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INTERACTIONS IN THE COMMUNITY**



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The FSCC soil reference material



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1 Introduction

Within the BioSoil project, it was the task of the Forest Soil Coordinating Centre (FSCC) to assure and control the quality of the data collection in the field and in the soil analytical laboratory.

One important aspect of the quality control on the physical and chemical analyses are the Interlaboratory Comparisons which FSCC is conducting every two years. The 4th FSCC Interlaboratory Comparison was conducted in 2005, prior to the start of the BioSoil project. The 5th Comparison took place in 2007 while the BioSoil survey and the related analyses were on-going.

The second component of the quality control in the laboratories is the analysis of the FSCC soil reference material. The purpose of this quality control component is to provide reference material for those analyses for which commercial reference materials are not easily available. While the interlaboratory comparisons assesses the between laboratory variability and the repeatability capacity of the individual laboratories, the analysis of the FSCC reference material assesses the long-term within laboratory reproducibility of the participating laboratories. The latter is part of the requested QA/QC information when reporting at EU level (ICP Forests, 2006).

2 Materials and Methods

2.1 The reference sample

In spring 2005 the FSCC reference material was taken from the 20 – 40 cm layer in the Aelmoeseneie forest in Gontrode, Belgium over a surface of 25 m² after the removal of the first 20 cm (Ah and Ap horizon). The total fresh weight was about 2 tonnes.

A subsample of 50 kg was set aside, dried and homogenised and served as sample B in the 4th FSCC Interlaboratory Comparison (Cools et al., 2006). The rest of the material passed several homogenisation and drying steps. First the material was mixed by quartering. Then it was oven-dried at 40°C and stored in 20 plastic containers. Subsequently the material was manually sieved on 2 mm sieves. Then a second homogenisation cycle followed where the material was dispersed over plastic containers. Of these containers 300 kg was distributed over 93 boxes of each minimum 3 kg. This was the first batch of FSCC reference material December 2006 which was sent at the beginning of 2007 to 30 laboratories that analyse soil samples within the framework of the BioSoil project.



Figure 1: Quartering of the FSCC soil reference sample

This FSCC soil reference material is representative for an acid, loamy forest soil. Since it is a very acid forest soil, the FSCC soil reference material Dec'06 will not be suitable as a reference sample for all mandatory and optional variables in the BioSoil project. Some of the

values for basic cations, heavy metals (Cd) and total nitrogen might be close to the limit of quantification (LOQ) of several laboratories.

FSCC recommended making the interval for analysing the reference sample dependent on the number of samples that the participating laboratory is analysing within the BioSoil project. For the first 200 soil samples, FSCC recommended to analyse the reference sample each 20 BioSoil soil samples. From sample 201 till sample 500, FSCC asked for one reference sample each 30 samples. In case the laboratory analyses more than 500 soil samples, FSCC recommended analysing the reference samples each 50 BioSoil soil samples, starting from sample 500.

The sample has a CEC of $\pm 2.53 \text{ cmol}(+)/\text{kg}$, a base saturation (BS) of 11 % and an Al-saturation of 80%. For a soil sample with a $\text{pH}(\text{CaCl}_2)$ of 3.85, it is of course irrelevant to measure the carbonate content. The moisture content was not requested. A disadvantage of not asking the latter variable, is that we are not sure whether all results have been reported on oven-dry basis. Probably most laboratories reported air-dried measurements, causing an extra source of variation of about one percentage. This report evaluates in total 34 soil variables defined in the ICP Forests Manual on Sampling and Analyses of Soil (ICP Forests, 2006).

The FSCC reference sample is seen as a way to help laboratories and not to control or punish them. In case of obvious mistakes, the laboratories were directly contacted to discuss the problem and correct the results when necessary. Often it concerned mistakes in the date (e.g. wrong year), reporting units,.... When it concerned mistakes in the analytical procedure, it is mentioned in the report.

2.2 Homogeneity tests

Randomly 10 samples were selected and tested for Kjeldahl N, $\text{pH}(\text{CaCl}_2)$, organic matter by loss-on-ignition (LOI) and the non-ferro aqua regia extractable elements. Of each sample, 4 subsamples were taken. The variability between the samples was compared with the variability within the samples taking the reproducibility of the laboratory into account.

2.3 Participation of the laboratories

27 of the 30 laboratories that requested material, submitted results obtained between March 2007 and June 2008. Table 1 in Annex I gives an overview of the reported data [N° of reported values, the mean, median, minimum, maximum reported value, the standard deviation and the reproducibility (CV) of the uncleaned data] by all participating laboratories. For the reference method of the analyses, please consult the ICP Forest Manual on Sampling and Analysis of Soil (ICP Forests, 2006).

2.4 Exploratory data analysis

A first step was the **data exploration** for each variable and laboratory in order to study the degree of homogeneity of the data sets. The following aspects were taken into consideration:

1. The number of reported replicates per variable: some laboratories reported only one analysis; others reported more than 30 replicates. When only one replicate was available, this value was not included in the histograms and the box plots.
2. Did analyse laboratories by regular time interval over the 16 months period?
3. Did they make replicates in one day? If so, how many?
4. A first assessment of visual outliers could be made.
5. When a sufficient number of replicates were made per variable, the standard deviation gives us information on the magnitude of the within laboratory variance (reproducibility). This quality indicator is requested in the data accompanying report when submitting the BioSoil data to the JRC by the end of 2008.

The exploratory data analysis included the study of following graphs per variable:

1. **Dot plot** of all the values reported by the participating laboratory for that variable. Very deviant outliers are reported with their values.
2. **Histogram of the means** of the reported values of each of the laboratories.
3. **Box plot of the means** of the reported values of each of the laboratories. Very deviant outliers are excluded, "normal" outliers are reported with their values.
4. **Histogram of the standard deviation** of the reported values of each of the laboratories.
5. **Box plot of the standard deviation** of the reported values of each of the laboratories.
6. **Notched box plot** of all the values reported by the participating laboratory for that variable. When the very deviant outliers disturbed the readability of the figure, the notch box plot was redrawn after the exclusion of these outliers (e.g. Exchangeable Mg, Mn and Na).
7. **Scatter plot** of the reported values for each individual laboratory, showing the distribution in function of the time of the reported measurements.

A laboratory can check its performance -relative to the other laboratories - by 1) studying the dot plots and, 2) the notched box plot. In the **dot plots**, every dot represents a reported value of a specific variable. 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. The x-axis corresponds to the variable unit. In order not to distort the graph, the reported values of the very deviant outlying results are written in text on the upper or lower side of the graph. The graph provides also an impression of the within-laboratory variability and can be compared with the other laboratories.

The **notched box plots** indicate whether significant differences between the individual laboratory can be expected. When the notches of the boxes of two laboratories do not overlap, there will be a significant difference for that variable between the two laboratories. So these plots allow a lab to compare its results with the results from the central laboratory.

The histograms provide a overview of the distribution of the means and the standard deviations per laboratory of all reported results for a certain variable. The information contained within the histograms is:

- **Visual outliers** that are very deviant (value of the variable value with lab N° between parentheses). Very deviant outliers means that they are located more than 3.5 times beyond the inter-quartile range (IQR). The IQR is defined as the distance between the 25 % and the 75% percentile.
- **Relative frequencies** in each class (in %)
- **Density curve** (smoothed trend-line)
- **N**: Number of laboratories in the histogram
- **NA**: Not Applicable
- **Z**: Number of reported zero's
- **E**: Number of excluded observations from the presentation in the histogram; separately mentioned for upper and lower limits of distribution. The first number refers to the left side of the diagram, the second number to the right side of the histogram.
- **U**: Number of laboratories included in the further analyses (box plots). [$U = N - E$]
- **a**: average value of the N laboratories
- **m**: median value of the N laboratories
- **s**: standard deviation of the N laboratories

The information in the box-plot starts from the dataset containing 'U' number of laboratories after the first rough cleaning done in the histograms where the very deviant visual outliers have been excluded. The box plot provides further information on the outliers, located at a distance further than 1.5* IQR from the median value (value of the variable with 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. The edges of the boxes are equal to the 25% and 75% percentiles. The value closest to the median is coloured black. Laboratories whose observations correspond to the median value, are indicated between brackets "< >"; observations between the 25% and the median are between "< <", and between the median and 75% percentile are between "> >".

Both histograms and box-plots are based on the observations after the 'very deviant' outliers have been excluded. 'The criterion to exclude observations is thus stronger than the criterion for 'visual' outliers as represented in the box-plot (Whiskers are placed at $1.5 * IQR$). It is possible that whiskers are placed on a closer distance than $1.5 * IQR$ from the box-plot, in case there are no observations outside the $1.5 * IQR$.

In case there would be a drift of the chemical soil variables in the soil samples (instability over time), it would be indicated by the **scatterplot** of the individual laboratories.

To allow a minimum statistical data analysis (as the calculation of the standard deviation), a least two replicates per variable had to be reported. This means that some data of Lab N° 13, 35, 37 and 58 (see Annex I, Table 1) were not included in the exploratory data analysis.

2.5 Tolerable limits for interlaboratory comparisons

Although the tolerable limits for soil have been developed for soil interlaboratory comparisons - where the replicates for one laboratory are measured under repeatability conditions - it is interesting to apply these limits on the FSCC reference sample, although these measurements have been spread over a period of 16 months and so include an additional source of variation (which is the long-term within laboratory variance or the laboratory's reproducibility).

On the **notched box plots** of each variable, the general cleaned mean after elimination of the outliers is indicated by a green line. The upper and lower tolerable limits for this mean value are indicated by two red lines. The procedure for the determination of the tolerable limits is described by De Vos, 2008. In this way the laboratories can evaluate their results on the FSCC reference sample as if they would have participated in a long-term interlaboratory comparison. When the measurements are outside the tolerable limits, actions are required to correct and improve their results.

2.6 Within laboratory repeatability and between laboratory reproducibility

In the analyses of the results of FSCC Interlaboratory Comparisons, we used a ring test protocol developed by Paul Quataert and Pieter Verschelde (INBO, 2003 – 2005) which assesses the within and between laboratory variability based on the Mandel' h and k statistics. Though, this protocol could not be applied here because it assumes that 1) the replicates of each laboratory are made under repeatability conditions and that 2) more or less the same number of replicates were analysed by each of the laboratories. By aggregating the submitted data by reporting period (covering each three months) we tried to homogenise the data set to fulfil the second condition. However, since a high number of laboratories only reported during one reporting period, the aggregated dataset showed often only one replicate meaning that the concerning laboratory would not be included in the data evaluation. So it was decided not to use the Mandel's h and k statistics but to rely on the graphs produced during the data exploration.

The coefficient of variation is the proportion of the standard deviation over the mean ($CV = sRepr/Mean * 100$). The overall mean of each variable maintained in this study is the mean after the elimination of the outlying laboratories, defined in the histograms and the box plots of the means and the standard deviations (see above). The reproducibility variance ($sRepr^2$) is the sum of the between laboratory variance ($sLab^2$) and the within laboratory variance ($sRep^2$).

$$s\text{Repr}^2 = s\text{Lab}^2 + s\text{Rep}^2$$

In the ideal situation, when there are no differences between the laboratories, the $s\text{Lab}^2$ and the $s\text{Rep}^2$ should be of the same magnitude.

2.7 Within laboratory reproducibility

Also at the level of the individual laboratory, a coefficient of variation can be defined as the percentage of reproducibility of the annual mean. Laboratories reported the results of the reference material over a maximum period of 16 months, so data suitable to assess the laboratory's reproducibility. The latter is requested quality information for the data submission in the BioSoil project.

2.8 Within and between day variability

When several replicates per day were available, the within and between day variability of the laboratory under consideration could be assessed. This within and between day variability can be assessed with the ring test protocol using the Mandel' h and k statistics (Quataert and Verschelde, 2003 – 2005).

De Vos (2008) also derived tolerable limits for the within laboratory variability under repeatability conditions. When several replicates were made on one day, FSCC recommends the laboratory to check whether it meets this quality requirement.

2.9 Construction of control charts

The results obtained from the analysis of the FSCC reference sample, can be used to set out the statistical control limits in the X-control charts (Nordic Innovation Centre, 2007). The control limits are set based on the analytical performance of the control sample. For a longer period of time, in the case of the FSCC reference sample a maximum period of 16 months, the standard deviation s is calculated from the control values. Warning limits are then $+2s$ and $-2s$ and action limits are $+3s$ and $-3s$. The mean central line is estimated from the same control values as the mean value over the considered period.

As this is a first line quality control action for the daily laboratory practise, it will not be further discussed in this report.

3 Results and discussion

3.1 Homogeneity

Table 1 compares the variability between the subsamples with the variability within the subsamples. For most variables the variation between the subsamples is lower than or equal to the variation within the subsamples. So for these variables, the subsamples can be considered homogeneous. For the elements Ca, P, Zn, LOI and pH(CaCl₂) the % variance between the subsamples is larger than the variation within the subsamples which can be an indication of heterogeneity. Concerning Ca, the measured value is very low. When an element is present in such low concentrations, it is not very suitable to be assessed in a reference sample since variations become relatively high.

The imbalance between within and between sample variation for Zn, LOI and pH(CaCl₂) is not that extreme. For the pH(CaCl₂), the CV is even lower than the mean laboratory repeatability. So it was decided to consider the FSCC reference standard homogeneously enough for distribution among the laboratories.

Table 1: Variance components of the homogeneity test

Variable	N° sub-samples	Unit	Gen. mean	St. dev. within sub-samples	st. dev. between sub-samples	Gen. St. dev.	CV	% variation between sub-samples	% variation within sub-samples	Evaluation
ExCa	10	ppm	506.1	72.74	94.75	119.45	23.6	62.9	37.1	>
ExCd	10	ppm	0.07	0.010	0.000	0.01	13.3	0.00	100	OK
ExCr	10	ppm	25.5	1.54	1.52	2.16	8.5	49.4	50.6	OK
ExCu	10	ppm	5.2	0.26	0.13	0.29	5.5	20.1	79.9	OK
ExK	10	ppm	2463.6	204.23	170.79	266.23	10.8	41.2	58.8	OK
ExMg	10	ppm	1527.5	93.46	25.07	96.77	6.3	6.7	93.3	OK
ExMn	10	ppm	126.9	11.14	2.29	11.37	9.0	4.1	95.9	OK
ExNa	10	ppm	105.3	17.38	15.38	23.20	22.0	43.9	56.1	OK
ExNi	10	ppm	5.5	0.29	0.24	0.38	6.9	40.4	59.6	OK
ExP	10	ppm	115.4	4.79	7.69	9.06	7.9	72.1	27.9	>
ExPb	10	ppm	8.9	0.36	0.16	0.40	4.5	16.6	83.4	OK
ExS	10	ppm	79.9	3.03	2.87	4.17	5.2	47.4	52.6	OK
ExZn	10	ppm	25.9	3.22	3.47	4.73	18.3	53.6	46.4	>
LOI	10	%	2.5	0.03	0.04	0.05	2.1	63.5	36.5	>
TotN	10	g/kg	0.05	0.004	0.002	0.004	8.5	29.6	70.4	OK
pH(CaCl ₂)	10	-	3.79	0.011	0.015	0.019	0.49	66.9	33.1	>

3.2 Exploratory data analysis

Consult Table I in Annex I and the figures organised per variable in the 34 Microsoft Powerpoint –files, compressed in one zip-file. Put your view in the 'Normal' mode to view the titles of the slide, facilitating scrolling through the presentations.

3.2.1 Particle size distribution

16 laboratories made use of the FSCC reference sample to evaluate their within laboratory reproducibility. The number of replicates per laboratory varied from 2 (Lab N° 80) till 33 (Lab N° 40, the central BioSoil laboratory). Overall the results were quite satisfactory.

The histograms and box plots identified for the sand and silt fraction one outlying laboratory (Lab N° 60) for the within laboratory variability. Their reported data show a reproducibility of 10-11% while most laboratories reach a reproducibility of maximum 5%.

The reported sand and silt content by Lab N° 60 was removed to calculate the outlier free mean.

Based on the overall uncleaned mean (10 % clay, 42% sand and 48% silt), the sample falls within the 'loam' textural class (USDA, 1951). After data cleaning, the mean silt fraction increased till 49% which is close to the boundary of 50% with the silt loam textural class. This means that the 5 laboratories, among which the central BioSoil laboratory, with a mean silt content of > 50% would report a silty loam textural class.

3.2.2 Soil reaction

24 of the 27 laboratories measured the pH(CaCl₂) and 19 measured the pH(H₂O). The required N° of reported digits is one, although most laboratories reported 2 digits. The notched box plots of most labs showed the shape of a normal distribution though for the labs reporting only one digit the shape was less conformal. Note that the reference method is a volumetric 1:5 measurement while in many laboratories the routine method is weight based.

Neither for pH(CaCl₂) nor for pH(H₂O) very deviant outliers were identified in the histograms (See Table 2). But several outlying laboratories popped up in the box plot of the standard deviations of pH(CaCl₂) (Labs N° 63, 60 and 71) and for pH(H₂O) in the box plots of the means (Labs N° 63 and 71) and the standard deviations (Labs N° 34, 60, 63 and 71). The observations of these laboratories were removed from the data set to estimate the outlier-free mean used in the further evaluation.

3.2.3 Total Organic Carbon

After the exclusion of Lab N° 35 that reported only one NA value, the dot plot contains the measurements of 19 laboratories.

Lab N° 71 reported during the third data submission completely different results from their first and second data submission. The laboratory was contacted and found a calculation mistake which could easily be corrected.

Lab N° 36 has been identified as an outlier in both the box plots of the means and of the standard deviations. In the beginning of the measurements there was a high variation and a high deviation from the mean. The results reported from June 2007 onwards were much better. The reproducibility decreased from 19.5% to 8%. So probably the problem has been solved in the meantime.

3.2.4 Total Nitrogen

21 laboratories reported results on the total Nitrogen. Lab N° 37 reported only one replicate. Lab N° 59 reported a very wide range of results and was therefore already in the histograms of the standard deviations identified as an outlier. In the box plot of the standard deviation labs N° 58 and 36 popped up with a high within-laboratory variability.

The exclusion of Lab N° 59 in the histogram was due to one very deviant outlier. After contact with the laboratory, it seemed the error was caused by the catalyst which was replaced afterwards.

Lab N° 60 reported in one data submission in the wrong units (% instead of g/kg). These values were corrected after contact between FSCC and the lab.

Although Total N is for many laboratories a routine analysis and usually has low variation in interlaboratory comparisons, the comparability for the reference sample is quite low. This is most probably due to the low N concentration in the sample (mean of 0.42 g/kg, cleaned mean of 0.44 g/kg) which is very close to the limit of quantification of many laboratories.

3.2.5 Exchangeable elements

While about 20 laboratories reported the common exchangeable elements (Al, Fe, Mn, Ca, Mg, K and Na) only 15 laboratories analysed the exchangeable acidity and/or the free H⁺. Especially the latter shows a very high variation both among and within the laboratories.

The laboratories N° 11, 42, 55, 59 and 64 had for at least some of the variables of this groups very deviant outliers, either for the between or for the within-laboratory variability. In the box plots of the means 12 laboratories (N° 8, 11, 23, 26, 34, 35, 55, 56, 59, 60 64 and 71) had an outlier for at least one variable. In the box plots of the standard deviations laboratories N° 8, 11, 23, 40, 58, 59, 60, 64 and 71 had also some problems.

The variation of the acid cations (Fe, Al and Mn) is clearly lower than the variation of the basic cations (Ca, K, Mg and Na) which is due to the acid nature of the sample where the concentrations of the basic cations are low and close to the LOQ.

Table 2: Outlying laboratories identified in the histograms and the box plots of the means and standard deviations reported for each variable by the individual laboratories.

Variable	no replicates	histograms			boxplots		
		means		standard deviations	means		standard deviations
		lower	higher	higher	lower	higher	higher
Pclay							
Psand							60
Psilt							60
pH(CaCl ₂)							63, 60, 71
pH(H ₂ O)						63, 71	63, 60, 34, 71
OC	35					36	36
TotN	37			59			36, 58
EcAcidity					23	26	
EcAl					55, 34	11	59, 71
EcCa			42, 64	59, 42	55	59	64
EcFe					55	11	71
EcK			11	11		71, 64	8, 64, 71
EcMg			42, 64	42	55		71, 58, 59
EcMn		55	64		34, 56	8, 59, 11	23, 71
EcNa			64			71, 11	11, 71
FreeH ⁺				42		35, 60	40
ExAl	58				56	37, 55	60
ExCa						42	
ExCd				6		6, 55, 64	55
ExCr					8		
ExCu	35			11	11	42, 64	64
ExFe							37, 34, 60
ExHg			6	6		64	8, 64
ExK						55, 42	11, 55
ExMg					58, 24, 56, 23	55, 71, 42	59, 60
ExMn							58, 34, 71, 11, 37
ExNa				40		71, 40, 64	71, 55
ExNi					59, 23, 7	34, 8, 11, 64	34, 59
ExP				34			23, 37, 40, 56
ExPb					59, 13	54, 60, 55	60, 64, 71
ExS				59	8	54, 64	6, 8, 71
ExZn				24		71, 55, 24	56, 64
ReAl	37					23, 40	40, 23
ReFe	37				64	40	

3.2.6 Extractable elements

Depending on the element, between 18 and 25 laboratories analysed the aqua regia extractable elements. 17 of these laboratories pop up in the exploratory graphs for at least one variable as an outlier either for the within or for the between lab variability (see Table 2 and the Figures). All the laboratories mentioned in Table 2 have been removed from the

dataset, to calculate the cleaned mean. FSCC recommends to all labs to check their position in the graphs and send their comments and/or corrections.

No significant declining or increasing trend in any of the chemical soil variables could be detected in any of the laboratories over the period of time under consideration.

Aluminium

Laboratory N°58 was not included in the exploratory graphs because they reported only one replicate, so neither the mean, standard deviation,... could be calculated.

The results of laboratory N° 56 were systematically lower compared to the other laboratories. Laboratories N° 37 and 55 had always higher results. The explanation can probably be found in the digestion method. Although not asked in this study, these two laboratories reported previously (in the FSCC interlaboratory comparisons) to use the microwave digestion method, while the reflux method is currently the only accepted reference method. Since losses during the digestion by microwave are minimal, it can be expected that the results of these two labs are relatively higher than the results obtained by laboratories using the reference method.

Laboratory N° 60 showed a relatively high within laboratory variability.

Calcium

Laboratory N° 42 reported systematically higher results compared to the other labs and was excluded for further analyses. This element has a relatively high overall coefficient of variation which is probably partly due to the low concentration of the element in the test sample.

Cadmium

The concentration of Cadmium was below the limit of quantification for many laboratories. So the FSCC reference sample is not a good reference sample for Cd to be included in a quality control programme.

Though, we might still learn from the scatter plots of the individual laboratories. Laboratory N°6 has a very high reproducibility. When measuring an element in low concentrations, the variation on the measurements might provide us information on the possible limit of quantification. When a first very deviant outlier is removed (see histograms of the means and Table 2), the standard deviation is 0.065 ppm. Taking $LOQ = 10 * \text{standard deviation}$, it would be equal to 0.65 ppm. It is strange that all the lab reported values are below this value.

Again laboratory N° 55 reported relatively high values compared to the other laboratories which showed additionally a high within laboratory variability.

Chromium

Again laboratory N° 37 and 55 reported the highest concentrations but were not identified as outliers. Laboratory N° 8 had exceptionally low results and was excluded in the box plot of the means.

Copper

In total, 25 laboratories reported values for extractable Copper. Lab N° 35 reported only one value = 2.7 ppm. Since there was only one replicate, the lab is not included in the exploratory data analysis. However, after the exclusion of Lab N° 11, outlying in the histogram of the box plot of the means, we see that Lab N° 35 would also be an outlier. So the lab was not only removed from the exploratory data graphs, but also from the final dataset to calculate the corrected mean value. On the upper side of the range two

laboratories were excluded based on the boxplot of the means (Lab N°42 and 64) while laboratory N° 64 also had a very high within laboratory variability.

Iron

Three laboratories were excluded based on their within laboratory reproducibility (Labs N° 34, 37 and 60). The maximum values are reported by Lab N° 37, while the results of Lab N° 55, a second laboratory digesting the samples by microwave, were close to the overall mean.

Mercury

Note that only eight laboratories reported the Hg content. The results of two laboratories (N° 6 and 64) were very deviant from the results of the remaining 6 laboratories. Laboratory N°6 is the only of these 8 laboratories measuring Hg with ICP AES, the other mainly use mon atom spectrometry techniques. It has an enormous variation (standard deviation = 0.17 ppm) on a mean of 0.39 ppm. Of the remaining 6 laboratories, Lab N° 8 showed a relative high standard deviation. For Mercury we can conclude, as for Cadmium, that the element is present in such a low concentrations that it can not be satisfactory measured by the majority of the laboratories.

Note that besides the method described in the manual according to ISO11466 for the determination of trace elements in aqua regia, ISO has developed a separate ISO norm for determination of Mercury in aqua regia solution by cold vapour spectrometry (ISO 16772:2004). FSCC recommends to include this method in the Manual IIIa on Sampling and Analysis of Soil.

Potassium

For K the two laboratories (Lab N° 42 and 55) on the upper side of the range, were excluded based on their mean values and Lab N° 11 and 55 were excluded based on their relatively poor within laboratory reproducibility.

Magnesium

Although the overall variability of the whole data set is relatively low (CV = 10.5%), the graphs reveal a relatively high number of laboratories with mean values on the lower (Labs N° 58, 24, 56 and 53) or the upper range (Labs N° 55, 71 and 42). Lab N° 59 and 60 showed a relatively high within laboratory variability.

Manganese

No laboratories were excluded based on their mean reported values. Five laboratories had relatively high standard deviations (Labs N° 11, 34, 37, 58 and 71).

Sodium

After Cd and Hg, Na was the extractable element with the poorest reproducibility among the different laboratories. It is an element with often high limits of quantification, meaning that many laboratories are measuring close to their detection limit. Laboratory N° 40 had a very high within laboratory variability and reported some exceptionally high results. Laboratories N° 40, 71 and 64 were excluded based on their relatively high mean values and labs N° 40, 71 and 55 based on their within laboratory reproducibility.

Nickel

21 laboratories reported values above the limit of quantification. Remarkable it that laboratory N° 56 had for Nickel, as for several other aqua regia extractable elements, very high LOQ values.

One third of these labs were excluded either on the low or high mean values (Lab N° 7, 8, 11, 23, 64), or combined with a high within laboratory variability (Labs N° 34 and 59).

Phosphorus

Concerning P, we see that there is a good reproducibility of the mean reported values. Also, overall the within laboratory variance was very good, except for the laboratories N° 34 (outlier in the histogram), 23, 56, 37 and 40.

Lead

Laboratory N° 56 had a very high LOQ and could not measure the concentration. Laboratory N° 13 and 59 reported relatively low values, while laboratories N° 54, 55 and 60 reported relatively high values. Labs N° 60, 64 and 71 showed a poor reproducibility within the lab.

Sulphur

For S, we see that the variation with Lab N° 59 is larger than the variation we see within all the other laboratories together. For this laboratory the S concentration in the FSCC reference sample is close to the LOQ. The laboratory was removed in the histogram of the standard deviations. Subsequently new laboratories popped up in the boxplots of the means (Labs N° 8, 54 and 64). Laboratories N° 6, 8 and 71 had relatively high within laboratory variability.

Zinc

For Zn, laboratory N° 24 reported some very deviant outliers and was therefore excluded in the histograms of the standard deviations. Laboratory N° 24, 71 and 55 were excluded in the boxplots based on their high mean values and Labs N° 56 and 64 had a very high within laboratory variability.

3.2.7 Oxalate extractable elements

14 laboratories reported results for the acid oxalate extractable Al and 15 for Fe, which is compared to the other elements, a relatively poor participation. Lab N° 37 reported only one value so was further excluded from the histograms and boxplots. Concerning Al, Lab N° 23 and 40 were excluded based both on their high mean values in the boxplots and their high within-laboratory variability. Concerning Fe, the mean values of Lab N° 64 and 40 deviated from the other labs.

3.3 Tolerable limits for interlaboratory comparisons

Concerning particle size distribution (see the slides with the notched box plots), all silt results were within the tolerable range. For the clay fraction one observation by Lab N° 59 was above the upper limit. For sand three observation of Lab N° 60 were outside the acceptable range.

Concerning the ring test tolerable limits for $\text{pH}(\text{CaCl}_2)$, two laboratories reported values above the upper limit (Labs N° 63 and 71) and two laboratories values below the tolerable limit (Labs N° 34 and 60). For $\text{pH}(\text{H}_2\text{O})$ four laboratories (N° 8, 34, 63 and 71) had values above the upper limit.

For Total Organic Carbon, three labs had results outside the tolerable range: Labs N° 36, 42 and 59 on the upper side and Lab N° 42 on the lower side. For Lab N° 42 this immediately implies that it has a wide within-laboratory variation (reproducibility).

For Total Nitrogen, there was no laboratory with all its results outside the tolerable range. Labs N° 7, 8, 36, 42, 58 and 59 reported values below the lower tolerable limit and 6 (out of 21) laboratories reported values above the upper tolerable limit for soil ring tests (Lab N° 8, 54, 56, 59, 60 and 64).

Table 3: Tolerable limits for soil ring tests applied on the results of the FSCC soil reference sample

Variable	Unit	cleaned mean	Tolerable limits					
			Obs range	ring test	min ring test	max ring test	% Labs outside	
Pclay	%	9.5	lower	±50%	50	4.7	14.2	0
Psand	%	41.2	higher	±25%	25	30.9	51.6	0
Psilt	%	48.6	higher	±30%	0	48.5	48.7	0
pH(CaCl ₂)		3.84		±5%	5	3.65	4.04	0
pH(H ₂ O)		4.24		±5%	5	4.03	4.46	0
OC	g/kg	6.37	lower	±20%	20	5.09	7.64	0
TotN	g/kg	0.44	lower	±30%	30	0.31	0.57	5
EcAcidity	cmol(+)/kg	3.21	higher	±35%	35	2.08	4.33	0
EcAl	cmol(+)/kg	2.85	higher	±30%	30	1.99	3.70	16
EcCa	cmol(+)/kg	0.10	lower	±65%	65	0.04	0.17	10
EcFe	cmol(+)/kg	0.10	higher	±50%	50	0.05	0.16	11
EcK	cmol(+)/kg	0.06	lower	±45%	45	0.03	0.08	10
EcMg	cmol(+)/kg	0.04	lower	±50%	50	0.02	0.06	10
EcMn	cmol(+)/kg	0.03	lower	±45%	45	0.02	0.05	11
EcNa	cmol(+)/kg	0.03		±80%	80	0.01	0.05	11
FreeH	cmol(+)/kg	0.16		±100%	100	0	0.32	13
ExAl	ppm	9017.1	higher	±20%	20	7213.7	10820.5	22
ExCa	ppm	353.6	lower	±70%	70	106.1	601.1	17
ExCd	ppm	0.027	lower	±100%	100	0.000	0.054	17
ExCr	ppm	22.0	higher	±25%	25	16.5	27.5	5
ExCu	ppm	3.9	lower	±40%	40	2.4	5.5	13
ExFe	ppm	11609.8	higher	±15%	15	9868.3	13351.3	0
ExHg	ppm	0.029		±75%	75	0.007	0.051	25
ExK	ppm	1640.5	lower	±60%	60	656.2	2624.8	4
ExMg	ppm	1348.2	higher	±15%	15	1146.0	1550.4	17
ExMn	ppm	112.9	lower	±30%	30	79.0	146.7	0
ExNa	ppm	39.0	lower	±65%	65	13.7	64.4	21
ExNi	ppm	4.0	lower	±40%	40	2.4	5.6	0
ExP	ppm	105.4	lower	±45%	45	58.0	152.8	0
ExPb	ppm	7.3		±30%	30	5.1	9.5	17
ExS	ppm	76.1		±35%	35	49.4	102.7	6
ExZn	ppm	20.2	lower	±40%	40	12.1	28.3	0
ReAl	ppm	1317.0	higher	±15%	15	1119.5	1514.6	36
ReFe	ppm	2764.0	higher	±15%	15	2349.4	3178.6	20

The tolerable limits for soil ring tests have been defined in such a way that about 75 -80 % of the laboratories ought to fall within these limits (De Vos, 2008). Most of the variables fit these requirements. The 'problem variables' are the oxalate extractable Al and Fe and the aqua regia extractable Al, Hg and Na were more than 20% of the laboratories fail to report median results within the tolerable range.

In an interlaboratory comparison a laboratory will fail to pass the tolerable limits in case more than 50% of all its results for all ring test samples fall outside the limits. In this exercise only one sample is included. Since it has been analysed numerous times, the laboratories have been evaluated on the median values. When the median value is outside the tolerable range, 50% of its results are outside the tolerable range and the laboratory does not meet the required quality.

This first application of the tolerable limits on a sample analysed by different laboratories, shows that the number and the identity of the excluded labs following this procedure is not necessary the same as identified in the exploratory graphs of the histograms and the boxplots.

3.4 Within and between laboratory variability

Since the number of replicates was different for each laboratory, it was not possible to evaluate the laboratories based on their (relative) 'within laboratory' variability. However, an estimation of the relative importance 'within' versus 'between laboratory variability' of the whole data set could be made.

Table 4 shows the variance components of the cleaned dataset, after the elimination of the outliers defined in Table 2. Ideally the within and between laboratory variance should be of the same magnitude. For most elements the between laboratory variability is larger than the within laboratory variability. This was also the main reason for the BioSoil project to have a subset of all samples analysed by one central laboratory.

For Exchangeable Mn all the variation is included in the within laboratory variability meaning that some laboratories have internal variability which is higher than the variation compared to other labs.

Pb is an example of an element where a large portion of the total variation is due to a poor within laboratory reproducibility.

Table 4: Variance components of the cleaned dataset

Variable	Unit	Mean	stdev within	gen stdev	Between lab variance (%)	Within lab variance (%)	CV (%)
pH(CaCl2)		3.84	0.040	0.083	76.36	23.64	1.05
pH(H2O)		4.24	0.045	0.081	69.23	30.77	1.90
Psand	%	41.2	1.416	3.228	80.76	19.24	7.83
Psilt	%	48.6	1.677	3.332	74.68	25.32	6.86
Pclay	%	9.5	0.747	1.802	82.84	17.16	19.0
OC	g/kg	6.4	0.373	0.554	54.68	45.32	8.7
TotN	g/kg	0.4	0.042	0.099	82.24	17.76	22.6
EcAcidity	cmol(+)/kg	3.21	0.225	0.464	76.53	23.47	14.5
EcAl	cmol(+)/kg	2.85	0.121	0.369	89.17	10.83	13.0
EcCa	cmol(+)/kg	0.10	0.021	0.035	64.88	35.12	34.2
EcFe	cmol(+)/kg	0.10	0.012	0.020	64.42	35.58	18.9
EcK	cmol(+)/kg	0.06	0.007	0.025	92.43	7.565	42.7
EcMg	cmol(+)/kg	0.04	0.007	0.020	88.48	11.52	50.7
EcMn	cmol(+)/kg	0.03	0.003	0.003	-4.53	104.53	10.2
EcNa	cmol(+)/kg	0.03	0.006	0.015	83.82	16.18	54.1
FreeH	cmol(+)/kg	0.16	0.051	0.080	59.23	40.77	49.9
ExAl	g/kg	9017.1	522.3	875.2	64.4	35.6	9.7
ExCa	g/kg	353.6	52.4	140.8	86.1	13.9	39.8
ExCd	g/kg	0.027	0.014	0.037	85.4	14.6	136.4
ExCr	g/kg	22.0	1.74	2.61	55.6	44.4	11.9
ExCu	g/kg	3.9	0.42	1.79	94.5	5.5	45.5
ExFe	g/kg	11609.8	366.7	889.0	83.0	17.0	7.7
ExHg	g/kg	0.029	0.003	0.005	54.6	45.4	16.7
ExK	g/kg	1640.5	129.8	302.2	81.6	18.4	18.4
ExMg	g/kg	1348.2	58.4	74.6	38.8	61.2	5.5
ExMn	g/kg	112.9	5.69	12.38	78.9	21.1	11.0
ExNa	g/kg	39.0	8.17	24.78	89.1	10.9	63.5
ExNi	g/kg	4.0	0.44	2.33	96.4	3.6	58.5
ExP	g/kg	105.4	5.81	20.30	91.8	8.2	19.3
ExPb	g/kg	7.3	0.78	3.41	94.8	5.2	46.8
ExS	g/kg	76.1	4.28	8.91	76.9	23.1	11.7
ExZn	g/kg	20.2	1.29	1.86	52.3	47.7	9.2
ReAl	g/kg	1317.0	57.2	128.1	80.0	20.0	9.7
ReFe	g/kg	2764.0	123.9	174.6	49.6	50.4	6.3

Concerning the coefficients of variation, which include both within and between laboratory variability, we see a very wide range depending on the analytical variable. For the soil reaction, the variation is very low. Also the CV of the texture analysis and the organic carbon content is below 20 %. The highest variability is seen for the basic exchangeable elements Ca, K, Mg, Na and Free H⁺ and for the extractable elements Cd, Cu, Na, Ni and Pb. For most of these elements the concentration in the FSCC reference sample could have been close to the limit of quantification of many of the laboratories. The heavy metals Ni and Cr had a

relatively low coefficient of variation. Also the variation for Hg was quite low, but remembering that this only concerns the results of 6 laboratories after data cleaning.

Note that in this report we compare the magnitude of standard deviations between laboratories. Besides the fact that the number of replicates strongly differs between the laboratories, FSCC does not know whether a pre-selection on the data had been done before sending us the results. Some laboratories reported all replicates while others might have removed (some of) the outliers. This makes the comparison between the laboratories a bit tricky.

3.5 Within and between day variability

A few laboratories made several replicates a day and this for several days usually spread over the full reporting period, allowing us to assess the within and between day variability within one laboratory.

3.5.1 Laboratory N° 59

Laboratory N° 59 reported for the exchangeable elements, free H⁺ and exchangeable acidity between 2 and 6 replicates on one day and this for 16 till 18 days (between 15 Feb '07 and 16 May '08). This data allow us to evaluate whether the within laboratory variability is mainly situated within one day or whether it is mainly caused by differences between the days. Outliers, stragglers and tail values (95 and 99% confidence limits) based on differences in the means between the days and/or on differences within one day can be identified. After 3 iterations the following results were obtained.

Table 5: Variance components of Laboratory N°59 of the between and within day variability

Variable	Outliers and stragglers	Step	Ntot	Ndays	Neff	Mgen	Min	Max	sRep	sDay	sRpr	CV	PDay
EcAcidity	k 05/05/2008 S	1	73	16	4.55	3.63	3.35	3.98	0.25	0.17	0.30	8.3	31
EcAl	k 05/07/2008 S	1	73	16	4.55	3.32	3.05	3.74	0.23	0.16	0.28	8.4	34
EcCa		1	67	16	4.17	0.16	0.08	0.41	0.09	0.08	0.11	73.3	45
EcFe	k07/04/2007	2	68	15	4.52	0.12	0.10	0.14	0.01	0.01	0.01	8.6	55
EcK	hk04/02/2008	2	71	15	4.73	0.07	0.07	0.07	0.00	0.001	0.004	5.7	8
EcMg	hk04/02/2008;k07/12/2007	3	73	16	4.55	0.05	0.03	0.06	0.02	0	0.02	38.3	0
EcMn	k 07/11/2007 S	1	73	16	4.55	0.04	0.03	0.04	0.002	0.001	0.002	5.5	34
EcNa	k05/30/2007;h10/11/2007; hk 10/11/2007 S	2	65	14	4.63	0.03	0.02	0.03	0.001	0.001	0.002	5.9	47
FreeH		1	73	17	4.28	0.11	0.06	0.16	0.03	0.02	0.04	35.8	38

Legend:

Step	Number of steps applied in the iteration procedures to identify the outliers
Ntot	Total number of observations for this variable
Ndays	Number of days on which the variable has been measured
Mgen, min, max	The general cleaned mean, mean minimum and mean maximum after the exclusion of the outliers
sRep	Within day standard deviation
sDay	Between day standard deviation
sRepr	Reproducibility standard deviation where $sRepr^2 = sRep^2 + sDay^2$
CV	Coefficient of variation of the cleaned dataset of the reproducibility standard deviation $CV = sRepr/Mgen * 100$
PDay	Percentage of the between day variance in the total variance

By way of an examples, let us consider exchangeable acidity. No outliers but one straggler was identified: the 5th of May 2008. Since only real outliers have been excluded from the data set, stragglers were retained. The coefficient of variation = 8.3% is a good indication of the long-term within laboratory variance. Since 31 % of the variance is due to differences between the day, 69% of the variance can be attributed to difference within one day.

Logically it is expected that the variance between the days is larger than the variation within one day. When the opposite is true, it is probably difficult to further improve.

For exchangeable calcium we see again a very high CV. 45% of this variance is due to differences between different days. After the exclusion of two outliers for exchangeable Mg, all the variance is due to differences within one day.

3.5.2 Laboratory N° 40, the central laboratory

The central laboratory made during 8 – 11 weeks, 3 replicates a day of most of the variables.

Table 6: Variance components of Laboratory N°40 of the between and within day variability

Variable	Outliers and stragglers	Step	Ntot	Ndays	Neff	Mgen	Min	Max	sRep	sDay	sRpr	CV	PDay
pHCaCl2		1	33	11	3	3.94	3.88	4.00	0.01	0.03	0.04	0.9	84
pHH2O	k06/10/2007	2	30	10	3	4.22	4.18	4.32	0.02	0.05	0.05	1.2	89
Pclay		1	33	11	3	8.9	7.87	9.87	0.24	0.65	0.70	7.8	88
Psand	k03/27/2007	2	30	10	3	39.4	38.60	41.47	0.59	0.72	0.93	2.4	60
Psilt	k03/27/2007	2	30	10	3	51.7	50.07	52.77	0.59	0.81	1.01	1.9	65
OC		1	33	11	3	6.62	6.33	6.93	0.31	0	0.31	4.7	0
TotN		1	33	11	3	0.40	0.36	0.44	0.01	0.02	0.02	5.8	75
EcAcidity	k11/27/2007	2	30	10	3	3.18	3.06	3.31	0.04	0.08	0.09	2.9	77
EcAl		1	33	11	3	3.01	2.89	3.15	0.04	0.08	0.09	2.9	79
EcCa	k 6/16/2007 S	1	33	11	3	0.11	0.09	0.15	0.02	0.01	0.03	23.0	23
EcFe		1	33	11	3	0.12	0.11	0.13	0.004	0.010	0.011	9.1	82
EcK		1	33	11	3	0.07	0.06	0.07	0.002	0.004	0.005	7.5	75
EcMn	h12/03/2007	2	30	10	3	0.03	0.03	0.03	0.001	0.001	0.001	3.4	53
EcNa	k06/10/2007	2	30	10	3	0.03	0.03	0.03	0.001	0	0.001	4.5	0
ExAl		1	33	11	3	9732	9027	10423	362	402	541	5.6	55
ExCa		1	33	11	3	488	385	568	61	56	83	16.9	45
ExCd	hk03/27/2007	2	25	9	2.77	0.022	0.013	0.031	0.004	0.005	0.006	29.2	65
ExCr	k12/17/2007	2	30	10	3	22.7	22.13	23.30	0.43	0.32	0.53	2.3	36
ExCu	hk07/25/2007; h 03/12/2007 S	2	30	10	3	4.9	4.67	5.27	0.24	0.12	0.26	5.4	19
ExFe		1	33	11	3	12357.6	11867	12667	280	202	344.69	2.8	34
ExHg		1	33	11	3	0.032	0.026	0.039	0.0012	0.0036	0.004	11.7	91
ExK	h 03/13/2007 S	1	33	11	3	2185.2	1900	2460	165	156	227.23	10.4	47
ExMg		1	33	11	3	1388.2	1316.7	1440.0	31.6	36.1	47.99	3.5	57
ExMn		1	33	11	3	127.7	118.3	134.0	4.2	4.8	6.36	5.0	56
ExNa		1	33	11	3	172.2	115.3	228.0	52.5	34.1	62.63	36.4	30
ExNi	h 06/16/2007 S	1	33	11	3	5.61	5.20	6.66	0.66	0.21	0.69	12.3	9
ExP		1	33	11	3	72.2	35.00	90.97	1.47	23.87	23.91	33.1	100
ExPb		1	33	11	3	9.0	7.87	9.67	0.38	0.47	0.60	6.7	60
ExS		1	33	11	3	84.1	77.40	89.20	2.55	3.21	4.10	4.9	61
ExZn		1	33	11	3	21.3	20.33	22.23	0.42	0.54	0.68	3.2	62
ReAl		1	24	8	3	1823.8	1646.7	2046.7	142.3	129.4	192.3	10.5	45
ReFe		1	33	11	3	3241.8	3056.7	3440.0	167.3	112.9	201.8	6.2	31

Legend: see Table 5

By comparing the CVs of the central laboratory with the overall CVs in Table 4, one may gain insight on the quality improvement that will be made by analysing BioSoil soil samples by one central laboratory. Only concerning the extractable P however, the central laboratory has a remarkable poor within-laboratory reproducibility compared to the other laboratories. This variance is nearly completely caused by differences between different days. Other problem variables in this reference samples are exchangeable Calcium, and Aqua Regia extractable Ca, Cd and Na.

3.5.3 Laboratory N° 26

Laboratory N° 26 made duplicates in one day for the exchangeable elements, the textural analysis, the oxalate extractable elements, the pH, organic carbon and total Nitrogen. Based on the provided data, no outliers were identified. Only a few stragglers were observed. Compared to the Lab N° 59,40 and 34, this laboratory had a good reproducibility for the exchangeable Calcium.

Table 7: Variance components of Laboratory N°26 of the between and within day variability

Variable	Stragglers	Step	Ntot	Ndays	Mgen	Min	Max	sRep	sDay	sRpr	CV	PDay
EcAl		1	14	7	3.339	3.250	3.465	0.036	0.073	0.081	2.4	80.7
EcCa		1	14	7	0.109	0.105	0.115	0.008	0	0.008	7.0	0
EcFe		1	14	7	0.097	0.090	0.105	0.008	0	0.008	7.8	0
EcK		1	14	7	0.081	0.075	0.090	0.004	0.004	0.005	6.7	52.0
EcMg		1	14	7	0.047	0.040	0.050	0.004	0.003	0.005	10.1	36.8
EcMn		1	14	7	0.030	0.030	0.030	0	0	0	0	
EcNa		1	14	7	0.044	0.035	0.060	0.008	0.006	0.010	21.5	36.8
OC		1	18	7	6.419	6.020	6.920	0.198	0.219	0.295	4.6	54.8
Pclay		1	24	12	7.397	7.035	7.660	0.168	0.167	0.237	3.2	49.6
Psand	k 03/26/2007	1	24	12	38.009	37.100	39.175	0.923	0.000	0.923	2.4	0.0
Psilt		1	24	12	48.915	46.810	50.825	1.264	0.859	1.528	3.1	31.6
ReAl		1	12	6	1296.2	1276.6	1342.3	26.2	16.2	30.8	2.4	27.6
ReFe	k 05/23/2007	1	12	6	2812.1	2734.2	2940.8	72.1	55.8	91.2	3.2	37.4
TotN		1	14	7	0.4	0.385	0.425	0.011	0.010	0.015	3.7	42.2
pHCaCl2		1	24	11	3.75	3.71	3.82	0.031	0.022	0.038	1.0	32.4
pHH2O	k 03/30/2007	1	21	10	4.17	4.10	4.23	0.016	0.041	0.044	1.0	86.5

Legend: see Table 5

3.5.4 Laboratory N°34

Laboratory N° 34 reported for the exchangeable and extractable elements, organic carbon and total nitrogen between 3 and 5 replicates a day, for 5 till 8 days.

Table 8: Variance components of Laboratory N°34 of the between and within day variability

Variable	Outliers and stragglers	Step	Ntot	Ndays	Mgen	Min	Max	sRep	sDay	sRpr	CV	PDay
EcAcidity		1	28	8	2.546	2.280	3.080	0.151	0.228	0.273	10.7	69.4
EcAl	h02/07/2008; h02/04/2008; h02/04/2008 S	3	24	6	1.885	1.863	1.945	0.186	0.000	0.186	9.9	0
EcCa	k03/20/2008	2	25	7	0.115	0.090	0.150	0.015	0.021	0.026	22.4	66.4
EcFe		1	28	8	0.086	0.075	0.100	0.011	0.006	0.013	14.6	24.5
EcK		1	20	7	0.058	0.047	0.070	0.008	0.007	0.010	18.2	40.4
EcMg		1	28	8	0.053	0.040	0.065	0.008	0.005	0.010	18.1	28.3
EcMn		1	28	8	0.026	0.023	0.030	0.005	0.000	0.005	21.0	0
EcNa		1	21	7	0.030	0.025	0.040	0.004	0.004	0.006	20.0	45.3
ExAl	hk05/07/2008; h05/07/2008 S	2	39	7	8762.5	8599.1	9065.8	499.2	0.0	499.2	5.7	0.0
ExCa	05/07/2008 S	1	42	8	281.6	254.8	323.4	36.2	20.9	41.8	14.8	24.9
ExCr	k05/07/2008	2	39	7	24.6	21.6	28.2	1.5	2.5	2.9	11.8	72.9
ExCu		1	22	7	4.8	4.3	5.3	0.2	0.3	0.4	7.4	64.1
ExFe		1	42	8	11496.9	10943.4	12048.8	596.6	183.8	624.3	5.4	8.7
ExHg		1	13	5	0.028	0.027	0.030	0	0	0.002	6.2	12.6
ExK	h04/05/2007 S	1	42	8	1637.4	1548.8	1858.1	166.2	50.0	173.5	10.6	8.3
ExMg		1	42	8	1309.0	1226.5	1399.8	88.7	38.0	96.5	7.4	15.5
ExMn		1	42	8	112.9	105.4	128.0	8.9	5.4	10.4	9.2	26.9
ExNa	h04/20/2007 S	1	42	8	45.0	41.6	53.2	7.5	1.0	7.5	16.7	1.7
ExNi		1	12	5	5.9	4.8	7.8	0.7	1.2	1.4	23.9	75.1
ExP		1	42	8	149.0	114.1	192.3	19.9	24.5	31.6	21.2	60.4
ExPb		1	17	5	9.1	6.6	10.3	0.9	1.4	1.6	17.9	72.1
ExZn	k05/13/2008 S	1	42	8	22.5	20.7	24.4	1.5	1.2	1.9	8.5	40.0
FreeH	h03/11/2008; k07/27/2007 S	2	26	7	0.2	0.2	0.3	0.0	0.0	0.0	20.1	90.0
OC		1	24	5	6.7	6.6	6.9	0.2	0.1	0.2	3.7	25.7
TotN		1	24	5	0.4	0.4	0.5	0.0	0.0	0.0	7.0	50.5

Legend: see Table 5

4 Conclusions and recommendations

Some laboratories are mentioned more frequently with errors and outliers than others. Though, one need to be careful in judging a laboratory based solely on this report. Some laboratories reported all measured values of the reference sample, also when, based on the first line control, immediate actions were taken to investigate the problem and to correct or redo the measurement. Other laboratories might not have reported doubtful results, which they could identify using the control charts or by other quality control measures. Also the amount of analytical results we received, differed greatly between the laboratories making statistical tests unbalanced.

On the other hand, we see that sometimes doubtful results ('noise') were reported probably below the quantification limit. This would indicate that there are still laboratories that are not fully aware of their detection and quantification limits.

So the results of the report reveal different levels of quality management within the BioSoil laboratories. To improve quality management in all the labs, the next FSCC interlaboratory comparison could be a good opportunity to gain a better insight on these practises e.g. on the method of determination of the quantification limits. This can shed more light on the reason for the high differences in LOQ values between the different labs.

The, in the meantime, traditional mistakes in reporting soil data were again met in the data reported for the reference material (e.g. factor 10 too high or too low, relative data where the sum is not 100%, wrong reporting dates, mixing of variables etc.). The frequency of this mistakes should be drastically lowered when the data undergo automatically run quality checks during the data submission. Within BioSoil, JRC/INRA Orléans is taking care of this part of the quality control programme.

Further the results on the aqua regia extractable elements in this report, let us assume that a part of the high variation between the labs, is still due to differences in the methods. Laboratories that use the microwave digestion methods have for several elements systematically higher results. And since this digestion method is less laborious, these labs are very reluctant to change again to the 'old fashion' reflux method.

Within this report, the reproducibility of the central laboratory was estimated for all the variables. As expected, a large quality improvement is seen when the coefficient of variations are compared with the overall dataset except for aqua regia extractable Phosphorus. Other problem variables are extractable Sodium and the oxalate extractable elements.

Annex I

		Lab.ID																											
Variable	Statistic	6	7	8	11	13	23	24	26	30	34	35	36	37	40	42	54	55	56	58	59	60	61	63	64	69	71	80	All labs
Pclay	Max	10.6	12.0				10.0		7.8		13.5		13.0	8.9	10.1	8.9				12.0	14.3	13.0		10.1	10.0		10.0	10.5	14.26
	Min	9.5	10.0				8.6		6.8		10.7		12.0	6.8	7.8	5.2				10.0	9.7	9.0		8.0	8.0		8.0	10.1	5.20
	Mean	9.9	11.0				9.3		7.4		11.5		12.3	8.0	8.9	7.3				10.8	12.2	10.4		9.3	8.8		9.4	10.3	9.47
	Median	9.7	11.0				9.2		7.5		11.4		12.0	8.1	8.7	7.5				11.0	12.1	10.0		9.4	9.0		9.0	10.3	9.27
	Total N	4	15				15		24		21		3	17	33	21				5	18	15		9	5		16	2	223
	Std Dev.	0.48	0.38				0.47		0.23		0.61		0.58	0.56	0.68	0.91				0.84	1.10	1.06		0.68	0.84		0.90	0.28	1.74
CV	4.87	3.44				5.04		3.17		5.27		4.68	7.00	7.62	12.57				7.75	9.01	10.15		7.38	9.51		9.55	2.75	18.37	
Psand	Max	41.2	39.0				48.7		40.9		42.0		36.0	41.7	43.6	45.4				50.0	47.0	52.0		49.4	50.0		44.3	47.1	52.0
	Min	41.1	37.0				45.0		37.1		39.7		35.0	40.3	37.3	38.9				43.0	39.2	39.0		40.5	45.0		40.0	47.1	35.0
	Mean	41.15	37.7				46.8		38.0		40.7		35.7	41.1	39.6	41.7				47.0	41.4	47.2		44.6	46.6		42.7	47.1	41.6
	Median	41.15	38.0				47.1		37.7		40.5		36.0	41.1	39.3	41.3				48.0	41.1	50.0		45.3	46.0		43.0	47.1	41.0
	Total N	2	15				15		24		21		3	17	33	21				5	18	15		9	5		16	2	223
	Std Dev.	0.07	0.72				1.11		0.87		0.72		0.58	0.41	1.16	1.78				2.65	1.64	5.10		2.94	2.07		1.55	0.00	3.59
CV	0.17	1.92				2.38		2.29		1.77		1.62	1.01	2.93	4.27				5.63	3.97	10.81		6.59	4.45		3.63	0.00	8.63	
Psilt	Max	50.1	52				45.845		51.53		49.0593		53	52.5	53.4	54.1				46	48.82	52		50.385	46		51	42.9	54.1
	Min	48.2	49				41.142		45.79		46.1947		51	49.9	47.8	45.7				40	39.6	38		42.573	42		44	42.5	38.0
	Mean	49.2	51.3				43.3		48.9		47.4		52.0	50.9	51.5	51.0				42.2	46.0	42.4		46.2	44.6		47.9	42.7	48.2
	Median	49.4	52.0				43.2		49.4		47.3		52.0	50.8	51.7	51.1				42.0	46.8	40.0		44.8	45.0		48.0	42.7	49.0
	Total N	3	15				15		24		21		3	17	33	21				5	18	15		9	5		16	2	223
	Std Dev.	0.96	0.90																										

		Lab.ID																												
Variable	Statistic	6	7	8	11	13	23	24	26	30	34	35	36	37	40	42	54	55	56	58	59	60	61	63	64	69	71	80	All labs	
ExS	Max	112.2	85.3	75.0	77.9	79.1			80.7	90.0		74.9	72.6	89.44	91.7		103.0	99.0			160.0		85.0		105.2	71.9	72.6		388.86	
	Min	69.6	68.5	31.0	67.7	57.0			61.6	70.0		74.9	66.0	74.71	75.5		95.4	86.0			3.0		73.3		96.0	49.9	38.2		3.00	
	Mean	77.2	73.2	48.3	73.0	67.6			68.4	80.0		74.9	69.9	83.05	84.1		98.9	93.3			64.7		78.9		100.5	62.1	56.2		72.74	
	Median	75.1	72.7	46.0	73.2	67.1			66.9	80.0		74.9	70.1	83.74	84.1		98.6	95.0			68.2		78.2		98.7	63.2	48.6		74.40	
	Total N	34	43	32	7	26			19	25		2	8	17	33		4	11			98		21		5	10	13		431	
	Std Dev.	9.19	3.39	13.33	3.27	5.29			5.03	2.89		0.00	1.92	4.59	4.02		3.31	4.17			31.87		3.10		4.30	6.97	14.17		25.1	
	CV	11.89	4.63	27.61	4.49	7.83			7.36	3.61		0.00	2.75	5.53	4.78		3.35	4.48			49.24		3.93		4.27	11.22	25.20		34.56	
ExZn	Max	22.1	23.3	21.6	21.5	19.7	17.4	37.5	21.0	22.2	26.8	18.2	20.7	24.32	22.7	23.0	22.2	28.6	24.1	19.7	21.1	24.3	26.9		23.4	19.5	26.5		37.50	
	Min	18.9	18.1	16.5	18.0	17.5	15.8	22.0	15.2	18.2	19.3	18.0	17.0	18.73	20.0	20.0	20.1	22.5	9.3	16.6	16.6	19.0	15.9		16.8	18.1	21.8		9.28	
	Mean	20.2	19.6	19.8	19.7	18.5	16.7	28.8	19.1	19.8	22.4	18.1	19.5	22.07	21.3	21.1	20.9	25.8	18.0	18.0	18.4	21.8	19.2		19.9	18.9	24.0		20.69	
	Median	20.1	19.4	20.1	19.6	18.5	16.8	25.5	19.3	19.8	22.1	18.1	20.1	22.18	21.2	21.0	20.7	25.8	18.0	18.0	18.3	21.9	19.0		19.4	19.0	23.5		20.19	
	Total N	34	43	32	7	27	4	5	19	25	48	2	7	17	33	30	4	12	51	10	13	15	21		5	10	7		492	
	Std Dev.	0.57	1.20	1.23	1.38	0.54	0.87	6.44	1.37	1.20	1.80	0.14	1.39	1.73	0.87	1.06	0.91	1.64	2.70	0.88	1.45	1.41	2.16		3.17	0.43	1.68		3.14	
	CV	2.84	6.11	6.22	7.03	2.93	5.21	22.35	7.16	6.04	8.03	0.78	7.12	3.13	5.03	4.33	6.36	14.99	4.91	7.88	6.46	11.23		15.88	2.29	6.99		15.16		
OC	Max		7.0	7.1	6.8	6.4	6.9		7.2	7.2	7.1	NA	12.9		7.3	8.4	6.6		7.2	7.0	8.1	7.3		7.4	6.1	7.4		12.9		
	Min		6.4	5.2	6.3	6.3	6.3		5.9	6.6	6.2	NA	6.2		6.1	4.8	5.5		5.5	6.0	5.2	5.6		6.7	5.8	6.1		4.76		
	Mean		6.7	6.2	6.5	6.4	6.6		6.4	6.8	6.7	NA	7.4		6.6	6.0	6.0		6.0	6.7	6.3	6.5		7.0	5.9	6.7		6.05		
	Median		6.7	6.2	6.5	6.4	6.6		6.5	6.7	6.8	NA	6.9		6.6	6.0	6.0		6.0	7.0	6.2	6.6		7.0	5.9	6.7		6.45		
	Total N		54	27	24	4	8		19	20	41	1	40		33	40	16		87	3	98	15		5	5	22		562		
	Std Dev.		0.15	0.40	0.13	0.05	0.20		0.28	0.16	0.27		1.44		0.30	0.53	0.35		0.35	0.58	0.50	0.49		0.26	0.14	0.34		0.641		
	CV		2.30	6.48	1.93	0.84	3.09		4.37	2.40	4.04		19.50		4.47	8.86	5.88		5.79	8.66	8.00	7.55		3.64	2.40	5.10		10.59		
ReAl	Max		1446	1304		1760	2029.1		1383.5	1400	1445	1430	1387.8	1075	2290			1623	1315.9						1226.6			2290.0		
	Min		1208	1294		1576	1508		1184.5	1210	1180	1200	1279.2	1075	1590			1537	1205.4						1141.5			1075.0		
	Mean		1281.18	1299		1672.13	1792.5		1288.83	1293.68	1315	1260	1330.14	1075	1823.8			1577.6	1245.9						1177.1			1400.5		
	Median		1268	1299		1665	1816.4		1287.25	1300	1335	1205	1324	1075	1775			1562	1233.0						1170.7			1307.0		
	Total N		22	2		8	4		38	19	12	4	7	1	24			5	14						5			165		
	Std Dev.		55.91	7.071		56.16	254.3		41.68	54.79	80.48	113.4	44.48	0	188.5			39.76	37.29						35.1			233.6		
	CV		4.36	0.54		3.36	14.19		3.23	4.24	6.12	9.00	3.34	0	10.34			2.52	2.99						2.98			16.68		
ReFe	Max		3123.0	2832.0		2935.0	3376.8		3055.0	2930.0	2875.0	3030.0	2780.3	2174.0	3650.0			2988.0	2800.4						2197.6		3002.2	3650.0		
	Min		2620.0	2775.0		2784.0	2872.8		2626.7	2410.0	2345.0	2580.0	2399.2	2174.0	2970.0			2846.0	2507.1						2080.3		2796.3	2080.3		
	Mean		2858.9	2803.5		2843.0	3118.1		2769.2	2693.2	2594.6	2720.0	2583.8	2174.0	3241.8			2940.4	2612.0						2149.1		2884.6	2837.6		
	Median		2847.5	2803.5		2825.0	3114.7		2751.1	2680.0	2572.5	2635.0	2571.8	2174.0	3210.0			2958.0	2589.9						2169.5		2865.9	2800.7		
	Total N		22	2		6	6		38	19	12	4	7	1	33			5	14						3		9	181		
	Std Dev.		121.8	40.31		58.26	166.7		97.28	135.9	153.4	213.1	127.9	0	199.8			58.05	86.35						61.24		72.32	272.8		
	CV		4.26	1.44		2.05	5.35		3.51	5.05	5.91	7.83	4.95	0	6.16			1.97	3.31						2.85		2.51	9.61		
TotN	Max		0.40	0.60	0.35	0.49	0.39		0.43	0.47	0.49	0.54	0.50	0.4	0.45	0.45	0.63		0.68	0.50	3.56	0.60		0.50	0.60		0.50	3.56		
	Min		0.23	0.30	0.32	0.41	0.31		0.38	0.43	0.39	0.45	0.20	0.4	0.35	0.26	0.50		0.45	0.30	0.10	0.40		0.50	0.48		0.40	0.04		
	Mean		0.32	0.40	0.33	0.46	0.36		0.40	0.44	0.43	0.51	0.33	0.4	0.40	0.38	0.55		0.57	0.43	0.38	0.48		0.50	0.54		0.41	0.42		
	Median		0.31	0.40	0.33	0.47	0.36		0.40	0.44	0.42	0.51	0.30	0.4	0.40	0.40	0.54		0.57	0.50	0.33	0.50		0.50	0.55		0.40	0.40		
	Total N		54	27	13	4	11		18	20	41	9	40	1	33	40	16		87	3	96	15		2	5		16	551		
	Std Dev.		0.038	0.071	0.011	0.038	0.028		0.013	0.009	0.028	0.028	0.076	0	0.023	0.046	0.033		0.048	0.116	0.342	0.068		0	0.056		0.034	0.17		
	CV		11.94	17.64	3.34	8.33	7.80		3.22	2.01	6.50	5.60	22.98	0	5.70	12.29	6.00		8.44	26.66	90.78	14.09		0	10.37		8.28	41.1		

Annex II

All Figures are electronically available on the attached CD-rom.

References

Cools, N., Verschelde P., Quataert P. 2006. Quality Assurance and Quality Control in Forest Soil Analysis: 4th FSCC Inter-laboratory Comparison. INBO.R.2006.6.

De Vos, 2008. Tolerable limits for interlaboratory forest soil ringtests. FSCC supporting studies to the EU BioSoil demonstration project INBO.R. 2008.43. Research Institute for Nature and Forest, Brussels.

ICP Forests. 2006. Manual on methods and criteria for harmonised sampling, assessment, monitoring and analysis of the effects of air pollution on forests. Part IIIa. Sampling and Analysis of Soil. Update 06/2006 to be applied from 2006 on. Elaborated by the Expert Panel on Soil and the Forest Soil Co-ordinating Centre.

ISO 16772:2004. Soil quality -- Determination of mercury in aqua regia soil extracts with cold-vapour atomic spectrometry or cold-vapour atomic fluorescence spectrometry

Nordic Innovation Centre. 2007. NT Technical Report. Nordtest report TR569. Internal Quality Control. Handbook for Chemical Laboratories.

U.S. Dept. of Agriculture. Soil Conservation Service. Soil Survey Staff. 1951. Soil Survey Manual. U.S. Dept. of Agric. Handb. 18. U.S. Govt. Print. Off. Washington, DC. 503 pp., illus.

van Reeuwijk, L.P. and Houba, V.J.G. 1998. Guidelines for Quality Management in Soil and Plant Laboratories. (FAO Soils Bulletin - 74)

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