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Manual of Standard Methods
for
Establishing the Global Geochemical Reference Network

Chapter 7

Quality Control Procedures

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7.1. Introduction

The analytical data that will be produced for the Global Geochemical Reference Network project are environmentally sensitive and important for the present and future generations of humankind because, apart from their use as reference data for levelling the more detailed national geochemical data sets, they will be used by many disciplines and for different purposes (Fig. 7.1). Consequently, they must be of proven quality and integrity.

To ensure the quality of generated geochemical data, a rigorous quality control and assurance procedure must be installed from the start of the project. The same quality control procedure should be in place for any geochemical survey at any mapping scale.

The quality control procedure for each generated geochemical data set should end with the estimation of sampling, analytical, and geochemical variance, and measurement uncertainty[1] (Ramsey, 1997, 1998; Ramsey and Argyraki, 1997; Ellison *et al.*, 2000; Ramsey and Ellison, 2007; Ellison and Williams, 2007, 2012; Demetriades, 2011; Majcen *et al.*, 2011; Ramsey *et al.*, 2019).

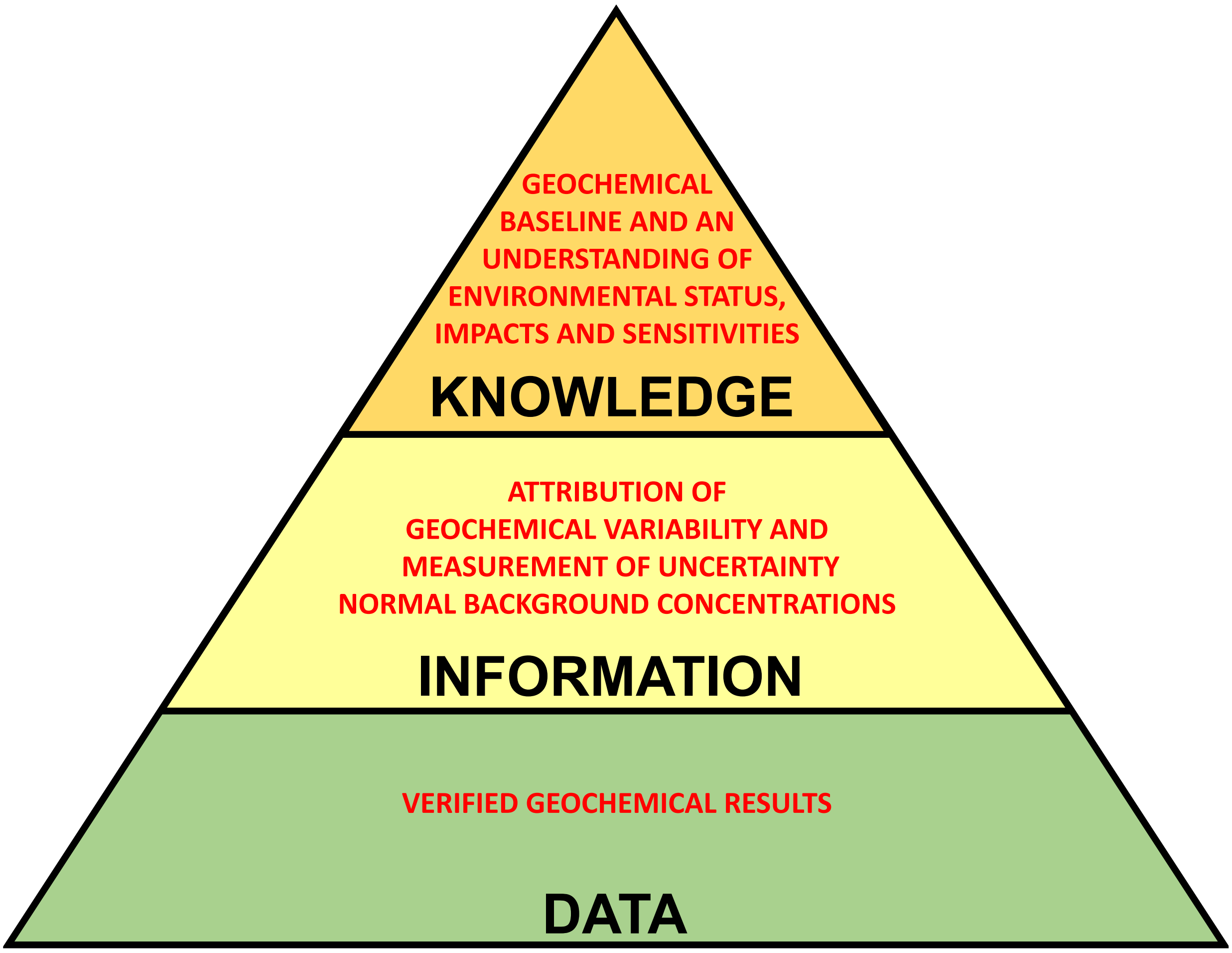

Figure 7.1. The triangular diagram shows how quality control procedures can contribute to two levels of the DATA + INFORMATION = KNOWLEDGE equation. Quality control produces the DATA set (verified geochemical results). This along with attribution of geochemical variability and measurement of uncertainty, plus other parameters such as threshold and normal background concentration determinations (INFORMATION) contribute to the KNOWLEDGE of the geochemical baseline and an understanding of environmental status, impacts and sensitivities. Plotted by Christopher C. Johnson (GeoElementary/IUGS-CGGB) with Microsoft™ PowerPoint.

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[1] Course on "*Estimation of Measurement Uncertainty in Chemical Analysis*": https://sisu.ut.ee/measurement/uncertainty

7.1.1. Obligations of leading applied geochemist

At present, most commercial laboratories are accredited. It is very important to understand, however, the accreditation process. A laboratory is considered competent in the application of specific documented laboratory methods and standard operating procedures. Accreditation mandates keeping a record of all procedures that a batch of samples undergoes in the laboratory. Hence, any errors can be located by backtracking. Accreditation requires that quality control and quality assurance programmes be in place for all aspects of the laboratory operations. All facilities and equipment are tightly scrutinised to assure adequacy for intended applications, and the laboratory must be participating in a proficiency analytical testing programme. To put it simply, an accredited laboratory has the right '*internal*'[2] procedures in place to analyse samples. It is, therefore, the professional responsibility of the leading applied geochemist of the project to install his/her own independent '*external*'[2] quality control procedures to ensure that the results received are of a good standard and fit for the purposes of the project. Hence, *the project manager must ensure that there is in the team a professional applied geochemist with the skills to organise the project's quality control procedure, and to check the quality and integrity of the analytical results received from the laboratory*.

It is important to remember that the analytical results of the Global Geochemical Reference Network project must be of high quality and integrity, as has already been stressed. Therefore, the leading applied geochemist must not rely on the '*element concentration numbers*' given by the laboratory. He/she must ensure that these '*numbers*' are meaningful, and are validated by his/her independent external quality control results. Consequently, the leading applied geochemist, upon receipt of the analytical results, must check them thoroughly to verify their quality and integrity.

For the Global Geochemical Reference Network project, it is proposed that there should be an international Quality Control Committee, which will organise the quality control procedure from sampling to sample preparation, and subsequently the randomisation of samples and insertion of project reference samples, and splits of routine and field duplicate samples.

Upon receipt of the analytical results, the Quality Control Committee studies the analytical report of the laboratory, before proceeding to check the quality of the project analytical results. Afterwards, proceeds in the arduous task of verification of the quality of the analytical data, using the project's external quality control results, and the laboratory's internal quality control results. If the leading applied geochemist, or the Quality Control Committee, is not satisfied with the quality of analytical results, then the laboratory is obliged to reanalyse the problematic batch or batches of samples, or even the whole sample suite. Verifying the quality of the generated analytical results is an important condition that should be included in the contract with the laboratory, and even an in-house laboratory.

When satisfied with the quality of the analytical results, an analysis of variance (ANOVA) is the final step of quality control for any geochemical mapping project. A procedure to estimate the geochemical, sampling and analytical variation, as well as measurement uncertainty, is performed by using the robust statistical method proposed by Ramsey (1998; Lee and Ramsey, 2001; Lyn *et al.*, 2007, Boon, 2009; Demetriades, 2011). The results of robust analysis of variance show the contribution to measurement uncertainty that arises from the processes of primary sampling and chemical analysis. In the Global Geochemical Reference Network project, the estimation of measurement uncertainty of the analytical results of each determinand or measurand is of paramount importance, because it is a parameter that describes quantitatively the quality of geochemical results. Some laboratories nowadays report measurement uncertainty, but it is prudent for the leading applied geochemist or the Quality Control Committee to estimate

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[2] An accredited laboratory has its own '*internal*' quality control procedure installed. The applied geochemist for the verification of the integrity and quality of the analytical results should install his/her independent '*external*' quality control procedure, which is unknown to the laboratory.

measurement uncertainty using the project's own independent quality control results. The requirement is that the combined sampling and analytical variances should be considerably smaller than the regional or spatial variability (geochemical variance) for the construction of a reliable geochemical map.

When satisfied with the quality of analytical results, then and only then the leading applied geochemist or Quality Control Committee should sanction the second step, which is the processing of geochemical data leading to map plotting.

As the generated data of the Global Geochemical Reference Network project are of interest to the whole geoscientific community, and not only, it is important to write a detailed quality control report for all the different geochemical data sets generated by different analytical methods and laboratories. Hence, the statement that *the generated Global Geochemical Reference Network project data must be legally defensible, according to international guidelines or national legislation*. So, *the first and foremost obligation of the Global Geochemical Reference Network project manager is the delivery of good quality geochemical data for multipurpose use*.

7.2. Quality control report

Upon receiving the analytical results from the laboratory the quality and integrity of the data should be verified, using various statistical techniques (see Section §7.3). The assessment report of the quality of analytical data is an integral part of any geochemical project, and must be compiled and made available as an open file report.

For further information, the freely available quality control reports of the EuroGeoSurveys project *'Geochemical Mapping of Agricultural and Grazing land soil'* (GEMAS) should be consulted (Reimann *et al.*, 2009, 2011, 2012; Demetriades *et al.*, 2014), and the procedures discussed by Johnson (2011) and Demetriades (2011).

7.3. Data checking

7.3.1. Checking of raw analytical data

Johnson (2011) has written a well-documented chapter "*Understanding the Quality of Chemical Data from the Urban Environment − Part 1: Quality Control Procedures*" in the textbook "*Mapping the Chemical Environment of Urban Areas*" (Johnson *et al.*, 2011), which should be consulted. The procedure for checking the raw analytical data upon receipt from the laboratory is given below.

The first assessment of data quality will consist of simple and obvious procedures that involve looking at the analytical results, as they are received from the laboratory. This needs to be done systematically, directly after the results are received, so any quality issues can be dealt with promptly. A series of questions should be addressed:

1. Are all the elements specified in the contract reported?
2. Is the number of samples reported, the same as the number of samples submitted?
3. Are the samples analysed in the correct order and date/time stamps provided?
4. Are the results reported with the correct concentration units?
5. Have results outside detection limits and/or missing data been reported correctly?
6. Have the values been reported with the requested number of significant digits?
7. Does the range of element values for each element look reasonable for the survey area?
8. Can any systematic trends (analytical drift or cross-sample contamination) be identified in samples reported in the order they were analysed?

Answers to the above questions will give an immediate impression of the quality of the analytical results, and it is at this stage that the most obvious problems with the data can be identified.

At this point, something should also be done for missing, semi-quantitative and unreliable data (see Johnson *et al.*, 2018), as such data will affect the data analysis process (see Reimann *et al.*, 2008, Chapter 2, p.13-28).

An archive of the original analytical data file, as received from the laboratory, should always be saved before any changes are made, and for data processing a work file should be prepared.

If the project samples have been given new random numbers, then the first task is to associate them with those in the original field database, where all control samples are characterised. For extracting all control sample analytical results, such as those of duplicates, replicates, project reference materials, and project blanks, it is recommended that the samples should be suitably coded in the original database, before the assigning of new random numbers, and the submission to the laboratory as proposed by Johnson (2011), *i.e.*:

- Field duplicate samples: DUPA and DUPB.
- Field replicate samples: REPA and REPB.
- Project reference material[3](s): REF1, REF2, REF3, REF4 and REF5 (in case more than one Project reference material has been prepared), and
- Project solid blank material: BLK1 and BLK2 (refer to Chapters 4 & 5 in this Manual).

Upon preparing different files of the quality control data, the leading applied geochemist or Quality Control Committee can proceed to check the quality of analytical results by a variety of statistical techniques, which are described below. Most of these descriptions have been abstracted from Johnson (2011) and Demetriades (2011). Other open file quality control reports that should be consulted are by Reimann *et al.* (2009, 2011, 2012).

7.3.1.1. Laboratory reagent blank samples

Firstly, check the analytical results of the laboratory reagent blank samples, which should be all below the laboratory's lower detection limit (LDL) for all elements determined. The reagent blank is made-up of the same acids (plus deionised water), which are added to the solid[4] samples for bringing into solution the chemical elements (Johnson, 2011; Magnusson and Örnemark, 2014; Cantwell, 2019). The primary purpose of the reagent blank samples is to trace any interferences or contamination introduced during any part of the measurement procedure in the laboratory. Therefore, if elevated values are observed for any element, then laboratory contamination is suspected, and it should be checked by reanalysis of the sample batch or batches analysed during that particular period. Once satisfied with this particular visual test, the verification of the quality of the analytical results can proceed.

7.3.1.2. Project solid blank materials

Secondly, check the analytical results of project solid blank materials. It is noted that the aliquots of solid blank materials are packed in the field, and go through the sample preparation procedure as the routine project samples, and their main purpose is to indicate contamination during sample preparation (Schermann, 1990).

If the solid blank material is pure silica, then the concentration of all elements, except Si, should be below the laboratory's lower detection limit. However, if the solid blank material is kaolinite (Schermann, 1990), then the analytical results should be within the accepted limits, as estimated by the standardisation procedure (see Chapter 5 in this Manual). If the results deviate

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[3] Project reference materials are called Secondary Reference Materials (SRMs)

[4] 'Solid' samples are the analysed aliquots of the collected rock, soil and sediment samples.

from the accepted limits, then most likely the aliquots of the solid blank material have been contaminated either during sample preparation or laboratory analysis. If the laboratory blank samples (*e.g.*, reagent blank or pure silica sand) are below the lower detection limit in that particular analytical batch or batches, then the project solid blank material has been contaminated during sample preparation.

It should be noted that the duplicate-replicate splits or secondary reference materials (SRMs) can be used also to indicate introduced contamination. A duplicate-replicate split would only indicate *'within batch*' contamination, while a secondary reference material could give an indication of *'between batch*' contamination.

The results of the suspected batch or batches of contaminated routine samples (rock, soil, sediment) should be studied carefully to assess the extent of contamination, and examine if it can be corrected by applying a correction factor, otherwise, new samples should be collected.

7.3.1.3. Project blank water samples

The analytical results of filtered blank water samples (see Chapter 3.3 in this Manual) are checked to ensure that all values are below the lower detection limit. If not, then the filtered blank water samples may have been contaminated during sampling or acidification. The results of the suspected batch or batches of contaminated routine stream water samples should be studied carefully to assess the extent of contamination, and if it can be corrected by applying a correction factor, otherwise new samples should be collected.

7.3.1.4. Control charts

According to Johnson (2011, p.67-71), the results for reference materials can be plotted on a control chart (also referred to as a Shewhart control chart or X-Chart), which is a time-sequenced graph with fixed defining limits (Miller and Miller, 2005). An example of such a chart is given in Figure 7.2. The X-axis shows the date of analysis or the laboratory batch, if batch numbers are assigned sequentially. The Y-axis displays the element concentration and the accepted value (AV) for the reference material, a value calculated from previous repeated analyses of the certified secondary reference materials (see Chapter 8 in this Manual). The AV will depend on the method of chemical extraction and analysis, *i.e.*, a partial method of extraction will yield a lower AV than a total extraction method. The AV used on the control chart must be that which has been determined by the same analytical method as the one used for the sample analyses undergoing the quality control procedures. It is impossible to know what the 'true' value of the reference material is, but the AV should be a good approximation of it. Defining limits of the secondary reference material are also plotted on the chart; in Figure 7.2, these are calculated as the AV ±2 and ±3 standard deviations (SD).

The AV±2SD threshold is normally used as an alert to possible analytical problems, and exceeding the AV±3SD requires an explanation, and a possible indication that the batch of samples needs reanalysis, particularly if this is a trend, observed for more than one element. This process of plotting a control chart is something that is usually done by the laboratory with its internal reference materials. Using the secondary reference materials (SRMs) inserted in each sample batch, the applied geochemists can check accuracy for themselves by visual inspection of these plots.

Accuracy is a measurement of how close to a 'true' or 'accepted' value a result is. A scattering of results about the AV line is to be expected, though a consistent trend to a higher or lower value would be referred to as *analytical bias*.

Control charts are invaluable in detecting analytical shifts that can occur over time, as, *for example*, after the installation of a new X-ray tube in X-ray fluorescence spectrometry (XRFS) or when any analytical instrument has been recalibrated. This can be used to identify levelling factors, required to level chemical results collected over a long period (Johnson *et al.*, 2018; and Chapter 8 in this Manual).

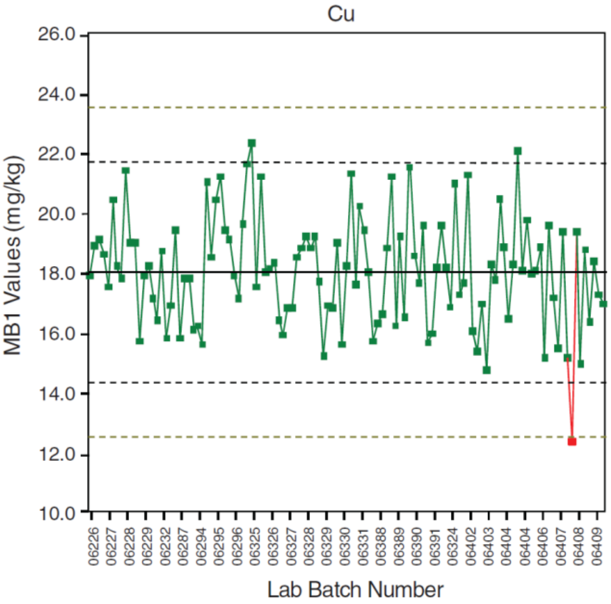

Figure 7.2. Example of a control chart plot using QI Analyst software for the BGS Moroccan secondary reference material MB1 (after Johnson et al., 2001, Fig. 2.4, p.10). The central solid line represents the accepted value (AV) of the secondary reference material; outer black and olive colour dashed lines are at AV ± 2SD and ± 3SD, respectively. The red dot and line represent a batch that fails QC criteria. Source: Johnson (2011, Fig. 5.4, p.68).

The second example is a control chart of a project reference material (Fig. 7.3), which does not show the expected random variation of the individual sub-sample results about the accepted value (AV). It has many outliers, and even time trends. Such data cannot be accepted when the objective is to compare the analytical results among different countries (in this example, different cities); in this plot, problems (time trends) are shown even between two analytical batches of the same city.

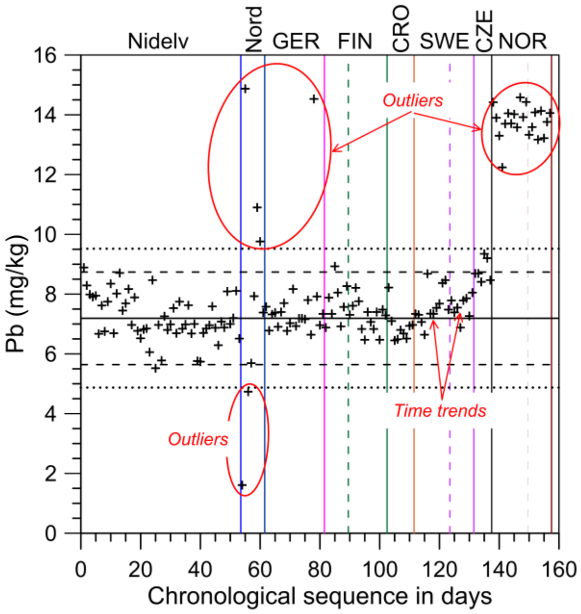

Figure 7.3. Example of a control chart for a secondary reference material used in the EuroGeoSurveys URGE I project. The central solid line represents the accepted value (AV); outer dashed lines are at AV ±2SD and dotted lines at AV ±3SD. The secondary reference material was used in the urban geochemical mapping projects in different European cities, the results of which are separated by solid coloured lines. In some cases, the city samples were analysed in two different batches and at different times, and dashed lines separate the two batches. Plotted by Alecos Demetriades, Hellenic Institute of Geology and Mineral Exploration (IGME) and IUGS Commission on Global Geochemical Baselines (IUGS-CGGB) with Golden Software's Grapher™ v20.

7.3.1.5. Precision

Analytical precision can be calculated by different statistical methods as described by Johnson (2011) and Demetriades (2011).

Precision is a measurement of how closely the analytical results can be reproduced, and is independent of the true value (*i.e.*, results can all show close agreement, but they may be a long way from the accepted value, AV). A visual impression of precision can be gained from the control chart (Figs. 7.2 & 7.3), since data will plot in a much narrower band if the method has good precision. Similar visual impressions of precision can be given by X-Y plots (Fig. 7.4) and Thompson and Howarth plots (see Section §7.3.1.9), which are described below. Overall precision at the 95% confidence level can be also estimated quantitatively, based on the mean ($\bar{x}$) and standard deviation (SD) expressed as a percentage:

$$\text{Overall Precision, P (\%)} = \frac{1.96^{5} * \text{SD}}{\bar{x}} * 100 \qquad (1)$$

$$\text{Coefficient of variation, CV (\%)} = \frac{\text{SD}}{\bar{x}} * 100 \qquad (2)$$

Substituting CV in Equation 1:

$$\text{P (\%)} = 1.96 * \text{CV} \qquad (3)$$

It should be noted that the calculation of the '*overall precision*' by the above equations is an oversimplification because it estimates the average precision for a range of element concentrations, which are assumed to follow a normal Gaussian distribution about their mean ($\bar{x}$) concentration (Fletcher, 1981). However, it is well known that most geochemical distributions are multimodal. Hence, the reason for referring to this parameter as '*overall precision*'.

An important feature of precision is that it varies with concentration (Thompson and Howarth, 1976; Fletcher, 1981, 1986; Demetriades, 2011). At low concentrations, near to the detection limit precision is poor, and normally improves with increasing concentration.

Other methods for the estimation of precision are described below.

7.3.1.6. Duplicate-replicate X-Y plot

According to Johnson (2011, p.69-70), a simple X-Y plot of duplicate-replicate pair results for an element gives an immediate visual appreciation of the laboratory precision for that particular element (Fig. 7.2). If in these plots the cluster of points does not follow closely the line of gradient 1, but instead forms a dispersed scatter of points, then data for that element should either be rejected or used with caution. A random scatter would indicate that variability in the results is most likely generated in the laboratory (for replicate samples) or includes significant within-site variability (if seen in the duplicate plots).

Figure 7.4 displays example plots from the British Geological Survey G-BASE soil samples for East Midlands urban samples. The Cu plot shows that the sampling and analytical variances are low, so there is confidence that the Cu results reflect actual between site variability. The Ni plot exhibits a few outlying DUPA versus DUPB points, indicating that when a site is sampled for a second time there are occasional significant within-site variations, a feature displayed for

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[5] The value for which P = 0.05, or 1 in 20, is 1.96 (Fisher, 1973). As the normal distribution is symmetric, $P(-1.96<X<1.96) \approx 0.95$, approximately 95% of the area under a normal distribution curve lies within roughly 1.96 standard deviations of the mean (JCGM 100, 2008, p.70). Due to the central limit theorem, 1.96 is used in the construction of the 95% confidence intervals (Dixon and Massey, 1969).

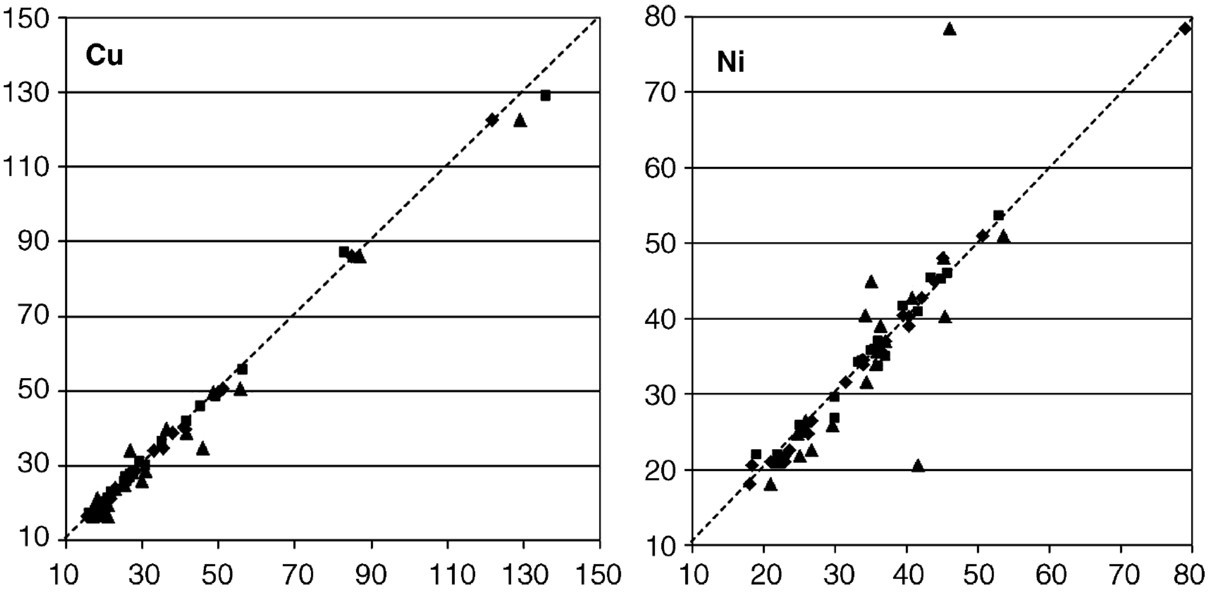

Figure 7.4. Duplicate-replicate plots for Cu and Ni for G-BASE urban soil (35-50 cm) from United Kingdom East Midlands. Axis units in mg/kg. Triangle = DUPA versus DUPB; Square= REPA versus DUPA; and Diamond = REPB versus DUPB (all x-axis versus y-axis). Notation: DUPA = Routine sample; REPA = Replicate split of routine sample; DUPB = Field duplicate sample; REPB = Replicate split of field duplicate sample. Source: Johnson (2011, Fig. 5.6, p.69).

the same duplicate pairs by other elements (*e.g.*, Fe, V, Cr and Co - not illustrated herein). This is to be expected in urban areas, where there is greater inhomogeneity in soil over short distances due to anthropogenic contamination.

This method is only applicable if there is a sufficient number of duplicate-replicate pairs with a range of element concentrations that can produce a meaningful plot. When only a single or a small number of duplicate-replicate pairs are available, Thompson-Howarth plots (Thompson and Howarth, 1976, 1978; Thompson, 1983; AMC, 2002) described below, can be used.

A quantitative measure of variability can be determined from the duplicate and replicate pairs for each element:

$$\text{Variability (Var)} = \frac{\sum(X_{\text{DUPA}}-X_{\text{DUPB}})^2}{N} \tag{4}$$

where X is an element concentration and N the number of sample pairs. Standard deviation (SD) is estimated by:

$$\text{Standard deviation (SD)} = \sqrt{\text{Var}} \tag{5}$$

Substituting SD in equation 2 with the terms of equation 5 gives the:

$$\text{Coefficient of Variation (CV) \%} = \frac{\sqrt{\text{Var}}}{\bar{x}} * 100 \tag{6}$$

Substituting CV in equation 6 with the terms of equation 3 gives the:

$$\text{Precision, P (\%)} = 1.96 * \frac{\sqrt{\text{Var}}}{\bar{x}} * 100 \tag{7}$$

Software for X-Y plots is readily available and Microsoft™ Excel or R routines provide satisfactory graphs (Reimann *et al.*, 2008). The BGS G-BASE project uses the macro facility of

Microsoft™ Excel rapidly to plot duplicate-replicate graphs for some 50 elements simultaneously. Charts of interest can be subsequently extracted and formatted suitably for publication. A Microsoft™ Excel workbook, 'IUGS-CGGB_Chapter-7_ DUPREPPLOT.xlsm' by Christopher C. Johnson is available (refer to the Supplementary material). See also worked example in Section §7.4.1.

7.3.1.7. Practical detection limit and analytical precision

The analytical precision can be calculated by another method as described below (Demetriades 2011, p.81−83).

The practical detection limit and analytical precision can be estimated by using the method proposed by Howarth and Thompson (1976) and Thompson and Howarth (1976, 1978), with modifications made by Demetriades (2011) at a particular step of the procedure. Replicated analyses are performed on at least 55 randomly selected samples. The steps followed are:

1. Calculate the mean values of the 55 pairs [$(X_1+X_2)/2$]. According to Thompson and Howarth (1978), this mean value is an estimate of the true concentration of an element for the particular analytical method used.
2. Calculate the absolute differences between each pair $|X_1-X_2|$. The absolute difference is an estimate of the standard deviation, σ_c, at that particular concentration. $|X_1-X_2|$ is assumed to be normally distributed and relates to the parent population, with a standard deviation, σ_c, such that:

$$\sigma_d = \sqrt{1.96 * \sigma_c} \qquad (8)$$

where σ_d is the standard deviation of the difference $|X_1-X_2|$.

$$d = 1.128 * \sigma_c \qquad (9)$$

where d is the mean value for the difference; and

$$M_d = 0.954 * \sigma_c \qquad (10)$$

where M_d is the median value for the difference. The statistic σ_c can be obtained from each of these relationships, but the median (M_d) is the most convenient estimator, because it is (i) relatively little affected by wild or extreme values; (ii) readily estimated graphically, and (iii) corresponds very closely to σ_c without further calculation (Fletcher, 1981).

3. Arrange the list in increasing order of concentration means.
4. From the first 11 results, calculate the mean concentration (*Group mean*) and the median difference (*Group median*).
5. Repeat step 4 for each successive group of 11 samples, ignoring any remainder less than 11. *Hence, the reason for suggesting that replicated analyses should be performed on at least 55 randomly selected samples, which gives 5 groups of 11 samples*.
6. Calculate the linear regression of the median difference (*Y-axis, dependent variable*) on the means (*X-axis, independent variable*). At this point, the first author introduced a modification. In classical regression, ($Y = B*X + A$), a linear relationship is quantified by fulfilling the following requirements of (a) dependency and (b) knowing one variable without error. Thompson and Howarth (1978) assumed that the group means are the

independent variable or predictor (*X*), by which the group median difference (*Y*) is estimated. The question posed is the following: *Which is the dependent variable?* Since both variables are derived from the grouping of the same analytical data set, they are subject to errors of the same order of magnitude. It is concluded, therefore, that the requirements of classical regression cannot be met. To overcome this situation Kermack and Haldane (1950) developed the reduced major axis line, which is the line of best-fit between a set of points (Fig. 7.5; Till, 1974). Essentially, is the best-fit line between the two regression lines of ($Y = B*X + A$) and ($X = B*Y + A$). Hence, errors of estimation are minimised.

7. Obtain from the reduced major axis regression line of the group median differences, $|X_1 - X_2|$, on the group means, $(X_1+X_2)/2$, the intercept, A, and coefficient, B.

8. Multiply by 1.048 (*i.e.*, 1/0.954) the intercept, A, and coefficient, B, to obtain σ_o and k, respectively; from the regression $\sigma_c = \sigma_o + kc$, so that the precision, P_c, is given by

$$P_c = \frac{1.96 * \sigma_o}{X_{ci}} + 1.96 * k \qquad (11)$$

which is the variation at the 95% confidence level (approximately at two standard deviations).

9. Calculate the percentage precision, $P_c\%$, by using the equation:

$$P_c\,\% = \left(\frac{1.96 * \sigma_o}{X_{ci}} + 1.96 * k \right) * 100 \qquad (12)$$

$$P_c\,\% = \frac{196 * \sigma_o}{X_{ci}} + 196 * k \qquad (13)$$

where X_{ci} is the element concentration determined on individual samples. Hence, it is possible to estimate, by this method, the precision of every determination.

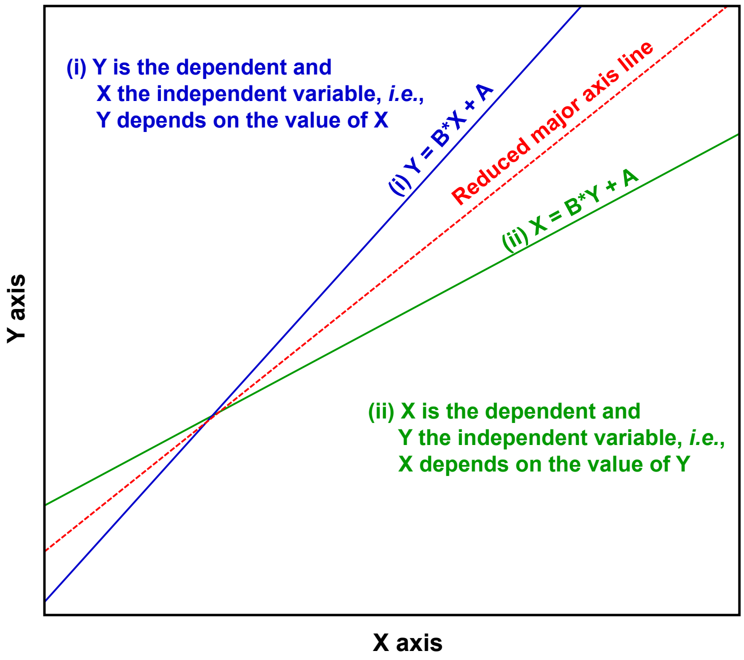

Figure 7.5. The reduced major axis line is the best fit line of Y on X and X on Y. Source: Demetriades (2011, Fig. 6.2, p.82, slightly modified).

10. Calculate the detection limit. The detection limit is normally defined as the concentration that gives rise to a signal equal to twice the standard deviation of blank fluctuations, *i.e.*, at a value of $P_c = 100\%$ and $X_{ci} = 1.96\sigma_o$. At concentrations higher than the detection limit, precision falls asymptotically towards the value of 1.96k as defined in the expression $P_c = (1.96\sigma_o / X_{ci}) + 1.96k$ (Equation 11). For further information, and the implications involved in the estimation of these quality control parameters, Thompson and Howarth (1976) should be consulted. It is important to understand the asymptotic nature of precision, and that it is incorrect to quote a single value for precision, *i.e.*, at concentrations higher than the detection limit, precision falls asymptotically towards the value of 1.96k or 196k in the above expressions (refer to Fletcher, 1981, Fig. 2-5, p.32; see Fig. 7.6 below). On the geochemical distribution maps, the relative precision equation should be given, so that the reader can estimate precision at any specific concentration.

Practical detection limits determined by this method are subject to the variation of element concentrations in the selected random samples. In case the samples have a distribution of element concentrations, approaching a normal Gaussian distribution, the practical detection limits of these elements are either the same or remarkably close to instrument detection limits. For element concentrations that have a non-Gaussian distribution, their practical detection limits are normally quite different from those quoted by the analysts.

Ideally, the samples selected for replicate measurements should include extremely low, low, moderate, high, and exceedingly high concentrations of the determinands or measurands studied. However, this selection can only be made upon completion of the routine geochemical survey, and evaluation of analytical results. In practice, the duplicate samples are selected in a completely random manner across the project area, and in such a case, the most dominant features are replicated.

For the estimation of precision by the above method, a Microsoft™ Excel workbook 'IUGS-CGGB_Chapter-7_PDLPRECIS.xlsx' by Alecos Demetriades is available (refer to the Supplementary material).

Further, Lee and Ramsey (2001) modelled measurement uncertainty as a function of concentration and they estimate analytical precision and detection limit, among other parameters.

The asymptotic nature of precision is shown in Figure 7.6, using the Be duplicate-replicate results from the *aqua regia* GEMAS grazing land soil data set (Reimann *et al.*, 2014). In this case, the laboratory provided uncensored data, and even sub-zero (negative) values. Using the procedure described above, two different estimations were made, with and without the negative values. The precision in both cases falls asymptotically towards the value of 1.96k or 196k in the above expressions. Beyond this limit, the curve reaches a plateau, and this is considered to be the overall precision. The practical detection limit (PDL), as mentioned above, is defined as the concentration that gives rise to a signal equal to twice the standard deviation of blank fluctuations, *i.e.*, at a value of $P_c = 100\%$ and $X_{ci}=1.96\sigma_o$. On the graph (Fig. 7.6), it is the tangent to the curve leading to $P_c = 100\%$. As expected, there are differences in the estimation, even by removing a single pair of negative values: -

(a) PDL = 0.072 mg Be/kg (with negative value and N=94 pairs), and an overall precision of 18.4% at the 95% confidence level, and a precision equation (Fig. 7.6a):

$$P_c\,\% = \frac{5.86}{X_{ci}} + 18.4 \tag{14}$$

(b) PDL=0.046 mg Be/kg (without negative values and N=93 pairs), and an overall precision of 24.5% at the 95% confidence level, and a precision equation (Fig. 7.6b):

$$P_c\,\% = \frac{3.44}{X_{ci}} + 24.5 \tag{15}$$

where X_{ci} in both cases is any concentration of Be that one is interested to know its precision at the 95% confidence level. *For example*, a Be concentration of 5 mg/kg has a precision of 19.6% and 25.2% for (a) and (b), respectively. As Be concentrations approach the detection limit, the precision becomes poorer, *e.g.*, for a Be concentration of 1.5 mg/kg, the precision for (a) is 22.3%, and for (b) is 26.8% at the 95% confidence level.

The reported laboratory's lower detection limit is 0.1 mg Be/kg, which is higher than the values estimated for the practical detection limit with and without negative values, *i.e.*, 0.072 and 0.046 mg Be/kg, respectively (see Fig. 7.6). For elements, such as Be, where most of the values are extremely low, and near to the analytical method's lower detection limit, it is an advantage to estimate the practical detection limit, using actual recorded analytical data.

Otherwise, if the laboratory provided censored analytical data at the laboratory's detection limit of 0.1 mg Be/kg, all values below this limit would have been given half the value of the lower detection limit (LDL), *i.e.*, 0.05 mg Be/kg, if chosen imputation method is to replace values <LDL by 0.5*LDL. Of course, there are other imputation techniques (refer to Chapter 8). Thus, losing many actual background values.

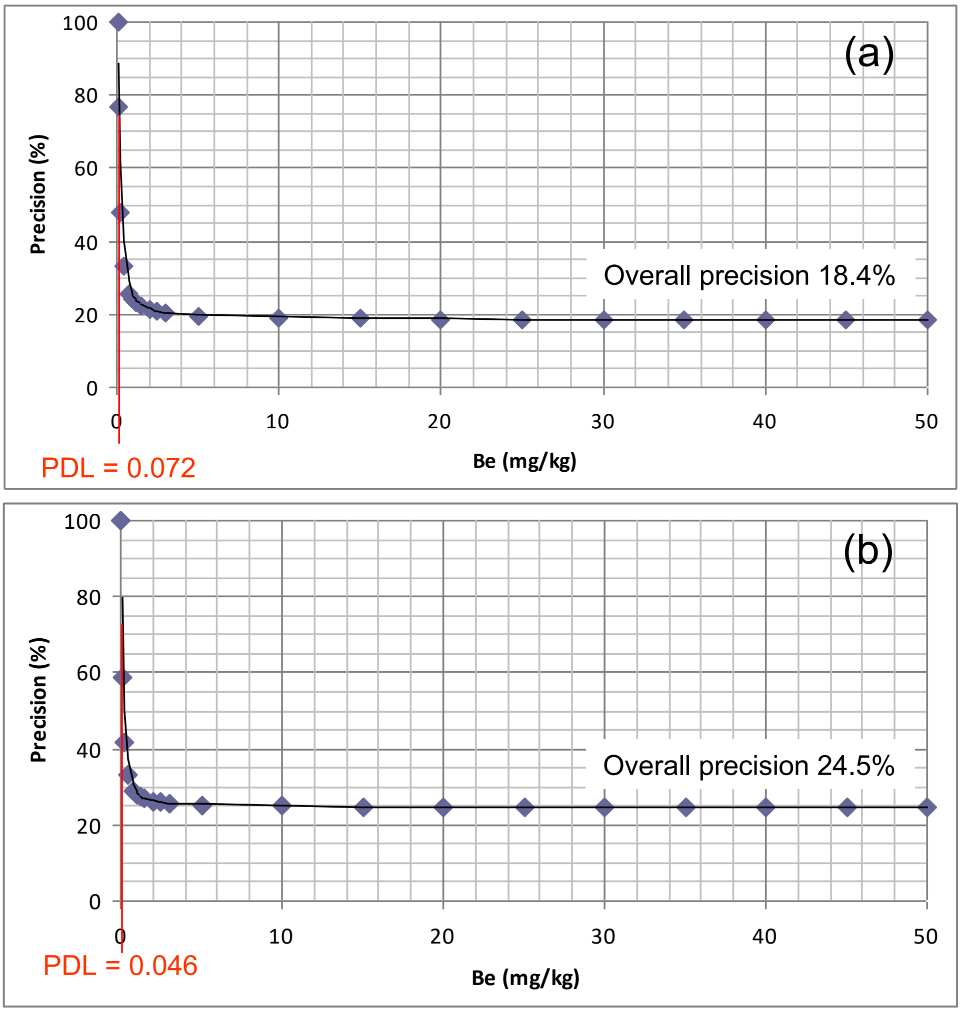

Figure 7.6. Variation of precision with concentration. Two examples of Be from the aqua regia GEMAS grazing land soil data set (Reimann et al., 2014) plotted with 'IUGS-CGGB_Chapter-7_PDLPRECIS.xlsx' Microsoft™ Excel file (see Supplementary material): ***(a)*** *With negative values (N=94 pairs), and* ***(b)*** *With negative values removed (N=93 pairs). The former gives a PDL at 0.072 mg/kg and an overall precision of 18.4% at the 95% confidence level, and the latter a PDL at 0.046 mg/kg and an overall precision of 24.5% at concentrations beyond 50 mg Be/kg. Plotted by Alecos Demetriades (IGME/IUGS-CGGB).*

7.3.1.8. Cumulative probability plot

According to Johnson (2011, p.68−69), replacing the value below the lower detection limit (LDL) with an arbitrary value (usually half the cited detection limit) will introduce a distortion in the data distribution at low concentrations, and this will have an impact on both descriptive and multivariate statistics. Analysts tend to be conservative with their LDLs, while many results reported as below detection have recordable useful values that show structure in the data distribution below the laboratory's cited LDL. This is illustrated in Figures 7.7 and 7.8 by cumulative probability plots, where the flattening of the graph indicates a more realistic limit of detection, which is much lower than that cited by the analyst.

Cumulative probability plots have long been used by applied geochemists to partition results into a combination of different populations (Tennant and White, 1959; Lepeltier, 1969; Sinclair, 1976, 1983, 1986), and their usefulness in establishing more realistic detection limits is shown herein.

The first example in Figure 7.7 is from the FOREGS Geochemical Atlas of Europe topsoil survey (Salminen *et al.*, 2005), where Ni was determined by two different analytical methods The second example in Figure 7.8 uses the As and Tl uncensored aqua regia analytical results from the EuroGeoSurveys project of Geochemical Mapping of Agricultural and Grazing land Soil of Europe (GEMAS; Reimann *et al.*, 2014). The third example in Figure 8.14 (Chapter 8) is from the British Geological Surveys' stream water survey where Al was determined by two different analytical methods. It is quite evident in these figures that the actual lower detection limit of Ni, As, Tl and Al is lower than that given by the laboratory.

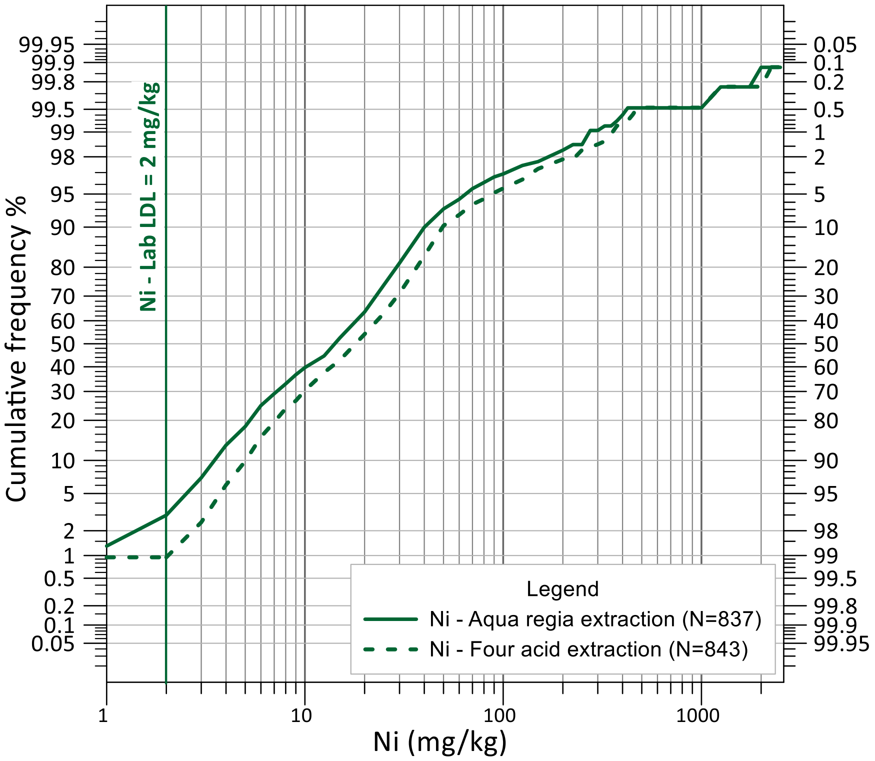

Figure 7.7. Cumulative probability plots of Ni indicating true detection limits for topsoil samples determined by two different analytical methods (data from the FOREGS Geochemical Atlas of Europe – Salminen et al., 2005). Plotted by Alecos Demetriades (IGME/IUGS CGGB) with Golden Software's Grapher^{TM} *v20.*

A procedure for estimating practical detection limits for chemical elements determined on project samples according to Thompson and Howarth (1978) has already been described in Section §7.3.1.7.

Reporting values below the cited LDL, as a single value <u>MUST BE</u> discouraged (AMC, 2001) ***in favour of delivering the recorded values as measured by the analytical instrument***. Users of uncensored analytical data can then better utilise values at the lower end of the data distribution without degrading the quality of the data. A single below detection value applied to many samples will distort statistically estimated parameters that may be significant in determining at which side of a statutory guideline value a result will fall.

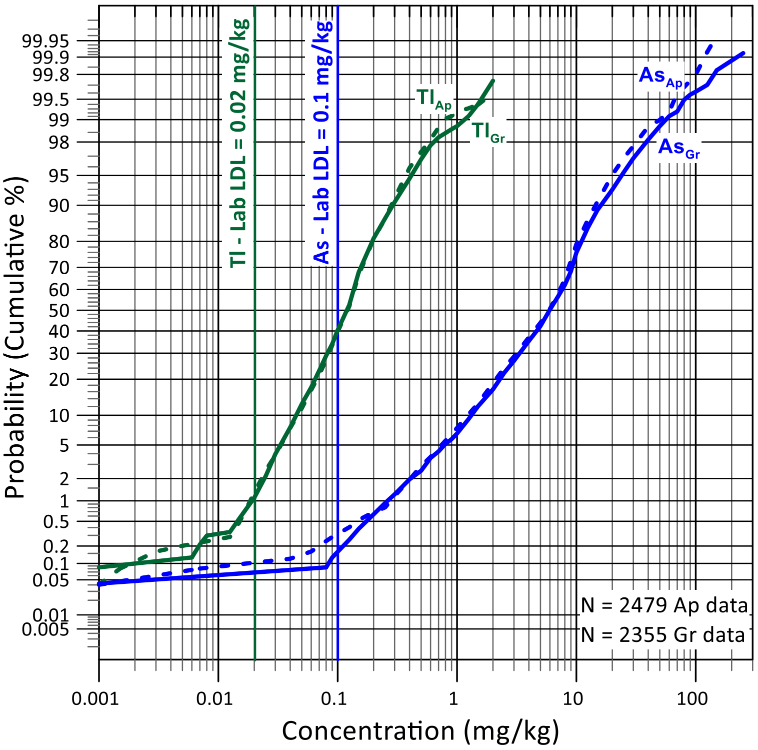

Figure 7.8. Cumulative probability plots indicating that the conservative laboratory lower detection limits (LDL) of hot aqua regia extractable As and Tl for the agricultural (Ap) and grazing land (Gr) soil samples of the EuroGeoSurveys project of Geochemical Mapping of Agricultural and Grazing land Soil (GEMAS) of Europe, using uncensored data (Reimann et al., 2014), are higher than the true detection limits. In this case, the practical detection limit can be as low as 0.005 and 0.00009 mg/kg for As and Tl, respectively (Reimann et al., 2009). Plotted by Alecos Demetriades (IGME/IUGS CGGB) with Golden Software's Grapher^{TM} v20.

7.3.1.9. Thompson-Howarth plot

Thompson and Howarth (1978) and Thompson (1983) describe a method of estimating analytical precision using duplicate-replicate sample pairs (Johnson, 2011, p.70). This is a graphical method, which can be used even for a single replicate pair that gives an immediate visual impression of precision of the analytical method (see Fig. 7.9).

The absolute difference between the two replicate analyses is plotted against the mean of the replicate results. On the graph, the fitness-for-purpose criteria are defined by the detection limit (herein 0.2 µg/l As) and 99th, 90th, and 50th percentile lines. In Figure 7.9, precision is generally good with only a small percentage of duplicate-replicate pairs plotting above the 90th percentile line. The example graph shown here was plotted using SigmaPlot software. Reimann *et al.* (2008, 2009, 2011, 2012) give examples of Thompson-Howarth plots generated using R.

The second Thompson and Howarth plot (Fig. 7.10) is a variant using normal linear axes. In this case, the 10% precision at the 95% confidence level is generally good as only 4 duplicate-replicate pairs plot above the 99th percentile line.

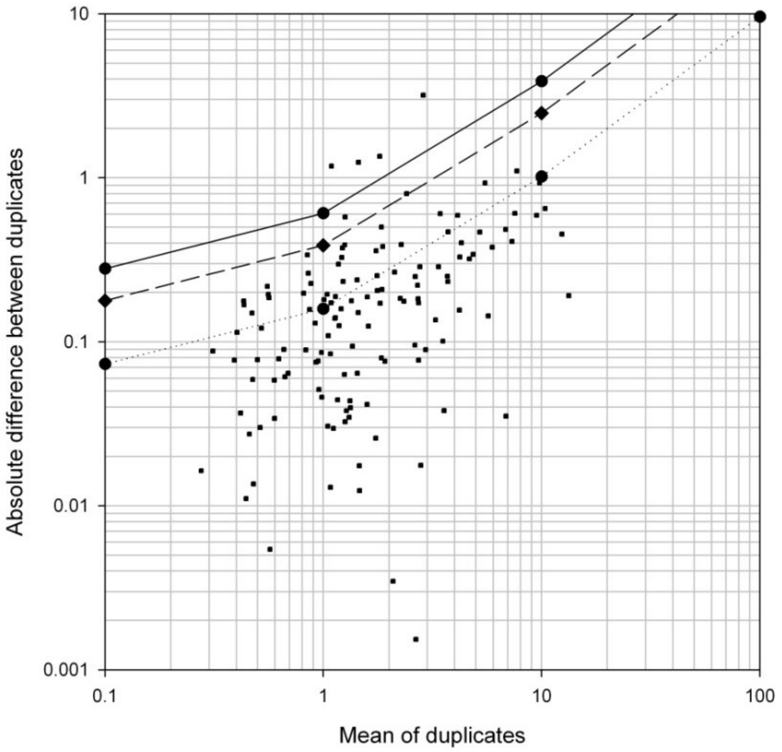

Figure 7.9. A logarithmic-scale Thompson-Howarth plot was used for visualising analytical precision. This is a plot of G-BASE stream water duplicates for As with probabilities calculated at 0.2 µg/l detection limit using SigmaPlot v10 software by E.L. Ander (BGS). See AMC (2002) for the rationale behind the Thompson-Howarth plot. Solid, dashed, and dotted lines represent 99th, 90th, and 50th per cent confidence levels, respectively. Source: Johnson (2011, Fig. 5.7, p.71).

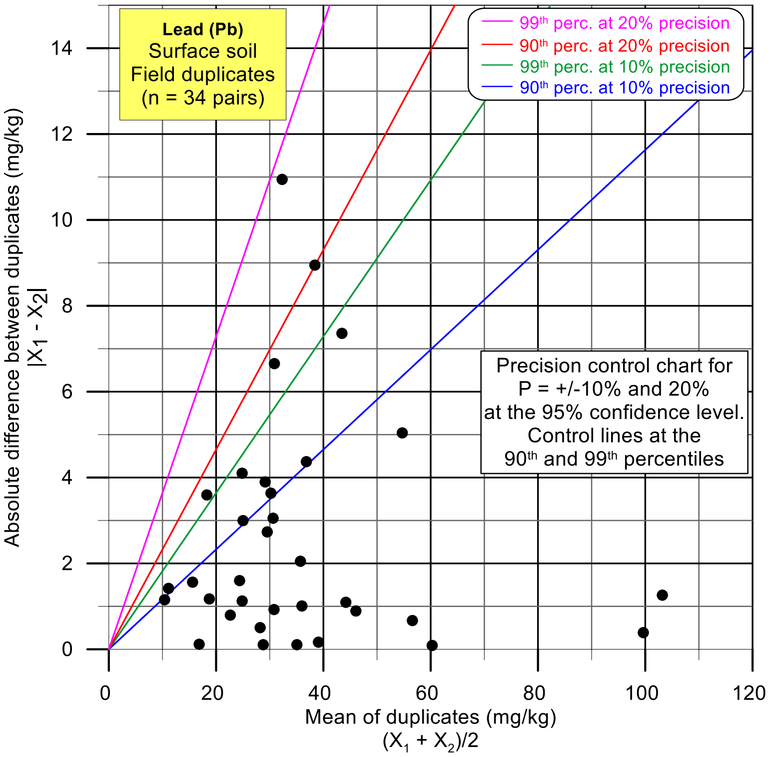

Figure 7.10. A normal linear scale Thompson and Howarth plot was used for visualising the precision of Pb. This is a plot from the results of the Hellenic Institute of Geology and Mineral Exploration's urban soil geochemistry project at Thrakomakœdónœs, a suburb of Athens. Colour lines represent 10% and 20% precision at the 95% confidence level, and the 90th and 99th percentiles. Plotted by Alecos Demetriades (IGME/IUGS-CGGB) with Golden Software's Grapher^{TM} v20.

7.3.1.10. Robust ANOVA for estimation of uncertainty due to sampling and analysis

The geochemical, sampling and analytical variance is normally estimated by classical analysis of variance (ANOVA), which is a statistical method strongly affected by a few outlying values, and also is based on three assumptions, *i.e.*, (i) the variances should be independent; (ii) each level of variance should be homogenous, meaning that it should not vary systematically within one level, and (iii) the distribution of errors within each level of variance should be approximately Gaussian (Ramsey, 1998). These problems are largely overcome by using robust analysis of variance (RANOVA).

The balanced RANOVA method proposed by Ramsey (1998), apart from estimating the geochemical, sampling and analytical variance, calculates measurement uncertainty, which is an essential parameter for the qualification of the determinands or measurands of any geochemical mapping project. According to Ramsey *et al.* (2019, p.1) "*Uncertainty of measurement is the most important single parameter that describes the quality of measurements. This is because uncertainty fundamentally affects the decisions that are based upon the measurement result*". *Uncertainty of measurement*, or *measurement uncertainty*, is defined in metrological terminology as the:

> "*Parameter, associated with the result of a measurement, that characterises the dispersion of the values that could reasonably be attributed to the measurand*" (Ramsey and Argyraki, 1997, p.244; ISO/IEC, 2008, p.2 & 36; Ramsey *et al.*, 2019, p. 6).

Uncertainties in the measurement process arise from a variety of sources, which are discussed in detail by Ellison and Williams (2012) and Ramsey *et al.* (2019). In their simplest form, the sources of measurement uncertainty can be categorised into two groups: (i) sampling and (ii) laboratory treatment of samples (*i.e.*, sample preparation and analysis). Hence, the two categories of measurement uncertainty discussed are '*sampling uncertainty*' and '*analytical uncertainty*', as well as the geochemical or spatial variance.

For the estimation of measurement uncertainty two different methodologies have been proposed, *i.e.*, (i) the '*bottom up*' (or 'modelling', 'theoretical', 'predictive'), and (ii) the '*top down*' (or 'empirical', 'experimental', 'retrospective') (Ramsey, 1998; Ramsey and Ellison, 2007). Whichever approach is followed, the general objective is to obtain a sufficiently reliable estimate of the overall measurement uncertainty. The '*top down*' approach does not require all the individual sources of uncertainty to be quantified, but only the combined effect to be assessed. If, however, the overall level of uncertainty is found to be unacceptable, according to the requirements of the project, *i.e.*, the measurements are not '*fit for intended use*', then actions should be taken to reduce the uncertainty. Alternatively, the estimated measurement uncertainty may be unnecessarily small, and in such a case there may be justification for increasing the analytical uncertainty, thereby decreasing the cost of analysis.

In the '*bottom-up*' approach the random error from each component of a method is quantified separately as a standard deviation, *s*, and then a model is used to combine them (Ramsey, 1998; Ellison *et al.*, 2000; Ellison and Williams, 2012; Ramsey *et al.*, 2019). Its limitation is the requirement to identify all sources of uncertainty. However, it is relatively easy to consider the obvious sources of error, which are explicit parts of a method, *e.g.*, weighing, and volumetric additions.

The '*top-down*' approach is intended to obtain a reliable estimate of the uncertainty, without necessarily knowing any of the sources individually, and has the widest applicability in measurement systems and applications (Ramsey *et al.*, 2019). It relies on overall precision measurements from either in-house or inter-organisational measurement trials. The latter is more difficult to use, comparatively impractical and somewhat costly for a project, because for the estimation of the total uncertainty of a measurement sampling, proficiency tests or collaborative trials are required (Argyraki *et al.*, 1995). Thus, in this case, many laboratories (N>8) are involved in the sampling and analysis by using the same protocol (collaborative trial in sampling – CTS, or by applying different protocols that are selected to be the most appropriate for the tested objective (sampling proficiency test – SPT). The scatter of measurements reported by all laboratories is then used to derive an overall estimate of uncertainty.

The '*duplicate method*' is the simplest and probably most cost-effective of the '*empirical methods*' for estimating combined uncertainty including sampling. It is based upon a single sampler duplicating a small proportion of the primary project samples. The field duplicate samples are taken from a minimum number of eight sampling target sites, selected at random to represent the typical composition of the target sites (it is stressed that this minimum concerns small projects, and definitely not the Global Geochemical Reference Network project).

To collect the field duplicated samples, a sampler is repeating the same sampling protocol with permitted variations that reflect the ambiguity in the protocol and the effect of small-scale heterogeneity of the determinand or measurand. Worked examples of the 'duplicate method' can be found in the Eurachem Guide on measurement uncertainty arising from sampling (Ramsey *et al.*, 2019), and herein (Section §7.4). Note that this method does not include any contribution from sampling bias, which in most instances is assumed to be negligible.

A balanced hierarchical sampling and analytical scheme should be used for the estimation of *geochemical, sampling,* and *analytical variances* and *random components of measurement uncertainty* (Fig. 7.11). Robust analysis of variance (RANOVA) is preferred, because it accommodates outlying values that exceed a certain distance from the mean (usually 1.5 times the standard deviation) by down-weighting them rather than rejecting them (Ramsey, 1998; Lee and Ramsey, 2001; Boon, 2009). The RANOVA method was proposed by Ramsey (1998), and subsequently verified by Lyn *et al.* (2007) for the minimum number of sampling sites that should be duplicated. In case, for some reason, the routine and duplicate samples from the same location cannot be split into two sub-samples for analysis, then two different aliquots of each routine and duplicate sample should be analysed randomly within the sample suite of the project.

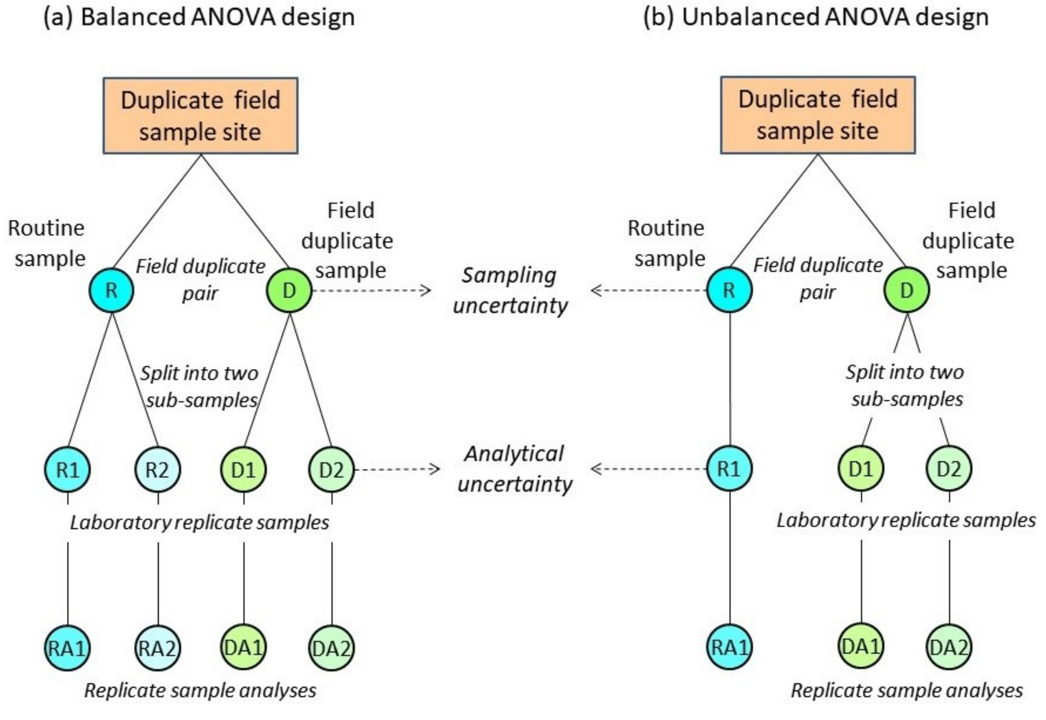

Figure 7.11. (a) Balanced and (b) unbalanced hierarchical geochemical sampling and analytical schemes for the estimation of geochemical, sampling, and analytical variance and random components of measurement uncertainty. Source: Demetriades et al. (2014, Fig. 6.4, p.56) slightly modified.

Collection of field duplicate samples is an inherent part of the *field geochemical investigation* itself, because the different types of variation of a parameter in the study area should be known. As pointed out by Ramsey (1998) two of the component variances can be classed as *measurement uncertainty*, and these are the *sampling,* s^2_{samp}, and *analytical,* s^2_{anal}, *variances*. The third component is the between location variance, the spatial variance, due to real variation of the determinand or measurand across the investigated area. This is called the *geochemical variance,* s^2_{geoch}, or *spatial variance*, in this particular case of a geochemical investigation. According to Ramsey *et al.* (1992) and Ramsey (1998), the "*sampling & analytical noise*", the "*measurement uncertainty*", should satisfy the following conditions:

Sampling + Analytical variance must be <20% of the total variance in the project area for each determinand studied. The analytical variance should not exceed 4% of the total variance (Garrett 1969; Ramsey et al., 1992; Ramsey, 1998). Thus, the maximum sampling variance should not exceed 16% of the total variance.

As pointed out by Ramsey (1998) if the measurement uncertainty is >20%, it does not mean that the analytical results are unusable. In such cases, emphasis must be placed on the interpretation of apparent differences between element concentrations at different sampling sites, which means that the quality control raw data should be visually inspected.

Sampling uncertainty, or *within-location variance*, is partially due to small scale geochemical variation within the location (or sampling target), and represents the uncertainty in all samples that can be collected from that particular 'location' or 'target', as specified by the investigation, *e.g.*, one- or two-metre radius, depending, however, on the distance of grid nodes. In the case of the Global Geochemical Reference Network project, the duplicate field samples are taken within the selected drainage basin, and the distance between the routine and duplicate locations of each sample type (*i.e.,* rock, residual soil, stream sediment, stream water, overbank sediment, floodplain sediment) could vary from 10 to 50 metres.

All three variances of a particular determinand or measurand in a material, such as rock, soil, stream sediment, overbank/floodplain sediment and stream water, can be summed up to give the *total variance,* s^2_{total}, of a geochemical survey. This figure would be estimated when calculating the variance of all analyses, and can be expressed by:

$$s^2_{total} = s^2_{geoch} + s^2_{samp} + s^2_{anal} \tag{16}$$

Ramsey *et al.* (1992) proposed initially the term *technical variance,* s^2_{tech}, for the sum of the *sampling*, s^2_{samp}, and *analytical*, s^2_{anal}, *variance* of a particular determinand or measurand in a material. It has been replaced since then by the term *measurement variance*, s^2_{meas} (Ramsey and Argyraki, 1997; Ramsey, 1998), *i.e.*,

$$s^2_{meas} = s^2_{samp} + s^2_{anal} \tag{17}$$

Hence, the total variance (s^2_{total}) of a particular determinand in a material becomes:

$$s^2_{total} = s^2_{geoch} + s^2_{meas} \tag{18}$$

The *measurement uncertainty*, *u*, can be estimated using this *bottom-up* approach from the combination of sampling and analytical variance:

$$\text{measurement uncertainty, } u = s_{meas} = \sqrt{(s^2_{samp} + s^2_{anal})} \tag{19}$$

It is a normal statistical procedure to increase the confidence interval of the uncertainty by multiplying by a *coverage factor* $k = 1.96$ (at the 95% confidence level) or 2.00 (at the 95.44% confidence level) to give the *expanded* or *extended uncertainty* *U*:

$$\textit{expanded uncertainty, } U = k * u = 2.00 * s_{meas} \tag{20}$$

In the statistics of the normal gaussian distribution, the coverage factor is 1.96 for the 95% confidence interval, and 2.00 for the 95.44% confidence interval. These coverage factors apply to an entire population when the true values for the mean and standard deviation are known. However, in geochemical mapping, the values of mean and standard deviation are estimated from 'samples' of this entire population. Because of the extra uncertainty in the estimates of standard deviation, it is necessary to increase the coverage factor to achieve a stated level of confidence. Consequently, international guidance recommends a coverage factor of 2 (*i.e.*, 2.00) for the expression of measurement uncertainty at *approximately 95% confidence*, to allow for this extra uncertainty that arises from using estimates of standard deviation (JCGM 100, 2008; ISO/IEC, 2008). This more reliable coverage factor is generally calculated using a t-distribution for the numbers of measurement values typically used (as explained in Annex G of JCGM 100, 2008, p.70−78). Further, the choice of coverage factor is discussed in detail in other publications that should be consulted (Ellison and Williams, 2012), and the key principles for its selection are given by Ramsey *et al.* (2019). If anyone wants to understand this more deeply, Section §G6.6.6 in JCGM 100 (2008, p.77) should be consulted, where it is stated: "*Then, based on the discussion given in this annex, including that emphasizing the approximate nature of the uncertainty evaluation process and the impracticality of trying to distinguish between intervals having levels of confidence that differ by one or two percent, one may do the following:*

- *adopt k = 2 and assume that U = 2u*$_c$*(y) defines an interval having a level of confidence of approximately 95 percent*".

Whichever coverage factor is used, it is important to state its value and confidence level when reporting expanded uncertainty.

The *expanded or extended uncertainty U*, expressed as a percentage of the mean concentration of a particular determinand, gives the *relative expanded uncertainty U' %*:

$$\textit{relative expanded uncertainty, } U'\,\% = \frac{(100 * 2.00) * s_{meas}}{\bar{x}} \tag{21}$$

where:

$\bar{x}$ is the estimated mean concentration of a determinand at the investigated site.

Similarly, the relative expanded uncertainty for sampling and/or analysis can be expressed (Ramsey *et al.*, 2019):

$$\textit{relative sampling uncertainty, } U'_{samp}\,\% = \frac{(100 * 2.00) * s_{samp}}{\bar{x}} \tag{22}$$

$$\textit{relative analytical uncertainty, } U'_{anal}\,\% = \frac{(100 * 2.00) * s_{anal}}{\bar{x}} \tag{23}$$

The calculated value of the uncertainty is applied to measurements on single samples taken during the investigation. According to Ramsey (1998), if *N* multiple samples are collected at any individual location within the investigated site, the uncertainty on the average for that location is the value given by Equation 21 divided by $\sqrt{N}$; this is equal to the standard error on the mean value ($s_{total} / \sqrt{N}$); *for example*, the estimated relative uncertainty at a location, where four measurements (1A, 1B, 2A, 2B) have been made, would be half ($1 / \sqrt{4}$) of the value as given by Equation 21. However, after due consideration, Ramsey and Ellison (2007) have proposed that the uncertainty at a duplicated site should not be divided by the square root of 4 ($\sqrt{4}$), but by the square root of 2 ($\sqrt{2} = 1.414$), because the sampling uncertainty is the limiting factor. It is, in fact, the duplicated field sampling (x2) that reduces the confidence interval on the uncertainty estimate. Thus, the value of the *relative expanded uncertainty* in Equation 21 should be divided by the square root of 2 ($\sqrt{2}$), as is shown below:

$$\textit{relative expanded uncertainty, } U'\,\% = \left(\frac{100 * 2.00 * s_{meas}}{\bar{x}} \right) \div \sqrt{2} \tag{24}$$

The *upper limit of relative expanded uncertainty U'* % at the 95% confidence level is estimated by the equation:

$$X + U = X * \left(1 + \frac{U'\,\%}{100} \right) \tag{25}$$

and the lower limit of relative expanded uncertainty is calculated by the equation:

$$X - U = X * \left(1 - \frac{U'\,\%}{100} \right) \tag{26}$$

where:

X = the concentration of the determinand or measurand in the sample medium

U = the expanded uncertainty at the 95% confidence level

$U'\,\%$ = the relative expanded uncertainty at the 95% confidence level.

The above Equations 25 and 26 may be refined if the *analytical bias*, B_a, is estimated using certified reference materials, CRMs (Ramsey and Argyraki, 1997; Ramsey, 1998; Ramsey *et al.*, 2019), which is a procedure employed by conventional accredited laboratories. The *upper limit of expanded uncertainty*, *U*, at the 95% confidence level is estimated by:

$$X + U = X \left(1 + \frac{U'\,\%}{100} \right) \left(1 - \frac{B_a}{100} \right) \tag{27}$$

and the lower limit of expanded uncertainty by:

$$X - U = X \left(1 - \frac{U'\,\%}{100} \right) \left(1 - \frac{B_a}{100} \right) \tag{28}$$

where:

X = the concentration of the determinand or measurand in the sample medium
U = the expanded uncertainty at the 95% confidence level
$U'\,\%$ = the relative expanded uncertainty at the 95% confidence level
B_a = the analytical bias is estimated as a percentage by regression.

Ramsey and Argyraki (1997) pointed out that the interpretation of *relative uncertainty* in the measurements of a particular determinand or measurand in soil, *for example*, assumes that it does not vary with concentration. Such a case has been observed in determinands, the analytical precision of which is considerably higher than the detection limit (Thompson and Howarth, 1976, 1978). Since the *relative analytical precision*, $P_c\%$, varies according to the concentration of the determinand, the above equations 25 and 26 may be improved, by incorporating precision, estimated on survey samples (Ramsey 1997, 1998; Ramsey and Argyraki, 1997). The *upper limit of expanded uncertainty*, *U*, at the 95% confidence level can be calculated, therefore, by:

$$X + U = X \left(1 + \frac{U'\%}{100} \right) \left(1 - \frac{P_c\%}{100} \right) \qquad (29)$$

and the *lower limit of expanded uncertainty* is calculated by the equation:

$$X - U = X \left(1 - \frac{U'\%}{100} \right) \left(1 - \frac{P_c\%}{100} \right) \qquad (30)$$

where:

X = the concentration of the determinand or measurand in the sample medium
U = the expanded uncertainty at the 95% confidence level
$U'\%$ = the relative expanded uncertainty at the 95% confidence level
$P_c\%$ = the analytical precision at the 95% confidence level

The practical detection limit, and analytical precision can easily be estimated using the method described above (see Section §7.3.1.5).

7.3.1.10.1. Calculation of standard and expanded uncertainty factor

It is well known that geochemical data generally follow a log-normal distribution (*e.g.*, Razumovsky, 1941; Ahrens, 1953, 1954a, 1954b; Chayes, 1954; Tennant & White, 1959; Vistelius, 1960; Shaw, 1961; Lepeltier, 1969; Sinclair, 1976, 1983, 1986; Reimann and Filzmoser, 2000; Buccianti *et al.*, 2006; Mateu-Figueras and Pawlowsky-Glahn, 2008; Zhao *et al.*, 2018), which can be seen in Figures 7.7 and 7.8. It is, therefore, advisable before embarking on the statistical treatment of the quality control results and analytical data from any geochemical mapping project, to check their statistical distribution. This can be done either by plotting a histogram or a cumulative frequency curve or both.

Figure 7.12 shows two graphs of Zn in topsoil samples of the FOREGS Geochemical Atlas of Europe (Salminen *et al.*, 2005). The first (a) is a histogram with the fitted normal distribution curve exhibiting a positive skewness. The second (b) is a cumulative frequency curve depicting the existence of at least four log-normal populations. From these two graphs, it can be concluded that the cumulative frequency distribution is a much better and more powerful visualisation tool than the histogram because it shows more effectively the pictorial statistical distribution of a determinand or measurand.

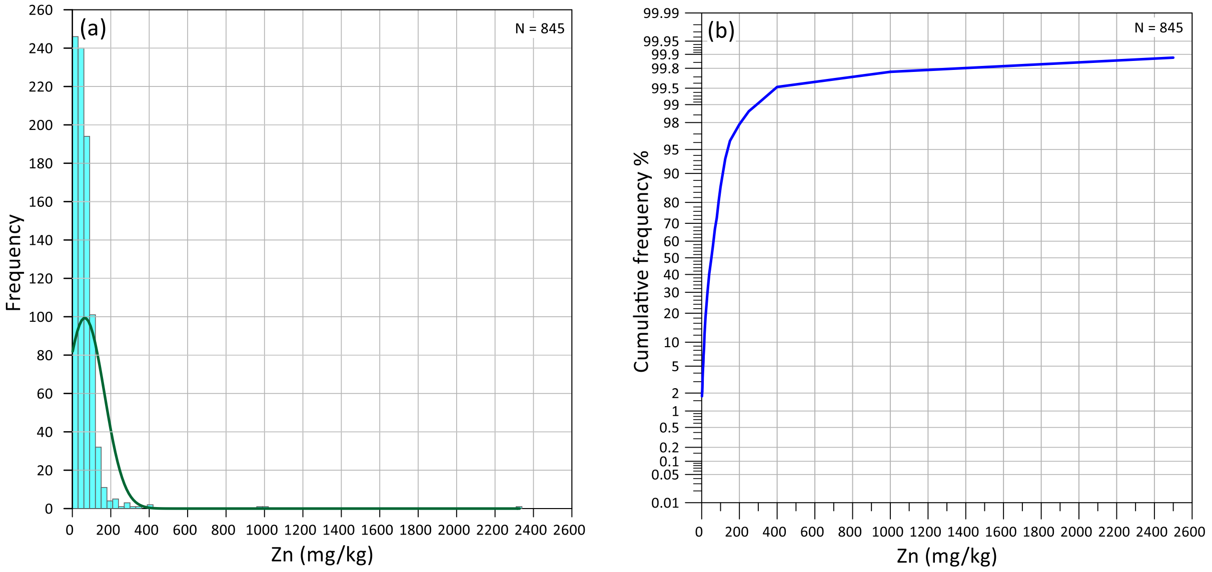

*Figure 7.12. **(a)** Histogram of Zn distribution with fitted normal distribution curve, and **(b)** Cumulative frequency plot of Zn in topsoil samples determined by XRF, FOREGS Geochemical Atlas of Europe (Salminen et al., 2005). It is noted that most of the topsoil samples have Zn concentrations <400 mg/kg. Plotted by Alecos Demetriades (IGME/IUGS- CGGB) with Golden Software's Grapher^{TM} v20.*

Figure 7.13 shows the log-normal distribution of Zn in the routine and duplicate quality control topsoil samples from the same geochemical mapping project; (a) displays the linear and (b) the $\log_e$ distribution. In both cases, the curves depict the existence of at least two log-normal populations.

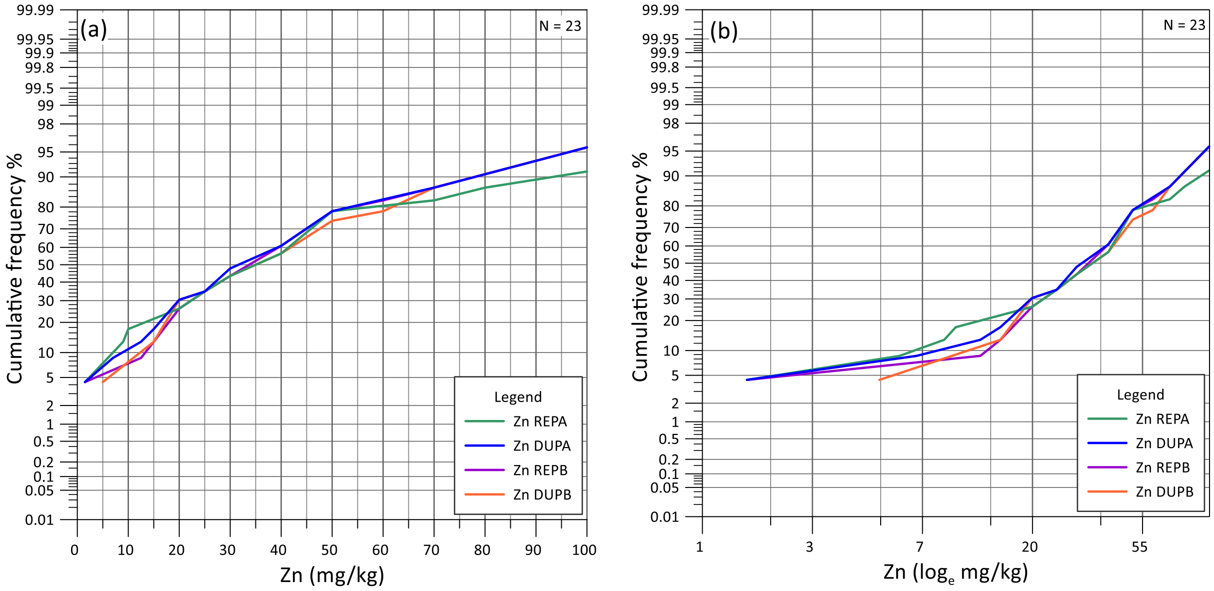

Figure 7.13. Cumulative frequency curves of Zn in routine and field duplicate topsoil samples determined by XRF, FOREGS Geochemical Atlas of Europe (Salminen et al., 2005). ***(a)*** *Linear graph and* ***(b)*** *$\log_e$ graph. Notation: DUPA = Routine sample; REPA = Replicate split of routine sample; DUPB = Field duplicate sample; REPB = Replicate split of field duplicate sample. Plotted by Alecos Demetriades (IGME & IUGS CGGB) with Golden Software's Grapher^{TM} v20.*

Ramsey and Argyraki (1997) already stated that the uncertainty interval of any concentration X_i (*e.g.*, the estimated mean for the site) becomes asymmetric (log-normal). However, they did not elaborate on the procedure that should be followed when expressing uncertainty to account for this asymmetry.

Ramsey *et al.* (2019) to accommodate this known asymmetry in the statistical distribution of geochemical data proposed the calculation of a *standard* ($^F u$) and an *expanded* ($^F U$) *uncertainty factor* by using natural logarithms. The reason for suggesting this transformation is that ANOVA assumes that the frequency distribution of a determinand (or measurand) is approximately normal, *i.e.*, Gaussian (Scheffé, 1959, 1999; Davis, 1973, 1986, 2002; Till, 1974; Reimann *et al.*, 2008), which is not the case of most geochemical statistical distributions, as has already been stated (see Figs. 7.7, 7.8, 7.12 & 7.13). Thus, according to Ramsey *et al.* (2019), it is more appropriate to express measurement uncertainty by using the *expanded uncertainty factor* ($^F U$), especially when the frequency distribution is approximately log-normal, a feature common at high values of sampling uncertainty. In such cases, the ANOVA is performed on the natural logarithms of the measurement values and, consequently, the results are not in the original units of elemental concentration.

To estimate the upper and lower confidence limits of the uncertainty interval about a determinand concentration value (X), Ramsey *et al.* (2019) proposed the multiplication and division of the measured concentration X by the *expanded uncertainty factor* ($^F U$), respectively.

The *standard uncertainty factor* ($^F u$) is calculated from the standard deviation (s_G) of $\log_e$–transformed determinand or measurand values [$s(\ln(X)) = s_G$], where $^F u = \exp(s_G)$.

The *expanded uncertainty factor* ($^F U$), using a *coverage factor* k = 2.00 at the ≈95% confidence interval, can be calculated, according to Ramsey *et al.* (2019), in two ways, either:

(i) *expanded uncertainty factor*, $^F U = \exp(2.00 * s_G)$ (31)

Or, alternatively, because multiplying by k in log-space is the same as raising to the power of k in linear space, *i.e.*, $^{F}U = (^{F}u)^{k}$, it can be calculated more simply as shown below:

$$\text{(ii)} \qquad \textit{expanded uncertainty factor, } {}^{F}U = ({}^{F}u)^{2.00} \qquad (32)$$

The upper and lower confidence limit for the expanded uncertainty interval about a determinand concentration X_i is calculated as follows:

a) *Upper Confidence Limit (UCL)* at the 95% confidence level is estimated by the equation:

$$UCL = X_i * {}^{F}U \qquad (33)$$

(Measured concentration X_i is *multiplied* by the Expanded uncertainty factor, ^{F}U)

b) and the Lower Confidence Limit (LCL) at the 95% confidence level is estimated by the equation:

$$LCL = X_i / {}^{F}U \qquad (34)$$

(Measured concentration X_i is *divided* by the Expanded uncertainty factor, ^{F}U)

Consequently, this confidence interval is not symmetrical about the measured concentration X_i in normal linear concentration space.

Finally, the *relative uncertainty*, *u'*, expressed as a fraction, can be calculated by the following expression:

$$\textit{relative uncertainty, } u' = \sqrt{\exp(s_G^2) - 1} \qquad (35)$$

which for modest values of u' (*for example*, <0.2, which is the usual case according to Ramsey *et al.*, 2019) is approximately equal to s_G.

Worked examples for estimating all parameters discussed in this Section will be found in Section §7.4.

7.3.1.10.2. Interpretation of uncertainty statements for regulatory purposes

The main aim of the Global Geochemical Reference Network project is the establishment of the geochemical baseline of chemical elements and compounds in natural surficial materials against which future changes can be quantified, whether natural or human-induced. Further, the generated analytical data, apart from their use as reference data for levelling the more detailed national geochemical data sets, will be used by many disciplines and for different purposes, including possible compliance with international or national regulatory limits. Therefore, it is important to take uncertainty into account, especially in the interpretation for regulatory purposes. A full discussion is beyond the scope of the present Manual, and the interested reader should consult Ellison and Willams (2007, 2012). Ramsey *et al.* (2019, p.32) have given the basic principles to be followed for regulatory purposes, *i.e.*:

- "*Decide whether the decision requires proof of compliance, proof of non-compliance, or a 'shared risk' approach, and set an appropriate level of confidence.*
- *For proof of compliance, the result and its uncertainty interval must be entirely within the permitted range.*
- *For proof of non-compliance, the result and its uncertainty interval must be entirely outside the permitted range.*

- *For shared risk approaches, set a range for acceptable measurement results based on the permitted interval, adjusted to provide a specified probability of false acceptance and false rejection rates. More recent guidance gives useful details of the procedure (ISO/IEC, 2012).*"

For regulatory purposes, it is important to consult the specific international or national regulations applicable, as no general guidance can currently cover all cases.

7.4. Worked examples

For the worked examples, software packages and data sets are provided, and which can be downloaded from the Publications web page of the IUGS Commission on Global Geochemical Baselines (https://www.globalgeochemicalbaselines.eu/) – Refer to Supplementary material.

7.4.1. Program for plotting X-Y diagrams

The following files should be downloaded from the Publications web page of the IUGS Commission on Global Geochemical Baselines (see Supplementary material):-

- ➢ IUGS-CGGB_Chapter-7_DUPREPPLOT.xlsm: Microsoft™ Excel Workbook with a macro for plotting X-Y diagrams. The Workbook consists of two Worksheets. The first, "INFO" gives general information, author and instructions on how to use the macro routine; the test duplicate-replicate analytical results are included on this page and come from samples of topsoil from the FOREGS Geochemical Atlas of Europe project (Salminen *et al*., 2005). The second worksheet, 'ControlData', contains the topsoil duplicate-replicate analytical results used for plotting the X-Y diagrams when running the macro.
- ➢ IUGS-CGGB_Chapter-7_DUPREPPLOT_Output.xlsm: Microsoft™ Excel Workbook with the output of X-Y plots in different worksheets with the symbol of each element.
- ➢ IUGS-CGGB_Chapter-7_FOREGS_Topsoil_QC_XRF_data.xlsx: Example quality control data set from the FOREGS Geochemical Atlas of Europe project (Salminen *et al.*, 2005). The Microsoft™ Excel workbook contains the original balanced ANOVA quality control XRF topsoil data, which have been transferred to "DUPPREPPLOT" after cleaning, *i.e.*, deleting columns of determinands with many values below the analytical method's lower detection limit, such as F, Bi, Cu, Hf, La, Mo, Sb, Sn, Ta, U and W. It also includes other worksheets: (a) Lower_detection_limit; (b) Notation_of_Control-ID; (c) Legal_Notice, and (d) Reference.

To obtain a visual appreciation of the analytical laboratory's precision simple X-Y plots of duplicate-replicate pair results for each determinand or measurand are plotted. Two examples, Zn and Th, have been extracted from the 'IUGS-CGGB_Chapter-7_DUPREPPLOT_Output.xlsm' Microsoft™ Excel file to show good and poor precision, respectively (Figs. 7.14 & 7.15). If all X-Y plots are studied in this output file, it will be observed that apart from Th, the elements As, Ce, Co, Cs, Ga, Nb, Ni, Pb, Sc and V show poor precision and, therefore, were rejected for further treatment. Consequently, this first step is important for apart from obtaining an appreciation of the analytical laboratory's precision, within-site variability can also be assessed, and poor data are rejected.

7.4.2. Program for the estimation of practical detection limit and precision

For the estimation of the practical detection limit and precision according to the method described in Section §7.3.1.7, a Microsoft™ Excel workbook '**IUGS-CGGB_Chapter-7_PDLPRECIS.xlsx**' is available (see Supplementary material).

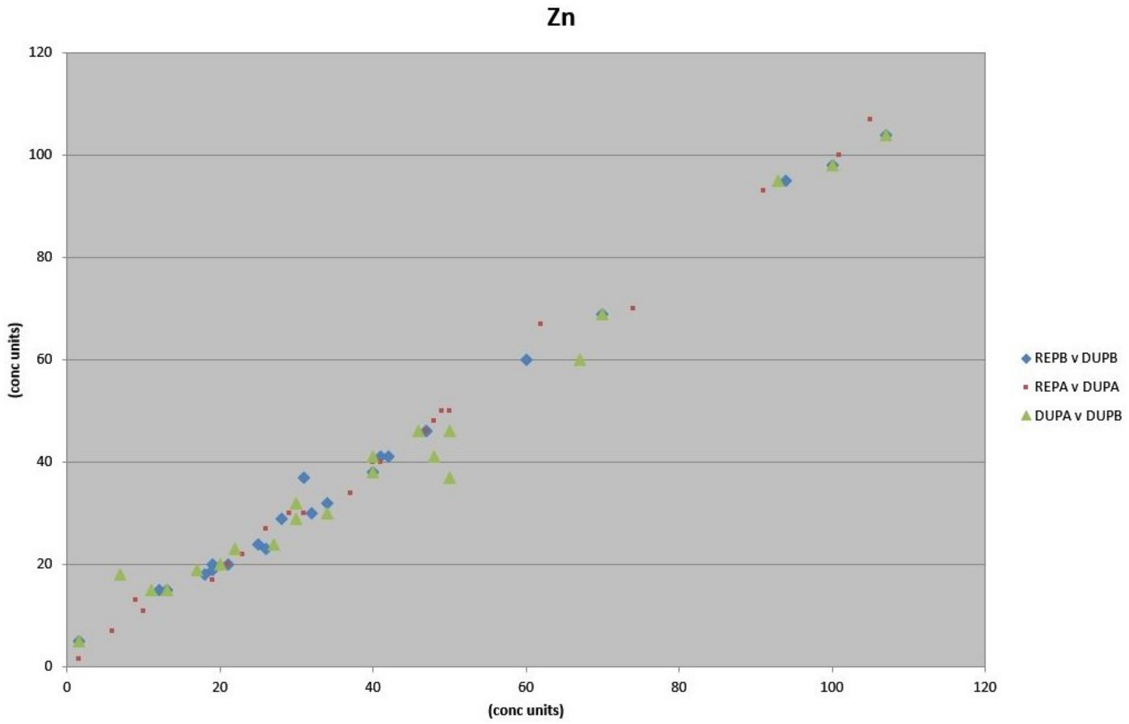

Figure 7.14. Duplicate-replicate plots for Zn from FOREGS Topsoil XRF quality control data (N=23 duplicated sites). It shows that the duplicate-replicate results are aligned close to the 1:1 gradient line. Plotted with 'DUPREPPLOT.xlsm', a Microsoft™ Excel Workbook macro routine developed by Christopher C. Johnson. Axis concentration units in mg/kg. Notation: Blue diamond = REPB versus DUPB; Red square = REPA versus DUPA; Green triangle = DUPA versus DUPB; and (all X-axis versus Y-axis). Notation: DUPA = Routine sample; REPA = Replicate split of routine sample; DUPB = Field duplicate sample; REPB = Replicate split of field duplicate sample. Plotted by Christopher C. Johnson (GeoElementary/IUGS-CGGB) with Microsoft™ Excel.

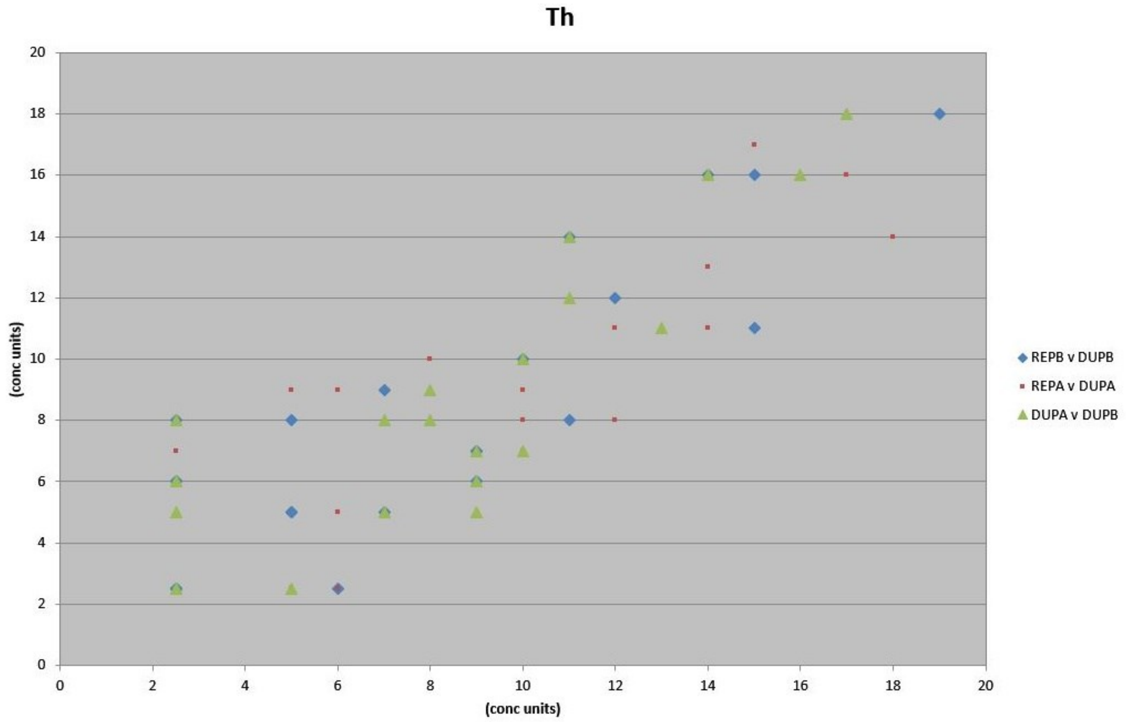

*Figure 7.15. Duplicate-replicate plots for Th from FOREGS Topsoil XRF quality control data (N=23 duplicated sites). It shows a wide scatter of **(i)** Routine and field duplicate results (within site variability), and **(ii)** Duplicate-replicate results (analytical variability). Plotted with 'DUPREPPLOT.xlsm', a Microsoft™ Excel Workbook having an embedded macro routine developed by Christopher C. Johnson. Axis concentration units in mg/kg. Notation: See Figure 7.14. Plotted by Christopher C. Johnson (GeoElementary/IUGS-CGGB) with Microsoft™ Excel.*

The PDLPRECIS Microsoft™ Excel Workbook comprises the following worksheets:

- **Contents**: Description of included worksheets, as given below.
- **Read-Me**: Contains the procedure described in Section §7.3.1.7.
- **Citation**: How PDLPRECIS should be cited when used.
- **Important cautions**: These cautions are very significant. They must be read carefully and understood, otherwise the calculations performed within the 'PDLPRECIS.xlsx' worksheet for the estimation of practical detection limit and precision will give erroneous results.
- **GEMAS-Gr_Be_QC_data**: The worksheet contains an uncensored data set: (a) Be analytical results including one sample with a negative value, and (b) the same Be analytical results without the sample pair without the negative value. These Be quality control results are from the GEMAS grazing land soil (Gr) samples (Reimann *et al*., 2009, 2014). The reason for their selection is because the Be analytical results are uncensored and, thus, suitable for the estimation of the practical detection limit. Here a question is raised: *Can the "PDLPRECIS" Worksheet be used for the estimation of the practical detection limit for censored or rather truncated data sets*, *i.e*., data sets that the laboratory does not report values below its estimated lower detection limit. Censored or truncated analytical results can be used for the estimation of the practical detection limit (PDL). The drawback here is if the value of the practical detection limit is lower than the laboratory detection limit. In such a case, the estimated PDL, cannot be used because of the laboratory's truncation. However, the estimation of the PDL, even for censored or truncated analytical results by the laboratory, verifies the laboratory's lower detection limit.
- Two worksheets: (i) **GEMAS-Gr_Be-1_PDLPRECIS** (with the Be negative value, N=94 pairs), and (ii) **GEMAS-Gr-Be-PDLPRECIS** (without the Be negative value, N=93 pairs): Worksheets with all the calculations leading to the estimation of (a) the practical detection limit; (b) precision and precision equation, and (c) a graph showing the distribution of precision with respect to concentration (see Fig. 7.6).
- **GEMAS-Ap_Be_Lab-replicate-data**: This worksheet contains the laboratory Be replicate analyses performed on the agricultural soil samples of the GEMAS project (Reimann *et al*., 2009, 2014). The reason for selecting this data set is because it has 146 pairs of Be analyses.
- **GEMAS-Ap_Be_Lab_PDLPRECIS**: Contains all the calculations leading to the estimation of the practical detection limit, precision, precision equation, and graph showing the distribution of precision with respect to concentration.
- **Summary_Table**: The worksheet contains the estimated results of Be from the different PDLPRECIS worksheets.
- **CLEAN-PDLPRECIS_Worksheet**: It is a clean worksheet for copying the pair of duplicate-replicate results of any geochemical project. Up to 440 pairs of analyses can be handled, and the calculations are carried out automatically, provided the underlying instructions and cautions are observed. If the data set exceeds 440 pairs of analyses, the Worksheet can be modified according to the instructions given below.

The Microsoft™ Excel Worksheet performing the calculations leading to the estimation of practical detection limit and precision is annotated with instructions on how to use it, and to modify it, if necessary, according to the number of pairs of analyses. The most important procedures that must be followed exactly when using the 'CLEAN-PDLPRECIS'_Worksheet are:

a) Copying the analytical results: This must be done by selecting from the relevant Microsoft™ Excel Worksheet the range of analytical results and then using the ‘Copy’ command.
b) Pasting the analytical results in the PDLPRECIS Worksheet: It is important to use the ‘Paste Special & Values’ command for the succeeding automated procedures to work properly.
c) Deleting all zero values in Columns: G ‘(X1+X2)/2’ (mean), and H ‘|X1-X2|’ (absolute difference). These two columns have entries until line 444. So, if your data set has fewer pairs of sample values, the zeros below your data set must be deleted. This is a very important action, otherwise, in the next step, all lines with ‘zero’ values will be transferred to the top of the worksheet.
d) Directly afterwards, you must ‘Sort’ the analytical results in Columns ‘A’ to ‘G’, with respect to their mean values, *i.e.*, Column G ‘(X1+X2)/2’, which means you mark all columns from ‘A’ to ‘G’ and use the ‘Data/Sort’ command to order the mean values from ‘Smallest to Largest’.
e) Delete all zero (0) or no values in Columns N, O, P, Q, R and S. This is a very important action for the Excel range commands in the calculations part of the Worksheet to work properly.
f) Finally, if your data set has pairs of values exceeding 440 (= 11 groups of pairs x 40 groups), you must first extend the calculation of the mean ‘(X1+X2)/2’, and absolute difference ‘|X1-X2|’ in columns G and H, respectively. Secondly, you must extend the estimation of ‘Group Mean’ and ‘Group Median’ in groups of 11 pairs of values in columns I and J, respectively, and to number each group of 11 pairs in Column K, and enter the corresponding line number in Column L. Thirdly, modify Columns N, O, P, Q, R and S by increasing the entry lines according to the additional groups of 11 pairs of values, and fourthly, modify accordingly the range commands in the calculations part of the Worksheet. The last action, *i.e.*, modification of equations, should be tested by using the Be results to ensure that the range commands work properly.

7.4.3. Programs for estimation of classical and robust ANOVA

The following two programs are freely available for downloading from the website of the Royal Society of Chemistry (https://www.rsc.org/membership-and-community/connect-with-others/through-interests/divisions/analytical/amc/software/)[6]:

- **RANOVA2** is a stand-alone program, running in Microsoft™ Excel and executes robust and classical analysis of variance with nested data. It is suitable for both balanced (Fig. 7.11a) and unbalanced (Fig. 7.11b) experimental designs. Output is expressed as standard uncertainty, expanded relative uncertainty, and Uncertainty Factor.
- **RANOVA3** is a stand-alone program, running in Microsoft™ Excel, and executes robust and classical analysis of variance with nested data. It is suitable for both balanced (Fig. 7.11a), and unbalanced experimental designs (Fig. 7.11). Output is expressed as standard uncertainty, expanded relative uncertainty, and Uncertainty Factor. Version 3 includes an option to calculate confidence intervals on uncertainties for balanced designs.

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[6] As new versions of software programs may be released from time to time, it is recommended to consult the web page of the Royal Society of Chemistry at regular intervals. The same applies to all recommended web pages with software programs.

The drawback of both programs is that the data of only one element can be processed each time, which means many runs of the two programs for processing multi-element data sets.

Ramsey with his 1998 paper made available the ROBCOOP4.EXE program, which runs on 32-bit computers, and processes multi-element data sets. This program has been updated to **ROBCOOP4A** (Vassiliades, 2022). There are two variants to run on both 32- and 64-bit computers, and it is available for download from the Publications web page of the IUGS Commission on Global Geochemical Baselines' website together with test data sets.

7.4.3.1. Classical and robust balanced ANOVA

According to Ramsey (1998, p.102) the ROBCOOP4.EXE and, consequently the new version ROBCOOP4A.EXE program (Vassiliades, 2022) is "*adjusted for a specified maximum incidence of outlying values, in this case, 10% of the total population. If there is a higher proportion of outlying values, then this would be expected to lead to somewhat erroneous estimates of the component variances*." Therefore, the first step is to check if there are more than 10% outlying values of the total population for each determinand in the duplicate-replicate data set. This can be done by plotting boxplots to see if there are any outlying values (Tukey, 1977; Hoaglin *et al.*, 1983; Kürzl, 1988). The FOREGS XRF duplicate-replicate data set of topsoil is used as an example (Salminen *et al.*, 2005).

Figures 7.16 and 7.17 are multiple-boxplots of the major and trace element XRF duplicate-replicate topsoil data sets, respectively. The multiple-boxplots can be plotted with any statistical software package. In this case, they were plotted with Golden Software's Grapher^{TM} v20.

The major elements multiple boxplot plot displays outliers for Fe_2O_3, MnO, MgO, CaO, SO_3, F and LOI (Fig. 7.16), and the trace element multiple-box plot shows outliers for As, Bi, Ce, Co, Cr, Cu, Hf, Mo, Pb, Rb, Sb, Sc, Sn, Sr, Ta, U, V, Zn and Zr (Fig. 7.17). Hence, these elements must be closely examined by either plotting boxplots for each element or studying visually the table of duplicate-replicate results or both. It is quite apparent that F in Figure 7.16, and Bi, Co, Cu, Mo, Sb, Ta and U in Figure 7.17 have more than 10% outlying values, which means that the classical and robust ANOVA will most likely give erroneous results with the ROBCOOP4A.EXE program.

Let us select CaO and Zn for a more detailed study. The multiple-boxplots (Fig. 7.18) and tabulated concentrations (Table 7.1) of CaO and Zn, show that there are 10 outlying values for CaO and 8 for Zn above the upper whisker at 1.63% and 95 mg/kg, respectively. Their corresponding percentages out of the total number of sample splits (N=92) are 10.9% for CaO and 8.69% for Zn. From this analysis, CaO exceeds slightly the upper limit of 10%, while Zn is within the upper limit.

The other elements with outliers should be subjected to the same rigorous treatment before running the ROBCOOP4A.EXE program.

The output results of the ROBCOOP4A.EXE program for CaO and Zn are shown in Tables 7.2 and 7.3, respectively, and the pie charts in Figure 7.19 display the proportion of geochemical (spatial), sampling, and analytical classical and robust analysis of variance results.

Tables 7.2 and 7.3 show distinct differences in the expanded relative uncertainty at the 95% confidence level between classical and robust ANOVA results, especially for CaO. The overall measurement uncertainty of classical ANOVA is 55.9% compared to 23.9% in robust ANOVA. In both cases, the greatest contribution to measurement uncertainty is due to sampling, as there is a small within sample site variation of CaO, which is shown in the pie chart (Fig. 7.19a).

For Zn again, the greatest contribution to measurement uncertainty in both classical and robust balanced ANOVA results is due to sampling (Table 7.3; Fig. 7.19b).

In both cases, the robust measurement variance out of the total is comparatively small, 2.40% for CaO and 0.93% for Zn. Consequently, the robust geochemical variance for both CaO (97.6%) and Zn (99.1%) has the greatest contribution to the total variance. The results are, therefore, considered to be fit for their intended use and the maps can be plotted, and the geochemical distribution interpreted (Fig. 7.20).

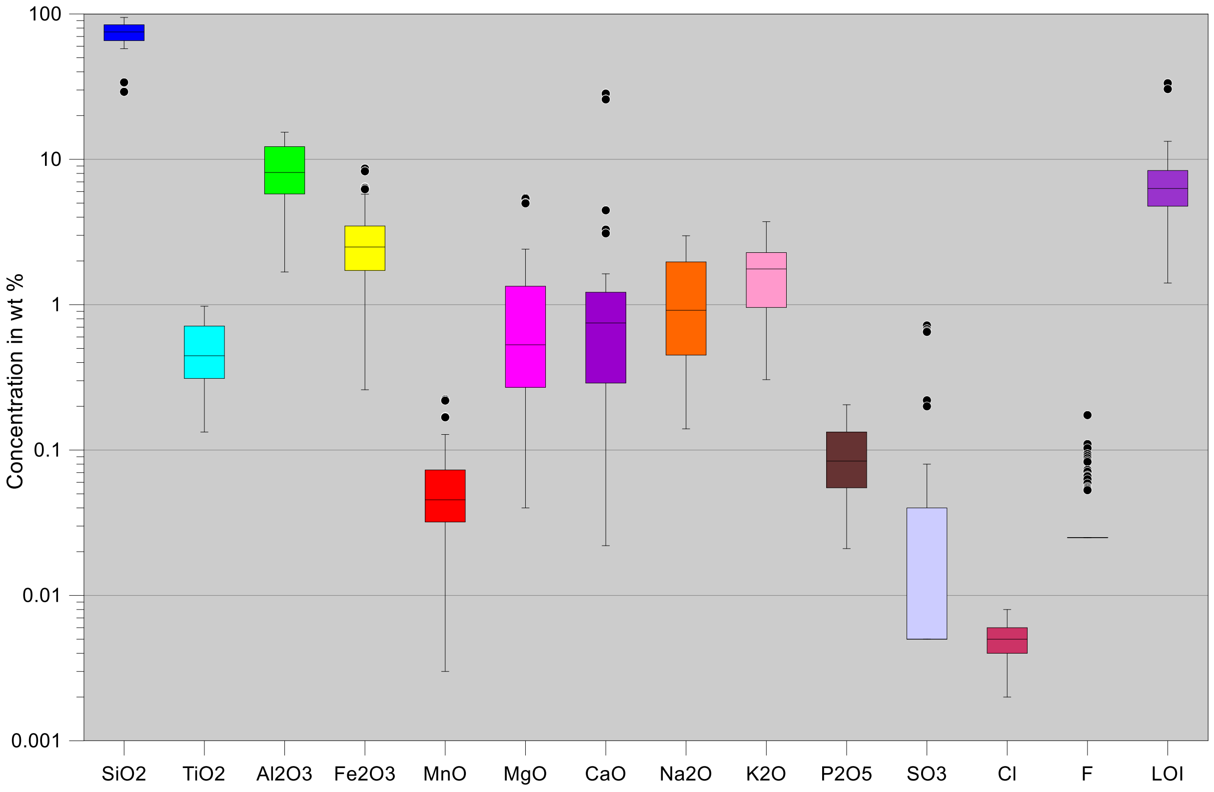


Figure 7.16. Multiple-boxplot of major element quality control data in European topsoil (N=23 duplicated sites). Plotted by Alecos Demetriades (IGME/IUGS-CGGB) with Golden Software's Grapher^{TM} v20.

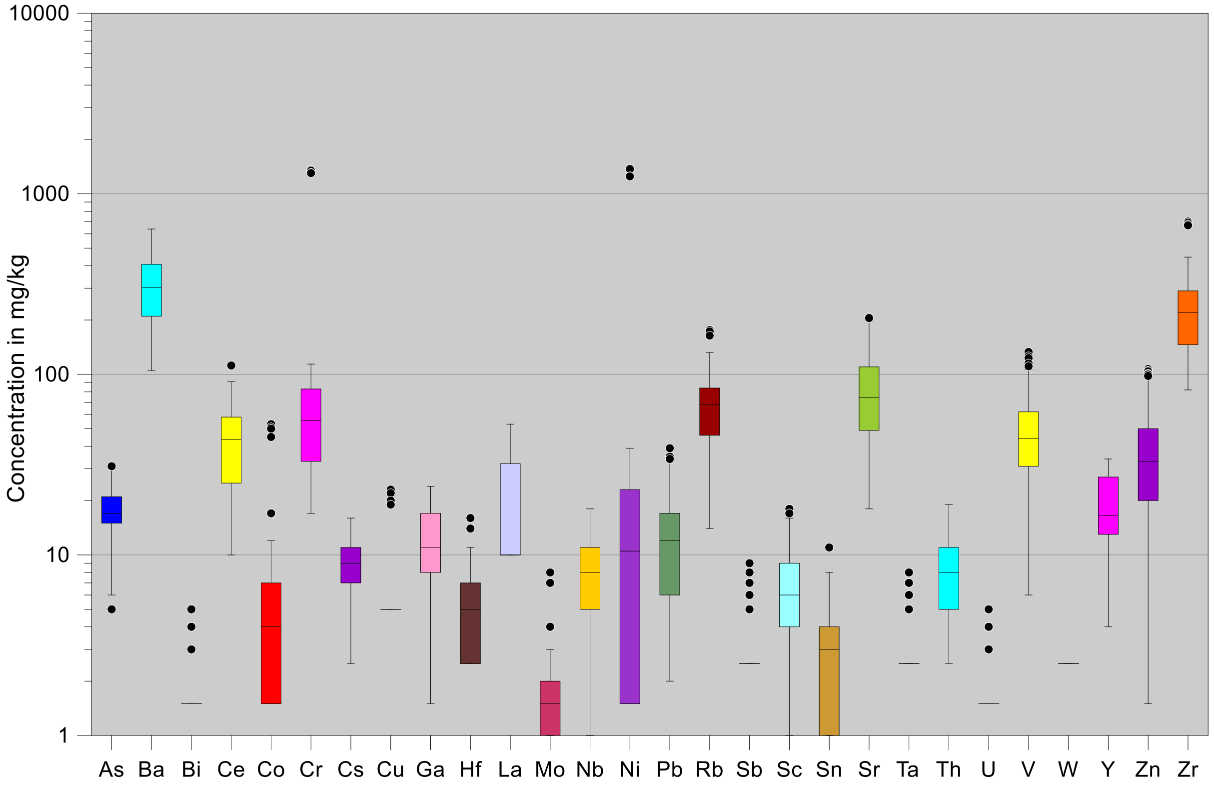
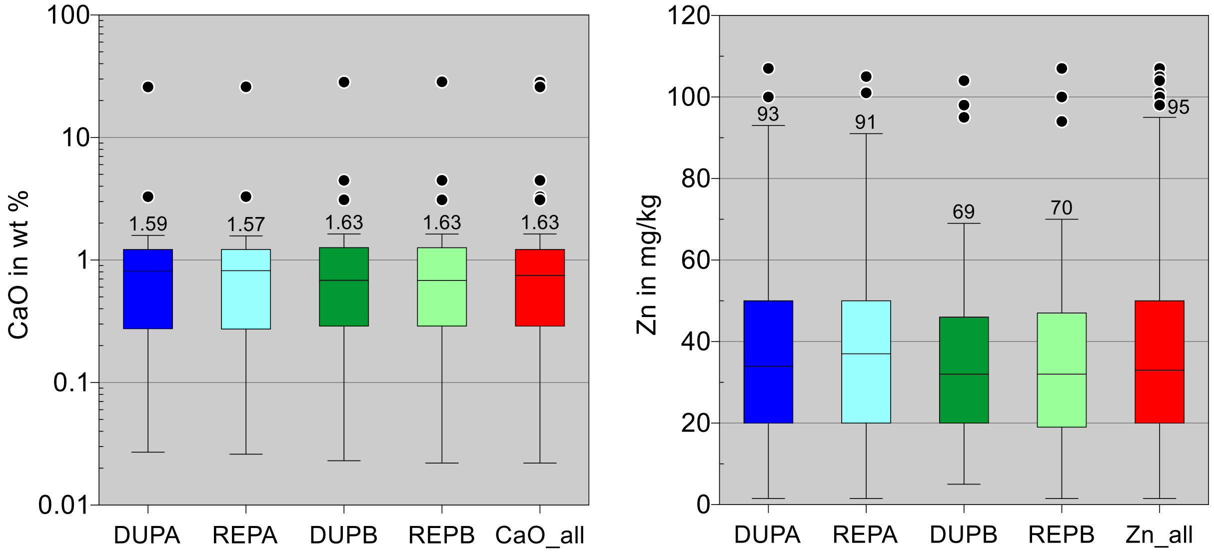


Figure 7.17. Multiple-boxplot of trace element quality control topsoil data (N=23 duplicated sites; Total number of sample splits, N=92) – FOREGS project (Salminen et al., 2005). Plotted by Alecos Demetriades (IGME & IUGS-CGGB) with Golden Software's Grapher^{TM} v20.



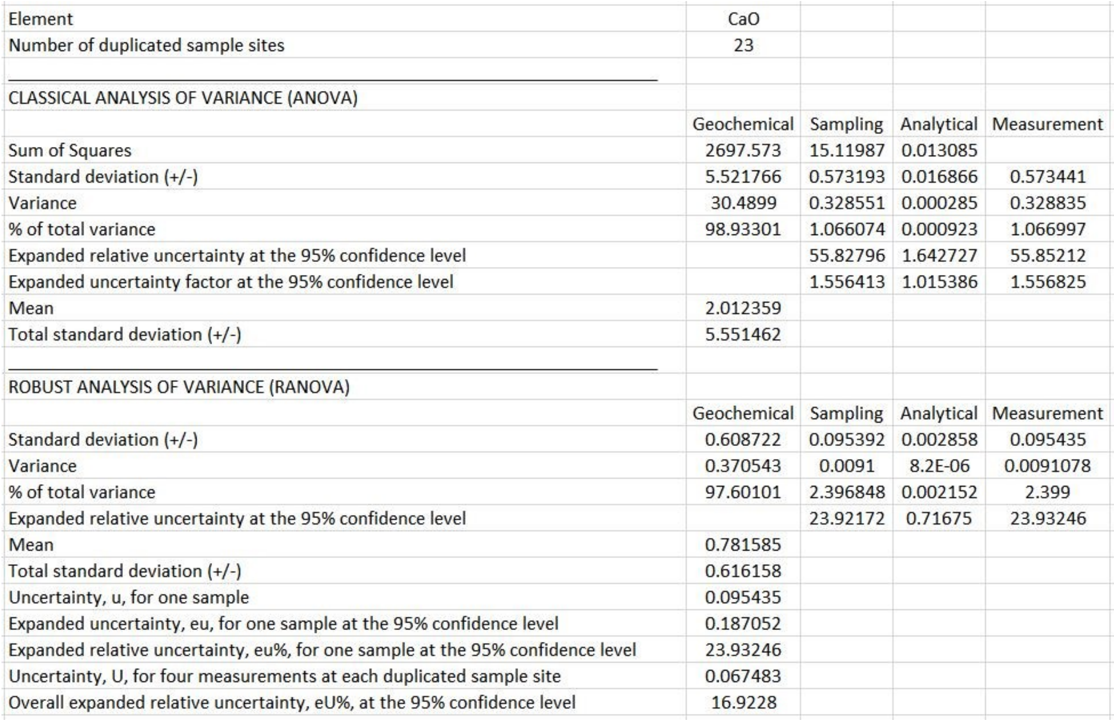
(a) (b)

Figure 7.18. Multiple-boxplots of routine and field duplicate sample splits of ***(a)*** *CaO and* ***(b)*** *Zn, FOREGS Topsoil QC data set (N=23 duplicated sites) (Salminen et al., 2005). The value of the upper whisker of all duplicate-replicate splits (N=92) is 1.63 wt% CaO, and 95 mg/kg Zn. Samples with values greater than these limits are considered outliers (see Table 7.1). Notation: DUPA = Routine sample; REPA = Replicate split of routine sample; DUPB = Field duplicate sample; REPB = Replicate split of field duplicate sample. Plotted by Alecos Demetriades (IGME/IUGS-CGGB) with Golden Software's Grapher^{TM} v20.*

Table 7.1. CaO (wt%) and Zn (mg/kg) results of routine and field duplicate sample splits of FOREGS Topsoil samples (Salminen et al., 2005). According to the results of the total number of samples (N=92), the outlying values for CaO are >1.63%, and for Zn >95 mg/kg. The outlying values are indicated by bold red numbers. Notation: DUPA = Routine sample; REPA = Replicate split of routine sample; DUPB = Field duplicate sample; REPB = Replicate split of field duplicate sample.

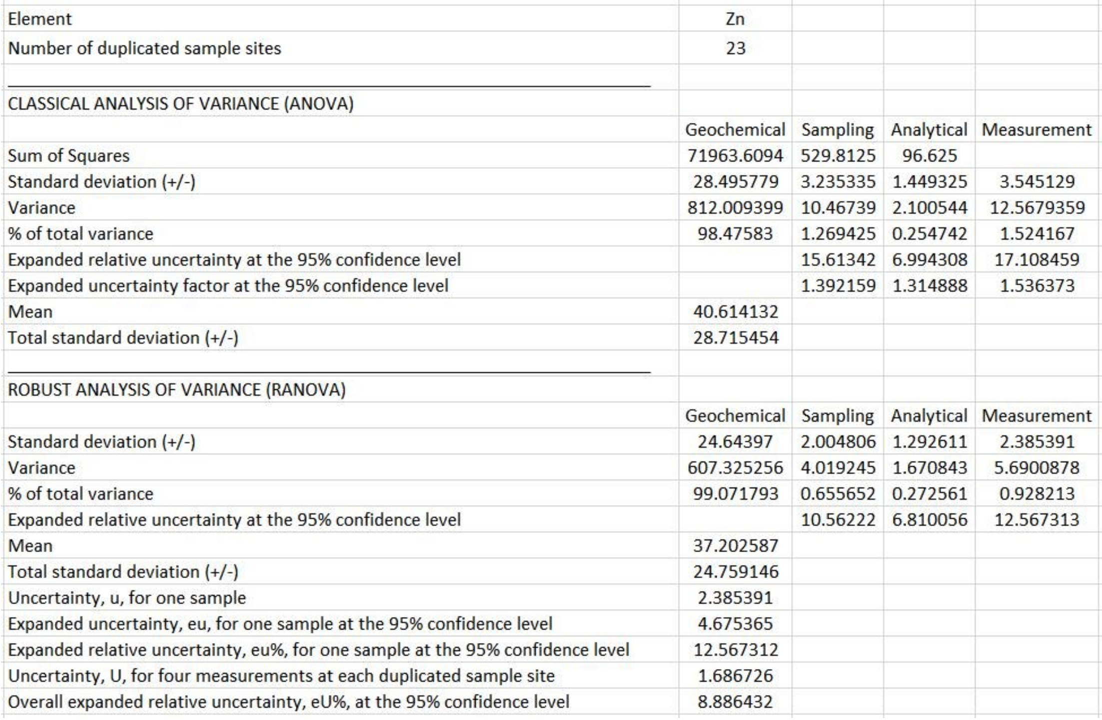
Sample Number	***CaO in wt%***				***Zn in mg/kg***			
	DUPA	***REPA***	***DUPB***	***REPB***	***DUPA***	***REPA***	***DUPB***	***REPB***
N31E05T2	0.655	0.654	0.683	0.681	67	62	60	60
N37W04T4	0.128	0.129	0.119	0.121	11	10	15	12
N32E04T5	0.363	0.363	0.36	0.355	40	41	41	42
N34E07T3	0.963	0.964	0.976	0.981	93	91	95	94
N35E01T1	0.896	0.888	1.01	0.997	40	40	38	40
N37W01T4	0.027	0.026	0.023	0.022	1.5	1.5	5	1.5
N42E10T2	1.29	1.28	1.26	1.26	20	21	20	19
N43E09T4	1.22	1.22	1.34	1.33	13	9	15	13
N34E03T3	0.489	0.489	0.486	0.484	**100**	**101**	**98**	**100**
N32E01T1	0.337	0.337	0.257	0.256	30	31	32	34
N40E10T5	1.38	1.37	1.63	1.63	48	48	41	41
N33E08T5	0.23	0.232	0.234	0.232	22	23	23	26
N42E04T5	0.816	0.818	0.954	0.961	20	20	20	21
N43E04T5	**3.29**	**3.29**	**3.10**	**3.10**	50	49	37	31
N30E06T1	0.275	0.273	0.289	0.289	46	47	46	47
N38E04T4	0.549	0.55	0.539	0.548	27	26	24	25
N28E11T1	1.03	1.02	0.815	0.829	**107**	**105**	**104**	**107**
N34E10T5	0.147	0.149	0.11	0.110	17	19	19	19
N36E08T3	0.142	0.143	0.303	0.302	7	6	18	18
N31E03T4	1.59	1.57	**4.46**	**4.47**	50	50	46	47
N33E02T3	**25.8**	**25.9**	**28.3**	**28.5**	30	29	29	28
N34E01T1	1.03	1.04	0.566	0.57	34	37	30	32
N32E10T1	0.953	0.952	1.02	1.02	70	74	69	70

Table 7.2. Classical and robust analysis of variance results of CaO from the FOREGS Topsoil XRF data set (Salminen et al., 2005). Output as given by ROBCOOP4A.EXE program (Vassiliades, 2022). The coverage factor used in this case is 1.96 at the 95% confidence level. Note: The output is exactly as given by the program. In practice, the results should not be quoted with more than two or three significant figures to the right of the decimal point depending on the number of integers.

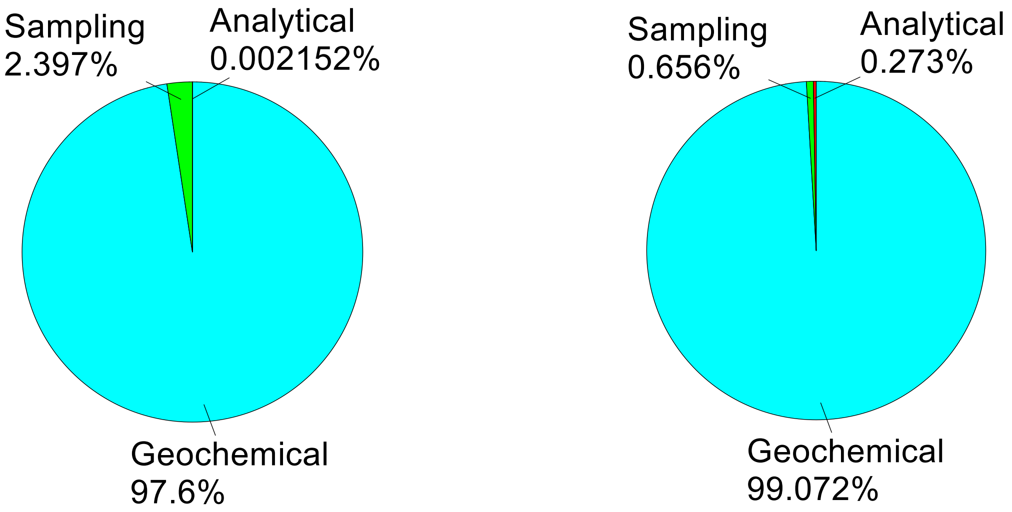


Element	CaO			
Number of duplicated sample sites	23			
CLASSICAL ANALYSIS OF VARIANCE (ANOVA)				
	Geochemical	Sampling	Analytical	Measurement
Sum of Squares	2697.573	15.11987	0.013085	
Standard deviation (+/-)	5.521766	0.573193	0.016866	0.573441
Variance	30.4899	0.328551	0.000285	0.328835
% of total variance	98.93301	1.066074	0.000923	1.066997
Expanded relative uncertainty at the 95% confidence level		55.82796	1.642727	55.85212
Expanded uncertainty factor at the 95% confidence level		1.556413	1.015386	1.556825
Mean	2.012359			
Total standard deviation (+/-)	5.551462			
ROBUST ANALYSIS OF VARIANCE (RANOVA)				
	Geochemical	Sampling	Analytical	Measurement
Standard deviation (+/-)	0.608722	0.095392	0.002858	0.095435
Variance	0.370543	0.0091	8.2E-06	0.0091078
% of total variance	97.60101	2.396848	0.002152	2.399
Expanded relative uncertainty at the 95% confidence level		23.92172	0.71675	23.93246
Mean	0.781585			
Total standard deviation (+/-)	0.616158			
Uncertainty, u, for one sample	0.095435			
Expanded uncertainty, eu, for one sample at the 95% confidence level	0.187052			
Expanded relative uncertainty, eu%, for one sample at the 95% confidence level	23.93246			
Uncertainty, U, for four measurements at each duplicated sample site	0.067483			
Overall expanded relative uncertainty, eU%, at the 95% confidence level	16.9228			

Table 7.3. Classical and robust analysis of variance results of Zn from the FOREGS Topsoil XRF data set (Salminen et al., 2005) as given by the output of ROBCOOP4A.EXE program (Vassiliades, 2022). The coverage factor used in this case is 1.96 at the 95% confidence level. Note: The output is exactly as given by the program. In practice, the results should not be quoted with more than two or three significant figures to the right of the decimal point depending on the number of integers.



Element	Zn			
Number of duplicated sample sites	23			
CLASSICAL ANALYSIS OF VARIANCE (ANOVA)				
	Geochemical	Sampling	Analytical	Measurement
Sum of Squares	71963.6094	529.8125	96.625	
Standard deviation (+/-)	28.495779	3.235335	1.449325	3.545129
Variance	812.009399	10.46739	2.100544	12.5679359
% of total variance	98.47583	1.269425	0.254742	1.524167
Expanded relative uncertainty at the 95% confidence level		15.61342	6.994308	17.108459
Expanded uncertainty factor at the 95% confidence level		1.392159	1.314888	1.536373
Mean	40.614132			
Total standard deviation (+/-)	28.715454			
ROBUST ANALYSIS OF VARIANCE (RANOVA)				
	Geochemical	Sampling	Analytical	Measurement
Standard deviation (+/-)	24.64397	2.004806	1.292611	2.385391
Variance	607.325256	4.019245	1.670843	5.6900878
% of total variance	99.071793	0.655652	0.272561	0.928213
Expanded relative uncertainty at the 95% confidence level		10.56222	6.810056	12.567313
Mean	37.202587			
Total standard deviation (+/-)	24.759146			
Uncertainty, u, for one sample	2.385391			
Expanded uncertainty, eu, for one sample at the 95% confidence level	4.675365			
Expanded relative uncertainty, eu%, for one sample at the 95% confidence level	12.567312			
Uncertainty, U, for four measurements at each duplicated sample site	1.686726			
Overall expanded relative uncertainty, eU%, at the 95% confidence level	8.886432			



(a) (b)

Figure 7.19. Pie charts of robust balanced ANOVA results for ***(a)*** *CaO and* ***(b)*** *Zn in topsoil samples of the FOREGS Geochemical Atlas of Europe, determined by XRF (Salminen et al., 2005). Plotted by Alecos Demetriades (IGME/IUGS-CGGB) with Golden Software's Grapher^{TM} v20.*

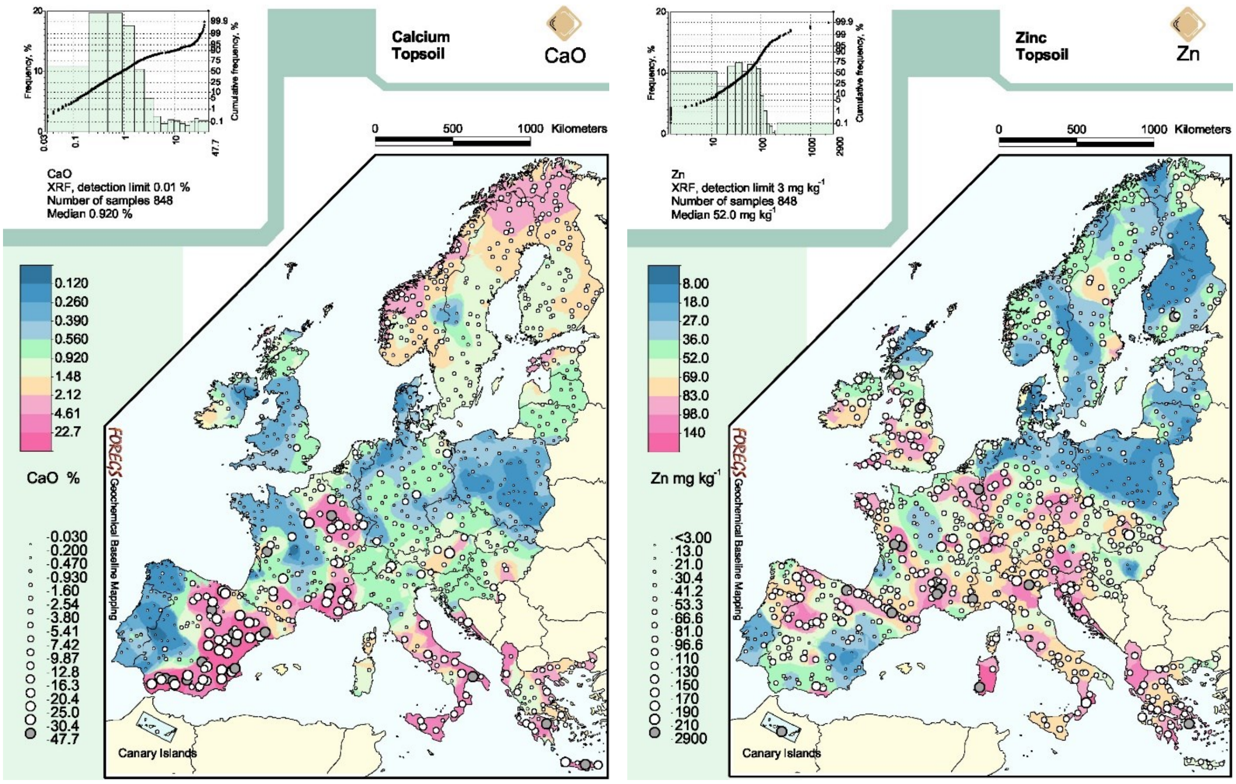
7.4.3.1.1. Use of expanded uncertainty factor

The example in Table 7.4 shows the advantage of using the expanded uncertainty factor (^{F}U) in comparison to the robust expanded relative uncertainty (U'). The former takes into account the positive skewness in the Zn topsoil analytical data (Figs. 7.12 & 7.20b - inset), and gives a much higher upper confidence limit (UCL) on the Zn concentration in comparison to the lower confidence limit (LCL), *i.e.*, the confidence interval from -23.5 to +36 mg/kg is asymmetrical around the measured value of 67 mg/kg Zn. While using the robust expanded uncertainty (U'), a symmetrical confidence interval of ±8.4 mg/kg Zn on the measured value of 67 mg Zn/kg is given.

The notable difference between the two estimations is shown in the X-Y plot of Figure 7.21. Using the robust expanded relative uncertainty (U'), the UCL and LCL remain constant at ±12.6% on the Zn values through the entire concentration range. While the UCL and LCL, estimated by the expanded uncertainty factor (^{F}U) on the Zn values, allow for the asymmetry due to the positive skewness of the Zn concentrations (Fig. 7.12a). This feature is quite evident in Figure 7.21 as the upper and lower confidence limits become distinctly larger at higher Zn concentrations.

Table 7.4. Calculations using the Zn concentration of 67 mg/kg in topsoil sample N31E05T2 (see Tables 7.1 and 7.3) with respect to the robust expanded relative uncertainty (U'=±12.6%), and expanded uncertainty factor (^{F}U=1.54). The much higher UCL for the ^{F}U approach better reflects the positive skewness of the underlying logarithmic frequency distribution (see histogram and cumulative frequency curve in Fig. 7.12). The coverage factor used in this case is 1.96 at the 95% confidence level. See Table 7.5 for the calculations and Figure 7.21. Notation: LCL = Lower confidence limit; UCL = Upper confidence limit; CI = Confidence interval.

Measurement uncertainty and factor at the 95% confidence level		***Calculation of LCL***	***LCL (mg/kg)***	***Calculation of UCL***	***UCL (mg/kg)***	***CI around measured value (mg/kg)***
Robust expanded relative uncertainty (U')	12.6%	67 – (67*12.6%) (Equation 26)	58.6	67 + (67*12.6%) (Equation 25)	75.4	±8.44
Expanded uncertainty factor (^{F}U)	1.54%	67/1.54 (Equation 34)	43.5	67*1.54 (Equation 33)	103	-23.5, +36



(a) (b)

Figure 7.20. FOREGS Geochemical Atlas of Europe maps of topsoil ***(a)*** *CaO and* ***(b)*** *Zn determined by XRF. Source: Salminen et al. (2005, p.158 CaO - http://weppi.gtk.fi/publ/foregsatlas/maps/Topsoil/t_xrf_cao_edit.pdf; p.513 Zn - http://weppi.gtk.fi/publ/foregsatlas/maps/Topsoil/t_xrf_zn_edit.pdf). It is noted that the number of topsoil samples analysed by XRF is 845 and not 848.*

Table 7.5. Extract from the example used for plotting Figure 7.21 to show the calculations presented in Table 7.4 with respect to the Expanded uncertainty factor (^FU). The Microsoft Excel worksheet is provided in the Supplementary material (IUGS-CGGB_Chapter-7_FOREGS_Topsoil_LCL_&_UPL.xlsx). Numbers were rounded to the first decimal place <99.9 and nearest integer >100.

GTN Sample No.	**Zn_i (mg/kg) ordered**	**Zn_i LCL (mg/kg) ($Zn_i / {}^FU\%$)**	**Zn_i UCL (mg/kg) ($Zn_i * {}^FU\%$)**	**E_i (mg/kg) ($Zn_i * U'\%$)**	**$Zn_i - E_i$ (mg/kg)**	**$Zn_i + E_i$ (mg/kg)**
	Zn_i	**$Zn_i / 1.54$**	**$Zn_i * 1.54$**	**$E_i = Zn_i * 0.126$**		
………	………	………	………	………	………	………
N42E11T3	114	74.0	176	14.4	99.6	128
N25E13T1	115	74.7	177	14.5	101	129
N38W03T3	117	76.0	180	14.7	102	132
N32E07T1	118	76.6	182	14.9	103	133
N26E13T2	120	77.9	185	15.1	105	135
N30E06T4	130	84.4	200	16.4	114	146
N33E06T1	141	91.6	217	17.8	123	159
N29W02T5	142	92.2	219	18.0	124	160
N37W01T3	295	192	454	37.2	258	332
N31W01T5	314	204	484	39.6	274	354
N26E14T4	358	232	551	45.1	313	403
N27E05T1	396	257	610	50.0	346	446
………	………	………	………	………	………	………

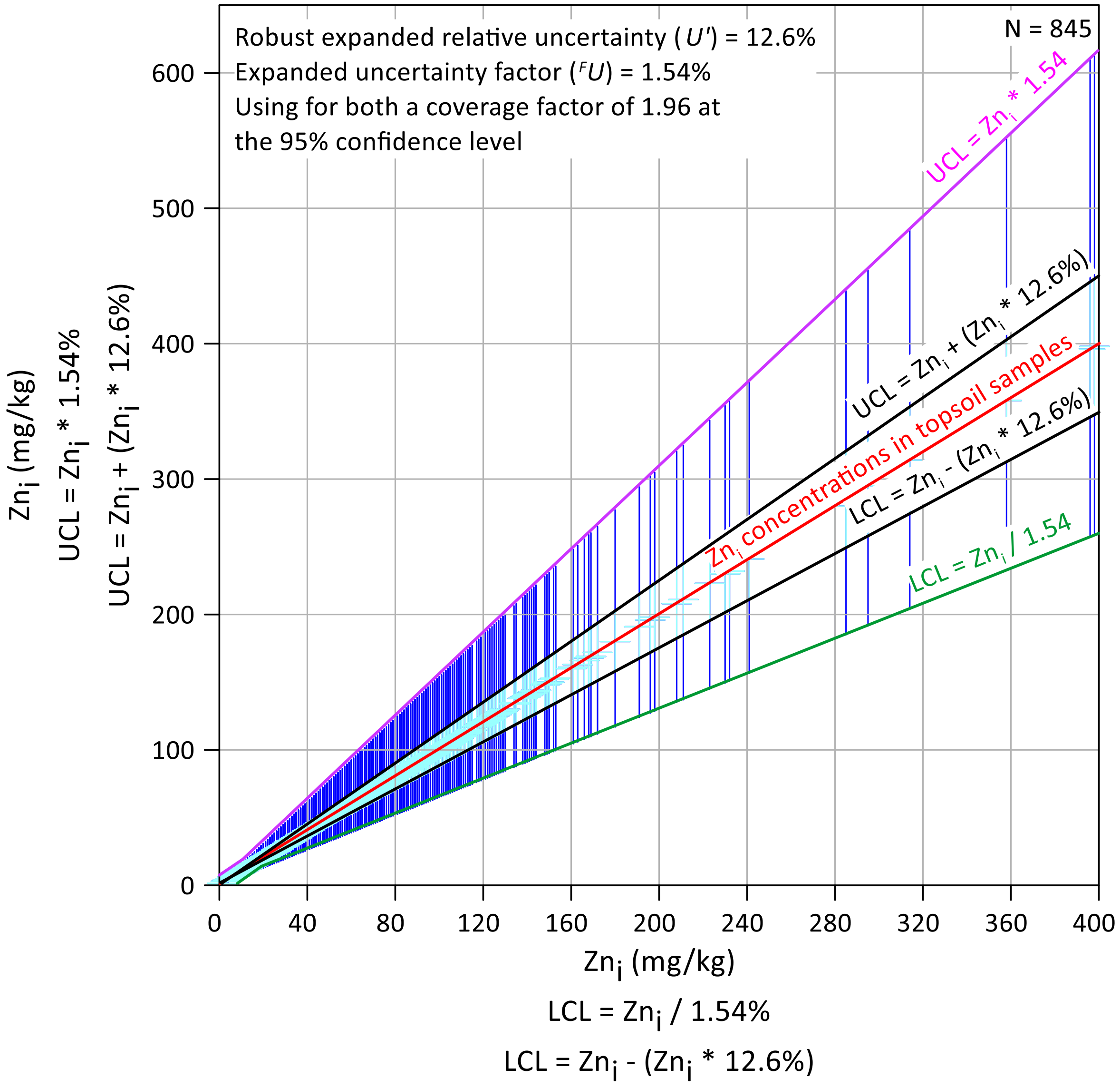


Figure 7.21. Composite high-low-close plot of Zn_i versus Zn_i concentrations in topsoil samples showing the upper (UCL) and lower (LCL) confidence limits estimated by the robust expanded relative uncertainty (U') and expanded uncertainty factor (^FU) on the Zn_i concentrations. The most notable feature is the exhibited asymmetry of the UCL and LCL on the Zn_i concentrations calculated with the use of the expanded uncertainty factor (^FU). It is noted that the plot shows Zn concentration values up to 400 mg/kg in the abscissa and 600 mg/kg in the ordinate. Plotted by Alecos Demetriades (IGME/IUGS-CGGB) with Golden Software's Grapher^{TM} v20.

Supplementary material

The following files can be downloaded from the Publications web page of the IUGS Commission on Global Geochemical Baselines (http://www.globalgeochemicalbaselines.eu/):

- IUGS-CGGB_Chapter-7_DUPREPPLOT.xlsm
- IUGS-CGGB_Chapter-7_DUPREPPLOT_Output.xlsm
- IUGS-CGGB_Chapter-7_DUPREPPLOT_ExcelMacroEMPTY.xlsm
- IUGS-CGGB_Chapter-7_PDLPRECIS_Clean_worksheet.xlsx
- IUGS-CGGB_Chapter-7_PDLPRECIS_Worked-example.xlsx
- IUGS-CGGB_Chapter-7_FOREGS_Topsoil_XRF_QC_data.xlsx
- IUGS-CGGB_Chapter-7_FOREGS_Topsoil_XRF_LCL_&_UCL.xlsx

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Note: All hyperlinks were checked on the 4th of February 2022.

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