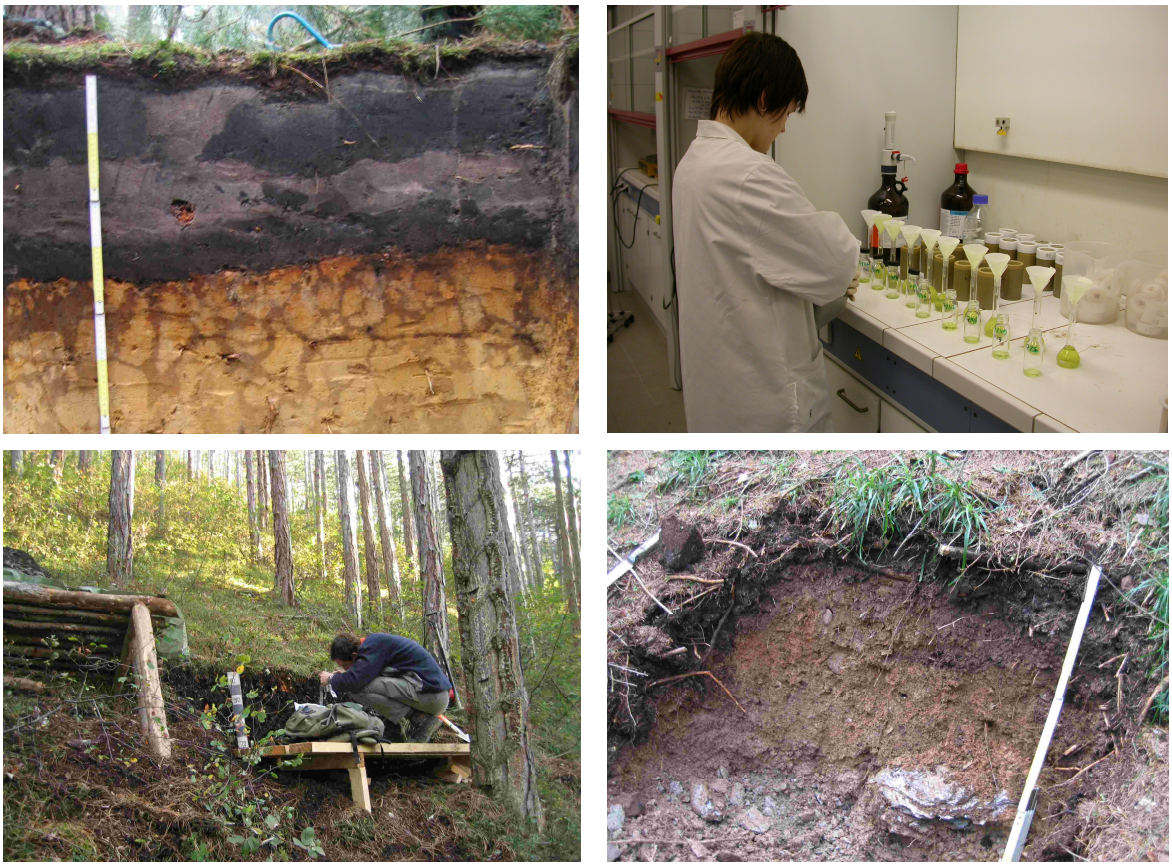
CONVENTION ON LONG-RANGE TRANSBOUNDARY AIR POLLUTION
INTERNATIONAL CO-OPERATIVE PROGRAMME ON ASSESSMENT AND MONITORING OF AIR POLLUTION EFFECTS ON FORESTS
AND
THE FOREST FOCUS REGULATION EEC 2152/2003 OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL CONCERNING MONITORING OF FORESTS AND ENVIRONMENTAL INTERACTIONS IN THE COMMUNITY

United Nations Economic Commission for Europe | European Commission | Flemish Community Forest and Green Division

Quality Assurance and Quality Control in Forest Soil Analysis: 4th FSCC Interlaboratory Comparison



N. Cools, P. Verschelde, P. Quataert, J. Mikkelsen, B. De Vos
2006

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LIST OF ABBREVIATIONS

ICP	International Co-operative Programme
FSCC	Forest Soil Co-ordinating Centre
EU	European Union
QA/QC	Quality assurance – Quality Control
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

52 laboratories participated in the 4th FSCC Interlaboratory Comparison 2005-2006. Seven laboratories reported outliers and stragglers for more than 20 % of the analyses, based on the between-laboratory variability, and six laboratories based on the within-laboratory variability. Problem parameters are (1) the heavy metals and S extracted by Aqua Regia, (2) the exchangeable elements, (3) carbon content in samples with low organic carbon content and (4) the calcium carbonate determinations. Three years after the 3rd FSCC Interlaboratory Comparison 2002-2003, more laboratories use the reference methods, have a higher experience with these reference methods, make more use of reference material and control charts but less laboratories are accredited for the reference methods. The coefficients of variation of all groups of analysis have improved except for the total nitrogen which was probably due to the fact that three samples had very low nitrogen content.

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 is 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 'Manual 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.

On the onset of the EC Forest Focus demonstration project "BioSoil", the FSCC proceeded in 2005 the FSCC with a **fourth Interlaboratory Comparison**. All analyses in the BioSoil project will need to be done by laboratories which perform well in the FSCC Intercalibration Exercises. The analytical methods allowed in this interlaboarotry comparison were exactly the same as in 2002-2003. Also the methodology of the statistical analysis of the ring test was exactly the same, allowing to detect possible progr

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 ring test. Initially 55 laboratories from 27 European countries registered by the end of May 2005. Three laboratories (n° 17, 25 and 65) registered but did not further participate in the ring test. These laboratories will not be mentioned in the further discussion. This means that a total of fifty two laboratories analysed the soil samples and reported their results to FSCC. Their addresses are listed in Annex 1.

2.2 Sample characterisation

2.2.1 Sampling location

Seven samples were sent to each of the participating laboratories in June 2005. This included 4 mineral soil samples (A, B, C and D), one forest floor sample (E) and two digested samples in an Aqua Regia extraction (F and G). These samples were taken under forest conditions in different regions of Europe (Austria, France, Belgium, Norway, Germany). Since the previous ring test was criticised for its selection of extreme soil samples - sample A was very poor in nutrients, and sample B was very calcareous – more moderate soil samples were selected.

Sample A was taken from the 20-40 cm depth layer in a monoculture beech (*Fagus sylvatica*) forest in Austria. This silty clay sample is a relatively nutrient rich forest soil sample (CEC > 25 cmol(+)/kg soil). Sample B is a loamy soil sample also taken from the 20 -40 cm layer of a mixed Flemish deciduous forest where Pedunculate oak (*Quercus robur*) and beech (*Fagus sylvatica*) dominate. Sample C is a sandy loam soil from a mixed beech *(Fagus sylvatica)* and Sessile oak *(Quercus petraea)* in north France. The soil profile is decarbonated following an irregular boundary and shows clay elevation/illuviation [FAO (1989) Calcic Luvisol]. Sample D is a poor sandy soil sample from Germany. Sample E is a Flemish forest floor sample from the F-layer of a beech forest (*Fagus sylvatica*). Samples F and G were samples which have been distributed after digestion for the analysis of aqua regia extractable elements only. Sample F is the same sample as Sample B. Sample G comes from the B horizon, enriched in Fe and Al, of a Cambic Arenosol in Norway.

Table 1 gives an overview of the properties of the seven soil samples, based on the results of the analyses of all participating laboratories in the 4th 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

Element		A		B		C		D		E		F			G		
		N°	Mean	N°	Mean	N°	Mean	N°	Mean	N°	Mean	N°	Mean		N°	Mean	
Moisture content	%	36	3.7	39	0.8	39	0.6	36	0.4	39	3.0						
Particle size: clay	%	32	40.4	31	10.7	31	10.1	27	3.9								
Particle size: sand	%	27	10.9	29	44.4	32	55.5	29	88.5								
Particle size: silt	%	31	43.0	28	41.4	30	32.8	30	7.4								
pH($CaCl_2$)		45	5.7	46	3.8	47	4.1	46	4.3	45	3.7						
pH(H_2O)		42	6.4	41	4.3	43	4.9	42	4.6	43	4.5						
Carbonates	g/kg	20	1.5	21	1.5	20	1.4	21	1.6	19	1.7						
Organic Carbon	g/kg	41	45.4	39	6.5	36	5.9	34	1.7	37	244.1						
Total N	g/kg	45	3.4	42	0.4	43	0.4	47	0.2	43	11.1						
Exchangeable Ac.	cmol(+)/kg	34	0.27	36	3.64	37	1.83	38	0.76	38	4.06						
Exchangeable Al	cmol(+)/kg	36	0.04	36	3.41	33	1.56	38	0.58	37	1.16						
Exchangeable Ca	cmol(+)/kg	42	21.17	38	0.12	43	2.60	33	0.04	44	15.35						
Exchangeable Fe	cmol(+)/kg	35	0.02	37	0.11	40	0.07	39	0.02	40	0.33						
Exchangeable K	cmol(+)/kg	37	0.47	37	0.07	35	0.06	36	0.02	38	1.49						
Exchangeable Mg	cmol(+)/kg	37	3.72	32	0.04	35	0.14	35	0.03	39	2.87						
Exchangeable Mn	cmol(+)/kg	40	0.25	33	0.03	28	0.02	41	0.03	36	1.52						
Exchangeable Na	cmol(+)/kg	38	0.12	31	0.04	36	0.06	36	0.04	35	0.25						
Free H+ acidity	cmol(+)/kg	34	0.16	35	0.31	30	0.27	35	0.21	35	2.28						
Extractable Al	mg/kg	33	28719	31	8429	32	7940	32	6495	32	4911.4	28	118.6	mg/l	29	193.6	mg/l
Extractable Ca	mg/kg	38	4153.8	37	258.6	38	717.1	38	360.9	42	3413.2	31	8.3	mg/l	37	29.6	mg/l
Extractable Cd	mg/kg	31	*0.542*	*28*	*0.116*	*30*	*0.130*	*30*	*0.128*	*33*	*0.403*	*25*	*0.01*	mg/l	27	*0.003*	mg/l
Extractable Cr	mg/kg	35	49.8	35	20.4	34	15.9	30	6.3	36	21.6	30	0.3	mg/l	29	0.3	mg/l
Extractable Cu	mg/kg	39	40.5	40	2.8	41	2.5	37	1.9	39	13.6	28	*0.04*	mg/l	31	0.1	mg/l
Extractable Fe	mg/kg	34	34952	37	11556	36	7788	36	7392	37	9307.4	32	129.9	mg/l	36	219.2	mg/l
Extractable Hg	mg/kg	14	*0.158*	*14*	*0.154*	*13*	*0.022*	*12*	*0.020*	*13*	*0.210*	*7*	*0.0003*	mg/l	8	*0.0002*	mg/l
Extractable K	mg/kg	39	3321.5	39	1351.3	39	697.9	39	321.2	41	1734.7	32	24.2	mg/l	33	29.2	mg/l
Extractable Mg	mg/kg	37	4482.7	41	1231.1	39	878.9	38	1544.8	38	1345.2	31	16.0	mg/l	33	37.6	mg/l
Extractable Mn	mg/kg	38	1987.4	41	106.4	40	74.3	41	255.8	41	500.7	32	1.2	mg/l	32	5.1	mg/l
Extractable Na	mg/kg	32	184.9	34	51.9	35	52.9	29	36.3	31	86.1	28	4.6	mg/l	30	4.5	mg/l
Extractable Ni	mg/kg	34	45.6	35	4.9	33	6.0	33	7.0	33	10.2	23	0.1	mg/l	27	0.2	mg/l
Extractable P	mg/kg	33	489.4	33	101.6	31	66.9	33	272.4	33	635.6	28	1.2	mg/l	26	7.5	mg/l
Extractable Pb	mg/kg	35	45.7	41	8.0	37	7.3	37	3.3	40	59.3	30	0.1	mg/l	32	0.1	mg/l
Extractable S	mg/kg	22	357.2	16	76.7	21	52.5	18	76.0	24	1195.0	18	1.1	mg/l	19	1.3	mg/l
Extractable Zn	mg/kg	36	117.4	41	19.0	41	16.6	42	20.3	41	59.8	33	0.3	mg/l	31	0.7	mg/l
Reactive Al	mg/kg	24	2487.8	21	1365.2	23	743.6	23	1082.3	21	733.7						
Reactive Fe	mg/kg	25	6876.4	21	2834.6	24	935.3	24	1855.4	24	2204.9						

2.2.2 Sample preparation and homogenisation

Prior to sending the soil samples to the laboratories, the samples were checked for homogeneity. Samples were air dried at 40°C and subsequently milled above a 2 mm sieve. The samples have been homogenised by riffling and divided over 100 subsamples (2 riffling cycles). Of each of the five sample (A, B, C, D and E), 8 subsamples were selected at random and sent to the laboratory for organic carbon and Modified Kjeldahl N. The variation between the subsamples was not bigger than the variation within the sample and therefore they were considered to be homogeneous.

2.2.3 Distribution of samples and submission of results

Samples were sent to the participating laboratories on the 22nd of June 2005, one week later than initially announced. Since FSCC was late to distribute the soil samples, the submission deadline was postponed with two weeks, 28 October 2005 instead of the initially announced deadline of 14 October 2005, for both the questionnaire and the ring test results.

2.3 Soil Analysis Methods

2.3.1 Guidelines for soil sampling and analysis

Laboratories were requested to use the methods as described in the revised 'Submanual on Sampling and Analysis of Soil' (FSCC, 2003). As seen from Table 2, all these methods are based on the ISO-standards. In contrast to the previous interlaboratory comparison, the analysis of total elements was not included in this comparison because these parameters are of no immediate relevance for the "BioSoil" project (where total elements are only optional parameters on Level II plots). However this did not increase the overall participation in the ring test. Many laboratories analysed only a limited set of parameters, which is worrying toward the upcoming BioSoil survey where all mandatory and optional parameters on all Level I plots should be analysed following the reference methods. For example only 69 % (36 laboratories) did determine the soil texture by analytical laboratory procedures. Not more than 26 of these laboratories used the reference method, which is the pipette method, which means that only 50% of the laboratories could analyse soil texture according to the reference method.

Table 2: Methods recommended by the manual on soil sampling and analysis

Analysis	Reference Method	Decription
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 $BaCl_2$
Aqua Regia Extractant Determinations	ISO 11466	Extraction by Aqua Regia
Reactive Fe and Al	ISRIC 1992	Extraction by Acid Oxalate

Although the use of the reference methods will be mandatory during the next soil survey, not all the laboratories used these reference methods for all types of analysis. More details on the use of the reference methods in this interlaboratory comparison can be consulted in Annex 2 and 3. Annex 3 contains a proposal for a coding system on the methodology. This coding system is based on the system proposed by Fürst (2006).

2.3.2 Questionnaire

All participating laboratories were asked to fill in a questionnaire in which they were asked to provide additional information to the FSCC on the laboratory practices. Questions were arranged according to eight groups of analyses. In contrast to the previous FSCC Interlaboratory Comparison, the group N° 8 of the Total elements was not included. The full questionnaire can be consulted in Annex 6 of the report, which can be found on the attached CD.

The questionnaire addressed the following topics:

- **General information on the laboratory:**
  - Statute of the laboratory (university, government, private and other)
  - Type of the laboratory (soil, plant or general laboratory)
  - Whether the laboratory is specified in forestry or not
  - N° of laboratory personnel
  - Since when the laboratory is operational
  - Whether the laboratory is certified
  - Whether the laboratory participates in other interlaboratory comparisons

- **Information on the conducted analyses:**
  - Analysis performed by own laboratory or subcontracted
  - Used methods (reference methods versus non-reference methods)
  - Accreditations
  - Frequency of use of the reference method (daily, weekly, monthly, few times a year, annually, less than once a year)
  - Information on the used laboratory equipment
  - Experience of the laboratory with the reference method
  - Quality assurance programme:
    - Use of reference material (international, national or local reference material)
    - Type of reference material (matrix or method reference material)
    - Use of calibration standards
    - Use of control charts
    - Repeatability/reproducibility conditions

2.3.3 Data reporting

Each parameter had to be measured in three replicates. Laboratories reported the values of the three replicates of each analytical in a preformatted Excel-spreadsheet or as a hard copy, using a separate sheet for each soil sample by the end of October 2005.

2.3.4 Problems of rounding

Laboratories reported the fixed number of digital numbers according to manual. However, concentrations were sometimes very low, especially of the aqua regia extractable Cd, Hg and Cu. The manual requires results of the aqua regia elements of up to one digit after the comma (unit = mg/kg). In these few case, reporting a limited fixed number of digits, caused a false reporting of null values. Therefore FSCC suggests to increase the number of digits to at least one significant digit. Otherwise no distinction can be made between real null values (reported as “0”) and false null values (truncated small values) once the data have been entered in the database.

2.3.5 Problems of quantification limit

Laboratories were asked to indicate a negative value sign in front of the measured value, when the concentration of the parameter was below quantification limit. However, still some zero values have been reported when these values were no real zero's (see also 2.4.2). Therefore it would be better to follow the methodology which is also applied in the other disciplines of the ICP Forests programme. When a laboratory measures 0.4 ppm and its quantification limit is 0.5 ppm, the laboratory should report "<0.5 ppm". Information on the reported LOQ values is given in Table 3.

Table 3: Average of reported LOQ values

	Sample						
Element	**A**	**B**	**C**	**D**	**E**	**F**	**G**
Moisture content	0.1	0.1	0.1	0.1	0.1		
Particle size: clay	1.5	0.6	0.6	0.6			
Particle size: sand	1.5	0.6	0.6	0.6			
Particle size: silt	0.4	0.4	0.4	0.4			
pH(CaCl2)	0.3	0.3	0.3	0.3	0.3		
pH(H2O)	0.3	0.3	0.3	0.3	0.3		
Carbonates	2.5	2.8	2.8	2.8	3.2		
Organic Carbon	1.3	1.2	1.2	1.2	1.7		
Total N	0.1	0.1	0.2	0.1	0.5		
Exchangeable Acidity	0.20	0.21	0.21	0.21	0.23		
Exchangeable Aluminium	0.21	0.20	0.20	0.20	0.22		
Exchangeable Ca	0.22	0.21	0.23	0.22	0.25		
Exchangeable Fe	0.05	0.04	0.05	0.04	0.05		
Exchangeable K	0.23	0.23	0.23	0.23	0.23		
Exchangeable Mg	0.18	0.18	0.18	0.18	0.19		
Exchangeable Mn	0.03	0.03	0.03	0.03	0.03		
Exchangeable Na	0.18	0.18	0.18	0.17	0.18		
Free H+ acidity	0.21	0.25	0.23	0.21	0.25		
Extractable Al	77.0	78.4	76.9	77.1	76.1	1.7	1.9
Extractable Ca	52.8	50.4	49.6	49.6	45.9	8.0	7.8
Extractable Cd	0.53	0.48	0.52	0.52	0.52	0.30	0.29
Extractable Cr	3.1	3.2	3.3	3.3	3.3	2.2	2.2
Extractable Cu	2.2	1.9	2.0	2.0	1.9	1.3	1.3
Extractable Fe	118.0	74.0	86.8	78.3	75.5	0.9	1.5
Extractable Hg	0.34	0.24	0.34	0.34	0.34	0.04	0.04
Extractable K	96.7	81.3	81.4	80.4	74.2	30.8	29.9
Extractable Mg	42.9	38.3	38.1	38.6	33.3	9.1	8.9
Extractable Mn	17.9	7.6	7.5	8.0	7.2	0.6	0.6
Extractable Na	21.7	20.9	21.3	20.9	20.6	4.0	4.0
Extractable Ni	1.6	1.5	1.6	1.6	1.5	0.8	0.4
Extractable P	41.6	35.3	35.0	34.3	32.8	0.5	0.5
Extractable Pb	2.5	2.4	2.4	2.4	2.4	0.4	0.4
Extractable S	135.0	136.0	134.2	134.2	128.6	0.5	0.5
Extractable Zn	2.2	2.0	2.0	2.2	2.0	0.4	0.4
Reactive Al	44.6	44.6	44.6	44.6	44.6		
Reactive Fe	48.4	48.4	48.4	48.4	48.4		

2.3.6 Data entering and data integrity check

After data have been entered in the database, each of the laboratories received a copy of their data in a PDF-file by the 16th of December 2005. The documents were in exactly the same format (same number of digits, etc.) as the data were entered in the system. Laboratories could check, comment and correct the reported values if needed till the 6th of January 2006.

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 6.2 Professional (2003).

This transparent and easily to interpret add 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.
3. The procedure allows the comparison of different sources of variance:

$$sRepr^2 = sLab^2 + sRep^2$$

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 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. Usually reported zero's are truncated small values. A truncated small value is a small measured value (but still higher than the quantification limit) that, by rounding to a certain precision is truncated to a zero in the database.

After the first statistical analysis, all laboratories reporting zero values have been contacted. In most of the cases the truncated small values could be defined and have been replace by the small positive values if above the quantification limit. This means that the number of zero's in the dataset is minimized.

"Values below quantification limit": Laboratories have been asked to indicate a negative value when the concentration of a certain parameter was below detection limit and to report the quantification limit. However, this rule was not always consistently applied by all laboratories. To guarantee consistency throughout the dataset, FSCC replace the values below the quantification limit (whether they were negative values, zero's or small positive values) by the "LOQ/2".

"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 reported for certain parameters only one or two replicates. When only one replicate was reported, this observation could not be included in the final evaluation of the inter- and intralaboratory variability for basic statistical reasons. When two observations have been reported, the parameter was included in the statistical analysis.

During the first analysis round, some "missing values" did received also the LOQ/2 values because in some cases laboratories did report LOQ values but not measurement. The replacement by LOQ/2 was performed automatically but erroneously on these empty cells. In the next analytical round, these false observations have been removed from the dataset.

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:

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

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.

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:

$sRepr^2 = sLab^2 + sRep^2$ Where : $sRep^2 < sLab^2$

In other words, we 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. Since the FSCC does not have any information on the repeatability conditions, a few additional questions were added to the questionnaire.

3. Not all the laboratories reported all parameters. Can laboratories improve their performance in the statistical analysis by reporting less parameters, especially of more complex analysis methods, in order to lower the risk of being evaluated as a poor performing laboratory?

3 RESULTS AND DISCUSSION

3.1 Questionnaire

3.1.1 Participation

Table 4 gives an overview of the registered and participating laboratories of each country. The column 'questionnaire' shows whether the laboratories delivered a completed questionnaire or not. Contact addresses of the participating laboratories can be consulted in Annex 1. Three laboratories (N° 48, 49 and 68) did not send in the questionnaire. When analyses were conducted by a subcontractor, the information related to the subcontracted analyses, has been filled under the name of the head laboratory. One exception is for the case of the UK where a second subcontractor for texture analyses joined the ring test later and received its own laboratory number.

Table 4: List of participating countries

Country	Registered	Results	Questionnaire
Austria	1	1	1
Belarus	1	0	0
Belgium	3	2	2
Bulgaria	3	3	3
Croatia	1	1	1
Cyprus	1	1	1
Czech Republic	1	1	1
Denmark	1	1	1
Estonia	1	1	1
Finland	2	2	2
France	1	1	1
Germany	15	14	12
Greece	1	1	1
Hungary	2	2	2
Ireland	1	1	1
Italy	2	2	2
Latvia	2	2	2
Lithuania	1	1	1
Poland	1	1	1
Portugal	1	1	1
Romania	1	1	1
Russia	3	3	2
Serbia and Montenegro	1	1	1
Slovak Republic	1	1	1
Slovenia	1	1	1
Spain	2	2	2
Sweden	1	1	1
United Kingdom	3	3	3
Total	**55**	**52**	**49**

3.1.2 General information on the laboratory

The general information on the laboratories is summarized in Table 5. 69 % of the laboratories are governmental institutes. Most of the participant laboratories are forestry laboratories, which conduct besides soil and plant analysis also other types of analyses. The majority of them is participating in other ring tests too. The size of the laboratories varies largely: from 1 to 60 laboratory workers.

Table 5: General information on the laboratories

Statute	**N° Labs**	**%**
Governmental Institute	34	69
University	9	18
Other	3	6
Private laboratory	3	6
Type	**N° Labs**	**%**
General	23	47
Plant & Soil	16	33
Soil	10	20
Forestry	**N° Labs**	**%**
Specialised in forestry	35	71
Not specialised in forestry	14	29
Permission public use info	**N° Labs**	**%**
Yes	25	51
No	24	49
Participation other RT	**N° Labs**	**%**
Yes	44	90
No	5	10
	N° personnel	**Working since**
Average	14	1970
Median	7	1972
Max	60	1999
Min	1	1857

3.1.3 Use of the reference methods

Although the use of the reference methods was mandatory for the ring test, still several laboratories used the national methods. Of all analyses, 82% was done according to the manual while in the 3rd FSCC Interlaboratory Comparison this was only 65%. Figure 1 gives an overview of the use of the reference methods for the different groups of types of analyses. Annex 2 provides this information for each laboratory.

As shown in Figure 1 the reference method is nearly always used for the determination of the *pH*. The *calcium carbonate* analysis by the use of the calcimeter is the least successful reference method. Of the non reference method users, most laboratories used an element analyser (e.g. LECO) or titration, a TOC analyser or by colorimetric detection of CO_2 for the carbonate determination. More information on the methods used can be found in Annex 3.

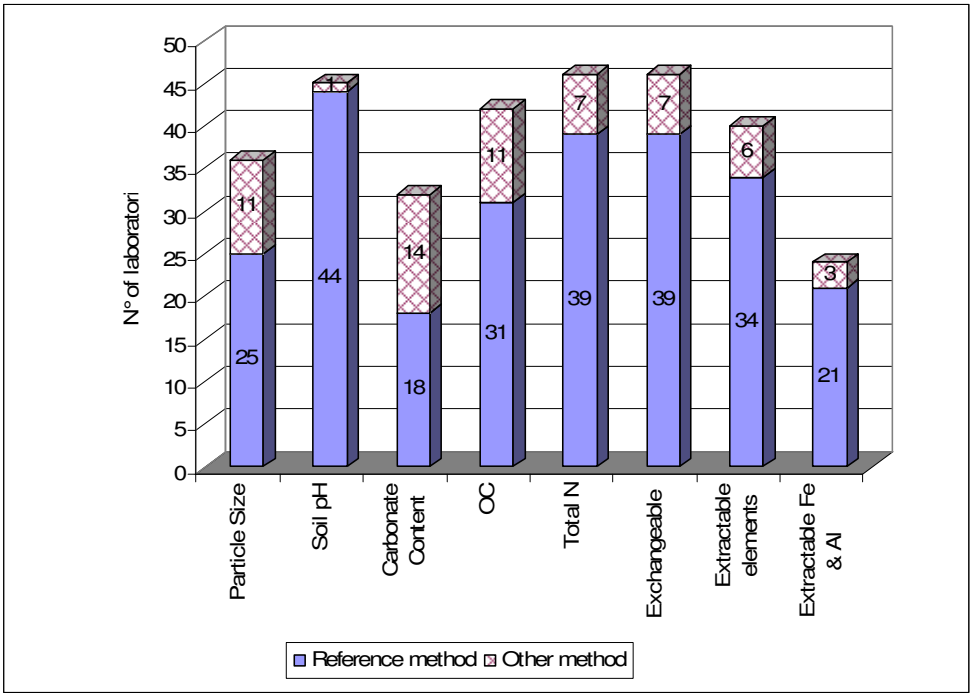


Figure 1: Use of the reference methods

The experience of the laboratories with the reference methods is shown in Figure 2. Only laboratories that effectively used the reference methods are included in this figure.

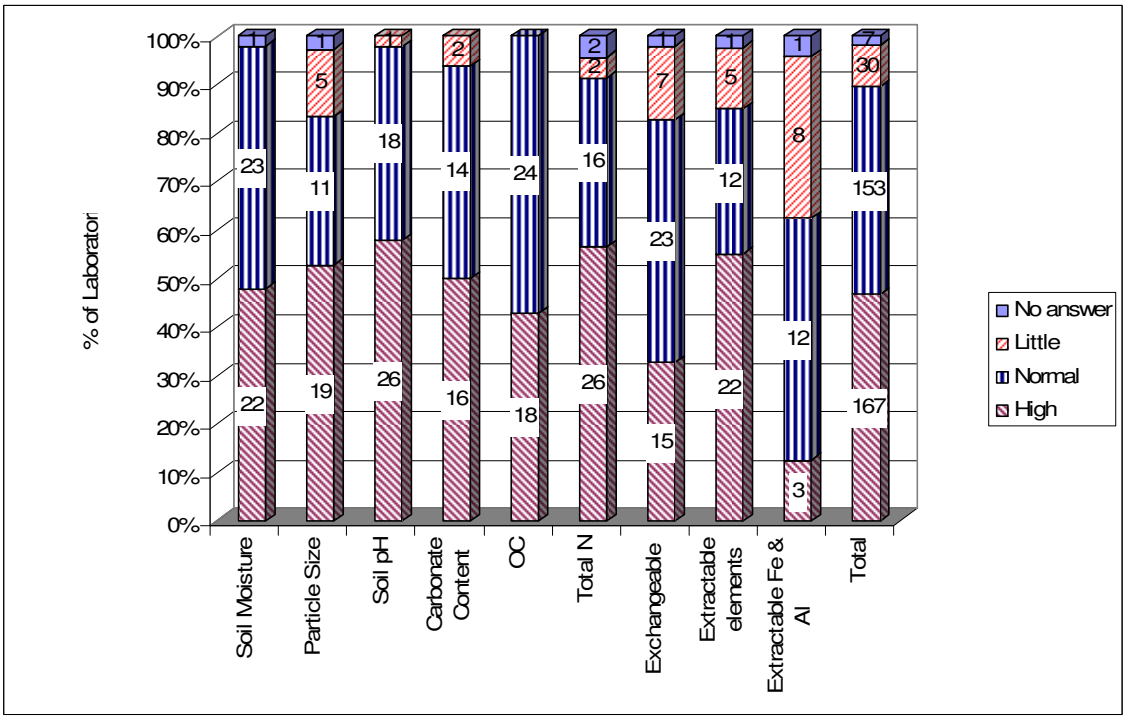


Figure 2: Experience with the reference methods

Three years after the previous ring test, laboratories have become more familiar with the reference methods. They report to have a high level of experience with the reference method in 47 % (>< 3RT:

30%) of the analyses, normal level of experience in 43 % (>< 3RT: 45%) and low level of experience in 8 % (>< 3RT: 24%) of the analyses.

3.1.4 Quality assurance and quality control

Reference materials come in various sorts and prices. International Reference Materials (IRM) are expensive and are only used when really needed. National Reference Materials (NRM) are in many cases easier to get and often not that expensive. They are in most cases issued by national laboratories and very useful to ensure the quality over the laboratories within a country. Local Reference Materials (LRM) are (to be) prepared by the laboratory itself and can be easily prepared in large quantities, very cheaply. It can also be made in the correct concentration ranges for the more important parameters. Especially these LRM have a high importance for the QA/QC activities. Guidelines for the preparation of local reference materials are included in the FSCC Manual on sampling analysis and of soils (FSCC, 2003).

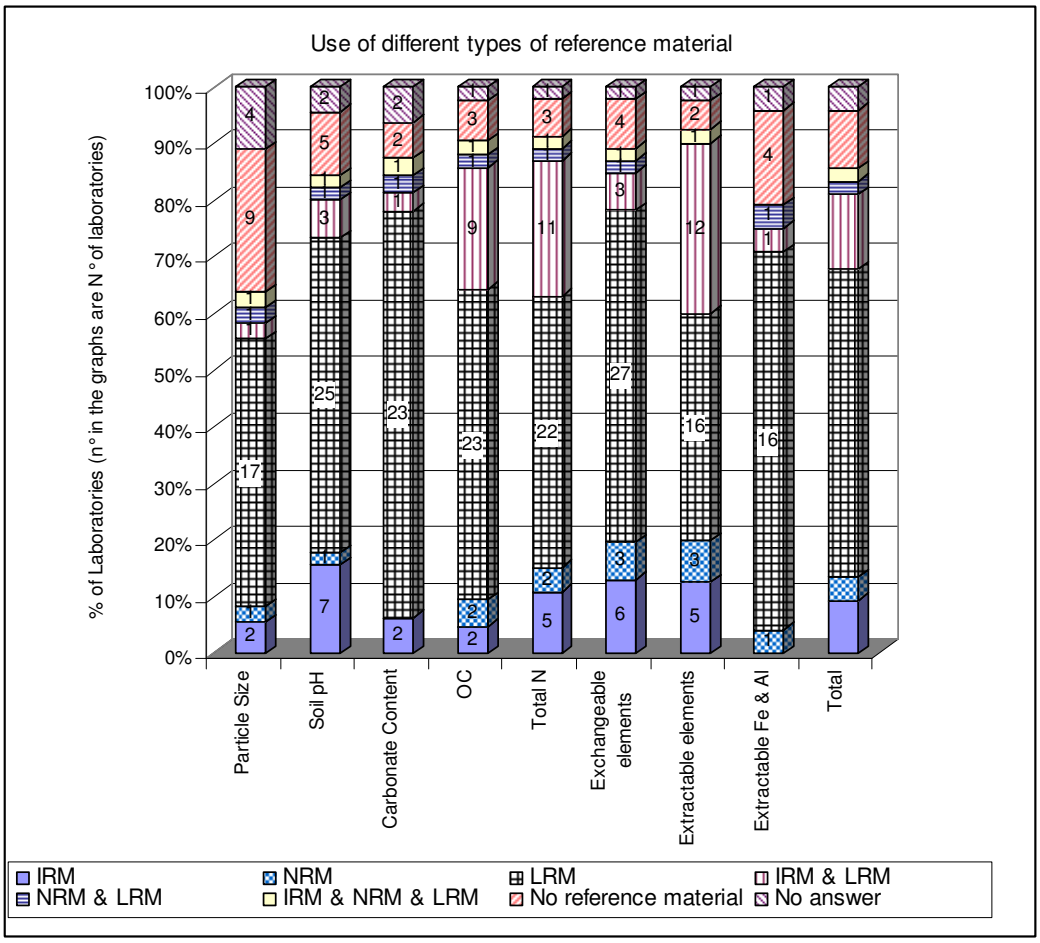


Figure 3: Use of reference material for the different parameters

Figure 3 provides an overview of the types of reference material used in the 4th FSCC Interlaboratory Comparison. Overall, reference material is used for 86 % of the analyses. For 71 % of the analyses,

local reference material has been used, either on its own, or in combination with NRM or IRM. In the 3rd FSCC Interlaboratory Comparison reference material was only used in 77 % of the analyses. The use of reference material is common for most of the analyses, but rather on the poor side for texture analysis.

The most common and transparent follow up of LRM is through control charts. The LRM is systematically resampled in each batch or series of soil samples. The results of the repeated analysis of the LRM allow the evaluation of the stability of the method/equipment overtime. The manual strongly recommends to map all LRM analyses over time in a control chart. There is an improvement in the use of control charts. For 65% of all analyses, control charts were used to evaluate the internal variance of the laboratory, compared to 50 % in the 3rd FSCC Interlaboratory Comparison (see Figure 4).

Calibration standards are commonly used, as 63% of the analyses included internal calibration standards, compared to 73 % in the previous FSCC Interlaboratory Comparison (see Figure 5).

It seems that only a small minority of the participating laboratories has received an accreditation for one of the reference methods. Only 11% of the analyses were done by laboratories that were specially accredited for these particular analyses compared to 13 % in the previous FSCC Interlaboratory Comparison.

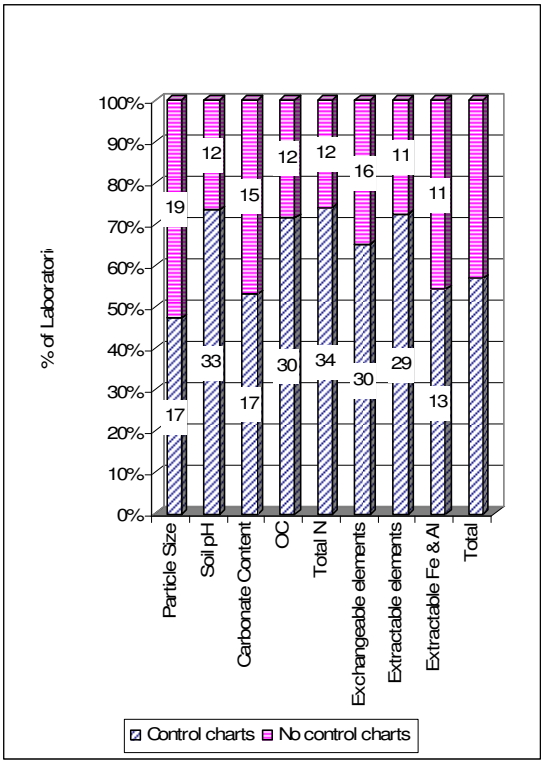


Figure 4: Use of control charts

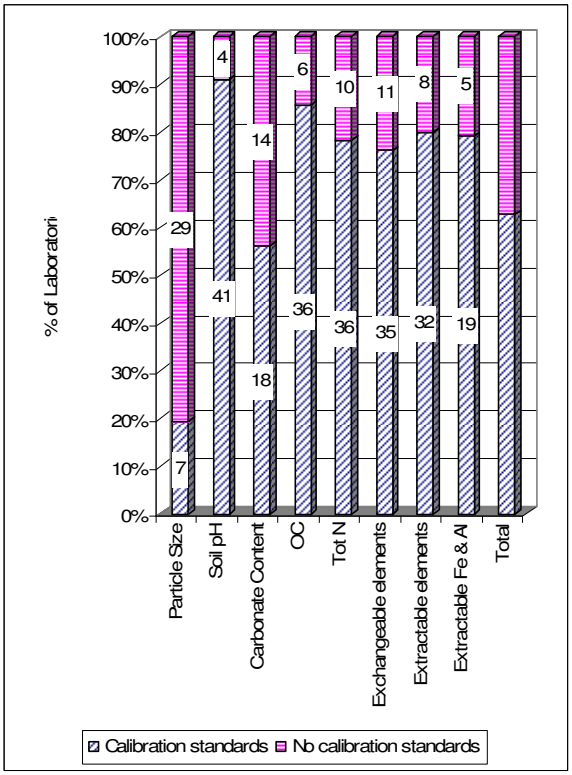


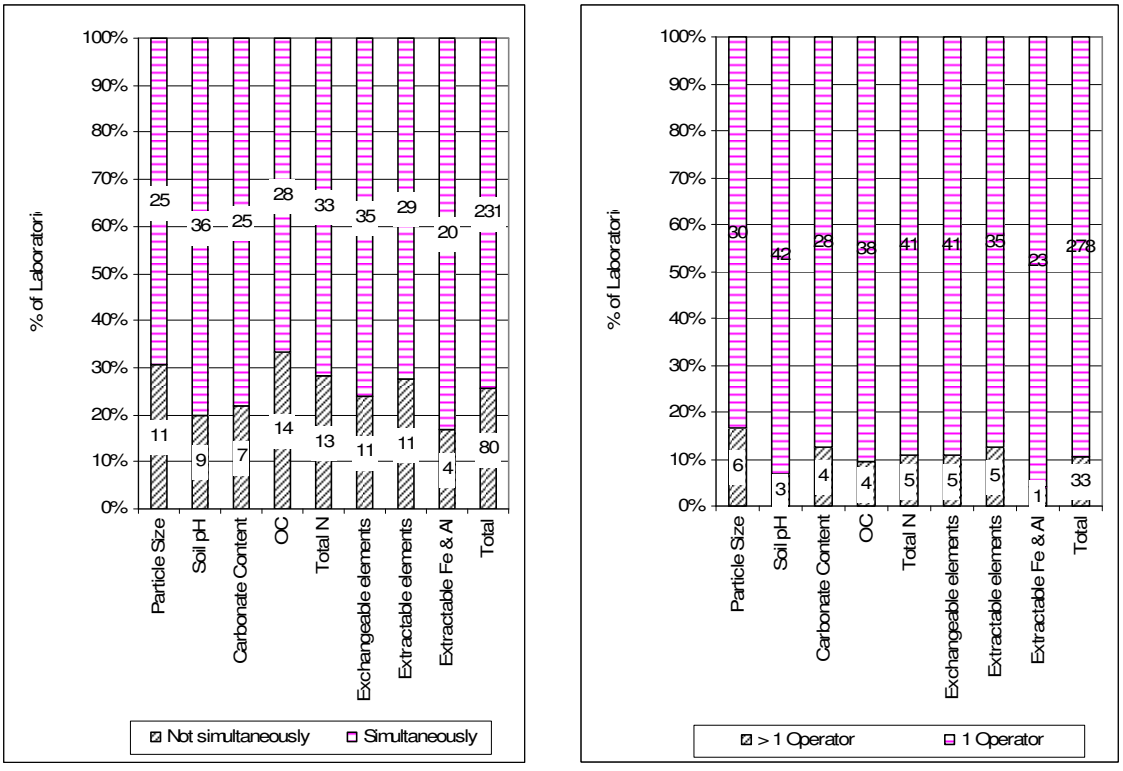
Figure 5: Use of calibration standards

3.1.5 Repeatability and/or reproducibility conditions in the laboratories

This ring test evaluates the laboratories both on the interlaboratory (between the laboratories) and on the intralaboratory variability (within the laboratory). However, within the laboratory there are also different levels of variability. One possibility is that the three replicates should have been analysed on different days, and by a different operator. Another possibility are perfect repeatability conditions: same operator and same day. Since FSCC can impossibly check these conditions, two simple questions have been added to the questionnaire:

1. Have the 3 replicates been conducted simultaneously (i.e. on the same day)?
2. Have the 3 replicates been analysed by the same operator?

Some laboratories prefer to maximise the within laboratory variability by analysing the soil samples on different days and by different operators. But most laboratories tried to minimise this variability by analysing the soil samples on one day and conducted by the same operator (See Figure 6). To improve the comparability of the ring test results, one strategy should be maintained. Or perfect repeatability conditions should be maintained or the within-laboratory reproducibility should be maximised (different days, different operators).



Figures 6a and 6b: Information on the repeatability/ reproducibility conditions

3.2 Statistical data analysis

The data analysis within S-plus produced for each parameter (each analysed element) and each sample (A, B, C, D, E, F and G) a total of 7 figures: one histogram and one boxplot of the mean of the three reported values, one histogram and one boxplot of the standard deviations, one dotplot of all reported values and one Mandel's h and one Mandel's k plot. Below the case of 'particle size clay' in sample C is given as an example. All the figures, arranged per parameter in the same sequence as discussed below, can be consulted in Annex 4 on the attached CD-rom.

3.2.1 Exploratory Data Analysis

The objectives of the exploratory data analysis are 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 are 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 7 and Figure 8 represent the inter-laboratory variance. They indicate the position of each laboratory in the population of all laboratories. Figure 9 and Figure 10 represent the standard deviations of each laboratory. They yield information on the within-laboratory variance. Figure 7 and 9 are histograms, while Figure 8 and 10 are box-plots. This 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 (lab N° between parentheses and parameter value)
- 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 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

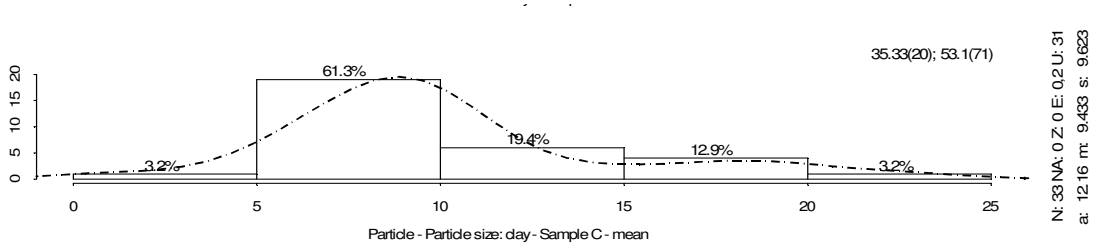


Figure 7: Histogram showing relative percentages and a rescaled density curve of the mean of 3 replicates of the measured parameter 'Particle size – clay' on Sample C. The units of the x-axis are in %.

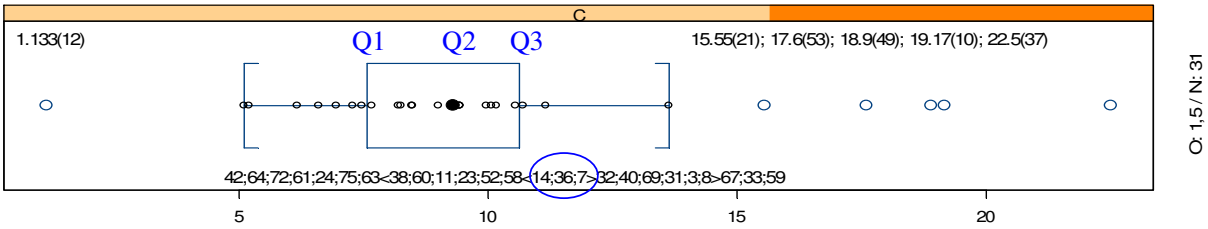


Figure 8: Box-plot of the mean values reported for sample A for the parameter 'Particle size - clay'. The units of the x-axis are in %.

The information in the box-plot start 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 particle size, clay of sample C, it means that laboratories N° 20 and 71 are not included in the boxplot. The boxplot provides following information:

- Visual outliers (lab N° between parentheses and parameter value). 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.
- Percentiles Q1 (25%), Q2 (50% or median) and Q3 (75%)
- N: Number of observations in the box-plot. This N is equal to the 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 "< <", between Q2 and Q3 "> >"

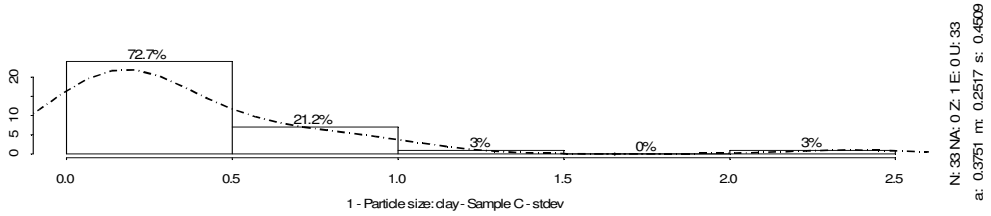


Figure 9: Histogram showing relative percentages and a rescaled density curve of the standard deviation based on 3 replicates of the measured parameter 'Particle size – clay' on Sample C.

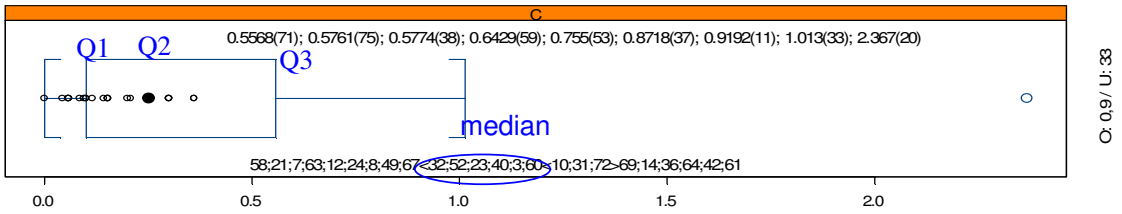


Figure 10: Box-plot of the standard deviations for sample C for the parameter 'Particle size distribution – clay'. The units of the x-axis are in %.

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 7, can be observed that the histogram is based on results from **N=33** laboratories. None of the reported values, was a "0" (**Z: 0**). Two laboratories (laboratory N° 20 and 71) are excluded from the histogram, so **U: 31** are used. Both laboratories reported extremely high clay content (35.3% and 53.1%). The average reported clay content of sample C is **a: 12.16 %**; the median clay content is **m: 9.4 %** and standard **deviation s: 9.6 %.** 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 8 shows that the laboratories N° 14, 36 and 7 reported the median value of 9.4%. Laboratories N° 38, 60, 11, 23, 52 and 58 reported values between the first quartile (**Q1**) and the median; laboratories N° 32, 40, 69, 31, 3 and 8 reported values between the median and the third quartile (**Q3**). Laboratories N° 42, 64, 72, 61, 24, 75 and 63 reported values below the first quartile (**Q1**) and laboratories N° 67, 33 and 59 reported clay contents above the third quartile (**Q3**). The laboratories outside the 1.5 * IQR whiskers, are given with their laboratory number and average value above the boxplot. Laboratory N° 12 reported a very low clay content of 1.1 % and laboratory N° 21 reported a clay content of 15.6 % which is rather high.

Based on the histogram we would expect that laboratories 20 and 71 will be outliers in the in-depth statistical analysis. Based on the boxplots which are more severe, we see that also laboratories N° 12, 21, 53, 49, 10 and 37 have doubtful results.

A laboratory can check its performance compared to the other laboratories by studying the dot plots (Figure 11). 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. Two laboratories (N°20 and 71) reported extremely deviant results for the clay content of sample C. The values are given at the top of the graph

Laboratory N° 20 reported 32.6, 36.7 and 36.7 % and laboratory N° 71 reported 52.3, 53.2 and 53.6 %. Values reported by other laboratories can be read on the x-axis. 50 % of the reported values are located between 8 % and 12.7 %. Again is seen that laboratories N° 12, 21, 53, 49, 10 and 37 tend to be outliers.

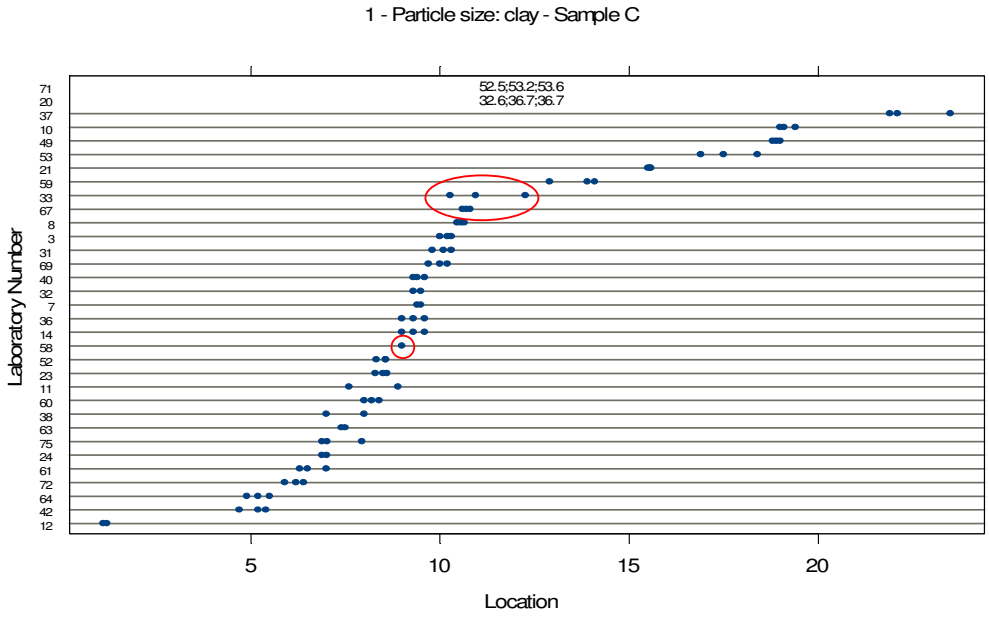


Figure 11: Dot plot of reported values for each laboratory, cumulatively ordered

This figure also tells something about the internal variance within one laboratory. By way of an example, laboratory N° 33 reported three very different results – represented by 3 dots widely separated from each other – whereas laboratory N° 67 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° 33 will have a poor within-laboratory repeatability whereas laboratory N° 67 and 58 will have a very good within-laboratory repeatability.

For layout reasons, the dots of laboratory N° 20 and 71 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° 20 and 71 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 12 and 13 present the Mandel's h and k statistics for the parameter 'Particle size - clay' 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 ring test from 0 till 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 $(\sigma/\mu)*100$ = 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 h statistics
- "k (K) + Laboratory N°": laboratory which has been excluded based on the k statistics
- E: Excluded observations, mentioning whether it was based on the h or k statistics

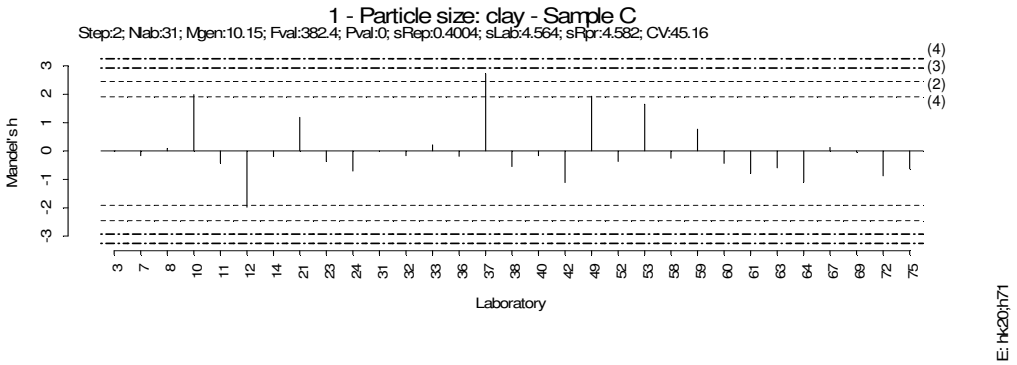


Figure 12: Mandel's h statistic for sample C for the parameter 'Particle size – clay'

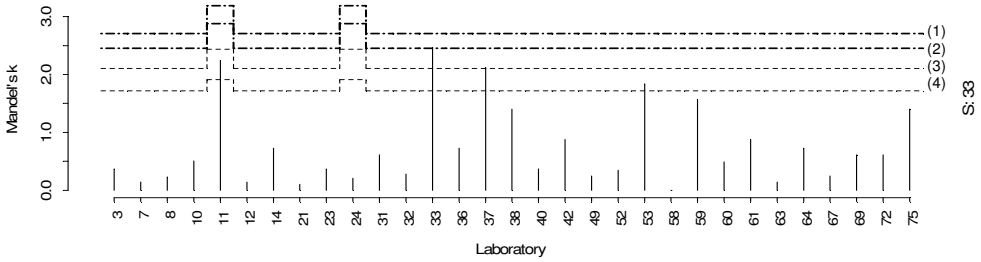


Figure 13: Mandel's k statistics for sample C for the parameter 'Particle size – clay'

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 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 12 and 13 form the core of the statistical analysis and contain all necessary information. They usually confirm the expectations after studying Figures 7 till 11.

The Mandel's h statistic of laboratory N° 37 is high, but does not reach critical limit N° (3) (Figure 12). Together with laboratories N° 10 and 49 it forms the tail of the distribution on the higher range. Laboratory N° 12 is located in the tail on the lower side. Laboratories N° 20 and 71 have been excluded from the statistical analysis based on the Mandel's h and laboratory N° 20 also based on the Mandel's k statistics (see lower right corner of Figure 12 ('E: hk20, h71'). In the exploratory study, these same laboratories were indeed excluded from the histograms in Figure 7 (showing the between-laboratory variance). Laboratory N° 20 was in Figure 10 (showing the within-laboratory variation) the one observation point on the right with st.dev. = 2.367.

From Figure 13 is seen that laboratory N° 33 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 7 and 8, where the box plot of the mean values and the dotplot was given. Observed stragglers are indicated on the right side of the figure behind the symbol 'S'.

Note that in Figure 13, the critical limits for laboratory N° 11 and 24 are different. This happens when laboratories have reported only two replicates instead of three, which results in wider confidence limits.

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". 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').

   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. In the case of calcium carbonate content of sample C and D, many laboratories reported a "0" value. In such a case, laboratories reporting positive values, have been excluded based on the h or k statistic. When during the check, these laboratories are compared to the population of laboratories reporting "0" values, a problem arises in calculating any of the statistics (mean of 0, standard deviations of 0,...). When this happens, the small 'h' or 'k' has been altered in a capital 'H' or 'K'.

3.2.3 Laboratory performance based on the number of outliers

The Mandel's h and k plots in Annex 4 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, it is considered as an indicator of poor quality of that laboratory.

Table 6 summarizes the Mandel's h and k plots given in Annex 4. For each laboratory and each analysed parameters a score has been given based on the frequency that a laboratory has been excluded:

(+++): all reported values are within the bulk of the data

(++): between 80 and 100 % of the reported values are within the bulk of the data (80 % included)

(+): between 60 and 80 % of the reported values are within the bulk of the data (60 % included)

(-): between 40 and 60 % of the reported values are within the bulk of the data (40 % included)

(--): between 0 and 40 % of the reported values are within the bulk of the data (0 % not included)

(---): none of the reported values are within the bulk of the data.

Empty cell = not analysed

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 4 to study the problem parameter more into detail. In Annex 4 for each sample the reported values are visualize and can easily be compared with the bulk of the data. Details on the statistical procedures are given in Annex 5.

Most of the laboratories measured many parameters. So it is interesting to study the frequencies of the exclusion of a laboratory. Figures 14 till 27 compare the performance of the 52 laboratories for each individual sample and separately for the between (based on the Mandel's h statistics) and within-laboratory variability (based on the Mandel's k statistics), showing the absolute number of outliers.

Table 6: Scoring of the laboratories for each individual element

Laboratory	Particle size: clay	Particle size: sand	Particle size: silt	pH(CaCl2)	pH(H2O)	Carbonates	Organic Carbon	Total N	Exchangeable Ac.	Exchangeable Al	Exchangeable Ca	Exchangeable Fe	Exchangeable K	Exchangeable Mg	Exchangeable Mn	Exchangeable Na	Free H+ acidity
2				+	+			+++	+++	++	+++	+++	++	+++	++	+++	+++
3	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++
6				+++	+++				+++	+++	+++	+++	+++	++	++	+++	+++
7	+++	+++	+++	+++	+++	+++	+++	+++	++	+++	+++	+++	+++	++	+++	+++	
8	+++	+++	+++	++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++
10	+++	+++	+++	+++	+++	+	---	+	+++	+++	+++	+	+++	++	+	+++	+
11	+++	+++	+++	+++			+++	+++	+++	+++	+++	++	++	+++	-	+++	+++
12	+++	-	+++	+++	+++		+++	+++	+++		+++	+++	+++	+++	+++	+++	+++
13				+++	+++	+++	+++	+++	++	+++	+++	++	+++	+++	+++	+++	+++
14	+++	+++	+++	+++	+++	+++	+++	++	+++	+++	+++	+++	+++	+++	+++	+++	+++
18				+++	++		++	+++									
19				+++	+++		+++	+++		-	+	+++	-	-	-	+++	
20	---	-		+++	+++		--	++		++	-	+++	-	-	+	++	-
21	+++	+++	+++	+++	+++		+++	++									
23	+++	+++	+++	+++	+++	+++	+++	++	+	++	+++	++		+++	+		+++
24	+++	+	+	+++	+++		+++	+++	+++	++	+++	+++	--	+++	+++	---	+++
26				+++	+++	---	+++	+++	+++	+++	+++	+++	+++	+++	+++	+	+
30				+++	+++	+++	+++	+++	+++	++	+++	+	+++	++	+++	+++	+++
31	+++	+++	+++	+++	+++	+++	+++	+++	+	---	---	---	---	---	---	---	+
32	+++	+	+	+++	++	-	+++	+++	+++	+++	+++	+++	++	+++	++	+++	+++
33	+++	+	+	+++	+++		+++	+++	++	+++	+++	+++	+++	+++	+++	+++	+++
34				+++	+++	+++	+++	+++	+++	++	+++	++	++	++	+	+++	+++
35				+++	+++	+++	++	+++	+++	+++	+++	+++	+++	+++	+	+++	+++
36	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++
37	+	+	+	+	+++	++	++	-	+++	++	+++	+++	++	+++	++	+	+++
38	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++
40	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	++	+++	+++	+++	+++
42	+++	++	+++	+++	-		++	+++			++		+	+		++	
45				+++	+++			+++	+++	+++	+++	+++	+++	+++	+++	++	
48				+++	+++	+++	+++	+++		+++	++	+++	++	+	+	++	
49	+++	+++	+++	+++	+++	--	+	+++	+++	++	+	+++	+++	---	++	-	+++
52	+++	+++	+++	+++	+++		++	+		+++	+++	+++	++	+++	+	--	
53	+	+	+++	+++	+++		---	+++									
54				+++	+++			+++	+++	+++	+++	+	+++	+++	+++	+++	
55				+++	++			+	+++	+++	+++	+++	+++	+	-	+++	+
56				++	+		+++	+++	-	+++	+++	+++	+++	+++	+++	+++	+
58	+++	+++	+++	+++		+++	++	++	+++	+++	+++	+++	+++	+++	+++	++	+++
59	+++	+++	+++	+++	+++	+++	++	++	++	-	+++	+++	+++	+++	+++	++	+++
60	+++	+++	+++	+++	+++	-	+	+++	++	+	++	-	++	+	-	---	++
61	+	+++	+++	+++	+++		+++	+++	-	+++	++	+++	+++	+	+++	---	-
62							+++	++			+	+++	---	-	+	+++	
63	+++	+++	+	++	+++	+++	++	+++	+++	+	+	++	+++	-	++	++	+++
64	+++	+	+++	+++	-	+++	+++	+	++	--	-	--	--	--	---	++	++
67	+++	+++	+++	+++	++	++	+++	+++	+++	++	++	+	+++	+	+++	+++	++
68				+++	+++	+++	+++	+++	+++	++	+++	-	+++	+++	+++	+++	+++
69	+++	+++	+++	+++	+++	+	+++	+++	+++	+++	+++	++	+++	+++	+++	+++	+++
70				+	+		-	+++									
71	--	-	+++	+	-	+++	-	++	+++		--	--	---	-	+	---	+++
72	+++	+++	+++	+++	+++	++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++
73											---	--	---	---	---	---	
74									+++	+++	+	+++	+++	---	++	--	+++
75	+++	-	-														

(+++): all reported values are within the bulk of the data

(++): between 80 and 100 % of the reported values are within the bulk of the data (80 % included)

(+): between 60 and 80 % of the reported values are within the bulk of the data (60 % included)

Table 6 (continued): Scoring of the laboratories for each individual element

Laboratory	Extractable Al	Extractable Ca	Extractable Cd	Extractable Cr	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
2	+++	+++	+	++	+	+++	+	+++	+++	+++	+++	+++	+++	+++		++		
3	+++	+++	++	+++	+++	+++		+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++
6	+++	+++	-	+++	+++	+++	--	+++	+++	+++	+++	+++	+++	+	+++	+++	+++	+++
7	+++	+++	+++	+++	+++	+++		+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++
8	-	+++	+++	+++	+++	+++		+	+	+		+++	++	+++	++	+	+++	+++
10	+++	+++	---	+++	++	+++		+++	+++	+	+++	---	+++	+++	--	+		
11	++	+++	+++	-	+++	++		+++	+++	+++	++		+	+++	+++	+++	+++	+++
12		+++	---		-	++		+++	-	+	-	--		-		+		
13	++	++	+++	+++	+++	++		+++	++	+++	+++	++	+++	+++	+++	+++	+++	+++
14	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	++	+++	+++	++	+++	+++	+++
18			--	-	-					++		--	-	-		+		
19		+++	+++		+++			+++	+++	+++			+++	+++		+++		
20		+++	--		-	--		+++	-	-	+++		--	++		-		
21																		
23		++	++		++			+++	+++	+++				-		-		
24	+++	+++		---	+++	+++		+++	+++	+++	+	++		+++		+	+++	+++
26	+++	++	+++	+++	+++	+++		+++	+++	+++	+++	+++	+++	+++	+++	+++		
30	+++	+++	++	+++	+++	+++		+++	+++	+++	+++	++	+++	+++	--	+++	+++	+++
31	+++	+++	+++	+++	+++	+++	++	+++	+++	+++	++	+++	+++	+++	++	+++	+++	+++
32	+++	+++	-	+	+	+++		+++	+++	+++	+++	+	+++	+	+++	+++	+++	+++
33	+++	+++	+++	+++	++	+++		+++	+++	+++	+	+++	+++	+++	+	+++	+++	+++
34	+++	+++	+++	++	++	++	++	+	+++	++	+		-	+++		+++		
35	+++	++	+++	++	++	+++		+++	+++	+++	++	++	+++	++		++		
36	+++	++	++	+++	++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++
37	++	-	+++	+	+++	+		+	+	++	--	+++	+++	+++	+	+++	+++	+++
38		+++				+++		+++	---	---	---							
40	+++	+++	-	+++	+++	+++	+	+++	+++	+++	++	+++	+++	+++	+++	+++	+++	+++
42		+			+	---		+	+	+	+					+		+++
45	++	+++	+++	+++	+++	+++		+++	++	+++	+++	+++	+++	+++		+++		
48	+++	++	++	++	+++	+++	+++	+++	+++	++	++	+++	++	+++	+++	++		
49	+++	+++	++	+++	-	+++		++	+++	++	+++	+++		+++	---	+++		
52		+++	-	++	+++	+++		++	-	+++	++	+++		++	--	+	+	+++
53								+++					+					
54	++	+++	+++	+++	+++	+++		+++	+++	+++	+++	+++	+++	+++	+++	+++		
55																		
56	+++	++	--	-	+	++	--	+++	+++	+++	+++	++	---	--		++	+++	++
58																	+++	+++
59	-	-	+	-	++	+++		-	+++	+++		+	-	++	+	+++		
60			+	+++	++		++					+++		+++		+++		
61	+++	+++	++	+++	+++	+++	--	+++	++	++	+++	+++	++	+++	+++	+++	+++	+
62		+	--	++	+++	+++		+++	++	+++	+++		+++	+++		+++		
63	++	+++	-	++	++	+++	++	+++	+++	+++	+++	+++	+++	++	++	+++		
64	+++	+	++	-	--	+	+++	+	+	+	+	+	+	+++	++	+	--	-
67	+++	++	++	+++	++	+++	--	+++	+++	+++	++	+++	+++	+		+++	+	++
68	+++	+++	++	+++	+++	+++	+++	+++	++	+++		++	+++	+		+++	+++	+++
69	+++	+++	+	+++	++	+++	-	+++	+++	+++	+++	++	+++	++		+++	+++	+++
70																		
71		+++	+	+++	--	+++		++	+	-	++	+	-	-		--		
72	+++	+++	+++	++	+++	+++	+	+++	+++	+++	+++	+++	+++	--	++	+++	+++	+++
73	++	+++	+	+++	-	++	+	+	+++	+++	+++	+	+++	+++	+++	+		
74																		
75																		

(-): between 40 and 60 % of the reported values are within the bulk of the data (40 % included)

(--): between 0 and 40 % of the reported values are within the bulk of the data (0 % not included)

(---): none of the reported values are within the bulk of the data; Empty cell = not analysed

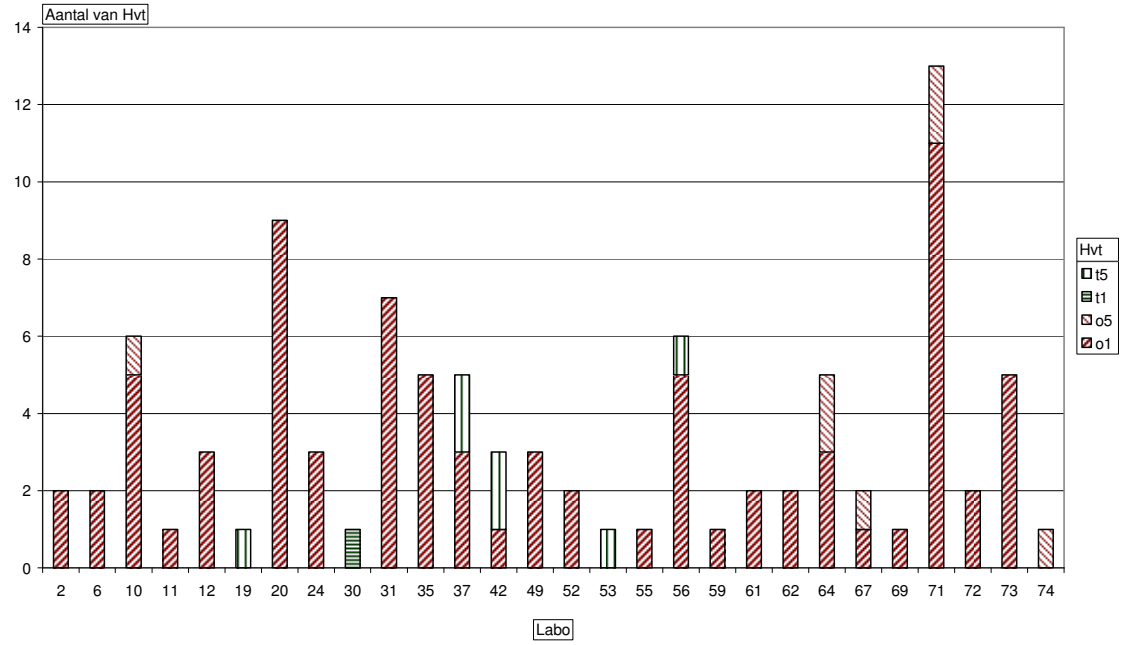


Figure 14: Sample A – Absolute N° of outliers (o1), N° of stragglers (o5) and N° of tail values per laboratory for the between-laboratory variability. Laboratories that are not mentioned in this graph did not have any outlier, straggler or tail value.

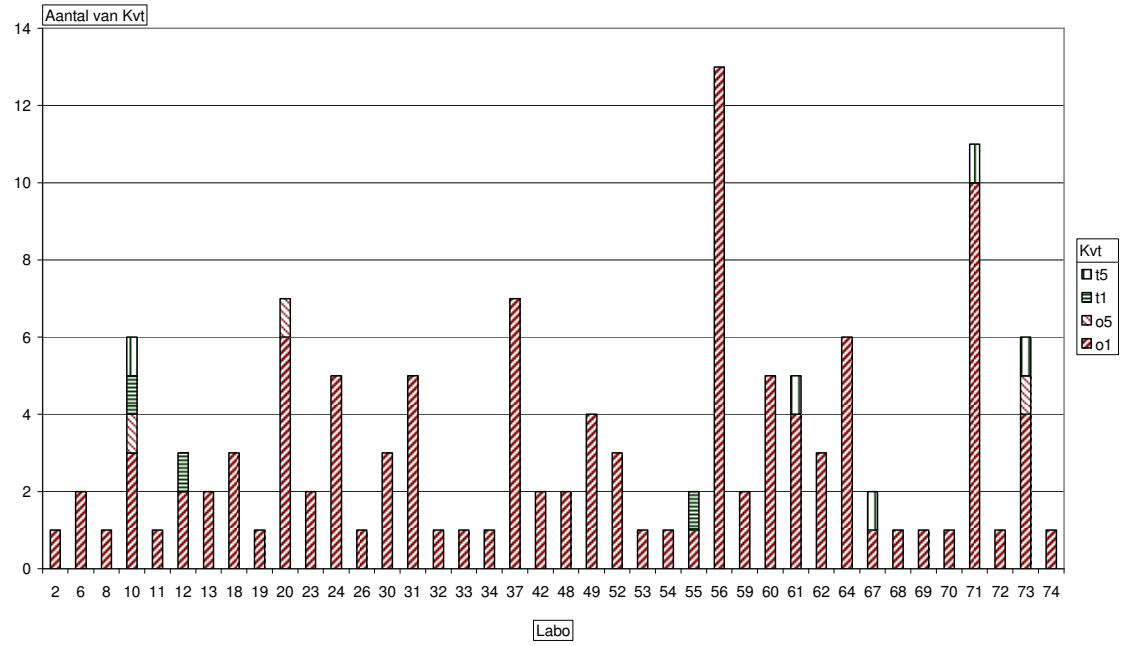


Figure 15: Sample A – Absolute N° of outliers (o1), N° of stragglers (o5) and N° of tail values per laboratory for the within-laboratory variability. Laboratories that are not mentioned in this graph did not have any outlier, straggler or tail value.

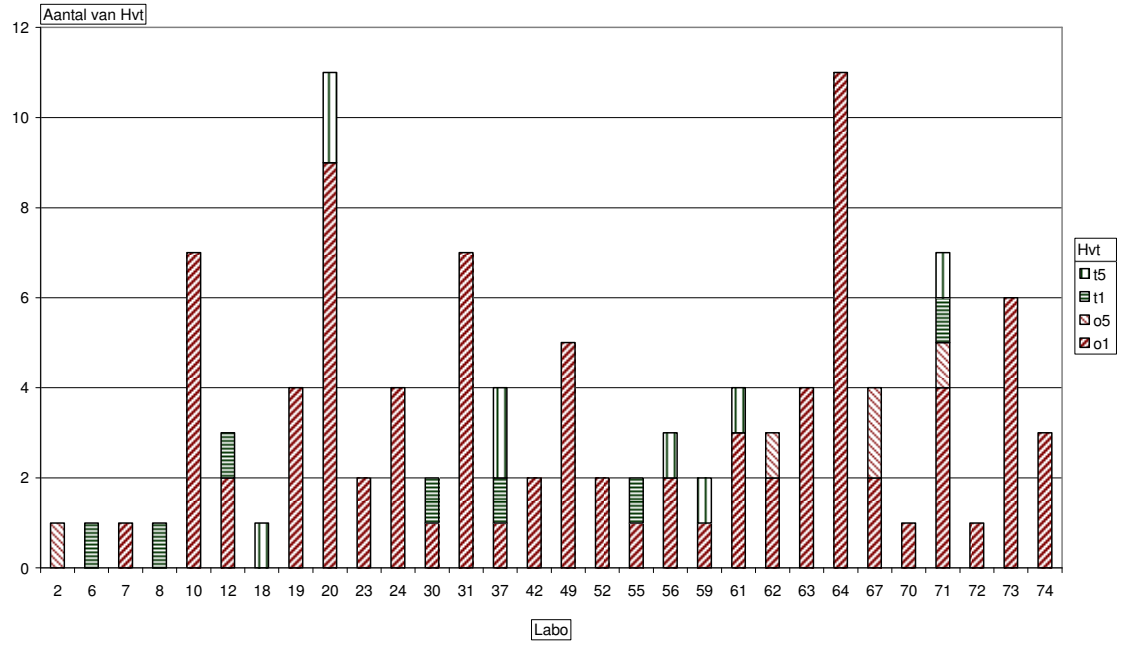


Figure 16: Sample B – Absolute N° of outliers (o1), N° of stragglers (o5) and N° of tail values per laboratory for the between-laboratory variability. Laboratories that are not mentioned in this graph did not have any outlier, straggler or tail value.

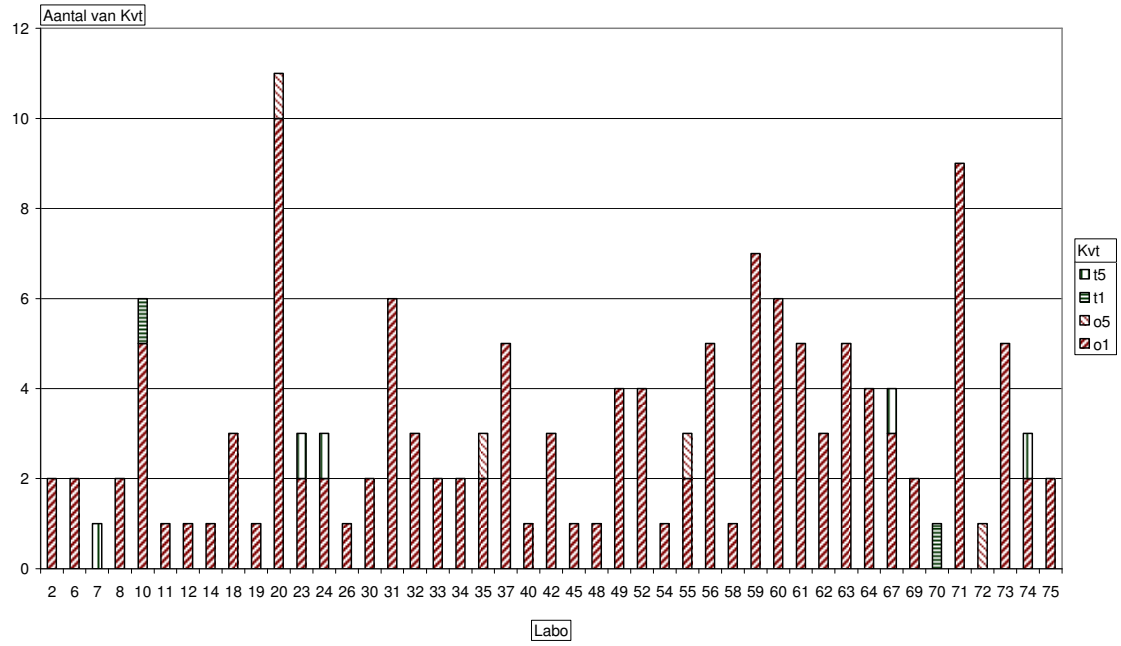


Figure 17: Sample B – Absolute N° of outliers (o1), N° of stragglers (o5) and N° of tail values per laboratory for the within-laboratory variability. Laboratories that are not mentioned in this graph did not have any outlier, straggler or tail value.

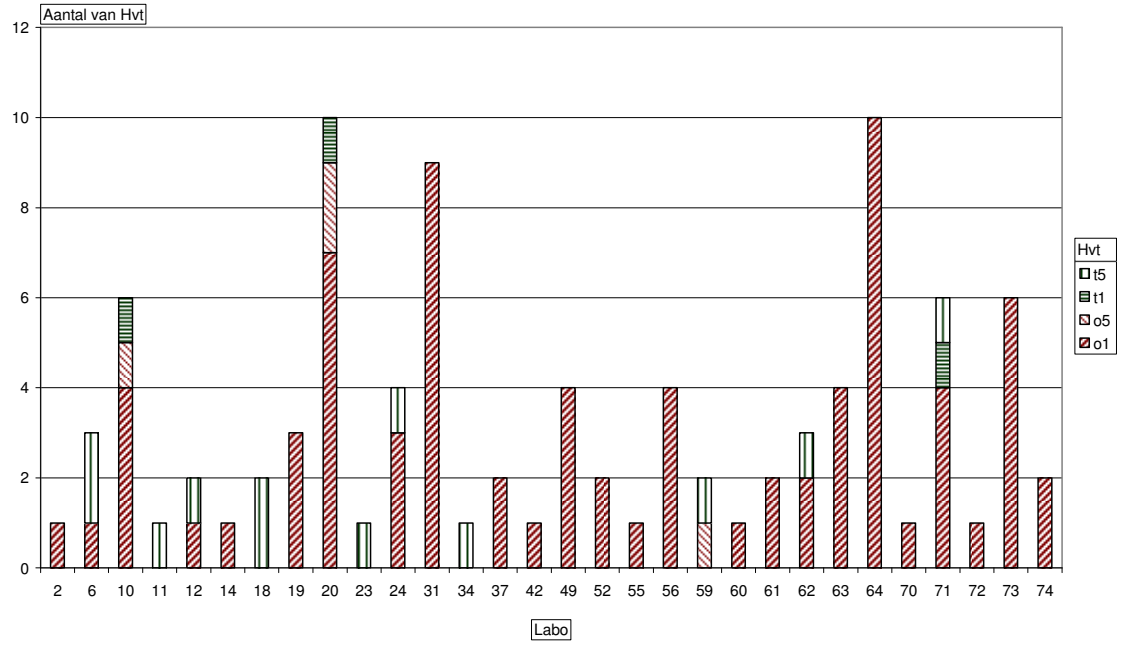


Figure 18: Sample C – Absolute N° of outliers (o1), N° of stragglers (o5) and N° of tail values per laboratory for the between-laboratory variability. Laboratories that are not mentioned in this graph did not have any outlier, straggler or tail value.

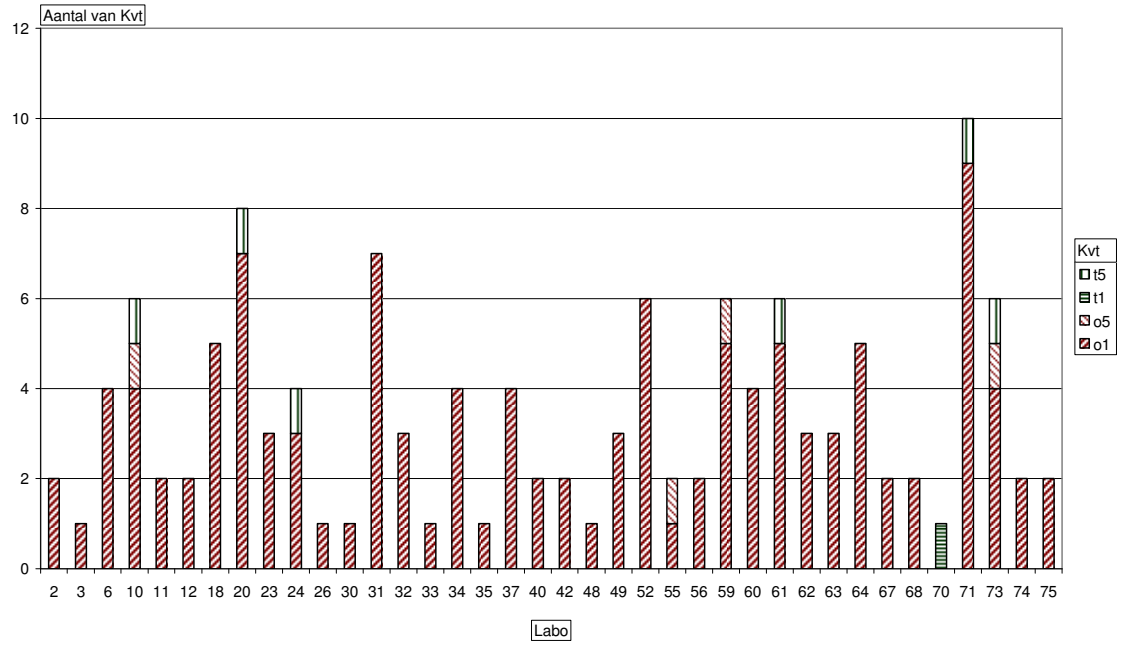


Figure 19: Sample C – Absolute N° of outliers (o1), N° of stragglers (o5) and N° of tail values per laboratory for the within-laboratory variability. Laboratories that are not mentioned in this graph did not have any outlier, straggler or tail value.

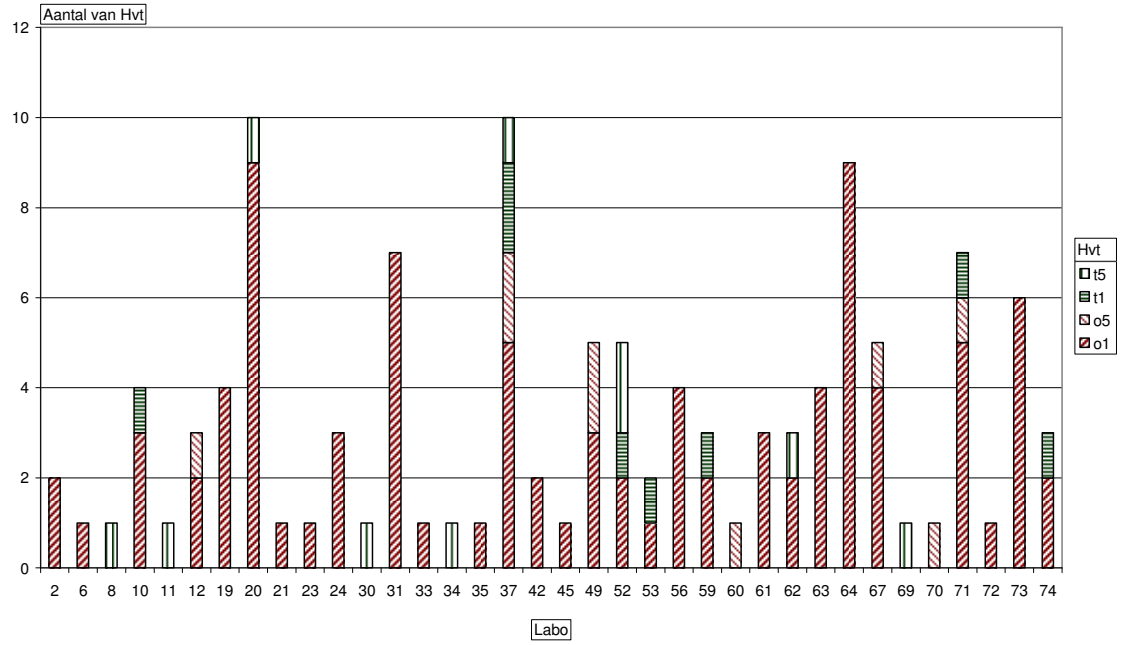


Figure 20: Sample D – Absolute N° of outliers (o1), N° of stragglers (o5) and N° of tail values per laboratory for the between-laboratory variability. Laboratories that are not mentioned in this graph did not have any outlier, straggler or tail value.

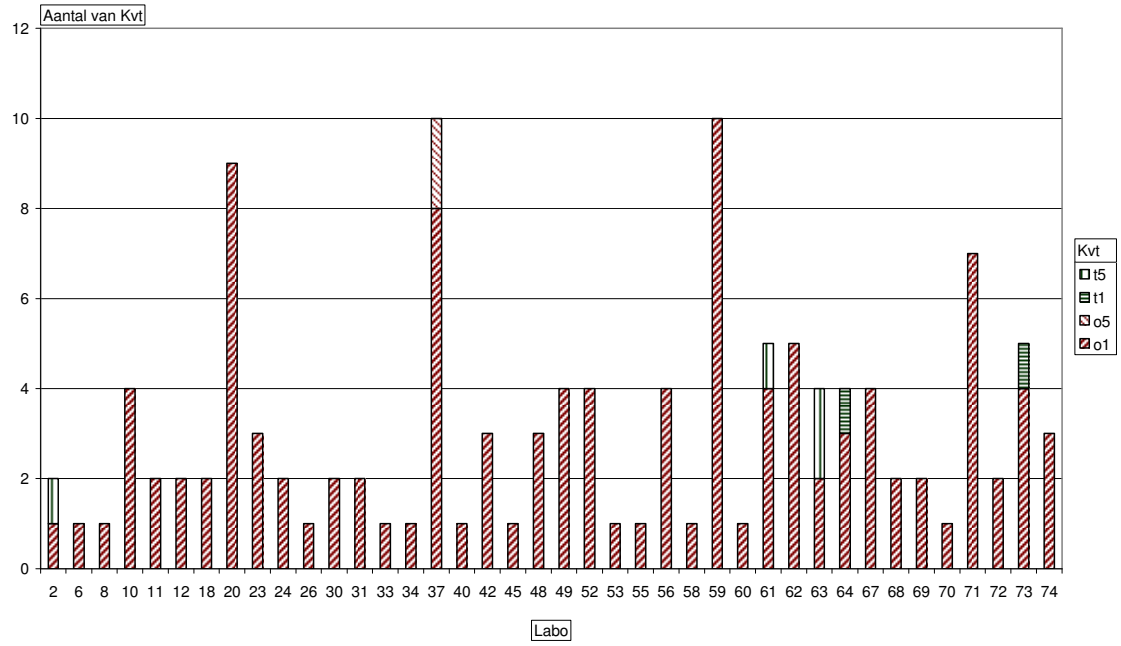


Figure 21: Sample D – Absolute N° of outliers (o1), N° of stragglers (o5) and N° of tail values per laboratory for the within-laboratory variability. Laboratories that are not mentioned in this graph did not have any outlier, straggler or tail value.

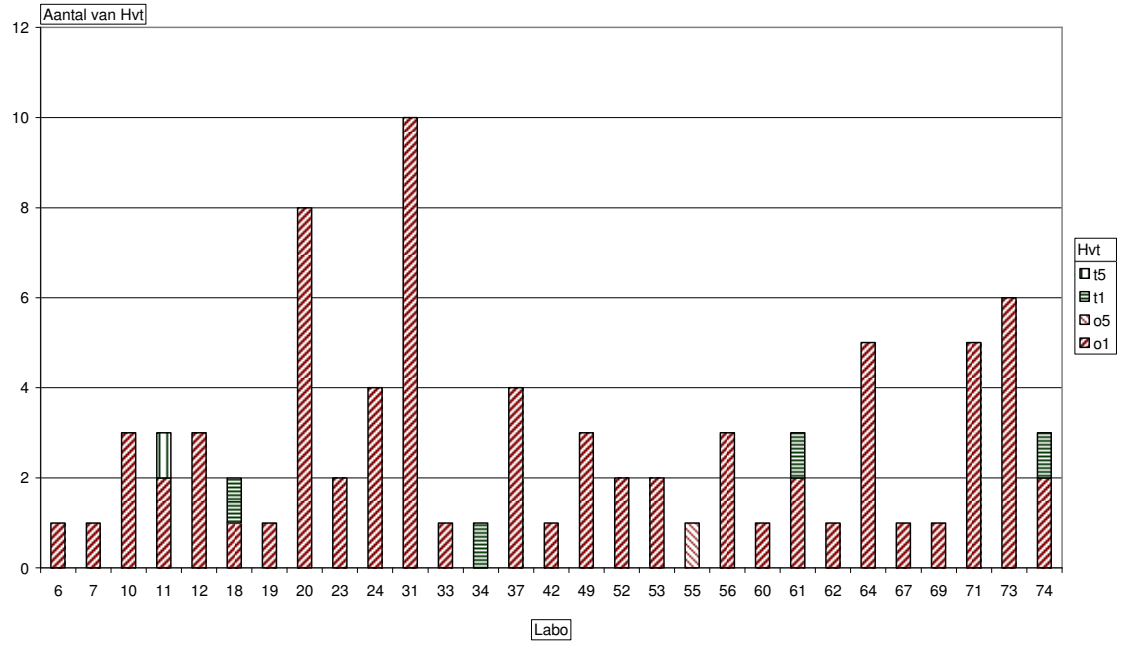


Figure 22: Sample E – Absolute N° of outliers (o1), N° of stragglers (o5) and N° of tail values per laboratory for the between-laboratory variability. Laboratories that are not mentioned in this graph did not have any outlier, straggler or tail value.

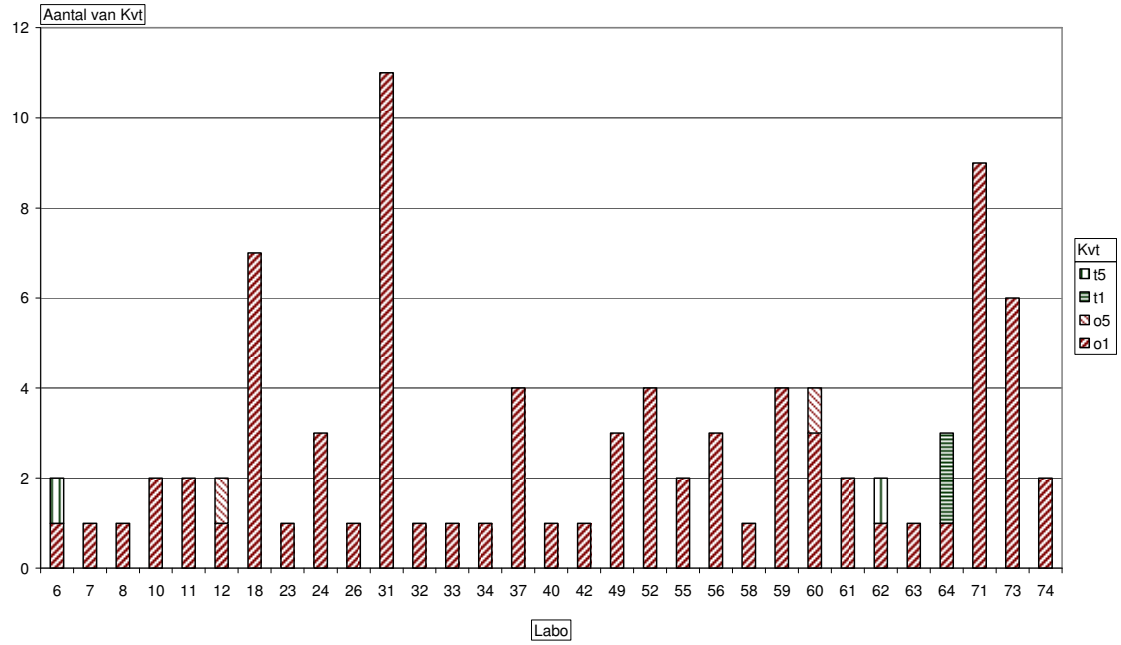


Figure 23: Sample E – Absolute N° of outliers (o1), N° of stragglers (o5) and N° of tail values per laboratory for the within-laboratory variability. Laboratories that are not mentioned in this graph did not have any outlier, straggler or tail value.

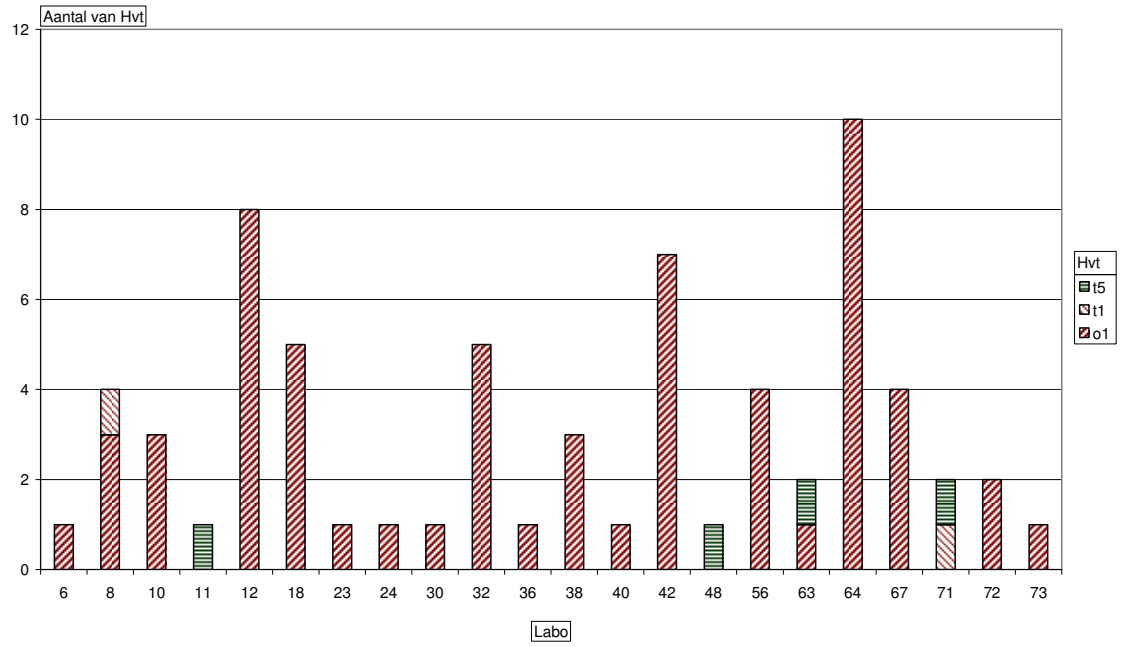


Figure 24: Sample F – Absolute N° of outliers (o1), N° of stragglers (o5) and N° of tail values per laboratory for the between-laboratory variability. Laboratories that are not mentioned in this graph did not have any outlier, straggler or tail value.

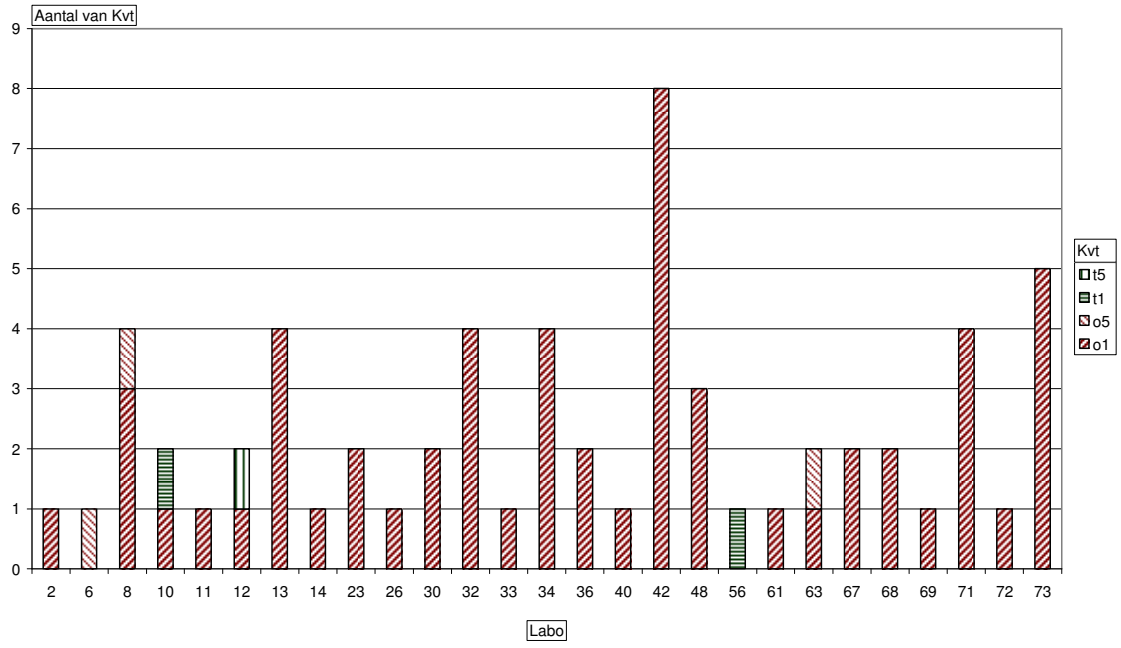


Figure 25: Sample F – Absolute N° of outliers (o1), N° of stragglers (o5) and N° of tail values per laboratory for the within-laboratory variability. Laboratories that are not mentioned in this graph did not have any outlier, straggler or tail value.

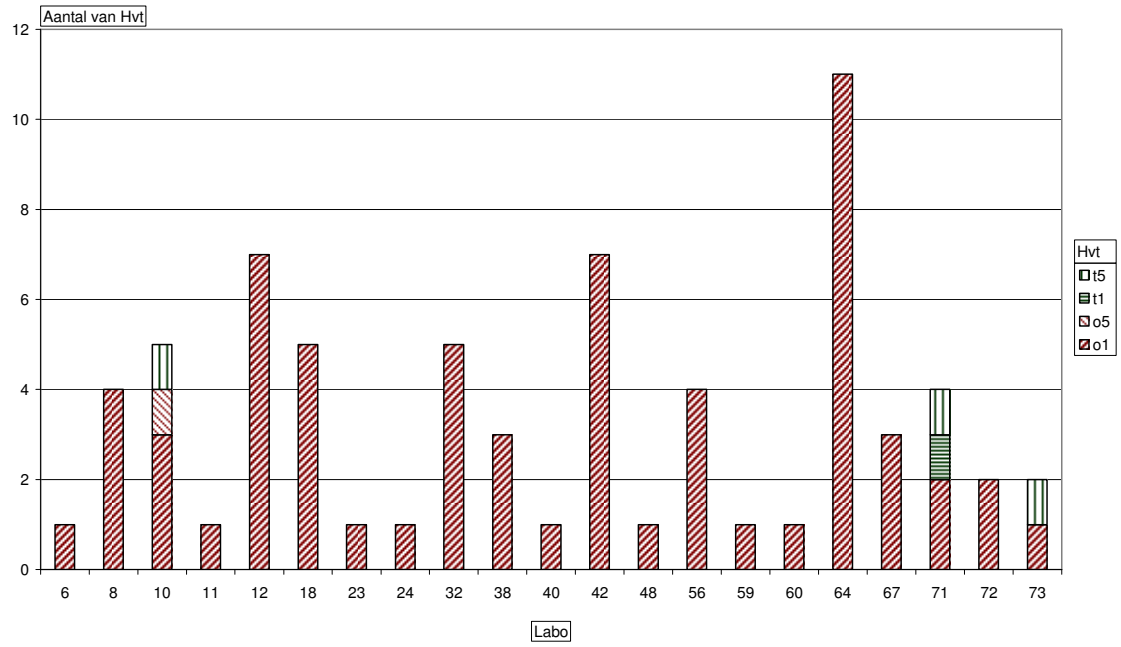


Figure 26: Sample G – Absolute N° of outliers (o1), N° of stragglers (o5) and N° of tail values per laboratory for the between-laboratory variability. Laboratories that are not mentioned in this graph did not have any outlier, straggler or tail value.

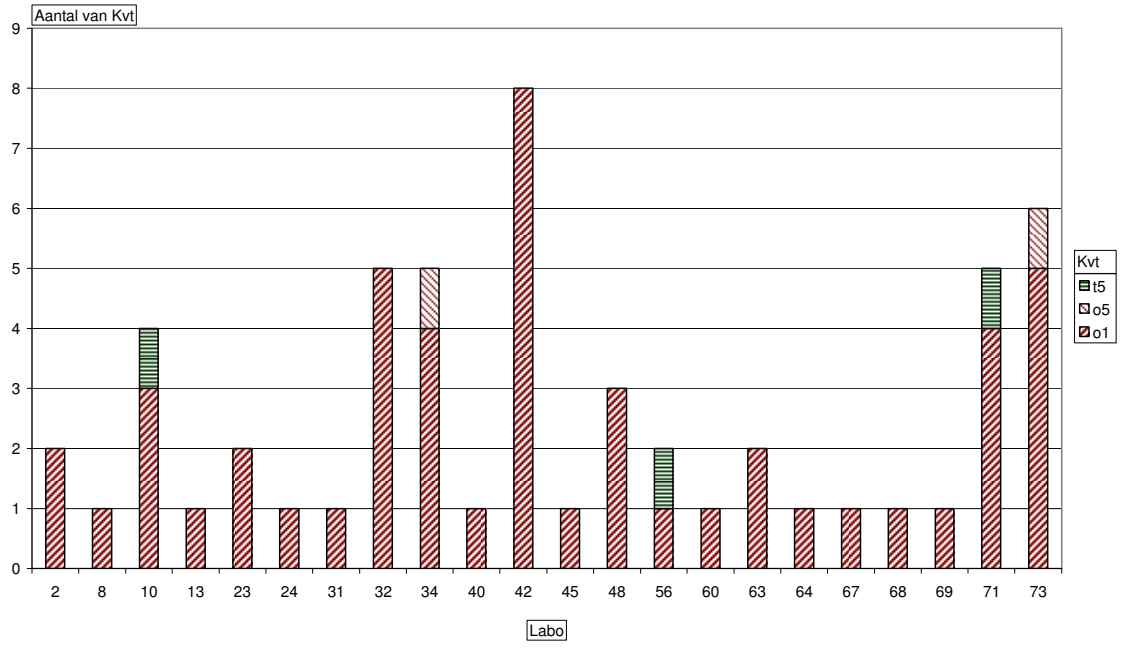


Figure 27: Sample G – Absolute N° of outliers (o1), N° of stragglers (o5) and N° of tail values per laboratory for the within-laboratory variability. Laboratories that are not mentioned in this graph did not have any outlier, straggler or tail value.

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 reported parameters of each laboratory. Table 7 gives an overview of the total number of reported parameters per laboratory and per soil sample. A parameter was included when at least two replicates were reported.

Table 7: N° reported parameters per sample by the individual laboratories

	Sample						
Labo	A	B	C	D	E	F	G
2	27	27	27	27	27	14	14
3	34	33	33	33	30	15	15
6	29	29	29	29	29	16	16
7	32	32	32	32	29	15	15
8	33	33	33	33	30	14	14
10	32	31	31	32	28	15	15
11	31	31	31	31	28	14	14
12	26	26	26	26	23	11	11
13	31	31	31	31	31	15	15
14	33	33	33	33	30	16	16
18	12	12	12	12	12	7	7
19	15	15	15	15	20	3	3
20	23	25	25	25	23	9	9
21	7	7	7	7	4		
23	23	23	23	23	18	8	8
24	30	29	29	30	27	11	11
26	29	28	28	28	28	15	15
30	31	31	31	31	31	15	15
31	35	35	35	35	32	16	16
32	34	34	34	34	31	15	15
33	33	33	33	33	30	15	15
34	28	28	28	28	28	13	13
35	28	28	28	28	28	14	14
36	35	35	35	35	32	16	16
37	34	34	34	34	31	15	15
38	16	17	17	16	14	6	6

	Sample						
Labo	A	B	C	D	E	F	G
40	35	35	35	35	32	16	16
42	20	20	20	20	17	8	8
45	25	25	25	25	25	14	14
48	28	27	27	27	27	16	16
49	28	30	30	30	26		
52	29	29	29	29	26		
53	8	8	8	8	6		
54	22	26	24	24	26	15	15
55	12	12	12	12	12		
56	30	30	30	30	30	15	15
58	18	18	18	18	15		
59	31	31	31	31	28		13
60	22	22	23	23	21	6	6
61	34	34	34	34	31	16	16
62	20	20	20	19	14		
63	32	31	31	31	29	15	14
64	35	35	35	35	31	14	14
67	34	34	34	32	31	15	15
68	30	30	30	30	30	12	12
69	34	33	33	33	30	15	15
70	4	4	4	4			
71	28	28	28	28	25	13	13
72	35	35	35	35	32	16	16
73	22	22	22	22	22	16	16
74	9	9	9	9	9		
75	3	3	3	3			

The percentage of outliers and stragglers was calculated relatively to the number of reported parameters (excluding the moisture content). Figures 28 to 41 give nearly the same information as the previous figures but now expressed as a percentage of the total number of reported parameters excluding the moisture content.

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.

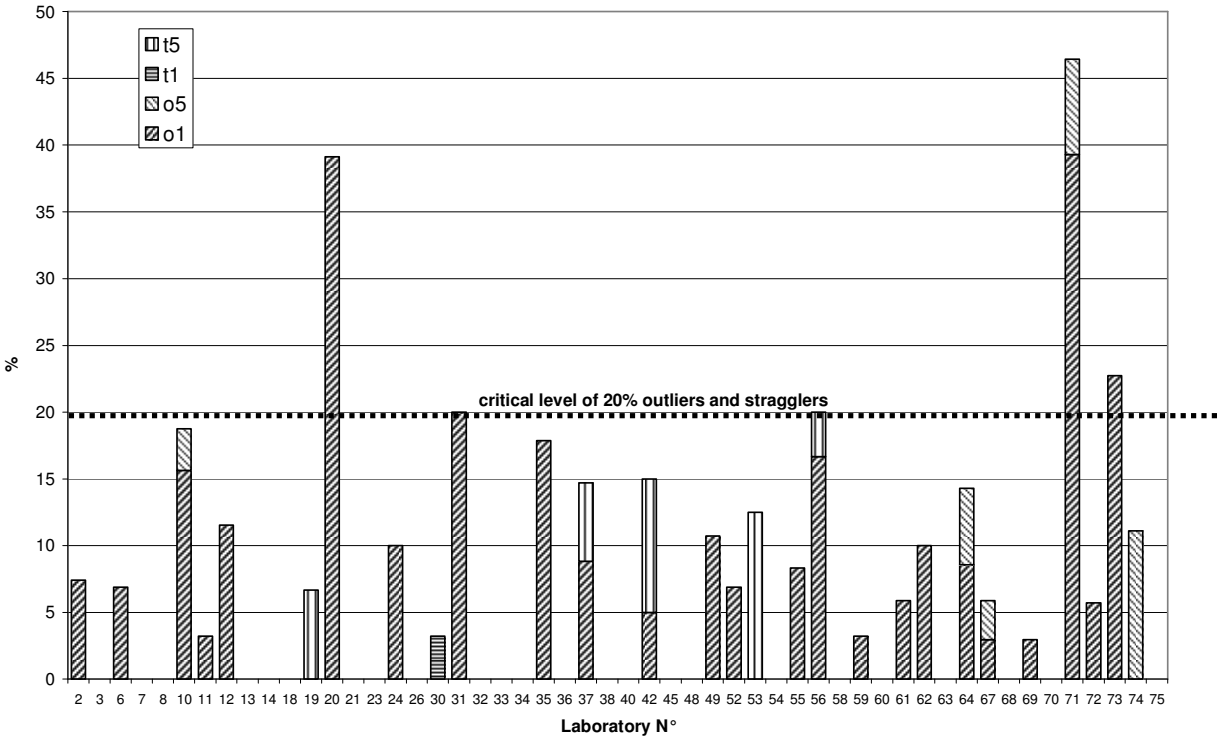


Figure 28: Sample A – Percentage of outliers (o1), stragglers (o5) and tail values per laboratory for the between-laboratory variability.

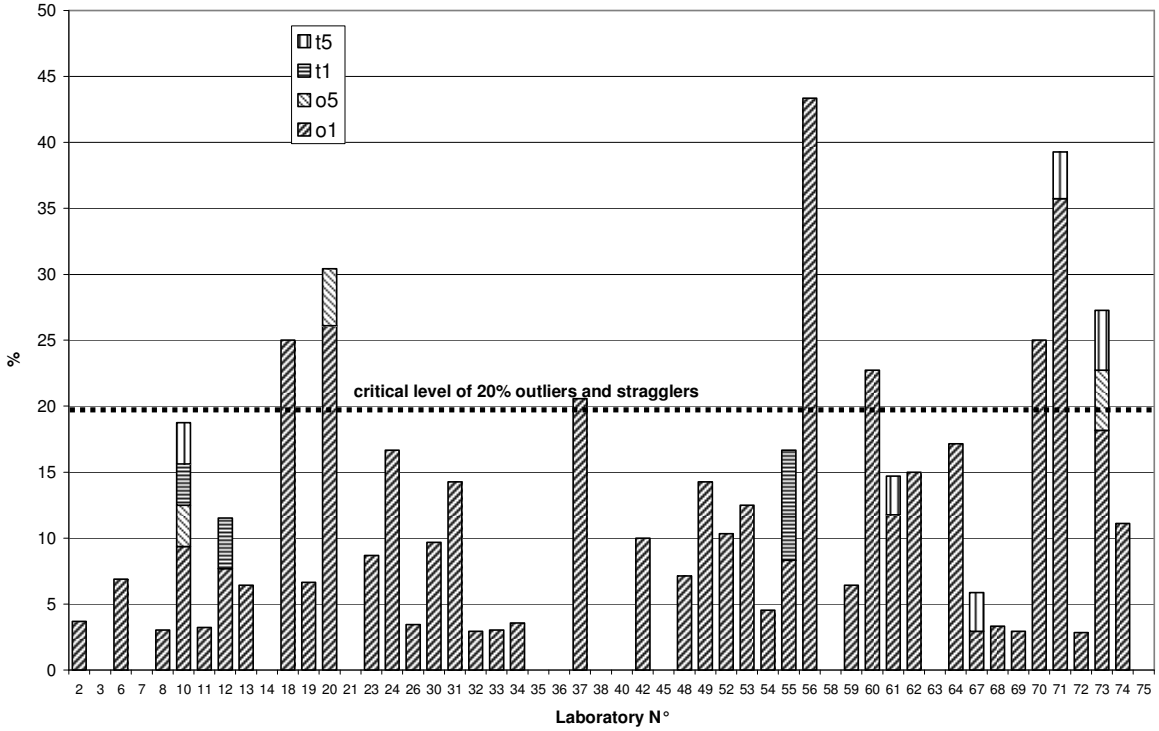


Figure 29: Sample A – Percentage of outliers (o1), stragglers (o5) and tail values per laboratory for the within-laboratory variability.

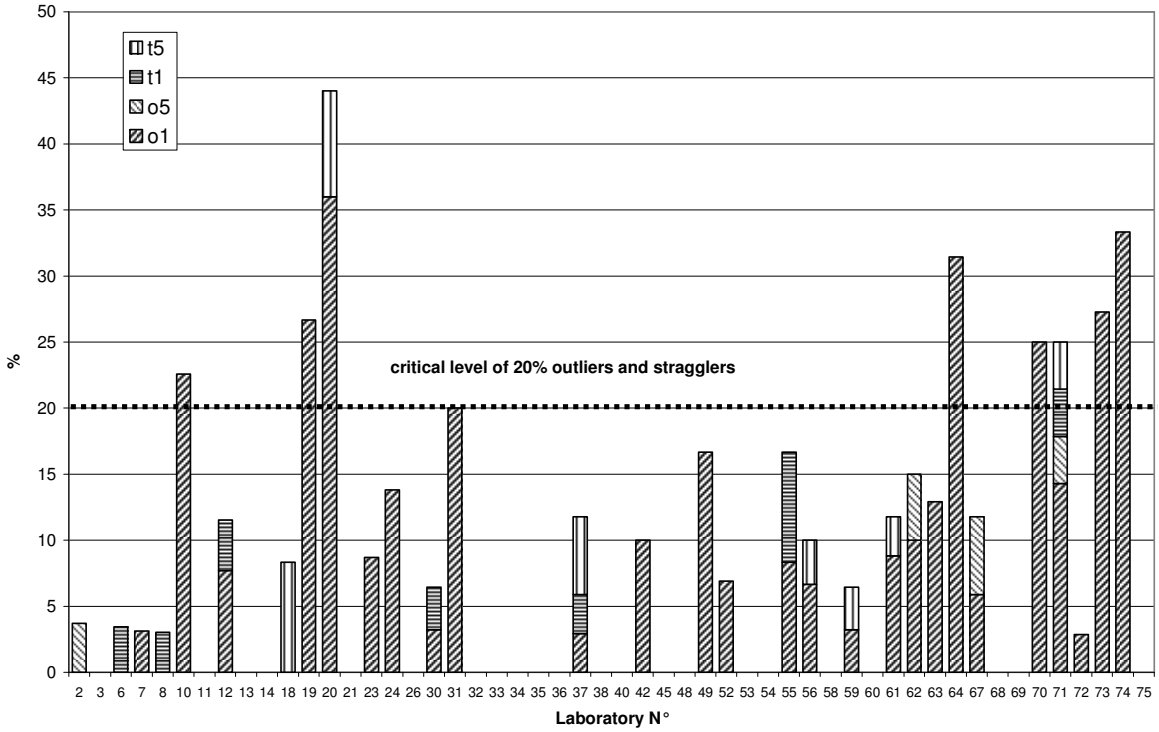


Figure 30: Sample B – Percentage of outliers (o1), stragglers (o5) and tail values per laboratory for the between-laboratory variability.

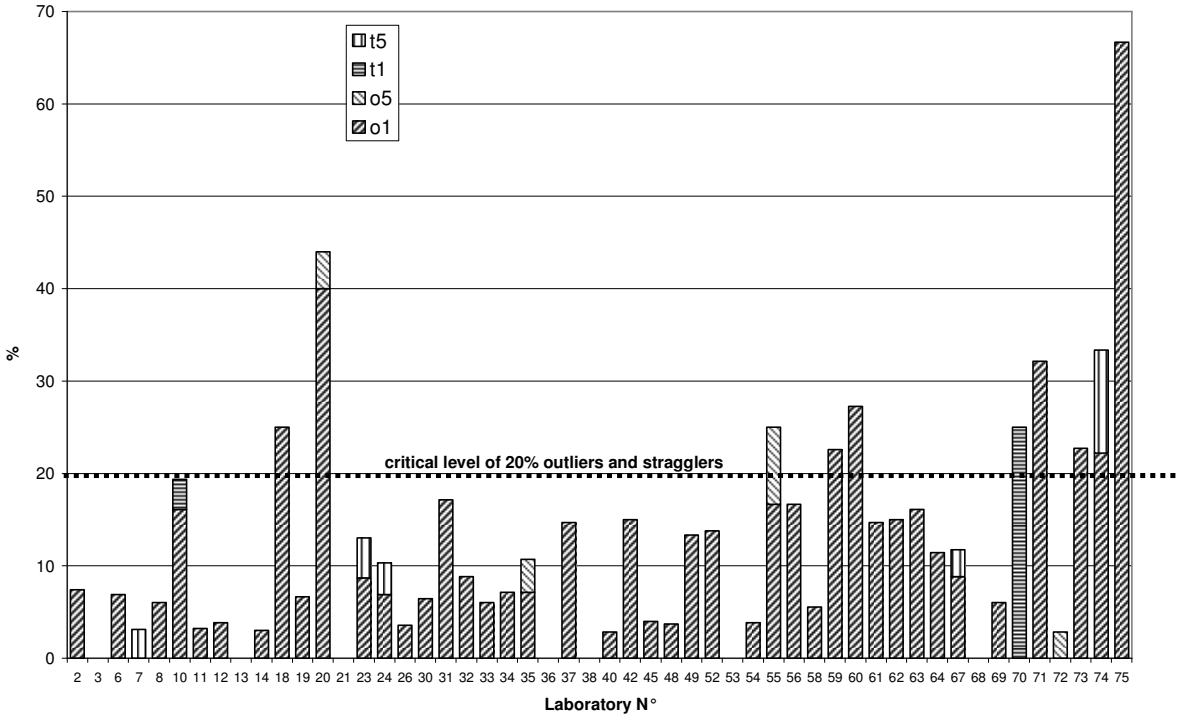


Figure 31: Sample B – Percentage of outliers (o1), stragglers (o5) and tail values per laboratory for the within-laboratory variability.

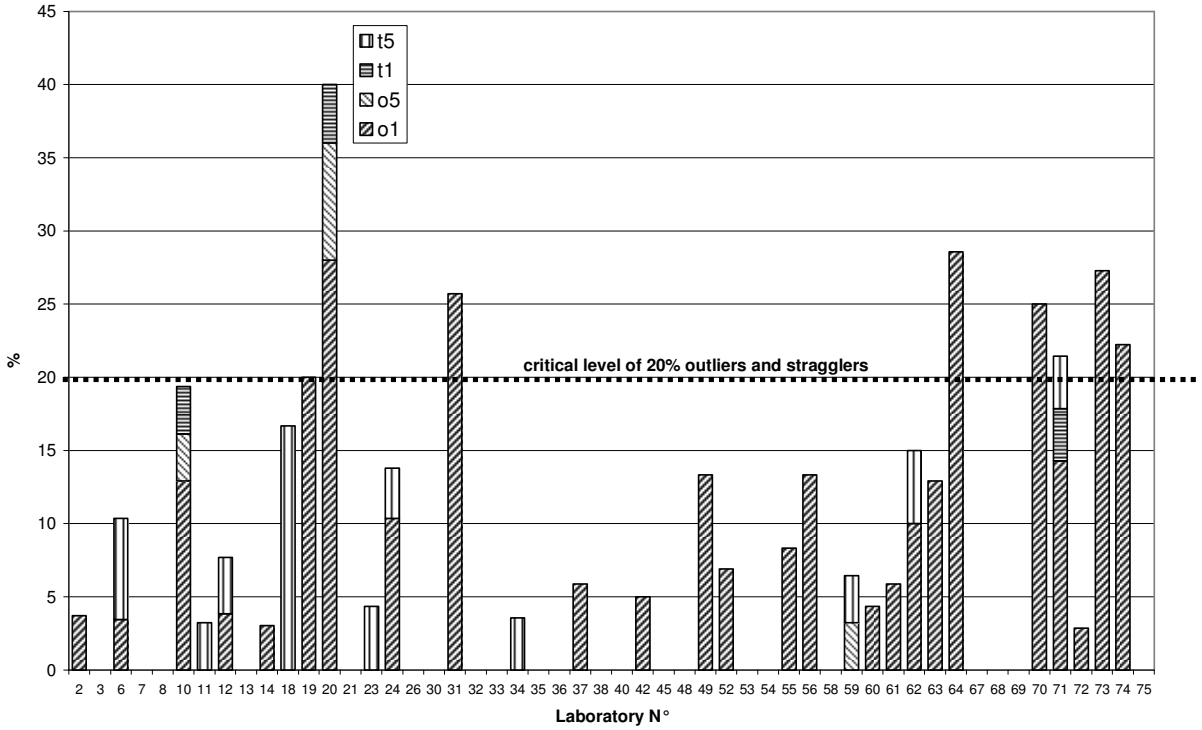


Figure 32: Sample C – Percentage of outliers (o1), stragglers (o5) and tail values per laboratory for the between-laboratory variability.

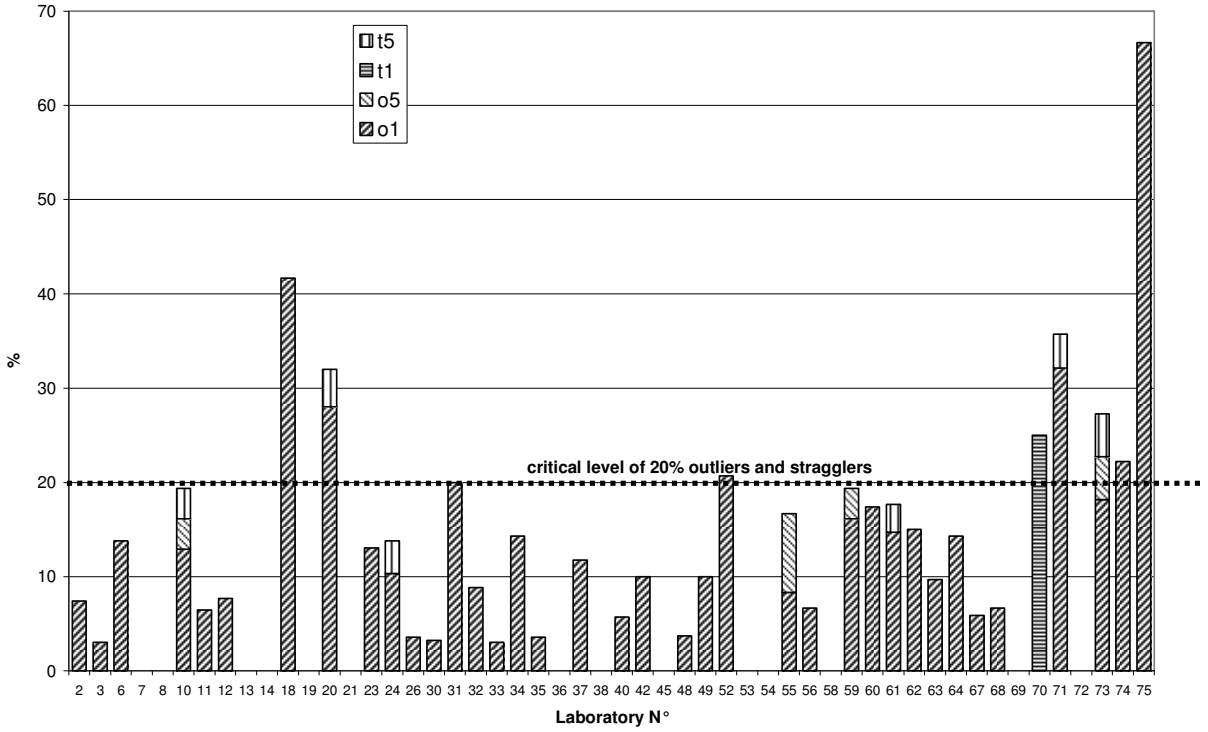


Figure 33: Sample C – Percentage of outliers (o1), stragglers (o5) and tail values per laboratory for the within-laboratory variability.

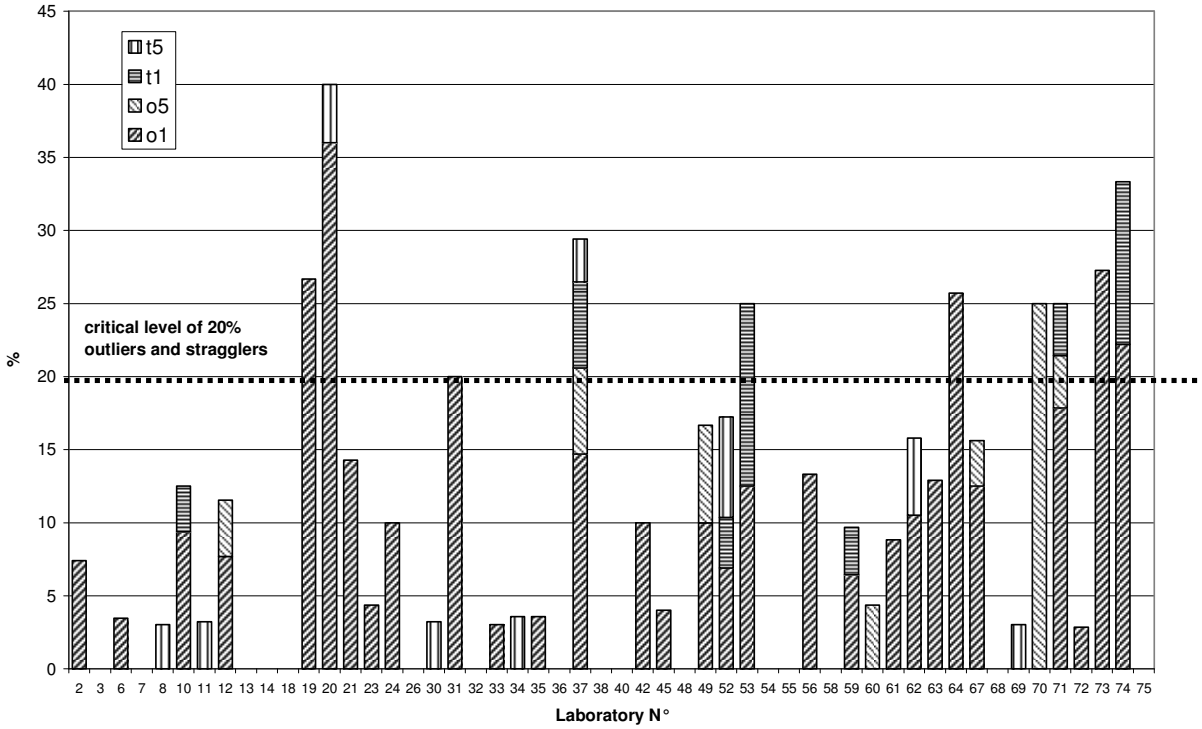


Figure 34: Sample D – Percentage of outliers (o1), stragglers (o5) and tail values per laboratory for the between-laboratory variability.

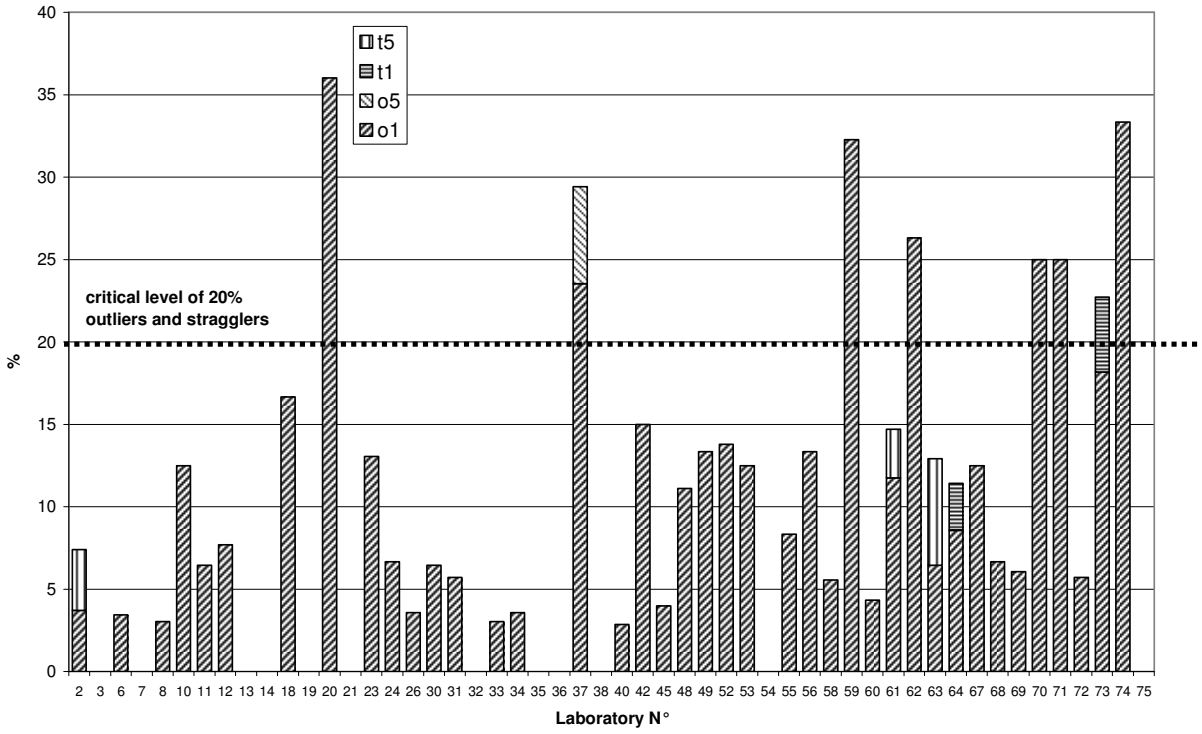


Figure 35: Sample D – Percentage of outliers (o1), stragglers (o5) and tail values per laboratory for the within-laboratory variability.

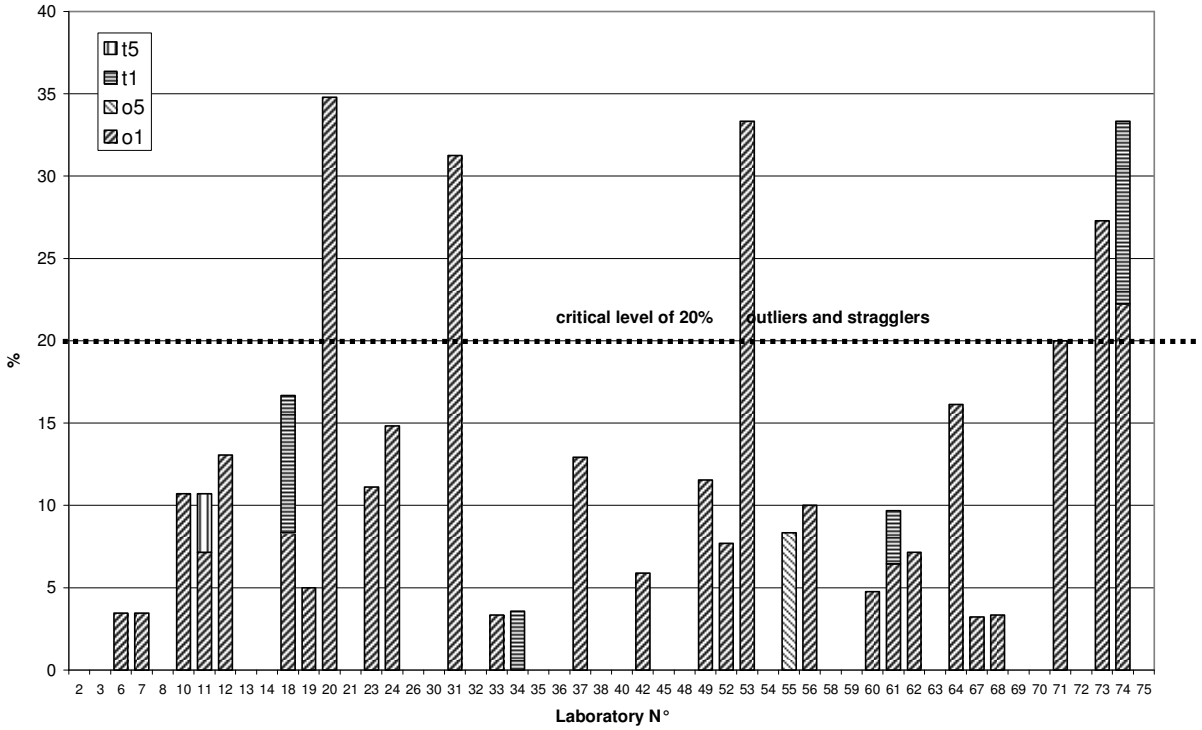


Figure 36: Sample E – Percentage of outliers (o1), stragglers (o5) and tail values per laboratory for the between-laboratory variability.

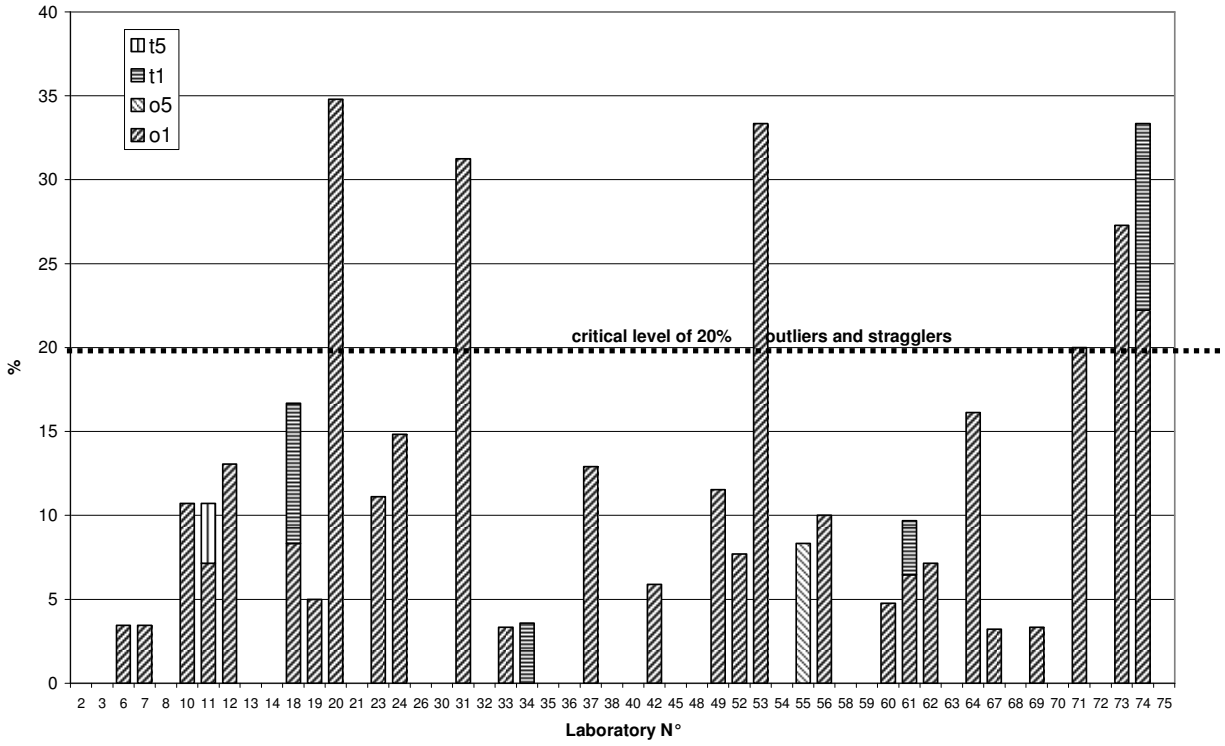


Figure 37: Sample E – Percentage of outliers (o1), stragglers (o5) and tail values per laboratory for the within-laboratory variability.

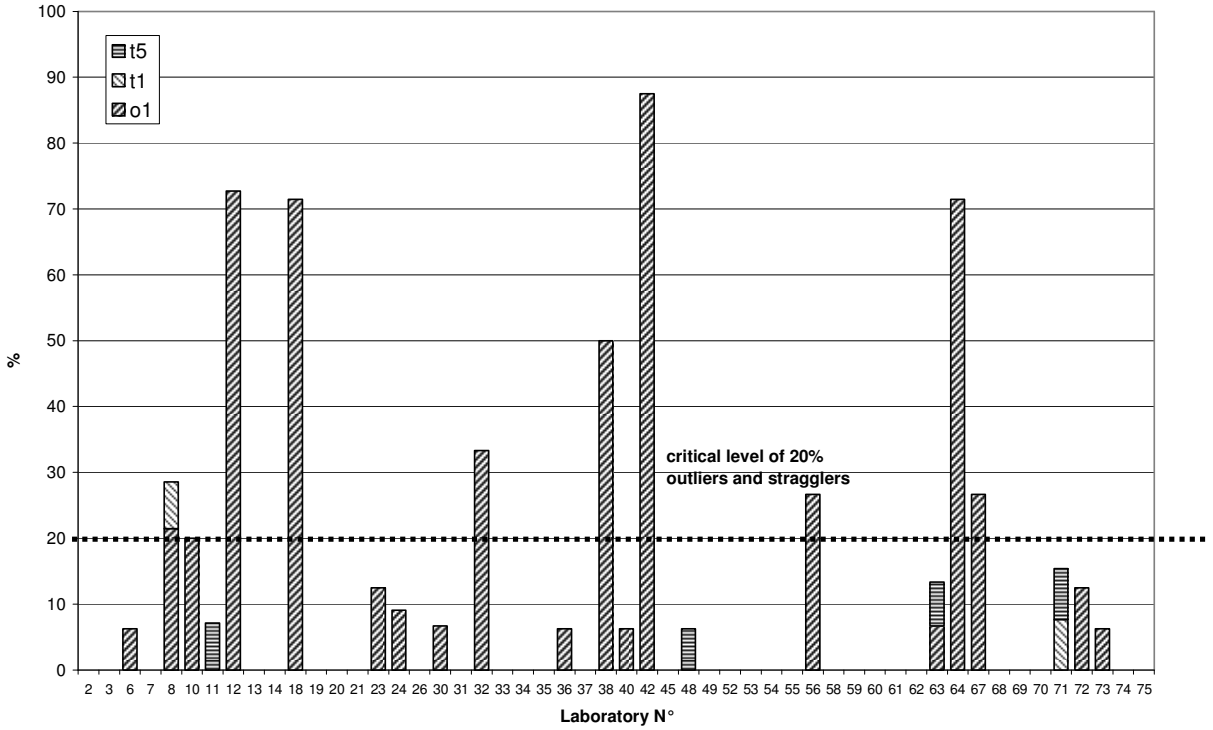


Figure 38: Sample F – Percentage of outliers (o1), stragglers (o5) and tail values per laboratory for the between-laboratory variability.

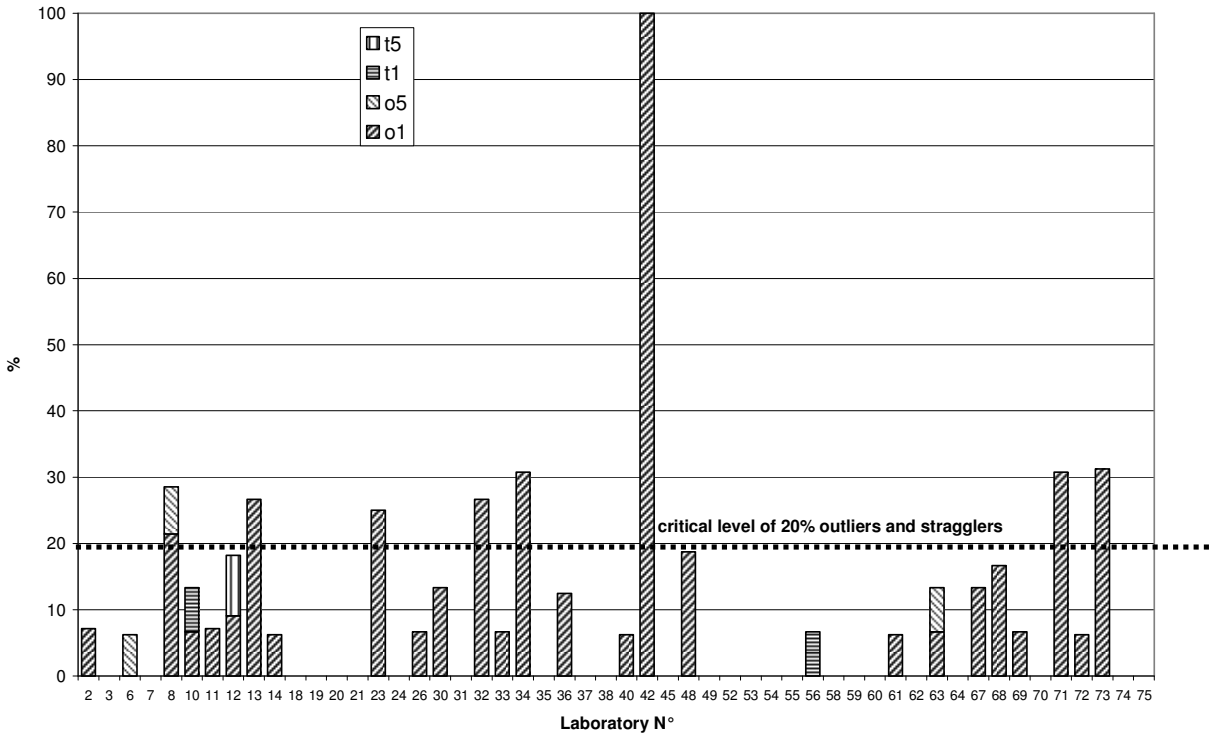


Figure 39: Sample F – Percentage of outliers (o1), stragglers (o5) and tail values per laboratory for the within-laboratory variability.

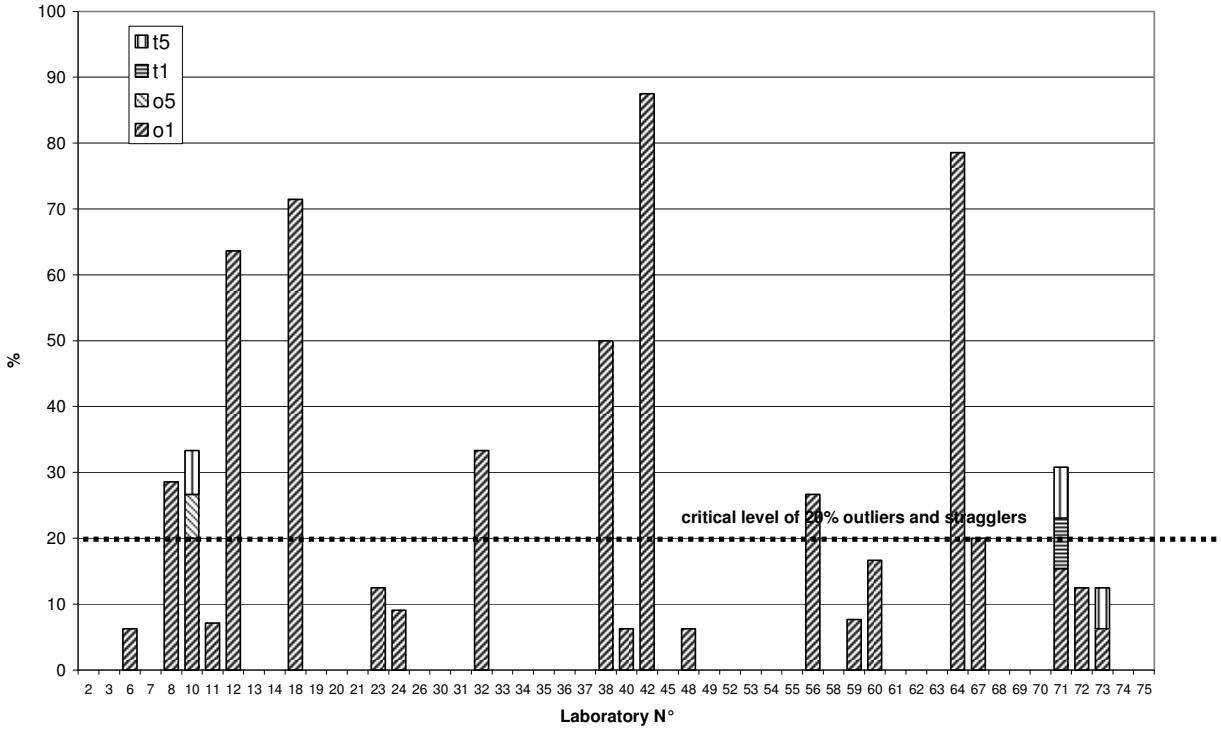


Figure 40: Sample G – Percentage of outliers (o1), stragglers (o5) and tail values per laboratory for the between-laboratory variability.

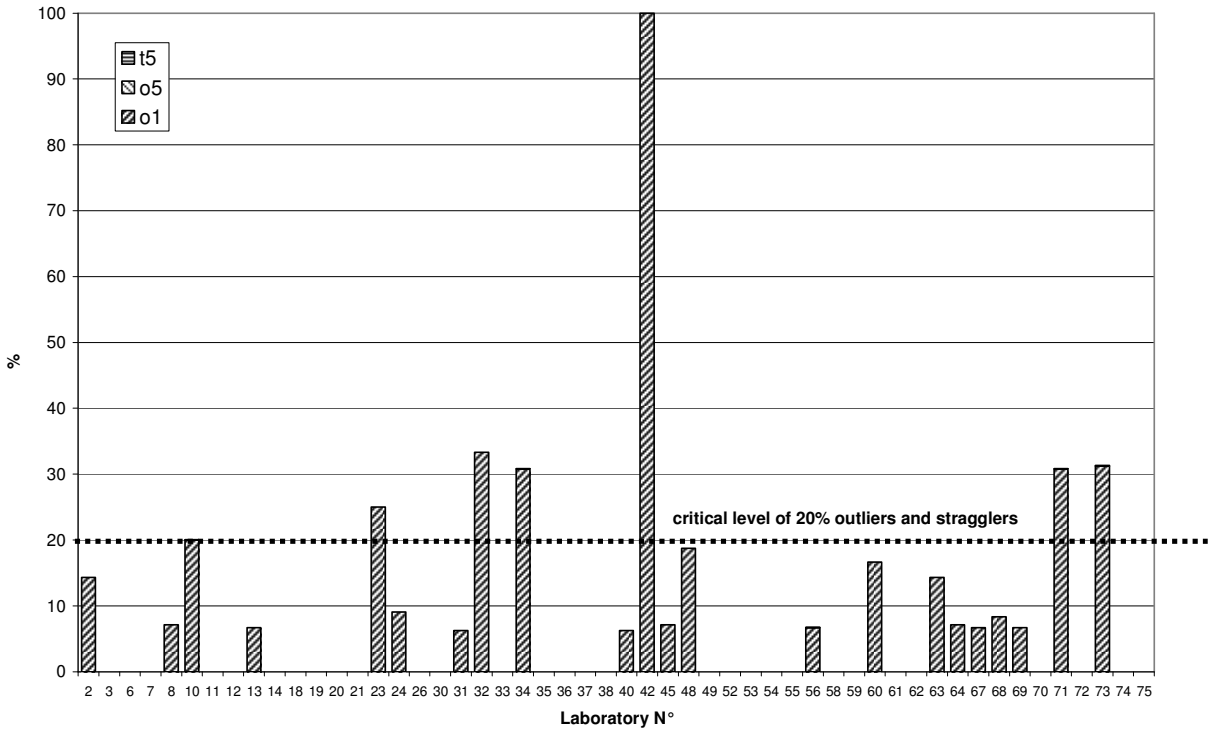


Figure 41: Sample G – Percentage of outliers (o1), stragglers (o5) and tail values per laboratory for the within-laboratory variability.

Table 8: Summary of % of outliers and stragglers per laboratory and per sample, separately for the between (Hvt) and the within laboratory (Kvt) variability. The last 2 columns give an average of all the samples.

	Hvt	Kvt	Hvt	Kvt	Hvt	Kvt	Hvt	Kvt	Hvt	Kvt	Hvt	Kvt	Hvt	Kvt	Hvt	Kvt
Labo	A	A	B	B	C	C	D	D	E	E	F	F	G	G	average	average
2	7	4	4	7	4	7	7	4	0	0	0	7	0	14	3	6
3	0	0	0	0	0	3	0	0	0	0	0	0	0	0	0	0
6	7	7	0	7	3	14	3	3	3	3	6	6	6	0	4	6
7	0	0	3	0	0	0	0	0	3	3	0	0	0	0	1	0
8	0	3	0	6	0	0	0	3	0	0	***21***	***29***	***29***	7	7	7
10	19	13	***23***	16	16	16	9	13	11	11	20	7	***27***	20	18	14
11	3	3	0	3	0	6	0	6	7	7	0	7	7	0	3	5
12	12	8	8	4	4	8	12	8	13	13	***73***	9	***64***	0	***26***	7
13	0	6	0	0	0	0	0	0	0	0	0	***27***	0	7	0	6
14	0	0	0	3	3	0	0	0	0	0	0	6	0	0	0	1
18	0	***25***	0	***25***	0	***42***	0	17	8	8	***71***	0	***71***	0	***22***	17
19	0	7	***27***	7	20	0	***27***	0	5	5	0	0	0	0	11	3
20	***39***	***30***	***36***	***44***	***36***	***28***	***36***	***36***	***35***	***35***	0	0	0	0	***26***	***25***
21	0	0	0	0	0	0	14	0	0	0	NA	NA	NA	NA	3	0
23	0	9	9	9	0	13	4	13	11	11	13	***25***	13	***25***	7	15
24	10	17	14	7	10	10	10	7	15	15	9	0	9	9	11	9
26	0	3	0	4	0	4	0	4	0	0	0	7	0	0	0	3
30	0	10	3	6	0	3	0	6	0	0	7	13	0	0	1	6
31	20	14	20	17	***26***	20	20	6	***31***	***31***	0	0	0	6	17	14
32	0	3	0	9	0	9	0	0	0	0	***33***	***27***	***33***	***33***	10	12
33	0	3	0	6	0	3	3	3	3	3	0	7	0	0	1	4
34	0	4	0	7	0	14	0	4	0	0	0	***31***	0	***31***	0	13
35	18	0	0	11	0	4	4	0	0	0	0	0	0	0	3	2
36	0	0	0	0	0	0	0	0	0	0	6	13	0	0	1	2
37	9	***21***	3	15	6	12	***21***	***29***	13	13	0	0	0	0	7	13
38	0	0	0	0	0	0	0	0	0	0	***50***	0	***50***	0	14	0
40	0	0	0	3	0	6	0	3	0	0	6	6	6	6	2	3
42	5	10	10	15	5	10	10	15	6	6	***88***	***100***	***88***	***100***	***30***	***37***
45	0	0	0	4	0	0	4	4	0	0	0	0	0	7	1	2
48	0	7	0	4	0	4	0	11	0	0	0	19	6	19	1	9
49	11	14	17	13	13	10	17	13	12	12	NA	NA	NA	NA	14	12
52	7	10	7	14	7	***21***	7	14	8	8	NA	NA	NA	NA	7	13
53	0	13	0	0	0	0	13	13	***33***	***33***	NA	NA	NA	NA	9	12
54	0	5	0	4	0	0	0	0	0	0	0	0	0	0	0	1
55	8	8	8	***25***	8	17	0	8	8	8	NA	NA	NA	NA	7	13
56	17	***43***	7	17	13	7	13	13	10	10	***27***	0	***27***	7	16	14
58	0	0	0	6	0	0	0	6	0	0	NA	NA	NA	NA	0	2
59	3	6	3	***23***	3	19	6	***32***	0	0	NA	NA	8	0	4	13
60	0	***23***	0	***27***	4	17	4	4	5	5	0	0	17	17	4	13
61	6	12	9	15	6	15	9	12	6	6	0	6	0	0	5	9
62	10	15	15	15	10	15	11	***26***	7	7	NA	NA	NA	NA	11	16
63	0	0	13	16	13	10	13	6	0	0	7	13	0	14	6	9
64	14	17	***31***	11	***29***	14	***26***	9	16	16	***71***	0	***79***	7	***38***	11
67	6	3	12	9	0	6	16	13	3	3	***27***	13	20	7	12	8
68	0	3	0	0	0	7	0	7	3	0	0	17	0	8	0	6
69	3	3	0	6	0	0	0	6	0	3	0	7	0	7	0	5
70	0	***25***	***25***	0	***25***	0	***25***	***25***	NA	NA	NA	NA	NA	NA	19	13
71	***46***	***36***	18	***32***	14	***32***	***21***	***25***	20	20	0	***31***	15	***31***	19	***30***
72	6	3	3	3	3	0	3	6	0	0	13	6	13	0	6	3
73	***23***	***23***	***27***	***23***	***27***	***23***	***27***	18	***27***	***27***	6	***31***	6	***31***	***21***	***25***
74	11	11	***33***	***22***	***22***	***22***	***22***	***33***	***22***	***22***	NA	NA	NA	NA	***22***	***22***
75	0	0	0	***67***	0	***67***	0	0	NA	NA	NA	NA	NA	NA	0	***33***

Based on the between laboratory variability, 7 laboratories reported outliers and stragglers for more

than 20% of the total number of reported parameters. These laboratories are **N° 12, 18, 20, 42, 64, 71, 73 and 74.** These laboratories will be contacted by the FSCC and asked to fill in a questionnaire to trace the source of the problem. For example, for laboratory N° 42 it will be clear that the wrong reporting form and wrong units have been used. They used the old reporting form where units in mg/kg have been asked while the correct reporting units was mg/l.

Six laboratories (**Lab N° 20, 42, 71, 73, 74 and 75**) reported outliers and stragglers for more than 20 % of the analyses based on the within-laboratory variability.

In Figure 42 the mean % of outliers and stragglers for the seven samples based on the Mandel's k is plotted against the mean % of outliers and stragglers for the seven samples based on the Mandel's h. The size of the circles is a measure of the mean number of reported parameters for each sample. The laboratories appearing in the upper right corners are the same laboratories as mentioned above.

From the location of the observations in the scatter plot, is seen that the balance is slightly 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 of the graph, have performed relatively poor for the 4th Interlaboratory Test.

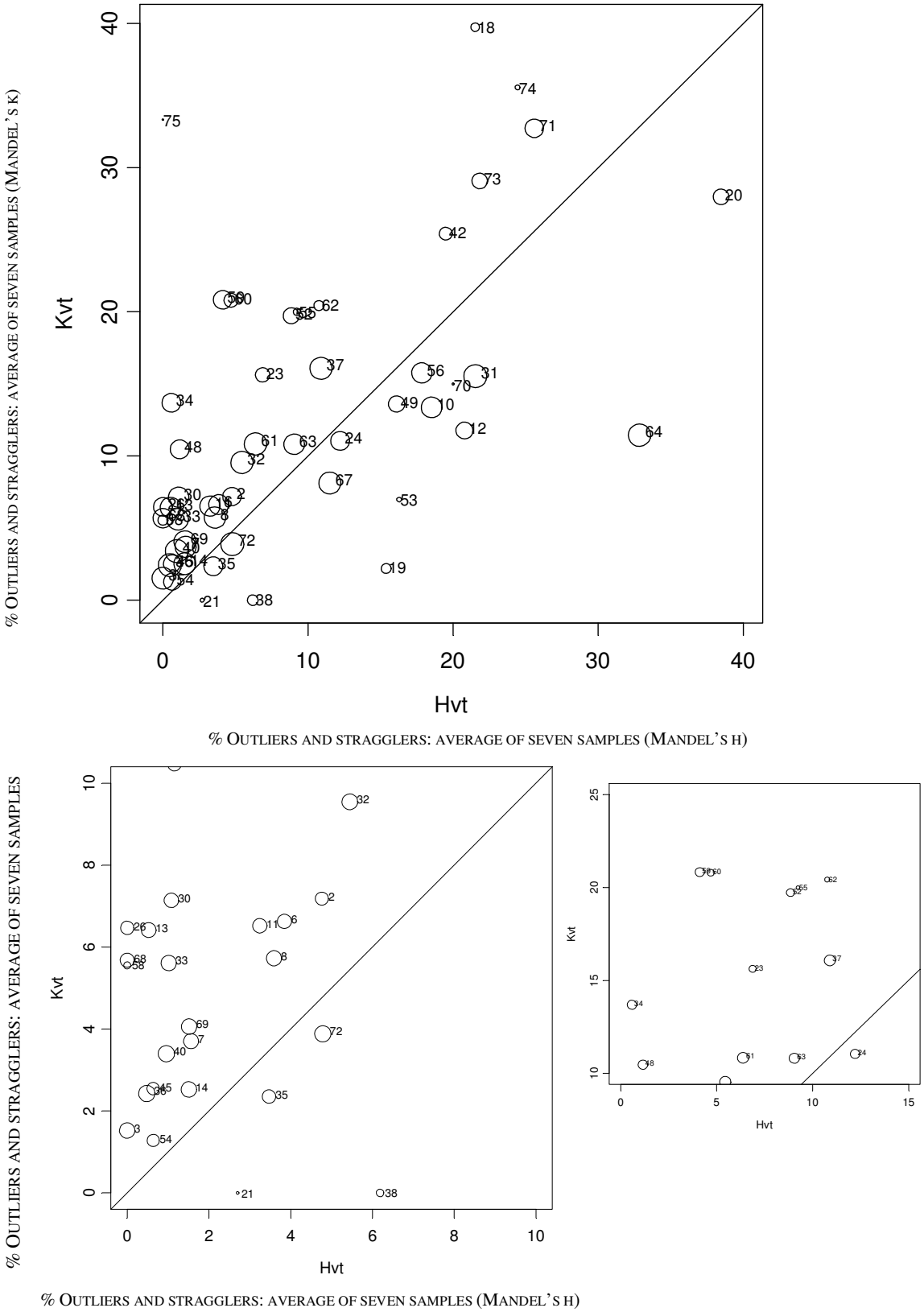


Figure 42: Scatter plot showing the 'h and k strategists' (above: all laboratories, below: zoom on 0 – 10 % scale)

Figure 43 and 44 provide an idea of the distribution of the laboratories in relation to the percentage of 'mistakes' – outliers and stragglers according to the h statistics (Figure 43) and the k statistics (Figure 44).

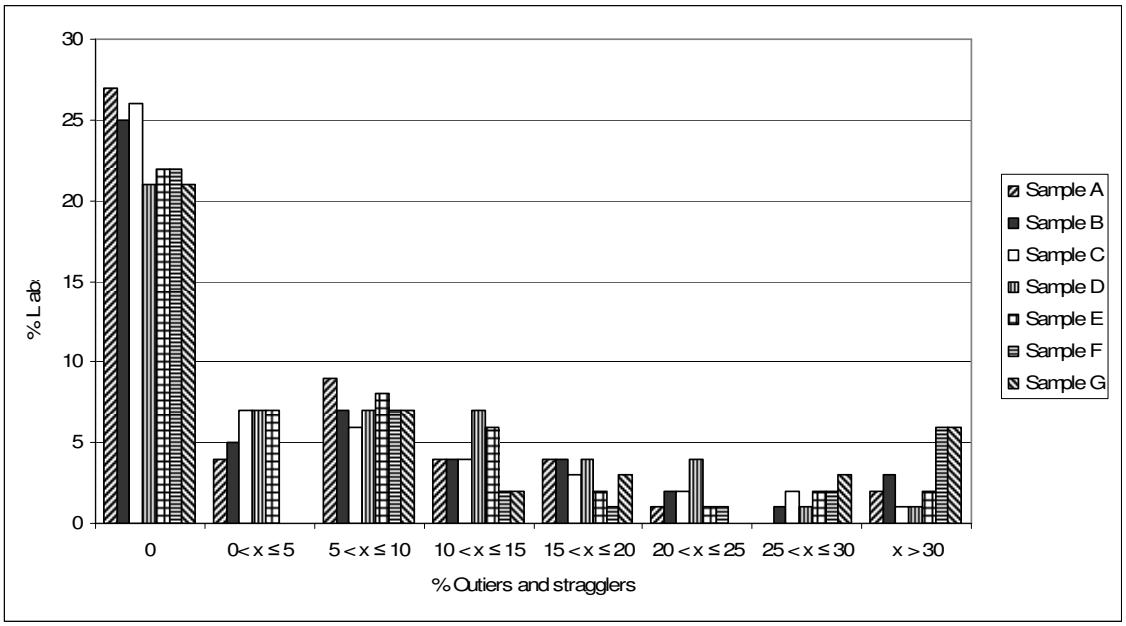


Figure 43: Outliers and stragglers based on Mandel's h statistics

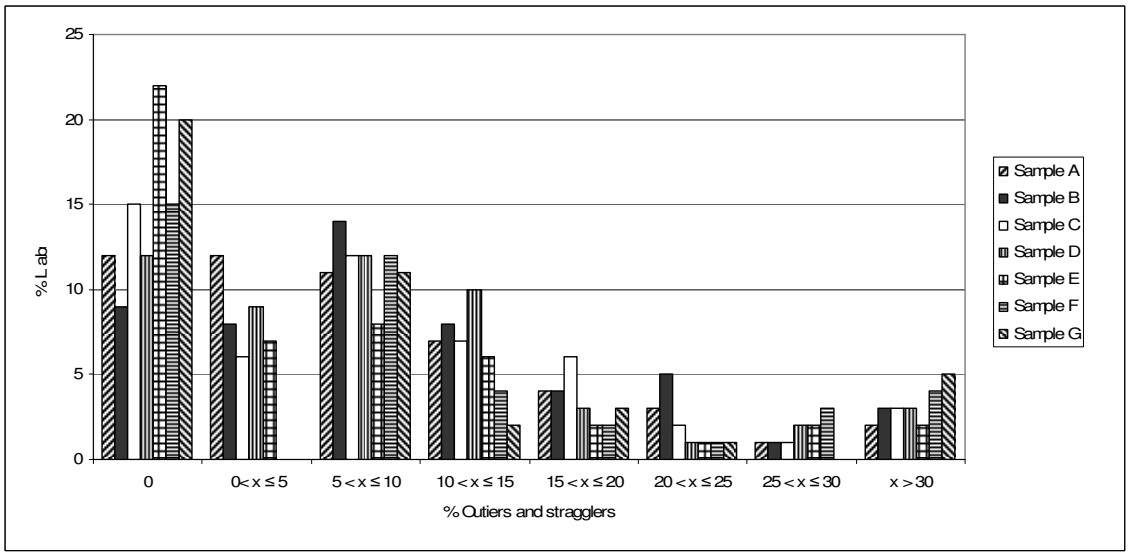


Figure 44: Outliers and stragglers based on Mandel's k statistics

3.2.5 Percentage of outliers and as a measure of difficulty of analysis

Based on Table 9 the 'problem 'elements can be identified. For each element and sample, the percentage of outlying laboratories is given. Concerning the aqua regia elements, the heavy metals clearly pop-up as problem parameters: Cadmium (Cd), chrome (Cr), copper (Cu), mercury (Hg), nickel (Ni), lead (Pb), zink (Zn) but also sulphur (S).

Table 9: % of outliers (99% confidence) per element and per sample

% outliers	Sample						
Element	**A**	**B**	**C**	**D**	**E**	**F**	**G**
Particle size: clay	3	6.1	6.1	16			
Particle size: sand	18	12	3	12			
Particle size: silt	3.1	13	6.3	3.2			
pH(CaCl2)	6.3	4.2	2.1	4.2	4.3		
pH(H2O)	8.7	11	6.5	8.7	4.4		
Carbonates	***29***	8.7	13	13	5		
Organic Carbon	4.7	9.3	16	***21***	12		
Total N	6.3	13	10	2.1	8.5		
Exchangeable Acidity	13	10	7.5	5	5		
Exchangeable Al	12	14	***21***	9.5	12		
Exchangeable Ca	11	19	8.5	***30***	4.3		
Exchangeable Fe	***22***	20	11	13	11		
Exchangeable K	20	20	***22***	20	16		
Exchangeable Mg	***21***	***30***	***26***	***24***	15		
Exchangeable Mn	13	***28***	***39***	11	20		
Exchangeable Na	16	***31***	20	***22***	***22***		
Free H+ acidity	5.6	7.9	***21***	5.4	7.9		
Extractable Al	2.9	6.1	3	5.9	5.9	9.7	9.4
Extractable Ca	7.3	9.8	7.3	7.3	0	18	5.1
Extractable Cd	***24***	***32***	***27***	***27***	20	***31***	***27***
Extractable Cr	7.9	10	13	***23***	7.7	14	19
Extractable Cu	11	9.1	6.8	16	11	***30***	***24***
Extractable Fe	13	5.1	7.7	7.7	5.1	14	5.3
Extractable Hg	***22***	***22***	***28***	***33***	***28***	***50***	***43***
Extractable K	2.5	4.9	4.9	4.9	2.4	14	13
Extractable Mg	9.8	0	4.9	7.3	9.5	18	15
Extractable Mn	9.5	2.4	4.8	0	4.7	18	20
Extractable Na	8.6	5.6	2.8	19	14	18	12
Extractable Ni	8.1	5.4	11	11	11	***32***	***23***
Extractable P	11	11	16	11	13	9.7	19
Extractable Pb	17	2.4	14	14	7	***23***	20
Extractable S	12	***36***	13	***25***	4	18	9.5
Extractable Zn	16	6.8	6.8	4.5	6.8	18	***24***
Reactive Al	0	13	4.2	4.2	13		
Reactive Fe	0	16	4	4	4		

The second group which deserves more attention for quality improvement are the exchangeable elements. Also the determination of the organic carbon content in a poor sandy sample was not without any problems. Which is also remarkable, is the carbonate content of sample A. There is only need to measure the carbonate content with the pH($CaCl_2$) > 6.0 (mineral soil sample) or > 5.5 (organic soil sample). Since the average reported pH($CaCl_2$) of sample A was 5.7, there was no need for carbonate analysis. So measured concentrations were low and close to detection limit. On top of that different methods with varying precision have been used causing a high level of variation (CV = 129 %) and a large number of outliers.

3.6 Coefficients of variation

Table 10 provides the CV for each analysed parameter. The last column of the table gives the CV per group of analyses, calculated over all samples. In the last row, the average CV per sample is given. In general, the coefficients of variation for the different parameters are high which implies high deviations among the results of the participating laboratories. The inter-laboratory variation is thus an important source of variation.

Table 10: Coefficients of variation 4th FSCC ring test 2005-2006 (CV = sRepr/Mgen)

Element	A	B	C	D	E	F	G	all samples	group
Particle size: clay	32.7	40.1	45.2	67.3				46.3	
Particle size: sand	47.3	27.1	28.8	4.0				26.8	37
Particle size: silt	28.7	37.5	39.6	50.9				39.2	
pH(CaCl2)	2.4	2.8	3.0	2.1	2.4			2.5	
pH(H2O)	3.1	3.9	3.7	4.2	3.4			3.7	3.1
Carbonates	120.8	134.1	139.0	130.5	120.7			129.0	129
Organic Carbon	9.6	11.8	7.5	25.9	9.9			12.9	13
Total N	5.1	23.7	32.6	63.8	7.3			26.5	27
Exchangeable Acidity	96.8	37.9	37.9	45.3	27.4			49.0	
Exchangeable Al	115.2	21.5	18.6	33.2	33.3			44.3	
Exchangeable Ca	18.7	60.6	27.3	90.8	24.2			44.3	
Exchangeable Fe	125.9	29.2	42.6	132.1	31.9			72.4	54
Exchangeable K	30.6	34.9	38.4	66.0	13.3			36.6	
Exchangeable Mg	19.5	34.8	31.8	87.6	24.4			39.6	
Exchangeable Mn	25.7	32.3	35.6	25.1	13.0			26.3	
Exchangeable Na	55.8	72.5	70.8	126.5	25.8			70.3	
Free H+ acidity	147.7	96.1	91.4	131.0	48.6			103.0	
Extractable Al	30.4	19.7	20.7	17.3	29.8	7.3	7.7	19.0	
Extractable Ca	32.0	53.8	38.2	54.4	28.0	36.9	31.5	39.2	
Extractable Cd	24.0	126.4	102.3	121.2	21.7	155.1	132.1	97.5	
Extractable Cr	20.8	22.3	17.8	30.0	27.3	13.6	13.9	20.8	
Extractable Cu	8.5	27.2	36.9	38.0	13.0	54.0	22.9	28.6	
Extractable Fe	8.7	9.8	7.5	10.2	17.6	12.4	13.7	11.4	
Extractable Hg	19.7	357.5	52.6	52.6	15.7	53.4	45.3	85.3	33
Extractable K	65.5	38.4	42.0	51.3	38.6	10.3	13.5	37.1	
Extractable Mg	16.2	23.4	25.3	17.4	20.3	9.1	6.9	17.0	
Extractable Mn	10.6	12.7	18.2	16.2	13.8	7.3	6.1	12.1	
Extractable Na	48.3	53.4	53.2	56.6	42.7	12.6	19.7	40.9	
Extractable Ni	11.7	24.1	20.7	17.1	14.3	58.2	15.0	23.0	
Extractable P	31.3	34.4	39.5	16.3	10.3	35.7	8.0	25.1	
Extractable Pb	12.0	37.0	28.3	52.6	14.5	32.1	33.0	29.9	
Extractable S	17.1	13.0	24.0	15.6	14.2	30.0	29.2	20.5	
Extractable Zn	11.7	15.3	20.9	21.3	15.0	18.3	8.6	15.8	
Reactive Al	16.6	7.4	11.6	10.6	7.6			10.7	12
Reactive Fe	18.4	9.2	17.8	10.9	11.7			13.6	
Average per sample	**37**	**45**	**36**	**48**	**23**	**34**	**25**		

It is clear that the CV varies according to the analysed sample. Where sample E (23%), G (25%) have rather low CV's and sample F (34%), A (37%) and C (36%) medium CV's, the CV's of B and D are rather large (respectively 45 and 48%). Sample F is the same sample as sample B. Sample B was extracted by Aqua Regia and bulked into one big extracted liquid sample. All the laboratories received a homogenous subsample. The average CV of the aqua regia elements of sample B is 54% and of sample F 34%. This means that 20 % of the variation of sample B finds its origin in the extraction

procedure of the soil sample.

The extremely high CV of the calcium carbonate analysis is due to the extremely low concentration or even complete absence of carbonates. Not analysing the carbonate content when the pH($CaCl_2$) is below 6.0 or below 5.5 in the case of an organic sample, will give more reliable results.

4 DISCUSSION

4.1 Evaluation by element

All results which are discussed here are presented in Annex 4 which can be consulted on the attached CD-rom. See also Table 6 pg. 28 – 29.

4.1.1 Moisture Content

Although the moisture content was not included in the evaluation of the interlaboratory variability, a limited exploratory data evaluation provided QA/QC information. Three laboratories **(N° 18, 31 and 56)** reported the dry matter instead of the moisture content.

A few laboratories **(N° 26, 30, 73 and 74)** did not report the moisture content but did report results where this moisture content is required.

Such a basic mistake can not be accepted. When laboratories do not succeed to report this correctly in an interlaboratory comparison, it is clear that during the data submission of the survey results this problem should be taken into account. This can easily be done by applying a simple data integrity rule on the moisture content.

4.1.2 Particle size distribution

A maximum of 32 results per soil sample have been included in the analysis (61.5 %). This is a slight improvement compared to the previous ring test where a maximum of 28 results per soil sample were included (54%). This number is lower than the information which was obtained based on the questionnaire. This means that some laboratories did complete the questionnaire but did not report the data.

In the statistical analysis the three particle size fraction of the four mineral soil samples have been considered separately and in total 13 outlying laboratories have been identified **(N° 12, 20, 24, 32, 33, 37, 42, 53, 61, 63, 64, 71 and 75).** This means that 41 % of the participating laboratories is outside the normal range for one or more samples.

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Based on the questionnaire, we know that 5 of these laboratories **(Lab N° 20, 24, 33, 37, 53)** did not use the reference method. One of these laboratories **(N° 20)** did only recognise a sand and a clay particle size class and ignored completely the silt fraction. Their sand + clay fractions are equal to 100 %. This laboratory already performed poorly in the previous ring test, but then they did not analyse the particle size distribution. Lab **N° 24** (outlier Sample A, sand fraction) and **N° 37** (outlier, sample D, all fractions) use the laser diffraction method. Lab **N° 12** used the national method of which we do not

know in how far it does correspond with the ISO standard. Lab **N° 33** did not respond on the question whether they followed the reference method or not.

Related to the reference material, six of them use local reference material and one used national reference material. Two laboratories did not answer the question and five laboratories said not to use any reference material. Of the seven laboratories which use reference material, not more than two laboratories used control charts to follow up the quality of their analysis. So FSCC strongly recommends the use of control charts and to take actions accordingly.

Remarkable is that although Lab N° 64 received an accreditation for this analysis following the ISO standard, they did report an outlier for the sand fraction for sample A. On the other hand Lab N° 64 and 71 do not participate in any other ring tests besides the FSCC ring test. This could be a recommendation towards these two laboratories. Lab N° 71 had very extreme outliers with the clay and the sand fraction, but not with the silt fraction. It would be worthwhile to check whether both fractions have not been mixed by filling in the reporting form.

4.1.3 Soil reaction

The pH is a parameter with a small coefficient of variation. This makes statistical procedure for detecting outliers more strict. For pH(H_2O) and pH($CaCl_2$) together, 13 laboratories have been excluded at least for one sample and one pH method: **Lab N° 2, 8, 18, 32, 37, 42, 55, 56, 63, 64, 67, 70 and 71.** For this analysis it is important to differentiate between the within - and between-laboratory variability. When tree replicates are measured, most laboratories will become exactly the same results for the pH or with maximum difference of 0.1 pH unit. So when a laboratory reports two values which differ more than 0.1 pH, they will be excluded based on the Mandel's k statistic as is the case for Lab N° 18, 55, 56, 71, 42 and 64. The remaining laboratories however do have a problem in producing comparable results with the other laboratories. Laboratory N° 56 however, did not use the reference method. Four of the 13 laboratories did not use reference material and four (no necessarily the same) did not use control charts.

4.1.4 Carbonate content

The samples contained no or very little $CaCO_3$. The majority of the laboratories did not measure the carbonate content (because of pH($CaCl_2$) values below 5.5 or 6.0) or reported values below the LOQ. Nine laboratories were excluded at least for one sample (**Lab N° 32, 37, 49, 10, 60, 72, 26, 67, 69**). Five of them purely based on the within laboratory variability (N° 32, 37, 60, 26, 67, 69), Lab N° 49 reported unacceptably high values for all mineral samples. They did not send in a questionnaire. Lab N° 37, 10 and 72 reported too high $CaCO_3$ content for Sample A. Lab N° 37, 67 and 72 did not use the reference method and only 4 of the 8 laboratories use control charts (N° 32, 37, 60 and 72).

4.1.5 Organic carbon

46 laboratories reported results for the organic carbon content. Fifteen laboratories reported for at least one sample outlying results **(Lab N° 10, 18, 20, 35, 37, 42,49, 52, 53, 58, 60, 70 and 71**). Lab N° 10 probably reported in the wrong units because their results are more than a factor of 10 higher than the average reported result. Of them 14 Labs completed the questionnaire. Eight of them did not the reference method. When comparing this number with Figure 1, this means that only 3 laboratories using another method than the reference method manage to obtain acceptable results.

4.1.6 Total nitrogen content

In total 13 laboratories of the 48 laboratories which reported N values have been excluded for at least one sample, namely **Labs N° 10, 14, 20, 21, 23, 37, 52, 55, 58, 59, 62, 64 and 71.** Lab N° 20 used the Kjeldahl method, which is not a reference method. Laboratories N° 10, 20, 23 and 64 do not use control charts although Lab N° 20, 23 and 64 do use reference material. Since it does not require such an big effort to monitor the evolution of the reference method throughout the year, FSCC recommends to follow the QA/QC guidelines related to the control charts as described in the manual.

4.1.7 Exchangeable cations

Except for laboratories N° 3, 8, 12, 14, 36 and 38, all laboratories reported outliers for at least one of the nine parameters in this group or for at least one of the five sample (A, B, C, D and E).

From Table 6 we see immediately that there are quite some laboratories which are facing problems with the determination of the exchangeable cations. Laboratory **N° 31** probably reported in the wrong units. Laboratory **N° 73** did not follow the reference method, neither did they specify in the questionnaire which method they are using. Labs **N° 64 and 71** did have very bad results for the exchangeable cations but reasonably good results for the exchangeable acidity and Free H^+ which they determined by titration. Laboratories **N° 19** and **20** used the reference method but unfortunately did not use any control charts. Laboratories **N° 60, 61, 74** also had poor results although they used the reference method and make use of control charts. Laboratory **N° 49** did not complete the questionnaire. Lab N° **24** had some analyses done by a subcontractor which gave reasonably good results but had mainly problems with two elements which Lab N° 24 analysed in its own laboratory, namely exchangeable K and Na. Lab **N° 62** did not use the reference method and could only obtain comparable results for exchangeable Fe and Na. All other laboratories reported between 1 and 7 outliers (out of a max. of 45).

4.1.8 Aqua Regia extractable elements

The aqua regia is the largest group of elements: 16 parameters have been determined on a maximum of 7 sample, including mineral and organic samples and the digested soil samples. Although considered as one group, not all elements are measured by the same technique. For example, the

extractable Hg was only measured by 18 laboratories. Nine of them used cold vapour absorption spectrometry (CV AAS), three used ICP-AES and four used atomic fluorescence spectrometry (AFS). See Annex 3.

Of the six laboratories which were very successfully in the determination of exchangeable elements, we see that laboratories N° 8, 12 and 38 are remarkably less good.

None of the laboratories that analysed all 16 parameters did have zero outliers. Lab **N° 7** did not have any outliers but did not analyse mercury. Lab **N° 19** analysed 9 parameters without any outlier. Labs **N° 3, 26 and 54** did not analyse Hg and had only one outlier. Lab **N° 14 and 45** had only 2 outliers (Lab **N° 53** too but only reported extractable K and P). Lab **N° 31 and 36** analysed all 16 parameters and had three outliers.

On the other side of the scale, there are the laboratories which reported 20% or more outliers, therefore QA/QC measures should be taken. Lab **N° 18** reported only 8 parameters but had 52% outliers. Based on the questionnaire we do not see an immediate explanation. Lab **N° 38** reported 6 parameters for sample F and G but had 50 % outliers. They did not fill in the questionnaire on the used method.

Lab N° 12 reported results for 11 parameters and **Lab N° 71** for 13 parameters but both had 30 outliers (respectively 39 and 35%). They conduct this type of analyses only few times a year. Lab **N° 42** reported 7 parameters and had 38% outliers; they conduct the analysis only once a year. Lab **N° 20** also had 38 % percent outliers based on 11 parameters. The use of control charts could possibly improve the results of Lab N° 20.

Lab N° 56 reported 33 outliers on 15 parameters. This makes 31 % outliers. This laboratory conducts this analysis less than once a year and does not use control charts (which is indeed not relevant for an analysis which is only done once a year). Lack of experience is possibly the main cause of the poor performance of this laboratory.

Other laboratories with more than 20 % outliers for the aqua regia elements are **59** (28%), **64** (26%) and **10** (24%), Lab **N° 37** had exactly 20 % outliers. Lab N° 59 did not use the reference method and Lab N° 64 and 10 could possibly improve their performance by the use of control charts.

4.1.9 Reactive Fe and Al

Although the reactive Fe and Al has been determined by less laboratories (N° = 25) than the other elements, it seems that there are not so many problems. Sample A did not have any outliers. Remarkable is the result of **Lab N° 64**, showing outliers for 70 % of the analyses while they laboratory is accredited and the analysis is been conducted on a weekly basis. Their results are usually 50 % than the average of all participating laboratories. Lab **N° 67** had three outliers (30%), Lab **N° 52** and **61** two outliers and **Lab N° 56** one outlier.

4.2 Comparison with the 3rd FSCC Interlaboratory Comparison

4.2.1 Questionnaire

Compared to the 3rd FSCC Interlaboratory Comparison, improvements have been made related to use of the reference method, the level of experience with the reference methods, the use of reference materials and control charts.

Table 11: Comparison between the questionnaire of the 3rd and the 4th FSCC Interlaboratory Comparison

	3rd FSCC Interlaboratory Comparison (2002 - 2003)	4th FSCC Interlaboratory Comparison (2005 - 2006)
Use of reference method	65 %	82 %
Experience level of reference methods	30 % (high) 45 % (normal) 24 % (low)	47 % (high) 43 % (normal) 8 % (low) 2 % (no answer)
Use of reference material	77 %	86 %
Use of control charts	50 %	65 %
Accreditation for the reference method	13 %	11 %
Use of calibration standards	73 %	63 %

To improve the transparency of the applied analytical methods and detection techniques, the use of a coding system in the data accompanying report is suggested. See Annex 3. This coding system is based on the list which is used for the foliar ring test and has been elaborated for soil analysis.

4.2.2 The group coefficients of variation

The CV's have improved except for total nitrogen (see Table 12). The high variation in the 4th FSCC ring test can be explained by the low nitrogen content of sample B, C and D (respectively 0.4, 0.4 and 0.2 g/kg), while the LOQ varies between 0.01 and 2 g/kg (average 0.16 g/kg). 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.

Table 12: Group CV's of the 2nd, 3rd and 4th FSCC Interlaboratory Comparison

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

4.3 Data Integrity Expert Rules

Many of the defined outliers were due to errors which could easily be avoided by the application of data integrity expert rules on the reported results. Since the manual has been changed after the first survey, these rules should be updated and new rules need to be defined. FSCC used the opportunity of the data submission for the 4th FSCC Interlaboratory Comparison, to test the data integrity rules.

Although the previous ring test report contained 10 basic "Data Integrity Expert Rules" (see Table 13), it seems that the laboratories or contact persons who did submit the data for the ring test did not remember to check these 10 basic rules. When a system of direct web submission of data will be used, these rules need to be inserted because they can trace data problems in a very early stage. Often it concerns problems related to the reporting units. Laboratories routinely report in a certain unit according to the national methods and forget to convert the data into the proper unit.

Table 13: Data integrity expert rules as defined in the Forest Soil Condition Report (Van Mechelen et al., 1997)

Rule N°	Parameter	Description	Permissible limit values		Conditions for application
			lower	upper	
1	pH	Checks pH results in presence of carbonates	5.5 6.0	- -	$CaCO_3$>0 for Organic Horizons $CaCO_3$>0 for Mineral Horizons
2	Organic Carbon	Checks organic C content (g/kg) in organic layers	80	-	Organic Horizons
3	C/N	Checks the C/N ratio in organic and mineral layers	5 3	100 75	Organic Horizons Mineral Horizons
4	C/P	Checks the C/P ratio in organic and mineral layers	100 10	2500 750	Organic Horizons Mineral Horizons
5	$CaCO_3$	Checks the carbonate content (g/kg) in soils with low pH	0	0	pH<5
6	AcExc	Checks the exchangeable acidity value($cmol_{(+)}$/kg) in organic and mineral layers	0.5 0	250 150	Organic Horizons Mineral Horizons
7	ACE (1)	Checks the exchangeable acid cation concentration ($cmol_{(+)}$/kg) in organic and mineral layers	0.5 0	250 150	Organic Horizons Mineral Horizons
8	BCE (2)	Checks the exchangeable basic cation concentration ($cmol_{(+)}$/kg) in organic and mineral layers	0.5 0.1	400 150	Organic Horizons Mineral Horizons
9	CEC (3)	Checks the cation exchange capacity ($cmol_{(+)}$/kg) in organic and mineral layers	1 0.5	400 150	Organic Horizons Mineral Horizons
10	BS (4)	Checks the base saturation (%) in presence of carbonates	90	100	$CaCO_3$>0

Legend:
(1) ACE:Exchangeable acid cation concentration (cmol(+)/kg) =Sum of exchangeable acid cations (Al + Fe + Mn + H)
(2) BCE:Exchangeable basic cation concentration (cmol(+)/kg) =Sum of exchangeable basic cations (Ca + K + Mg + Na)
(3) CEC:Cation Exchange Capacity (cmol(+)/kg) =Sum of exchangeable cations (ACE + BCE)
(4) BS:Base Saturation =100*BCE/CE

The results of the data integrity expert rules conducted on the submitted ring test data are shown below:

Rule 1 checks the pH in presence of carbonates: "if $CaCO_3$ > 0 then the organic layer pH($CaCl_2$)> 5.5 or in mineral layer > 6.0"

Twelve laboratories reported [$CaCO_3$] > 0 but none of them measured a sufficienly high pH($CaCl_2$). See Table 14.

Table 14: Laboratories reporting $CaCO_3$ values > 0 with the reported pH($CaCl_2$) values

	$CaCO_3$ (g/kg)					pH($CaCl_2$)				
Lab	**A**	**B**	**C**	**D**	**E**	**A**	**B**	**C**	**D**	**E**
3	4.0					5.8				
10	18.0			2.3		5.7			4.3	
26	3.3					5.7				
30	0.3					5.8				
32	5.4	2.0	2.2	2.2	2.8	5.6	4.3	3.9	3.8	3.6
36	2.0					5.8				
37	19.6					5.4				
49	42.0	11.6	14.3	10.6		5.8	3.9	4.2	4.3	
60	5.0	5.3	3.7	5.0	3.0	5.9	4.3	4.1	3.9	3.7
67	8.7				1.8	5.8				3.7
69	1.0					5.8				
72	12.3					5.8				

On the other hand **Lab N° 2** and **N° 70** measured a pH($CaCl_2$) > 6.0 for the mineral soil Sample A but did not conduct any $CaCO_3$ analysis. To be sure that laboratories are reporting significant amounts of $CaCO_3$ the rule better includes "$CaCO_3$ > LOQ".

Rule 5 checks the carbonate content in soils with low pH "if pH($CaCl_2$) < 5 than $CaCO_3$ should be 0"

Several laboratories did submit significant $CaCO_3$ concentration (above LOQ) when the pH($CaCl_2$) < 5. See Table 14 for the sample B, C, D and E.

Rule 2: "The organic carbon content in the organic layer should be at least 80 g/kg"

This rule can be put even more strict, following the definitions of the manual *where the OC content should be at least 120 g/kg*. When this rule is applied on the OC results for sample E, all results passed the test.

Rule 3: "The C/N ratio in the mineral layers should be between 3 and 75 and in the organic layer between 5 and 100.

Lab N° 62 becomes for Sample B a C/N ratio of less than 3 because of the high reported concentration of N. The lab reports a concentration of 3.6 g/kg while the average reported values is 0.4 g/kg. **Lab N° 64,** Sample C reports a N concentration of 2.0 g/kg which also results in a C/N ratio below 3. During the statistical analysis, the lab result of both laboratories was defined as an outlier for the between laboratory variability at the first step.

Rule 4: "The C/P ratio in the mineral layer should be between 10 and 750 and in the organic layer between 100 and 2500."

Lab N° 10 reported for Sample C a C/P value above 750. This is due to their high OC content. The average reported OC content of sample C is 6 g/kg while this laboratory reports more than 60 g/kg.
But applying this rule on sample D seems to be problematic. This rule was initially based on a different type of P measurement. For sample D, the average OC is 1.8 g/kg and the average extracted P by Aqua Regia is 0.27 g/kg, which results in a C/P proportion of 6.6 which is below 10 but probably correct. This rule is probably only applicable on surface soil samples. So this rule should be adapted or removed form the list of the integrity rules.

Rule 6, Rule 7, Rule 8 and Rule 9, related to the exchangeable elements

Lab N° 31 reported for all its exchangeable cations in the wrong units (probably by a factor of 100). After sending the file for correction to the laboratory, they adjusted some wrong units for the extractable elements but did not correct any of the exchangeable elements. Especially when checking rule 7 (ACE),8 (BCE) and 9 (CEC) this becomes very clear.
Lab N° 73 possibly has similar problems: their results of the exchangeable elements differ about a factor of 10 with the average reported values. When the results were sent for feedback to the laboratory, FSCC did not receive any comments.
For sample D, Rule 9 might be difficult to apply since the nutrient content of this sample is extremely low. Therefore the values are often below detection limit which may results in CEC values below 0.5. So FSCC recommends to put the minimum equal to 0 and not 0.5.

Rule 10 checks the base saturation (%) in presence of carbonates: should be between 90 and 100 % when $CaCO_3$ > 0 g/kg.

The average $CaCO_3$ content is 1 g/kg for sample A, D and E. Since the concentration of $CaCO_3$ was extremely low this values often corresponds to the detection limit. Sample D and E cannot contain any (indicated by the low pH values). The measurement of $CaCO_3$ was not mandatory for sample A but a concentration of 1 g/kg might be possible. So we should check rule 10 only on sample A.
Nearly all results of Sample A fulfil this rule, except Lab N° 67. But since their own measurement of the $CaCO_3$ was = 0, their BS of 89 % should still be accepted.

Suggestions for additional quality rules

1. In European forest soils the pH measured in water will always be larger (usually 0.5 pH unit) than the pH measured in $CaCl_2$. When however, the difference between pH(H_2O) and pH($CaCl_2$) is negative or zero, this may be a strong indication of a wrong pH measurement. For example, Lab N° 19 in Sample D measures both in $CaCl_2$ and in H_2O a pH of 4.4.

2. When laboratories do not report the moisture content, they should not be able to report oven dry results (for example **Lab N° 74**). The determination of the moisture content is a prerequisite to be able to report carbonate content, OC, Total N, exchangeable, extractable elements, total elements and reactive Fe and Al.

5 CONCLUSIONS

52 laboratories participated in the 4th FSCC Interlaboratory Comparison 2005-2006. Seven laboratories reported outliers and stragglers for more than 20 % of the analyses, based on the between-laboratory variability, and six laboratories based on the within-laboratory variability. Problem parameters are (1) the heavy metals and S extracted by Aqua Regia, (2) the exchangeable elements, (3) carbon content in samples with low organic carbon content and (4) the calcium carbonate determinations. Three years after the 3rd FSCC Interlaboratory Comparison 2002-2003, more laboratories use the reference methods, have a higher experience with these reference methods, make more use of reference material and control charts but less laboratories are accredited for the reference methods. The coefficients of variation of all groups of analysis have improved except for the total nitrogen which was probably due to the fact that three samples had very low nitrogen content.

6 RECOMMENDATIONS AND FOLLOW-UP

1. **The particle size distribution** could probably improve strongly when all laboratories would use the reference method and would take more care of the quality control in the laboratory by the use of **local reference material** and simple **control charts**.
2. Although the use of reference material and **control charts** has increased, the results of this ring test show that the quality could further improve by an even wider application of reference material and control charts. Many of the poor performing laboratories were not applying this simple control technique. Overall the use of reference material was 20 % higher than the use of control charts (86 % versus 65%). As has been suggested by the QAQC group of the Expert Panel on Deposition and Soil Solution, FSCC wants to stimulate the efficient use of control charts. Suggested reading:
    - ISO 8258 (1991) Shewart control charts
    - ISO 7870 (1993) Control charts – General Guide and introduction
    - ISO 7873 Control charts for arithmetic average with warning limits
    - ISO 7966 Acceptance control charts
    - ISO 7871 Cumulative sum charts – Guidance on quality control and data analysis using CUSUM techniques – technical report
    - Internal Quality Control, Handbook for Chemical Laboratories, NT Technical report, TR 569, 2005, revised for the demands of ISO/IEC 17025 standard. Handbook available at www.nordicinnovation.net/nordtest.cfm (choose Rapporter/NT tech 569)

3. FSCC also suggests to use one common international reference material in all the laboratories participating in the BioSoil project. This reference material is being prepared by the FSCC. The reference material is sample B of this ring test. Eeach laboratory can receive a maximum amount of 5 kg. Laboratories should use this reference material to make control charts which should be reported to FSCC.
4. Since many of the problems which showed up during the analysis of the ring test data, were due to the reporting of the data itself, it can be concluded that the quality of the data will benefit largely from the application of updated data integrity expert rules. Therefore it is absolutely needed that during the submission of the data, the data is checked by applying these few simple rules, preferably in an automated manner.
5. To be able to report the heavy metals such as Hg and Cd, FSCC suggests to report to at least one significant number.
6. The nine laboratories which reported more than 20 % outliers (within- or between-laboratory variation) will be contacted by the FSCC and have to fill in a follow-up questionnaire to be able to trace back the problem(s). These poorly performing laboratories can receive new material from the 4th FSCC ring test to reanalyse the samples.
7. FSCC will try to create an internet platform as soon as possible. On this platform laboratories will be able to post questions and have discussions co-ordinated by the FSCC.
8. At the 13th Forest Soil Expert Panel Meeting in Alton (UK) on 29-30 March was suggested to analyse the subset of the 14 German laboratories separately. Germany has developed a QA/QC programme by bringing the laboratory responsibles together. The results of this analysis can be an indication whether this approach works or not. In case the results are positive, Germany would recommend that the laboratories of neighbouring countries get in touch with each other and exchange experiences. FSCC should indicate for each region one well performing laboratory (can depend on the analysis). This laboratory will then be asked whether they are prepared to help the poorer performing laboratories.

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