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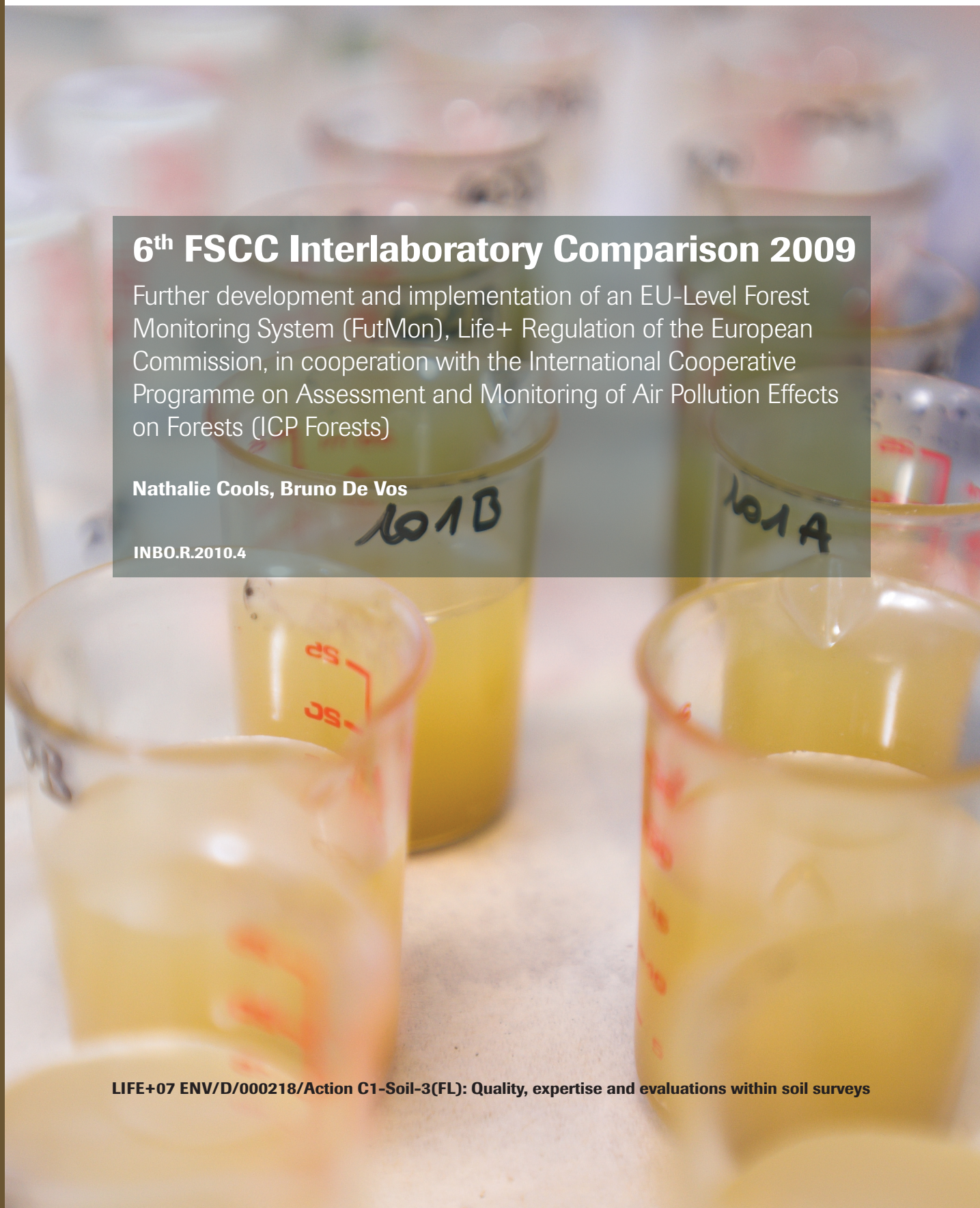

6th FSCC Interlaboratory Comparison 2009

Further development and implementation of an EU-Level Forest Monitoring System (FutMon), Life+ Regulation of the European Commission, in cooperation with the International Cooperative Programme on Assessment and Monitoring of Air Pollution Effects on Forests (ICP Forests)

Nathalie Cools, Bruno De Vos

INBO.R.2010.4

LIFE+07 ENV/D/000218/Action C1-Soil-3(FL): Quality, expertise and evaluations within soil surveys

Vlaamse overheid

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FURTHER DEVELOPMENT AND IMPLEMENTATION OF AN EU-LEVEL FOREST MONITORING SYSTEM (FUTMON)

AND

UNITED NATIONS ECONOMIC COMMISSION FOR EUROPE

CONVENTION ON LONG-RANGE TRANSBOUNDARY AIR POLLUTION

INTERNATIONAL COOPERATIVE PROGRAMME ON ASSESSMENT AND MONITORING OF AIR POLLUTION EFFECTS ON FORESTS (ICP FORESTS)

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Summary

Fifty laboratories from 29 countries took part in the 6th FSCC Interlaboratory Comparison in 2009. The ring test included five samples of which three were mineral soil samples, one was a peat sample and one was an organic layer sample. Nine laboratories reported outliers and stragglers for more than 20 % of the total reported analyses: two laboratories for both the between- and the within- laboratory variability, four laboratories based on the within-laboratory variability and three for the between-laboratory variability. Based on the coefficient of variation, the problem parameters were (1) exchangeable elements, especially Na and the acid exchangeable cations Al, Fe, Mn, free H^+ and acidity, (2) aqua regia extractable elements Na and Cd, (3) the carbonate content in Sample C with low $CaCO_3$ content and (4) the determination of the clay content. In general there were more problems when the concentration of the concerning element was low. Compared to the 5th FSCC Interlaboratory Comparison conducted in 2007, the coefficients of variation of all groups of analysis remained at a similar level except for the $CaCO_3$ content and the total elements which were higher in this ring test.

New in this 6th Interlaboratory Comparison was the application of preset tolerable limits. When a laboratory had more than 50% of its reported means outside the tolerable range or when it did not report a mandatory parameter, requalification was required. All laboratories received an individual qualification report and a follow-up questionnaire in order to correct errors and mistakes. Corrected results could be submitted for requalification. Only one laboratory qualified immediately for all mandatory and optional parameters. Two more laboratories qualified immediately for all their reported parameters and yet two more for all mandatory parameters. After requalification 16 labs could qualify for all their reported parameters. This new approach assured an individual and intensive follow up which will eventually lead to an improved quality of the solid soil parameters measured in the current and future forest soil monitoring programme.

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1 Introduction

ICP-Forests of the 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 better understand the ecological impact of air pollution processes. An important part of this monitoring programme is the study of forest soil condition across Europe.

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 test samples, was conducted in 1993, simultaneously with the analysis of the collected soil samples of the Level I plots. Laboratories using national methods were recommended to analyse the standard soil samples with both national and reference methods, in order to provide a basis for comparison. Once more the existing variance, especially between different methods, asked for the uniform use of reference methods.

In view of a second European wide soil survey, harmonisation and improvement of the analytical techniques was indispensable. In order to assure the quality of the data obtained by soil analysis, the 10th Forest Soil Expert Panel (Warsaw, 2000) decided to proceed to a **third Intercalibration Exercise**. This third ring test (2002-2003) provided insight in the quality of soil analysis results and thus the quality of the future Forest Soil Database. A revision of the ICP Forests Submanual on sampling and analysis of soil (FSCC and the Expert Panel on Soil and Soil Solution, 2003) was a first step in this harmonisation process. All participating countries in the third ring test were requested to use the 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 (Cools *et al.,* 2003).

At the onset of the EC Forest Focus demonstration project 'BioSoil', the FSCC proceeded in 2005 with a **fourth Interlaboratory Comparison** (Cools *et al.*, 2006) prior to the BioSoil survey and in 2007 with the **fifth Interlaboratory Comparison** (Cools *et al.*, 2007) at the time that most laboratories were performing the BioSoil analyses. All analyses in the BioSoil project had to be done by laboratories that performed well in the FSCC Intercalibration Exercises. The analytical methods allowed in these comparisons and the procedure for the statistical analysis were exactly the same as in the 3rd Interlaboratory Comparison, allowing to detect possible progress.

The laboratories gained more experience in the reference methods and used more control charts, though the general use of these quality control measures was still limited. The evolution was that the coefficients of variation of most parameters improved except for elements present in low concentrations. Problem parameters remained heavy metals (such as Hg and Cd) and the $BaCl_2$ exchangeable elements.

Within the **EU LIFE$^+$ "Further Development and Implementation of an EU-level Forest Monitoring System (FutMon)" project**, the action group C1 implements quality assurance and quality control (QAQC) procedures by means of interlaboratory comparisons. In order to enhance the quality and comparability of the analytical data for the laboratories of all beneficiaries within FutMon, action C1-QALab-30(NWD), developed a FutMon protocol (Clarke *et al.*, 2009) on methods for quality control and data checks in the laboratories.

At the kick-off meeting of the FutMon project in January 2009, it was decided to harmonise the organisation and the follow up of all laboratory ring tests in the LIFE$^+$ FutMon project.

This has the following immediate implications for this **6th FSCC Interlaboratory Comparison 2009,** which is part of Action C1-Soil-3(FL)**:**

1. In order to improve the communication among the laboratories, it was decided to open the laboratory codes within the group of the laboratories, the NFCs and the QAQC working group.

2. Before submitting the results to FSCC, the laboratories were asked to perform the data checks as outlined in the FutMon protocol to be downloaded from the FutMon homepage (Clarke *et al.*, 2009) (http://www.futmon.org/documents_results/Field_protocols_final/QualLabs_v4.pdf).

3. Preset tolerable limits were applied on the ring test results. When a laboratory does not meet for 50% of its results the limits for a certain parameter, it will be marked in the qualification report. The tolerable limits for soil ring test are listed in the FutMon protocol (Clarke *et al.*, 2009).

4. One month after the data submission, each laboratory received a qualification report. In case a FutMon laboratory failed for a certain parameter, it was urged to re-qualify. The information on qualification and re-qualification will be stored in the central FutMon database to assure an actual link with the reported survey results.

The aim of this report is to present the statistical evaluation of the between – and within-laboratory variability of the results of the laboratories participating in the 6th FSCC Interlaboratory Comparison 2009 according to the methods defined, established and used in the previous FSCC Interlaboratory Comparisons. Subsequently, the predefined tolerable ranges, accepted at the 14th meeting of the Expert Panel on Soil and Soil Solution, April 2008 in Firenze, are applied on the ring test results and discussed thoroughly.

2 Materials and methods

2.1 Selection and registration of the laboratories

According to the FutMon proposal and in line with the outcome of the FutMon kick-off meeting of 12-16 January 2009 in Hamburg, all laboratories which analyse samples (either on deposition, soil, soil solution, soil water retention curve, foliage, litterfall or ground vegetation) had to take part in a number of ring tests during the two project years, amongst other the 6th FSCC Interlaboratory Comparison 2009. All associated beneficiaries provided contact details of the participating laboratories to the chair of the Working Group of QAQC in the laboratories. The laboratories received their new lab code (harmonised for the different ring tests in the project) and password for the registration procedure which had to be performed online (http://www.bfw.ac.at/fscc/ring_boden.login) by the end of February 2009.

Countries participating within the ICP Forests programme without being associated beneficiary of the EU Life+ FutMon project were invited to take part of the ring test on a voluntary basis.

2.2 Sample preparation

2.2.1 Characteristics of the test samples

The interlaboratory comparison included five European forest soil samples: three mineral samples (A, B and C), one forest floor sample (D) and one peat sample (E). With the samples, FSCC tried to cover a broad geographic area. They were taken in Slovakia, France, Spain, Belgium and Finland.

Sample A was taken from 3 till 10 cm in an Ah horizon under a uniform beech stand (*Fagus sylvatica*) in the Carpathians in Slovakia. The soil was described and classified according to WRB (IUSS Working Group WRB, 2006) as a Haplic Cambisol (Humic, Eutric, Endoskeletic, Siltic). So it is a soil characterised by a high amount of organic material throughout the soil profile, with a base saturation of 50% or more in the major part between 20 and 100 cm from the soil surface, having 40% or more gravel or other coarse fragments averaged over a depth between 50 and 100 cm and having a texture of silt, silt loam, silty clay loam or silty clay in a layer, 30 cm or more thick, within 100 cm from the soil surface.

Sample B comes from a mixed oak-beech-hornbeam stand (*Quercus petraea, Quercus robur, Fagus sylvatica, Carpinus betulus*) in the forest of Fontainebleau south of Paris, France. The soil developed on a sand substrate. The sampled depth is between 20 and 60 cm and comprises the E and Bhs horizon. The soil was according to FAO (1990) classified as a Cambic Podzol.

Sample C is a clay loam sample taken from the Bt_1 horizon in Valdeaveruelo (between 13 and 36 cm of depth) in central Spain. The profile is classified as a Calcic Cutanic Luvisol (Endosodic, Hypereutric, Chromic) (IUSS Working Group WRB, 2006).

Sample D is taken from the F+H layer of a Haplic Alisol (Abruptic, Alumic, Hyperdystric, Profondic, Arenic) (IUSS Working Group WRB, 2006) under a scotch pine forest (*Pinus sylvestris*) in Flanders, Belgium. The forest floor was classified as a Hemimoder.

Sample E is a Finnish peat sample taken from a bog or fen with a vegetation cover consisting of Sphagnum mosses under dwarf birch (Betula nana).

2.2.2 Sample preparation and homogenisation

The samples were dried at 40°C and sieved by the institutes that collected the samples in the field following ISO 11464 (1994). Subsequently they were packed and sent to FSCC in Belgium. The peat sample was milled by a Variable speed rotor mill (PULVERISETTE 14) equipped with a titanium sieve ring.

Prior to sending the soil samples to the laboratories, the samples were checked for homogeneity. The FSCC prepared 100 subsamples of each of the mineral soil samples A, B and C (about 300 g each) and 70 subsamples (about 250 g each) of the organic samples D and E. Of each sample, 8 subsamples were randomly selected for laboratory analysis. Of each of the subsamples, 4 sub – subsamples were taken and analysed. The variation within the subsamples was compared with the variation between the subsamples. In case the variation between the subsamples was larger then the variation within the subsamples, it could be an indication of heterogeneity.

The elements Loss-on-Ignition (LOI), Total N by the Modified Kjeldahl method and aqua regia extractable elements (microwave digestion, HNO_3 + HCl, 3 + 1, v/v) have been measured. Note that the measurements were made on the air-dried samples without recalculation to oven-dry mass. The mean results, on air-dried basis, are presented in Table 1.

On Sample B, several elements were below the limit of quantification (LOQ) (total N, Ca, Na, Cd and S). For sample C there were no data above LOQ for total N and Cd. In sample E, the concentrations for aqua regia extractable Cd, Mn, Na, Zn, As were below the LOQ and there were only limited data for K.

Samples A, C and D were homogeneous for all measured soil variables. The variation between the subsamples was lower than variation within the subsamples. For sample B, the variation of the variable Fe and P was slightly higher between the subsamples than within the subsamples, because of some deviant results in one subsample 3J. This might indicate a heterogeneity in that particular subsample. For sample E, the variation of the variable Pb was slightly higher between the subsamples than within the subsamples, because of deviant results in one subsample. Note that the element is present in only low concentrations. The variance components are listed in Table 1. Consult Annex 2 on the attached CD for the dot plots showing the results of the homogeneity tests.

2.2.3 Distribution of the samples and submission of results

Samples were sent to the participating laboratories by the 2nd March 2009. The on-line data submission at http://bfw.ac.at/fscc/ring_boden.send_results was open till the 30th of June 2009. Corrections sent till the 15th of July 2009 were all included in the statistical analysis.

Table 1: Variance components of the homogeneity tests

Element	Sample	General mean	General St.dev.	General CV(%)	St.dev. within subsamples	St.dev. between subsamples	%variation within subsamples	%variation between subsamples	
Al (ppm)	A	59519.3	4199.9	7.1	4072.1	1028.4	94.0	6.0	OK
	B	3670.0	645.3	17.6	489.8	420.2	57.6	42.4	OK
	C	56146.2	7712.5	13.7	7705.0	340.2	99.8	0.2	OK
	D	2030.3	249.2	12.3	222.7	111.9	79.8	20.2	OK
	E	3600.8	61.7	1.7	61.7	1.7	99.9	0.1	OK
As (ppm)	A	5.5	0.5	9.9	0.5	0.0	100.0	0.0	OK
	B	1.1	0.1	8.0	0.1	0.0	100.0	0.0	OK
	C	14.5	1.6	11.2	1.4	0.9	69.5	30.5	OK
	D	6.0	0.8	13.1	0.7	0.4	78.8	21.2	OK
Ca (ppm)	A	5377.5	179.5	3.3	151.4	96.5	71.1	28.9	OK
	C	10237.3	1001.1	9.8	963.2	272.9	92.6	7.4	OK
	D	5383.7	219.9	4.1	219.9	0.0	100.0	0.0	OK
	E	3951.7	106.4	2.7	106.4	0.0	100.0	0.0	OK
Cd (ppm)	A	0.3	0.0	15.0	0.0	0.0	100.0	0.0	OK
	D	1.3	0.0	3.6	0.0	0.0	100.0	0.0	OK
Cr (ppm)	A	24.0	1.6	6.5	1.4	0.6	83.7	16.3	OK
	B	5.0	1.0	19.3	0.7	0.7	54.2	45.8	OK
	C	33.6	2.3	6.8	2.3	0.0	100.0	0.0	OK
	D	12.1	1.4	11.7	1.3	0.6	83.7	16.3	OK
	E	9.3	0.2	2.2	0.2	0.1	88.1	11.9	OK
Cu (ppm)	A	14.4	0.8	5.7	0.8	0.0	100.0	0.0	OK
	B	1.6	0.2	14.0	0.2	0.0	100.0	0.0	OK
	C	14.4	0.7	5.2	0.7	0.0	100.0	0.0	OK
	D	23.6	0.5	2.3	0.5	0.0	100.0	0.0	OK
	E	6.6	0.3	4.6	0.3	0.0	100.0	0.0	OK
Fe (ppm)	A	44243.5	2084.2	4.7	2041.3	420.5	95.9	4.1	OK
	B	***2341.9***	***168.7***	***7.2***	***102.5***	***134.0***	***36.9***	***63.1***	***>***
	C	33051.4	1680.7	5.1	1675.3	134.7	99.4	0.6	OK
	D	13980.6	2492.1	17.8	2290.3	982.4	84.5	15.5	OK
	E	2582.6	44.9	1.7	40.8	18.8	82.4	17.6	OK
K (ppm)	A	1019.3	121.0	11.9	93.2	77.2	59.3	40.7	OK
	B	460.6	104.8	22.8	88.2	56.6	70.9	29.1	OK
	C	6884.0	639.3	9.3	592.0	241.2	85.8	14.2	OK
	D	1567.3	209.0	13.3	184.2	98.9	77.6	22.4	OK
	E	57.1	5.4	9.4	3.9	3.7	51.9	48.1	OK
Mg (ppm)	A	3045.3	100.2	3.3	93.8	35.4	87.5	12.5	OK
	B	296.3	29.4	9.9	22.1	19.4	56.5	43.5	OK
	C	9247.5	412.2	4.5	412.2	0.0	100.0	0.0	OK
	D	669.4	66.9	10.0	58.3	32.8	75.9	24.1	OK
	E	187.0	4.9	2.6	4.9	0.0	100.0	0.0	OK
Mn (ppm)	A	1140.6	116.7	10.2	110.2	38.4	89.1	10.9	OK
	B	223.7	12.6	5.6	10.5	6.8	70.4	29.6	OK
	C	167.9	9.9	5.9	9.9	0.0	100.0	0.0	OK
	D	794.2	27.5	3.5	25.7	10.0	86.8	13.2	OK
Na (ppm)	A	478.2	49.6	10.4	37.3	32.7	56.6	43.4	OK
	C	218.2	30.8	14.1	26.2	16.2	72.5	27.5	OK
	D	107.4	7.0	6.5	6.9	0.9	98.2	1.8	OK
Ni (ppm)	A	6.5	0.44	6.74	0.44	0.00	100.0	0.00	OK
	B	2.8	0.20	7.25	0.16	0.12	63.0	36.97	OK
	C	18.4	0.84	4.57	0.84	0.00	100.0	0.00	OK
	D	6.3	0.38	6.16	0.37	0.10	92.7	7.26	OK
	E	5.4	0.09	1.63	0.08	0.03	87.4	12.62	OK
OM (%)	A	10.2	0.23	2.27	0.23	0.00	100.0	0.00	OK
	B	0.43	0.02	4.20	0.02	0.01	78.5	21.53	OK
	C	3.2	0.40	12.54	0.40	0.00	100.0	0.00	OK
	D	74.7	1.22	1.63	0.99	0.71	65.6	34.43	OK
	E	81.0	2.64	3.26	2.64	0.00	100.0	0.00	OK
P (ppm)	A	293.0	18.8	6.4	17.4	7.1	85.8	14.2	OK
	B	***56.4***	***3.4***	***6.0***	***2.0***	***2.8***	***34.2***	***65.8***	***>***
	C	127.3	8.9	7.0	8.7	1.6	96.6	3.4	OK
	D	799.9	15.1	1.9	15.1	0.0	100.0	0.0	OK
	E	982.7	25.5	2.6	25.4	2.4	99.1	0.9	OK
Pb (ppm)	A	36.7	1.2	3.2	1.2	0.1	99.6	0.4	OK
	B	2.6	0.2	6.8	0.1	0.1	50.3	49.7	OK
	C	15.7	0.4	2.7	0.4	0.2	86.5	13.5	OK
	D	68.2	1.8	2.6	1.8	0.0	100.0	0.0	OK
	E	***2.9***	***0.2***	***5.6***	***0.1***	***0.1***	***38.0***	***62.0***	***>***
S (ppm)	A	314.2	12.5	4.0	10.9	6.1	75.8	24.2	OK
	C	79.3	3.6	4.5	3.6	0.0	100.0	0.0	OK
	D	2085.1	45.9	2.2	45.9	0.0	100.0	0.0	OK
	E	3118.1	43.0	1.4	41.7	10.6	93.9	6.1	OK
TotN (g/kg)	A	0.3	0.0	14.1	0.0	0.0	100.0	0.0	OK
	D	1.5	0.2	12.2	0.2	0.0	100.0	0.0	OK
	E	2.4	0.2	8.0	0.2	0.0	100.0	0.0	OK
Zn (ppm)	A	83.1	2.7	3.2	2.5	1.0	86.9	13.1	OK
	B	8.6	1.0	11.7	0.8	0.6	65.1	34.9	OK
	C	57.7	2.2	3.9	2.2	0.5	95.8	4.2	OK
	D	332.0	5.4	1.6	5.4	0.0	100.0	0.0	OK

2.3 Soil Analytical Methods

Laboratories were requested to use the methods as described in the ICP Forests Submanual on Sampling and Analysis of Soil (FSCC and the Expert Panel on Soil and Soil Solution, 2006). As seen from Table 2, nearly all these methods are based on the ISO-standards. Following the requirements of the EU LIFE$^+$ FutMon project, all associated beneficiaries needed to analyse in this 6th FSCC Interlaboratory Comparison all mandatory parameters. Optional parameters could be analysed voluntarily. However, the qualification report took into account both mandatory and optional parameters. The latter because the quality requirements apply to all submitted data to the central FutMon database. When an optional parameter does not meet the minimum quality requirements in this ring test, the associated beneficiary had two options: either requalification, either not reporting the concerning parameter until the next ring test where a new qualification can be obtained.

The distributed test material consisted of the fraction < 2 mm of air-dried samples so no further grinding of the samples was allowed except for the analysis of total element contents such as carbonates, TOC, total Nitrogen and the total elements.

As all results had to be reported on oven-dried basis, it was necessary to determine the soil moisture content following ISO 11465 (1993). As a validation check, the soil moisture content had to be reported. However, as moisture content might change during transport and storage it was not included in the evaluation and the qualification report.

Table 2: Methods recommended by the manual IIIa on sampling and analysis of soil (ICP Forests, 2006)

Analysis	Reference Method	Description
Particle Size Distribution	ISO 11277	Pipette method
Soil pH	ISO 10390	Potentiometric pH (volumetric)
Carbonate Content	ISO 10693	Calcimeter
Organic Carbon Content	ISO 10694	Total Organic Carbon by dry combustion
Total Nitrogen Content	ISO 13878 ISO 11261	Elemental analysis by dry combustion Modified Kjeldahl method
Exchangeable Acidity and Free H^+ Exchangeable Cations	ISO 14254 ISO 11260	Titration or German method Extraction by 0.1 M $BaCl_2$, single extraction
Aqua Regia Extractant Determinations	ISO 11466	Extraction by Aqua Regia
Reactive Fe and Al	ISRIC 1992	Extraction by Acid Ammonium Oxalate
Total Elements	ISO 14869 ISO 14869	Dissolution with hydrofluoric and perchloric acids Total element analysis by fusion with lithium metaborate

2.4 Statistical data analysis

2.4.1 General characteristics of the data analysis methodology

The aim of the statistical analysis is to answer the question "Which laboratories are performing well and which poorly?" based on the between-laboratory and the within-laboratory variance.

This analysis is 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, 1994). Data analysis was done by means of the statistical software package TIBCO Spotfire S$^+$ 8.1 for Windows (November 2008).

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

1. The interpretation of statistics has been facilitated by graphs integrating multiple statistical parameters.

2. The procedure is iterative. The presence of very deviant outliers can distort the view of the whole distribution. Multiple outliers can mask each other; by eliminating outliers, new outliers and stragglers may pop up. After outliers are eliminated, the statistical analysis is repeated to study the distributions in order to trace new outliers or stragglers. This iterative procedure will continue until no new outliers are found or in this ring test, up to a maximum of eight iterations.

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 under the same conditions (job done by one person, in the same laboratory, with the same equipment, at the same time or within 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, missing values and limits of quantification

In theory, reporting analytical results equal to 0 is not possible. Since there is always some uncertainty on the test result, very small values should be reported as being below the limit of quantification by reporting '< LOQ'. Sometimes it might be possible that artificially 0 values are created in the database due to rounding. This is for example the case for exchangeable Mn in sample C or E where several laboratories could measure below 0.01 cmol(+)/kg while the required detail of precision is only two decimal numbers. It was therefore recommended to increase the reporting precision up to three decimal places.

Due to the data formats of the database where the on-line submitted results were stored, missing values and reported zero values were all stored as the number '0'. This means that during the statistical analysis, it was not possible to distinguish between the different origins of these zero values. In the analyses, all zero values were removed from the dataset and considered as non reported values.

The calculation of the general cleaned mean was in rule based on the values of the really measured data. So LOQ values were not included. Theoretically, this will result in an overestimation of the cleaned mean. However, in practise the exercise was made where the cleaned means were once calculated including the LOQ values and once without. Difference in the cleaned means were generally minor except for the free H^+ on sample C where most labs reported below LOQ and the total Na on sample E. In these two cases the cleaned mean included the absolute values of the reported LOQ values.

So, when for a certain laboratory no statistical evaluation is available for a certain parameter, either the laboratory did not report that parameter, either the reported values were below the LOQ of that specific laboratory.

In the application of the tolerable limits, the LOQ values were however again included in the evaluation (see § 2.5). So the LOQ values were evaluated against the tolerable range.

All analyses had to be analysed in triplicate. When only one replicate was reported, this observation could not be included in the final evaluation of the inter- and intralaboratory variability for statistical reasons. When two observations have been reported, the parameter was included in the statistical analysis.

2.4.3 Coefficients of variation (CV)

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

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

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 among the different parameters, and rank the analysed parameters according to their CV.

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

2.5 Tolerable limits

At the meeting of the 14th Expert Panel on Soil and Soil Solution in April 2008 in Firenze, the members approved tolerable limits on the between laboratory variability to be applied from next ring test onwards.

The tolerable limits are a driving force towards reduced measurement uncertainty and increased comparability of the results among participating laboratories. With time, these tolerable limits should be narrowed in order to maintain their role as driver for quality improvement. This is possible when an increasing number of laboratories meet the quality requirements (De Vos, 2008).

The initial tolerable limits shown in Table 3 till 8 have been set to a z-score of 1 (± 1*SD). So theoretically 68 % of the labs will fall within these limits. Tolerable limits on the within-laboratory variability have been derived but are not yet applied in this ring test.

Table 3: Tolerable limits for soil moisture content, pH, total organic carbon (OC), total nitrogen (TotN) and carbonate for inter-laboratory comparison

Parameter	Observation Range	Level	Ring Test Tolerable limit (% of mean)
Moisture content (%)	lower	≤ 1.0	± 25
	higher	> 1.0	± 15
pH(H_2O)	whole	2.0 – 8.0	± 5
pH($CaCl_2$)	whole	2.0 – 8.0	± 5
OC g kg-1	lower	≤ 25	± 20
	higher	> 25	± 15
Total N g kg-1	lower	≤ 1.5	± 30
	higher	> 1.5	± 10
$CaCO_3$ g kg-1	lower	≤ 50	± 130
	higher	> 50	± 40

Table 4: Tolerable limits for exchangeable elements and free acidity for inter-laboratory comparison

Parameter	Observation Range	Level $_{(cmol(+).kg-1)}$	Ring Test Tolerable limit (% of mean)
Exch Acidity	lower	≤ 1.00	± 90
	higher	> 1.00	± 35
Exch K	lower	≤ 0.10	± 45
	higher	> 0.10	± 30
Exch Ca	lower	≤ 1.50	± 65
	higher	> 1.50	± 20
Exch Mg	lower	≤ 0.25	± 50
	higher	> 0.25	± 20
Exch Na	whole	0.01-0.14	± 80
Exch Al	lower	≤ 0.50	± 105
	higher	> 0.50	± 30
Exch Fe	lower	≤ 0.02	± 140
	higher	> 0.02	± 50
Exch Mn	lower	≤ 0.03	± 45
	higher	> 0.03	± 25
Free H^+	whole	0.02-1.20	± 100

Table 5: Tolerable limits for soil texture for inter-laboratory comparison

Parameter	Observation Range	Level (%)	Ring Test Tolerable limit (% of mean)
Clay content	lower	≤ 10.0	± 50
	higher	> 10.0	± 35
Silt content	lower	≤ 20.0	± 45
	higher	> 20.0	± 30
Sand content	lower	≤ 30.0	± 45
	higher	> 30.0	± 25

Table 6: Tolerable limits for aqua regia extractable elements for inter-laboratory comparison

Parameter	Observation Range	Level ($mg.kg^{-1}$)	Ring Test Tolerable limit (% of mean)
Extr P	lower	≤ 150	± 45
	higher	> 150	± 20
Extr K	lower	≤ 500	± 60
	higher	> 500	± 40
Extr Ca	lower	≤ 500	± 70
	higher	> 500	± 30
Extr Mg	lower	≤ 500	± 60
	higher	> 500	± 15
Extr S	whole	35 - 1300	± 35
Extr Na	lower	≤ 75.0	± 65
	higher	> 75.0	± 50
Extr Al	lower	≤ 2500	± 50
	higher	> 2500	± 20
Extr Fe	lower	≤ 2500	± 40
	higher	> 2500	± 15
Extr Mn	lower	≤ 150	± 30
	higher	> 150	± 15
Extr Cu	lower	≤ 5	± 40
	higher	> 5	± 15
Extr Pb	whole	3 - 70	± 30
Extr Ni	lower	≤ 10	± 40
	higher	> 10	± 15
Extr Cr	lower	≤ 10	± 40
	higher	> 10	± 25
Extr Zn	lower	≤ 20	± 40
	higher	> 20	± 20
Extr Cd	lower	≤ 0.25	± 100
	higher	> 0.25	± 55
Extr Hg	whole	0 - 0.16	± 75

Table 7: Tolerable limits for reactive iron and aluminium for inter-laboratory comparison

Parameter	Observation Range	Level (mg.kg^{-1})	Ring Test Tolerable limit (% of mean)
Reactive Al	lower	≤ 750	± 30
	higher	> 750	± 15
Reactive Fe	lower	≤ 1000	± 30
	higher	> 1000	± 15

Table 8: Tolerable limits for total elements for inter-laboratory comparison

Parameter	Observation Range	Level (mg.kg^{-1})	Ring Test Tolerable limit (% of mean)
Tot Al	Lower range	≤ 20000	± 35
	Higher range	> 20000	± 10
Tot Ca	Lower range	≤ 1500	± 20
	Higher range	> 1500	± 15
Tot Fe	Lower range	≤ 7000	± 20
	Higher range	> 7000	± 10
Tot K	Lower range	≤ 7500	± 15
	Higher range	> 7500	± 10
Tot Mg	Lower range	≤ 1000	± 60
	Higher range	> 1000	± 10
Tot Mn	Lower range	≤ 200	± 25
	Higher range	> 200	± 10
Tot Na	Lower range	≤ 1500	± 20
	Higher range	> 1500	± 10

After the calculation of the outlier free mean based on the iterative procedure described above, the tolerable ranges for each parameter and sample were calculated using the limits for the lower or higher range, depending on the mean level. Subsequently, it was checked whether the laboratory means were within these tolerable ranges.

When a laboratory reported values below the limit of quantification (LOQ), the LOQ was compared with the tolerable range. When the LOQ was within the tolerable range, the result was accepted. When the LOQ was below the tolerable range, the reported value was not accepted. When the LOQ was above the tolerable lower limit, the reported value was accepted but a remark was added to the qualification report that the LOQ reported by the laboratory was too high as the majority of the laboratories did manage to produce meaningful results.

2.6 Qualification report and requalification procedure

Based on the evaluation of the tolerable limits for the between-laboratory variability, individual laboratory qualification reports were generated. Together with the qualification report, the laboratory received a detailed report with the laboratory mean for each sample and parameter together with the tolerable ranges.

When less than 50% of the reported samples were within the preset tolerable range, the parameter was marked as 'not passed' or 'not qualified' and the laboratory had to requalify for this parameter if it wanted to report data to the central FutMon database in the course of the project.

The requalification procedure consisted of 1) identification of the problem, followed by 2) reanalysis of the ring test samples when necessary. Additional test material was available upon request. Non-FutMon laboratories were invited to follow the same procedure.

1) To identify the problem, FSCC asked the laboratory to fill in a questionnaire for each failed parameter. In case the results could be corrected without re-analysis, the laboratory had to sent FSCC its corrected results and the reason for failure of the original results. In case the corrected results were satisfactory, the laboratory received a positive requalification report.

2) Based on the answers to the questionnaire, FSCC could decide that re-analysis was necessary. Then the new results together with the original reports of the instruments and information about weight factors, dilution factors etc. had to be provided to FSCC. This was to prove that the reanalysis had actually been conducted and that the results were genuine. When the problem could not be solved in this way, a limited number of FutMon laboratories could make use of the laboratory assistance programme where a specialist was asked to visit the laboratory. The requalification report was provided by the beginning of December 2009 after positive decision by FSCC in consultation with the Working Group on QAQC in the labs.

3 Results and discussion

3.1 Participation

In total 52 laboratories registered the ring test and 51 laboratories received the samples. By the beginning of July, 50 laboratories, of which 41 FutMon laboratories, submitted their results. One non FutMon laboratory reported its first results only in November 2009 during the requalification period after the publication of the draft report. The results of this laboratory were evaluated against the tolerable limits but were not included in the statistical data analysis of this report.

The list of the participating laboratories can be consulted in Annex 1.

Table 9 gives an overview of the number of reported analyses. From the moment a value was reported it is included in the table, even when it was below the LOQ. A reported zero value has been considered as a missing value (hence not included) since the database receiving the input data did not distinguish between 'missing values' and 'zero values' as they were all stored as zero values.

In total 5 samples were included in the ring test, all analysed in triplicate. The top line of Table 9 indicates whether a parameter was mandatory or optional. The aqua regia extractable macronutrients (Ca, K, Mg and P) are mandatory on the organic samples but optional on the mineral soil samples.

It is clear that there are a high number of missing values in this table, although many of the parameters are mandatory. Sometimes this can be explained by the fact that some associated beneficiary contracted two laboratories to conduct the full list of mandatory analyses. For example, lab S02 and F18, or S33 and S08, or F21 and S34, or S03 and F19 worked complementary. Laboratory A43, A61, F12, etc… contracted the particle size analysis to one of the other successfully participating laboratories.

Four laboratories (F05, F18, F28 and S33) did not report the moisture content and lab F07 did report it only for the three mineral samples. Although this is not a parameter in the evaluation of the ring test, it is mandatory to measure since it is essential for the calculation of the results on oven-dry basis.

The determination of the $CaCO_3$ was only relevant for sample C which had a $pH(CaCl_2)$ = 7.0. For the other samples, most laboratories reported either nothing, or 'NA values' or values below the LOQ. A limited number of labs did however report real values (see further).

In the qualification reports, missing data on mandatory parameters will result in a non-qualification for this particular parameter and requalification will be necessary. So it should become clear from the follow up on this ring test how the grey zones will be filled in during the planned surveys.

Table 9: N° of reported results by the participating laboratories (green). When no results were submitted the cell is coloured grey.

LabID	FutMon	Moisture	Particle size clay	Particle size sand	Particle size silt	pHCaCl2	pHH2O	CaCO3	OC	Total N	Exchangeable Acidity	Exchangeable Al	Exchangeable Ca	Exchangeable Fe	Exchangeable K	Exchangeable Mg	Exchangeable Mn	Exchangeable Na	Free H	Extractable Al	Extractable Ca	Extractable Cd
Opt./Mand.		*M*	*M*	*M*	*M*	*M*	*O*	*M*	*M*	*M*	*M*	*M*	*M*	*M*	*M*	*M*	*M*	*M*	*M*	*O*	*M/O*	*M*
A39	*N*	15				15	15		15	15	15	13	15	15	15	15	12	15	15	15	15	15
A42	*Y*	15	9	9	9	15	15	3	15		12		15	3	15	15	15	15			12	9
A43	*Y*	15				15							15		15	15		15			15	
A47	*N*	15				15	15		15	15	15	15	15	15	15	15	15	15	15	15	15	15
A61	*Y*	15				15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15
A66	*N*	15	9	9	9	15	15	15	15	15	6	15	15		15	15		15		15	15	
A69	*Y*	15	9	9	9	15	15	3	15	15	15	15	15	6	15	15	15	12	11	15	15	15
A71	*N*	15				15	15		15	15	15	15	15	13	15	15	12	15	15			
F03	*Y*	15	9	9	9	15	15	3	15	15	15	15	15	15	15	15	15	15	15	15	15	15
F04	*Y*	15	9	9	9	15	15	15	15	15	15	15	15	15	15	15	15	15	15		15	15
F05	*Y*					15	15		15	15	15	15	15	15	15	15	15	15		15	15	15
F06	*Y*	15	9	9	9	15			15	15		15	15	15	15	15	15	15	13	15	15	15
F07	*Y*	9	9	9	9	15	15	3	15	15	15	15	15	15	15	15	15	15	12	15	15	15
F08	*Y*	15	9	9	9	15	15	15	15	15	15	15	15	15	15	15	15	15		15	15	15
F10	*Y*	15	6	9	9	15	15	15	15	15	12	15	15	15	15	15	11	15	9	15	15	15
F11	*Y*	15	9	9	9	15	15	3	15	15	15	15	15	15	15	15	15	15	15	15	15	15
F12	*Y*	15				15	15	3	15	15	15	15	15	15	15	15	15	15	12	15	15	15
F14	*Y*	15				15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15
F15	*Y*	15	9	9	9	15	15	3	15	15	12	15	15	15	15	15	15	15	15	15	15	15
F16	*Y*	15	9	9	9	15	15	3	15	15	15	15	15	15	15	15	15	15	15	15	15	15
F17	*Y*	15	9	9	9	15		3	15	15	15	15	15	15	15	15	15	15	15		15	15
F18	*Y*					15	15	6	15	15	15	15	15	15	15	15	15	15	15	15	15	15
F19	*Y*	15				15			15	15	15	15	15	15	15	15	15	15	15		15	15
F21	*Y*	15		9	9	15	15	3	15	15	15		15	15	15	15	15	15	15			
F23	*Y*	15	9	9	9	15		3	15	15	12	12	15	9	15	15	12	15	12	15	15	15
F24	*Y*	15	9	9	9	15	15	9		15	15	15	15	15	15	15	15	15	15		6	15
F25	*Y*	15	9	9	9	15	15	3	15	15	15	15	15	15	15	15	15	15	15	15	15	15
F26	*Y*	15	9	9	9	15	15	3	15	15	9	9	9	9	9	9	9	9			15	
F27	*Y*	15	9	9	9	15	15	3	15	15	12	9	15	6	15	15	12	14	12	15	15	15
F28	*Y*		9	9	9	15	15	3	15	15	12	15	15	15	15	15	15	15	12	15	15	15
F29	*Y*	15	9	9	9	15	15		15	15									15			15
F32	*Y*	15	9	9	9	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15
S01	*Y*	15	9	9	9	15	15	3	15	15	15	15	15	15	15	15	15	15	15	15	15	15
S02	*Y*	3	9	9	9																	
S03	*Y*	15	6	9	9	15	15			15	15	15	15	15	15	15	15	15	15			
S04	*Y*	15	9	9	9	15	15	3	15	15	15	15	15	15	15	15	15	15	15	15	15	15
S05	*Y*	15	9	9	9	15	15	3	15	15	15	15	15	15	15	15	15	15	15	15	15	15
S08	*Y*	15				15	15		15	15	15	15	15	15	15	15	15	15	15	15	15	15
S12	*N*	15	9	9	9	15	15		15		15	15	15	15	15	15	15	15				
S13	*N*	15	9	9	9	15	15	3	15	15	15	15	15	15	15	15	15	15	12	15	15	15
S14	*Y*	15	9	9	9	15		3	15	15	11		15	15	15	15	15	15	11		6	15
S16	*Y*	15	9	9	9	15	15	3	15	15											6	15
S17	*N*	15				15	15	6	15	15												
S18	*Y*	15				15	15	3	15	15	15	15	15	15	15	15	15	15	15	15	15	15
S20	*N*	15	9	9	9	15	15	15	15	15	15	15	15	15	15	15	15		15	15	15	15
S22	*N*	15				15	15	3														
S23	*Y*	15	9	9	9	15	15	3	15	15	15	15	15	15	15	15	15	15	15	15	15	15
S25	*Y*	15	9	9	9	15		15	15	15	15	15	15	15	15	15	15	15	15	15	15	15
S33	*Y*		9	9	9			3														
S34	*Y*	15										15								15	15	15
Total N°labs with results		46	34	35	35	47	40	37	43	43	41	40	43	41	43	43	41	42	37	32	41	39

Table 9 (continued): N° of reported results by the participating laboratories (green). When no results were submitted the cell is coloured grey.

LabID	*FutMon*	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	Total Al	Total Ca	Total Fe	Total K	Total Mg	Total Mn	Total Na
Opt./Mand.		*O*	*M*	*O*	*O*	*M/O*	*M/O*	*M/O*	*O*	*O*	*M/O*	*M*	*O*	*M*	*M*	*M*	*O*	*O*	*O*	*O*	*O*	*O*	*O*
A39	*N*	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15
A42	*Y*	9	15	15		15	15	15				15		15									
A43	*Y*		12	15		15	15	15				12		15									
A47	*N*	15	15	15		15	15	15	15	15	15	15	15	15			15	15	15	15	15	15	15
A61	*Y*	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15							
A66	*N*	12	15	15		15	15	15	12	15	15	15	6	15		3							
A69	*Y*	15	15	15		15	15	15		15	15	15		15	15	15							
A71	*N*														15	15							
F03	*Y*	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15							
F04	*Y*		15			15	15	15			15	15		15	15	15							
F05	*Y*	15	15	15		15	15	15	15	15	15	15	15	15									
F06	*Y*	15	15	15		15	15	15	15	15	15	15	15	15	15	15							
F07	*Y*	15	15	15		15	15	15	15	15	15	15	15	15	9	9							
F08	*Y*	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15
F10	*Y*		15	15		15	15	15	15		15	15		15	15	15							
F11	*Y*	15	15	15		15	15	15	15	15	15	15	15	15	9	9							
F12	*Y*	15	15	15		15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15
F14	*Y*	15	15	15		15	15	15	15	15	15	15	15	15	15	15							
F15	*Y*	15	15	15		15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15
F16	*Y*	15	15	15		15	15	15	15	15	15	15	15	15	15	15	9	9	9	9	9	9	9
F17	*Y*		15			15	15	15			15	15		15									
F18	*Y*	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15							
F19	*Y*		15			6	6	15			6	15		15	9	9							
F21	*Y*																						
F23	*Y*	15	15	15	15		15	15		15	15	15	15	15	15	15							
F24	*Y*		15			6	6	6			15	15	15	15	9	15							
F25	*Y*	15	15	15		15	15	15	15	15	15	15	15	15									
F26	*Y*		15			15	15	15			15	15		15									
F27	*Y*	15	15	15		15	15	15	15	15	15	15	15	15	15	15							
F28	*Y*	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15							
F29	*Y*		15								15	15		15									
F32	*Y*	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15
S01	*Y*	15	15	15	15	15	15	15		15	15	15	15	15	15	15							
S02	*Y*																						
S03	*Y*														15	15							
S04	*Y*	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	9	9	9	9	9	9	9
S05	*Y*	15	15	15	15	15	15	15	15	15	15	15	15	15									
S08	*Y*	15	15	15		15	15	15	15	15	15	15	15	15	15	15							
S12	*N*														15	15	9	9	9	9	9	9	9
S13	*N*	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	9	9	9	9	9	9	9
S14	*Y*		15			6	6	6			6	15		15		9							
S16	*Y*		15			6	6	6			6	15	15	15	15	15							
S17	*N*					15					15												
S18	*Y*	15	15	15		15	15	15	15	15	15	15	15	15	15	15							
S20	*N*	15	15	15	15		15	15		15	15	15		15									
S22	*N*																						
S23	*Y*	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15							
S25	*Y*	15	15	15	15	15	15	15	15	15	15	15		15									
S33	*Y*																						
S34	*Y*	15	15	15	15	15	15	15	15	15	15	15	15	15									
Total N°labs with results		32	42	34	16	40	41	41	28	31	41	42	30	42	31	33	10	10	10	10	10	10	10

3.2 Statistical data analysis

The data analysis produced for each parameter (each analysed element) and each sample (A, B, C, D and E) yields a total of 7 figures: one dot plot of all reported values, one histogram and one box plot of the mean of the three reported values, one histogram and one box plot of the standard deviations, and one Mandel's h and one Mandel's k plot. All these graphs are provided in Annex 3 in MS PowerPoint-presentations and in PDF-files on the attached CD-Rom, and are arranged by parameter group. Below the case of 'Total Organic Carbon' in sample A is shown as an example.

3.2.1 Exploratory Data Analysis

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

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

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

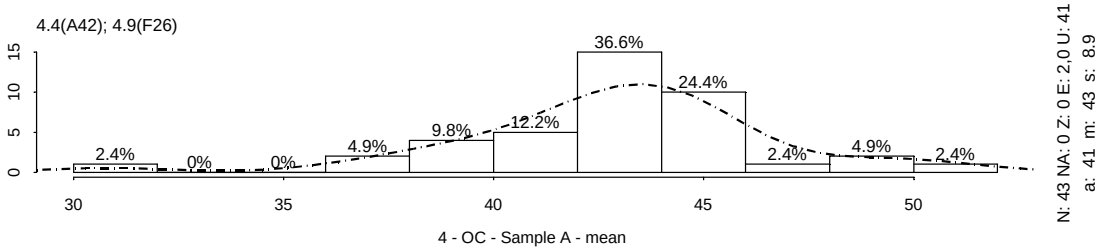

Figure 1: Histogram showing relative percentages and a rescaled density curve of the mean of three replicates of the measured parameter 'total organic carbon' in Sample A. The units of the X-axis are in g/kg.

The information in the box plot starts from the dataset after the first rough cleaning done in the histograms where the 'very deviant' outliers have been excluded. The box plot provides following information:

- 'Visual' outliers (parameter value and lab N° between parentheses). These are placed in the top left and top right corner of the figure. On the right side of the figure 'O' indicates the number of outliers excluded from the box plot, respectively on the lower and the higher range of the box-plot. So in this example, four outlying labs

have been identified in the box plot on the lower range and three on the upper range.

- The percentiles Q1 (25%) and Q3 (75%) coincide with the edges of the rectangular box and the 50 % percentile = Q2 = median is indicated by the black coloured dot.
- U: Number of observations in the box-plot where U=N-E in the histograms.
- Laboratories whose observations correspond to the median value, are put between brackets "< >"; observations between Q1 and Q2 are between "< <" and between Q2 and Q3 "> >".

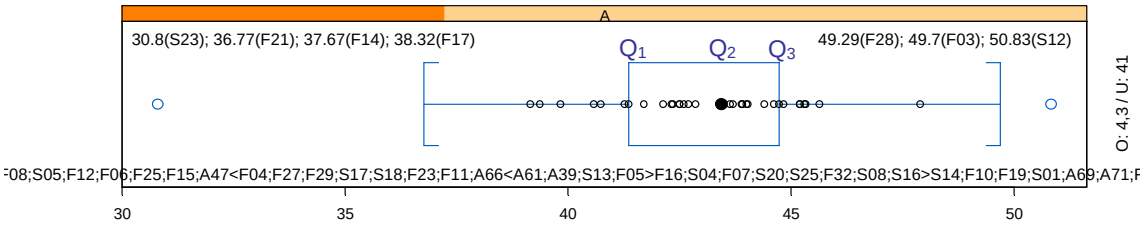

Figure 2: Box plot of the <u>mean</u> values reported for sample A for 'total organic carbon'. The units of the X-axis are in g/kg.

Both histograms and box plots show the distribution after exclusion of the 'very deviant' outliers. '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 (see Figure 2). In the box-plot the whiskers are placed at 1.5 * IQR. Observations outside the whiskers are the 'visual' outliers. It is possible that whiskers are placed on a closer distance than 1.5 * IQR in case there are no observations outside the 1.5 * IQR.

From the text on the right side of Figure 1 can be observed that the histogram is based on results from N=43 laboratories. None of the reported values, was a "0" (Z: 0). Two laboratories (A42 and F26) are excluded from the histogram, so the results of U=41 laboratories are included in the calculation of the general statistics. Laboratory A42 and F26 reported extremely lower TOC contents (4.4 and 4.9 g/kg whilst the average reported TOC content of sample A is a: 41 g/kg and the median TOC content is m: 43 g/kg and standard deviation s: 8.9 g/kg). In order to allow calculations of average, standard deviation and the Mandel's h and k statistics, data are supposed to have a normal distribution. The shape of the density curve (dotted line) should therefore approach the symmetrical shape of a normal distribution.

Figure 2 shows that the laboratories A61, A39, S13 and F05 reported the median value of 43 g/kg soil. Laboratories F04, F27, F29, S17, S18, F23, F11 and A66 reported values between the first quartile (Q1) and the median; laboratories F16, S04, F07, S20, S25, F32, S08 and S16 reported values between the median and the third quartile (Q3). Laboratories F08, S05, F12, F06, F25, F15 and A47 reported values below the first quartile (Q1) and laboratories S14, F10, F19, S01, A69, A71 and F18 reported values above the third quartile (Q3). The laboratories outside the 1.5 * IQR whiskers, are given with their laboratory number and average value above the box plot. Laboratories S23, F21, F14, and F17 reported very low and labs F28, F03 and S12 very high TOC contents.

Based on the histogram of the means (Figure 1) one would expect that laboratories A42 and F26 will be outliers in the in-depth statistical analysis for the between laboratory variability. Based on the box plot which is more severe (Figure 2), we see that also laboratories S23, F21, F14, F17, F28, F03 and S12 have doubtful results.

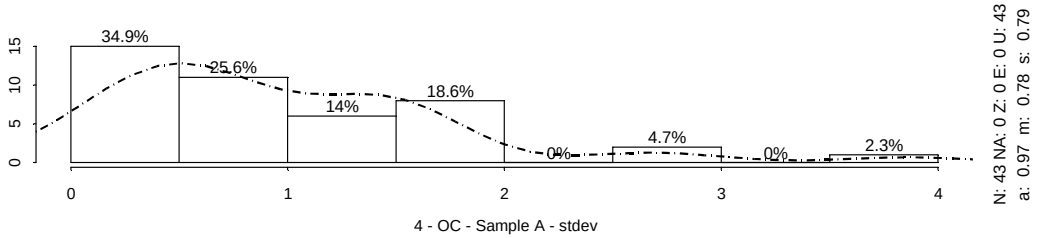

Figure 3: Histogram showing relative percentages and a rescaled density curve of the <u>standard deviation</u> of three replicates of the measured parameter 'total organic carbon' in Sample A. The units of the X-axis are in g/kg.

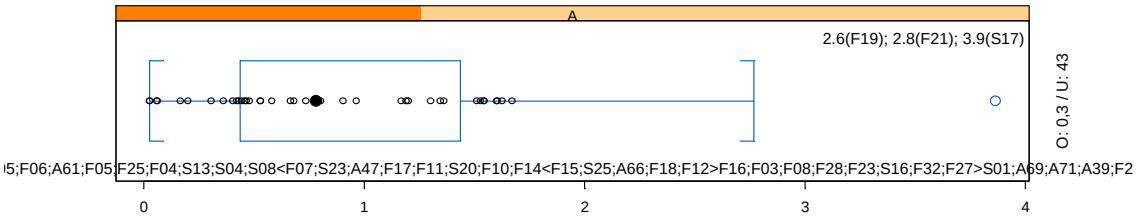

Figure 4: Figure 4: Box plot of the <u>standard deviations</u> reported for sample A for 'total organic carbon'. The units of the X-axis are in g/kg.

The histogram of the standard deviations (Figure 3) does not define any very deviant outliers for the within-laboratory variability. The more severe box plots show high within-laboratory variability for laboratories F19, F21 and S17.

A laboratory can also check its performance compared to the other laboratories by studying the dot plots (Figure 5). Every dot represents a reported value of a specific parameter. The shape of the dot plot follows the sigmoid curve shape of a normal distribution. Laboratories are plotted on the Y-axis, arranged according to the magnitude of the reported values. Two laboratories reported extremely deviant results for the TOC content of sample A. The values are given at the bottom of the graph Laboratory A42 reported 4.39, 4.40 and 4.44 g/kg and lab F26 reported 4.86, 4.87 and 4.91 g/kg. Values reported by other laboratories can be read on the X-axis.

This figure also tells something about the internal variance within one laboratory. For example, laboratories F21 and S17 reported three very different results – represented by 3 dots widely separated from each other – whereas laboratories S05 and F05 reported 3 very similar results – represented by 3 dots very close to each other. We expect that laboratory F21 and S17 will have a poor within-laboratory repeatability whereas laboratory S05 and F05 will have a very good within-laboratory repeatability.

For layout reasons, the dots of laboratories A42 and F26 have not been plotted. Their values are that deviant from the median value that showing these dots would completely disturb the figure. Therefore the reported values of laboratories A42 and F26 have been shown separately at the bottom of the figure.

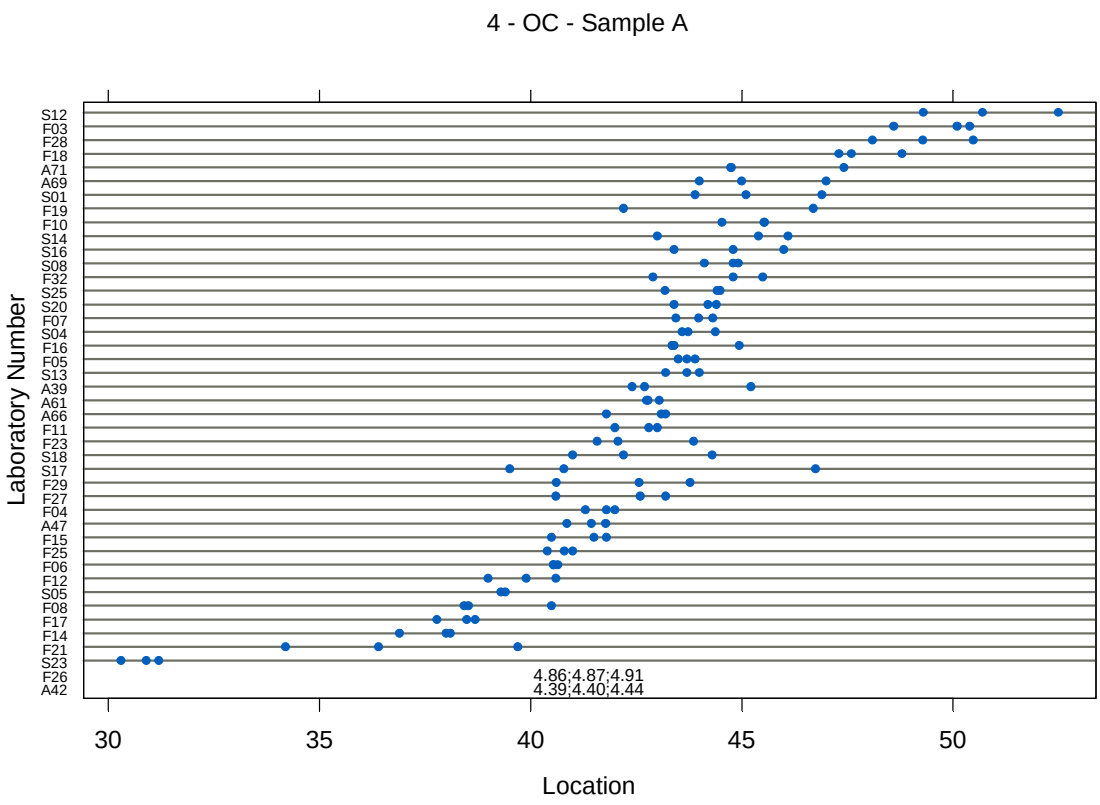

Figure 5: Dot plot of reported TOC values for sample A for each laboratory, ordered increasingly

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

Figure 6 presents an example of the Mandel's h and k plot for the TOC content of sample A. The Mandel's h statistic tests the between-laboratory variance. The Mandel's k statistic is a measure for the within-laboratory variance. The information contained within the two figures is:

- Step x: Iteration number of runs; varies in this interlaboratory comparison from 1 till maximum 8
- Nlab: Number of laboratories after elimination of outliers
- Mgen: General mean after outliers have been excluded
- Fval: tests whether interlaboratory variance $\sigma_L^2 \neq 0$, F test for laboratory effect
- Pval: tests whether interlaboratory variance $\sigma_L^2 \neq 0$, p value of the F test
- sRep^2: estimation of repeatability variance
- sLab^2: estimation of the between-laboratory variance
- sRepr^2: estimation of the reproducibility variance
- CV: coefficient of variation (σ/μ)*100 = sRepr/Mgen*100
- Excluded laboratories: excluded observations that are statistical outliers, mentioning whether it was based on the h or k statistic:
- "h (H) + Laboratory N°": laboratory has been excluded based on the Mandel's h statistics
- "k (K) + Laboratory N°": laboratory which has been excluded based on the Mandel's k statistics
- E: Excluded observations, mentioning whether it was based on the h or k statistics

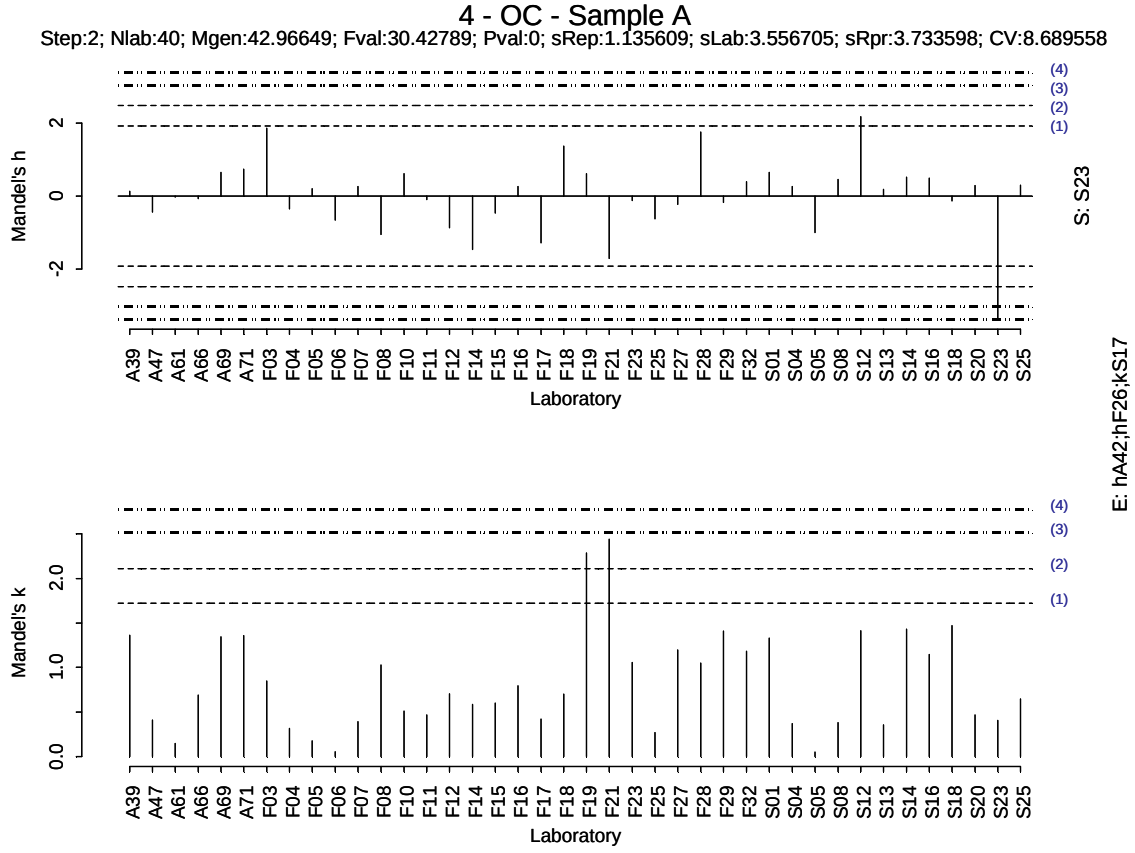

Figure 6: Mandel's h statistic for sample A for the TOC content

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

(1) Critical value where H_0 will be rejected at probability level of 95%
(2) Critical value where H_0 will be rejected at probability level of 99%
(3) Critical value where H_0 will be rejected at probability level of 95% after application of the Bonferroni rule.
(4) Critical value where H_0 will be rejected at probability level of 99% after application of the Bonferroni rule.

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

The Mandel's h statistic of laboratory S23 is low, but does not reach critical limit N° (4) (Figure 6). It is a straggler because the Mandel's k value is located between the critical value of the 95% and 99% confidence limits, and identified as such on the right side of the figure by the letter 'S' followed by the labID.

Laboratories A42 and F26 have been excluded from the statistical analysis based on the Mandel's h and laboratory S17 based on the Mandel's k statistics (see right side of Figure 6 'E'). In the exploratory study, Labs A42 and F26 were indeed excluded from the histogram of the means in Figure 1. Lab S17 was identified in the box plot of the standard deviations (Figure 4).

Labs F19 and F21 show a Mandel's k value between the critical levels (2) and (3). They are located in the tail of the distribution. In the box plot of the standard deviations (Figure 4) they were indeed already located outside 1.5 times the interquartile range.

Remarks:

1. 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').
2. Sometimes it happens that, when performing the check in subsequent steps, a laboratory which was an outlier before, suddenly is not an outlier any more. This is possible when many laboratories have been excluded from the population and confidence limits have become wider till the original outlier falls again within the normal population. In that case, the original exclusion is restored, indicated on the right side of the Figures showing the Mandel's h statistics, by the laboratory number, followed by a small 'k' or 'h'.

3.2.3 The outlier free mean (Mgen)

The Mgen value in the upper line of Figure 6 shows the general mean after outliers, either based on the Mandel's h or k statistics, have been excluded. A overview of the outlier free mean for each reported parameter and sample is given in Table 10. The outlier free mean is the best approximation that can be made of the real value of the sample. After the laboratories provide feedback and correct their results, the outlier free mean will be calculated again and will probably be slightly different from the figures presented at this moment.

In Figure 7 the mean % of outliers and stragglers for the five samples based on the Mandel's h is plotted against the mean % of outliers and stragglers based on the Mandel's k. The size of the 'bubbles' is a measure of the mean number of reported parameters for each laboratory. Laboratories that are located in the centre of the 'cloud' are performing normally well. Laboratories situated in the upper right corner of the graph, have performed poorly for the 6th FSCC Interlaboratory Comparison.

At the 12th Meeting of the Expert Panel on Soil and Soil Solution it was decided to identify those labs with more than 20% of their results outside the acceptable limits [outliers (o1) and stragglers (o5)] because they clearly have QA/QC problems and need follow-up.

In the upper right corner two laboratories are situated with more than 20% outliers and stragglers for both the within- and between-laboratory variability. These are labs S17 and F21. Both did report a relatively small number of parameters. Laboratory A42 reported more parameters but it is the worst performing laboratory concerning the between laboratory variability.

Other labs with 20% or more outliers and stragglers for the between laboratory variability are F26 and S34. Other labs with more than 20% outliers and stragglers for the within laboratory variability are F24, S33, S08 and S14.

Especially when zooming into the 0 - 10% range of the graph (Figure 8), it may be observed that the balance is in favour of the 'h strategist': 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 (indicated by a small Mandel's h statistic) than to focus on a low within-laboratory variability (indicated by a high Mandel's k statistic).

Table 10: The outlier free mean and number of laboratories (N°) included in the calculation of the outlier free mean for each parameter ad each sample

	Unit	Sample A		Sample B		Sample C		Sample D		Sample E	
Element		N¶abs	Mean	N¶abs	Mean	N¶abs	Mean	N¶abs	Mean	N¶a bs	Mean
Moisture	%	41	9.7	35	0.2	42	4.8	41	9.3	42	14.3
Particle size clay	%	34	20.8	30	2.9	33	36.7				
Particle size sand	%	32	27.6	32	86.2	31	36.9				
Particle size silt	%	31	50.7	34	11.0	33	24.7				
pHCaCl2		43	4.7	44	5.2	47	7.0	42	3.8	46	3.4
pHH2O		36	5.5	35	6.3	39	7.6	40	4.4	39	4.2
CaCO3	g/kg					33	10				
OC	g/kg	40	43.0	38	1.3	38	4.0	40	465.5	38	529.7
Total N	g/kg	40	2.7	34	0.13	43	0.4	42	18.0	42	30.1
Exchangeable Acidity	cmol(+)/kg	34	0.61	25	0.11	14	0.08	35	3.56	39	5.45
Exchangeable Al	cmol(+)/kg	34	0.32	25	0.05	14	0.05	33	0.43	35	2.76
Exchangeable Ca	cmol(+)/kg	36	17.25	38	0.89	43	27.31	41	20.33	40	16.94
Exchangeable Fe	cmol(+)/kg	15	0.010	15	0.009	12	0.009	37	0.07	36	0.24
Exchangeable K	cmol(+)/kg	37	0.24	33	0.05	37	0.27	38	1.23	27	0.07
Exchangeable Mg	cmol(+)/kg	38	3.80	38	0.08	41	3.84	40	2.12	38	1.22
Exchangeable Mn	cmol(+)/kg	40	0.18	39	0.021	10	0.004	38	1.73	20	0.007
Exchangeable Na	cmol(+)/kg	31	0.09	21	0.03	31	0.14	37	0.33	21	0.03
Free H	cmol(+)/kg	27	0.19	20	0.07	21	0.10	33	2.37	32	1.97
Extractable Al	mg/kg	31	54501.4	27	2722.4	29	45203.6	29	2148.2	30	3520.4
Extractable Ca	mg/kg	37	6251.7	33	314	37	9744.6	37	6226.7	38	4826.8
Extractable Cd	mg/kg	28	0.41	21	0.04	19	0.08	34	1.42	19	0.07
Extractable Cr	mg/kg	30	24.4	28	4.3	31	31.5	31	14.7	28	10.1
Extractable Cu	mg/kg	40	14.1	30	1.04	39	13.3	40	24	36	6.7
Extractable Fe	mg/kg	33	42994.2	29	2258.0	32	29373.4	33	14729.5	32	2678.9
Extractable Hg	mg/kg	15	0.099	12	0.017	9	0.017	15	0.268	15	0.069
Extractable K	mg/kg	34	715.9	33	316.4	31	5192.3	39	1800.8	24	64.55
Extractable Mg	mg/kg	33	3124.8	35	267.1	36	8786.9	39	776.7	31	202.12
Extractable Mn	mg/kg	35	1251.5	37	210.6	38	161.3	38	856.6	30	5.45
Extractable Na	mg/kg	28	773.7	18	22.6	24	139.9	24	110.8	20	48.4
Extractable Ni	mg/kg	28	6.6	27	2.9	28	18.0	29	7.4	29	5.9
Extractable P	mg/kg	34	276.5	31	43.1	32	115.1	37	748.6	39	947.7
Extractable Pb	mg/kg	38	40.9	27	2.6	34	15.0	41	71.3	28	3.2
Extractable S	mg/kg	23	306.9	20	20.8	22	61.9	26	1974.2	29	3127.3
Extractable Zn	mg/kg	40	81.4	35	6.5	38	52.5	39	336.3	27	4.0
Total Al	mg/kg	10	80430.0	9	11435.0	8	84304.2	6	4059.0	5	3850.2
Total Ca	mg/kg	10	17117.5	9	635.6	8	11043.6	5	6587.8	6	5002.0
Total Fe	mg/kg	9	64025.3	10	2713.2	10	31403.2	6	15417.3	5	2744.5
Total K	mg/kg	10	7489.4	10	8277.5	9	24936.5	6	2848.9	5	124.6
Total Mg	mg/kg	9	19118.7	9	380.6	10	9992.7	5	905.5	5	233.6
Total Mn	mg/kg	10	1697.0	10	218.8	10	187.6	5	857.7	5	8.4
Total Na	mg/kg	10	7712.5	9	1224.7	9	4456.1	6	326.1	6	87.6
Reactive Al	mg/kg	30	2852.2	29	271.3	31	839.2	26	650.7	27	2927.1
Reactive Fe	mg/kg	32	3270.0	28	339.1	30	865.2	27	1296.2	28	2401.0

As sample C is a slightly calcareous sample, containing 10 g/kg $CaCO_3$, the amount of acid exchangeable cations (exchangeable Al, Fe and Mn, free H^+ and exchangeable acidity) is very low.

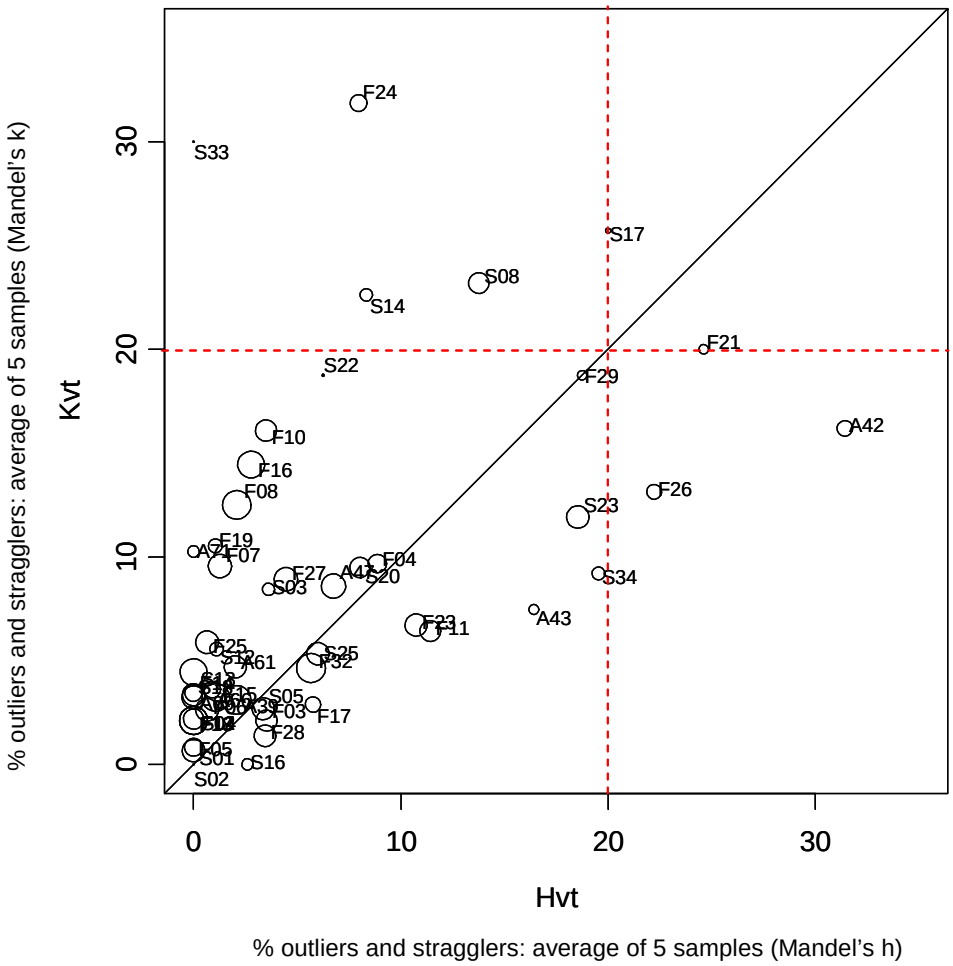

Figure 7: Bubble plot showing the 'h and k strategists.'

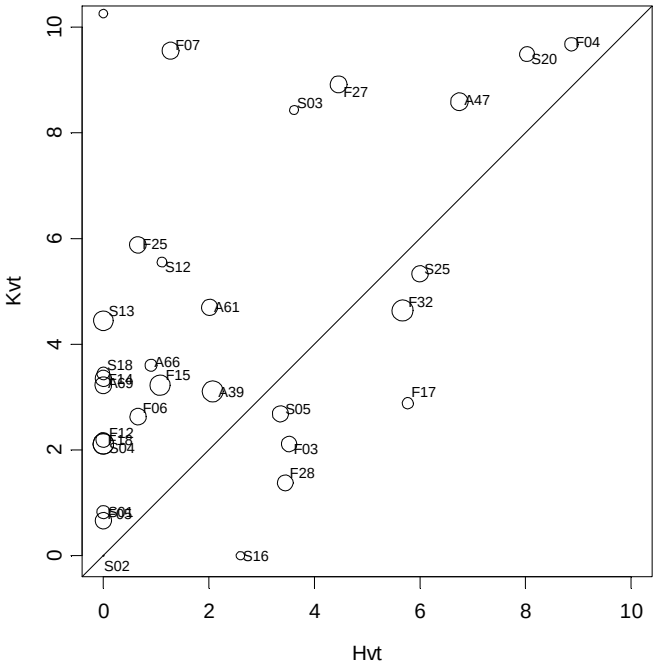

Figure 8: Bubble plot showing the 'h and k strategists' (zoomed on the 0 – 10% scale).

3.2.4 Coefficients of variation

The topline in Figure 6 also shows the coefficient of variation (CV) of the cleaned dataset. Table 11 provides the CV of each analysed parameter before and after the exclusion of the outliers. The last column of the table gives the CV by analysis group, calculated over all the samples. In the last row, the average CV by sample is given. The CV of the different samples are comprised between 19 and 27%.

The highest coefficients of variation are situated within the groups of the exchangeable and aqua regia extractable elements, for the latter especially in the peat sample. Many labs also faced difficulties with the $CaCO_3$ and OC content in the slightly calcareous sample C.

Table 11: Coefficients of variation in the 6th FSCC Interlaboratory Comparison 2009 (CV = sRepr/Mgen) before and after removal of the outliers

Element	M/O	Sample A		Sample B		Sample C		Sample D		Sample E		All samples		Group	
Moisture	M	15.7	6.5	90.4	26.6	16.0	9.5	22.1	22.4	19.4	15.8	33	16	33	16
Particle size clay	M	29.6	29.6	42.6	34.1	32.8	33.3					35	32		
Particle size sand	M	36.6	19.9	11.4	2.6	30.8	10.7					26	11	33	23
Particle size silt	M	17.0	12.2	52.2	19.5	43.5	43.5					38	25		
pHCaCl2	M	3.8	1.8	4.0	2.2	2.8	2.8	2.5	1.6	2.7	2.3	3.2	2.1	3.2	2.4
pHH2O	O	3.9	2.1	3.2	1.8	3.2	3.2	2.7	2.7	3.6	3.1	3.3	2.6		
CaCO3	M					110.3	61.30					110	61	110	61
OC	M	21.7	8.7	58.5	20.8	111.6	28.5	10.0	5.4	6.7	6.2	42	14	42	14
Total N	M	7.5	6.7	41.7	39.3	29.1	29.1	5.5	5.5	5.3	5.3	18	17	18	17
Exchangeable Acidity	M	116.5	43.2	104.1	65.6	150.3	69.8	58.3	47.9	65.3	54.4	99	56		
Exchangeable Al	M	42.1	36.4	78.3	74.7	107.1	102.9	70.8	43.5	46.0	47.1	69	61		
Exchangeable Ca	M	20.5	11.0	86.9	17.4	25.5	25.5	25.9	25.9	27.4	27.6	37	21		
Exchangeable Fe	M	89.8	74.4	109.2	86.6	96.4	95.9	60.2	60.2	38.4	38.3	79	71		
Exchangeable K	M	49.3	24.6	65.0	26.7	86.4	23.5	49.4	35.1	139.9	43.4	78	31	91	49
Exchangeable Mg	M	17.2	10.5	327.4	39.1	18.6	14.5	27.6	28.0	26.2	26.4	83	24		
Exchangeable Mn	M	48.3	28.2	39.7	26.3	130.0	72.4	30.7	31.0	382.8	41.5	126	40		
Exchangeable Na	M	107.0	26.5	205.4	100.4	83.7	16.9	78.2	42.4	190.0	45.8	133	46		
Free H	M	130.8	90.0	163.4	103.0	94.5	99.2	86.7	75.9	87.0	75.3	112	89		
Extractable Al	O	20.9	14.9	20.1	11.7	22.2	14.1	86.7	13.0	16.4	12.7	33	13		
Extractable Ca	M/O	21.8	14.5	41.5	19.8	18.8	9.8	33.8	10.2	34.7	17.7	30	14		
Extractable Cd	M	119.1	23.6	38.6	29.4	188.9	96.1	581.2	20.6	142.1	18.4	214	38		
Extractable Cr	O	18.8	15.2	24.9	17.6	16.3	15.8	25.4	25.4	21.8	13.6	21	18		
Extractable Cu	M	23.7	20.8	58.2	31.1	18.3	15.3	16.3	16.1	48.8	18.4	33	20		
Extractable Fe	O	23.0	16.3	42.8	4.4	17.8	10.7	36.1	17.2	64.8	10.0	37	12		
Extractable Hg	O	13.2	13.2	52.3	36.1	79.2	21.2	20.0	20.0	27.8	27.8	38	24		
Extractable K	M/O	70.5	32.1	38.1	21.1	44.3	13.7	59.6	22.4	262.2	33.4	95	25	63	21
Extractable Mg	M/O	24.9	10.6	27.7	9.5	17.1	12.4	33.3	17.6	108.0	10.4	42	12		
Extractable Mn	M/O	16.9	11.3	7.3	5.7	11.0	11.0	18.0	8.4	285.5	40.8	68	15		
Extractable Na	O	21.6	21.6	133.0	42.7	79.6	20.1	47.8	29.1	103.2	108.4	77	44		
Extractable Ni	O	25.1	25.5	16.1	16.2	17.5	10.7	15.3	14.9	17.8	17.4	18	17		
Extractable P	M/O	60.6	13.2	52.8	18.2	66.0	17.3	127.5	26.1	108.6	33.4	83	22		
Extractable Pb	M	21.5	15.6	160.0	14.4	53.0	19.3	15.4	12.9	188.8	20.4	88	17		
Extractable S	O	31.5	9.7	72.1	45.1	59.7	43.0	28.3	19.3	28.1	20.6	44	28		
Extractable Zn	M	12.9	12.0	98.3	13.5	16.3	12.1	15.6	11.0	311.5	46.3	91	19		
Total Al	O	15.0	15.0	7.3	5.7	24.2	4.3	15.3	15.3	4.7	1.7	13	8		
Total Ca	O	4.6	4.6	21.3	21.9	6.8	5.3	3.5	2.9	2.3	2.3	8	7		
Total Fe	O	5.6	5.6	9.8	9.8	9.9	9.9	23.6	23.6	4.1	4.3	11	11		
Total K	O	3.3	3.3	6.6	6.6	14.9	5.1	20.3	20.3	30.1	31.0	15	13	15	12
Total Mg	O	15.8	7.8	8.6	7.2	4.2	4.2	14.1	13.5	13.9	2.5	11	7		
Total Mn	O	8.9	8.9	9.2	9.2	8.3	8.3	4.3	4.3	65.6	20.6	19	10		
Total Na	O	4.4	4.4	10.6	9.5	6.3	3.3	36.0	36.0	78.0	78.0	27	26		
Reactive Al	M	11.0	11.0	21.2	12.3	12.2	12.2	20.1	10.2	13.1	13.1	15	12	17	13
Reactive Fe	M	14.5	13.7	24.4	10.3	24.5	21.5	15.4	11.8	10.4	10.4	18	14		
Average		**32.5**	**18.5**	**59.2**	**26.6**	**46.7**	**27.0**	**47.3**	**21.8**	**77.8**	**26.8**	**52.9**	**24.8**		

3.2.5 Identification of the problem parameters

Several indicators can be used to identify the problem parameters in this 6th FSCC Interlaboratory Comparison. Firstly, by studying the coefficients of variation of each parameter before and after the exclusion of the outliers, as shown in the table above. Secondly, based on the percentage of laboratories that for each parameter reported outlying results. So it is the proportion of laboratories which you need to remove from the population to come to a normal distribution without outliers. When more than 20% of the labs have been identified as outliers, it is indicated in Table 12 in bold italic underlined.

In the previous interlaboratory comparisons, these two indicators have been applied.

Especially for the sample E, the peat sample, the number of outlying laboratories was high for a substantial number of parameters. Most of the levels of these parameters are relatively

low compared to a 'normal' organic sample. Concerning the aqua regia extractable elements there were a high number of outlying laboratories for the heavy metals Cd, Zn and Pb.

Table 12: Percentage (%) of outlying laboratories (99 % confidence) by parameter and by sample

Parameter	A	B	C	D	E	average	average per group
Particle size clay	0	6	3			3	
Particle size sand	9	9	11			10	6
Particle size silt	11	3	6			7	
pH($CaCl_2$)	9	6	0	11	2	6	6
pH(H_2O)	10	13	3	0	3	6	
$CaCO_3$			6			6	6
OC	7	7	10	7	12	8	9
Total N	7	11	0	2	2	4	4
Exchangeable Acidity	11	7	18	13	3	10	
Exchangeable Al	11	11	7	11	10	10	
Exchangeable Ca	16	10	0	2	5	7	
Exchangeable Fe	17	6	14	0	10	9	
Exchangeable K	12	11	14	10	***23***	14	11
Exchangeable Mg	12	7	5	5	7	7	
Exchangeable Mn	2	5	***38***	3	***26***	15	
Exchangeable Na	16	16	***21***	5	***34***	18	
Free H	16	9	8	11	14	11	
Extractable Al	3	16	9	9	6	9	
Extractable Ca	3	6	3	10	7	6	
Extractable Cd	13	9	***21***	6	***21***	14	
Extractable Cr	6	3	3	0	10	5	
Extractable Cu	5	12	7	5	14	9	
Extractable Fe	3	15	6	3	6	6	
Extractable Hg	0	14	***36***	0	0	10	
Extractable K	6	8	14	3	***27***	12	9
Extractable Mg	11	5	3	5	***24***	10	
Extractable Mn	8	3	0	7	***21***	8	
Extractable Na	0	***22***	14	14	9	12	
Extractable Ni	7	4	10	3	3	5	
Extractable P	11	16	14	10	5	11	
Extractable Pb	10	18	19	2	20	14	
Extractable S	18	5	15	13	3	11	
Extractable Zn	5	15	10	7	***25***	12	
Total Al	0	10	20	0	17	9	
Total Ca	0	10	20	17	0	9	
Total Fe	10	0	0	0	17	5	
Total K	0	0	10	0	17	5	7
Total Mg	10	10	0	17	17	11	
Total Mn	0	0	0	17	17	7	
Total Na	0	10	10	0	0	4	
Reactive Al	3	6	0	4	0	3	4
Reactive Fe	3	13	6	4	0	5	

Thirdly one may consider the percentage of laboratories which failed to meet the tolerable limits. Using the latter indicator involves some risks. The tolerable limits have been fixed based on the mean coefficients of variation met in previous ring tests (De Vos, 2008). In the determination of these limits 12 mineral soil samples and three organic samples were involved. When we see in this ring test, a high number of laboratories not meeting the tolerable ranges, it might rather depend on the specific characteristics of the samples in this ring test than on the capacity of the laboratories to meet the quality requirements.

In the example of aqua regia extractable Cu, the proportion of laboratories showing outliers is on average not more than for other parameters. The mean CV of the 5 samples is 20% which is slightly below the group average. But on the other hand, the extractable Cu has the highest percentage of laboratories that fail to meet the tolerable limits. Note that compared to the other aqua regia extractable elements, the limits are relatively narrow.

On the opposite, only 5% of the laboratories failed to fall within the tolerable limits of Cd. On the other hand, the coefficient of the uncleaned data set was the highest amongst the ring test parameters. Also the percentage of excluded labs was amongst the highest.

So this ring test showed that laboratories faced the most difficulties meeting the tolerable limits for the parameters exchangeable acidity, aqua regia extractable Cu and a number of total elements but this evaluation does not necessarily indicate the variables with the largest variability.

Concerning aqua regia extractable Hg, and the total elements Ca and Mg, none of the laboratories failed which would be an argument to narrow the tolerable ranges of these elements toward the future. So it would be useful to calculate new tolerable limits including the results of the five test samples in this interlaboratory comparison.

3.2.6 Application of the tolerable limits

The tolerable ranges are calculated with reference to the outlier free mean. See Table 13.

Table 13: The tolerable ranges of the parameters analysed on 5 samples in the 6th FSCC Interlaboratory Comparison as applied in the qualification reports

	units	Sample A		Sample B		Sample C		Sample D		Sample E	
		lower	upper	lower	upper	lower	upper	lower	upper	lower	upper
Particle size clay	%	13.5	28.0	1.5	4.4	23.8	49.5				
Particle size sand	%	15.2	40.0	64.7	107.8	27.7	46.2				
Particle size silt	%	35.5	65.9	6.1	16.0	17.3	32.1				
pH($CaCl_2$)		4.47	4.94	4.98	5.51	6.67	7.37	3.65	4.04	3.25	3.60
pH(H_2O)		5.25	5.81	5.94	6.57	7.20	7.96	4.20	4.64	4.01	4.44
$CaCO_3$	g/kg					0	23				
OC	g/kg	36.5	49.4	1.1	1.6	3.2	4.8	395.7	535.4	450.3	609.2
Total N	g/kg	2.4	3.0	0.1	0.2	0.3	0.5	16.2	19.8	27.1	33.2
Exchangeable Acidity	cmol(+)/kg	0.06	1.15	0.01	0.21	0.01	0.14	2.31	4.80	3.54	7.36
Exchangeable Al	cmol(+)/kg	0	0.67	0	0.09	0	0.11	0	0.88	1.93	3.58
Exchangeable Ca	cmol(+)/kg	13.80	20.70	0.31	1.46	21.85	32.77	16.27	24.40	13.55	20.32
Exchangeable Fe	cmol(+)/kg	0	0.02	0	0.02	0	0.02	0.03	0.10	0.12	0.36
Exchangeable K	cmol(+)/kg	0.17	0.31	0.03	0.07	0.21	0.38	0.86	1.60	0.04	0.10
Exchangeable Mg	cmol(+)/kg	3.04	4.56	0.04	0.13	3.07	4.61	1.70	2.55	0.98	1.47
Exchangeable Mn	cmol(+)/kg	0.134	0.223	0.011	0.030	0.002	0.006	1.301	2.168	0.004	0.010
Exchangeable Na	cmol(+)/kg	0.02	0.17	0.01	0.05	0.03	0.25	0.07	0.60	0.01	0.08
Free H	cmol(+)/kg	0	0.38	0	0.14	0	0.20	0	4.74	0	3.94
Extractable Al	ppm	43601.1	65401.7	2177.9	3266.9	36162.9	54244.4	1074.1	3222.3	2816.3	4224.5
Extractable Ca	ppm	4376.2	8127.3	94.2	533.8	6821.2	12668.0	4358.7	8094.8	3378.7	6274.8
Extractable Cd	ppm	0.183	0.630	0	0.089	0	0.159	0.639	2.200	0	0.146
Extractable Cr	ppm	18.3	30.5	2.6	6.0	23.6	39.4	11.0	18.4	7.6	12.6
Extractable Cu	ppm	12.02	16.27	0.62	1.45	11.28	15.26	20.44	27.65	5.73	7.75
Extractable Fe	ppm	36545.1	49443.3	1354.8	3161.1	24967.4	33779.4	12520.1	16938.9	2277.1	3080.7
Extractable Hg	ppm	0.0248	0.1736	0.0041	0.0289	0.0042	0.0294	0.0671	0.4694	0.0172	0.1201
Extractable K	ppm	429.5	1002.2	126.6	506.3	3115.4	7269.3	1080.5	2521.2	25.5	102.0
Extractable Mg	ppm	2656.1	3593.5	106.8	427.4	7468.8	10104.9	660.2	893.2	81.1	324.5
Extractable Mn	ppm	1063.7	1439.2	179.0	242.2	137.1	185.5	728.1	985.1	3.8	7.1
Extractable Na	ppm	386.8	1160.5	7.9	37.3	70.0	209.9	55.4	166.3	16.9	79.8
Extractable Ni	ppm	4.0	9.3	1.8	4.1	15.3	20.6	4.5	10.4	3.5	8.2
Extractable P	ppm	221.2	331.8	23.7	62.5	63.3	166.9	598.9	898.4	758.1	1137.2
Extractable Pb	ppm	28.6	53.2	1.8	3.4	10.8	20.0	49.9	92.6	2.3	4.2
Extractable S	ppm	199.5	414.3	13.5	28.1	40.2	83.5	1283.2	2665.2	2032.7	4221.8
Extractable Zn	ppm	65.2	97.7	3.9	9.2	42.0	63.0	269.1	403.6	2.5	5.8
Total Al	ppm	76408.5	84451.5	7432.7	15437.2	80089.0	88519.4	2638.3	5479.6	2502.6	5197.7
Total Ca	ppm	14549.9	19685.2	508.5	762.8	9387.0	12700.1	5599.6	7575.9	4251.7	5752.3
Total Fe	ppm	60824.0	67226.5	2170.6	3255.8	29833.1	32973.4	14646.4	16188.1	2195.6	3293.4
Total K	ppm	6366.0	8612.8	7863.7	8691.4	23689.7	26183.4	2421.6	3276.3	105.9	143.3
Total Mg	ppm	18162.8	20074.6	152.2	608.9	9493.1	10492.4	362.2	1448.8	93.4	373.8
Total Mn	ppm	1612.2	1781.9	207.8	229.7	140.7	234.5	814.8	900.5	6.3	10.5
Total Na	ppm	7326.9	8098.1	979.8	1469.7	4233.3	4678.9	260.9	391.4	70.1	105.2
Reactive Al	ppm	2424.3	3280.0	189.9	352.7	713.3	965.0	455.5	845.9	2488.1	3366.2
Reactive Fe	ppm	2779.5	3760.5	237.4	440.9	605.6	1124.7	1101.8	1490.7	2040.8	2761.1

Note that these tolerable ranges depend directly on the reported results. When during the follow up, corrected results are reported, no new cleaned means and tolerable ranges were calculated in order to keep the same reference.

While all the participating laboratories received a personal qualification report with more detailed information on their laboratory mean evaluated against the tolerable range, this part of the report discusses the application of the tolerable limits by parameter.

Using the current set of tolerable limits, the percentage of laboratories that reported results for a certain parameter and that did not qualify, is shown in the last line of Table 14. So these laboratories had less than 50% of their results within the tolerable range.

Table 14: Percentage (%) of reported results within the tolerable limits for each laboratory and parameter.

LabID	FutMon	Particle size clay	Particle size sand	Particle size silt	pHCaCl2	pHH2O	CaCO3	OC	Total N	Exchangeable Acidity	Exchangeable Al	Exchangeable Ca	Exchangeable Fe	Exchangeable K	Exchangeable Mg	Exchangeable Mn	Exchangeable Na	Free H	Extractable Al	Extractable Ca	Extractable Cd	Extractable Cr
Opt./Mand.		*M*	*M*	*M*	*M*	*O*	*M*	*M*	*M*	*M*	*M*	*M*	*M*	*M*	*M*	*M*	*M*	*M*	*O*	*M/O*	*M*	*O*
A39	*N*				100	100		100	100	100	75	100	100	100	100	100	60	80	100	100	80	100
A42	*Y*	67	33	67	100	60	100	40		50		60	100	40	0	80	0			0	0	0
A43	*Y*				100							100		20	80		60			60		
A47	*N*				100	80		80	60	80	80	60	80	80	60	60	100	100	40	100	40	100
A61	*Y*				100	100	100	100	80	100	80	60	100	80	60	100	100	80	100	100	60	100
A66	*N*	100	100	100	100	100	100	100	100	100	100	60		80	80		100		100	100		50
A69	*Y*	100	100	100	100	100	100	100	80	100	100	100	50	100	80	100	100	100	100	100	100	100
A71	*N*				100	100		80	100	100	60	100	100	80	100	75	100	100				
F03	*Y*	100	100	100	80	80	0	80	100	60	80	80	100	80	20	100	100	60	20	100	100	100
F04	*Y*	100	100	100	100	20	100	100	40	40	100	80	80	0	60	60	20	40		100	80	
F05	*Y*				100	100		80	100	100	100	100	60	100	100	40	100		100	100	100	100
F06	*Y*	67	100	67	80			80	100		100	100	100	100	100	100	100	100	100	100	60	100
F07	*Y*	100	100	100	100	100	100	80	40	60	40	60	80	80	60	100	100	100	100	100	100	100
F08	*Y*	100	100	100	100	100	100	100	100	40	100	100	80	100	100	100	80		100	100	100	100
F10	*Y*	50	100	67	80	100	100	100	100	100	100	80	40	80	100	100	100	100	100	100	80	
F11	*Y*	100	100	100	100	80	0	100	100	60	100	100	100	100	80	100	100	60	60	60	80	60
F12	*Y*				100	100	100	100	100	80	100	100	80	100	100	100	100	100	100	100	100	100
F14	*Y*				100	100	100	100	100	80	100	100	100	60	100	100	100	100	100	100	100	100
F15	*Y*	0	100	67	100	100	100	100	100	75	100	100	100	100	100	100	100	100	100	100	100	100
F16	*Y*	67	100	100	100	100	100	80	100	0	100	100	100	100	60	80	80	100	100	100	100	40
F17	*Y*	0	67	67	80		0	80	60	60	100	100	100	100	80	80	100	100		100	100	
F18	*Y*				100	100	100	100	100	60	80	100	80	80	100	80	100	80	40	100	100	100
F19	*Y*				100			80	60	60	80	60	60	80	80	60	80	80		100	100	
F21	*Y*		33	67	80	20	100	80	60	0		60	60	40	40	80	20	0				
F23	*Y*	67	100	67	20		100	100	100	75	75	100	100	0	40	100	0	100	100	100	100	100
F24	*Y*	100	100	100	80	100	100		80	100	60	100	60	80	80	80	80	80		100	60	
F25	*Y*	100	100	100	100	100	100	100	100	80	100	60	100	100	60	100	100	100	80	100	80	100
F26	*Y*	100	100	67	80	100	100	40	80	67	100	33	100	100	33	33	0			80		
F27	*Y*	100	100	100	100	100	100	60	60	100	67	20	100	80	40	75	100	100	80	80	100	100
F28	*Y*	67	100	67	100	100	100	60	80	50	80	60	60	80	60	60	100	50	100	100	100	40
F29	*Y*	33	33	33	60	60		100	100									40			80	
F32	*Y*	100	100	100	80	100	100	100	100	40	100	100	80	100	100	100	100	40	100	100	100	100
S01	*Y*	100	100	100	100	100	100	80	100	100	80	60	80	80	80	60	100	100	80	100	100	60
S02	*Y*	100	100	100																		
S03	*Y*	100	100	100	100	100			80	60	80	100	100	80	80	20	100	40				
S04	*Y*	100	100	100	100	100	100	80	80	100	100	80	100	80	60	80	100	100	100	100	100	100
S05	*Y*	100	100	100	100	100	100	80	100	80	60	80	60	60	60	60	60	100	100	100	100	100
S08	*Y*				100	80		100	100	60	100	60	80	40	80	40	40	100	0	100	80	80
S12	*N*	67	100	100	100	80		40		60	80	80	100	80	80	100	100					
S13	*N*	100	100	100	100	100	100	100	80	80	80	60	100	100	60	100	100	100	100	100	100	100
S14	*Y*	100	100	100	60		100	100	100	100		80	100	100	100	100	100	100		0	80	
S16	*Y*	100	100	100	100	100	100	80	40											100	80	
S17	*N*				100	100	100	60	60													
S18	*Y*				100	100	100	100	60	60	80	80	100	100	80	80	100	80	100	100	100	100
S20	*N*	100	67	67	100	80	100	60	40	40	100	20	100	80	60	80		80	100	100	100	100
S22	*N*				100	80	100															
S23	*Y*	33	33	0	100	100	100	80	60	60	40	40	100	0	100	40	100	60	100	80	60	40
S25	*Y*	100	100	100	100		100	100	80	40	80	0	60	0	0	0	60	100	100	100	100	100
S33	*Y*	67	100	100			100															
S34	*Y*										40								40	60	100	60
% failed labs		15	11	6	2	5	8	7	9	22	8	12	5	19	16	15	14	16	16	5	5	16

Legend:

Dark green: all the reported results for the concerning parameter were within the tolerable range

Light green: 50% or more of the reported results for the concerning parameter were within the tolerable range

Orange: Less than 50% of the reported values for the concerning parameter were within the tolerable range. When the cells do not contain any value, no results were reported.

Table 14 (continued): Percentage (%) of reported results within the tolerable limits for each laboratory and parameter.

LabID	FutMon	Extractable Cu	Extractable Fe	Extractable Hg	Extractable K	Extractable Mg	Extractable Mn	Extractable Na	Extractable Ni	Extractable P	Extractable Pb	Extractable S	Extractable Zn	Reactive Al	Reactive Fe	Total Al	Total Ca	Total Fe	Total K	Total Mg	Total Mn	Total Na
Opt./Mand.		M	O	O	M/O	M/O	M/O	O	O	M/O	M	O	M	M	M	O	O	O	O	O	O	O
A39	N	60	80	100	100	100	100	100	100	100	100	60	80	100	100	60	100	40	60	80	80	40
A42	Y	20	0		20	0	20				40		40									
A43	Y	25	60		40	60	80				25		60									
A47	N	100	100		100	80	100	60	100	100	20	80	80			60	100	40	60	80	20	80
A61	Y	80	60	100	100	100	100	100	100	80	60	100	100	100	100							
A66	N	60	80		100	80	60	100	80	100	100	100	100		100							
A69	Y	60	100		100	100	80		80	100	100		100	100	100							
A71	N													100	100							
F03	Y	40	60	100	80	100	80	80	100	100	100	100	100	40	60							
F04	Y	0			100	40	80			100	40		40	100	80							
F05	Y	60	100		100	100	100	80	100	100	100	100	100									
F06	Y	100	100		100	100	80	100	100	100	100	100	100	100	100							
F07	Y	60	40		100	100	80	40	80	100	100	100	80	100	33							
F08	Y	100	100	100	100	100	100	100	100	100	100	100	100	40	60	80	100	60	40	80	80	60
F10	Y	60	40		100	100	40	80		80	100		100	100	100							
F11	Y	100	60		60	60	60	60	100	60	60	60	60	100	100							
F12	Y	80	100		100	100	100	100	100	100	100	100	80	100	100	80	100	80	100	100	80	80
F14	Y	80	100		100	80	80	100	80	100	100	100	80	100	100							
F15	Y	100	100		80	100	100	100	100	80	100	80	80	100	100	100	100	100	80	80	100	40
F16	Y	0	80		100	100	80	40	40	60	100	100	80	100	100	100	100	67	67	67	67	100
F17	Y	100			40	100	100			100	100		80									
F18	Y	100	60	100	100	60	100	60	100	100	100	100	100	60	40							
F19	Y	100			100	100	100			100	80		80	67	33							
F21	Y																					
F23	Y	60	80	100		80	100		100	100	100	0	80	80	40							
F24	Y	0			100	50	100			80	0	60	100	100	80							
F25	Y	60	100		100	100	100	80	100	100	80	100	80									
F26	Y	60			80	60	40			0	40		20									
F27	Y	80	100		80	100	80	100	100	40	100	60	100	100	100							
F28	Y	100	100	100	100	80	80	100	100	80	100	60	80	100	100							
F29	Y	60								20	80		100									
F32	Y	20	100	100	100	100	100	100	80	100	100	80	40	100	100	80	100	60	60	60	60	60
S01	Y	100	80	100	100	80	100		100	60	100	80	100	100	100							
S02	Y																					
S03	Y													80	60							
S04	Y	80	80	100	100	80	100	100	100	100	100	100	80	60	100	33	67	100	67	67	67	100
S05	Y	80	100	100	100	100	80	100	80	100	100	80	80									
S08	Y	60	40		0	40	60	60	40	60	80	40	80	100	100							
S12	N													80	80	33	67	100	33	100	33	100
S13	N	100	80	100	100	100	100	100	80	100	80	100	100	100	100	100	100	100	100	67	100	100
S14	Y	40			100	50	50			0	60		60		0							
S16	Y	60			100	100	50			100	60	100	80	100	100							
S17	N				20					0												
S18	Y	40	100		100	100	100	100	100	60	100	100	100	100	100							
S20	N	100	80	60		80	60		100	100	100		60									
S22	N																					
S23	Y	20	100	100	80	80	80	20	0	60	60	0	60	80	80							
S25	Y	60	80	100	80	100	60	100	100	100	100		80									
S33	Y																					
S34	Y	40	80	60	100	20	40	20	100	80	100	0	20									
% failed labs		26	12	0	12.5	14.6	14.6	14	9.7	12.2	14	13	12	6.5	13	20	0	20	20	0	20	20

Legend:

Dark green: all the reported result for the concerning parameter were within the tolerable range

Light green: 50% or more of the reported results for the concerning parameter were within the tolerable range

Orange: Less than 50% of the reported values for the concerning parameter were within the tolerable range. When the cells do not contain any value, no results were reported.

The following graph provides a ranking of the laboratories based on the number of reported and qualified parameters.

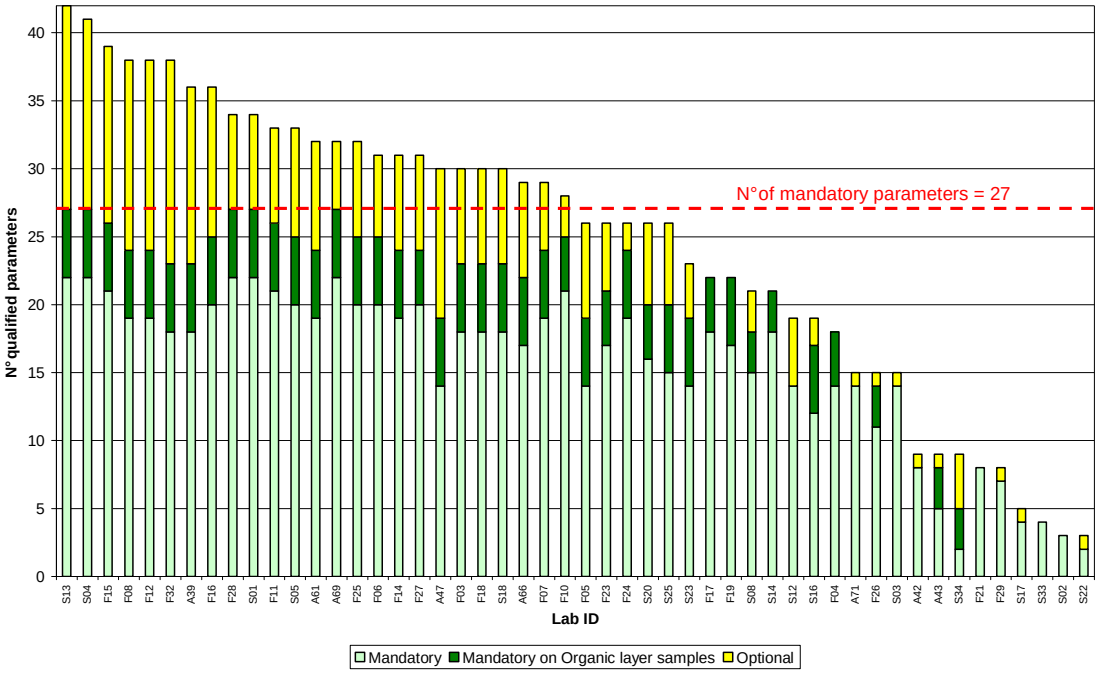

Figure 9: Ranking of the laboratories based on N° of qualified parameters in the 6th FSCC Interlaboratory comparison

Dark green: mandatory in organic layer but optional in mineral. These are the macro-nutrients Ca, K, Mg, Mn and P determined by aqua regia analysis.

One laboratory qualified immediately for all mandatory and optional parameters (Lab S13). Three additional laboratories qualified immediately for all their reported parameters (A69, S01, S13). Two more labs qualified immediately for all mandatory parameters (S04, F28). Two labs participated only for textural analysis (and $CaCO_3$) while another lab in the same country analysed the other parameters (S33 and S02). S03 did the analysis together with F19 but it is not clear which lab was responsible for which analysis. It is possible that some labs did not qualify for certain parameters because they simply did not report any results for the concerning parameter.

From this figure it is clear that further improvement is still possible. The first objective should be that all laboratories manage to meet the agreed quality requirements of at least the mandatory parameters.

3.2.7 Number of non qualified laboratories/parameters after requalification

After requalification, 16 laboratories could qualify for all the mandatory parameters and for the reported optional parameters: Lab A69, F08, F10, F23, F24, F25, F27, F28, F32, S01, S04, S13, S16, S18 and S23. Lab S33 and S02 are subcontracted to another lab for a limited number of analyses and qualified for all their conducted analyses.

This means that 33 laboratories listed in the figure below could not qualify by the end of 2009 for at least one mandatory parameter. A number of the poor performing laboratories are not participating in the EU Life+ FutMon programme (S17, S22, A39, A40, A47, A66, A71, S12, S20). Lab A43 is already subcontracting a well performing laboratory for the parameters that they cannot analyse.

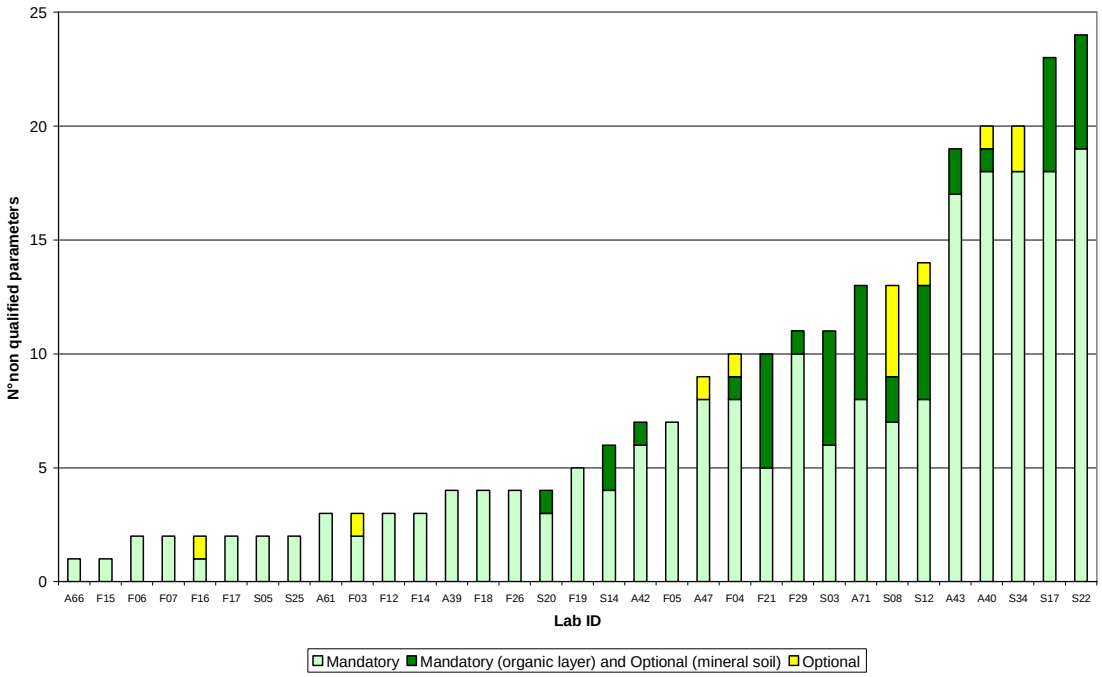

Figure 10: Ranking of laboratories that did not requalify for at least one mandatory parameter by the end of 2009

3.3 Soil analytical methods

3.3.1 Sieving and milling

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

It is clear from Table 15 that this rule was respected by most of the laboratories. However, for the aqua regia extractable elements, three laboratories (F08, F25 and F29) did further mill the samples.

One laboratory (F26) did report to mill the samples before the determination of the particle size distribution which is highly questionable. However, for lab F26 the silt content in sample C was the only real outlier while the sand content of the same sample was identified as a straggler.

While for the total elements (Al, Ca, Fe, K, Mg, Mn, Na) the sample had to be milled, this was only done by five out of ten laboratories that reported these elements.

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

3.3.2 Removal of compounds

The removal of certain compounds such as organic matter, carbonates and salts as a pre-treatment prior to the determination, is mainly relevant for the particle size distribution. According to the Manual (FSCC and Expert Panel on Soil and Soil Solution, 2006, SA03, ISO

11277) all cementing materials such as organic matter, salts, iron oxides and carbonates should be removed. This is of paramount importance to have a complete dispersion of the primary particles.

Table 16 shows that there is a high difference in this pre-treatment amongst the participating laboratories. Ten laboratories did not respect this rule and did not do any additional pre-treatment. Twelve laboratories removed the organic matter and two laboratories the carbonates. Six labs removed organic matter and the carbonates and 4 labs also removed the soluble salts and gypsum which were probably only present in negligible amounts.

Note that for the determination of the aqua regia extractable elements, the amount of aqua regia is sufficient for the oxidation of about 0.5 g of organic carbon in a 3 g sample, so 16.6%. So this would mean that it was necessary to add additional nitric acid in the determination of the aqua regia extractable elements of the organic samples D and E. Due to the submission format of the reported methods, i.e. asked once for all samples, it was however not possible to report in such a detail on the methods used in this interlaboratory comparison.

For the total elements determined by the method SA12A (dissolution with hydrofluoric and perchloric acids), it is necessary to pre-treat the sample to destroy the organic matter. When using method S12B the organic matter should be destroyed by pre-ignition at 850°C.

Table 15: Methods used for sieving and milling in the 6th FSCC Interlaboratory Comparison

PARAMETER	A39	A42	A43	A47	A61	A66	A69	A71	F03	F04	F05	F06	F07	F08	F10	F11	F12	F14	F15	F16	F17	F18	F19	F21	F23	F24	F25	F26	F27	F28	F29	F32	S01	S03	S04	S05	S08	S12	S13	S14	S16	S17	S18	S20	S22	S23	S25	S33	S34
Moisture	0	0	0	0	0	0	0	0	0	0		0	0	0	0	0	2	0	0	0	0		0	0	0	0	0	0	0		0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0		0
Particle size clay		0				0	0		0	0		0	0	0	0	0			0	0	0				0	0	0	2	0	0	0	0	0	0	0	0		0	0	0	0			0		0	0	0	
Particle size sand		0				0	0		0	0		0	0	0	0	0			0	0	0			0	0	0	0	2	0	0	0	0	0	0	0	0		0	0	0	0			0		0	0	0	
Particle size silt		0				0	0		0	0		0	0	0	0	0			0	0	0			0	0	0	0	2	0	0	0	0	0	0	0	0		0	0	0	0			0		0	0	0	
pHCaCl2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0		
pHH2O	0	0		0	0	0	0	0	0	0	0		0	0	0	0	0	0	0	0		0		0		0	0	0	0	0	0	0	0	0	0	0	0	0			0	0	0	0	0	0			
CaCO3		0			2	0	0		0	0			2	0	0	0	2	0	2.2	0	2	0		0	0	0	0	0	0	1		0	0		2.2	2.2			0	1	0	0	0	0	0	0	0	0	0	
OC	0	0		0	2	0	0	0	0	0	0	0	2	2.1	0	0	2	0	2.2	2.2	2	0	0	0	2.2		2	0	0	1	2.1	0	0		2.2	2.2	2	2.2	1	2.2	0	0	0	0		0	0		
Total N	0			0	2	0	0	0	0	0	0	0	2	2.2	0	0	2	0	2.2	2.2	2	0	0	0	2	0	2	2	0	1	2.1	0	0	0	2.2	2.2	2		1	2.2	0	0	0	0		0	0		
Exchangeable Acidity	0	0		0	0	0	0	0	0	0			0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0		0	0	0	0	0	0	0	0	0			0	0	0	0		
Exchangeable Al	0			0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0		0	0	0	0	0	0		0	0	0	0	0	0	0	0				0	0	0	0		0
Exchangeable Ca	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0		0	0	0	0	0	0	0	0	0			0	0	0	0		
Exchangeable Fe	0	0		0	0		0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0		0	0	0	0	0	0	0	0	0			0	0	0	0		
Exchangeable K	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0		0	0	0	0	0	0	0	0	0			0	0	0	0		
Exchangeable Mg	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0		0	0	0	0	0	0	0	0	0			0	0	0	0		
Exchangeable Mn	0	0		0	0		0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0		0	0	0	0	0	0	0	0	0			0	0	0	0		
Exchangeable Na	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0		0	0	0	0	0	0	0	0	0			0		0	0		
Free H	0			0	0		0	0	0	0		0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0		0	0	0	0	0	0	0		0	0				0	0	0	0		
Extractable Al	0			0	0	0	0		0		0	0	0	2.2	0	0	0	0	0	0		0		0		0	2		0	0		0	0		0	0	0		0				0	0	0	0		0
Extractable Ca	0	0	0	0	0	0	0		0	0	0	0	0	2.2	0	0	0	0	0	0	0	0	0		0	0	2	0	0	0		0	0		0	0	0		0	0	0		0	0	0	0		0
Extractable Cd	0	0		0	0		0		0	0	0	0	0	2.2	0	0	0	0	0	0	0	0	0		0	0	2		0	0	2.1	0	0		0	0	0		0	0	0		0	0	0	0		0
Extractable Cr	0	0		0	0	0	0		0		0	0	0	2.2		0	0	0	0	0		0			0		2		0	0		0	0		0	0	0		0				0	0	0	0		0
Extractable Cu	0	0	0	0	0	0	0		0	0	0	0	0	2.2	0	0	0	0	0	0	0	0	0		0	0	2	0	0	0	2.1	0	0		0	0	0		0	0	0		0	0	0	0		0
Extractable Fe	0	0	0	0	0	0	0		0		0	0	0	2.2	0	0	0	0	0	0		0			0		2		0	0		0	0		0	0	0		0				0	0	0	0		0
Extractable Hg	0			0					0					2.2								0			0					0	0		0				0					0		0	0		0
Extractable K	0	0	0	0	0	0	0		0	0	0	0	0	2.2	0	0	0	0	0	0	0	0	0			0	2	0	0	0		0	0		0	0	0		0	0	0	0	0		0	0		0
Extractable Mg	0	0	0	0	0	0	0		0	0	0	0	0	2.2	0	0	0	0	0	0	0	0	0		0	0	2	0	0	0		0	0		0	0	0		0	0	0		0	0	0	0		0
Extractable Mn	0	0	0	0	0	0	0		0	0	0	0	0	2.2	0	0	0	0	0	0	0	0	0		0	0	2	0	0	0		0	0		0	0	0		0	0	0		0	0	0	0		0
Extractable Na	0			0	0	0			0		0	0	0	2.2	0	0	0	0	0	0		0					2		0	0		0			0	0	0		0				0	0	0	0		0
Extractable Ni	0			0	0	0	0		0		0	0	0	2.2		0	0	0	0	0		0			0		2		0	0		0	0		0	0	0		0				0	0	0	0		0
Extractable P	0			0	0	0	0		0	0	0	0	0	2.2	0	0	0	0	0	0	0	0	0		0	0	2	0	0	0	2.1	0	0		0	0	0		0	0	0	0	0	0	0	0		0
Extractable Pb	0	0	0	0	0	0	0		0	0	0	0	0	2.2	0	0	0	0	0	0	0	0	0		0	0	2	0	0	0	2.1	0	0		0	0	0		0	0	0		0	0	0	0		0
Extractable S	0			0	0	0			0		0	0	0	2.2		0	0	0	0	0		0			0	0	2		0	1		0	0		0	0	0		0				0		0	0		0
Extractable Zn	0	0	0	0	0	0	0		0	0	0	0	0	2.2	0	0	0	0	0	0	0	0	0		0	0	2	0	0	0	2.1	0	0		0	0	0		0	0	0		0	0	0	0		0
Total Al	0			0										2.2			2		0	0											0			2.2			2.2	1										
Total Ca	0			0										2.2			2		0	2.2											0			2.2			2.2	1										
Total Fe	0			0										2.2			2		0	2.2											0			2.2			2.2	1										
Total K	0			0										2.2			2		0	2.2											0			2.2			2.2	1										
Total Mg	0			0										2.2			2		0	2.2											0			2.2			2.2	1										
Total Mn	0			0										2.2			2		0	2.2											0			2.2			2.2	1										
Total Na	0			0										2.2			2		0	2.2											0			2.2			2.2	1										
Reactive Al	0				0		0	0	0	0		0	0	0	0	0	0	0	0	2.2		0	0		0	0			0	0		0	0	0	0		0	0	0		0		0		0				0
Reactive Fe	0				0	0	0	0	0	0		0	0	0	0	0	0	0	0	0		0	0		0	0			0	0		0	0	0	0		0	0	0	0	0		0		0				0

Legend: 1= Crushing; 2= Milling (2.1 to 150 µm and 2.2 as fine as possible); 9 = Other method; 0 = No information because done by FSCC.

3.3.3 Pre-treatment

The pre-treatment describes the extraction/dissolution/digestion procedure. So concerning pH, the extract should have been specified in this submethod which was either not well explained to or understood by a number of laboratories.

From Table 17, it seems that three laboratories use the Walkley and Black method for the determination of the total organic carbon content which is not the reference method.

When the total nitrogen was measured by the modified Kjeldahl method, the extract and the catalyst should have been reported here.

For the exchangeable elements, the single $BaCl_2$ extraction method had to be used. Six laboratories however followed the ISO method and applied the triple $BaCl_2$ extraction. One laboratory (F15) used a $CaCl_2$ extraction and one laboratory (S08) made the free H^+ and exchangeable acidity titration on a KCl extract.

The majority of the laboratories used the reflux system to digest the soil samples in aqua regia. However six laboratories digested the soil samples using a closed microwave system where we would expect that the results will be higher. Laboratory S17 did not further specify which extraction procedure they followed.

Total elements, which are optional, have been reported by 10 laboratories but amongst these labs, 6 different extraction/digestion methods have been used.

Concerning the acid oxalate extractable Al and Fe, only one method is available. The reporting of method '1' by lab S34 is an error since the laboratory did not report any values for these two variables.

3.3.4 Determination methods

The methods used for the final determination are shown in Table 18.

Four laboratories did not provide the method of the determination of the particle size distribution, 26 labs use the pipette method, three labs reported to use another detection method. One laboratory used laser diffraction for the clay and silt content while it measured the sand content gravimetrically. At the meeting of the heads of the laboratories (Warsaw, 2009) it was once more confirmed that the laser diffraction method cannot be used as this method does not give comparable results with the pipette method.

Thirthy-five out of the 43 laboratories measured the total organic carbon by elemental analysers. So eight laboratories (19%) still do not use the reference method which is a relatively high number for a very important and common analysis.

For the measurement of the exchangeable, aqua regia extractable, and acid oxalate elements, the majority of the laboratories use an ICP-AES.

The colour coding in Table 18 allows the reader to detect those laboratories whose methods clearly deviate from the majority of the labs which are using the reference methods. For example, although laboratory F29 is a FutMon laboratory, it analyses only a limited number of parameters and mostly according to different methods.

Table 16: Methods used for removal of compounds prior to the pre-treatment and the determination method in the 6th FSCC Interlaboratory Comparison

PARAMETER	A39	A42	A43	A47	A61	A66	A69	A71	F03	F04	F05	F06	F07	F08	F10	F11	F12	F14	F15	F16	F17	F18	F19	F21	F23	F24	F25	F26	F27	F28	F29	F32	S01	S03	S04	S05	S08	S12	S13	S14	S16	S17	S18	S20	S22	S23	S25	S33	S34
Moisture	1	1	1	1	1	1	1	1	1	1		1	1	1	1	1	1	1	1	1	1		1	1	1	1	1	1	1		1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1		1
Particle size clay		6				6	2		5	2		2.1	5	1	5	4			5	6	1				1	2	2	1	1	4.1	1	1	2	2	1	2		2	2.1	2.1	2.1			1		5	1	5	
Particle size sand		6				6	2		5	4.1		2.1	5	1	1	4			5	6	1			6	1	2	2	1	1	4.1	1	1	2	2	1	2		2	2.1	2.1	2.1			1		5	1	5	
Particle size silt		6				6	2		5	2		2.1	5	1	1	4			5	6	1			6	1	2	2	1	1	4.1	1	1	2	2	1	2		2	2.1	2.1	2.1			1		5	1	5	
pHCaCl2	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1		
pHH2O	1	1		1	1	1	1	1	1	1	1		1	1	1	1	1	1	1	1		1		1		1	1	1	1	1	1	1	1	1	1	1	1	1	1	1		1	1	1	1	1	1			
CaCO3		1			2	1	1		1	1			1	1	1	1	1	1	1	1	1	1		1	1	1	1	1	1	1		1	1		1	1			1	1	1	1	1	1	1	1	1	1	
OC	2.2	1		1	1	4.1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1		1	1	1	1	1	1	1		1	1	1	1	1	1	1	1	1	1		1	1		
Total N	2.2			1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1		1	1	1	1	1	1		1	1		
Exchangeable Acidity	1	1		1	1	1	1	1	1	1	1		1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1		1	1	1	1	1	1	1	1	1			1	1		1	1	
Exchangeable Al	1			1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1		1	1	1	1	1	1		1	1	1	1	1	1	1	1				1	1		1	1		1
Exchangeable Ca	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1		1	1	1	1	1	1	1	1	1			1	1		1	1		
Exchangeable Fe	1	1		1	1		1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1		1	1	1	1	1	1	1	1	1			1	1		1	1		
Exchangeable K	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1		1	1	1	1	1	1	1	1	1			1	1		1	1		
Exchangeable Mg	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1		1	1	1	1	1	1	1	1	1			1	1		1	1		
Exchangeable Mn	1	1		1	1		1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1		1	1	1	1	1	1	1	1	1			1	1		1	1		
Exchangeable Na	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1		1	1	1	1	1	1	1	1	1			1			1	1		
Free H	1			1	1		1	1	1	1		1	1	1	1	1	1	1	1	1	1	1	1	1	1	1		1	1	1	1	1	1	1	1	1		1	1			1	1		1	1		
Extractable Al	1			1	1	1	1		1		1	1	1	1	1	1	1	1	1	1		1		1		1		1	1		1	1		1	1	1		1				1	1		1	1		1
Extractable Ca	1	1	1	1	1	1	1		1	1	1	1	1	1	1	1	1	1	1	1	1	1	1		1	1	1	1	1	1		1	1		1	1	1		1	1	1		1	1		1	1		1
Extractable Cd	1	1		1	1		1		1	1	1	1	1	1	1	1	1	1	1	1	1	1	1		1	1	1		1	1	1	1	1		1	1	1		1	1	1		1	1		1	1		1
Extractable Cr	1	1		1	1	1	1		1		1	1	1	1		1	1	1	1	1		1			1		1		1	1		1	1		1	1	1		1				1	1		1	1		1
Extractable Cu	1	1	1	1	1	1	1		1	1	1	1	1	1	1	1	1	1	1	1	1	1	1		1	1	1	1	1	1	1	1	1		1	1	1		1	1	1		1	1		1	1		1
Extractable Fe	1	1	1	1	1	1	1		1		1	1	1	1	1	1	1	1	1	1		1			1		1		1	1		1	1		1	1	1		1				1	1		1	1		1
Extractable Hg	1				1				1				1									1			1					1		1	1				1					1			1	1		1
Extractable K	1	1	1	1	1	1	1		1	1	1	1	1	1	1	1	1	1	1	1	1	1	1			1	1	1	1	1		1	1		1	1	1		1	1	1	1	1	1		1	1		1
Extractable Mg	1	1	1	1	1	1	1		1	1	1	1	1	1	1	1	1	1	1	1	1	1	1		1	1	1	1	1	1		1	1		1	1	1		1	1	1		1	1		1	1		1
Extractable Mn	1	1	1	1	1	1	1		1	1	1	1	1	1	1	1	1	1	1	1	1	1	1		1	1	1	1	1	1		1	1		1	1	1		1	1	1		1	1		1	1		1
Extractable Na	1			1	1	1			1		1	1	1	1	1	1	1	1	1	1		1					1		1	1		1			1	1	1		1				1	1		1	1		1
Extractable Ni	1			1	1	1	1		1		1	1	1	1		1	1	1	1	1		1			1		1		1	1		1	1		1	1	1		1				1	1		1	1		1
Extractable P	1			1	1	1	1		1	1	1	1	1	1	1	1	1	1	1	1	1	1	1		1	1	1	1	1	1	1	1	1		1	1	1		1	1	1	1	1	1		1	1		1
Extractable Pb	1	1	1	1	1	1	1		1	1	1	1	1	1	1	1	1	1	1	1	1	1	1		1	1	1	1	1	1	1	1	1		1	1	1		1	1	1		1	1		1	1		1
Extractable S	1			1	1	1			1		1	1	1	1		1	1	1	1	1		1			1	1	1		1	1		1	1		1	1	1		1		1		1			1			1
Extractable Zn	1	1	1	1	1	1	1		1	1	1	1	1	1	1	1	1	1	1	1	1	1	1		1	1	1	1	1	1	1	1	1		1	1	1		1	1	1		1	1		1	1		1
Total Al	1			1										1			1		1	1											1		1			1	2											
Total Ca	1			1										1			1		1	1											1		1			1	2											
Total Fe	1			1										1			1		1	1											1		1			1	2											
Total K	1			1										1			1		1	1											1		1			1	2											
Total Mg	1			1										1			1		1	1											1		1			1	2											
Total Mn	1			1										1			1		1	1											1		1			1	2											
Total Na	1			1										1			1		1	1											1		1			1	2											
Reactive Al	1				1		1	1	1	1		1	1	1	1	1	1	1	1	1		1	1		1	1			1	1		1	1	1	1		1	1	1		1			1			1		1
Reactive Fe	1				1	1	1	1	1	1		1	1	1	1	1	1	1	1	1		1	1		1	1			1	1		1	1	1	1		1	1	1	1	1			1			1		1

Legend: 1 = No removal; 2 = Removal of organic carbon (2.1 by hydrogen peroxide or 2.2 by pre-ignition at 850°C); 3 = Removal of soluble salts and gypsum (3.1 by washing with water); 4 = Removal of carbonates (4.1 by hydrochloric acid or 4.2 by hydrochloric acid/Calcium chloride); 5 =Removal of OC and carbonates; 6 = Removal of OC, carbonates, soluble salts and gypsum.

Table 17: Methods used for the pre-treatment in the 6th FSCC Interlaboratory Comparison

PARAMETER	A39	A42	A43	A47	A61	A66	A69	A71	F03	F04	F05	F06	F07	F08	F10	F11	F12	F14	F15	F16	F17	F18	F19	F21	F23	F24	F25	F26	F27	F28	F29	F32	S01	S03	S04	S05	S08	S12	S13	S14	S16	S17	S18	S20	S22	S23	S25	S33	S34
Moisture	1	1	1	1	1	1	1	1	1	1		1	1	1	1	1	1	1	1	1	1		1	1	1	1	1	1	1		1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1		1
Particle size clay		1				1	1		1	1		1	1	1	1	1			1	1	1				1	1	1	1	1	1		1	1	1	1	1		1	1	1	1			1		1	1	1	
Particle size sand		1				1	1		1	1		1	1	1	1	1			1	1	1			1	1	1	1	1	1	1	1	1	1	1	1		1	1	1	1			1		1	1	1	
Particle size silt		1				1	1		1	1		1	1	1	1	1			1	1	1			1	1	1	1	1	1	1	1	1	1	1	1		1	1	1	1			1		1	1	1	
pHCaCl2	2.9	1	1	2.9	2.9	2.9	2.9	2.9	2.9	1	1	2.9	2.9	1	1	1	1	1	1	2.9	1	2.9	1	2.9	1	1	2.9	1	2.9	2.9	2.9	1	2.9	1	1	2.9	2.9	1	2.9	1	1	2.9	2.9	1	2.9	1	1	
pHH2O	2.7	1		2.7	2.7	2.7	2.7	1	1	1	1		2.7	1	1	1	1	1	1	2.7		2.7		2.7		1	2.7	1	2.7	2.7	2.7	1	2.7	1	1	2.7	2.7	1	2.7		1	2.7	2.7	1	2.7	1		
CaCO3		1			1	1	1		2	1			1	1	1	1	1	1	1	1	1	1		1	1	1	1	1	1	1		1	1		1	1			1	1	1	1	1	1	1	1	1	1	
OC	1	3.32		1	1	7.3	1	3.32	1	3.32	1	1	1	6.7	1	1	1	1	1	1	1	1	1	1	1		1	1	1	1	3.32	1	1		1	1	1	1	1	1	1	1	1	1		1	1		
Total N	1			1	1	7.3	1	3.51	3.51	1	1	1	1	3.51	1	1	1	1	1	1	1	3.51	1	1	1	3.52	1	1	1	1	3.5	1	1	1	1	1	1		1	1	1	1	1	1	1		1	1		
Exchangeable Acidity	2.11	2.11		2.11	2.11	2.11	2.11	2.11	2.11	1	1		2.11	2.11	2.11	2.11	2.11	2.11	2.9	2.11	2.11	2.12	2.11	2.11	2.11	2.11	2.11	2.12	2.11	2.11		2.11	2.11	2.11	2.11	2.11	2.2	2.12	1	2.11			2.11	2.12		2.12	2.11		
Exchangeable Al	2.11			2.11	2.11	2.11	2.11	2.11	2.11	2.12	2.11	2.11	2.11	2.11	2.11	2.11	2.11	2.11	2.9	2.11	2.11	2.12	2.11		2.11	2.11	2.11	2.12	2.11	2.11		2.11	2.11	2.11	2.11	2.11	2	2.12	2.11				2.11	2.12		2.12	2.11		2.11
Exchangeable Ca	2.11	2.11	2.11	2.11	2.11	2.11	2.11	2.11	2.11	2.12	2.11	2.11	2.11	2.11	2.11	2.11	2.11	2.11	2.9	2.11	2.11	2.12	2.11	2.11	2.11	2.11	2.11	2.12	2.11	2.11		2.11	2.11	2.11	2.11	2.11	2	2.12	2.11	2.11			2.11	2.12		2.12	2.11		
Exchangeable Fe	2.11	2.11		2.11	2.11		2.11	2.11	2.11	2.12	2.11	2.11	2.11	2.11	2.11	2.11	2.11	2.11	2.9	2.11	2.11	2.12	2.11	2.11	2.11	2.11	2.11	2.12	2.11	2.11		2.11	2.11	2.11	2.11	2.11	2	2.12	2.11	2.11			2.11	2.12		2.12	2.11		
Exchangeable K	2.11	2.11	2.11	2.11	2.11	2.11	2.11	2.11	2.11	2.12	2.11	2.11	2.11	2.11	2.11	2.11	2.11	2.11	2.9	2.11	2.11	2.12	2.11	2.11	2.11	2.11	2.11	2.12	2.11	2.11		2.11	2.11	2.11	2.11	2.11	2	2.12	2.11	2.11			2.11	2.12		2.12	2.11		
Exchangeable Mg	2.11	2.11	2.11	2.11	2.11	2.11	2.11	2.11	2.11	2.12	2.11	2.11	2.11	2.11	2.11	2.11	2.11	2.11	2.9	2.11	2.11	2.12	2.11	2.11	2.11	2.11	2.11	2.12	2.11	2.11		2.11	2.11	2.11	2.11	2.11	2	2.12	2.11	2.11			2.11	2.12		2.12	2.11		
Exchangeable Mn	2.11	2.11		2.11	2.11		2.11	2.11	2.11	2.12	2.11	2.11	2.11	2.11	2.11	2.11	2.11	2.11	2.9	2.11	2.11	2.12	2.11	2.11	2.11	2.11	2.11	2.12	2.11	2.11		2.11	2.11	2.11	2.11	2.11	2	2.12	2.11	2.11			2.11	2.12		2.12	2.11		
Exchangeable Na	2.11	2.11	2.11	2.11	2.11	2.11	2.11	2.11	2.11	2.12	2.11	2.11	2.11	2.11	2.11	2.11	2.11	2.11	2.9	2.11	2.11	2.12	2.11	2.11	2.11	2.11	2.11	2.12	2.11	2.11		2.11	2.11	2.11	2.11	2.11	2	2.12	2.11	2.11			2.11			2.12	2.11		
Free H	2.11			2.11	2.11		2.11	2.11	2.11	2.12		2.11	2.11	1	2.11	2.11	2.11	1	2.9	2.11	2.11	2.12	2.11	2.11	2.11	2.11	2.11		2.11	2.11	2.12	2.11	2.11	2.11	2.11	2.11	2.2		2.11	2.11			2.11	2.12		2.12	2.11		
Extractable Al	3.11			3.11	3.11	3.11	3.11		5.8		3.11	3.11	3.11	3.11	3.11	3.11	3.11	3.11	3.11	3.11		5.8			3.11		3.11		3.11	3.11		3.11	3.11		3.11	3.11	5.8		3.11				3.11	5.8		5.8	3.11		3.11
Extractable Ca	3.11	3.11	3.11	3.11	3.11	3.11	3.11		5.8	3.11	3.11	3.11	3.11	3.11	3.11	3.11	3.11	3.11	3.11	3.11	3.11	5.8	5.8		3.11	3.11	3.11	3.11	3.11	3.11		3.11	3.11		3.11	3.11	5.8		3.11	3.11	1		3.11	5.8		5.8	3.11		3.11
Extractable Cd	3.11	3.11		3.11	3.11		3.11		5.8	3.11	3.11	3.11	3.11	3.11	3.11	3.11	3.11	3.11	3.11	3.11	3.11	5.8	5.8		3.11	3.11	3.11		3.11	3.11	3.11	3.11	3.11		3.11	3.11	5.8		3.11	3.11	1		3.11	5.8		5.8	3.11		3.11
Extractable Cr	3.11	3.11		3.11	3.11	3.11	3.11		5.8		3.11	3.11	3.11	3.11		3.11	3.11	3.11	3.11	3.11		5.8			3.1		3.11		3.11	3.11		3.11	3.11		3.11	3.11	5.8		3.11				3.11	5.8		5.8	3.11		3.11
Extractable Cu	3.11	3.11	3.11	3.11	3.11	3.11	3.11		5.8	3.11	3.11	3.11	3.11	3.11	3.11	3.11	3.11	3.11	3.11	3.11	3.11	5.8	5.8		3.1	3.11	3.11	3.11	3.11	3.11	3.11	3.11	3.11		3.11	3.11	5.8		3.11	3.11	1		3.11	5.8		5.8	3.11		3.11
Extractable Fe	3.11	3.11	3.11	3.11	3.11	3.11	3.11		5.8		3.11	3.11	3.11	3.11	3.11	3.11	3.11	3.11	3.11	3.11		5.8			3.11		3.11		3.11	3.11		3.11	3.11		3.11	3.11	5.8		3.1				3.11	5.8		5.8	3.11		3.11
Extractable Hg	3.11				3.11				1					3.11					5.8						1				1			3.11	1		3.11	3.11			3.1					5.8		5.8	3.11		3.11
Extractable K	3.11	3.11	3.11	3.11	3.11	3.11	3.11		5.8	3.11	3.11	3.11	3.11	3.11	3.11	3.11	3.11	3.11	3.11	3.11	3.11	5.8	5.8			3.11	3.11	3.11	3.11	3.11		3.11	3.11		3.11	3.11	5.8		3.11	3.11	1	2	3.11			5.8	3.11		3.11
Extractable Mg	3.11	3.11	3.11	3.11	3.11	3.11	3.11		5.8	3.11	3.11	3.11	3.11	3.11	3.11	3.11	3.11	3.11	3.11	3.11	3.11	5.8	5.8		3.1	3.11	3.11	3.11	3.11	3.11		3.11	3.11		3.11	3.11	5.8		3.11	3.11	1		3.11	5.8		5.8	3.11		3.11
Extractable Mn	3.11	3.11	3.11	3.11	3.11	3.11	3.11		5.8	3.11	3.11	3.11	3.11	3.11	3.11	3.11	3.11	3.11	3.11	3.11	3.11	5.8	5.8		3.11	3.11	3.11	3.11	3.11	3.11		3.11	3.11		3.11	3.11	5.8		3.11	3.11	1		3.11	5.8		5.8	3.11		3.11
Extractable Na	3.11			3.11	3.11	3.11			5.8		3.11	3.11	3.11	3.11	3.11	3.11	3.11	3.11	3.11	3.11	3.11	5.8					3.11		3.11	3.11		3.11			3.11	3.11	5.8		3.11				3.11			5.8	3.11		3.11
Extractable Ni	3.11			3.11	3.11	3.11	3.11		5.8		3.11	3.11	3.11	3.11		3.11	3.11	3.11	3.11	3.11		5.8			3.11		3.11		3.11	3.11		3.11	3.11		3.11	3.11	5.8		3.11				3.11	5.8		5.8	3.11		3.11
Extractable P	3			3.11	3.11	3.11	3.11		5.8	3.11	3.11	3.11	3.11	3.11	3.11	3.11	3.11	3.11	3.11	3.11	3.11	5.8	5.8		3.11	3.11	3.11	3.11	3.11	3.11	3.11	3.11	3.11		3.11	3.11	5.8		3.11	3.11	1	2	3.11	5.8		5.8	3.11		3.11
Extractable Pb	3.11	3.11	3.11	3.11	3.11	3.11	3.11		5.8	3.11	3.11	3.11	3.11	3.11	3.11	3.11	3.11	3.11	3.11	3.11	3.11	5.8	5.8		3.1	3.11	3.11	3.11	3.11	3.11	3.11	3.11	3.11		3.11	3.11	5.8		3.11	3.11	1		3.11	5.8		5.8	3.11		3.11
Extractable S	3.11			3.11	3.11	7.3			5.8		1	3.11	3.11	3.11		3.11	3.11	3.11	3.11	3.11		5.8			3.11	1	3.11		1	1		3.11	3.11		3.11	3.11	5.8		3.11		1		3.11			1			3.11
Extractable Zn	3.11	3.11	3.11	3.11	3.11	3.11	3.11		5.8	3.11	3.11	3.11	3.11	3.11	3.11	3.11	3.11	3.11	3.11	3.11	3.11	5.8	5.8		3.1	3.11	3.11	3.11	3.11	3.11	3.11	3.11	3.11		3.11	3.11	5.8		3.11	3.11	1		3.11	5.8		5.8	3.11		3.11
Total Al	3.4			5.4										4.2			4.2		2.4	5.2											3.2			4.2			3.4	2.4											
Total Ca	3.4			5.4										4.2			4.2		2.4	5.2											3.2			4.2			3.4	2.4											
Total Fe	3.4			5.4										4.2			4.2		2.4	5.2											3.2			4.2			3.4	2.4											
Total K	3.4			5.4										4.2			4.2		2.4	5.2											3.2			4.2			3.4	2.4											
Total Mg	3.4			5.4										4.2			4.2		2.4	5.2											3.2			4.2			3.4	2.4											
Total Mn	3.4			5.4										4.2			4.2		2.4	5.2											3.2			4.2			3.4	2.4											
Total Na	3.4			5.4										4.2			4.2		2.4	5.2											3.2			4.2			3.4	2.4											
Reactive Al	2.6				2.6		2.6	2.6	2.6	2.6		2.6	2.6	2.6	2.6	2.6	2.6	2.6	2.6	2.6	2.6	2.6	2.6		2.6	2.6			2.6	2.6		2.6	2.6	2.6	2.6		2.6	2.6	2.6		2.6		2.6			2.6				1
Reactive Fe	2.6				2.6	2.6	2.6	2.6	2.6	2.6		2.6	2.6	2.6	2.6	2.6	2.6	2.6	2.6	2.6	2.6	2.6	2.6		2.6	2.6			2.6	2.6		2.6	2.6	2.6	2.6		2.6	2.6	2.6	2.6	2.6		2.6			2.6				1

Legend: 1 = No pretreatment; 2 = Extraction (2.11 single by $BaCl_2$, 2.12 triple by $BaCl_2$, 2.2 by KCl, 2.4 total with HF/HClO4; 2.6 by acid ammonium oxalate, 2.7 by H_2O, 2.9 by $CaCl_2$); Wet ashings at room pressure (open system) (3.11 by aqua regia, 3.2 by HNO_3/HF; 3.32 = by H_2SO_4/K_2CrO_7; 3.4 by $HNO_3/HClO_4$/HF; 3.5 HNO_3/H_2O_2; 3.51 Kjeldahl H_2SO_4/Se-catlyst; 3.52 Kjeldahl H_2SO_4/Ti-Cu catalyst; 3.11 by aqua regia); 4 = pressure digestion (closed system) (4.2 by HNO_3/HF); 5 = microwave pressure digestion (closed system)(5.2 by HNO_3/HF; 5.4 by $HNO_3/HClO_4$/HF; 5.8 by aqua regia); 6.7 = dry ashing dissolution with H_2SO_4; 7.3 oxygen ashing calorimetric bomb

Table 18: Methods used for the determination in the 6th FSCC Interlaboratory Comparison

PARAMETER	A39	A42	A43	A47	A61	A66	A69	A71	F03	F04	F05	F06	F07	F08	F10	F11	F12	F14	F15	F16	F17	F18	F19	F21	F23	F24	F25	F26	F27	F28	F29	F32	S01	S03	S04	S05	S08	S12	S13	S14	S16	S17	S18	S20	S22	S23	S25	S33	S34
Moisture	91	1	91	81	91	81	81	81	81	1		91	81	1	81	81	81	81	81	81	1		81	81	81	81	81	1	81		90	81	81	81	81	81	1	1	81	81	81	1	81	81	81	81	1		81
Particle size clay		81.1				81.1	81.1		81.1	81.1		90	81.1	1	81	81.1			90	81.1	81.1				81.1	81.1	81.1	1	81.1	81.1	48	81	81.1	81.1	81.1	81.1	81.1			81.1	81.1	81.1	81.1			90		81	1	1	
Particle size sand		81.1				81.1	81		81	81.1		90	81.1	1	81	81.1			90	81	81.1			81.1	81.1	81	81.1	1	81.1	81.1	81	81	81	81	81	81		81.1	81.1	81.1	80			90		81	1	1	
Particle size silt		81.1				81.1	81.1		81.1	81.1		90	81.1	1	81	81.1			90	81.1	81.1			81.1	81.1	81.1	81.1	1	81.1	81.1	48	81	81.1	81.1	81.1	81.1		81.1	81.1	81.1	81.1			90		81	1	1	
pHCaCl2	72	72.1	72.1	72.1	72.1	72.1	72.1	72.1	72.1	72.1	1	72.1	72	72.1	72.1	72.1	72.1	72.1	72.1	72.1	72	72.1	72.1	72.1	72.1	72.1	72	1	72.1	72.1	72.1	72.1	72.1	72.1	72.1	72.1	72.1	72.1	72.1	72.1	72.1	72	72.1	72.1	72.1	72.1	72.1	72.1	
pHH2O	72	72.1		72.1	72.1	72.1	72.1	72.1	72.1	72.1	1		72	72.1	72.1	72.1	72.1	72.1	72.1	72.1		72.1		72.1		72.1	72	1	72.1	72.1	72.1	72.1	72.1	72.1	72.1	72.1	72.1	72.1	72.1	72.1	72.1	72.1	72.1	72.1	72.1	72.1	72.1		
CaCO3		83			15.1	83	83		82	83			83	13	15.5	13.1	13.1	13.3	15.2	83	82	13.2		83	83	83	83	1	83	83		83	83		90	83			83	83	83	83	90	73	83	83	13.1	1	
OC	15.1	82		15	91	17.1	15.2	84.3	13.2	82	17.2	15.4	17.1	13	91	17.2	13.1	15.3	15.2	15.3	18.1	13.2	15.2	17	13		15.3	17.1	17.1	17.3	50	15.3	15.2		15.3	15.3	15.1	13.2	15	15.3	17.4	91	17.1	84.2		13.1	13			
Total N	15.1			15	15.1	17.1	15.2	11	11.2	11	17.2	15.4	17.1	12.2	15.5	17.2	15.5	15.3	15.2	15.3	18.1	11.2	15.2	17	11.2	11	15.3	11.2	17.1	17.3	73	15.3	15.2	13.1	15.3	15.3	15.1		15	15.3	17.4	17.1	17.1	13		12.3	12.3		
Exchangeable Acidity	82	82		82	73	73	82	82	82	91	72		31	91	82	91	91	31	91	91	82	71.1	82	82	82	82	82	1	91	73		82	91	82.1	91	91	82	82	91	82		73	90		82	91		
Exchangeable Al	31			31	31	31	21.2	21	31	31	21.2	31	31	31	21.2	31	31	31	31	31	31	31	31		31	21.2	31	31	21.2	31		31	31	31	31	31	31	21.2	31			31	31		31	31		35
Exchangeable Ca	31	21.1	21.1	31	31	21.1	21.1	21	31	31	21.2	31	31	31	21.2	31	31	31	31	31	31	31	31	21.1	31	21.1	31	31	21.1	31		31	31	31	31	31	31	21.2	31	21.1			31	31		31	31		
Exchangeable Fe	31	21.1		31	31		21.1	21	31	31	21.2	31	31	31	21.1	31	31	31	31	31	31	31	31	21.1	31	21.1	31	31	21.1	31		31	31	31	31	31	31	21.1	31	21.1			31	31		31	31		
Exchangeable K	31	21.1	21.1	31	31	28	21.1	21	31	31	21	31	31	31	28	31	31	31	31	31	31	31	31	21.1	28	28	31	31	21.1	21.1		31	31	31	31	31	31	21.1	31	28			31	31		31	31		
Exchangeable Mg	31	21.1	21.1	31	31	21.1	21.1	21	31	31	21.2	31	31	31	21.1	31	31	31	31	31	31	31	31	21.1	31	21.1	31	31	21.1	31		31	31	31	31	31	31	21.1	31	21.1			31	31		31	31		
Exchangeable Mn	31	21.1		31	31		21.1	21	31	31	21.2	31	31	31	21.1	31	31	31	31	31	31	31	31	21.1	31	21.1	31	31	21.1	31		31	31	31	31	31	31	21.1	31	21.1			31	31		31	31		
Exchangeable Na	31	21.1	21.1	31	31	28	21.1	21	31	31	21.2	31	31	31	28	31	31	31	31	31	31	31	31	21.1	28	21.1	31	31	21.1	21.1		31	31	31	31	31	31	21.1	28	28			31			21.1	31		
Free H	82			82	91		91	82	82	82		91	31	1	82	91	91	72.1	91	91	82	71.1	82	82	82	82	82		72.1	73	72.1	82	72	91	72.1	91	82		82	82			73	31		82	82		
Extractable Al	31			31	31	31	35		31		31	31	31	31	21.2	31	31	31	31	31		31			31		31		21.2	31		31	31		31	35	31		31				31	31		31	31		35
Extractable Ca	31	21.1	21.1	31	31	31	35		31	31	31	31	31	31	21.2	31	31	31	31	31	32	31	31		31	21.1	31	31	21.1	31		31	31		31	35	31		31	21.1	21		31	31		31	31		35
Extractable Cd	31	21.1		31	31		35		31	31	31	31	31	31	31	35	22	22	22	35	32	31	31		22	21.1	31		22	21.1	22	22	31		22	35	31		35	21.1	22		31	31		31	35		35
Extractable Cr	31	21.1		31	31	31	35		31		31	31	31	31		35	31	31	31	35		31				31			22	31		31	31		31	35	31		31				31	31		31	31		35
Extractable Cu	31	21.1	21.1	31	31	31	35		31	31	31	1	31	31	31	35	31	31	31	35	32	31	31		31	21.1	31	31	22	21.1	21	31	31		31	35	31		31	21.1	22		31	31		31	31		35
Extractable Fe	31	21.1	21.1	31	31	31	35		31		31	31	31	31	21.1	31	31	31	31	31		31			31		31		21.1	31		31	31		31	35	31		31				31	31		31	31		35
Extractable Hg	31				31				10					51.2								25			25					25.1		25	10		26	24			25					90		25	25		35
Extractable K	31	21.1	21.1	31	31	31	35		31	31	31	31	31	31	28	31	31	31	31	31	32	31	31			21.1	31	31	21.1	31		31	31		31	35	31		28	28	21	28	31			31	31		35
Extractable Mg	31	21.1	21.1	31	31	31	35		31	31	31	31	31	31	21.1	31	31	31	31	31	32	31	31		31	21.1	31	31	21.1	31		31	31		31	35	31		31	21.1	21		31	31		31	31		35
Extractable Mn	31	21.1	21.1	31	31	31	35		31	31	31	31	31	31	21.1	31	31	31	31	31	32	31	31		31	21.1	31	31	21.1	31		31	31		31	35	31		31	21.1	21		31	31		31	31		35
Extractable Na	31			31	31	31			31		21.2	31	31	31	28	31	31	31	31	31		31					31		21.1	31		31			31	35	31		31				31			21.1	31		35
Extractable Ni	31			31	31	31	35		31		31	31	31	31		31	31	31	31	35		31			31		31		22	31		31	31		31	35	31		31				31	31		31	31		35
Extractable P	31			31	31	31	35		31	31	31	31	31	31	31	31	31	31	31	31	32	31	31		31	53.1	31	31	53.1	31	50	31	31		31	35	31		31	50	53.1	50	31	31		53	31		35
Extractable Pb	31	21.1	21.1	31	31	31	35		31	31	31	31	31	31	31	31	31	31	31	35	32	31	31		31	21.1	31	31	22	21.1	21	31	31		31	35	31		31	21.1	22		31	31		31	35		35
Extractable S	31			31	31	17.1			31		17.2	31	31	31		31	31	31	31	31		31			31	14	31		17.1	14.1		31	31		31	31	31		31		17.4		31			14.1			35
Extractable Zn	31	21.1	21.1	31	31	31	35		31	31	31	31	31	31	31	31	31	31	31	31	32	31	31		31	21.1	31	31	21.1	31	21	31	31		31	35	31		31	21.1	21		31	31		31	31		35
Total Al	31			31										31			31		31	31												31			31			21.2	31										
Total Ca	31			31										31			31		31	31												31			31			21.2	31										
Total Fe	31			31										31			31		31	31												31			31			21.1	31										
Total K	31			31										31			31		31	31												31			31			21.1	31										
Total Mg	31			31										31			31		31	31												31			31			21.1	31										
Total Mn	31			31										31			31		31	31												31			31			21.1	31										
Total Na	31			31										31			31		31	31												31			31			21.1	31										
Reactive Al	31				31		21.2	21	31	31		31	31	31	21.2	31	31	31	31	31		31	31		31	21.2			21.2	31		31	31	31	31		31	21.2	31		31			31				1
Reactive Fe	31				31	21.1	21.1	21	31	31		31	31	31	21.1	31	31	31	31	31		31	31		31	21.1			21.1	31		31	31	31	31		31	21.1	31	21.1	21.1		31			31			1

Legend:

1	No detection	15	C/N-Analyzer	17.4	C/N/S-Analyzer (Carlo-Erba=CE Instrume	24	AAS-hydride technique	48	Laser diffraction	81	Gravimetry	82.5	AgNO3-Titration
10	Elemental analysers	15.1	C/N-Analyzer (Carlo-Erba=CE Instruments)	18	C/N/H-Analyzer	25	AAS-cold vapor technique	50	UV-VIS-spectrophotometry-techniques	81.1	Pipette	83	Calcimeter (Scheibler unit)
11	Kjeldahl-apparatus	15.2	C/N-Analyzer (Leco)	18.1	C/N/H-Analyzer (Leco)	25.1	AAS-LECO/ALTEC Mercury Analyzer	53	Colorimetric P-Determination	81.2	Hydrometer	84	Carbon determinations
11.2	Kjeldahl-apparatus (Gerhardt)	15.3	C/N-Analyzer (Heraeus/Elementar)	18.2	C/H/N-Analyzer (Heraeus/Elementar)	26	AFS-hydride-technique	53.1	Molybdene-blue-method	82	Titration	84.2	Walkley-Black
12.2	N-Analyzer (Vario)	15.4	C/N-Analyzer (Vario)	20	Mono-Atom-Spectrometry-Techniques	28	AES-Flame photometer	71.1	Conductometric titration	82.1	NH4-back titration	84.3	Tjurin method
13	C-Analyzer	17	C/N/S-Analyzer	21	AAS-flame technique	30	Multi-Atom-Spectrometry-techniques	72	Potentiometry	82.2	Thiocyanate-titration	90	other detections
13.1	C-Analyzer (Leco)	17.1	C/N/S-Analyzer (Leco)	21.1	AAS-flame technique (C2H2/Air)	31	ICP-AES without Ultrasonic nebulisation	72.1	pH	82.3	FeNH4SO4-Titration	91	Calculation
13.2	TOC Analyzer	17.2	C/N/S-Analyzer (Heraeus/Elementar)	21.2	AAS-flame technique (C2H2/N2O)	32	ICP-AES with Ultrasonic nebulisation	73	Potentiometric titrations	82.4	Barimetric titration		
13.3	C-Analyzer (Heraeus/Elementar)	17.3	C/N/S-Analyzer (Thermo Electron)	22	AAS-flameless (electrothermal technique	35	ICP-MS	80	Classical analytical techniques				

3.4 Follow-up questionnaire

The FSCC asked all laboratories that did not qualify for at least one parameter to fill in a questionnaire on the possible problem(s) causing a failure in the ring test. In the majority of the cases the laboratories could identify and solve the problem. They were given the opportunity to send their corrected results to FSCC till mid November 2009 in order to requalify.

Labs were asked to answer the questions for each individual parameter. So when the problem applied to all basic exchangeable cations, the problem was counted four times. The problems are not mutually exclusive so more than one answer for one parameter could be given.

Table 19: Reasons given by the laboratories for not reporting in the tolerable range. Numbers are percentages by analytical group.

Reason	Texture	pH	OC	Tot N	$CaCO_3$	Exch. el.	Extr. El.	Tot. El.	Ox. Extr. el.	Total
N° of answers	**79**	**9**	**6**	**10**	**19**	**147**	**192**	**18**	**36**	**516**
No reason found (%)						7	2	11	8	4
Not analysed (%)	62	44	67	30	63	32	29	39	75	41
Sample preparation (%)	6		17	10	11	20	23		6	17
Determination (%)	6	22		30	16	18	24	11	6	18
Laboratory Conditions (%)	22	33	17	10	11	16	20	39	6	18
Other (%)	4			20		6	1			

The main reason for failure was the fact that the parameter was not analysed (41% of the answers). So the first objective to improve the quality of the soil database should be that all laboratories are able to analyse the whole set of mandatory parameters. When this is not possible, the analysis should be conducted by another (qualified) laboratory. In order to evaluate the ring test results, FSCC should be informed on the cooperation between the labs.

A distinction can be made between the different types of analyses. Table 20 provides a more detailed overview.

A high number of labs did not conduct the particle size distribution, the carbonate analysis and the acid oxalate extractable aluminium and iron. These labs will usually solve the problem by having the analysis done by another lab. Several laboratories do not have the required equipment to conduct the pipette analysis. The same problem arises for the calcimeter necessary for the analysis of the carbonates. As the acid oxalate extractable aluminium and iron is not a standard method in many labs and as this is not a standard parameter on the ICP Forests Level I plots, the experience with this method in many labs is rather low, and so, several decided not to conduct this analysis in the ring test.

For a number of parameters the level of experience of the personnel with the method in general or with the (new) instrument forms an important problem.

Although problems such as mixing up of samples, reporting in the wrong units,… are easy to detect by applying basic quality checks, these problems still appear in our interlaboratory comparison exercises. It is cumbersome that such mistakes happen in a ring test programme as such kind of checks should be part of the general internal laboratory quality control programme.

Table 20: Detailed reasons given by the laboratories for not reporting in the tolerable range. Numbers are percentages by analytical group.

	Texture	pH	OC	Tot N	$CaCO_3$	Exch. el.	Extr. El.	Tot . El.	Ox. Extr. el.
No reason found						7	2	11	8
The analysis was not conducted		11	17		5		3		6
By another laboratory	34	11	33	20	21	10	16		28
No required equipment	19				21	5	1		11
No qualified personnel	8	22	17	10	11	10	8	39	22
Did not reach the deadline						6	1		
Other	1				5	1	1		8
Sample preparation									
Wrong sample weight				10		3	3		
Mixing-up of samples	3					10	8		
Dilution error						1	3		
No use of reference method			17		11	4	1		
Contamination of sample						2	3		3
Losses	4								
Other						1	5		3
Determination									
Calibration problem		11		10		10	19		6
Wrong units					16	2			
Instrument error	6	11		10		3	4	11	
Contamination						3	2		
Error in recalculation on oven-dry basis				10					
Laboratory Conditions									
New (or poorly educated) staff						4			
No experience with a new instrument	8	33	17	10	5	6	11	39	6
No experience with this method	14				5	6	8		
Other problems	4			20		6	1		

3.5 Evaluation by element group

3.5.1 Moisture content

Although, the soil moisture content was mandatory to report, this was not done by four laboratories for the mineral soil (F05, F18, F28 and S33) and by one laboratory (F08) for the organic layer.

It is mandatory to report the moisture content since the moisture content is essential to express the results on an oven-dry basis (at 105°C). Especially for sample A, where the moisture content was relatively high, this makes large differences in the ring test results of many parameters. This leaves us in the assumption that the concerning laboratories did not report their results on a oven-dry basis.

The report of the previous ring test did already bring up this point. Most of the laboratories not reporting the moisture content at that time, did report it this time but one laboratory (F18) seems reluctant to do so.

3.5.2 Particle size distribution

This is a second group of mandatory parameters which is only analysed by 35 out of the 50 laboratories. A number of laboratories (S02, S08, S34, A43, A61, F12, F19) have the particle size analysed by another laboratory which is participating for this parameter in the FSCC Interlaboratory Comparisons. The follow-up questionnaire should shed more light on the

plans of the concerning laboratories on how they will deal with these missing parameters in future ring tests and monitoring work.

The percentage of laboratories which did not qualify is 15% for clay, 11% for sand and 6% for silt. See Table 13. More problems were seen in sample C (slightly calcareous, clay loam) compared to sample A (silt loam) and B (loamy sand).

3.5.3 Soil reaction

Forty-seven out of the 50 laboratories reported pH($CaCl_2$) which is a mandatory parameter. Two of the three remaining laboratories work complementary to other laboratories in their own country. Only one laboratory (F23) failed for pH($CaCl_2$) and needs requalification.

Forty laboratories reported pH(H_2O) which is indeed optional. This is clearly lower compared to previous ring tests. Two laboratories (5%) (F04 and F21) failed for pH(H_2O) and need requalification.

From the exploratory data analysis, it was seen that laboratory F29 had very deviant visual outliers in both the analysis of pH($CaCl_2$) and pH(H_2O) for samples A and B where it reported values of one pH unit below the general mean. Since the laboratory was successful in measuring the pH in the three other samples, it qualified for this ring test. On the other hand, we strongly recommend this laboratory to check what went wrong in samples A and B.

3.5.4 Carbonate content

Note it was only relevant to measure $CaCO_3$ for sample C since this was the only sample with a pH($CaCl_2$) above 6.0. For all other samples, the content was extremely low or theoretically equal to 0. Though, for samples A, B, D and E there were a limited number of laboratories reporting a measured value above the LOQ. To guarantee a representative statistical analysis, the reported $CaCO_3$ data on samples A, B, D and E were too few to calculate a general cleaned mean and so, the samples A, B, D and E were not included in the statistical evaluation of $CaCO_3$ content.

Three out of 37 laboratories (equals 8%) (labID F03, F11 and F17) failed for the determination of $CaCO_3$ content on sample C and so need requalification.

3.5.5 Organic carbon

Forty-three laboratories analysed the mandatory organic carbon content. Three labs failed, two of them are located within one country (A42 and F26), the other lab is not a FutMon laboratory (S12).

3.5.6 Total Nitrogen content

Four laboratories (F04, F07, S16 and S20) failed out of the 43 labs that reported results. Especially sample B with low N content posed the most problems.

3.5.7 Exchangeable cations

Forty-three laboratories reported results for exchangeable Ca, K and Mg but concerning the remaining exchangeable elements less results were reported. Following the rules outlined in the Manual IIIa (FSCC and the Expert Panel on Soil and Soil Solution, 2006), it was mandatory to analyse the exchangeable acidity and cations on samples A, B, D and E but not on sample C, since the latter is a calcareous sample containing 10 g/kg $CaCO_3$. In calcareous soils, the measurement of these parameters is optional.

We see in this group the highest values for the coefficients of variation. Also the tolerable ranges have been set relatively wide for this group of parameters. The percentage of laboratories failing for exchangeable element varies, depending on the element, between 5 (Fe) and 22% (acidity).

Exchangeable acidity and free H^+ pose the most problems. Although mandatory, participation is low and although the tolerable limits are wide, the percentage of failing laboratories is relatively high.

Exactly 19% of the laboratories also failed for exchangeable K. In sample B and D the general cleaned mean was far below the LOQ of a number of laboratories. Additionally, a high number of labs failed for the organic samples.

For exchangeable Fe, 95 % of the laboratories had satisfactory results. This will rather be an indication that the tolerable range of 140% should be narrowed.

3.5.8 Aqua Regia extractable elements

A relatively high percentage of the 42 laboratories will need a requalification for the mandatory heavy metals Cu, Pb, Zn. Concerning Cd, less labs need requalification. On the other hand, Cd has a tolerable range of ± 100%. The results of this ring test indicate that it would be realistic to aim for a lower variability and to narrow the tolerable range.

Forty-one laboratories analysed the macro-nutrients P, Ca, K, Mg and Mn. Four of them measured them only on the organic samples, where these parameters are mandatory. All other measured it on organic and mineral samples. Especially a high number of failing laboratories is seen for sample E, the peat sample. Laboratories were clearly more successful in measuring the macro-nutrients in the 'standard' organic layer sample D.

The optional elements Al, Fe, Cr, Ni, S, Na were on average reported by a lower number of laboratories (31 labs or 62%). On average 13.5% of the laboratories failed for these optional parameters and will need requalification if they want to report these parameters to the FutMon database. Hg was analysed by 16 labs (32%) which all qualified.

3.5.9 Total elements

The optional total elements were only reported by 10 laboratories, of which 4 laboratories only analysed the mineral soil samples. This is a relatively small number to come to a reliable cleaned mean. An additional source of variation in this group of parameters, is that the laboratories used six different methods to measure these total elements.

Depending on the element, one or two laboratories failed to report results within the tolerable range.

3.5.10 Reactive Fe and Al

Although it are mandatory parameters on the mineral soil samples on the Level II plots, a relatively small number of laboratories reported these analyses (31 for Al and 33 for Fe, 62% and 66% respectively).

3.6 Comparison of the CV with previous FSCC Interlaboratory Comparisons

Compared to the previous FSCC Interlaboratory Comparisons, the CVs have improved for pH, organic carbon, aqua regia extractable elements and acid oxalate extractable elements. For calcium carbonate and total elements CV increased. As sample C was low in $CaCO_3$ content (10 g/kg), the high coefficient of variation follows the expectations. It stayed at the same level for particle size distribution, total N and exchangeable cations.

Table 21: Group CVs of the 2nd, 3rd, 4th, 5th and 6th FSCC Interlaboratory Comparison

FSCC Interlaboratory Comparison	2nd	3rd	4th	5th	6th
Group 1: Particle size distribution	NA	53	37	23	23
Group 2: pH	3.25	3.5	3.1	3.2	2.4
Group 3: Carbonate content	NA	206	129	45	61.3
Group 4: Organic carbon	41.5	18	13	16	14
Group 5: Total N	25	17	27	17	17
Group 6: Exchangeable cations	52	71	54	49	49
Group 7: Aqua regia extractable elements	35	47	33	26	21
Group 8: Total elements	NA	21	NA	9	12
Group 9: Acid oxalate extractable Fe & Al	NA	44	12	20	13

4 Conclusions and Recommendations

4.1 Towards the participating laboratories

4.1.1 Application of data quality checks

The laboratories should better apply the data quality checks, outlined in the ICP Forests quality check paper (www.icp-forests.org) or the FutMon QA/QC Guide for laboratory work (1st version) (www.futmon.org) (Clarke *et al.* 2009). When applying the related quality checks on the exchangeable elements, we see that several laboratories report data that should not have passed the checks.

For example, the free H^+ and exchangeable acidity (EA) check asks to perform the algorithm: **Free H^+ < EA**. Table 20 shows that this rule is violated by 7 laboratories as the EA values are smaller than the Free H^+ values.

Table 22: Failed free H^+ and exchangeable acidity checks

LabID	SAMPLE	EA	Free_H+
A39	C	0.063	0.407
A47	D	3.067	3.182
A71	C	0.090	0.107
F21	B	0.743	0.783
F21	C	0.170	0.590
F24	C	<0.003	0.410
F25	C	0.160	0.170
S23	C	0.093	1.087

It is obvious from Table 22 that this type of problem is mainly situated in the slightly calcareous sample where there is as good as no free H^+.

Secondly, the exchangeable acidity should more or less be equal to the sum of the acid cations (Al + Fe + Mn + Free H^+). In some cases the difference between exchangeable acidity and the sum of the acid cations is nearly 4 cmol(+)/kg. The concerning laboratories indeed need a requalification either for EA or free H^+ or both.

4.1.2 Use of reference methods

In the current qualification procedure, the application of the correct methods (as described in the Submanual on Sampling and Analysis of Soils), has not been included. It was however stressed by the heads of the laboratories (Warsaw, 2009) that in order to come to more harmonised results, it is indispensible to use the ISO reference methods.

In practise this means that a number of current practises in the FSCC interlaboratory comparisons will not be allowed any longer:

- The reference method for the particle size distribution is the analyses by the pipette method. Particle size distribution by laser diffraction analysis is not allowed. As the method is based on a different concept, there is no unique relationship between both methods valid for all types of soils.
- Note that in the future, the reference method for pH will follow the updated ISO 10390 standard (2005) with following differences:
    - Shaking of suspension for 60 min +/- 10 min (previously 5 min)
    - Waiting at least 1 hour but not longer than 3 hrs prior to reading (previously 2 readings: after 2h and < 24 hrs)
- The organic carbon is determined by a total analysis (TOC or elemental analyser). The more traditional methods (e.g. the Walkley and Black method, Loss-on-Ignition or the Tjurin method) cannot be used.
- In the analyses of total Nitrogen, the modified Kjeldahl method can be used as an alternative method to the total N analyser unlike the traditional Kjeldahl method which will underestimate N concentration.
- The exchangeable elements are measured in a single extraction $BaCl_2$ solution, this in contrast to the ISO standard. Other extracts cannot be used.
- The aqua regia digestions should be done by the reflux method. The digestion by microwave, as done by six laboratories in this ring test is not allowed.

4.2 Towards the Manual on Sampling and Analysis of Soil

4.2.1 Exchangeable elements

The method description of the exchangeable elements should be made more clear and transparent. The exchangeable acidity is a parameter with a very high coefficient of variation when measured by the titration method. When it is calculated starting from the calculated data on the free H^+, results might be slightly different from the titration method but these are better reproducible.

4.2.2 Problems due to rounding of results

Several parameters were that low in concentration that when reporting according to the precision presently described in the manual, important information would be lost. In some cases it was difficult to match the results according to the minimum required precision with the calculated tolerable range based on the general cleaned mean. To avoid this problem both in future interlaboratory comparisons and in the survey data, FSCC suggests to increase the precision requirements in the Manual. Since the data reporting format in the FutMon database is a floating point format, no changes to the reporting data forms will be necessary. It would suffice to state that at least two significant numbers (so numbers different from 0) should be reported if the first of these two significant numbers is 1 or 2.

For example, the total Nitrogen in sample B (general mean 0.13 g/kg) should be reported minimum up to two decimal places while the manual presently only asks for one decimal place. So 0.13 g/kg fits the reporting precision requirement but 0.2 g/kg does not. In sample C, the cleaned mean value was 0.4 g/kg. In this case reporting up to one decimal is sufficient. Similar with the exchangeable Fe and Mn where reporting up to three decimal places will be necessary or for extractable Cd in sample B, C and E were two decimal places will be necessary.

4.3 Towards future Interlaboratory Comparisons

The results of the ring test on the exchangeable elements are not suitable to statistically prove whether the results of the German calculation method of the free H^+ give the same results as the titration method but they show that the variability amongst the results obtained by the calculation method are less variable. A dedicated study should reveal which method will be recommended for use in future ringtests.

In this 6th FSCC Interlaboratory Comparison tolerable limits have been applied for the first time. The success/failure to meet the requirements set by the calculated tolerable ranges have been translated into individual qualification reports for the laboratories. By relating this qualification report to the reported survey data, laboratories are encouraged to provide feedback to the FSCC on the reasons for failure in the ring test and correct their results when possible. Laboratories make clearly more efforts to improve compared to the past since they want to requalify.

A better estimation of the general cleaned mean can be obtained when real zero values are distinguished from missing values in the data submission. Real zero values are only possible in a limited number of cases. For example when the pH of a samples is acid, the content of carbonates will be zero.

5 Conclusions

Fifty laboratories took part in the 6th FSCC Interlaboratory Comparison in 2009. Nine laboratories reported outliers and stragglers for more than 20 % of the total reported analyses: two laboratories for both the between- and the within- laboratory variability, four laboratories based on the within-laboratory variability and three for the between-laboratory variability. Based on the coefficient of variation, the problem parameters are: (1) exchangeable elements, especially Na and the acid cations Al, Fe, Mn, free H^+ and acidity, (2) aqua regia extractable elements Na and Cd, (3) the carbonate content in Sample C with low $CaCO_3$ content and (4) the determination of the clay content. In general there are more problems when the concentration of the concerning element is low, which is recognised by setting different tolerable ranges depending on lower and higher concentration levels. Compared to the 5th FSCC Interlaboratory Comparison in 2007, the coefficients of variation of all groups of analysis remained at a similar level except for the $CaCO_3$ content and the total elements.

New in this 6th Interlaboratory Comparison was the application of preset tolerable limits. When a laboratory had more than 50% of its reported means outside the tolerable range or when it did not report a mandatory parameter, requalification was required. All laboratories received an individual qualification report and a follow-up questionnaire in order to correct errors and mistakes. Corrected results could be submitted for requalification. Only one laboratory qualified immediately for all mandatory and optional parameters. Two more laboratories qualified immediately for all their reported parameters and yet two more for all mandatory parameters. After requalification 16 labs could qualify for all their reported parameters. This new approach assured an individual and intensive follow up which will eventually lead to an improved quality of the solid soil parameters measured in the current and future forest soil monitoring programmes.

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