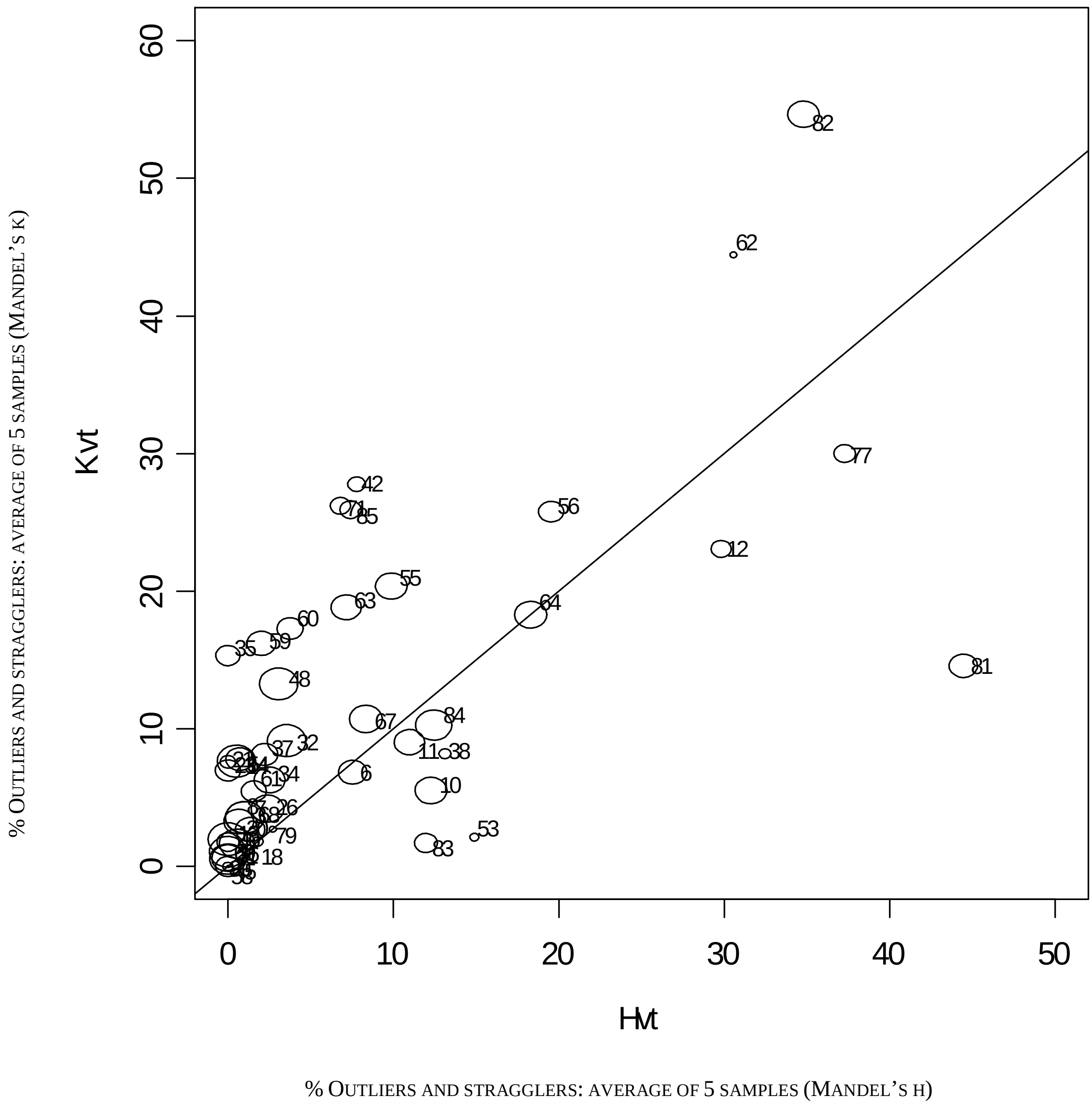


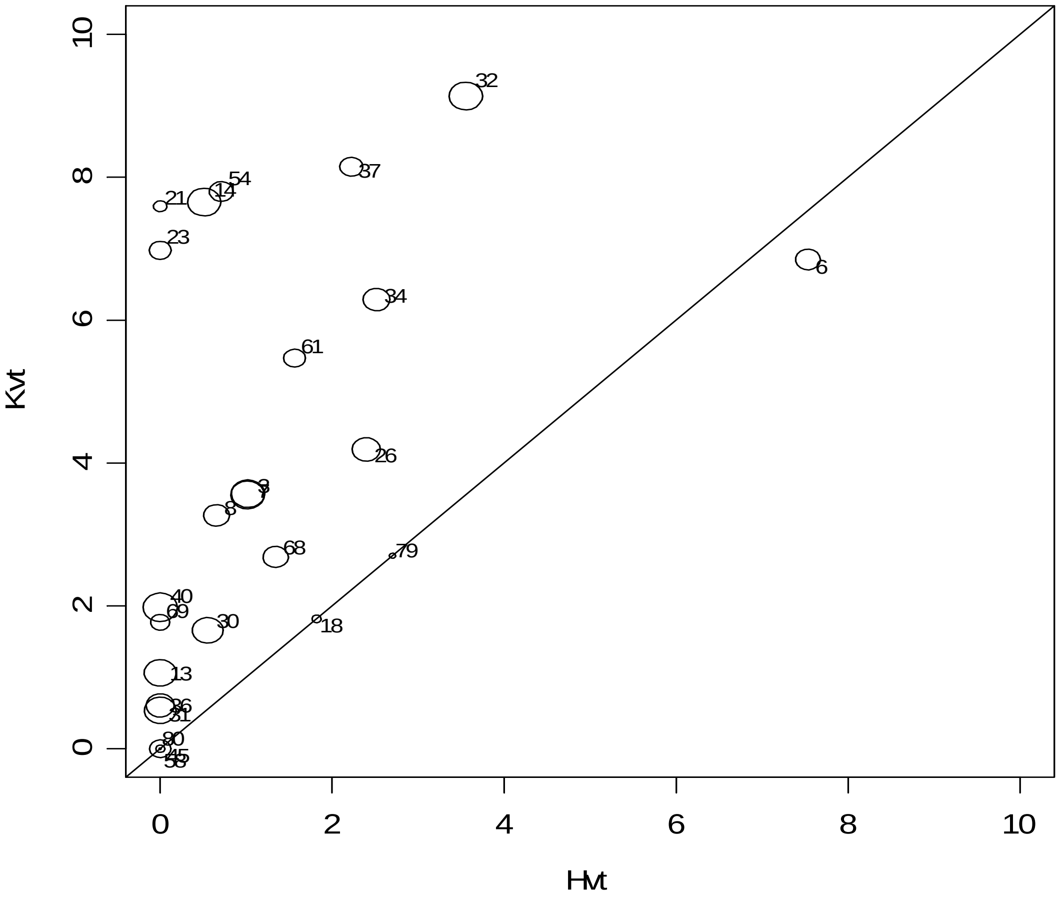
Figure 23: Percentage of outliers (o1) and stragglers (o5) per laboratory for the between-laboratory variability (Mandel's h in red) and within-laboratory variability (Mandel's k in blue) over all samples and all reported parameters.

Figure 23 shows the percentage of outliers and stragglers for all the samples and all the reported parameters (above LOQ). Nine laboratories reported outliers and stragglers for more than 20 % of their total N° of reported parameters: five based on the between-laboratory variability (Lab N° 12; 62, 77, 81 and 82), and eight laboratories based on the within-laboratory variability (12, 42, 56, 62, 71, 77, 82 and 85).

In Figure 24 the mean % of outliers and stragglers for the five samples based on the Mandel's k is plotted against the mean % of outliers and stragglers for the five samples based on the Mandel's h. The information in Figure 24 is more or less similar to Figure 23 but where the size of the circles is a measure of the mean number of reported parameters per sample for each laboratory.

From the location of the observations in the scatter plot, is seen that the balance is clearly in favour of the 'h strategists'; most of the observations are located above the 1:1 diagonal. This means that laboratories rather preferred to minimize the number of outliers concerning the between-laboratory variability (Mandel's h statistic) in stead of focussing on a low within-laboratory variability (Mandel's k statistics). Laboratories that are located in the centre of the 'cloud' are performing normally well. Laboratories situated in the perimeter (upper right corner) of the graph, have performed relatively poor for the 5th FSCC Interlaboratory Comparison.





% OUTLIERS AND STRAGGLERS: AVERAGE OF 5 SAMPLES (MANDEL'S K)

% OUTLIERS AND STRAGGLERS: AVERAGE OF 5 SAMPLES (MANDEL'S H)

Figure 24: Scatter plot showing the 'h and k strategists' (above: all laboratories, below: zoom on 0 – 10 % scale)

Figure 25 summarizes the results of the statistical evaluation when only the laboratories participating in the BioSoil project are included in the overall statistical evaluation. Now 6 laboratories pop up as 'problem laboratories' with more than 20 % of their reported results as outliers or stragglers. Three laboratories are identified based on their between-laboratory variability (Labs N° 12, 56 and 64) but all six based on their within-laboratory variability (Labs N° 12, 42, 55, 56, 64 and 71). So the problems in Laboratory N°12 become more outstanding and two new problem laboratories (Labs N° 55and 64) have been identified. Lab N° 63 reached but not exceeded the critical limit of 20% for the within-laboratory variability.

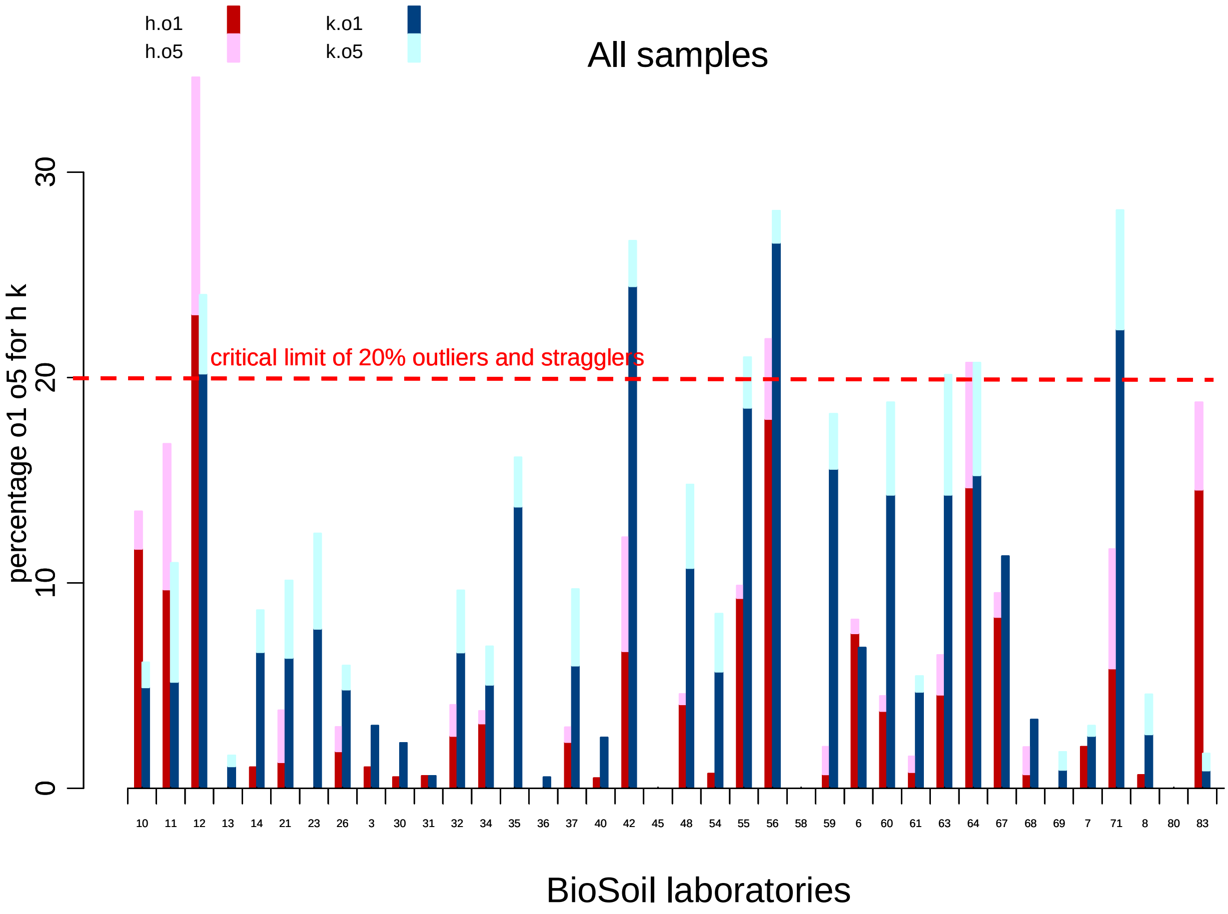


Figure 25: Percentage of outliers (o1) and stragglers (o5) per laboratory for the between-laboratory variability (Mandel's h in red) and within-laboratory variability (Mandel's k in blue) over all samples and all reported parameters for the BioSoil laboratories

3.2.5 Percentage of outliers

Based on Table 7 possible 'problem 'elements can be identified. For each element and sample, the percentage of outlying laboratories is given. The first group which deserves more attention for quality improvement are the exchangeable elements. Concerning the aqua regia elements, the heavy metals Cadmium (Cd) and Mercury (Hg) clearly pop-up as problem parameters. These are – not accidentally - the two elements present in the lowest concentrations. Also the determination of the organic carbon content in a poor loamy sample was not without any problems. Then there was also a problem determining the pH($CaCl_2$) in the peat sample.

Table 7: % of outlying laboratories (99% confidence) per element and per sample

	sample				
Element	**A**	**B**	**C**	**D**	**E**
Particle size clay	3	9	9	6	
Particle size sand	9	6	0	9	
Particle size silt	0	3	9	12	
pHCaCl2	4	13	9	6	***21***
pHH2O	7	4	2	2	2
CaCO3			0		
OC	10	2	2	***22***	7
Total N	9	0	14	0	2
Exchangeable Acidity	3	12	***33***	3	16
Exchangeable Al	3	8	7	3	6
Exchangeable Ca	***28***	***26***	15	***30***	8
Exchangeable Fe	***21***	13	16	18	8
Exchangeable K	16	18	20	13	11
Exchangeable Mg	18	***23***	10	13	***21***
Exchangeable Mn	8	5	17	8	8
Exchangeable Na	***37***	***29***	***31***	***30***	***26***
Free H	***41***	4	***38***	***23***	7
Extractable Al	14	11	20	***23***	3
Extractable Ca	18	8	13	11	14
Extractable Cd	19	***35***	***25***	***36***	***24***
Extractable Cr	0	3	3	11	8
Extractable Cu	10	10	17	15	14
Extractable Fe	14	14	11	11	11
Extractable Hg	20	18	***35***	***25***	***33***
Extractable K	14	8	8	8	11
Extractable Mg	***21***	18	5	5	5
Extractable Mn	3	5	5	13	5
Extractable Na	12	15	6	15	6
Extractable Ni	13	18	10	13	15
Extractable P	11	13	11	5	5
Extractable Pb	7	7	15	12	15
Extractable S	4	11	7	7	7
Extractable Zn	12	5	5	7	20
Total Al	9	***27***	9	9	10
Total Ca	18	***27***	9	18	***40***
Total Fe	9	9	9	9	20
Total K	9	9	9	9	***22***
Total Mg	9	***27***	9	18	10
Total Mn	9	18	9	***27***	10
Total Na	18	9	***36***	***27***	0
Reactive Al	11	11	7	11	0
Reactive Fe	7	7	7	11	4

3.3 Coefficients of variation

Table 8 provides the CV for each analysed parameter. The last column of the table gives the CV per group of analysis, calculated over all the samples. In the last row, the average CV per sample is given. The CV of the different samples lay all within a relatively narrow range (between 22 and 29%).

Table 8: Coefficients of variation 5th FSCC interlaboratory comparison 2007 (CV = sRepr/Mgen)

	Sample					All samples	Group
Element	**A**	**B**	**C**	**D**	**E**		
Moisture	20.3	22.6	17.1	16.4	41.0	23.5	
Particle size clay	34.2	20.3	28.5	14.2		24.3	**23**
Particle size sand	4.9	30.8	19.6	16.5		18.0	
Particle size silt	37.9	28.6	23.1	13.4		25.8	
pHCaCl2	2.5	2.4	2.7	2.0	2.3	2.4	**3.2**
pHH2O	3.4	3.4	3.4	3.9	5.8	4.0	
CaCO3			45.3			45.3	**45**
OC	14.6	17.3	28.7	9.6	7.5	15.5	**16**
Total N	21.9	27.0	4.7	21.8	10.2	17.1	**17**
Exchangeable Acidity	39.7	16.1	81.1	30.0	42.9	42.0	**49**
Exchangeable Al	35.0	26.7	90.8	29.2	37.2	43.8	
Exchangeable Ca	62.6	38.5	18.2	39.4	35.4	38.8	
Exchangeable Fe	64.3	29.5	89.3	103.1	47.1	66.7	
Exchangeable K	48.7	33.3	29.2	31.5	34.7	35.5	
Exchangeable Mg	58.4	34.0	12.6	31.8	30.4	33.5	
Exchangeable Mn	29.2	27.6	85.2	25.7	36.6	40.8	
Exchangeable Na	88.7	53.3	93.2	65.9	38.3	67.9	
Free H	84.2	91.1	61.7	67.3	54.5	71.8	
Extractable Al	14.9	13.6	17.7	14.9	25.8	17.4	**26**
Extractable Ca	40.0	44.9	8.4	48.2	12.3	30.7	
Extractable Cd	48.7	57.1	35.8	44.6	24.9	42.2	
Extractable Cr	23.3	18.8	24.9	27.2	62.9	31.4	
Extractable Cu	9.9	14.1	11.4	14.4	48.2	19.6	
Extractable Fe	13.2	8.3	14.7	33.2	21.0	18.1	
Extractable Hg	30.4	22.7	40.1	16.0	17.0	25.2	
Extractable K	43.3	22.0	36.4	45.0	22.9	33.9	
Extractable Mg	10.4	7.1	14.1	31.0	12.1	15.0	
Extractable Mn	22.4	12.6	19.0	9.4	25.5	17.8	
Extractable Na	52.3	50.4	47.6	54.0	58.9	52.6	
Extractable Ni	9.8	13.1	11.6	9.7	49.1	18.7	
Extractable P	6.7	17.3	11.1	29.7	28.4	18.7	
Extractable Pb	31.1	23.1	17.9	26.7	15.1	22.8	
Extractable S	35.9	33.0	54.2	29.5	26.1	35.7	
Extractable Zn	11.9	14.3	15.7	14.6	13.5	14.0	
Total Al	4.3	3.3	5.1	11.8	20.8	9.1	**9.0**
Total Ca	11.0	4.0	4.7	12.5	4.9	7.4	
Total Fe	8.9	4.3	4.7	4.0	19.4	8.2	
Total K	4.0	3.3	3.0	3.3	19.7	6.7	
Total Mg	6.7	2.5	6.0	2.7	8.5	5.3	
Total Mn	11.3	7.6	9.4	3.4	11.0	8.6	
Total Na	4.4	3.3	4.9	6.7	69.8	17.8	
Reactive Al	7.7	9.6	21.1	33.0	39.0	22.1	**20**
Reactive Fe	10.0	8.1	17.9	20.2	32.5	17.7	
Average per sample	**27.6**	**22.6**	**28.1**	**25.4**	**28.2**	**26.7**	

In Table 9, the coefficients of variation are shown for each parameter and each sample including only those laboratories that participate in the BioSoil project. For most of the parameters the CVs were slightly lower, however not for all.

Table 9: Coefficients of variation 5th FSCC interlaboratory comparison 2007 (CV = sRepr/Mgen) including only the BioSoil laboratories

	Sample					All samples	Group
Element	**A**	**B**	**C**	**D**	**E**		
Moisture	22.1	23.3	13.0	16.9	30.7	13.0	
Particle size clay	35.3	21.5	30.2	14.2		30.2	**23**
Particle size sand	3.4	27.8	19.5	15.1		16.5	
Particle size silt	34.1	16.0	21.9	11.0		21.9	
pHCaCl2	2.3	2.3	3.0	1.9	2.1	2.3	**2.9**
pHH2O	2.3	2.0	3.6	3.4	5.3	3.6	
CaCO3			39.2			39.2	**39**
OC	10.7	11.1	13.2	8.1	7.4	10.1	**10**
Total N	22.1	24.7	4.9	18.9	10.7	16.3	**16**
Exchangeable Acidity	38.7	13.8	81.4	16.8	43.1	38.8	**50**
Exchangeable Al	26.4	21.3	92.5	23.6	36.6	92.5	
Exchangeable Ca	62.6	39.1	18.6	39.4	35.6	39.0	
Exchangeable Fe	64.1	29.5	84.7	98.4	41.8	84.7	
Exchangeable K	46.4	22.1	22.5	27.4	34.7	30.6	
Exchangeable Mg	59.3	33.5	12.4	29.8	28.5	12.4	
Exchangeable Mn	26.7	25.0	92.0	22.5	35.5	40.3	
Exchangeable Na	88.7	53.3	27.1	54.6	39.2	27.1	
Free H	88.7	80.1	152.9	58.6	48.5	85.8	
Extractable Al	13.7	13.6	16.1	15.0	22.4	16.2	**20**
Extractable Ca	26.7	38.7	7.9	40.2	12.5	7.9	
Extractable Cd	31.8	29.6	72.0	44.9	18.0	39.3	
Extractable Cr	20.1	15.7	18.7	22.5	62.6	18.7	
Extractable Cu	9.4	13.2	9.6	13.8	44.1	18.0	
Extractable Fe	13.5	8.5	15.1	8.9	12.8	15.1	
Extractable Hg	26.3	23.3	41.8	15.9	16.9	24.8	
Extractable K	33.3	13.2	27.0	36.7	19.3	27.0	
Extractable Mg	9.5	6.4	8.0	9.6	12.1	9.1	
Extractable Mn	19.0	9.4	11.9	8.6	23.4	11.9	
Extractable Na	45.5	47.2	44.2	49.6	54.9	48.3	
Extractable Ni	9.7	13.6	11.9	9.7	42.6	11.9	
Extractable P	6.7	13.5	9.0	6.8	12.6	9.7	
Extractable Pb	29.1	20.3	18.5	21.9	15.0	18.5	
Extractable S	32.9	29.9	45.3	16.9	21.7	29.3	
Extractable Zn	10.8	13.4	14.8	12.9	20.9	14.8	
Total Al	3.8	3.3	5.2	2.5	20.7	7.1	**5.4**
Total Ca	8.6	4.0	4.9	12.5	4.9	4.9	
Total Fe	6.1	4.5	4.8	3.4	17.2	7.2	
Total K	3.4	3.4	2.9	3.0	21.5	2.9	
Total Mg	5.7	2.5	6.0	2.3	8.5	5.0	
Total Mn	9.8	4.8	6.0	3.4	11.4	6.0	
Total Na	4.4	3.0	4.9	6.7	58.3	4.9	
Reactive Al	7.6	9.9	22.0	33.7	34.3	21.5	**20**
Reactive Fe	10.3	9.0	18.6	20.9	16.2	18.6	
Average per sample	**27.5**	**20.4**	**31.0**	**23.1**	**28.1**	**23.3**	

3.4 Soil analytical methods

Tables 8 and 9 showed that even in this 5th Interlaboratory Comparison, the CVs remain relatively high. This raises the question whether all laboratories effectively use the reference methods. The following information was available from the method information provided by the laboratories at the on-line data submission.

3.4.1 Sieving and milling

Since the methods described in the Manual on Sampling and Analysis of Soil (2006) had to be applied, also the rules on preparation of the soil samples had to be followed. This means that the analysis had to be done on the < 2 mm fraction without further milling for the determination of moisture, particle size distribution, pH, exchangeable, aqua regia extractable and oxalate extractable elements. Further grinding was only allowed for the determination of $CaCO_3$, total organic carbon, total Nitrogen and total elements.

From Table 3.1 in Annex 3 is seen that at least five laboratories did not respect these rules. Laboratory N ° 67 milled the sample for exchangeable elements and Lab N° 18, 48 and 67 did it for the extractable elements. Unless it is due to an error in reporting, Lab N° 53 milled the sample for the measurement of the silt content. Lab N° 53 and 67 milled the sample for the determination of the soil pH. Lab N° 40 milled the sample for the determination of the reactive Fe and Al. While for the total elements (Al, Ca, Fe, K, Mg, Mn, Na) the sample had to be milled, this was only done by three of the eleven laboratories that reported these elements.

These differences in sample preparation are not immediately reflected in the ring test results. However this does not mean that the way of sample preparation would not be a source of variation of the results.

3.4.2 Removal of compounds

Since this question was not 100 % clear, it is difficult to draw any conclusions. Though, when following the manual, certain analyses such as the determination of particle size distribution, total analyses did require an additional step to remove organic carbon, soluble salt, gypsum or $CaCO_3$. Some laboratories did report this, other not.

3.4.3 Pretreatment

Concerning the Exchangeable elements, one laboratory (Lab N°26) reported to have used the triple extraction method. A quick exploration of their results show rather high concentrations for most of the acid cations, but reasonably good results for the basic cations.

When using the reference method, the laboratories should have indicated the aqua regia extraction by reflux method (code 3.11). Six laboratories indicated that they digested the sample by microwave (code 5.7 and 5.8). Though, most laboratories did not specify whether they used the reflux method or the microwave digestion and used code 2.3. Towards the next ring test, the method list should be more clear and the reflux digestion method should be better indicated.

Concerning $CaCO_3$, the manual writes ‘the soil is treated with a strong acid = HCl’. Since the reaction takes place in the calcimeter, it is not clear whether this is a pretreatment or not. Since theoretically the strong acid can be another reagant, it is worthwhile reporting the HCl ashing.

Laboratory N° 10 used a KCl extraction in stead of acid ammonium oxalate. They had one outlier (sample D, Fe).

Following the manual, there were two possibilities for the pre-treatment of the total element determination: either 2.4 (HF + $HClO_4$) or 2.5 ($LiBO_2$). The digestion with $_{HNO3}$ + HF (either pressure digestion or microwave digestion) is not described in the manual. This means that eight of the eleven laboratories did not use the reference method for this analysis.

Related to the OC determination, it is not clear which methods some of the labs used. Lab N°36 reported that they made a dry ashing and Lab N°84 an oxygen ashing in the pretreatment. Possibly they were talking about the dry combustion method which is included in the description of the determination method of the element analysers (Lab N° 36 used a CN analyser and Lab N° 84 a CNS analyser). The results of these two labs were good (no outliers). Lab N°18 did a pretreatment with H_2SO_4/K_2CrO_7 followed by a spectrophotometric UV-VIS measurement. Lab N° 53 did not do any pretreatment but said to calculated the OC content (?). Labs N° 82 and 85 did not report any pretreatment and reported to have done ‘C determinations’. The latter four laboratories had each one outlier.

3.4.4 Determination

When studying Table 3.4 in Annex 3, we see that some laboratories used a very general code to name their determination technique, which should be avoided in future ring test questionnaires.

Related to the spectrometry techniques, most laboratories used ICP-AES, except for the Hg determination. Only Lab N° 6 used ICP but their results were out of the normal range. One laboratory determined the total elements by AAS but nearly all its results were outliers.

For the determination of total N, the majority of the laboratories use total analysers. Eight laboratories reported to use the Kjeldahl apparatus and two reported ‘titration’, also possibly referring to the Kjeldahl determination method.

Concerning exchangeable acidity there should only have been two possibilities: either titration (code 82 or 73) or calculation (code 91). Some laboratories reported the code ’72 = potentiometry’ but this is the method to determine the free H^+ since the German calculation method calculates the free H^+ based on pH measurements of the $BaCl_2$ extract before and after extraction. Based on the pH difference, the amount of protons is calculated, so the free H^+. Subsequently the exchangeable acidity is calculated as the sum of free H^+ and exchangeable acid cations.

Thirty five laboratories reported results for the particle size determination. Based on their answers, at least 24 laboratories used the pipette method. Eight laboratories did not report any determination method. Two laboratories answered they used other techniques. One laboratory (Lab N° 7) reported that they used the calcimeter, which must be a misunderstanding. Though, all these 11 laboratories performed well in the ring test for this analysis.

Of the 27 laboratories that analysed the reactive Fe and Al, only two laboratories measured the content using AAS. All others used ICP. No differences were seen in the quality of the results.

Lab N° 81 reported for all parameters (and Lab N° 62 for all parameters except Total N) ‘no information’. So we can only conclude that these laboratories did not make the effort to fill in the questions properly. For the determination method of the particle size distribution, several more laboratories reported ‘no information’.

4 DISCUSSION

4.1 Evaluation by element

While reading this section, please consult the figures in Annex 5 on the attached CD-Rom and Table 5 on pages 28 and 29.

4.1.1 Moisture Content

Although, the soil moisture content was mandatory to report, this was only done by 42 of the 48 laboratories for the mineral soil (not reported by laboratories n° **12, 18, 35, 62, 69 and 80**) and by 41 of 48 for the organic layer (not reported by the laboratories mentioned above and Lab N° **83**). Some of the laboratories that participated in the previous interlaboratory comparison, reported the moisture content but decided this time not to do so.

Since nearly 15% of the laboratories did not report the soil moisture content, we assume that no corrections were made between the results on air-dried and oven-dried basis. This means that they did not work according to the methods described in the manual where reporting on oven-dry basis is obligatory. This is remarkably since this parameter seems easy to measure.

Since it is an essential link in a harmonised data set across Europe, the moisture content should be a strictly mandatory parameter: when the parameter is not reported, a country should not be able to submit the whole file containing the analytical laboratory results. This should be added as an extra quality rule when submitting the survey data to the central database.

In contrast to the 4th FSCC Interlaboratory Comparison, all reported moisture contents were indeed the moisture content and no confusion was made with the dry matter content.

4.1.2 Particle size distribution

Thirty-five out of the 48 laboratories reported the particle size distribution (73%) which is an increase of more than 10% compared to the previous ring test. One laboratory (Lab N° 56) did only report one replicate so could only be included in the dot plot, the histogram and box plot of the means but not in the further statistical analysis.

Most of the laboratories used the reference method (N°= 24). Eight laboratories did not report the method and three laboratories reported using another method (see Annex 3, Table 3.4).

Over the three particle size classes, a total of 11 outlying laboratories (Labs N° **11, 23, 37, 53, 59, 60**, **82** and **85** based on the within-laboratory variability and Labs N° **34, 37** and **55** based on the between-laboratory variability) have been identified for at least one sample.

Each ring test it happens again, that correct analyses are reported in the wrong fields or better that a laboratory analyses well its samples but makes it all undone by reporting carelessly. Lab N° 34 clearly mixed up the sand and clay content. For the silt fraction their results are nicely within the bulk of the data. So please be more careful in reporting!

Good news is that the coefficients of variation improved compared to the previous interlaboratory comparisons.

4.1.3 Soil reaction

In total 46 of the 48 participating laboratories reported pH(H_2O) and 49 reported pH($CaCl_2$). There were more outliers for the pH($CaCl_2$) than for the pH(H_2O). Concerning pH($CaCl_2$), 16 laboratories reported outlying results for at least one of their samples, either for the within or for the between-laboratory variability (see Table 5). The poorest performing laboratories for pH are laboratories N° 42 and 62, failing for their within-laboratory variability.

Studying the pH, the applied statistical procedure seemed not waterproof concerning the different levels of rounding . Most laboratories are able to report up to two decimals, while strictly seen the database only asks for one decimal place. The statistical analysis was done on the data as they have been reported giving a possible advantage to laboratories that reported only one decimal and so decreasing the within laboratory variability. Therefore the analysis was redone using the results rounded to one decimal place. Doing so, the number of excluded laboratories decreases. See Table 10.

Table 10: The list with excluded laboratories where 1) all decimals were kept as reported and 2) all results have been rounded to one decimal place

Parameter	Sample	Excluded labs (all decimals included)	Excluded labs (one decimal included)	Mgen	CV
pH($CaCl_2$)	A	k42;k82	k42	4.2	2.6
	B	k62;k63;k26;k82;k83;k42	k62;k63	3.8	2.4
	C	k62;k67;k36;k42	k62;k67;k36;k42	7.3	2.7
	D	k62;h71k;k42	k62;h71;k42	4.0	2.0
	E	h18;k62;k63;k21;k40; k61;k81;k42;h85;k48	h18;k62;k63	2.9	2.9
pH(H_2O)	A	k42;k62;h71	h71	4.6	3.6
	B	k62;k63	k62	4.2	3.5
	C	k62	k62	7.9	3.4
	D	h71	h71	4.6	3.9
	E	h85		4.0	6.6

When more laboratories are included in the cleaned dataset, it influences the other statistics. The mean of the pH($CaCl_2$) in sample E increased from 2.8 to 2.9. The coefficients of variations also increased for pH($CaCl_2$) for samples A and E and for pH(H_2O) for sample A, B and E.

4.1.4 Carbonate content

4.1.4.1 Sample A, B, D and E

$CaCO_3$ should only have been measured when the pH($CaCl_2$) was above 5.5 (organic) or 6.0 (mineral soil). So in practise, only sample C had to be analysed (mean pH($CaCl_2$) = 7.3). The values for samples A, B, D and E should have been ‘NA’, meaning that the analysis was not done. Another possibility was to report that the value was below the detection limit. However, strictly seen, reporting a ‘0’ value is not correct since it is never possible to really measure ‘0’. There is always some noise on a measurement. In the statistical evaluation, the $CaCO_3$ content of sample A, B, D and E has not been taken on board.

4.1.4.2 Sample C

In the statistical analysis of the $CaCO_3$ content of sample C another particularity was found. Eight of the 39 laboratories reported values of about 10 times smaller than the average of the remaining 31 laboratories, suggesting a mistake in the reporting unit (see Figure 26). The $CaCO_3$ content had to be reported in g/kg and not in %, which might be the routine unit in a number of laboratories. These 8 laboratories have been defined in the histogram of the means (Figure 27) as very deviant outliers and were excluded from the box plots. But in contrast to what we expect, they have not been identified as outliers in the Mandel’s h and k statistical evaluation. Only Lab N° 60, 81 and 34 had a tail value for the Mandel’s h statistics at 5% significance level. This case clearly shows the importance of combining the exploratory and the in-depth statistics to come to a good interpretation of the ring test results.

The eight laboratories which should check their reported values are Lab N° **6, 34, 56, 60, 64, 68, 81 and 84.** When these eight laboratories are manually removed from the dataset, the **mean** reported values of the remaining 31 laboratories is **181.5 g/kg** and the **CV = 7.9%.**

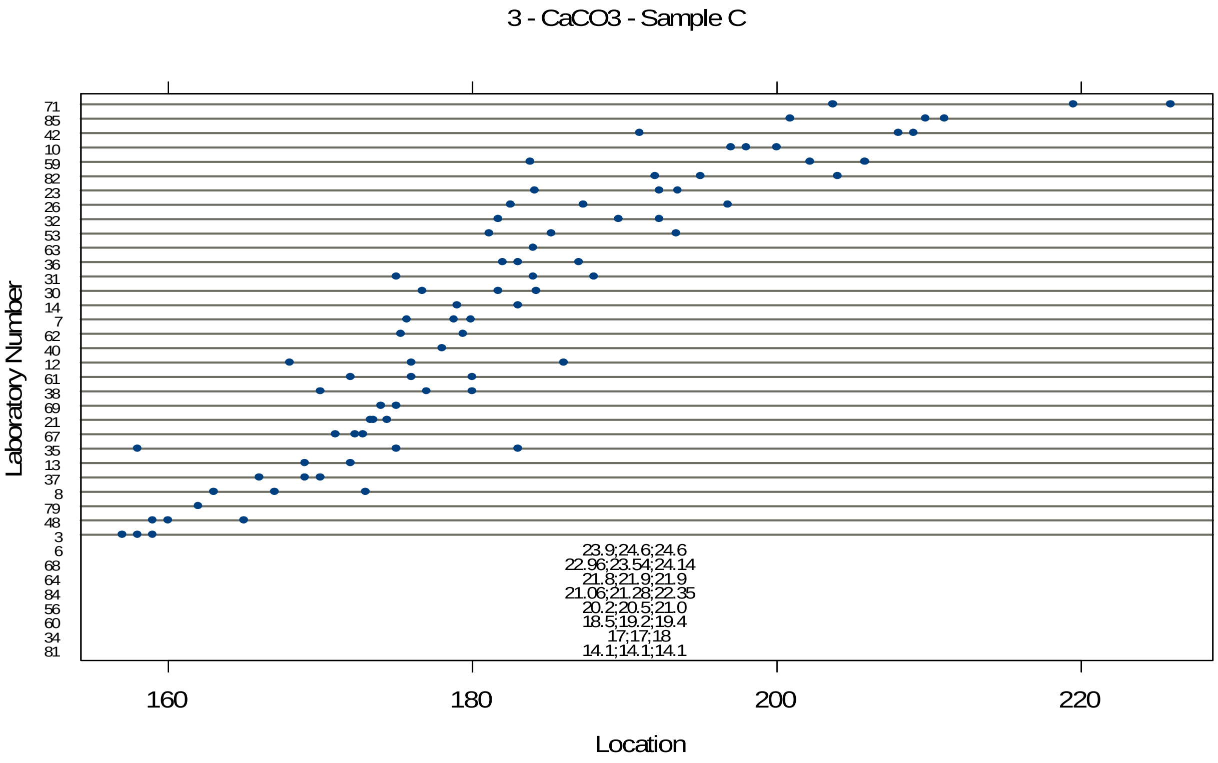


Figure 26: Dot plot of the reported $CaCO_3$ content of sample C

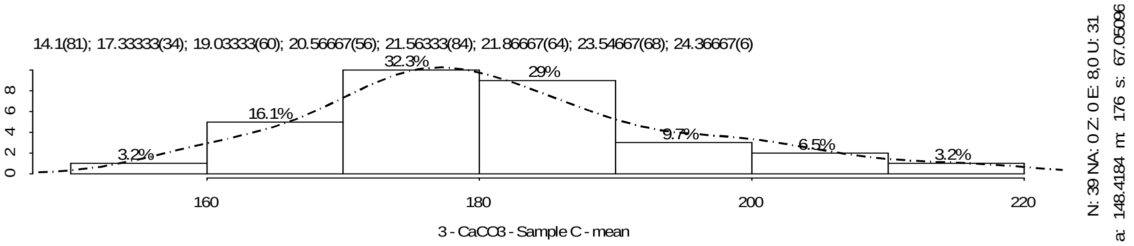


Figure 27: Histogram of the means of the reported $CaCO_3$ content of sample C

4.1.5 Organic carbon

In total 43 laboratories reported results for the organic carbon content. Due to a very high limit of quantification of 10 g/kg, Laboratory N° **35** could not report a significant OC content for the mineral soil samples. Also the detection limit in Laboratory N° **54** was too high (5 g/kg) to measure the concentration of OC in sample D.

Lab N° **81** probably reported the OC in the wrong units for sample A, B, C and D (a factor of 10 too high). For sample C, three laboratories report values which are about double the average of the other labs (Lab N° **34, 40** and **54**). Although the histogram of the means identified them as outliers, the Mandel’s h statistics did not throw them out. The reported values of sample D of Lab N° **63** have been corrected by the laboratory on the 27th of Sept. ’07: the value of three replicates should be 4.5 g/kg. This error must have been introduced – according to the lab responsible - while entering the data through the on-line web application. What went wrong in sample D and E for labs N° **85, 83** is unclear.

4.1.6 Total nitrogen content

10 laboratories of the 43 laboratories which reported N values have been excluded for at least one sample (namely Labs N° **11, 12, 42, 53, 55, 59, 62, 64, 81, 82**). The low total nitrogen content in three of the five samples (below 1 g/kg) probably explains the relatively high coefficients of variation (between 22 and 27%). In sample C and E, the total nitrogen content is higher and the samples have significant lower CV’s (between 5 and 10%).

4.1.7 Exchangeable cations

Except for laboratories N° **21, 31, 36, 40, 45, 48, 54, 58** and **83**, all laboratories reported outliers for at least one of the nine parameters in this group for at least one of the five samples. Note that laboratory N° **45** did not report free H^+ and laboratory N°**48** reported ‘0’ values for exchangeable acidity. Lab N° **58** did not report exchangeable acidity and free H^+. Lab N° **83** did not report free H^+ and exchangeable Na and reported ‘0’ values for some other parameters.

In the dataset, we still face problems with the ‘0’ values. In theory it is not possible to report a ‘0’ value since it is not possible to quantify an element below the limit of quantification and certainly not below the limit of detection. Some laboratories reported ‘0’ values while they probably should have reported the determination limit or limit of quantification. In the statistical analysis the 0 values and the values below the determination limit have been removed from the dataset. This means for example that Lab N°48 was not included in the analysis for the exchangeable acidity.

Also, it might have happened that some laboratories did not analyse a certain parameter on a sample and also put a ‘0’ value (since the on-line submission programme did no accept empty cells).

Lab N° **77** reported results which are completely different from what is expected. Also other laboratories that participated for the first time in a FSCC Interlaboratory Comparisons, performed poorly.

Another factor that may influence the variability between the labs is the single versus the triple extraction. According to Annex 3, Table 3.3, Lab N° 26 used triple extraction. For the basic cations, their results are always within the bulk of the data, except for Na where it had a tail value for sample A and a straggler for sample B based on the between-laboratory variability. For the acid cations, their values are above the mean, with occasionally a tail value, straggler or outliers, namely an outlier for sample A for Fe and for sample C for Free H^+, a straggler for sample A for Free H^+ and a tail value for sample B exchangeable acidity.

4.1.8 Aqua Regia extractable elements

Five laboratories did not analyse the aqua regia extractable elements. Of the remaining 43 laboratories, several did only analyse a subset of the 16 elements. Lab N° 62 only analysed extractable P and had poor results. Lab N° 53 only analysed K and P and neither had good results. Elements which are regularly skipped are Hg, S and K. Of the 43 laboratories, 9 laboratories failed for more than 20% of their reported results (Lab N° **12, 42, 53, 55, 56, 62, 64, 81** and **82**).

A first 'problem' element, identified as an element where more than 20% of the laboratories reported outliers, is Cadmium (Cd). 40 laboratories reported values for the extractable Cd of which 33 laboratories reported values above the limit of quantification. Of these 33 laboratories, 4 laboratories (Lab N° **6, 10, 12, 56**) failed for all samples and 2 laboratories for nearly all samples (Lab N° **55** and **63**).

The second problem element is Mercury (Hg). Only 17 laboratories reported values above the limit of quantification. Two of these laboratories failed for all their samples (Lab N° **6** and **48**) and two for nearly all of them (Lab N° **64** and **67**) . So Hg remains a difficult element to analyse.

Other elements where frequently problems are met are Al, Cu, Na, Ni and Pb (between 10 and 20 % of the reported values are outliers).

4.1.9 Total elements

In contrast to the 4th FSCC Interlaboratory Comparison, the Total elements were again included in the evaluation. Eleven laboratories reported their results. In the evaluation per element and per samples, between 1 and 4 laboratories were excluded based on the Mandel's h and k statistics. Laboratory N° **13, 30 and 36** passes the test for all the samples and elements. Laboratoy N° **82** scores very badly for most of the elements.

4.1.10 Reactive Fe and Al

In total 27 laboratories analysed the oxalate extractable Fe and Al. Laboratory N° **67** failed for nearly all the samples for the between-laboratory variability by reporting far too low concentrations. In the previous FSCC Interlaboratory Comparison, they had neither good results, but then they always measured far above the mean concentration.

4.2 Comparison with the 4th FSCC Interlaboratory Comparison

4.2.1 The coefficients of variation

Compared to the 4th FSCC Interlabratory Comparison, the CV's have improved for particle size distribution, carbonates, total nitrogen, exchangeable cations, aqua regia extractable elements (see Table 11) but remained at the same level or were even worse for pH, organic carbon, acid oxalate extractable Fe and Al.

While the average CV per sample in the 4th FSCC ring test varied between 23 % (organic sample) and 48% (sample D), there is now a clear improvement with a maximum CV of 28% in the peat sample. Note, that this is only a very rough comparison, since it concerns the average of different soil samples and the CV largely depend on the kind of sample. To allow better comparison, sample B in the 4th and the 5th FSCC Interlaboratory Comparison were nearly the same sample. The sample B in the previous ring test was a subsample of the sample in the 5th ring test, taken before the homogenisation of the sample was completed. Concerning the average coefficient of variation, the improvement is remarkable, it decreased with more than 20% (the CV of the total analyses not included).

Table 11: Group CV's of the 2nd, 3rd, 4th and 5th FSCC Interlaboratory Comparison after elimination of the outliers

	2nd FSCC RT	3rd FSCC RT	4th FSCC RT	5th FSCC RT
Group 1: Particle size distribution	NA	53	37	23
Group 2: pH	3.25	3.5	3.1	3.2
Group 3: Carbonate content	NA	206	129	45
Group 4: Organic carbon	41.5	18	13	16
Group 5: Total N	25	17	*27*	17
Group 6: Exchangeable cations	52	71	54	49
Group 7: Aqua regia extractable elements	35	47	33	26
Group 8: Total elements		21		9
Group 9: Acid oxalate extractable Fe & Al	NA	44	12	20

4.2.2 The poor performing laboratories

In the 4th FSCC ring test 9 laboratories reported outliers and stragglers for more than 20% of the total number of reported parameters. Seven laboratories (N° 12, 18, 20, 42, 64, 71, 73 and 74) reported outliers and stragglers for more than 20 % of the analyses based on the between-laboratory variability and six laboratories (Lab N° 20, 42, 71, 73, 74 and 75) based on the within-laboratory variability.

Laboratories N° 20, 73, 74 and 75 did not participate any more in the 5th FSCC Interlaboatory Comparison. The problems in Lab N° 12 remained. Lab N° 18 improved their results largely. Lab N° 42 has now better results, though still had problems with sample A and did not analyse an important set of parameters which are mandatory in the BioSoil project. Labs N° 64 and 71 improved their results but need to continue improving because still have problems with certain parameters (especially the exchangeable elements). Laboratories N° 12 and 42 mainly had problems with the aqua regia extractable elements. Lab N° 12 did not know the cause of their problems and clearly could not solve the problem in the meantime. Laboratory N° 42 installed in the meantime new equipment (AAS instrument) but is still not measuring all the mandatory parameters of the BioSoil project.

Concerning sample B, 9 laboratories reported more than 20% of outliers (summed over all reported parameters) in the 4th FSCC Interlaboratory Comparison. Five of these laboratories did not participate in the 5th FSCC Interlaboratory Comparison. Two laboratories still face problems and laboratories N° 10 and 18 improved. Lab N° 18 improved significantly its results for the aqua regia elements, although their total set of analysed parameters remains very limited (pH, OC, Tot N and Extractable Cd, Cr, Cu, Ni, P, Pb and Zn). Lab N° 10 analysed all parameters (except Total elements and Hg) and improved for most of the parameters except for extractable Cd and Mg.

4.3 Data Integrity Expert Rules

Together with the test samples all laboratories received a list (see Table 12) with updated data integrity rules and plausibility ranges.

4.3.1 $0 < pH(H_2O) – pH(CaCl_2) < 1.2$

Laboratory **N° 85** reported higher $pH(CaCl_2)$ results for samples A, B and E. The laboratory was identified for sample E as an outlier [$pH(CaCl_2)$] and a straggler [$pH(H_2O)$].

For the peat sample E, the majority of the laboratories (27 of 46 = 59%) reported $pH(H_2O)$ values which were more than 1.2 pH units higher than the $pH(CaCl_2)$. This could mean that rather the rule should be revised concerning the organic layer or more specifically for peat soils. This problem needs further clarification.

4.3.2 For organic layers: $5 < C/N$ ratio < 200 and for mineral soil: $3 < C/N$ ratio < 75

Except for Laboratory **N° 53** which reported a too low OC content for sample C (see the histogram in annex) and for Laboratory **N° 81** which reported an unacceptably high OC content for the mineral soil samples, the integrity rule on the C/N ratio was respected by all laboratories.

Table 12: Updated data integrity expert rules (FSCC, May ’07)

	Organic Sample	Mineral sample
Parameter	Rule	Rule
pH(CaCl2)	0 < [pH(H2O) - pH(CaCl2)] <= 1.2	0 < [pH(H2O) - pH(CaCl2)] <= 1.2
pH(H2O)	0 < [pH(H2O) - pH(CaCl2)] <= 1.2	0 < [pH(H2O) - pH(CaCl2)] <= 1.2
Organic carbon	(CaCO3-C)+TOC<=TC	(CaCO3-C)+TOC<=TC
Total N	5 < C/N ratio < 100	3 < C/N ratio < 75
CaCO3	if pH(CaCl2) < 6.0, CaCO3 = 0	if pH(H2O) < 5, CaCO3 = 0 or: if pH(CaCl2)<5.5, CaCO3 = 0
Particle size: clay		100-clay%-silt%-sand% = 0
Particle size: silt		100-clay%-silt%-sand% = 0
Particle size: sand		100-clay%-silt%-sand% = 0
Extracted P	100 < C/P ratio < 2500	10 < C/P ratio < 750
Extracted Ca		Extracted Ca <= Total Ca
Extracted K		Extracted K <= Total K
Extracted Mg		Extracted Mg <= Total Mg
Extracted Mn		Extracted Mn <= Total Mn
Extracted Al		Extracted Al <= Total Al
Extracted Fe		Extracted Fe <= Total Fe
Extracted S	20 < C/S ratio < 1000	
Exchangeable acidity		EA = Al-exch+Fe-exch+Mn-exch+Free H+
Exchangeable Ca		(Ca-exch * 200) <= Extracted Ca <= Total Ca
Exchangeable Mg		(Mg-exch*122) <= Extracted Mg <= Total Mg
Exchangeable K		(K-exch*391) <= Extracted K <= Total K
Exchangeable Na		(Na-exch *230) <= Extracted Na <= Total Na
Exchangeable Al		(Al-exch*89) <= Extracted Al <= Total Al
Exchangeable Fe		(Fe-exch*186) <= Extracted Fe <= Total Fe
Exchangeable Mn		(Mn-exch*274) <= Extracted Mn <= Total Mn
Total Al		Total Al >= Extracted Al
Total Ca		Total Ca >= Extracted Ca
Total Fe		Total Fe >= Extracted Fe
Total K		Total K >= Extracted K
Total Mg		Total Mg >= Extracted Mg
Total Mn		Total Mn >= Extracted Mn
Total Na		Total Na >= Extracted Na
Free H+		Free H+ < Exchangeable Acidity
Reactive Fe		Reactive Fe <= Total Fe
Reactive Al		Reactive Al <= Total Al

4.3.3 For organic layers: if pH($CaCl_2$) < 6.0 then $CaCO_3$ = 0 and for mineral soil: if pH(H_2O) < 5 then $CaCO_3$ = 0 or: if pH(CaCl2) < 5.5, then $CaCO_3$ = 0

The laboratories that reported other values than ‘NA’, a ‘0’ or a value below the limit of determination made a serious mistake and are considered to have failed for this parameter and the concerning sample(s). The outlying labs and their reported values are given in Table 13.

Table 13: Mean reported $CaCO_3$ content for samples A, B, D and E different from 'NA', 0 or below detection limit

Lab ID	Mean reported value			
	Sample A	**Sample B**	**Sample D**	**Sample E**
Mean pH($CaCl_2$)	*4.2*	*3.8*	*4.0*	*2.8*
68	Value < LOQ	Value < LOQ	Value < LOQ	***3 g/kg***
81	***0.2 g/kg***	0 g/kg	0 g/kg	0 g/kg
85	***17.7 g/kg***	***24.5 g/kg***	***7 g/kg***	***9.8 g/kg***

4.3.4 Particle size distribution: Σ [clay (%), silt (%), sand (%)] = 100 %.

Taking one digit into account, not more than the results of 13 laboratories out of 35 fulfil this rule. For most of the other 22 labs, the differences were smaller than 1% and can still be accepted. Though, laboratory N° **55** (with an outlier for silt content on sample D) reported results where the sum of the sand and silt fraction was exactly 100% but on top of that they still measured a clay fraction, resulting in total percentage way above 100%. Other laboratories with great deviations from the 100 % were Labs N° **7, 26 and 34.**

4.3.5 For organic layers: 100 < C/P ratio < 2500 and for mineral soil: 10 < C/P ratio < 750

Concerning the organic layer, all laboratories reported C/P ratio's above 100 but more than 50 % (18/35) of the laboratories reported C/P ratio's above 2500. This raises again the question whether the data quality rule is also valid for a peat soil.

Concerning the mineral samples, the C/P ratio in samples A and D is quite often close to 10 and for a number of laboratories below 10 (Labs N° 8, 18, 31, 32, 34, 54, 56, 59 and 85). The upper limit for the mineral samples was respected by most of the laboratories except for Lab N°53 which reported too low extractable P values (see also Annex 5).

4.3.6 For organic layers: 20 < C/S < 1000

All results of the organic sample for which both the C and S content was reported, fulfilled this criterion.

4.3.7 [Exchangeable elements] ≤ [Extractable elements] ≤ [Total elements]

These rules check whether the total content of a certain elements is larger than the extractable content which should be larger than the exchangeable content. Table 14 and Table 15 show the Lab IDs of the laboratories violating these rules.

Table 14: Laboratories for which violations have been observed for Ca, Mg, K, Na and Mn

Violation	[Ex Ca] < [Ec Ca]	[Tot Ca] < [Ex Ca]	[Ex Mg] < [Ec Mg]	[Tot Mg] < [Ex Mg]
A	77, 81	-	-	-
B	77, 81	-	-	-
C	77	3, 7, 13, 14, 30, 32, 40, 48, 82	77	-
D	77, 81, 83, 84	-	-	82
E	6, 12, 77	14, 30, 32, 40, 48	6, 8, 12, 14, 23, 26	14, 30, 32, 40, 48
Violation	**[Ex K] < [Ec K]**	**[Tot K] < [Ex K]**	**[Ex Na] < [Ec Na]**	**[Tot Na] < [Ex Na]**
A	**77**	**-**	77, 81, 82	-
B	77	-	6, 64, 77, 81, 82	-
C	77	-	77, 82, 84	-
D	77	-	56, 77, 81, 82	-
E	8, 11, 63, 64, 77, 82	32	3, 6, 11, 13, 26, 31, 45, 54, 64, 77, 82, 84	7, 32, 40, 82
Violation	**[Ex Mn] < [Ec Mn]**	**[Tot Mn] < [Ex Mn]**		
A	77	32		
B	77	-		
C	77	7, 30, 32, 40, 48		
D	77	7, 14, 30, 32, 48, 84		
E	3, 11, 14, 23, 42, 59, 60, 77, 82	7, 13, 32, 40, 48		

Based on the Mandel's h and k statistics, laboratory N° **77** had outlying results for all its measured exchangeable elements and for all samples. They easily could have identified this problem before submitting the results to FSCC by checking these rules. Most of the laboratories mentioned in the second column have been excluded from the Mandel's h and k statistics of the exchangeable elements meaning that the reason behind the violation of the rules should be sought in the too high levels of exchangeable elements reported by these laboratories.

Calcium: It is remarkable that 9 of the 11 laboratories that measured total Ca on sample C reported total Ca content lower than the extractable Ca. This inconsistency can be related to the $CaCO_3$ content of the sample and the pre-treatment of the sample. On the peat sample, 10 laboratories determined total elements. Five of them measured values lower than the extractable elements. These differences can e.g. be due to an improper destruction of the organic matter. These two problems have to be analysed in more detail.

Potassium: Lab N° 77 reported too high exchangeable K for all the samples. Concerning sample E, Lab N° 77 and 82 were identified as outliers for the exchangeable elements and Labs N° 11 and 64 as stragglers. The extractable K measured by Lab N°32 in sample E was higher compared to the other laboratories and by consequence identified as an outlier.

Magnesium: Five out of the ten laboratories that reported total Mg for the peat samples obtained results which were lower than the concentrations obtained by the aqua regia extractions. It are exactly the same laboratories that failed this rule for Ca.

Sodium: In the previous sections of the report, problems were seen for many laboratories concerning the exchangeable sodium content. Again we face higher extractable concentrations than total concentrations for the organic sample.

Manganese: Lab N° 77 reported exchangeable Mn values far too high for all the samples. Lab N° 3, 11, 42 and 60 were tail values in the dot plots of extractable Mn for sample E on the lower range of the distribution. Lab N° 32 had relatively high extractable values for sample A and Lab N° 48 was identified as outlier for extractable Mn for sample E. Lab N° 14 and 84 were identified as outliers for the total Manganese and Lab N° 32 in sample E.

Aluminium and Iron: For these two elements two additional rules could be included concerning the total and the oxalate extractable elements.

Table 15: Laboratories for which violations have been observed for Fe and Al

Sample	[Ex Al] < [Ec Al]	[Tot Al] < [Ex Al]	[Tot Al] < [Re Al]
A	-	-	-
B	-	-	-
C	-	-	-
D	-	-	-
E	30, 82	-	-
Sample	**[Ex Fe] < [Ec Fe]**	**[Tot Fe] < [Ex Fe]**	**[Tot Fe] < [Re Fe]**
A	-	-	-
B	-	32	-
C	-	13	-
D	-	32, 48, 82	-
E	77	3, 13, 32, 40, 48	3, 13

Aluminium: Lab N° 30 was an outlier for exchangeable Aluminium since they measured a concentration which was too high and Lab N° 82 was identified as an outlier for the extractable Al in the boxplots (measurement was too low).

Iron: Lab N° 77 is an outlier for the exchangeable Fe and Lab N° 82 and 32 were identified as outliers for respectively samples D and E. The differences between total Fe and extractable Fe for laboratories n° 3 and 13 were relatively small (< 5%), but were 10% for Lab N° 32 and between 10 and 20 % for laboratories 40 and 48.

4.3.8 Exchangeable acidity = Σ (acid cations, free H^+)

This rule can be used to check two methods: the calculation of the exchangeable acidity by making the sum of the acid cations and Free H^+ and the direct titration method to measure the exchangeable acidity. FSCC suggests to apply this rule on the results in cmol(+)/kg without decimal values. For sample C this rule was difficult to check since many of the acid cations were below the limit of determination. Concerning sample A, the exchangeable acidity of 5 laboratories was higher than the sum of the acid cations and Free H^+ (Labs N° 26, 40, 54, 63 and 71) and for other 6 laboratories (Labs

N° 32, 37, 42, 55 and 81) the sum of the acid cations and Free H^+ was clearly higher than the (directly measured) exchangeable acidity.

4.3.9 Exchangeable acidity > Free H^+

Some laboratories reported Exchangeable acidity concentrations which were lower than the Free H^+ (Table 16). Sometimes this is due to the low concentration in the sample and that the measurement(s) is (are) close to the limit of quantification. For example, Lab N° 54 measured exchangeable acidity below the LOQ and positive Free H^+ values. Some laboratories (Lab N° 48 and 64) reported '0' values for exchangeable acidity and positive numbers for Free H^+. As written before, these '0' values cannot be correct and should be replaced by the LOQ values. In Lab N° 26 and 63 there must have gone something wrong in the measurement of Free H^+.

Table 16: Laboratories violating the rule: Exchangeable acidity > Free H^+

Laboratory	Sample (s) where [Free H^+] > [Ec Ac]
26	C
48	A, B, C, D
54	C
63	D, E
64	C

5 CONCLUSIONS

A total of 48 laboratories reported their results in the 5th FSCC Interlaboratory Comparison 2007. Nine laboratories reported outliers and stragglers for more than 20 % of the total; five based on the between-laboratory variability, and eight laboratories based on the within-laboratory variability. Problem parameters are (1) exchangeable elements, especially Na, Ca, free H^+, Mg, Acidity and Fe, (2) the heavy metals Hg and Cd extracted by Aqua Regia, Extractable Al and Mg, (3) carbon content in sample D with low organic carbon content and (4) the pH determination of a peat sample. In general there are more problems when the concentration of the concerning element is relatively low. Compared to the 4th FSCC interlaboratory comparison in 2005, the coefficients of variation of all groups of analysis have improved or remained at a similar level. The CV of the blind sample B improved by 20% mainly because of a large improvement of determination of the Aqua Regia extractable elements.

6 RECOMMENDATIONS AND FOLLOW-UP

1. Certain easily identifiable errors appear over and over again in each interlaboratory comparison. A number of them can be overcome by the application of the data integrity rules. The application of

the data integrity expert rules by the laboratories could have been better. Several laboratories reported data which violated the rules. Those errors often resulted in the exclusion of the laboratory in the final statistical evaluation. So the application of the data integrity rules would strongly improve the ring test results. Certain rules might need further refinement, for example concerning the pH checks in the organic layer.

2. A second set of errors concern the reporting units. This ring test showed a clear example where the $CaCO_3$ by a number of laboratories was reported in % instead of g/kg. Plausibility rules could help the laboratories to identify such errors, though since the programme covers a very wide range of soil types, the plausibility range we can set is often too wide to detect these errors. Therefore FSCC suggests that all laboratories set up their plausibility ranges according to the soil types which are frequently met in their country.
3. In the 4th FSCC Interlaboratory Comparison 14 German laboratories reported their results. The coefficients of variation of this subset of laboratories were significantly better compared to the whole set of 52 laboratories. This may indicated that the German approach is a possible effective way to improve the quality in the laboratories. In Germany regular laboratories meetings are organised with the laboratories heads, where information between the laboratories can be exchanged. Therefore the QAQC laboratory group of ICP Forest, under the chairmanship of Dr. N. König, will organise a laboratory head meeting. FSCC fully supports this initiative.
4. In the framework of the BioSoil project, a separate statistical evaluation was made of the subset of 39 laboratories participating in BioSoil. Now 6 laboratories were identified as outlying labs, of which 4 laboratories were already identified in the overall interlaboratory comparison. While overall the CVs were slightly lower, this was not the case for all parameters and samples.

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