CONVENTION ON LONG-RANGE TRANSBOUNDARY AIR POLLUTION
INTERNATIONAL CO-OPERATIVE PROGRAMME ON ASSESSMENT AND MONITORING
OF AIR POLLUTION EFFECTS ON FORESTS
AND
EUROPEAN UNION SCHEME
ON THE PROTECTION OF FORESTS AGAINST ATMOSPHERIC POLLUTION

United Nations
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Quality Assurance and Quality Control in Forest Soil Analysis:

3rd FSCC Interlaboratory Comparison

Forest Soil Co-ordinating Centre
Institute for Forestry and Game Management
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3rd FSCC Interlaboratory Comparison

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LIST OF ABBREVIATIONS

ICP	International Co-operative Programme
FSCC	Forest Soil Co-ordinating Centre
EU	European Union
QA/QC	Quality assurance – Quality Control
NFC	National Focal Centre
ISO	International Standardisation Organization
$sRepr^2$	Estimation of the reproducibility variance
$sLab^2$	Estimation of the between-laboratory variance
$sRep^2$	Estimation of the repeatability variance
CV	Coefficients of variation
NA	Not Applicable
IQR	Inter quartile range
KW	Kruskal-Wallis test

SUMMARY

Fifty two laboratories from 27 European countries took part in the **3rd ICP-Forest Soil Interlaboratory Test** (2002-2003). As the statistical analysis of the ring test is revised, the used statistical procedures have become more transparent and consistent compared to the procedures used in the previous ring tests. The data analysis and interpretation has been made more accessible. This manuscript reports the results of phase I and phase II.

Phase I focuses on the in-depth statistical analysis of the performance of the laboratories with relevance to their between and within-laboratory variance. The results of the ring test reveal that a certain group of laboratories need quality improvement. As based on the between-laboratory variance, 4 laboratories had more than 20 % outliers for sample A, 1 laboratory for sample B and 2 for sample C. However, more laboratories have been excluded based on the Mandel's k than on the Mandel's h: 11 laboratories for sample A, 2 for sample B and 6 for sample C. Until now, most ring tests did not assess this within-laboratory variance. As seen from these results, it becomes obvious that this variance should not be ignored. Concerning the between-laboratory variance, 16 laboratories had no outliers for sample A, 24 no outliers for sample B and 30 no outliers for sample C. While for sample B and sample C these numbers fall within an acceptable range, it is clear that sample A was more difficult to analyse and caused many problems.

The linkage with secondary information, obtained trough a laboratory questionnaire, is foreseen in the second phase of the analysis. **Phase II** links the different possibly influencing factors with the performance of the laboratories. As the sampling design is mainly aimed at the ring test 'sensu stricto', the necessary caution should be taken into account when searching for significant influencing factors. There is no consistent trend spotted through the data; significant influencing factors differ depending on the group of analysis. The sampling design is not powerful enough to come to overall conclusions concerning the influencing factors for laboratory performance.

PHASE I

I.1 INTRODUCTION

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

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

In view of a second European wide soil survey, harmonisation and improvement of the analytical techniques is indispensable. In order to assure the quality of the data obtained by soil analysis, the 10^{th} Forest Soil Expert Panel (Warsaw, 2000) decided to proceed to a **Third Intercalibration Exercise.** This third ring test (2002-2003) should provide insight in the quality of soil analysis results and thus the quality of the future Forest Soil Database. A revision of the 'Manual on sampling and analysis of soil' (FSCC, 2003) was a first step in this harmonisation process. All participating countries in the third ring test were requested to use the recently proposed reference methods which are mainly based on ISO-standards.

The effect of the adaptation of one single reference analysis method for each parameter will be evaluated on the basis of the results of this third ring test. This ring test is seen as a first testing phase of the newly developed manual (FSCC, 2003) and provides information on the quality control activities of the participating laboratories. All this information is essential for the preparation of a new Level I Soil Survey. Results of the ring test will supply the information necessary in the preparation of a Quality Assurance/Quality Control follow-up programme.

This manuscript reports both phases of the data analysis. The first phase consists of an in depth statistical analysis, in which the performance of the laboratories is evaluated. The extra information, obtained by the questionnaires is linked to the data in the second phase of this report.

I.2 MATERIALS AND METHODS

I.2.1 Participating laboratories and countries

FSCC asked the National Focal Centres (NFC) to select laboratories for the ring test. Initially 59 laboratories from 27 European countries registered by the end of May 2002. Seven laboratories (n° 1, 22, 29, 39, 46, 49, 56) registered but did not further participate in the ring test. These laboratories will not be mentioned in the further discussion. This means that a total of fifty two laboratories analysed the soil samples and reported their results to FSCC. All participating laboratories were asked to fill in a questionnaire concerning the analysis. Table I.1 gives an overview of the registered and participating laboratories of each country. The column 'questionnaire' shows whether the laboratories delivered a completed questionnaire or not. Contact addresses of the participating laboratories can be consulted in Annex 1. One laboratory (Swedish) did not deliver a filled-in questionnaire.

Table I.1: List of participating countries

Country	Registered	Results	Questionnaire
Austria	1	1	1
Belgium	5	5	5
Bulgaria	3	3	3
Canada	1	1	1
Croatia	1	1	1
Cyprus	1	1	1
Czech Republic	1	1	1
Denmark	1	1	1
Estonia	3	2	2
Finland	2	2	2
France	1	1	1
Germany	15	13	13
Greece	1	1	1
Hungary	2	2	2
Ireland	1	1	1
Italy	4	4	4
Latvia	1	1	1
Lithuania	1	1	1
Poland	1	1	1
Portugal	2	1	1
Russian Federation	2	1	1
Slovak republic	1	1	1
Slovenia	1	1	1
Spain	2	2	2
Sweden	3	1	0
The Netherlands	1	1	1
United Kingdom	1	1	1
Total	59	52	51

I.2.2 Sample characterisation

I.2.2.1 Sampling location

Three soil samples were sent to each of the participating laboratories in July 2002. These samples were taken under forest conditions in different regions of Belgium (June 2002). Sample A and B are mineral samples, sample C is an organic layer sample.

Sample A was taken from the Ah horizon under a coniferous forest, where Scots Pine (*Pinus sylvestris*) is the dominating tree species. The nutrient content of this loamy sandy soil is generally spoken very low. This sample is thus an example of a chemically poor soil.

Sample B on the contrary is a mineral top soil sample (0-10 cm) originating from a very calcareous silty clay soil, with a very high nutrient content. The sample was taken under a mixed deciduous forest where ash (*Fraxinus excelsior*), pedunculate oak (*Quercus robur*) and maple (*Acer pseudoplatanus*) are the major tree species.

Sample C is taken from the organic layer, on the same site as the soil sample A.

It is important to mention that the chosen soil samples are not very easy to analyse, as sample A is very poor in nutrients, and sample B is very calcareous (± 45% $CaCO_3$). The element concentration of sample A might have been below the detection limit of some laboratories but this can be solved using standard addition techniques. Nevertheless the chosen samples are representative for common forest soils in Europe. From this point of view, the choice of the samples is well-founded.

Table I.2 gives an overview of the properties of the three soil samples. This table is based on the results of the analyses of all participating laboratories, making abstraction of the outliers.

Table I.2: List of measured parameters with per sample, the mean value and standard deviation and the detection limits, mentioning the number of laboratories (N°) on which the values are based

Parameter	Unit	Sample A			Sample B			Sample C			Detection limit	
		N°	Mean	St. dev.	N°	Mean	St. dev.	N°	Mean	St. dev.	N°	Median
Particle Size - Clay	%	28	2.4	2	26	23.5	13.3	28	ND	ND	6	0.4
Particle Size – Silt	%	28	7.8	3.5	26	33.3	15	28	ND	ND	6	0.4
Particle Size – Sand	%	28	76.7	31.3	26	41.4	19.6	28	ND	ND	6	0.4
pH (CaCl2)	-	47	3.1	0.1	47	7.4	0.1	47	3	0.1	5	0.02
pH (H2O)	-	45	4	0.2	45	7.9	0.2	45	3.9	0.2	5	0.02
Carbonates	g/kg	19	0	0	37	447	169	19	ND	ND	19	1
Organic Carbon	g/kg	40	10	1.1	40	75.7	25.1	40	480	46.7	22	0.25
Total N	g/kg	43	0.3	0.1	43	4.5	0.3	43	17.9	1.1	24	0.1
Exchangeable Acidity	cmol(+)/kg	37	1.27	0.73	29	0.18	0.26	37	8.08	3.29	8	0.075
Exchangeable Al	cmol(+)/kg	38	0.43	0.21	33	0.01	0.01	38	1.58	0.77	15	0.02
Exchangeable Ca	cmol(+)/kg	41	0.12	0.1	40	29.4	8.83	41	6.28	1.84	16	0.015
Exchangeable Fe	cmol(+)/kg	42	0.04	0.02	39	0	0	42	0.3	0.15	16	0.006
Exchangeable K	cmol(+)/kg	41	0.02	0.01	41	0.55	0.1	41	0.95	0.15	16	0.01
Exchangeable Mg	cmol(+)/kg	41	0.03	0.02	41	1.18	0.39	41	1.6	0.35	17	0.01
Exchangeable Mn	cmol(+)/kg	39	0	0	40	0.01	0.01	39	0.16	0.05	16	0.003
Exchangeable Na	cmol(+)/kg	39	0.04	0.04	38	0.07	0.05	39	0.31	0.13	15	0.02
Free H+ Acidity	cmol(+)/kg	33	0.66	0.43	26	0.06	0.13	33	5.84	3.38	4	0.055
Extractable Al	mg/kg	34	361	172	35	5491	1085	34	1193	309	17	3
Extractable Ca	mg/kg	36	77.1	98.6	37	220989	226555	36	1712	806	16	5.5
Extractable Cd	mg/kg	36	0	0	41	1	0.5	36	1.1	0.5	21	0.04
Extractable Cr	mg/kg	35	2.3	1.3	39	29.6	6.9	35	49.2	12.3	19	0.33
Extractable Cu	mg/kg	40	1.3	1.1	42	29.7	4.6	40	22	6.7	21	0.6
Extractable Fe	mg/kg	40	231	97.1	41	12378	1596	40	3459	750	19	1.5
Extractable Hg	mg/kg	11	0	0	14	0.1	0.1	11	0.3	0.1	10	0.007
Extractable K	mg/kg	38	69.9	52.6	40	2408	436	38	465	197	16	10
Extractable Mg	mg/kg	38	19.9	16.5	39	2119	206	38	303	74.7	15	1
Extractable Mn	mg/kg	41	4.4	2.7	42	255	39	41	74	9.5	19	0.5
Extractable Na	mg/kg	30	25.5	26.6	32	593	216	30	96.9	54.7	13	2.5
Extractable Ni	mg/kg	34	0.5	0.5	36	11.8	2.8	34	35.1	6.2	20	0.7
Extractable P	mg/kg	33	17.6	14.5	36	9147	1278	33	576	105	18	7.5
Extractable Pb	mg/kg	41	6.9	1.5	42	51.7	23.7	41	130	30.1	20	1
Extractable S	mg/kg	25	35	23.3	26	1295	692	25	2150	158	15	15
Extractable Zn	mg/kg	42	1.7	1.6	44	93.4	12	42	102	24.9	21	0.58
Total Al	mg/kg	16	2791	922	16	10721	3669	16	2964	323	8	23
Total Ca	mg/kg	16	148	54.7	17	216682	50187	16	1677	324	8	11
Total Fe	mg/kg	17	504	106	17	13664	1495	17	3990	287	7	1
Total K	mg/kg	17	1827	222	17	4777	669	17	1064	76.9	7	37.5
Total Mg	mg/kg	17	99.1	62.7	17	2406	186	17	374	28.7	8	2.7
Total Mn	mg/kg	17	12.2	4.67	18	276	15.3	17	76.9	10.8	8	0.23
Total Na	mg/kg	16	504	110	16	1485	585	16	310	22.2	8	9.5
Reactive Al	mg/kg	21	113	48	20	400	164	21	496	245	8	13.5
Reactive Fe	mg/kg	20	87.1	36.5	20	1564	617	20	760	393	8	6.25

Note: ND = not determined; Carbonates and particle size distribution were not determined for sample C, which is an organic sample

I.2.2.2 Sample homogenisation

The soil samples were homogenised by an independent institute (VITO, Geel, Belgium) by means of riffling. VITO is qualified for preparing homogenised samples and for organising ring test (e.g. BELTEST) in Belgium. A test of homogeneity was carried out following the below described procedure. Eight sub samples of each of the three bulk samples, distributed over 8 containers by the VITO were analysed on loss-on-ignition and total nitrogen. Three replicates of each kind of analyses were done on each of the containers. Results were submitted to analysis of variance in order to test the homogeneity between the eight containers.

I.2.2.3 Distribution of samples

Samples were sent to the participating laboratories during the first week of July. This timing caused for certain laboratories some difficulties due to summer holidays.

I.2.3 Soil Analysis Methods

I.2.3.1 Guidelines for soil sampling and analysis

Laboratories were requested to use the methods as described in the revised 'Submanual on Sampling and Analysis of Soil' (FSCC, 2003). As seen from Table I.3, most of these methods are based on the ISO-standards.

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

Analysis	Reference Method
Particle Size Distribution	ISO 11277
Soil pH	ISO 10390
Carbonate Content	ISO 10693
Organic Carbon Content	ISO 10694
Total Nitrogen Content	ISO 13878
Exchangeable Acidity and Free H^+ Acidity Exchangeable Cations	ISO 14254 ISO 11260
Aqua Regia Extractant Determinations	ISO 11466
Total Elements	ISO 14869 Michopoulos 1995
Acid Oxalate Extractable Fe and Al	ISRIC 1992

In general, most of the laboratories used the reference methods: 65% of the total of reported analyses were done according to the new soil manual. Figure I.1 shows the use of the reference methods for each parameter-group. Details on the reported methods by each laboratory can be consulted in Annex 2.

All laboratories (N=52) analysed soil pH; 77% (N=40) of them used the reference method. Total elements were analysed by less than 40% of the laboratories (N= 21) and half of them (N = 11) used the reference method.

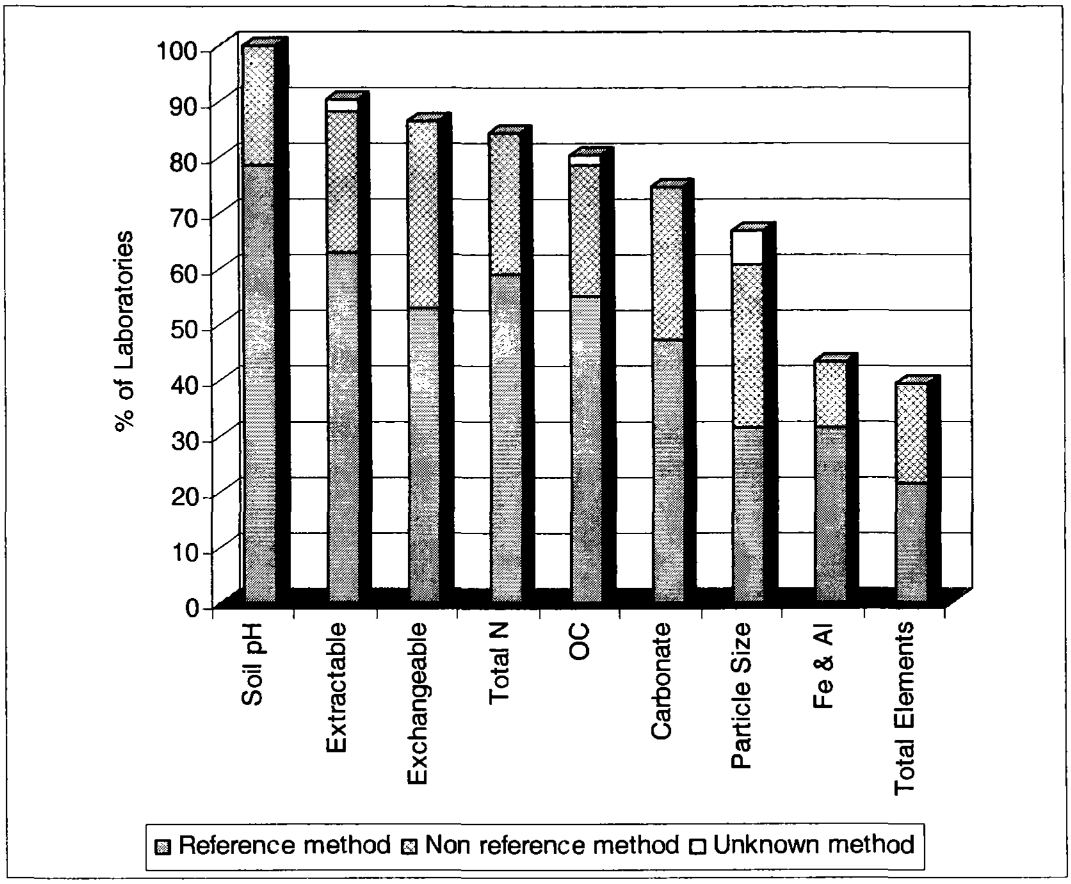


Figure I.1: Reported analysis methods by the different laboratories

I.2.3.2 Questionnaire

Each laboratory provided:

(1) General information on the laboratory;

(2) Analysis information. Information was collected under the format of multiple choice questions concerning analysis method, used equipment, experience of the personnel and procedures of quality assurance. The full questionnaire can be consulted in Annex 7 of the report.

I.2.3.3 Data reporting

Each parameter was measured in three replicates. Laboratories reported the values of the three replications of each analytical in a preformatted Excel-spreadsheet or as a hard copy, using a separate sheet for each soil sample (see Annex 3) by the end of October 2002.

I.2.3.4 Problems of rounding

Laboratories reported a fixed number of digital numbers according to ISO and/or to the Forest Soil Condition database. Though, it has not been taken into account that sample A was extremely poor in nutrients. Concentrations were sometimes extremely low. Reporting a limited fixed number of digits, could cause a false reporting of null values. After entering the results in the database, no distinction could be made between real null values (reported as "0") and false null values (truncated small values).

I.2.3.5 Problems of detection limit

Laboratories were asked to indicate a negative value sign in front of the measured value, when the concentration of the parameter was below detection limit. Since this request was made after some laboratories did already submit their results, this late correction could not correct the mistake made. In combination with the problem of rounding, the consequence is that null values have been reported when these values are no real zero's (see I.2.4.2).

Next to the average values of the measured parameters in Table I.2, the mean of the reported detection limits by the laboratories is given. The shaded numbers indicate case where the reported value was below the median detection limit. For sample A, this was the case for 'Carbonates', 'Exchangeable Mn' and 'Extractable Cd, Hg, Ni'. For sample B, this was the case for 'Exchangeable Fe'.

I.2.3.6 Data entering and data integrity check

After data have been entered in the database, each of the laboratories was sent a copy of their data in a PDF-file by the beginning of November 2002. The documents were in exactly the same format (same number of digits, etc.) as the data were entered in the system. Laboratories could check, comment and correct the reported values if needed till the beginning of December 2002.

I.2.4 Statistical data analysis

I.2.4.1 General characteristics of data analysis methodology

The statistical data analysis was based on the international standard ISO 5725-2 'Accuracy (trueness and precision) of measurement methods and results – part 2: Basic method for determination of repeatability and reproducibility of a standard measurement method' (ISO, 1994c). Data analysis was done by means of the statistical software package S-plus 6.1 Professional (2002).

This method has been made more straightforward, transparent and easily to interpret. The disadvantage of the black box character of the Ring 4.0 programme (used in the Needle/Foliar Interlaboratory Tests) has been overcome (Bartels, 2002).

Specific items have been added to the procedure.

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

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

where $sRepr^2$ estimation of the reproducibility variance

$sLab^2$ estimation of the between-laboratory variance

$sRep^2$ estimation of the repeatability (within-laboratory) variance

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

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

"Zero" values: Many laboratories reported "zero's" which could be real zero's or truncated small values. A real zero means that the analysed element is not present in the soil sample. A truncated small value is a small measured value (but still higher than the detection limit) that, by rounding to a certain precision is truncated to a zero in the database. In practice, it became impossible to distinguish these two types of zero's in the database.

"Values below detection limit": Laboratories have been asked to indicate a negative value when the concentration of a certain parameter was below detection limit.

The questionnaire asked for the detection limit for each specific parameter. Nevertheless, certain laboratories reported their results below detection limit as zero's.

"Missing values": Parameters that where not analysed by a certain laboratory where reported as missing values (NA: Not Analysed). The number of missing values are reported at the right side of the histograms (see Figure I.2).

Different laboratories reported inconsistently for certain parameters. Examples of some problems are shown in Table I.4.

Table I.4: Different cases of reported "zero's", "missing values" and "below detection limit"

	Replication 1	Replication 2	Replication 3
Parameter 1	0	Missing	- Detection limit
Parameter 2	0	0	Missing
Parameter 3	- Detection limit	0	0
Parameter 4	0	Missing	Missing
Parameter 5	Missing	- Detection limit	Missing

As there was often no clear distinction between zero's and values below detection limits, it was decided to treat these two cases similarly. All zero's and values below detection limit are thus reduced to zero's, as shown in Table I.5. These zero's are reported as 'Z' at right side of the histogram (Figure I.2).

Table I.5: Revised definition of the "zero's" in Table 4

	Replication 1	Replication 2	Replication 3
Parameter 1	Zero	NA	Zero
Parameter 2	Zero	Zero	NA
Parameter 3	Zero	Zero	Zero
Parameter 4	Zero	NA	NA
Parameter 5	NA	Zero	NA

Parameters where only 1 replication was reported have been rejected for further analysis, as it was not possible to calculate averages, standard deviations nor Mandel's h or k statistics for these cases. This means for the examples given in Table I.5, that parameters 4 and 5 will be excluded from further analysis.

I.2.4.3 Coefficients of variation (CV)

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

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

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

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

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

I.2.5 Research objectives

The aim of the statistical analysis in phase I is to investigate the research questions:

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

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

In other words, we expect that laboratories will be rather discarded from the laboratory population – and the calculation of the mean and standard deviation - based on the between-laboratory variance and not on the within-laboratory variance.

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

I.3 RESULTS

I.3.1 Interpretation of the data analysis

The data analysis within S-plus produced for each parameter (each analysed element) and each sample (A, B and C) a total of 7 figures. Below the case of 'exchangeable acidity' in sample A is given as an example. The other figures arranged per parameter in the same sequence as discussed below, can be consulted in Annex 4.

I.3.2 Exploratory Analysis

The objectives of the exploratory data analysis are to 'explore' the observations. It allows a visual evaluation of the data and gives an indication of possible outliers. However, based on these exploratory analysis, no observations nor laboratories are excluded from further analysis.

Two sources of variance are investigated: the inter-laboratory variance (between-laboratory variance) and the intra-laboratory variance (within-laboratory variance). Figure I.2 and Figure I.3 represent the inter-laboratory variance. They indicate the position of each laboratory in the population of all laboratories. Figure 4 and Figure 5 represent the standard deviations of each laboratory. They yield information on the within-laboratory variance. Figure I.2 and I.4 are histograms, while Figure I.3 and I.5 are box-plots. The information contained within the histograms is:

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

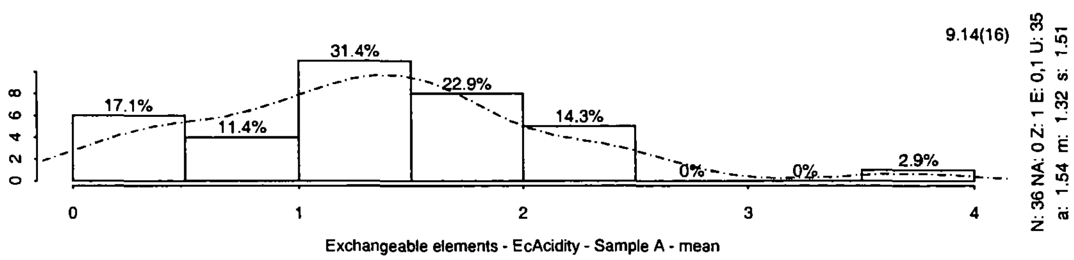


Figure I.2: Histogram showing relative percentages and a rescaled density curve of the <u>mean</u> of 3 replicates of the measured parameter 'exchangeable acidity' on Sample A. The units of the x-axis are in cmol(+)/kg.

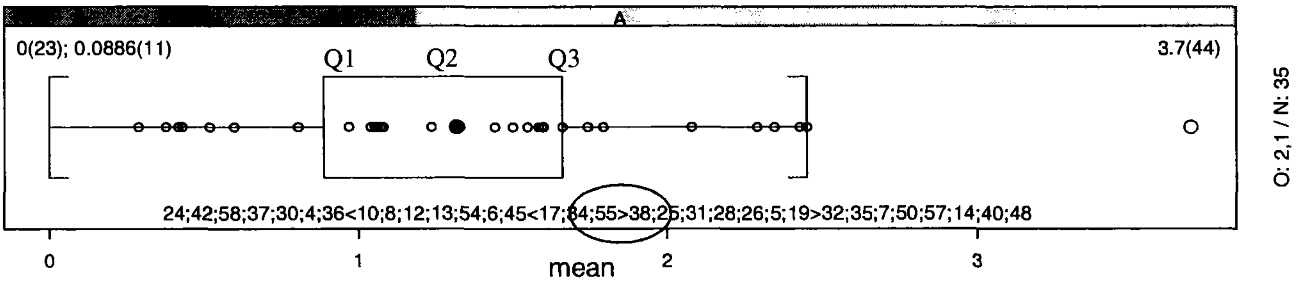


Figure I.3: Box-plot of the <u>mean</u> values reported for sample A for the parameter 'exchangeable acidity'. The units of the x-axis are in cmol(+)/kg.

The box-plot provides following information:

- Visual outliers (lab N° between parentheses and parameter value). These are placed in the top left and top right corner of the figure. On the right side of the figure 'O' indicates the number of outliers excluded from the box plot, respectively on the lower and the higher range of the box-plot.
- Percentiles Q1, Q2 (median) and Q3
- N: Number of observations in the box-plot

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

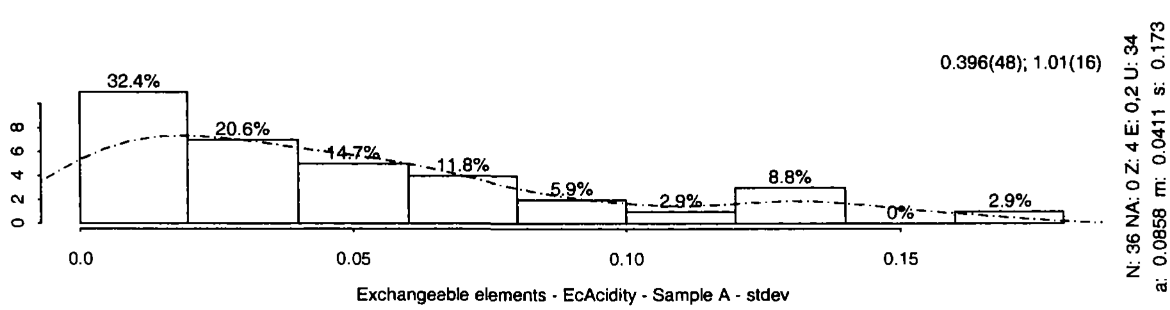


Figure I.4: Histogram showing relative percentages and a rescaled density curve of the standard deviation based on 3 replicates of the measured parameter 'exchangeable acidity' on Sample A.

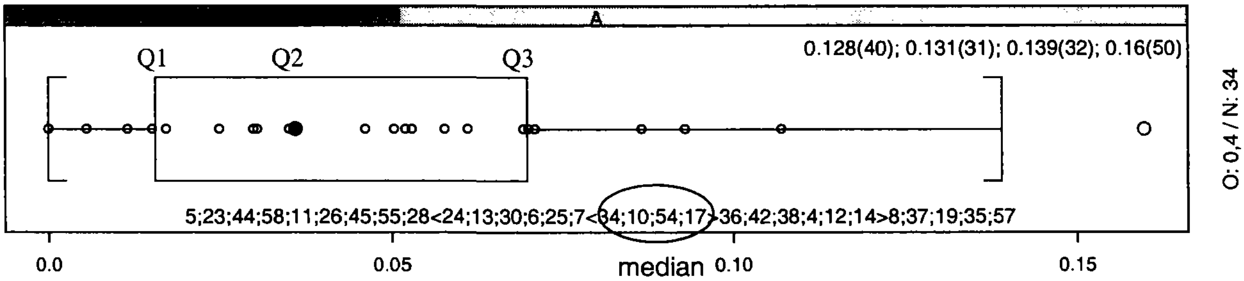


Figure I.5: Box-plot of the standard deviations for sample A for the parameter 'exchangeable acidity'. The units of the x-axis are in cmol(+)/kg.

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

From the text on the right side of Figure I.2, can be observed that the histogram is based on results from **N=36** laboratories. One of the reported values, was a "0" (**Z: 1**). One laboratory (laboratory N° 16) is excluded from the histogram, so **U: 35** are used. Laboratory N° 16 reported extremely high exchangeable acidity levels (9.14 cmol(+)/kg). The average reported concentration of exchangeable acidity is **a: 1.54 cmol(+)/kg**; the median concentration is **m: 1.32 cmol(+)/kg** and standard **deviation s: 1.51 cmol(+)/kg.** In order to allow calculations of average, standard deviation and the Mandel's h and k statistics, data are supposed to have a normal distribution. The shape of the density curve (dotted line) should therefore approach the symmetrical shape of a normal distribution.

Figure I.3 shows that the laboratories N° 17, 34 and 55 reported the median value of 1.32 cmol(+)/kg. Laboratories N° 10, 8, 12, 13, 54, 6 and 45 reported values between the first quartile (**Q1**) and the mean; laboratories N° 38, 25, 31, 28, 26, 5 and 19 reported values between the median and the third quartile (**Q3**). Laboratories N° 24, 42, 58, 37, 30, 4 and 36 reported values below the first quartile

(**Q1**) and laboratories N° 32, 35, 7, 50, 57, 14, 40, and 48 reported exchangeable acidity concentrations above the third quartile (**Q3**). The first line in the figures shows that laboratory N° 23 reported a "0" value. This was the Z = 1 in Figure I.2. Laboratory N° 11 reported a value close to 0 and laboratory N° 44 reported a concentration of 3.7 cmol(+)/kg which is rather high. From this plot, we expect that laboratories 23, 11 and 44 will be outliers in the in-depth statistical analysis.

A laboratory can check its performance compared to the other laboratories by studying the dot plots (Figure I.6). Every dot represents a reported value of a specific parameter. The shape of the dot plot follows the sigmoid curve shape of a normal distribution. Laboratories are plotted on the y-axis, arranged according to the magnitude of the reported values. One laboratory (N°16) reported extremely deviant results for the exchangeable acidity of sample A. The laboratory reported values of 8.21, 9.00 and 10.21 cmol(+)/kg soil. These values are given at the top of the graphic. Values reported by other laboratories can be read on the x-axis. The majority measured values between ±0.3 and ±2.3. Again is seen that laboratories N° 44, 23 and 11 tend to be outliers.

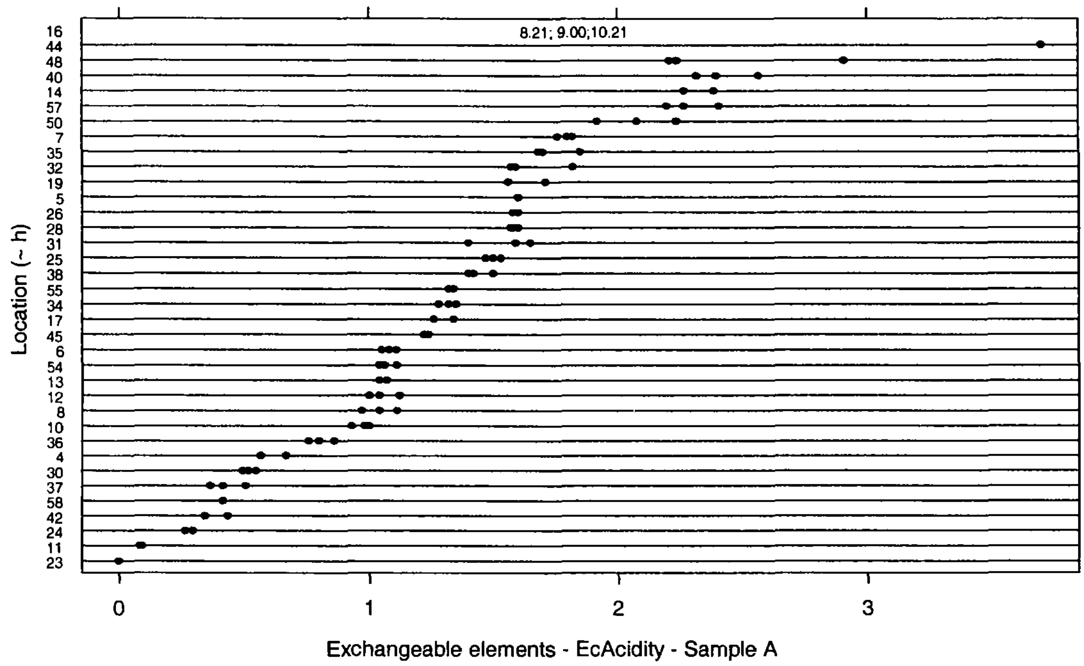


Figure I.6: Dot plot of reported values for each laboratory, cumulatively ordered

This figure also tells something about the internal variance within one laboratory. By way of an example, laboratory N° 50 reported three very different results – represented by 3 dots widely separated from each other – whereas laboratory N° 28 reported 3 very similar results – represented by 3 dots very close to each other. We expect that laboratory N° 50 will have a poor within-laboratory repeatability whereas laboratory N° 28 will have a very good within-laboratory repeatability.

I.3.3 In-depth statistical data analysis: Mandel's h and Mandel' k statistics

Figure I.7 and I.8 present the Mandel's h and k statistics for the parameter 'Exchangeable acidity' of the test sample A. The Mandel's h statistics test the between-laboratory variance. The Mandel's k statistic is a measure for the within-laboratory variance. The information contained within the two figures is:

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

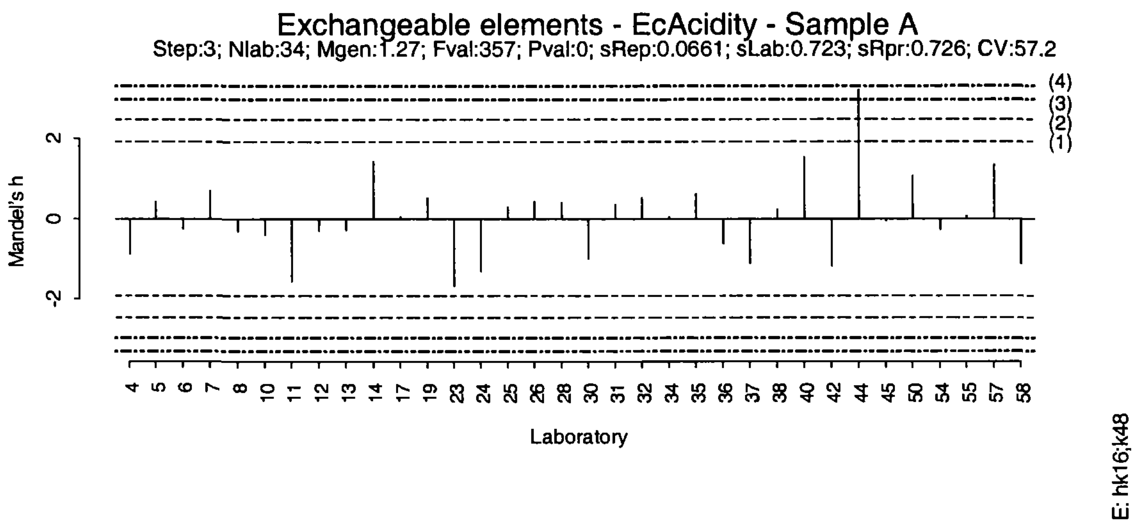


Figure I.7: Mandel's h statistic for sample A for the parameter 'Exchangeable acidity'

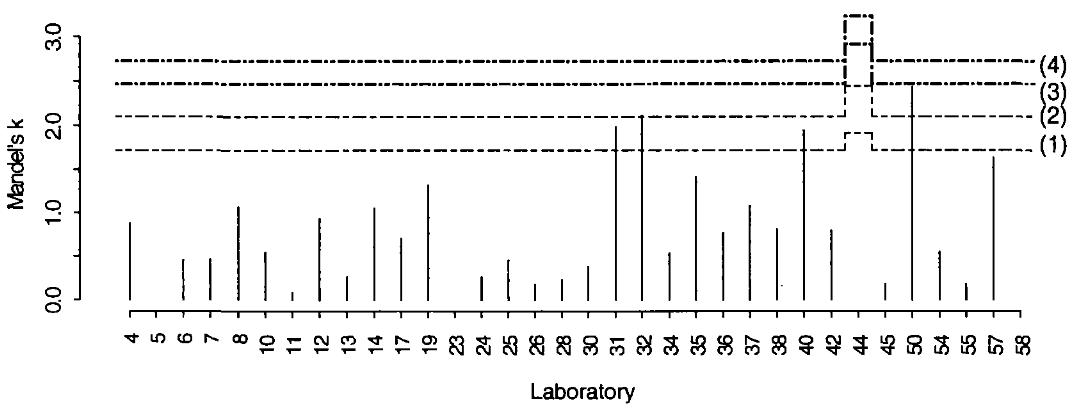


Figure I.8: Mandel's k statistics for sample A for the parameter 'Exchangeable acidity'

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 <u>outliers</u> are the observations of which the h or k-statistic exceeds the critical value at probability level of 99% after application of the Bonferroni rule. Statistical <u>stragglers</u> are the observations of which the h or k-statistic are situated between the critical values of probability level 95 and 99% after application of the Bonferroni-rule.

Figures I.7 and I.8 form the core of the statistical analysis and contain all necessary information. They usually confirm the expectations after studying Figures I.2 till I.6.

From Figure I.7 is seen that laboratory N° 44 can be considered to be a straggler because the Mandel's h value is located between the critical value of the 95% and 99% confidence limits. This was already expected by studying Figure I.3, where the box plot of the mean values was given. The Mandel's h statistics of laboraties 23 and 11 are low, but do not reach critical limits (Figure I.7). Laboratory 16 has been excluded from the statistical analysis based on the Mandel's h and the Mandel's k statistics (see lower right corner of Figure I.7 ('E: hk16'). The same laboratory was indeed excluded from the histograms in Figure I.2 and I.4 (showing both the within and between-laboratory variance) in the exploratory study.

Laboratory 48 has been excluded based on the Mandel's k statistics. Again this could be confirmed by Figure I.4, where laboratory N° 48 was excluded from the histogram. Figure I.8 shows that laboratory N° 50 is characterised by a high Mandel's k value, reaching the critical level of 95%. This was expected when studying the dot plot in Figure I.6. Also the k values of laboratories 31, 32 and 40 are high as was expected from Figure I.5 and I.6.

Note that in Figure I.8, the critical limits for laboratory 44 are different. This happens when laboratories have reported only two replications instead of three, which results in wider confidence limits.

<u>Remarks:</u>

1. Sometimes no vertical 'line' is seen in the Mandel's h and k plots. This is because the calculated h and k values are close to "0". The limit becomes a dot which can disappear in the printed version of the output.
2. Laboratories are excluded through an iterative procedure. A laboratory can, for example, be excluded based on the k statistic in the first step. In that case, it cannot be excluded any more in an subsequent step if it would have been an outlier for the h statistic in a subsequent step after a

number of laboratories have been removed and the population composition was altered. A check has been included in the procedure where the excluded laboratory is compared with the laboratories left in the population, in this case, for the h statistic. If the laboratory appears to be an outlier for the h statistics as well, it receives a 'h' (in addition to the 'k') in front of its lab number. A similar procedure is applied when a laboratory is excluded based on the h statistic and checked for the k statistics in a later step (a 'k' in front of the 'h + lab number').

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

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

I.3.4 'Percentage of outliers and stragglers' as a measure of laboratory performance

The Mandel's h and k plots in Annex 4 visualise the occurrence of outliers and stragglers. The Mandel's h statistics inform about the performance of the laboratory compared to the whole population of laboratories. The Mandel's k statistics says something about the within-laboratory variance. When a laboratory is excluded from the h statistics because its reported value is very deviant from the mean value, it is considered as an indicator of poor quality of that laboratory. Since most of the laboratories measured many parameters, it becomes interesting to study the frequencies of this event, namely the exclusion of a laboratory. Since the numbers of measured parameters are differing from laboratory to laboratory, the percentage of outliers and stragglers was calculated relatively to the number of reported parameters.

A question that first needs to be answered is whether laboratories that analysed only few selected parameters can perform better in this ring test compared to laboratories that analysed and reported most of the parameters, even if their personnel was not familiar with the analysing method requested for the ring test. This hypothesis is verified in Figures I.9 till I.11 where the number of reported parameters has been put on the x-axis and the % of reported outliers and stragglers on the y-axis for each of the three soil samples. A linear regression line has been fit and the correlation coefficient has been given together with the equation. For each of the three samples correlation coefficients are very close to 0 which is a clear indication that there is no correlation between the number of reported parameters and the performance of the laboratory within the ring test.

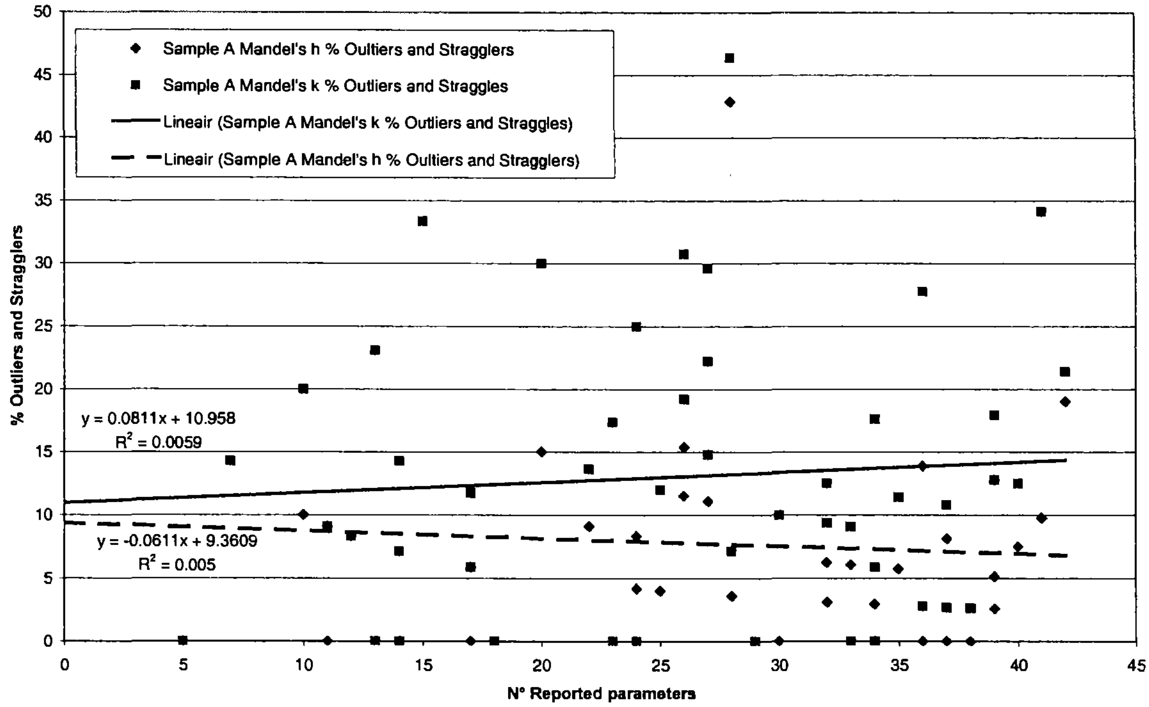


Figure I.9: Relation between number of reported parameters and % of outliers and stragglers (sample A)

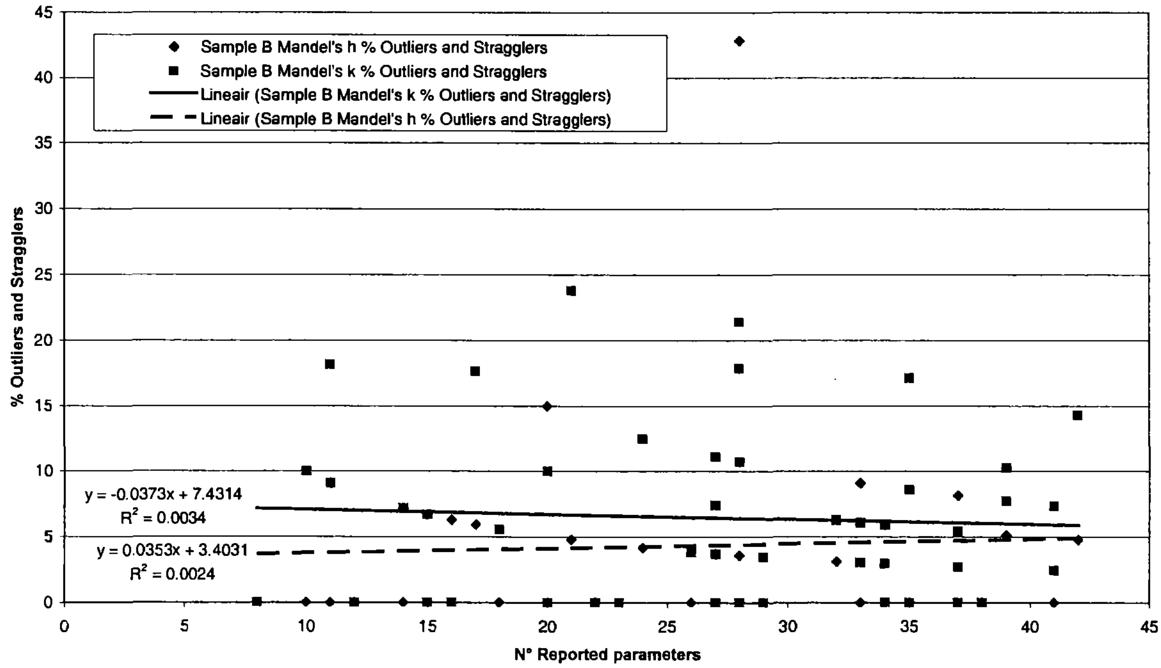


Figure I.10: Relation between number of reported parameters and % of outliers and stragglers (sample B)

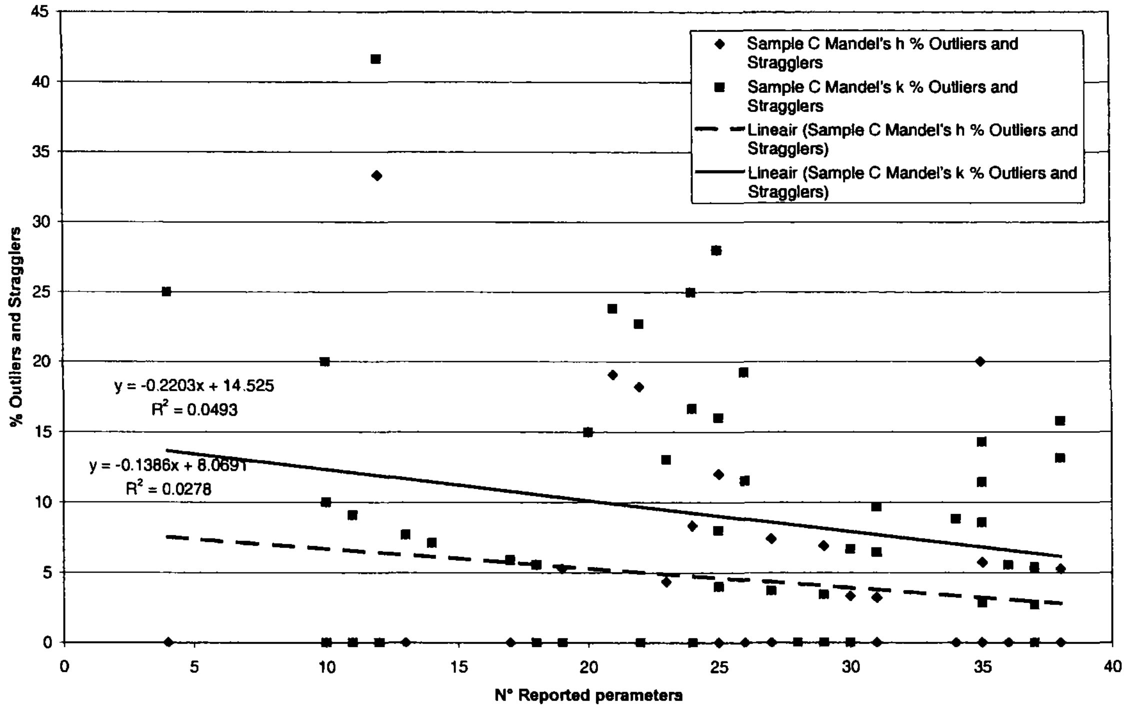


Figure I.11: Relation between number of reported parameters and % of outliers and stragglers (sample C)

I.3.5 Laboratory performance

Figure I.12 compares the performance of the 52 laboratories based on the Mandel's h statistics. Figure I.13 compares the performance of the laboratories based on the Mandel's k statistics.

Figure I.12 shows the % of outliers and stragglers for the Mandel's h statistics for sample A, B and C and for each laboratory. This figure allows evaluating the performance of each laboratory with reference to the other laboratories. Laboratories N° 3, 15, 26, 30, 36, 45 and 54 score well for all the samples. These laboratories never reported outlying results nor stragglers. Laboratory N° 50 has serious problems for each of the three samples. Laboratory N° 16, 58 and 60 reported more than 20% outlying results or stragglers for at least one of the three samples. Laboratory N° 41 did not report any results for sample A or B.

Figure I.13 is a similar figure showing the within-laboratory variance based on the Mandel's k statistics. Laboratories with poor between-laboratory performance, are generally performing poorly for the within-laboratory variance. Laboratories N° 16, 19, 20, 21, 24, 27, 33, 40, 50, 52, 57, 58, 59 and 60 all reported for at least one sample more than 20% stragglers and outliers.

Only three laboratories (N° 45, 51 and 54) did not show any outliers nor stragglers for the Mandel's k. Note that, though Figures I.9 to I.11 did not show any relation between the number of reported parameters and the percentage of outliers, laboratories N° 45 and 51 only reported few parameters. On top of that laboratory N° 51 reported maximum two replications for each of the samples (see dot plots in Annex 4).

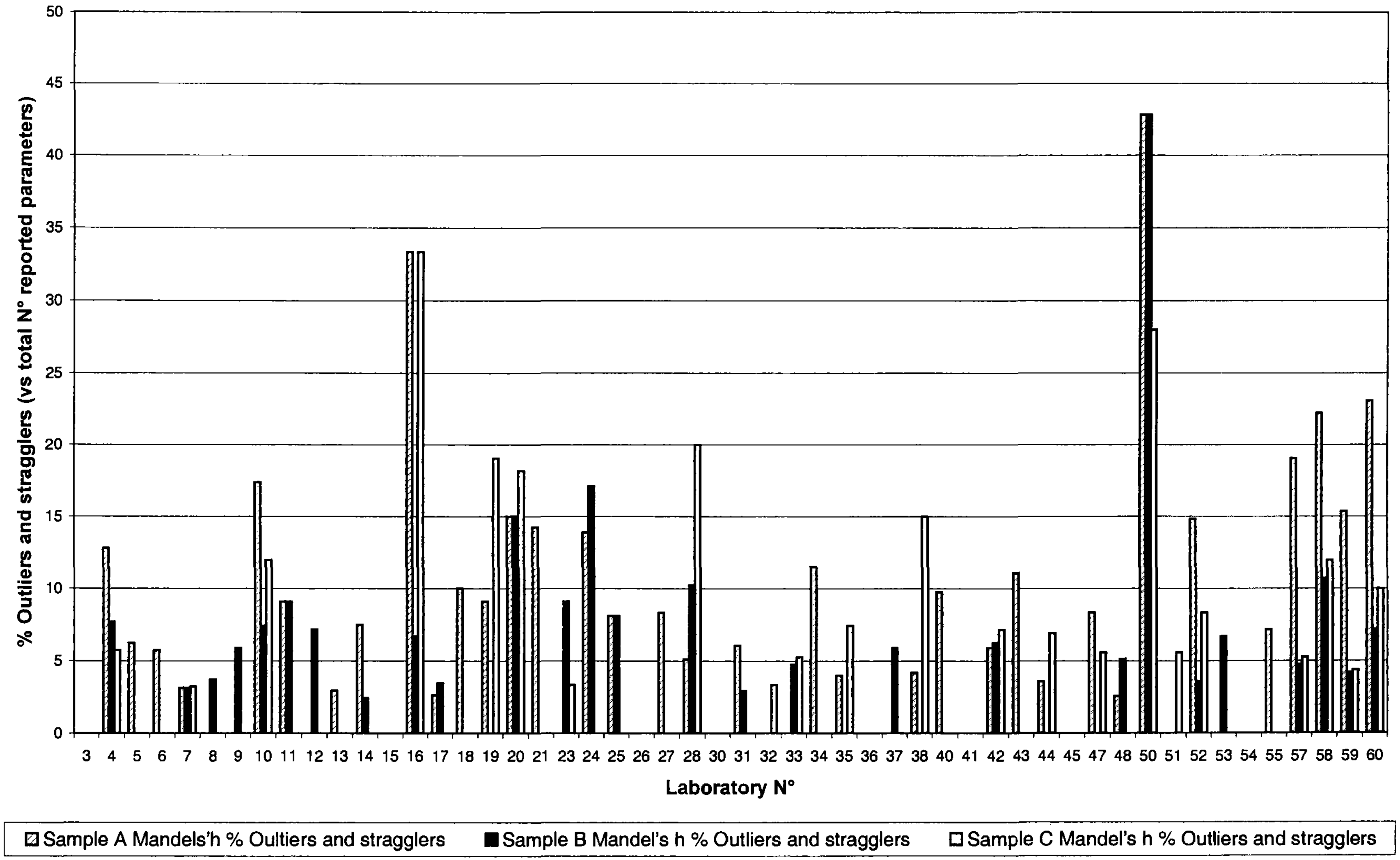


Figure I.12: Performance of the participatory laboratories in the third ring test based on the between-laboratory variance

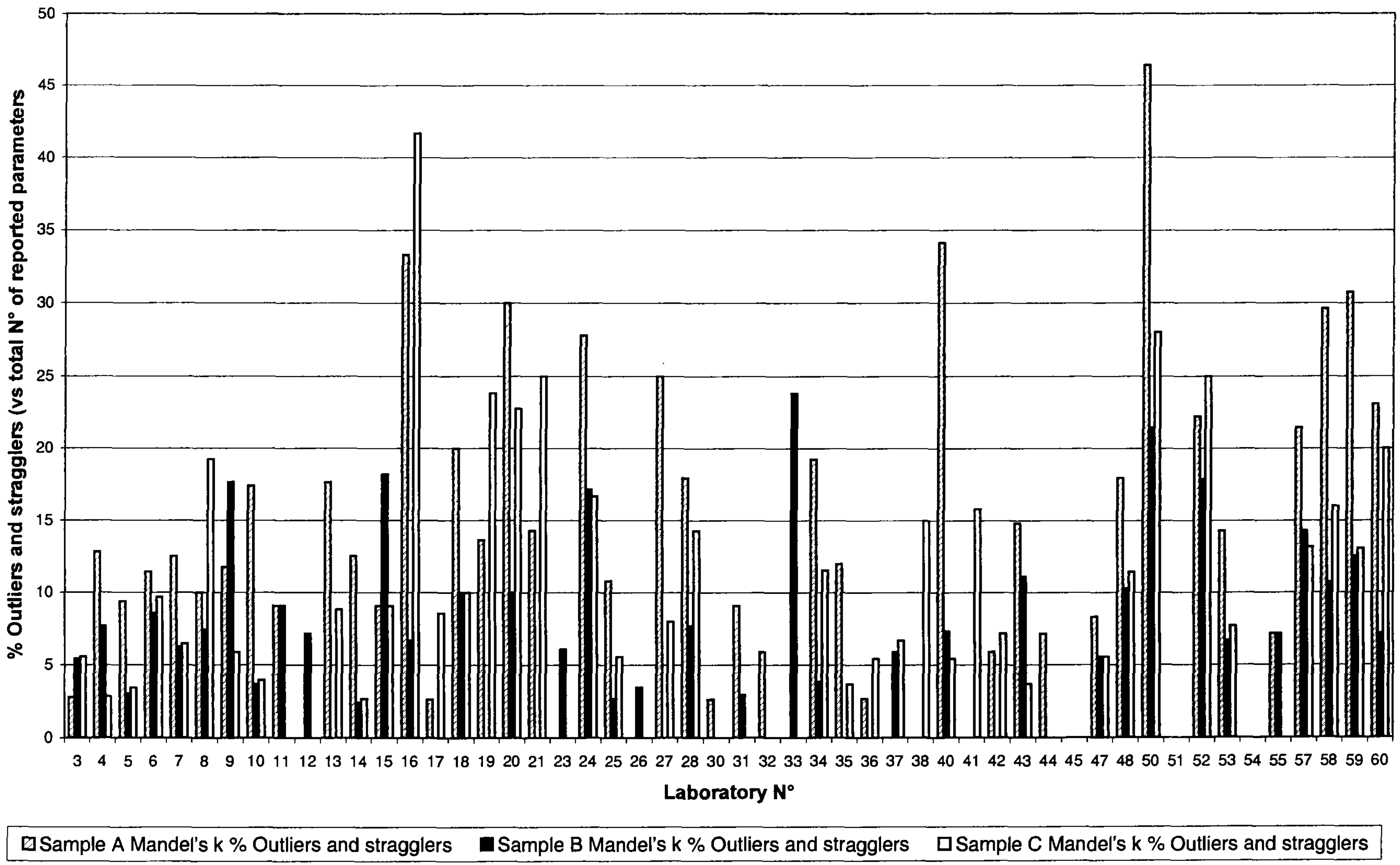


Figure I.13: Performance of the participatory laboratories in the third ring test based on the within-laboratory variance

In Figure I.14, the mean % of outliers and stragglers for the three samples based on the Mandel's k is plotted against the mean % of outliers and stragglers for the three samples based on the Mandel's h. The size of the circles is a measure of the mean number of reported parameters for each sample. From the location of the observations in the scatter plot, is seen that the balance is in favour of the 'h strategists'; most of the observations are located above the 1:1 diagonal. This means that laboratories rather preferred to minimize the number of outliers concerning the between-laboratory variability (Mandel's h statistic) in stead of focussing on a low within-laboratory variability (Mandel's k statistics).

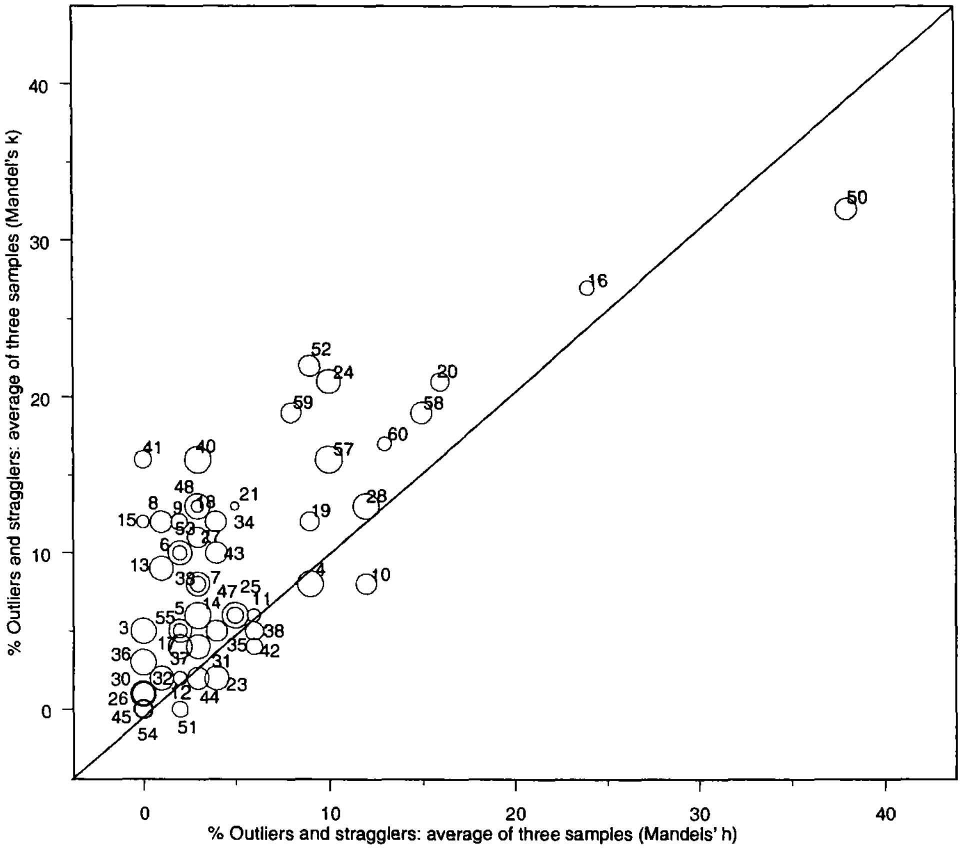


Figure I.14: Scatter plot showing the 'h and k strategist'

Laboratories that are located in the centre of the 'cloud' are performing normally well. Laboratories situated in the perimeter of the graph, have performed relatively poor for the 3rd Interlaboratory Test. Figure I.15 and I.16 provide an idea of the distribution of the laboratories in relation to the percentage of 'mistakes' – outliers and stragglers according to the h statistics (Figure I.15) and the k statistics (Figure I.16). It is obvious from these figures that laboratories have been more excluded based on sample A than on the other 2 soil samples.

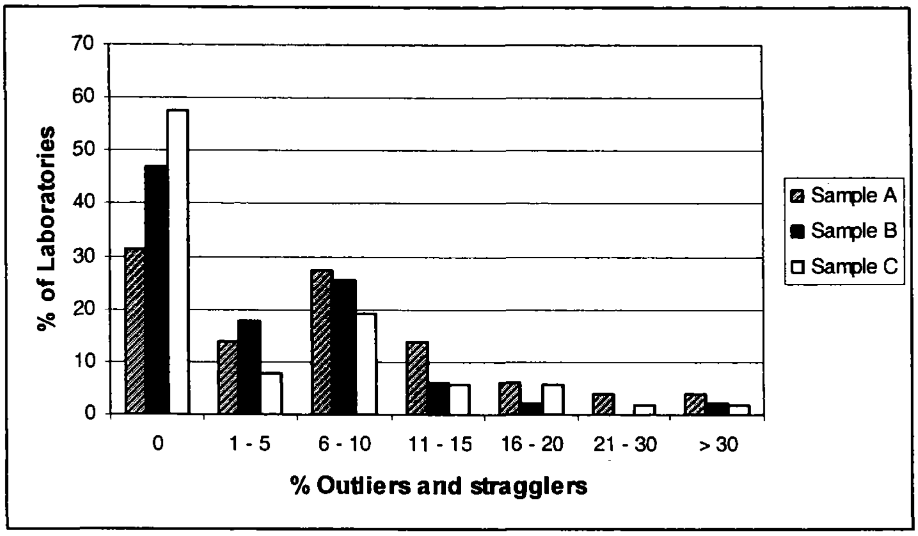


Figure I.15: Outliers and stragglers based on Mandel's h statistics

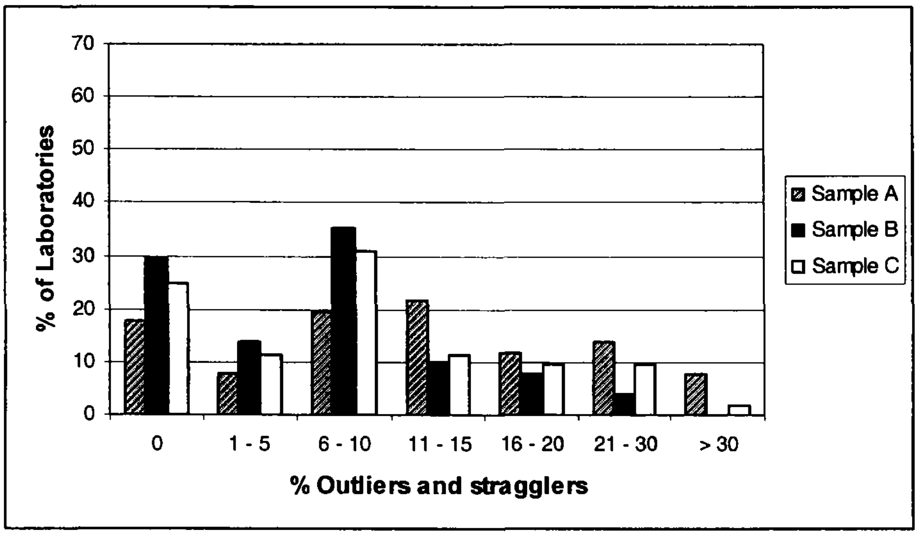


Figure I.16: Outliers and stragglers based on Mandel's k statistics

I.3.6 Coefficients of variation

Table I.6 gives the CV for each analysed parameter. The last column of the table gives the CV per group of analyses, calculated over all samples. In the last row, the average CV per sample is given.

In general, the coefficients of variation for the different parameters are very high which implies high deviations among the results of the participating laboratories. The inter-laboratory variation will thus be an important source of variation.

It is clear that the CV varies according to the analysed sample. Where sample A and B have rather high CV's (respectively 69.7 and 43.5), the CV of C is rather small (26.2). These results were expected, knowing that sample A (chemically poor) and B (calcareous) are quite difficult to analyse. Sample C, on the contrary has a moderate nutrient content, and could be more easily measured.

Table I.6: Coefficients of variation 3rd ring test 2002-2003 (CV = sRepr/Mgen)

Parameter	A	B	C	3 Samples	Group
pH($CaCl_2$)	3,8	1,9	2,7	2,8	3,5
pH(H_2O)	4,4	2,6	5,3	4,1	
Particle Size Clay	83,1	56,6	NA	69,9	53
Particle Size Sand	40,8	47,4	NA	44,1	
Particle Size Silt	45,2	45	NA	45,1	
Carbonates	374	37,7	NA	205,9	206
Organic Carbon	11,1	33,1	9,72	18	18
Total N	36,3	6,88	6,3	16,5	17
Exchangeable Acidity	57,2	143	40,7	80,3	71
Exchangeable Al	49,6	168	48,7	88,8	
Exchangeable Ca	83,5	30,1	29,4	47,7	
Exchangeable Fe	61,7	210	47,9	106,5	
Exchangeable K	55,3	18,8	16	30	
Exchangeable Mg	86,8	28,7	21,8	45,8	
Exchangeable Mn	NA	62,3	32,9	47,6	
Exchangeable Na	118	70	40,5	76,2	
Free H^+ Acidity	66	213	57,9	112,3	
Extractable Al	47,6	19,8	25,9	31,1	47
Extractable Ca	128	12	47,1	62,4	
Extractable Cd	260	46,9	42,5	116,5	
Extractable Cr	54,2	23,4	25	34,2	
Extractable Cu	85,9	15,6	30,6	44	
Extractable Fe	42	12,9	21,7	25,5	
Extractable Hg	NA	76	41,8	58,9	
Extractable K	75,2	18,1	42,4	45,2	
Extractable Mg	83	9,71	24,6	39,1	
Extractable Mn	61,1	15,3	12,8	29,7	
Extractable Na	104	36,4	56,5	65,6	
Extractable Ni	89	24,1	17,6	43,6	
Extractable P	82,6	14	18,2	38,3	
Extractable Pb	22,3	45,7	23,2	30,4	
Extractable S	66,6	53,4	7,37	42,5	
Extractable Zn	98	12,9	24,3	45,1	
Total Al	33	34,2	10,9	26	21
Total Ca	36,8	23,2	19,3	26,4	
Total Fe	21	10,9	7,2	13	
Total K	12,2	14	7,22	11,1	
Total Mg	63,3	7,71	7,67	26,2	
Total Mn	38,2	5,55	14	19,3	
Total Na	21,8	39,4	7,15	22,8	
Reactive Al	42,6	40,9	49,3	44,3	44
Reactive Fe	41,9	39,5	51,7	44,4	
Average per Sample	**69,7**	**43,5**	**26,2**		

Key: NA: Not analysed

The coefficient of variation gives a good indication of the level of difficulty of a specific analysis. Based on the CV, the different analysis can be grouped according to increasing level of difficulty, as shown in Table I.6.

Table I.7: Parameters grouped according to level of difficulty of analysis

Parameter	Group	Level of difficulty
pH	1	Low
Total nitrogen content	1	Low
Organic Carbon	1	Low
Total elements	2	Medium
Aqua regia extractant determinations	2	Medium
Acid oxalate extractions	3	High
Particle size	3	High
Exchangeable elements	3	High
Total carbonates	3	High

Note that the analysis of carbonates has an extremely high CV. Nevertheless this CV is dominated by the large CV for sample A; sample B has an acceptable CV for this parameter. The high CV of sample A can be explained by the absence of calcium carbonate. It is also the only parameter for which the CV increases after exclusion of the outliers (see Annex 5).

Figure I.17 shows for each parameter and each sample, the % of laboratories, that participated for that particular parameter, reporting outlying results. For sample A, more than 20% of the laboratories have been excluded based on the carbonate analysis, exchangeable K and Mn, extractable Cd, Hg, Ni and P and total Ca. Parameters causing problems in sample B, are exchangeable Al, Free H and extractable Hg. For sample C, more than 20% of the laboratories were excluded based on pH($CaCl_2$), reactive Fe and total Na. Hence, there is no particular parameter, except perhaps extractable Hg, that causes consequently problems in each of the three samples. The identity of the 'problem parameters' seems to depend on the nature of the soil sample.

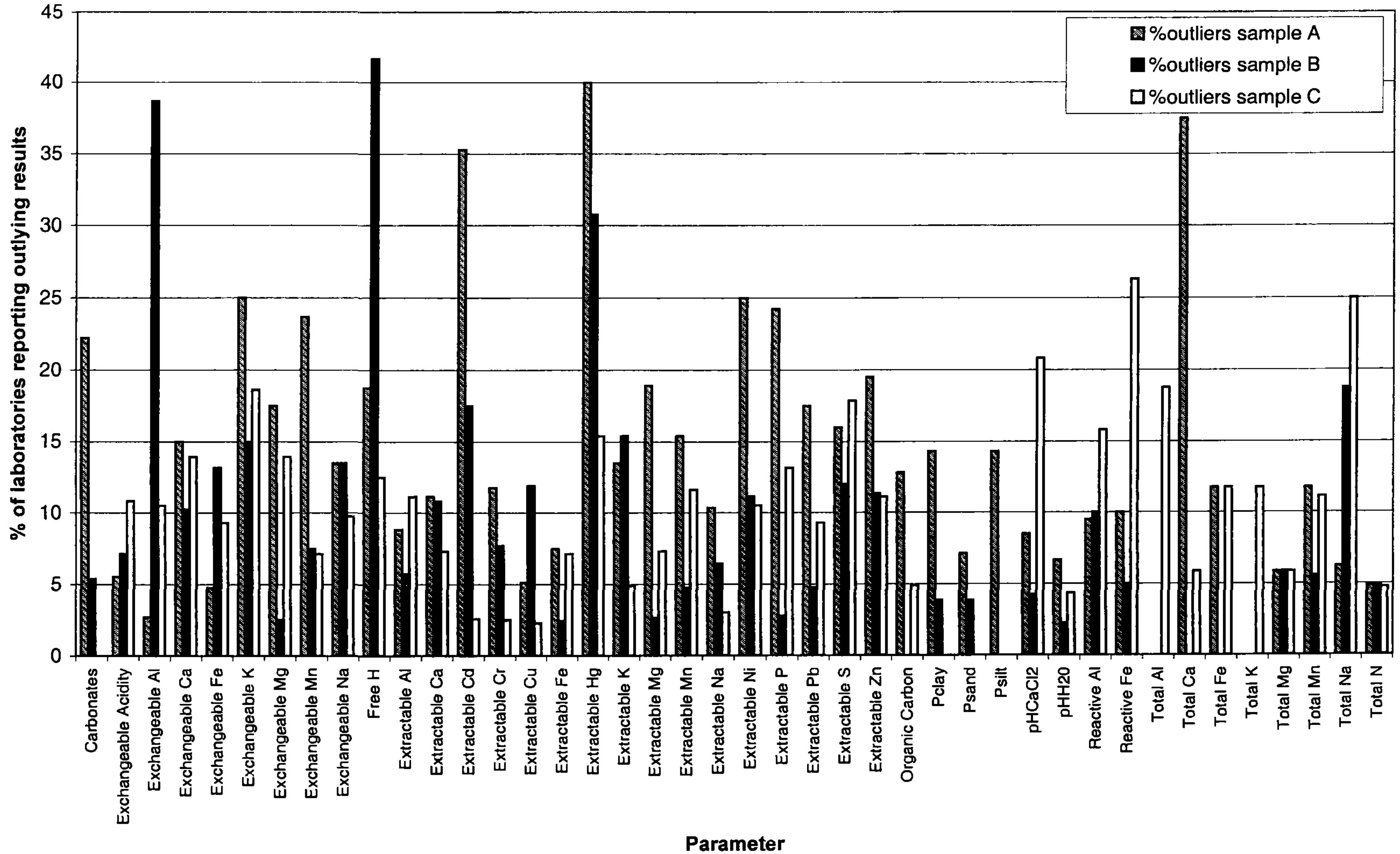


Figure I.17: % of number of laboratories, which participated for that particular parameter, reporting outlying results (probability level 99%)

I.4 Discussion

Laboratories are more often excluded based on the Mandel's k statistics than based on the Mandel's h. This means that many laboratories have **poor internal repeatability**. One possible explanation is that the laboratories were not explicitly asked to report under repeatability conditions, although it has been assumed in this statistical analysis. It is a fact that some laboratories did report values that are a measure of laboratory reproducibility. This means that the model: "$sRepr^2=sLab^2 + sRep^2$" needs to be refined. $SRep^2 = SRep(sensu\ stricto)^2 + SRepr(laboratory)^2$. The fact that the samples were rather extremes - representative for European forest soils, but not a standard sample typically used in ring tests- might have contributed to this poor internal repeatability.

Although laboratories have been contacted to check the reported values after the test results have been entered, some laboratories still reported values in the wrong units (see also §II.3.3). This explains many of the excluded observations (E) in the histograms and box-plots.

Can laboratories mask 'tricky' results by not reporting them? In other words, do laboratories that report less results, score better than laboratories that do their best to do most of the analysis, even if they are not acquainted with the analysis method? Although Figures I.8 till I.10 suggested that no correlation between the number of reported parameters exist, the two laboratories having good results in the Mandel's k evaluation happened to be two laboratories reported few results and/or few replications.

The bonus of this new analysis method is that the procedures becomes more transparent and it becomes possible to interpret and explain in-depth the results of the analysis.

In order to answer the question: When a laboratory scores bad for one sample, will this poor performance be valid for all the samples and both for the inter-laboratory and within-laboratory variance, study again Figures I.11 and I.12.

Table I.8 compares the CV's of the 2nd FSCC ring test (Van Mechelen *et al.*, 1997) to the CV's of the 3rd FSCC ring test. The samples of the second ring test were taken from a Podzolic B horizon enriched in OM (Sample A) and from a Bt of a loess soil (sample B) and were submitted to the same statistical procedure. The CV's for both tests were calculated after the outliers were excluded. Unlike the results in Forest Soil Condition Report (Van Mechelen *et al.*, 1997), the reported values measured by the countries Bulgaria, Estonia, Belarus and Ukraine are included in the calculations for this table. However, it should be noted that samples of completely different origin are chemically difficult to compare. So the same is valid for comparing the CV's.

Careful comparison of some general trends shows that:

The CV's of pH-$CaCl_2$ are of same magnitude. The CV's of Total Nitrogen and Organic Carbon have slightly improved. For sample A of the 3rd ring test, the CV's of the extractable and exchangeable elements are higher compared to the previous ring test. For sample B and C CV values are smaller or of comparable magnitude, except for some exchangeable elements in sample B. For the exchangeable elements Na, Fe and H – some of the problem elements in the 2nd ring test - still cause problems in the 3rd ring test. The same is valid for the measurement of extractable Cd. These elements have both relatively high CV's in the second and the third ring test. Also the degree of difficulty, as was presented in Table I.7, remains largely the same.

Table I.8: Coefficients of variation: 2nd ring test versus 3rd ring test

			2nd ring test						3rd ring test		
		Sample:	A	A	A	B	B	B	A	B	C
Parameter		unit	Mgen	St dev	CV	Mgen	St dev	CV	CV	CV	CV
pH-$CaCl_2$			3.3	0.08	2.4	4.1	0.17	4.1	4	2	3
Organic carbon		g kg^{-1}	203	30	15	2.02	1.38	68	11	33	10
Total Nitrogen		g kg^{-1}	8.9	1.2	14	0.3	0.10	36	36	7	6
Extractable	P	mg kg^{-1}	253.6	64.6	25	389.5	68.4	18	83	14	18
Extractable	K	mg kg^{-1}	468.8	261	56	3065	1608	52	75	18	42
Extractable	Ca	mg kg^{-1}	951.5	225	24	1594.2	745.4	47	128	12	47
Extractable	Mg	mg kg^{-1}	355.1	111	31	3378.9	633.3	19	83	10	25
Extractable	Na	mg kg^{-1}	85.4	48	56	109.6	70.5	64	104	36	57
Extractable	Al	mg kg^{-1}	4735.5	1218	26	17564.6	5326	30	48	20	26
Extractable	Fe	mg kg^{-1}	4024.6	875.1	22	222122	12417.1	18	42	13	22
Extractable	Cr	mg kg^{-1}	10.5	1.3	12	27.2	15.0	55	54	23	25
Extractable	Ni	mg kg^{-1}	9.47	5.9	63	19.7	2.57	13	89	24	18
Extractable	Mn	mg kg^{-1}	26.9	8.7	32	334.5	39.8	12	61	15	13
Extractable	Zn	mg kg^{-1}	175.9	37.4	21	40.2	7.9	20	98	13	24
Extractable	Cu	mg kg^{-1}	10.3	3.4	33	10.3	2.3	22	86	16	31
Extractable	Pb	mg kg^{-1}	70.2	26.1	37	11.7	3.6	31	22	46	23
Extractable	Cd	mg kg^{-1}	3.0	1.2	39	0.7	0.8	110	260	47	43
Exchangeable	K	cmol$^+$ kg^{-1}	0.18	0.05	28	0.09	0.03	28	55	19	16
Exchangeable	Ca	cmol$^+$ kg^{-1}	4.40	0.97	22	3.85	0.57	15	84	30	29
Exchangeable	Mg	cmol$^+$ kg^{-1}	1.09	0.26	23	1.88	0.14	7	87	29	22
Exchangeable	Na	cmol$^+$ kg^{-1}	0.13	0.02	18	0.12	0.18	154	118	70	41
Exchangeable	Al	cmol$^+$ kg^{-1}	5.43	1.82	34	1.58	0.35	22	50	168	49
Exchangeable	Fe	cmol$^+$ kg^{-1}	0.22	0.16	70	0.001	0.003	238	62	210	48
Exchangeable	Mn	cmol$^+$ kg^{-1}	0.06	0.02	29	0.05	0.01	25	0	62	33
Exchangeable	H	cmol$^+$ kg^{-1}	1.17	0.68	58	0.14	0.16	106	66	213	58
Exchangeable	Acidity	cmol$^+$ kg^{-1}	6.51	2.20	34	2.00	0.36	18	57	143	41

The ISO standards report ring test results from interlaboratory comparisons carried out by Wageningen Agricultural University using the same statistical procedures (ISO, 1994a, 1994b, 1994d, 1995, 1998). Table I.9 mentions the mean value of the parameter under consideration in order to characterise the sample. Note that the Wageningen Tests used different soil samples for the different elements whereas the 3rd FSCC Interlaboratory reports for all the parameters on 3 exactly the same samples. It is seen that, except for the measurement of the carbonates and the exchangeable calcium, coefficients of variations are very similar. The reason behind the high CV's of sample A in the 3rd ring test, was the nature of the sample. Sample A was a poor, acid sample without carbonates. Most of the laboratories reported a zero-value, resulting in an extremely small mean value. From the moment that laboratories reported a (even a small) concentration, the standard deviation will be large, resulting in high CV's. The same reasoning is valid for the measurement of the exchangeable calcium.

Table I.9: Ring test results reported by ISO standards compared with the 3rd FSCC Interlaboratory ring test

	Interlaboratory tests ISO standards						3rd FSCC Interlaboratory test			
sample	1	2	3	4	5	mean	A	B	C	mean
PH(H_2O)										
mean value	8.07	8.26	5.47	8.09	4.50		4.0	7.9	3.9	
CVRepr	3.42	2.81	3.33	3.20	3.93	3.34	4.37	2.63	5.34	4.11
pH($CaCl_2$)										
mean value	7.37	7.41	4.93	7.38	4.26		3.1	7.4	3.0	
CVRepr	3.53	3.24	3.51	3.20	4.18	3.53	3.75	1.94	2.67	2.79
Carbonates	**g/kg**									
mean value	662.00	540	158	66	1		0.0	447	NA	
CVRepr	5.11	3.6	4.2	10.4	117.9	28.24	374	37.7	NA	205.9
OC	**g/kg**									
mean value	410.42	63.30	83.88	41.54	2.47		10.0	75.7	480	
CVRepr	31.04	18.89	23.10	13.30	62.96	29.86	11.1	33.1	9.72	17.97
Total Nitrogen	**mg/g**									
mean value	1.46	2.05	11.16				0.3	4.5	17.9	
CVRepr	14.07	16.21	8.80			13.03	36.3	6.88	6.3	16.49
Exchangeable Sodium		**cmol(+)/kg**								
mean value	0.12	0.07	0.05	0.10			0.04	0.07	0.31	
CVRepr	44.35	57.58	57.41	101.02		65.09	104	36.4	56.5	65.63
Exchangeable Potassium			**cmol(+)/kg**							
mean value	0.68	0.63	0.29	0.40			0.02	0.55	0.95	
CVRepr	69.51	62.94	43.06	38.00		53.38	75.2	18.1	42.4	45.23
Exchangeable Calcium		**cmol(+)/kg**								
mean value	9.05	8.03	3.27	13.96			0.12	29.4	6.28	
CVRepr	13.35	20.96	12.11	33.99		20.10	128	12	47.1	62.37
Exchangeable Magnesium			**cmol(+)/kg**							
mean value	0.95	2.27	0.40	0.45			0.03	1.18	1.6	
CVRepr	41.39	57.74	48.48	55.73		50.83	86.6	28.7	21.8	45.70

I.5 CONCLUSIONS

52 laboratories participated at the 3rd FSCC Interlaboratory Ring Test. Although explicitly asked, only 65% of the analyses were done following the reference methods as outlined in the manual (FSCC, 2003). The general trend is that most of the laboratories are making 'mistakes'. Some laboratories have more problems than others. Laboratories reporting more than 20% outliers and/or stragglers need to improve strongly and may need to be helped through a follow up programme. Based on the between-laboratory variance, 4 laboratories had more than 20 % outliers for sample A, 1 laboratory for sample B and 2 for sample C. However, more laboratories have been excluded based on the Mandel's k than on the Mandel's h: 11 laboratories for sample A, 2 for sample B and 6 for sample C. Until now, most ring tests did not assess this within-laboratory variance. As seen from these results, it becomes obvious that this variance should not be ignored. Concerning the between-laboratory variance, 16 laboratories had no outliers for sample A, 24 no outliers for sample C and 30 no outliers for sample C. While for sample B and sample C these numbers fall within an acceptable range, it is clear that sample A was more difficult to analyse and caused many problems.

Phase 2 of the analysis will try to explain the causes that are on the basis of the poor performance of some laboratories. Based on these results further recommendations will be possible.

After analysing the results of the 2nd Interlaboratory Ring Test can be concluded that laboratories might have improved for the 'easy' analysis like pH, organic carbon and total nitrogen. For the analysis of extractable and exchangeable elements no clear improvements can be seen.

Phase II

II.1. INTRODUCTION

While Phase I studied the within-laboratory and between-laboratory variance, Phase II will try to retrieve the causes of this variability. This will be done based on the information obtained from the questionnaire and based on the reactions received from the laboratories after reporting the results of Phase I. All laboratories have been given the opportunity to send FSCC their comments with respect to the results of Phase I (reasons for the good/bad performance, projects to improve the performance, etc.).

Phase II consists of two parts: a **quantitative analysis**, where the relationship is sought between the within- and between-laboratory variability and a **qualitative part** where a closer look is taken at the comments of the laboratories on Phase I.

The quantitative part will try to answer the next research questions:

1. Do laboratories using the reference methods, report better results than laboratories using other methods?
2. Do laboratories with high experience (concerning personnel, analysis method, etc.) score better?
3. Does the region where the laboratory is located play a role in the variability? The problems that laboratories face when analysing soil samples can depend on the type of sample. Laboratories in the southern (Mediterranean) countries may be more experienced in analysing calcareous soil samples (like sample B) and could be expected to report better results than the laboratories in the northern countries which may be more experienced in analysing nutrient poor soil samples (like sample A).
4. Based on the coefficient of variation, the different methods of analysis were grouped according to the 'level of difficulty of analysis'. It will be interesting to find out whether the exclusion of laboratories for further analysis is related to the difficulty of the analysis method.

The ultimate objective is to be able to fine tune the recommendations to the participating laboratories in order to decrease the variability between the laboratories.

As the sampling design aimed in the first place at a ring test 'sensu stricto', the design might not be powerful enough to give a final satisfying answer to the above stated research questions. In this second phase we will try to detect possible trends in the data set which was collected especially for the objectives of phase I. This second phase is seen as an opportunity to check some questions we have in mind and explore some very general answers. It is very important during the reading of the remaining part of the report, to keep the limited value of the results in mind.

II.2 MATERIALS AND METHODS

II.2.1 Questionnaire

The participating laboratories were asked to provide additional information to FSCC by filling in the accompanying questionnaire with the distribution of the soil samples. This questionnaire interrogated on the laboratory practices (used methods, experience, QA/QC programme, etc.) and can be consulted in Annex 7. Questions were arranged according to nine groups of analyses. Throughout the discussion of Phase II, these same nine groups will be retained. Almost all participating laboratories (except for laboratory N° 51) returned a completed questionnaire to FSCC.

In the following paragraphs, the information of the questionnaires will be discussed. The questionnaire addressed the following topics:

- used methods (reference methods versus non-reference methods)
- experience of the laboratory with the used method, with the equipment, experience of the laboratory assistants
- accreditation
- statute of the laboratory (university, state, private and other)
- type of the laboratory (soil, plant or general laboratory)
- whether the laboratory was specified in forestry or not
- training of the personnel
- region of the laboratory (Northern, Southern, Eastern and Western Europe)

More information concerning the used analytical techniques and equipment can be consulted in Annex 8.

II.2.1.1 Use of the reference methods

Although the use of the reference methods was mandatory for the ring test, several laboratories preferred to use their national methods. Of all analyses, only 65% was done according to the manual. Figure II.1 gives an overview of the use of the reference methods for the different groups of types of analyses. Laboratories that gave no (or an unclear) answer to this question are classified within the category 'Unknown method'.

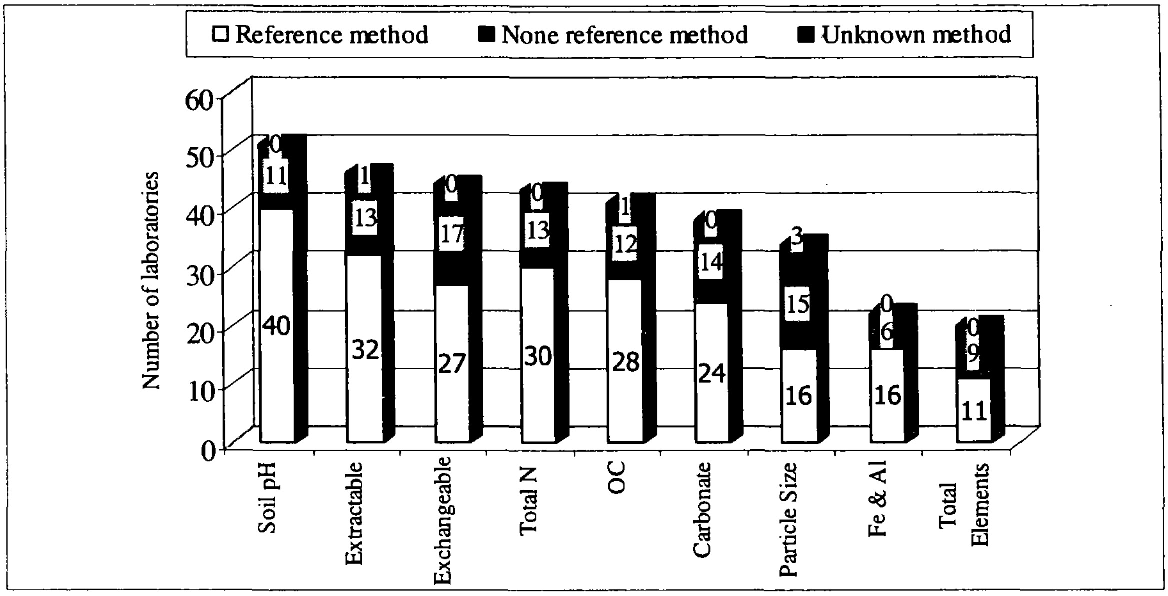


Figure II.1: Use of the reference methods

As shown in Figure II.1 the reference methods are frequently used for the determination of the *pH* and the *Reactive Fe and Al*. For the analysis of the *Particle size distribution*, less than half of the participating laboratories (47 %) uses the recommended method.

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

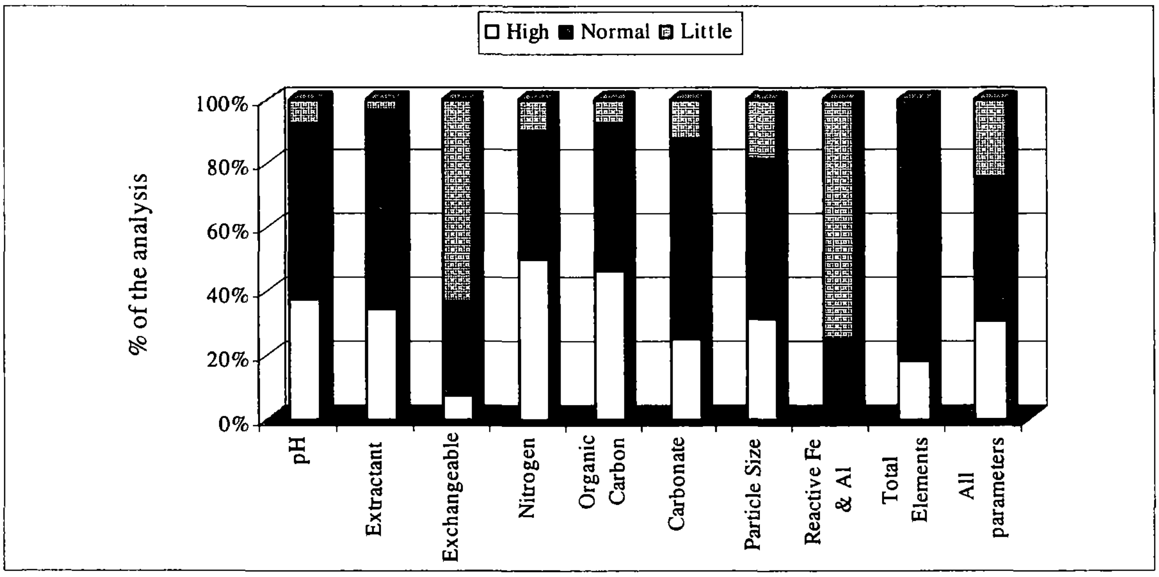


Figure II.2: Experience with the reference methods

More than sixty percent report low experience with the determination of *oxalate extractable Fe and Al* and *Exchangeable Element*. For the latter this is quite remarkable, first because of its important in the assessment of soil acidification and secondly because the extraction with BaCl2 has already been the standard method within the programme for many years. Different motivations exist to use other methods than the reference methods: laboratories do not have any experience with the reference methods, they lack the necessary apparatus, they want to keep comparability with analyses done by national methods, etc.

II.2.1.2 Experience of the participating laboratories

Laboratories were asked to report on their experience with the used methods, the experience with the used equipment and the experience and training of the personnel.

As shown in figure II.3, the experience of the personnel is in most cases high: 75 % of the analysis was done by lab assistants with more than 3 years experience. Most of the laboratories have a lot of experience with the determination of the *Soil pH* and the *Extractable cations*. The determination of the *Reactive iron and aluminium* on the contrary is for most laboratories rather new.

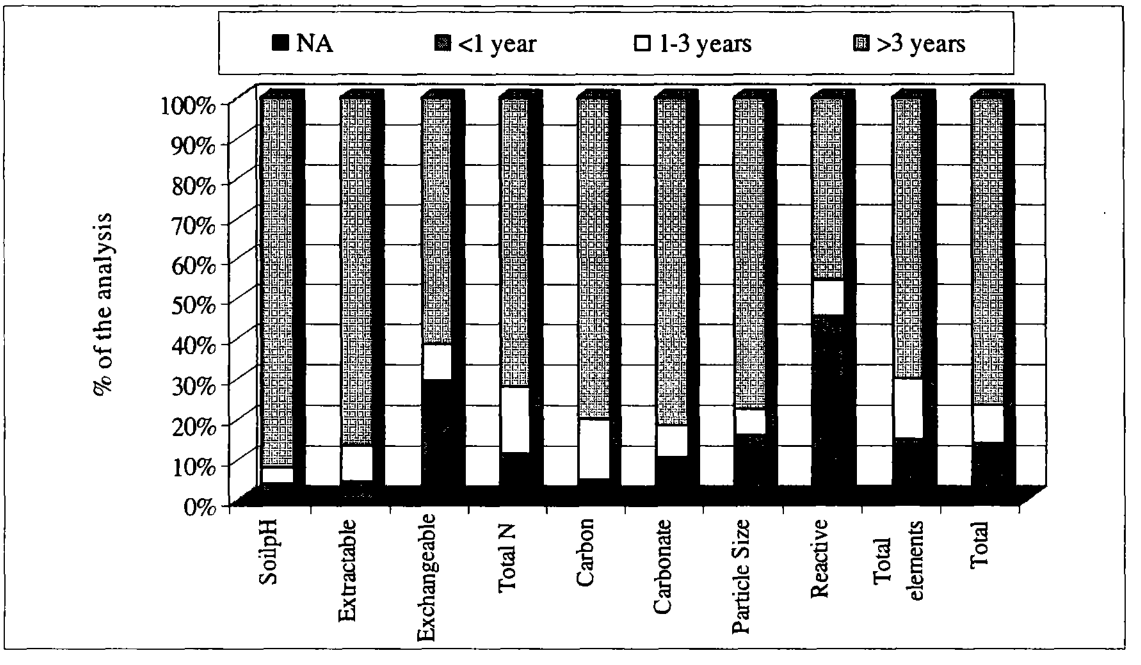


Figure II.3: Experience of the personnel

Next to the experience of the personnel, the laboratories were asked whether the personnel is specifically trained for the different analyses. Results are given in Figure II.4.

For most of the analysis (71.5%) the personnel is specifically trained. The determination of the *Total Elements* is clearly the method where the lowest percentage of trained personnel is reported (only 40% is specifically trained for this analysis).

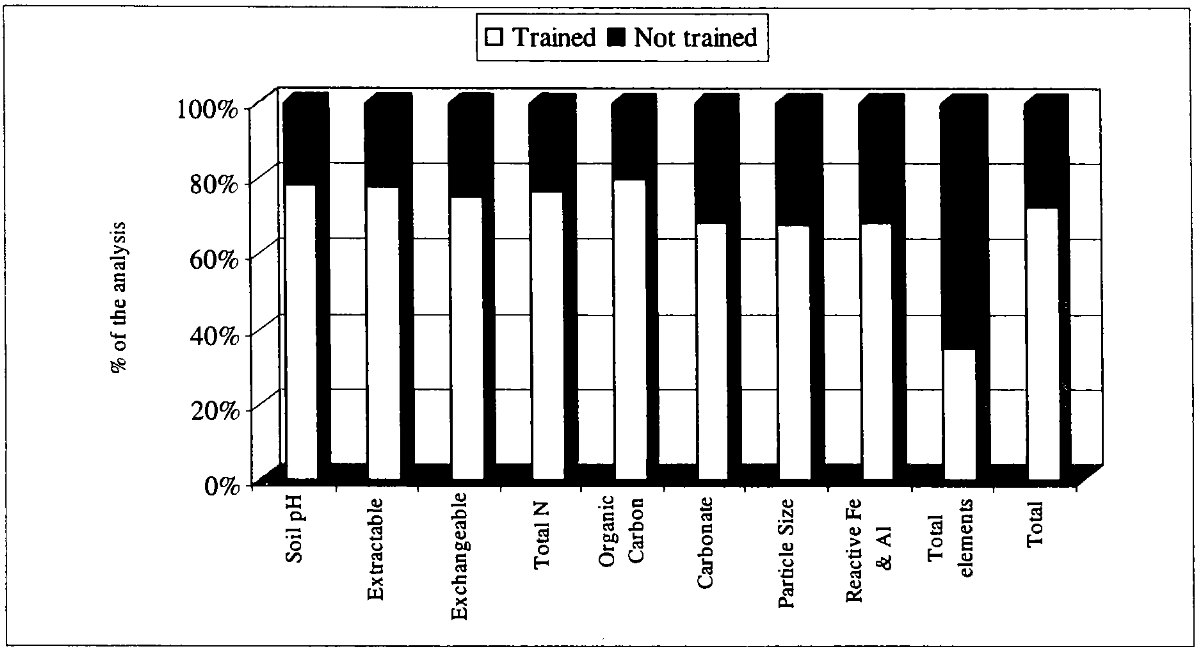


Figure II.4: Training of the personnel

As shown in figure II.5, the experience with the used equipment is usually normal to high.

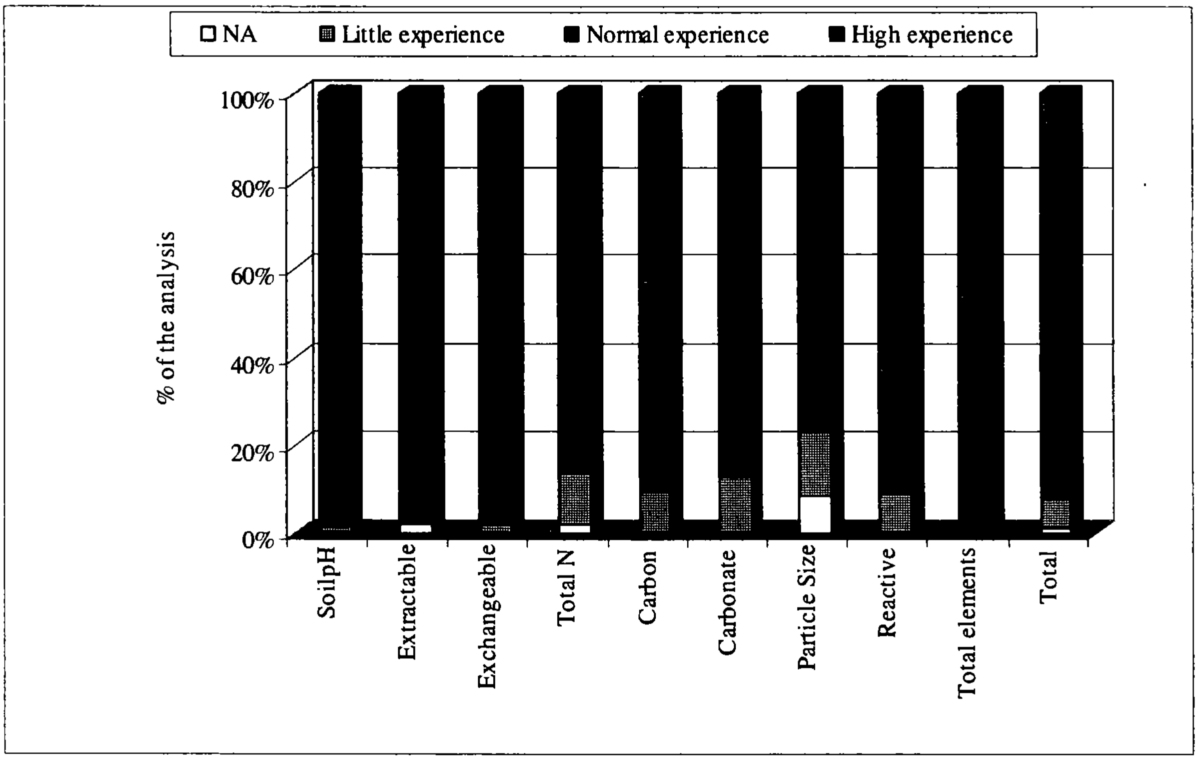


Figure II.5: Experience of the laboratories with the used equipment

Most of the laboratories that participate in the third FSCC ring test are experienced. The determination of the *Reactive Fe and Al* and *Total Elements* are the analyses in which the laboratories are less experienced.

II.2.1.3 Quality assurance and quality control

Reference materials come in various sorts and prices. International Reference Materials (IRM) are expensive and should be used only when really needed. In many cases the concentrations are not in the ranges encountered in the daily practices.

National Reference Materials (NaRM) are in many cases easier to get and often not that expensive. They are in most cases issued by national laboratories and very useful to ensure the quality over the laboratories within a country.

Local Reference Materials (LRM) are (to be) prepared by the laboratory itself and can be easily prepared in large quantities, very cheaply. It can also be made in the correct concentration ranges for the more important parameters. Especially these LRM have a high importance for the QA/QC activities (FSCC, 2003).

Guidelines for the preparation of local reference materials are included in the FSCC Manual on sampling analysis and of soils (FSCC, 2003).

Table II.1: Use of different types of Reference Material

Type of Reference Material	Analysis (%)
International Reference Material (IRM)	13
National Reference Material (NaRM)	4
Local Reference Material	46
IRM & LRM	10
NaRM & LRM	1
IRM & NaRM & LRM	3
No Reference Material	18
NA	5

Form Table II.1, it is obvious that LRM is the most popular type of reference material. 60% of the laboratories uses LRM either on its own, or in combination with NaRM or IRM.

Figure II.6 provides a closer look at the use of types of reference material. Reference material is common for most of the analyses, except for the determination of *Reactive Fe and Al*, where less than 40% of the laboratories make use of RM.

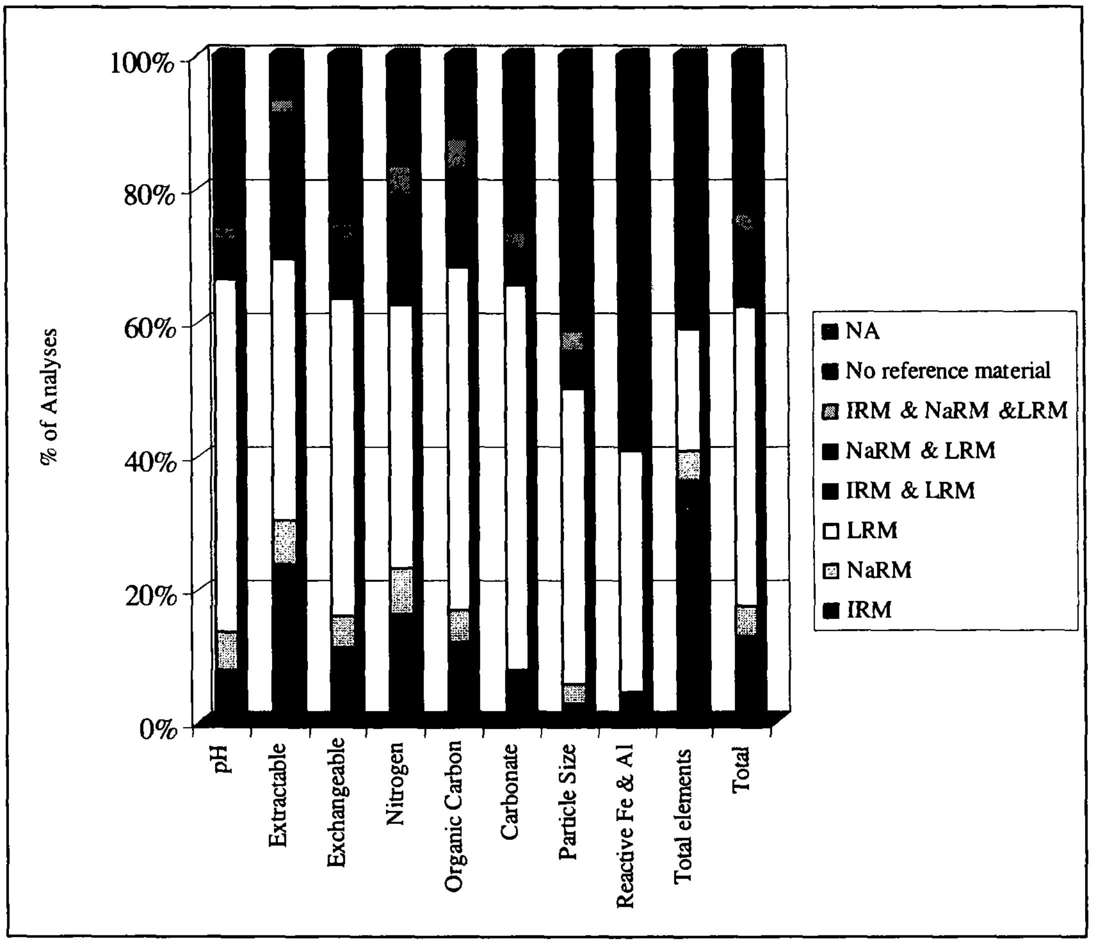


Figure II.6: Use of reference material for the different parameters

For 50% of all analysis, Shewhart control charts were used to evaluate the internal variance of the laboratory. Calibration standards are commonly used, as 73% of the analyses included internal calibration standards.

It seems that only a small minority of the participating laboratories has received an accreditation for a certain type of analysis, only 13% of the analyses were done by laboratories that were specially accredited for these particular analyses.

II.2.2 Description of the exploratory variables

For the sake of the interpretation, single contrasts are preferred to multiple contrasts. For this reason most exploratory variables were reduced to single contrasts (binary factor levels).

1. Use of reference method **(RefmC)**

67 % of the analyses of the ring test were done according to the reference methods. Note that the laboratories that did not clearly answer the question of the used method (in Figure II.1 marked as 'Unknown Method'), are here classified within the group of 'no use of reference method'.

(0) No use of reference methods

(1) Use of reference methods

Factor Levels	0	1
Frequency	1144	2326
%	33	67

2. Experience level **(ExpLevC)**

In the questionnaire laboratories were asked to report on three types of experience. These three exploratory variables (experience with the method – experience with equipment – experience personnel) have been combined for analytical reasons to one factor with two levels:

(0): Little experience

(1): High experience

Factor Levels	0	1
Frequency	2128	1342
%	61	39

The level 1 of the exploratory variable 'Experience' combines all laboratories reporting the highest level of experience for all three types of experience (high experience with the method and the equipment and personnel with more than three years of experience). All other laboratories are included in the group '0'.

3. Training of the personnel **(Trained)**

For each of the analysis, the laboratories where asked whether the personnel was specifically trained to conduct this analysis.

(0): no trained personnel

(1): trained personnel

Factor Levels	0	1
Frequency	865	2555
%	25	75

4. Accreditation **(Accr)**

(0): No accreditation

(1): Accreditation

Factor Levels	0	1
Frequency	2858	562
%	84	16

It should be noted that in total laboratories received accreditation for only 16 % of the analyses. Care is needed in interpreting this unbalanced design.

5. Statute of laboratory **(Statute)**

The exploratory variable 'Statute' has four levels:

(1) or (U) *: University laboratory

(2) or (S): State laboratory

(3) or (P): Private institute or laboratory

(4) or (O): Other

Factor Levels	1 or U	2 or S	3 or P	4 or O
Frequency	524	2205	351	301
%	16	65	10	9

6. Type of laboratory **(Type)**

(1) or (B): Soil laboratory

(2) or (P): Plant and soil laboratory

(3) or (G): General laboratory

Factor Levels	1 or B	2 or P	3 or G
Frequency	463	1635	1283
%	14	48	38

7. Specialised in forestry **(Forest)**

(0): Not specialised forestry laboratory

(1): Specialised forestry laboratory

Factor Levels	0	1
Frequency	1993	1388
%	59	41

* In the univariate analysis the factor levels are coded with numbers. In the multivariate analyses the numbers were recoded into characters.

8. Region (**Region**)

(1): Northern Europe and Canada

(2): Southern Europe

(3): Eastern Europe

(4): Western Europe

Factor Levels	1	2	3	4
Frequency	230	458	825	1957
%	7	13	24	56

The countries are distributed over the different classes as shown in Table II.2.

Table II.2: Countries and regions

Country	Region
Austria	4
Belgium	4
Bulgaria	3
Canada	1
Croatia	3
Cyprus	2
Czech Republic	3
Denmark	1
Estonia	3
Finland	1
France	4
Germany	4
Greece	2
Hungary	3

Country	Region
Ireland	4
Italy	2
Latvia	3
Lithuania	3
Poland	3
Portugal	2
Russian Federation	3
Slovak republic	3
Slovenia	3
Spain	2
Sweden	1
The Netherlands	4
United Kingdom	4

Again, the grouping is unbalanced. Much more laboratories from Western Europe participated in the ring test than from the other parts of Europe. On top of that, 13 of the 23 Western laboratories are located in Germany and 5 in Belgium.

II.2.3. Description of the response variables

During this second phase, we will try to explain the variability of the Mandel's h (labelled in the remaining part of the report as 'Hv') and the Mandel's k ('Kv').

The influence of each possibly influencing factor will be assessed by Analysis of Variance (ANOVA). To meet the requirements for ANOVA, a normal distribution is needed. For this reason, the not normally distributed response variables will be transformed.

QQ-plots are drawn to check the values of two transformations: the **square root transformation** and the **logarithmic** transformation. Since the values of Hv, can either be positive or negative, the absolute value is taken before transformation.

Per group of analyses (a total of 9 groups) normal probability plots (QQ-plots) were drawn of the residuals, as presented in Table II.3 for the Hv (between-laboratory variability) and in Table II.4 for Kv (within-laboratory variability).

Table II.3: QQ-plots of possible transformations of Hv given per group

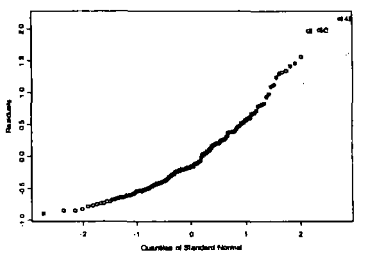
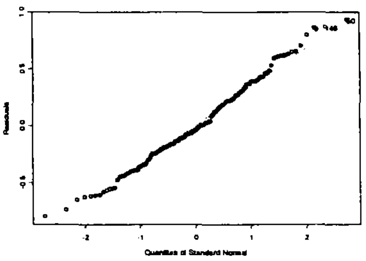
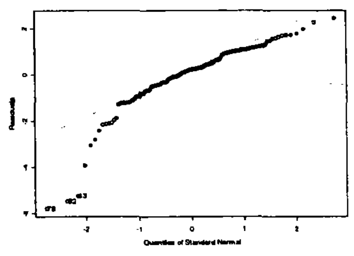
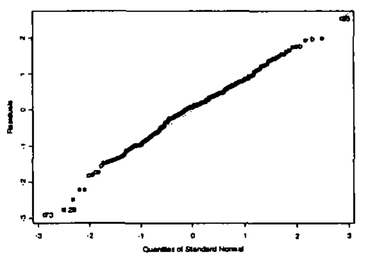
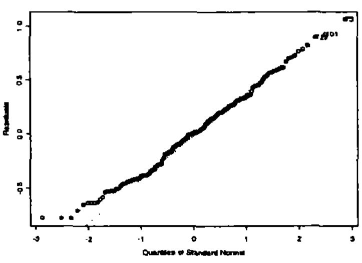
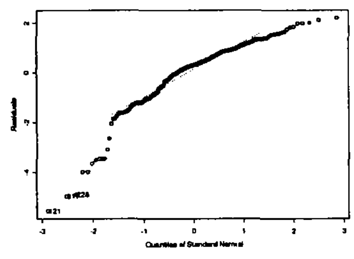
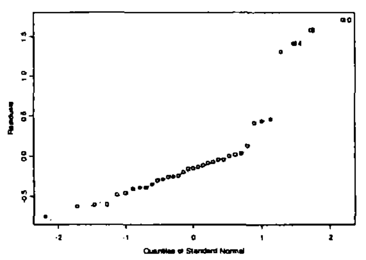
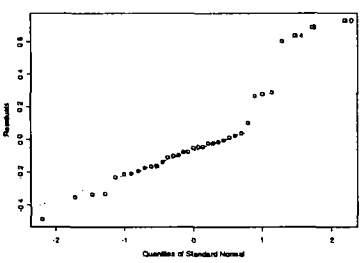
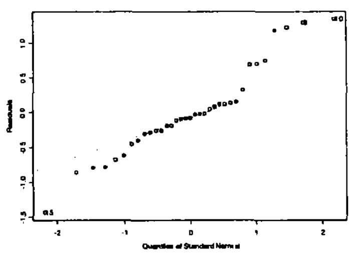
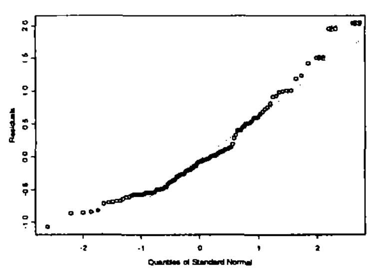
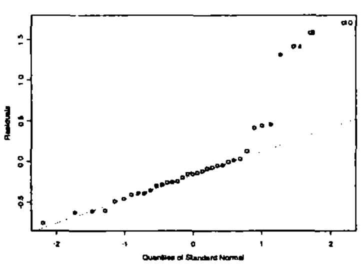
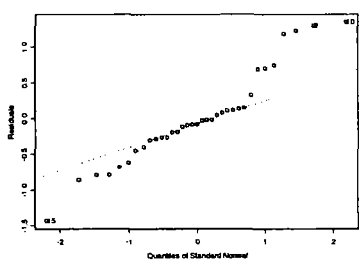
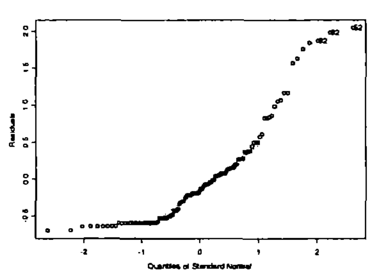
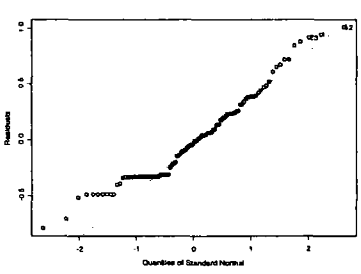
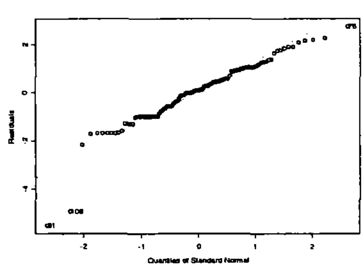
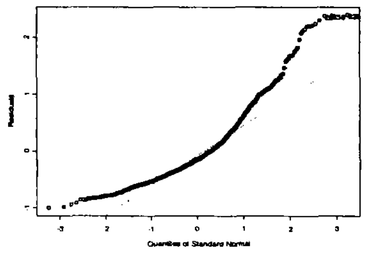
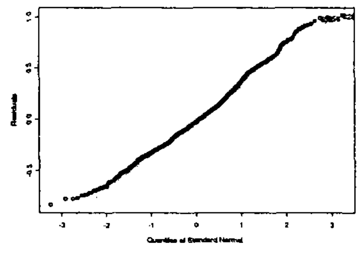
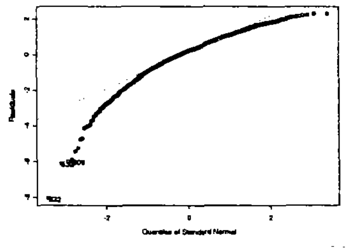
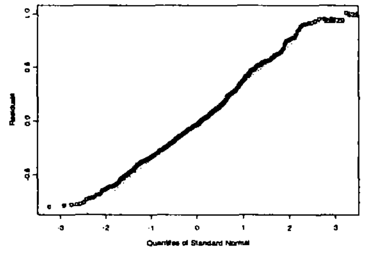
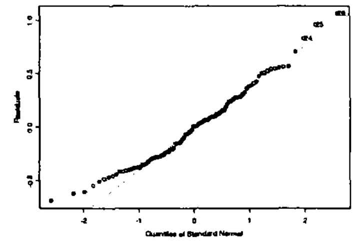
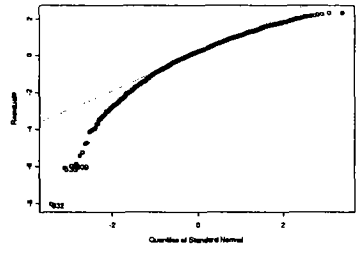
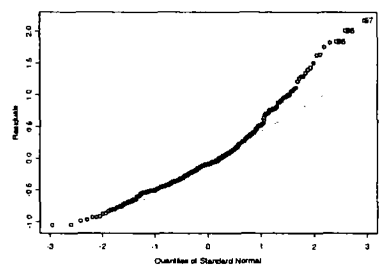
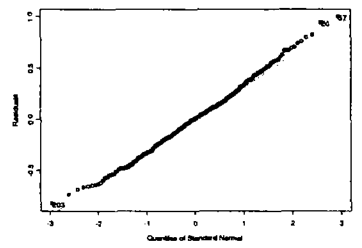
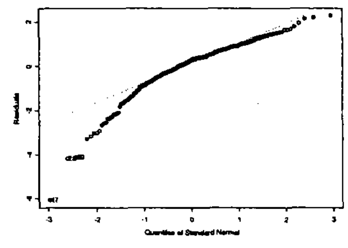
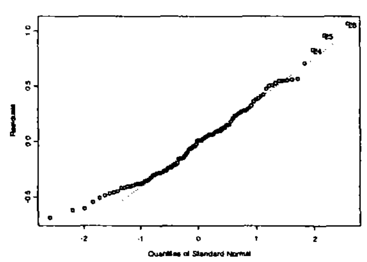
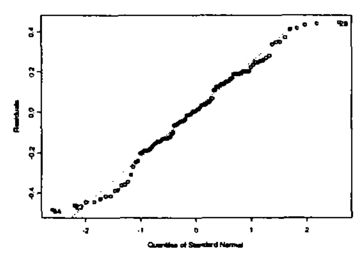
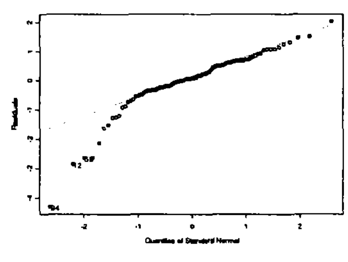
	abs(Hv)	sqrt[abs(Hv)]	log(Hv)
Particle size			
pH Soil			
Carbonates			
Organic Carbon			
Total Nitrogen			

Table II.3 (continued): QQ-plots of possible transformations of Hv given per group

	abs(Hv)	sqrt[abs(Hv)]	log(Hv)
Exchangeable Elements			
Aqua Regia			
Total Elements			
Reactive Elements			

Legend: Aqua Regia = Elements extractable by Aqua Regia = 'Extractable Elements'

Table II.4: QQ-plots of possible transformations of Kv given per group

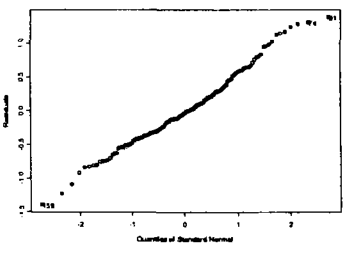
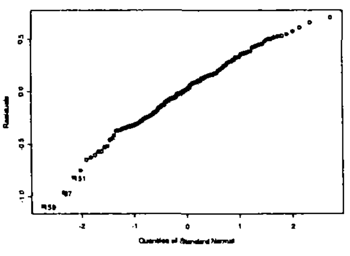
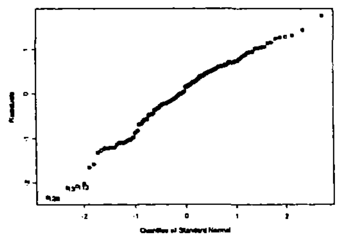
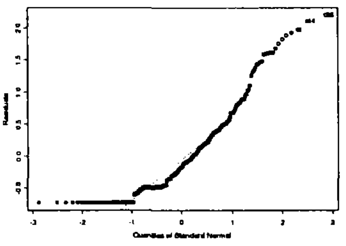
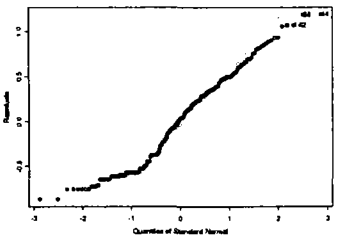
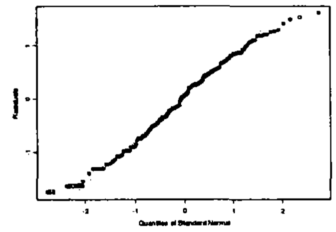
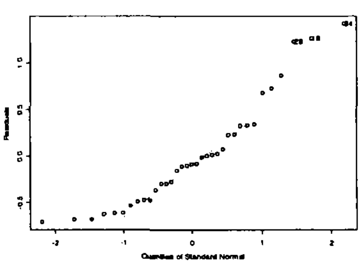
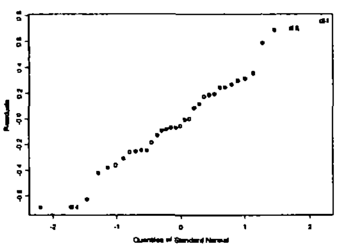
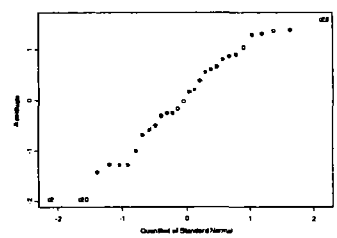
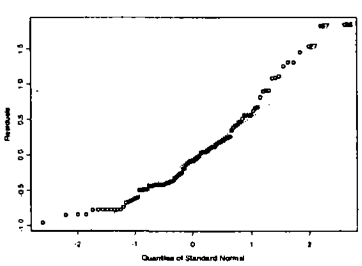
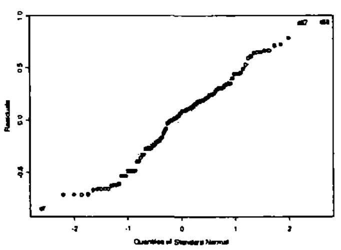
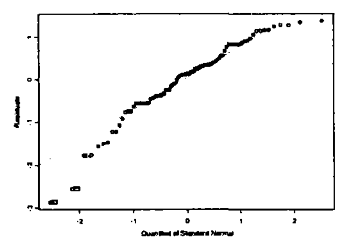
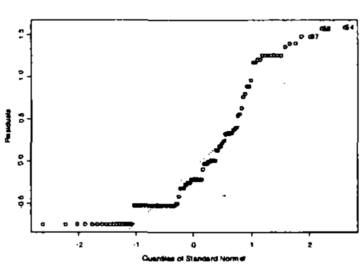
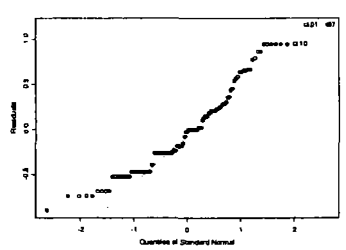
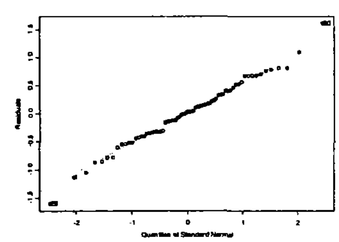
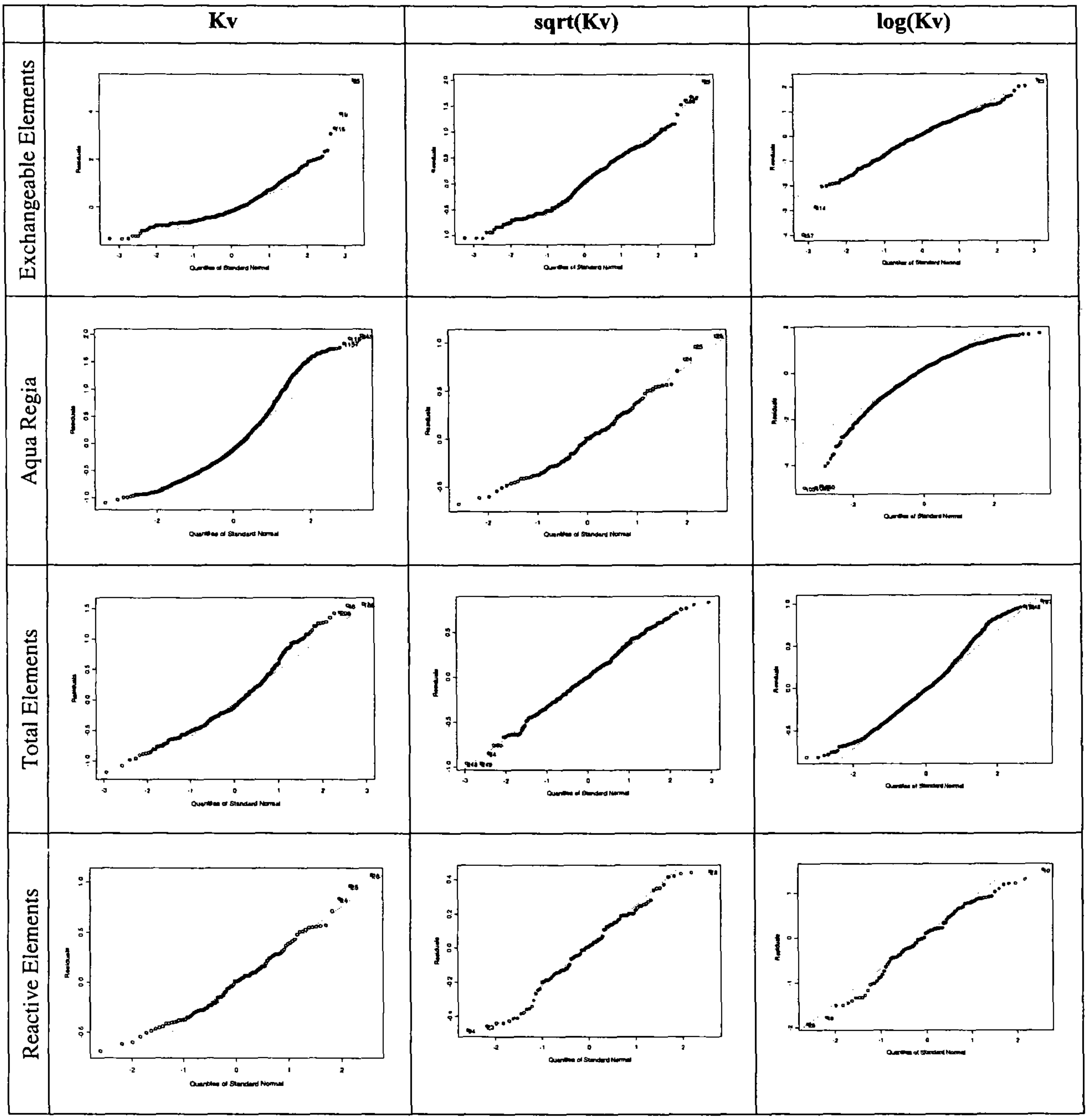
	Kv	sqrt(Kv)	log(Kv)
Particle Size			
pH Soil			
Carbonates			
Organic Carbon			
Total Nitrogen			

Table II.4 (continued): QQ-plots of possible transformations of Kv given per group



Legend: Aqua Regia = Extractable Elements; Reactive Elements= Fe and Al extractable oxalate

The most suitable transformation for each of the groups is presented in Table II.5.

Table II.5: Most suitable transformation for each of the groups (both for Hv and Kv)

Statistic	Hv	Kv
Particle size	square root	square root
pH Soil	square root	logarithmic
Carbonates	none	square root or logarithmic
OC	square root	square root
Total Nitrogen	square root	logarithmic
Exchangeable elements	square root	logarithmic
Aqua Regia	square root	square root
Total elements	square root	square root
Reactive	square root	square root

Concerning Hv, for most of the groups, the square root transformation provides the best fit. For *Carbonates*, none of the three proposed models meets normality conditions.

Concerning Kv, sometimes the square root and sometimes the logarithmic transformation gives the best fit. Generally spoken and in view of a consistent data analysis, a square root transformation will provide the best results and will be used in the remaining part of the analyses.

II.2.4. Statistical analysis

II.2.4.1. Statistical conceptual model

A two-step approach will be followed: first, the response variables will be explored in function of the exploratory variables by means of univariate tests. Subsequently a multivariate model will try to provide a more complete picture.

```
sqrt(abs(Hv)) ~ Sample + RefmC + ExpLevC + Trained + Accr + Statute + Type + Forest + Region
sqrt(Kv) ~ Sample + RefmC + ExpLevC + Trained + Accr + Statute + Type + Forest + Region
```

II.2.4.2. Univariate screening

The exploratory data analysis provides boxplots for each of the influencing factors per group of analyses. The 'notches' in the boxplots indicate the 95% confidence intervals. When the confidence intervals do not overlap, statistically significant differences can be expected.

Note that the 'true' values of the soil parameters of each of the three samples are not known which means that the accurateness of the analyses can not be assessed. In the analysis of the ring test, the precision is evaluated, which means that the results of the analyses are compared to the mean value, determined after exclusion of the outliers. Laboratories using a different, more accurate technique, might be penalized, because their results are too deviant from the general mean. When we say that certain laboratories perform 'better', it means that their results are more precise i.e. they are closer to the general mean of the measured parameter based on the results of all the laboratories, after exclusion of the outliers. An example is the determination of the particle size by laser diffraction (no reference method), which is considered to be a more accurate technique than determination by pipette method (reference method).

To check whether the expected differences are truly significant, univariate tests are used both parametric (ANOVA) and non-parametric (Kruskal-Wallis). While ANOVA works with the normally transformed data, the non-parametric tests use ranks and does not require normality.

II.2.4.3. Multivariate analysis

Multivariate analysis of variance is the extension of ANOVA techniques to multiple responses. Analysis of variance models are typically used to compare the effects of several treatments upon a

certain response. A multiple stepwise regression model has been fit to the response variable Hv (after square root transformation of the absolute value) and to Kv (after square root transformation).
After the analysis of variance model has been fit, it was determined whether any significant differences exist between the responses for the various treatment groups and, if so, the size of the differences was estimated by multiple comparisons tests.

II.2.4.4. Synthesis

The results obtained through the exploratory data analysis, the parametric a non-parametric univariate and multivariate tests are compared and possible pitfall are identified.

II.2.5 Qualitative analysis

The laboratories received the results of the first phase at the end of March 2003 and were given the opportunity to send their comments to FSCC. These comments have been summarized. Based on these comments and on experience that FSCC gained during the analysis of the ring test results, some guidelines for reporting have been compiled. This information is complementary to the statistical analysis.

II.3 RESULTS

II.3.1 Exploratory data analysis

As was decided in § II.2.3 Hv and Kv were transformed using the square root transformation. Hv was first transformed into positive values by taking the absolute value.

I. Between-laboratory variance (based on Mandel's h)

1. Effect of the sample

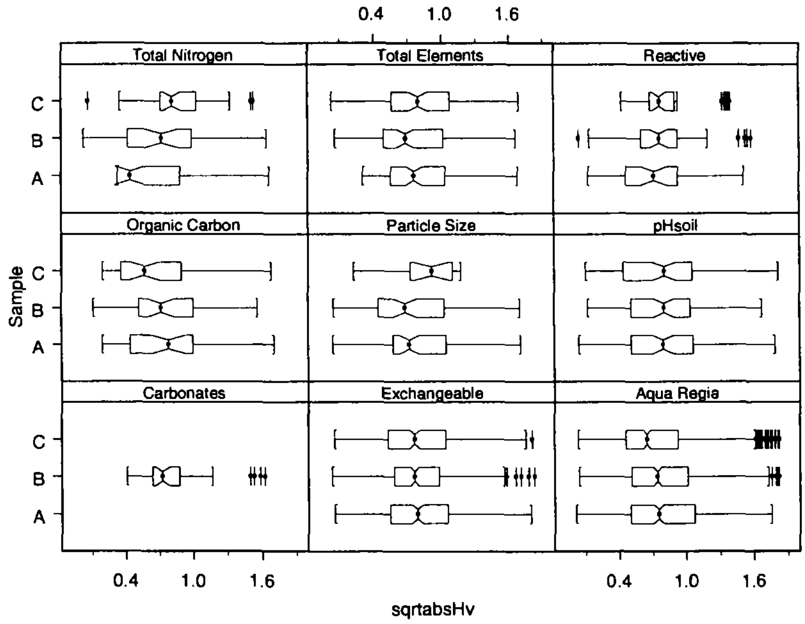


Figure II.7: Boxplot of Hv (square root transformation of absolute values) for (A): sample A, (B): sample B and (C): sample C

Studying the boxplots of Figure II.7, significant differences are expected when the 'notches' of the two factor levels do not overlap. This can be the case for the parameter *Total Nitrogen* where the between-laboratory variance for sample A is lower than for sample C and an opposite trend is expected for *Aqua Regia* (or *Extractable Elements*). Note that the *Aqua Regia extractable elements* show a lot of outliers for sample C, which lets us suspect that these observations are not normally distributed. Care is needed when interpreting the results of the statistical tests.

2. Use of reference method

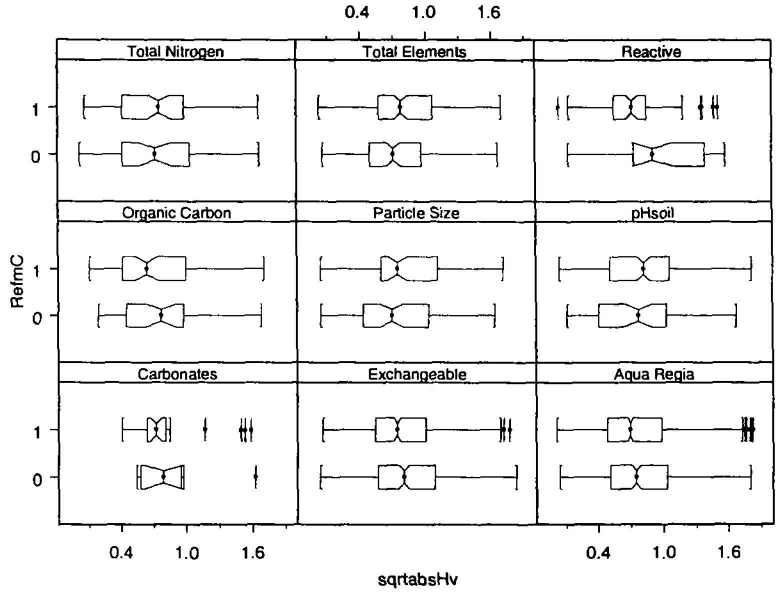


Figure II.8: Boxplot of Hv (square root transformation of absolute values) for (0): no reference method and (1): use of reference method

For *Exchangeable Elements, Reactive Elements* and *Aqua Regia* the square root transformation of the absolute value of Hv is lower when laboratories use reference methods compared to the laboratories that do not use the reference methods. In other words, laboratories that use the reference method are expected to report more precise results than laboratories that do not make use of the reference methods.

Note that in most cases the interquartile range (box length) seems to be of the same magnitude for reference and no reference method. This suggests still an important variation within the reference group laboratories.

3. Experience level

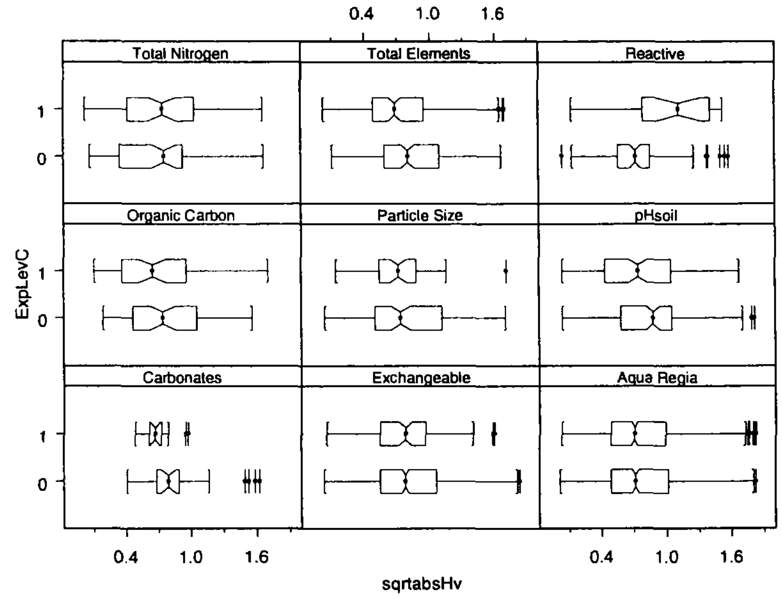


Figure II.9: Boxplot of Hv (square root transformation of absolute values) for (0): little experience and (1): high experience

It seems that laboratories with experience for the analysis of *Reactive Elements* show higher between-laboratory variability than laboratories without experience. For *Carbonates* and the *Total Elements* the opposite trend is seen.

4. Training of personnel

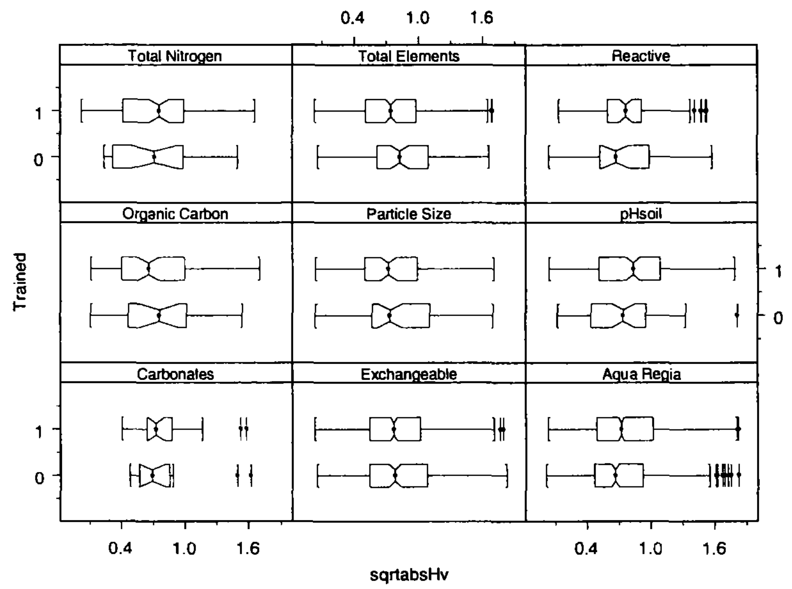


Figure II.10: Boxplot of Hv (square root transformation of absolute values) for (0): no trained personnel and (1): trained personnel

Difference might be expected for *Aqua Regia*, where the trained personnel reports less precise results than when the personnel is not trained. But note again the high number of outliers for the personnel without training.

5. Accreditation

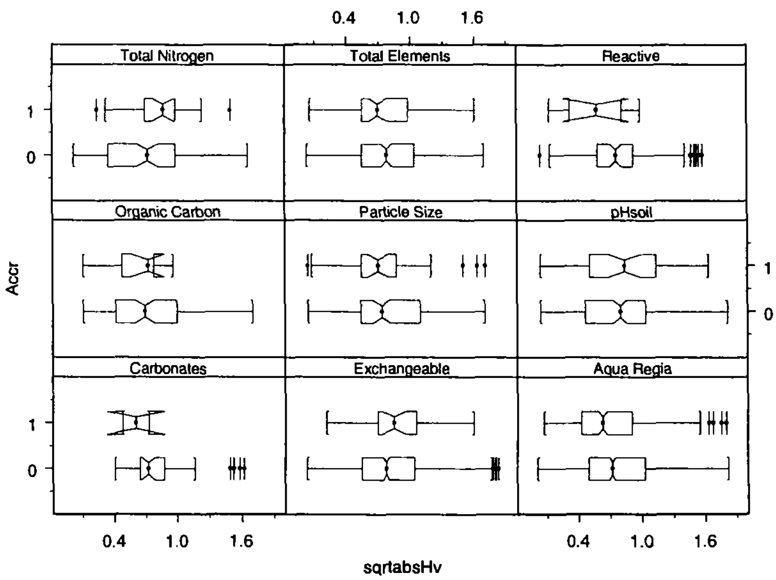


Figure II.11: Boxplot of Hv (square root transformation of absolute values) for (0): no accreditation and (1): accreditation

Laboratories that received accreditation for the analysis of *Aqua Regia* have more precise results than those that did not receive an accreditation for this analysis. All other parameters show no significant difference for accreditation.

6. Statute of laboratory

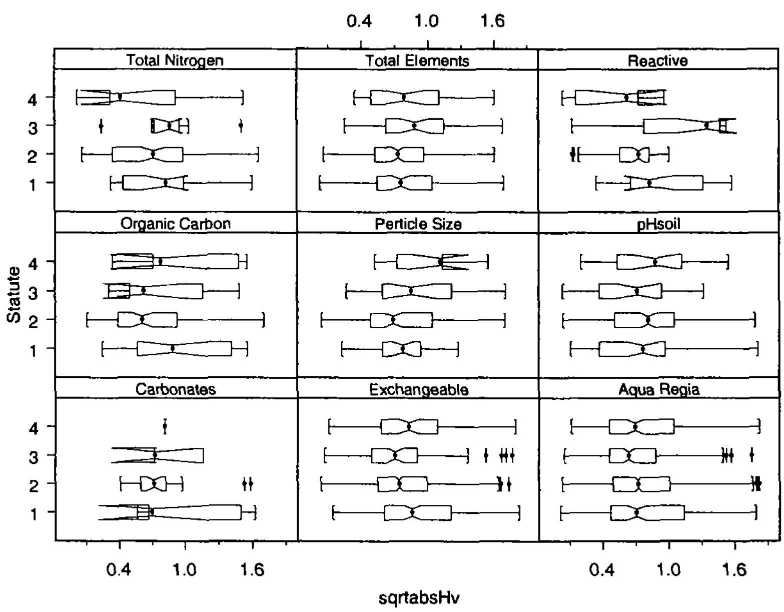


Figure II.12: Boxplot of Hv (square root transformation of absolute values) for statute of the laboratory (1): University, (2): State, (3): Private and (4): Other

Concerning the *Reactive elements*, 'University' (1), 'State' (2) and 'Other' (4) laboratories have lower in between-laboratory variability than the 'Private' laboratories. Concerning *Particle Size*, 'University' (1) and 'State' (2) laboratories might perform better than (4) 'Other' laboratories. Concerning *Exchangeable Elements*, 'State' (2) laboratories might do better than 'University' (1) laboratories.

7. Type of laboratory

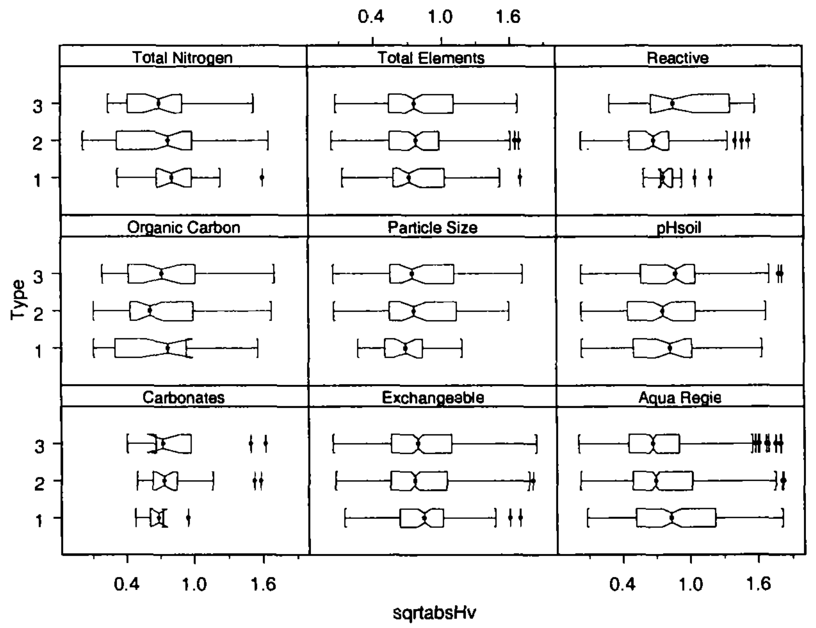


Figure II.13: Boxplot of Hv (square root transformation of absolute values) for the type of laboratory (1): Soil laboratory, (2): Plant and Soil laboratory and (3): General purpose laboratory

Differences are expected for *Aqua Regia* when the 'Soil' (1) laboratories have higher variability than the 'Plant and Soil' (2) and the 'General Purpose' (3) laboratories.

8. Specialised in forestry

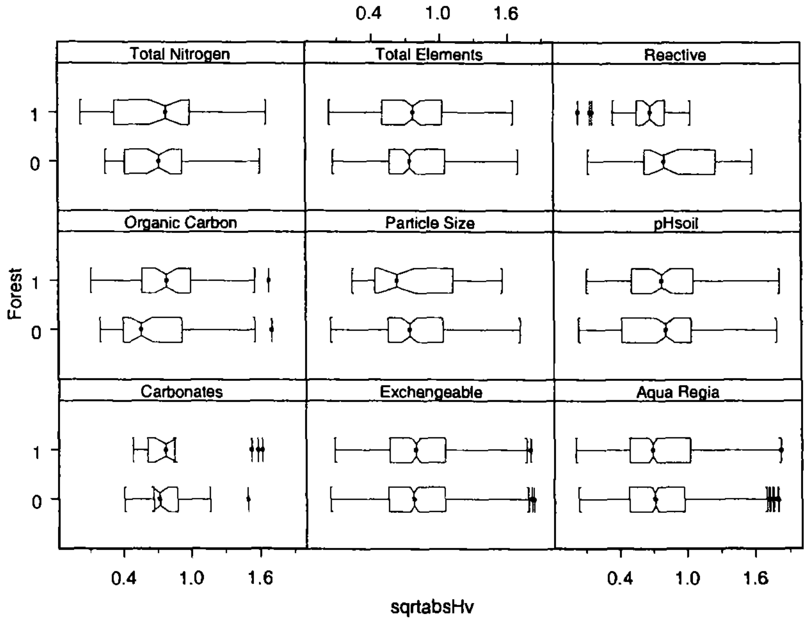


Figure II.14: Boxplot of Hv (square root transformation of absolute values) for (0): General laboratory and (1): Specific forestry laboratory

It is expected that for *Organic Carbon*, 'General' (0) laboratories perform better than 'Specialised Forestry' (1) laboratories.

9. Region

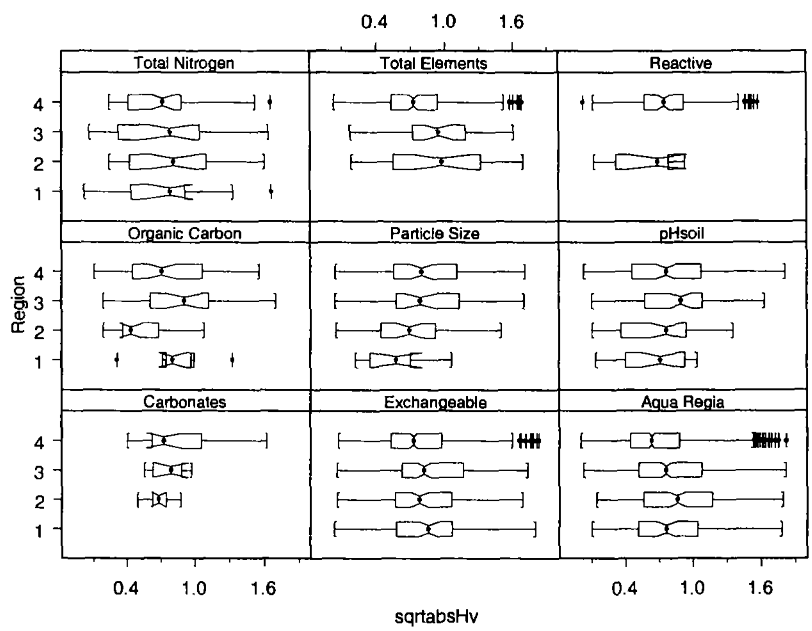


Figure II.15: Boxplot of Hv (square root transformation of absolute values) for (1): Northern Europe and Canada, (2): Southern Europe, (3): Eastern Europe and (4): Western Europe

For *Total Elements*, laboratories in Western Europe (4) have in general better results than laboratories in Eastern Europe (3). For *Organic Carbon*, Southern Europe (2) performs better than all the other regions. For *Exchangeable Elements*, Western European (4) laboratories perform better than Eastern

(3) and Northern (1) laboratories and for *Aqua Regia,* Western (4) laboratories seem to be better than all the other laboratories. But on the other hand, the Western laboratories show also the largest number of outliers, which let us suspect that the normal distribution model might not be appropriate.

II. Within-laboratory variance (based on Mandel's k)

1. Effect of the sample

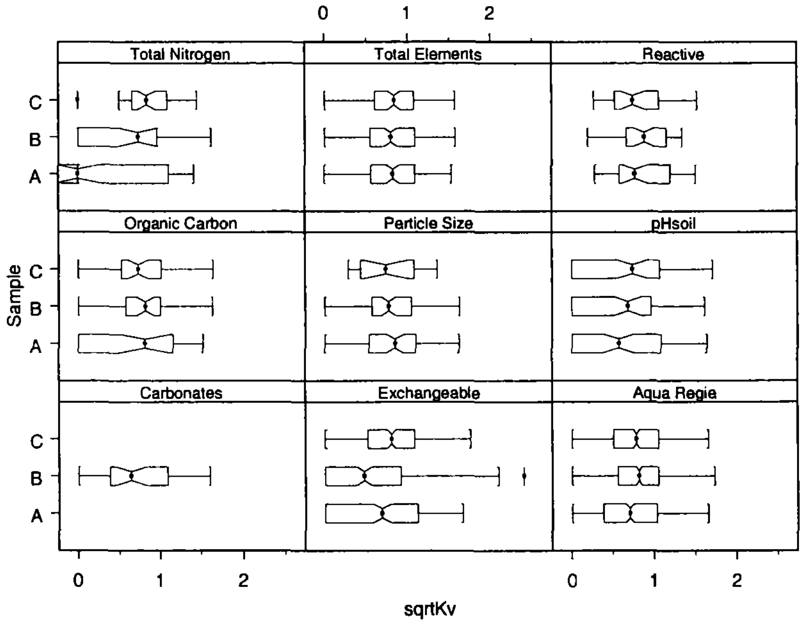


Figure II.16: Boxplot of Kv (square root transformation) for (A): Sample A, (B): Sample B and (C): Sample C

Concerning *Total Nitrogen,* sample A has lower within-laboratory variability than sample C. But since the confidence limits and the interquartile range are much wider for sample A and B than for sample C, care is needed in the interpretation of these boxplots. For *Exchangeable elements* sample B gives lower variances and for *Aqua Regia* the analyses on sample A shower smaller intra-laboratory variability.

2. Use of reference method

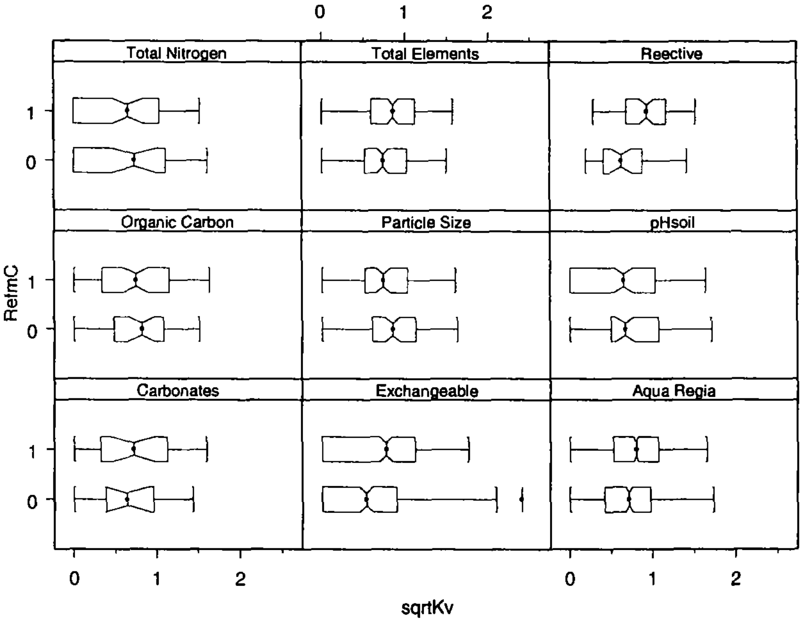


Figure II.17: Boxplot of Kv (square root transformation) for (0): no reference method and (1): use of reference method

For *Total Elements*, *Reactive Elements*, *Exchangeable Elements* and *Aqua Regia*, laboratories that do not use the reference method (0) have lower within-laboratory variance than laboratories that use the reference methods (1).

3. Experience level

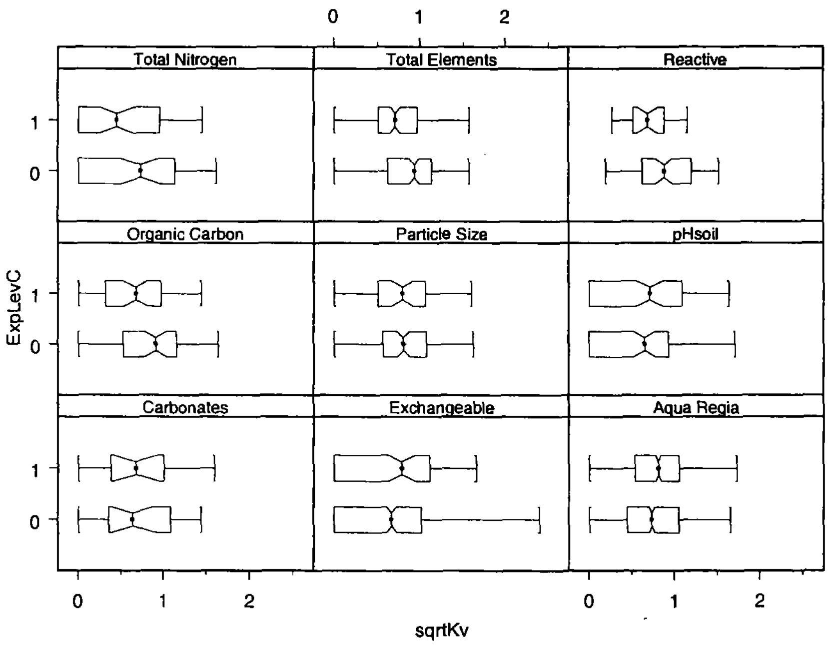


Figure II.18: Boxplot of Kv (square root transformation) for (0): little experience and (1): high experience

For *Total Elements*, laboratories with experience (1) have lower within-laboratory variance than laboratories without experience (0). For *Aqua Regia*, the opposite trend is expected.

4. Training of personnel

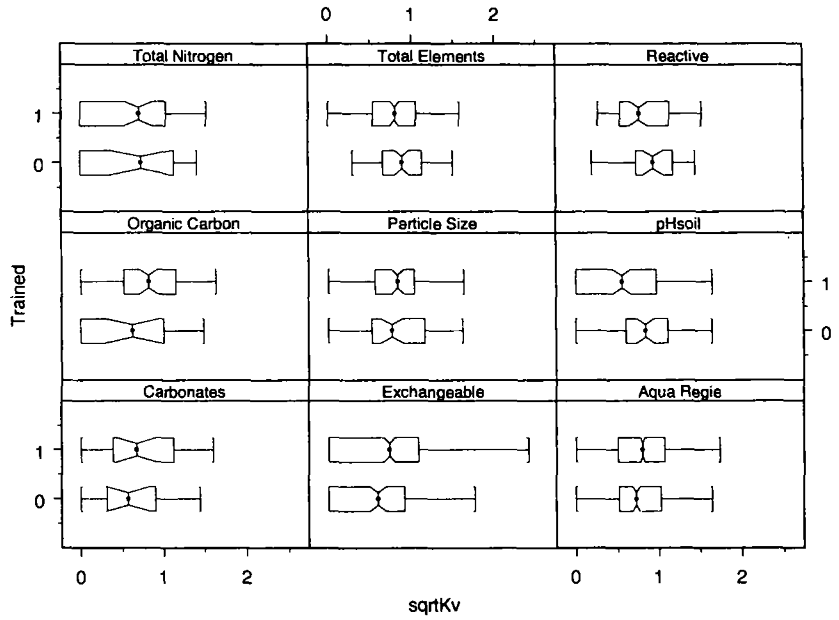


Figure II.19: Boxplot of Kv (square root transformation) for (0): no trained personnel and (1): trained personnel

The *pH* and *Total Elements*, measured by trained personnel (1), gives results with lower within-laboratory variability than measured by not trained personnel (0). For *Aqua Regia*, the opposite trend is observed.

5. Accreditation

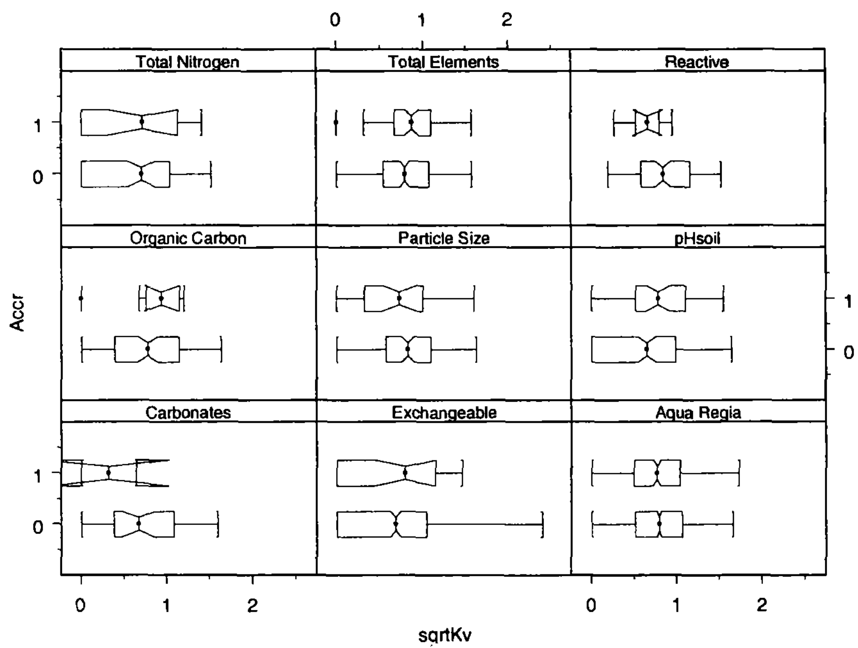


Figure II.20: Boxplot of Kv (square root transformation) for (0): no accreditation and (1): accreditation

No differences are observed, so accreditation does not seem to lower the intra-laboratory variability of this dataset.

6. Statute of laboratory

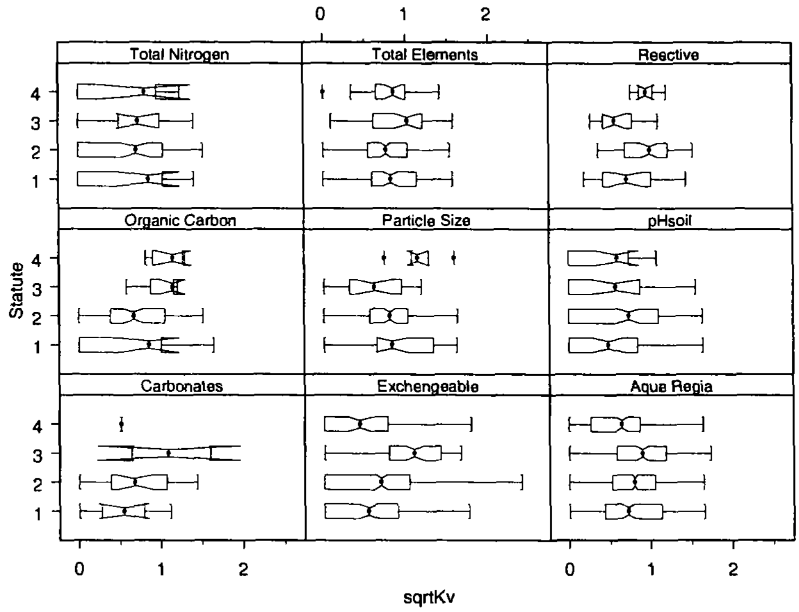


Figure II.21: Boxplot of Kv (square root transformation) for statute of the laboratory (1): University, (2): State, (3): Private and (4): Other

For *Total Elements*, 'State' laboratories (2) have lower within-laboratory variability than 'Private' laboratories (3). For *Reactive Elements*, 'Private' laboratories (3) seem to be better than academic laboratories (2) and than the 'Other' laboratories (4). For *Organic Carbon*, 'Universities' (2) score better than 'Private' (3) and 'Other' laboratories (4). For *Particle Size*, the 'Other' (4) laboratories are better than the rest. For *Exchangeable Elements* and *Aqua Regia,* 'Private' (3) laboratories are worse than the rest and the 'Other' (4) laboratories are better than the 'State' (2) laboratories.

7. Type of laboratory

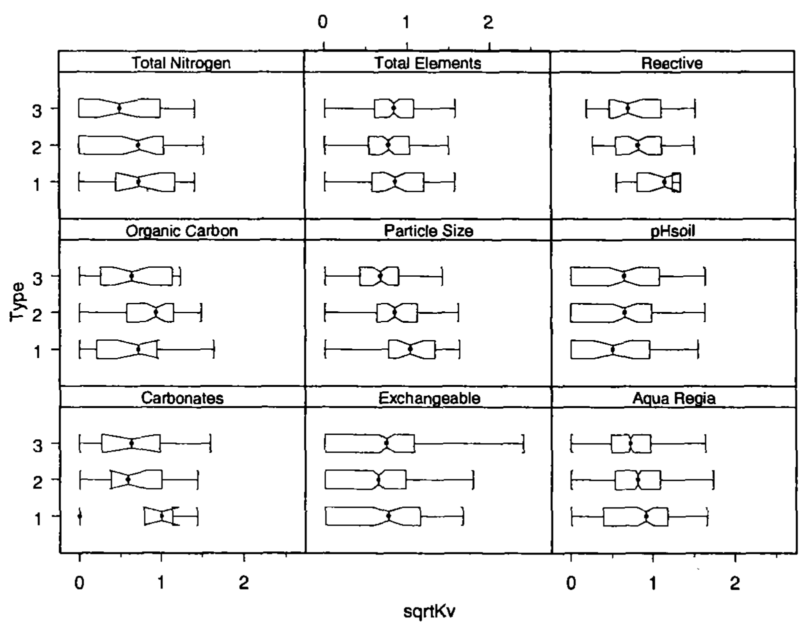


Figure II.22: Boxplot of Kv (square root transformation) for the type of laboratory (1): Soil laboratory, (2): Plant and Soil laboratory and (3): General purpose laboratory

'General purpose' laboratories (3) perform better in relation to the intra-laboratory variability than 'Soil' laboratories (1) for *Reactive Elements*, *Particle Size* and *Aqua Regia*.

8. Specialised in forestry

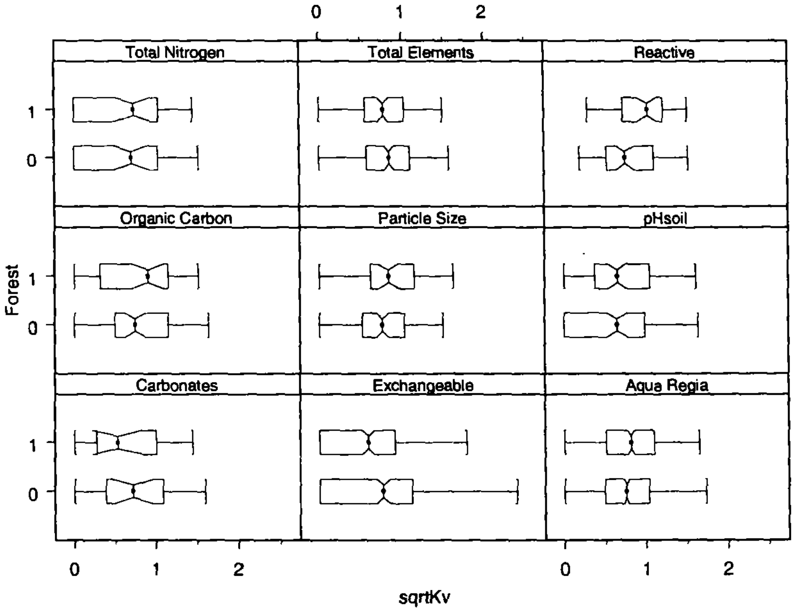


Figure II.23: Boxplot of Kv (square root transformation) for (0): General laboratory and (1): Specific forestry laboratory

Concerning *Reactive Elements*, 'General laboratories' (0) perform better than (1) 'Specialised forestry laboratories 'and for *Exchangeable Elements* the opposite trend is observed.

9. Region

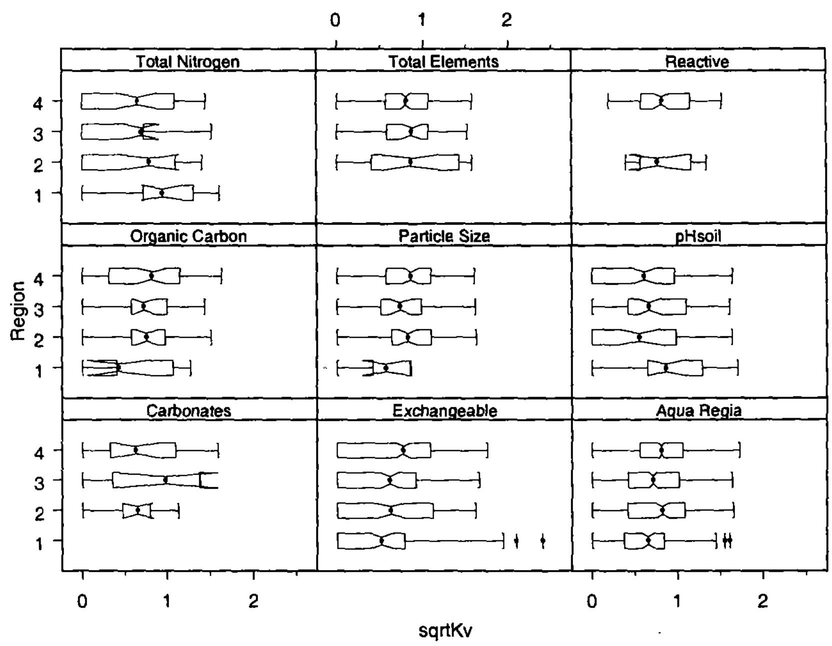


Figure II.24: Boxplot of Kv (square root transformation) for (1): Northern Europe and Canada, (2): Southern Europe, (3): Eastern Europe and (4): Western Europe

For *Exchangeable Elements* and *Aqua Regia*, Western laboratories (4) have poorer within-laboratory variance than the Northern and the Eastern laboratories.

II.3.2. Statistical analysis

II.3.2.1. Results of the individual models

The boxplots of § II.3.1. can be statistically evaluated by non-parametric tests (Kruskal-Wallis) or univariate analyses of variance of which the results are presented in Tables II.6 and II.7. It was opted to conduct both parametric and non-parametric tests as a way to check the validity of the transformations. The parametric test works with the square root transformed data, while the non-parametric test works with the ranks, which remain exactly the same after transformation.

For the multivariate analyses, the example of Exchangeable Elements is given below. The other results can be consulted in Annex 10. The significant factors are summarised in Table II.6 and II.7.

I. Between-laboratory variability

The tested model contains nine factors and is of the form:

```
sqrt(abs(Hv))=Sample+RefmC+ExpLevC+Trained+Accr+Statute+Type+Forest+Region
```

Of these nine factors, two factors contribute significantly to the between-laboratory variability of the Exchangeable elements at the 0.01 significance level, namely 'Statute' and 'Region'. This is seen from the next ANOVA table.

```
Analysis of Variance Table
Response: sqrt(abs(Hv))
Type III Sum of Squares
             Df          Sum of Sq    Mean Sq    F Value      Pr(F)
Statute       3                  2      0.725     6.04        0.00046
Region        3                  1      0.459     3.82        0.00974
Residuals   846                102      0.120
```

The factor levels of the significant factors are compared by means of multiple comparison tests:

```
Multicomp(Statute)
95 % simultaneous confidence intervals for specified linear combinations,
by the Tukey method
critical point: 2.5741
response variable: sqrt(abs(Hv))
intervals excluding 0 are flagged by '**'
    Estimate Std.Error Lower Bound Upper Bound
S-U  -0.1340    0.0327     -0.2180     -0.0496 **
S-P  -0.0157    0.0442     -0.1290      0.0981
S-O  -0.0701    0.0436     -0.1820      0.0421
U-P   0.1180    0.0508     -0.0126      0.2490
U-O   0.0637    0.0511     -0.0679      0.1950
P-O  -0.0545    0.0589     -0.2060      0.0971
```

One of the multiple comparisons is significant at the 0.05 level, namely between S (state laboratories) and U (university laboratories). The difference between S-U is negative (-0.1340) meaning that sqrt(abs(Hv)) of U is larger than the sqrt(Abs(Hv)) of S. So laboratories from government institutions have better results compared to academic laboratories.

```
Multicomp (Region)
95 % simultaneous confidence intervals for specified linear combinations,
by the Tukey method
critical point: 2.5741
response variable: sqrt(abs(Hv))
intervals excluding 0 are flagged by '**'
    Estimate Std.Error Lower Bound Upper Bound
W-E  -0.0958    0.0300     -0.1730     -0.0187 **
W-S  -0.0325    0.0384     -0.1310      0.0664
W-N  -0.0799    0.0427     -0.1900      0.0299
E-S   0.0633    0.0419     -0.0444      0.1710
E-N   0.0160    0.0456     -0.1010      0.1330
S-N  -0.0473    0.0523     -0.1820      0.0874
```

From the above multiple comparisons can be concluded that Western laboratories (W) score better than laboratories from Eastern Europe (E).

II. Within-laboratory variability

The tested model is:

```
sqrt(kv)= Sample+RefmC+ExpLevC+Trained+Accr+Statute+Type+Forest+Region
```

Three factors are retained at the 0.01 significance level.

```
Analysis of Variance Table

Response: sqrt(Kv)
Type III Sum of Squares
           Df Sum of Sq Mean Sq F Value       Pr(F)
   Sample   2        10    5.11    21.7   1.00e-009
    RefmC   1         6    6.07    25.8   4.71e-007
  Statute   3        15    5.10    21.7   0.00e+000
Residuals 846       199    0.24
```

```
Multicomp(Sample)
95 % simultaneous confidence intervals for specified linear combinations,
by the Tukey method
critical point: 2.3478
response variable: sqrt(Kv)

intervals excluding 0 are flagged by '**'
    Estimate Std.Error Lower Bound Upper Bound
A-B    0.108    0.0420     0.00974       0.207 **
A-C   -0.154    0.0404    -0.24900      -0.059 **
B-C   -0.262    0.0402    -0.35700      -0.168 **
```

From the multiple comparisons is seen that B is smaller than A, and that A is smaller than C (B<A<C). This means that, concerning the *Exchangeable Elements*, the within-laboratory variability for sample B is smaller than for sample A; and for sample A smaller than for sample C.

```
Multicomp(RefmC)
95 % non-simultaneous confidence intervals for specified linear
combinations, by the Fisher LSD method
critical point: 1.9628
response variable: sqrt(Kv)
intervals excluding 0 are flagged by '**'
    Estimate Std.Error Lower Bound Upper Bound
0-1   -0.175    0.0344      -0.242      -0.107 **
```

Laboratories that use the reference method (1) have higher within-laboratory variability than the laboratories that do not use the reference methods.

```
Multicomp(Statute)
95 % simultaneous confidence intervals for specified linear combinations,
by the Tukey method
critical point: 2.5741
response variable: sqrt(Kv)
intervals excluding 0 are flagged by '**'
    Estimate Std.Error Lower Bound Upper Bound
S-U   0.0832    0.0453     -0.0333       0.200
S-P  -0.3900    0.0595     -0.5430      -0.237 **
S-O   0.1980    0.0602      0.0435       0.353 **
U-P  -0.4730    0.0688     -0.6500      -0.296 **
U-O   0.1150    0.0695     -0.0637       0.294
P-O   0.5880    0.0796      0.3830       0.793 **
```

There are no significant differences between the academic laboratories (U) and the 'other' laboratories (O) or the government laboratories (S). But O is significantly smaller than S and S and U significantly smaller than P. This means that the laboratories that are grouped under the category 'Others' (O) have smaller within-laboratory variability in the analyses of the exchangeable elements compared to the other 'statutes' of laboratories (S and P), except the academic laboratories (U). Further, private laboratories (P) consistently reported results that showed higher within-laboratory variability when compared to the other categories.

II.3.2.2. Comparison between the different models and summaries

I. Between-laboratory variability

Table II.6. summarises the results of the Kruskal-Wallis tests, the univariate ANOVA and the stepwise multiple regression. This allows us to compare between the different models. When significant at the 0.05 level, the p-values is accompanied by an '*', when significant at the 0.01 level, it is indicated by a '**' and have been written in **bold** script.

Table II.6: Summary of the exploratory study (0) and p-values of the between-laboratory variability (Mandel's h) of (1) univariate Kruskal-Wallis test (2) univariate ANOVA and (3) the multiple linear regression model. The p-values of the latter are only given when significant at the $\alpha = 0.05$ level. 'E' means that based on the box plots, a significant difference could be expected.

Factor	Group	Sample	RefmC	ExpLevC	Trained	Accr	Statute	Type	Forest	Region
Particle Size	0						E			
	1	0.292	0.199	0.378	0.442	0.673	0.151	0.145	0.71	0.141
	2	0.524	0.151	0.303	0.434	0.691	0.108	0.124	0.873	0.113
	3									
pH soil	0									
	1	0.964	0.959	0.108	0.145	0.357	0.744	0.625	0.711	0.329
	2	0.903	0.847	0.165	0.174	0.311	0.679	0.617	0.639	0.375
	3									
Carbonates	0			E						
	1	NA	0.534	0.0488*	0.602	0.303	0.579	0.607	0.788	0.464
	2	NA	0.786	0.0523	0.933	0.339	0.608	0.548	0.338	0.322
	3									
OC	0								E	E
	1	0.392	0.924	0.172	0.556	0.478	0.0615	0.865	0.112	0.0074**
	2	0.616	0.964	0.182	0.682	0.313	0.0165*	0.803	0.233	0.00702**
	3						0.00997**			0.00432**
Total N	0	E								
	1	0.0194*	0.915	0.462	0.594	0.327	0.598	0.663	0.996	0.77
	2	0.0597	0.965	0.487	0.536	0.444	0.691	0.692	0.758	0.653
	3									
Exchangeable	0		E				E			E
	1	0.932	0.0577	0.574	0.574	0.231	0.0011**	0.667	0.294	0.0044**
	2	0.908	0.0591	0.41	0.487	0.344	2.45E-04**	0.893	0.407	0.00537**
	3						0.00046**			0.00974**
Extractable	0	E	E		E	E		E		E
	1	0.0116*	0.608	0.995	0.0542	0.0011**	0.0896	0**	0.629	0**
	2	0.0844	0.984	0.926	0.054	0.00106**	0.0418*	9.3E-09**	0.415	2.5E-014**
	3			7.2E-05**			5.89E-04**	00**		0**
Total elements	0			E						E
	1	0.305	0.0639	0.0035**	0.0895	0.438	0.153	0.949	0.611	0.0025**
	2	0.636	0.0554	0.00649**	0.12	0.553	0.775	0.919	0.502	0.00205**
	3				6.0E-06**	3.8E-04**	5.0E-06**			3.0E-06**
Reactive	0		E	E			E			
	1	0.498	0.0011**	0.003**	0.43	0.185	0.0009**	0.0073**	0.0058**	0.209
	2	0.545	1.1E-04**	3.8E-05**	0.751	0.118	1.72E-06**	0.00552**	0.00133**	0.0903
	3		0.00013**			0**	0**			

Concerning the groups of analysis *Particle Size, pH Soil, Carbonates, Total Nitrogen,* none of the exploratory variables could explain any significant part of the variability of Hv. For *Organic Carbon,* the **Region** was significant in all the tests. The variable **Statute** was only significant at α=0.01 in the multivariate model. For the *Exchangeable Elements* there were 2 significant factors in all the tests: **Statute** and **Region.**

For the remaining three groups *Extractable, Total* and *Reactive Elements,* more significant factors were found, though these effects were not always consistent between the different types of statistical tests. For *Extractable Elements,* **Type** and **Region** were significant for all types of tests; for *Total Elements,* the factor **Region** was significant for all the tests and for *Reactive Elements,* the factors

Reference Method and **Statute** were highly significant. Other effects were only significant for some of the four tests. Especially for the *Reactive Elements* the different ways of analysing gave very differing results.

From the point of view of the factors, the **Use of the reference method** does not explain any significant part of the between-laboratory variability, except for the *Reactive Elements*. The **Level of experience** was only relevant for the *Total Elements* and the *Reactive Elements* when using the Kruskal-Wallis test or univariate ANOVA but not in the multiple regression model. There the **Level of experience** was only significant for the *Extractable elements*. Whether the personnel followed a specialised **training** course was not important to explain the between-laboratory variability except for *Total elements* in the multivariate analysis. The **Statute** and **Region** were the most significant factors explaining between-laboratory variability. The consistency between the univariate and multivariate was low for the factors **Accreditation** and **Statute**. If an effect was found, it was usually not valid for the four approaches.

Usually the Kruskal-Wallis tests and the ANOVA tests confirm the trends that were seen in the boxplots. Sometimes visual effects were only significant at the $\alpha = 0.10$ level. A remarkable difference is seen for the *Reactive elements* and both the **Type** of laboratory and whether is a **specialised forestry** laboratory or not. No significant difference is expected when studying the boxplots nor from the multiple regression model but significant difference are seen in the Kruskal-Wallis test and the ANOVA tests.

Differences of significance between the Kruskal-Wallis tests and ANOVA tests are minor. It may happen that a certain factor is significant at the 0.05 level using the ANOVA model and only significant at the 0.1 level for the Kruskal-Wallis tests (e.g. **Sample** for *Extractable* and *Total Nitrogen*; **ExpLevC** for *Carbonates*, **Statute** for *Organic Carbon*).

II. Within-laboratory variability

Table II.7. summarises the results of the Kruskal-Wallis tests, the univariate ANOVA and the stepwise multiple regression. This allows us to compare between the different models. When significant at the 0.05 level, the p-values is accompanied by an '*', when significant at the 0.01 level, it is indicated by a '**' and have been written in **bold** script.

Table II.7: Summary of the exploratory study (0) and p-values of the within-laboratory variability of (1) univariate Kruskal-Wallis test (2) univariate ANOVA and (3) the multiple linear regression model. The p-values of the latter are only given when significant at the $\alpha = 0.05$ level. 'E' means that based on the box plots, a significant difference could be expected

Factor		Sample	RefmC	ExpLevC	Trained	Accr	Statute	Type	Forest	Region
		Group								
Particle Size	0						E	E		
	1	0.848	0.13	0.56	0.813	0.638	**0.0073****	**0.0001****	0.115	0.162
	2	0.88	0.15	0.44	0.663	0.057	**0.00478****	**6.03E-05****	0.0558	0.173
	3							**6.05E-05****		
pH soil	0				E					
	1	0.847	0.267	0.334	**0.0012****	0.0725	0.0453*	0.66	0.546	0.224
	2	0.932	0.221	0.369	**0.00181****	0.0961	0.0451*	0.672	0.394	0.205
	3				**0.00181****					
Carbon-ates	0									
	1	NA	0.845	0.826	0.413	0.27	0.35	0.438	0.303	0.914
	2	NA	0.767	0.913	0.473	0.233	0.35	0.542	0.365	0.804
	3									
OC	0						E			
	1	0.708	0.414	0.0149*	0.157	0.299	0.0237*	0.15	0.67	0.931
	2	0.41	0.335	0.016*	0.137	0.364	0.0393*	0.161	0.886	0.857
	3									
Total N	0	E								
	1	**0.0063****	0.365	0.0487*	0.653	0.742	0.722	0.35	0.775	0.397
	2	**0.00213****	0.382	0.0387*	0.663	0.754	0.782	0.325	0.808	0.494
	3	**0.00213****								
Exchange-able	0	E	E				E		E	E
	1	**0****	**0****	0.0265*	0.0109*	0.648	**0****	0.0126*	**0****	**0.0059****
	2	**3.03E-09****	**1.85E-05****	0.0333*	0.0113*	0.771	**5.05E-011****	**0.0082****	**4.18E-05****	0.0224*
	3	**1.00E-09****	**4.71E-07****				**0.00E+000****			
Extractable	0	E	E	E	E		E	E		E
	1	**0****	0.0293*	0.046*	0.252	0.139	**0****	**0.0039****	0.0833	**0.0028****
	2	**0.00247****	0.0369*	0.0512	0.392	0.166	**3.65E-010****	0.0157*	0.144	**0.00552****
	3	**0.000929****					**0****			
Total elements	0		E	E	E		E			
	1	0.649	**0.0156***	**0****	0.0324*	0.0767	0.0292*	0.187	0.196	0.704
	2	0.602	**0.0155***	**1.77E-05****	0.0311*	0.121	0.041*	0.191	0.181	0.908
	3			**0****					**0.00543****	
Reactive	0		E				E	E	E	
	1	0.654	**0.0014****	0.0122*	0.218	0.143	**0.0019****	0.0491*	**0.0078****	0.995
	2	0.747	**0.00102****	0.015*	0.241	0.134	**0.00142****	0.0631	**0.00959****	0.988
	3						**0.00420****	**0.00721****	**0.00725****	

For *Particle Size*, significant differences are found for **Type** and for **Statute**, but for the latter the effect was not significant in the multiple regression model. For *pH soil* there was an effect of **Training**. For *Carbonates* and *OC* no significant effects were found. For *Total Nitrogen* there was an effect of the **Sample**. For *Exchangeable, Extractable, Total and Reactive Elements*, many factors were significant but not necessarily for all the (statistical) tests.

Most of the exploratory variables could explain some parts of the variation, except for the variable **Accreditation.** The factor **Region** was significant in less groups compared to the **between-laboratory variability. The Experience Level, Training of the personnel, Type** of laboratory and **Forestry**

laboratory or not and the **use of the reference method** did matter for some groups. Again **Statute** significantly contributed to the within-laboratory variability of most of the groups.

Concerning differences between the Kruskal-Wallis tests and the ANOVA, levels of significant of the factor 'Type' may differ for the groups *Exchangeable* (KW at 0.05 and ANOVA at 0.01), *Extractable* (KW at 0.01 and ANOVA at 0.05) and *Reactive Elements* (KW at 0.05 and ANOVA at 0.1).

Most of the significant effects could already been seen from the boxplots although some discrepancies were observed. Sometimes boxplots might suggest that significant differences exist while the statistical analysis does not reveal any differences at the $\alpha = 0.01$ or 0.05 level, though often significant differences are seen at the $\alpha = 0.10$ level (e.g. Kv – **Trained** personnel – *Total Elements*).

III. Multiple comparisons

Based on the multiple stepwise regression, individual contrasts were made to detect the significant differences between the factor levels (when the factor levels were contributing to the variability of the response variables at the $\alpha = 0.01$ level. The results for the between-laboratory variability is given in Table II.8 and for the within-laboratory variability in Table II.9.

Table II.8: Summary of the multiple comparisons in the multiple stepwise regression models of the between-laboratory variability

Factor Group	Sample	RefmC	ExpLevC	Trained	Accr	Statute	Type	Forest	Region
Particle Size									
pH Soil									
Carbonates									
Organic Carbon						S < U			S<E
Total Nitrogen									
Exchangeable elements						S < U			W<E
Extractable elements			0 < 1			P,S<U	G<P<B		W<S,E N<S
Total elements				1 < 0	1 < 0	U,S < P			W<S,E
Reactive Fe and Al		1 < 0			1 < 0	S<U<P O<U,P			

Legend: 1: use of reference method, or has trained personnel, or has received accreditation
When indicated as smaller, Hv is smaller so between-laboratory variability is significantly smaller
S= State, U = University, P = Private, O = Other
W = West Europe, S = South, E = East

The variability between the laboratories is mostly influenced by the statute of the laboratory and the region where the laboratory is located. The factor **Statute** is significant for 5 groups of analysis (*Organic Carbon, Exchangeable Elements, Extractable Elements, Total Elements, Reactive Fe & Al*). Governmental laboratories perform significantly better than academic laboratories for four out of the five significant cases. The factor **Region** influences the variability between the laboratories significantly for four groups of analysis (*Organic Carbon, Exchangeable Elements, Extractable Elements and Total Elements*). Laboratories from Eastern Europe give significantly poorer results than laboratories from Western Europe for three groups (*Exchangeable Elements, Extractable Elements and total Elements*). For the determination of the *Extractable Elements* and *Total Elements*, Western laboratories perform significantly better then laboratories from Southern Europe.

The factors **Reference Method, Experience Level, Training, Accreditation** and **Type** are significantly influencing the variability between the laboratories occasionally.

Table II.9: Summary of the multiple comparisons in the multiple stepwise regression models of the within-laboratory variability

Factor	Sample	RefmC	ExpLevC	Trained	Accr	Statute	Type	Forest	Region
Group									
Particle Size							G<B,P		
pH Soil				1 < 0					
Carbonates									
Organic Carbon									
Total Nitrogen	A<C								
Exchangeable elements	B<A<C	0 < 1				O<S<P U<P			
Extractable elements	A<B,C					O<S<P O<U<P			
Total elements			1 < 0					1 < 0	
Reactive Fe and Al						U<S	P,G<B	0 < 1	

Legend: A,B and C = Sample names
1: use of reference method, or has experience, has trained personnel or is a specialised forest laboratory
S= State, U = University, P = Private, O = Other
When indicated as smaller, Kv is smaller so between-laboratory variability is significantly smaller.

The within-laboratory variance is significantly influenced by the **Statute** of the laboratory and the analysed **Sample**. Private laboratories suffer from a significantly larger internal variability than other laboratories (governmental, academic and other laboratories). The internal variability differs significantly with the analysed sample, sample C (organic sample) gives the largest internal variability. Some particular groups as **Reference Method, Experience Level, Training, Type** and **Forest** are significantly influencing the within-laboratory variance.

Note that while **Region** was an important factor contributing to the between-laboratory variance, it is not important any more in explaining the within-laboratory variance.

In summary, no consistent trends are seen throughout the data analysis, neither for the between-laboratory variance, nor for the within-laboratory variance. The different factors only show significant influences for some groups, but none of the factors is significant for all groups of analyses.

II.3.3. Qualitative analysis

FSCC sent the draft version of the ring test report (Phase I) to the participating laboratories. Certain laboratories sent some remarks and comments to FSCC; others gave some explanation concerning outlying results. As expected, several technical mistakes and inaccuracies showed up. Some examples are given below:

1. **Laboratory N° 13** reduced the sample weight for the $CaCO_3$ analysis from the requested 5 g to 2.5 g. Afterwards the $CaCO_3$ content was not multiplied by a factor 2 (Figure II.25).

2. **Laboratory N° 19** asked to correct the values for exchangeable Al (had to be divided by three). By reporting wrong results for 'exchangeable Al', the laboratory became an outlier for this parameter on each of the three samples. If the values would be reported correctly (divided by three), the laboratory results would be situated within the bulk of the data.

3. **Laboratory N° 23** reported wrong calculations for extractable Ca and Mg for the organic sample. Nevertheless they are not marked as a straggler or outlier for these parameters.

4. **Laboratory N° 30** made some technical mistakes:

- Results for $CaCO_3$ were reported as $CaCO_3$-C (see Figure II.25);
- Error in the calculation programme for exchangeable cations and free acidity;
- Some of the results for extracted elements (Fe, K, Mg, Mn, S – Sample A) were reported in a wrong unit (g/kg). For more detail, see Figure II.26.

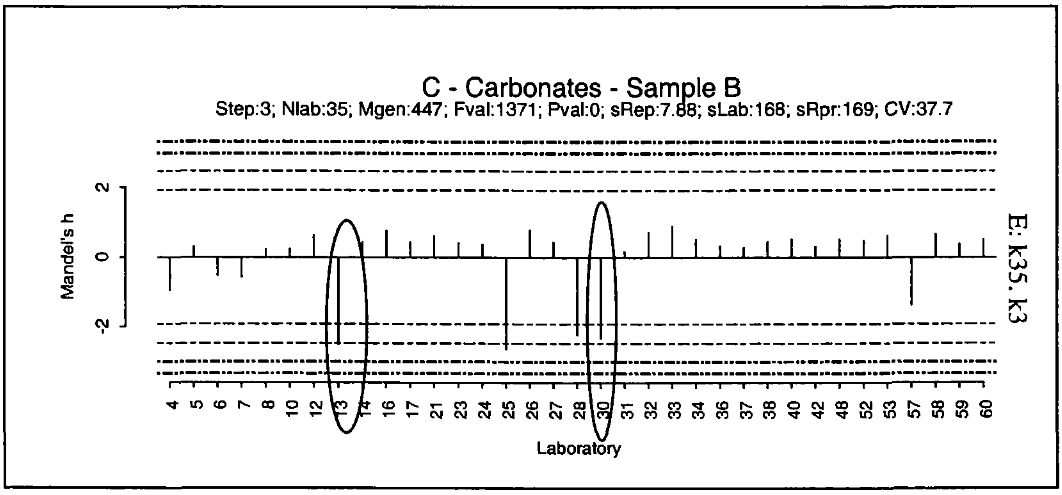


Figure II.25: Deviating results in reporting the $CaCO_3$ of sample B for laboratory N° 13 and 30

Figure II.25 shows Mandel's h statistic for the carbonates of sample B. Laboratories N° 13 and 30, who reported wrongly, calculated values are indicated. It is clear that the Mandel's h statistic is quite high for these specific laboratories, but despite their incorrect results, neither N° 13, nor N° 30 has been excluded from the ring test (no stragglers or outliers). This situation and the situation of laboratory N°23 indicate that the procedure for this ring test is not severe. All other laboratories, showing high values for Mandel's h made thus serious mistakes, probably caused by careless calculating and reporting.

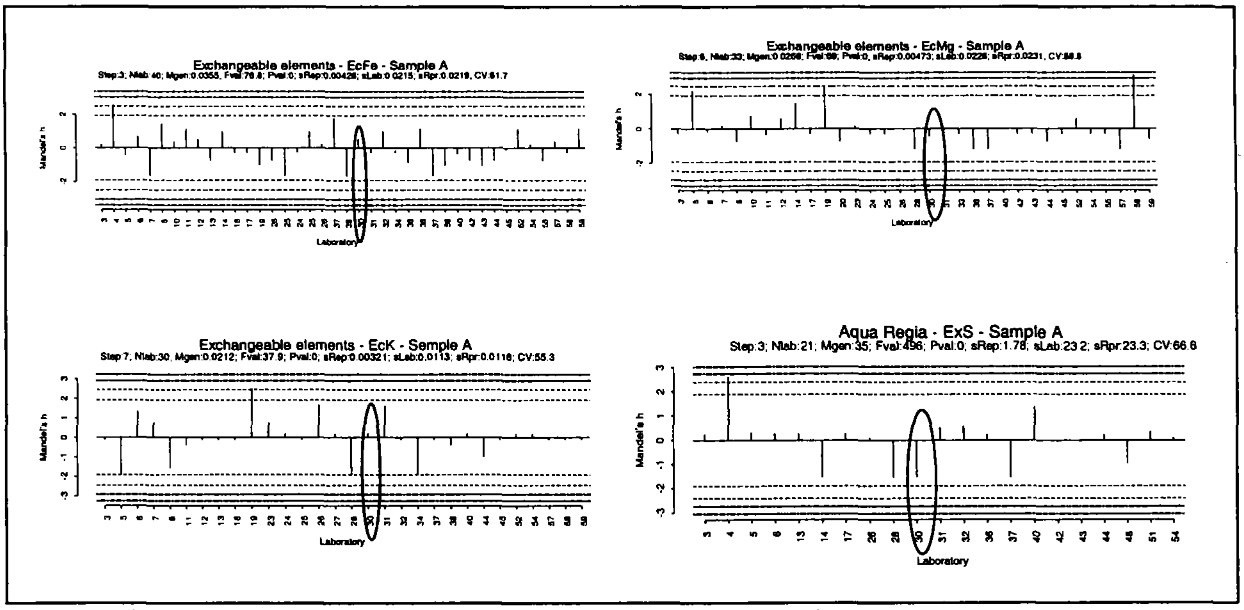


Figure II.26: Technical mistakes of laboratory N° 30 – wrong units

Figure II.26 takes a closer look at the results of laboratory N° 30, which reported certain values of *Extractable Elements* in the wrong units (g/kg). Note that none of the wrong values is indicated as an outlier or straggler. This indicates that the statistical procedure is mild, due to several large mistakes within the dataset. As the limits for stragglers and outliers are directly linked to the variance of the data, several mistakes within the data result in a less powerful statistical evaluation.

II.4 DISCUSSION

II.4.1 Questionnaires

The low percentage of analyses (65%) done according to the reference methods was disappointing FSCC has been stimulating laboratories to use the mandatory reference methods in an attempt to obtain more uniform and comparable data. Through this second phase of the ring test, an attempt was made to figure out whether the analyses done according to the reference methods were better than the ones that do not follow the reference method. Unfortunately the unbalanced design of the ring test was not strong enough to detect a consistent trend. Usually the reference method did not significantly reduce the variability.

Sometimes the phrasing of the questionnaire was not clear for all participants and caused some confusion. In some cases it was not clear whether the questionnaire asked for information on the daily laboratory practices, or particularly on the analysis for the ring test. There also arose some problems concerning the difference between a method detection limit and a detection limit for a certain apparatus. In the future, more attention should be given to the wording of questionnaires in order to avoid confusion as much as possible.

II.4.2 Statistical analysis

When comparing the univariate and the multivariate analysis, often differences are seen. Generally much more significance was found when the factors were considered separately. It also happened that a factor was not significant in the univariate analysis but became significant in the multivariate analysis. This could be expected because the individual factors are not necessarily independent. By consequence, some effects may be hidden behind possible interactions. Statistically this problem can be solved by studying the interaction terms in the regression model. However, because the current model already showed a high degree of complexity and in order to keep the analysis easily interpretable, it was chosen not to use more complex statistical models.

It should be noted that the sampling design was in the first place set out in view of an interlaboratory comparison with the objective to situate the variability among laboratory analysis. The investigation of the possible influences of the different factors on the quality of the results was not the main research question. For this reason the sampling design is not optimised to give an answer to the possible importance of the different factors.

As was already seen in II.2.2, most of the investigated factors are unbalanced, what means that one factor level consist of more observations than the other factor-levels. This might lead to an incorrect interpretation of the analyses, so it is recommended to evaluate the results of the statistical analysis with the necessary caution.

II.4.3 Qualitative analysis

It is clear that the impact of this kind of technical mistakes should not be underestimated. Probably more laboratories than mentioned in II.3.3 are confronted with this type of mistakes. Since the evaluation of the ring test is based on a statistical procedure that calculates its limits for stragglers and outliers based on the variation of the whole data set, the high variability of the population implies a less severe test (than when carried out with more precise results).

Laboratories should try to avoid this incorrectness by checking their data thoroughly (calculations, required units, etc) before reporting. This type of mistakes can rather easily be avoided, what would result in a more consistent data set of which the statistical evaluation could only profit.

A ring test expects laboratories to work as precise as possible. Concerning the possible 'hidden' amount of technical mistakes within this ring test, the follow-up should, next to the real analytical problems, give attention to this type of errors. Even when laboratories work as precise as possible, if they do not pay any attention to the reporting of the data (calculations, units, etc.), their results are of little value.

The willingness of the laboratories to report as precise and accurate as possible, is essential for the quality of the data and for the resulting databases. In order to help the laboratories in improving the reporting of the results, reference is made to Annex 10 'Guidelines for reporting'.

II.5 CONCLUSIONS

1. With reference to the research questions, as has been put forward in the introduction of Phase II:
   - The **use of the reference methods** could not explain significant parts of the observed variability. The second phase of the ring test does not provide arguments for the hypothesis that when all laboratories would use the same method, the variability between the laboratories would be smaller. However, the fact that the significance of use of reference method could not be proven, does not mean that lower variability would be met when all laboratories would continue the analyses with their own (national) methods.
   - The same applies for the **experience level**.
   - The **region** where the laboratory is located, seems to play a big role but is only important in the between-laboratory variability and not in the within-laboratory variance. The Western laboratories performed often better than the Eastern and/or the Southern laboratories. It should however be noted that the design for this test was very variable and not suitable for far-reaching conclusions. As seen from § II.2.2 the design was extremely unbalanced: the Western laboratories concerned a total of 23 laboratories (44%) of which 13 laboratories are enrolled in a national quality assurance and quality control programme.
   - Concerning the **degree of difficulty** of the laboratory analysis, it can be concluded that extremely little of the <u>between-laboratory variance</u> could be explained by the statistical procedure for the groups with the lowest coefficients of variations. So few significant effects were found for *Soil pH*, *Total Nitrogen* and *Organic Carbon*. It was very difficult to draw any other conclusions.

2. Since:

- In the statistical analysis often contradictory results were obtained. This happened for example with the results between the univariate and the multivariate analysis;
- The models were often based on very unbalanced data which might lead to misleading results;
- There was no single factor that contributed significantly to the variance of each of the nine groups of analysis;

no unambiguous conclusions can be made. This statistical analysis was a first attempt in explaining the high variability observed in Phase I. Though to be able to make valid judgements related to the causes of variability, it is recommended to use an appropriate design in a follow-up phase.

II.6 Recommendations Towards the Next Ring Test

- Develop a questionnaire containing less but more essential and straightforward questions. It is better to ask few but clear questions than asking more information but which can be ambiguous. For this reason it is not advisable to include an extra questionnaire in the fourth ring test without testing this questionnaire thoroughly before application. Testing can be realised by requesting 2 to 3 laboratories that do not participate in the ring test to fill in the questionnaire. A testing phase for the questionnaire is indispensable, only in this way efficient questioning of the laboratories is feasible.
- The design for Phase II could be improved largely by making the groups more balanced. A balanced design might be obtained by selecting more or less equal range of laboratories that meet certain criteria. The third ring test was however based on a voluntary participation. All participatory laboratories had the same right of being part of the sample in the statistical analysis in Phase II. Towards the next ring test, it will be important to chose an appropriate strategy: directed towards Phase I (an interlaboratory analysis sensu stricto) or directed towards Phase II that tries to reveal causes of variability between and within-laboratory results. Based on the results of Phase II, one can conclude that combining both strategies into one single ring test is not a valid option.

Acknowledgements

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ANNEXES

Annex 1: List of participating laboratories

Country	Name of laboratory and institute	Address	Zip code	City
Austria	Soil Laboratory - Branch of Pedology - Federal Office and Research Centre for Forests	Seckendorff-Gudent-Weg, 8	A-1131	Vienna
Belgium	Bodemkundige Dienst Van België	De Croylaan, 48	3001	Leuven
Belgium	Institute for Forestry and Game Management	Gaverstraat, 4	B-9500	Geraardsbergen
Belgium	Laboratory Soil Science - Ghent University	Krijgslaan, 281 (S8)	B-9000	Ghent
Belgium	Vlaamse Instelling voor Technologisch Onderzoek (VITO)	Boeretang, 200	B-2400	Mol
Belgium	Unité des Eaux et Forêts - Département des Sciences du Milieu et de l'Aménagement du Territoire - Faculté d'Ingénierie Biologique, Agronomique et Environnementale - Université Catholique de Louvain	Place Croix-du-Sud, 2 - Boîte 9	B-1348	Louvain-la-Neuve
Bulgaria	Laboratory Quality Control Soil, Analytical Department, Executive Agency of Environment	Tzar Boris III Blvd., 136; POB 251	BG-1618	Sofia
Bulgaria	Laboratory Pedology - University of Forest	Kliment Ohridski Blvd., 10		Sofia
Bulgaria	Laboratory Forest Pedology - Institute of Forest - Bulgarian Academy of Sciences	Kliment Ohridski Blvd., 132	1756	Sofia
Canada	Laboratoire de Chimie Organique et Inorganique - Direction de la Recherche Forestière	2700 Rue Einstein, Local B1.260	G1P 3W8	Sainte-Foy (Québec)
Croatia	Soil Laboratory - Forest Research Institute	Cvjetno Naselje, 41	10450	Jastrebarsko
Cyprus	Analytical Laboratories Section - Department of Agriculture	Louki Akrita	CY-1411	Lefkosia
Czech Republic	Department of Experimental Laboratories - Forestry and Game Management Research Institute (Výzkumný ústav lesního hospodárství a myslivost)	Jiloviste - Strnady 136	156 04	Praha 5 - Zbraslav
Denmark	Forest Research Laboratory	Hoersholm Kongevej, 11	DK-2970	Hoersholm
Estonia	Laboratory of Residues and Contaminants - Estonian Control Center of Plant Production	Teaduse Str., 6	75501	Saru, Haryu County
Estonia	Tartu Environmental Research	Akadeemia, 4	51003	Tartu
Estonia	Geological Survey of Estonia	Kadaka tee, 82	12618	Tallinn
Finland	Central Laboratory of the Finnish Forest Research Institute - Finnish Forest Research Institute	P.O. Box 18	FIN 01301	Vantaa
Finland	Rovaniemi Research Station - Finnish Forest Research Institute	P.O. Box 16	FIN 96301	Rovaniemi
France	Laboratoire d'Analyses des Sols - INRA	273, Rue de Cambrai	62000	Arras
Germany	Institut für Bodenkunde und Standortslehre - Technische Universität Dresden	Pienner Str., 7	D-01737	Tharandt
Germany	Abt. Bodenkunde - Forstliche Versuchs- und Forshungsanstalt Baden-Württemberg	Wonnhaldestr., 4	D-79100	Freiburg
Germany	Landesuntersuchungsamt für Gesundheits- Umwelt- und Verbraucherschutz Sachsen-Anhalt - LUA - Standort Halle-Lettin	Schiepziger Straße, 29	D-06120	Halle
Germany	Abt. Waldökologie, Landesforstanstalt Eberswalde	Alfred-Möller-Straße, 1	D-16225	Eberswalde
Germany	Dept. Soil Science and Plant Nutrition Analytical Laboratory - Saxon State Institute for Forestry	Bonnewitzer Str., 34	D-01796	Pirna - OT Graupa
Germany	Abteilung Untersuchungswesen - Thüringer Landesanstalt für Landwirtschaft	Naumburger Str., 98	D-07743	Jena
Germany	Institute of Soil Science and Forest Nutrition - Göttingen University	Büsgenweg, 2	D-37077	Göttingen
Germany	Umweltforschungszentrum Physische Geographie - Zeile 2 - AG Forst - der Universität des Saarlandes		D-66125	Saarbrücken

Country	Name of laboratory and institute	Address	Zip code	City
Germany	Niedersächsische Forstliche Versuchsanstanstalt	Grätzelstraße, 2	D-37079	Göttingen
Germany	Hessisches Dienstleistungszentrum für Landwirtschaft, Gartenbau und Naturschutz - LUFA Kassel	Am Versuchsfeld, 13	D-34128	Kassel
Germany	Bayerische Landesanstalt für Wald und Forstwirtschaft	Am Hochanger, 11	D-85354	Freising
Germany	Landeslabor Schleswig-Holstein - Aussenstelle Kiel 2 - Dezernat 830	Saarbrückenstraße, 38	D-24114	Kiel
Germany	Geologischer Dienst Nordrhein-Westfalen	De-Greiff-Straße, 195	D-47803	Krefeld
Germany	LUFA Rostock der LMS	Graf-Lippe-Str., 1	D-18059	Rostock
Germany	Oekologie Zentrum - Universität Kiel	Schanenburger Str., 112	D-24118	Kiel
Greece	Forest Soils Labarotory - Forest Research Institute of Athens	Terma Alkmanos, Ilisia		Athens
Hungary	Laboratory of Ecology - Forest Research Institute	Frankel Leó, 42-44	H-1023	Budapest
Hungary	Institute of Soil Site Survey - Faculty of Forestry, West-Hungarian University	Bajcsy-Zs. U. 4	9400	Sopron
Ireland	Coillte Research Laboratory	Newtownmountkennedy		County Wicklow
Italy	Istituto Agrario S. Michele All'Adige	Via E. Mach, 1	38010	San Michele All'Adige
Italy	Laboratorio di Chimica e Biochimica del Suolo - Di.PRO.VE.	Via Celoria, 2	20133	Milano
Italy	Agrikulturchemisches Labor Laimburg - Land- und Forstwirtschaftliches Versuchszentrum Laimburg		39040	Auer / Pfatten
Italy	Laboratorio di Pedologia - Università degli Studi di Firenze	Piazzale delle Cascine, 15	50144	Firenze
Latvia	Laboratory Department - Latvian Environment Agency (LEA)	Osu str., 5	LV-2015	Jurmala
Latvia	Laboratory Department of Latvian Environmental Agency - Latvian Environmental Agency	Maskavas Street 165	LV-1019	Riga
Lithuania	Laboratory of Forest Soils - Department of Forest Soils, Typology and Hydrology - Lithuanian Forest Research Institute	Liepu 1	LT-4312	Girionys - Kaunas reg.
Poland	Laboratory of Forest Environment Chemistry - Department of Forest Habitat Science - Forest Research Institute	Sekocin Las	05-090	Raszyn
Portugal	Soil and Plant Analysis Laboratory - Departamento de Ciencias Agrarias, Universidade dos Açores	Terra-Cha	9700	Angra do Heroismo
Portugal	Laboratório Químico Agrícola Rebelo da Silva	Tapada de Ajuda, Apartado 3228	P-1301-903	Lisboa
Russian Federation	Laboratory of Soil Biochemistry - Biological Research Institute of Sankt-Petersburg State University	Oranienbaumskoe Schosse 2, Petrodvoretz	198503	Sankt-Petersburg
Russian Federation	Analytical Forest Soil Laboratory - Forest Research Institute - Karelian Research Centre - Russian Academia of Sciences	Pushkinskaja St., 11	185610	Petrozavodsk
Slovak Republic	Laboratory of the Department of Forest Environment - Forest Research Institute	T.G. Masaryka 22	96092	Zvolen
Slovenia	Laboratory for Forest Ecology, Slovenian Forestry Institute	Vecna pot 2	SI-1000	Ljubiljana
Spain	Ecosistemas Forestales y Agrobiosistemas - INIA, Dto. Medio Ambiente	Apdo. Correos 8111	28080	Madrid
Sweden	Department of Environmental Assessment - Sveriges Lantbruksuniversitet (SLU)	PO Box 7050	SE-75007	Uppsala
Sweden	HS Miljölab AB - Hushållningssällskapet	Gas Jacobs gata, 1	SE-392 45	Kalmar
Sweden	Department of Forest Soils - Sveriges Lantbruksuniversitet (SLU)	Johan Brauners vag 1, Ultuna	SE-75007	Uppsala
Netherlands	Alterra Wageningen	Droevendaalsesteeg 3, P.O.Box 47	6708 PB	Wageningen
United Kingdom	Environmental Research Branch Laboratories - Forest Research, Alice Holt Lodge	Wrecclesham	GU104LH	Farnham, Surrey

Annex 2 - Details on analysis methods report by each of the laboratories

Labo Id	Extractable	Carbonate	Exchangeable	Fe & Al	OC	Particle Size	Soil pH	Total Elements	Total N
3	NRM	NRM	NRM	RM	RM	NRM	RM	NRM	RM
4	RM	NRM	RM	-	RM	RM	RM	RM	NRM
5	RM	NRM	RM	RM	RM	NRM	RM	-	RM
6	RM	RM	NRM	RM	RM	RM	RM	-	RM
7	RM	RM	NRM	NRM	-	-	NRM	NRM	-
8	RM	RM	RM	-	RM	RM	RM	-	RM
9	RM	-	-	-	-	-	RM	-	-
10	RM	RM	RM	-	NRM	NRM	RM	-	NRM
11	-	-	NRM	-	NRM	UM	NRM	-	NRM
12	-	RM	RM	-	-	RM	RM	-	-
13	RM	RM	RM	-	UM	UM	RM	RM	RM
14	RM	NRM	RM	RM	RM	NRM	RM	NRM	RM
15	RM	-	-	-	-	-	NRM	-	-
16	NRM	NRM	NRM	-	RM	NRM	NRM	-	RM
17	RM	RM	RM	RM	RM	RM	RM	RM	RM
18	RM	-	-	-	-	-	RM	-	RM
19	RM	-	RM	-	RM	-	RM	RM	RM
20	RM	-	NRM	-	NRM	-	NRM	-	NRM
21	-	NRM	-	-	RM	-	RM	-	RM
23	RM	RM	NRM	RM	NRM	NRM	NRM	-	RM
24	RM	RM	RM	RM	NRM	NRM	RM	RM	NRM
25	RM	NRM	RM	RM	NRM	-	RM	RM	NRM
26	RM	NRM	RM	-	RM	-	RM	-	NRM
27	NRM	RM	RM	-	RM	RM	RM	-	RM
28	RM	RM	NRM	NRM	RM	RM	RM	NRM	RM
30	RM	RM	NRM	RM	RM	NRM	NRM	NRM	RM
31	RM	RM	RM	RM	RM	NRM	RM	-	RM

Labo Id	Extractable	Carbonate	Exchangeable	Fe & Al	OC	Particle Size	Soil pH	Total Elements	Total N
32	RM	RM	RM	RM	RM	RM	RM	-	RM
33	RM	NRM	-	NRM	RM	-	RM	-	RM
34	RM	RM	RM	-	RM	-	RM	-	RM
35	NRM	NRM	RM	-	NRM	-	RM	-	NRM
36	RM	NRM	RM	NRM	RM	UM	RM	NRM	RM
37	NRM	NRM	RM	RM	RM	NRM	RM	-	NRM
38	-	RM	RM	RM	RM	RM	RM	RM	-
40	RM	RM	RM	RM	RM	RM	RM	RM	RM
41	RM	NRM	RM	RM	NRM	RM	RM	NRM	RM
42	NRM	RM	NRM	-	RM	NRM	NRM	-	RM
43	NRM	-	NRM	NRM	-	-	RM	-	-
44	NRM	-	NRM	-	NRM	-	RM	-	NRM
45	UM	-	NRM	-	-	-	RM	-	-
47	NRM	-	-	-	-	-	NRM	NRM	-
48	RM	RM	RM	-	RM	RM	RM	RM	RM
50	RM	-	RM	-	RM	NRM	RM	UM	NRM
51	UM	-	UM	-	UM	-	UM	-	UM
52	NRM	RM	RM	-	RM	RM	RM	RM	RM
53	RM	RM	-	-	NRM	NRM	RM	-	NRM
54	NRM	-	NRM	-	-	-	RM	-	RM
55	-	-	NRM	-	-	NRM	NRM	-	RM
57	RM	RM	RM	NRM	NRM	RM	RM	RM	RM
58	RM	RM	RM	RM	RM	RM	RM	-	RM
59	NRM	RM	NRM	-	RM	RM	RM	-	RM
60	NRM	NRM	NRM	-	NRM	NRM	NRM	NRM	NRM

Key: RM: reference method, UM: Unknown method, NRM: Non reference method

Annex 3 – Form for data reporting: Example for sample A

Country				
Form for the collection of the data of sample A				
Parameter	Unit	Replicate 1	Replicate 2	Replicate 3
Particle size: clay	%			
Particle size: silt	%			
Particle size: sand	%			
pH($CaCl_2$)	-			
pH(H_2O)	-			
Carbonates	g/kg			
Organic carbon	g/kg			
Total N	g/kg			
Exchangeable acidity	cmol+/kg			
Exchangeable Al	cmol+/kg			
Exchangeable Ca	cmol+/kg			
Exchangeable Fe	cmol+/kg			
Exchangeable K	cmol+/kg			
Exchangeable Mg	cmol+/kg			
Exchangeable Mn	cmol+/kg			
Exchangeable Na	cmol+/kg			
Free H^+ acidity	cmol+/kg			
Extracted Al	mg/kg			
Extracted Ca	mg/kg			
Extracted Cd	mg/kg			
Extracted Cr	mg/kg			
Extracted Cu	mg/kg			
Extracted Fe	mg/kg			
Extracted Hg	mg/kg			
Extracted K	mg/kg			
Extracted Mg	mg/kg			
Extracted Mn	mg/kg			
Extracted Na	mg/kg			
Extracted Ni	mg/kg			
Extracted P	mg/kg			
Extracted Pb	mg/kg			
Extracted S	mg/kg			
Extracted Zn	mg/kg			
Total Al	mg/kg			
Total Ca	mg/kg			
Total Fe	mg/kg			
Total K	mg/kg			
Total Mg	mg/kg			
Total Mn	mg/kg			
Total Na	mg/kg			
Reactive Al	mg/kg			
Reactive Fe	mg/kg			
Moisture content	%			

Annex 4: Statistical data analysis phase I

Group I: Particle Size distribution

Parameter: Particle Size Clay

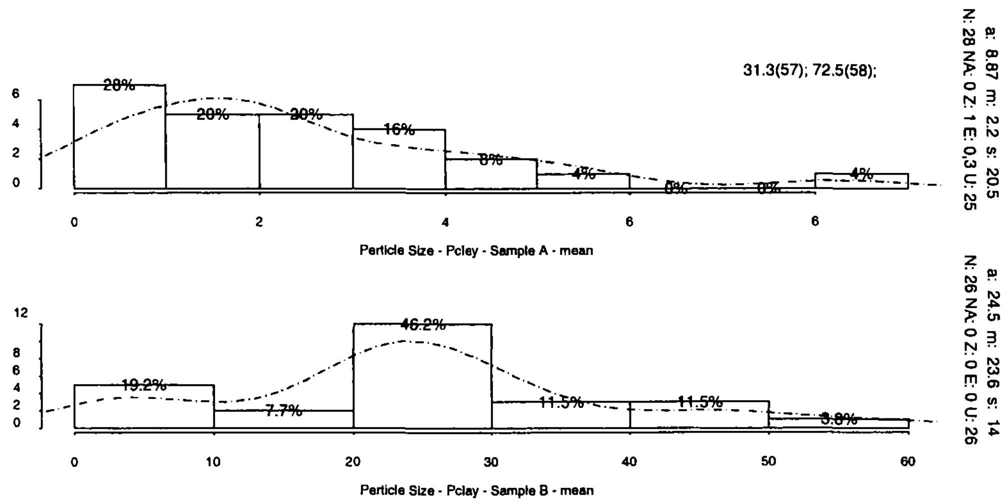


Figure IV. 1: Histogram showing the distribution of the reported mean values of clay

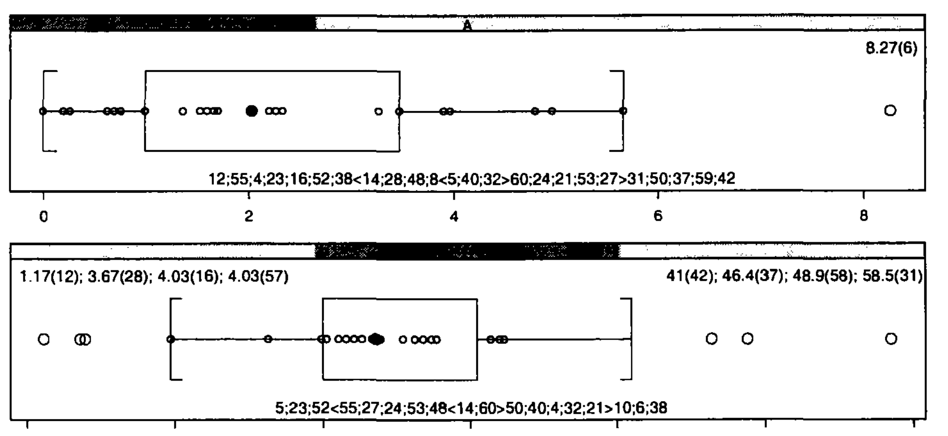


Figure IV. 2: Boxplot showing the distribution of the reported mean values of clay

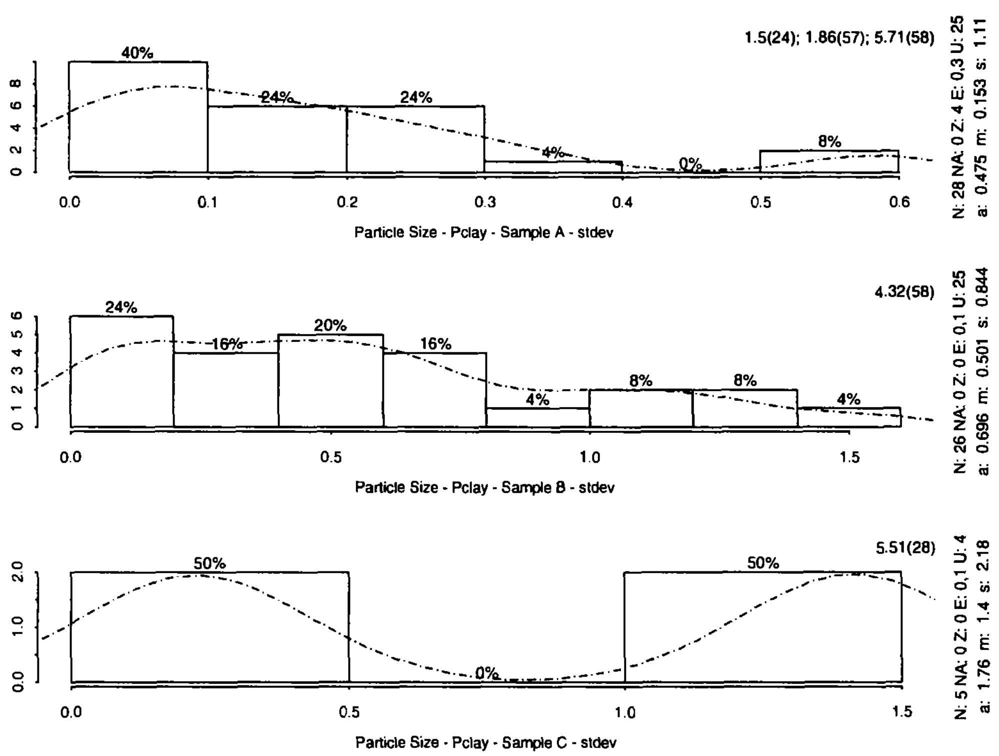


Figure IV. 3: Boxplot showing the distribution of the standard deviations of the reported values of clay

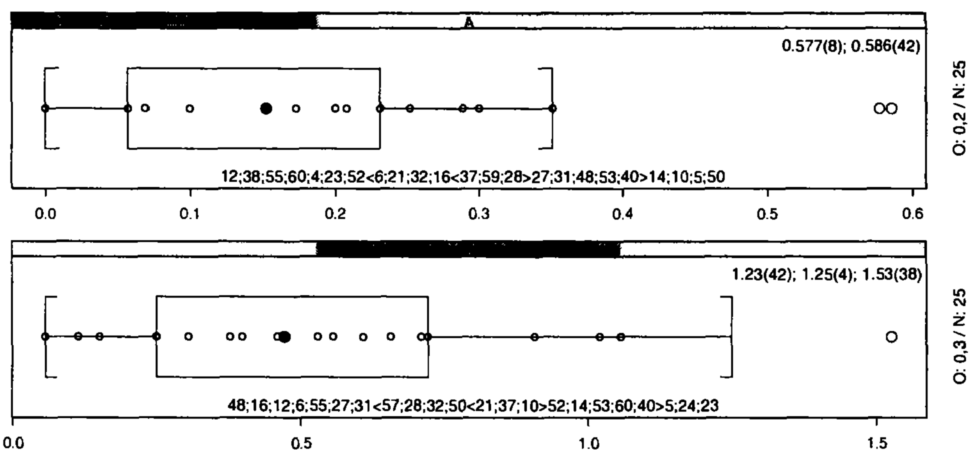


Figure IV. 4: Boxplot showing the distribution of the standard deviations of the reported values of clay

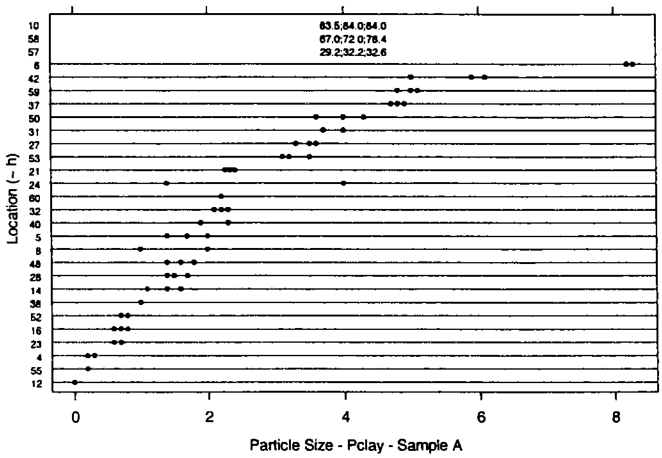


Figure IV.5: Dotplot of sample A of Particle size Clay

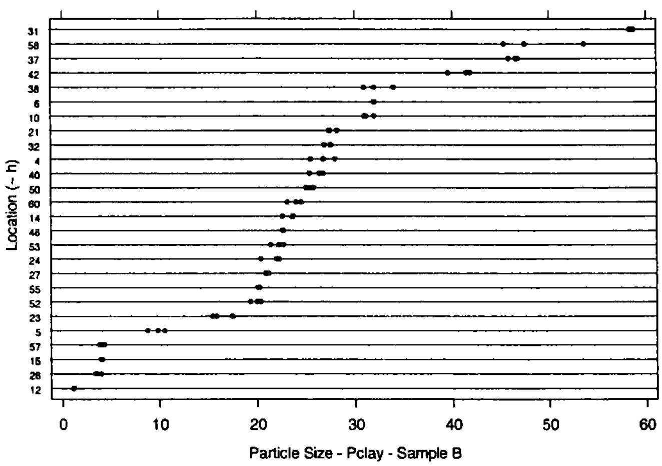


Figure IV.6: Dotplot of sample B of Particle size Clay

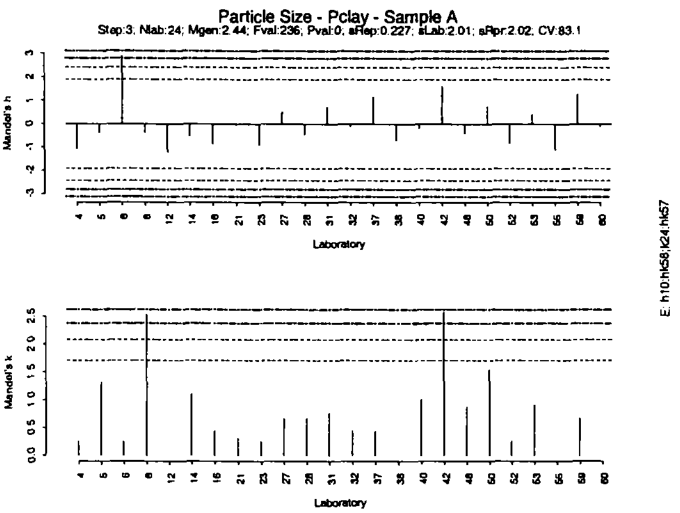


Figure IV.7: Mandel's h and k plot - Sample A – Particle Size Clay

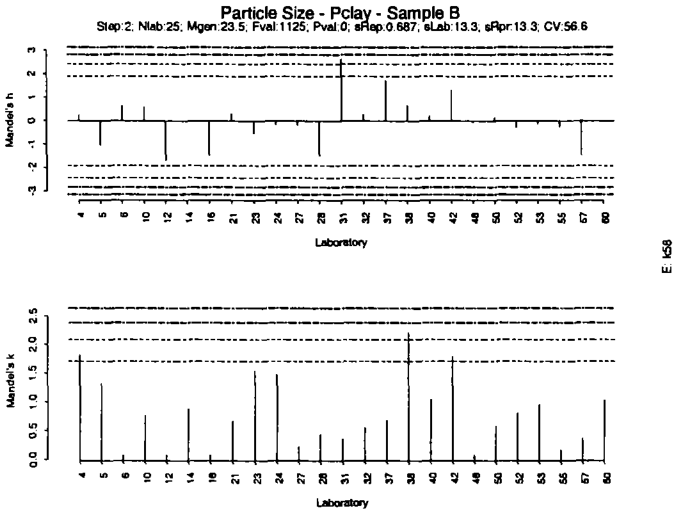


Figure IV.8: Mandel's h and k plot - Sample B – Particle Size Clay

Parameter: Particle Size Silt

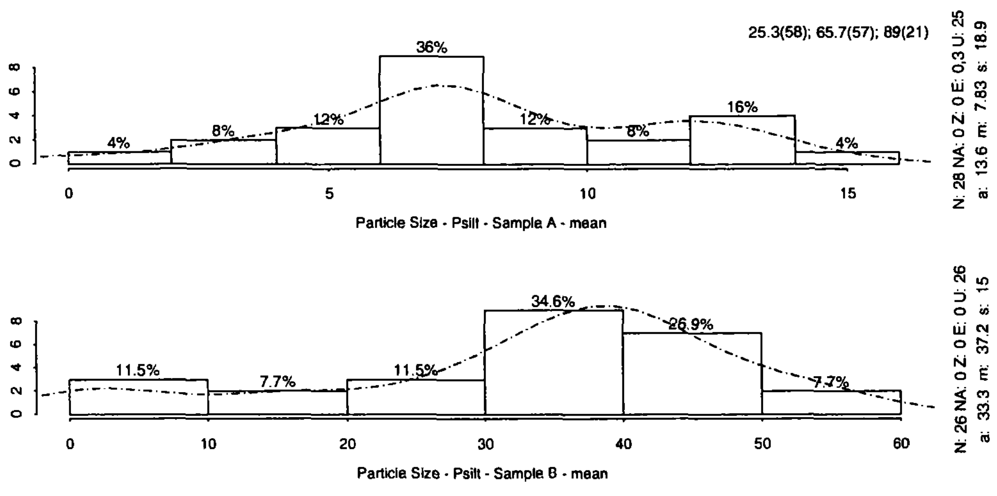


Figure IV. 9: Histogram showing the distribution of the reported mean values of silt

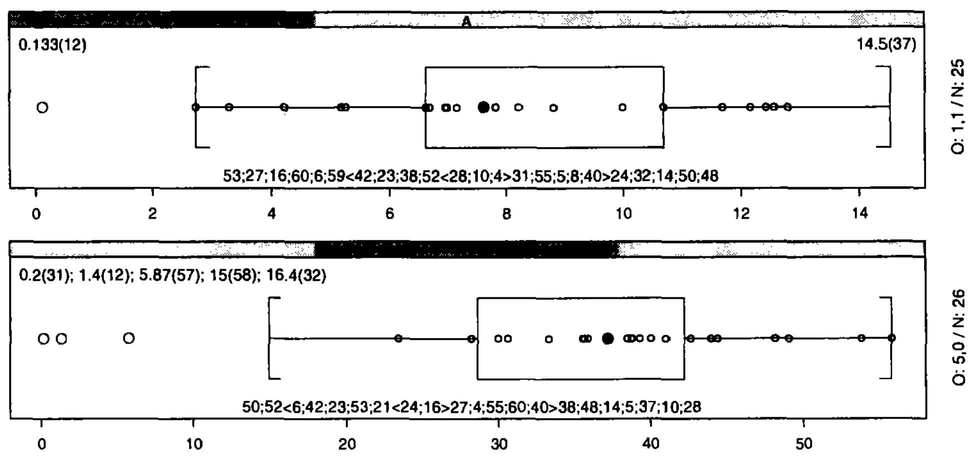


Figure IV.10: Boxplot showing the distribution of the reported mean values of silt

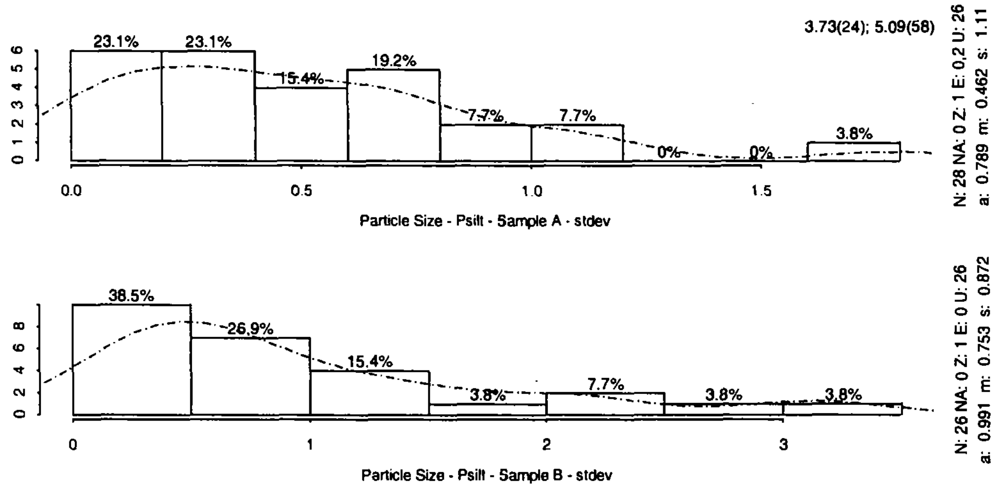


Figure IV.11: Histogram standard deviation – particle size silt

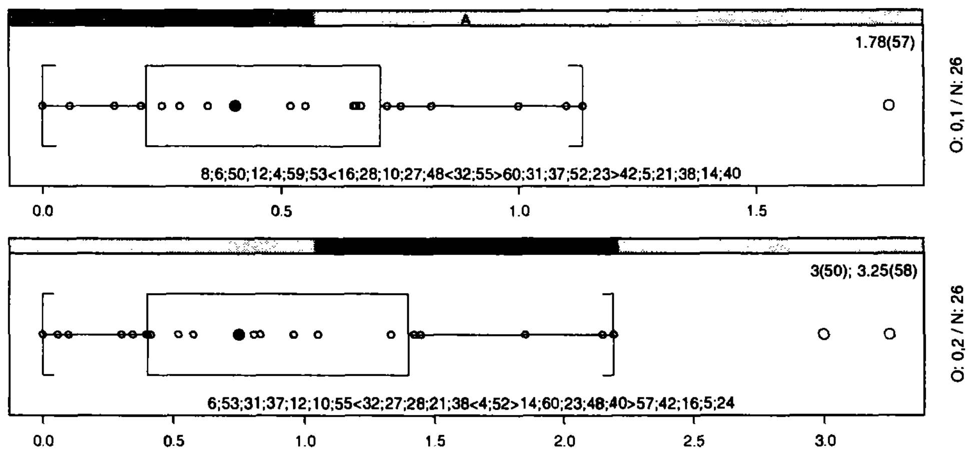


Figure IV.12: Boxplot stdev – particle size silt

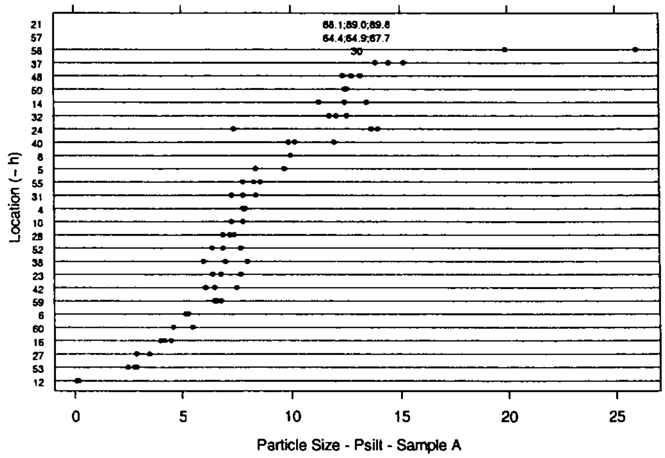


Figure IV.13: Dotplot - Sample A – particle size silt

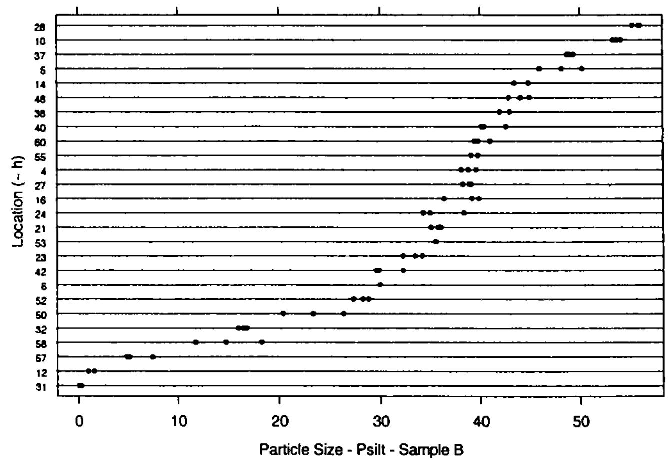


Figure IV.14: Dotplot – Sample B – particle size silt

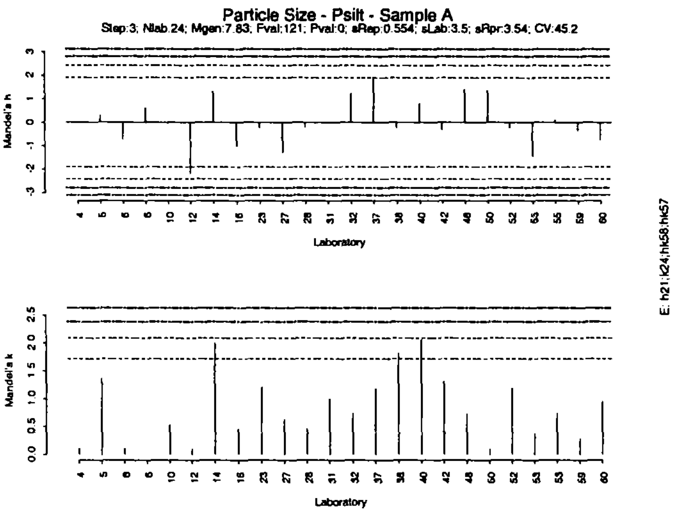


Figure IV.15: Mandel h/k plot - Sample A – particle size silt

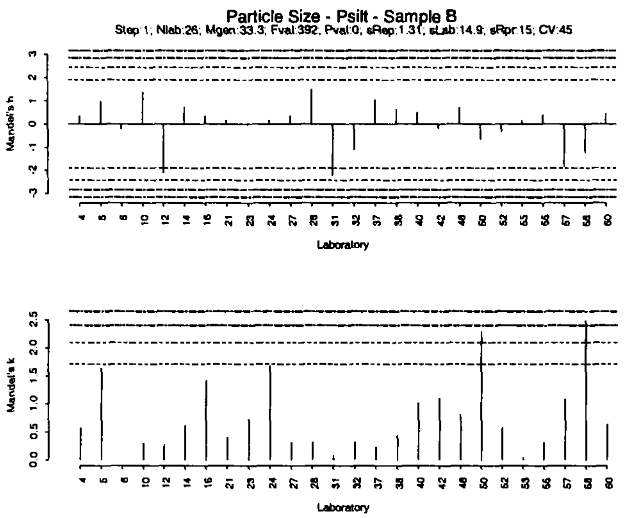


Figure IV.16: Mandel h/k plot – Sample B – particle size silt

Parameter: Particle Size Sand

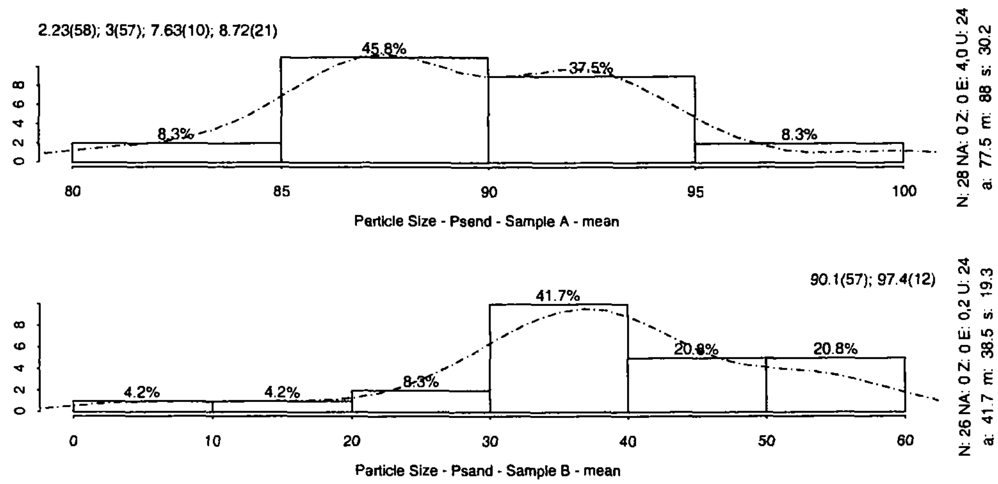


Figure IV. 17: Histogram showing the distribution of the reported mean values of sand

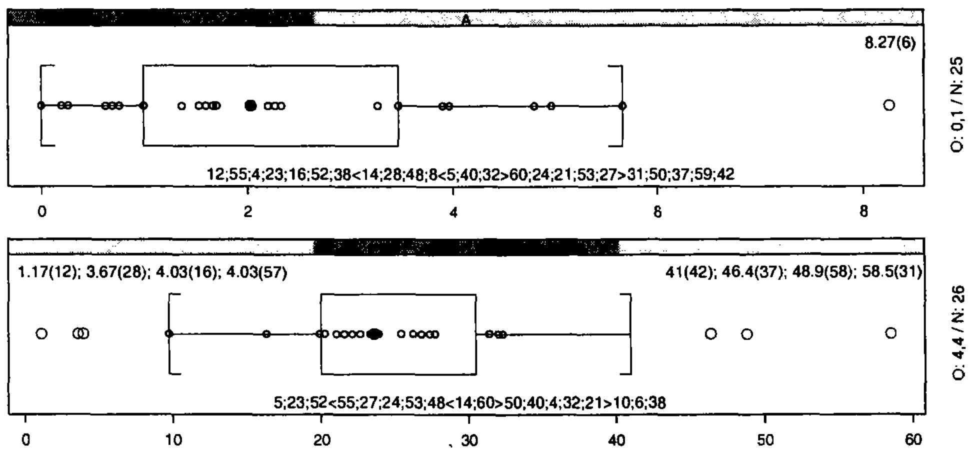


Figure IV.18: Boxplot showing the distribution of the reported mean values of sand

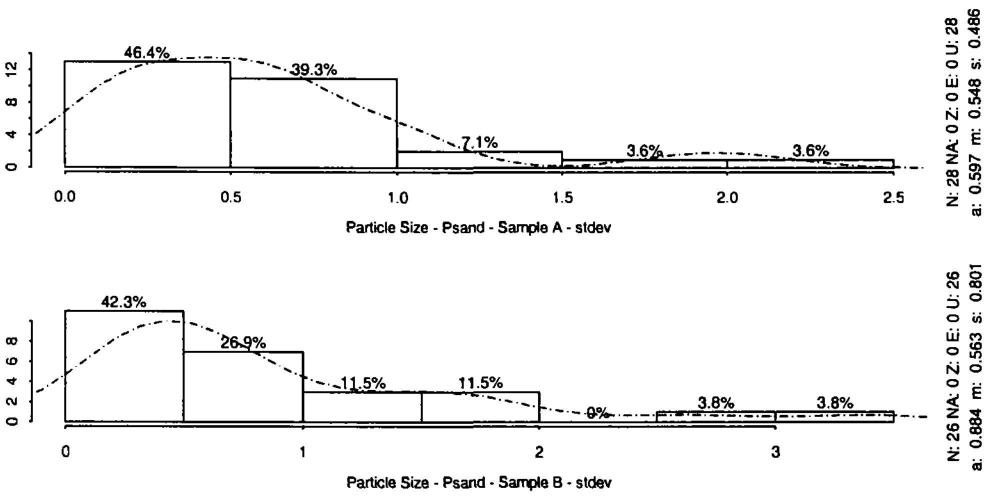


Figure IV.19: Histogram stdev – particle size sand

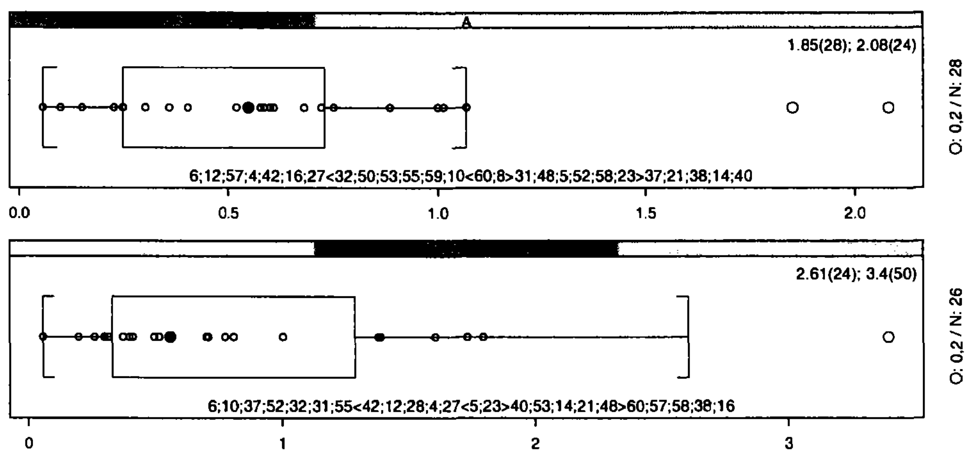


Figure IV.20: Boxplot stdev - particle size sand

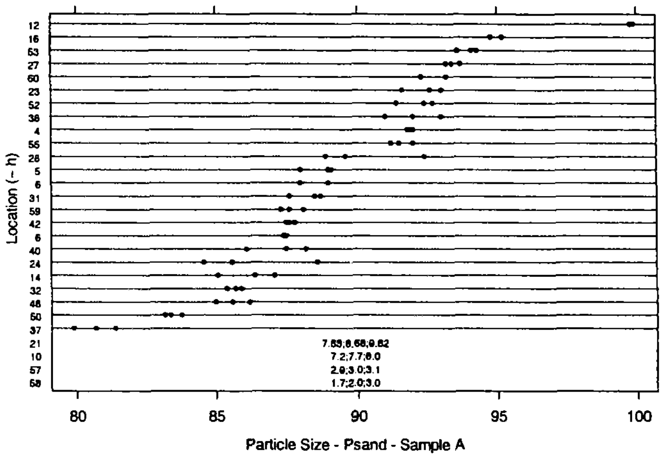


Figure IV.21: Dotplot - Sample A - particle size sand

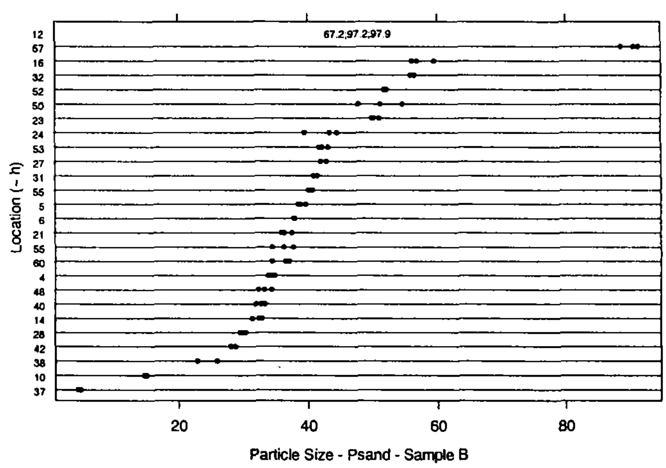


Figure IV.22: Dotplot - Sample B - particle size sand

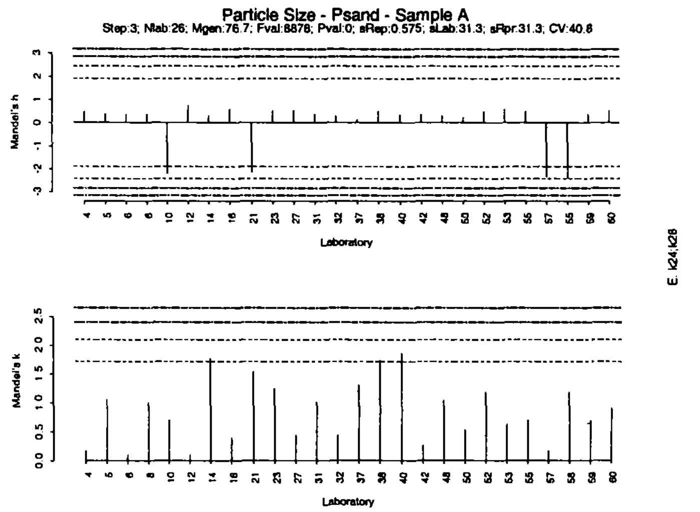


Figure IV.23: Mandel h/k plot - Sample A B - particle size sand

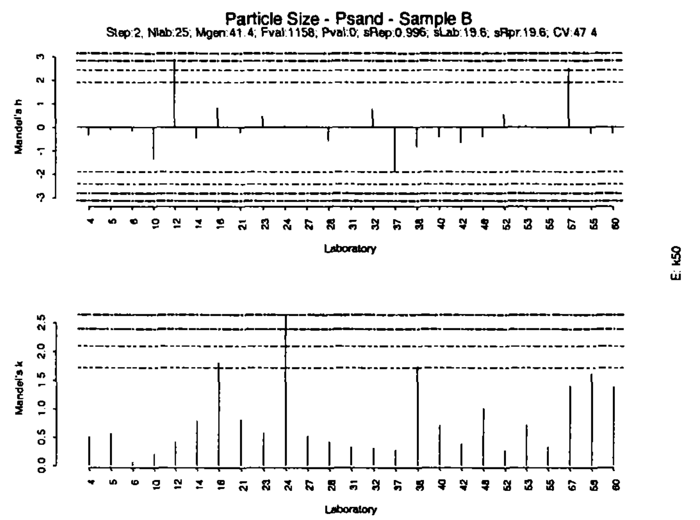


Figure IV.24: Mandel h/k plot - Sample B B - particle size sand

Group II: pH

Parameter: pH $CaCl_2$

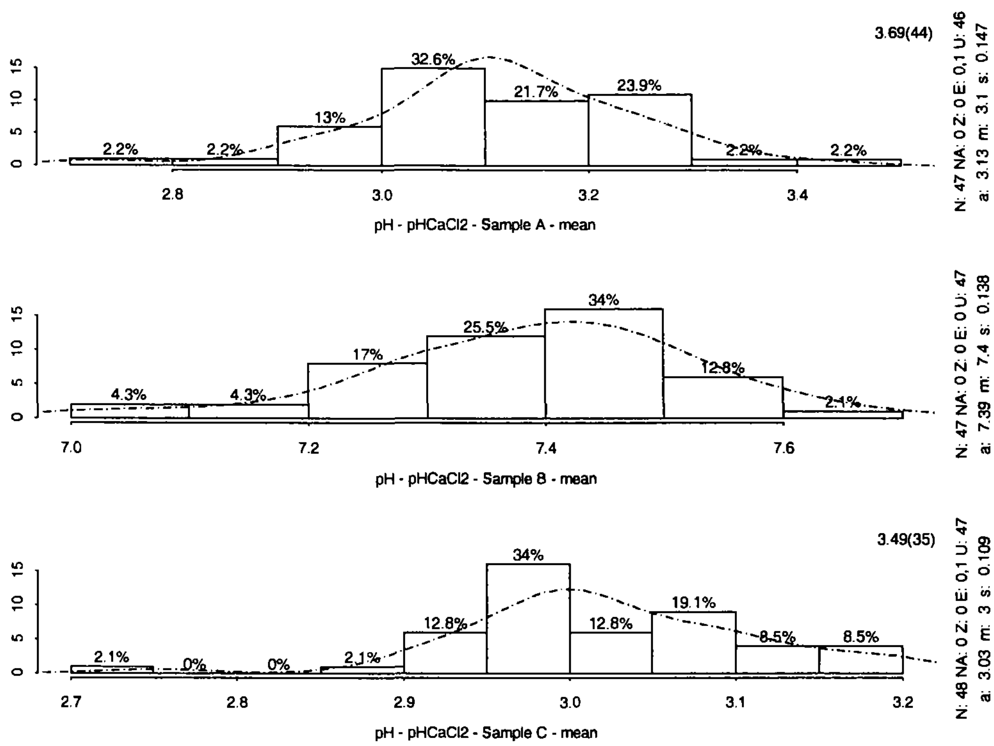


Figure IV. 25: Histogram showing the distribution of the reported mean values of pH($CaCl_2$)

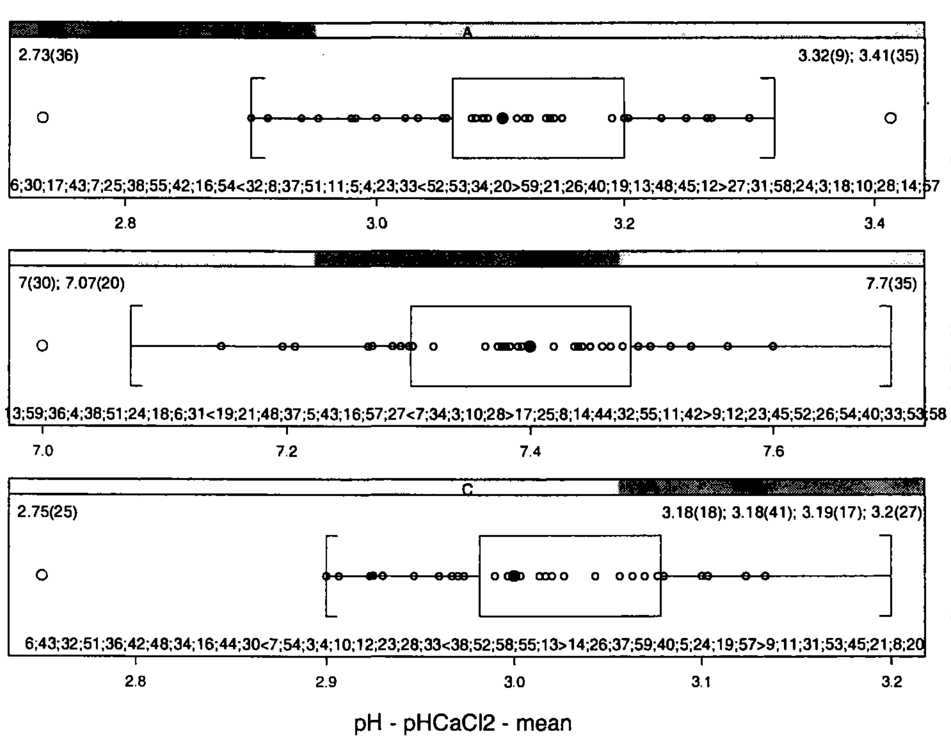


Figure IV.26: Boxplot showing the distribution of the reported mean values of pH($CaCl_2$)

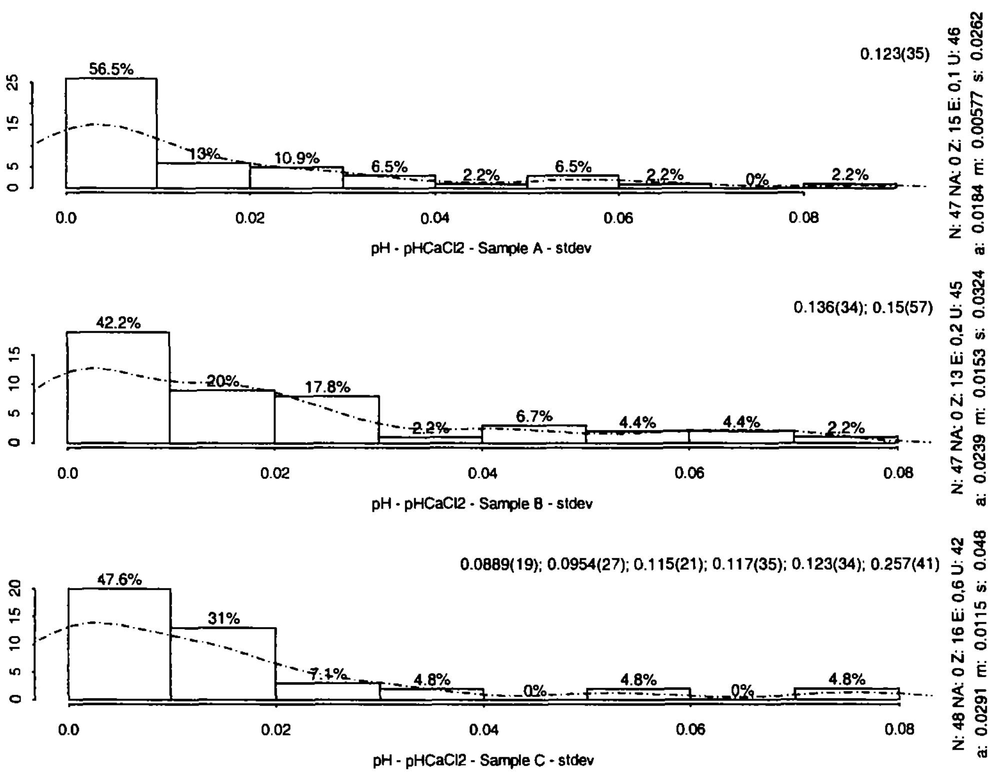


Figure IV.27: Histogram standard deviation - pH($CaCl_2$)

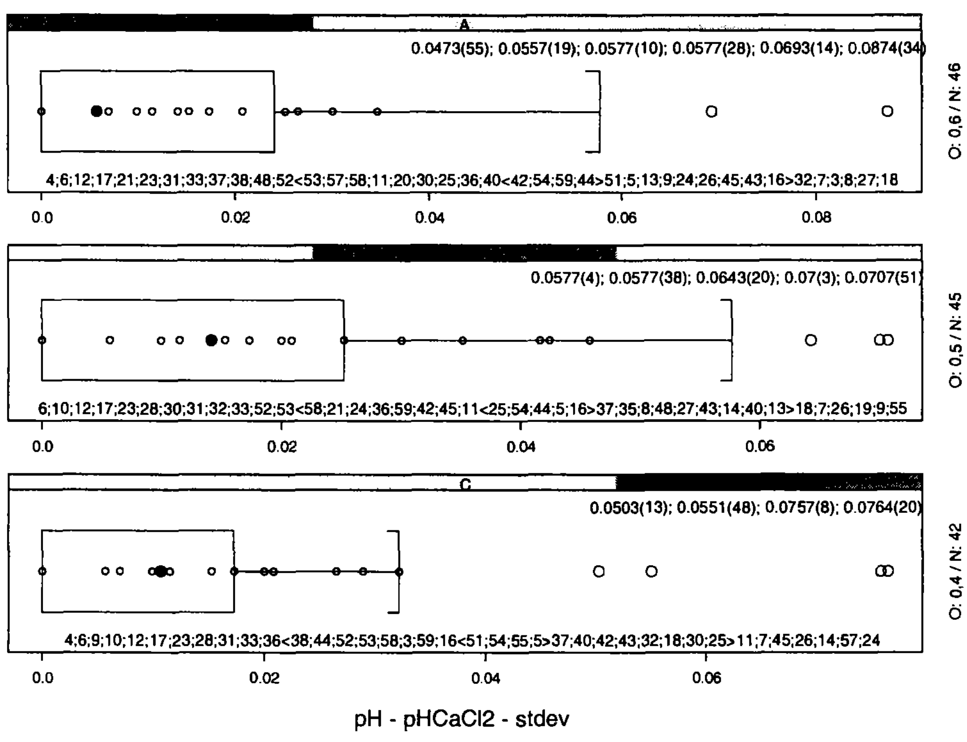


Figure IV.28: Boxplot standard deviation - pH($CaCl_2$)

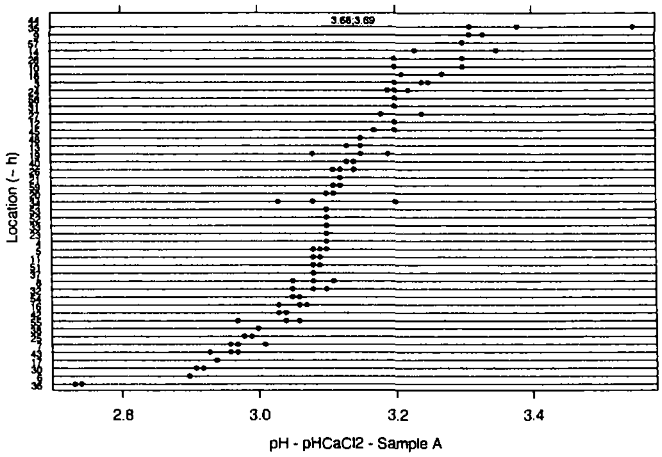


Figure IV.29: Dotplot - Sample A - pH($CaCl_2$)

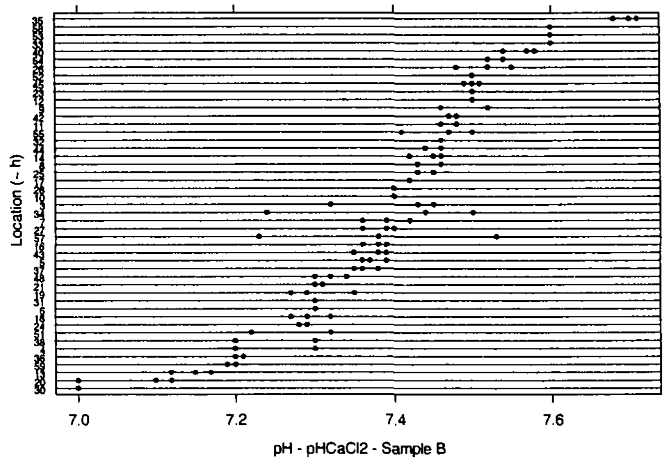


Figure IV.30: Dotplot - Sample B - pH($CaCl_2$)

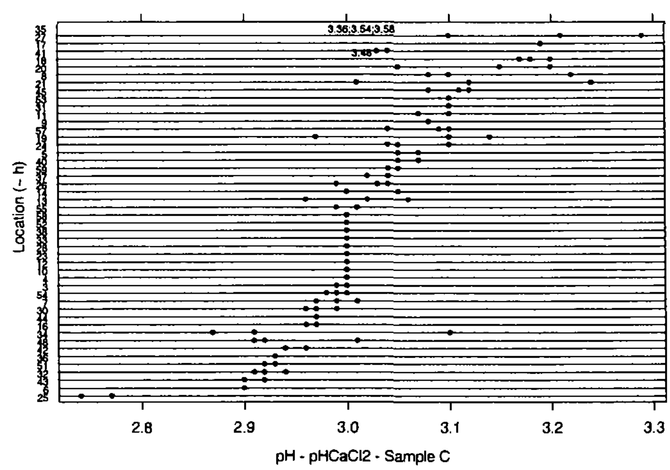


Figure IV.31: Dotplot - Sample C- pH($CaCl_2$)

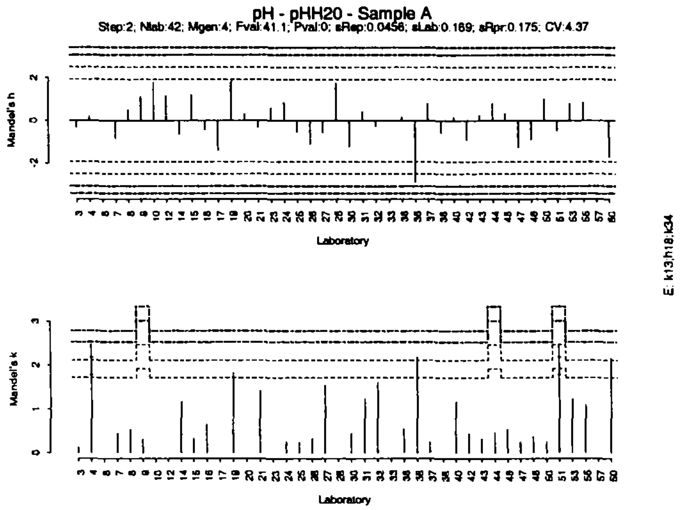


Figure IV.32: Mandel h/k plot - Sample A- pH($CaCl_2$)

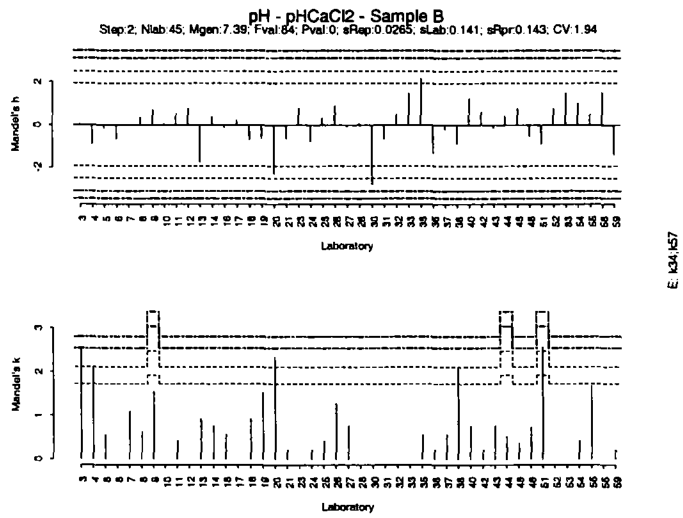


Figure IV.33: Mandel h/k plot - Sample B- pH($CaCl_2$)

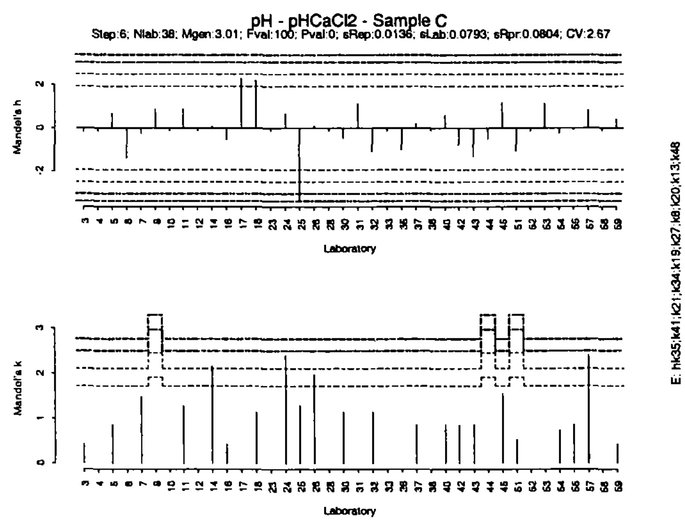


Figure IV.34: Mandel h/k –plot - Sample C- pH($CaCl_2$)

Parameter: pH (H_2O)

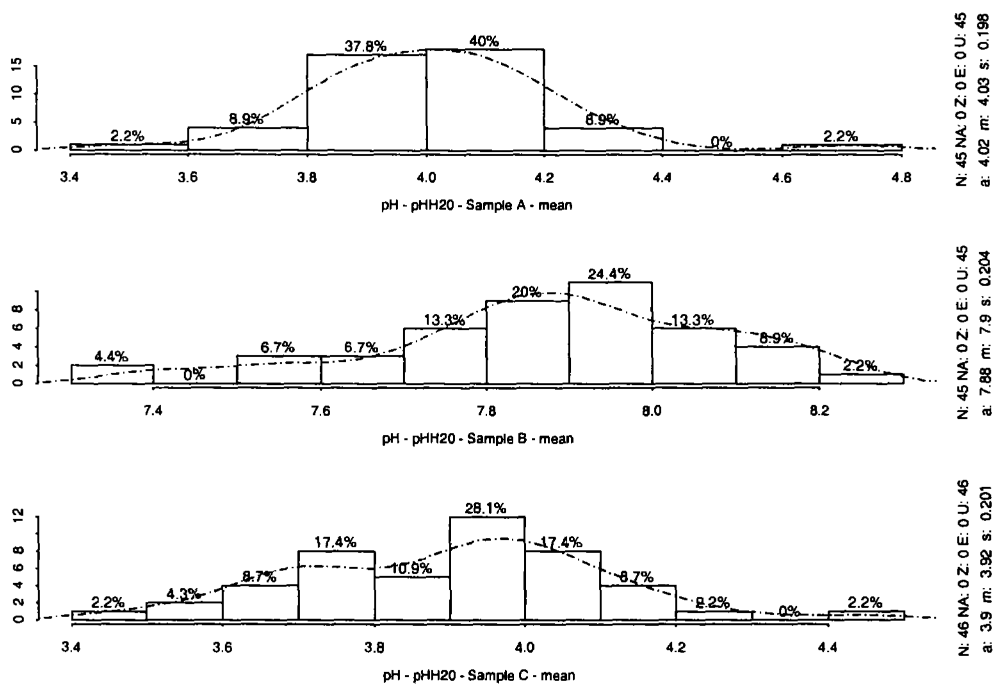


Figure IV. 35: Histogram showing the distribution of the reported mean values of pH(H_2O)

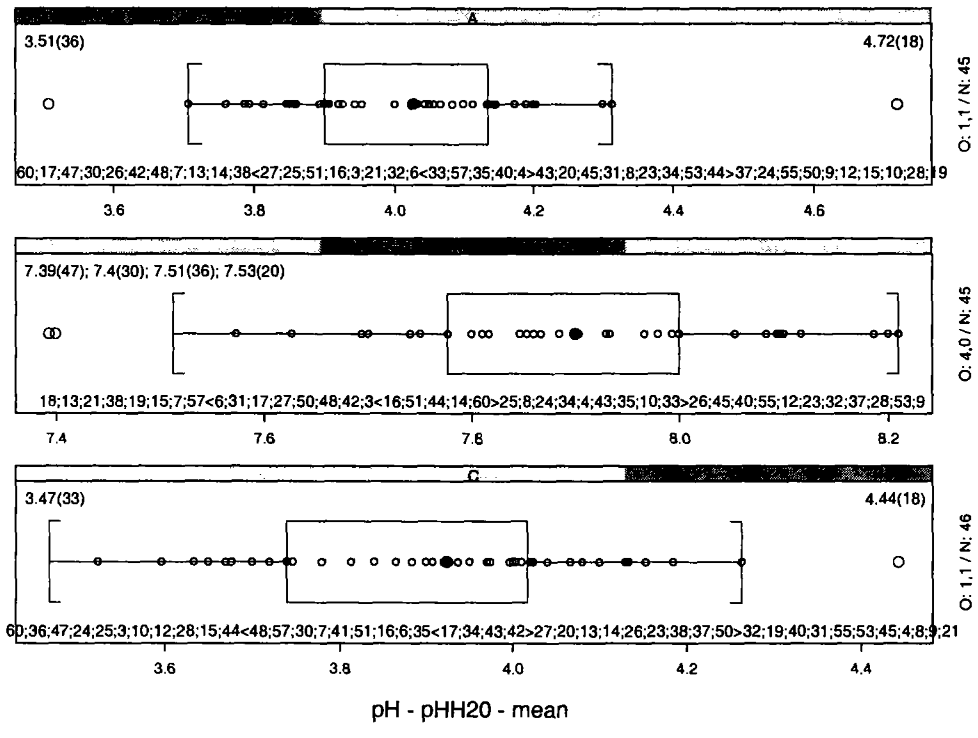


Figure IV.36: Boxplot showing the distribution of the reported mean values of pH(H_2O)

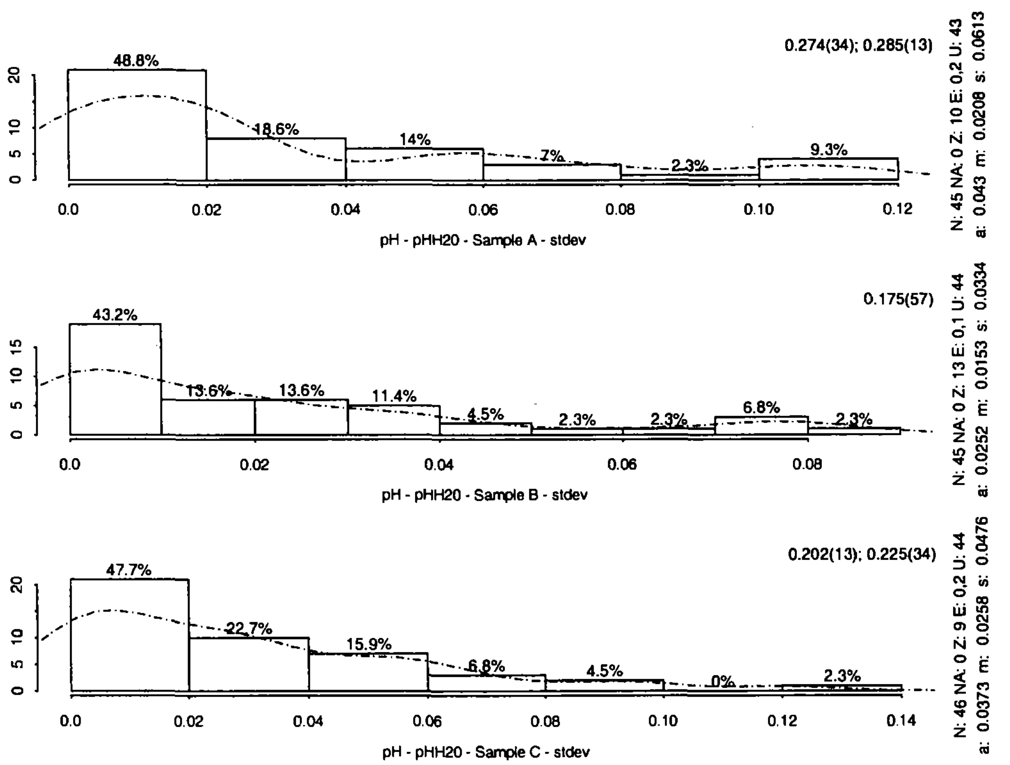


Figure IV.37: Histogram stdev - pH(H_2O)

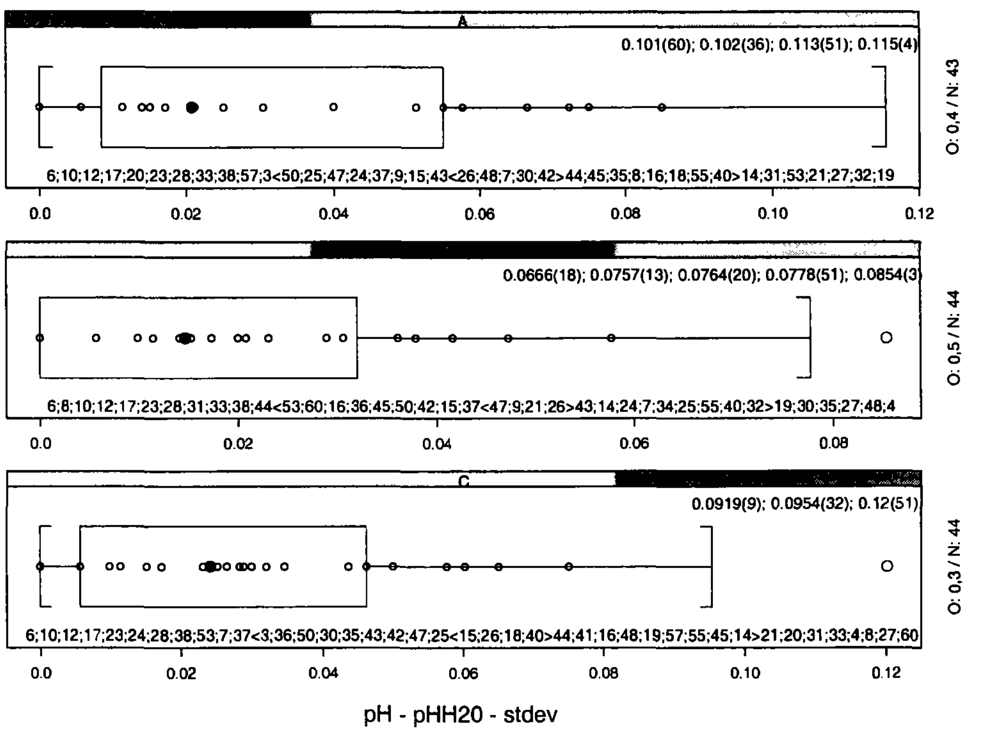


Figure IV.38: Boxplot standard deviation - pH(H_2O)

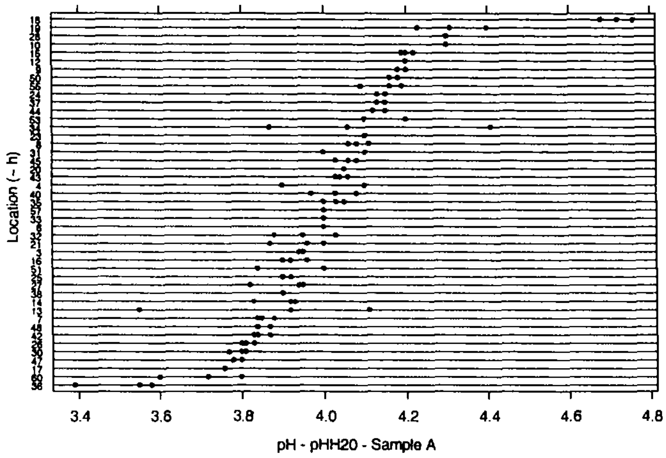


Figure IV.39: Dotplot - Sample A - pH(H_2O)

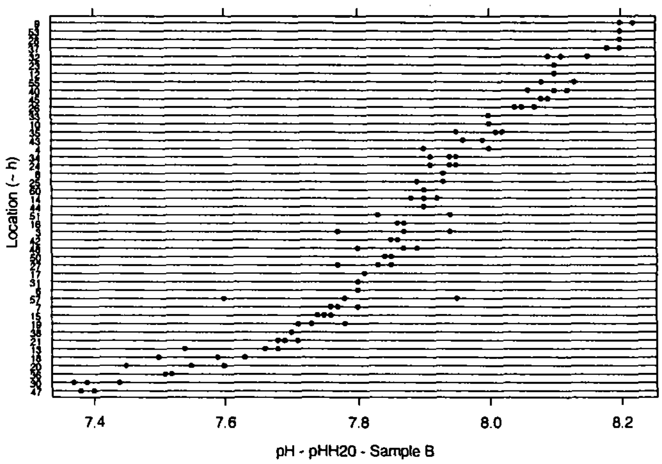


Figure IV. 40: Dotplot - Sample B - pH(H_2O)

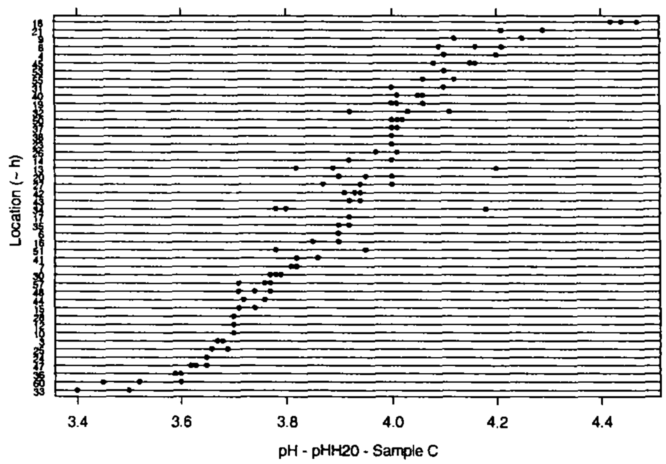


Figure IV.41: Dotplot - Sample C - pH(H_2O)

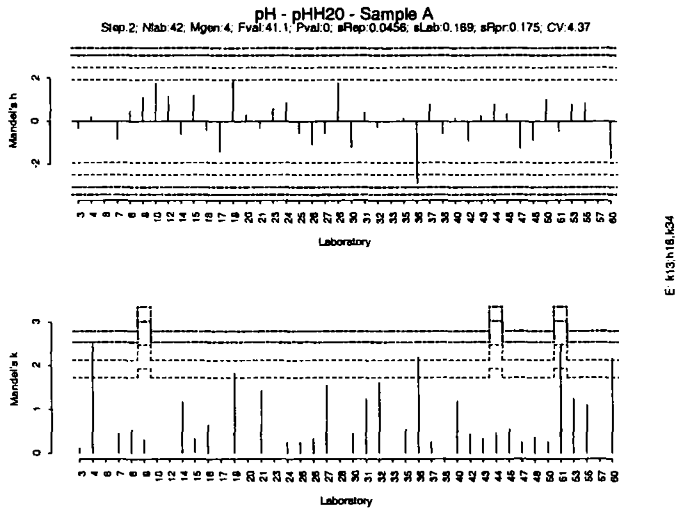


Figure IV.42: Mandel's h and k plot - Sample A - pH(H_2O)

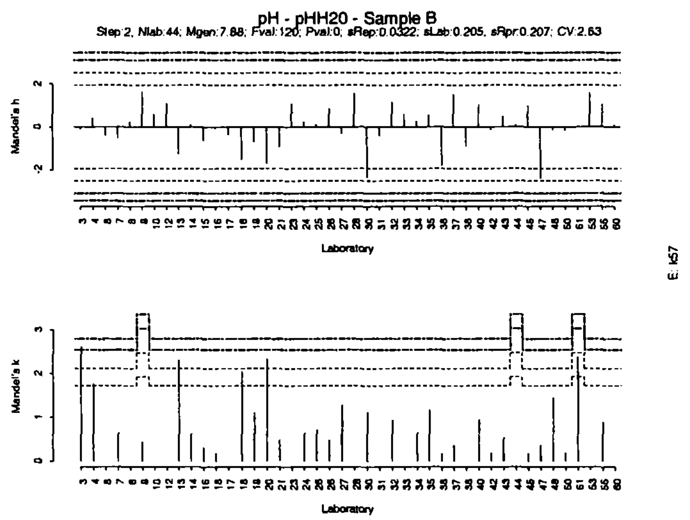


Figure IV.43: Mandel's h and k plot - Sample B - pH(H_2O)

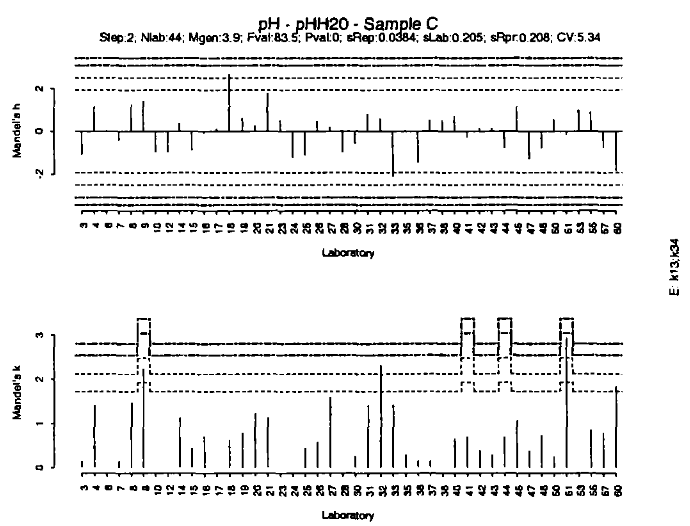


Figure IV. 44: Mandel's h and k plot - Sample C - pH(H_2O)

Group III: Carbonate content

Parameter: Carbonates

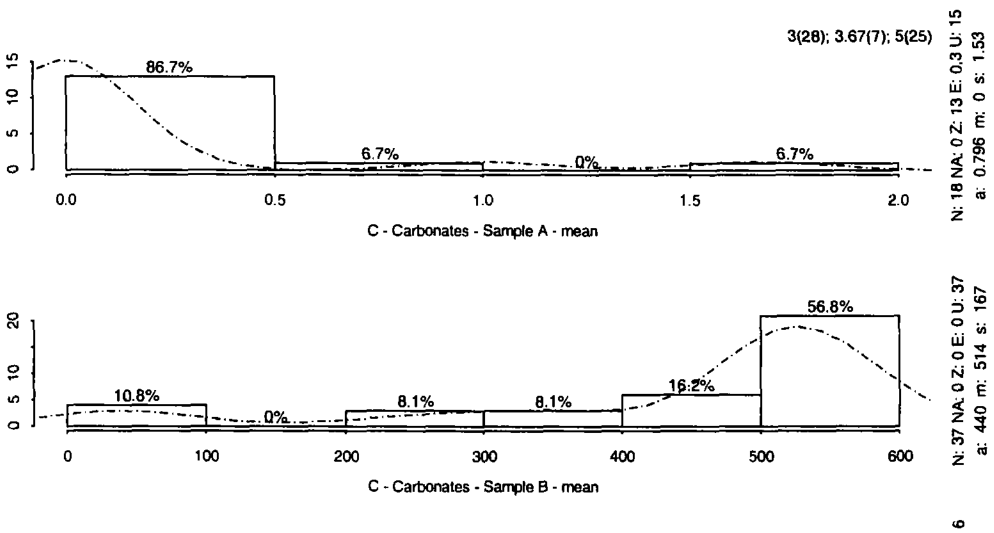


Figure IV. 45: Histogram mean - Carbonates

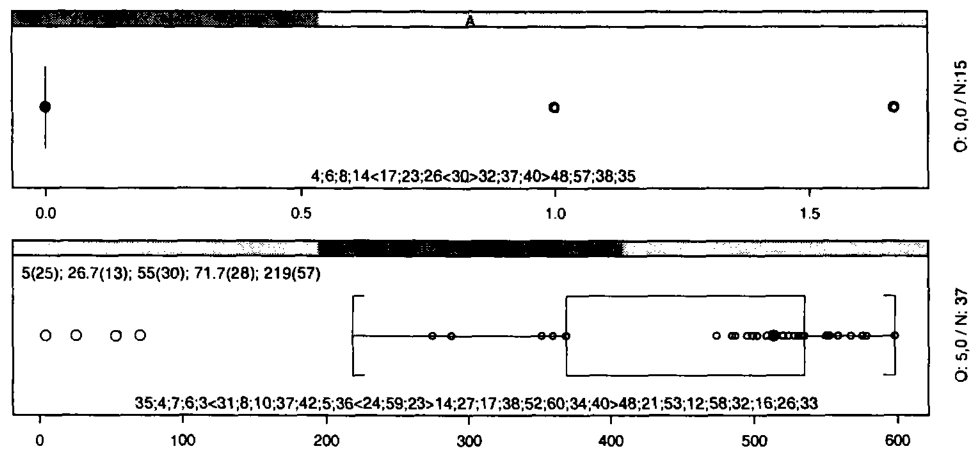


Figure IV. 46: Boxplot mean - Carbonates

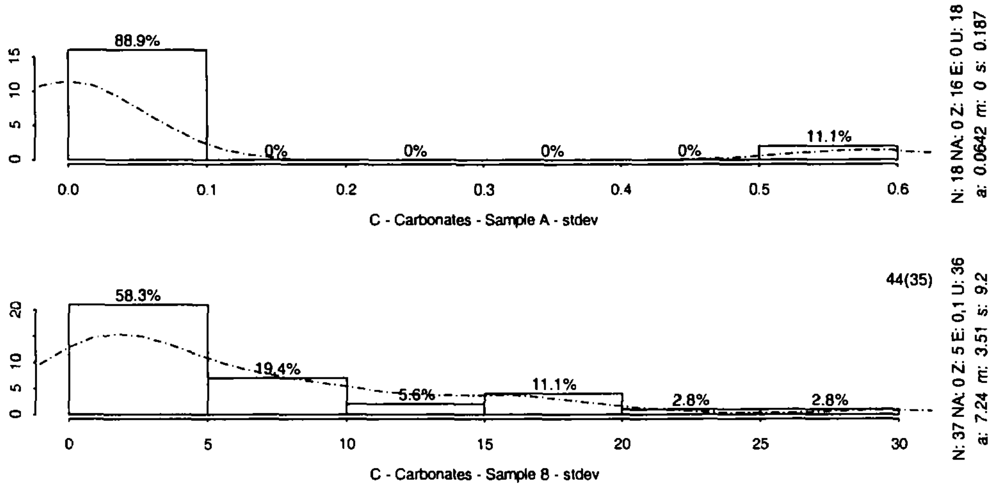


Figure IV. 47: Histogram stdev - Carbonates

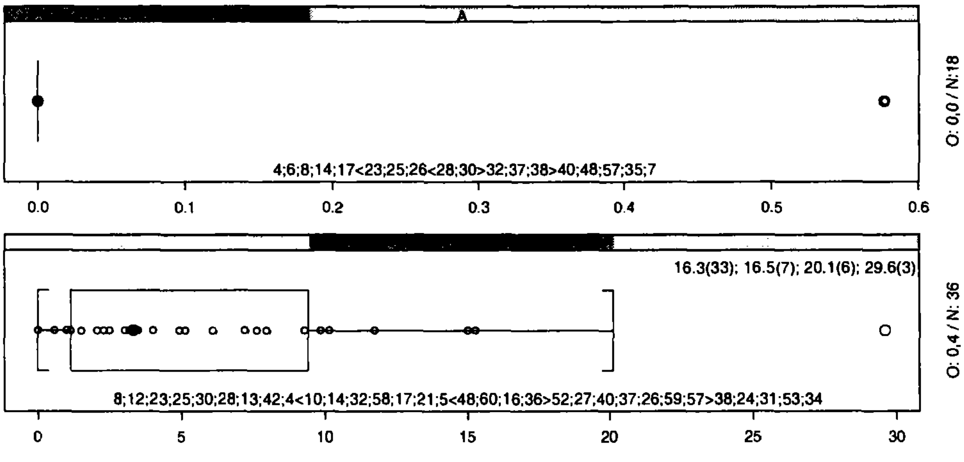


Figure IV. 48: Boxplot stdev - Carbonates

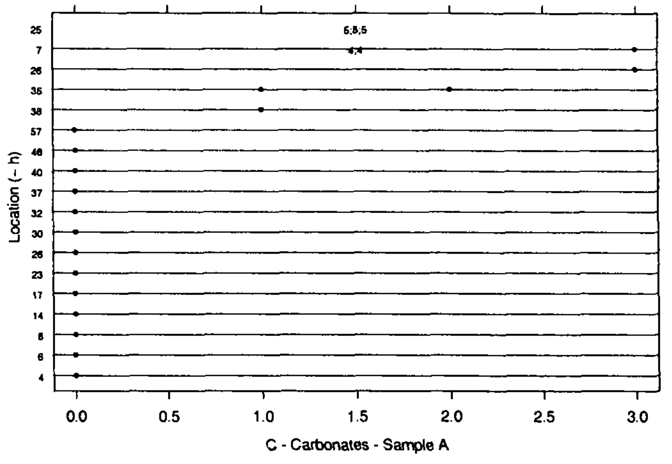


Figure IV. 49: Dotplot - Sample A - Carbonates

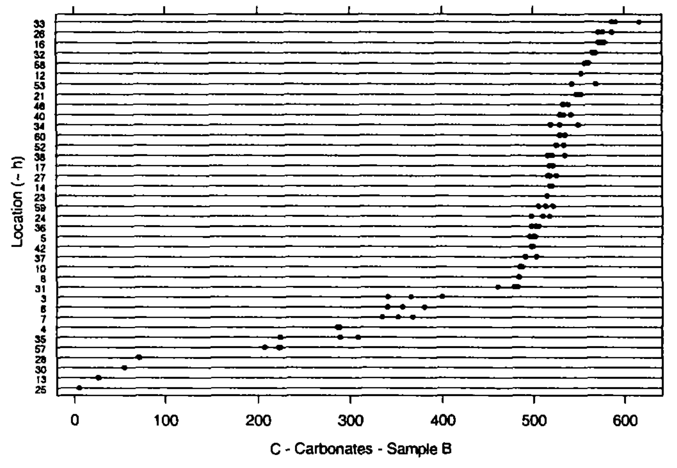


Figure IV. 50: Dotplot - Sample B - Carbonates

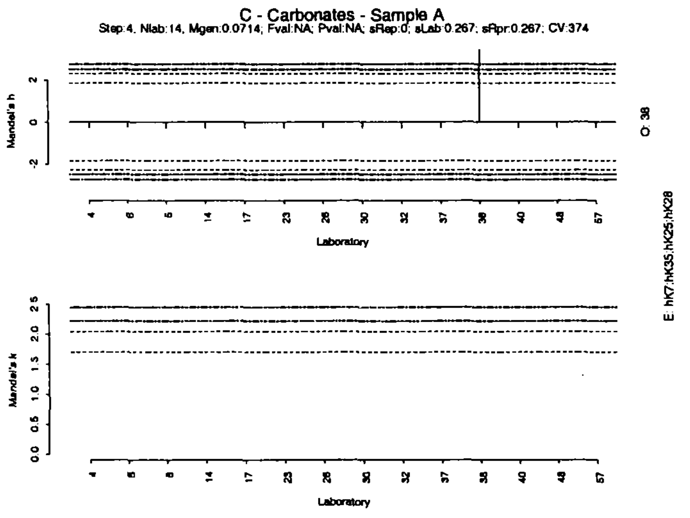


Figure IV. 51: Mandel h/k plot - Sample A - Carbonates

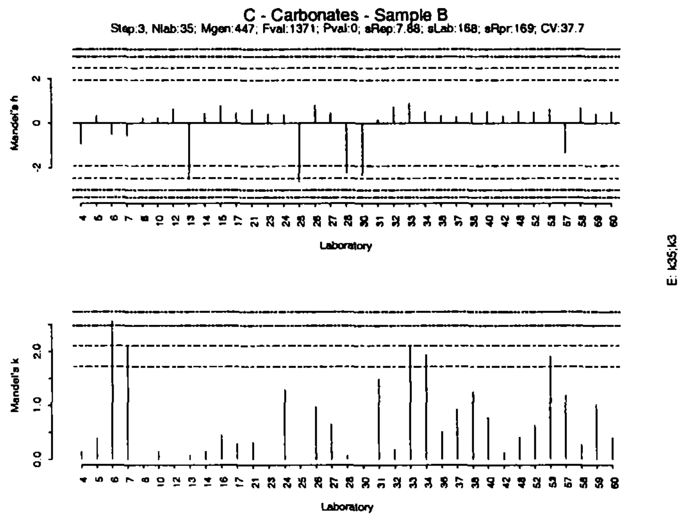


Figure IV. 52: Mandel h/k plot - Sample B mean - Carbonates

Group IV: Organic Carbon

Parameter: Organic Carbon

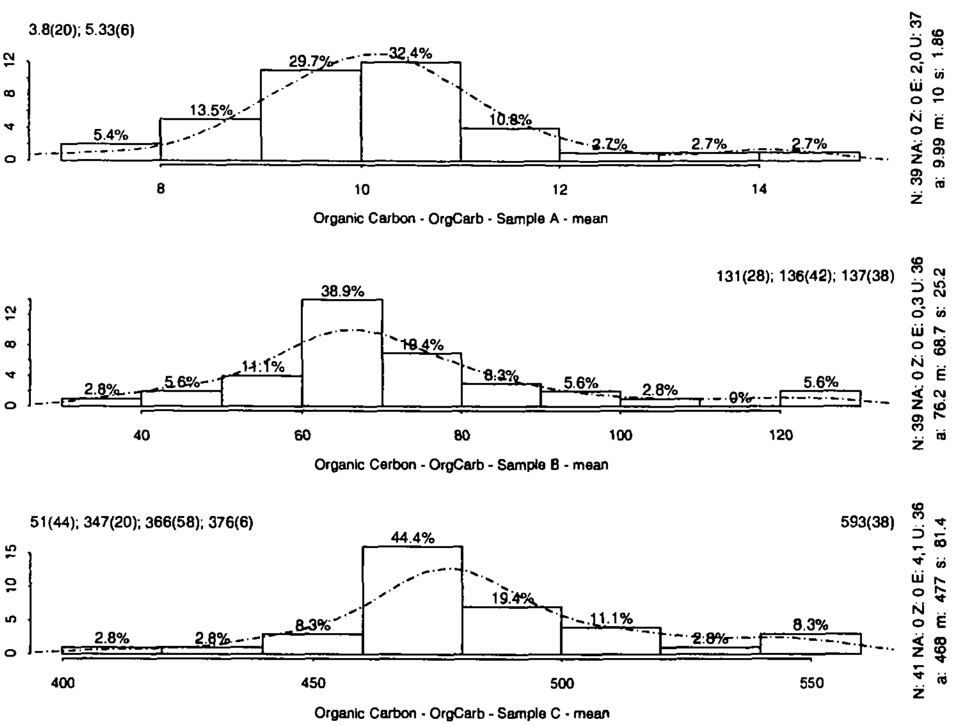


Figure IV. 53: Histogram mean – Organic carbon

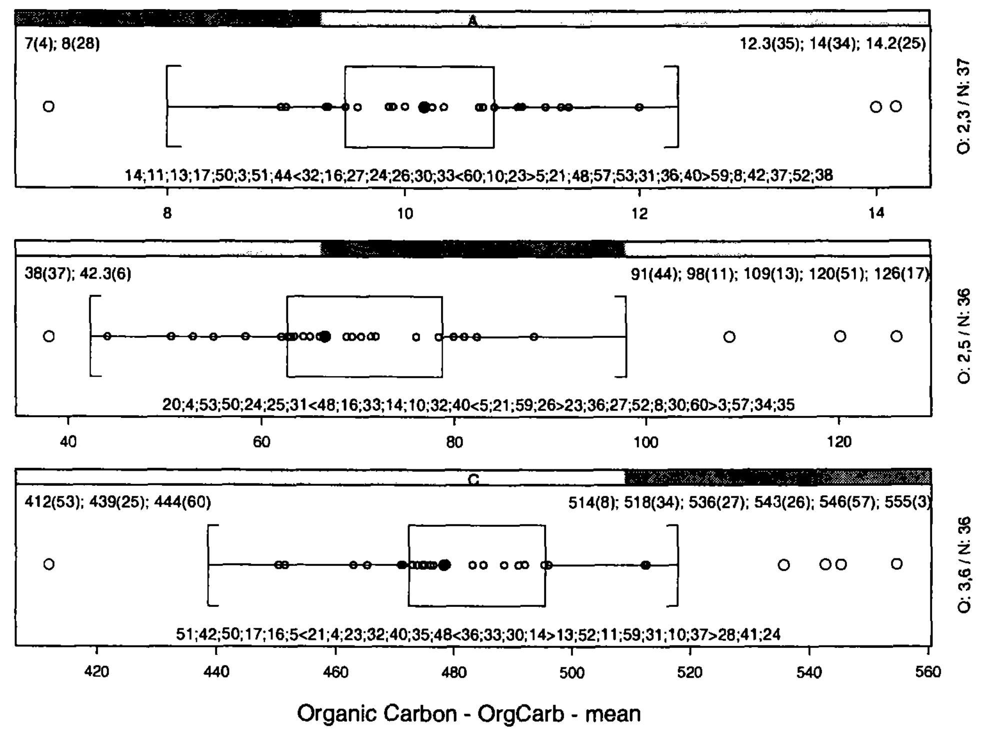


Figure IV. 54: Boxplot mean – Organic carbon

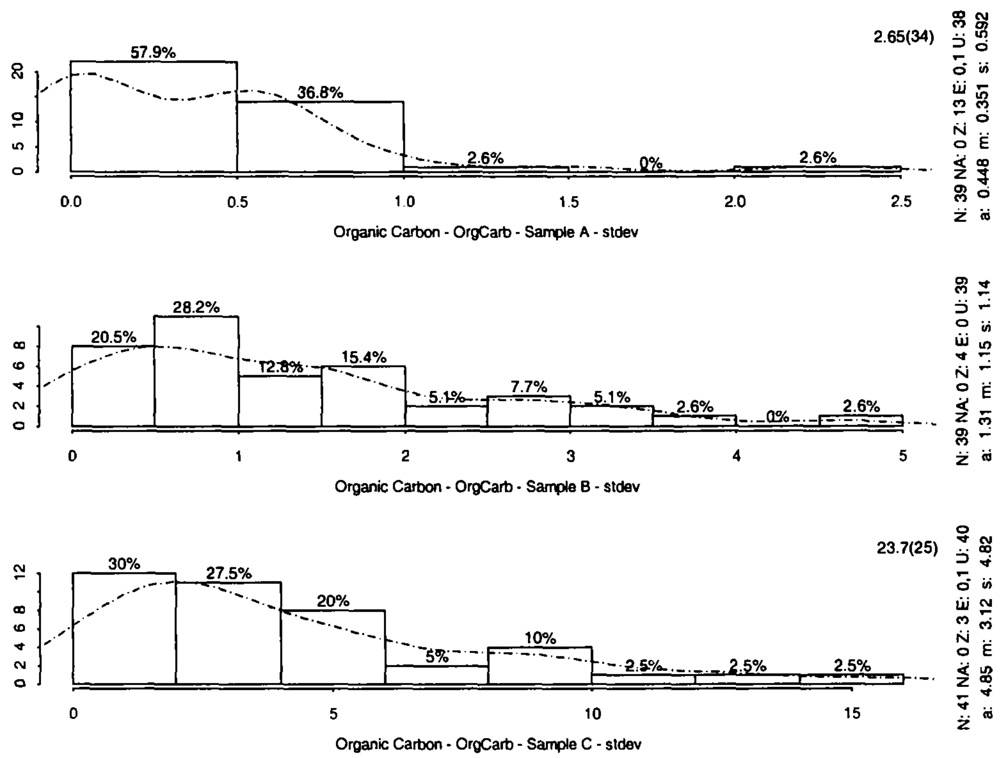


Figure IV. 55: Histogram stdev – Organic carbon

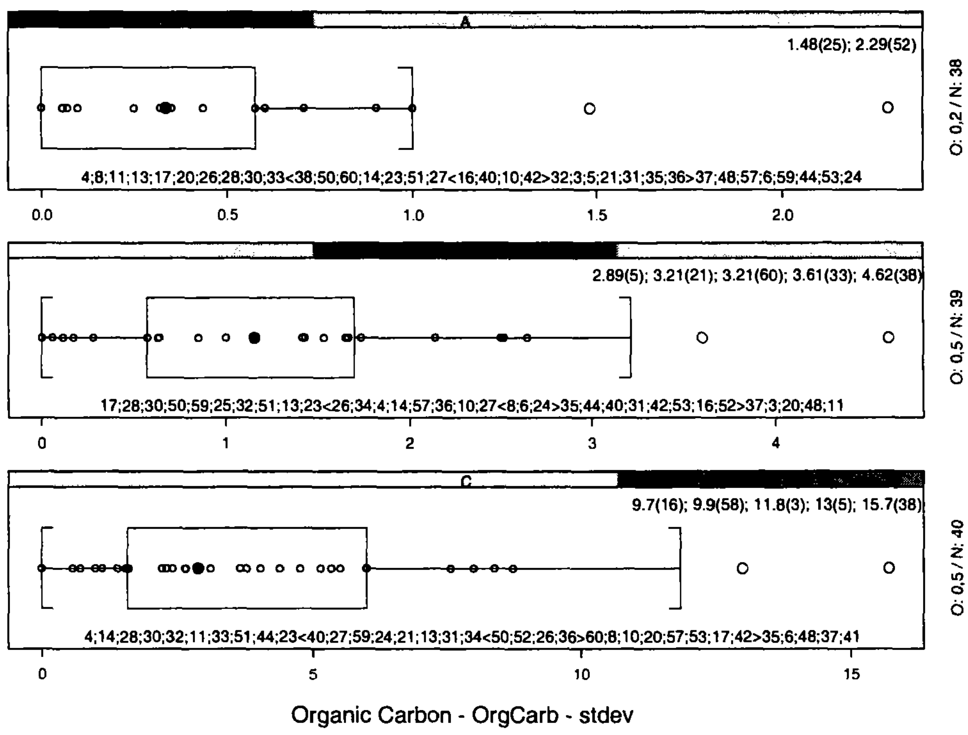


Figure IV. 56: Boxplot stdev – Organic carbon

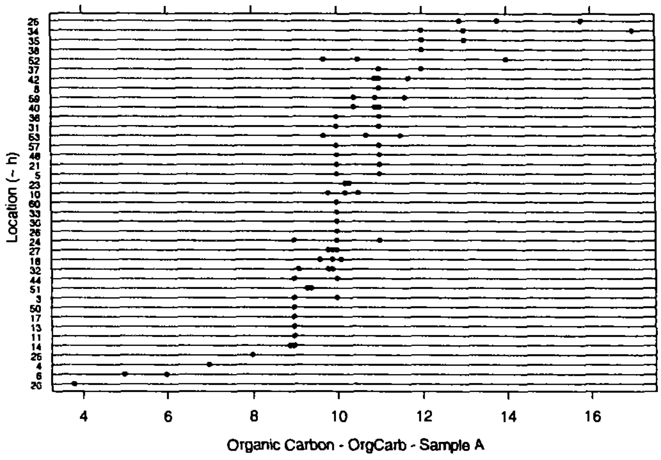


Figure IV. 57: Dotplot - Sample A – Organic carbon

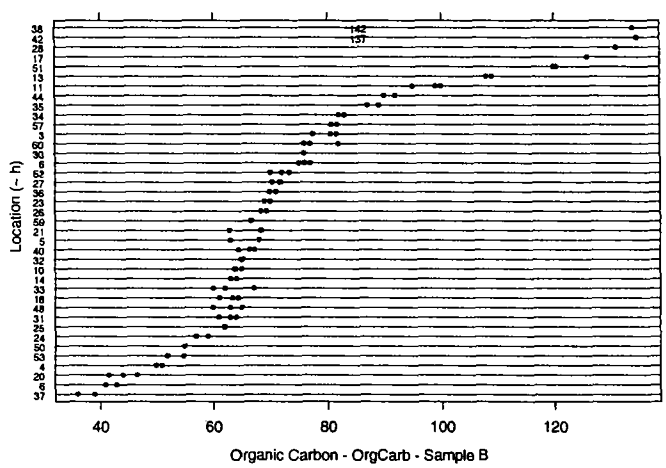


Figure IV. 58: Dotplot - Sample B – Organic carbon

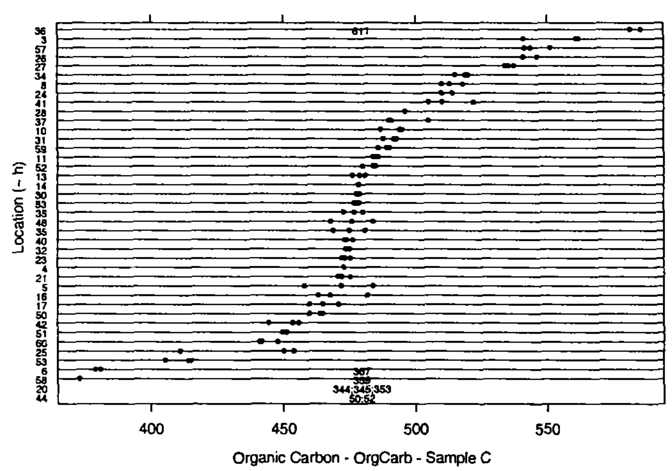


Figure IV. 59: Dotplot - Sample C – Organic carbon

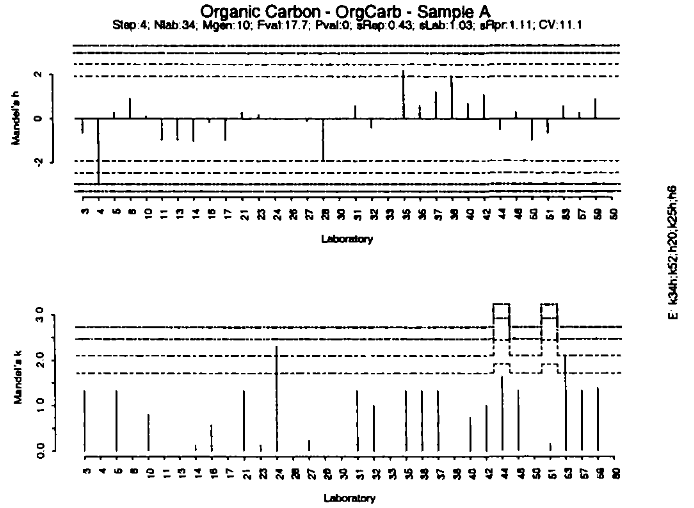


Figure IV. 60: Mandel's h and k plot - Sample A mean – Organic carbon

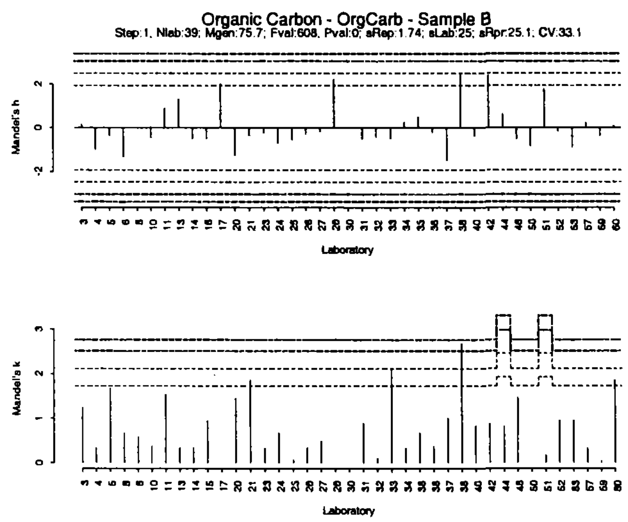


Figure IV. 61: Mandel's h and k plot - Sample B mean – Organic carbon

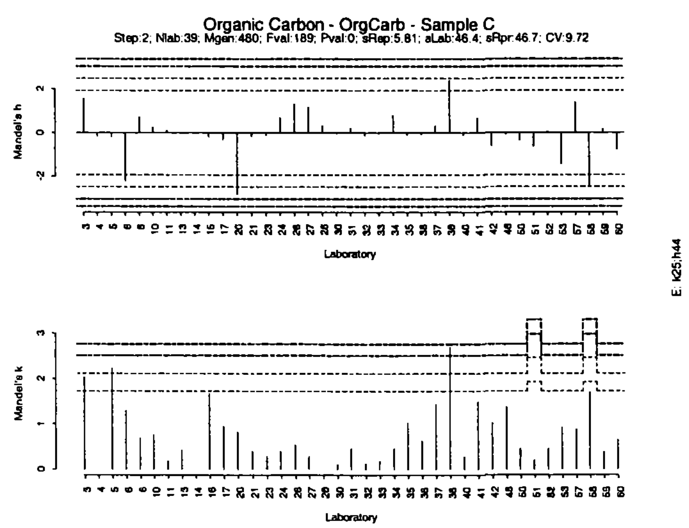


Figure IV. 62: Mandel's h and k plot - Sample C mean – Organic carbon

Group V: Total nitrogen content

Parameter: Total N

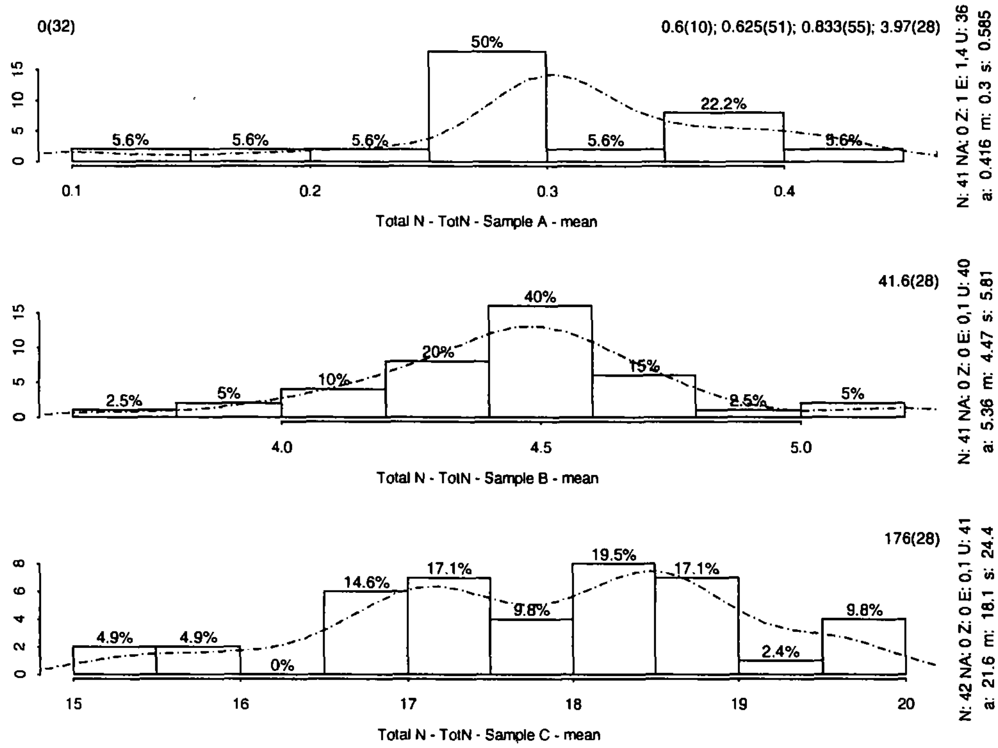


Figure IV. 63: Histogram mean – Total N

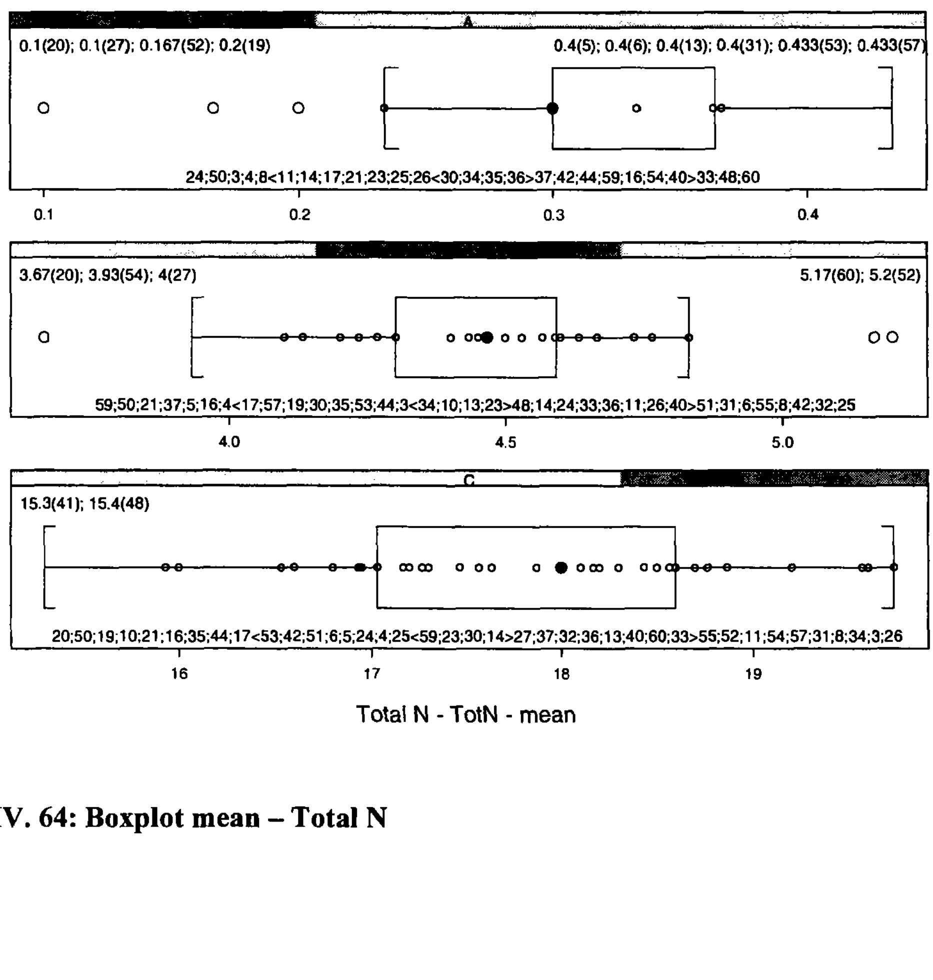


Figure IV. 64: Boxplot mean – Total N

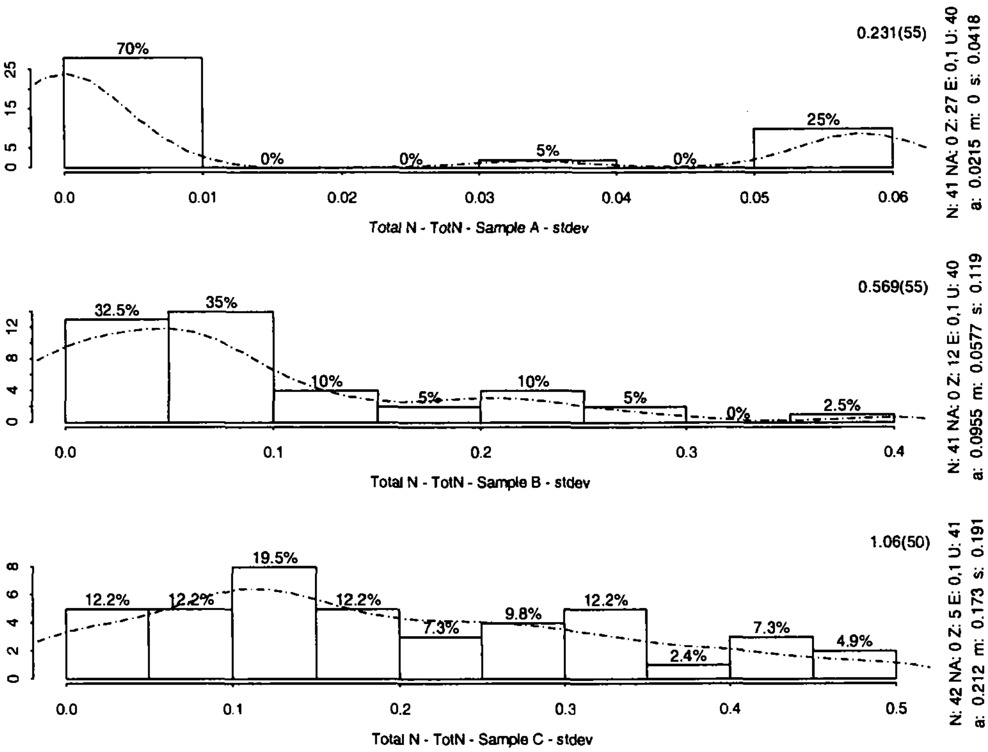


Figure IV. 65: Histogram stdev – Total N

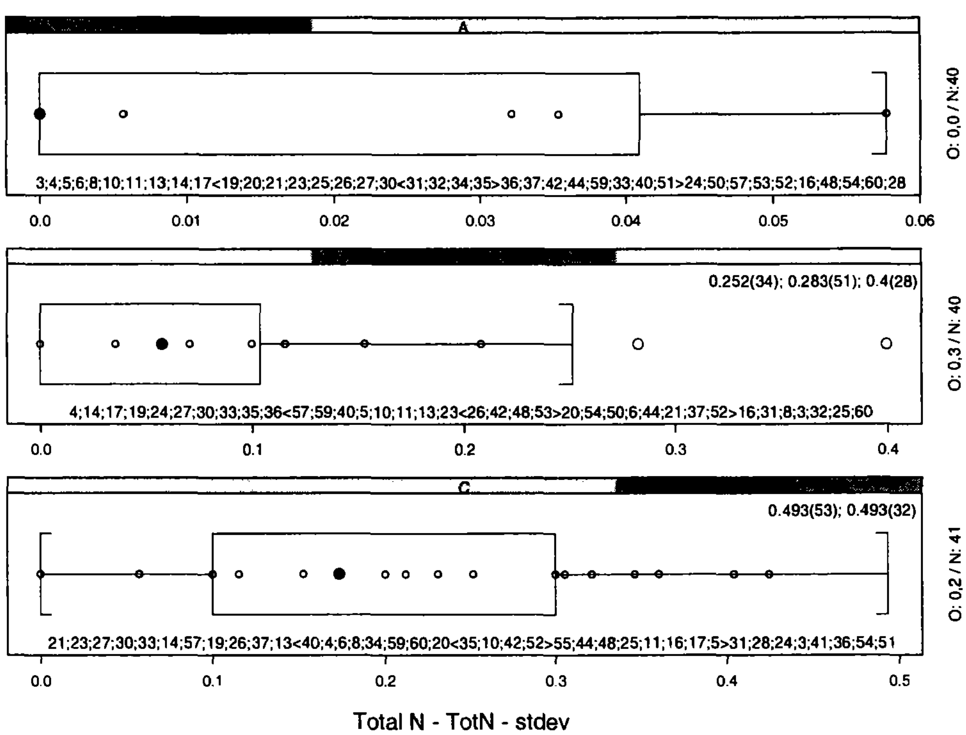


Figure IV. 66: Boxplot stdev – Total N

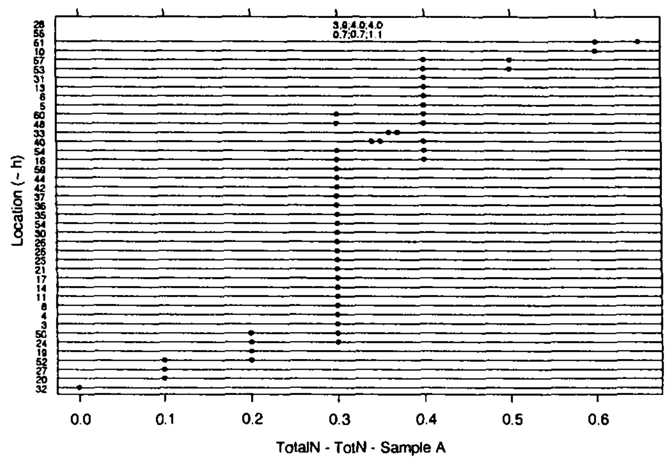


Figure IV. 67: Dotplot - Sample A – Total N

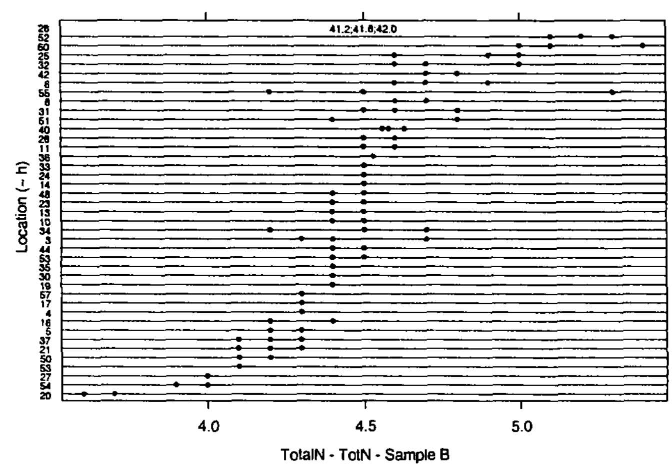


Figure IV. 68: Dotplot - Sample B – Total N

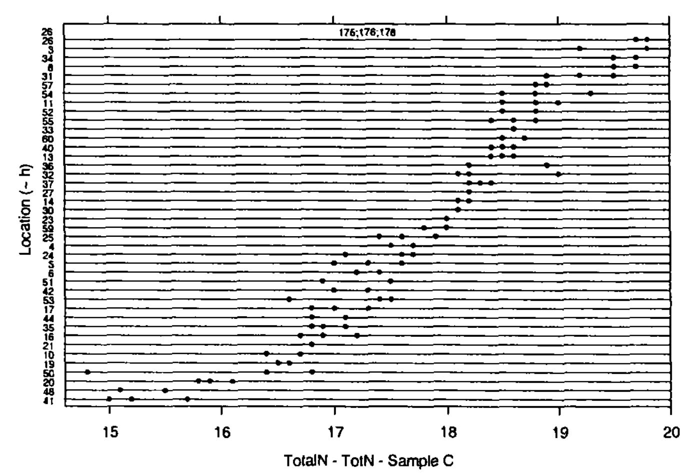


Figure IV. 69: Dotplot - Sample C – Total N

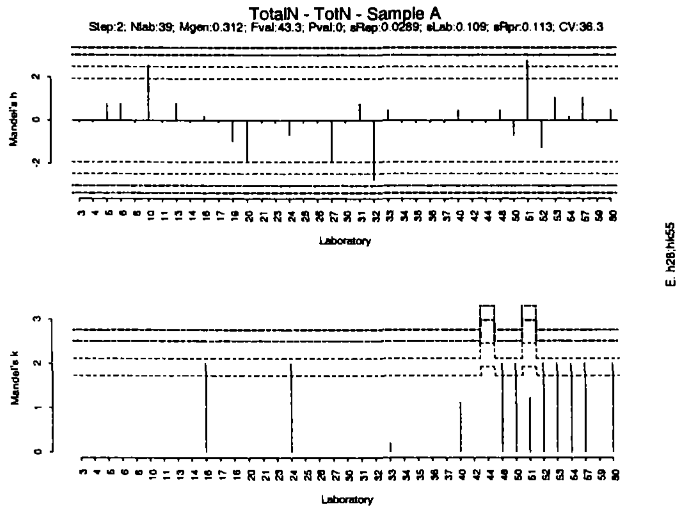


Figure IV. 70: Mandel h/k plot - Sample A – Total N

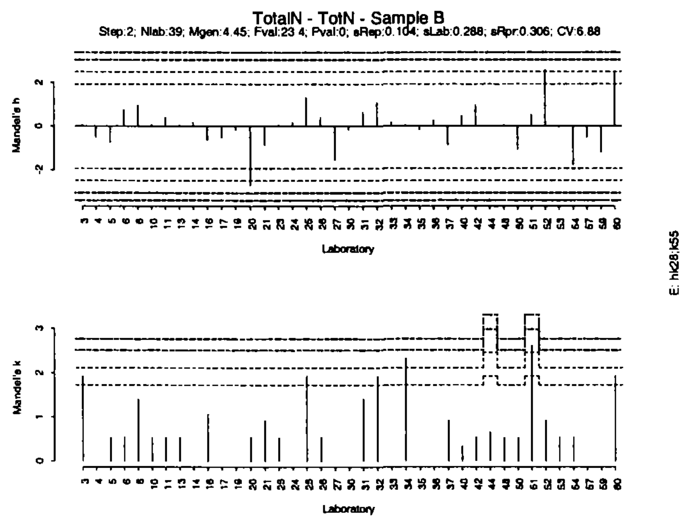


Figure IV. 71: Mandel h/k plot - Sample B – Total N

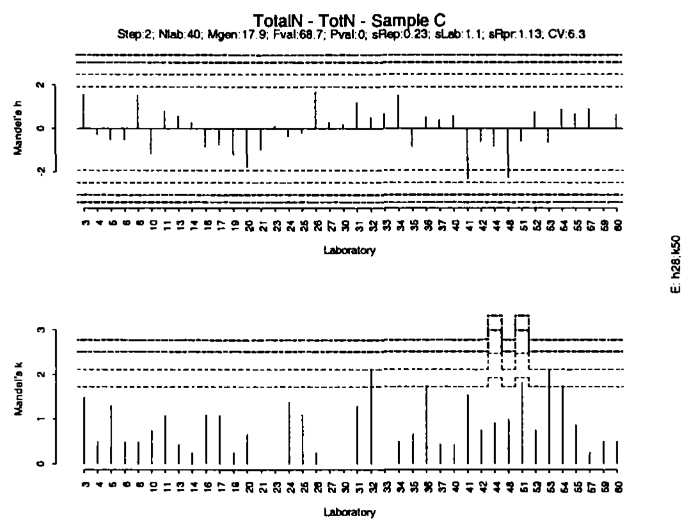


Figure IV. 72: Mandel h/k plot - Sample C – Total N

Group VI: Exchangeable cations

Parameter: Exchangeable Acidity

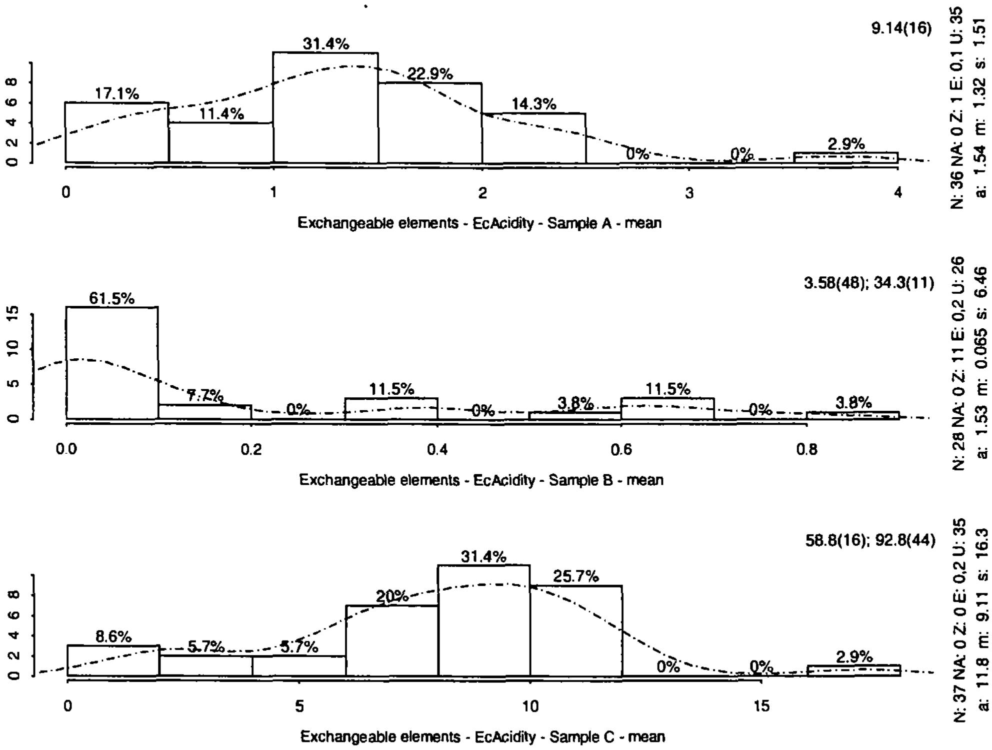


Figure IV. 73: Histogram mean – Exchangeable acidity

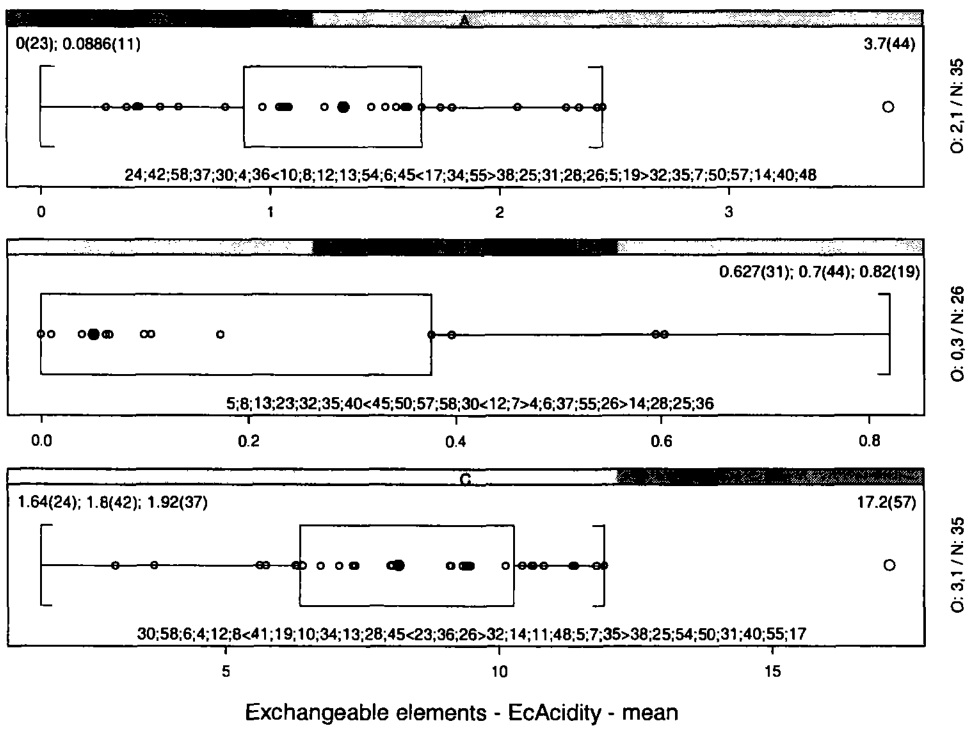


Figure IV. 74: Boxplot mean – Exchangeable acidity

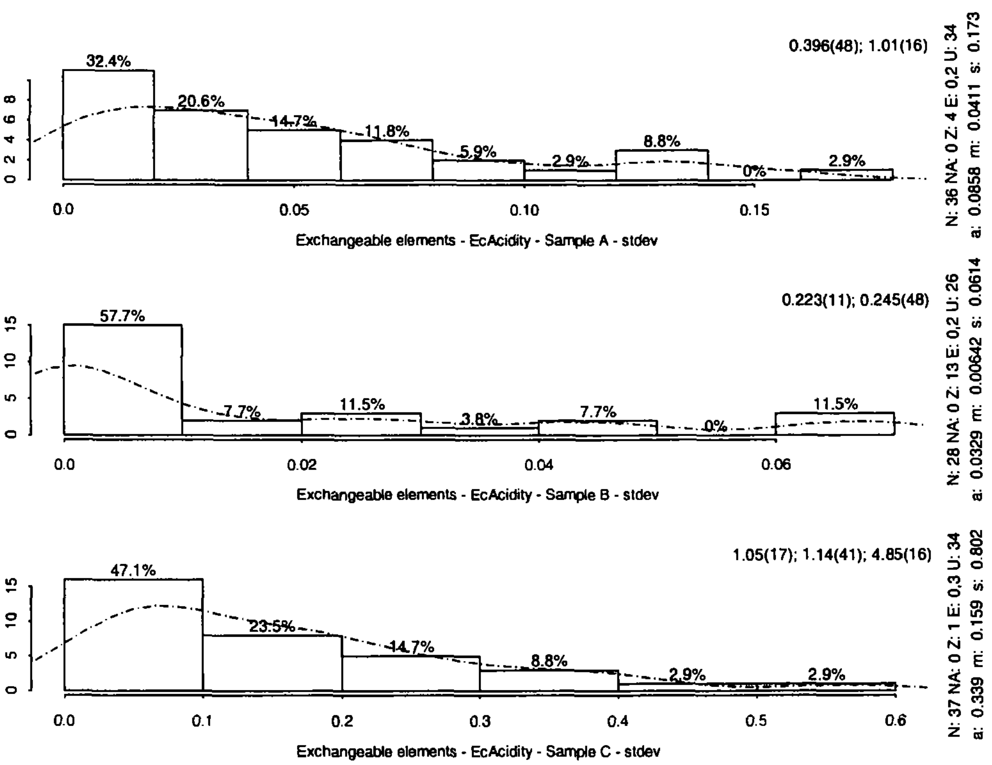


Figure IV. 75: Histogram stdev – Exchangeable acidity

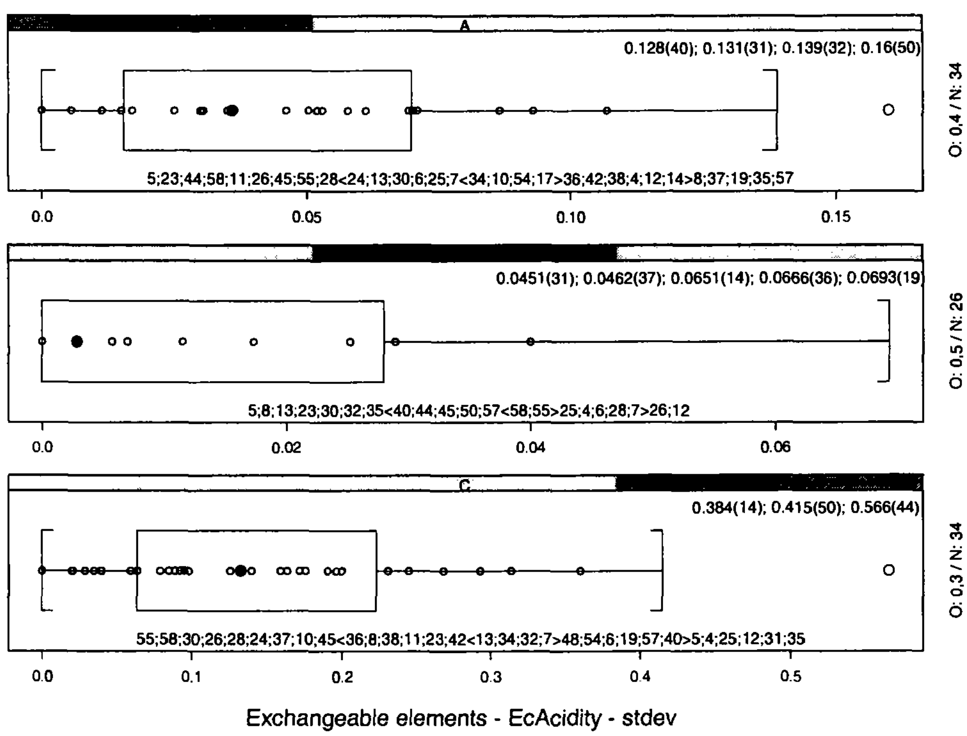


Figure IV. 76: Boxplot stdev – Exchangeable acidity

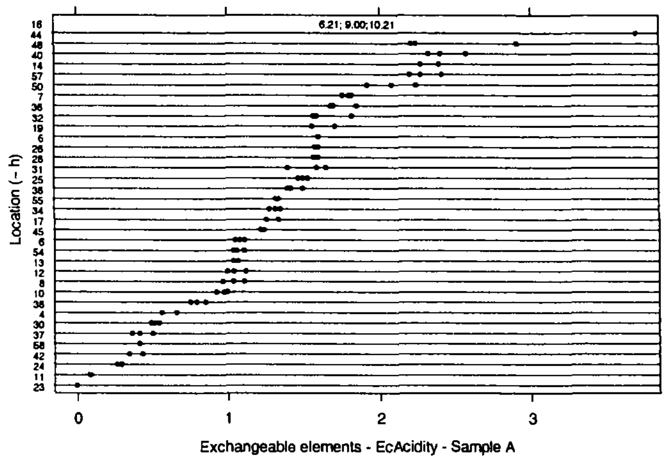


Figure IV. 77: Dotplot - Sample A – Exchangeable acidity

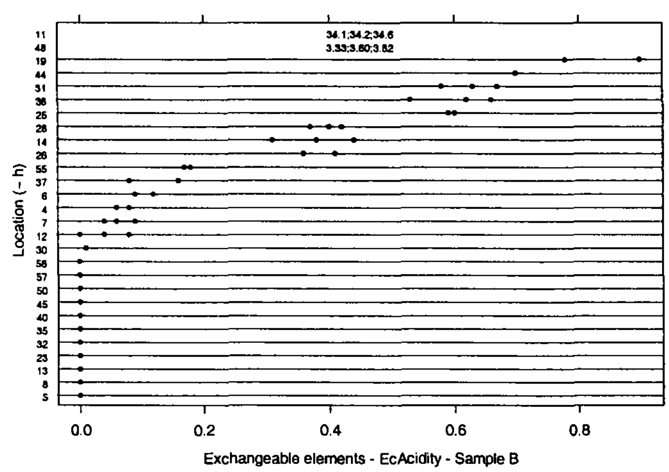


Figure IV. 78: Dotplot - Sample B– Exchangeable acidity

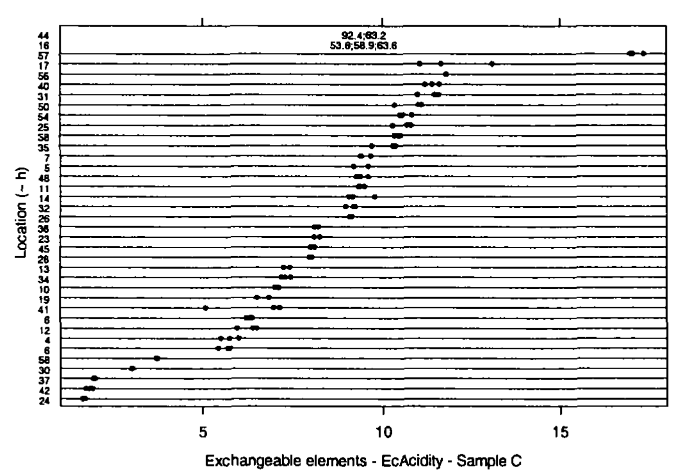


Figure IV. 79: Dotplot - Sample C – Exchangeable acidity

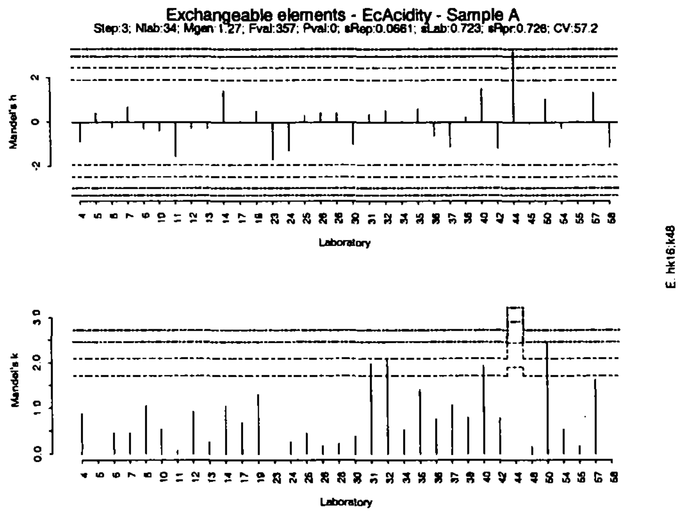


Figure IV. 80: Mandel's h and k plot - Sample A – Exchangeable acidity

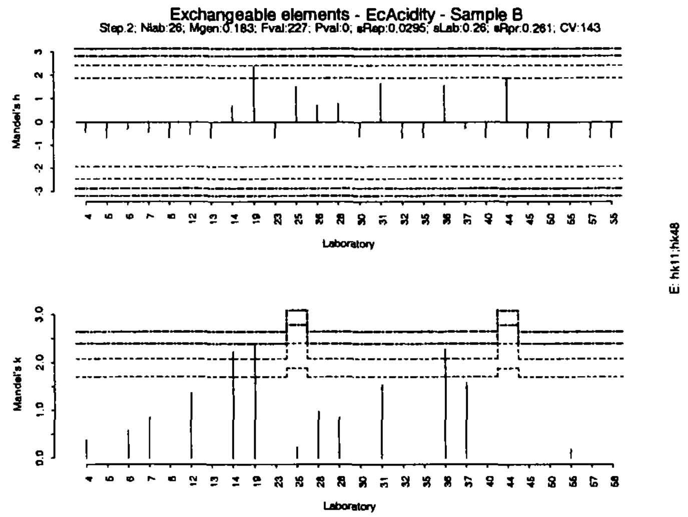


Figure IV. 81: Mandel's h and k plot - Sample B– Exchangeable acidity

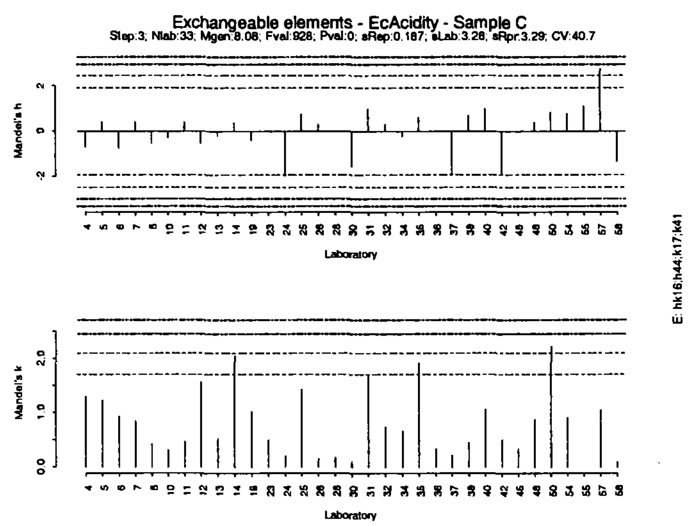


Figure IV. 82: Mandel's h and k plot - Sample C – Exchangeable acidity

Parameter: Exchangeable Al

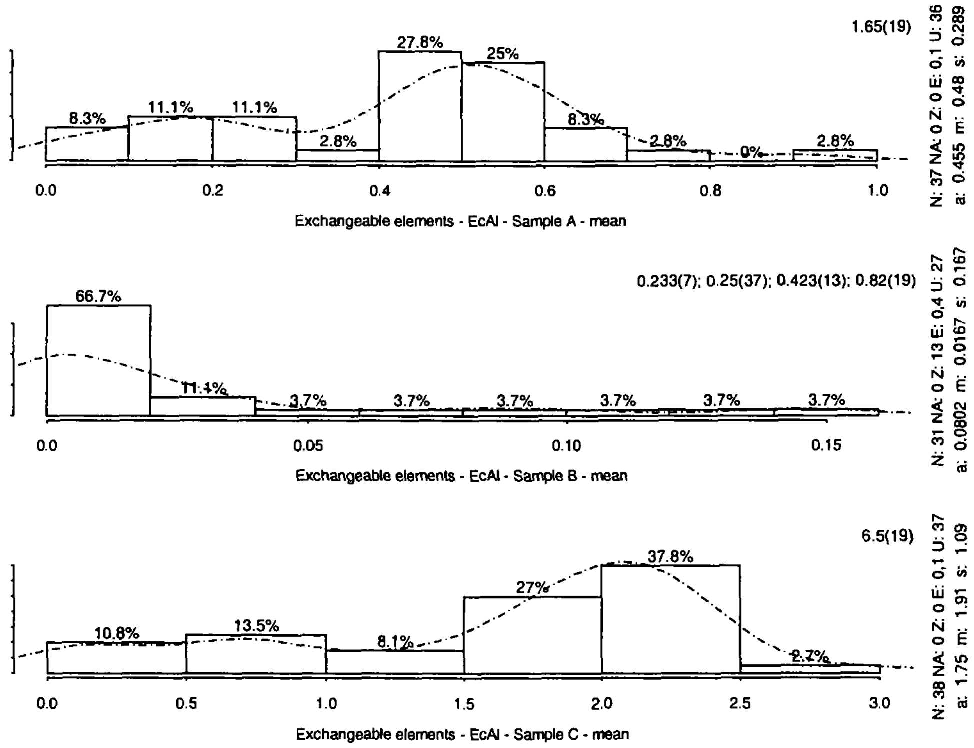


Figure IV. 83: Histogram mean – Exchangeable Al

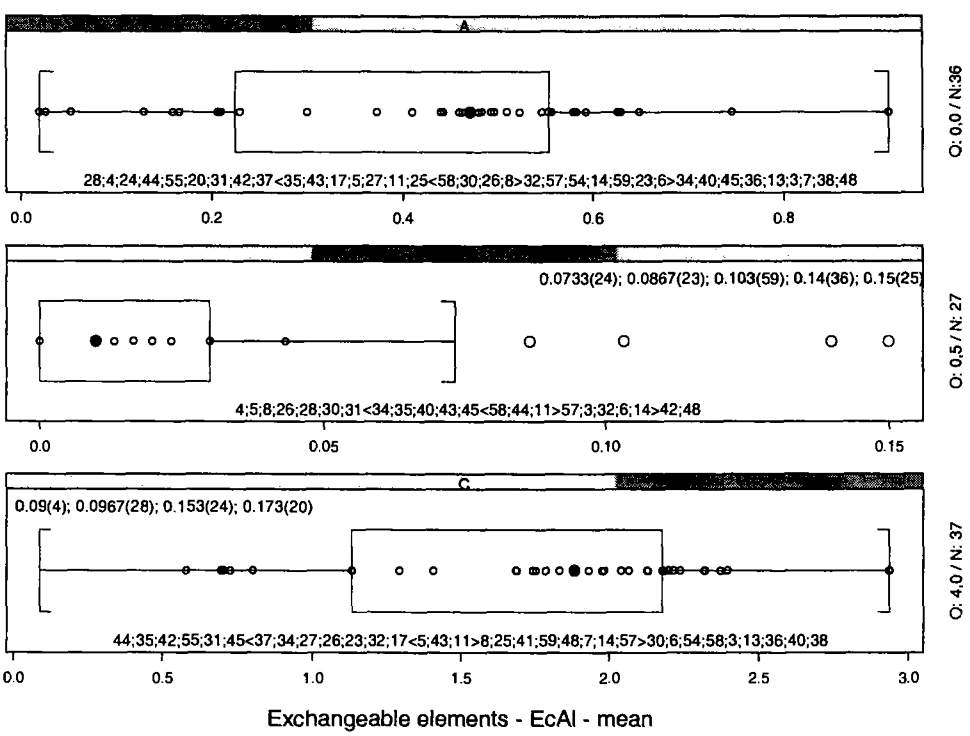


Figure IV. 84: Boxplot mean - Exchangeable Al

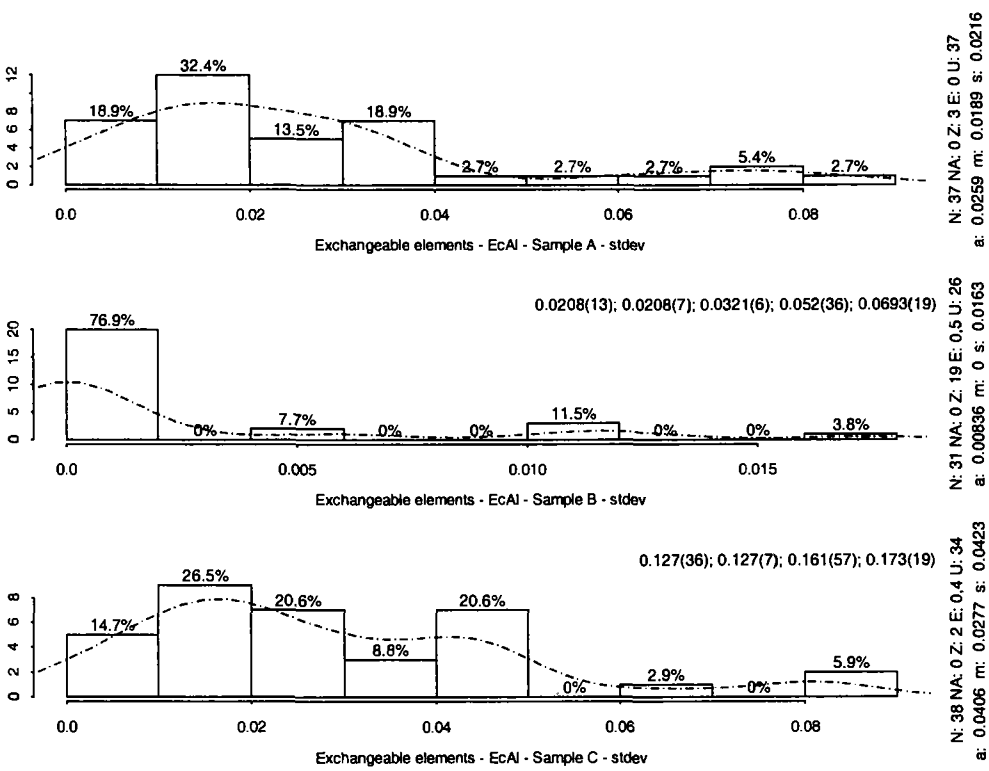


Figure IV. 85: Histogram stdev - Exchangeable Al

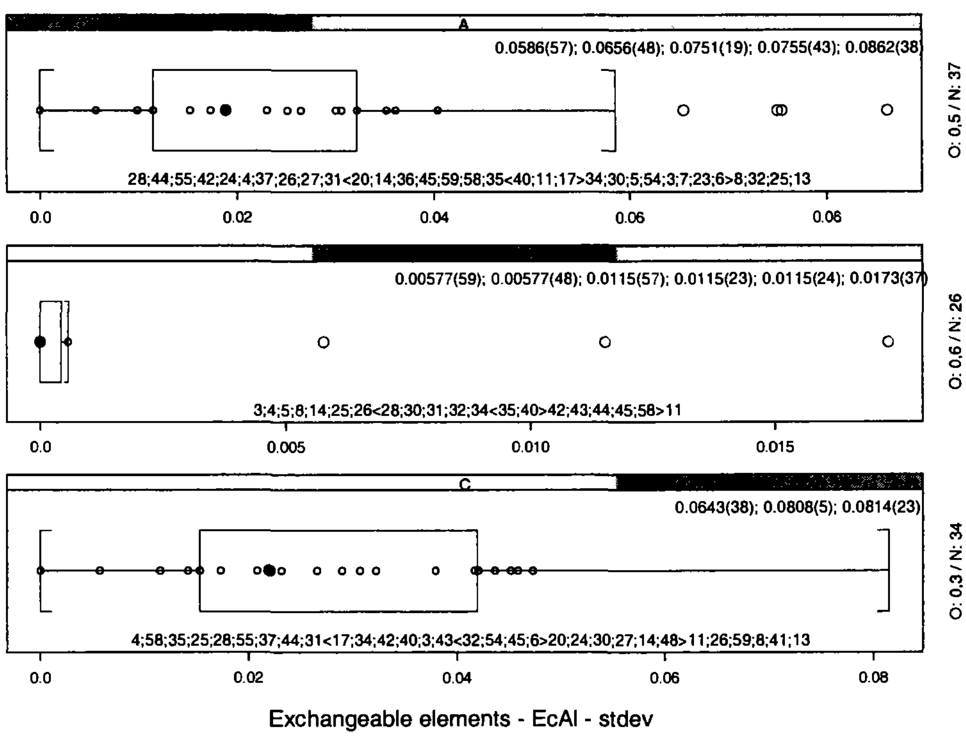


Figure IV. 86: Boxplot stdev - Exchangeable Al

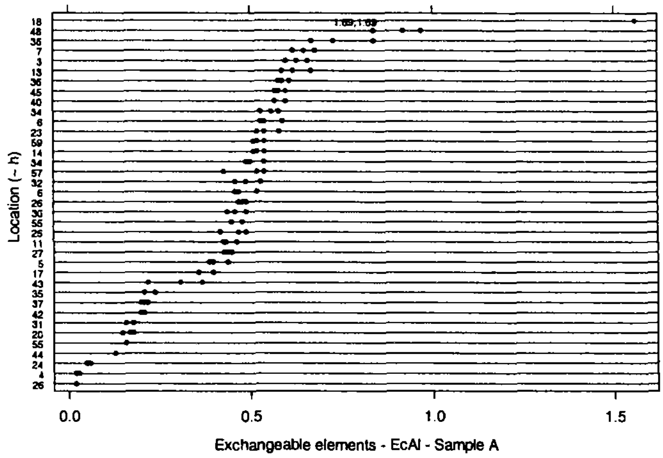


Figure IV. 87: Dotplot - Sample A - Exchangeable Al

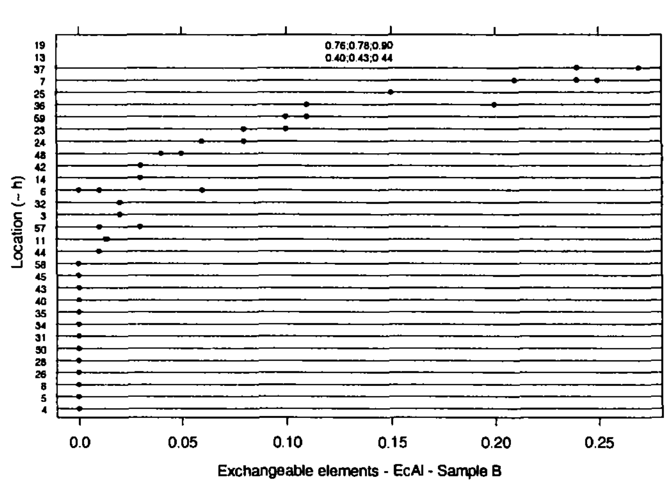


Figure IV. 88: Dotplot - Sample B - Exchangeable Al

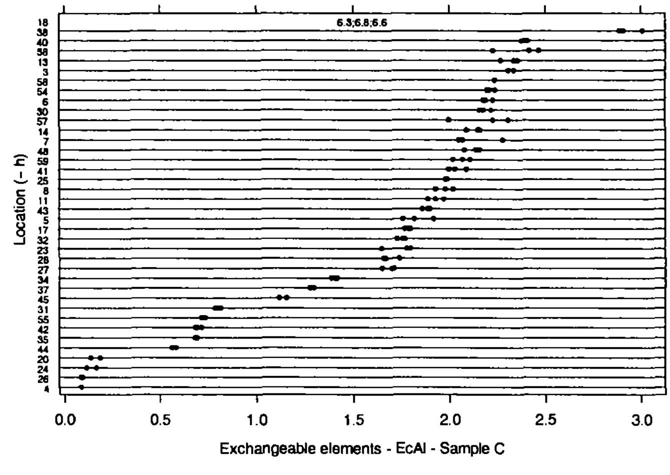


Figure IV. 89: Dotplot - Sample C - Exchangeable Al

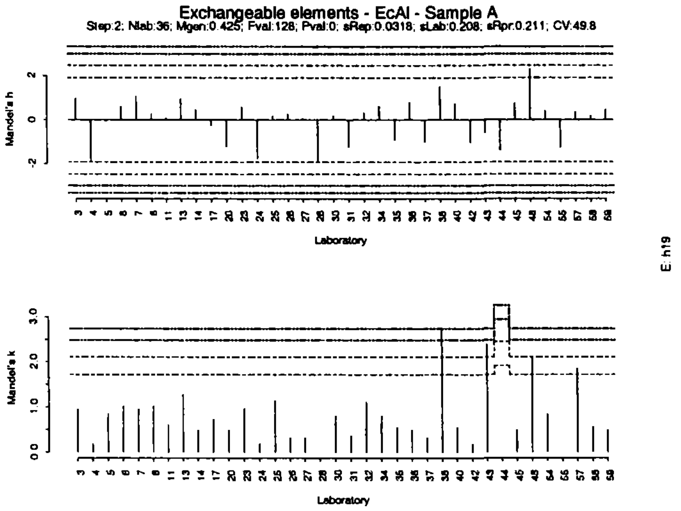


Figure IV. 89: Mandel h/k plot - Sample A - Exchangeable Al

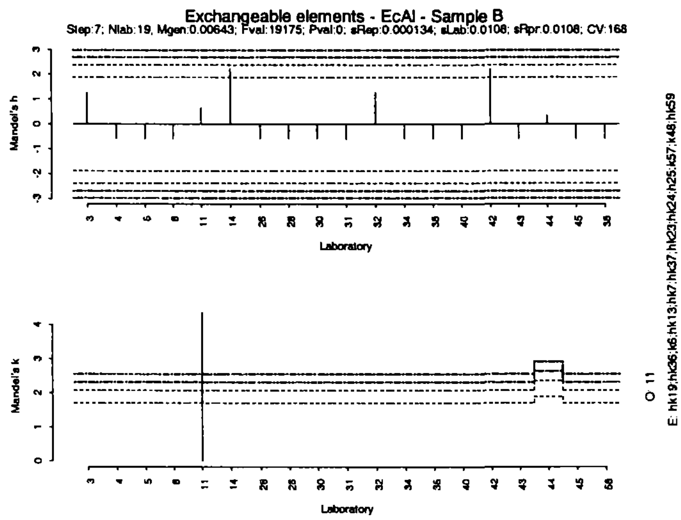


Figure IV. 90: Mandel h/k plot - Sample B - Exchangeable Al

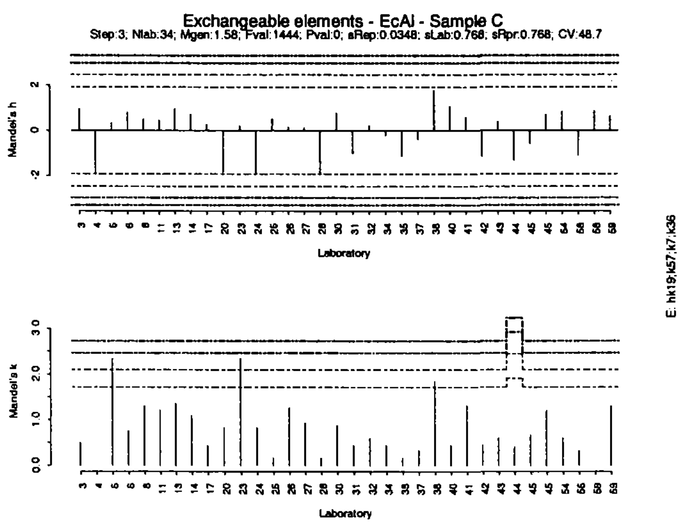


Figure IV. 91: Mandel h/k plot - Sample C - Exchangeable Al

Parameter: Exchangeable Ca

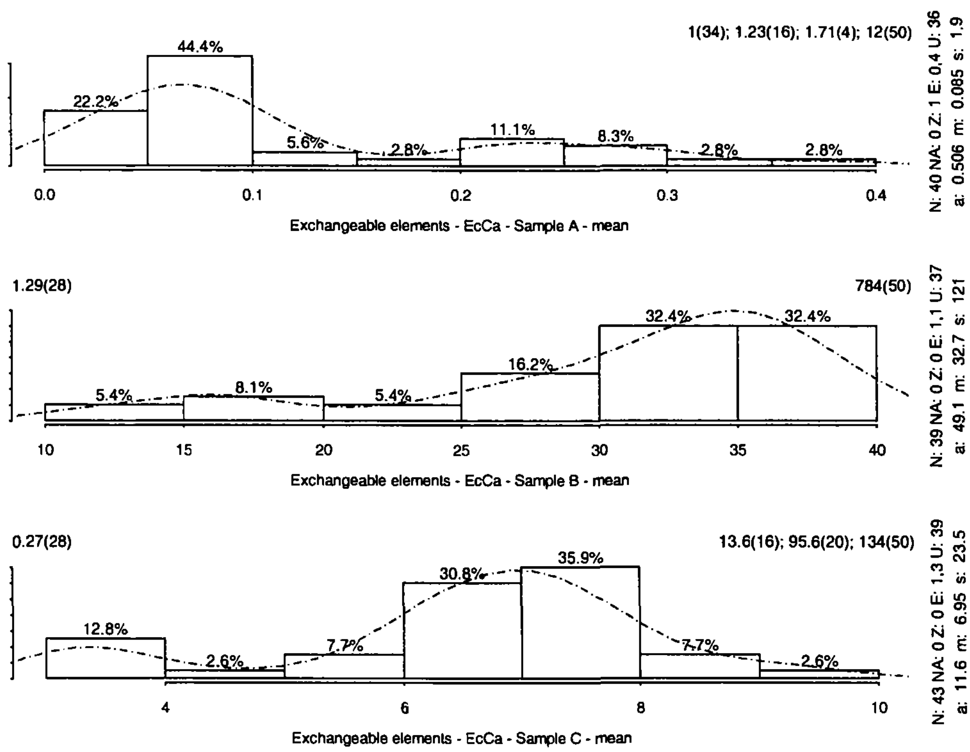


Figure IV. 92: Histogram mean - Exchangeable Ca

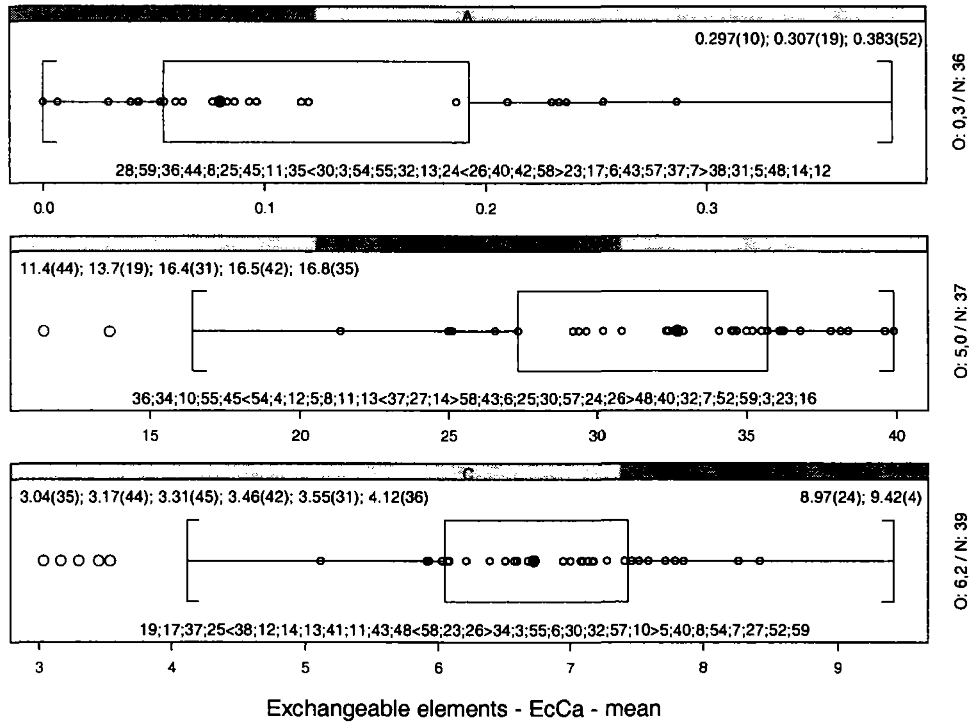


Figure IV. 93: Boxplot mean - Exchangeable Ca

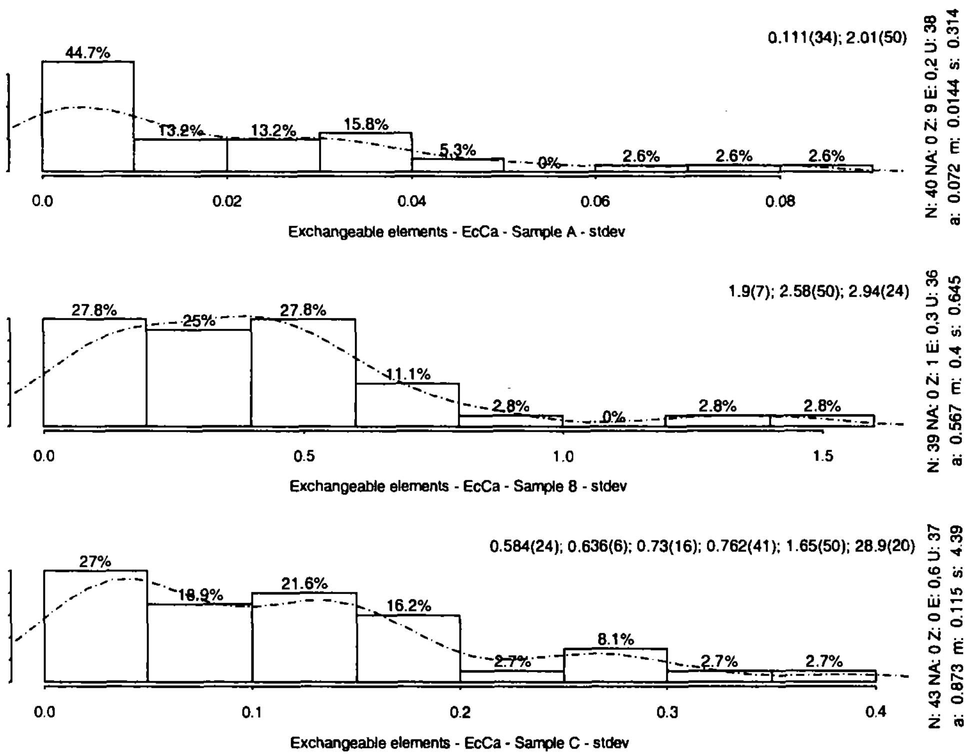


Figure IV. 94: Histogram stdev - Exchangeable Ca

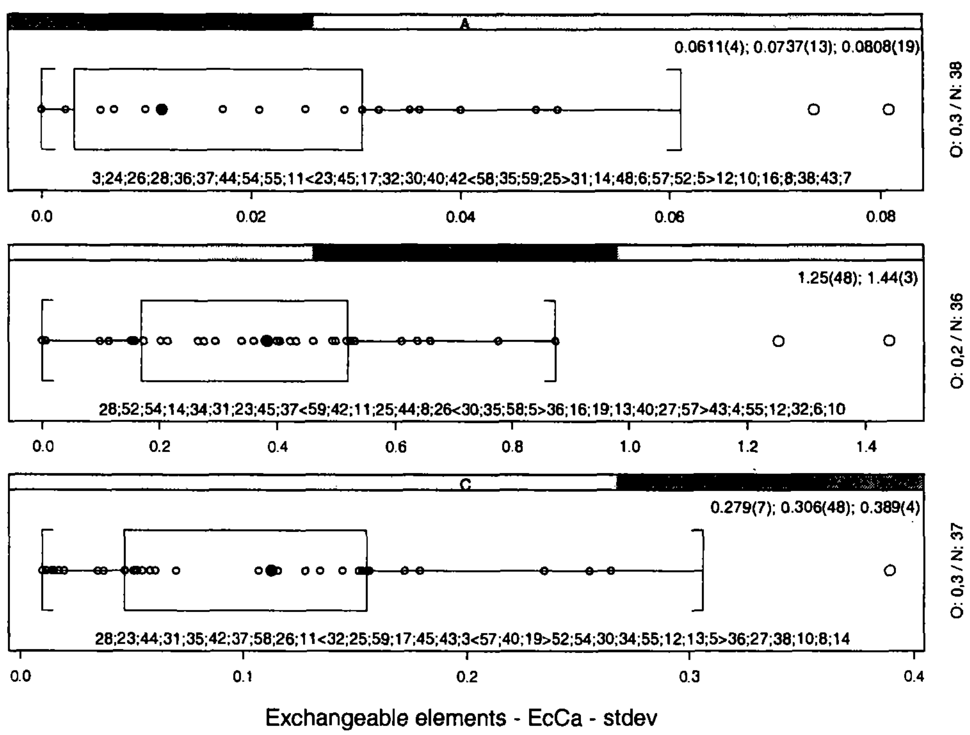


Figure IV. 95: Boxplot stdev - Exchangeable Ca

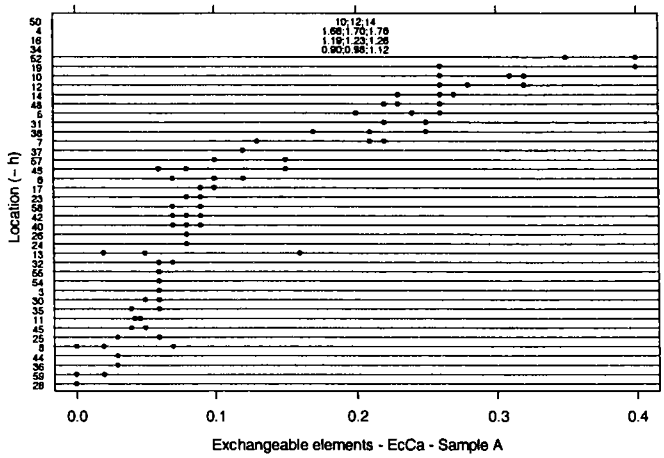


Figure IV. 96: Dotplot - Sample A - Exchangeable Ca

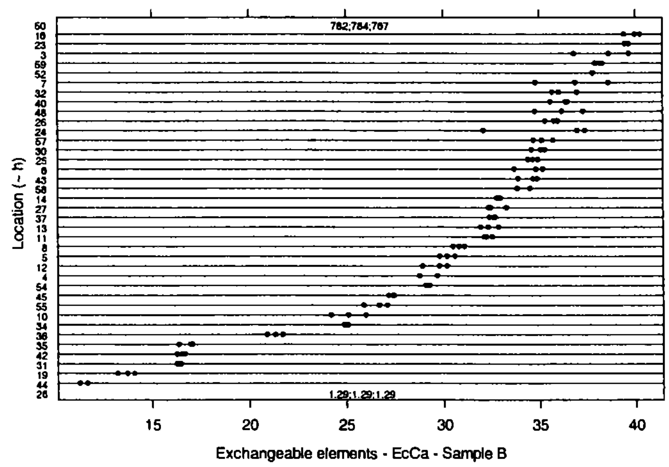


Figure IV. 97: Dotplot - Sample B - Exchangeable Ca

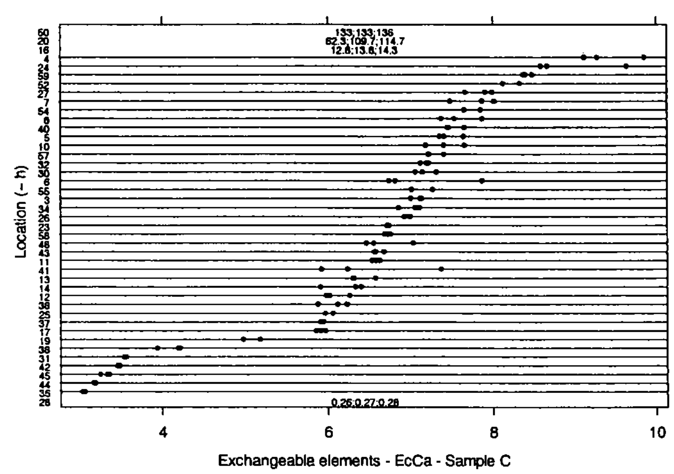


Figure IV. 98: Dotplot - Sample C - Exchangeable Ca

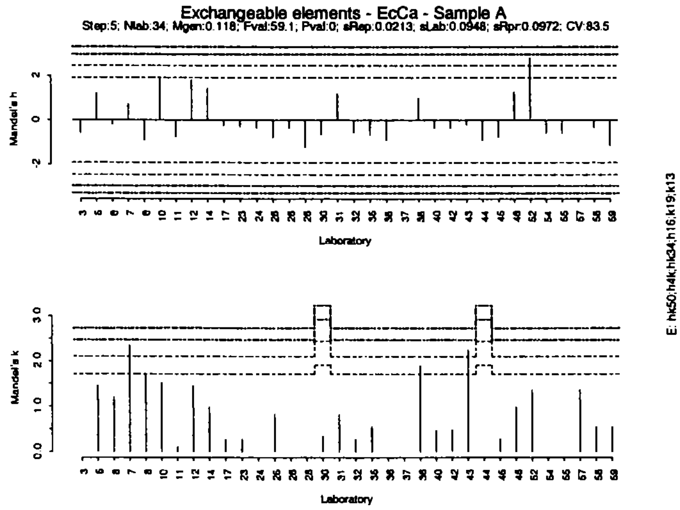


Figure IV. 99: Mandel h/k plot - Sample A - Exchangeable Ca

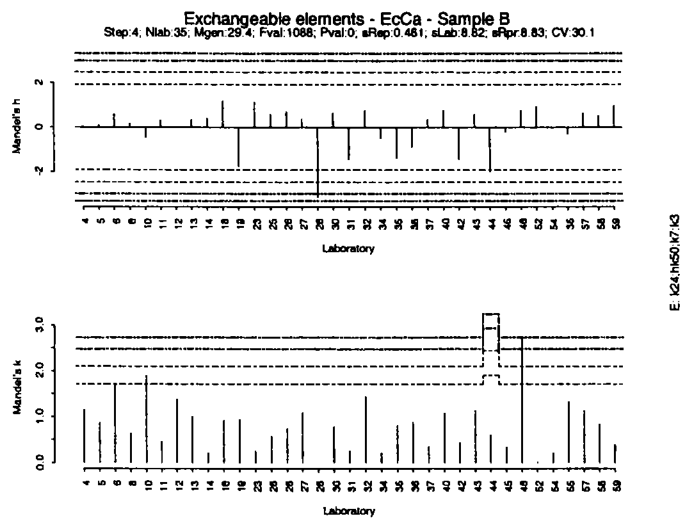


Figure IV. 100: Mandel h/k plot - Sample B mean - Exchangeable Ca

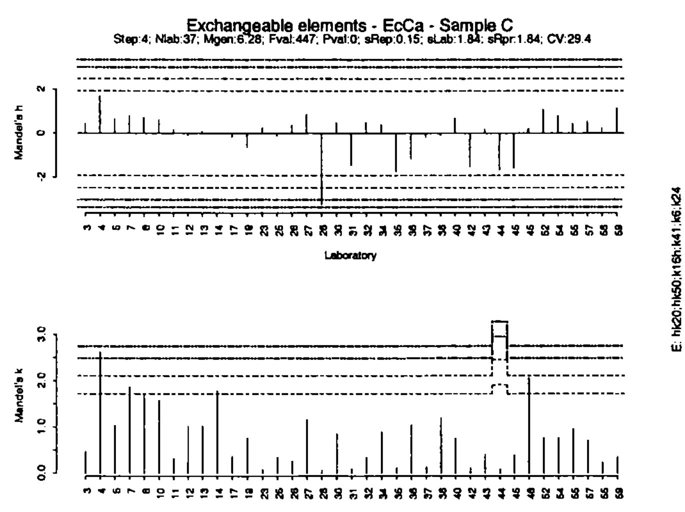


Figure IV. 101: Mandel h/k plot - Sample C mean - Exchangeable Ca

Parameter: Exchangeable Fe

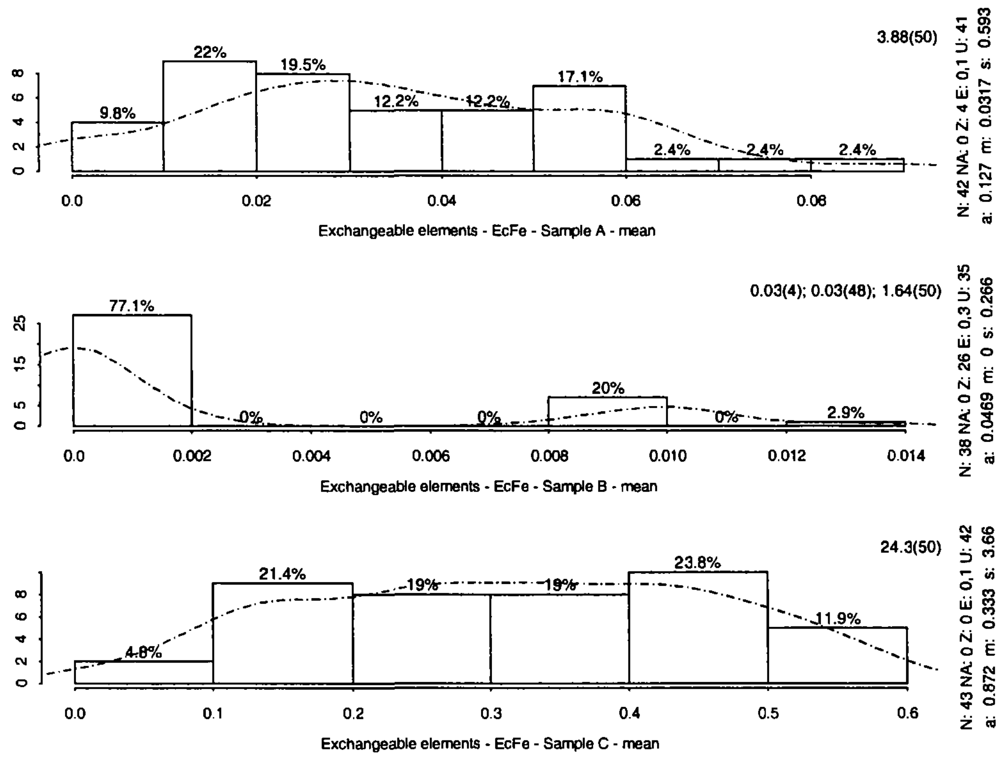


Figure IV. 102: Histogram mean - Exchangeable Ca

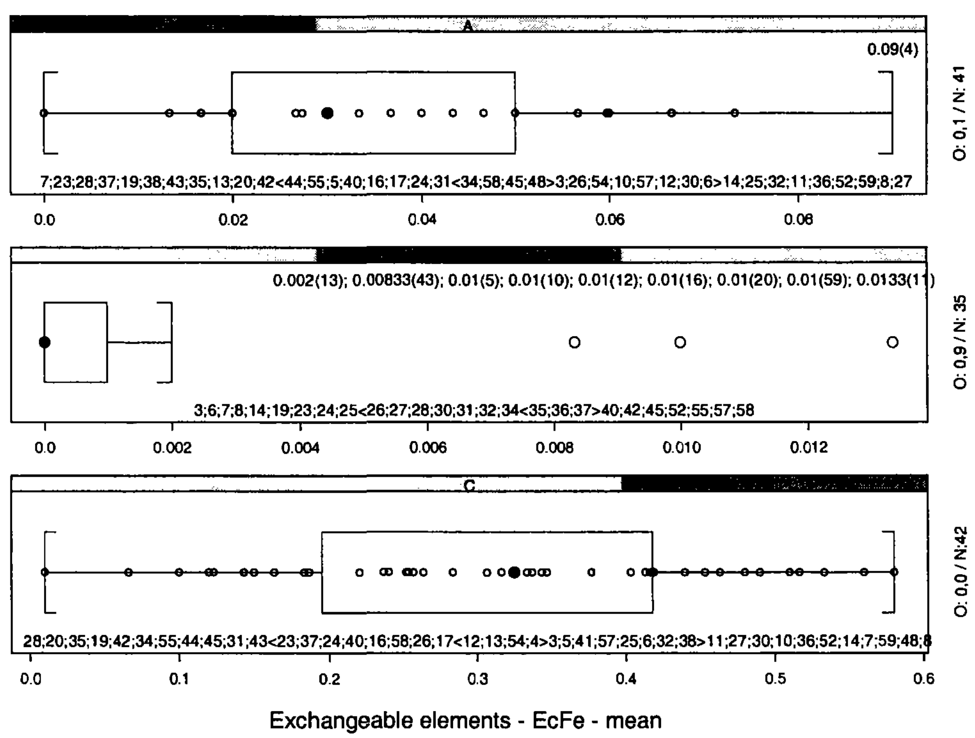


Figure IV.103: Boxplot mean - Exchangeable Ca

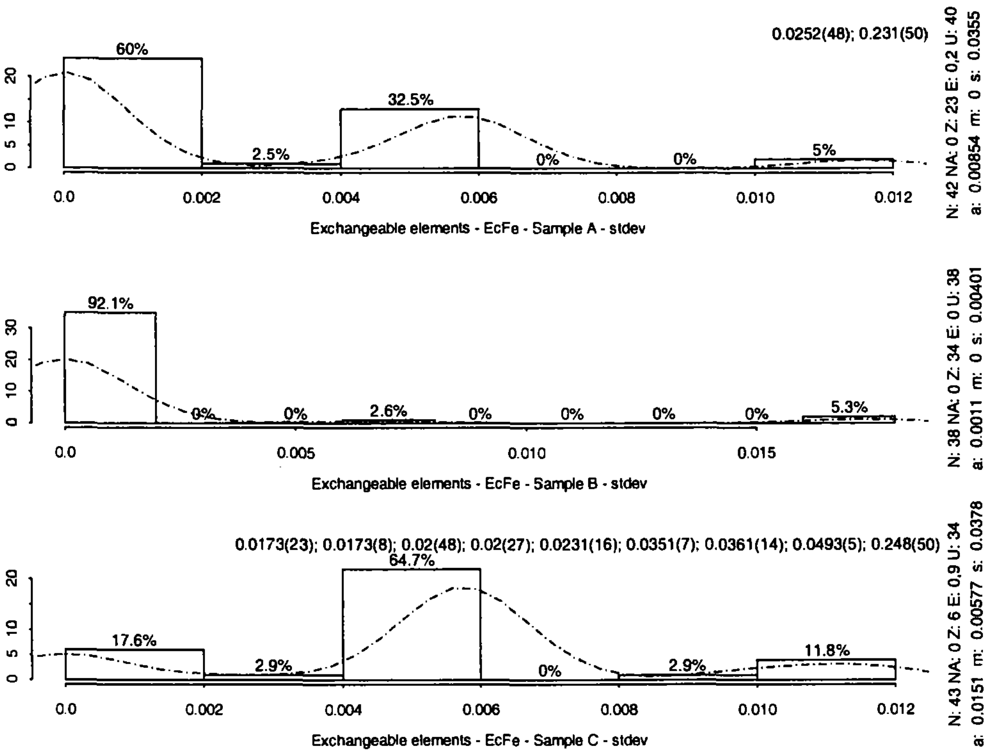


Figure IV.104: Histogram stdev - Exchangeable Ca

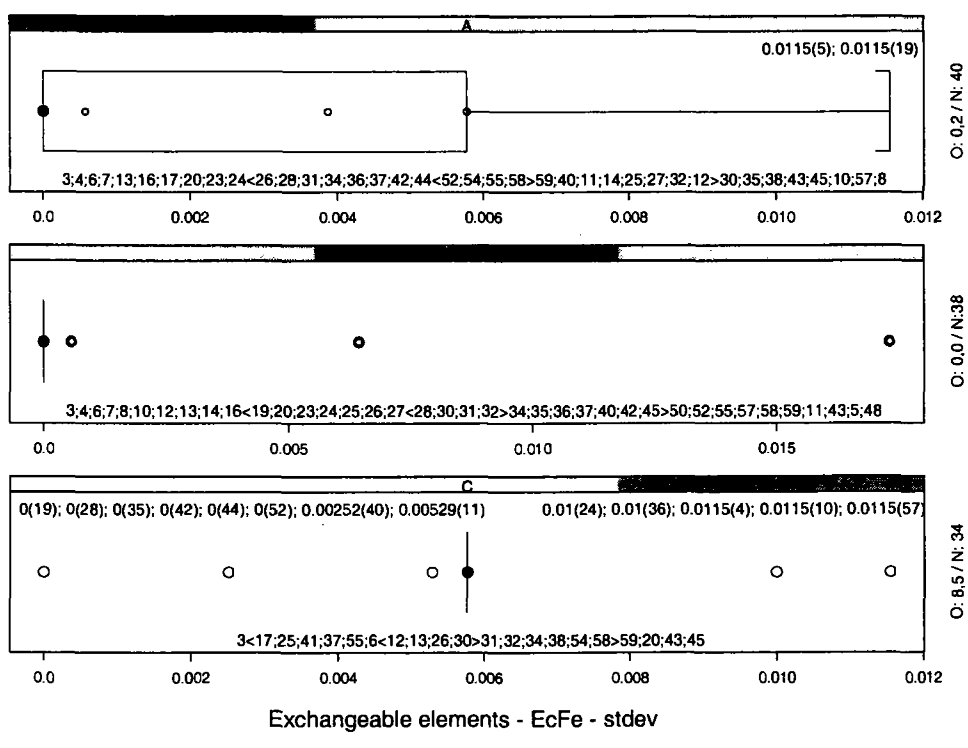


Figure IV.105: Boxplot stdev - Exchangeable Ca

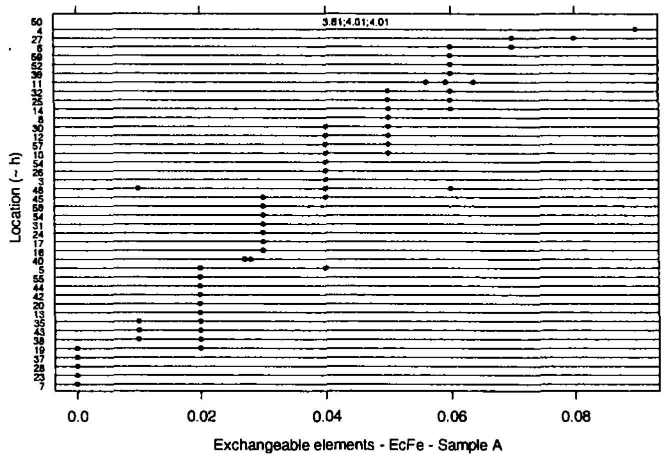


Figure IV.106: Dotplot - Sample A- Exchangeable Ca

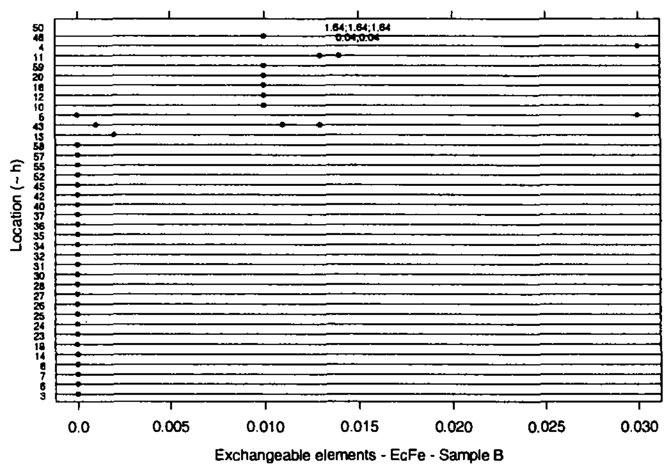


Figure IV.107: Dotplot - Sample B - Exchangeable Ca

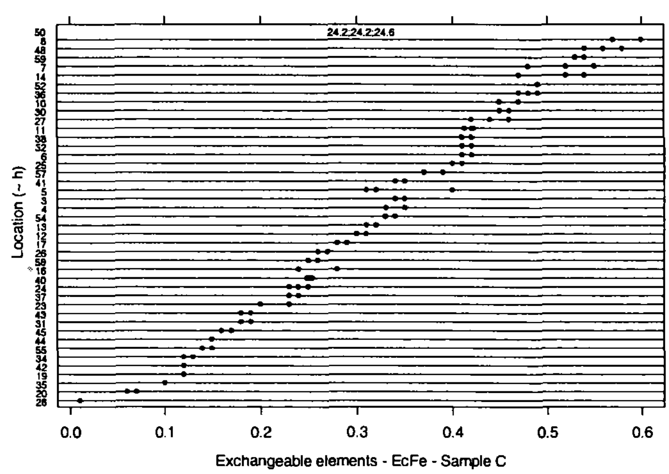


Figure IV.108: Dotplot – Sample Cv - Exchangeable Ca

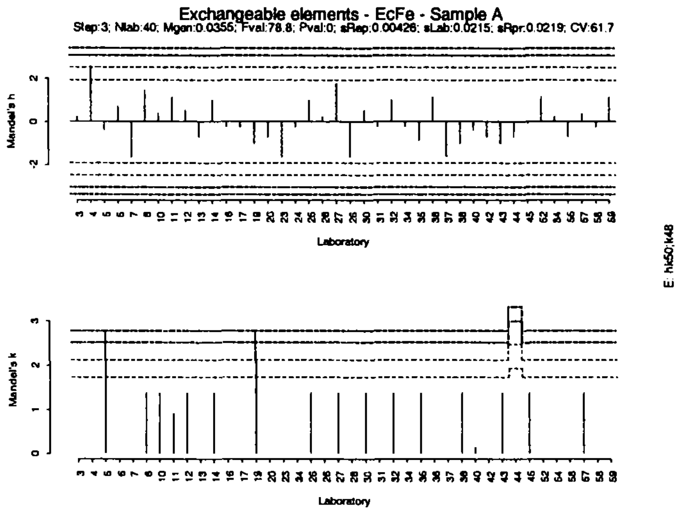


Figure IV.109: Mandel's h and k plot - Sample A - Exchangeable Ca

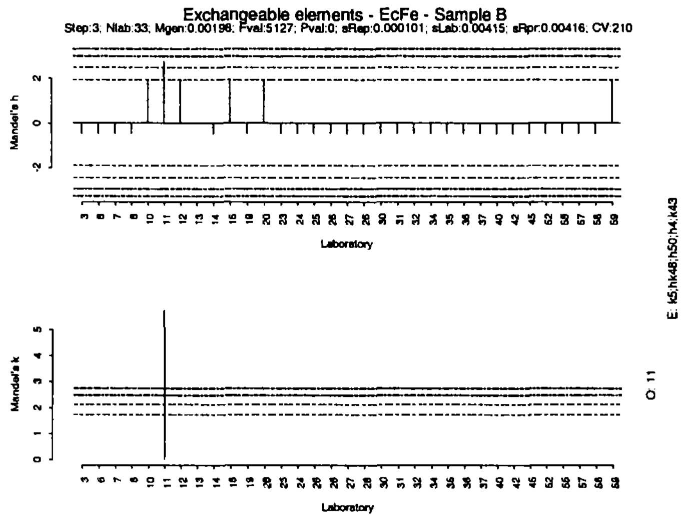


Figure IV.110: Mandel's h and k plot - Sample B - Exchangeable Ca

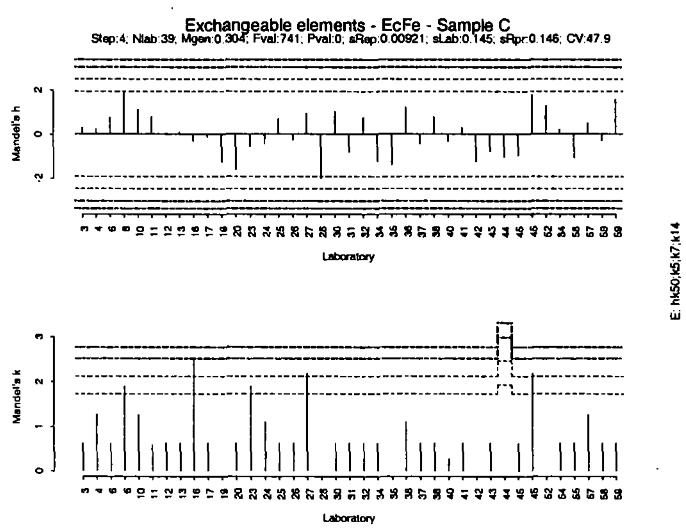


Figure IV.111: Mandel's h and k plot - Sample C - Exchangeable Ca

Parameter: Exchangeable K

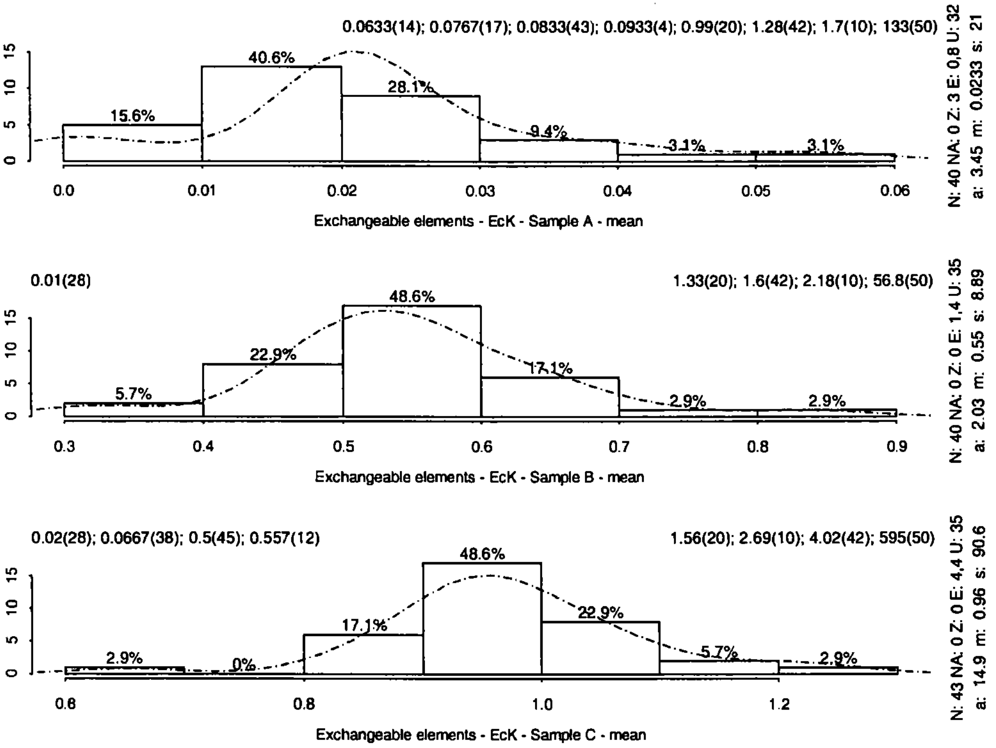


Figure IV.112: Histogram mean – Exchangeable K

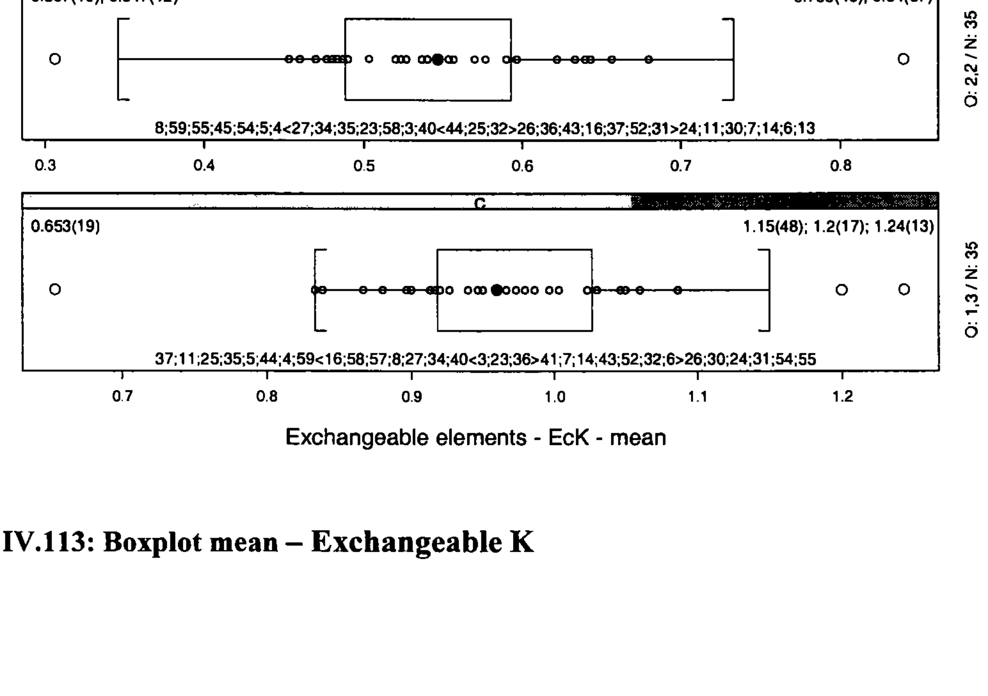


Figure IV.113: Boxplot mean – Exchangeable K

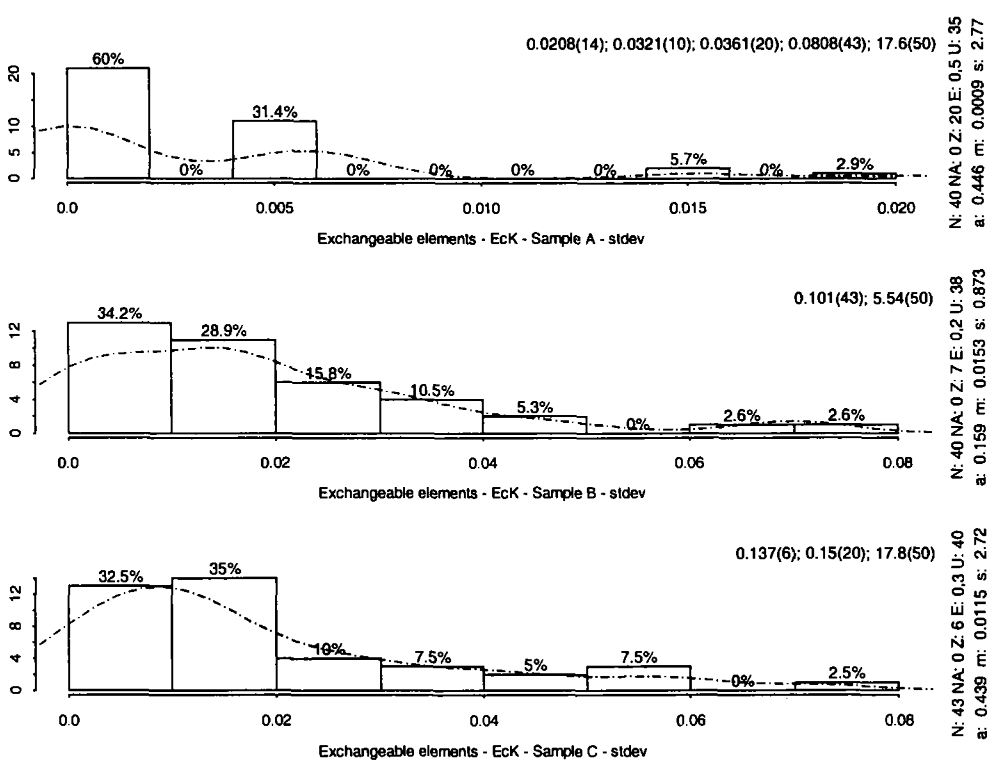


Figure IV.114: Histogram stdev – Exchangeable K

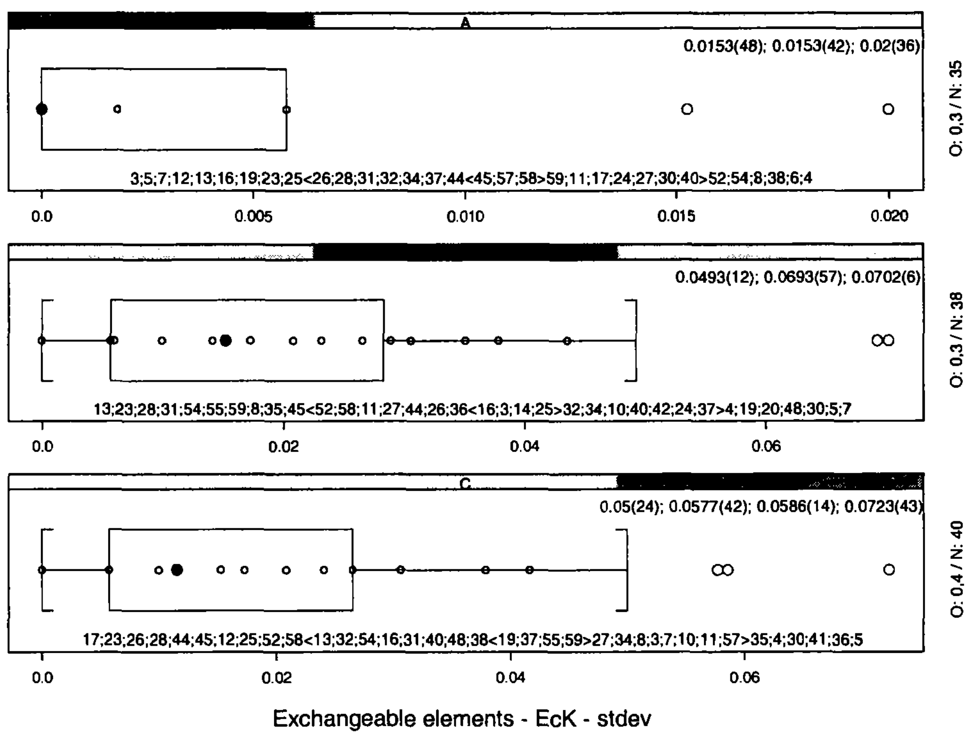


Figure IV.115: Boxplot stdev– Exchangeable K

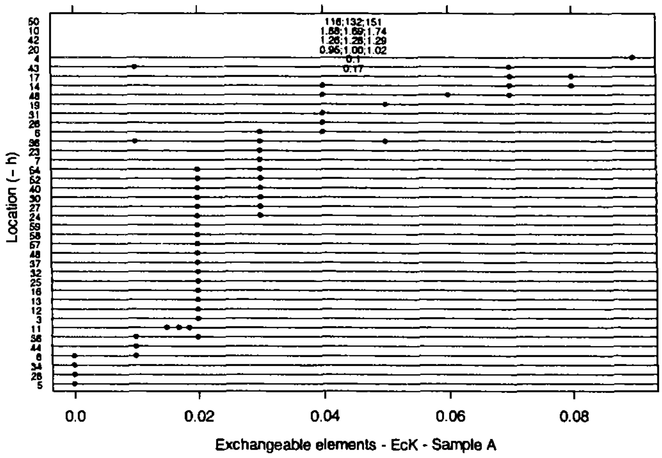


Figure IV.116: Dotplot - Sample A – Exchangeable K

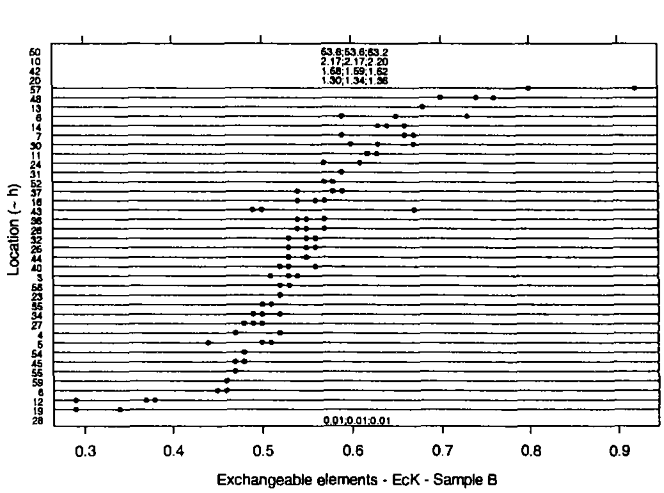


Figure IV.117: Dotplot - Sample B mean – Exchangeable K

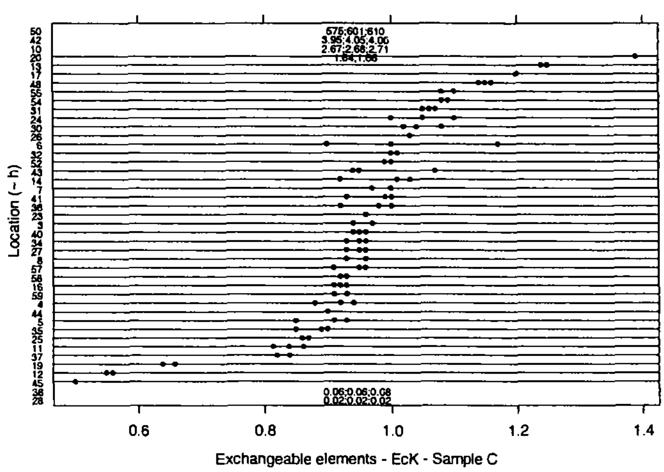


Figure IV.118: Dotplot - Sample C mean – Exchangeable K

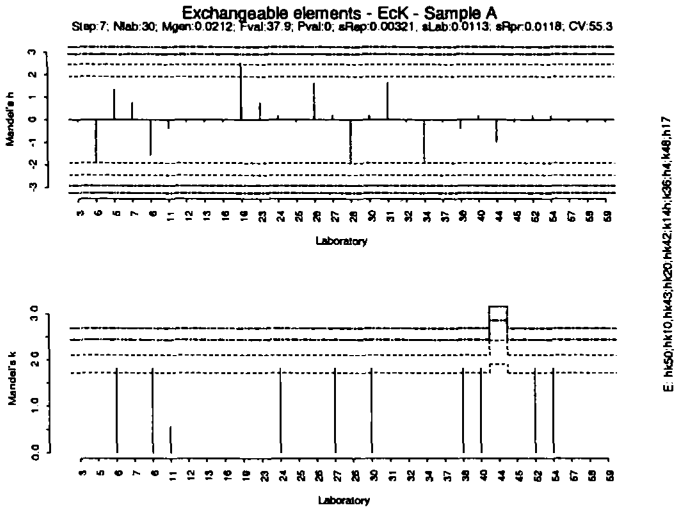


Figure IV.119: Sample A mean – Exchangeable K

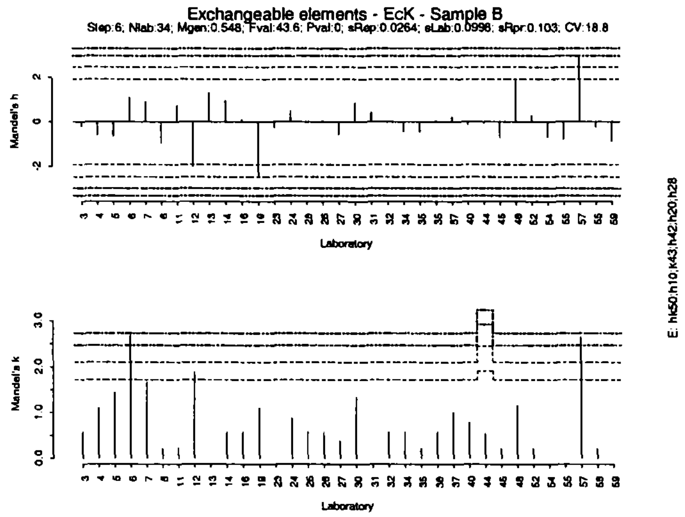


Figure IV.120: Sample B mean – Exchangeable K

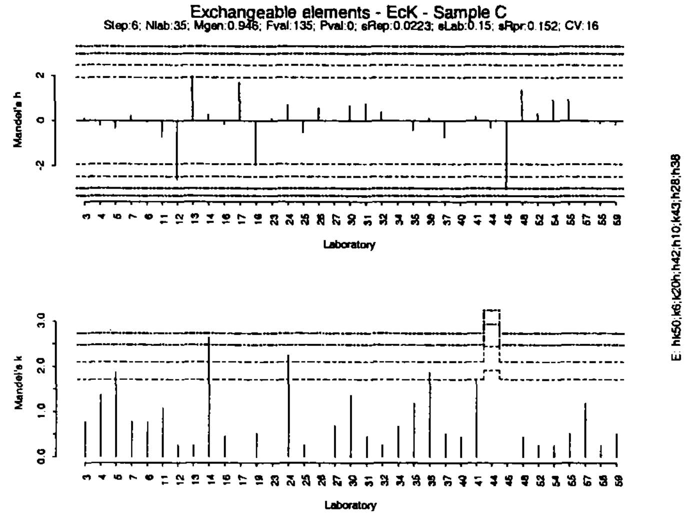


Figure IV.121: Sample C mean – Exchangeable K

Parameter: Exchangeable Mg

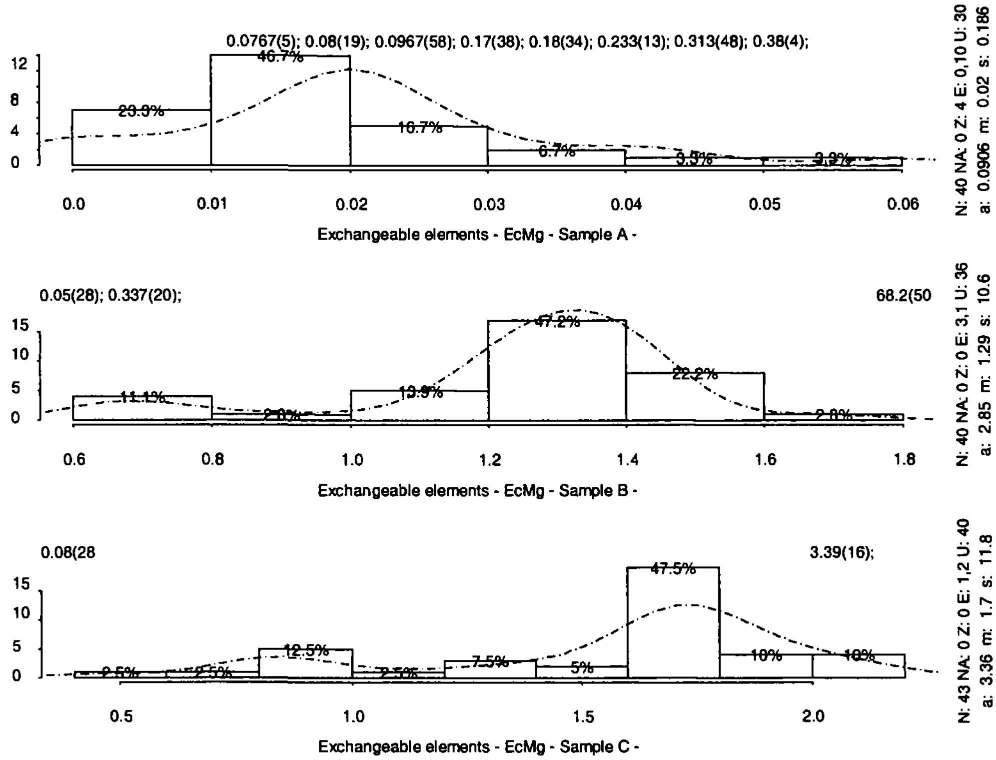


Figure IV.122: Histogram mean – Exchangeable Mg

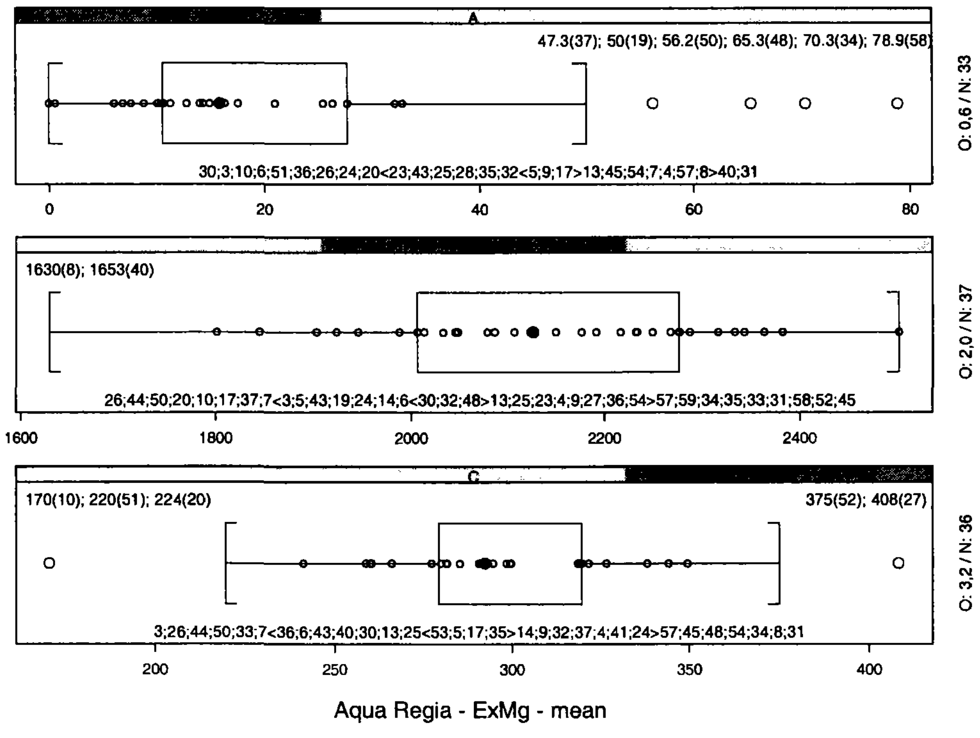


Figure IV.123: Boxplot mean – Exchangeable Mg

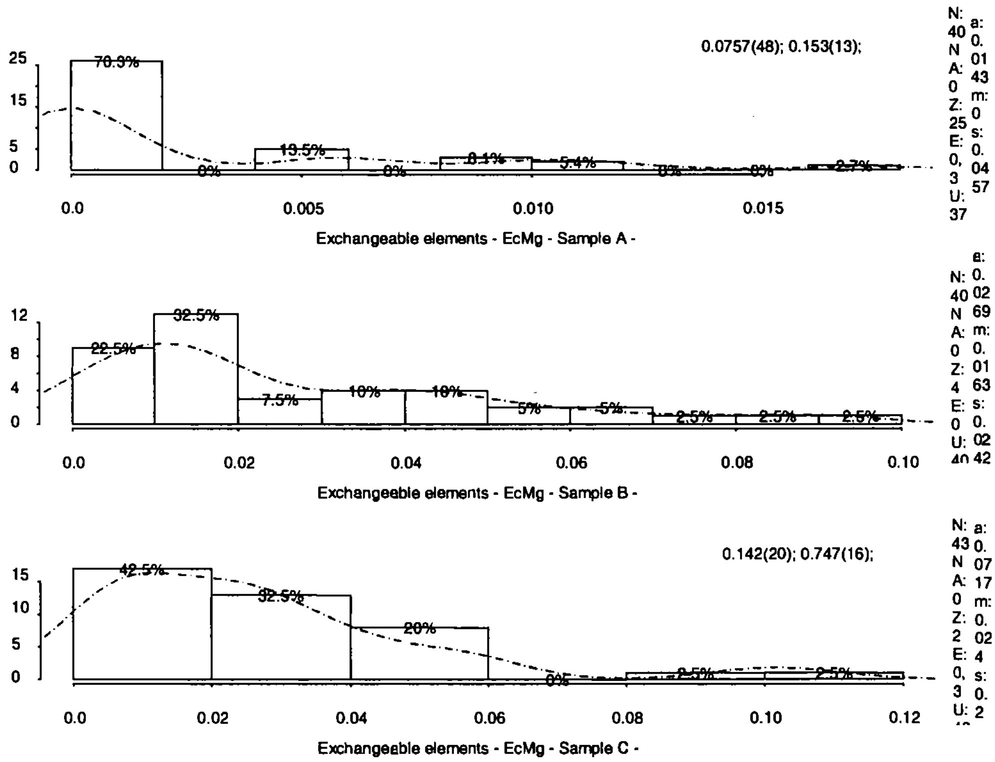


Figure IV.124: Histogram stdev – Exchangeable Mg

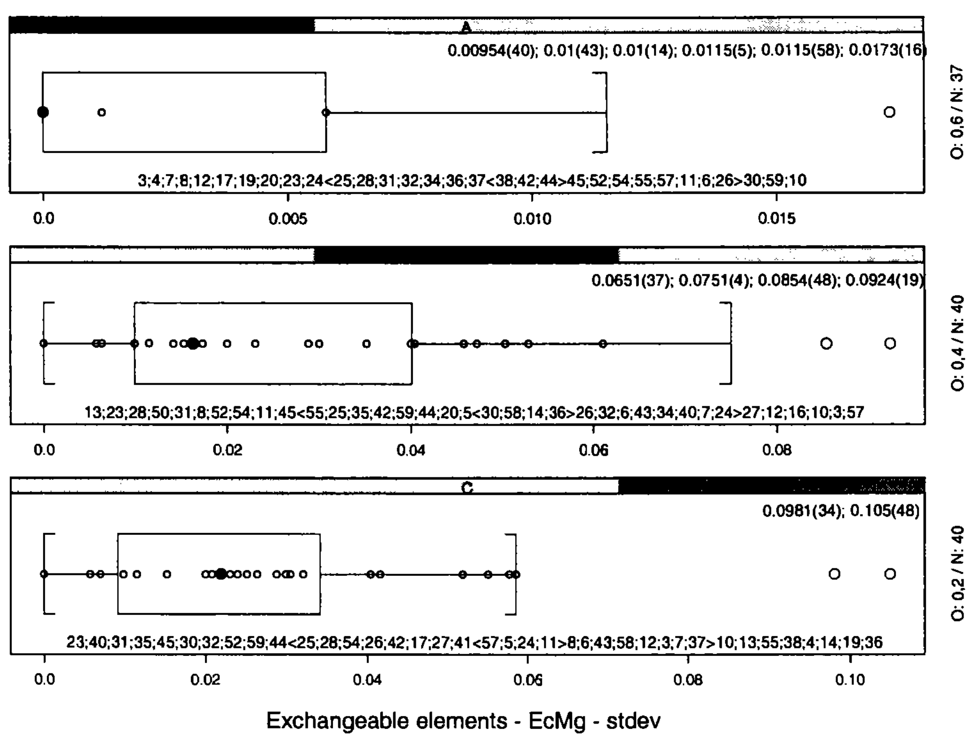


Figure IV.125: Boxplot stdev– Exchangeable Mg

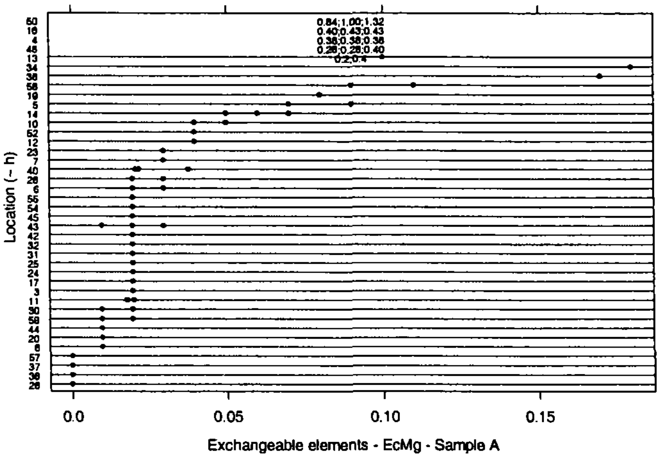


Figure IV.126: Dotplot - Sample A– Exchangeable Mg

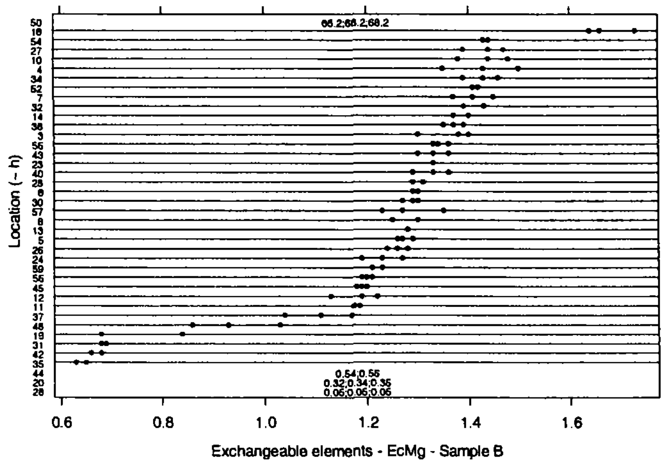


Figure IV.127: Dotplot – Sample B – Exchangeable Mg

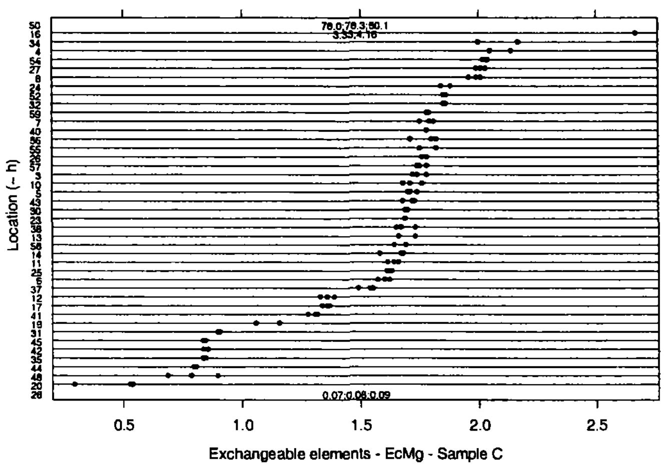


Figure IV.128: Dotplot - Sample C – Exchangeable Mg

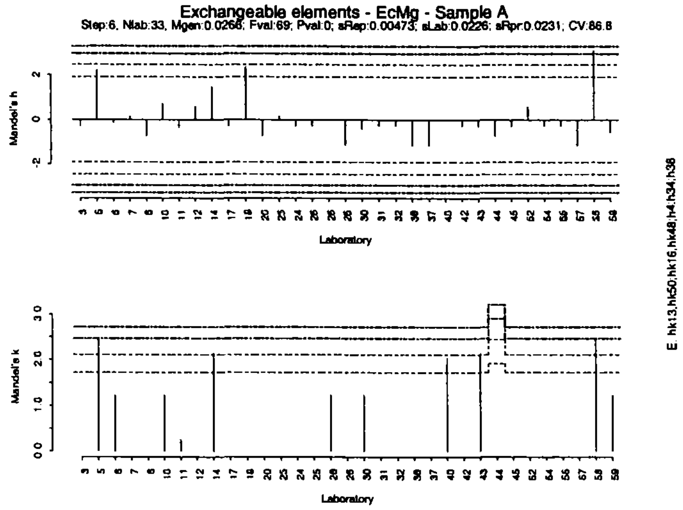


Figure IV.129: Mandel's h/k plot – Sample A – Exchangeable Mg

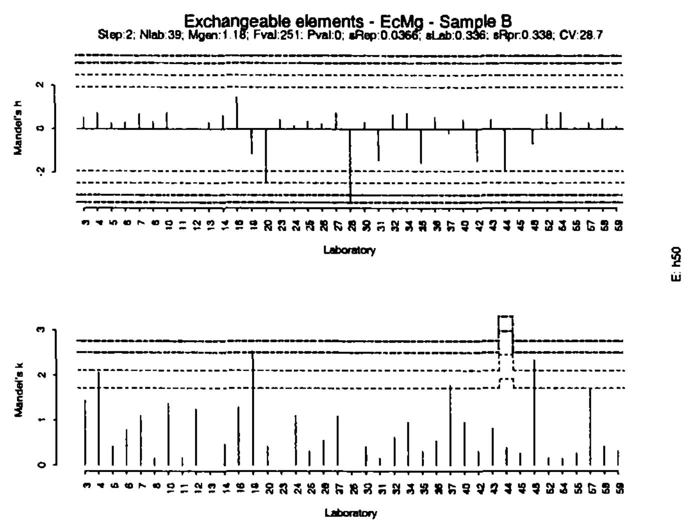


Figure IV.130: Mandel h/k plot – Sample B – Exchangeable Mg

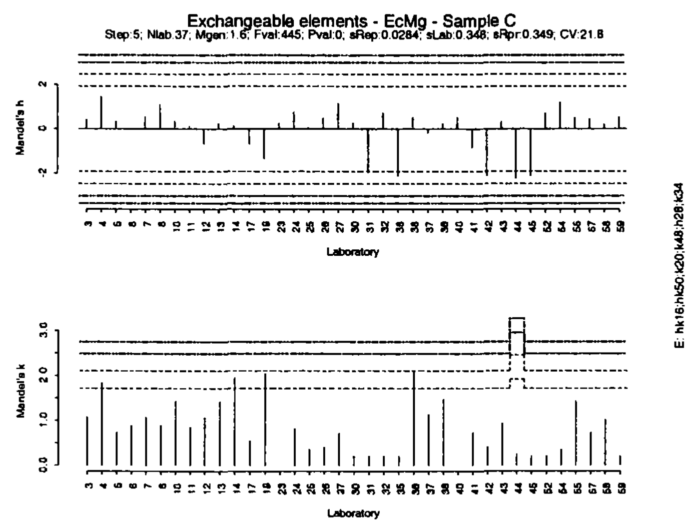


Figure IV.131: Mandel h/k plot – Sample C – Exchangeable Mg

Parameter: Exchangeable Mn

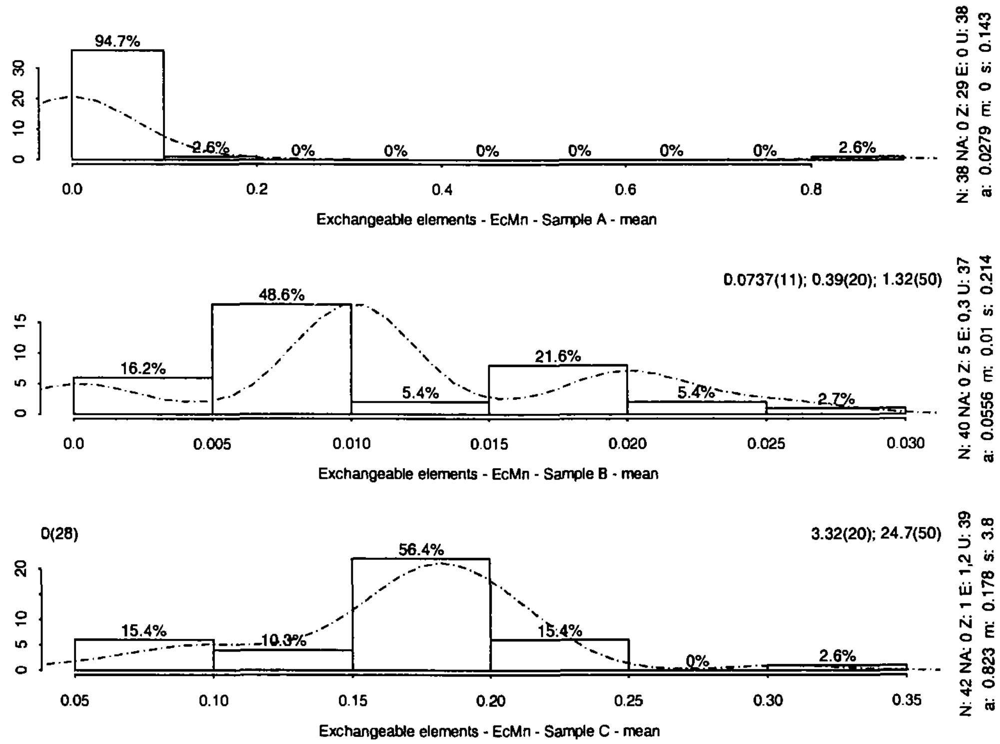


Figure IV.132: Histogram mean – Exchangeable Mn

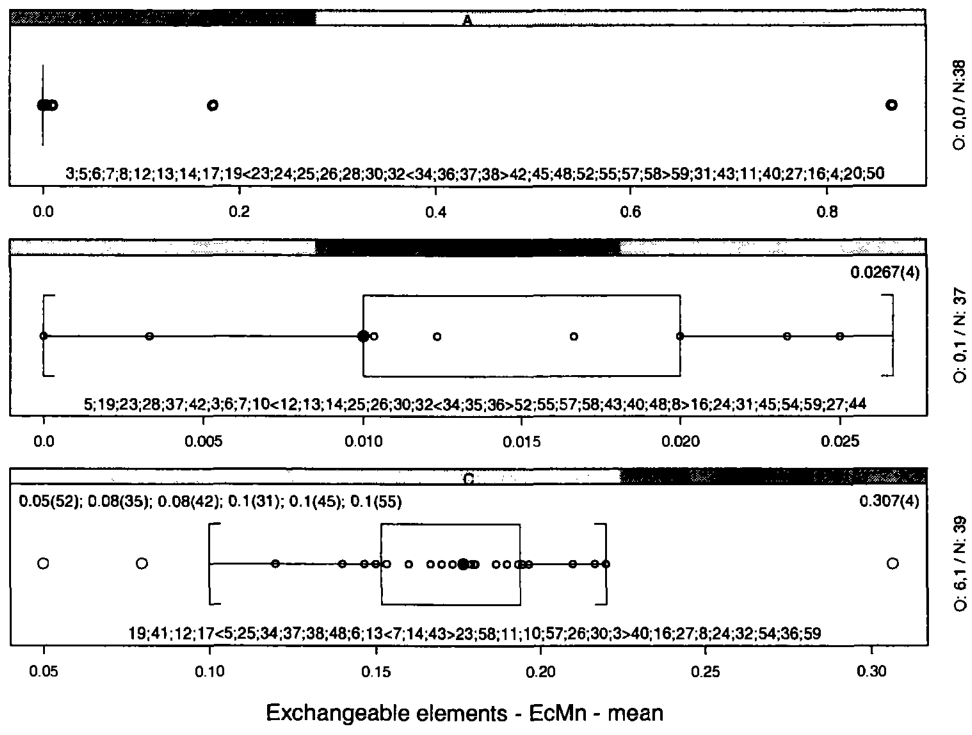


Figure IV.133: Boxplot mean – Exchangeable Mn

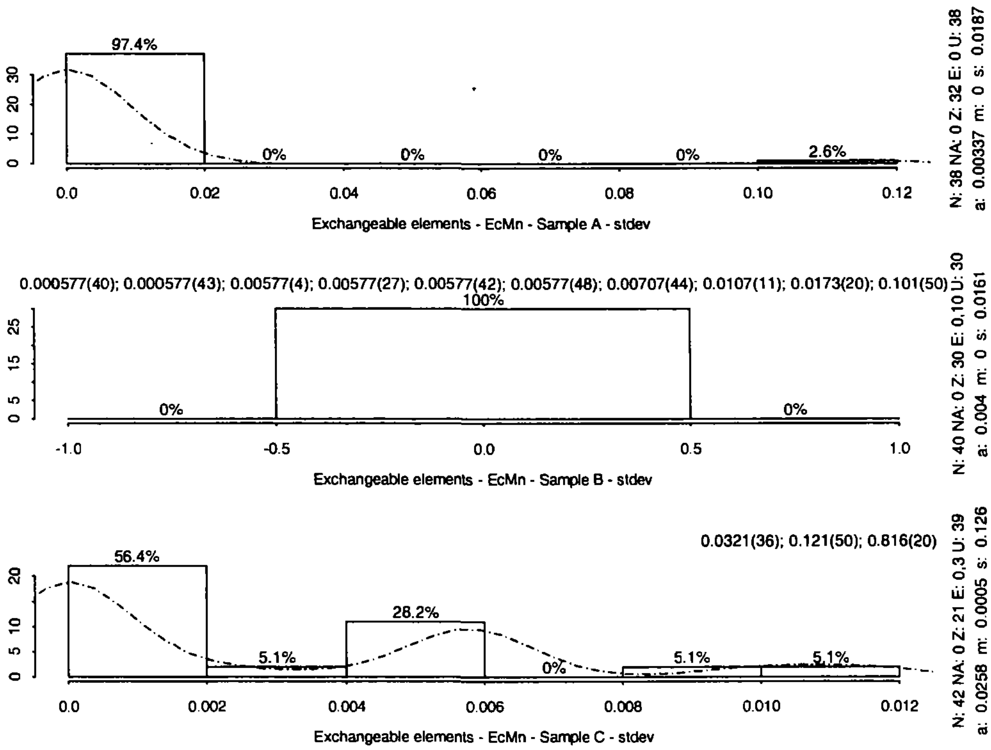


Figure IV.134: Histogram stdev – Exchangeable Mn

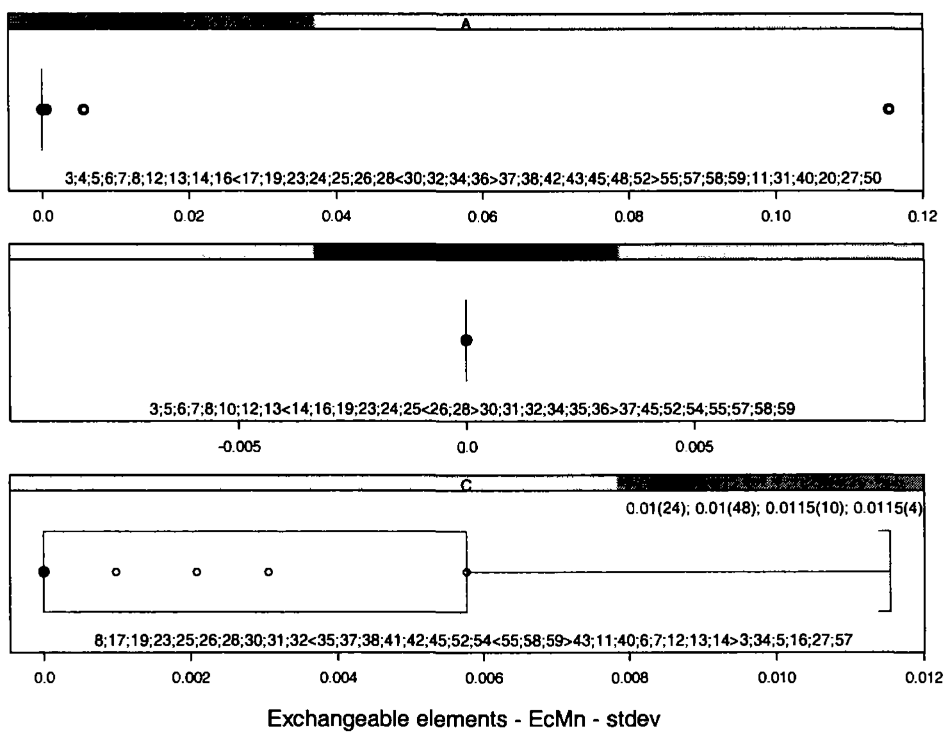


Figure IV.135: Boxplot stdev – Exchangeable Mn

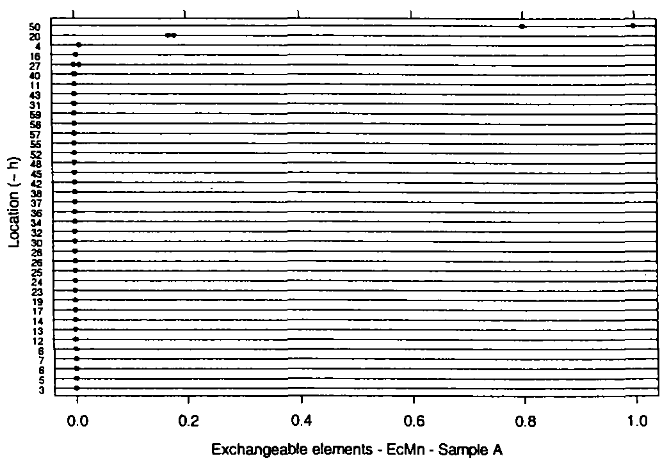


Figure IV.136: Dotplot - Sample A – Exchangeable Mn

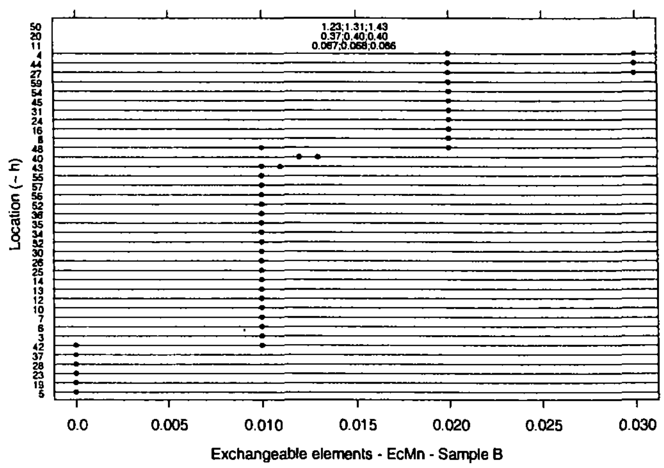


Figure IV.137: Dotplot - Sample B – Exchangeable Mn

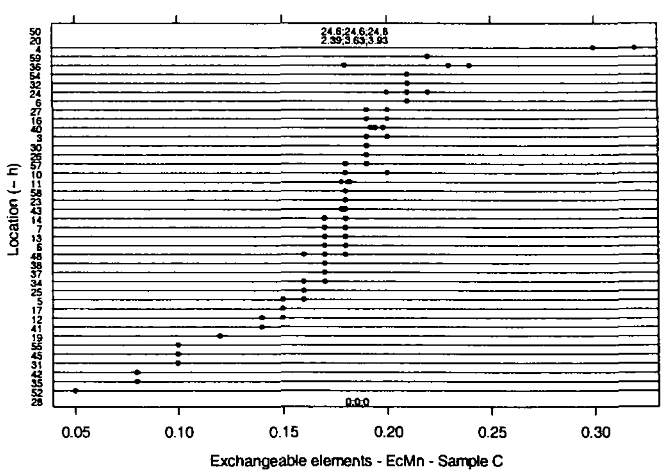


Figure IV.138: Dotplot - Sample C – Exchangeable Mn

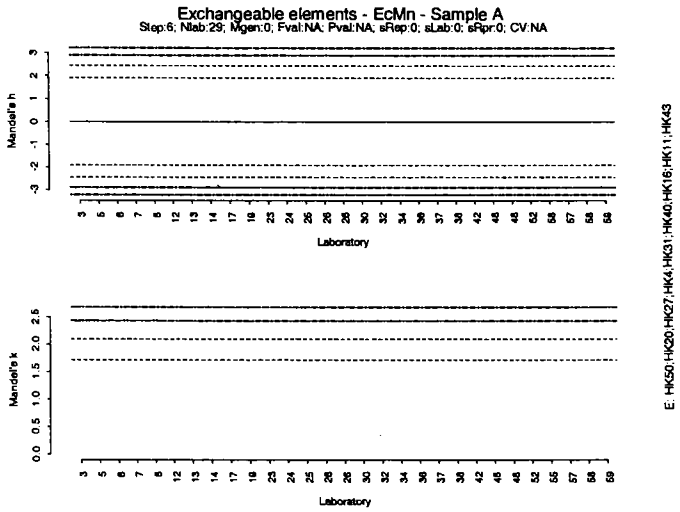


Figure IV.139: Mandel h/k plot - Sample A – Exchangeable Mn

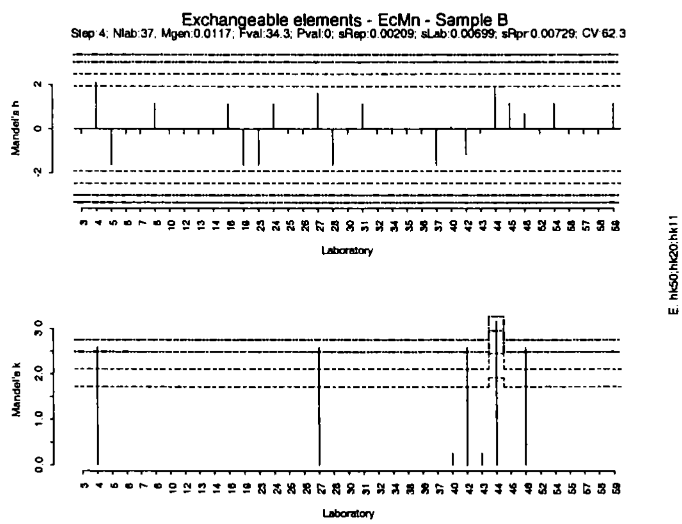


Figure IV.140: Mandel h/k plot - Sample B – Exchangeable Mn

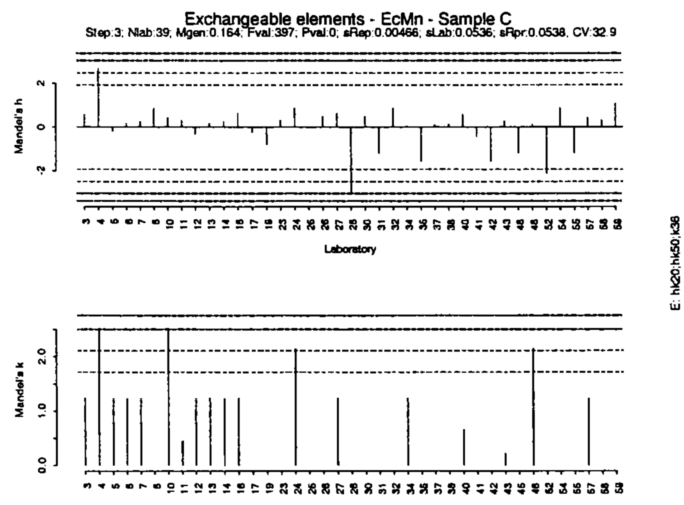


Figure IV.141: Mandel h/k plot - Sample C – Exchangeable Mn

Parameter: Exchangeable Na

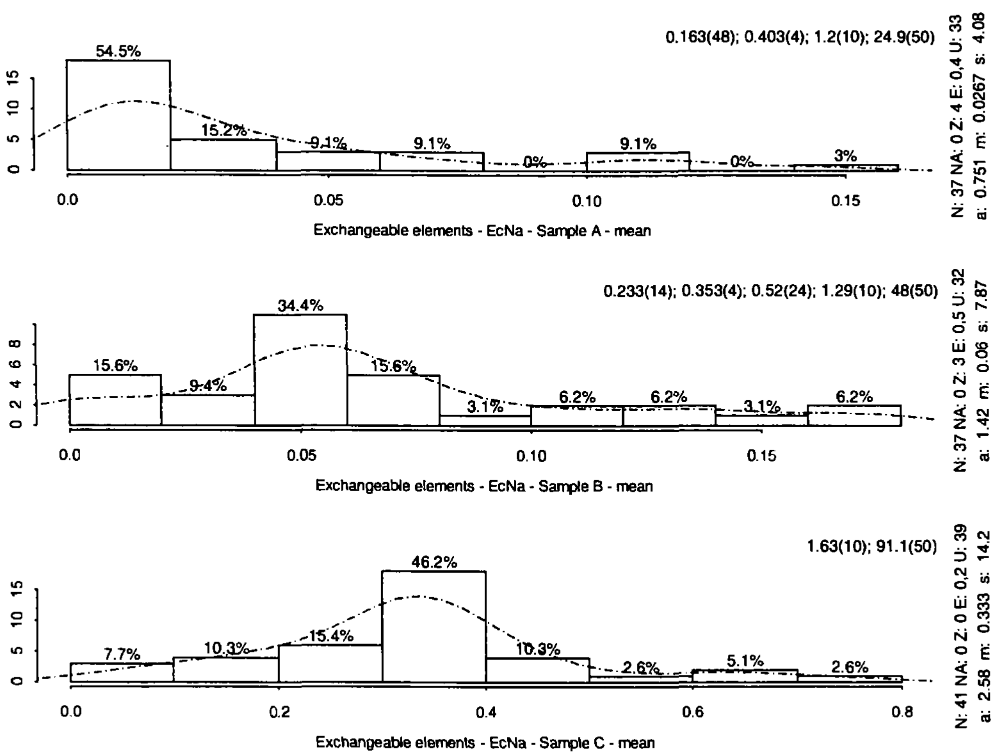


Figure IV.142: Histogram mean – Exchangeable Na

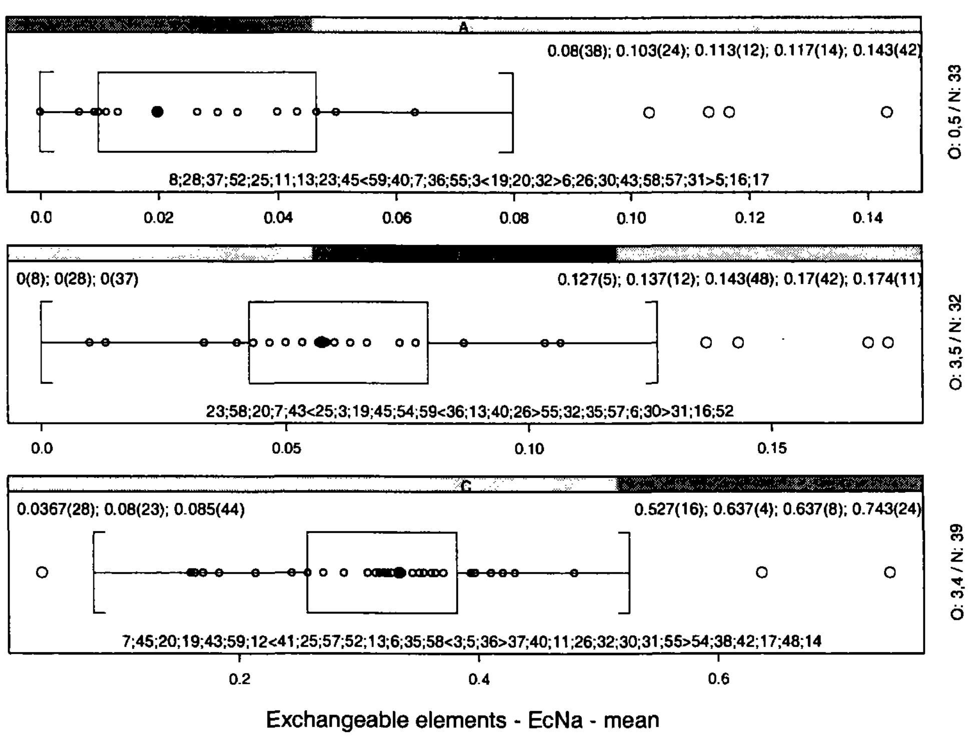


Figure IV.143: Boxplot mean – Exchangeable Na

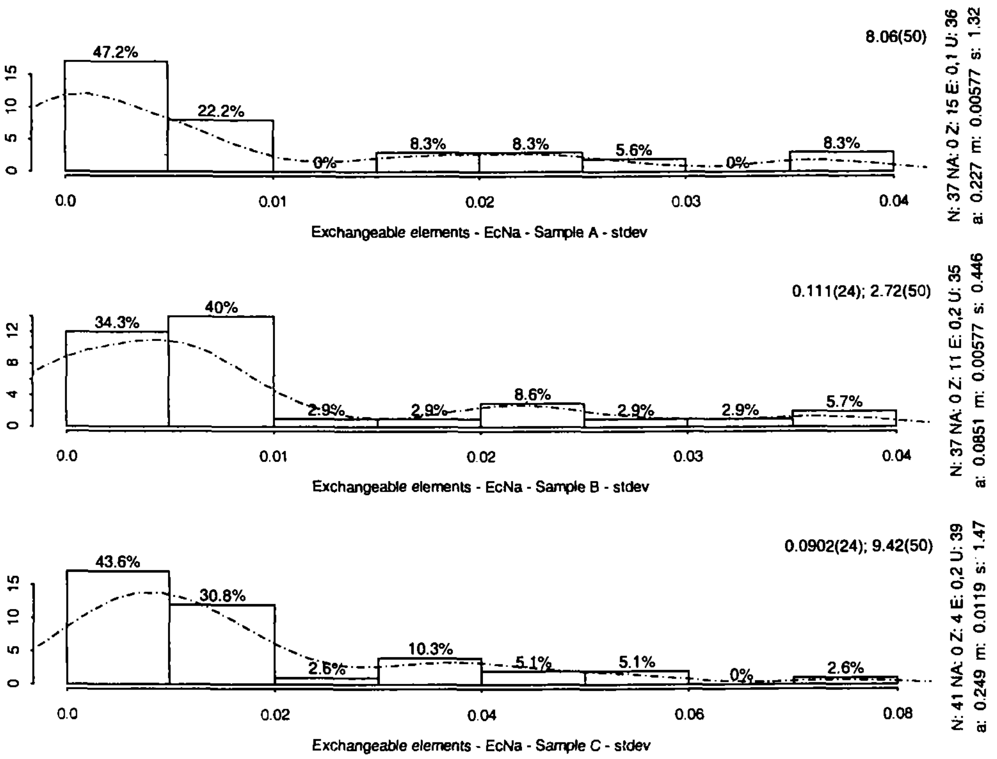


Figure IV.144: Histogram stdev – Exchangeable Na

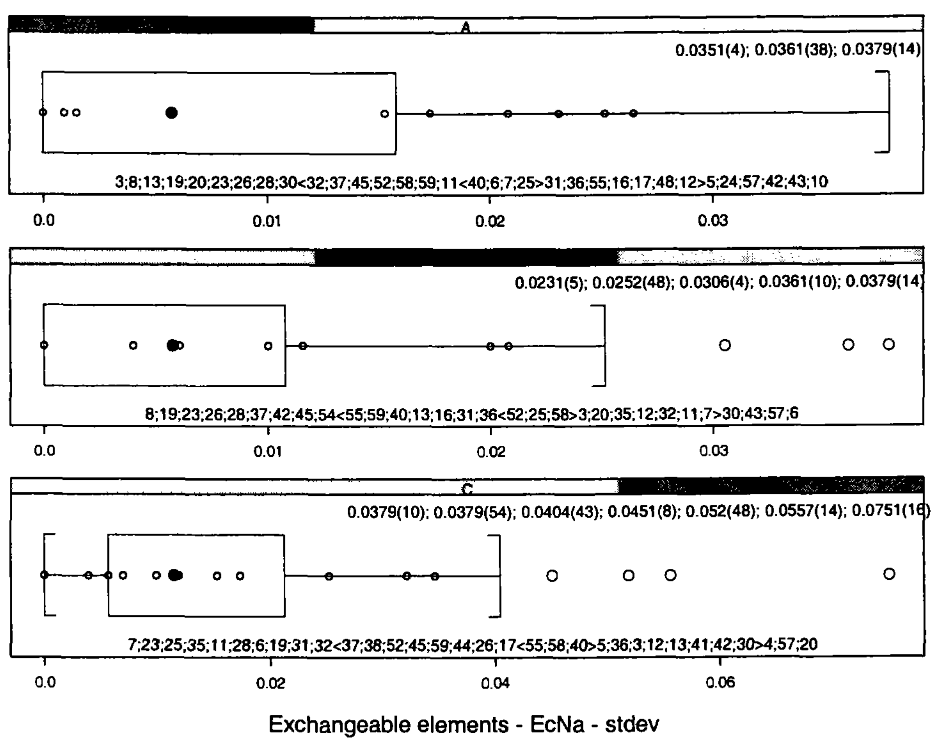


Figure IV.145: Boxplot stdev – Exchangeable Na

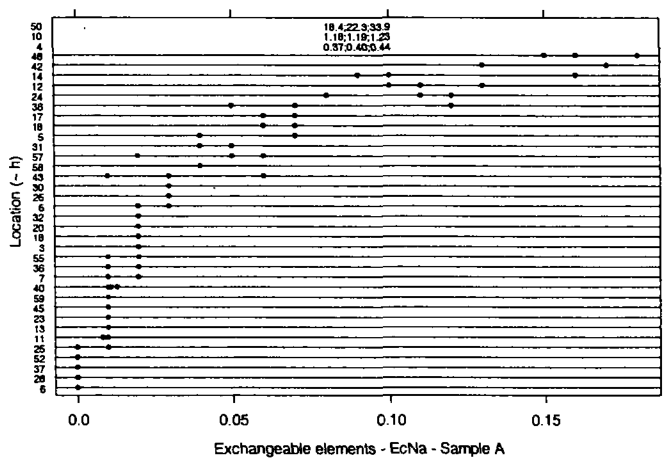


Figure IV.146: Dotplot - Sample A – Exchangeable Na

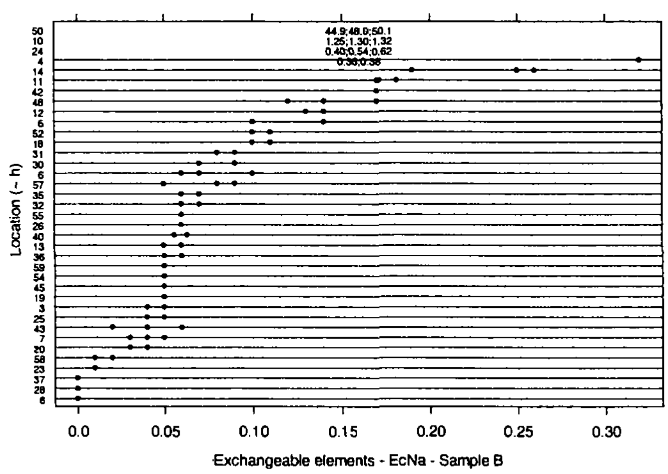


Figure IV.147: Dotplot - Sample B – Exchangeable Na

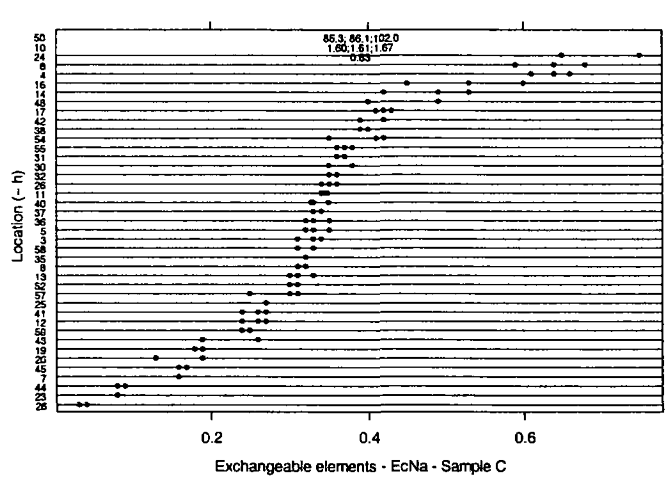


Figure IV.148: Dotplot - Sample C – Exchangeable Na

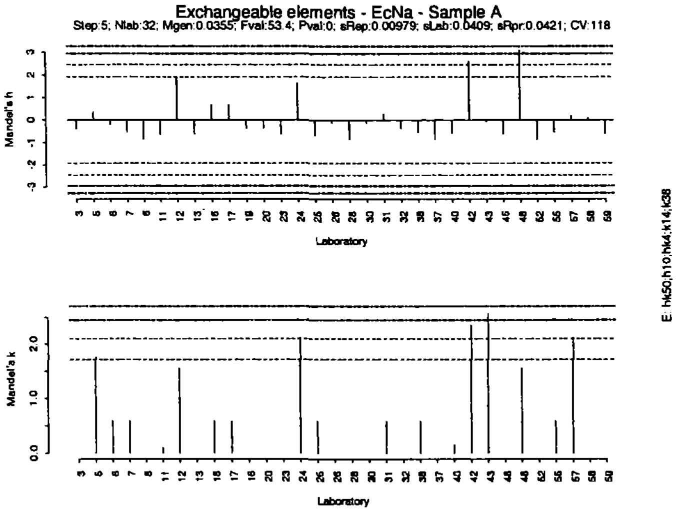


Figure IV.149: Mandel h/k plot - Sample A – Exchangeable Na

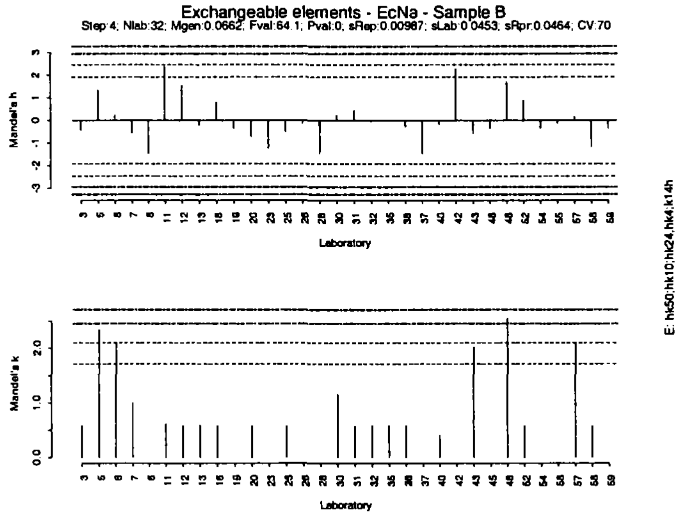


Figure IV.150: Mandel h/k plot – Sample B – Exchangeable Na

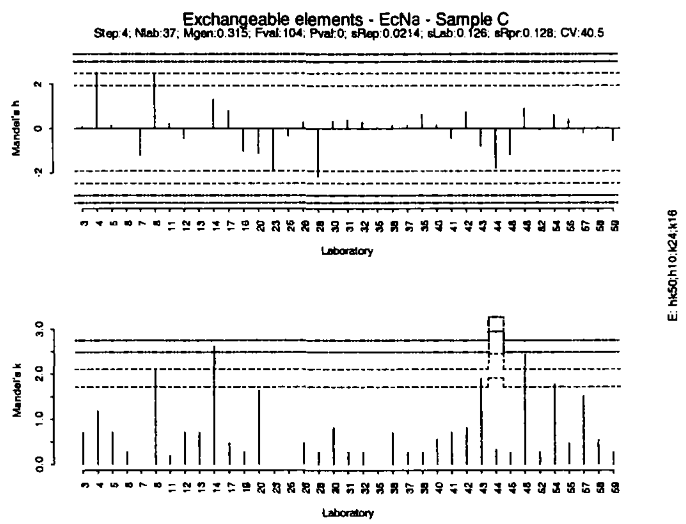


Figure IV.151: Mandel h/k plot - Sample C– Exchangeable Na

Parameter: Free H^+ Acidity

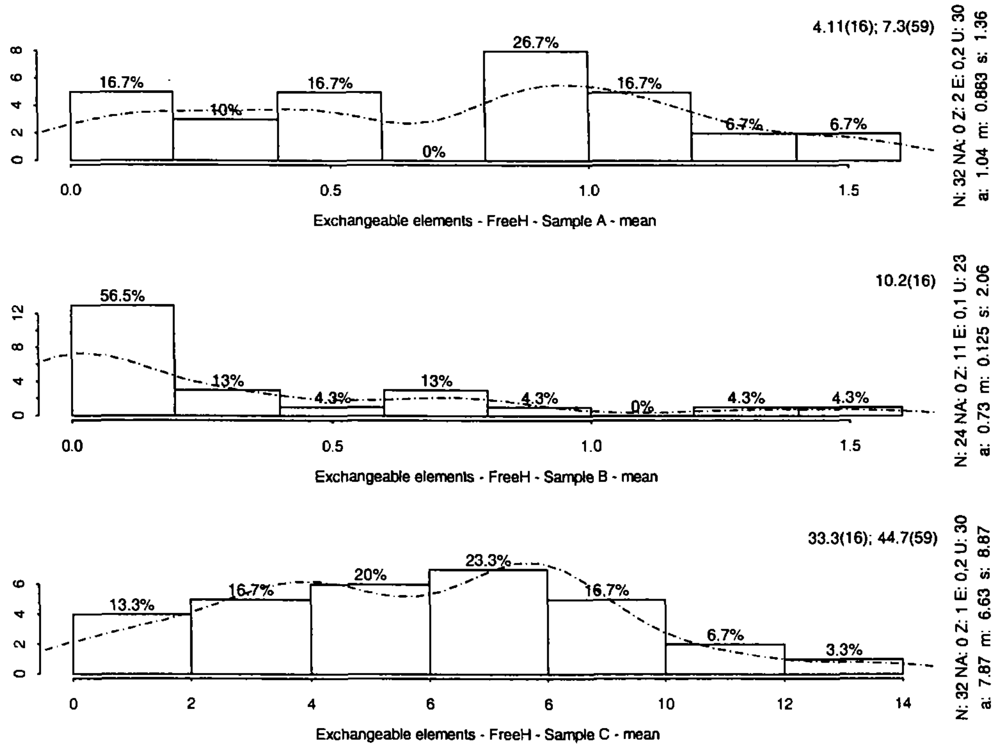


Figure IV.152: Histogram mean – Free H+ acidity

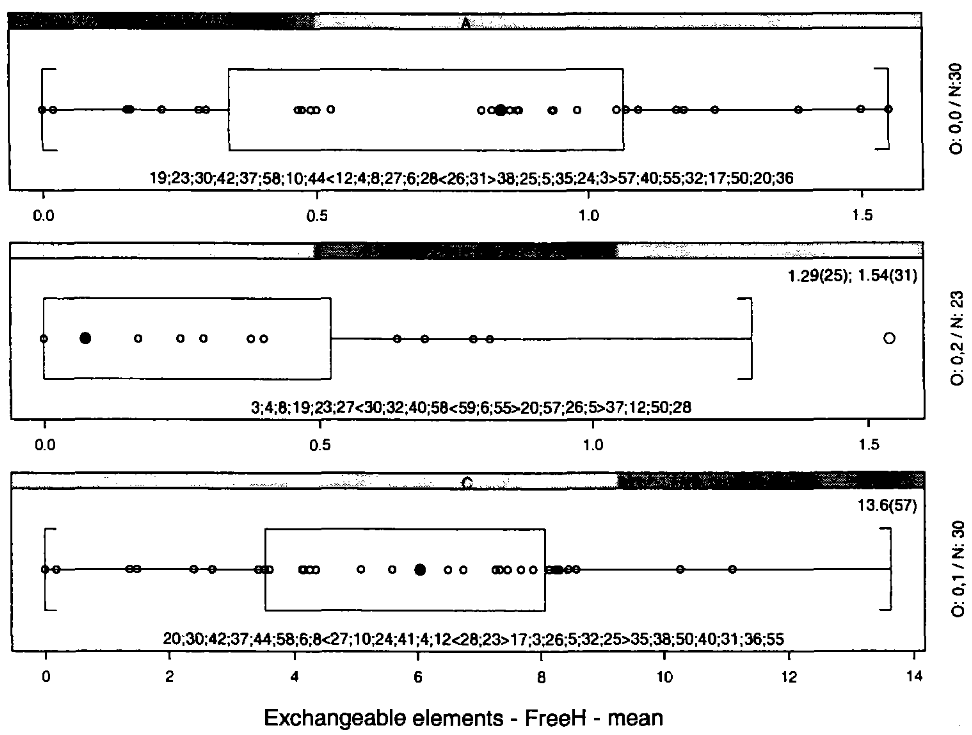


Figure IV.153: Boxplot mean - Free H+ acidity

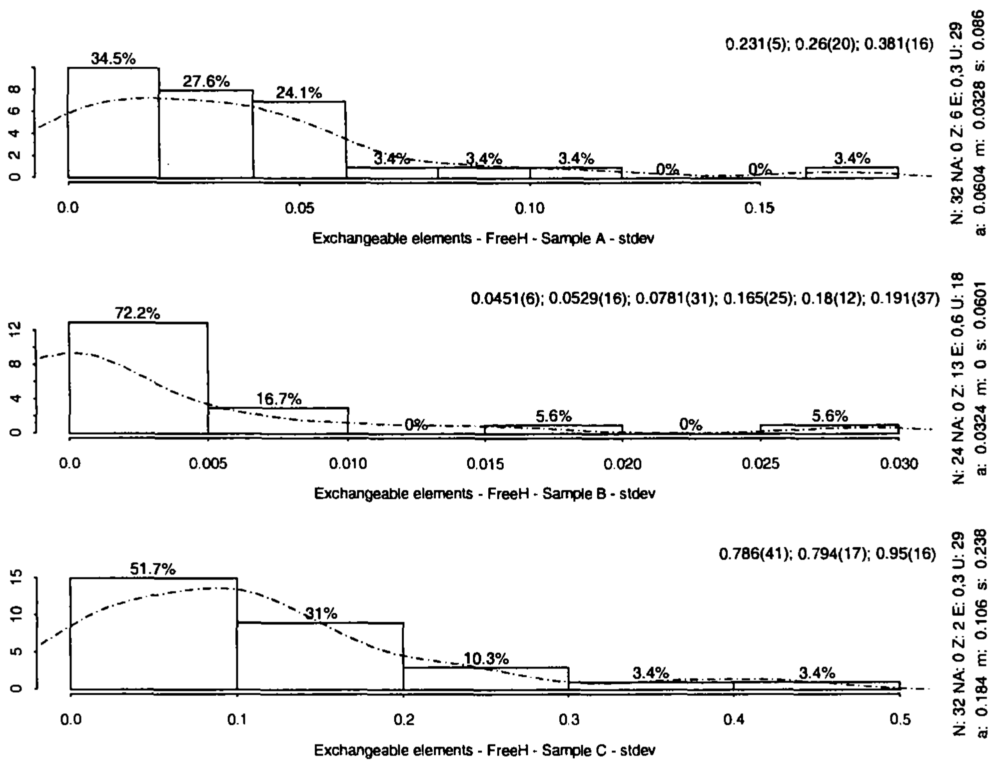


Figure IV.154: Histogram stdev - Free H+ acidity

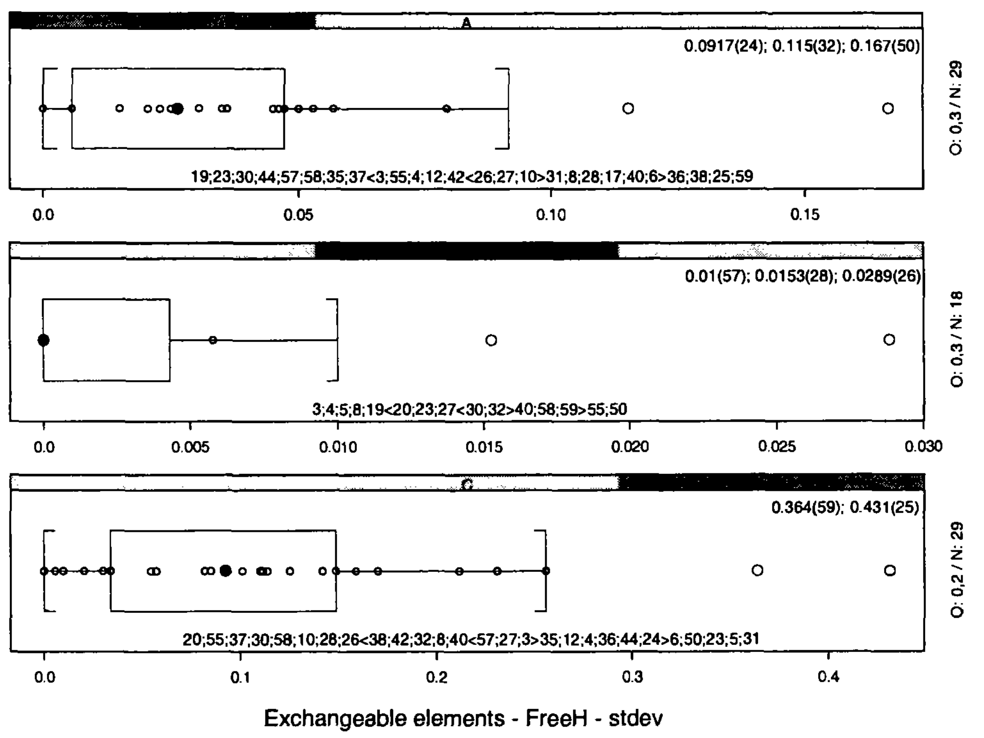


Figure IV.155: Boxplot stdev - Free H+ acidity

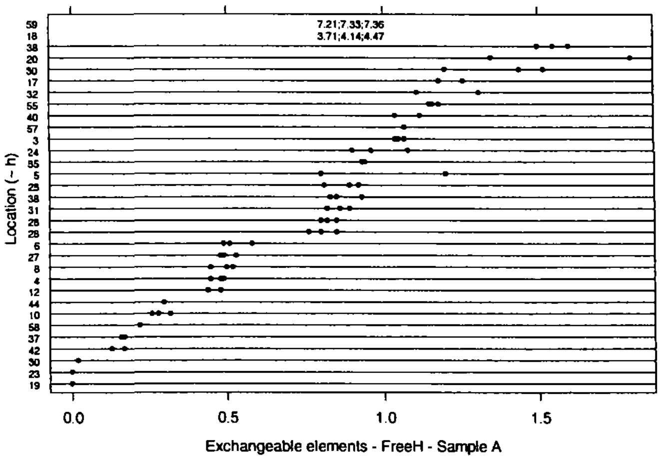


Figure IV.156: Dotplot - Sample A - Free H+ acidity

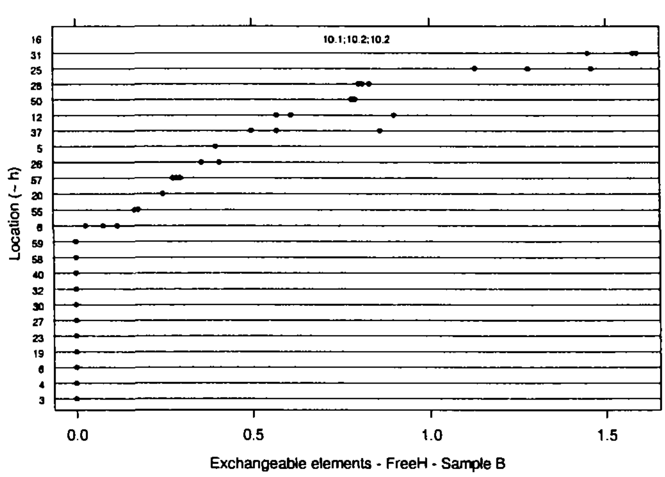


Figure IV.157: Dotplot - Sample B - Free H+ acidity

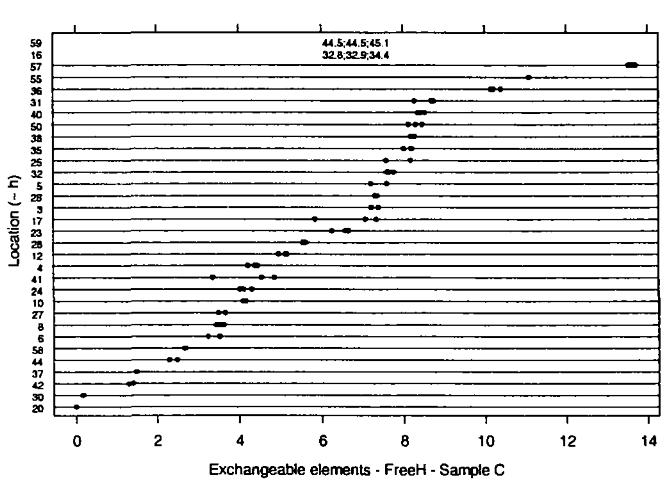


Figure IV.158: Dotplot - Sample C - Free H+ acidity

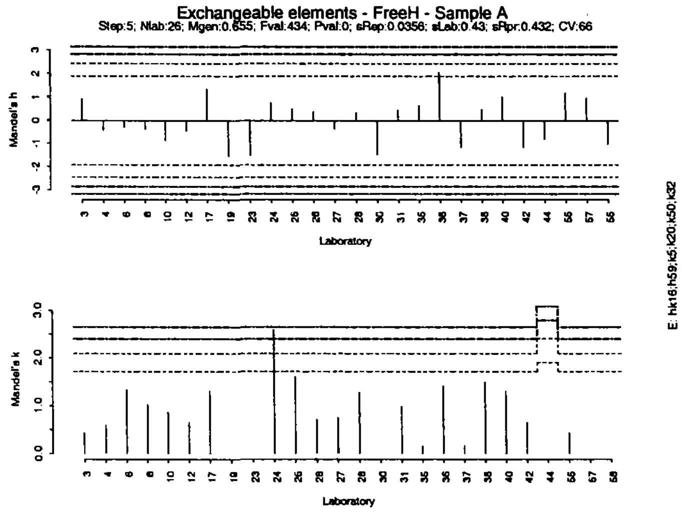


Figure IV.159: Mandel's h and k plot - Sample A - Free H+ acidity

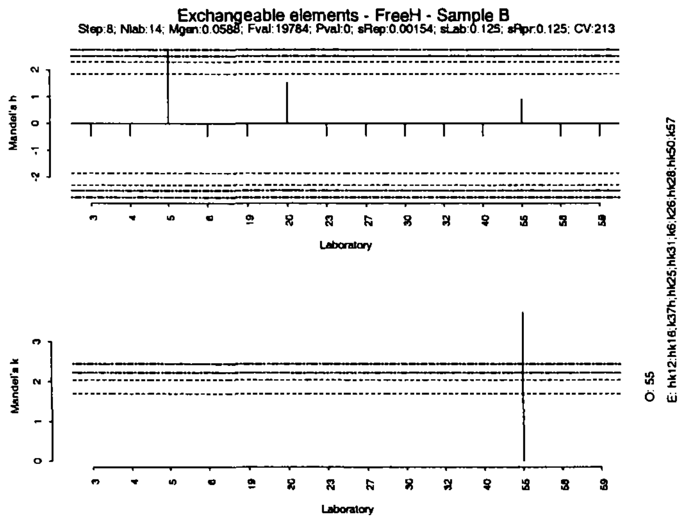


Figure IV.160: Mandel's h and k plot - Sample B - Free H+ acidity

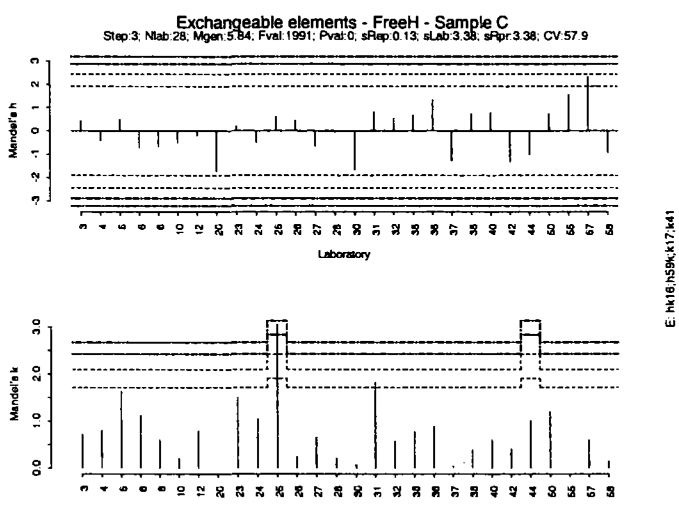


Figure IV.161: Mandel's h and k plot - Sample C - Free H+ acidity

Group VII: Aqua Regia Extractable elements

Parameter: Extractable Al

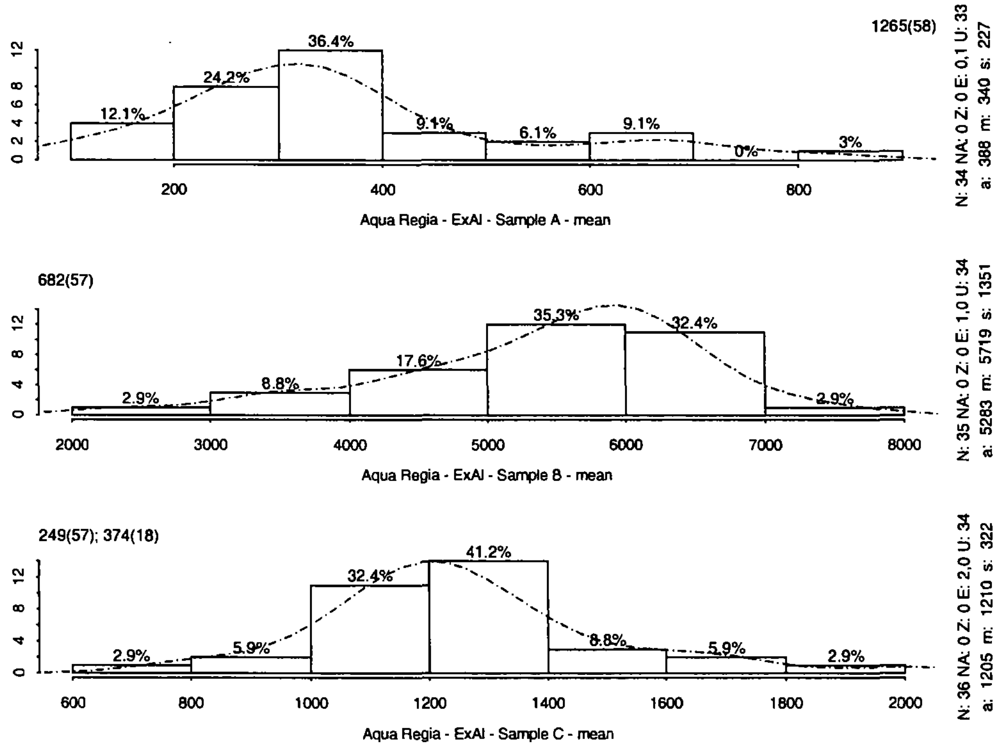


Figure IV.162: Histogram mean – Extractable Al

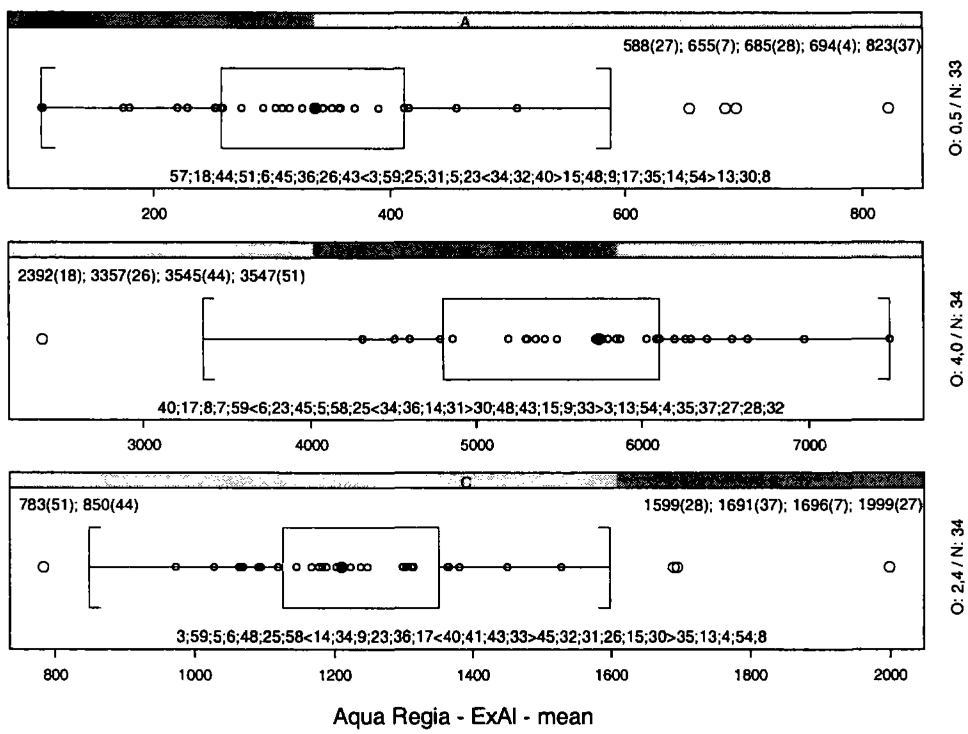


Figure IV.163: Boxplot mean – Extractable Al

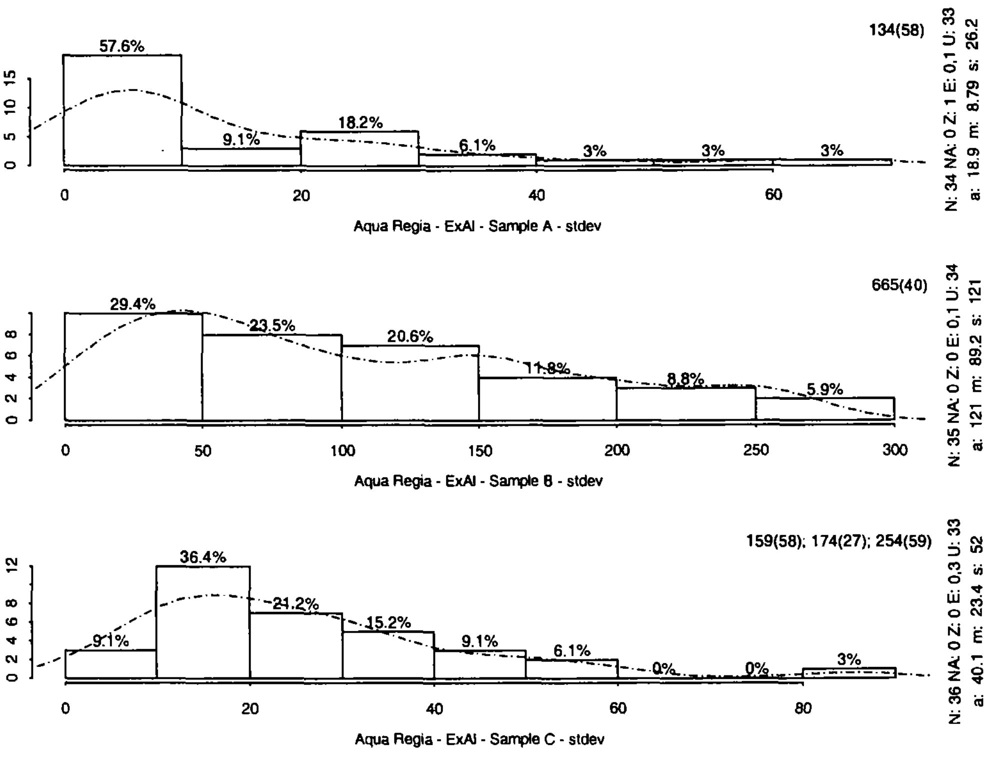


Figure IV.164: Histogram stdev – Extractable Al

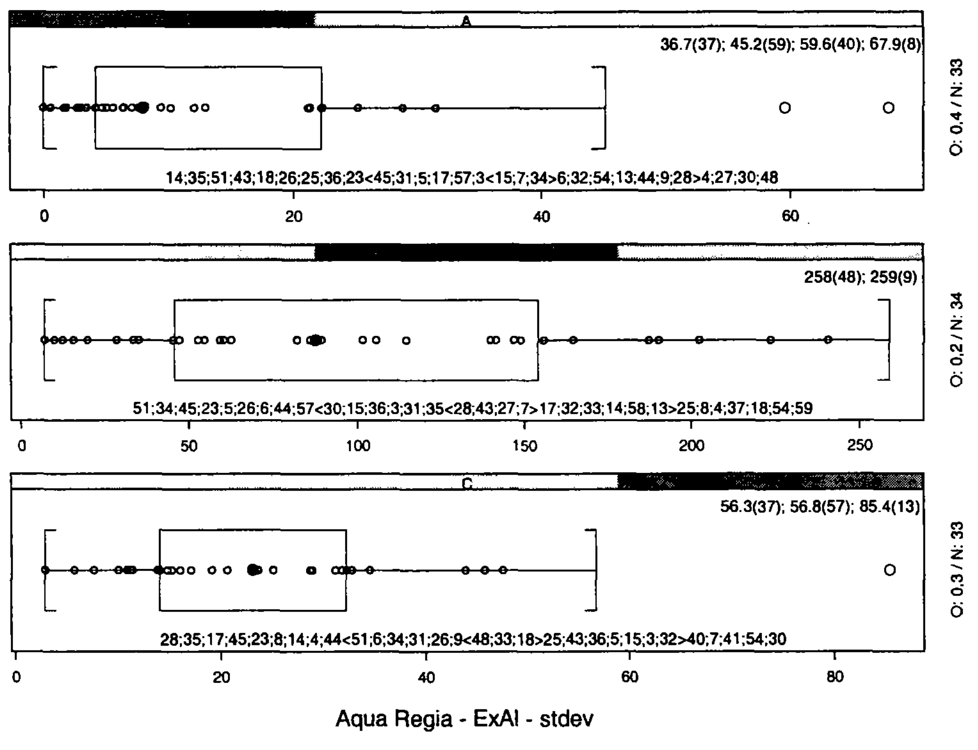


Figure IV.165: Boxplot stdev – Extractable Al

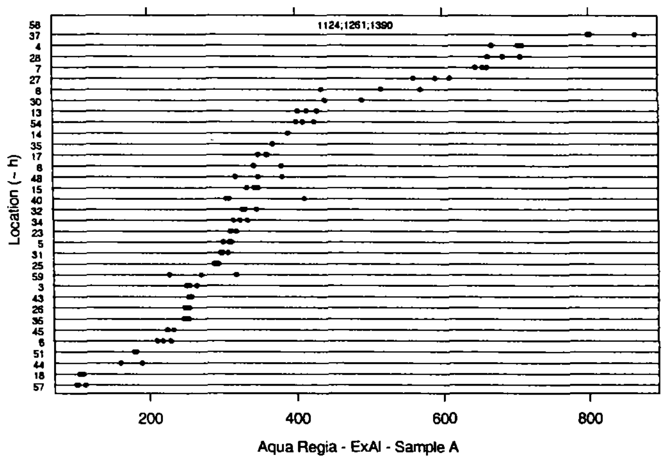


Figure IV.166: Dotplot - Sample A – Extractable Al

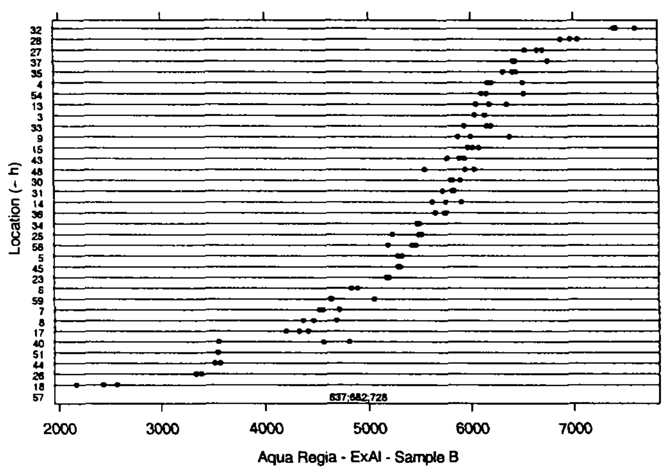


Figure IV.167: Dotplot - Sample B – Extractable Al

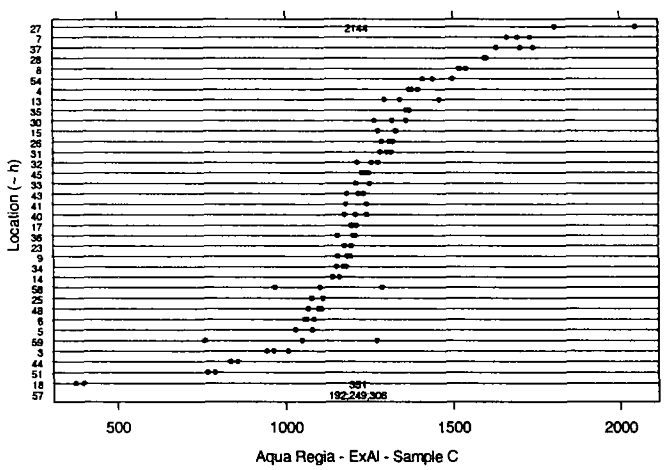


Figure IV.168: Dotplot - Sample C – Extractable Al

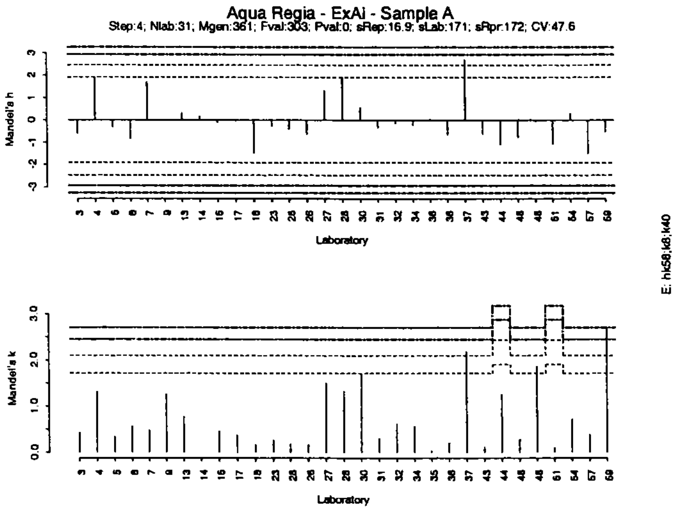


Figure IV.169: Mandel h/k plot - Sample A – Extractable Al

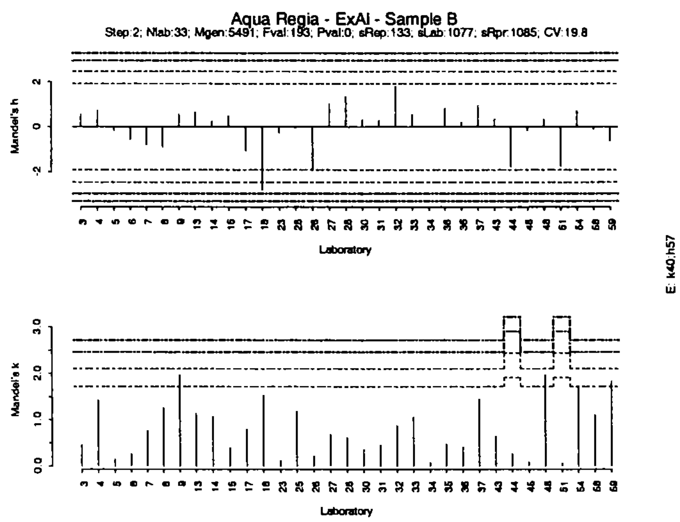


Figure IV.170: Mandel h/k plot - Sample B – Extractable Al

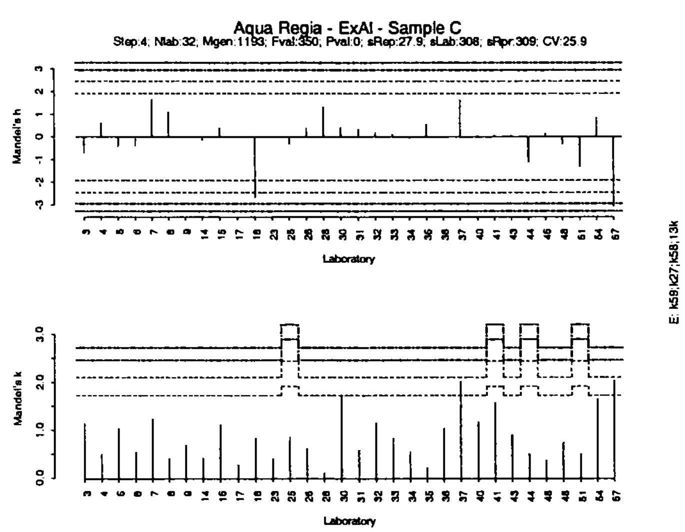


Figure IV.171: Mandel h/k plot - Sample C – Extractable Al

Parameter: Extractable Ca

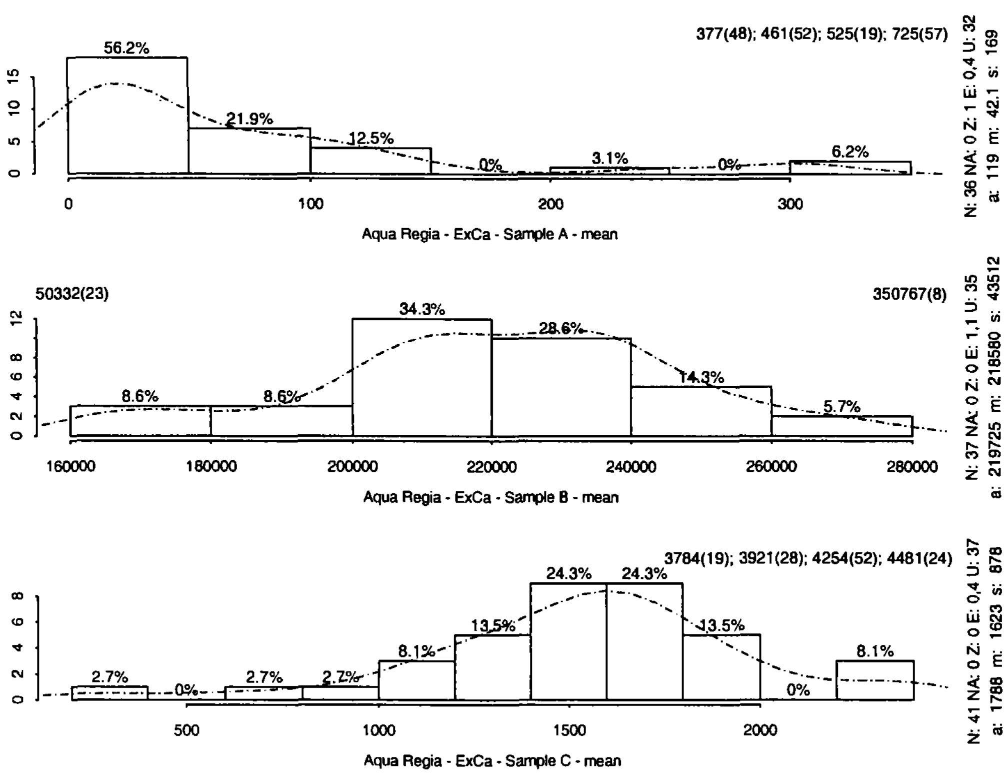


Figure IV.172: Histogram mean – Extractable Ca

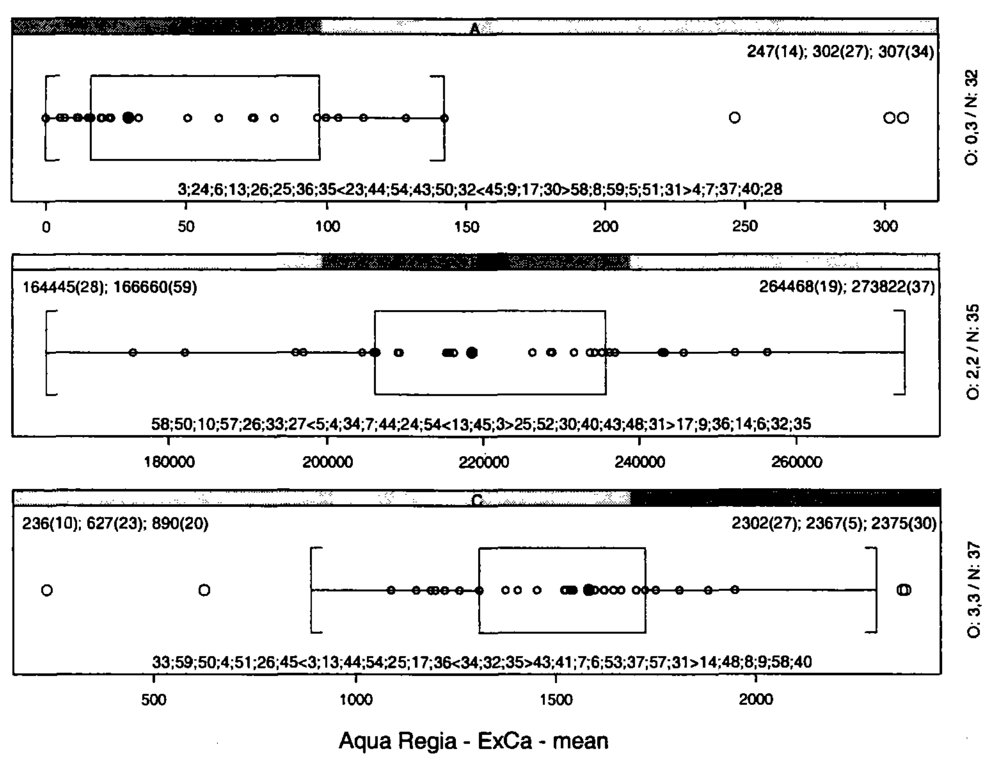


Figure IV.173: Boxplot mean – Extractable Ca

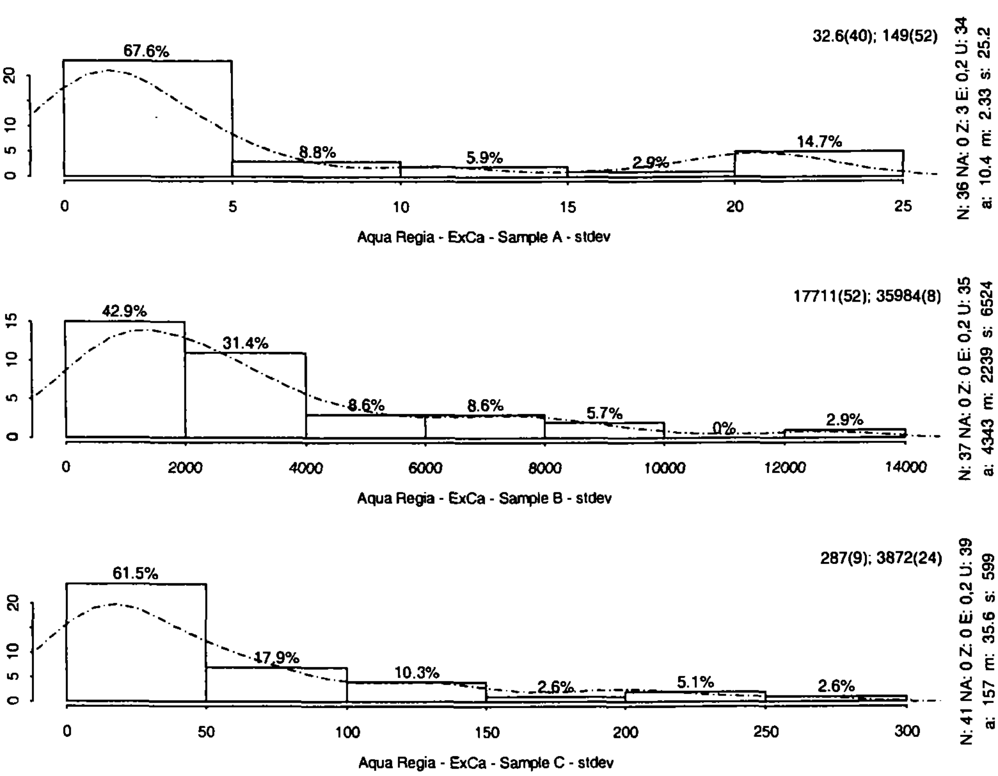


Figure IV.174: Histogram stdev – Extractable Ca

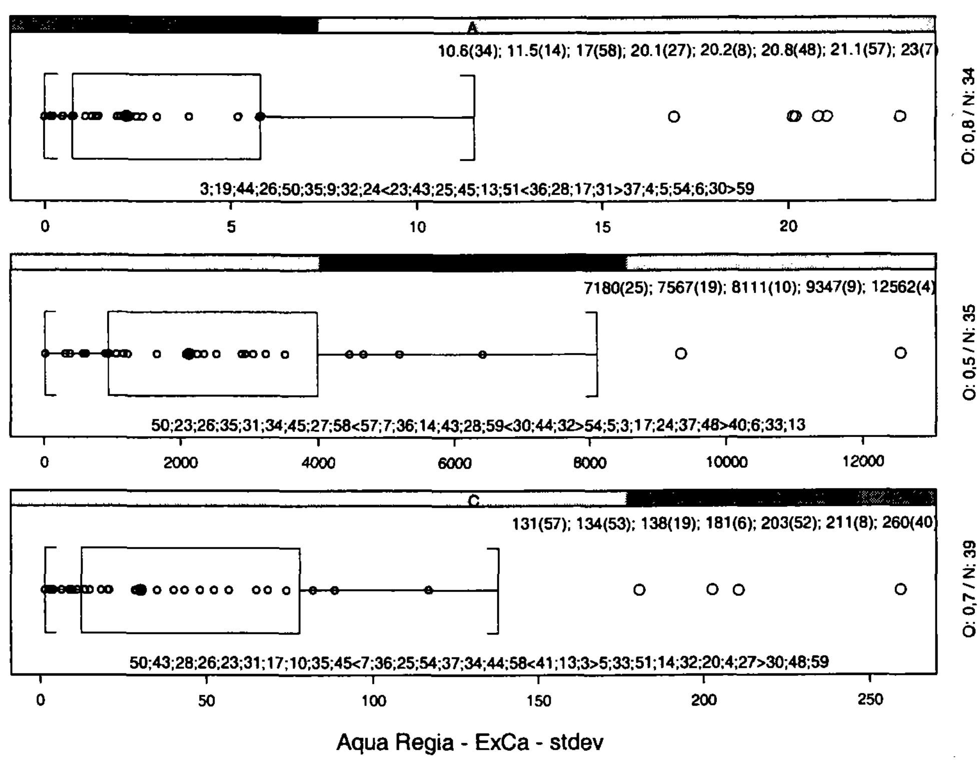


Figure IV.175: Boxplot stdev – Extractable Ca

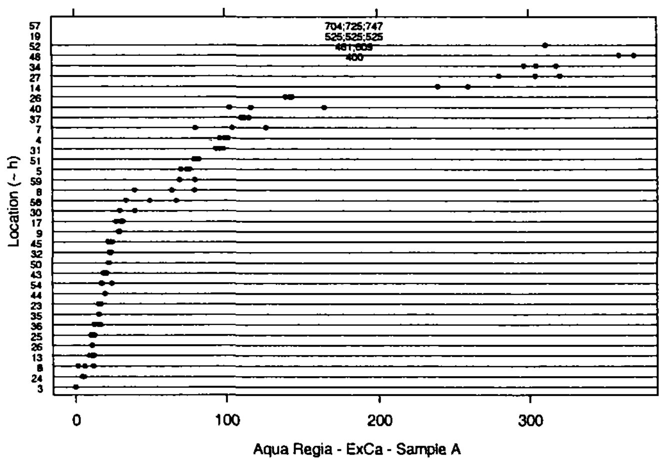


Figure IV.176: Dotplot - Sample A – Extractable Ca

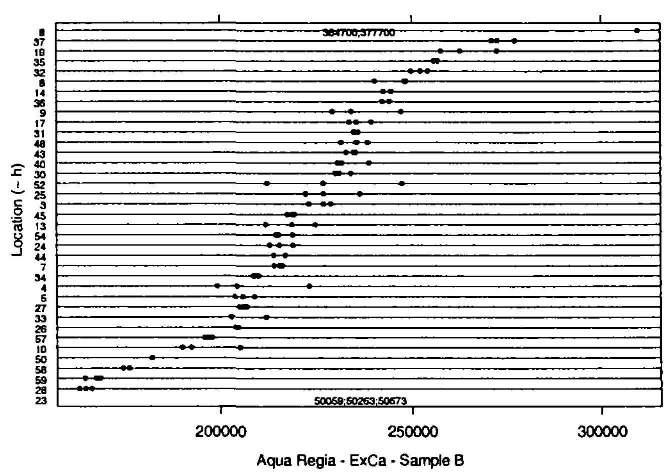


Figure IV.177: Dotplot - Sample B – Extractable Ca

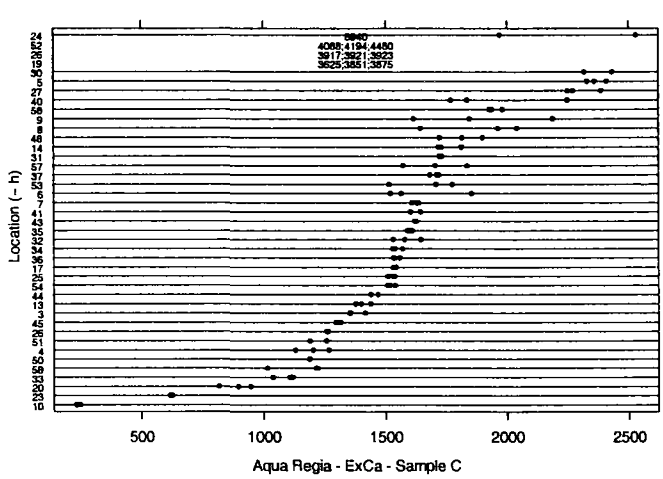


Figure IV.178: Dotplot - Sample C – Extractable Ca

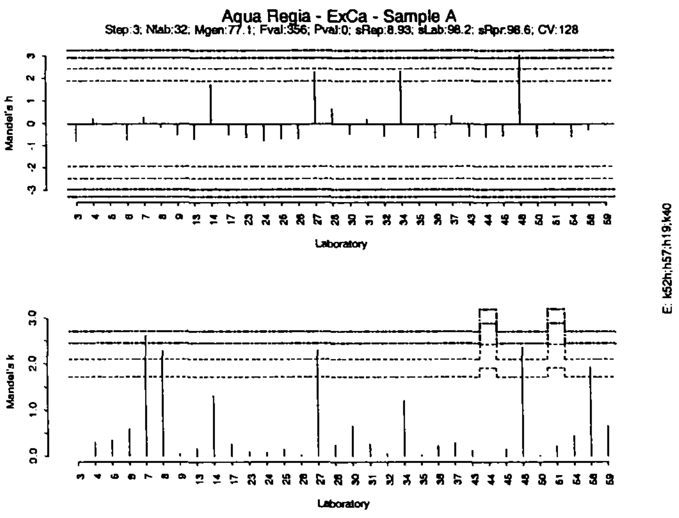


Figure IV.179: Mandel h/k plot - Sample A – Extractable Ca

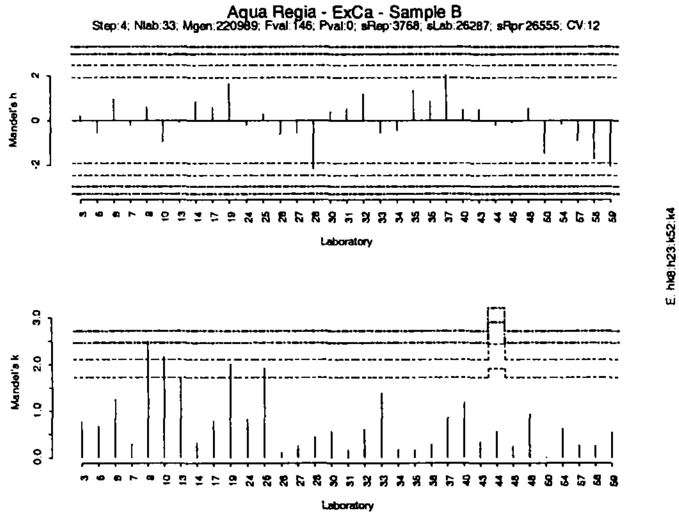


Figure IV.180: Mandel h/k plot - Sample B – Extractable Ca

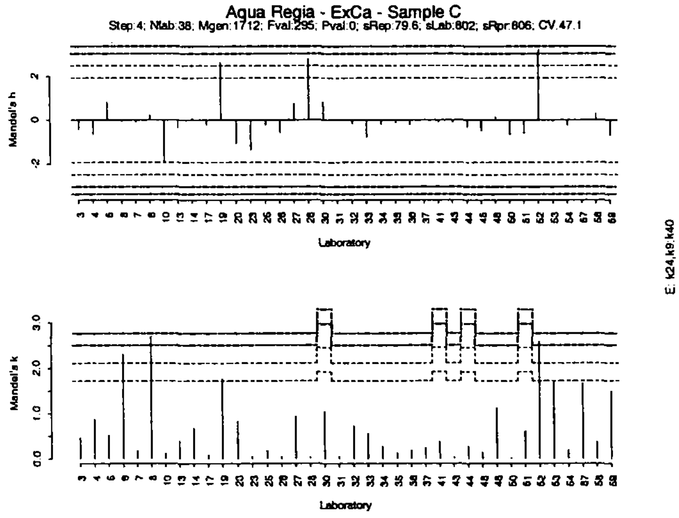


Figure IV.181: Mandel h/k plot - Sample C – Extractable Ca

Parameter: Extractable Cd

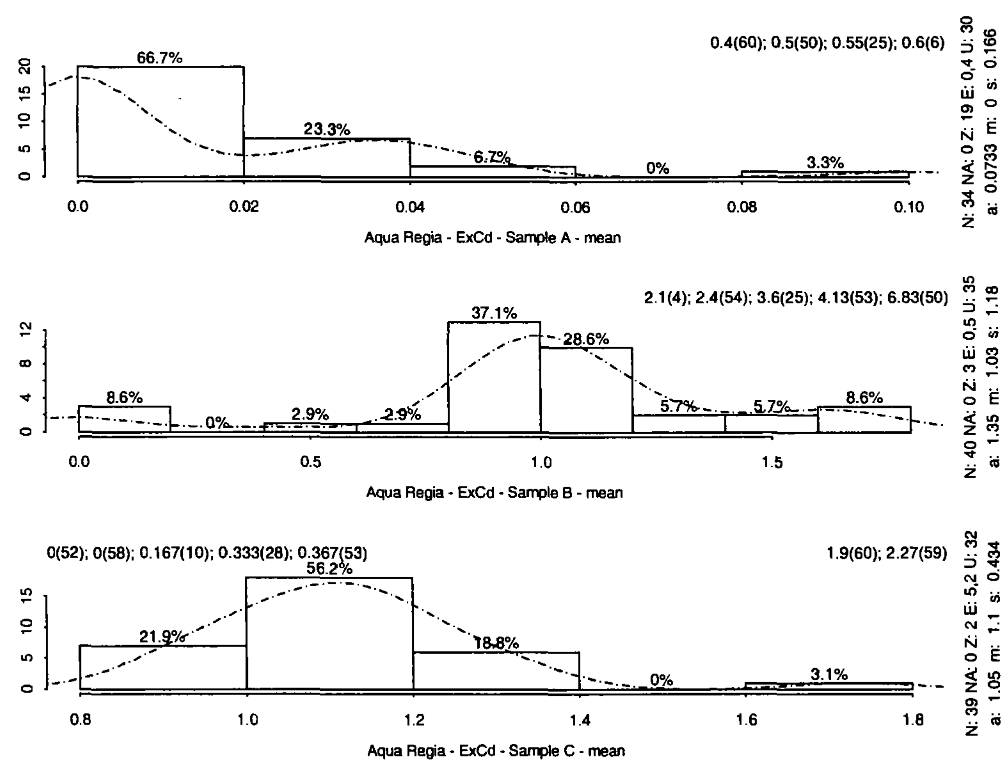


Figure IV.182: Histogram mean – Extractable Cd

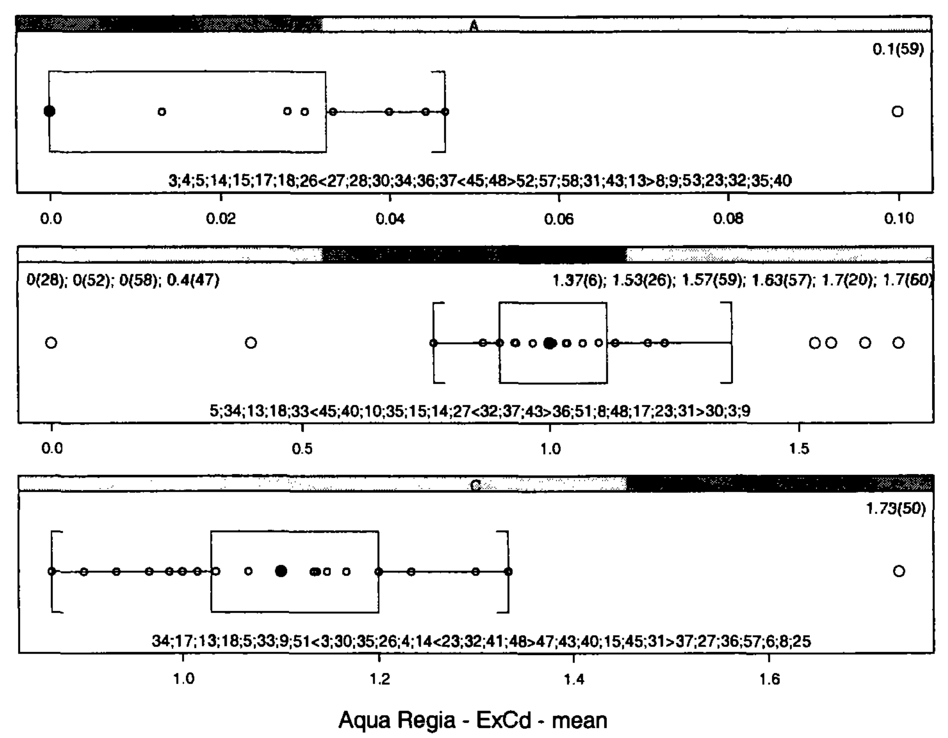


Figure IV.183: Boxplot mean – Extractable Cd

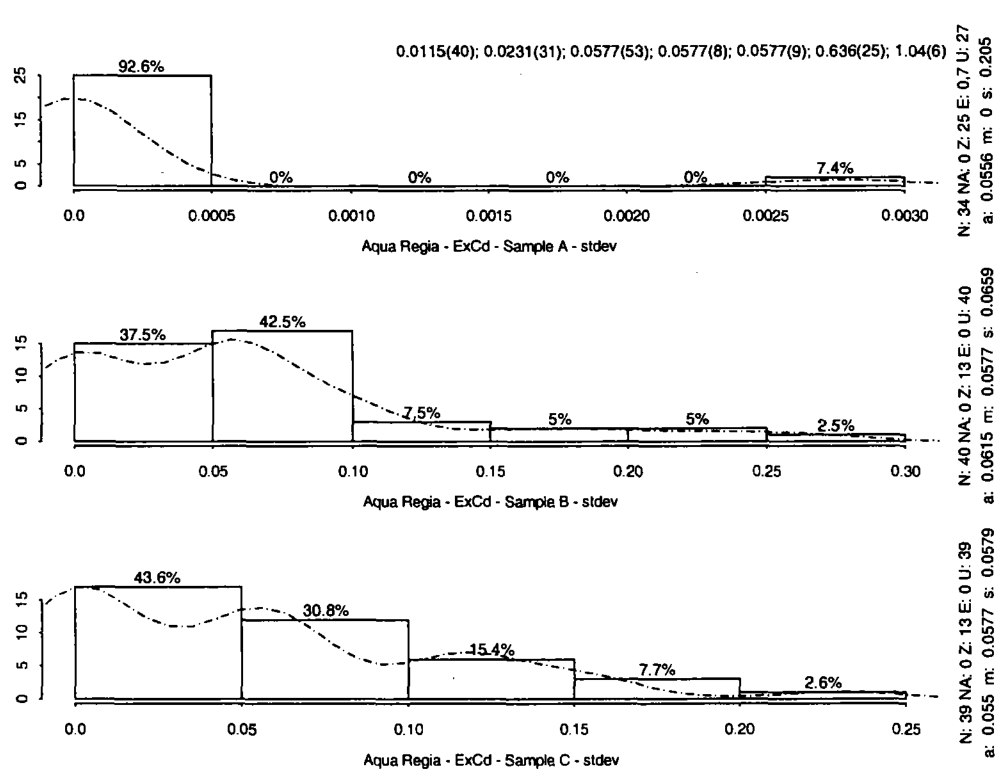


Figure IV.184: Histogram stdev – Extractable Cd

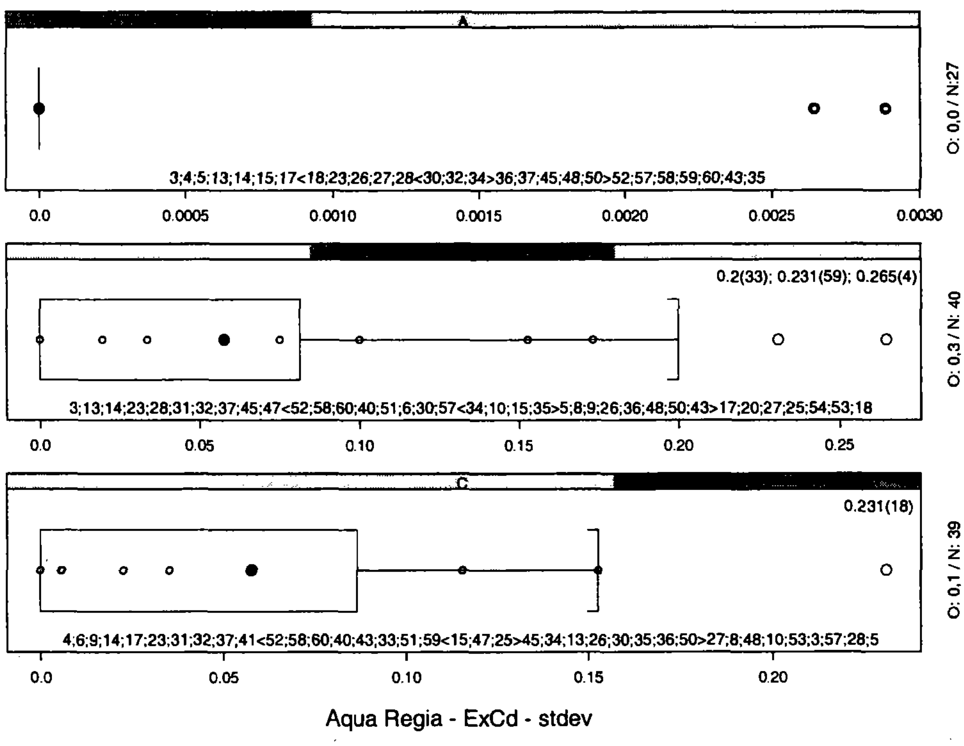


Figure IV.185: Boxplot stdev – Extractable Cd

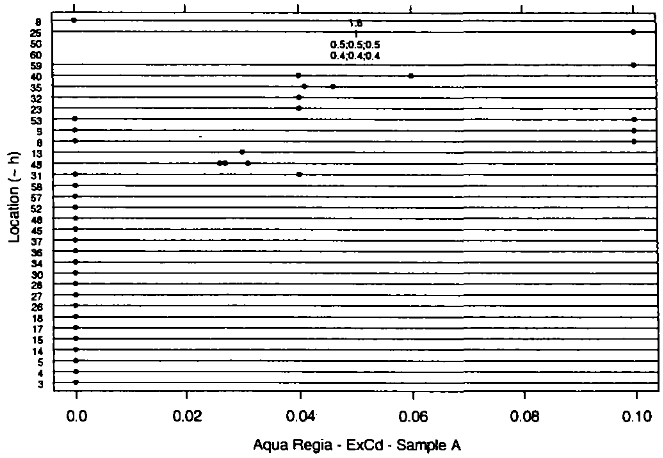


Figure IV.186: Dotplot sample A – Extractable Cd

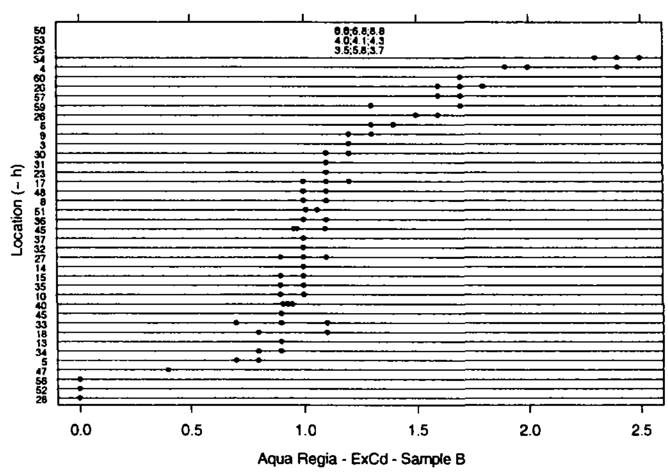


Figure IV.187: Dotplot sample B – Extractable Cd

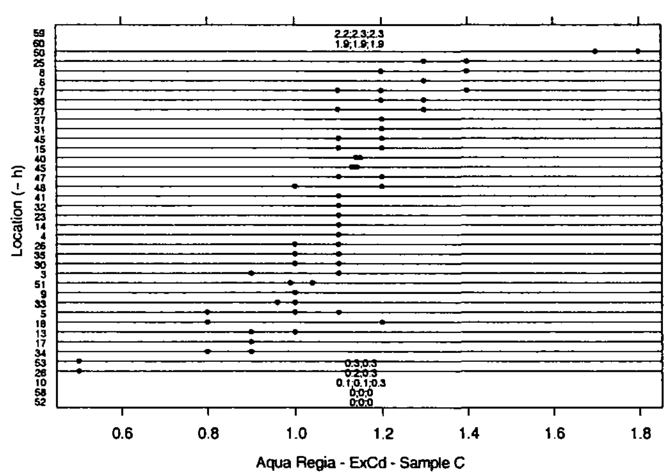


Figure IV.188: Dotplot sample C – Extractable Cd

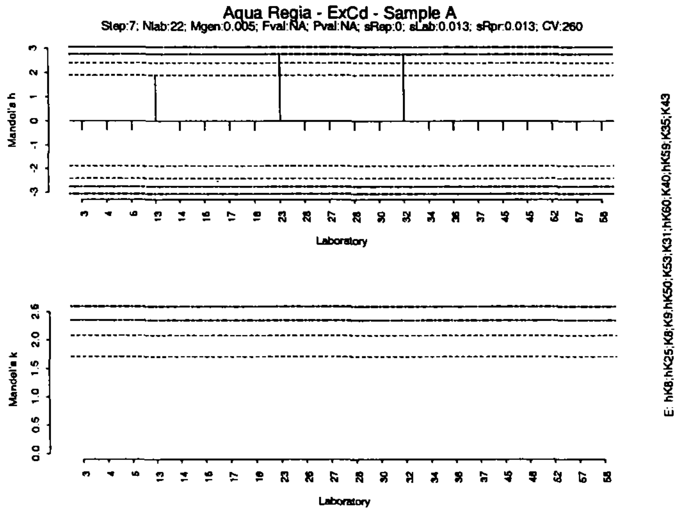


Figure IV.189: Mandel h/k plot - Sample A – Extractable Cd

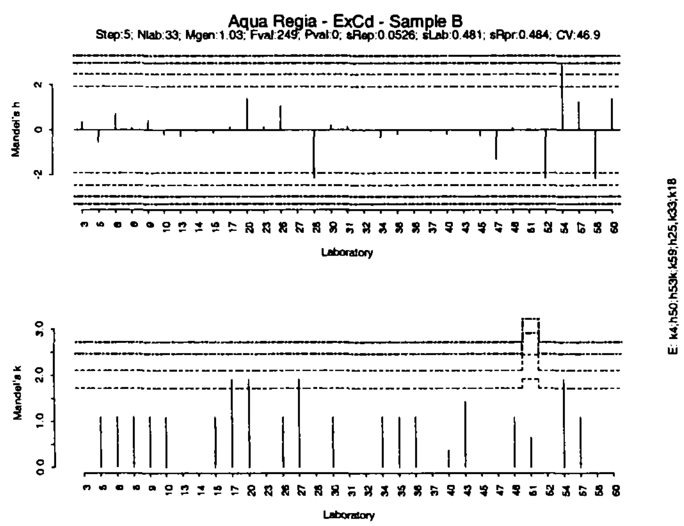


Figure IV.190: Mandel h/k plot - Sample B– Extractable Cd

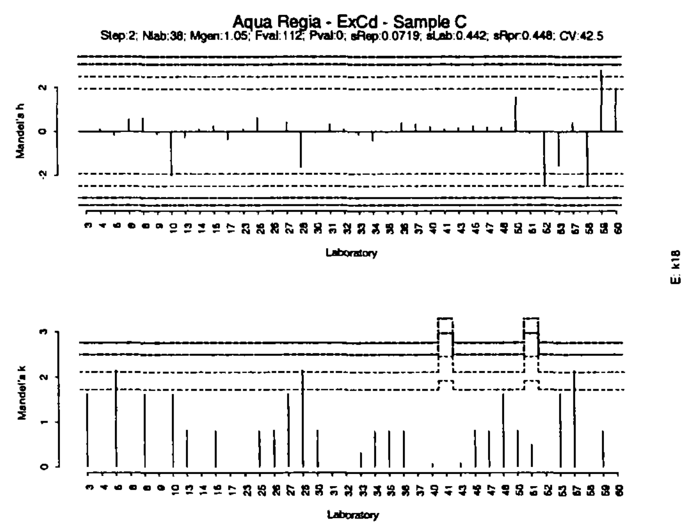


Figure IV.191: Mandel h/k plot – Sample C – Extractable Cd

Parameter: Extractable Cr

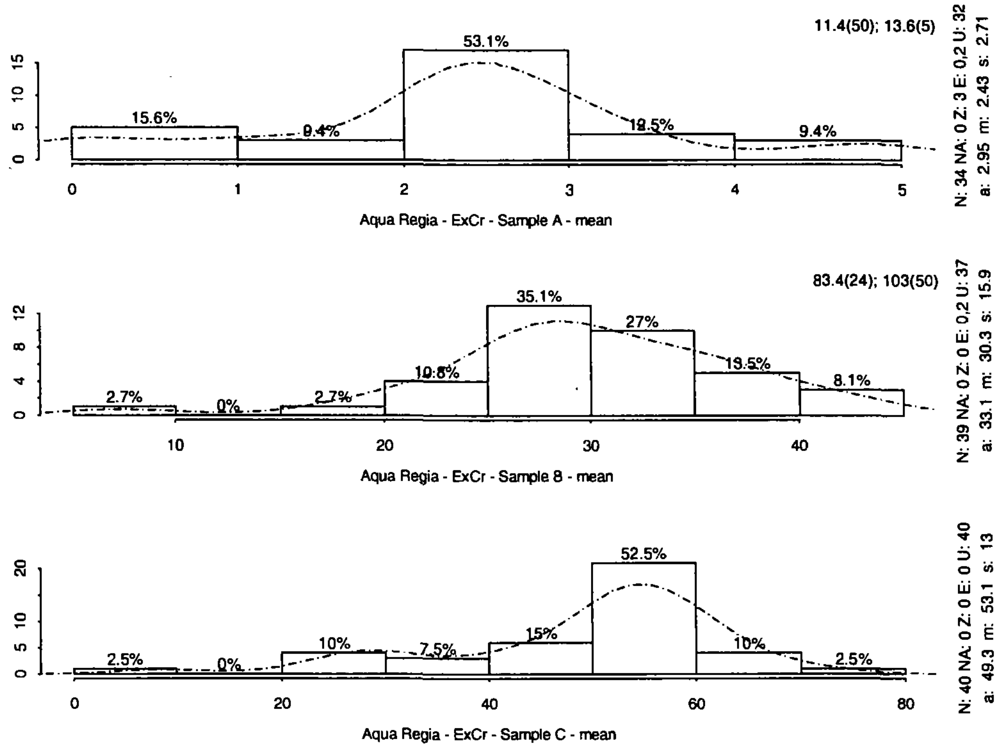


Figure IV.192: Histogram mean – Extractable Cr

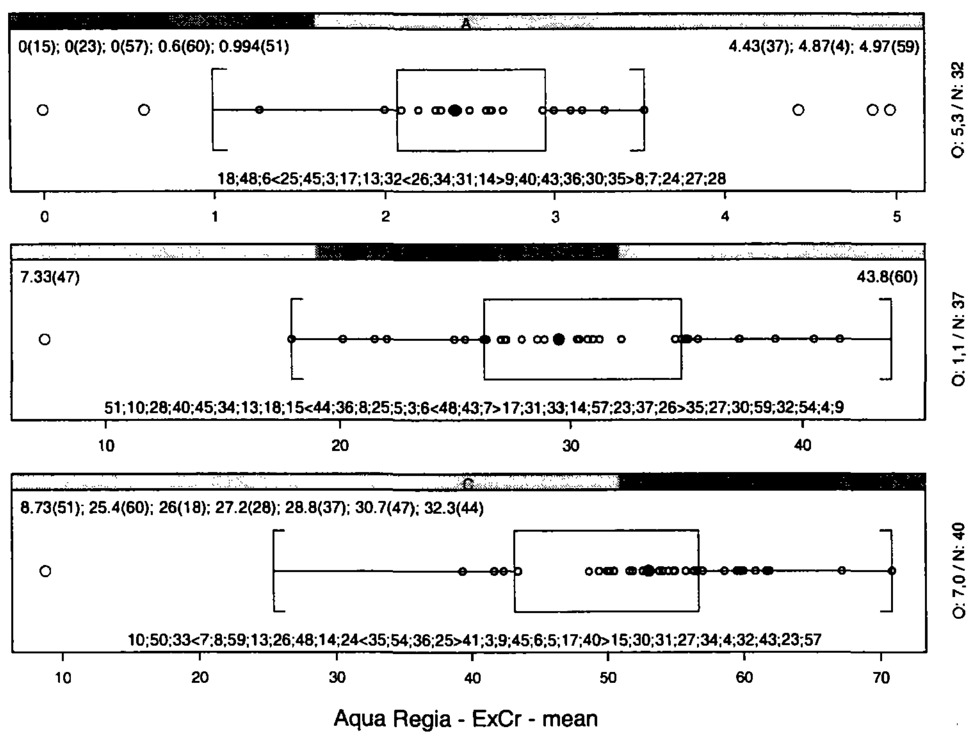


Figure IV.193: Boxplot mean – Extractable Cr

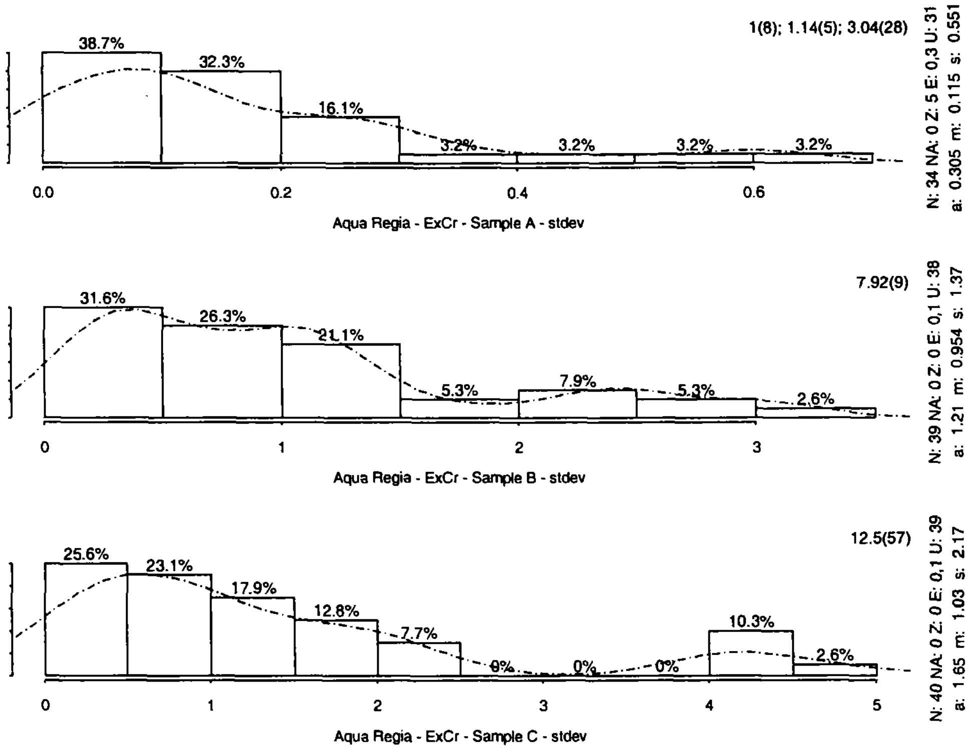


Figure IV.194: Histogram stdev – Extractable Cr

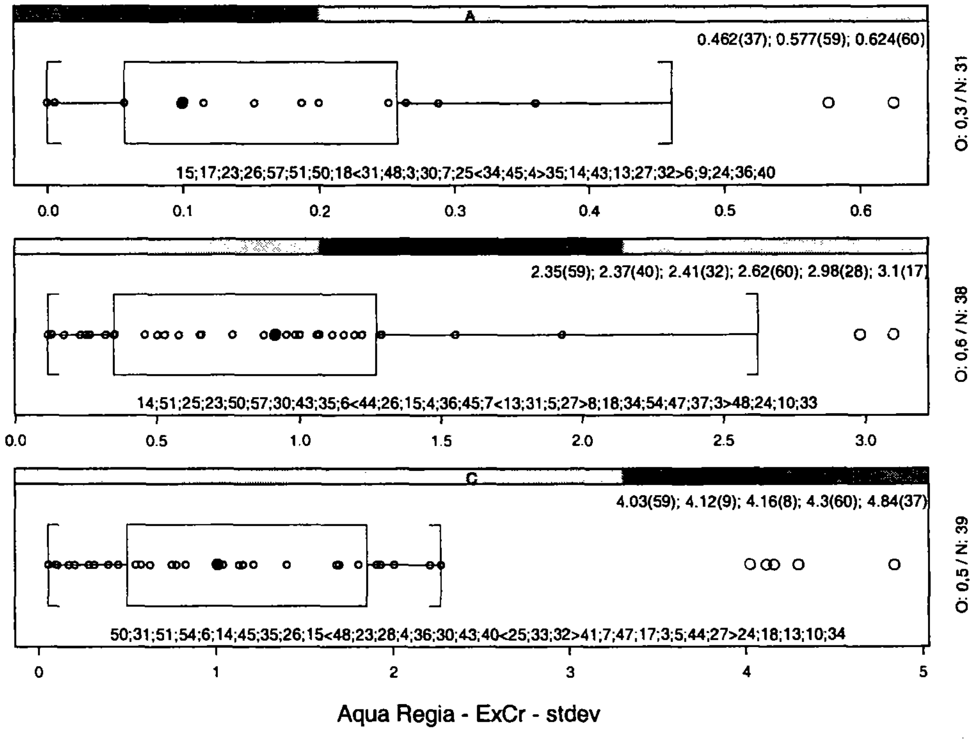


Figure IV.195: Boxplot stdev – Extractable Cr

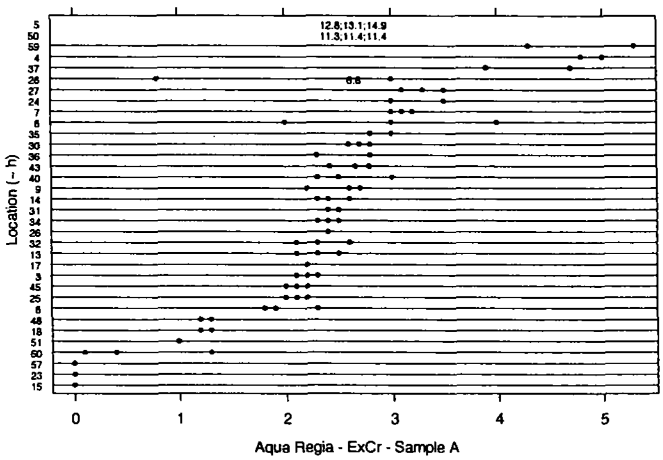


Figure IV.196: Dotplot - Sample A– Extractable Cr

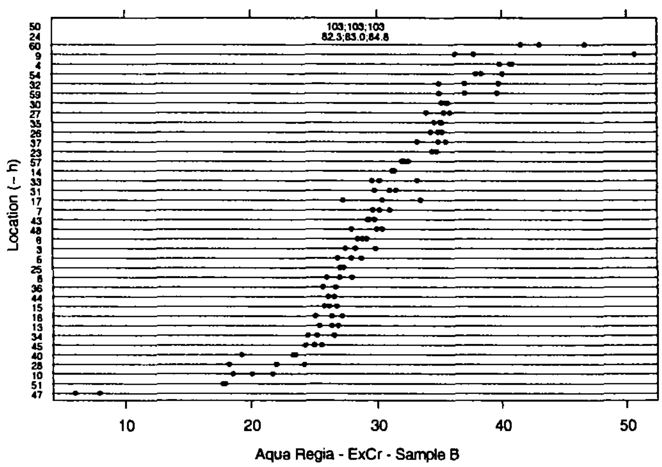


Figure IV.197: Dotplot- Sample B – Extractable Cr

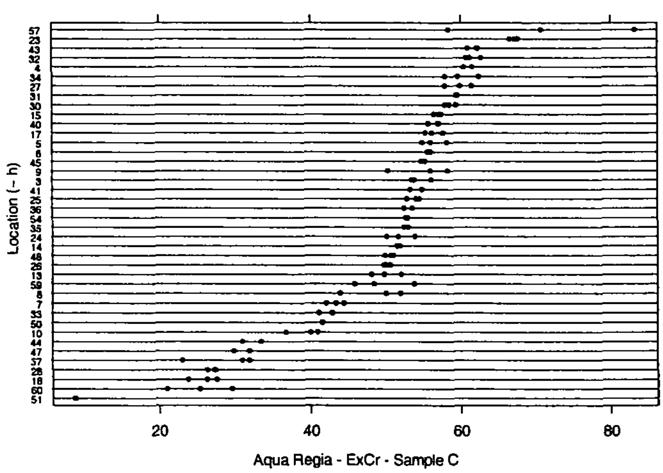


Figure IV.198: Dotplot - Sample C – Extractable Cr

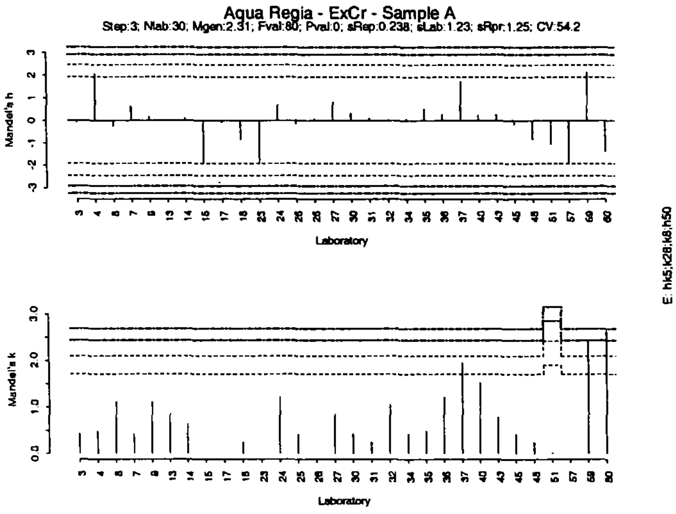


Figure IV.199: Mandel h/k plot - Sample A – Extractable Cr

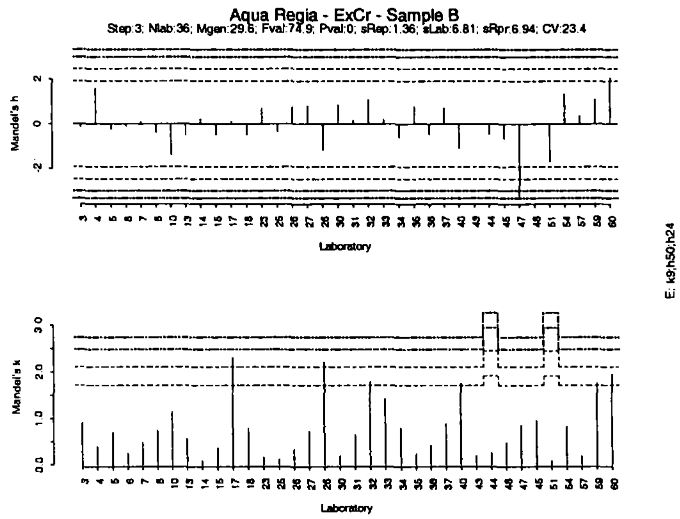


Figure IV.200: Mandel h/k plot - Sample B – Extractable Cr

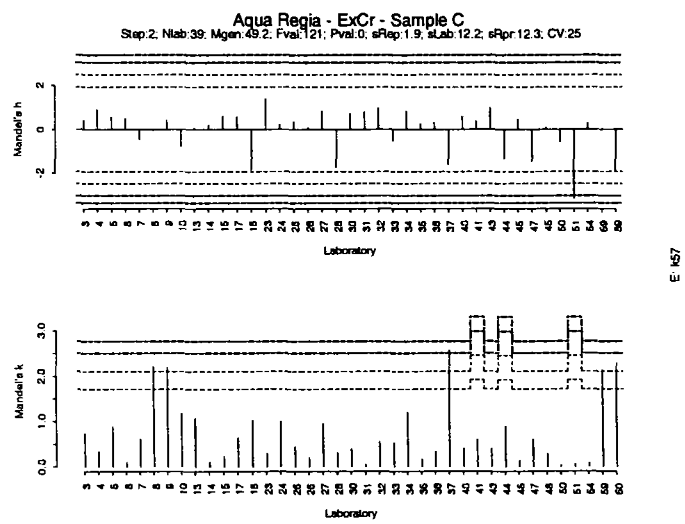


Figure IV.201: Mandel h/k plot - Sample C – Extractable Cr

Parameter: Extractable Cu

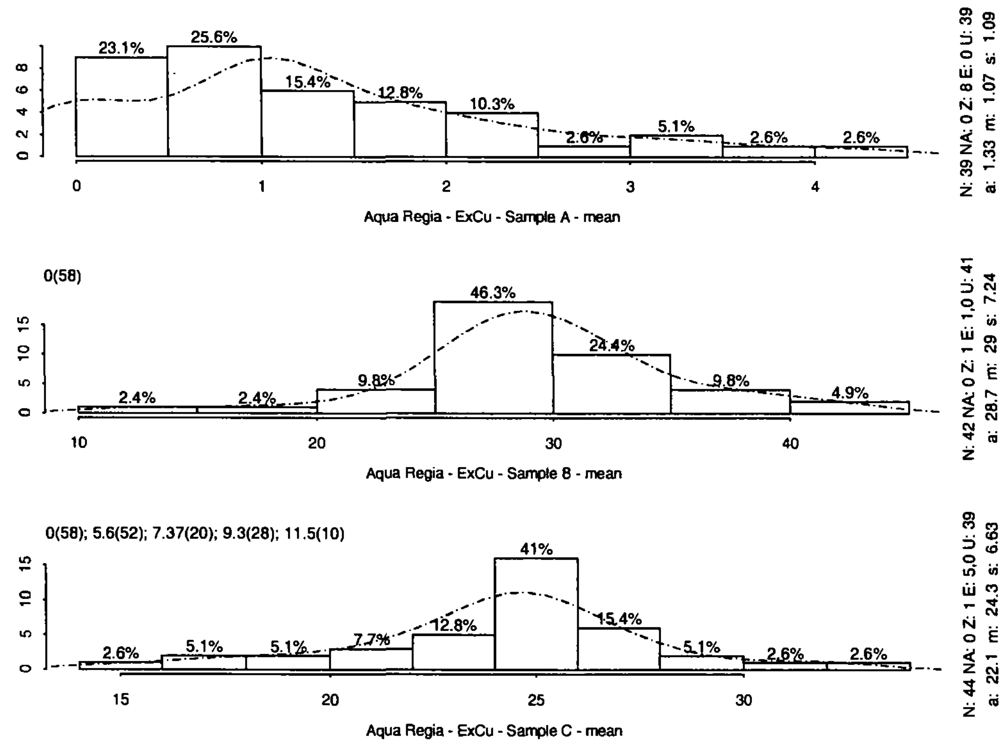


Figure IV.202: Histogram mean – Extractable Cu

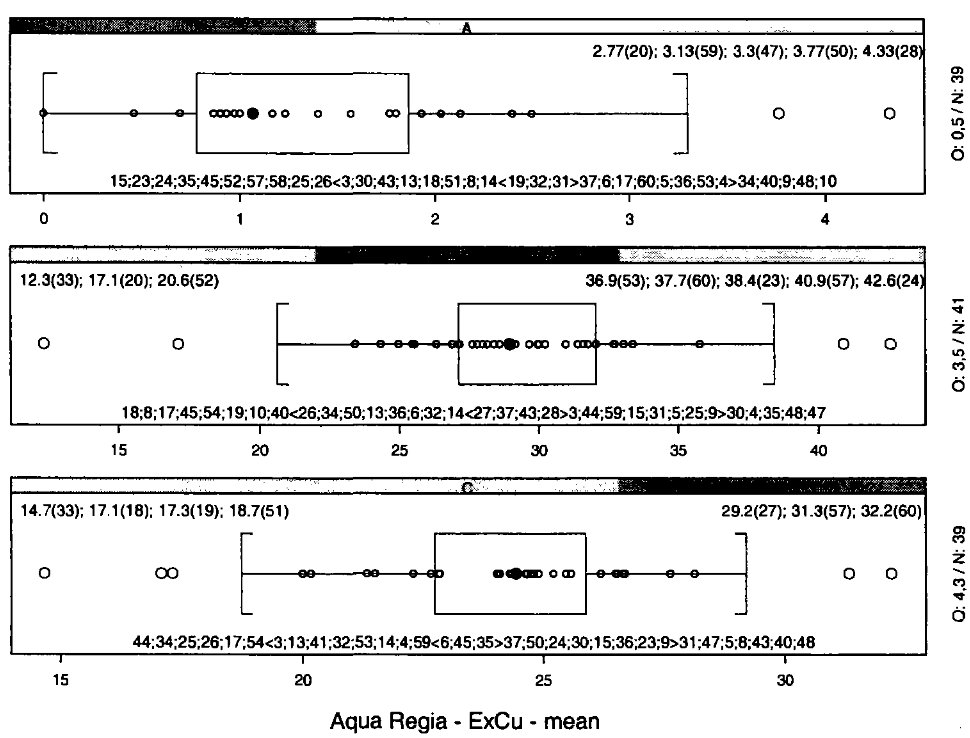


Figure IV.203: Boxplot mean – Extractable Cu

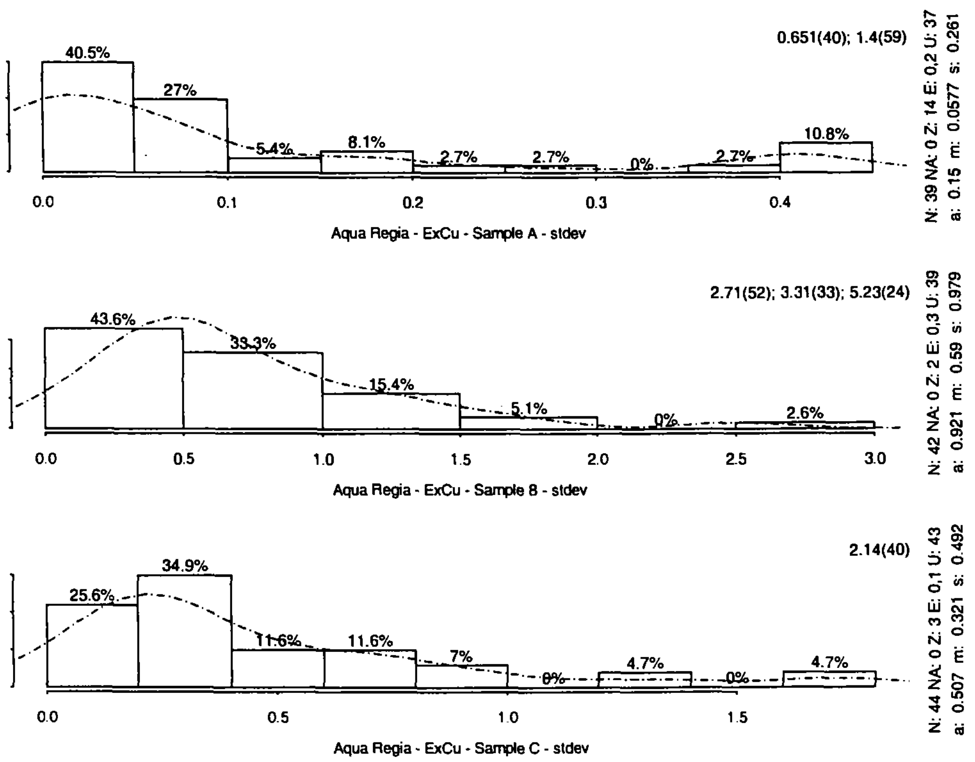


Figure IV.204: Histogram stdev – Extractable Cu

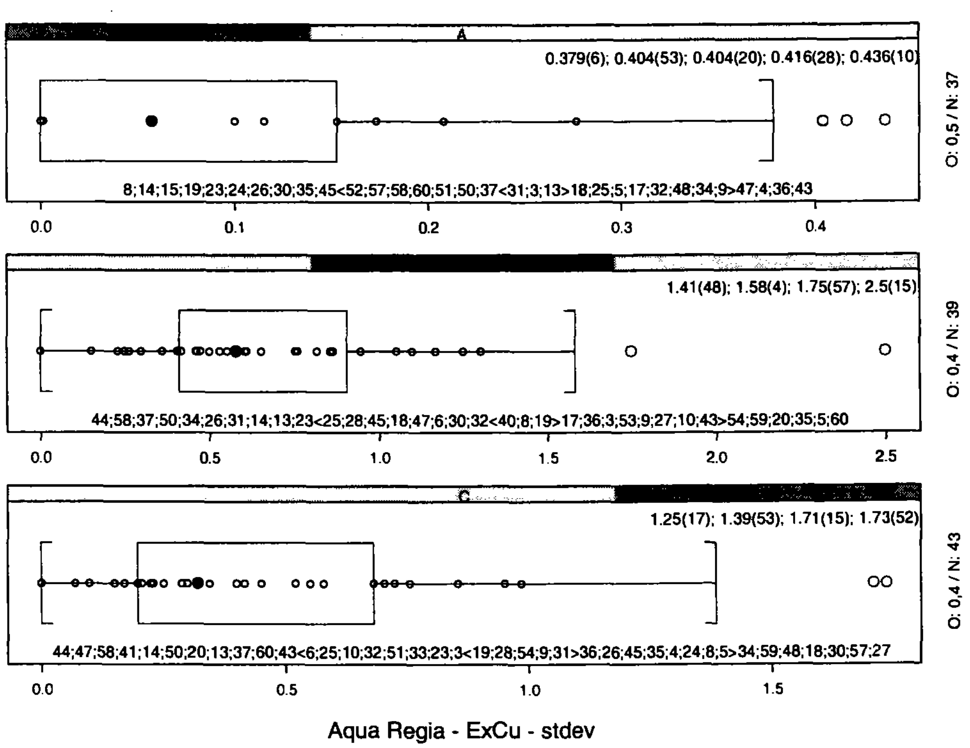


Figure IV.205: Boxplot stdev – Extractable Cu

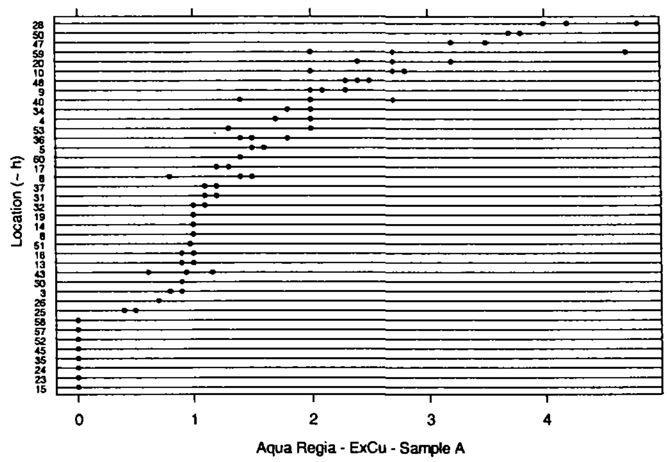


Figure IV.206: Dotplot - Sample A – Extractable Cu

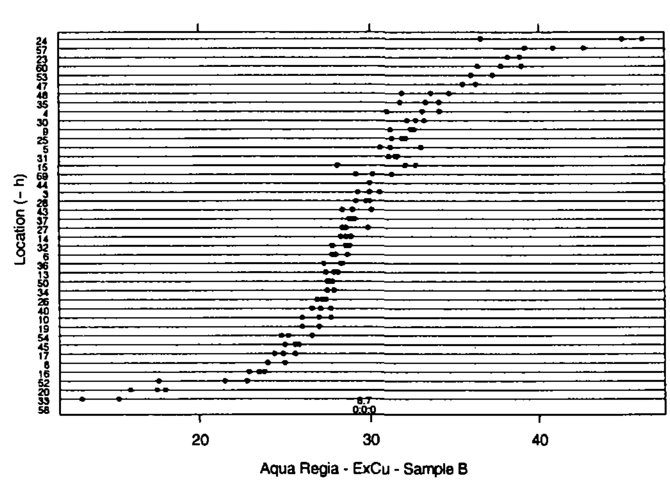


Figure IV.207: Dotplot - Sample B – Extractable Cu

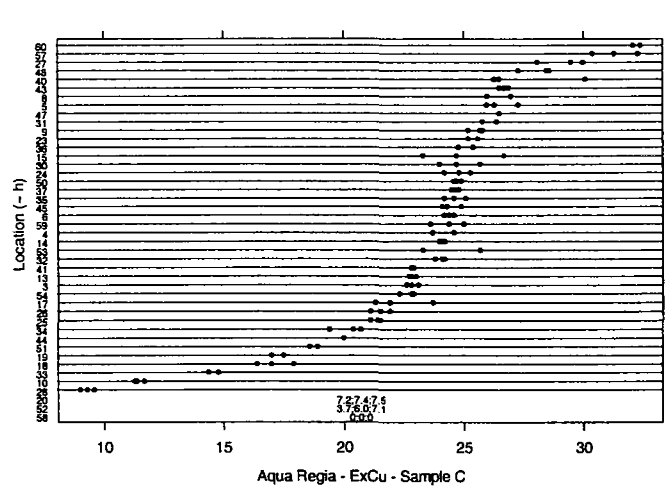


Figure IV.208: Dotplot - Sample C – Extractable Cu

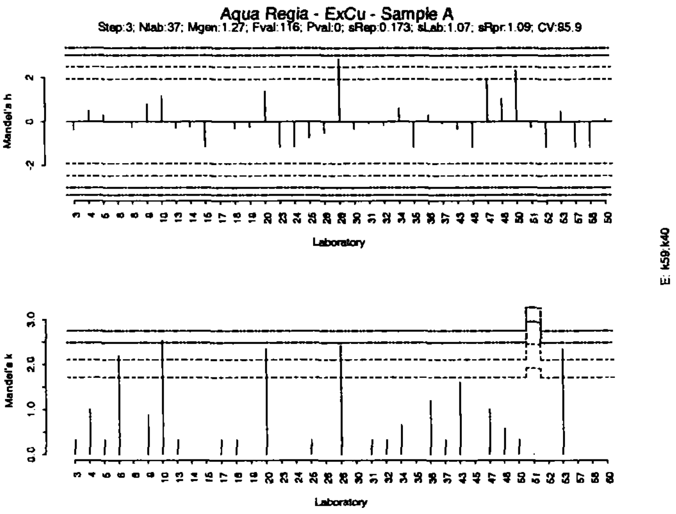


Figure IV.209: Mandel h/k plot - Sample A – Extractable Cu

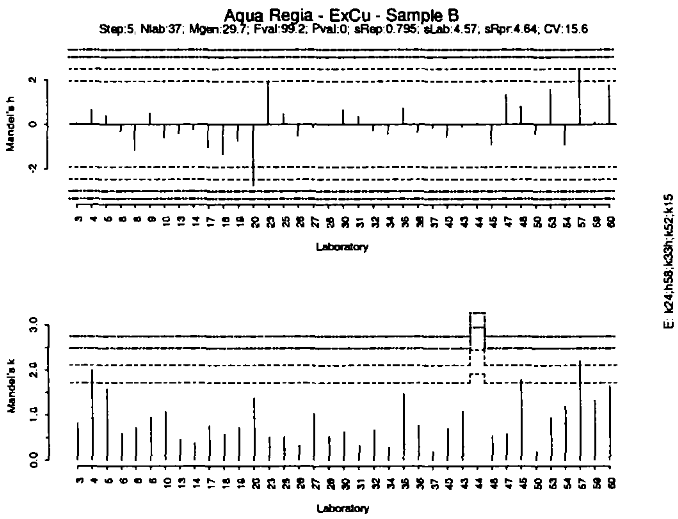


Figure IV.210: Mandel h/k plot - Sample B – Extractable Cu

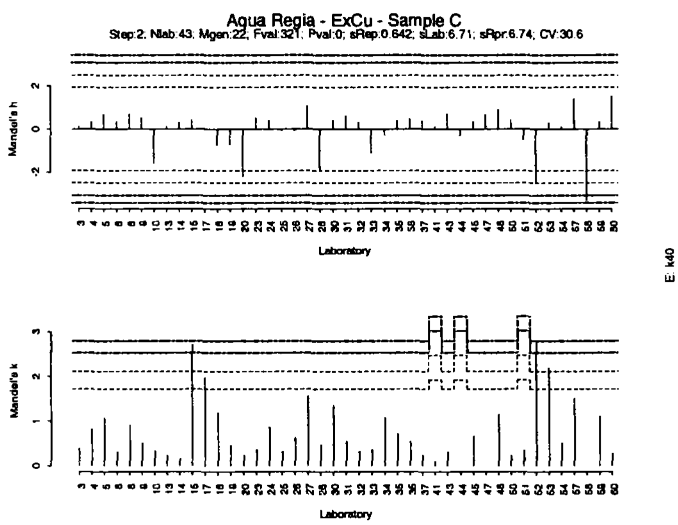


Figure IV.211: Mandel h/k plot - Sample C – Extractable Cu

Parameter: Extractable Fe

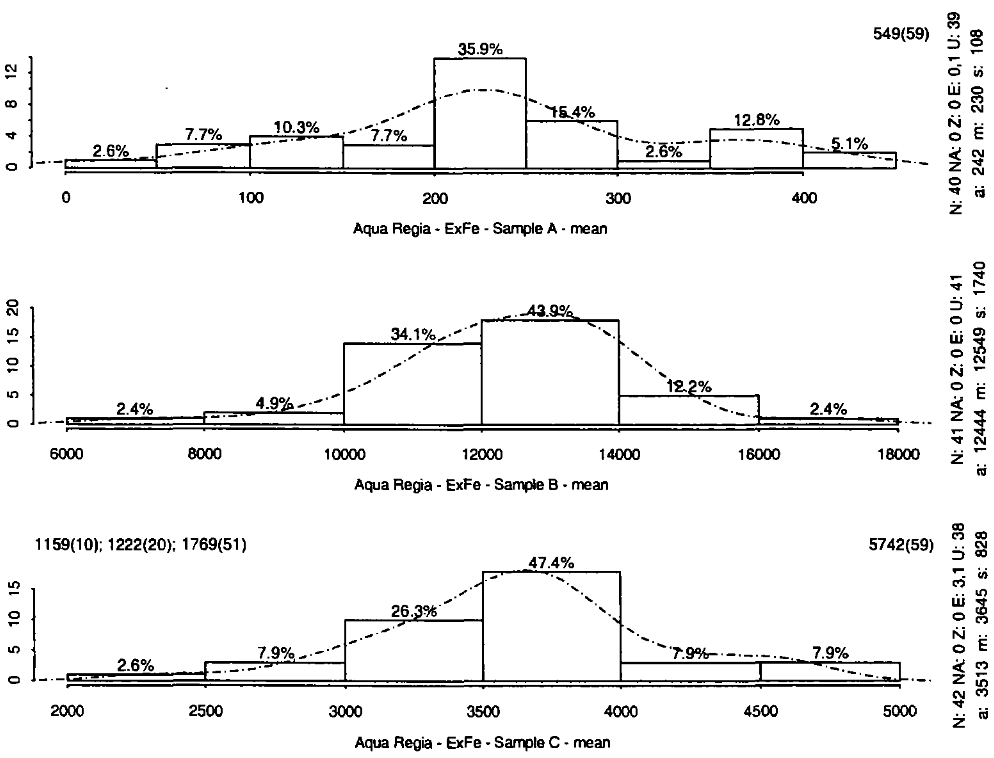


Figure IV.212: Histogram mean – Extractable Fe

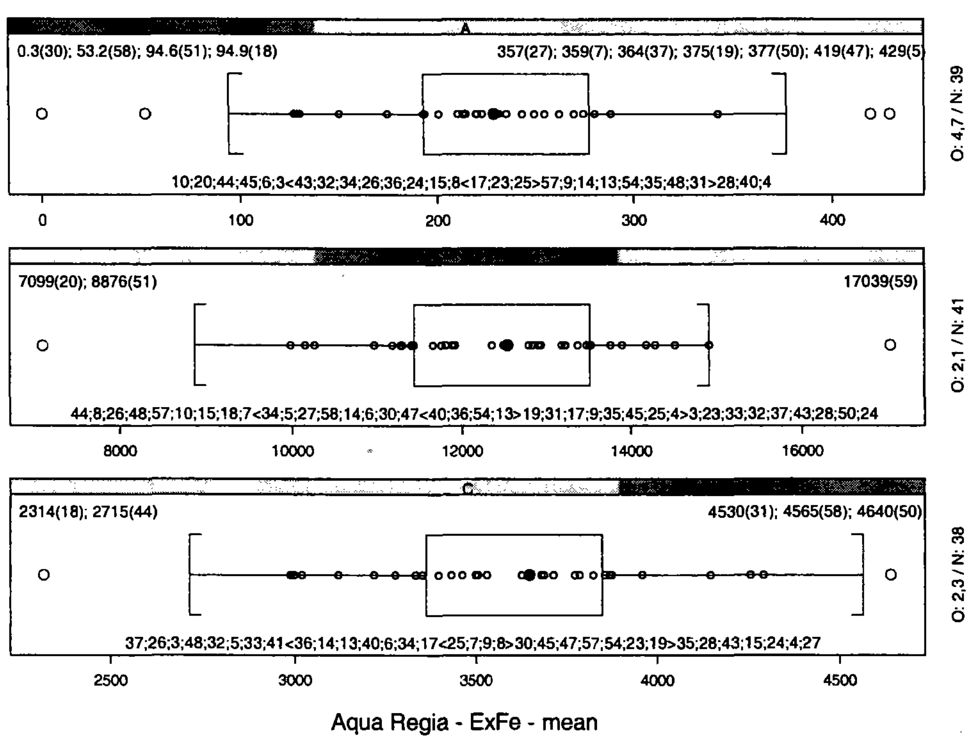


Figure IV.213: Boxplot mean – Extractable Fe

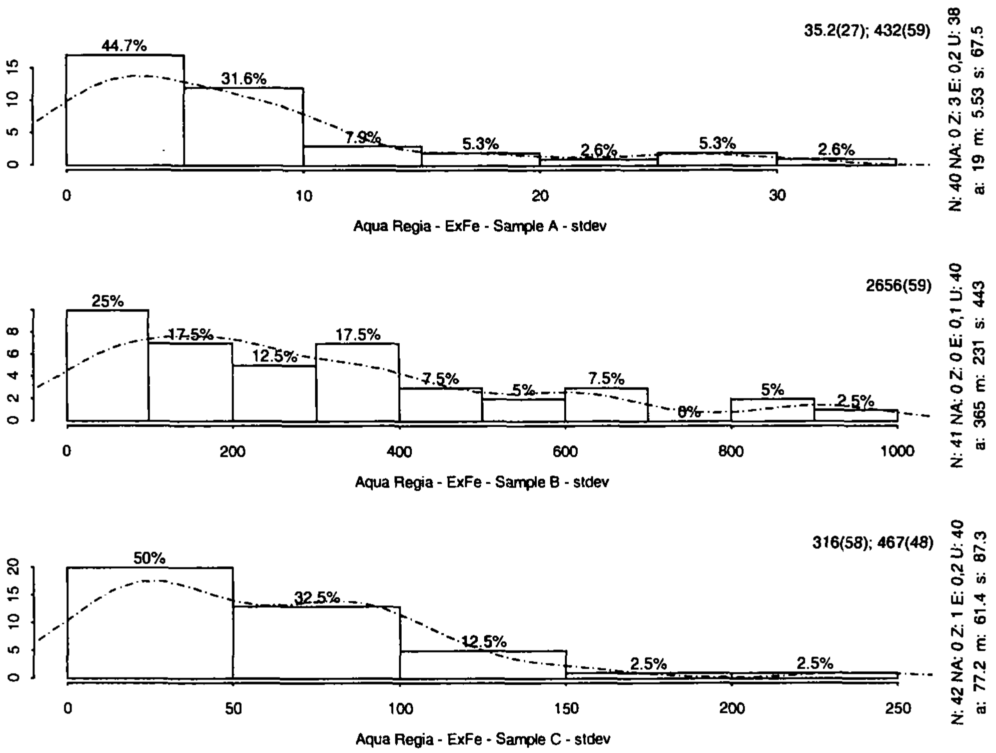


Figure IV.214: Histogram stdev – Extractable Fe

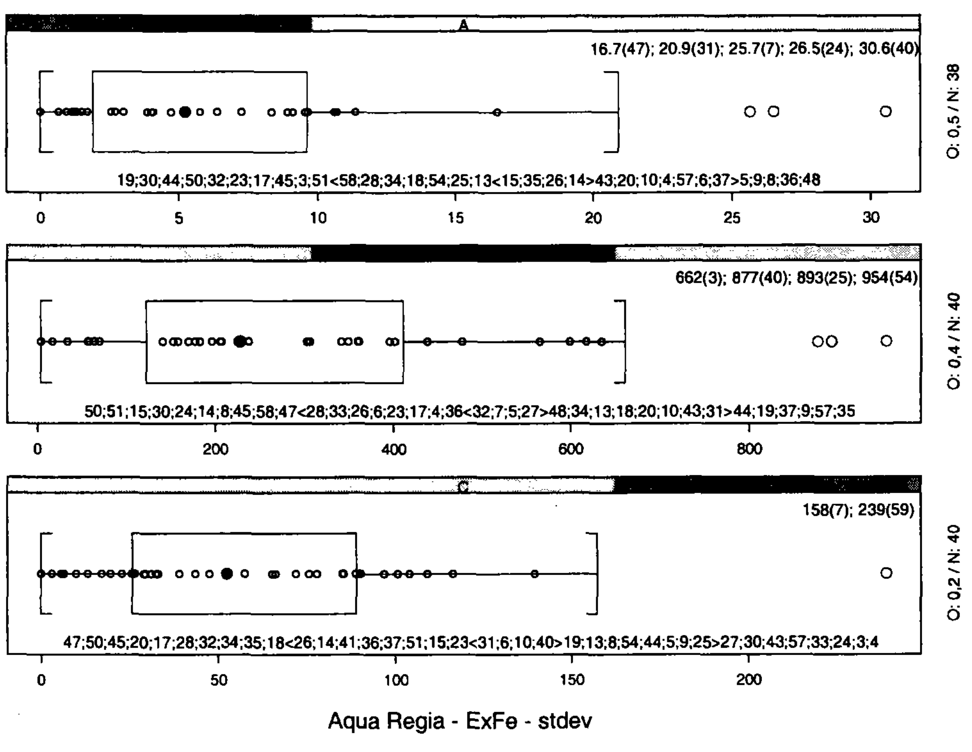


Figure IV.215: Boxplot stdev – Extractable Fe

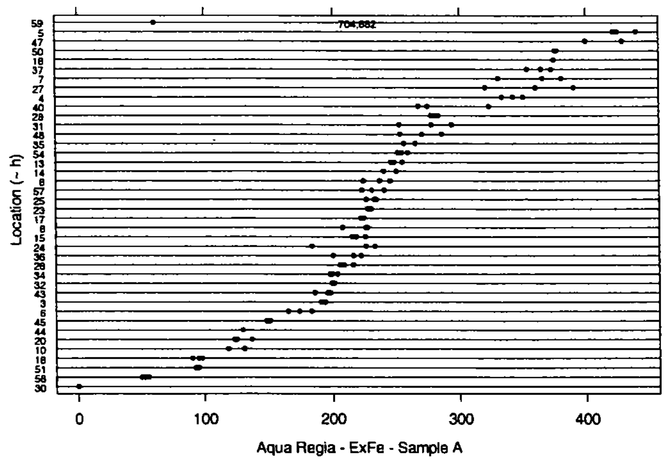


Figure IV.216: Dotplot - Sample A – Extractable Fe

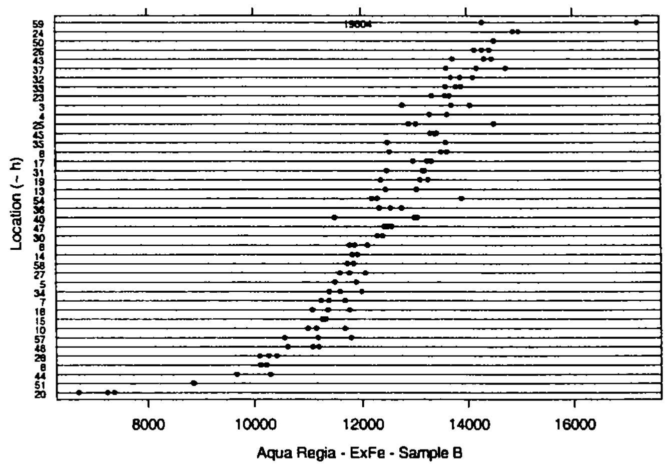


Figure IV.217: Dotplot - Sample B – Extractable Fe

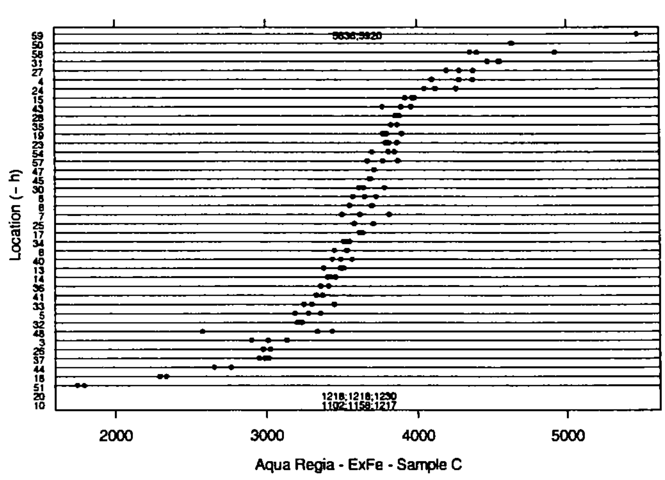


Figure IV.218: Dotplot - Sample C – Extractable Fe

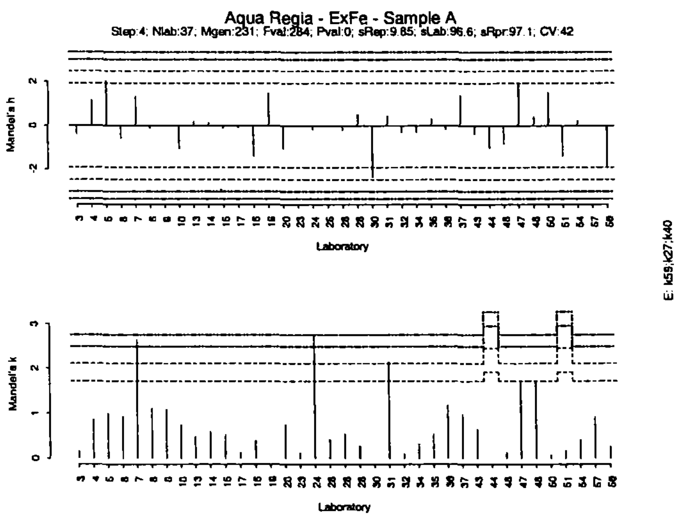


Figure IV.219: Mandel h/k plot - Sample A – Extractable Fe

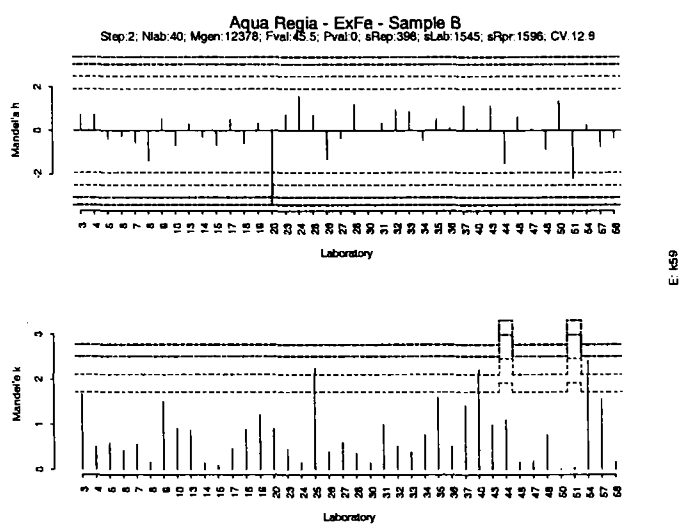


Figure IV.220: Mandel h/k plot - Sample B – Extractable Fe

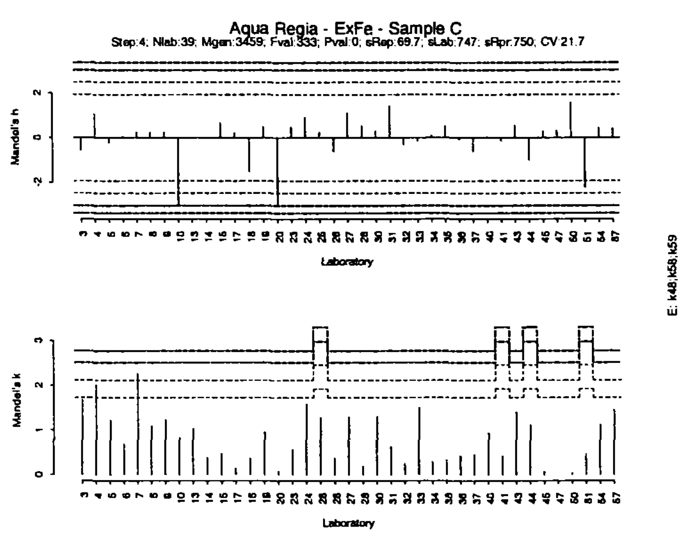


Figure IV.221: Mandel h/k plot - Sample C – Extractable Fe

Parameter: Extractable Hg

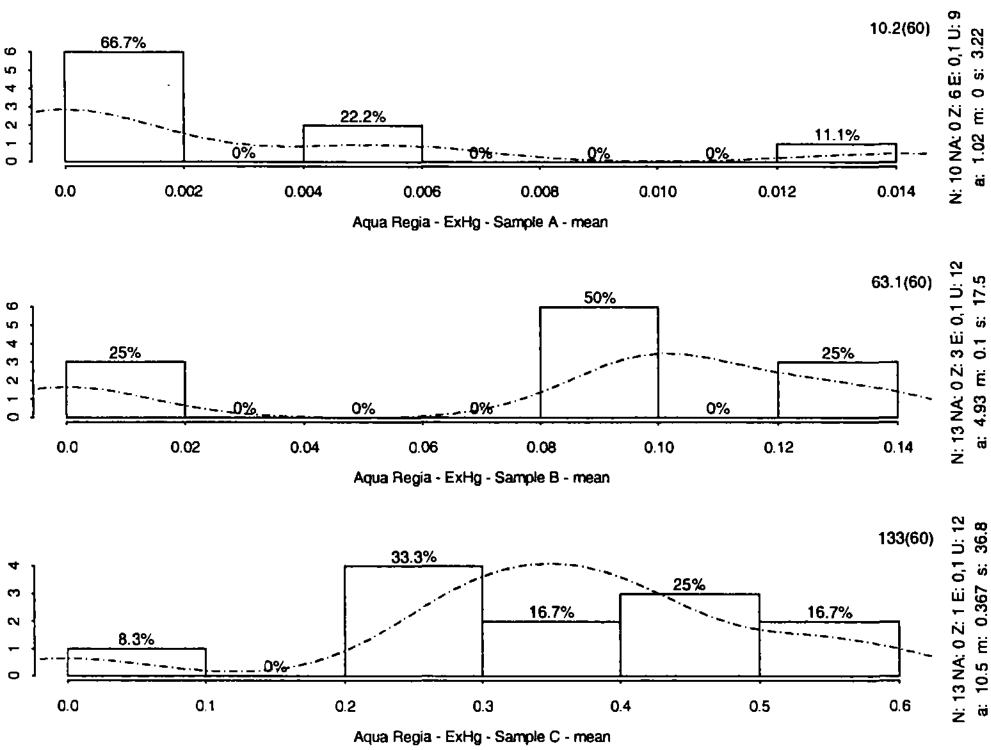


Figure IV.222: Histogram mean – Extractable Hg

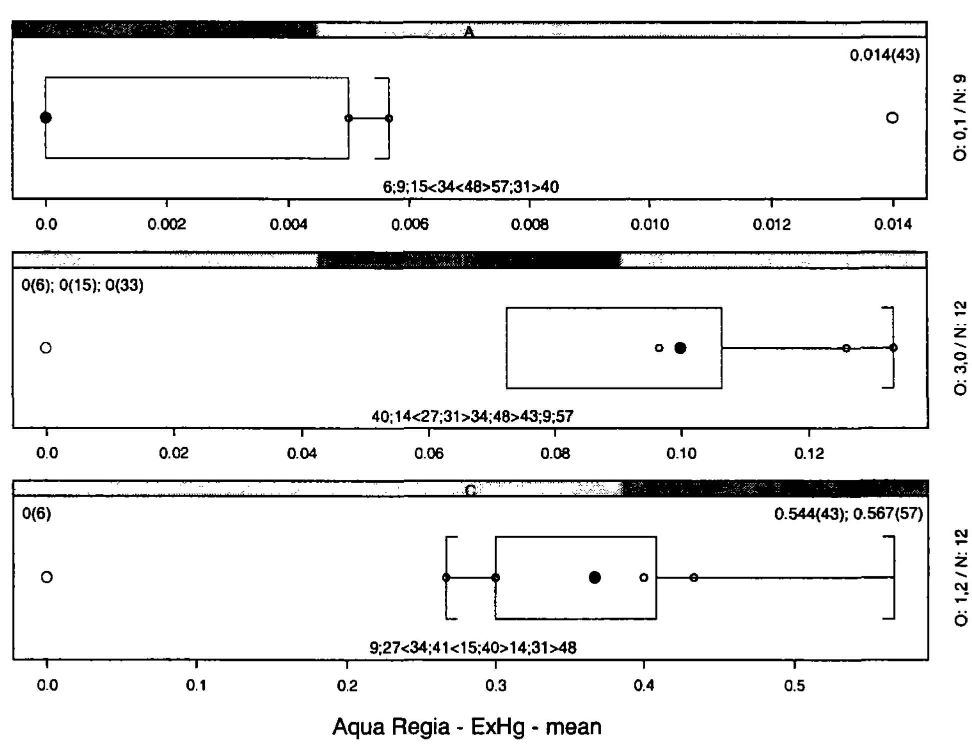


Figure IV.223: Boxplot mean – Extractable Hg

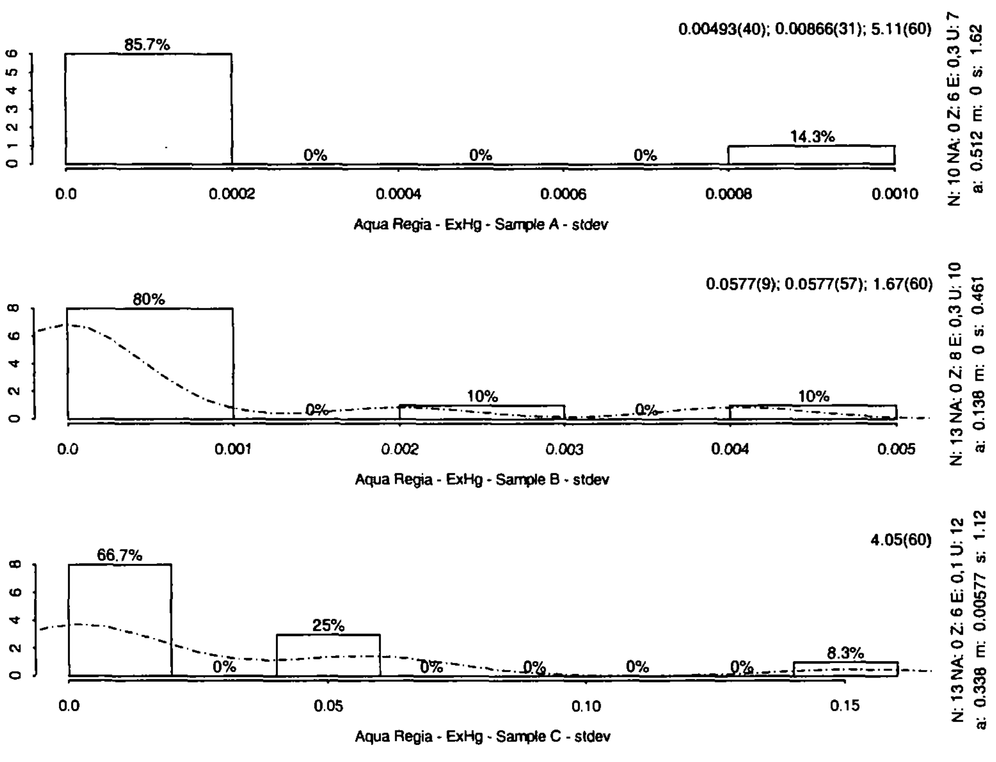


Figure IV.224: Histogram stdev – Extractable Hg

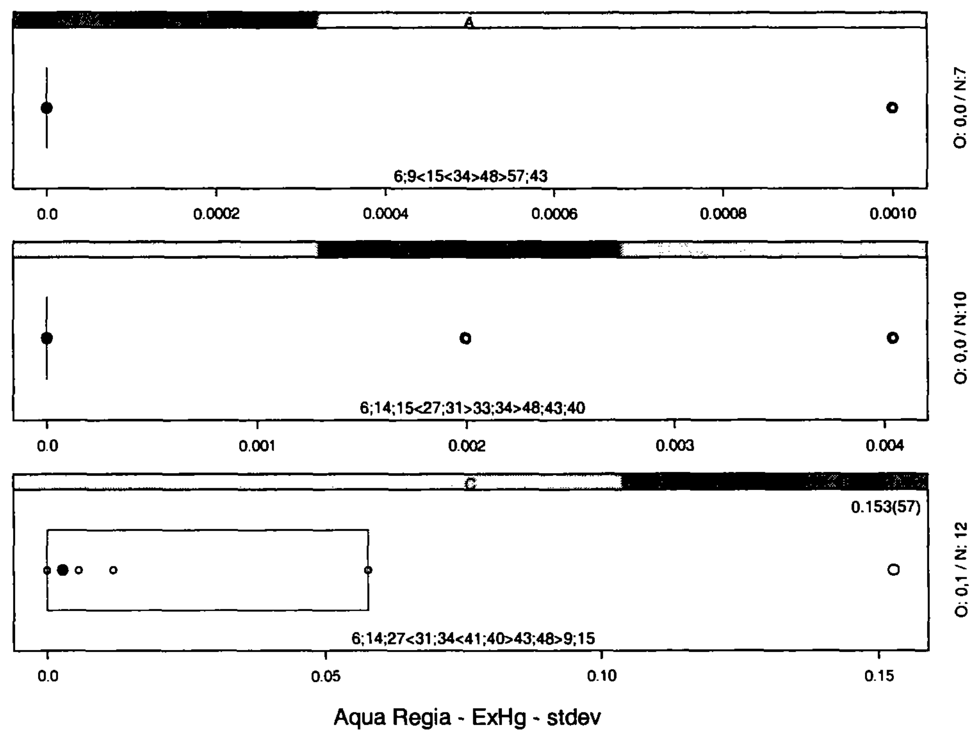


Figure IV.225: Boxplot stdev – Extractable Hg

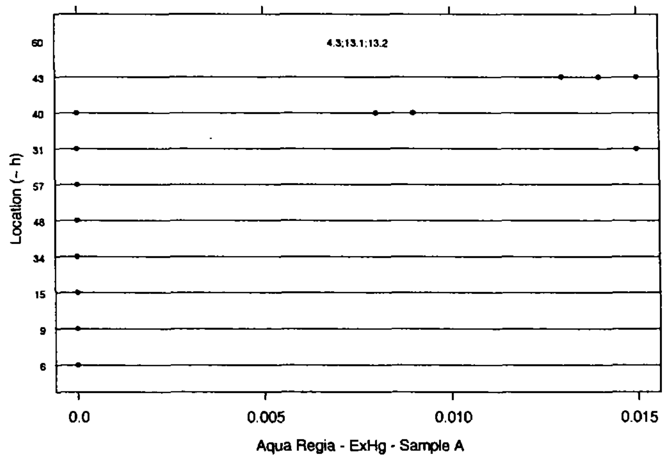


Figure IV.226: Dotplot - Sample A – Extractable Hg

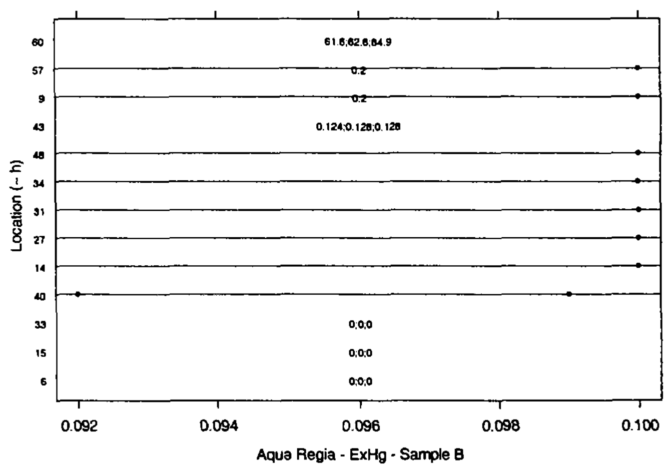


Figure IV.227: Dotplot - Sample B – Extractable Hg

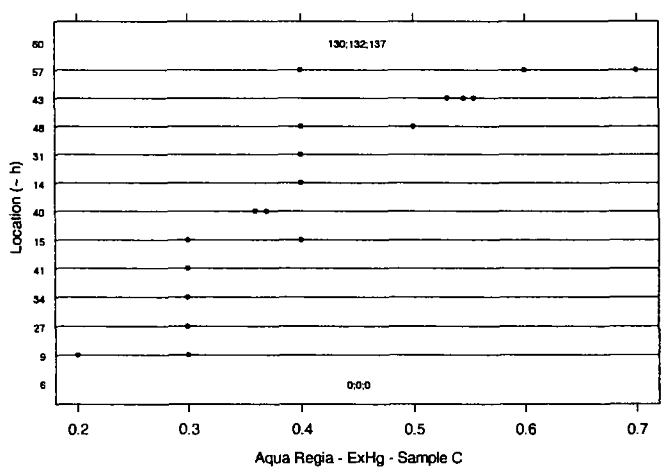


Figure IV.228: Dotplot - Sample C – Extractable Hg

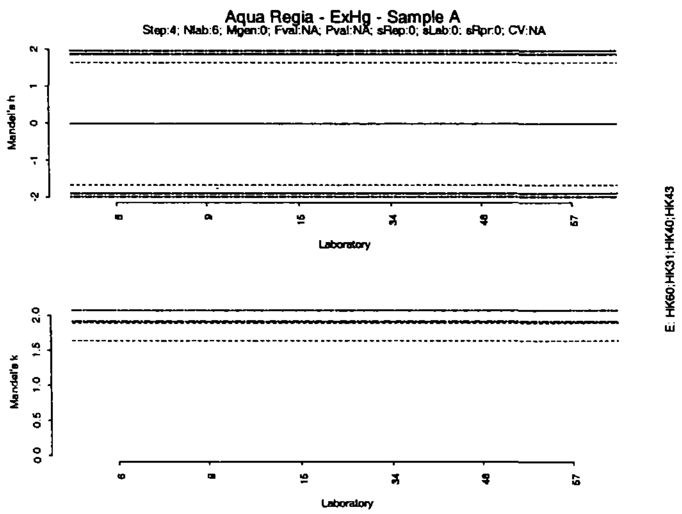


Figure IV.229: Mandel h/k plot - Sample A – Extractable Hg

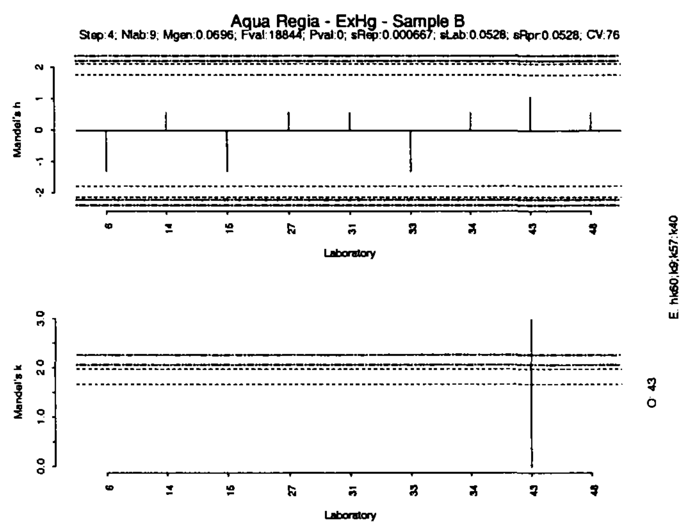


Figure IV.230: Mandel h/k plot - Sample B – Extractable Hg

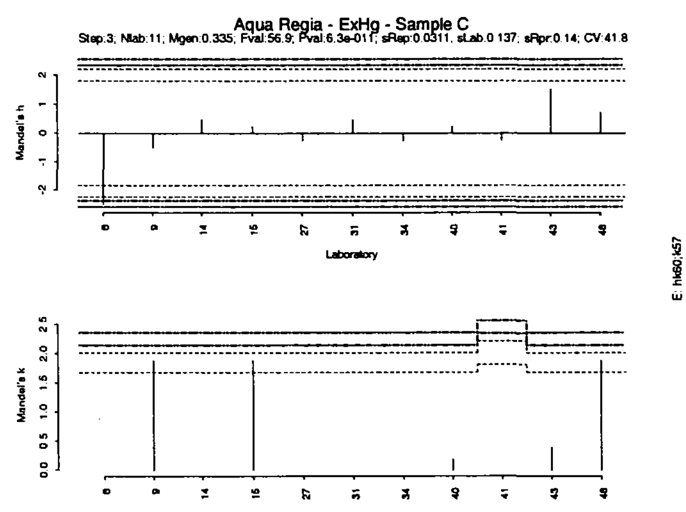


Figure IV.231: Mandel h/k plot - Sample C – Extractable Hg

Parameter: Extractable K

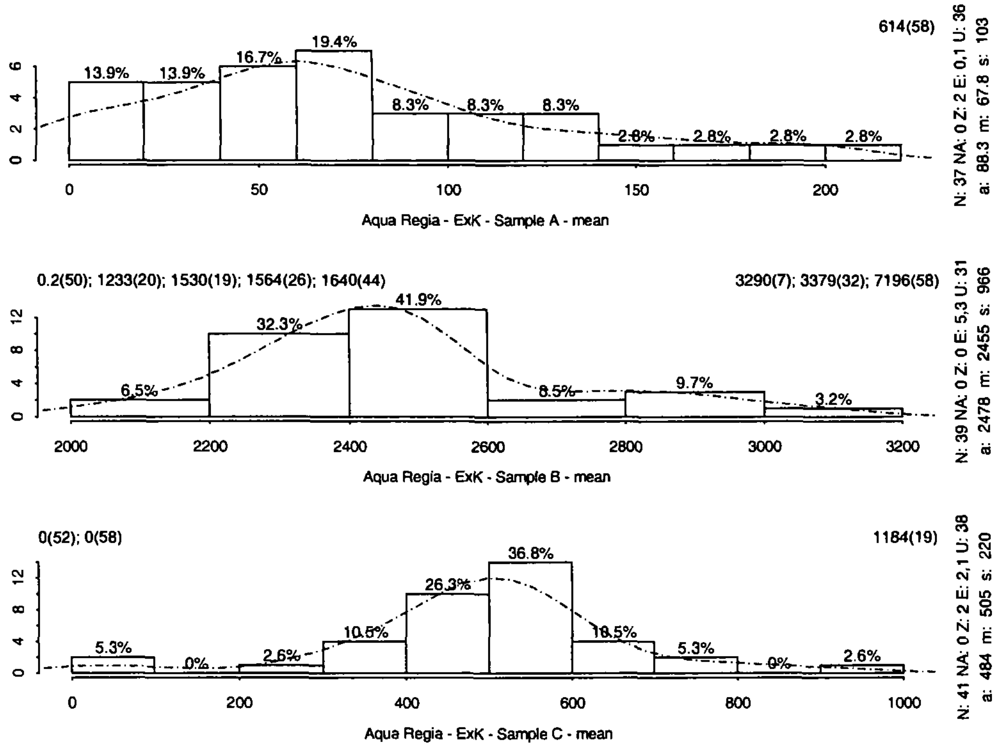


Figure IV.232: Histogram mean – Extractable K

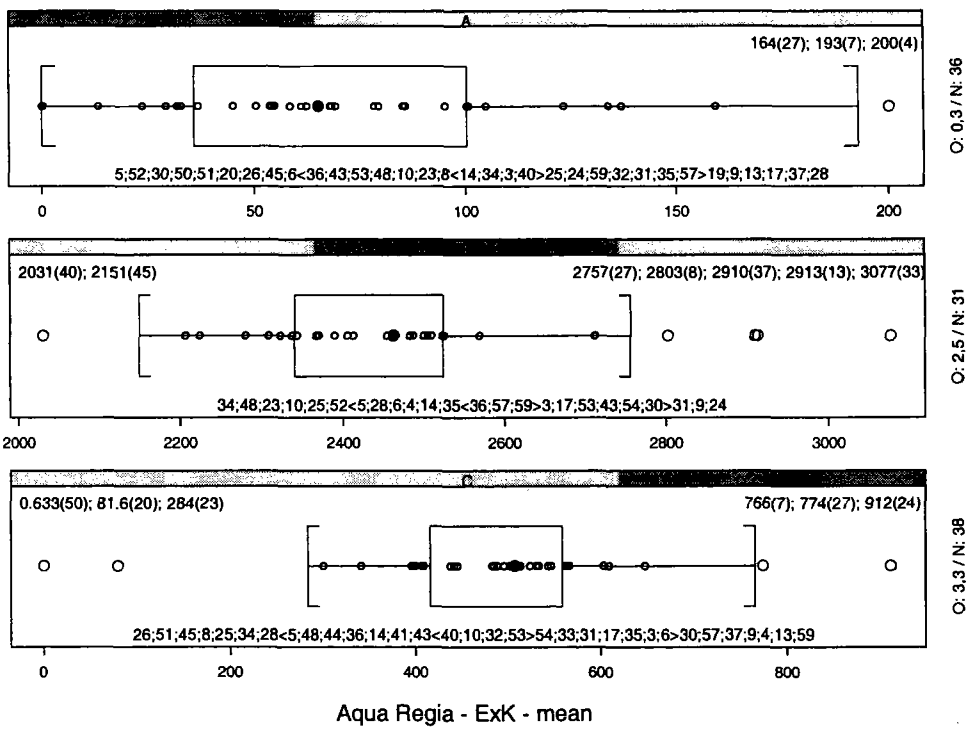


Figure IV.233: Boxplot mean – Extractable K

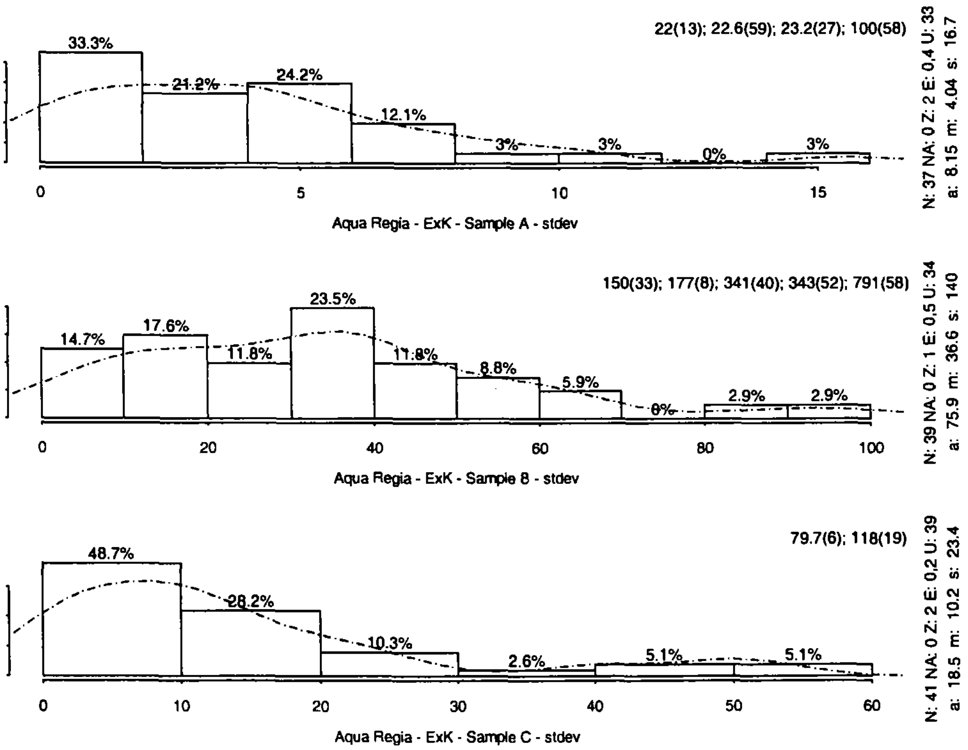


Figure IV.234: Histogram stdev – Extractable K

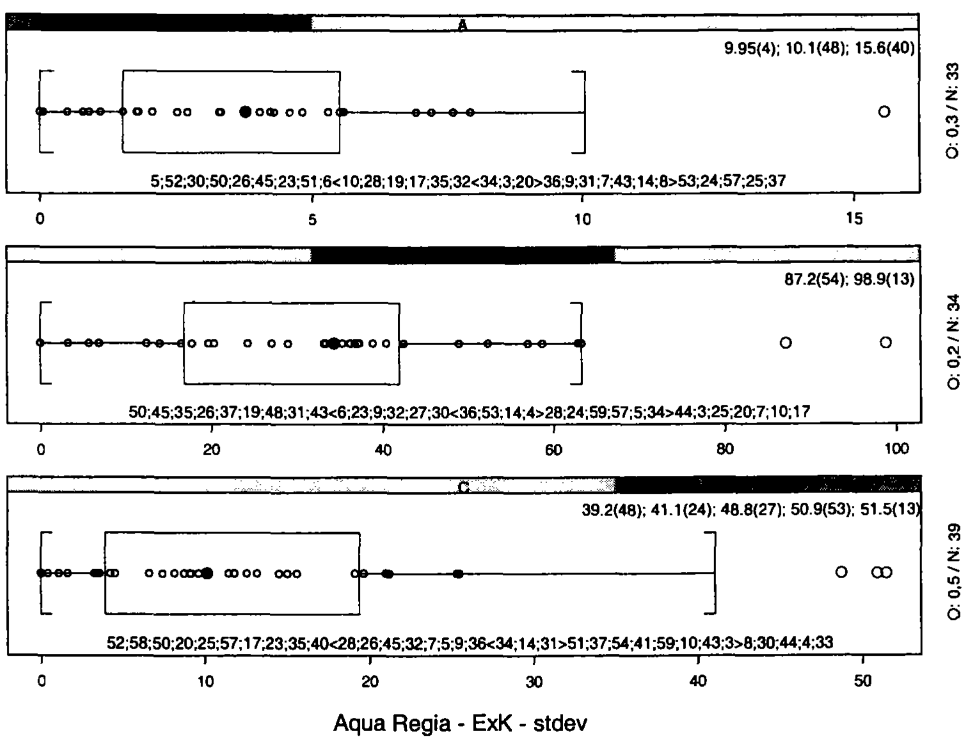


Figure IV.235: Boxplot stdev – Extractable K

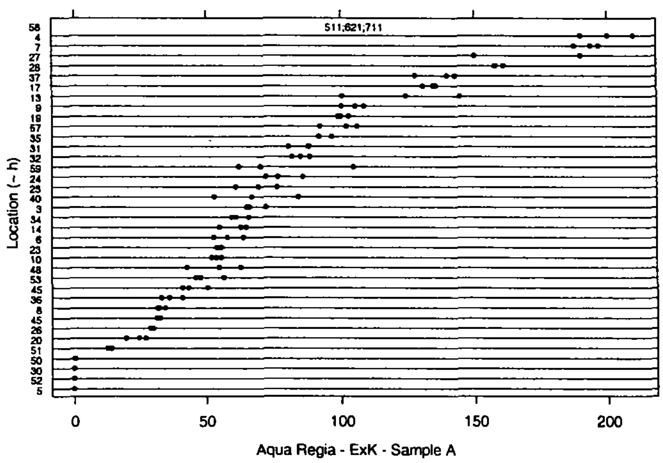


Figure IV.236: Dotplot - Sample A – Extractable K

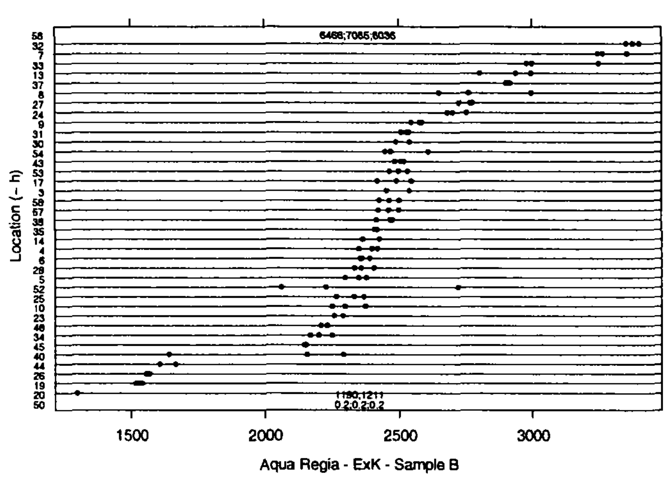


Figure IV.237: Dotplot - Sample B – Extractable K

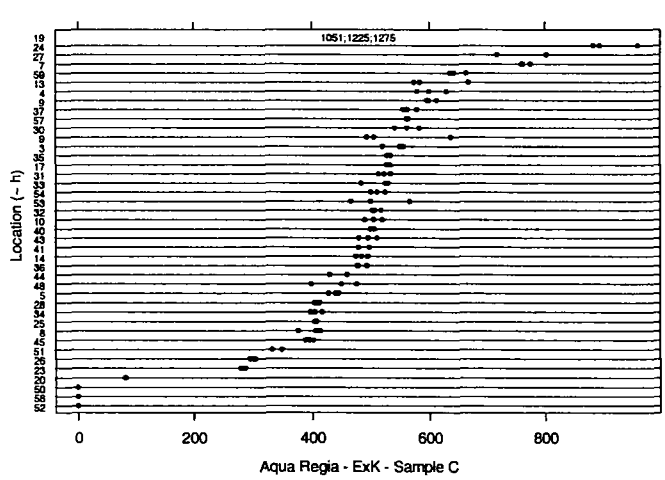


Figure IV.238: Dotplot - Sample C – Extractable K

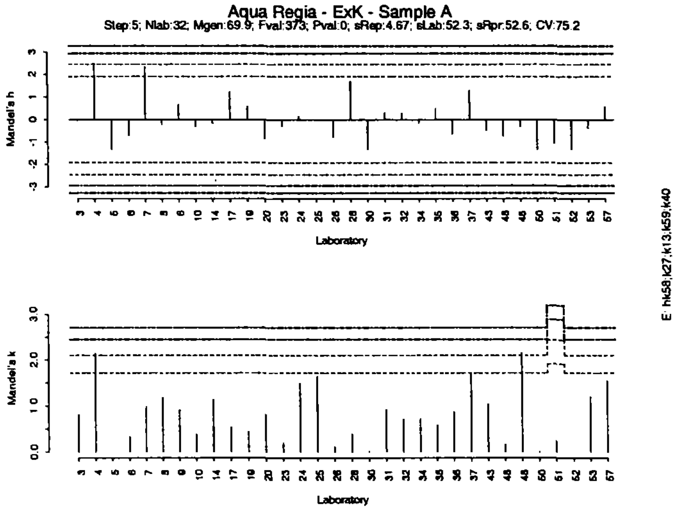


Figure IV.239: Mandel h/k plot - Sample A – Extractable K

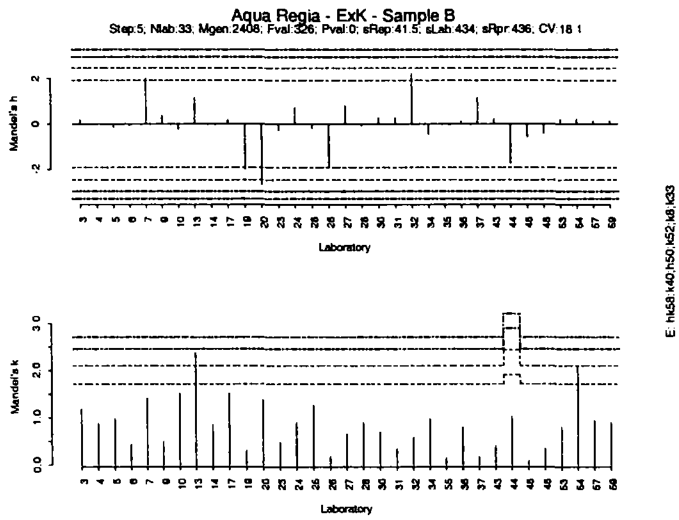


Figure IV.240: Mandel h/k plot - Sample B – Extractable K

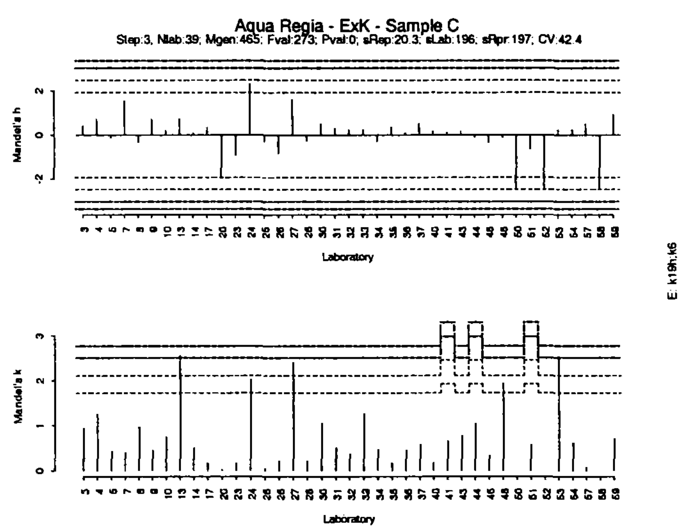


Figure IV.241: Mandel h/k plot - Sample C – Extractable K

Parameter: Extractable Mg

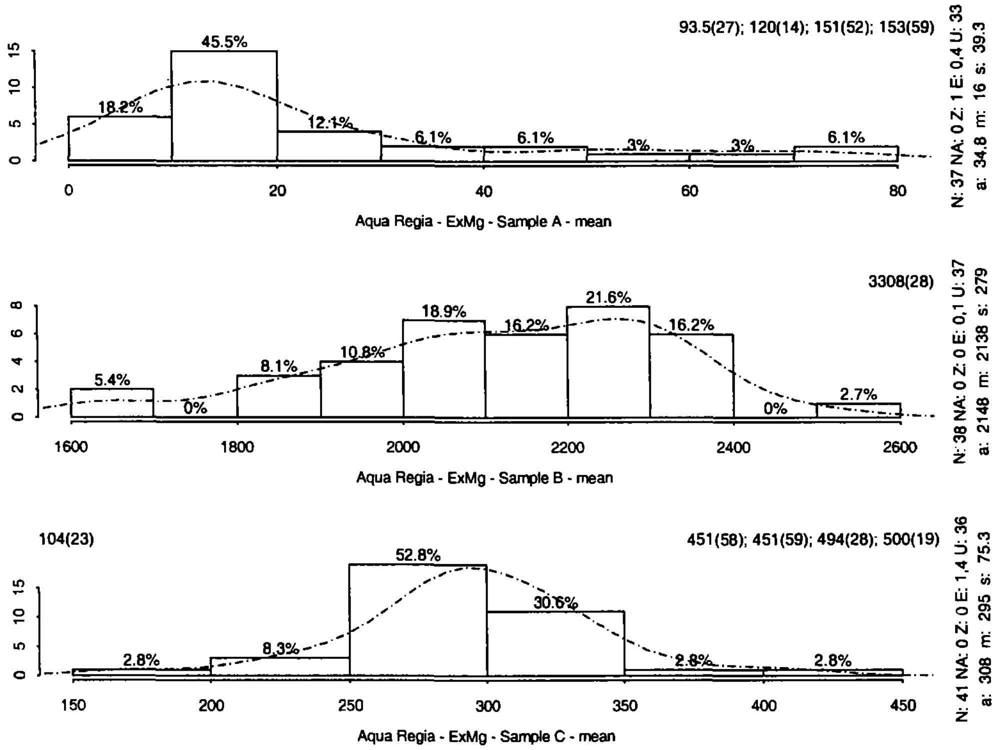


Figure IV.242: Histogram mean – Extractable Mg

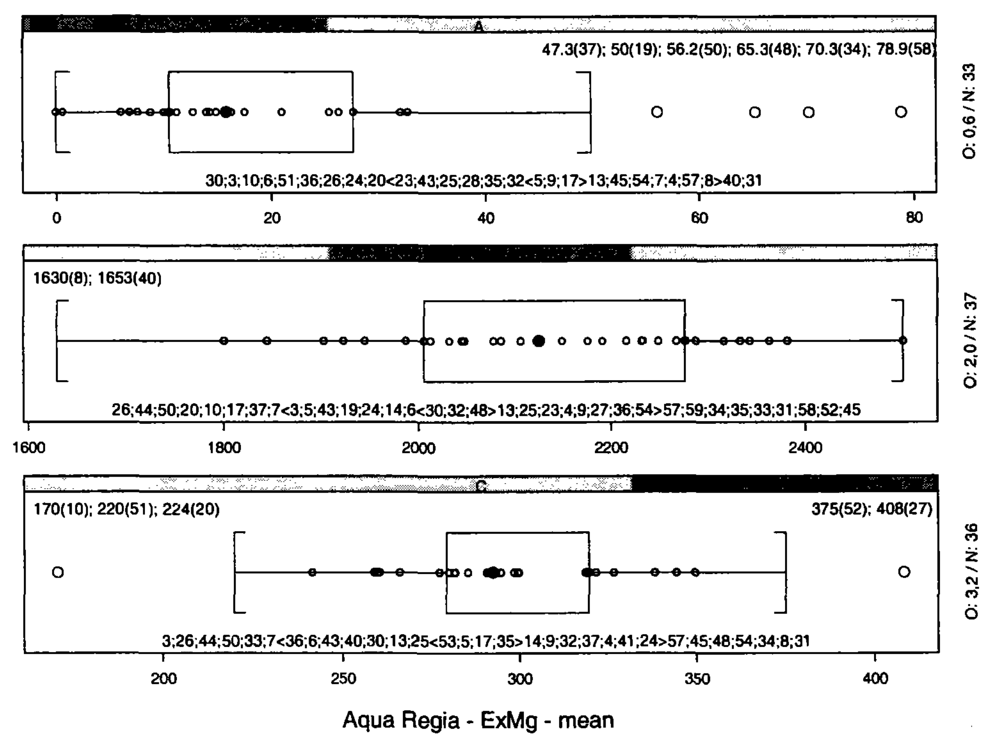


Figure IV.243: Boxplot mean – Extractable Mg

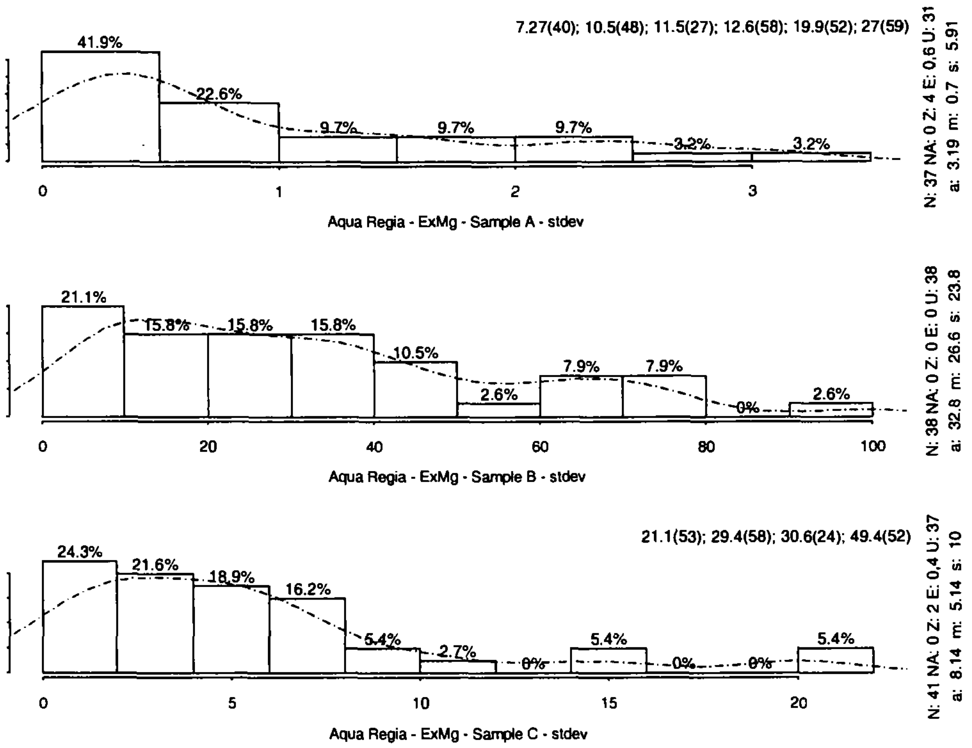


Figure IV.244: Histogram stdev – Extractable Mg

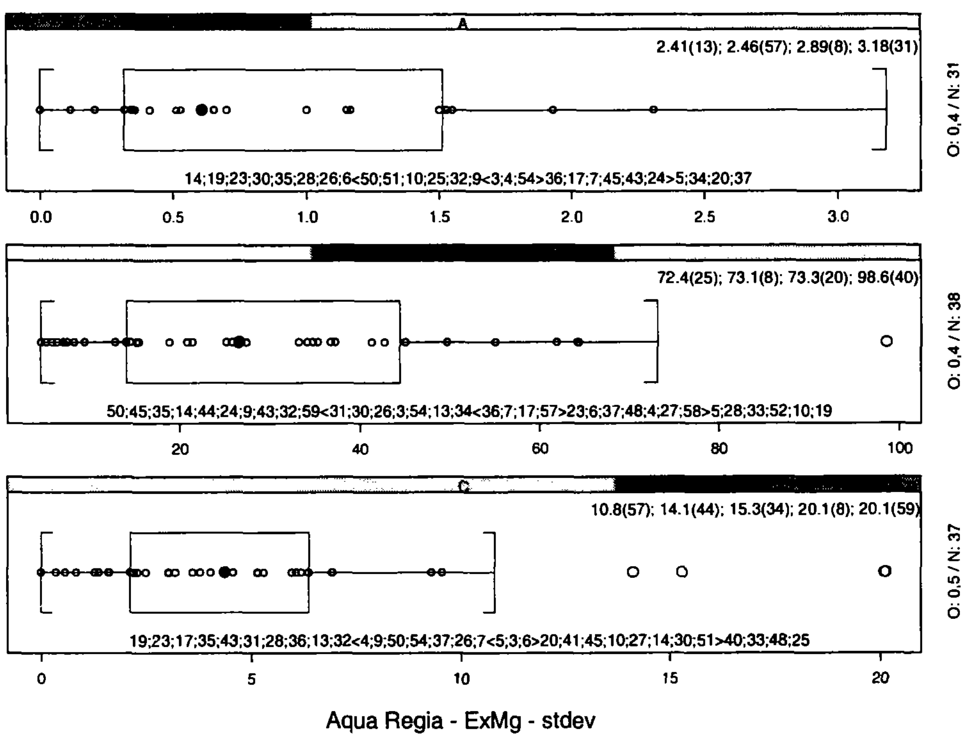


Figure IV.245: Boxplot stdev – Extractable Mg

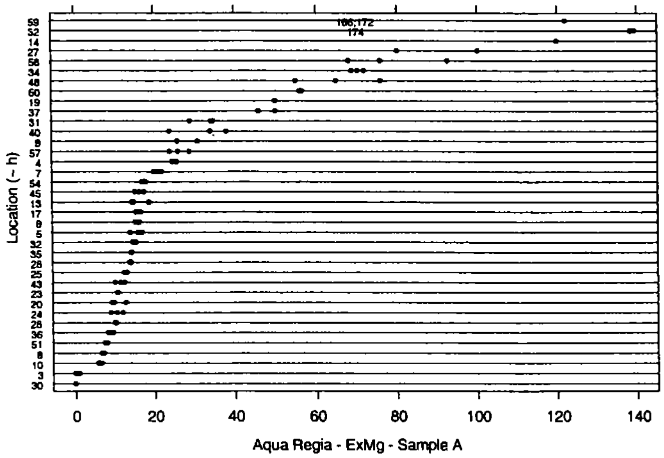


Figure IV.246: Dotplot - Sample A – Extractable Mg

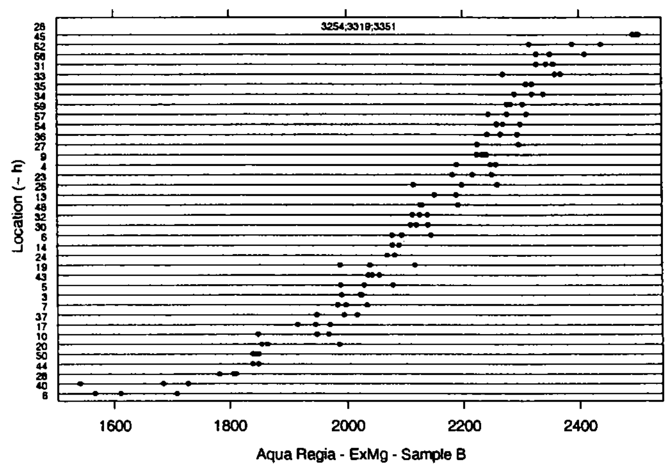


Figure IV.247: Dotplot - Sample B – Extractable Mg

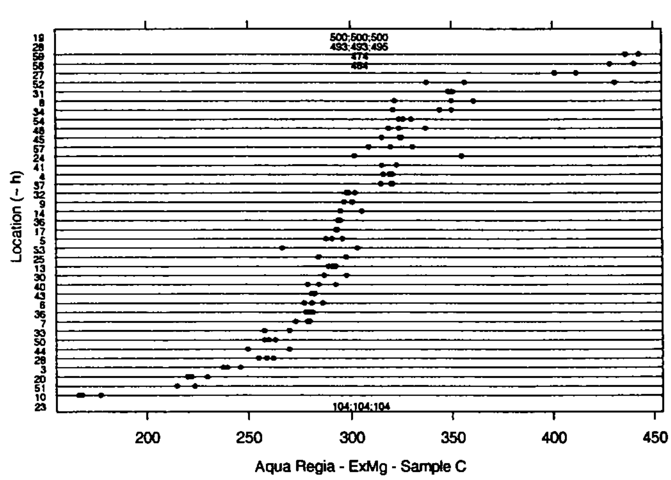


Figure IV.248: Dotplot - Sample C – Extractable Mg

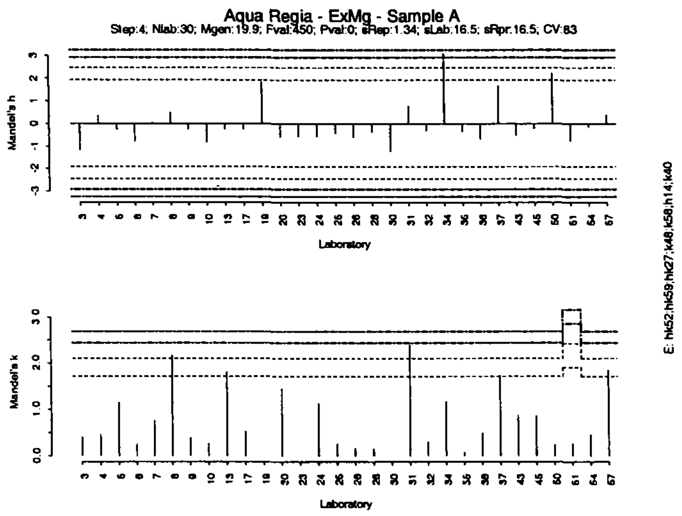


Figure IV.249: Mandel h/k plot - Sample A – Extractable Mg

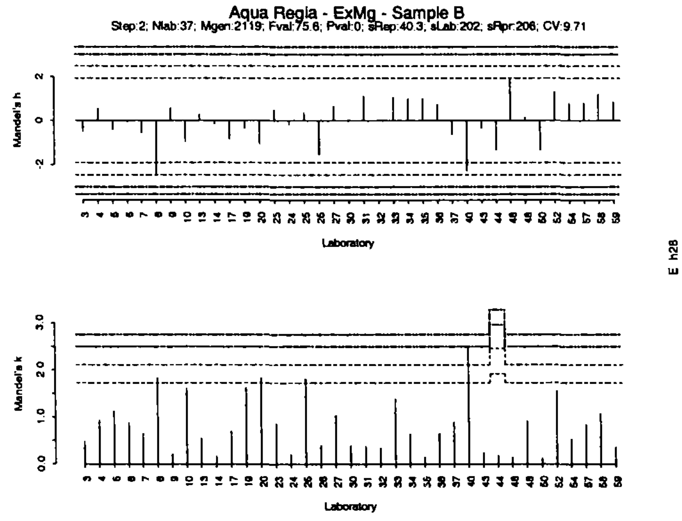


Figure IV.250: Mandel h/k plot - Sample B – Extractable Mg

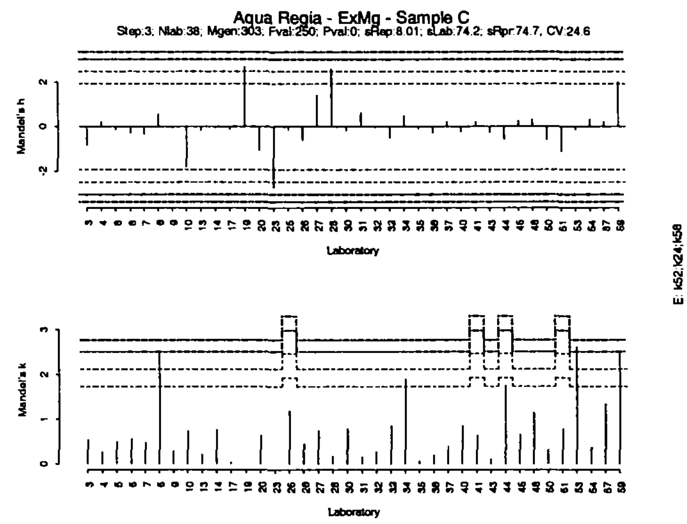


Figure IV.251: Mandel h/k plot - Sample C – Extractable Mg

Parameter: Extractable Mn

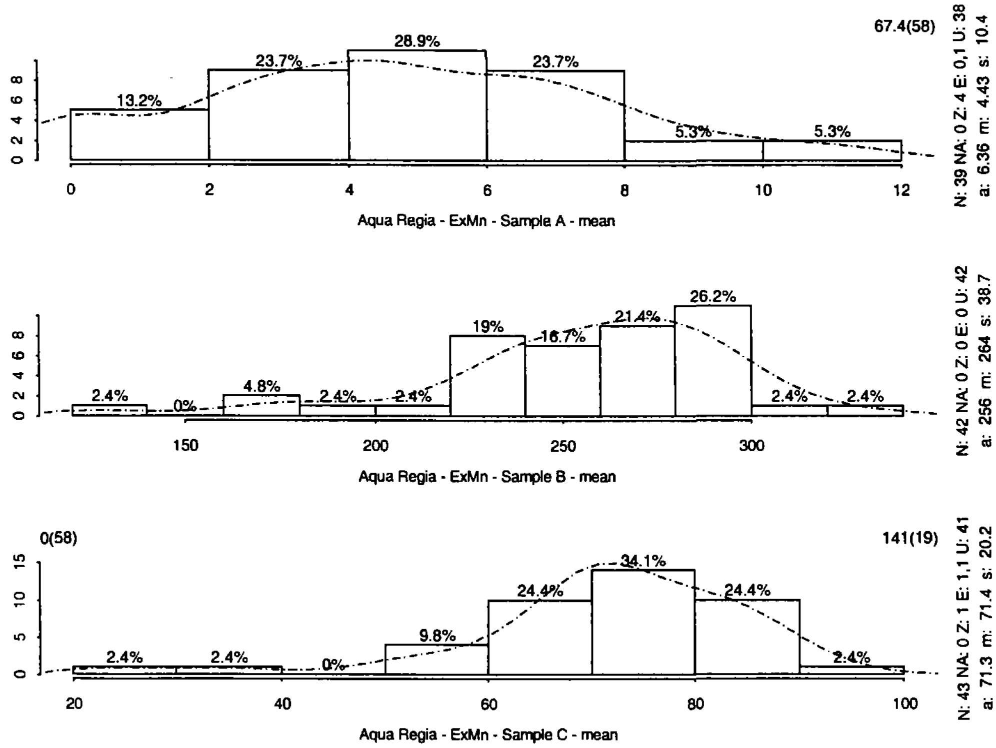


Figure IV.252: Histogram mean – Extractable Mn

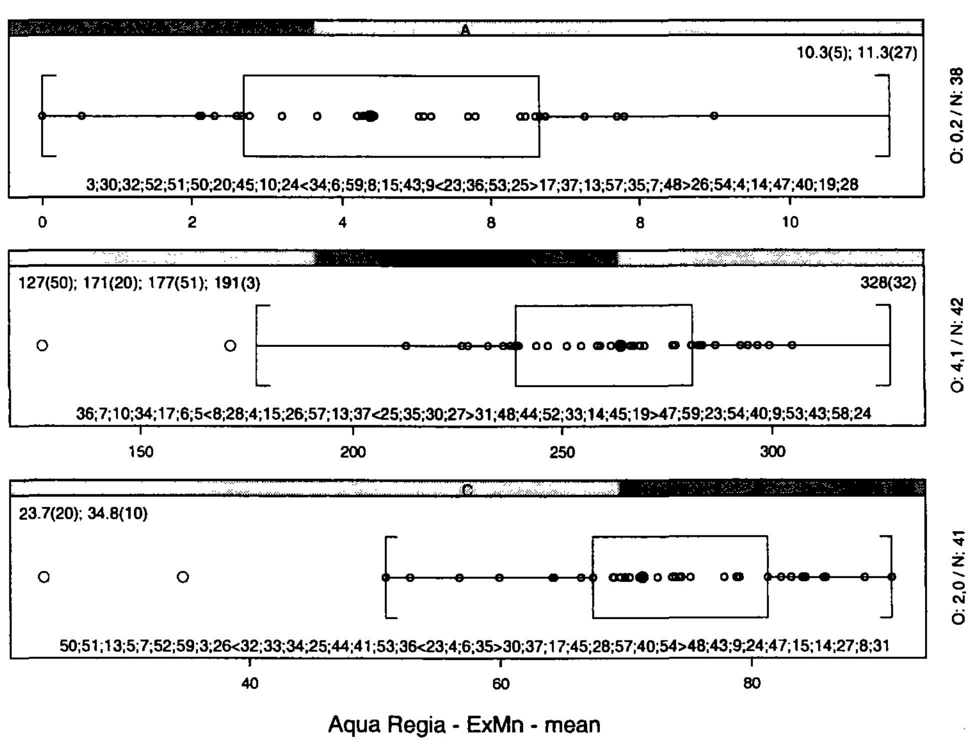


Figure IV.253: Boxplot mean - Extractable Mn

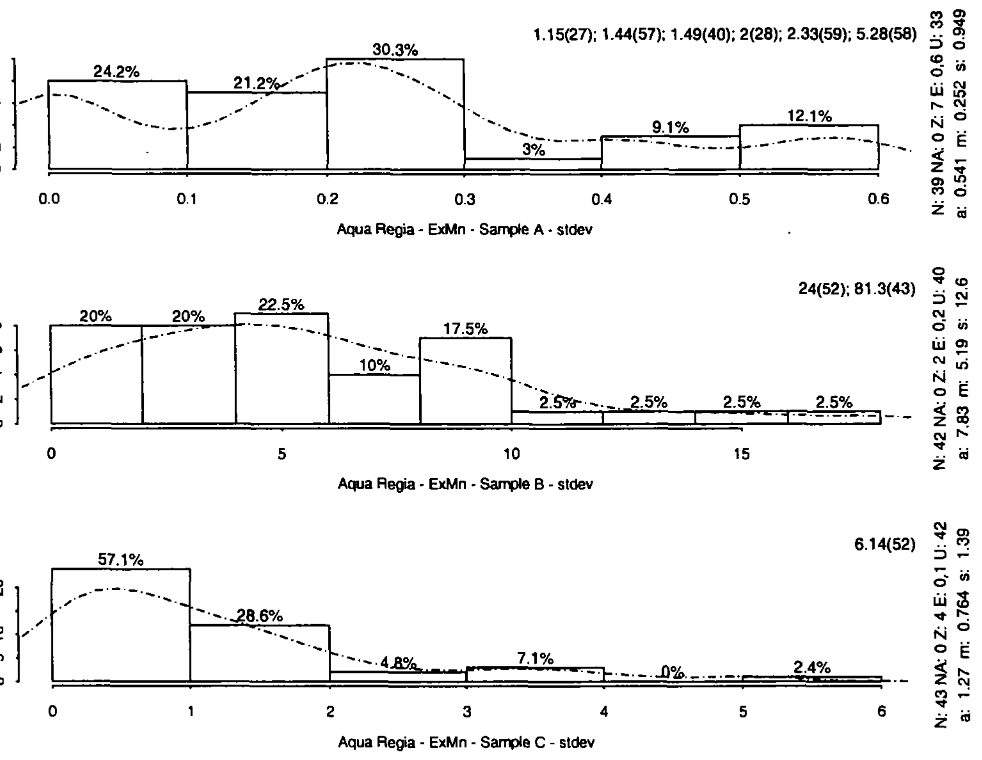


Figure IV.254: Histogram stdev - Extractable Mn

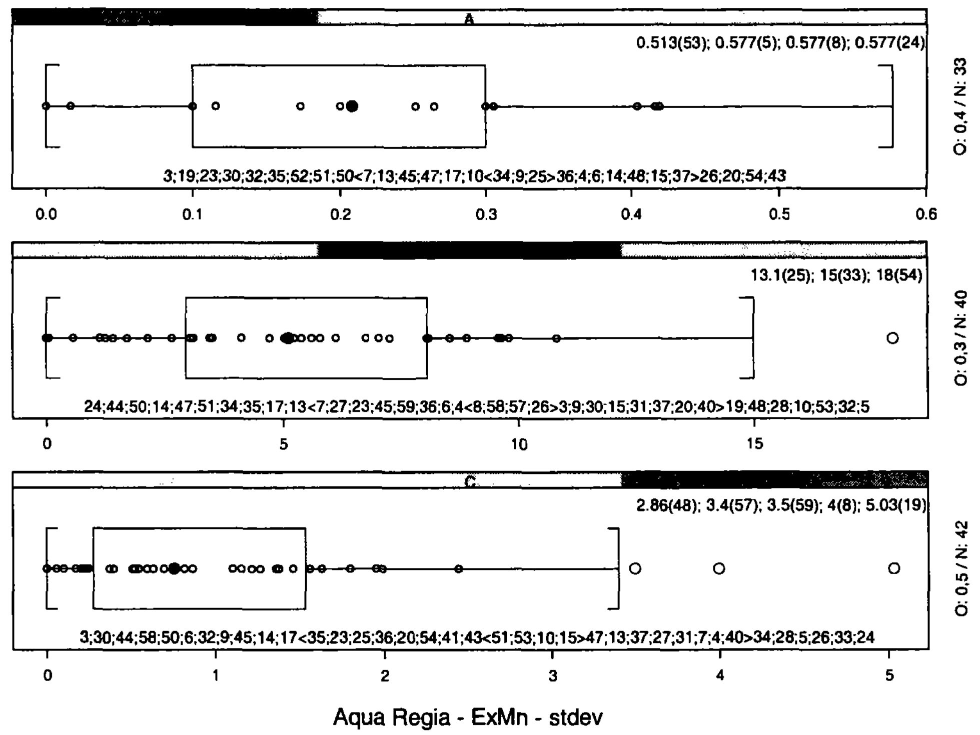


Figure IV.255: Boxplot stdev - Extractable Mn

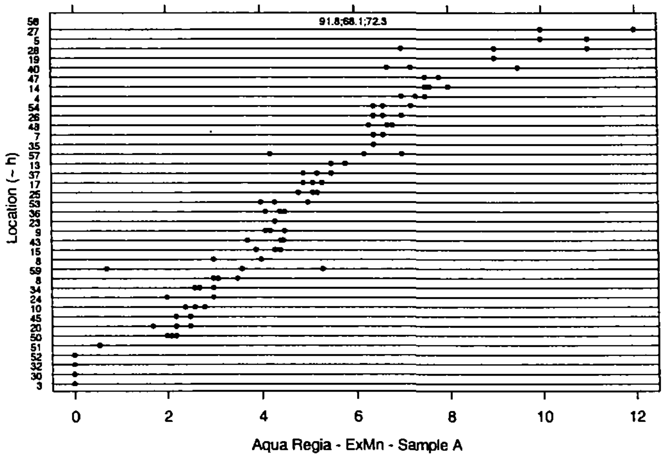


Figure IV.256: Dotplot - Sample A - Extractable Mn

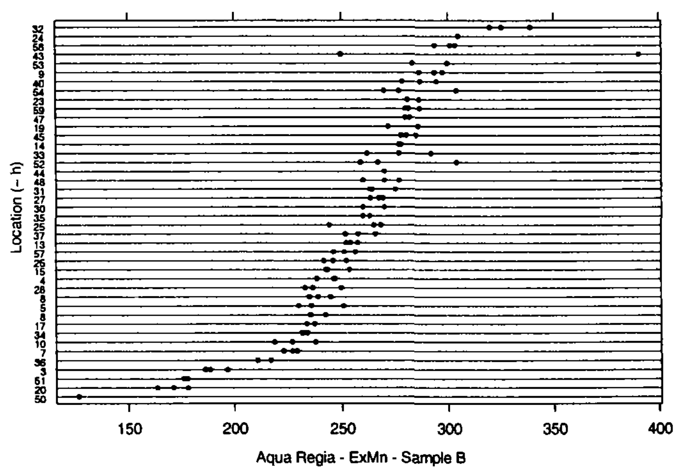


Figure IV.257: Dotplot - Sample Bv - Extractable Mn

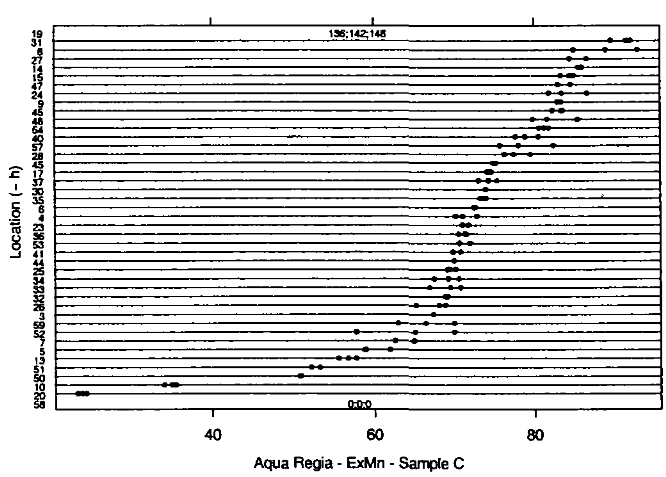


Figure IV.258: Dotplot - Sample C - Extractable Mn

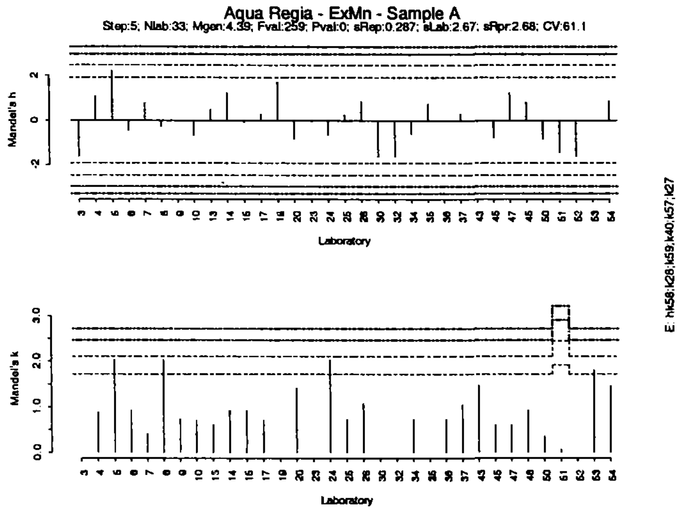


Figure IV.259: Mandel's h and k plot: Sample A - Extractable Mn

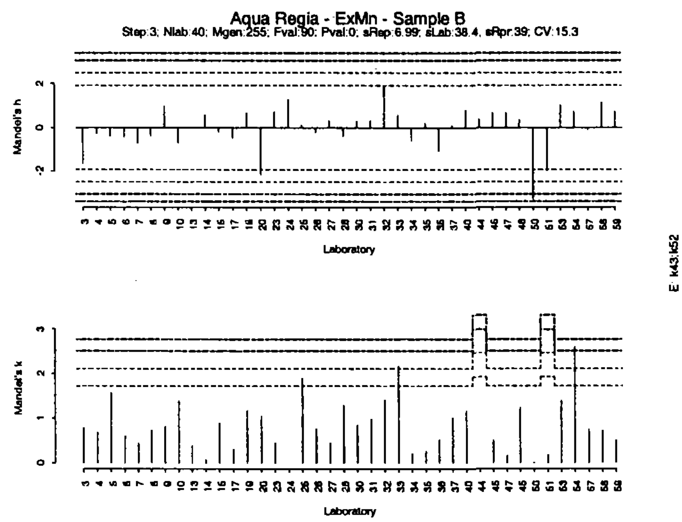


Figure IV.260: Sample B - Extractable Mn

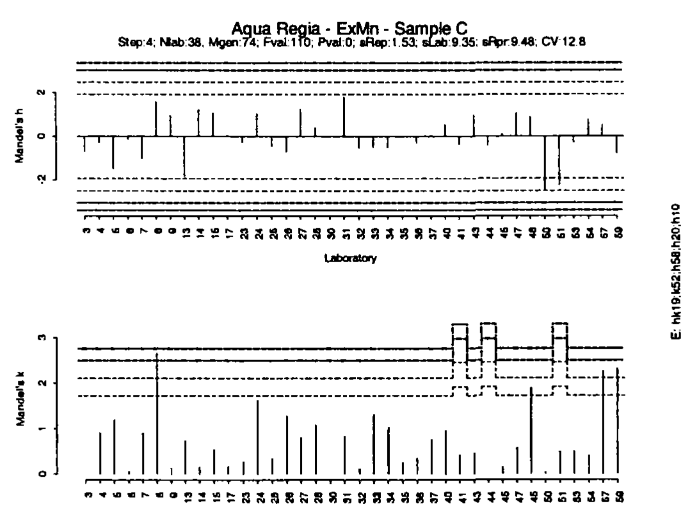


Figure IV.261: Sample Cv - Extractable Mn

Parameter: Extractable Na

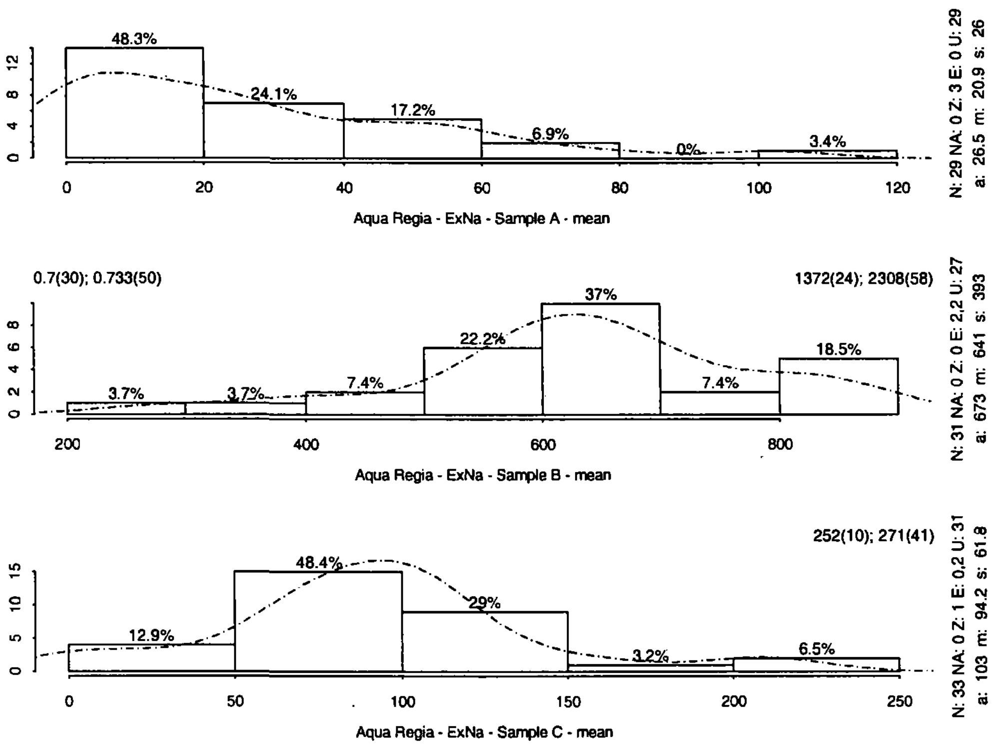


Figure IV.262: Histogram mean - Extractable Na

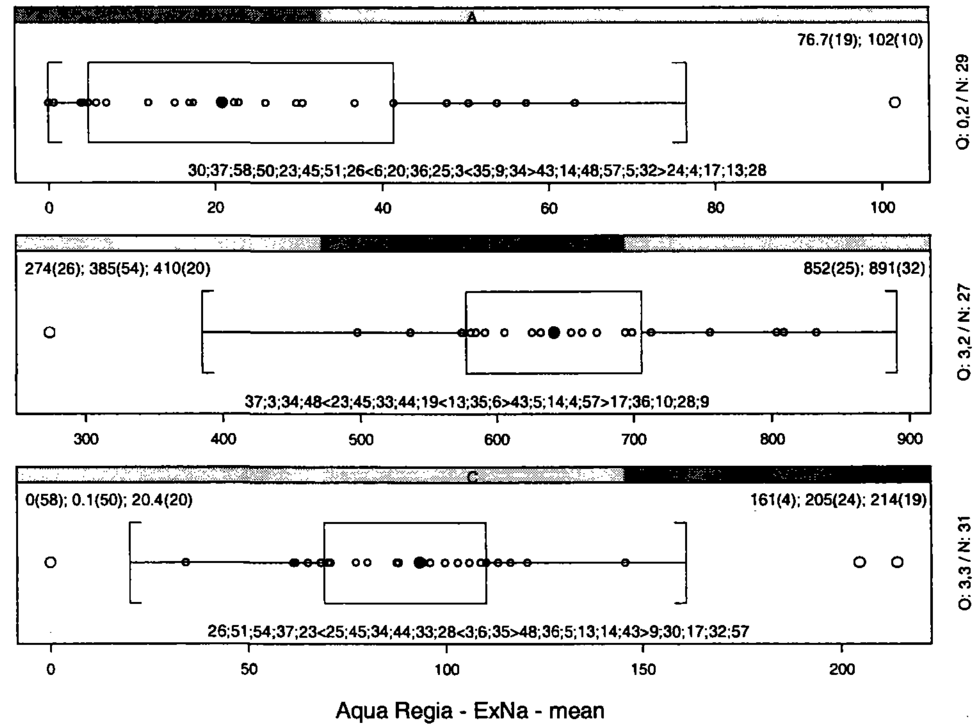


Figure IV.263: Boxplot mean - Extractable Na

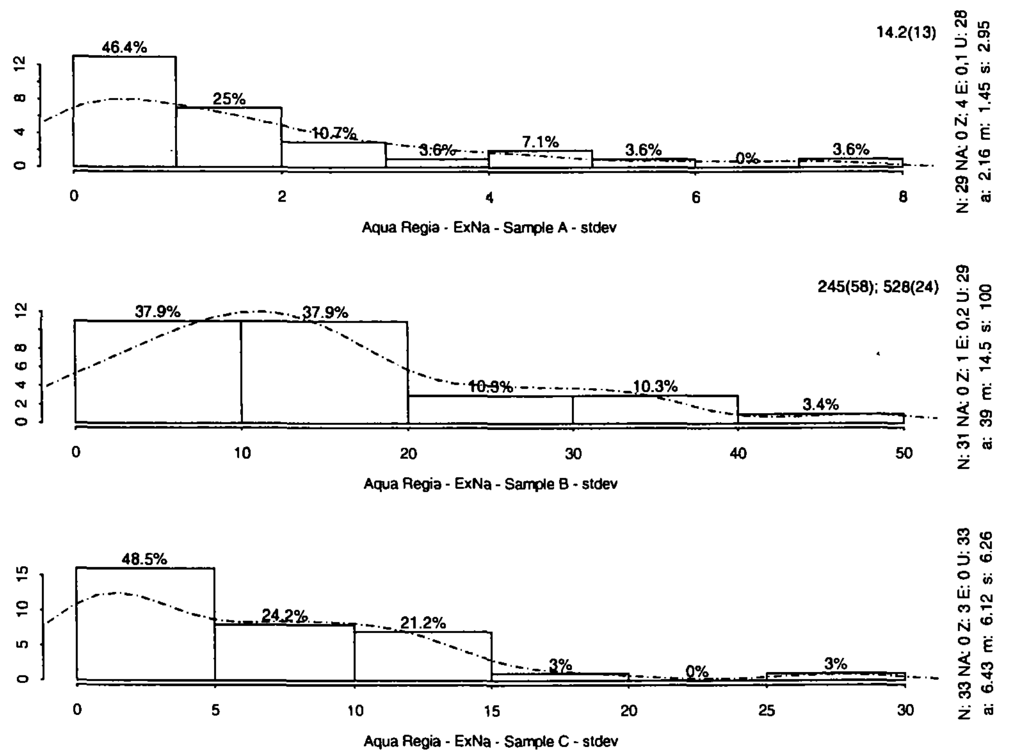


Figure IV.264: Histogram stdev - Extractable Na

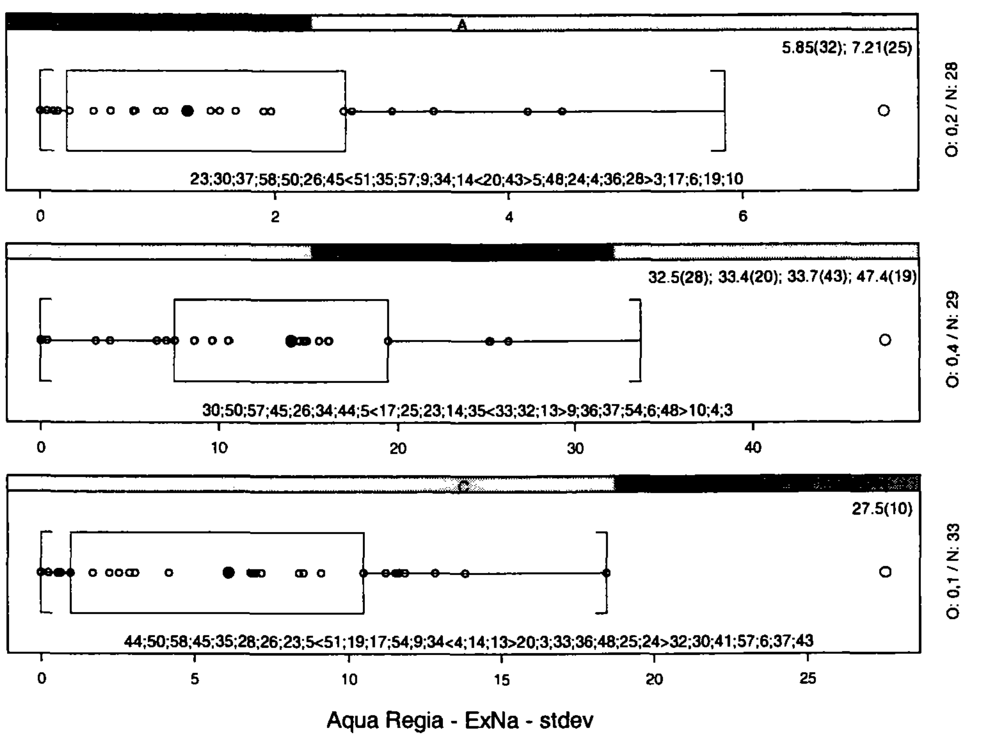


Figure IV.265: Boxplot stdev - Extractable Na

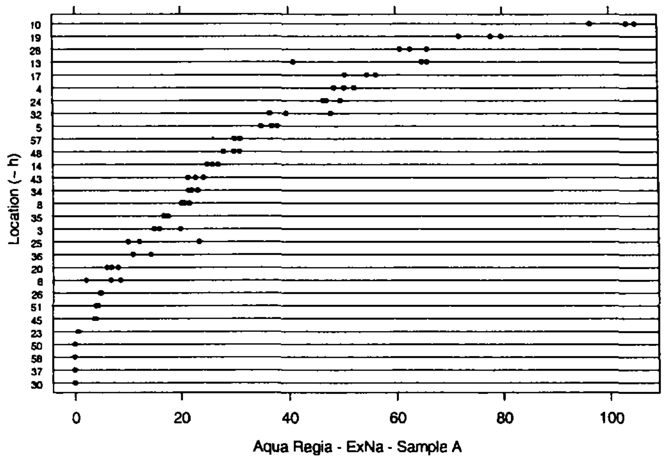


Figure IV.266: Dotplot - Sample A - Extractable Na

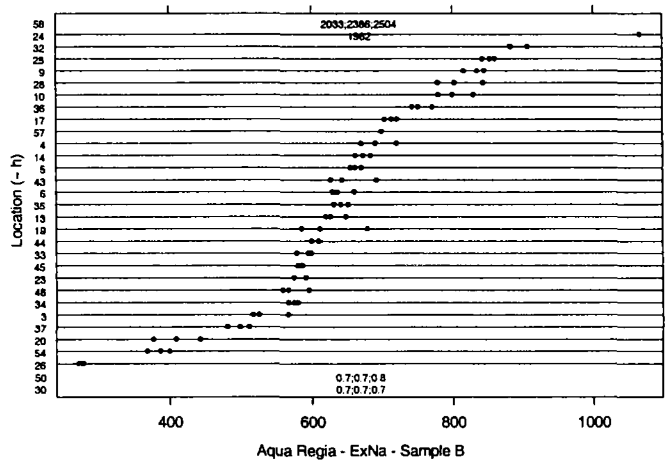


Figure IV.267: Dotplot - Sample B - Extractable Na

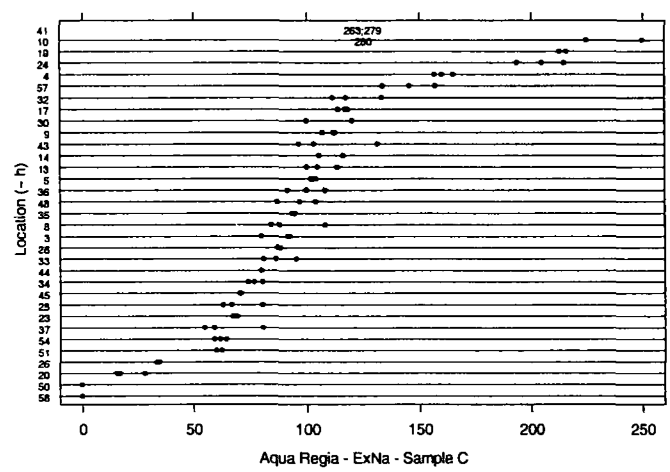


Figure IV.268: Dotplot - Sample C - Extractable Na

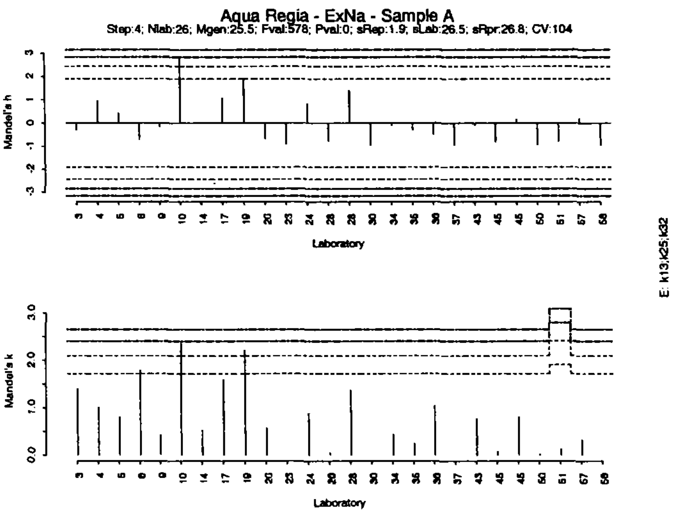


Figure IV.269: Mandel h/k plot - Sample A - Extractable Na

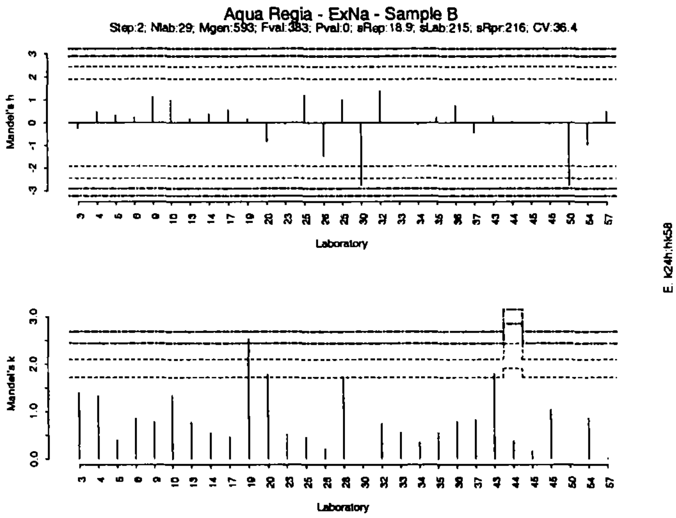


Figure IV.270: Mandel h/k plot - Sample B - Extractable Na

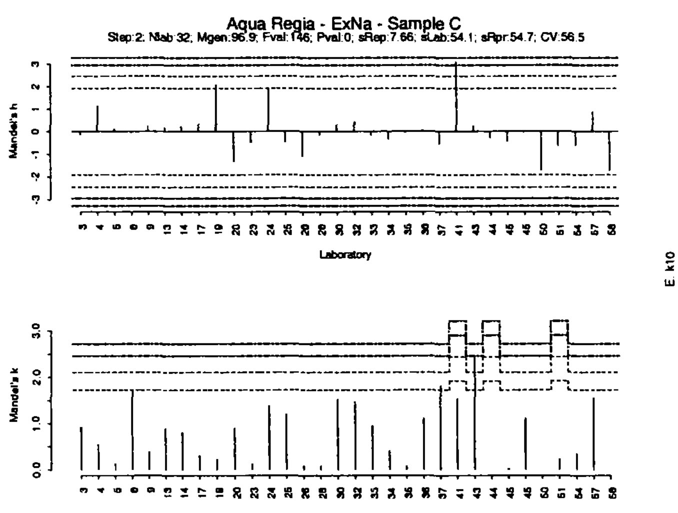


Figure IV.271: Mandel h/k plot - Sample C - Extractable Na

Parameter: Extractable Ni

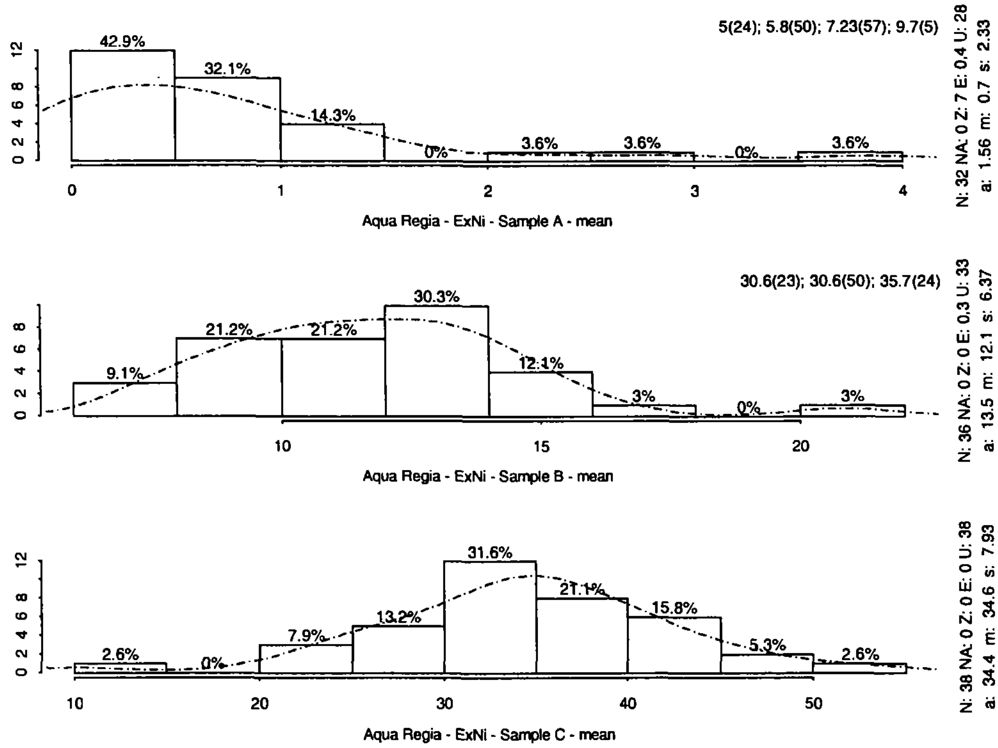


Figure IV.272: Histogram mean - Extractable Ni

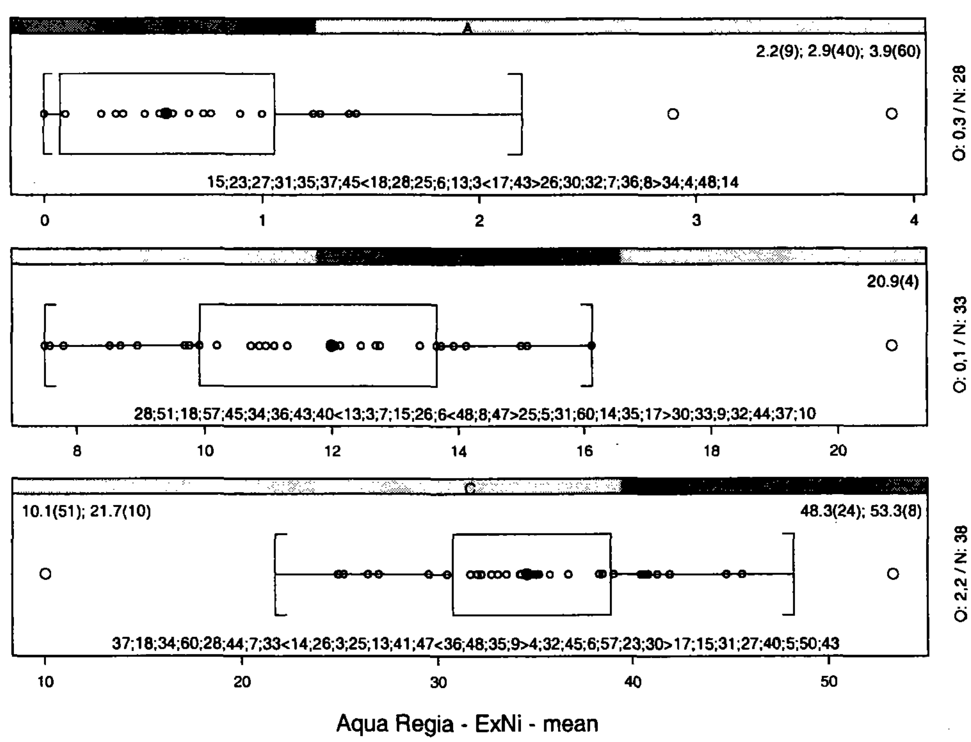


Figure IV.273: Boxplot mean - Extractable Ni

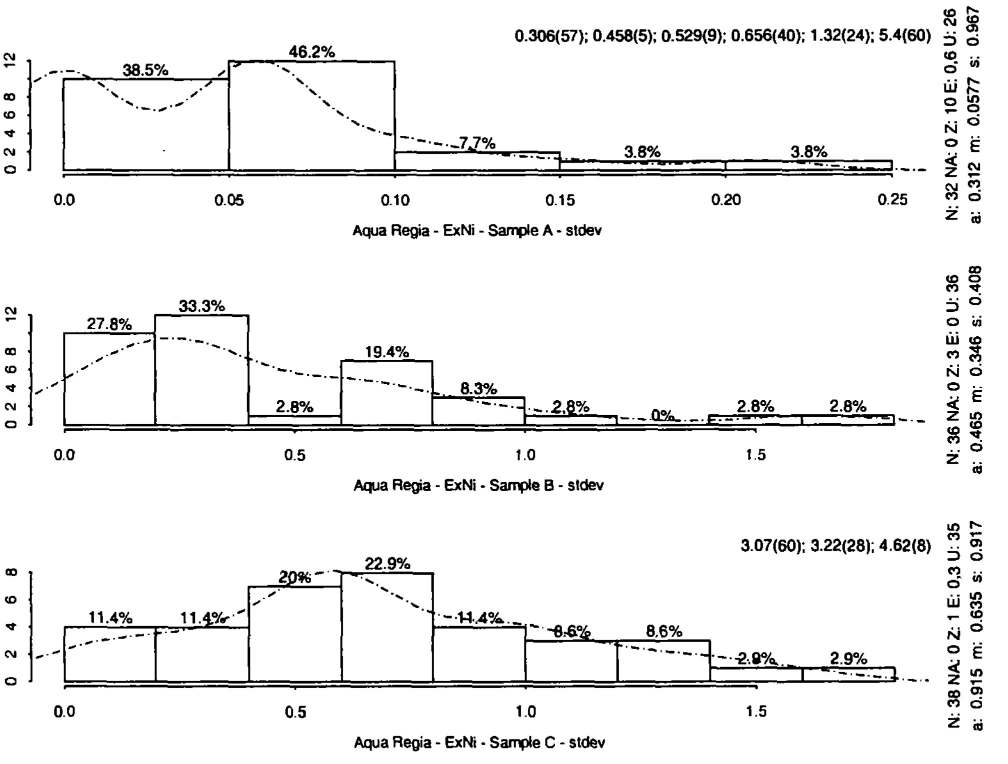


Figure IV.274: Histogram stdev - Extractable Ni

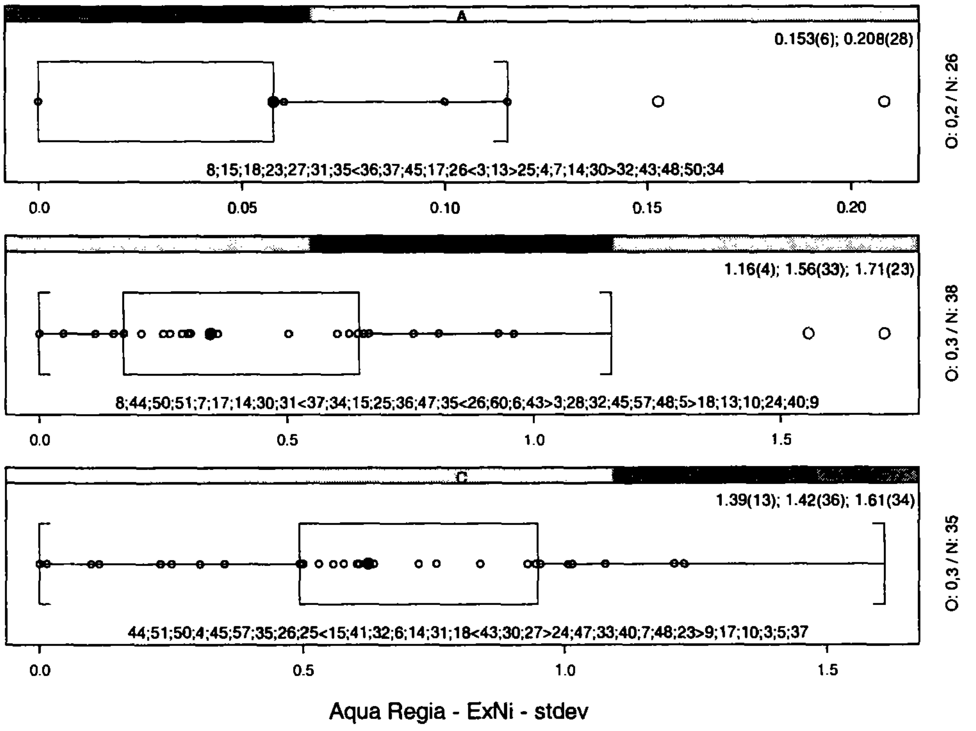


Figure IV.275: Boxplot stdev - Extractable Ni

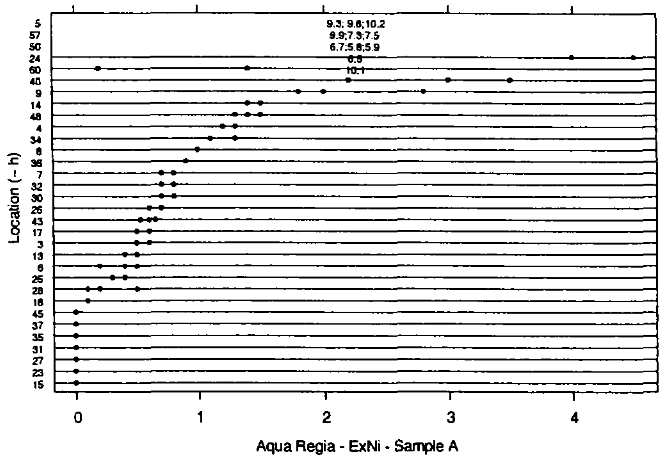


Figure IV.276: Dotplot - Sample A - Extractable Ni

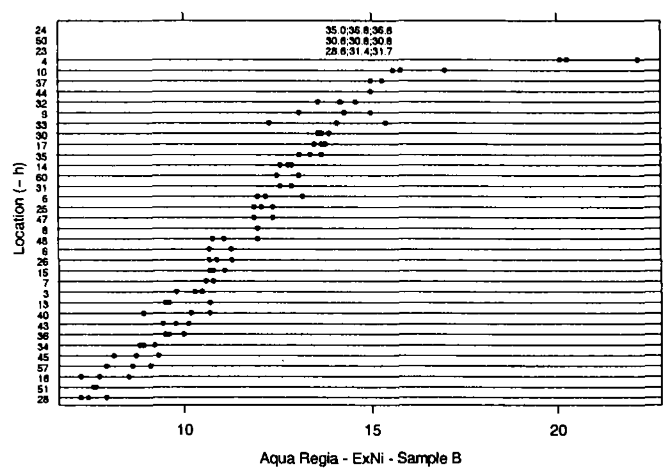


Figure IV.277: Dotplot - Sample B - Extractable Ni

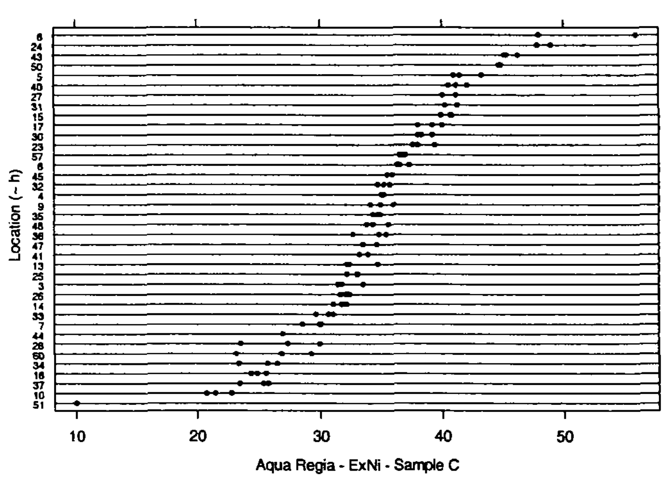


Figure IV.278: Dotplot - Sample C - Extractable Ni

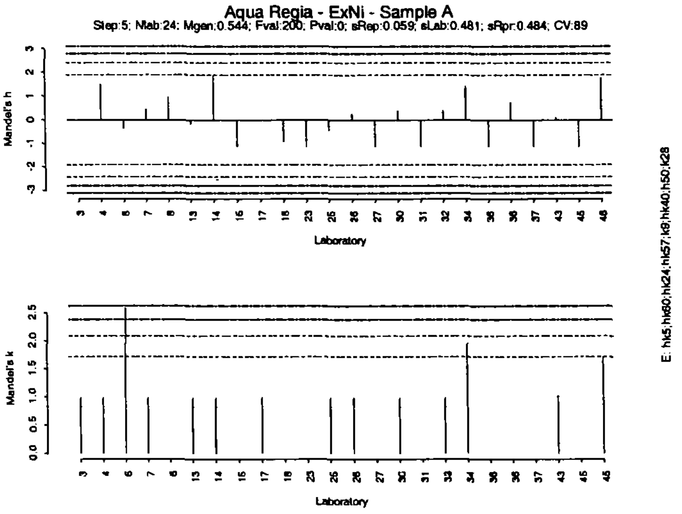


Figure IV.279: Mandel h/k plot - Sample A - Extractable Ni

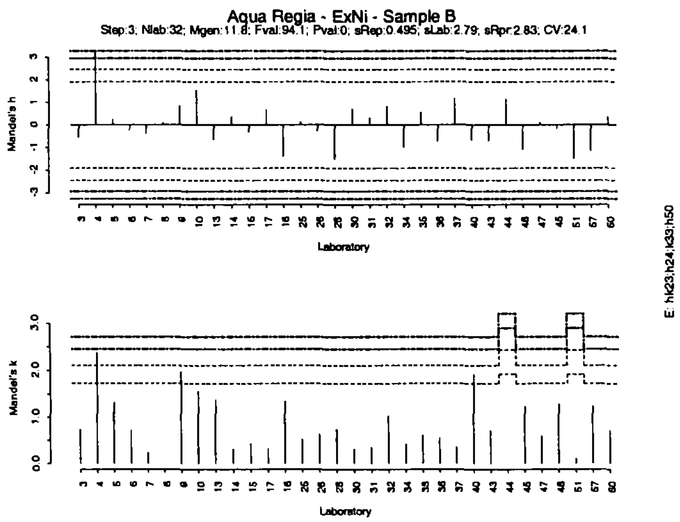


Figure IV.280: Mandel h/k plot - Sample B - Extractable Ni

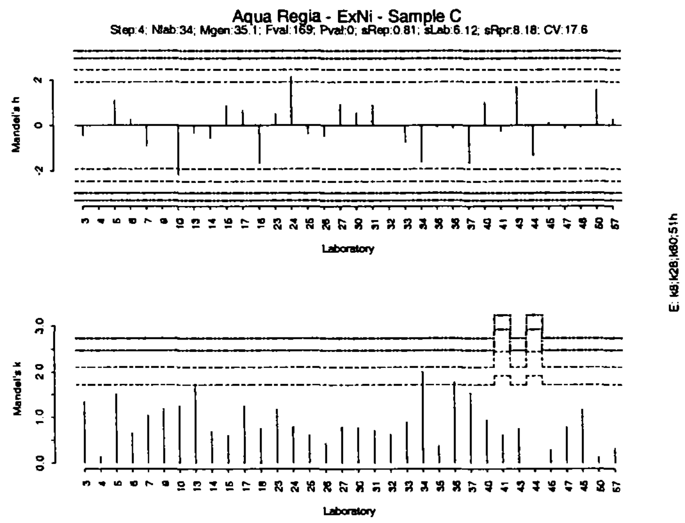


Figure IV.281: Mandel h/k plot – Sample C - Extractable Ni

Parameter: Extractable P

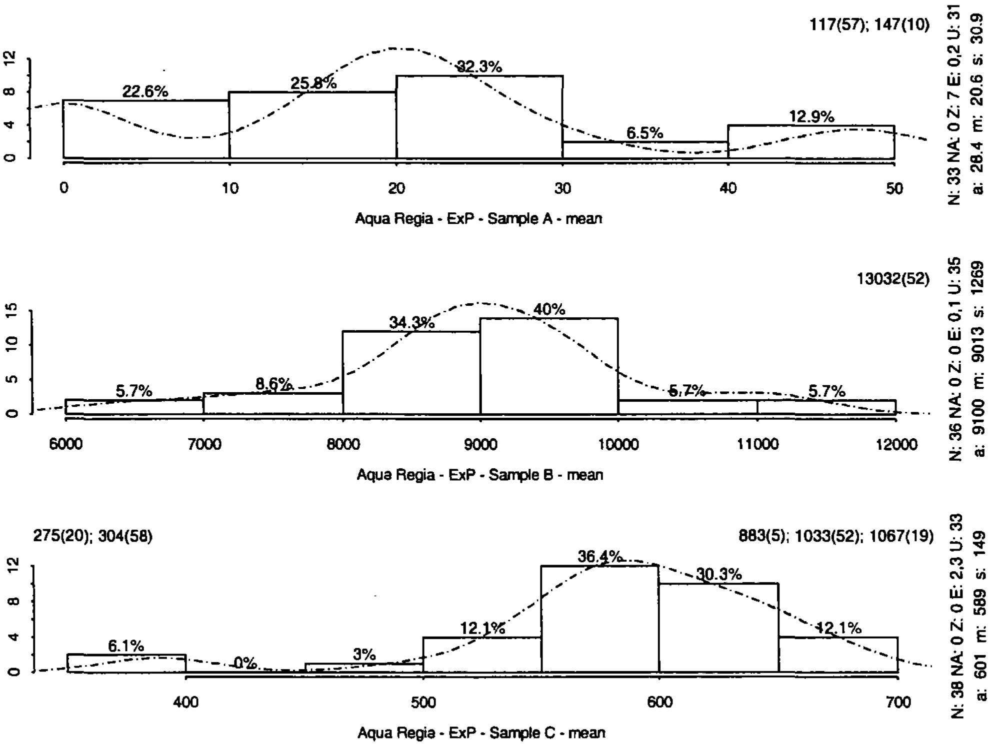


Figure IV.282: Histogram mean - Extractable P

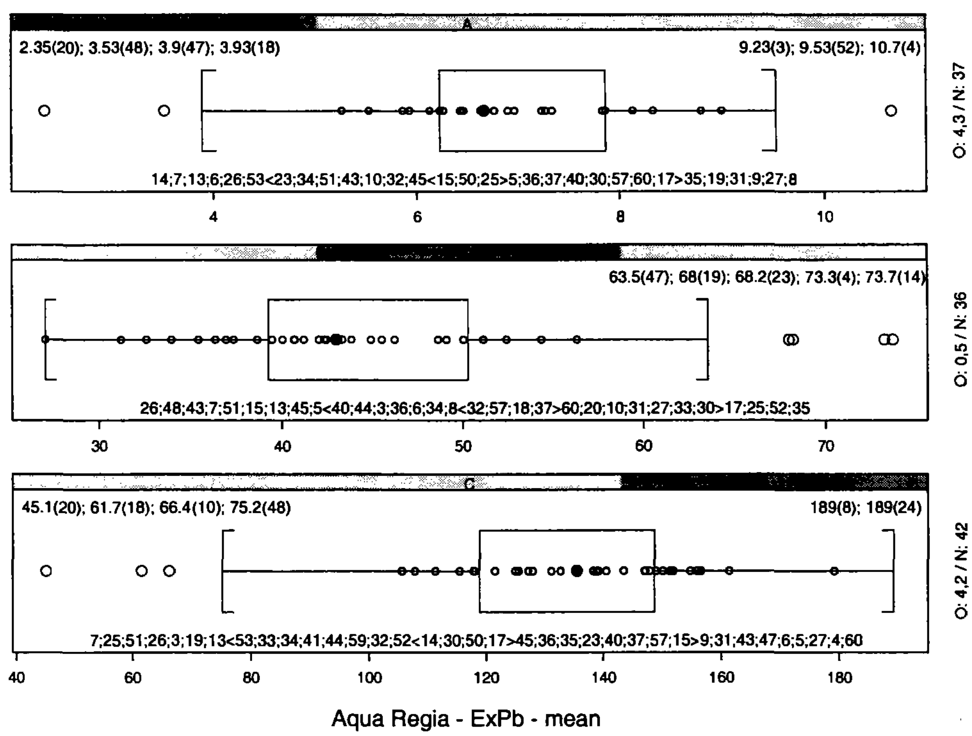


Figure IV.283: Boxplot mean - Extractable P

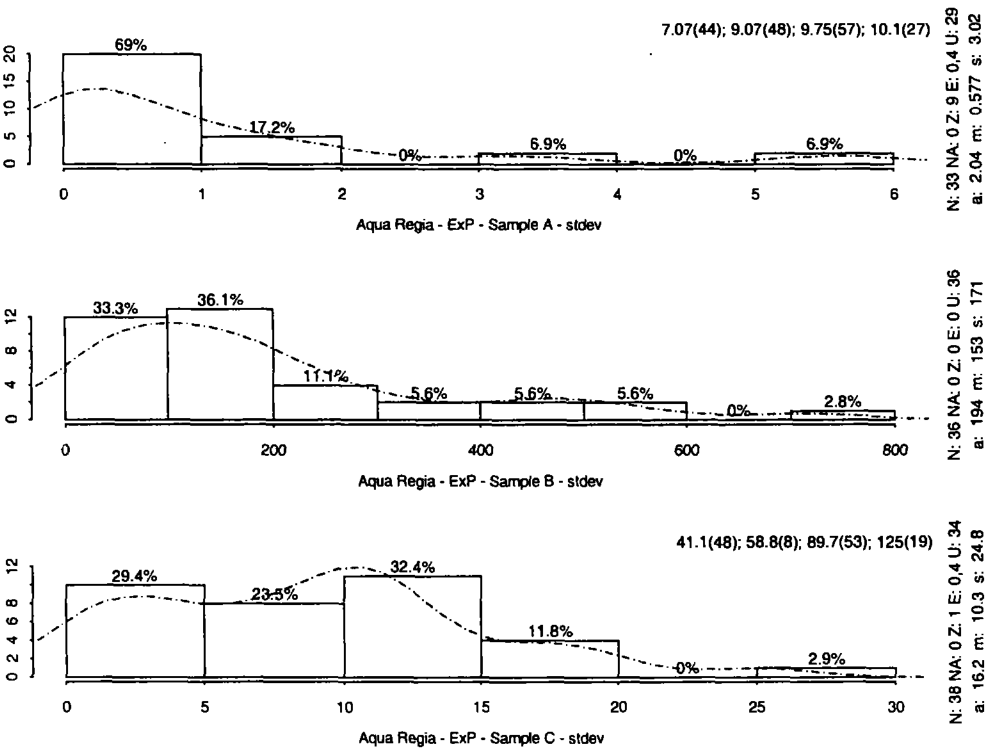


Figure IV.284: Histogram stdev - Extractable P

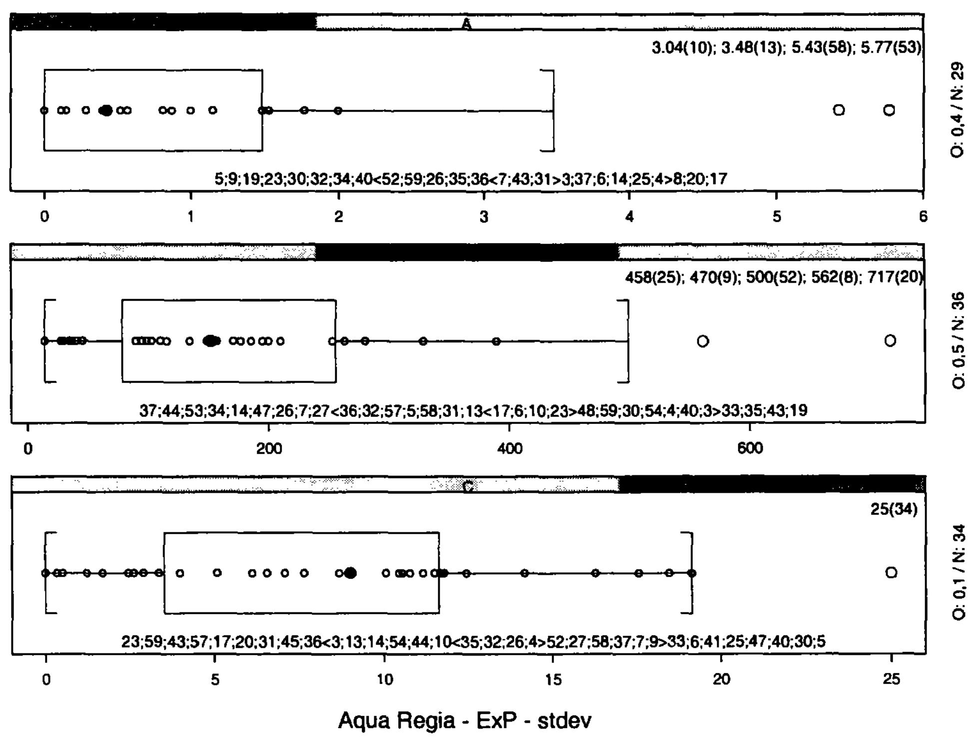


Figure IV.285: Boxplot stdev - Extractable P

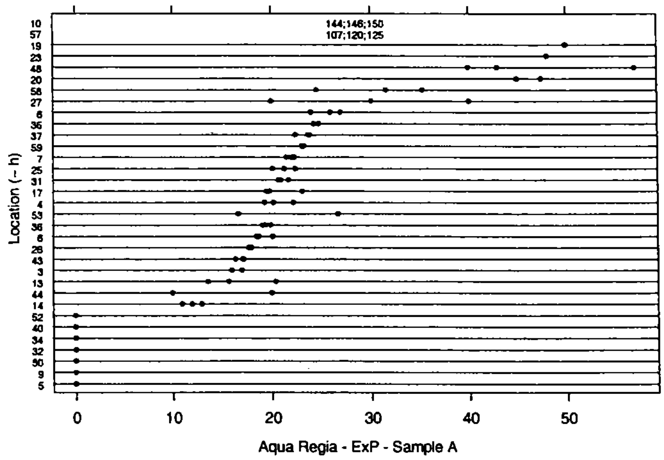


Figure IV.286: Dotplot - Sample A - Extractable P

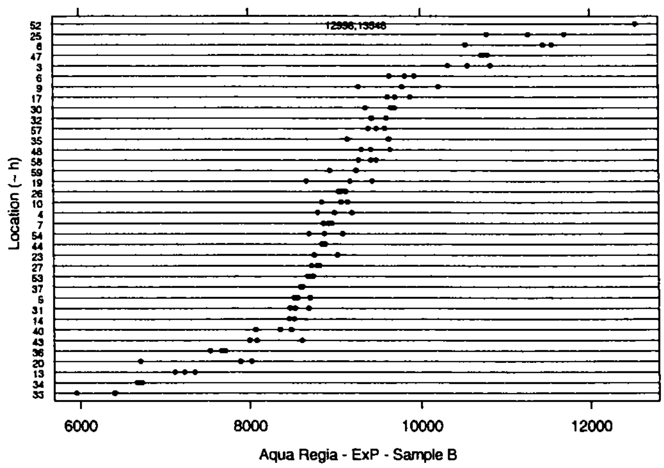


Figure IV.287: Dotplot - Sample B - Extractable P

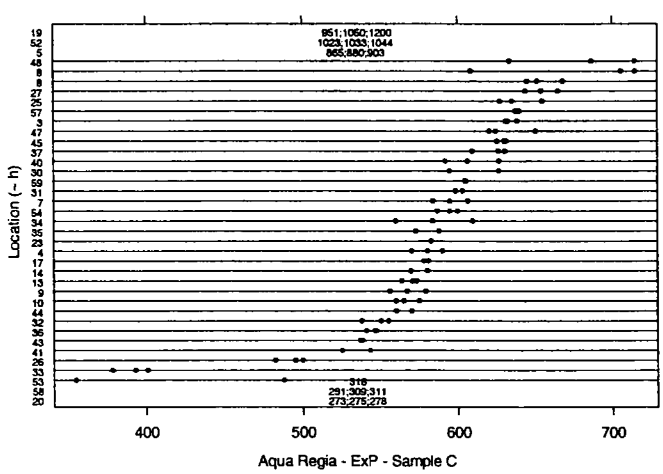


Figure IV.288: Dotplot - Sample C - Extractable P

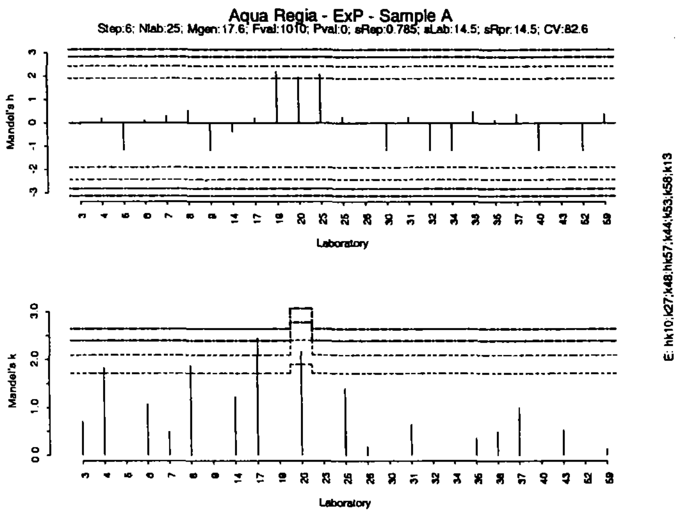


Figure IV.289: Mandel h/k plot - Sample A - Extractable P

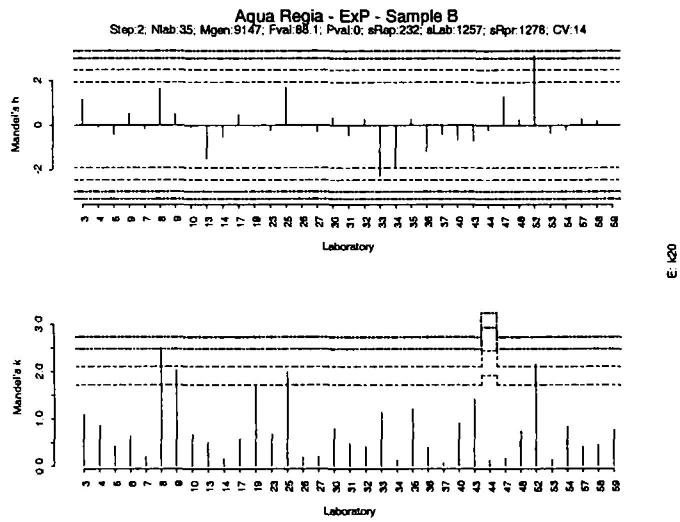


Figure IV.290: Mandel h/k plot - Sample B - Extractable P

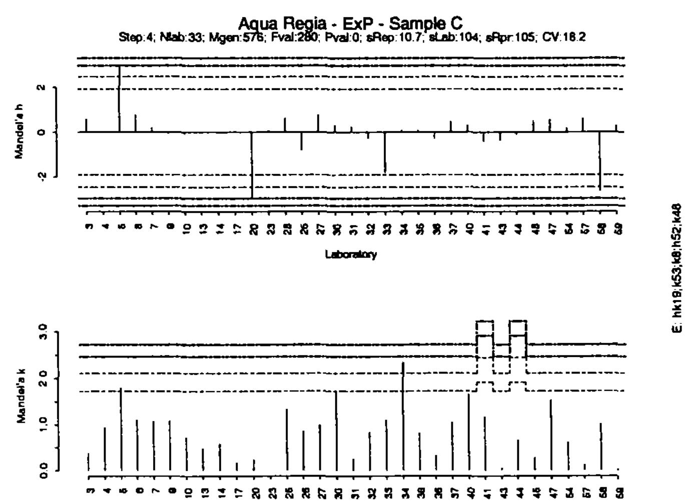


Figure IV.291: Mandel h/k plot - Sample C - Extractable P

Parameter: Extractable Pb

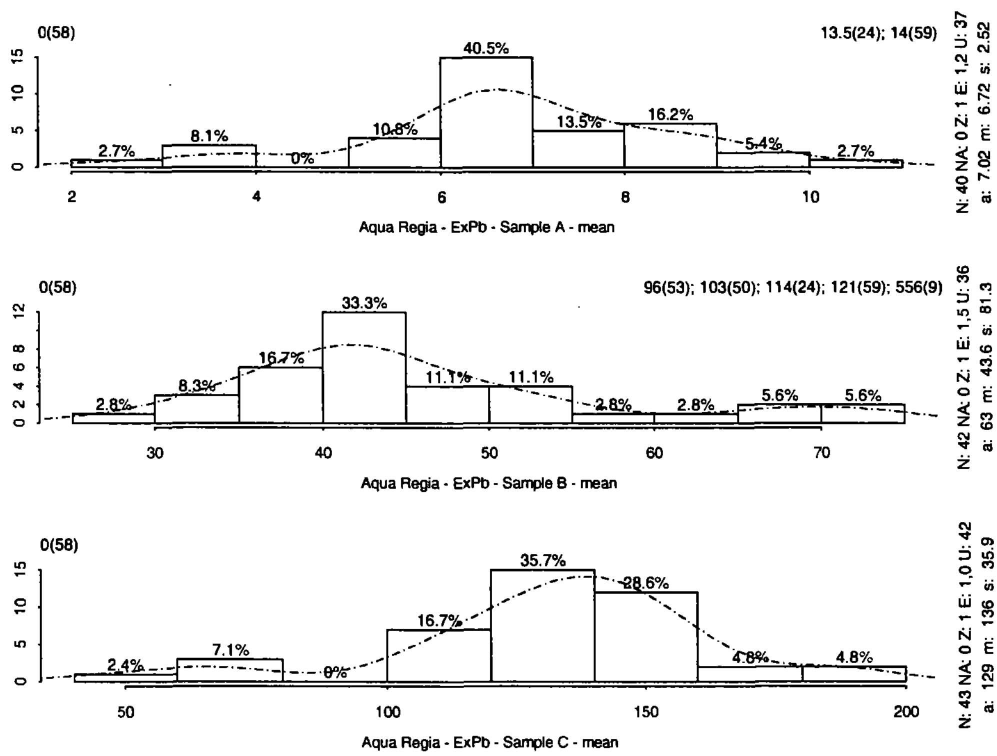


Figure IV.292: Histogram mean - Extractable Pb

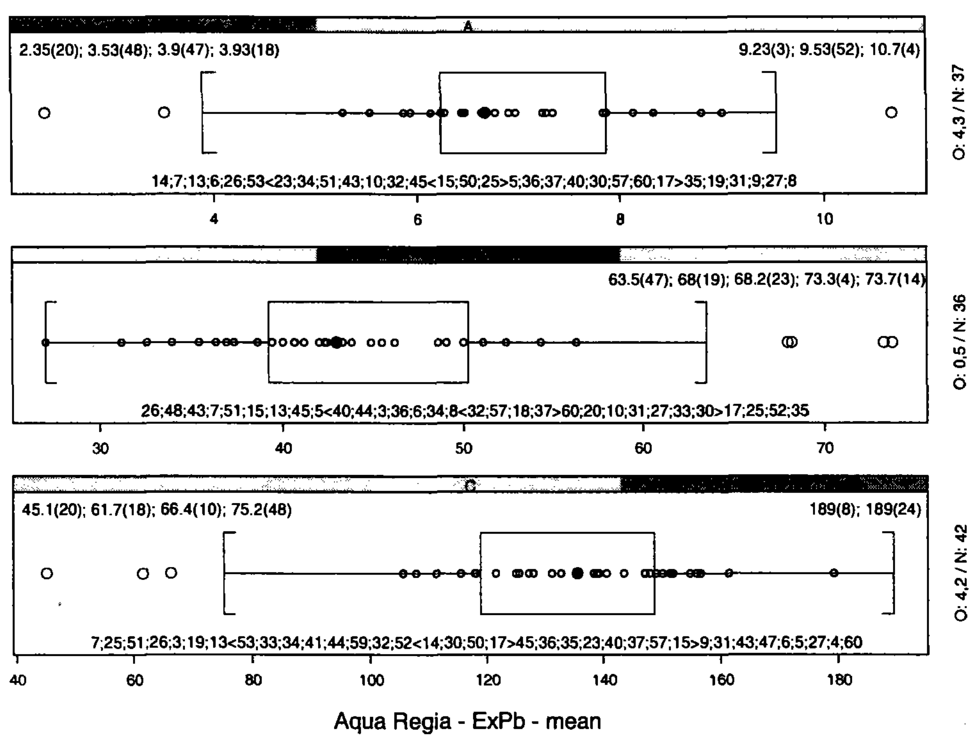


Figure IV.293: Boxplot mean - Extractable Pb

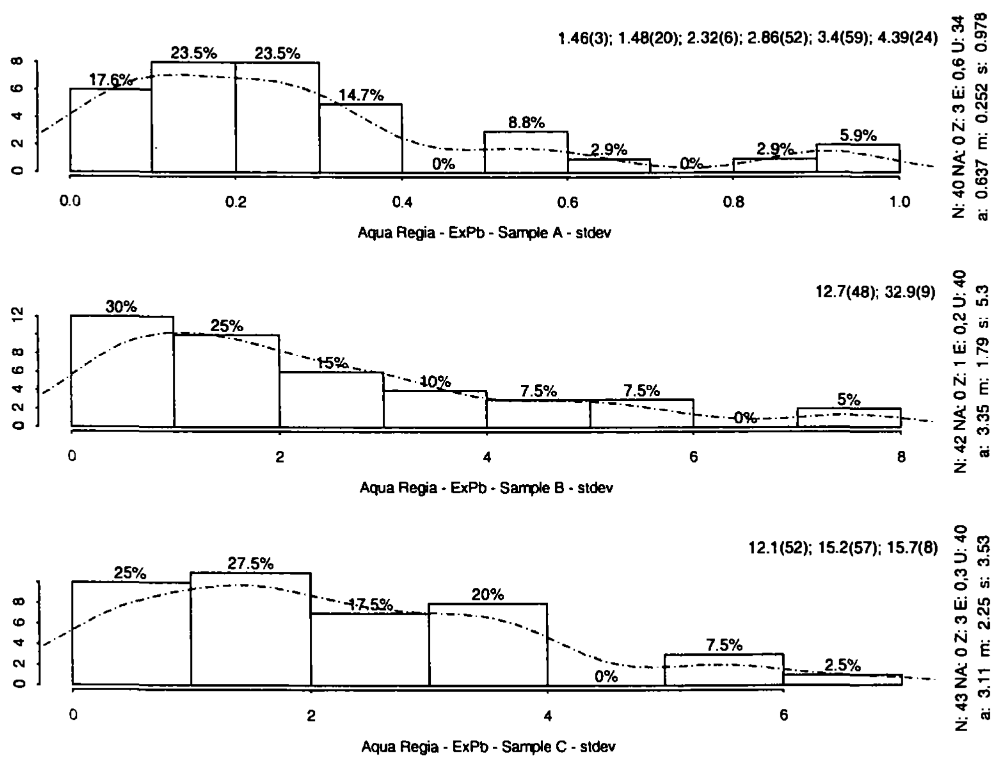


Figure IV.294: Histogram stdev- Extractable Pb

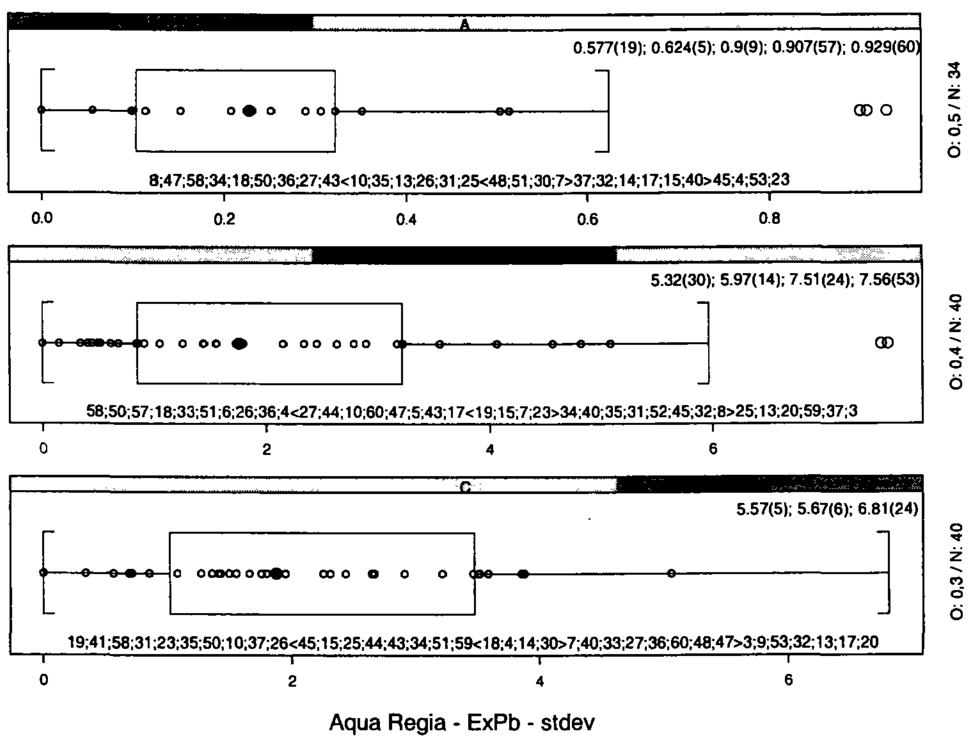


Figure IV.295: Boxplot stdev - Extractable Pb

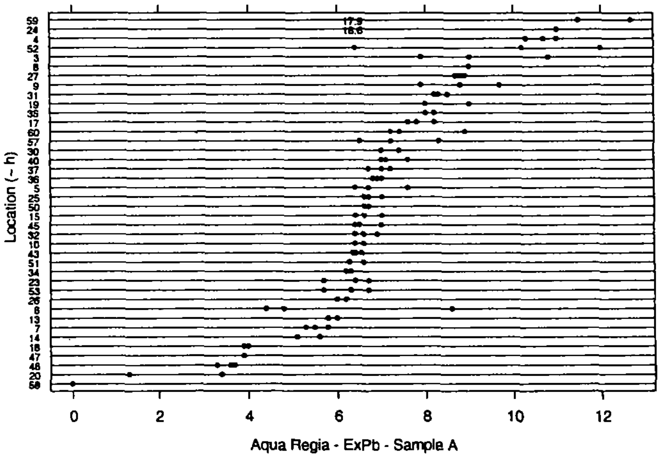


Figure IV.296: Dotplot - Sample A - Extractable Pb

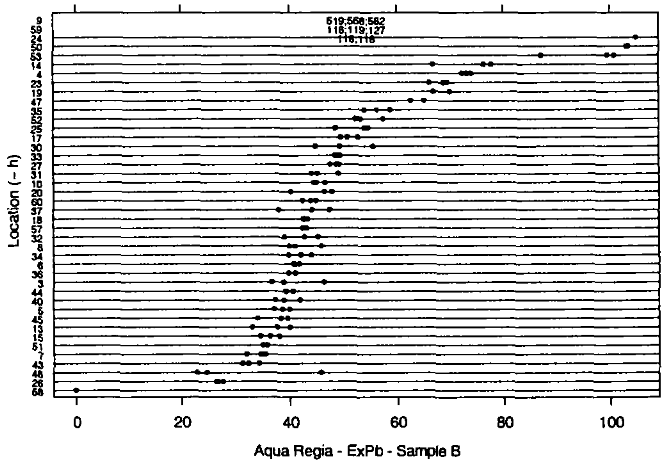


Figure IV.297: Dotplot - Sample B - Extractable Pb

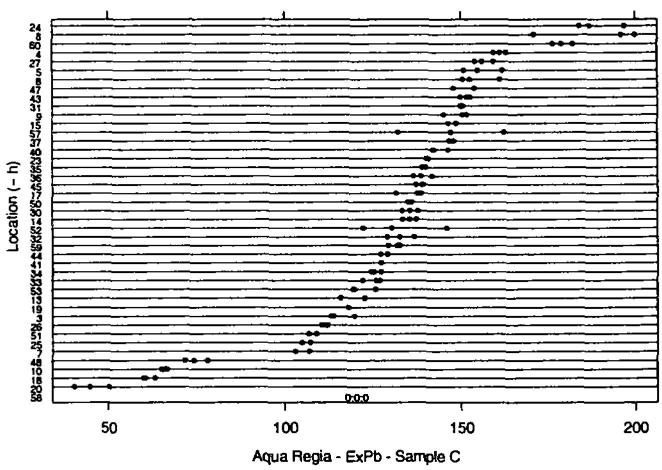


Figure IV.298: Dotplot - Sample C - Extractable Pb

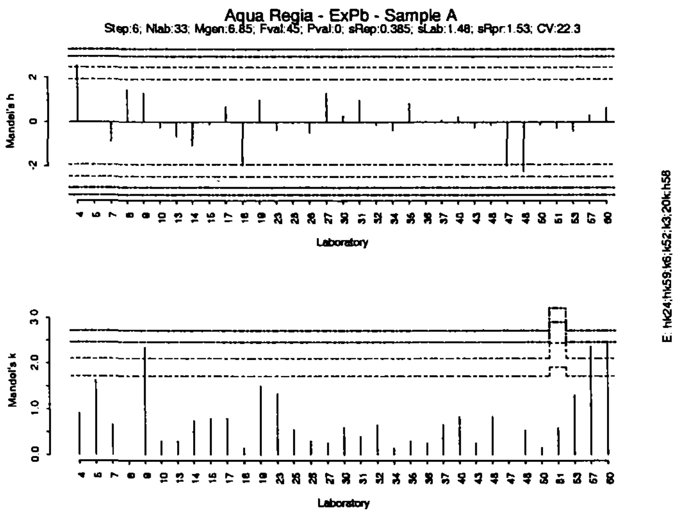


Figure IV.299: Mandel h/k plot - Sample A - Extractable Pb

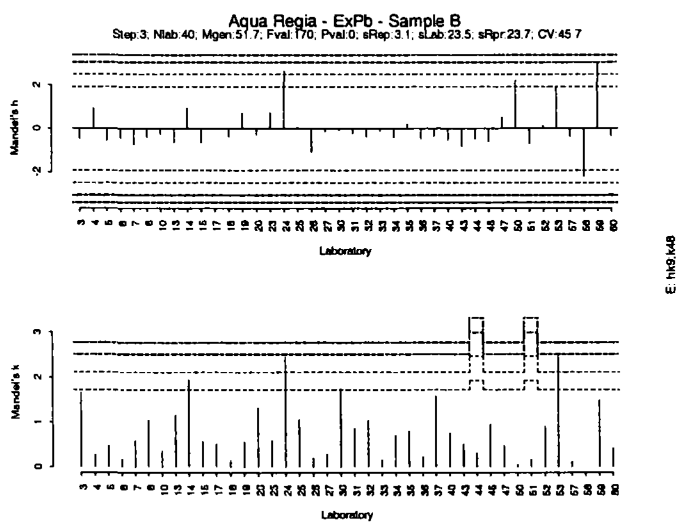


Figure IV.300: Mandel h/k plot - Sample B - Extractable Pb

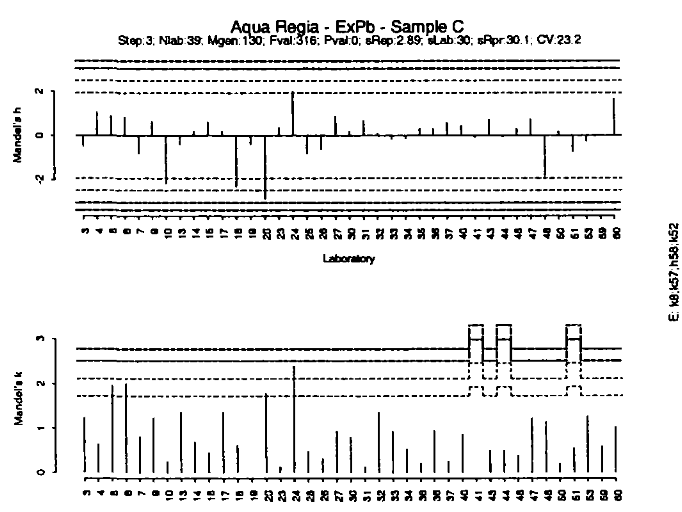


Figure IV.301: Mandel h/k plot - Sample C - Extractable Pb

Parameter: Extractable S

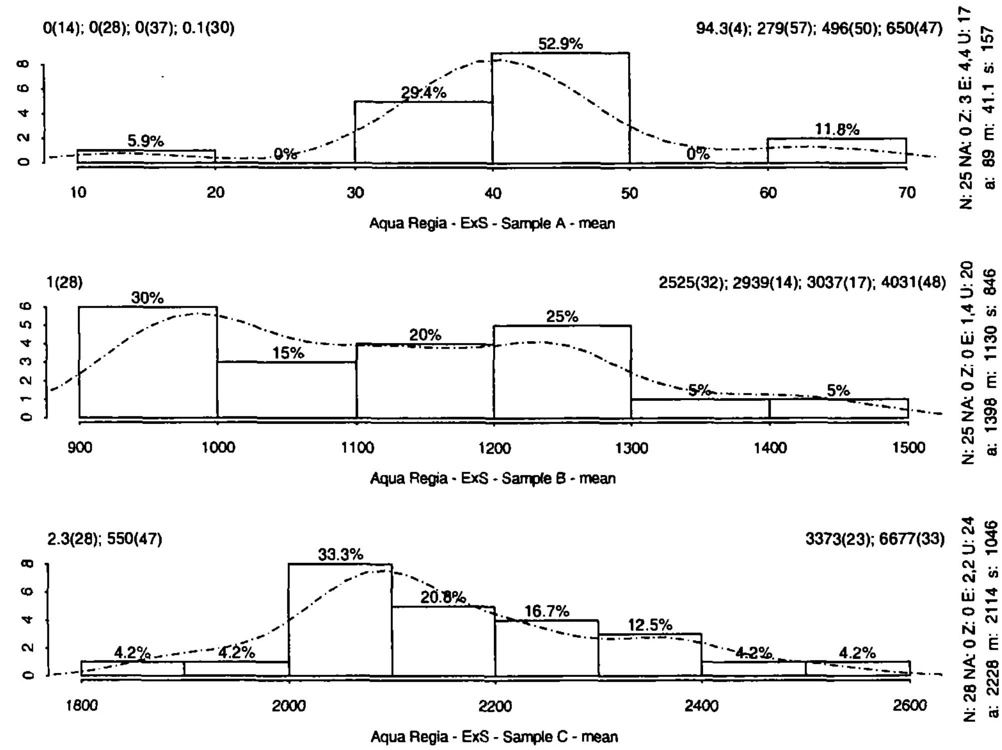


Figure IV.302: Histogram mean - Extractable S

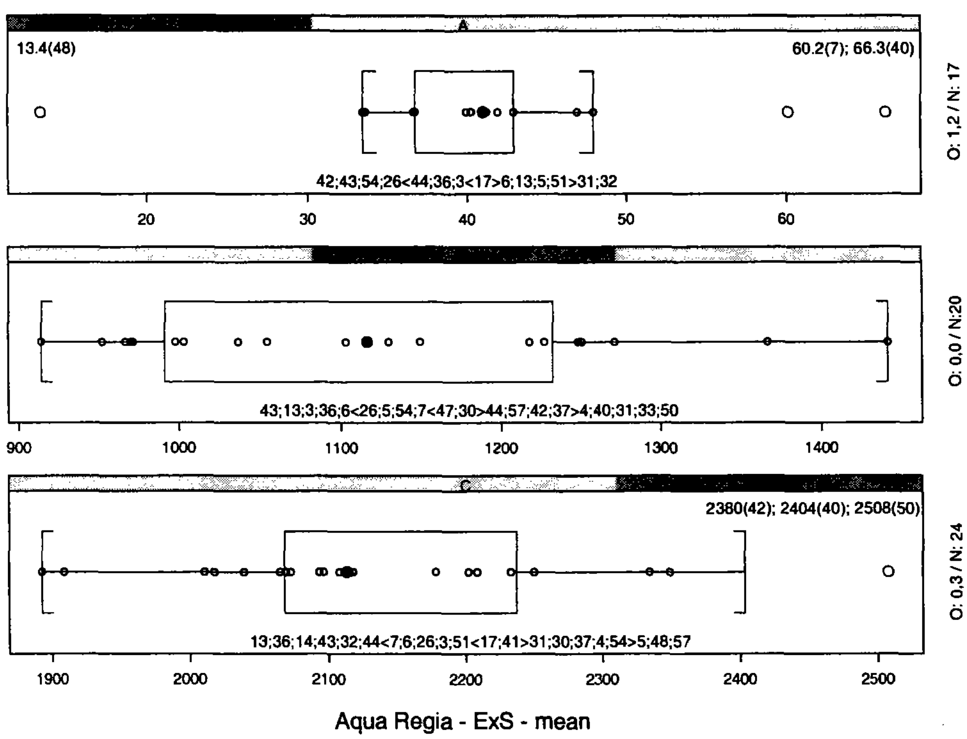


Figure IV.303: Boxplot mean - Extractable S

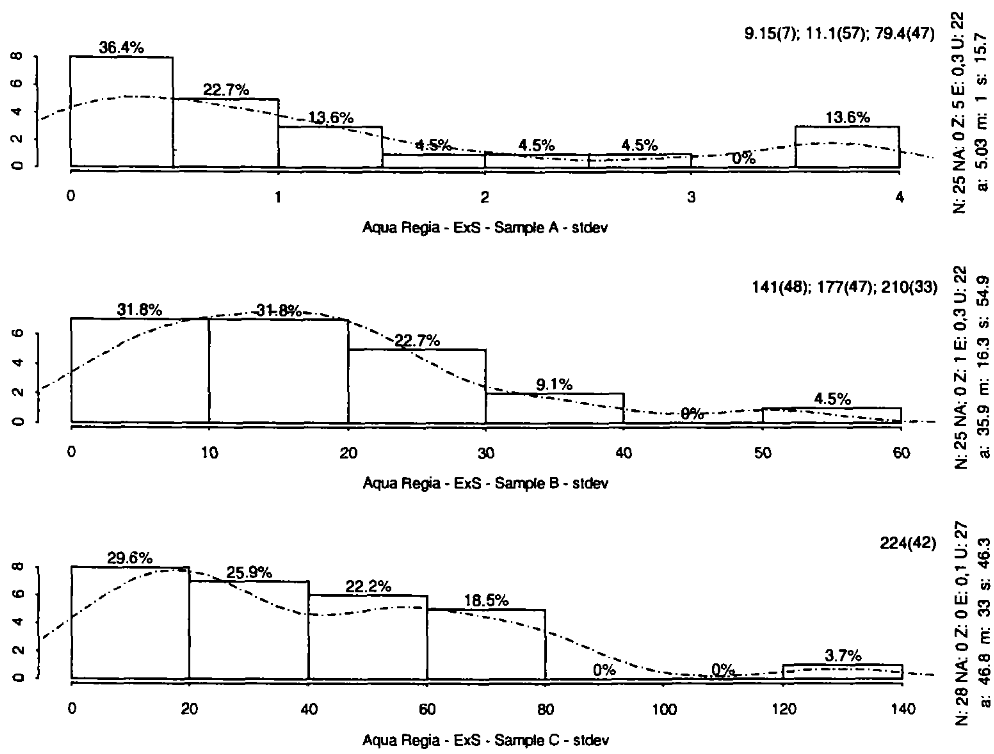


Figure IV.304: Histogram stdev - Extractable S

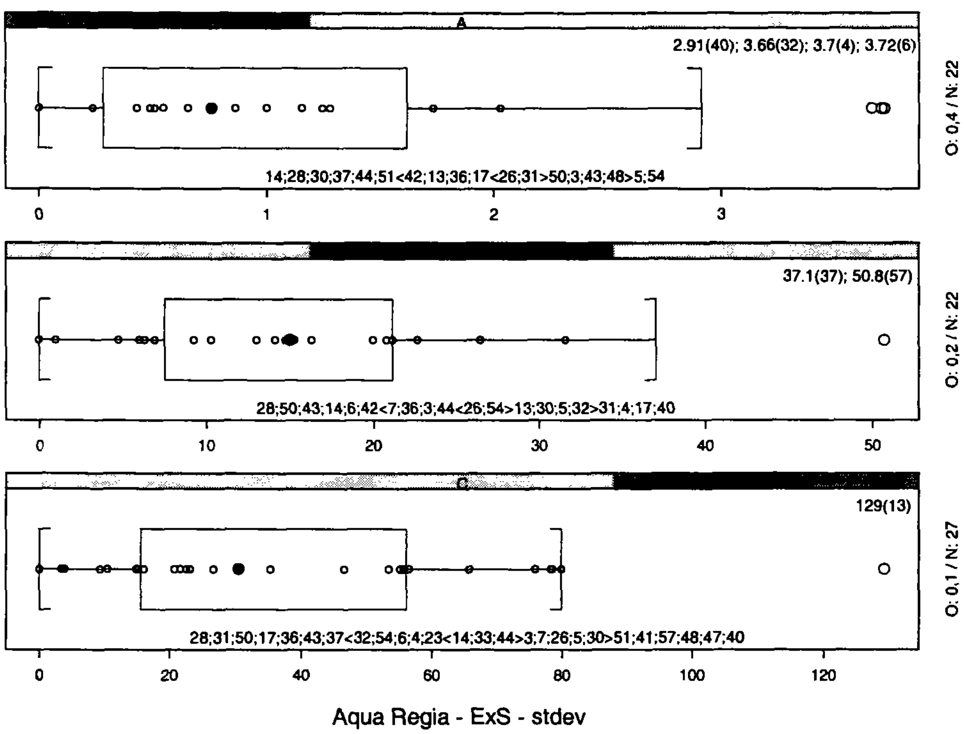


Figure IV.305: Boxplot stdev - Extractable S

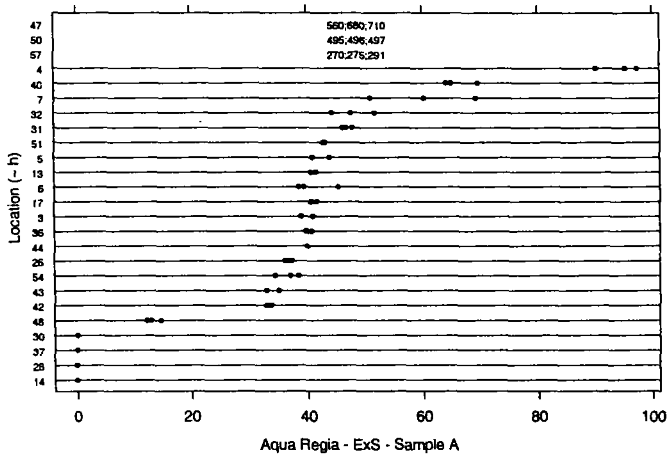


Figure IV.306: Dotplot - Sample A- Extractable S

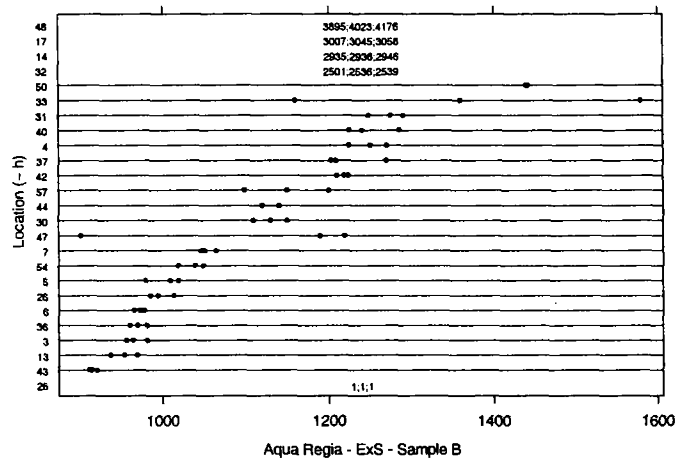


Figure IV.307: Dotplot - Sample B - Extractable S

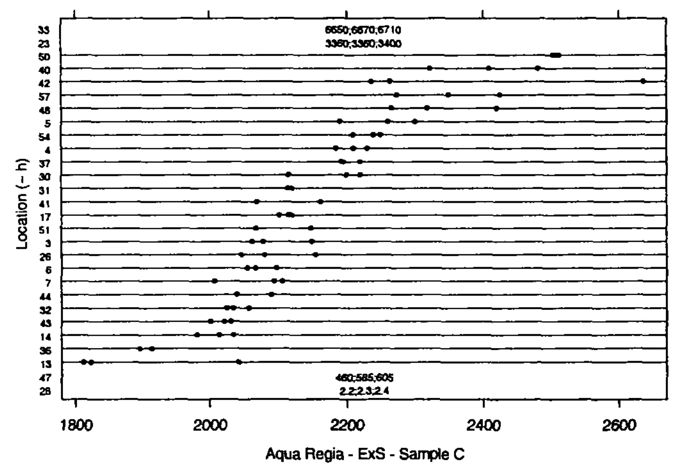


Figure IV.308: Dotplot - Sample C - Extractable S

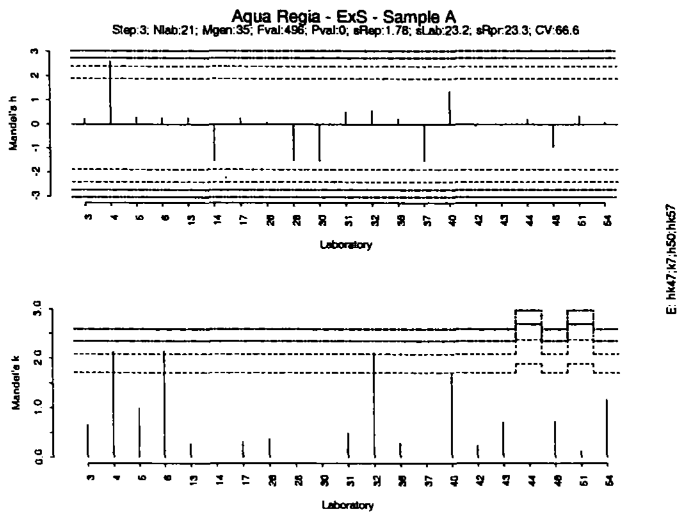


Figure IV.309: Mandel h/k plot - Sample A - Extractable S

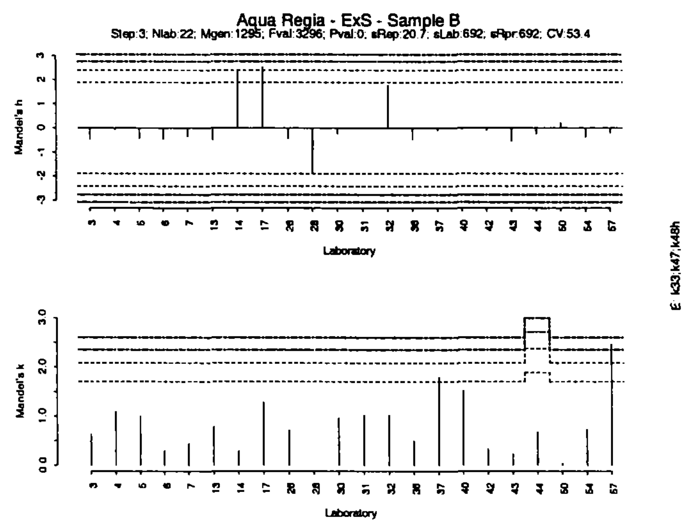


Figure IV.310: Mandel h/k plot - Sample B - Extractable S

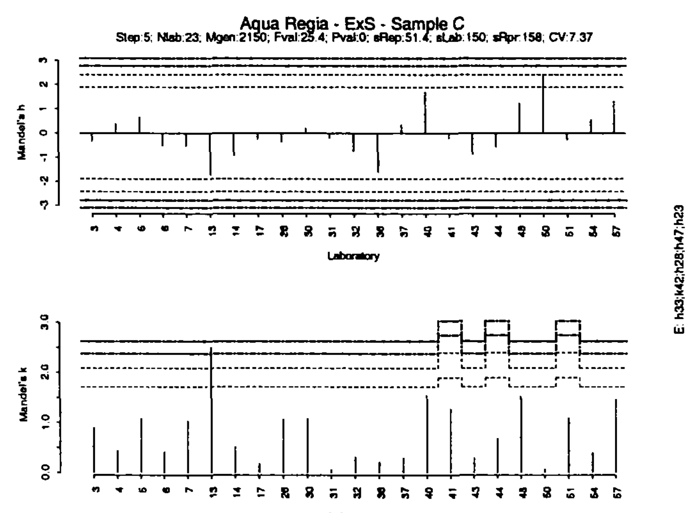


Figure IV.311: Mandel h/k plot - Sample C - Extractable S

Parameter: Extractable Zn

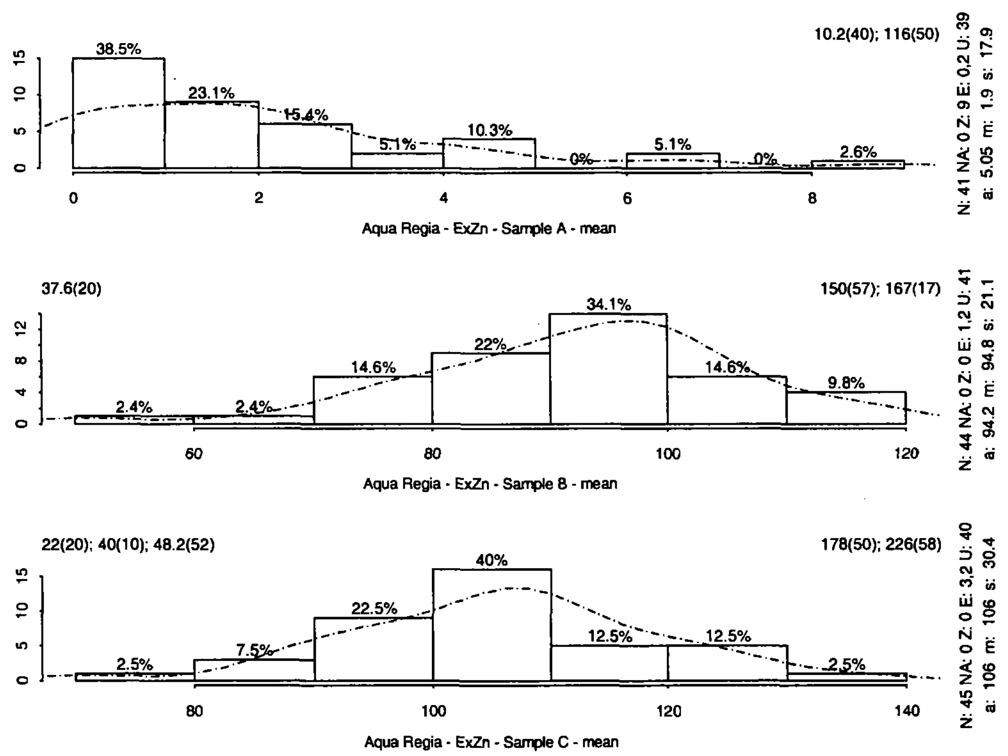


Figure IV.312: Histogram mean - Extractable Zn

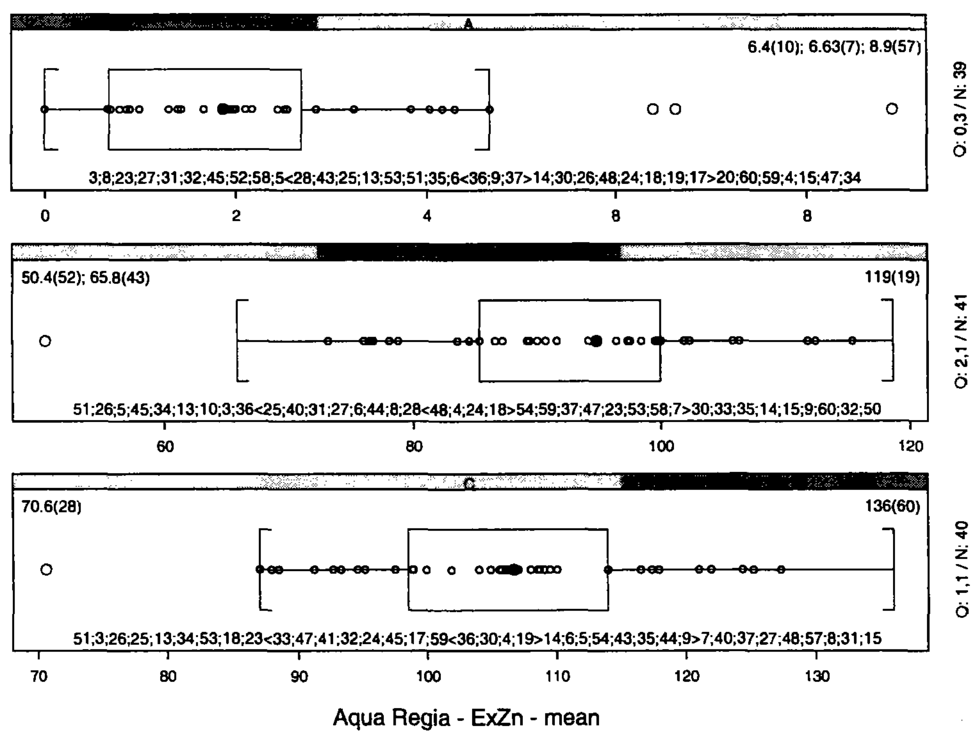


Figure IV.313: Boxplot mean - Extractable Zn

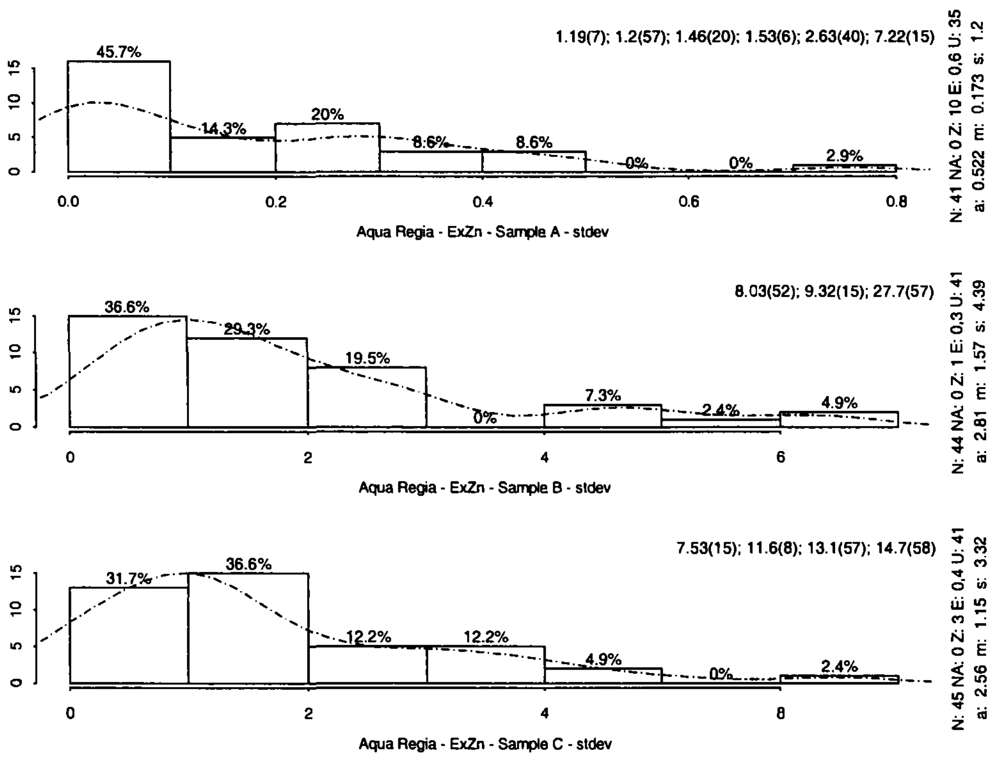


Figure IV.314: Histogram stdev - Extractable Zn

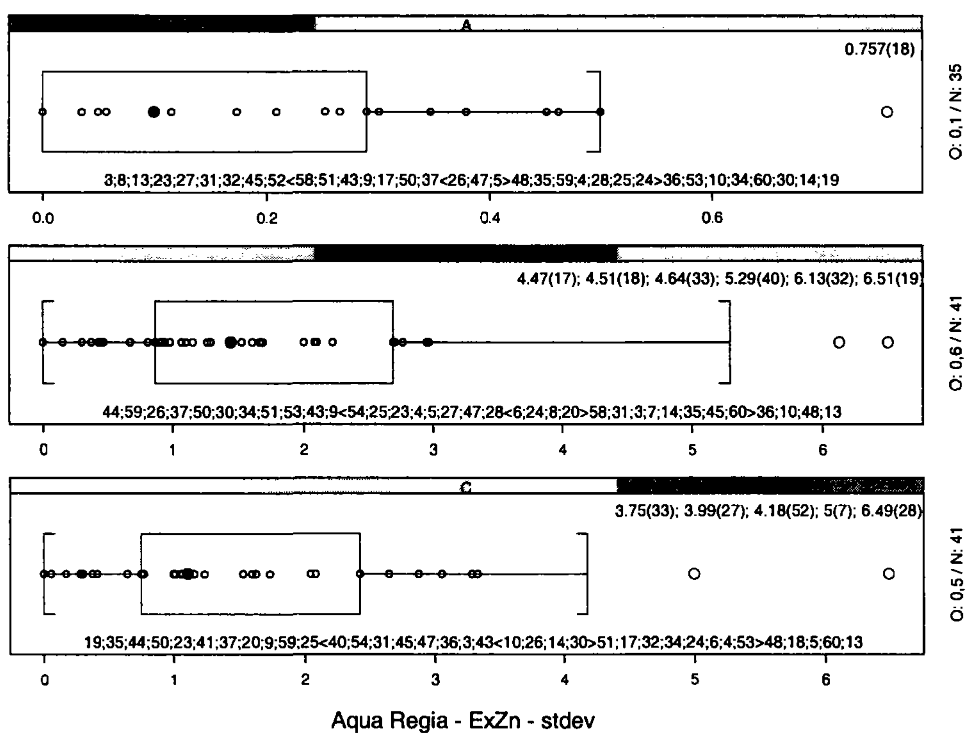


Figure IV.315: Boxplot stdev - Extractable Zn

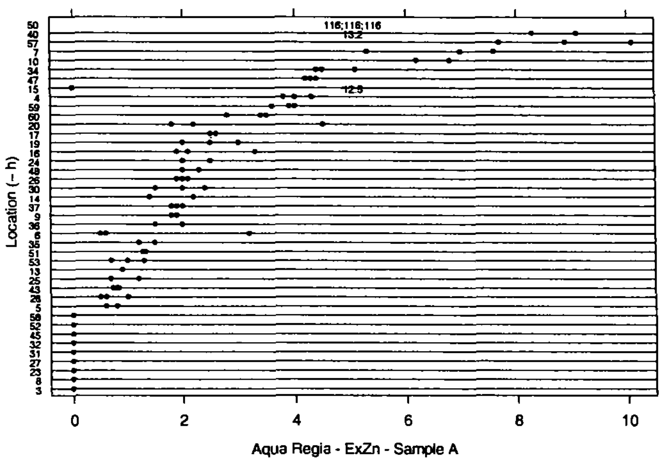


Figure IV.316: Dotplot - Sample A - Extractable Zn

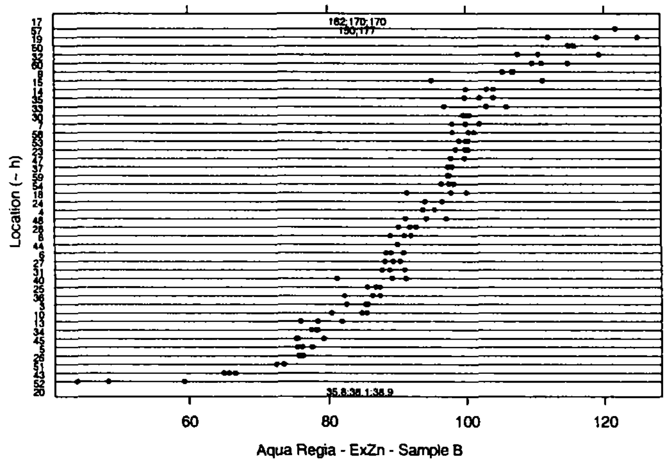


Figure IV.317: Dotplot - Sample B - Extractable Zn

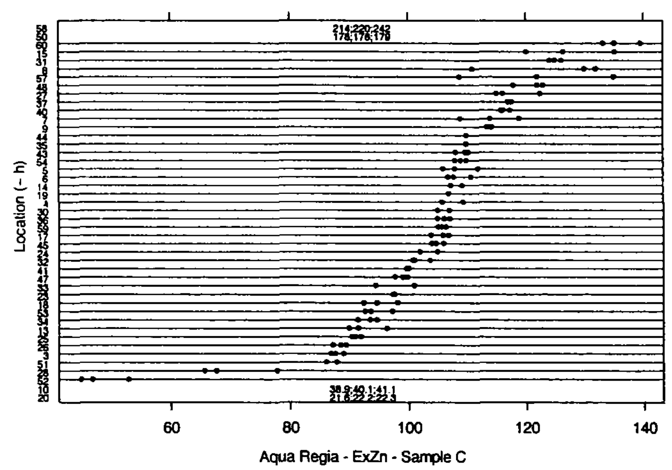


Figure IV.318: Dotplot - Sample C - Extractable Zn

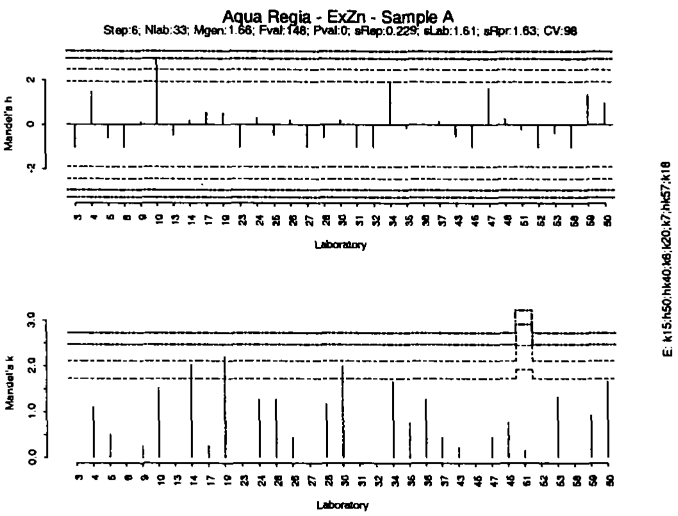


Figure IV. 319: Mandel h/k plot - Sample A - Extractable Zn

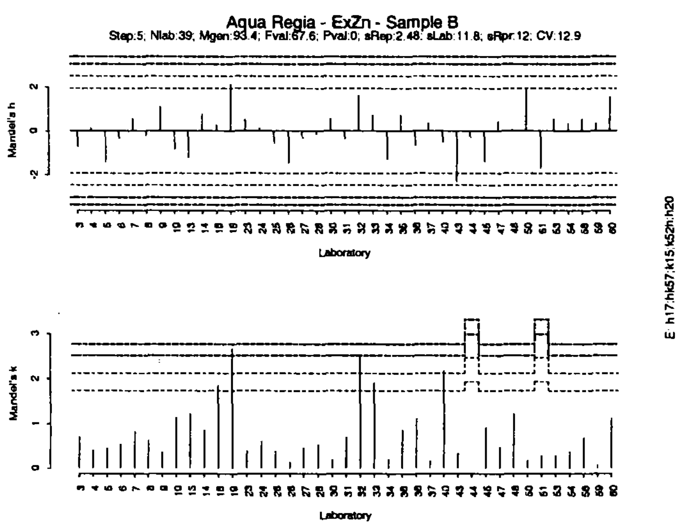


Figure IV.320: Mandel h/k plot – Sample B - Extractable Zn

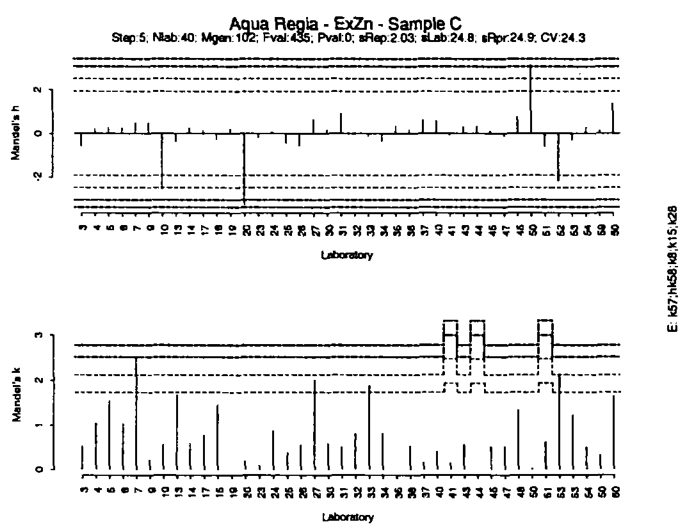


Figure IV.321: Mandel h/k plot - Sample C - Extractable Zn

Group VIII: Total Elements

Parameter: Total Al

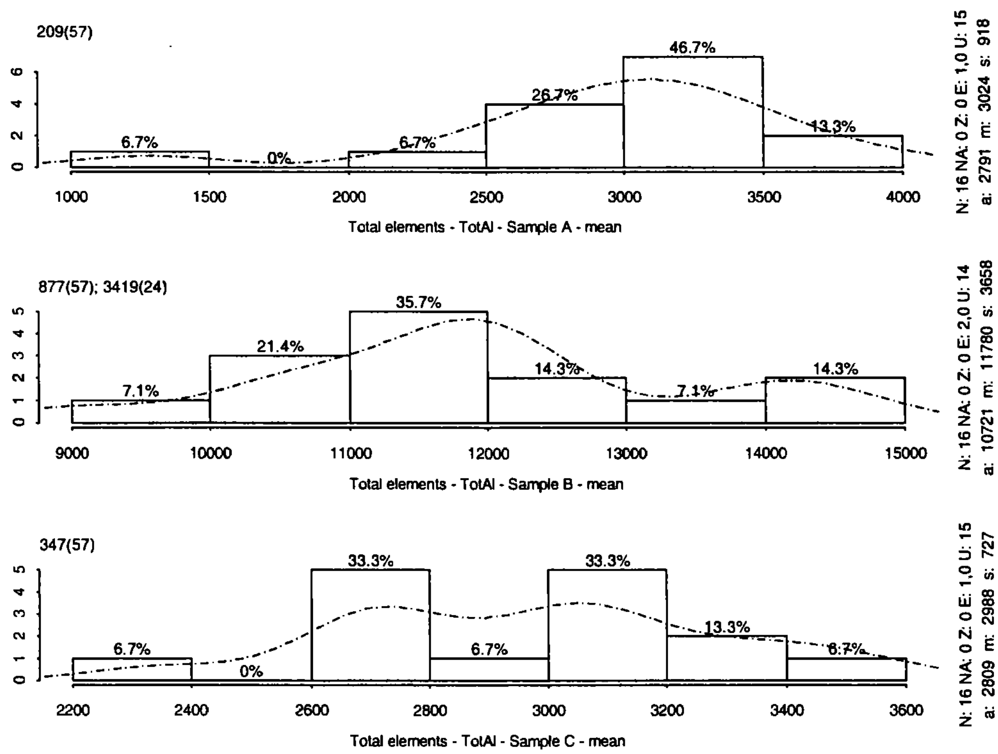


Figure IV.322: Histogram mean – Total Al

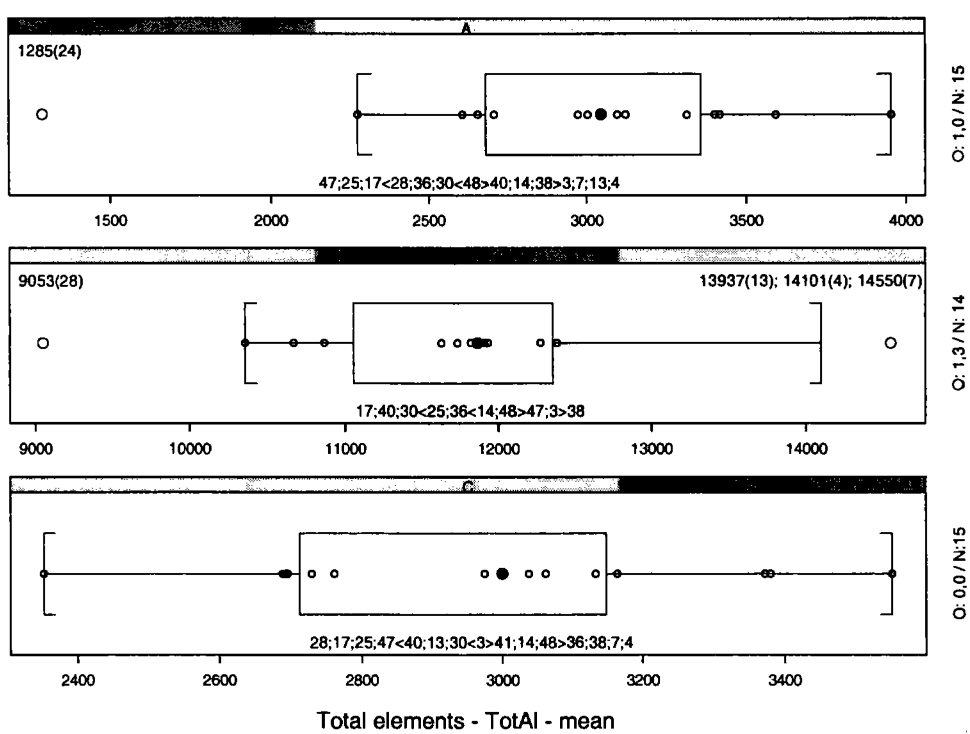


Figure IV.323: Boxplot mean – Total Al

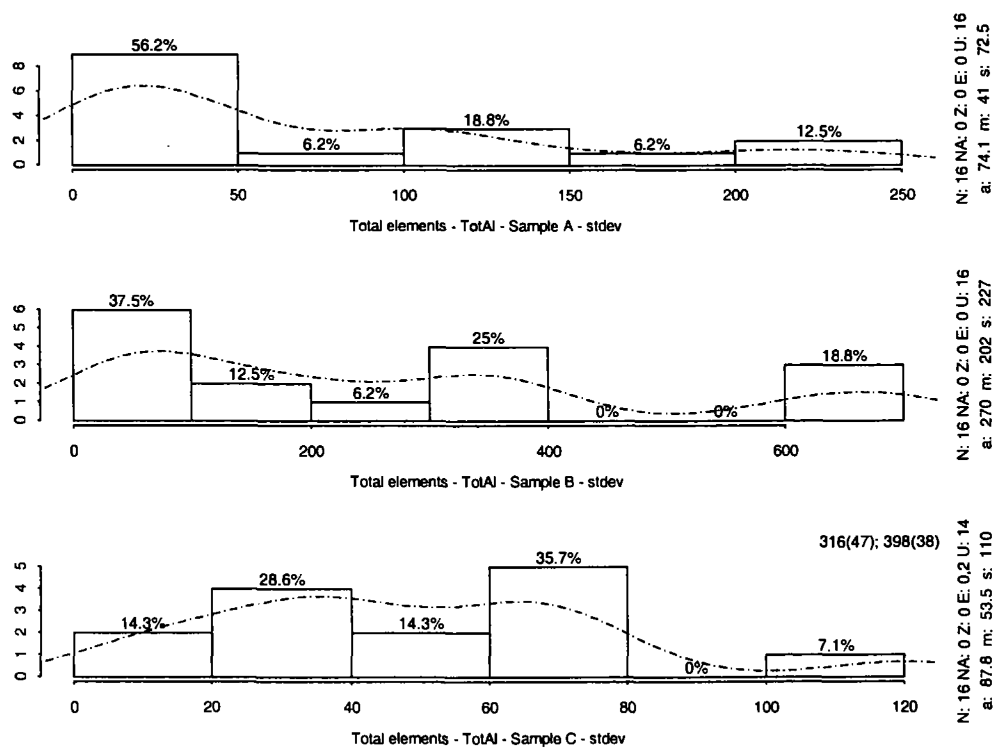


Figure IV.324: Histogram stdev – Total Al

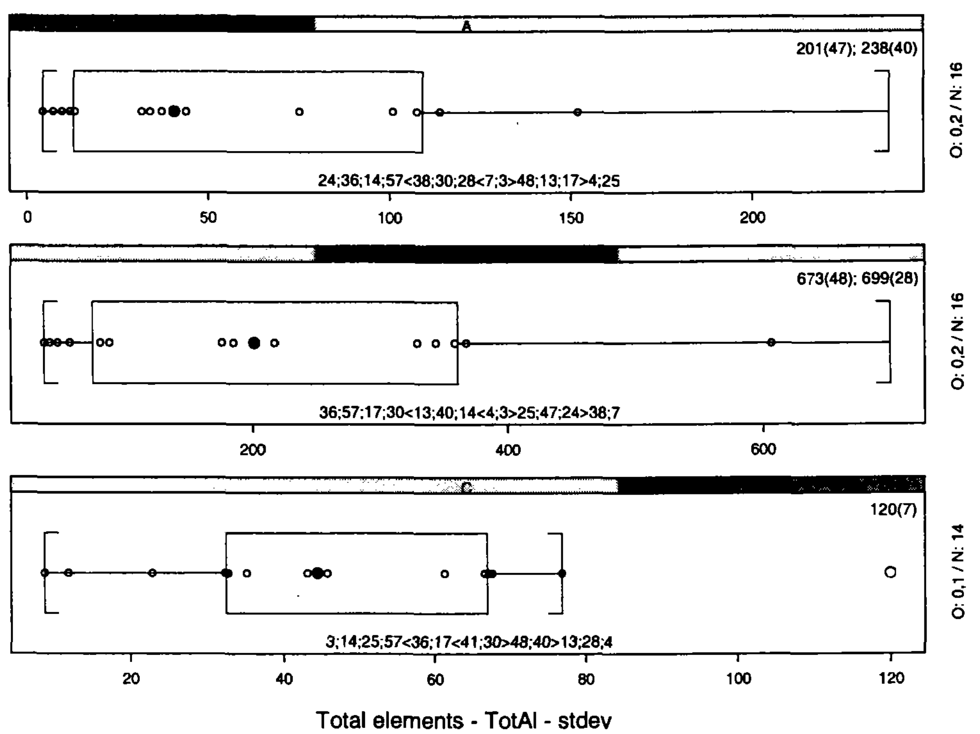


Figure IV.325: Boxplot stdev – Total Al

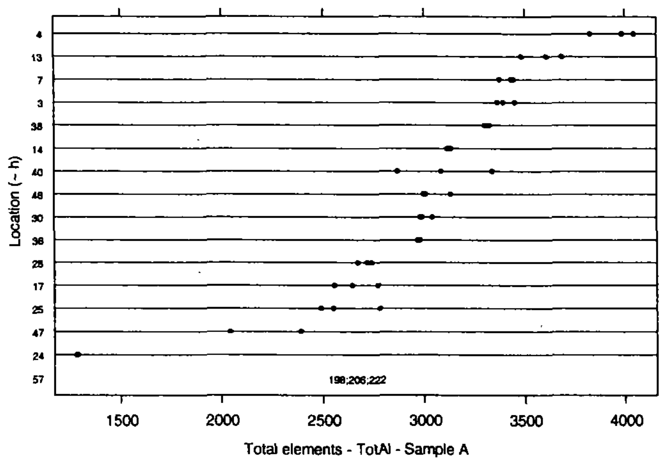


Figure IV.326: Dotplot - Sample A – Total Al

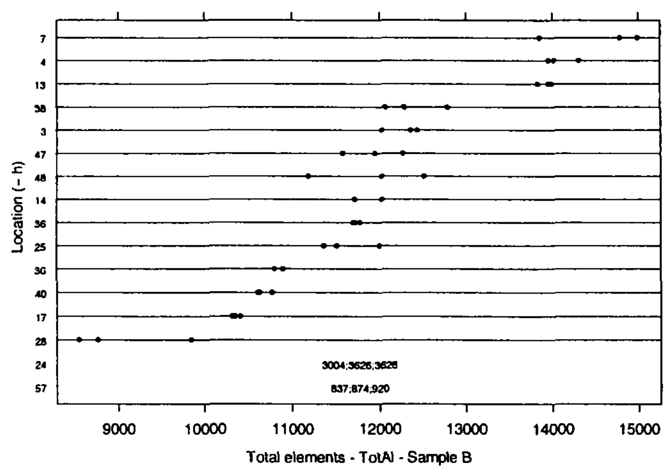


Figure IV.327: Dotplot - Sample B – Total Al

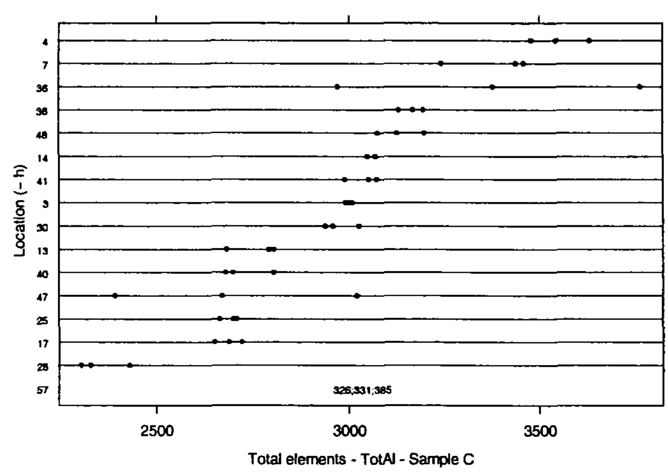


Figure IV.328: Dotplot - Sample C – Total Al

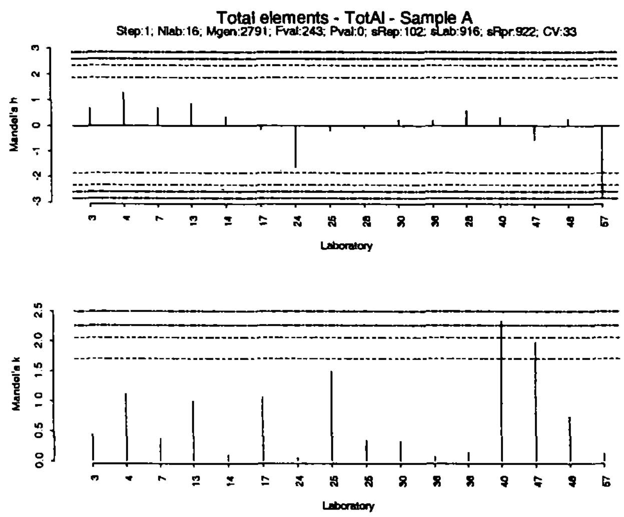


Figure IV.329: Mandel h/k plot - Sample A – Total Al

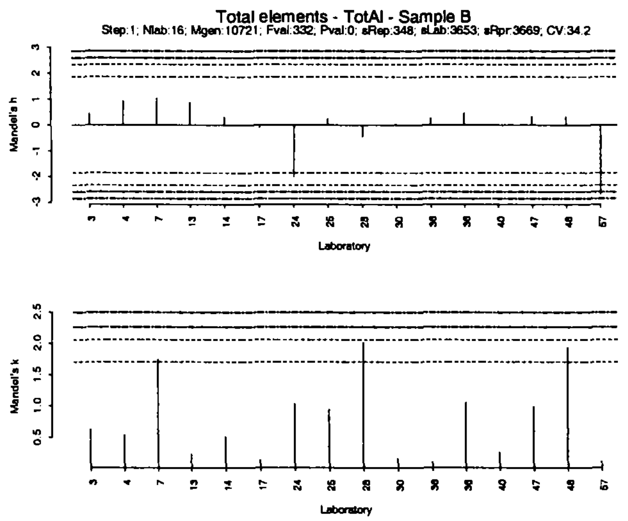


Figure IV.330: Mandel h/k plot - Sample B – Total Al

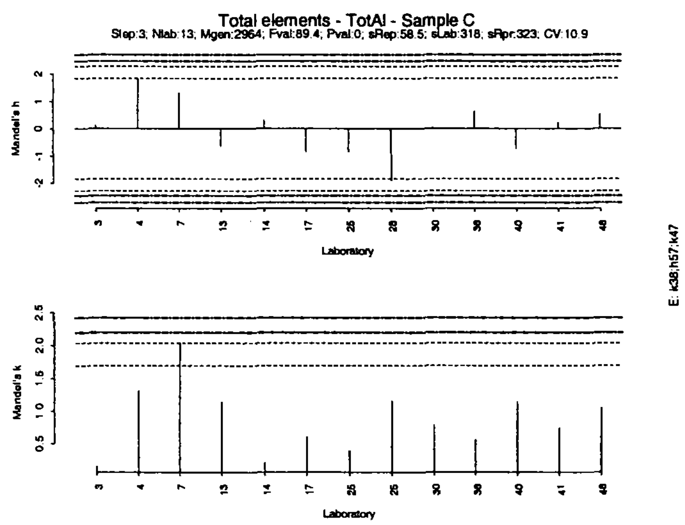


Figure IV.331: Mandel h/k plot - Sample C – Total Al

Parameter: Total Ca

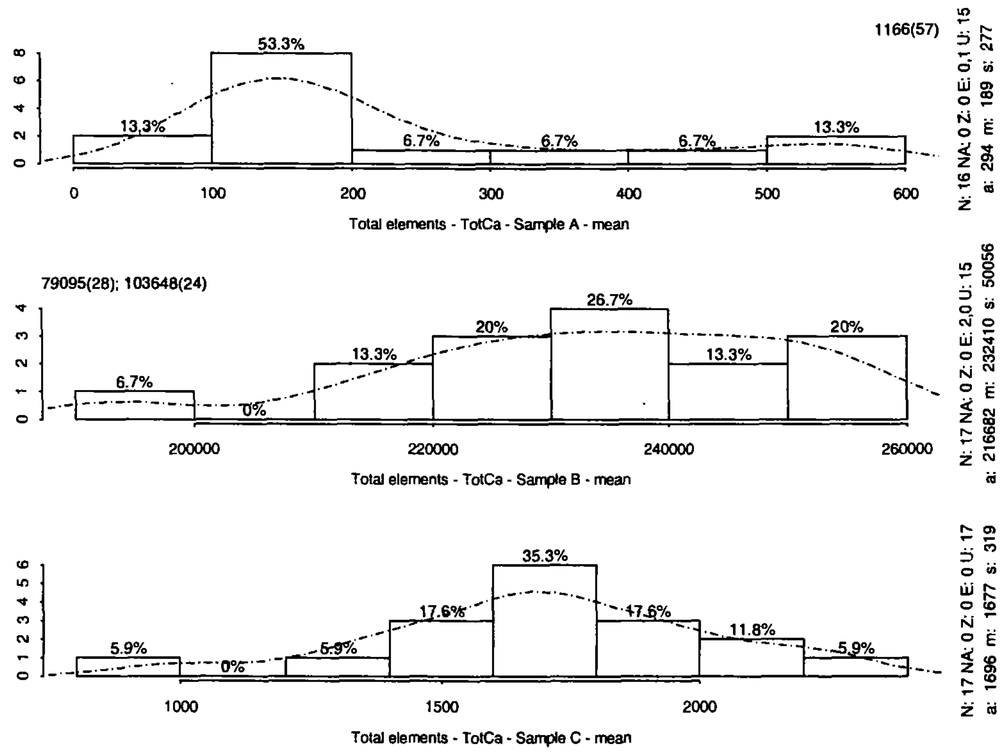


Figure IV.332: Histogram mean – Total Ca

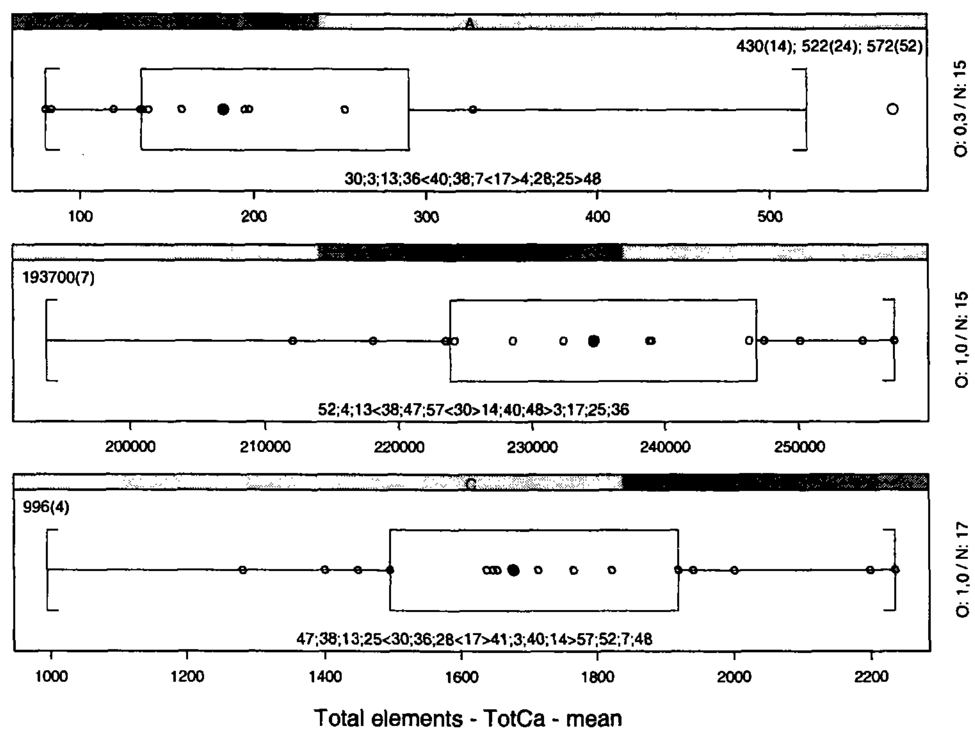


Figure IV.334: Boxplot mean – Total Ca

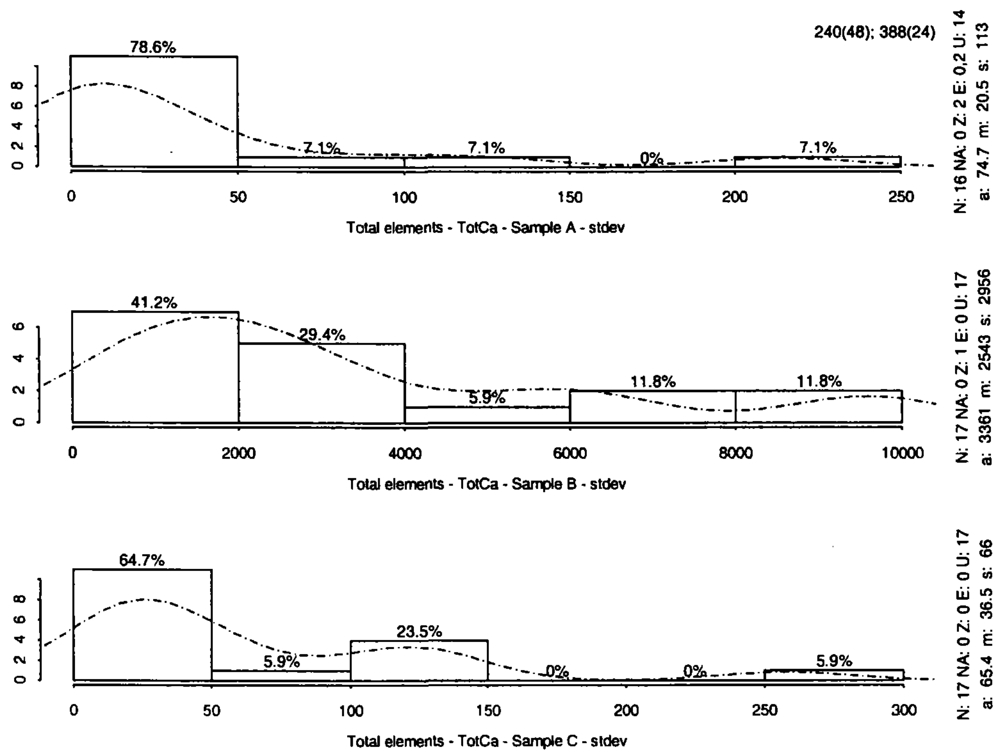


Figure IV.335: Histogram stdev – Total Ca

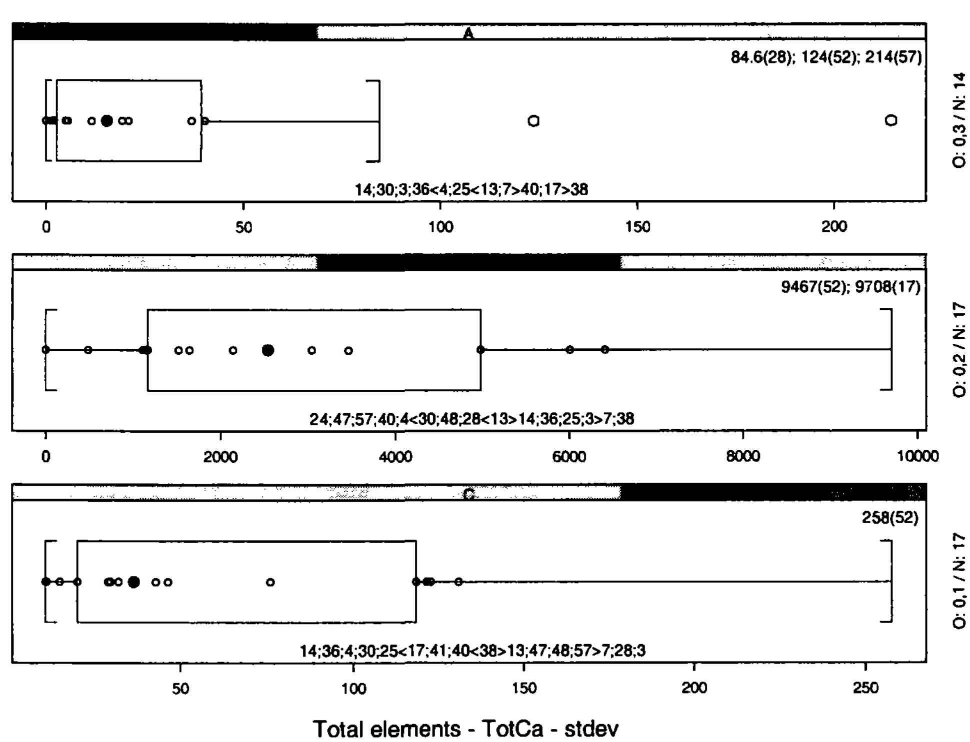


Figure IV.336: Boxplot stdev – Total Ca

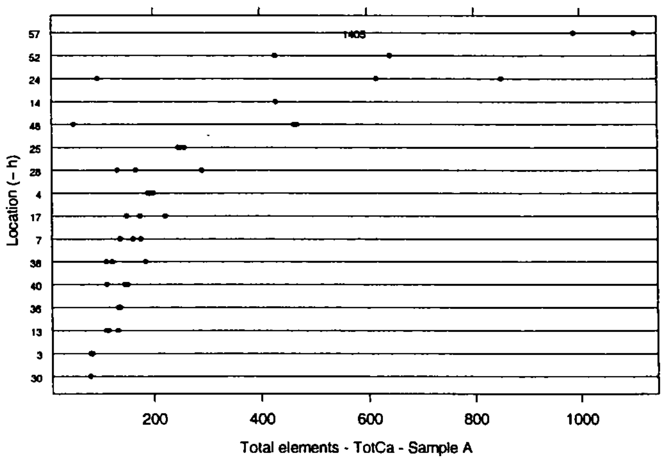


Figure IV.337: Dotplot - Sample A– Total Ca

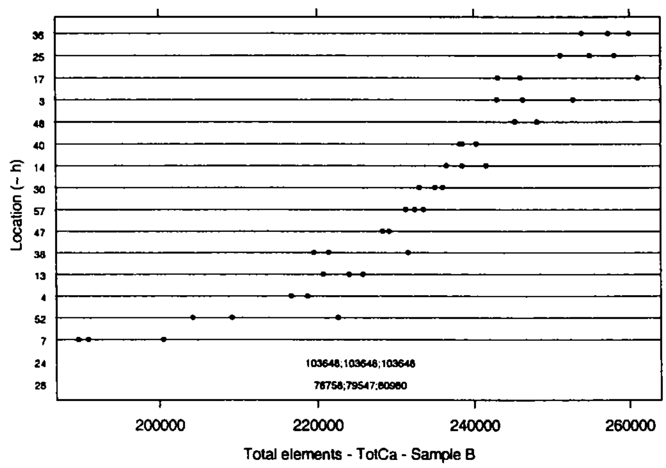


Figure IV.338: Dotplot - Sample B– Total Ca

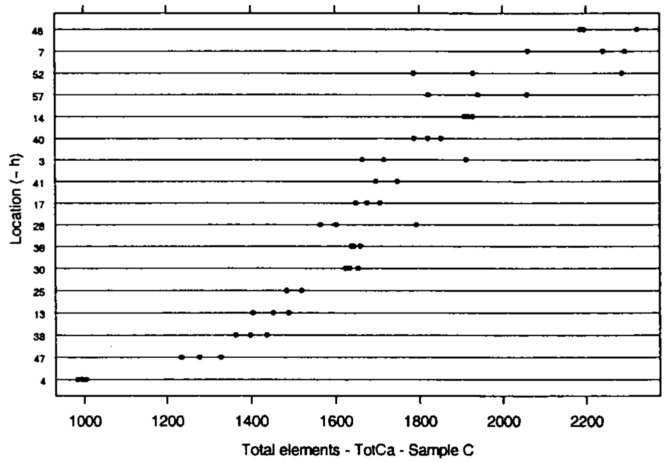


Figure IV.339: Dotplot - Sample C – Total Ca

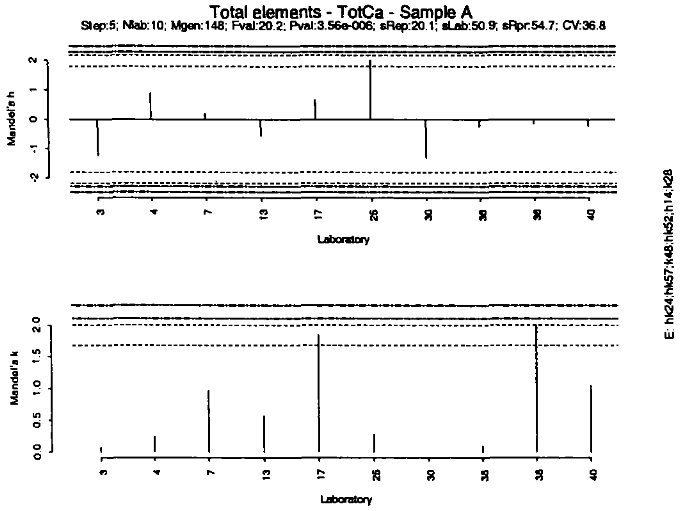


Figure IV.340: Mandel h/k plot - Sample A – Total Ca

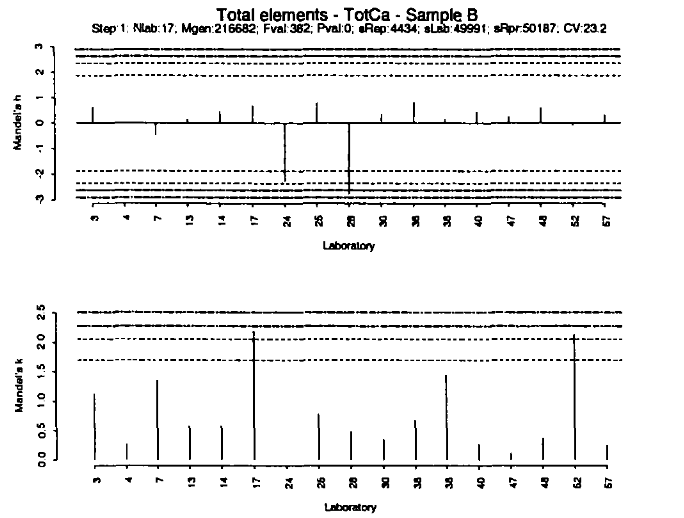


Figure IV.341: Mandel h/k plot - Sample B – Total Ca

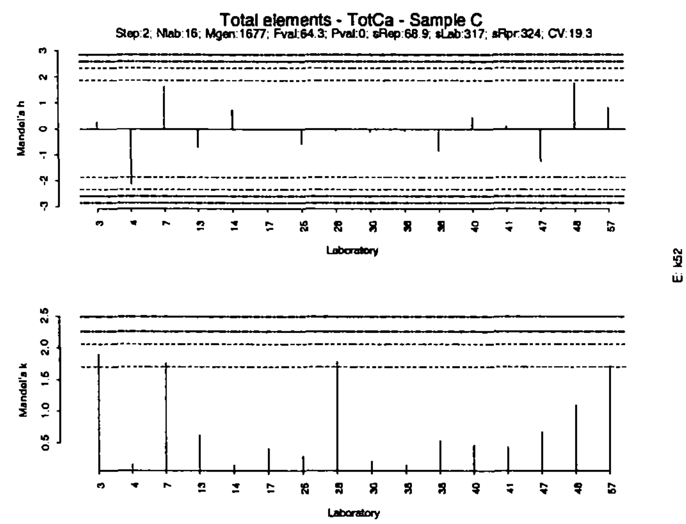


Figure IV.342: Mandel's h/k plot - Sample C – Total Ca

Parameter: Total Fe

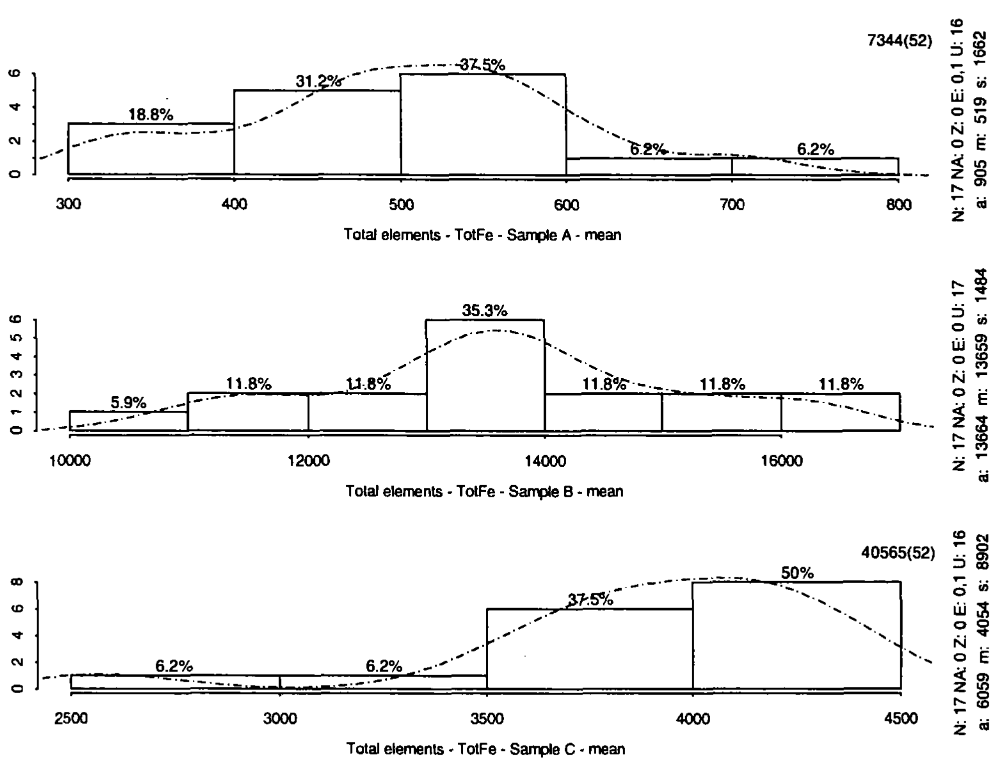


Figure IV.342: Histogram mean – Total Fe

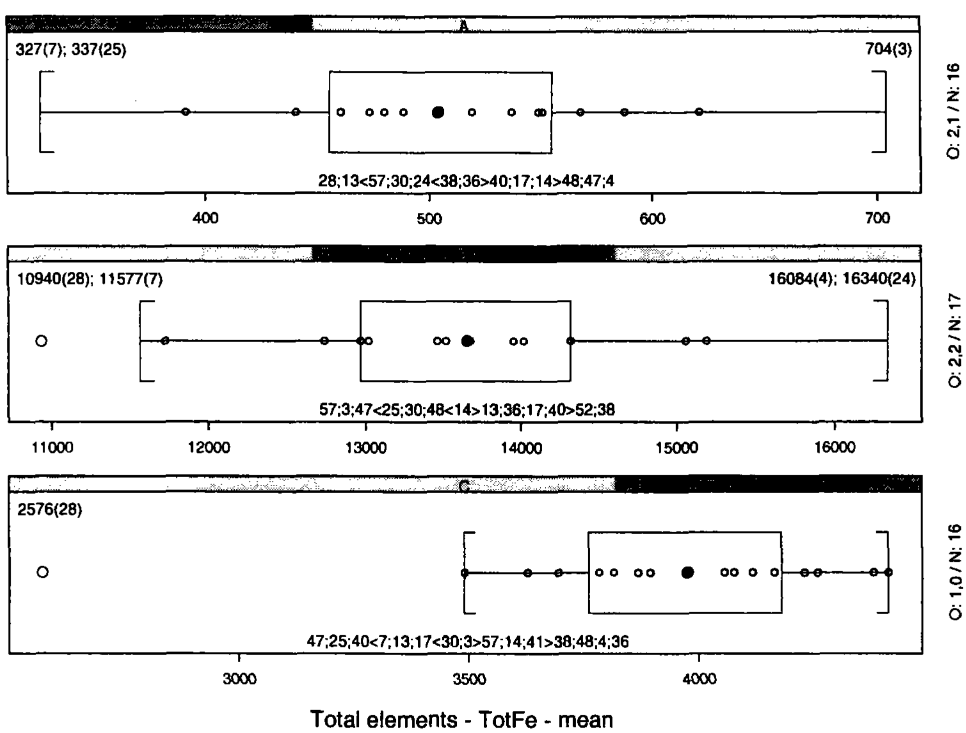


Figure IV.343: Boxplot mean – Total Fe

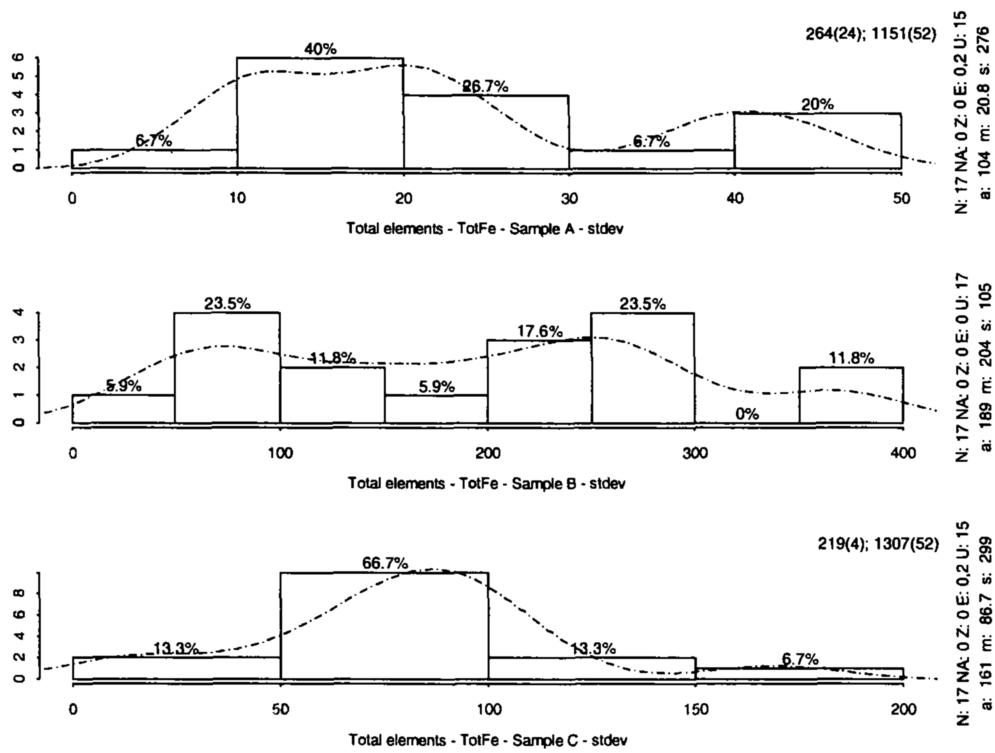


Figure IV.344: Histogram stdev – Total Fe

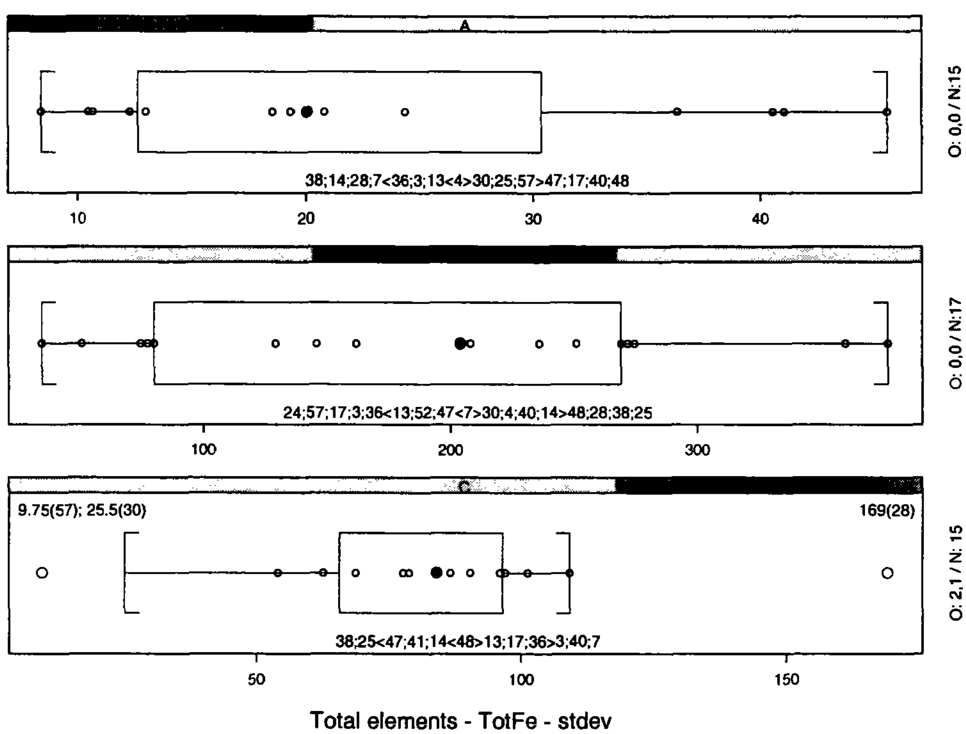


Figure IV.345: Boxplot stdev – Total Fe

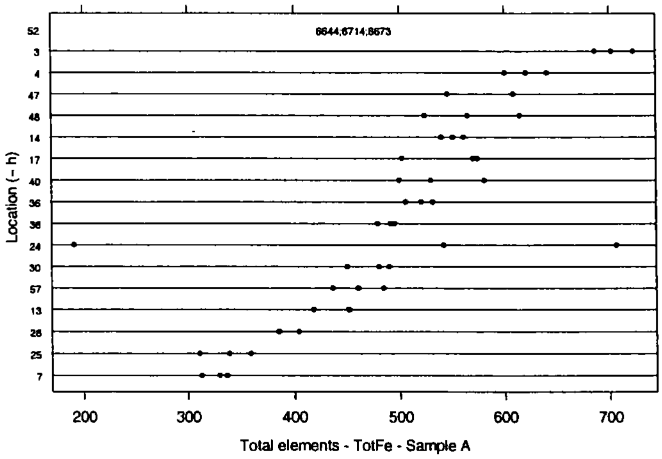


Figure IV.346: Dotplot - Sample A – Total Fe

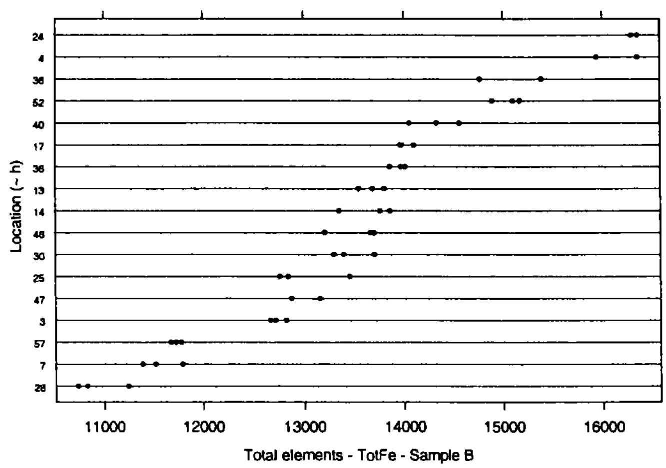


Figure IV.347: Dotplot - Sample B – Total Fe

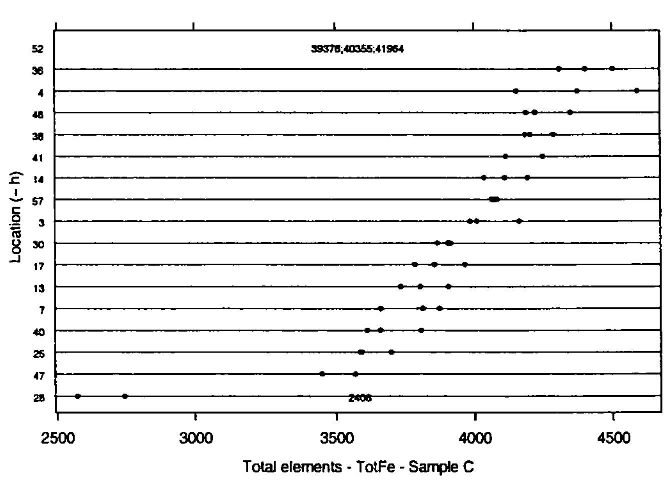


Figure IV.348: Dotplot - Sample C – Total Fe

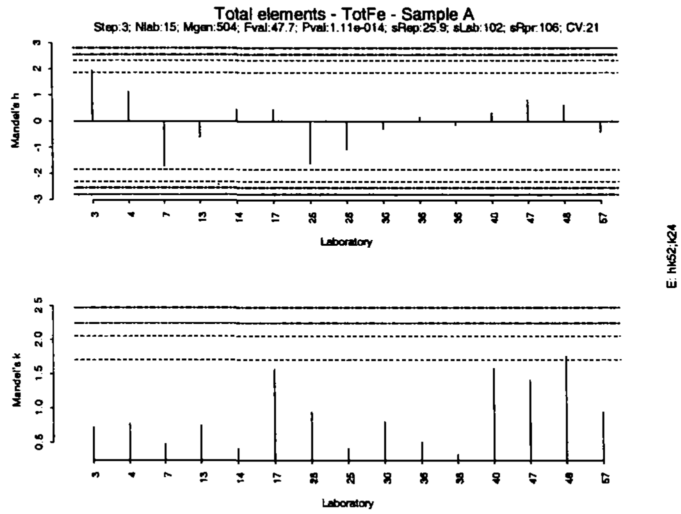


Figure IV.349: Mandel h/k plot - Sample A – Total Fe

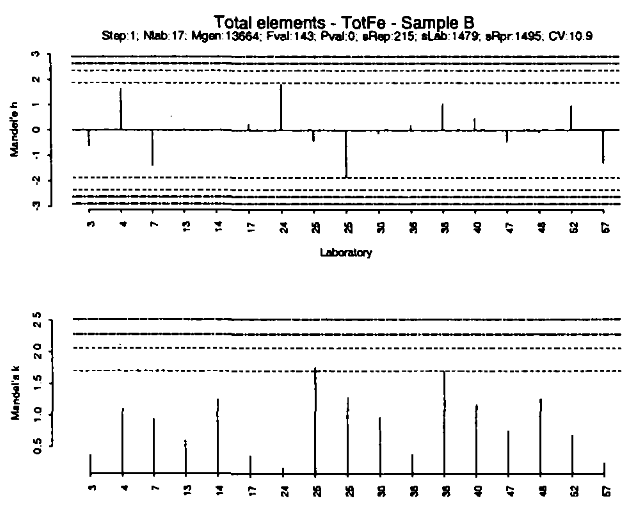


Figure IV.350: Mandel h/k plot - Sample B – Total Fe

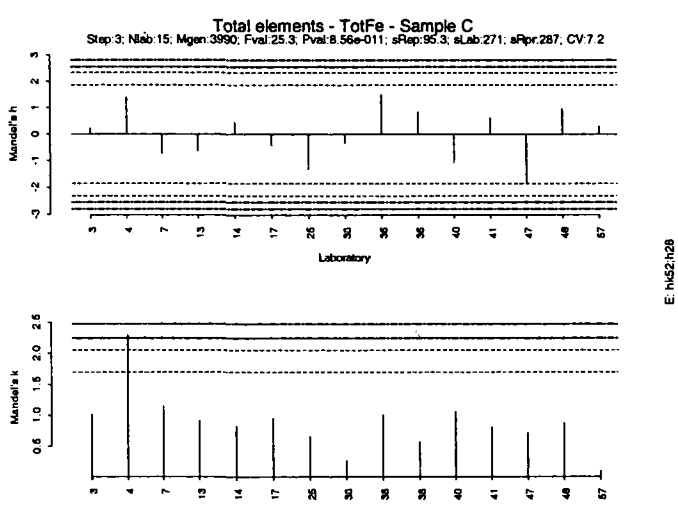


Figure IV.351: Mandel h/k plot - Sample C – Total Fe

Parameter: Total K

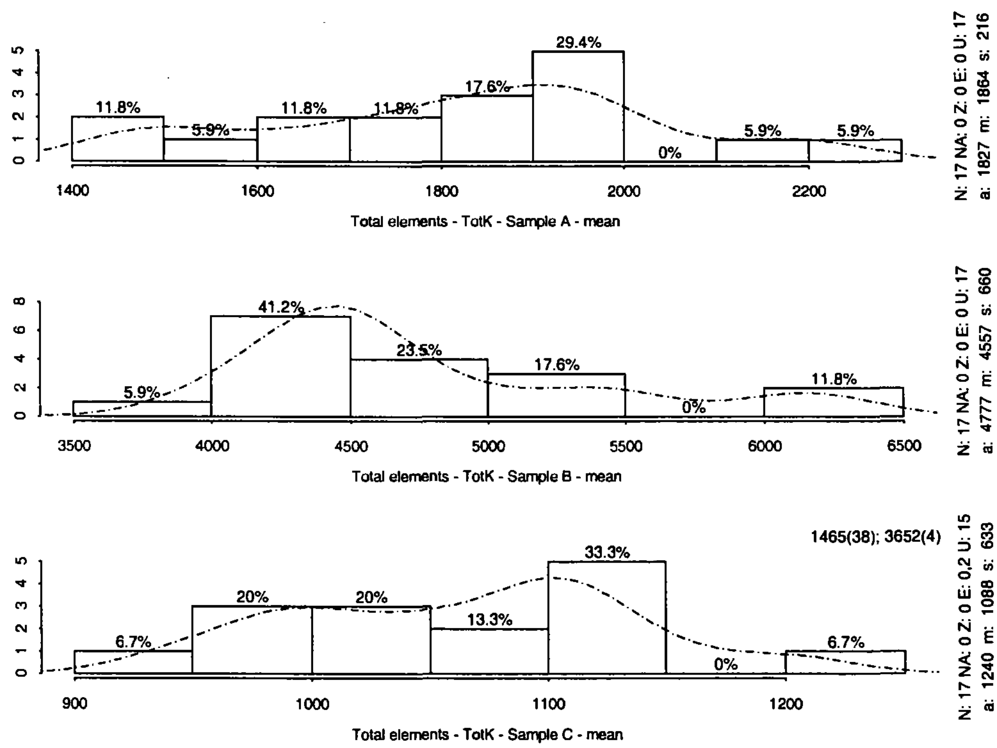


Figure IV.352: Histogram mean – Total K

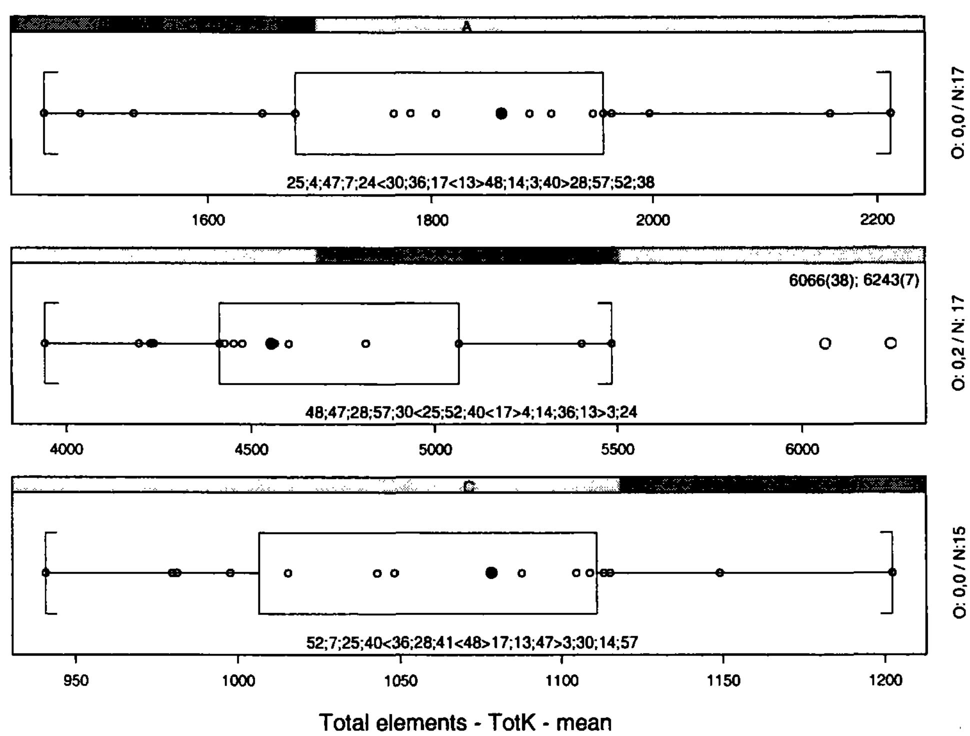


Figure IV.353: Boxplot mean – Total K

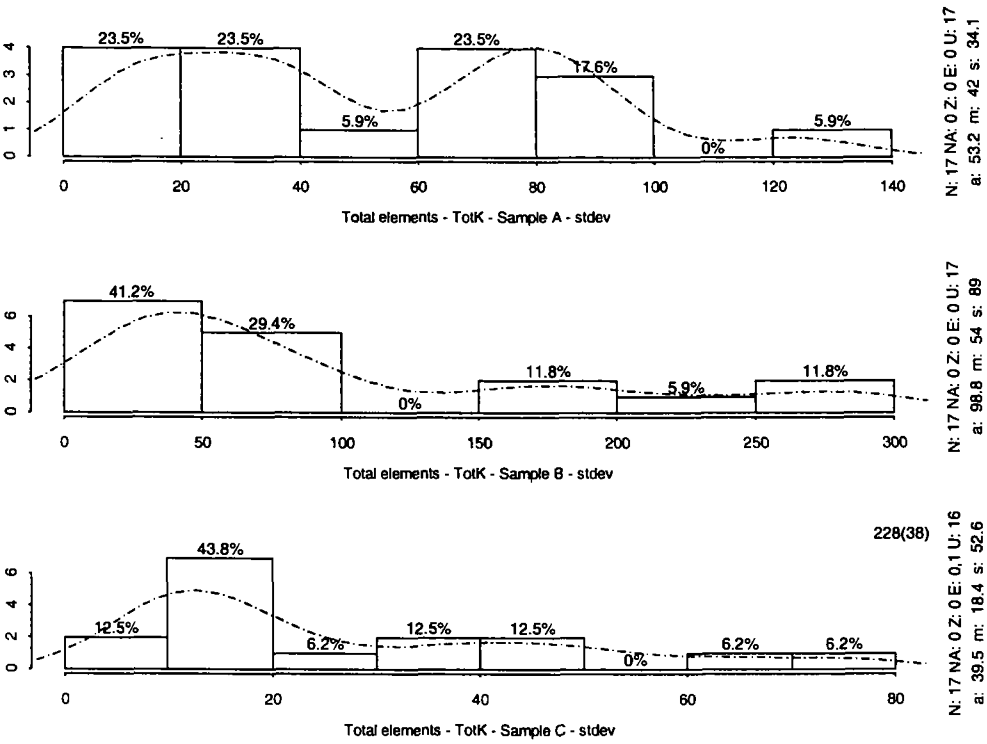


Figure IV.354: Histogram stdev – Total K

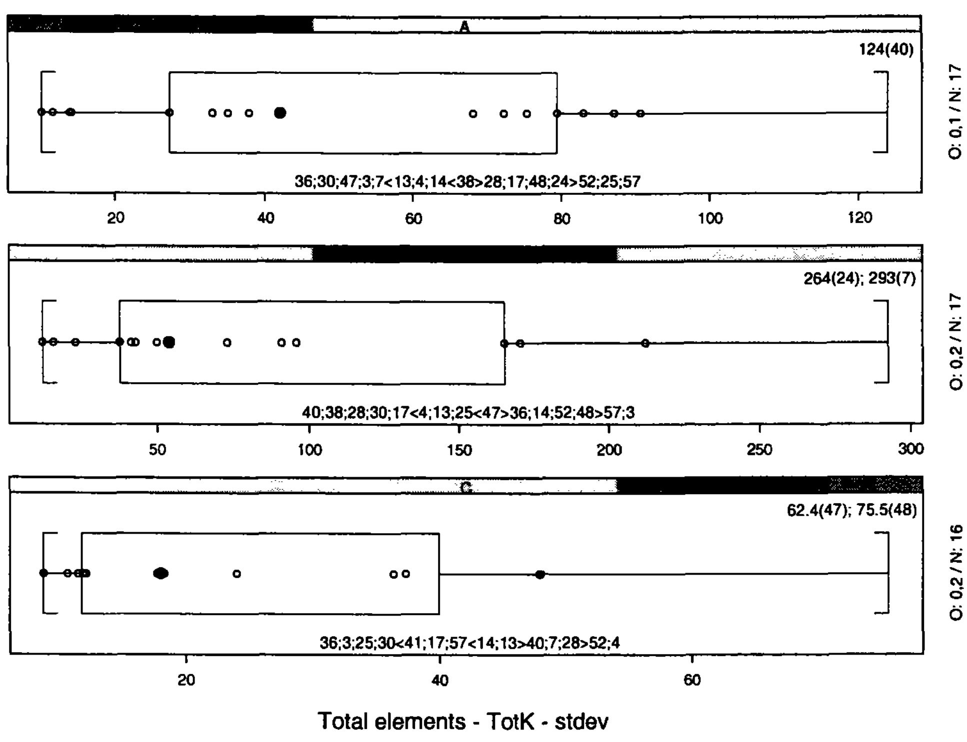


Figure IV.355: Boxplot stdev – Total K

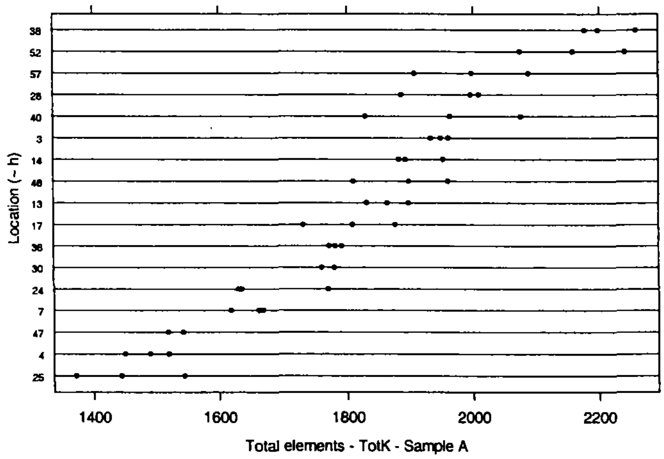


Figure IV.356: Dotplot - Sample A – Total K

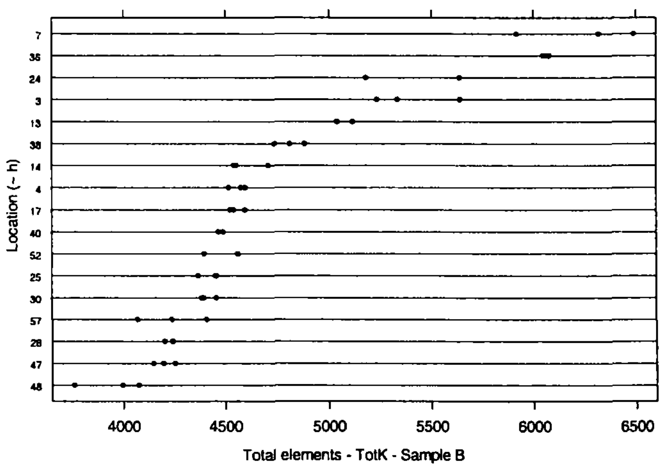


Figure IV.357: Dotplot - Sample B – Total K

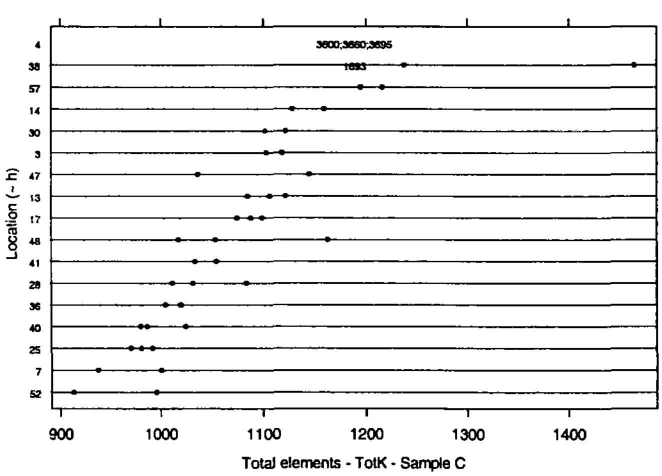


Figure IV.358: Dotplot - Sample C – Total K

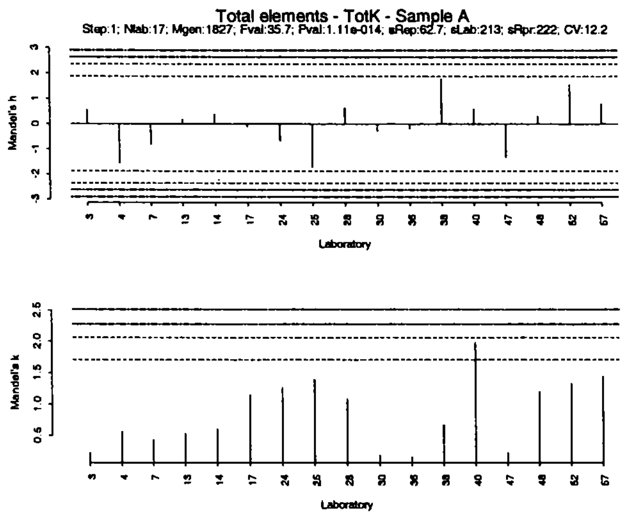


Figure IV.359: Mandel h/k plot - Sample A – Total K

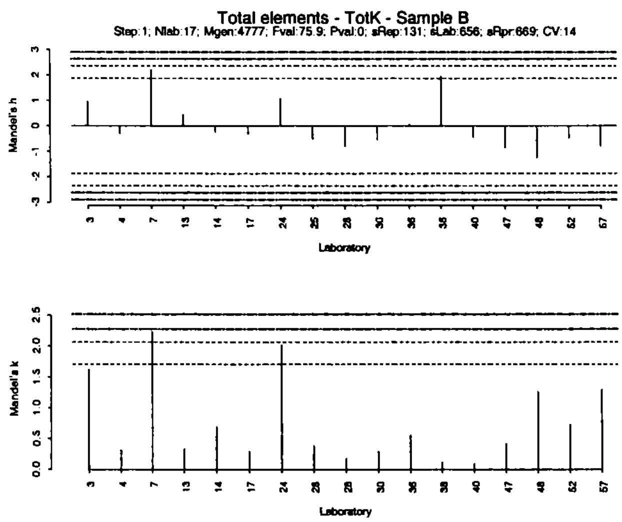
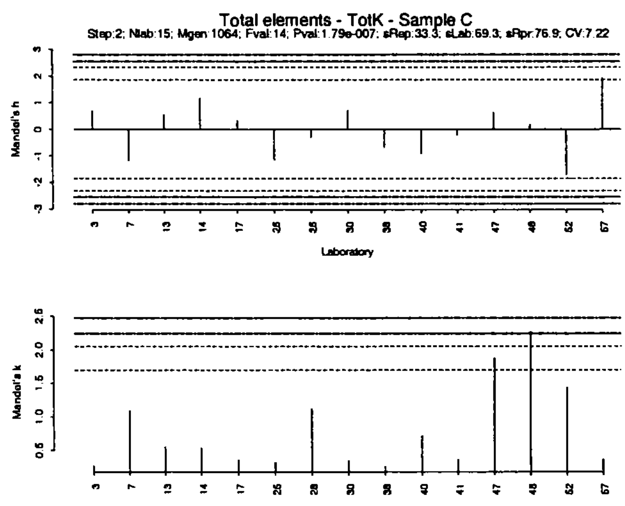


Figure IV.360: Mandel h/k plot - Sample B – Total K



E: h4;hk38

Figure IV.361: Mandel h/k plot - Sample C – Total K

Parameter: Total Mg

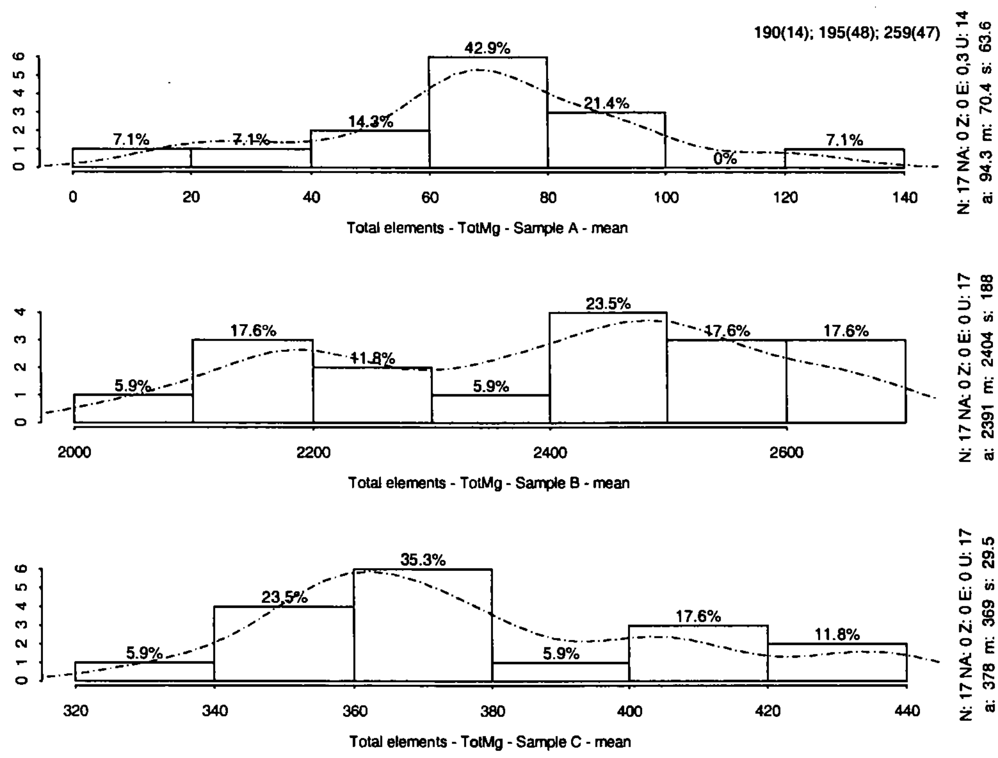


Figure IV.362: Histogram mean – Total Mg

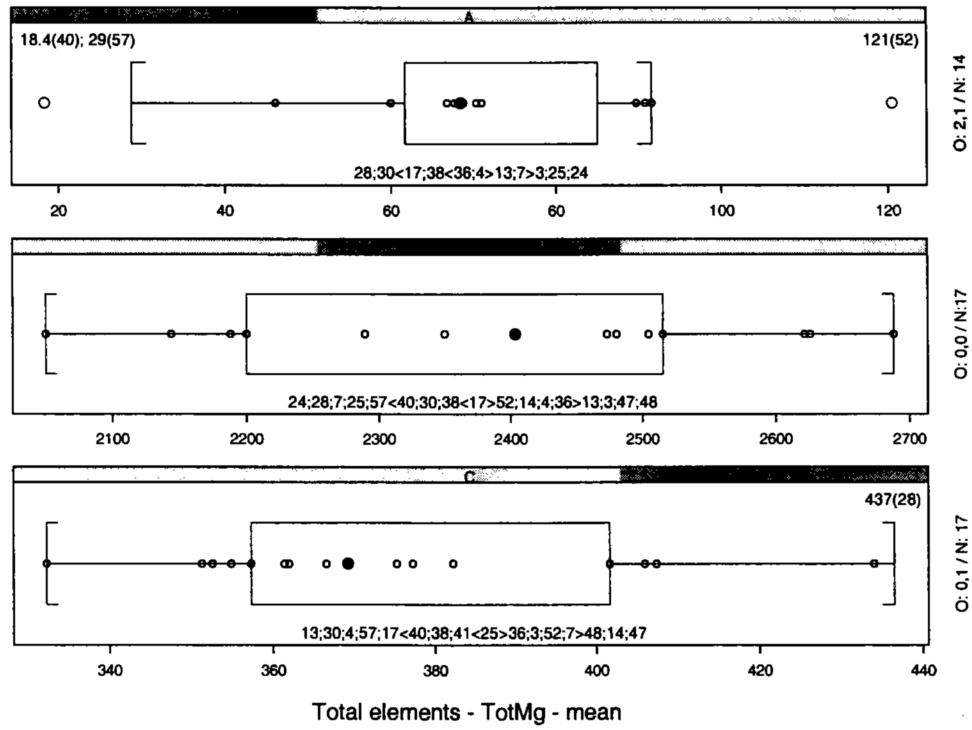


Figure IV.363: Boxplot mean – Total Mg

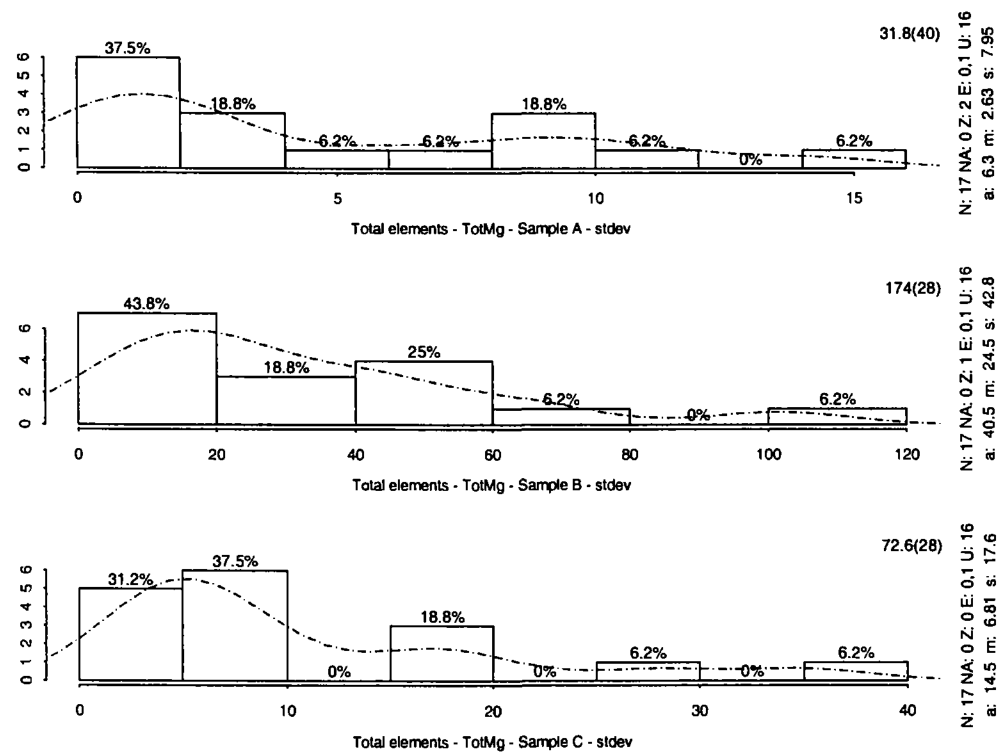


Figure IV.364: Histogram stdev – Total Mg

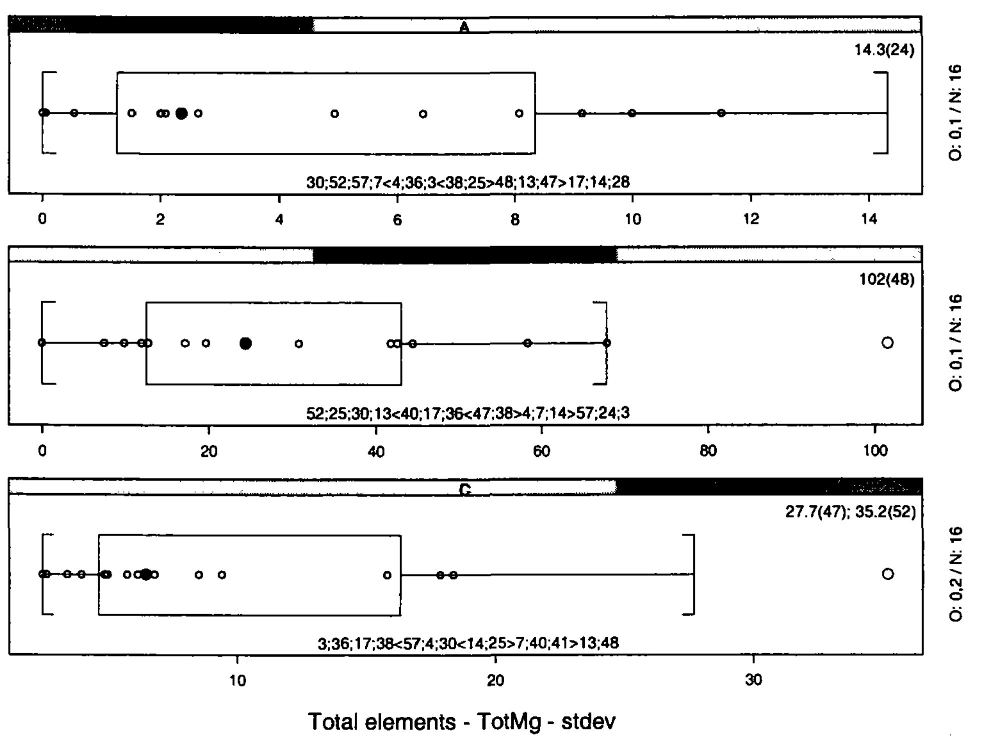


Figure IV.365: Boxplot stdev – Total Mg

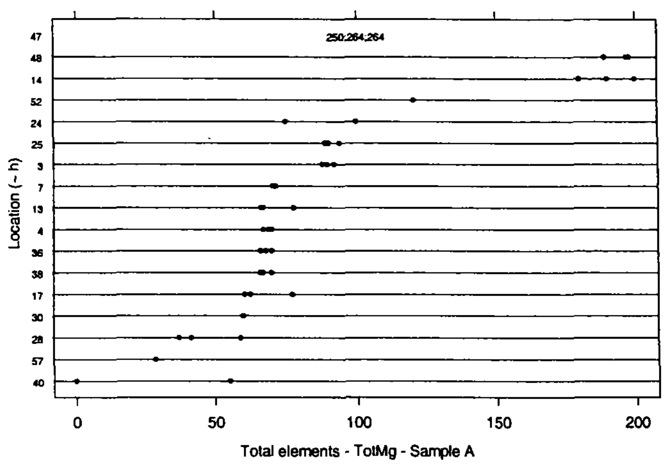


Figure IV.366: Dotplot - Sample A – Total Mg

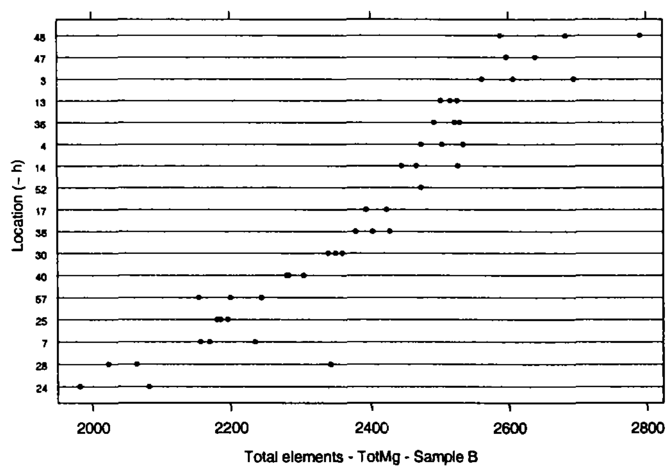


Figure IV.367: Dotplot - Sample B – Total Mg

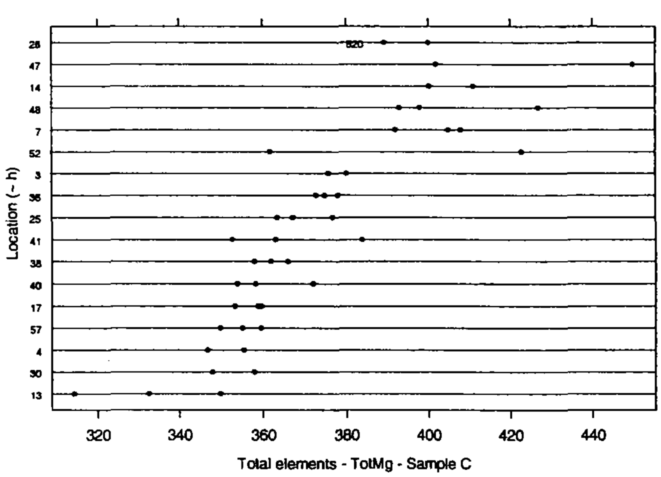


Figure IV.368: Dotplot - Sample C – Total Mg

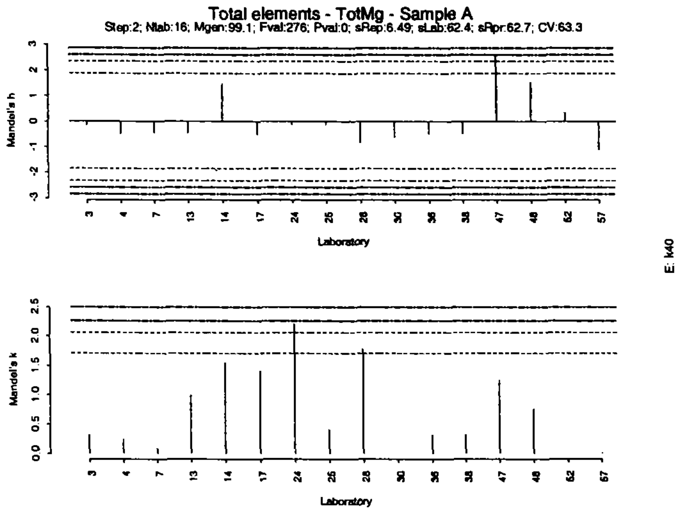


Figure IV.369: Mandel h/k plot - Sample A – Total Mg

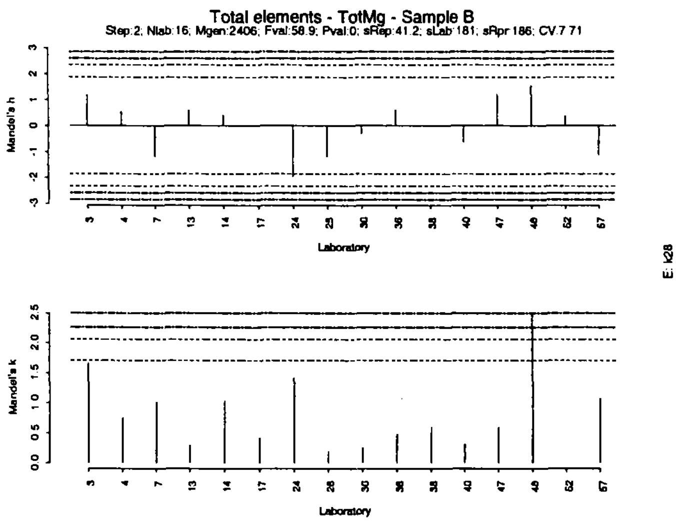


Figure IV.370: Mandel h/k plot - Sample B – Total Mg

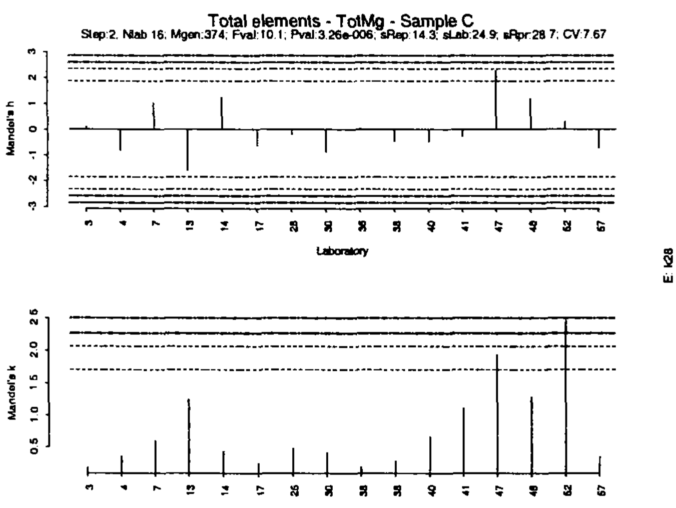


Figure IV.371: Mandel h/k plot – Sample C – Total Mg

Parameter: Total Mn

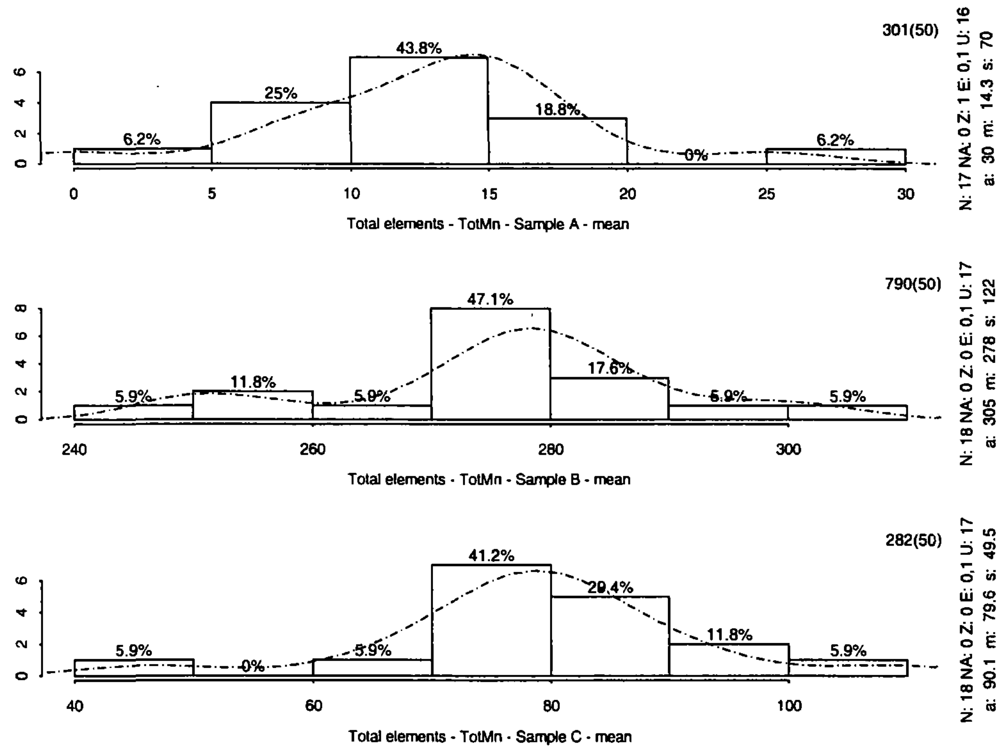


Figure IV.372: Histogram mean – Total Mn

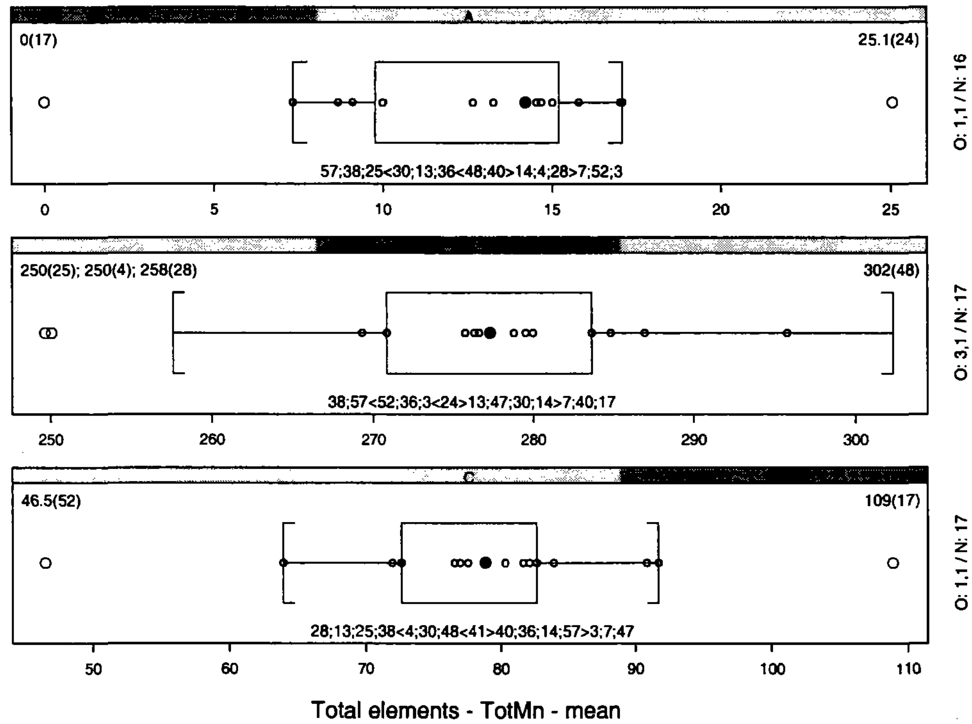


Figure IV.373: Boxplot mean – Total Mn

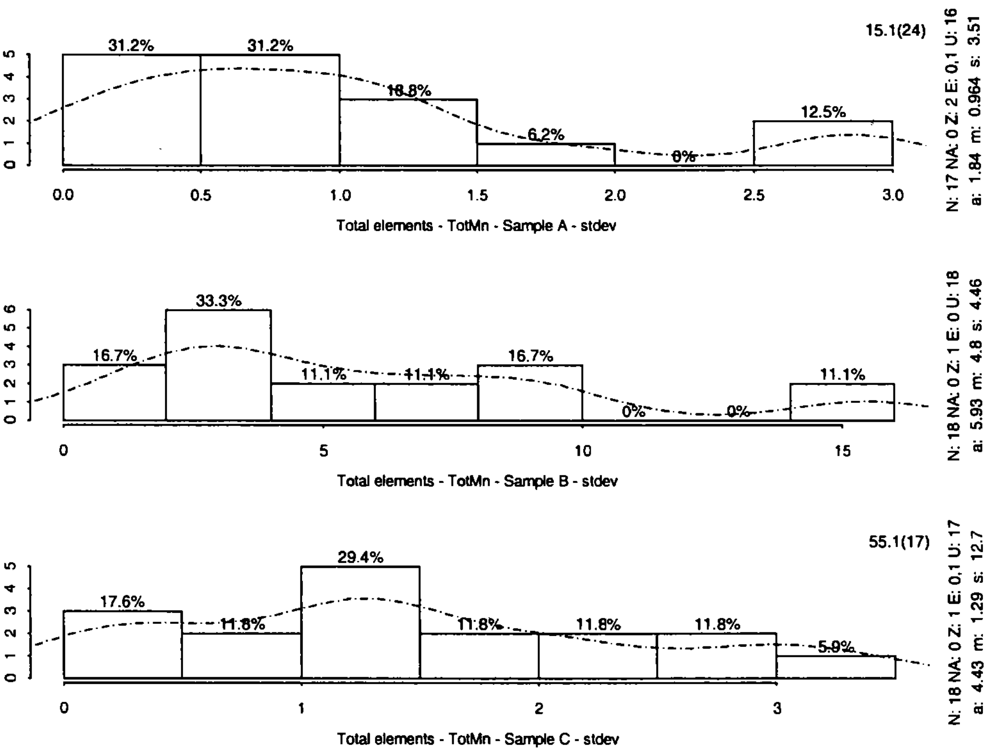


Figure IV.374: Histogram stdev – Total Mn

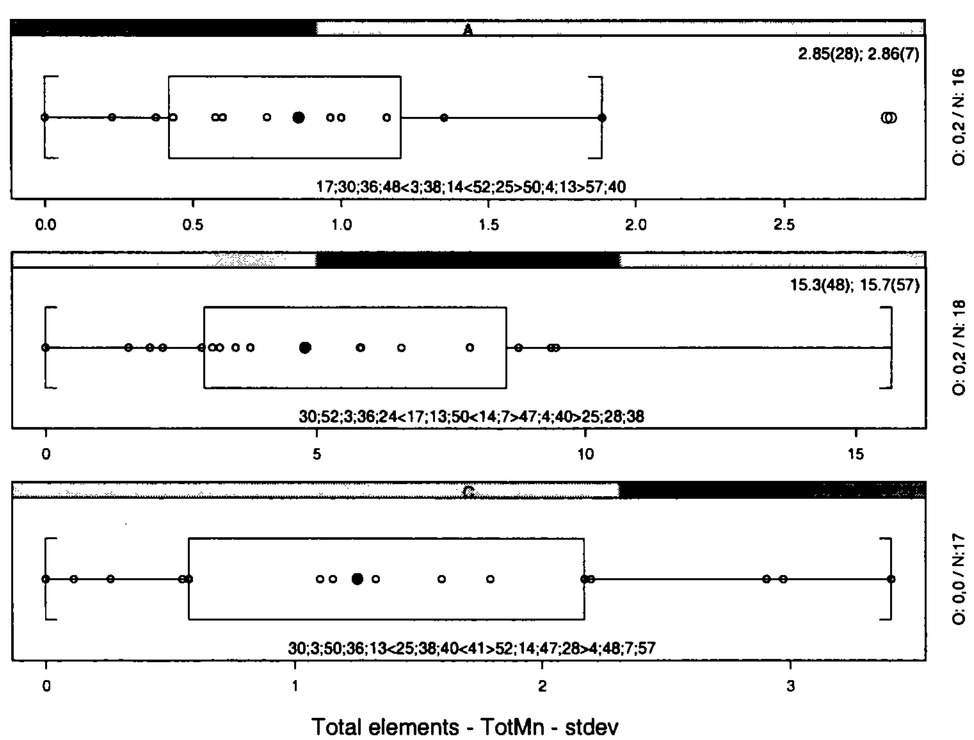


Figure IV.375: Boxplot stdev – Total Mn

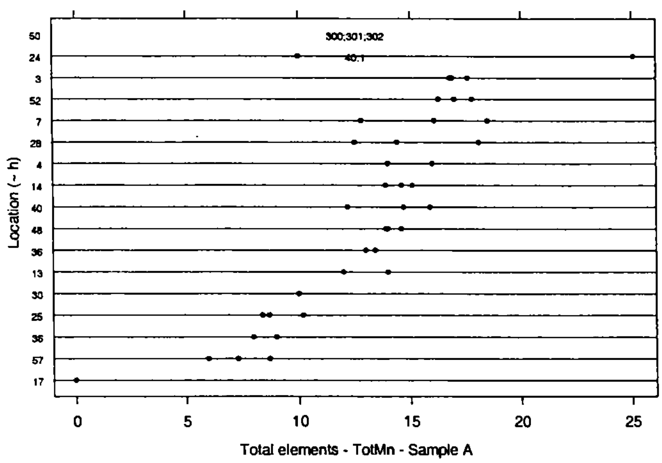


Figure IV.376: Dotplot - Sample A – Total Mn

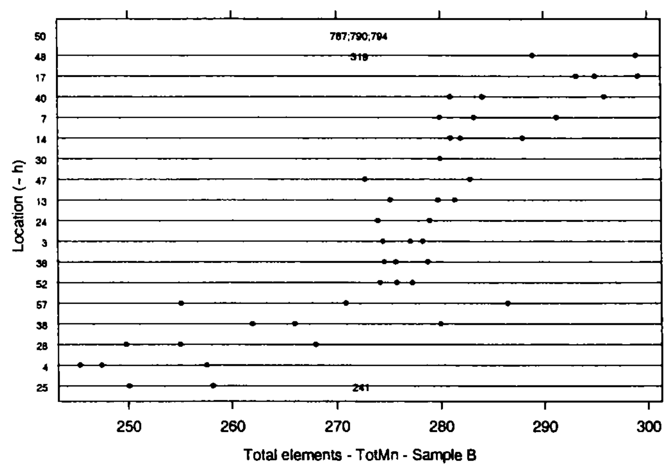


Figure IV.377: Dotplot - Sample B – Total Mn

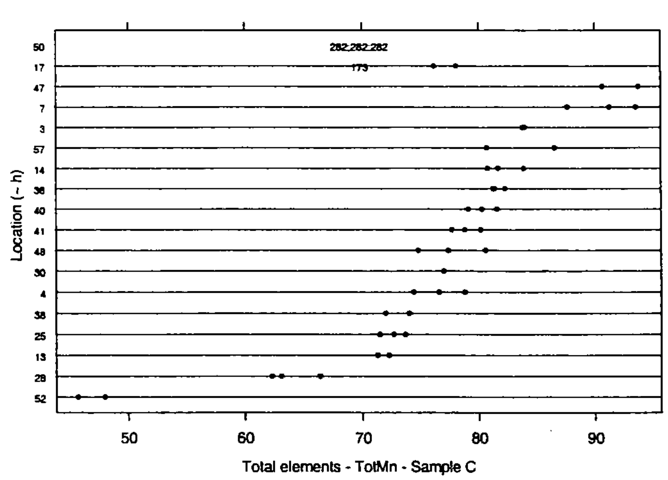


Figure IV.378: Dotplot - Sample C – Total Mn

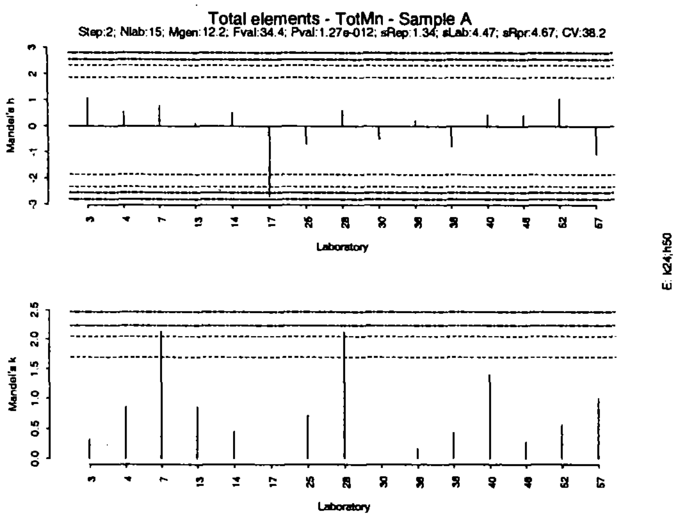


Figure IV.379: Mandel h/k plot - Sample A – Total Mn

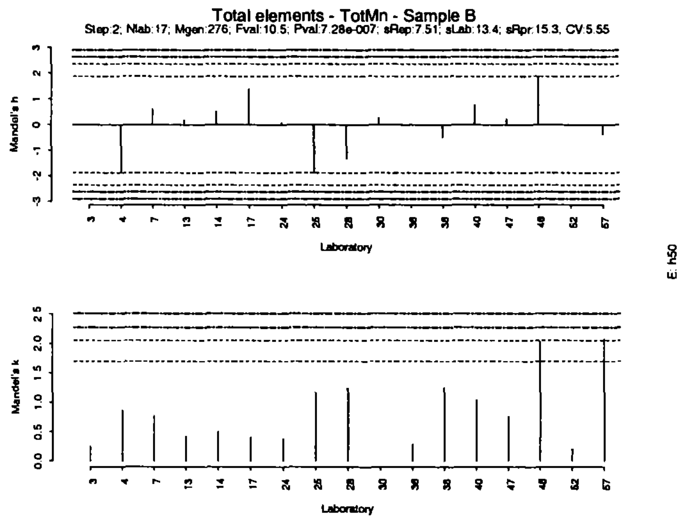


Figure IV.380: Mandel h/k plot - Sample B – Total Mn

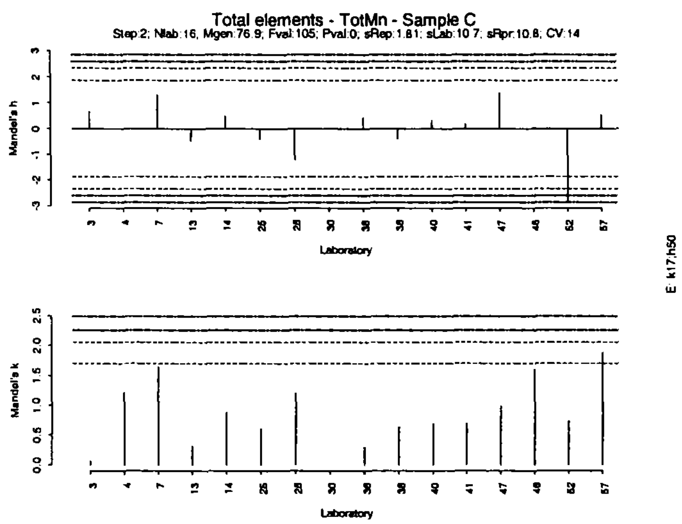


Figure IV.381: Mandel h/k plot - Sample C – Total Mn

Parameter: Total Na

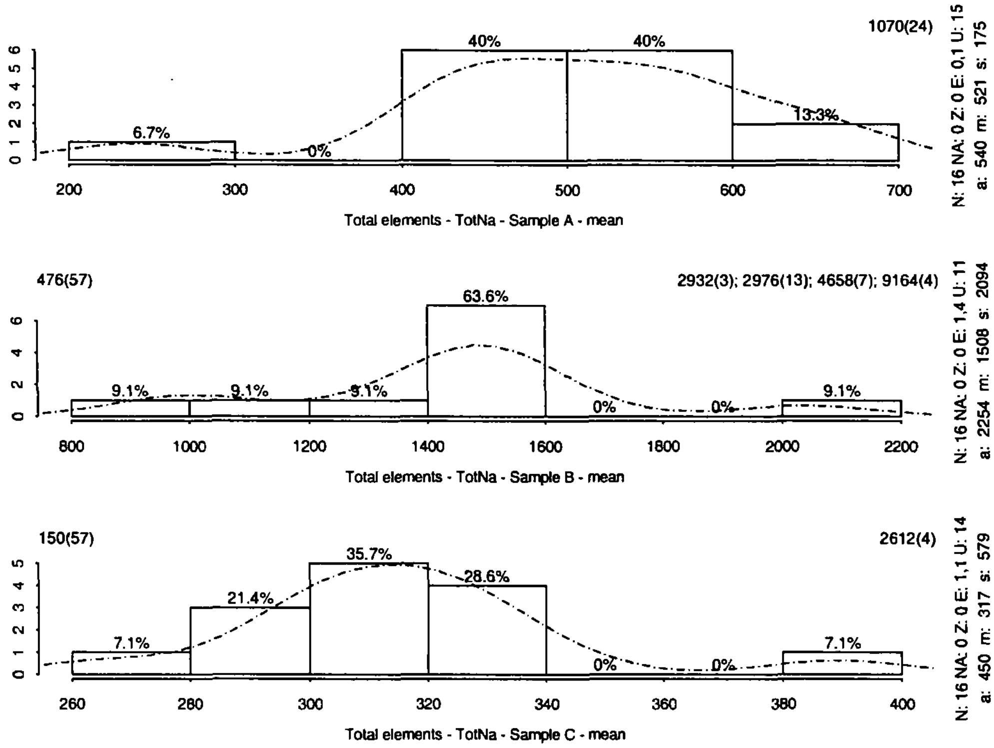


Figure IV.382: Histogram mean – Total Na

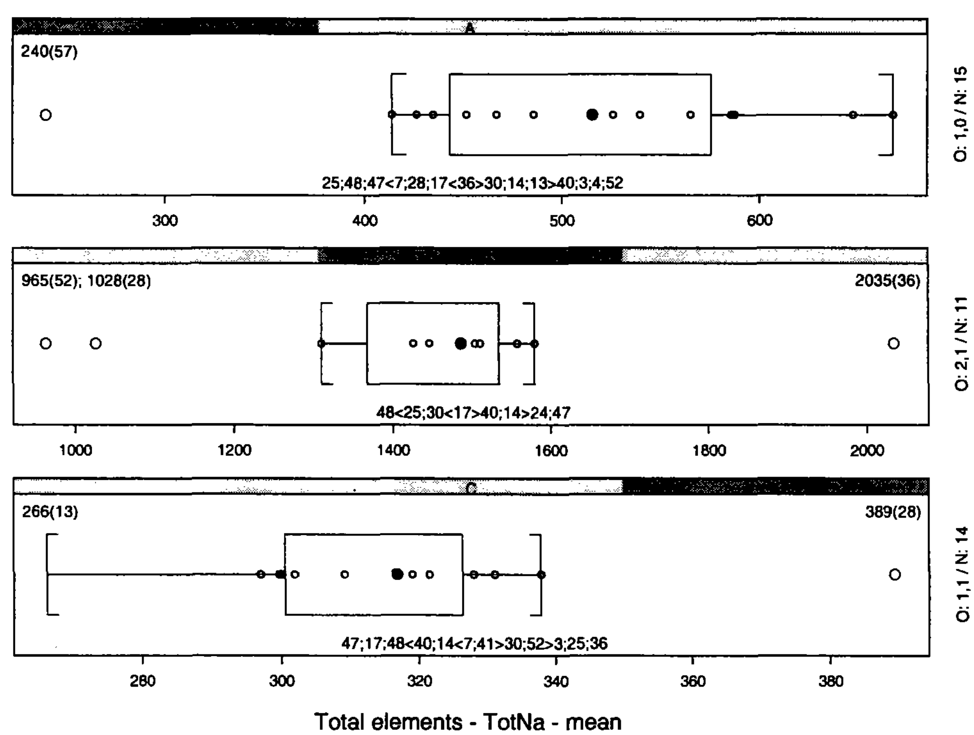


Figure IV.383: Boxplot mean – Total Na

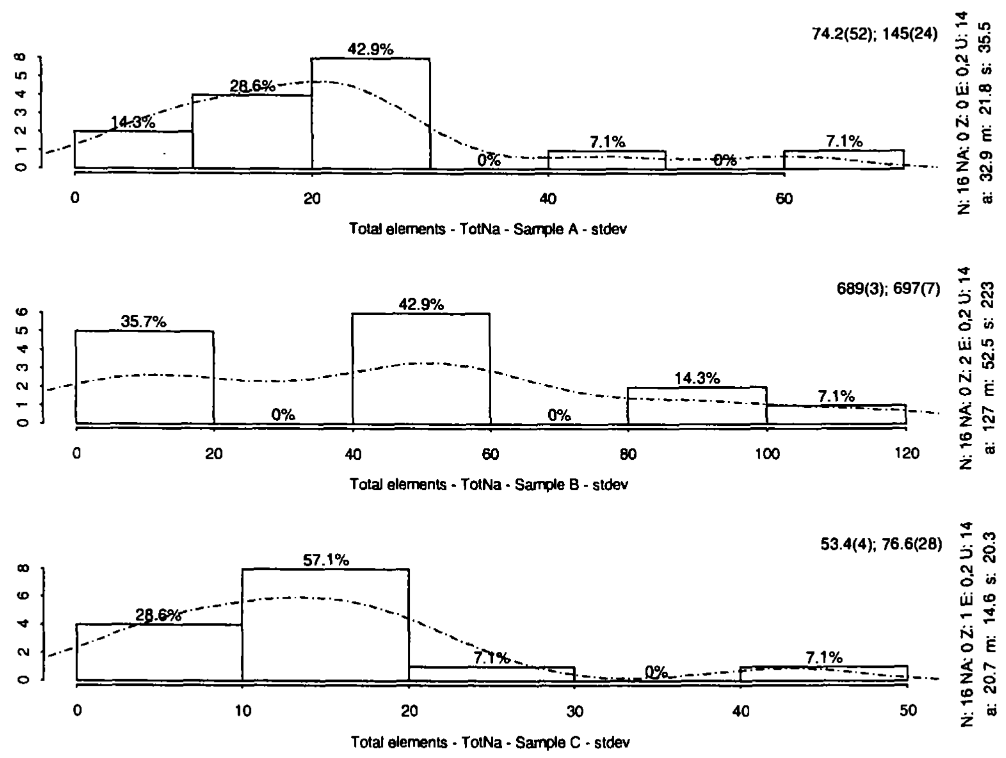


Figure IV.384: Histogram stdev – Total Na

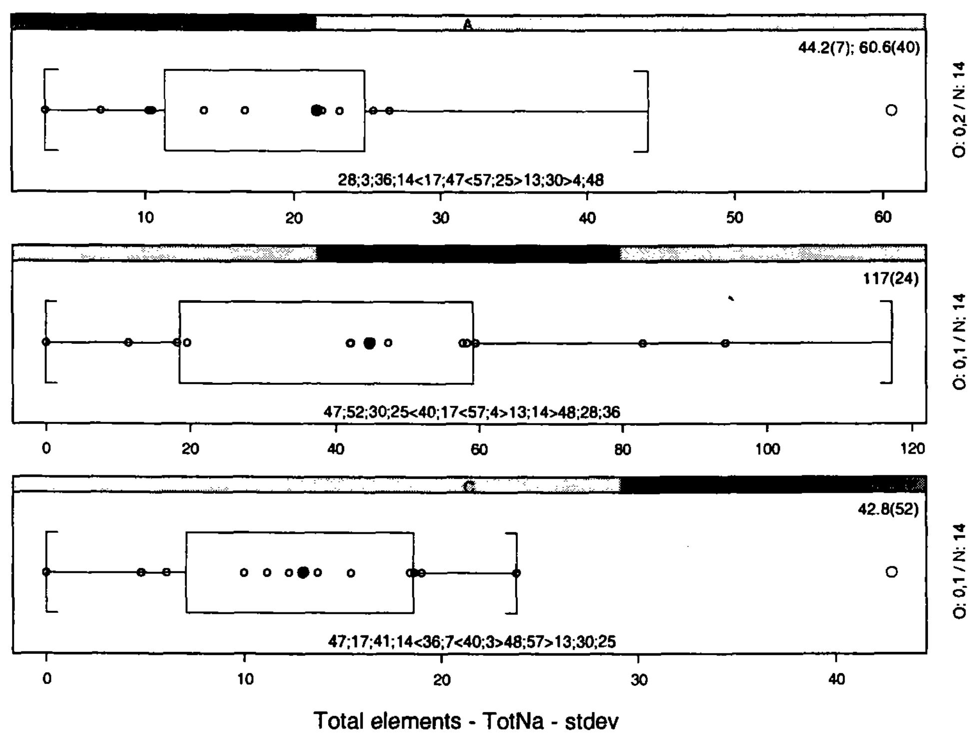


Figure IV.385: Boxplot stdev – Total Na

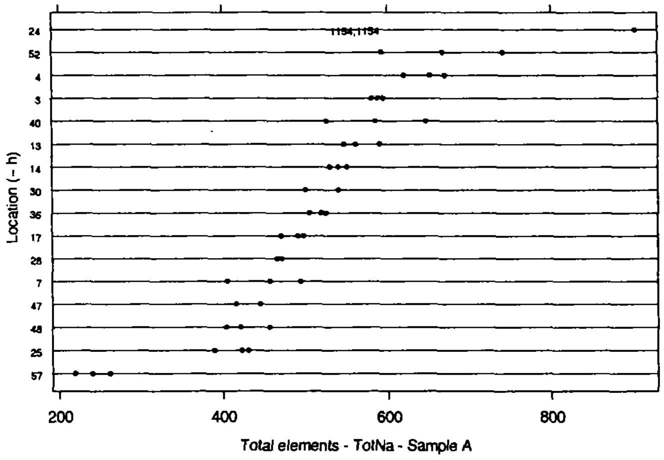


Figure IV.386: Dotplot - Sample A – Total Na

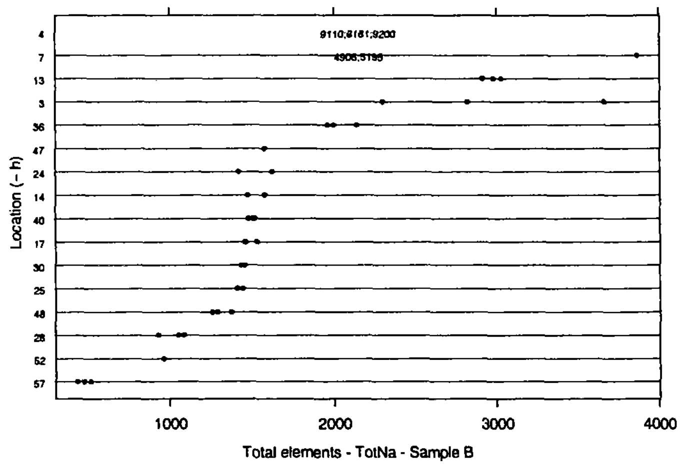


Figure IV.387: Dotplot - Sample B – Total Na

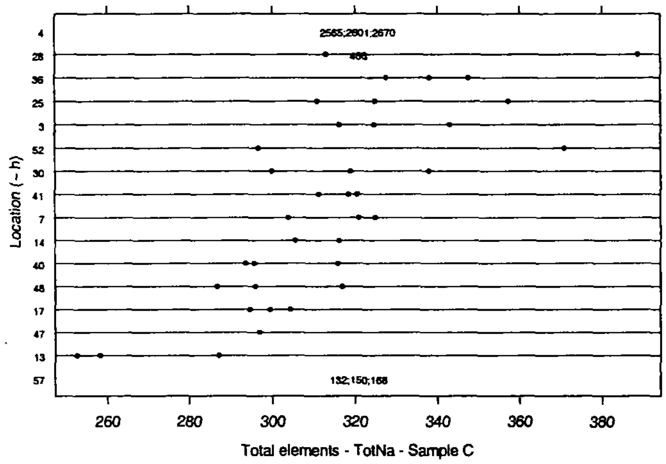


Figure IV.388: Dotplot - Sample C – Total Na

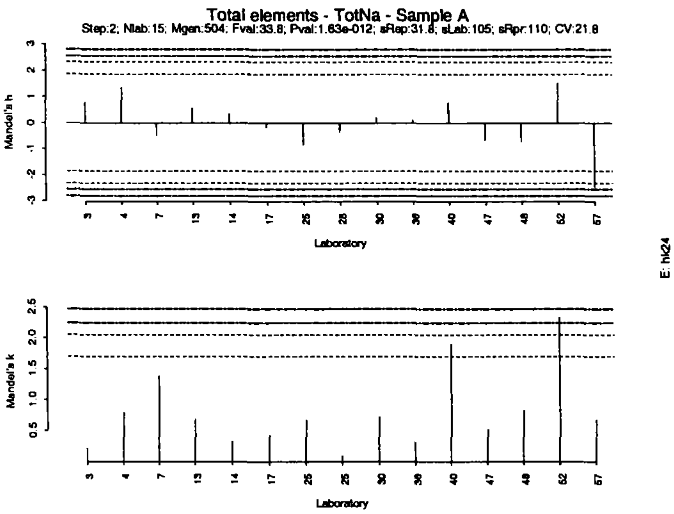


Figure IV.389: Mandel h/k plot - Sample A – Total Na

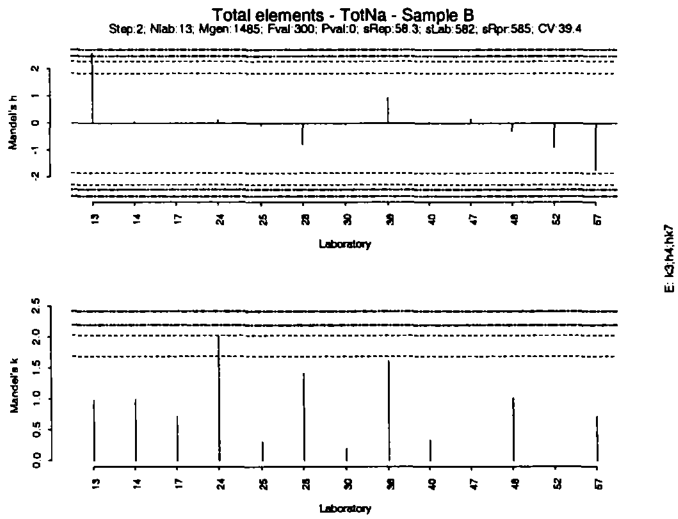


Figure IV.390: Mandel h/k plot - Sample B – Total Na

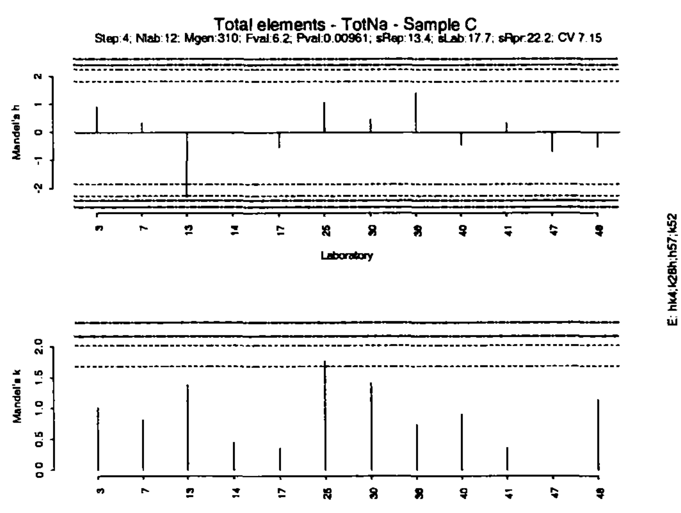


Figure IV.391: Mandel h/k plot - Sample C – Total Na

Group IX: Acid oxalate extractable Fe and Al

Parameter: Reactive Al

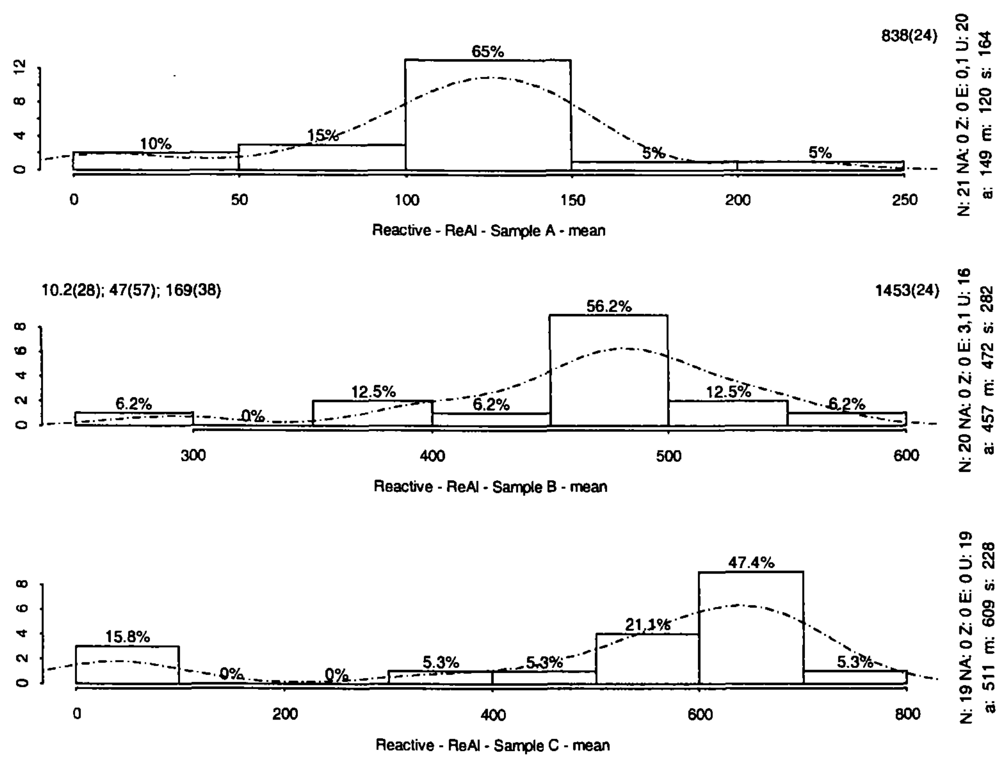


Figure IV.392: Histogram mean – Reactive Al

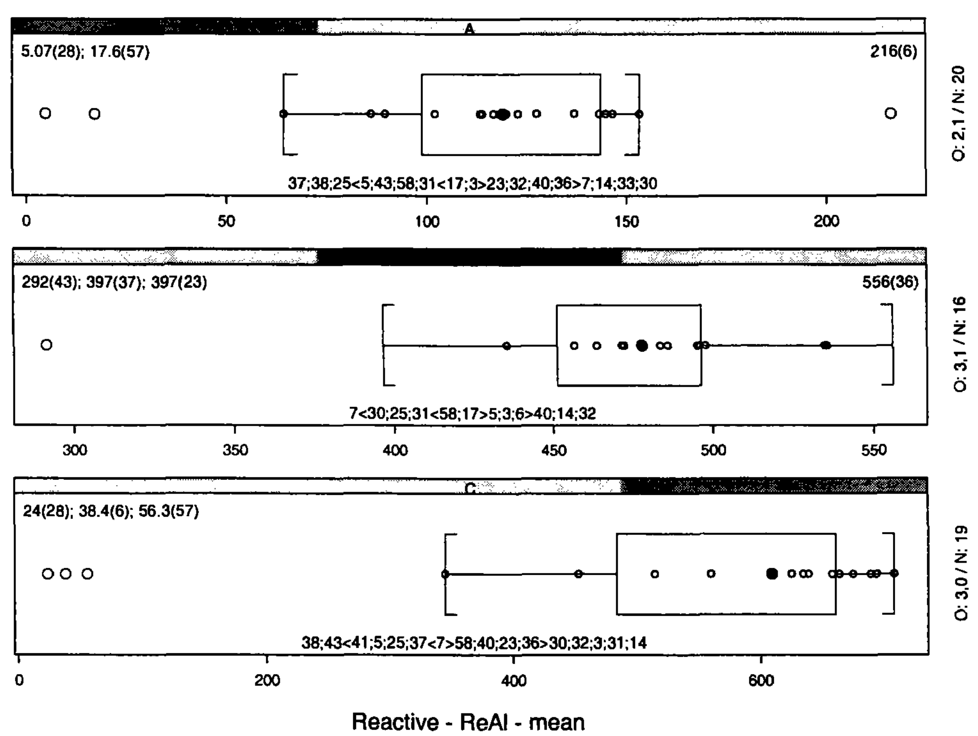


Figure IV.393: Boxplot mean – Reactive Al

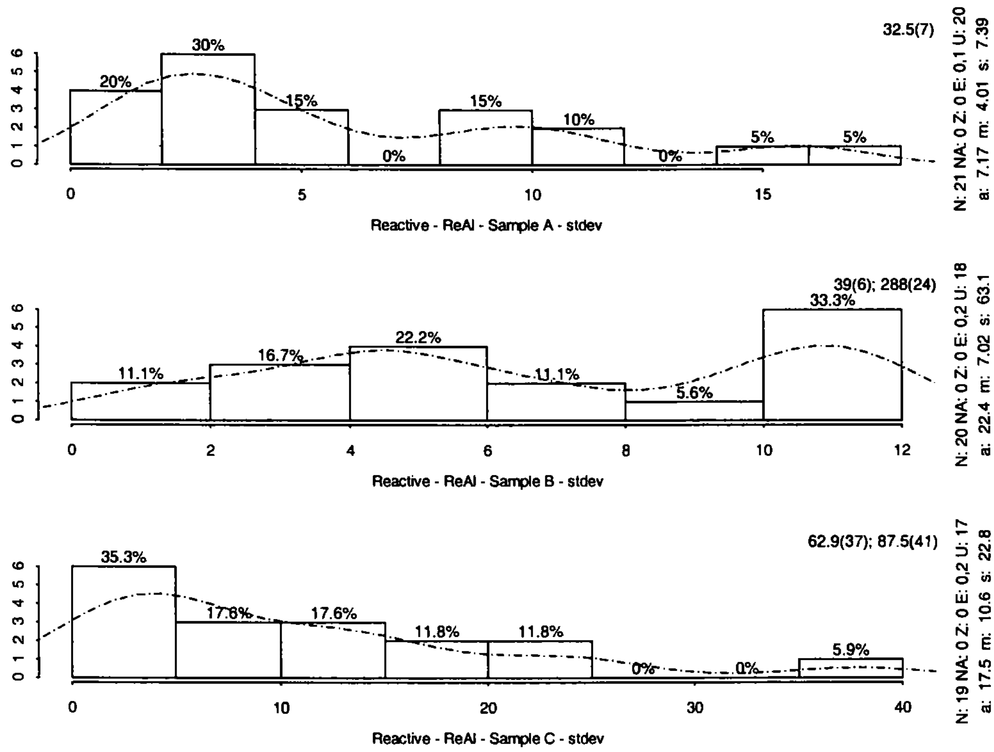


Figure IV.394: Histogram – Reactive Al

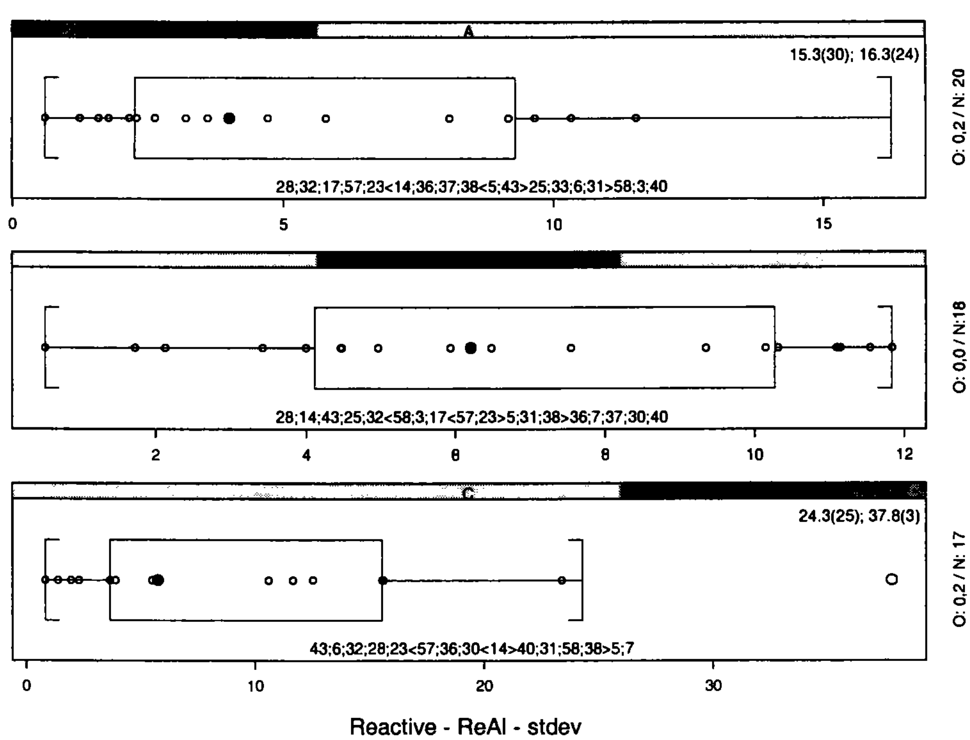


Figure IV.395: Boxplot stdev – Reactive Al

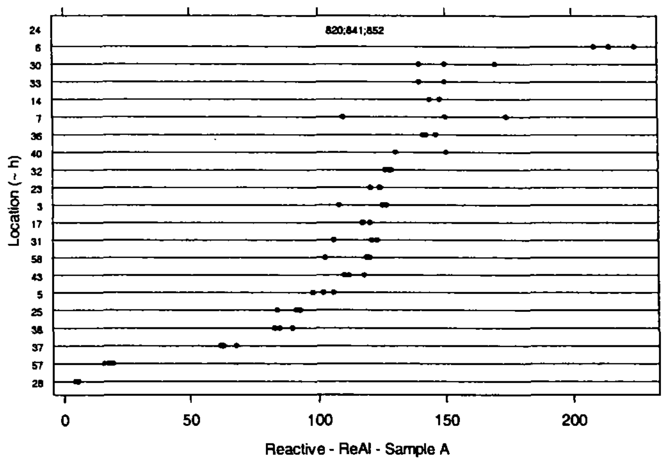


Figure IV.396: Dotplot - Sample A – Reactive Al

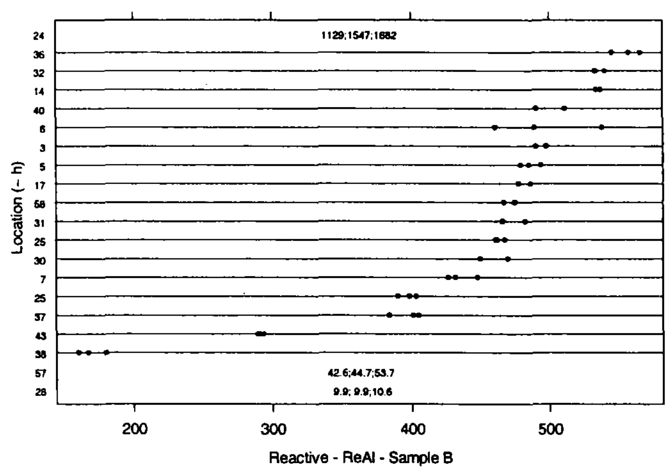


Figure IV.397: Dotplot - Sample B– Reactive Al

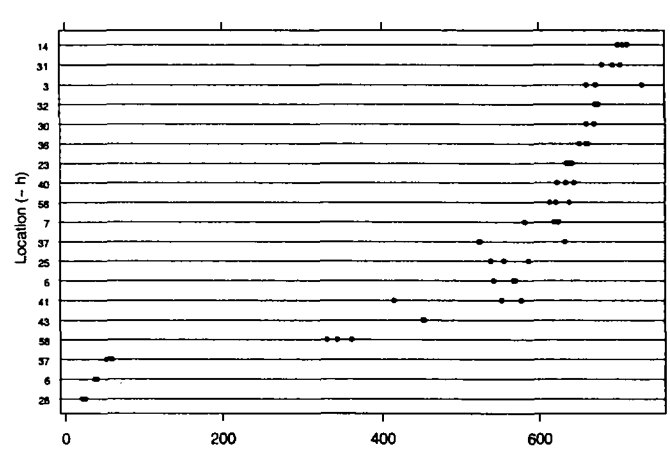


Figure IV.398: Dotplot - Sample C – Reactive Al

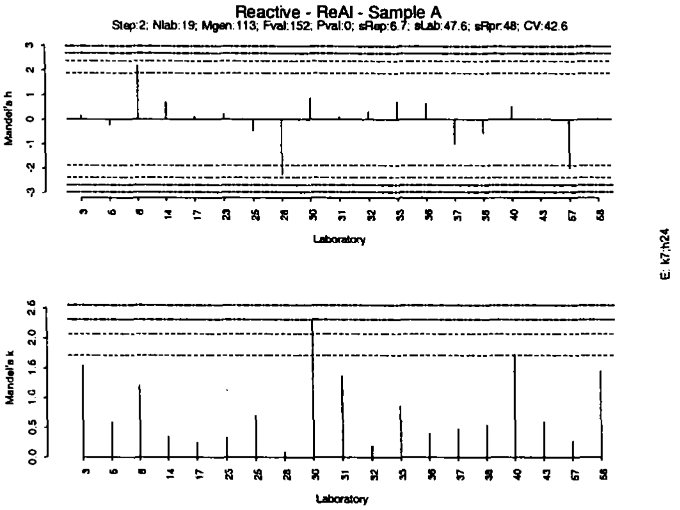


Figure IV.399: Mandel h/k plot - Sample A– Reactive Al

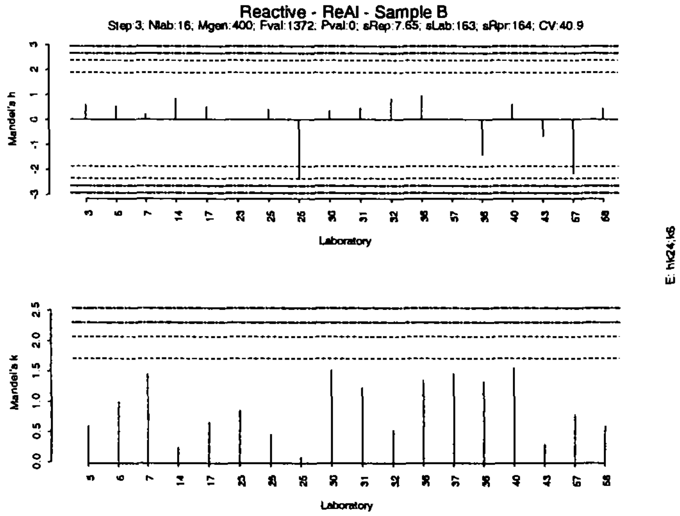


Figure IV.400: Mandel h/k plot - Sample B – Reactive Al

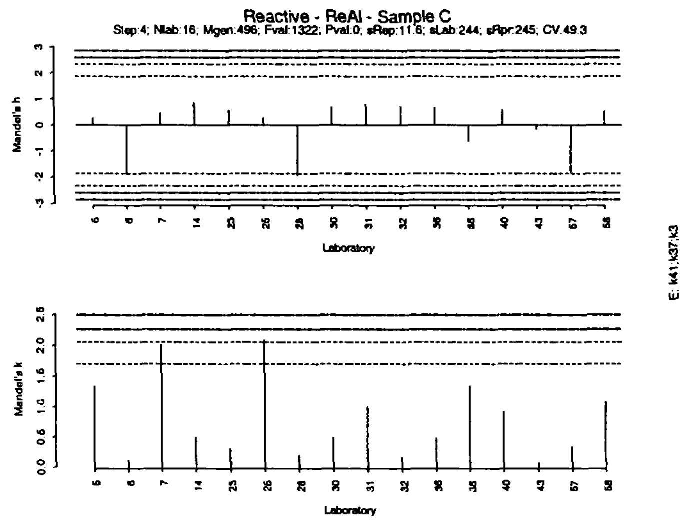


Figure IV.401: Mandelh/k plot - Sample C – Reactive Al

Parameter: Reactive Fe

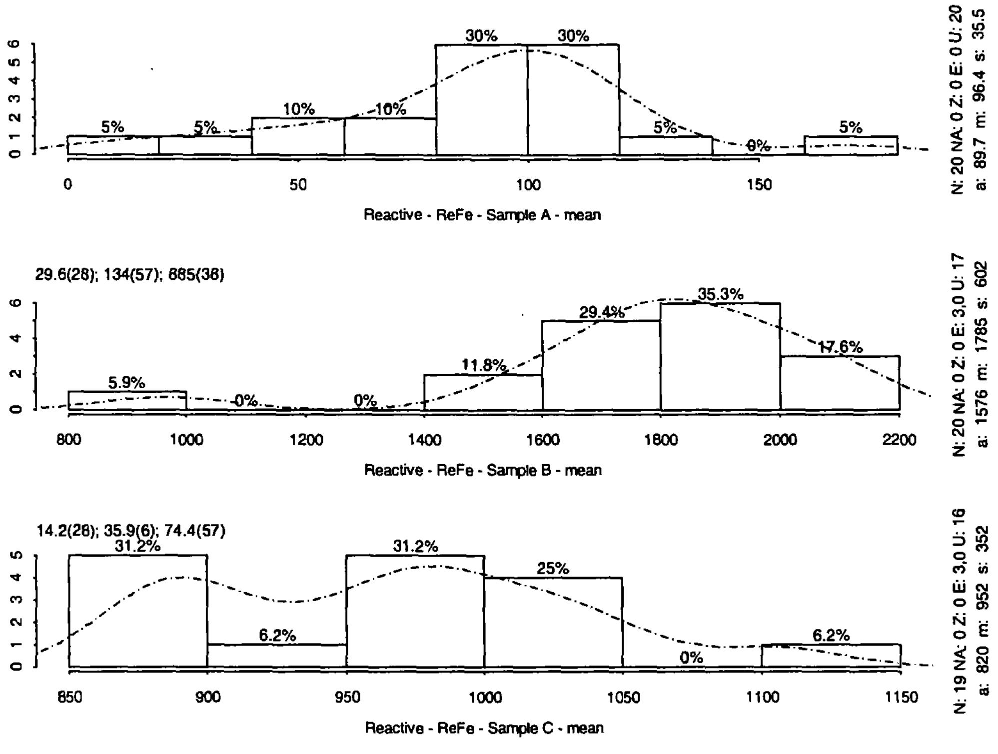


Figure IV.402: Histogram mean – Reactive Fe

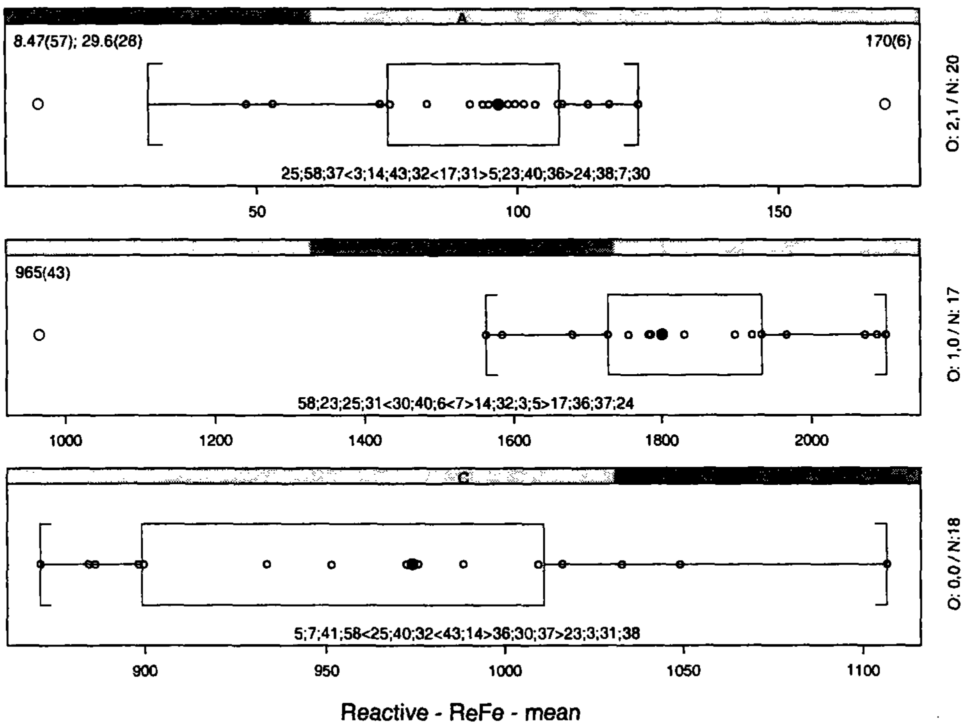


Figure IV.403: Boxplot mean – Reactive Fe

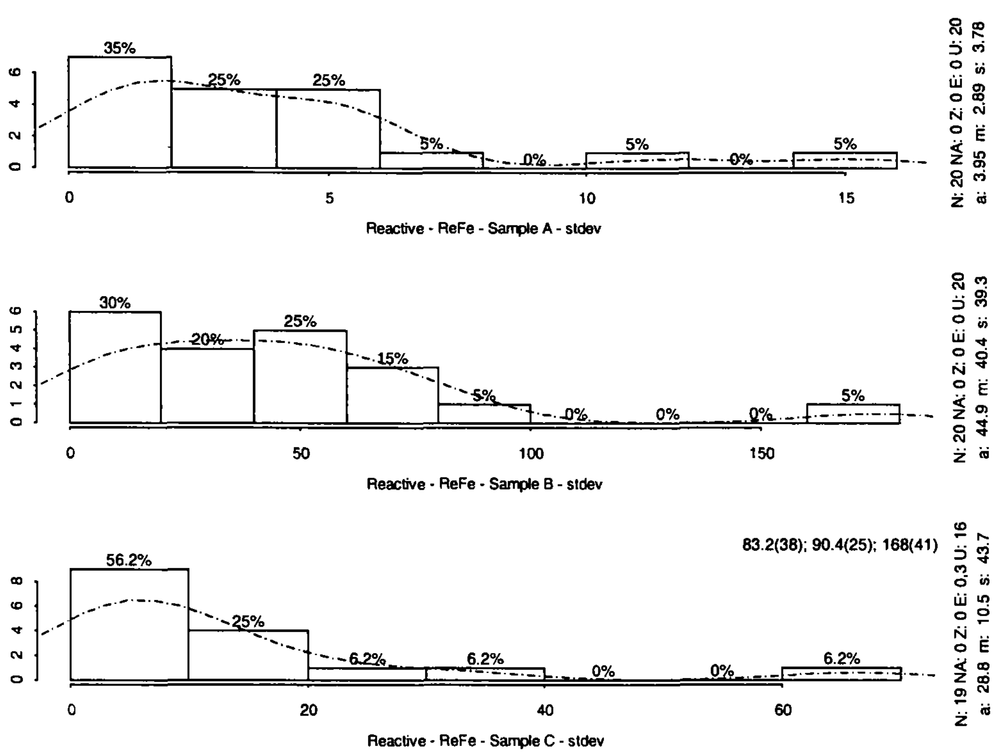


Figure IV.404: Histogram stdev – Reactive Fe

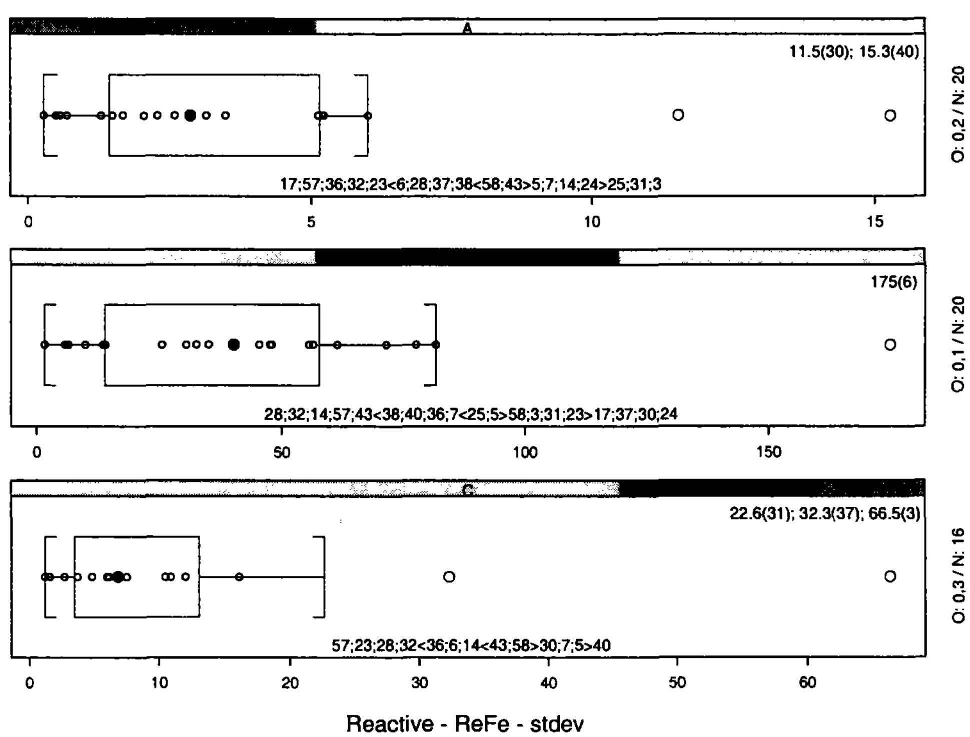


Figure IV.405: Boxplot stdev – Reactive Fe

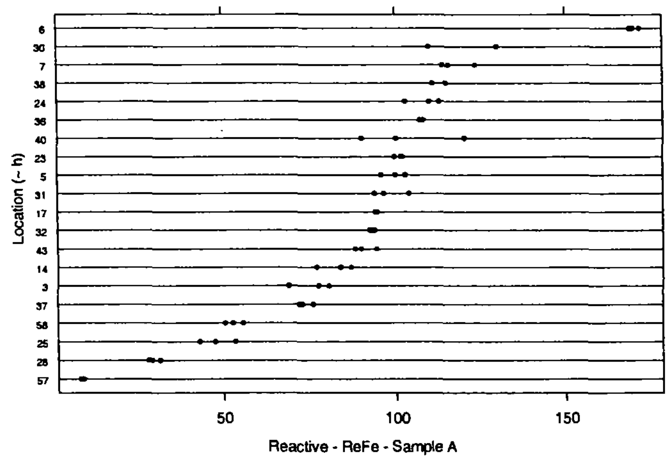


Figure IV.406: Dotplot - Sample A – Reactive Fe

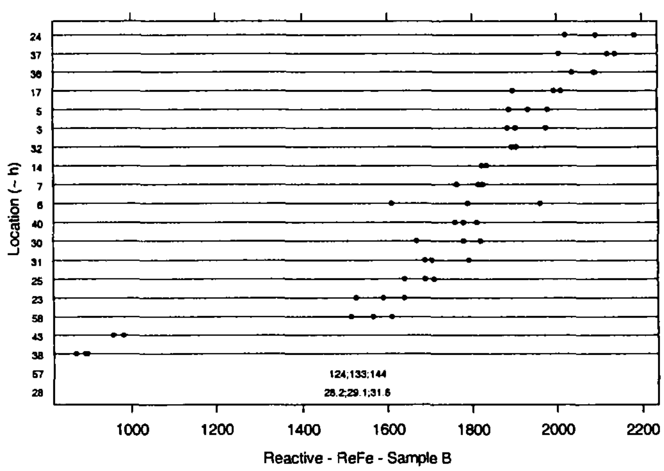


Figure IV.407: Dotplot - Sample B – Reactive Fe

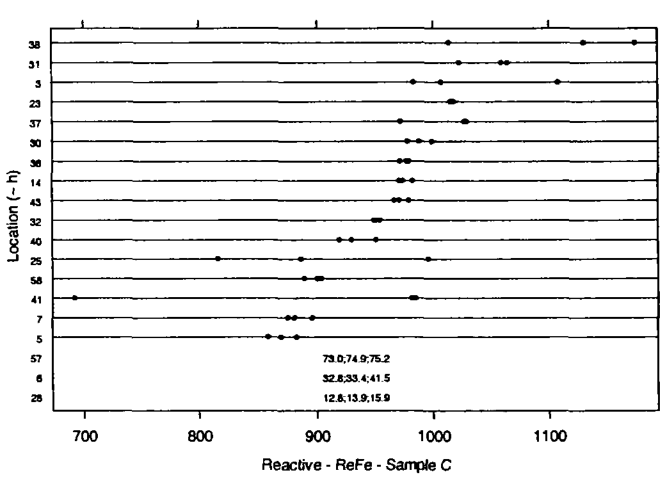


Figure IV.408: Dotplot - Sample C mean – Reactive Fe

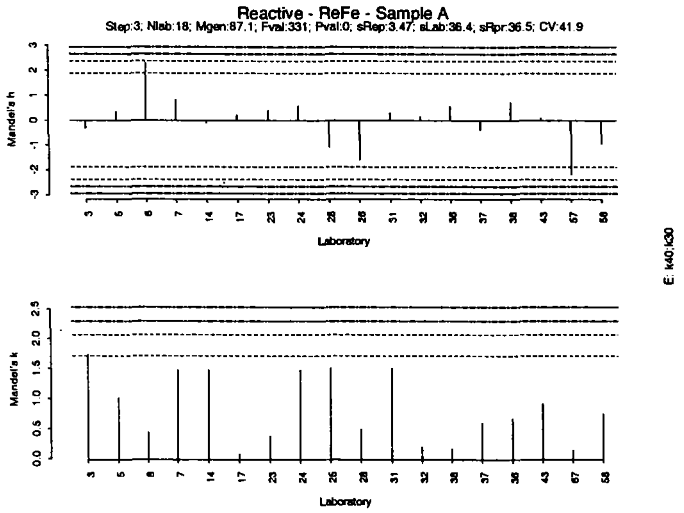


Figure IV.409: Mandel h/k plot - Sample A – Reactive Fe

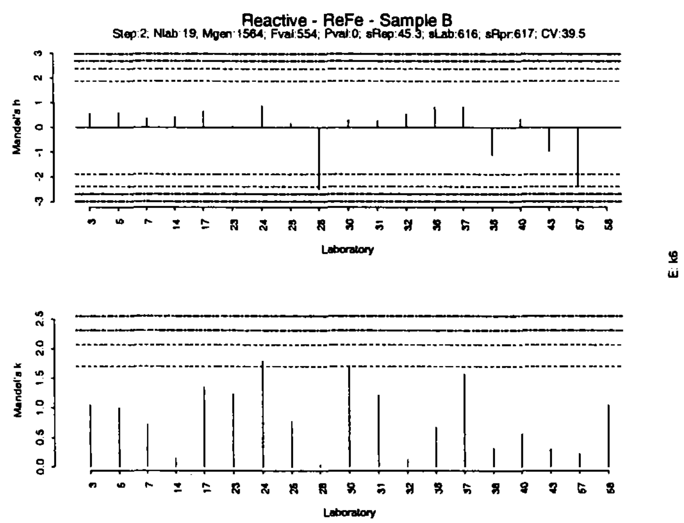


Figure IV.410: Mandel h/k plot - Sample B – Reactive Fe

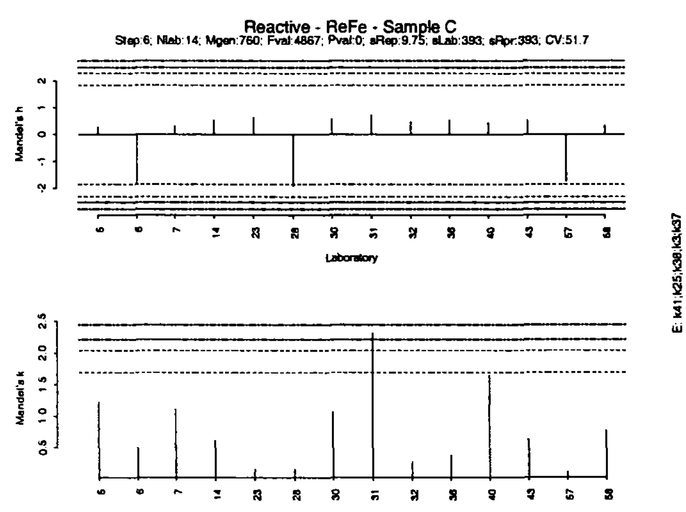


Figure IV.411: Mandel h/k plot - Sample C – Reactive Fe

Annex 5: Details on statistical procedures

Gnr	Element	Sample	Gnam	Labx	Labz	Step	Ntot	Nlab	Neff	Mgen	Min	Max	Fval	Pval	sRep	sLab	sRpr	CVr	CV	Plab
1	Carbonates	A	Carbonates			1	54	18	3.00	0.80	0.0	5.0	189.7	0.0E+00	0.2	1.5	1.5	24.2	193.2	99.2
1	Carbonates	A	Carbonates	hK7;hK35;hK25;hK28	k7;k35;h25;h28	4	42	14	3.00	0.07	0.0	1.0			0.0	0.3	0.3	0.0	374.2	100.0
1	Carbonates	B	Carbonates			1	111	37	3.00	440.14	5.0	598.3	616.9	0.0E+00	11.6	166.4	166.8	2.6	37.9	99.8
1	Carbonates	B	Carbonates	k35;k3	k35;k3	3	105	35	3.00	446.90	5.0	598.3	1371.5	0.0E+00	7.9	168.3	168.5	1.8	37.7	99.9
2	EcAcidity	A	Exchangeable			1	107	36	2.97	1.52	0.0	9.1	180.6	0.0E+00	0.2	1.5	1.5	12.6	99.1	99.2
2	EcAcidity	A	Exchangeable	hk16;k48	hk16;k48	3	101	34	2.97	1.27	0.0	3.7	357.0	0.0E+00	0.1	0.7	0.7	5.2	57.2	99.6
2	EcAcidity	B	Exchangeable			1	82	28	2.93	1.56	0.0	34.3	25593.6	0.0E+00	0.1	6.5	6.5	4.5	420.3	100.0
2	EcAcidity	B	Exchangeable	hk11;hk48	hk11;k48	2	76	26	2.92	0.18	0.0	0.8	226.9	0.0E+00	0.0	0.3	0.3	16.2	143.3	99.4
2	EcAcidity	C	Exchangeable			1	110	37	2.97	11.06	1.6	92.8	825.3	0.0E+00	0.9	14.4	14.4	7.8	130.3	99.8
2	EcAcidity	C	Exchangeable	hk16;h44;k17;k41	k16;h44;k17;k41	3	99	33	3.00	8.08	1.6	17.2	928.4	0.0E+00	0.2	3.3	3.3	2.3	40.7	99.8
2	EcAl	A	Exchangeable			1	110	37	2.97	0.46	0.0	1.6	217.0	0.0E+00	0.0	0.3	0.3	7.4	63.2	99.3
2	EcAl	A	Exchangeable	h19	h19	2	107	36	2.97	0.43	0.0	0.9	128.4	0.0E+00	0.0	0.2	0.2	7.5	49.6	98.9
2	EcAl	B	Exchangeable			1	92	31	2.97	0.08	0.0	0.8	251.6	0.0E+00	0.0	0.2	0.2	22.5	208.4	99.4
2	EcAl	B	Exchangeable	hk19;hk36;k6;hk13;hk7;hk37;hk23;hk24;h25;k57;k48;hk59	hk19;k36;k6;h13;k7;hk37;k23;k24;h25;k57;k48;hk59	7	56	19	2.95	0.01	0.0	0.0	19175.4	0.0E+00	0.0	0.0	0.0	2.1	168.5	100.0
2	EcAl	C	Exchangeable			1	113	38	2.97	1.76	0.1	6.5	1028.0	0.0E+00	0.1	1.1	1.1	3.3	62.0	99.9
2	EcAl	C	Exchangeable	hk19;k57;k7;k36	hk19;k57;k7;k36	3	101	34	2.97	1.58	0.1	2.9	1444.3	0.0E+00	0.0	0.8	0.8	2.2	48.7	99.9
2	EcCa	A	Exchangeable			1	118	40	2.95	0.51	0.0	12.0	103.7	0.0E+00	0.3	1.9	1.9	62.8	375.7	98.6
2	EcCa	A	Exchangeable	hk50;h4k;hk34;h16;k19;k13	hk50;h4;k34;h16;k19;k13	5	100	34	2.94	0.12	0.0	0.4	59.1	0.0E+00	0.0	0.1	0.1	18.3	83.5	97.6
2	EcCa	B	Exchangeable			1	116	39	2.97	49.46	1.3	784.1	59777.3	0.0E+00	0.9	121.6	121.6	1.7	245.8	100.0
2	EcCa	B	Exchangeable	k24;hk50;k7;k3	k24;hk50;k7;k3	4	104	35	2.97	29.36	1.3	39.9	1088.4	0.0E+00	0.5	8.8	8.8	1.6	30.1	99.9
2	EcCa	C	Exchangeable			1	128	43	2.98	11.62	0.3	133.8	83.8	0.0E+00	4.4	23.5	23.9	38.3	205.5	98.2
2	EcCa	C	Exchangeable	hk20;hk50;k16h;k41;k6;k24	hk20;h50;k16;k41;k6;k24	4	110	37	2.97	6.28	0.3	9.4	447.3	0.0E+00	0.1	1.8	1.8	2.4	29.4	99.7
2	EcFe	A	Exchangeable			1	125	42	2.98	0.13	0.0	3.9	800.7	0.0E+00	0.0	0.6	0.6	28.4	466.9	99.8
2	EcFe	A	Exchangeable	hk50;k48	hk50;k48	3	119	40	2.97	0.04	0.0	0.1	76.8	0.0E+00	0.0	0.0	0.0	12.0	61.7	98.1
2	EcFe	B	Exchangeable			1	114	38	3.00	0.05	0.0	1.6	12525.3	0.0E+00	0.0	0.3	0.3	8.8	565.7	100.0
2	EcFe	B	Exchangeable	k5;hk48;h50;h4;k43	k5;k48;h50;h4;k43	3	99	33	3.00	0.00	0.0	0.0	5127.3	0.0E+00	0.0	0.0	0.0	5.1	209.9	100.0
2	EcFe	C	Exchangeable			1	128	43	2.98	0.88	0.0	24.3	24475.6	0.0E+00	0.0	3.7	3.7	4.6	419.1	100.0
2	EcFe	C	Exchangeable	hk50;k5;k7;k14	hk50;k5;k7;k14	4	116	39	2.97	0.30	0.0	0.6	740.7	0.0E+00	0.0	0.1	0.1	3.0	47.9	99.8
2	EcK	A	Exchangeable			1	119	40	2.97	3.48	0.0	132.9	169.5	0.0E+00	2.8	21.0	21.2	80.3	609.9	99.1
2	EcK	A	Exchangeable	hk50;hk10;hk43;hk20;hk42;k14h;k36;h4;k48;h17	hk50;h10;k43;hk20;h42;k14;k36;h4;k48;h17	7	89	30	2.97	0.02	0.0	0.1	37.9	0.0E+00	0.0	0.0	0.0	15.1	55.3	96.2
2	EcK	B	Exchangeable			1	119	40	2.97	2.04	0.0	56.8	304.4	0.0E+00	0.9	8.9	9.0	43.2	438.8	99.5
2	EcK	B	Exchangeable	hk50;h10;k43;h42;h20;h28	hk50;h10;k43;h42;h20;h28	6	101	34	2.97	0.55	0.3	0.8	43.6	0.0E+00	0.0	0.1	0.1	4.8	18.8	96.7
2	EcK	C	Exchangeable			1	128	43	2.98	14.96	0.0	595.3	3290.3	0.0E+00	2.7	91.0	91.0	18.3	608.1	100.0
2	EcK	C	Exchangeable	hk50;k6;k20h;h42;h10;k43;h28;h38	hk50;k6;k20;h42;h10;k43;h28;h38	6	104	35	2.97	0.95	0.5	1.2	135.0	0.0E+00	0.0	0.2	0.2	2.4	16.0	98.9

Gnr	Element	Sample	Gnam	Labx	Labz	Step	Ntot	Nlab	Neff	Mgen	Min	Max	Fval	Pval	sRep	sLab	sRpr	CVi	CV	Plab
2	EcMg	A	Exchangeable			1	119	40	2.97	0.09	0.0	1.1	45.8	0.0E+00	0.0	0.2	0.2	52.3	209.4	96.8
2	EcMg	A	Exchangeable	hk13;hk50;hk16;hk48;h4;h34;h38	k13;hk50;h16;k48;h4;h34;h38	6	98	33	2.97	0.03	0.0	0.1	69.0	0.0E+00	0.0	0.0	0.0	17.8	86.8	97.9
2	EcMg	B	Exchangeable			1	119	40	2.97	2.87	0.1	68.2	257165	0.0E+00	0.0	10.6	10.6	1.3	371.1	100.0
2	EcMg	B	Exchangeable	h50	h50	2	116	39	2.97	1.18	0.1	1.7	251.2	0.0E+00	0.0	0.3	0.3	3.1	28.7	99.4
2	EcMg	C	Exchangeable			1	128	43	2.98	3.38	0.1	78.8	9294.7	0.0E+00	0.2	11.8	11.8	6.3	350.1	100.0
2	EcMg	C	Exchangeable	hk16;hk50;k20;k48;h28;k34	k16;hk50;k20;k48;h28;k34	5	110	37	2.97	1.60	0.8	2.1	445.4	0.0E+00	0.0	0.3	0.3	1.8	21.8	99.7
2	EcMn	A	Exchangeable			1	114	38	3.00	0.03	0.0	0.9	172.8	0.0E+00	0.0	0.1	0.1	67.2	513.3	99.1
2	EcMn	A	Exchangeable	HK50;HK20;HK27;HK4;HK31;HK40;HK16;HK11;HK43	hk50;hk20;k27;h4;k31;k40;h16;h11;h43	6	87	29	3.00	0.00	0.0	0.0			0.0	0.0	0.0			
2	EcMn	B	Exchangeable			1	119	40	2.97	0.06	0.0	1.3	508.5	0.0E+00	0.0	0.2	0.2	29.5	386.0	99.7
2	EcMn	B	Exchangeable	hk50;hk20;hk11	hk50;hk20;hk11	4	110	37	2.97	0.01	0.0	0.0	34.3	0.0E+00	0.0	0.0	0.0	17.8	62.3	95.8
2	EcMn	C	Exchangeable			1	126	42	3.00	0.82	0.0	24.7	2664.8	0.0E+00	0.1	3.8	3.8	15.5	461.8	99.9
2	EcMn	C	Exchangeable	hk20;hk50;k36	k20;h50;k36	3	117	39	3.00	0.16	0.0	0.3	396.9	0.0E+00	0.0	0.1	0.1	2.9	32.9	99.6
2	EcNa	A	Exchangeable			1	111	37	3.00	0.75	0.0	24.9	28.4	0.0E+00	1.3	4.0	4.2	176.4	561.7	94.9
2	EcNa	A	Exchangeable	hk50;h10;hk4;k14;k38	hk50;h10;h4;k14;k38	5	96	32	3.00	0.04	0.0	0.2	53.4	0.0E+00	0.0	0.0	0.0	27.6	118.4	97.3
2	EcNa	B	Exchangeable			1	111	37	3.00	1.42	0.0	48.0	924.6	0.0E+00	0.4	7.9	7.9	31.6	555.3	99.8
2	EcNa	B	Exchangeable	hk50;hk10;hk24;hk4;k14h	hk50;h10;k24;h4;k14	4	96	32	3.00	0.07	0.0	0.2	64.1	0.0E+00	0.0	0.0	0.0	14.9	70.0	97.7
2	EcNa	C	Exchangeable			1	122	41	2.98	2.60	0.0	91.1	275.1	0.0E+00	1.5	14.2	14.3	57.0	550.2	99.5
2	EcNa	C	Exchangeable	hk50;h10;k24;k16	hk50;h10;k24;k16	4	110	37	2.97	0.32	0.0	0.6	104.0	0.0E+00	0.0	0.1	0.1	6.8	40.5	98.6
2	FreeH	A	Exchangeable			1	95	32	2.97	1.05	0.0	7.3	505.6	0.0E+00	0.1	1.4	1.4	10.0	130.6	99.7
2	FreeH	A	Exchangeable	hk16;h59;k5;k20;k50;k32	k16;h59;k5;k20;k50;k32	5	77	26	2.96	0.65	0.0	1.6	434.2	0.0E+00	0.0	0.4	0.4	5.4	66.0	99.7
2	FreeH	B	Exchangeable			1	72	24	3.00	0.73	0.0	10.2	2818.8	0.0E+00	0.1	2.1	2.1	9.2	282.4	99.9
2	FreeH	B	Exchangeable	hk12;hk16;k37h;hk25;hk31;k6;k26;hk28;hk50;k57	k12;h16;k37;k25;hk31;k6;k26;k28;h50;k57	8	42	14	3.00	0.06	0.0	0.4	19784.4	0.0E+00	0.0	0.1	0.1	2.6	213.1	100.0
2	FreeH	C	Exchangeable			1	94	32	2.94	7.93	0.0	44.7	2663.4	0.0E+00	0.3	8.9	9.0	3.7	112.9	99.9
2	FreeH	C	Exchangeable	hk16;h59k;k17;k41	k16;h59;k17;k41	3	82	28	2.93	5.84	0.0	13.6	1990.8	0.0E+00	0.1	3.4	3.4	2.2	57.9	99.9
3	ExAl	A	Aqua Regia			1	100	34	2.94	392.44	104.8	1264.9	144.5	0.0E+00	32.4	226.4	228.7	8.3	58.3	99.0
3	ExAl	A	Aqua Regia	hk58;k8;k40	hk58;k8;k40	4	91	31	2.93	361.50	104.8	822.7	303.2	0.0E+00	16.9	171.2	172.0	4.7	47.6	99.5
3	ExAl	B	Aqua Regia			1	103	35	2.94	5317.08	682.3	7480.4	177.9	0.0E+00	172.6	1337.8	1348.9	3.2	25.4	99.2
3	ExAl	B	Aqua Regia	k40;h57	k40;h57	2	97	33	2.94	5491.49	2391.6	7480.4	192.9	0.0E+00	133.3	1076.9	1085.2	2.4	19.8	99.2
3	ExAl	C	Aqua Regia			1	104	36	2.89	1213.93	248.7	1999.4	67.9	0.0E+00	66.6	320.8	327.6	5.5	27.0	97.9
3	ExAl	C	Aqua Regia	k59;k27;k58;13k	k59;k27;k58;k13	4	92	32	2.87	1192.55	248.7	1696.0	349.7	0.0E+00	27.9	307.8	309.0	2.3	25.9	99.6
3	ExCa	A	Aqua Regia			1	106	36	2.94	120.40	0.0	725.4	114.4	0.0E+00	27.3	169.7	171.9	22.7	142.8	98.7
3	ExCa	A	Aqua Regia	k52h;h57;h19;k40	k52;h57;h19;k40	3	94	32	2.94	77.07	0.0	376.7	356.3	0.0E+00	8.9	98.2	98.6	11.6	128.0	99.6
3	ExCa	B	Aqua Regia			1	110	37	2.97	219763	50332	350767	93.1	0.0E+00	7812	43474	44171	3.6	20.1	98.4
3	ExCa	B	Aqua Regia	hk8;h23;k52;k4	k8;h23;k52;k4	4	98	33	2.97	220989	164445	273822	145.6	0.0E+00	3768	26287	26555	1.7	12.0	99.0
3	ExCa	C	Aqua Regia			1	119	41	2.90	1792.24	235.9	4480.7	5.8	1.8E-09	627.8	808.5	1023.7	35.0	57.1	79.0
3	ExCa	C	Aqua Regia	k24;k9;k40	k24;k9;k40	4	110	38	2.89	1712.10	235.9	4254.1	294.8	0.0E+00	79.6	802.3	806.2	4.7	47.1	99.5
3	ExCd	A	Aqua Regia			1	101	34	2.97	0.07	0.0	0.6	2.0	9.6E-01	0.2	0.1	0.2	286.5	329.9	49.6
3	ExCd	A	Aqua Regia	hK6;hK25;K8;K9;hK50;K53;K31;hK60;K40;hK59;K35;K43	k6;hk25;k8;k9;h50;k53;k31;h60;k40;h59;k35;k43	7	66	22	3.00	0.01	0.0	0.0			0.0	0.0	0.0	0.0	260.0	100.0
3	ExCd	B	Aqua Regia			1	119	40	2.97	1.35	0.0	6.8	518.3	0.0E+00	0.1	1.2	1.2	6.6	87.9	99.7
3	ExCd	B	Aqua Regia	k4;h50;h53k;k59;h25;k33;k18	k4;h50;h53;k59;h25;k33;k18	5	98	33	2.97	1.03	0.0	2.4	249.0	0.0E+00	0.1	0.5	0.5	5.1	46.9	99.4
3	ExCd	C	Aqua Regia			1	115	39	2.95	1.05	0.0	2.3	88.0	0.0E+00	0.1	0.4	0.4	7.6	42.2	98.3
3	ExCd	C	Aqua Regia	k18	k18	2	112	38	2.95	1.05	0.0	2.3	112.3	0.0E+00	0.1	0.4	0.4	6.8	42.5	98.7

Grt	Element	Sample	Gnam	Labx	Labz	Step	Ntot	Nlab	Neff	Mgen	Min	Max	Fval	Pval	sRep	sLab	sRpr	CVi	CV	Plab
3	ExCr	A	Aqua Regia			1	101	34	2.97	2.97	0.0	13.6	55.6	0.0E+00	0.6	2.7	2.8	21.1	92.9	97.4
3	ExCr	A	Aqua Regia	hk5;k28;k8;h50	h5;k28;k8;h50	3	89	30	2.97	2.31	0.0	5.0	80.0	0.0E+00	0.2	1.2	1.3	10.3	54.2	98.2
3	ExCr	B	Aqua Regia			1	115	39	2.95	33.28	7.3	103.1	221.6	0.0E+00	1.8	15.9	16.0	5.5	48.2	99.3
3	ExCr	B	Aqua Regia	k9;h50;h24	k9;h50;h24	3	106	36	2.94	29.85	7.3	43.8	74.9	0.0E+00	1.4	6.8	8.9	4.8	23.4	98.1
3	ExCr	C	Aqua Regia			1	117	40	2.92	49.74	8.7	70.8	61.0	0.0E+00	2.7	12.4	12.7	5.5	25.8	97.6
3	ExCr	C	Aqua Regia	k57	k57	2	114	39	2.92	49.18	8.7	67.2	120.8	0.0E+00	1.9	12.2	12.3	3.9	25.0	98.8
3	ExCu	A	Aqua Regia			1	116	39	2.97	1.33	0.0	4.3	39.7	0.0E+00	0.3	1.1	1.1	22.5	84.3	96.4
3	ExCu	A	Aqua Regia	k59;k40	k59;k40	3	110	37	2.97	1.27	0.0	4.3	115.6	0.0E+00	0.2	1.1	1.1	13.7	85.9	98.7
3	ExCu	B	Aqua Regia			1	125	42	2.98	28.72	0.0	42.6	87.0	0.0E+00	1.3	7.2	7.3	4.7	25.6	98.3
3	ExCu	B	Aqua Regia	k24;h58;k33h;k52;k15	k24;h58;k33;k52;k15	5	110	37	2.97	29.73	17.1	40.9	99.2	0.0E+00	0.8	4.6	4.6	2.7	15.6	98.5
3	ExCu	C	Aqua Regia			1	129	44	2.93	22.16	0.0	32.2	257.4	0.0E+00	0.7	6.7	6.7	3.2	30.3	99.4
3	ExCu	C	Aqua Regia	k40	k40	2	126	43	2.93	22.03	0.0	32.2	320.8	0.0E+00	0.6	6.7	6.7	2.9	30.8	99.5
3	ExFe	A	Aqua Regia			1	118	40	2.95	243.77	0.3	548.9	6.9	2.4E-11	70.2	99.6	121.9	28.8	50.0	81.8
3	ExFe	A	Aqua Regia	k59;k27;k40	k59;k27;k40	4	109	37	2.95	231.01	0.3	429.0	284.4	0.0E+00	9.8	96.6	97.1	4.3	42.0	99.5
3	ExFe	B	Aqua Regia			1	121	41	2.95	12493	7099	17039	26.0	0.0E+00	575.2	1875.1	1771.1	4.8	14.2	94.6
3	ExFe	B	Aqua Regia	k59	k59	2	118	40	2.95	12378	7099	14921	45.5	0.0E+00	398.0	1545.2	1595.7	3.2	12.9	96.8
3	ExFe	C	Aqua Regia			1	122	42	2.90	3534	1159	5742	141.8	0.0E+00	117.7	819.5	828.0	3.3	23.4	99.0
3	ExFe	C	Aqua Regia	k48;k58;k59	k48;k58;k59	4	113	39	2.90	3459	1159	4640	333.2	0.0E+00	69.7	746.8	750.1	2.0	21.7	99.8
3	ExHg	A	Aqua Regia			1	30	10	3.00	1.02	0.0	10.2	11.9	2.9E-04	1.6	3.1	3.5	158.0	340.8	88.6
3	ExHg	A	Aqua Regia	HK80;HK31;HK40;HK43	hk60;k31;k40;h43	4	18	6	3.00	0.00	0.0	0.0			0.0	0.0	0.0			
3	ExHg	B	Aqua Regia			1	39	13	3.00	4.93	0.0	63.1	4259.9	0.0E+00	0.5	17.5	17.5	9.4	354.6	100.0
3	ExHg	B	Aqua Regia	hk60;k9;k57;k40	hk60;k9;k57;k40	4	27	9	3.00	0.07	0.0	0.1	18844.5	0.0E+00	0.0	0.1	0.1	1.0	76.0	100.0
3	ExHg	C	Aqua Regia			1	38	13	2.92	10.82	0.0	132.9	3073.0	0.0E+00	1.1	37.2	37.2	10.6	344.1	100.0
3	ExHg	C	Aqua Regia	hk60;k57	hk60;k57	3	32	11	2.91	0.34	0.0	0.5	56.9	6.3E-11	0.0	0.1	0.1	9.3	41.8	97.5
3	ExK	A	Aqua Regia			1	110	37	2.97	88.94	0.0	614.0	92.3	0.0E+00	18.5	102.5	104.1	20.8	117.1	98.4
3	ExK	A	Aqua Regia	hk58;k27;k13;k59;k40	hk58;k27;k13;k59;k40	5	95	32	2.97	69.89	0.0	200.3	373.4	0.0E+00	4.7	52.3	52.8	6.7	75.2	99.6
3	ExK	B	Aqua Regia			1	116	39	2.97	2485.2	0.2	7195.6	110.5	0.0E+00	158.8	982.5	975.5	6.4	39.3	98.7
3	ExK	B	Aqua Regia	hk58;k40;h50;k52;k8;k33	hk58;k40;h50;k52;k8;k33	5	98	33	2.97	2407.7	1232.8	3378.6	326.0	0.0E+00	41.5	433.9	435.9	1.7	18.1	99.5
3	ExK	C	Aqua Regia			1	120	41	2.93	485.0	0.0	1183.7	160.6	0.0E+00	30.0	221.9	223.9	6.2	46.2	99.1
3	ExK	C	Aqua Regia	k19h;k6	k19;k6	3	114	39	2.92	465.0	0.0	912.0	272.8	0.0E+00	20.3	195.9	197.0	4.4	42.4	99.5
3	ExMg	A	Aqua Regia			1	110	37	2.97	35.1	0.0	153.2	103.2	0.0E+00	6.7	39.2	39.8	19.1	113.5	98.8
3	ExMg	A	Aqua Regia	hk52;hk59;hk27;k48;k58;h14;k40	k52;k59;k27;k48;k58;h14;k40	4	89	30	2.97	19.9	0.0	70.3	450.0	0.0E+00	1.3	18.5	16.5	6.7	83.0	99.7
3	ExMg	B	Aqua Regia			1	113	38	2.97	2150.7	1629.7	3308.0	140.4	0.0E+00	40.6	277.7	280.6	1.9	13.0	98.9
3	ExMg	B	Aqua Regia	h28	h28	2	110	37	2.97	2119.1	1629.7	2500.8	75.8	0.0E+00	40.3	201.8	205.8	1.9	9.7	98.1
3	ExMg	C	Aqua Regia			1	119	41	2.90	309.4	103.6	500.0	99.7	0.0E+00	13.0	75.6	78.7	4.2	24.8	98.6
3	ExMg	C	Aqua Regia	k52;k24;k58	k52;k24;k58	3	110	38	2.89	303.4	103.6	500.0	249.5	0.0E+00	8.0	74.2	74.7	2.6	24.8	99.4
3	ExMn	A	Aqua Regia			1	116	39	2.97	6.4	0.0	87.4	274.5	0.0E+00	1.1	10.4	10.5	17.0	183.7	99.5
3	ExMn	A	Aqua Regia	hk58;k28;k59;k40;k57;k27	hk58;k28;k59;k40;k57;k27	5	98	33	2.97	4.4	0.0	10.3	258.5	0.0E+00	0.3	2.7	2.7	6.5	61.1	99.4
3	ExMn	B	Aqua Regia			1	124	42	2.95	256.5	126.7	328.3	19.6	0.0E+00	14.9	37.4	40.2	5.8	15.7	92.9
3	ExMn	B	Aqua Regia	k43;k52	k43;k52	3	118	40	2.95	254.9	126.7	328.3	90.0	0.0E+00	7.0	38.4	39.0	2.7	15.3	98.4
3	ExMn	C	Aqua Regia			1	126	43	2.93	71.5	0.0	141.3	338.0	0.0E+00	1.9	20.4	20.5	2.7	28.8	99.6
3	ExMn	C	Aqua Regia	hk19;k52;h58;h20;h10	h19;k52;h58;h20;h10	4	111	38	2.92	74.0	50.8	91.1	109.6	0.0E+00	1.5	9.4	9.5	2.1	12.8	98.7
3	ExNa	A	Aqua Regia			1	86	29	2.97	28.8	0.0	101.7	151.1	0.0E+00	3.6	25.9	28.2	13.6	97.7	99.0
3	ExNa	A	Aqua Regia	k13;k25;k32	k13;k25;k32	4	77	28	2.96	25.5	0.0	101.7	578.0	0.0E+00	1.9	26.5	26.8	7.5	104.4	99.7
3	ExNa	B	Aqua Regia			1	92	31	2.97	673.9	0.7	2307.6	40.4	0.0E+00	107.0	390.0	404.4	15.9	80.0	96.4
3	ExNa	B	Aqua Regia	k24h;hk58	k24;h58	2	86	29	2.97	592.6	0.7	890.6	382.7	0.0E+00	18.9	214.9	215.7	3.2	36.4	99.6
3	ExNa	C	Aqua Regia			1	96	33	2.91	101.7	0.0	271.1	129.6	0.0E+00	9.0	59.8	80.5	8.8	59.5	98.9
3	ExNa	C	Aqua Regia	k10	k10	2	93	32	2.91	98.9	0.0	271.1	148.2	0.0E+00	7.7	54.1	54.7	7.9	56.5	99.0

Gnr	Element	Sample	Gnam	Labx	Labz	Step	Ntot	Nlab	Neff	Mgen	Min	Max	Fval	Pval	sRep	sLab	sRpr	CVi	CV	Plab
3	ExNi	A	Aqua Regia			1	96	32	3.00	1.56	0.0	9.7	16.2	0.0E+00	1.0	2.3	2.5	64.0	157.6	91.4
3	ExNi	A	Aqua Regia	hk5;hk60;hk24;hk57;k9;hk40;h50;k28	h5;k60;k24;h57;k9;k40;h50;k28	5	72	24	3.00	0.54	0.0	1.4	200.1	0.0E+00	0.1	0.5	0.5	10.8	89.0	99.3
3	ExNi	B	Aqua Regia			1	106	36	2.94	13.58	7.5	35.7	310.7	0.0E+00	0.6	6.4	6.4	4.6	47.3	99.5
3	ExNi	B	Aqua Regia	hk23;h24;k33;h50	k23;h24;k33;h50	3	94	32	2.94	11.78	7.5	20.9	94.1	0.0E+00	0.5	2.8	2.8	4.2	24.1	98.5
3	ExNi	C	Aqua Regia			1	111	38	2.92	34.72	10.1	53.3	99.3	0.0E+00	1.3	7.6	7.7	3.8	22.2	98.5
3	ExNi	C	Aqua Regia	k8;k28;k60;51h	k8;k28;k60;h51	4	100	34	2.94	35.13	21.7	48.3	169.2	0.0E+00	0.8	6.1	6.2	2.3	17.6	99.1
3	ExP	A	Aqua Regia			1	97	33	2.94	26.32	0.0	146.6	225.7	0.0E+00	3.5	31.0	31.2	13.5	118.6	99.4
3	ExP	A	Aqua Regia	hk10;k27;k48;hk57;k44;k53;k58;k13	h10;k27;k48;hk57;k44;k53;k58;k13	6	74	25	2.96	17.57	0.0	50.0	1010.1	0.0E+00	0.8	14.5	14.5	4.5	82.6	99.9
3	ExP	B	Aqua Regia			1	107	36	2.97	9101.97	6263.3	13031.8	72.2	0.0E+00	258.6	1265.5	1291.7	2.8	14.2	98.0
3	ExP	B	Aqua Regia	k20	k20	2	104	35	2.97	9146.74	6263.3	13031.8	88.1	0.0E+00	232.2	1257.2	1278.4	2.5	14.0	98.3
3	ExP	C	Aqua Regia			1	112	38	2.95	601.42	275.0	1067.0	75.6	0.0E+00	29.7	149.5	152.5	4.9	25.4	98.1
3	ExP	C	Aqua Regia	hk19;k53;k8;h52;k48	k19;k53;k8;h52;k48	4	97	33	2.94	575.59	275.0	882.7	279.7	0.0E+00	10.7	104.1	104.7	1.9	18.2	99.5
3	ExPb	A	Aqua Regia			1	118	40	2.95	7.06	0.0	14.0	13.7	0.0E+00	1.2	2.4	2.7	16.4	37.8	90.1
3	ExPb	A	Aqua Regia	hk24;hk59;k6;k52;k3;20k;h58	k24;k59;k6;k52;k3;k20;h58	6	98	33	2.97	6.85	3.5	10.7	45.0	0.0E+00	0.4	1.5	1.5	5.6	22.3	96.8
3	ExPb	B	Aqua Regia			1	124	42	2.95	63.46	0.0	556.3	500.6	0.0E+00	6.3	81.8	82.1	9.9	129.3	99.7
3	ExPb	B	Aqua Regia	hk9;k48	hk9;k48	3	118	40	2.95	51.74	0.0	121.5	170.2	0.0E+00	3.1	23.5	23.7	6.0	45.7	99.1
3	ExPb	C	Aqua Regia			1	126	43	2.93	128.79	0.0	189.3	170.8	0.0E+00	4.8	36.2	36.5	3.7	28.3	99.1
3	ExPb	C	Aqua Regia	k8;k57;h58;k52	k8;k57;h58;k52	3	114	39	2.92	130.00	45.1	189.3	315.7	0.0E+00	2.9	30.0	30.1	2.2	23.2	99.5
3	ExS	A	Aqua Regia			1	73	25	2.92	90.25	0.0	650.0	268.0	0.0E+00	16.5	158.3	159.1	18.3	176.3	99.5
3	ExS	A	Aqua Regia	hk47;k7;h50;hk57	hk47;k7;h50;k57	3	61	21	2.90	34.97	0.0	94.3	495.9	0.0E+00	1.8	23.2	23.3	5.1	66.6	99.7
3	ExS	B	Aqua Regia			1	74	25	2.96	1401.24	1.0	4031.3	503.3	0.0E+00	65.3	850.4	852.9	4.7	60.9	99.7
3	ExS	B	Aqua Regia	k33;k47;k48h	k33;k47;k48	3	65	22	2.95	1295.20	1.0	3036.7	3296.2	0.0E+00	20.7	692.0	692.3	1.6	53.4	100.0
3	ExS	C	Aqua Regia			1	81	28	2.89	2232.38	2.3	6676.7	757.0	0.0E+00	65.8	1064.4	1066.4	2.9	47.8	99.8
3	ExS	C	Aqua Regia	h33;k42;h28;h47;h23	h33;k42;h28;h47;h23	5	66	23	2.87	2149.65	1892.8	2508.0	25.4	0.0E+00	51.4	149.8	158.4	2.4	7.4	94.6
3	ExZn	A	Aqua Regia			1	122	41	2.98	5.08	0.0	115.6	564.8	0.0E+00	1.3	17.9	18.0	25.6	353.7	99.7
3	ExZn	A	Aqua Regia	k15;h50;hk40;k6;k20;k7;hk57;k18	k15;h50;k40;k6;k20;k7;k57;k18	6	98	33	2.97	1.66	0.0	6.4	148.2	0.0E+00	0.2	1.6	1.6	13.8	98.0	99.0
3	ExZn	B	Aqua Regia			1	130	44	2.95	94.37	37.6	167.1	48.3	0.0E+00	5.2	20.9	21.6	5.5	22.8	97.0
3	ExZn	B	Aqua Regia	h17;hk57;k15;k52h;h20	h17;k57;k15;k52;h20	5	115	39	2.95	93.36	65.8	118.7	67.6	0.0E+00	2.5	11.8	12.0	2.7	12.9	97.9
3	ExZn	C	Aqua Regia			1	132	45	2.93	105.88	22.0	225.6	154.3	0.0E+00	4.2	30.6	30.9	4.0	29.2	99.1
3	ExZn	C	Aqua Regia	k57;hk58;k8;k15;k28	k57;hk58;k8;k15;k28	5	117	40	2.92	102.28	22.0	178.4	435.4	0.0E+00	2.0	24.8	24.9	2.0	24.3	99.7
4	OrgCarb	A	Organic Carbon			1	115	39	2.95	10.00	3.8	14.2	18.9	0.0E+00	0.7	1.8	2.0	7.4	19.7	92.7
4	OrgCarb	A	Organic Carbon	k34h;k52;h20;k25h;h6	k34;k52;h20;k25;h6	4	100	34	2.94	10.04	7.0	12.3	17.7	0.0E+00	0.4	1.0	1.1	4.3	11.1	92.2
4	OrgCarb	B	Organic Carbon			1	115	39	2.95	75.72	38.0	136.7	608.1	0.0E+00	1.7	25.0	25.1	2.3	33.1	99.8
4	OrgCarb	C	Organic Carbon			1	120	41	2.93	472.20	51.0	593.0	325.8	0.0E+00	6.8	72.0	72.3	1.4	15.3	99.6
4	OrgCarb	C	Organic Carbon	k25;h44	k25;h44	2	115	39	2.95	480.40	347.3	593.0	188.8	0.0E+00	5.8	46.4	46.7	1.2	9.7	99.2
5	Pclay	A	Particle Size			1	84	28	3.00	8.87	0.0	83.8	885.8	0.0E+00	1.2	20.4	20.5	13.4	230.9	99.8
5	Pclay	A	Particle Size	h10;hk58;k24;hk57	h10;k58;k24;hk57	3	72	24	3.00	2.44	0.0	8.3	236.4	0.0E+00	0.2	2.0	2.0	9.3	83.1	99.4
5	Pclay	B	Particle Size			1	78	26	3.00	24.52	1.2	58.5	499.2	0.0E+00	1.1	13.9	14.0	4.4	57.0	99.7
5	Pclay	B	Particle Size	k58	k58	2	75	25	3.00	23.55	1.2	58.5	1125.0	0.0E+00	0.7	13.3	13.3	2.9	56.6	99.9

Gnr	Element	Sample	Gnam	Labx	Labz	Step	Ntot	Nlab	Neff	Mgen	Min	Max	Fval	Pval	sRep	sLab	sRpr	CVi	CV	Plab
5	Psand	A	Particle Size			1	84	28	3.00	77.50	2.2	99.8	4698.9	0.0E+00	0.8	30.2	30.2	1.0	39.0	100.0
5	Psand	A	Particle Size	k24;k28	k24;k28	3	78	26	3.00	76.67	2.2	99.8	8878.4	0.0E+00	0.6	31.3	31.3	0.7	40.8	100.0
5	Psand	B	Particle Size			1	78	26	3.00	41.73	4.5	97.4	796.4	0.0E+00	1.2	19.3	19.3	2.8	46.2	99.8
5	Psand	B	Particle Size	k50	k50	2	75	25	3.00	41.36	4.5	97.4	1157.6	0.0E+00	1.0	19.6	19.6	2.4	47.4	99.9
5	Psilt	A	Particle Size			1	84	28	3.00	13.55	0.1	89.0	587.0	0.0E+00	1.3	18.9	18.9	10.0	139.4	99.7
5	Psilt	A	Particle Size	h21;k24;hk58;hk57	h21;k24;k58;hk57	3	72	24	3.00	7.83	0.1	14.5	120.8	0.0E+00	0.6	3.5	3.5	7.1	45.2	98.8
5	Psilt	B	Particle Size			1	78	26	3.00	33.31	0.2	55.8	392.3	0.0E+00	1.3	14.9	15.0	3.9	45.0	99.6
6	pHCaCl2	A	pHsoil			1	138	47	2.94	3.12	2.7	3.7	55.3	0.0E+00	0.0	0.1	0.1	1.0	4.6	97.4
6	pHCaCl2	A	pHsoil	k35;h44;k34;k14	k35;h44;k34;k14	4	127	43	2.95	3.10	2.7	3.3	83.3	0.0E+00	0.0	0.1	0.1	0.7	3.7	98.3
6	pHCaCl2	B	pHsoil			1	138	47	2.94	7.39	7.0	7.7	35.8	0.0E+00	0.0	0.1	0.1	0.5	1.9	96.0
6	pHCaCl2	B	pHsoil	k34;k57	k34;k57	2	132	45	2.93	7.39	7.0	7.7	84.0	0.0E+00	0.0	0.1	0.1	0.4	1.9	98.3
6	pHCaCl2	C	pHsoil			1	141	48	2.94	3.03	2.8	3.5	11.0	0.0E+00	0.1	0.1	0.1	1.9	3.9	87.9
6	pHCaCl2	C	pHsoil	hk35;k41;k21;k34;k19;k27;k8;k20;k13;k48	h35;k41;k21;k34;k19;k27;k8;k20;k13;k48	6	111	38	2.92	3.01	2.8	3.2	100.1	0.0E+00	0.0	0.1	0.1	0.5	2.7	98.6
6	pHH20	A	pHsoil			1	132	45	2.93	4.02	3.5	4.7	21.0	0.0E+00	0.1	0.2	0.2	1.9	5.2	93.4
6	pHH20	A	pHsoil	k13;h18;k34	k13;h18;k34	2	123	42	2.93	4.00	3.5	4.3	41.1	0.0E+00	0.0	0.2	0.2	1.1	4.4	96.5
6	pHH20	B	pHsoil			1	132	45	2.93	7.88	7.4	8.2	71.0	0.0E+00	0.0	0.2	0.2	0.5	2.6	98.0
6	pHH20	B	pHsoil	k57	k57	2	129	44	2.93	7.88	7.4	8.2	119.7	0.0E+00	0.0	0.2	0.2	0.4	2.6	98.8
6	pHH20	C	pHsoil			1	134	46	2.91	3.90	3.5	4.4	33.8	0.0E+00	0.1	0.2	0.2	1.5	5.3	95.8
6	pHH20	C	pHsoil	k13;k34	k13;k34	2	128	44	2.91	3.90	3.5	4.4	83.5	0.0E+00	0.0	0.2	0.2	1.0	5.3	98.3
7	ReAl	A	Reactive			1	63	21	3.00	148.72	5.1	837.7	783.7	0.0E+00	10.2	164.3	164.6	6.8	110.7	99.8
7	ReAl	A	Reactive	k7;h24	k7;h24	2	57	19	3.00	112.67	5.1	216.3	152.3	0.0E+00	6.7	47.6	48.0	5.9	42.6	99.0
7	ReAl	B	Reactive			1	60	20	3.00	457.49	10.2	1452.7	55.5	0.0E+00	65.5	279.0	286.6	14.3	62.6	97.4
7	ReAl	B	Reactive	hk24;k6	hk24;k6	3	54	18	3.00	400.06	10.2	556.1	1372.5	0.0E+00	7.6	163.5	163.7	1.9	40.9	99.9
7	ReAl	C	Reactive			1	57	19	3.00	510.56	24.0	706.9	194.3	0.0E+00	28.3	227.2	228.9	5.5	44.8	99.2
7	ReAl	C	Reactive	k41;k37;k3	k41;k37;k3	4	48	16	3.00	496.07	24.0	706.9	1321.9	0.0E+00	11.6	244.3	244.6	2.3	49.3	99.9
7	ReFe	A	Reactive			1	60	20	3.00	89.73	8.5	170.3	129.9	0.0E+00	5.4	35.4	35.8	6.0	39.9	98.9
7	ReFe	A	Reactive	k40;k30	k40;k30	3	54	18	3.00	87.10	8.5	170.3	330.6	0.0E+00	3.5	36.4	36.5	4.0	41.9	99.5
7	ReFe	B	Reactive			1	60	20	3.00	1575.58	29.6	2100.0	311.8	0.0E+00	59.0	600.7	603.6	3.7	38.3	99.5
7	ReFe	B	Reactive	k6	k6	2	57	19	3.00	1564.47	29.6	2100.0	554.1	0.0E+00	45.3	615.5	617.2	2.9	39.5	99.7
7	ReFe	C	Reactive			1	57	19	3.00	819.75	14.2	1106.7	140.7	0.0E+00	51.4	350.6	354.3	6.3	43.2	98.9
7	ReFe	C	Reactive	k41;k25;k38;k3;k37	k41;k25;k38;k3;k37	6	42	14	3.00	760.03	14.2	1049.2	4866.8	0.0E+00	9.7	392.6	392.7	1.3	51.7	100.0
8	TotAl	A	Total Elements			1	48	16	3.00	2791	209	3954	242.6	0.0E+00	102.1	916.2	921.9	3.7	33.0	99.4
8	TotAl	B	Total Elements			1	48	16	3.00	10721	877	14550	331.5	0.0E+00	348.0	3652.9	3669.4	3.2	34.2	99.5
8	TotAl	C	Total Elements			1	48	16	3.00	2808.91	347.3	3551.7	83.7	0.0E+00	137.7	722.6	735.6	4.9	26.2	98.2
8	TotAl	C	Total Elements	k38;h57;k47	k38;h57;k47	3	39	13	3.00	2963.72	2352.5	3551.7	89.4	0.0E+00	58.5	317.7	323.0	2.0	10.9	98.3
8	TotCa	A	Total Elements			1	48	16	3.00	293.71	80.0	1166.0	13.2	1.1E-07	132.4	266.7	297.8	45.1	101.4	89.6
8	TotCa	A	Total Elements	hk24;hk57;k48;hk52;h14;k28	k24;h57;k48;k52;h14;k28	5	30	10	3.00	148.46	80.0	252.8	20.2	3.6E-06	20.1	50.9	54.7	13.5	36.8	93.0
8	TotCa	B	Total Elements			1	51	17	3.00	216682	79095	257116	362.4	0.0E+00	4433.9	49990.6	50186.8	2.0	23.2	99.6
8	TotCa	C	Total Elements			1	51	17	3.00	1696.27	995.5	2235.3	36.4	1.1E-14	91.5	314.5	327.5	5.4	19.3	96.0
8	TotCa	C	Total Elements	k52	k52	2	48	16	3.00	1677.21	995.5	2235.3	64.3	0.0E+00	68.9	316.7	324.1	4.1	19.3	97.7
8	TotFe	A	Total Elements			1	51	17	3.00	904.65	326.7	7343.7	100.3	0.0E+00	287.5	1653.8	1678.6	31.8	185.6	98.5
8	TotFe	A	Total Elements	hk52;k24	hk52;k24	3	45	15	3.00	503.69	326.7	704.4	47.7	1.1E-14	25.9	102.3	105.6	5.1	21.0	96.9
8	TotFe	B	Total Elements			1	51	17	3.00	13664.16	10940.0	16340.0	143.5	0.0E+00	214.6	1479.1	1494.6	1.6	10.9	99.0
8	TotFe	C	Total Elements			1	51	17	3.00	6058.69	2576.0	40565.2	2159.3	0.0E+00	331.8	8900.4	8906.6	5.5	147.0	99.9
8	TotFe	C	Total Elements	hk52;h28	hk52;h28	3	45	15	3.00	3990.44	3490.7	4407.6	25.3	8.6E-11	95.3	270.9	287.2	2.4	7.2	94.3

Gnr	Element	Sample	Gnam	Labx	Labz	Step	Ntot	Nlab	Neff	Mgen	Min	Max	Fval	Pval	sRep	sLab	sRpr	CVi	CV	Plab
8	TotK	A	Total Elements			1	51	17	3.00	1826.56	1453.7	2212.0	35.7	1.1E-14	62.7	213.3	222.3	3.4	12.2	95.9
8	TotK	B	Total Elements			1	51	17	3.00	4776.87	3943.0	6243.3	75.9	0.0E+00	131.2	655.7	668.7	2.7	14.0	98.1
8	TotK	C	Total Elements			1	51	17	3.00	1240.18	940.8	3651.7	288.5	0.0E+00	64.5	631.4	634.7	5.2	51.2	99.5
8	TotK	C	Total Elements	h4;hk38	h4;k38	2	45	15	3.00	1064.41	940.8	1202.2	14.0	1.8E-07	33.3	69.3	76.9	3.1	7.2	90.1
8	TotMg	A	Total Elements			1	51	17	3.00	94.31	18.4	259.3	122.2	0.0E+00	10.0	63.3	64.1	10.6	68.0	98.8
8	TotMg	A	Total Elements	k40	k40	2	48	16	3.00	99.05	29.0	259.3	277.7	0.0E+00	6.5	62.4	62.7	6.6	63.3	99.5
8	TotMg	B	Total Elements			1	51	17	3.00	2390.75	2049.3	2688.3	31.4	1.0E-13	58.1	184.8	193.7	2.4	8.1	95.4
8	TotMg	B	Total Elements	k28	k28	2	48	16	3.00	2406.16	2049.3	2688.3	58.9	0.0E+00	41.2	180.9	185.5	1.7	7.7	97.5
8	TotMg	C	Total Elements			1	51	17	3.00	378.12	332.2	436.5	5.2	2.7E-03	22.4	26.5	34.7	5.9	9.2	76.4
8	TotMg	C	Total Elements	k28	k28	2	48	16	3.00	374.47	332.2	434.0	10.1	3.3E-06	14.3	24.9	28.7	3.8	7.7	86.7
8	TotMn	A	Total Elements			1	51	17	3.00	29.98	0.0	301.0	983.3	0.0E+00	3.9	70.0	70.1	12.9	233.9	99.8
8	TotMn	A	Total Elements	k24;h50	k24;h50	2	45	15	3.00	12.24	0.0	17.1	34.4	1.3E-12	1.3	4.5	4.7	10.9	38.2	95.8
8	TotMn	B	Total Elements			1	54	18	3.00	304.78	249.7	790.3	827.3	0.0E+00	7.3	121.9	122.1	2.4	40.1	99.8
8	TotMn	B	Total Elements	h50	h50	2	51	17	3.00	276.22	249.7	302.3	10.5	7.3E-07	7.5	13.4	15.3	2.7	5.5	87.2
8	TotMn	C	Total Elements			1	54	18	3.00	90.10	46.5	281.8	42.8	0.0E+00	13.1	48.9	50.6	14.5	56.2	96.6
8	TotMn	C	Total Elements	k17;h50	k17;h50	2	48	16	3.00	76.94	46.5	91.7	105.2	0.0E+00	1.8	10.7	10.8	2.3	14.0	98.6
8	TotNa	A	Total Elements			1	48	16	3.00	539.50	240.1	1070.3	40.7	1.1E-14	47.5	173.0	179.4	8.8	33.3	96.4
8	TotNa	A	Total Elements	hk24	hk24	2	45	15	3.00	504.12	240.1	667.7	33.8	1.6E-12	31.8	105.2	109.9	6.3	21.8	95.7
8	TotNa	B	Total Elements			1	48	16	3.00	2253.56	475.9	9163.7	208.8	0.0E+00	250.9	2088.6	2103.6	11.1	93.3	99.3
8	TotNa	B	Total Elements	k3;h4;hk7	k3;h4;k7	2	39	13	3.00	1484.91	475.9	2976.3	300.1	0.0E+00	58.3	581.8	584.7	3.9	39.4	99.5
8	TotNa	C	Total Elements			1	48	16	3.00	449.76	149.9	2612.0	1232.3	0.0E+00	28.6	578.4	579.1	6.3	128.8	99.9
8	TotNa	C	Total Elements	hk4;k28h;h57;k52	h4;k28;h57;k52	4	36	12	3.00	310.28	266.1	337.9	6.2	9.6E-03	13.4	17.7	22.2	4.3	7.1	79.6
9	TotN	A	Total Nitrogen			1	121	41	2.95	0.42	0.0	4.0	463.6	0.0E+00	0.0	0.6	0.6	11.3	142.2	99.7
9	TotN	A	Total Nitrogen	h28;hk55	h28;k55	2	115	39	2.95	0.31	0.0	0.6	43.3	0.0E+00	0.0	0.1	0.1	9.3	36.3	96.7
9	TotN	B	Total Nitrogen			1	121	41	2.95	5.38	3.7	41.6	4510.3	0.0E+00	0.1	5.9	5.9	2.8	108.9	100.0
9	TotN	B	Total Nitrogen	hk28;k55	h28;k55	2	115	39	2.95	4.45	3.7	5.2	23.4	0.0E+00	0.1	0.3	0.3	2.3	6.9	94.0
9	TotN	C	Total Nitrogen			1	124	42	2.95	21.65	15.3	175.7	22306.8	0.0E+00	0.3	24.6	24.6	1.3	113.6	100.0
9	TotN	C	Total Nitrogen	h28;k50	h28;k50	2	118	40	2.95	17.87	15.3	19.7	68.7	0.0E+00	0.2	1.1	1.1	1.3	6.3	97.9

Name variable	Comment
Gnr	Group number
Element	Element code
Sample	Sample
Gnam	Group name
Labx	Excluded laboratories + evaluation (1st run)
Labz	Excluded laboratories + stepwise reason (after check)
Step	Number of exclusion steps
Ntot	Total number of observations
Nlab	Total number of laboratories
Neff	Average number of replicates, corrected for imbalance

Name variable	Comment
Mgen	Average value for measurements
Min	Minimum value
Max	Maximum value
Fval	F-test for laboratory-effect
Pval	p-value for the F-test
sRep	within laboratory standard deviation
sLab	between laboratory standard deviation
sRpr	reproducibility standard deviation where $sRepr^2 = sRep^2 + sLab^2$
Cvi	coefficient of variation of homogeneous set, of the within laboratory standard deviation Cvi = sRep/Mgen*100
CV	coefficient of variation of homogeneous set, of the reproducibility standard deviation CV = sRepr/Mgen*100
Plab	percentage of the between laboratory variance in the total variance Plab = sqrt(sLab²/sRepr²)*100

Annex 6: ISO precision limits on repeatability

The limits below are meant as best practise guidelines. Individual laboratories are urged strongly to accumulate such data as part of a continuous quality control exercise. The ring test did not evaluated the laboratories based on the criteria below.

Precision requirements set by ISO are, for air-dried soil:

Dry matter content	Water content	Acceptable variation
% (m/m)	% (m/m)	
<= 96	<= 4.0	0.2 % (m/m) absolute value
> 96	> 4.0	0.5 % of the mean measure value

Particle size

Size fraction	Acceptable variation
mm	as % of measured value
2.000 to 0.600	< 1
0.600 to 0.212	< 2.5
0.212 to 0.063	< 3
0.063 to 0.002	< 2
< 0.002	< 2

pH

pH - range	Acceptable variation
pH <= 7.00	0.15
7.00 < pH < 7.50	0.20
7.50 <= pH <= 8.00	0.30
pH > 8.00	0.40

Carbonates

Carbonate content g/kg	Acceptable variation
0 to 50	3 g/kg
> 50 to 150	6 % of the value
> 150 to 180	9 g/kg
> 180	5% of the value

Carbon content

Carbon content g/kg	Acceptable variation
<= 2.5	0.25 g/kg absolute
2.5 < OC <= 75	10 % relative
> 75	7.5 g/kg absolute

Total Nitrogen

Total Nitrogen content	Acceptable variation
mg/g	
<= 2.0	10 % relative
> 2.0	5 % relative

Annex 7: Questionnaire

<u>Guidelines</u>: **Please fill in all questions.**
For some questions more than one answer is allowed.
In case of subcontracted laboratories, each laboratory has to fill the General Information form.

A. General Information

Name of Laboratory:
Address
Street :
Number :
PO Box :
Postal Code :
City :
Country :

Telephone Number :
Fax Number :
Website :

Contact person
Name :
Email :

Responsible person (laboratory)
Name :
Email :

Statute (belonging to) :
- ☐ University, Name :
- ☐ State Institute, Name :
- ☐ Private Institute, Name :
- ☐ Private Lab
- ☐ Other, Specify :

Type of laboratory:
- ☐ Soil (Forest)
- ☐ Soil (General)
- ☐ Plant & Soil (Forest)
- ☐ Plant & Soil (General)
- ☐ General

Actual Number of laboratory personnel:

Lab is working since (year) :

Certificates of laboratory :

The results of the ring test will be published in a report. Do you agree that your laboratory is mentioned with full name in this evaluation report ? Laboratories indicating 'no' will be given a code only. In that case only the NFC will have knowledge of the laboratory codes of its country.
- ☐ Yes
- ☐ No

B. Analysis Information

Analysis: Determination of Particle Size Distribution

Laboratory that performed analysis

- ☐ Own laboratory
- ☐ Subcontracted laboratory, Specify

(subcontracted laboratory should fill in General Information and Analysis Information Forms)

Method

- Is the lab working according to the reference method (ISO 11277) ?
  - ☐ Yes
  - ☐ No, Lab method :
- Has the lab experience with reference method ?
  - ☐ High
  - ☐ Normal
  - ☐ Little
- Does the lab possess any accreditation for this method ?
  - ☐ Yes, delivered by :
  - ☐ No
- Does the lab encounters any specific problems analysing the samples according to this method ?

Equipment

- What is the used equipment for this analysis ?

Analysis	Analytical technique	Analytical instrument (+manufacturer)	Method detection limit

- What is the experience of the lab with the used equipment ?
  - ☐ High
  - ☐ Normal
  - ☐ Little

Personnel

- Has the lab personnel specifically trained for this analysis ?
  - ☐ Yes
  - ☐ No
- What is the experience of the lab personnel with this method
  - ☐ < 1 year
  - ☐ 1 - 3 years
  - ☐ > 3 years

Quality Assurance

- Does the lab use for this method
  - ☐ International Reference Material (IRM), Provider/Code :
  - ☐ National Reference Material (NRM), Provider/Code :
  - ☐ Local Reference Material (LRM)
  - ☐ No reference material
- Which reference material does the lab use ?
  - ☐ Matrix reference material
  - ☐ Method reference material
- Does the lab use Calibration Standards ?
  - ☐ Yes, Provider/Code :
  - ☐ No
- Does the lab use Control Charts ?
  - ☐ Yes (if possible, please provide)
  - ☐ No

Analysis: Determination of Soil pH

Laboratory that performed analysis
- ☐ Own laboratory
- ☐ Subcontracted laboratory, Specify
  (subcontracted laboratory should fill in General Information and Analysis Information Forms)

Method

- Is the lab working according to the reference method (ISO 10390) ?
  - ☐ Yes
  - ☐ No, Lab method :
- Has the lab experience with reference method ?
  - ☐ High
  - ☐ Normal
  - ☐ Little
- Does the lab possess any accreditation for this method ?
  - ☐ Yes, delivered by :
  - ☐ No
- Does the lab encounters any specific problems analysing the samples according to this method ?

Equipment

- What is the used equipment for this analysis ?

Analysis	Analytical technique	Analytical instrument (+manufacturer)	Method detection limit
pH			

- What is the experience of the lab with the used equipment ?
  - ☐ High
  - ☐ Normal
  - ☐ Little

Personnel

- Has the lab personnel specifically trained for this analysis ?
  - ☐ Yes
  - ☐ No
- What is the experience of the lab personnel with this method
  - ☐ < 1 year
  - ☐ 1 - 3 years
  - ☐ > 3 years

Quality Assurance

- Does the lab use for this method
  - ☐ International Reference Material (IRM), Provider/Code :
  - ☐ National Reference Material (NRM), Provider/Code :
  - ☐ Local Reference Material (LRM)
  - ☐ No reference material
- Which reference material does the lab use ?
  - ☐ Matrix reference material
  - ☐ Method reference material
- Does the lab use Calibration Standards ?
  - ☐ Yes, Provider/Code :
  - ☐ No
- Does the lab use Control Charts ?
  - ☐ Yes (if possible, please provide)
  - ☐ No

Analysis: Determination of Carbonate Content

Laboratory that performed analysis
- ☐ Own laboratory
- ☐ Subcontracted laboratory, Specify

(subcontracted laboratory should fill in General Information and Analysis Information Forms)

Method

- Is the lab working according to the reference method (ISO 10693) ?
  - ☐ Yes
  - ☐ No, Lab method :
- Has the lab experience with reference method ?
  - ☐ High
  - ☐ Normal
  - ☐ Little
- Does the lab possess any accreditation for this method ?
  - ☐ Yes, delivered by :
  - ☐ No
- Does the lab encounters any specific problems analysing the samples according to this method ?

Equipment

What is the used equipment for this analysis ?

Analysis	Analytical technique	Analytical instrument (+manufacturer)	Method detection limit
Carbonate content			

- What is the experience of the lab with the used equipment ?
  - ☐ High
  - ☐ Normal
  - ☐ Little

Personnel

- Has the lab personnel specifically trained for this analysis ?
  - ☐ Yes
  - ☐ No
- What is the experience of the lab personnel with this method
  - ☐ < 1 year
  - ☐ 1 - 3 years
  - ☐ > 3 years

Quality Assurance

- Does the lab use for this method
  - ☐ International Reference Material (IRM), Provider/Code :
  - ☐ National Reference Material (NRM), Provider/Code :
  - ☐ Local Reference Material (LRM)
  - ☐ No reference material
- Which reference material does the lab use ?
  - ☐ Matrix reference material
  - ☐ Method reference material
- Does the lab use Calibration Standards ?
  - ☐ Yes, Provider/Code :
  - ☐ No
- Does the lab use Control Charts ?
  - ☐ Yes (if possible, please provide)
  - ☐ No

Analysis: Determination of Organic Carbon Content

Laboratory that performed analysis
- ☐ Own laboratory
- ☐ Subcontracted laboratory, Specify
  (subcontracted laboratory should fill in General Information and Analysis Information Forms)

Method
- Is the lab working according to the reference method (ISO 10694) ?
  - ☐ Yes
  - ☐ No, Lab method :
- Has the lab experience with reference method ?
  - ☐ High
  - ☐ Normal
  - ☐ Little
- Does the lab possess any accreditation for this method ?
  - ☐ Yes, delivered by :
  - ☐ No
- Does the lab encounters any specific problems analysing the samples according to this method ?
  No

Equipment
- What is the used equipment for this analysis ?

Analysis	Analytical technique	Analytical instrument (+manufacturer)	Method detection limit
Organic Carbon			

- What is the experience of the lab with the used equipment ?
  - ☐ High
  - ☐ Normal
  - ☐ Little

Personnel
- Has the lab personnel specifically trained for this analysis ?
  - ☐ Yes
  - ☐ No
- What is the experience of the lab personnel with this method
  - ☐ < 1 year
  - ☐ 1 - 3 years
  - ☐ > 3 years

Quality Assurance
- Does the lab use for this method
  - ☐ International Reference Material (IRM), Provider/Code :
  - ☐ National Reference Material (NRM), Provider/Code :
  - ☐ Local Reference Material (LRM)
  - ☐ No reference material
- Which reference material does the lab use ?
  - ☐ Matrix reference material
  - ☐ Method reference material
- Does the lab use Calibration Standards ?
  - ☐ Yes, Provider/Code : Fisons Instruments, ThermoQuest Italia s.p.a.
  - ☐ No
- Does the lab use Control Charts ?
  - ☐ Yes (if possible, please provide)
  - ☐ No

Analysis: Determination of total Nitrogen Content

Laboratory that performed analysis
- ☐ Own laboratory
- ☐ Subcontracted laboratory, Specify
  (subcontracted laboratory should fill in General Information and Analysis Information Forms)

Method

- Is the lab working according to the reference method (ISO 13878) ?
  - ☐ Yes
  - ☐ No, Lab method :
- Has the lab experience with reference method ?
  - ☐ High
  - ☐ Normal
  - ☐ Little
- Does the lab possess any accreditation for this method ?
  - ☐ Yes, delivered by :
  - ☐ No
- Does the lab encounters any specific problems analysing the samples according to this method ?

Equipment

- What is the used equipment for this analysis ?

Analysis	Analytical technique	Analytical instrument (+manufacturer)	Method detection limit
Total Nitrogen Content			

- What is the experience of the lab with the used equipment ?
  - ☐ High
  - ☐ Normal
  - ☐ Little

Personnel

- Has the lab personnel specifically trained for this analysis ?
  - ☐ Yes
  - ☐ No
- What is the experience of the lab personnel with this method
  - ☐ < 1 year
  - ☐ 1 - 3 years
  - ☐ > 3 years

Quality Assurance

- Does the lab use for this method
  - ☐ International Reference Material (IRM), Provider/Code :
  - ☐ National Reference Material (NRM), Provider/Code :
  - ☐ Local Reference Material (LRM)
  - ☐ No reference material
- Which reference material does the lab use ?
  - ☐ Matrix reference material
  - ☐ Method reference material
- Does the lab use Calibration Standards ?
  - ☐ Yes, Provider/Code :
  - ☐ No
- Does the lab use Control Charts ?
  - ☐ Yes (if possible, please provide)
  - ☐ No

Analysis: Determination of Exchangeable Acidity, Exchangeable Cations (Al, Ca, Fe, K, Mg, Mn, Na) and Free H^+ Acidity

Laboratory that performed analysis
- ☐ Own laboratory
- ☐ Subcontracted laboratory, Specify
  (subcontracted laboratory should fill in General Information and Analysis Information Forms)

Method

- Is the lab working according to the reference method (ISO 11260 and ISO 14254) ?
  - ☐ Yes
  - ☐ No, Lab method :
- Has the lab experience with reference method ?
  - ☐ High
  - ☐ Normal
  - ☐ Little
- Does the lab possess any accreditation for this method ?
  - ☐ Yes, delivered by :
  - ☐ No
- Does the lab encounters any specific problems analysing the samples according to this method ?

Equipment

- What is the used equipment for this analysis ?

Analysis	Analytical technique	Analytical instrument (+manufacturer)	Wavelength	Method detection limit
Exchangeable acidity				
Free H^+ acidity				
Exchangeable Al				
Exchangeable Ca				
Exchangeable Fe				
Exchangeable K				
Exchangeable Mg				
Exchangeable Mn				
Exchangeable Na				

- What is the experience of the lab with the used equipment ?
  - ☐ High
  - ☐ Normal
  - ☐ Little

Personnel

- Has the lab personnel specifically trained for this analysis ?
  - ☐ Yes
  - ☐ No
- What is the experience of the lab personnel with this method
  - ☐ < 1 year
  - ☐ 1 - 3 years
  - ☐ > 3 years

Quality Assurance

- Does the lab use for this method
  - ☐ International Reference Material (IRM), Provider/Code :
  - ☐ National Reference Material (NRM), Provider/Code :
  - ☐ Local Reference Material (LRM)
  - ☐ No reference material
- Which reference material does the lab use ?
  - ☐ Matrix reference material
  - ☐ Method reference material
- Does the lab use Calibration Standards ?
  - ☐ Yes, Provider/Code :
  - ☐ No
- Does the lab use Control Charts ?
  - ☐ Yes (if possible, please provide)
  - ☐ No

Analysis: Aqua Regia Extractant Determinations (P, Ca, K, Mg, Mn, Cu, Pb, Cd, Zn, Al, Fe, Cr, Ni, S, Hg, Na)

Laboratory that performed analysis
- ☐ Own laboratory
- ☐ Subcontracted laboratory, Specify

(subcontracted laboratory should fill in General Information and Analysis Information Forms)

Method

- Is the lab working according to the reference method (ISO 11466) ?
  - ☐ Yes
  - ☐ No, Lab method :
- Has the lab experience with reference method ?
  - ☐ High
  - ☐ Normal
  - ☐ Little
- Does the lab possess any accreditation for this method ?
  - ☐ Yes, delivered by :
  - ☐ No
- Does the lab encounters any specific problems analysing the samples according to this method ?

Equipment

- What is the used equipment for this analysis ?

Analysis	Analytical technique	Analytical instrument (+manufacturer)	Wavelength	Method detection limit
Extracted Al				
Extracted Ca				
Extracted Cd				
Extracted Cr				
Extracted Cu				
Extracted Fe				
Extracted Hg				
Extracted K				
Extracted Mg				
Extracted Mn				
Extracted Na				
Extracted Ni				
Extracted P				
Extracted Pb				
Extracted S				
Extracted Zn				

- What is the experience of the lab with the used equipment ?
  - ☐ High
  - ☐ Normal
  - ☐ Little

Personnel

- Has the lab personnel specifically trained for this analysis ?
  - ☐ Yes
  - ☐ No
- What is the experience of the lab personnel with this method
  - ☐ < 1 year
  - ☐ 1 - 3 years
  - ☐ > 3 years

Quality Assurance

- Does the lab use for this method
  - ☐ International Reference Material (IRM), Provider/Code :
  - ☐ National Reference Material (NRM), Provider/Code :
  - ☐ Local Reference Material (LRM)
  - ☐ No reference material
- Which reference material does the lab use ?
  - ☐ Matrix reference material
  - ☐ Method reference material
- Does the lab use Calibration Standards ?
  - ☐ Yes, Provider/Code :
  - ☐ No

Analysis: Determination of Total Elements (Ca, Mg, Na, K, Al, Fe, Mn)

Laboratory that performed analysis

- ☐ Own laboratory
- ☐ Subcontracted laboratory, Specify
  (subcontracted laboratory should fill in General Information and Analysis Information Forms)

Method

- Is the lab working according to the reference method (ISO 14869 or Michopoulos, 1995) ?
  - ☐ Yes
  - ☐ No, Lab method :
- Has the lab experience with reference method ?
  - ☐ High
  - ☐ Normal
  - ☐ Little
- Does the lab possess any accreditation for this method ?
  - ☐ Yes, delivered by :
  - ☐ No
- Does the lab encounters any specific problems analysing the samples according to this method ?

Equipment

What is the used equipment for this analysis ?

Analysis	Analytical technique	Analytical instrument (+manufacturer)	Wavelength	Method detection limit
Total Al				
Total Ca				
Total Fe				
Total K				
Total Mg				
Total Mn				
Total Na				

- What is the experience of the lab with the used equipment ?
  - ☐ High
  - ☐ Normal
  - ☐ Little

Personnel

- Has the lab personnel specifically trained for this analysis ?
  - ☐ Yes
  - ☐ No
- What is the experience of the lab personnel with this method
  - ☐ < 1 year
  - ☐ 1 - 3 years
  - ☐ > 3 years

Quality Assurance

- Does the lab use for this method
  - ☐ International Reference Material (IRM), Provider/Code :
  - ☐ National Reference Material (NRM), Provider/Code :
  - ☐ Local Reference Material (LRM)
  - ☐ No reference material
- Which reference material does the lab use ?
  - ☐ Matrix reference material
  - ☐ Method reference material
- Does the lab use Calibration Standards ?
  - ☐ Yes, Provider/Code :
  - ☐ No
- Does the lab use Control Charts ?
  - ☐ Yes (if possible, please provide)
  - ☐ No

Analysis: Acid Oxalate Extractable Fe and Al

Laboratory that performed analysis

- ☐ Own laboratory
- ☐ Subcontracted laboratory, Specify

(subcontracted laboratory should fill in General Information and Analysis Information Forms)

Method

- Is the lab working according to the reference method (ISRIC 1992) ?
  - ☐ Yes
  - ☐ No, Lab method :
- Has the lab experience with reference method ?
  - ☐ High
  - ☐ Normal
  - ☐ Little
- Does the lab possess any accreditation for this method ?
  - ☐ Yes, delivered by :
  - ☐ No
- Does the lab encounters any specific problems analysing the samples according to this method ?

Equipment

What is the used equipment for this analysis ?

Analysis	Analytical technique	Analytical instrument (+manufacturer)	Wavelength	Method detection limit
Reactive Al				
Reactive Fe				

- What is the experience of the lab with the used equipment ?
  - ☐ High
  - ☐ Normal
  - ☐ Little

Personnel

- Has the lab personnel specifically trained for this analysis ?
  - ☐ Yes
  - ☐ No
- What is the experience of the lab personnel with this method
  - ☐ < 1 year
  - ☐ 1 - 3 years
  - ☐ > 3 years

Quality Assurance

- Does the lab use for this method
  - ☐ International Reference Material (IRM), Provider/Code :
  - ☐ National Reference Material (NRM), Provider/Code :
  - ☐ Local Reference Material (LRM)
  - ☐ No reference material
- Which reference material does the lab use ?
  - ☐ Matrix reference material
  - ☐ Method reference material
- Does the lab use Calibration Standards ?
  - ☐ Yes, Provider/Code :
  - ☐ No
- Does the lab use Control Charts ?
  - ☐ Yes (if possible, please provide)
  - ☐ No

Annex 8: Analytical Techniques and Equipment

Table VIII.1 summarises the different analytical techniques used for the third FSCC-ring test. Parameters are shown as rows of the table, while the columns are formed by the different analytical techniques. In the cells, the number of laboratories using a certain technique for a parameter are shown.

Particle size is in most cases determined by the 'Pipette Method', pH is mostly measured using potentiometry. For the analysis of the organic carbon, two methods (Dry combustion and the CNS-Analyser) are popular. The CNS-Analyser is also often used to determine the amount of nitrogen. Most laboratories measure the amount of carbonate gas-volumetric (by means of a Scheibler unit). For the determination of the exchangeable, extractable and total elements, ICP is the most popular method, by exception of the amount of extractable Hg, which is in most cases measured by use of AAS. The exchangeable acidity is frequently determined by titration. Whereas the amount of reactive Fe and Al is mostly measured by use of AAS.

The AAS (Atomic Absorption Spectrometry) and ICP (Inductively Coupled Plasma) are further subdivided, based on the method of detection.

AAS	:	NS	–	Not further Specified
		Fl	–	Flame AAS
		Ov	–	Oven AAS (Graphite furnace)
		CV	–	Cold vapour AAS
ICP	:	NS	–	Not further Specified
		AES	–	Atomic Emission Spectrometry
		MS	–	Mass Spectrometry

Table VIII.2 gives an overview of the wavelengths used for the detection of the different elements. The wavelengths used by laboratories that use ICP are given in bold, the wavelengths used for AAS are printed in italic.

Each dot in Figure VIII.1 represents a wavelength used by a laboratory to determine the amount of a specific element (either exchangeable, extractable, total or reactive). The symbols vary according to the used technique, as explained in the accompanying legend.

For more information concerning this topic, please do not hesitate to contact FSCC . Extra information on the used analytical techniques or apparatus can be provided on request.

TableVIII.1: Number of laboratories that used a certain analytical technique for each parameter

	AAS				Calculation	CNS-Analyser	Dry combustion	Elemental Analysis	Gas-Volumetric	ICP			Kjeldahl	Laser	Photometry	Pipette	Potentiometry	Spectrometry	Titration	W&B[1]	NA[2]
	NS	Fl	Ov	CV						NS	AES	MS									
Organic Carbon						13	12										1		1	2	7
Carbonates						4			26										3		5
Total N						21		3					6					2	2		6
Particle Size														1		20					4
pH															3		22				23
Exchangeable Acidity					2										1		9		18		4
Exchangeable Al	3	4	1							14	13							1	1		1
Exchangeable Ca	10	4								14	13							1			1
Exchangeable Fe	10	4								14	13							1			1
Exchangeable K	10	5								13	11							3			1
Exchangeable Mg	11	5								14	12							1			1
Exchangeable Mn	10	4								14	13							1			1
Exchangeable Na	9	5								13	11							2			2
Extractable Al	2	5								15	13							1			1
Extractable Ca	6	5								16	12							1			
Extractable Cd	6	5	4							14	9	2						1			
Extractable Cr	5	6	1							14	11	1						1			
Extractable Cu	6	8								15	11							1			
Extractable Fe	6	6								15	13							1			
Extractable Hg	4	1		4						3											2
Extractable K	4	5								16	12							3			
Extractable Mg	5	5								16	12							1			
Extractable Mn	6	7								16	13							1			
Extractable Na	4	4								13	9							2			1
Extractable Ni	5	7								13	11	1						1			
Extractable P										15	13				7			2			1
Extractable Pb	6	6	1							15	11	1						1			1
Extractable S						4				11	9				2			1			1
Extractable Zn	6	7								15	14							1			
Free H+ Acidity					1												9		12		5
Reactive Al	3	1								9	6							1			1
Reactive Fe	3	1								9	6							1			1
Total Al	2	2								5	7				1				1		
Total Ca	3	3								5	7										
Total Fe	3	3								5	7										
Total K	3	1								5	7				1			1			
Total Mg	3	3								5	7										
Total Mn	3	3								5	7										
Total Na	3	1								5	7				1			1			

[1] Method of Walkley and Black

[2] Not available, no information provided

Table VIII.2: Wavelenghts for the analysed elements (bold : ICP / italic : AAS)

Labo_Id	Exch. Al	Exch. Ca	Exch. Fe	Exch. K	Exch. Mg	Exch. Mn	Exch. Na	Extr. Al	Extr. Ca	Extr. Cd	Extr. Cr	Extr. Cu	Extr. Fe	Extr. Hg	Extr. K	Extr. Mg
2					*285.2*			*309.3*	*422.7*	*228.8*	*357.9*	*324.8*	*248.3*	*253.7*	*766.5*	
3	**308.215**	**315.887**	**259.94**	**766.49**	**279.553**	**257.61**	**589.592**	**308.215**	**317.933**	**228.802**	**267.716**	**324.754**	**273.358**		**766.491**	**277.983**
4		*422.7*	*248.3*		*285.2*	*279.5*		*309.3*	*422.7*	*228.8*	*357.9*	*324.8*	**248.3**			*285.2*
5	**395.152**	**317.933**	**259.94**	**766.49**	**279.079**	**257.61**	**589.592**	**396.152**	**317.933**	**228.802**	**267.715**	**324.754**	**259.94**		**766.49**	**279.079**
6	**308.215**	**422.673**	**259.94**	**765.491**	**285.213**	**257.61**	**589.592**	**308.15**	**422.673**	**214.438**	**283.553**	**324.754**	**259.94**	**184.95**	**766.491**	**285.213**
7	**167.081**	**317.393**	**259.94**	**766.491**	**279.078**	**293.306**	**588.995**	**308.215**	**317.933**		**267.716**		**271.441**		**766.491**	**279.078**
8	**308.215**	**210.324**	**238.204**	**769.897**	**279.078**	**293.931**	**588.995**	**256.798**	**210.324**	**228.802**	**267.716**	**327.395**	**273.368**		**769.897**	**279.078**
10		*422.7*	*248.3*		*285.2*	*279.5*			*422.7*	*228.8*	*357.9*	*324.8*	*248.3*			*285.2*
11	**396.152**	**315.887**	**239.562**	**766.491**	**280.27**	**260.569**	**588.995**									
12		*422.7*	*248.3*	*786.5*	*285.2*	*279.5*	*589*									
13	**257.61**	**318.128**	**271.441**	*766.5*	**279.079**	**293.93**	**589.592**	**257.61**	**318.128**	**228.802**	**267.716**	**324.754**	**271.441**		**769.896**	**279.079**
14	**167.08**	**315.887**	**259.94**	**766.491**	**279.663**	**257.61**	**589.592**	**396.157**	**315.892**	*228.8*	*358*	*324.8*	**234.349**	*253.7*	**766.604**	**279.079**
15								**237.313**		**228.802**	**205.560**	**324.752**	**238.863**	*253.7*		
16		*422.7*	*248.3*	*766.5*	*285.2*	*279.5*	*589*									
17	**167.08**	**317.93**	**259.94**	**786.49**	**285.21**	**257.61**	**589.59**	**167.08**	**317.93**	**228.2**	**357.9**	**324.7**	**259.94**		**766.49**	**285.21**
18								*309.3*		*228.8*	*357.9*	*324.8*	*248.3*	*253.65*		
20		*422.7*	*248.3*	*766.5*	*285.2*	*279.5*	*589*		*422.7*	*228.8*		*324.7*	*248.3*		*766.5*	*285.2*
23	*309.3*	*422.7*	*248.3*		*258.2*	*279.5*		*309.3*	*422.7*	*228.8*	*357.9*	*324.8*	*248.3*			*258.2*
24		*422.7*	*248.3*	*766.5*	*285.2*	*279.5*	*589*		*422.7*		*357.9*	*324.8*	*248.3*		*766.5*	*285.2*
25	**396.152**	**393.366**	**269.940**	**766.490**	**279.553**	**257.610**	**588.995**	**395.152**	**393.365**	**214.438**	**267.716**	**324.754**	**259.940**		**766.490**	**279.553**
26	**398.162**	**317.933**	**238.204**	**765.490**	**279.553**	**257.610**	**589.592**	**396.152**	**317.933**	**225.502**	**206.149**	**224.700**	**238.204**		**766.490**	**279.553**
27	**308.215**	**317.933**	**239.562**	**766.491**	**280.270**	**257.610**		**308.215**	**317.933**	**228.800**	**205.560**	**324.754**	**238.204**	*254*	**765.491**	**279.079**
28	*396.2*	*422.7*	*248.3*	*766.5*	*285.2*	*279.5*	*589*	*396.2*	*422.7*	*228.8*	*357.9*	*324.8*	*248.3*		*766.5*	*285.2*
30	**308.215**	**315.887**	**259.940**	*766.5*	**285.210**	**257.610**	*589*	**395.153**	**317.933**	**228.802**	**205.550**	**324.754**	**271.441**		**766.491**	**279.553**
31	**396.152**	**317.933**	**259.940**	**766.490**	**285.213**	**293.306**	**589.592**	**396.152**	**317.933**		**267.715**	**324.754**	**259.940**		**765.490**	**285.213**
32	**308**	**319**	**238**	**766**	**280**	**258**	**590**	**396**	**393**				**238**		**766**	**280**
33																
34	**394.4**	**317.93**	**238.2**	**766.49**	**282.21**	**257.61**		**394.4**	**317.93**	*228.8*	*357.9*	*324.8*	**238.2**	*253.65*	**766.49**	**285.21**
35	**398.152**	**317.933**	**259.940**	**769.896**	**285.213**	**260.589**	**589.592**	**396.152**	**317.933**	*228.8*	**267.716**	**324.754**	**259.940**		**769.896**	**285.213**
36	**396.152**	**317.933**	**259.940**	**766.491**	**285.213**	**257.610**	**588.995**	**237.3**	**317.9**	*228.8*	**205.5**	**223.0**	**215.5**		**768.4**	**280.3**
37	**396.152**	**317.933**	**239.68**	**769.896**	**383.826**	**293.93**	**689.592**	**396.152**	**317.933**	**228.802**	**267.716**	**324.754**	**239.56**		**769.896**	**383.826**
38	*309.3*	*422.7*	*248.3*	*766.5*	*285.2*	*279.2*	*598*									
40	**396.1**	**184**	**259.94**	**765.49**	**285.21**	**259.37**		**308.2**	**445.4**	**228.8**	**267.7**	**324.7**	**371.9**		**769.8**	**279**
41	**396.152**	**317.933**	**259.940**	**768.490**	**279.079**	**257.81**	**589.592**	**396.152**	**317.933**	**214.438**	**205.552**	**324.754**	**259.94**		**766.491**	**279.079**
42																
43	**396.152**	**317.933**	**260.709**	**766.490**	**280.270**	**257.610**	**589.592**	**257.510**	**315.887**	**228.802**	**267.716**	**324.754**	**239.562**	*253.7*	**766.490**	**280.270**
45	*309.3*	*422.7*	*248.3*	*766.5*	*285.2*	*279.5*	*589*	*309.3*	*422.7*	**228.802**	**267.716**	**324.754**	*248.3*		*766.5*	*285.2*
47										*228.8*	*357.9*	*324.7*	*248.3*			
48	**396.152**	**317.933**	**259.94**	*766.5*	*285.2*	**267.61**	**589.592**	**396.152**	**317.933**	**228.802**	**257.715**	**324.754**	**259.94**	**253.7**	**766.491**	**279.806**
52	*309*	*423*	*248*	*766*	*285*	*279*	*589*		**317.933**	**228.802**		**324.754**			**769.896**	**285.213**
53									*422.7*	*228.8*		*324.8*			*766.5*	*285.2*
54	**308.22**	**393.37**	**259.94**	**766.49**	**383.23**	**257.61**	**589.59**	**308.22**	**393.37**	**214.44**	**205.55**	**324.75**	**259.94**		**766.49**	**279.55**
55	**394.357**	**383.322**	**259.950**	**766.453**	**279.584**	**257.518**	**589.555**									
58	*309.3*	*422.7*	*248.3*	*769.9*	*202.6*	*279.5*	*589.6*									
59	*309.3*	*422.7*	*248.3*	*766.5*	*285.2*	*279.5*	*589*	*309.3*	*422.7*	*228.8*	*357.9*	*324.7*	*248.3*		*766.5*	*285.2*
60									**373.590**	**228.802**	**267.716**	**327.396**	**371.944**	*253*	**766.490**	**285.213**

Table VIII.2 (continued): Wavelenghts for the analysed elements (bold : ICP / italic : AAS)

Labo_Id	Extr. Mn	Extr. Na	Extr. Ni	Extr. P	Extr. Pb	Extr. S	Extr. Zn	Total Al	Total Ca	Total Fe	Total K	Total Mg	Total Mn	Total Na
2	*279.5*	*589*	*232*		*217*		*213.9*							
3	257.61	589.592	231.804	178.222	220.353	181.972	213.857	308.215	315.887	259.94	766.49	279.553	257.61	589.892
4	*279.5*		*232*		*283.3*		*253.9*							
5	257.61	589.592	231.604	214.914	220.353	181.978	213.856							
6	257.61	589.592	231.604	178.29	168.22	182.04	213.886							
7	293.306		231.604	178.287	220.352	182.04	213.856	308.215	317.933	271.441	766.491	279.078	293.306	588.955
8	260.568		231.604	214.914	220.353		213.857							
10	*279.6*		*232*		*217*		*213.9*							
11														
12														
13	293.93	589.592	231.604	178.284	220.353	182.034	213.856	257.51	318.128	271.441	769.896	279.079	293.93	589.592
14	257.612	589.594						396.152	315.887	234.349	766.491	279.079	257.610	589.592
15	*259.372*		231.604		220.353		213.857							
16														
17	257.61	589.59	232	178.29	283.3	180.73	213.86	167.08	317.93	259.94	766.49	285.21	257.61	589.59
18	*279.5*		*232*		*207.2*		*213.9*							
20	*279.5*	*589*			*283.3*		*213.9*							
23	*279.5*		*232*		*217*		*213.9*							
24	*279.5*	*589*	*232*		*283.3*		*213.9*		*422.7*	*248.3*	*766.5*	*285.2*	*279.5*	*589*
25	257.610	588.995	231.604	213.618	220.353		213.856	396.152	393.366	259.940	766.490	279.553	257.610	588.995
26	257.610	589.592	221.647	177.499	220.353	182.034	206.200							
27	257.610		231.604	213.618	220.353		213.856							
28	*279.5*	*589*	*232*				*213.9*	*396.2*	*422.7*	*248.3*	*766.5*	*285.2*	*279.5*	*589*
30	257.610	589.592	231.604	178.287	220.351	182.040	213.858	396.153	317.933	271.441	766.491	279.553	257.610	589.592
31	283.306		231.604	214.914	220.353	181.978	213.856							
32	260	689	*232*	213		180	213							
33														
34	257.61	589.59		214.91	*217*		213.86							
35	260.568	589.592	231.618	213.604	220.353		213.856							
36	257.6	588.9	227.0	185.9	220.3	182.0	206.2	237.3	317.9	218.6	766.4	280.3	257.6	588.9
37	293.83	589.592	341.476	213.618	220.353	182.034	213.856							
38								*309.3*	*422.7*	*248.3*	*766.5*	*285.2*	*279.5*	*589.6*
40	260.5		231.6	213.6			213.8	308.2	445.4	371.9	769.8	279	260.5	588.9
41	257.61	589.592	231.604	177.669	220.353	180.669	213.856	396.152	317.933	259.940	766.491	279.079	257.610	589.592
42														
43	257.610	588.592	231.604	213.618	220.353	182.034	202.548							
45	*279.5*	*589*	231.604	177.495	220.353		213.856							
47	*279.5*		*232*		*283.3*		*213.9*		*422.7*	*248.3*		*285.5*	*279.5*	
48	257.61	589.692	231.604	214.914	220.353	180.73	213.856	396.152	317.933	259.94	766.491	279.806	257.61	589.592
52	257.610				220.353		213.856	*309*	*422.7*	*248.3*	*766.5*	*285.2*	*279.5*	*589*
53	*279.5*				*283.3*		*213.9*							
54	257.61	589.59		178.29	220.35	180.73	213.86							
55														
58														
59	*279.5*		*232*		*217*		*213.9*							
60		589.592	221.647	214.914	220.353	182.034	213.856							

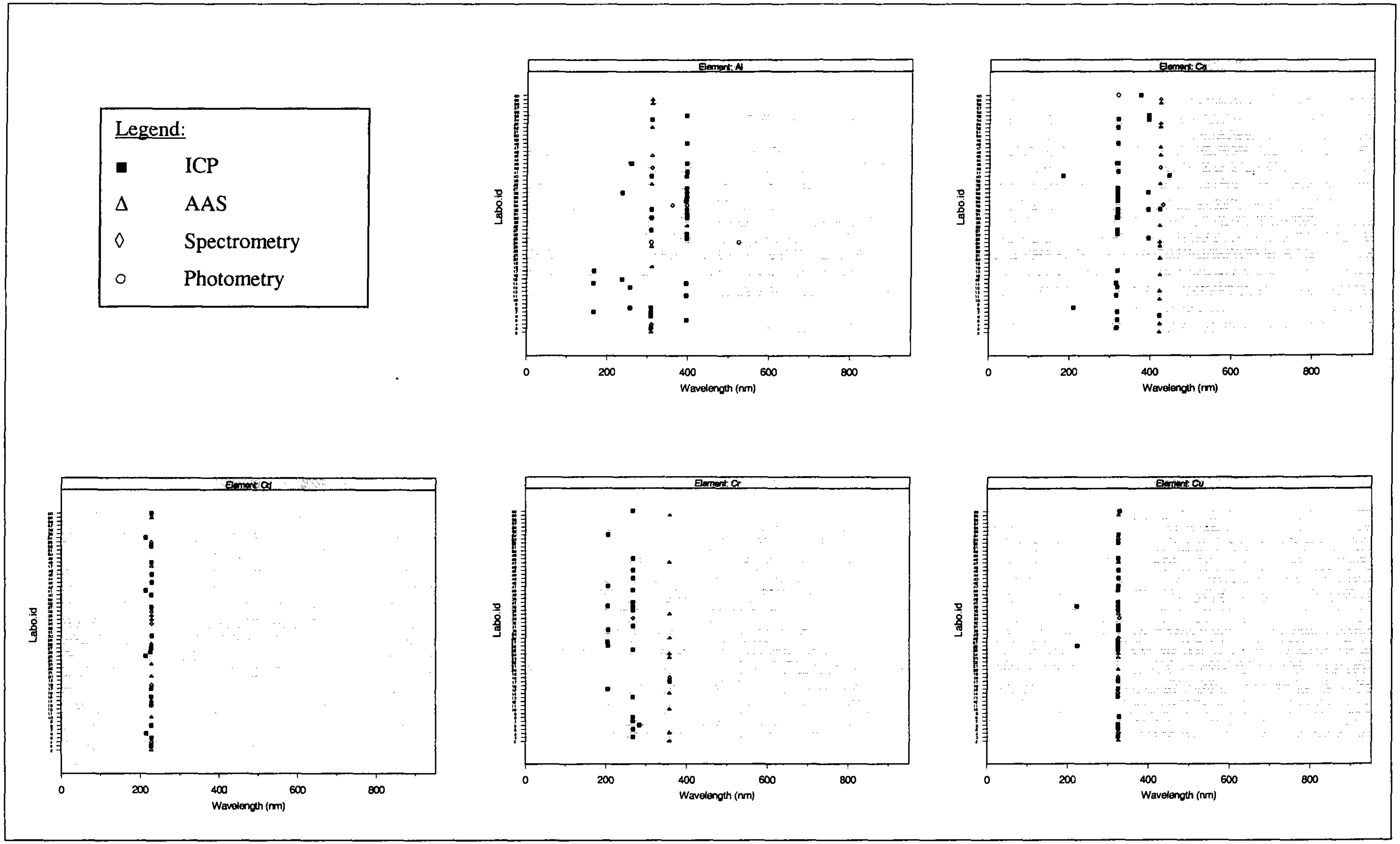


Figure VIII.1: Dotplots – Wavelengths used for the analysed elements

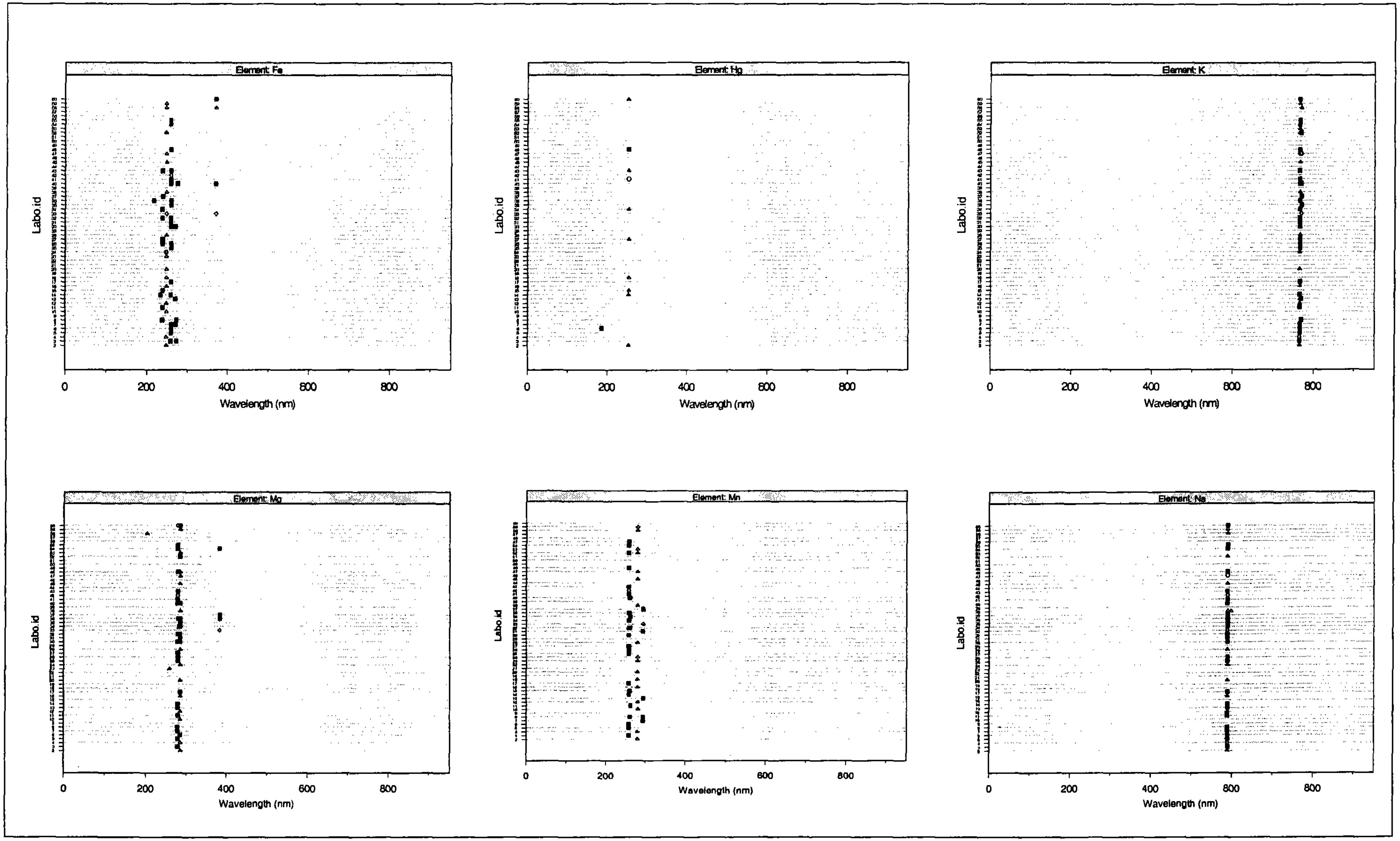


Figure VIII.1 (continued): Dotplots – Wavelengths used for the analysed elements

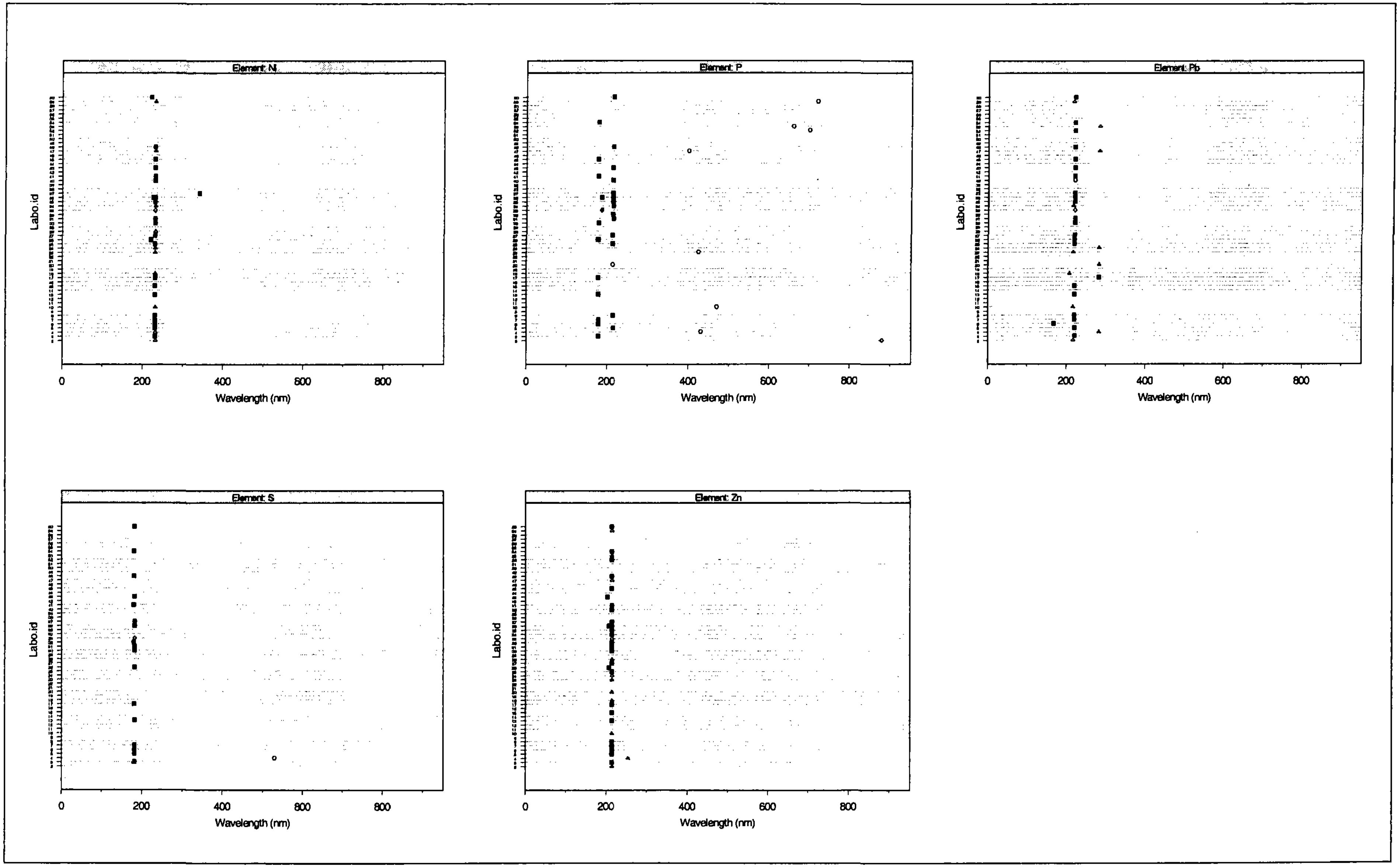


Figure VIII.1 (continued): Dotplots – Wavelengths used for the analysed elements

Annex 9: Statistical analysis phase II

In this annex, the statistical analysis of phase II for each of the analysis is set out. Factors are only retained if they are significant at the 0.01 level. Next to the ANOVA table, each significant factor is separately discussed by means of multiple comparisons ['Multicomp'-function, (S-plus,2002)]. This function compares all levels of the factor to each other. Significant differences are marked as **.

1. Particle Size

1.A Between-laboratory variability

No significant factors for Hv at the 0.01 level (after sqrt(abs(Hv)) transformation).

1.B Within-laboratory variability

```
Analysis of Variance Table

Response: sqrt(Kv)
Type III Sum of Squares
          Df  Sum of Sq  Mean Sq  F Value       Pr(F)
     Type   2        2.5     1.26     10.3  0.0000603
Residuals 156       19.0     0.12

Multicomp(Type)
95 % simultaneous confidence intervals for specified
linear combinations, by the Tukey method critical point: 2.3663
response variable: sqrt(Kv)
intervals excluding 0 are flagged by '**'
       Estimate    Std.Error    Lower Bound   Upper Bound
G-P      -0.189       0.0612         -0.334       -0.0443   **
G-B      -0.331       0.0775         -0.514       -0.1470   **
P-B      -0.142       0.0783         -0.327        0.0435
```

The General laboratories have significantly lower within-laboratory variability than the Soil laboratories and the Plant and Soil laboratories.

2. pHsoil

2.A Between-laboratory variability

No significant factors remain in the model at the 0.01 level. As was seen in the first phase of the analysis of the ring test, *soil pH* did not show a large variation (low coefficient of variation) between the laboratories participating in the ring test.

2.B Within-laboratory variability

```
Analysis of variance table
Response: sqrt(Kv)
Type III Sum of Squares
           Df Sum of Sq Mean Sq F Value   Pr(F)
  Trained   1       2.4    2.43    9.95   0.00181
Residuals 242      59.2    0.24

Multicomp(Trained)
95 % non-simultaneous confidence intervals for specified
linear combinations, by the Fisher LSD method
critical point: 1.9698
response variable: sqrt(Kv)
intervals excluding 0 are flagged by '**'
    Estimate Std.Error Lower Bound Upper Bound
0-1    0.239    0.0758      0.0897       0.388     **
```

The laboratories with especially trained personnel perform better (internal variability is lower) than other laboratories.

3. Carbonates

3.A Between laboratory variability

No significant factors at the 0.01 level (after sqrt-transformation).

3.B Within-laboratory variability

No significant factors at the 0.01 level (after sqrt-transformation).

4. Organic Carbon

4.A Between-laboratory variability

```
Analysis of Variance Table

Response: sqrt(abs(Hv))
Type III Sum of Squares
           Df  Sum of Sq   Mean Sq   F Value       Pr(F)
Statute     3        1.6    0.536      3.98        0.00997
Region      3        1.9    0.627      4.65        0.00432
Residuals 102         13.7       0.135

Multicomp(Statute)
95 % simultaneous confidence intervals for specified
linear combinations, by the Sidak method
critical point: 2.6806
response variable: sqrt(abs(Hv))
intervals excluding 0 are flagged by '**'
    Estimate Std.Error Lower Bound Upper Bound
S-U  -0.3230    0.0968      -0.583     -0.0635 **
S-P  -0.1270    0.1420      -0.507      0.2530
S-O  -0.1690    0.1540      -0.581      0.2430
U-P   0.1960    0.1600      -0.232      0.6240
U-O   0.1540    0.1740      -0.313      0.6220
P-O  -0.0419    0.2030      -0.586      0.5020

Multicomp(Region)
95 % simultaneous confidence intervals for specified linear combinations, by the Sidak method
critical point: 2.6806
response variable: sqrt(abs(Hv))
intervals excluding 0 are flagged by '**'
    Estimate Std.Error Lower Bound Upper Bound
W-E  -0.1700    0.0916     -0.4160      0.0755
W-S   0.2310    0.0933     -0.0187      0.4810
W-N  -0.0122    0.1820     -0.4990      0.4750
E-S   0.4020    0.1080      0.1120      0.6910 **
E-N   0.1580    0.1850     -0.3380      0.6540
S-N  -0.2440    0.1920     -0.7580      0.2710
```

The factors **Statute** and **Region** explain parts of the variability of the between-laboratory variability of the measurement of *Organic Carbon.* University laboratories are performing poorer than the State laboratories. Southern countries perform better than Eastern countries.

4.B Within-laboratory variability

No significant factors at the 0.01 level (after sqrt-transformation).

5. Total Nitrogen

5.A Between-laboratory variability

No significant factors at the 0.01 level (after sqrt-transformation).

5.B Within-laboratory variability

Analysis of Variance Table

```
Response: sqrt(Kv)
Type III Sum of Squares
              Df Sum of Sq Mean Sq F Value   Pr(F)
   Sample   2         3.4     1.70     6.5 0.00213
Residuals 112        29.3     0.26
```

Multicomp(Sample)

```
95 % simultaneous confidence intervals for specified
linear combinations, by the Tukey method
critical point: 2.3753
response variable: sqrt(Kv)
intervals excluding 0 are flagged by '**'
       Estimate Std.Error Lower Bound Upper Bound
A-B    -0.263     0.117      -0.542      0.0154
A-C    -0.416     0.117      -0.693     -0.1390     **
B-C    -0.153     0.117      -0.430      0.1240
```

Sample A gives better results than sample C concerning the internal variability.

6. Exchangeable elements

6.A Between-laboratory variability

Analysis of Variance Table

```
Response: sqrt(abs(Hv))
Type III Sum of Squares
                 Df            Sum of Sq        Mean Sq       F Value        Pr(F)
Statute          3              2               0.725          6.04         0.00046
Region           3              1               0.459          3.82         0.00974
Residuals      846            102               0.120
```

Multicomp(Statute)

```
95 % simultaneous confidence intervals for specified linear combinations, by the Tukey method
critical point: 2.5741
response variable: sqrt(abs(Hv))
intervals excluding 0 are flagged by '**'
    Estimate Std.Error Lower Bound Upper Bound
S-U  -0.1340    0.0327     -0.2180     -0.0496 **
S-P  -0.0157    0.0442     -0.1290      0.0981
S-O  -0.0701    0.0436     -0.1820      0.0421
U-P   0.1180    0.0508     -0.0126      0.2490
U-O   0.0637    0.0511     -0.0679      0.1950
P-O  -0.0545    0.0589     -0.2060      0.0971
```

Multicomp (Region)

```
95 % simultaneous confidence intervals for specified linear combinations, by the Tukey method
critical point: 2.5741
response variable: sqrt(abs(Hv))
intervals excluding 0 are flagged by '**'
    Estimate Std.Error Lower Bound Upper Bound
W-E  -0.0958    0.0300     -0.1730     -0.0187 **
W-S  -0.0325    0.0384     -0.1310      0.0664
W-N  -0.0799    0.0427     -0.1900      0.0299
E-S   0.0633    0.0419     -0.0444      0.1710
E-N   0.0160    0.0456     -0.1010      0.1330
S-N  -0.0473    0.0523     -0.1820      0.0874
```

Laboratories from government institutions have better results compared to academic laboratories. Western laboratories score better than laboratories from East Europe.

6.B Within-laboratory variability

```
Analysis of Variance Table

Response: sqrt(Kv)
Type III Sum of Squares
            Df Sum of Sq Mean Sq F Value      Pr(F)
   Sample  2        10    5.11     21.7 1.00e-009
    RefmC  1         6    6.07     25.8 4.71e-007
  Statute  3        15    5.10     21.7 0.00e+000
Residuals 846      199    0.24
Multicomp(Sample)
95 % simultaneous confidence intervals for specified
linear combinations, by the Tukey method
critical point: 2.3478
response variable: sqrt(Kv)
intervals excluding 0 are flagged by '**'
    Estimate Std.Error Lower Bound Upper Bound
A-B    0.108    0.0420     0.00974       0.207 **
A-C   -0.154    0.0404    -0.24900      -0.059 **
B-C   -0.262    0.0402    -0.35700      -0.168 **

Multicomp(RefmC)
95 % non-simultaneous confidence intervals for specified
linear combinations, by the Fisher LSD method
critical point: 1.9628
response variable: sqrt(Kv)
intervals excluding 0 are flagged by '**'
    Estimate Std.Error Lower Bound Upper Bound
0-1   -0.175    0.0344      -0.242      -0.107 **

Multicomp(Statute)
95 % simultaneous confidence intervals for specified
linear combinations, by the Tukey method
critical point: 2.5741
response variable: sqrt(Kv)
intervals excluding 0 are flagged by '**'
    Estimate Std.Error Lower Bound Upper Bound
S-U   0.0832    0.0453     -0.0333       0.200
S-P  -0.3900    0.0595     -0.5430      -0.237 **
S-O   0.1980    0.0602      0.0435       0.353 **
U-P  -0.4730    0.0688     -0.6500      -0.296 **
U-O   0.1150    0.0695     -0.0637       0.294
P-O   0.5880    0.0796      0.3830       0.793 **
```

Concerning the internal variability, the results for sample B are better then the results for the other samples. Sample C gives the poorest results. Laboratories working according to national methods perform better than laboratories using the reference methods. Private laboratories are providing poorer results than the other types of laboratories (state laboratories, universities and other).

7. Aqua regia extractable elements

7.A Between-laboratory variability

```
Analysis of Variance Table

Response: sqrt(abs(Hv))
Type III Sum of Squares
             Df Sum of Sq Mean Sq F Value      Pr(F)
  ExpLevC    1         2    2.10    15.9 0.000072
  Statute    3         2    0.77     5.8 0.000589
     Type    2         6    3.14    23.7 0.000000
   Region    3        10    3.35    25.3 0.000000
Residuals 1427       189    0.13


Multicomp (Statute)
95 % simultaneous confidence intervals for specified linear combinations, by the Sidak method
critical point: 2.6345
response variable: sqrt(abs(Hv))
intervals excluding 0 are flagged by '**'
    Estimate Std.Error Lower Bound Upper Bound
S-U -0.14900    0.0360     -0.2430     -0.0539 **
S-P -0.00505    0.0338     -0.0942      0.0841
S-O -0.06150    0.0365     -0.1580      0.0346
U-P  0.14400    0.0476      0.0181      0.2690 **
U-O  0.08710    0.0440     -0.0289      0.2030
P-O -0.05650    0.0489     -0.1850      0.0723

Multicomp (Region)
```

```
95 % simultaneous confidence intervals for specified linear combinations, by the Tukey method
critical point: 2.5721
response variable: sqrt(abs(Hv))
intervals excluding 0 are flagged by '**'
    Estimate Std.Error Lower Bound Upper Bound
W-E  -0.1780   0.0245    -0.24100     -0.1150 **
W-S  -0.2060   0.0311    -0.28600     -0.1260 **
W-N  -0.0427   0.0525    -0.17800      0.0922
E-S  -0.0276   0.0332    -0.11300      0.0577
E-N   0.1350   0.0531    -0.00137      0.2720
S-N   0.1630   0.0564     0.01800      0.3080 **
```

Multicomp (Type)

```
95 % simultaneous confidence intervals for specified linear combinations, by the Tukey method
critical point: 2.3462
response variable: sqrt(abs(Hv))
intervals excluding 0 are flagged by '**'
    Estimate Std.Error Lower Bound Upper Bound
P-G   0.110    0.0230     0.0559      0.1640 **
P-B  -0.111    0.0315    -0.1850     -0.0375 **
G-B  -0.221    0.0338    -0.3010     -0.1420 **
```

Multicomp(ExpLevC)

```
95 % non-simultaneous confidence intervals for specified
linear combinations, by the Fisher LSD method
critical point: 1.9616
response variable: sqrt(abs(Hv))
intervals excluding 0 are flagged by '**'
    Estimate Std.Error Lower Bound Upper Bound
0-1 -0.0987    0.0248      -0.147     -0.0501 **
```

Concerning the **Type** of laboratory, general purpose laboratories have better results than plant and soil laboratories and better than specialised soil laboratories.

With reference to the **Region**, Western laboratories are better than Southern and Eastern laboratories, and Northern are better than Southern. Note, however, than the factor **Region** is extremely unbalanced. Private and government laboratories have better results than academic laboratories. And experienced laboratories have poorer results than non-experienced laboratories.

7.B Within-laboratory variability

Analysis of Variance Table

```
Response: sqrt(Kv)
Type III Sum of Squares
            Df Sum of Sq Mean Sq F Value    Pr(F)
   Sample    2         2    1.18     7.0 0.000929
  Statute    3         8    2.78    16.5 0.000000
Residuals 1431       240    0.17
```

Multicomp (Sample)

```
95 % simultaneous confidence intervals for specified
linear combinations, by the Tukey method
critical point: 2.3461
response variable: sqrt(Kv)
intervals excluding 0 are flagged by '**'
    Estimate Std.Error Lower Bound Upper Bound
A-B  -0.0985   0.0274     -0.1630     -0.0342 **
A-C  -0.0791   0.0272     -0.1430     -0.0152 **
B-C   0.0194   0.0255     -0.0403      0.0792
```

Multicomp (Statute)

```
95 % simultaneous confidence intervals for specified linear combinations, by the Tukey method
critical point: 2.5721
response variable: sqrt(Kv)
intervals excluding 0 are flagged by '**'
    Estimate Std.Error Lower Bound Upper Bound
S-U   0.0233   0.0355     -0.0680     0.11500
S-P  -0.1040   0.0349     -0.1930    -0.01400 **
S-O   0.2090   0.0354      0.1180     0.30000 **
U-P  -0.1270   0.0461     -0.2460    -0.00834 **
U-O   0.1860   0.0466      0.0658     0.30500 **
P-O   0.3130   0.0461      0.1940     0.43100 **
```

Within laboratory variability was smaller for sample A than for sample B and C.
Private laboratories have poorer results than university, state and other laboratories.
Other laboratories have better results than university, state and private laboratories.

8. Total elements

8.A Between-laboratory variability

```
Analysis of Variance Table

Response: sqrt(abs(Hv))
Type III Sum of Squares
              Df     Sum of Sq      Mean Sq       F Value       Pr(F)
Trained        1           2.4         2.42          21.4     0.000006
Accr           1           1.5         1.46          12.9     0.000384
Statute        3           3.2         1.07           9.4     0.000005
Region         2           3.0         1.51          13.3     0.000003
Residuals    312          35.3         0.11

Multicomp (Statute)
95 % simultaneous confidence intervals for specified linear combinations, by the Sidak method
critical point: 2.6471
response variable: sqrt(abs(Hv))
intervals excluding 0 are flagged by '**'
        Estimate        Std.Error       Lower Bound Upper Bound
S-U    0.0259           0.0486          -0.1030        0.154
S-P      -0.3750        0.0712          -0.5630           -0.186       **
S-O      -0.1740        0.1100          -0.4650        0.117
U-P      -0.4000        0.0850          -0.6250           -0.175       **
U-O      -0.1990        0.1260          -0.5320        0.133
P-O    0.2010           0.1080          -0.0842        0.486

Multicomp(Region)
95 % simultaneous confidence intervals for specified
linear combinations, by the Tukey method  critical point: 2.355
response variable: sqrt(abs(Hv))
intervals excluding 0 are flagged by '**'
        Estimate        Std.Error       Lower Bound     Upper Bound
W-E     -0.3080         0.0741          -0.483          -0.1340     **
W-S     -0.2620         0.0771          -0.444          -0.0803     **
E-S     0.0461          0.1020          -0.195       0.2870

Multicomp(Trained)
95 % non-simultaneous confidence intervals for specified
linear combinations, by the Fisher LSD method
critical point: 1.9676
response variable: sqrt(abs(Hv))
intervals excluding 0 are flagged by '**'
    Estimate Std.Error Lower Bound Upper Bound
0-1    0.246    0.0533       0.142       0.351 **

Multicomp(Accr)
95 % non-simultaneous confidence intervals for specified
linear combinations, by the Fisher LSD method
critical point: 1.9676
response variable: sqrt(abs(Hv))
intervals excluding 0 are flagged by '**'
    Estimate Std.Error Lower Bound Upper Bound
0-1    0.255    0.0709       0.115       0.394   **
```

Four factors significantly contribute to the variability in the regression model: whether the personnel is **Trained** or not, whether the laboratory has received **Accreditation** for the method, the **Statute** of the laboratory and the **Region**. Note that these factors are rather unbalanced:

	0	1	2	3
Trained	77	273		
Experience level	166	154		
Accreditation	255	65		
Statute	171	86	38	25
Region	261	36	23	0

Laboratories with trained personnel or with accreditation score better. Private laboratories make more mistakes than state laboratories and university laboratories. Laboratories in Western Europe have better results than laboratories in Eastern or Southern Europe.

8.B Within-laboratory variability

The factors **ExpLevC** and **Forest** contribute significantly to the variability.

```
Analysis of Variance Table

Response: sqrt(Kv)
Type III Sum of Squares
            Df      Sum of Sq        Mean Sq      F Value       Pr(F)
ExpLevC     1             3.0    3.03        25.3           0.00000
Forest      1             0.9    0.94         7.8           0.00543
Residuals   317          37.9          0.12
```

Laboratories with experience have smaller within-laboratory variability compared to laboratories without experience.
General purpose laboratories have poorer results than specialised forest laboratories.

```
Multicomp (ExpLevC)
95 % non-simultaneous confidence intervals for specified
linear combinations, by the Fisher LSD method critical point: 1.9675
response variable: sqrt(Kv)
intervals excluding 0 are flagged by '**'
    Estimate Std.Error Lower Bound Upper Bound
0-1    0.204    0.0405       0.124        0.283    **

Multicomp(Forest)
95 % non-simultaneous confidence intervals for specified
linear combinations, by the Fisher LSD method
critical point: 1.9675
response variable: sqrt(Kv)
intervals excluding 0 are flagged by '**'
       Estimate        Std.Error       Lower Bound     Upper Bound
0-1    0.115           0.041           0.0341          0.196    **
```

9. Acid oxalate extractable Fe and Al

9.A Between-laboratory variability

```
Analysis of Variance Table

Response: sqrt(abs(Hv))
Type III Sum of Squares
          Df Sum of Sq Mean Sq F Value   Pr(F)
    RefmC  1      0.94    0.94    15.9 0.00013
     Accr  1      3.29    3.29    55.5 0.00000
  Statute  3      3.87    1.29    21.8 0.00000
Residuals 98      5.80    0.06

Multicomp(RefmC)
95 % non-simultaneous confidence intervals for specified
linear combinations, by the Fisher LSD method
critical point: 1.9845
response variable: sqrt(abs(Hv))
intervals excluding 0 are flagged by '**'
    Estimate Std.Error Lower Bound Upper Bound
0-1     0.24    0.0603       0.121        0.36 **

Multicomp(Accr)
95 % non-simultaneous confidence intervals for specified
linear combinations, by the Fisher LSD method
critical point: 1.9845
response variable: sqrt(abs(Hv))
intervals excluding 0 are flagged by '**'

    Estimate Std.Error Lower Bound Upper Bound
0-1    0.953     0.128       0.699        1.21    **

Multicomp(Statute)
95 % simultaneous confidence intervals for specified
linear combinations, by the Sidak method
critical point: 2.6827
response variable: sqrt(abs(Hv))
intervals excluding 0 are flagged by '**'
    Estimate Std.Error Lower Bound Upper Bound
S-U   -0.241    0.0629     -0.4100     -0.0723    **
S-P   -0.649    0.0864     -0.8810     -0.4170    **
S-O    0.106    0.1050     -0.1740      0.3870
U-P   -0.408    0.0959     -0.6650     -0.1510    **
U-O    0.347    0.1150      0.0398      0.6550    **
P-O    0.755    0.1310      0.4050      1.1100    **
```

Laboratories using the reference method or which are accredited for the analyses of *Reactive Fe and Al* have better results than the other laboratories. Private laboratories perform worse than all the other types of laboratories. State laboratories have better results than university or private laboratories. The laboratories, grouped under the name 'other' are better than university or private laboratories, but not significantly better than state laboratories.

9.B Within-laboratory variability

```
Analysis of Variance Table

Response: sqrt(Kv)
Type III Sum of Squares
          Df Sum of Sq Mean Sq F Value    Pr(F)
  Statute  3      1.24   0.413    4.69 0.00420
     Type  2      0.91   0.457    5.19 0.00721
   Forest  1      0.66   0.663    7.52 0.00725
Residuals 97      8.55   0.088

Multicomp(Statute)
95 % simultaneous confidence intervals for specified
linear combinations, by the Sidak method
critical point: 2.6832
response variable: sqrt(Kv)
intervals excluding 0 are flagged by '**'
    Estimate Std.Error Lower Bound Upper Bound
S-U   0.2750    0.0822      0.0542       0.495 **
S-P   0.1730    0.0935     -0.0779       0.424
S-O   0.0209    0.1330     -0.3360       0.377
U-P  -0.1020    0.1210     -0.4270       0.224
U-O  -0.2540    0.1480     -0.6510       0.143
P-O  -0.1520    0.1590     -0.5780       0.274

Multicomp(Type)
95 % simultaneous confidence intervals for specified
linear combinations, by the Tukey method
critical point: 2.3802
response variable: sqrt(Kv)
intervals excluding 0 are flagged by '**'

    Estimate Std.Error Lower Bound Upper Bound
P-G  -0.0947    0.0798      -0.285      0.0953
P-B  -0.3410    0.1060      -0.594     -0.0871 **
G-B  -0.2460    0.0979      -0.479     -0.0129 **

Multicomp(Forest)
95 % non-simultaneous confidence intervals for specified
linear combinations, by the Fisher LSD method
critical point: 1.9847
response variable: sqrt(Kv)
intervals excluding 0 are flagged by '**'
    Estimate Std.Error Lower Bound Upper Bound
0-1   -0.216    0.0787      -0.372     -0.0597 **
```

Specific forestry laboratories have poorer results than general laboratories. University laboratories have smaller within-laboratory variability than governmental laboratories and soil laboratories are better than plant and soil or general laboratories.

Annex 10: Guidelines for reporting

1. Introduction

The results of the third interlaboratory ring test revealed that several laboratories made technical mistakes in the data reporting. The importance of this type of errors should not be neglected. These 'guidelines for reporting' are meant to be a tool for correct and accurate reporting. Before data reporting, these guidelines could form a practical help for thorough verification of the laboratory results. In this way technical mistakes (as in the third ring test) could be avoided and data quality improved.
Below the different types of technical mistakes will be discussed. All necessary calculations, although often really basic, are mentioned in these guidelines. As a practical help, some data integrity expert rules are included.

2. Units

One of the most frequently made mistakes, is the use of wrong units. As the required unit might differ from the unit that is used on a daily basis in the laboratories, it is necessary to check all reported units carefully. The use of wrong units, wrong calculations, and the misreporting of results (e.g. filling in wrong columns) are mistakes that can easily avoided, by checking the data thoroughly, preferably by several different persons. Table X.1 gives an overview of the units and the accuracy required in the Manual for Sampling and Analysis of Soil (FSCC, 2003).

Table X.1 : Required units of the different parameters

Parameter	Unit	Decimals
Physical soil parameter		
Organic layer weight	kg/m^2	2
Coarse fragments	%	0
Bulk density	kg/m^3	0
Particle size distribution (FAO, 1990a)	-	-
Clay content	%	0
Silt Content	%	0
Sand Content	%	0
Chemical soil parameter		
$pH(CaCl_2)$	-	1
Organic carbon	g/kg	1
Total nitrogen	g/kg	1
Carbonates	g/kg	0
Aqua Regia extracted P, Ca, K, Mg, Mn	mg/kg	1
Aqua Regia extracted Cu, Pb, Cd, Zn	mg/kg	1
Aqua Regia extracted Al, Fe, Cr, Ni, S, Hg, Na	mg/kg	1
Exchangeable Acidity	$cmol_{(+)}/kg$	2
Exchangeable Cations:Ca, Mg, K, Na, Al, Fe, Mn, H	$cmol_{(+)}/kg$	2
$pH(H_2O)$	-	2
Total Elements:Ca, Mg, Na, K, Al, Fe, Mn	mg/kg	1
Oxalate extractable Fe, Al	mg/kg	1

To recalculate the results from one unit to another, the following guidelines can be used:
<u>Recalculation g/kg → $cmol_{(+)}/kg$</u>

$$\text{Result in } cmol_{(+)}/kg = \frac{\text{Result in } g/kg}{\text{Equivalent Weight}} \times 100 \qquad (1)$$

Note: All parameters are asked in $cmol_{(+)}/kg$. It is thus necessary to recalculate all elements that are multivalent (e.g. Al^{3+}, Fe^{2+},...) to $cmol_{(+)}/kg$. For this reason formula (1) uses the Equivalent weight in stead of the Molar Mass. Note that $cmol_{(+)}$ is equal to the notation $cmol_c$.

```
Example:     Exchangeable Mg   =    0.22 g/kg
             Equivalent weight =    Molar Mass/Valences
                               =    24.3 / 2
                               =    12.16
             Exchangeable Mg   =    (0.22 /12.16)*100
                               =    1.81  cmol(+)/kg
```

3. Moisture Content

FSCC asks to report the results on oven dry basis. If the analyses were carried on an air dry soil, a correction factor (moisture content of the soil) is necessary to convert the data.
The conversion from air dried soil to oven dried soil can be done according the following formula:

$$\text{Results on oven dry soil} = \text{Results on air dry soil} * (1 - \text{moisture content } (\%)) \quad (2)$$

Note: The soil moisture content is a mandatory parameter for both organic and mineral layers, reporting in % with one decimal place.

4. Data below the Quantification Limit

The processing of the ring test was hampered by the confusion concerning the values below the detection limit. Learning from the past experiences, a consistent strategy concerning this matter is set out.
It is chosen to make use of the **quantification limit (QL)** instead of the **detection limit (DL).** The quantification limit is a plural of the method detection limit. It is the lowest value that can be reported with a sufficient certainty.

$$QL = DL * \text{Correction factor} \quad (3)$$

Where the correction factor (>1) varies according to the analysis method.

The method detection limit includes the whole procedure, from sample preparation until the analysis result (including heating, shaking, making a solution, etc). Values situated between the method detection limit and the quantification limit can be measured, but with a big uncertainty. For this reason, **measured values below the quantification limit should not be reported**. The reporting of values below the quantification limit can lead to confusion and misunderstanding. For this reason, it was agreed during the 3rd ring test to **provide** for results below the quantification limit, a negative value, equal to the **negative quantification limit**.

5. Data integrity expert rules

The rules, shown in Table X.2 (adapted from Van Mechelen et al., 1997), can help to evaluate the analysis results. If one of the rules is broken, there is a severe indication that the results are not correct. In this case it is necessary to check all analysis and calculations, it might even be advisable to re-analyse the involved samples.

References

Forest Soil Co-Ordinating Centre, 2003. Manual on methods and criteria for harmonized sampling, assessment, monitoring and analysis of the effects of air pollution on forests. Part IIIa. Sampling and Analysis of Soil. UN/ECE Convention on Long-Range Transboundary Air Pollution, International Co-operative Programme on Assessment and Monitoring of Air Pollution Effects on Forests.

Vanmechelen, L., Groenemans R., Van Ranst E. 1997. Forest Soil Condition in Europe. Results of a Large-Scale Soil Survey. Prepared by Forest Soil Co-Ordinating Centre in Co-Operation with the Ministry of the Flemish Community. EC-UN/ECE, Brussels, Geneva.

Table X.2 : Data integrity expert rules

Rule N°	Parameter	Description	Permissible limit values		Conditions for application
			lower	upper	
1	pH	Checks pH results in presence of carbonates	5.5 6.0	- -	$CaCO_3$>0 for Organic Horizons $CaCO_3$>0 for Mineral Horizons
2	Organic Carbon	Checks organic C content (g/kg) in organic layers	80	-	Organic Horizons
3	C/N	Checks the C/N ratio in organic and mineral layers	5 3	100 75	Organic Horizons Mineral Horizons
4	C/P	Checks the C/P ratio in organic and mineral layers	100 10	2500 750	Organic Horizons Mineral Horizons
5	CaCO3	Checks the carbonate content (g/kg) in soils with low pH	0	0	pH<5
6	AcExc	Checks the exchangeable acidity value(cmol$_{(+)}$/kg) in organic and mineral layers	0.5 0	250 150	Organic Horizons Mineral Horizons
7	ACE (1)	Checks the exchangeable acid cation concentration (cmol$_{(+)}$/kg) in organic and mineral layers	0.5 0	250 150	Organic Horizons Mineral Horizons
8	BCE (2)	Checks the exchangeable basic cation concentration (cmol$_{(+)}$/kg) in organic and mineral layers	0.5 0.1	400 150	Organic Horizons Mineral Horizons
9	CEC (3)	Checks the cation exchange capacity (cmol$_{(+)}$/kg) in organic and mineral layers	1 0.5	400 150	Organic Horizons Mineral Horizons
10	BS (4)	Checks the base saturation (%) in presence of carbonates	90	100	$CaCO_3$>0

Legend:

(1) ACE: Exchangeable acid cation concentration (cmol(+)/kg) = Sum of exchangeable acid cations (Al + Fe + Mn + H)

(2) BCE: Exchangeable basic cation concentration (cmol(+)/kg) = Sum of exchangeable basic cations (Ca + K + Mg + Na)

(3) CEC: Cation Exchange Capacity (cmol(+)/kg) = Sum of exchangeable cations (ACE + BCE)

(4) BS: Base Saturation = 100*BCE/CE