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Monitoring of Air Pollution Effects on Forests (ICP Forests)

MANUAL

on

methods and criteria for harmonized sampling, assessment,
monitoring and analysis of the effects of air pollution on forests

Part XVI

Quality Assurance and Control in Laboratories

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Prepared by:

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1 Introduction

Chemical analyses are an essential part of monitoring activities related to observations and measurements of nutrients and pollutants fluxes in forest ecosystems. The value of data collected under the framework of the ICP-Forests programme depends to a great extent on the quality of the analytical work carried out in supporting laboratories across Europe. To gain full comparability of the spatial and temporal variability in the data, every effort must be taken to ensure accuracy of the analytical measurements.

To that end, considerable efforts have been made over the last number of years to improve the quality of laboratory analyses in the various monitoring programmes within the framework of the ICP Forests programme. The Soil & Soil Solution, Deposition and Foliage & Litterfall expert panels have carried out a number of ring tests and held extensive discussions on harmonising analytical methodology, including the most appropriate quality control (QC) and quality assurance (QA) to be employed by participating laboratories. An expert panel sub-group, 'Working Group on QA/QC in Laboratories', has extended its remit from optimising the quality control of water analyses to encompass all forms of laboratory analysis, and now also includes experts in the fields of soil, foliage and litterfall.

Presented quality assurance and control tools remain in line with the overall QA approach within the ICP Forests, as outlined in the Part III of the Manual.

2 Scope and application

This paper presents all the QC methods that have been devised for the relevant fields of analytical chemistry. The aim is to provide those laboratories carrying out analyses of water, soil solution, soil, foliage and litterfall within the ICP Forests programme with a complete overview of the QC options that can be applied in their laboratories.

The QA programme in each laboratory should be based on both: internal and external quality control. Among the range of internal control methods that can be employed, the use of reference materials is highly recommended (Chapter 3.1) as an extremely valuable tool to ensure accuracy of analytical results. Although the use of Certified Reference Materials can be limited by expense and availability in large quantities alternative Reference Materials, such as National or Local Reference Materials can be used on a routine basis to confirm the analytical methods accuracy and precision over time. The variation and the quality of the analytical results can be controlled with the use of control charts. The different types of control charts available, their construction and application are described in Chapter 3.2.

Analytical data must be validated prior to data submission to confirm the correctness of analyses and exclude the risk of errors. A wide range of data consistency checks are detailed depending on the type of matrix analysed (Chapter 3.3, 3.3.1-3.3.3), based on the relationship between the chemical components and/or chemical and physical properties of the samples.

Participation by laboratories in external inter-calibration exercises plays an integral role in the laboratory's QA programme (Chapter 3.4). Otherwise known as 'ring tests', they are carried out on a periodic basis and assess the performance of the participating laboratories as well as help to ensure the comparability of the data produced by different laboratories over time. Laboratories encountering difficulties with analytical methodology and/or associated QA/QC programmes are encouraged to take full advantage of the range of proposals contained within this document, which include the exchange of analytical expertise, and experiences between laboratories.

Evaluation of the quality performance of the participating laboratories within ICP Forests will be conducted through the use of quality indicators outlined in Chapter 3.5. Information gathered on the laboratories quality assurance processes/activities, will be linked via quality reports, with the submission of data to ICP Forests each year.

3 Quality assurance and control tools

3.1 Use of reference materials

Within the ICP-Forests programme the use of control charts for each variable and matrix is mandatory. In order to produce these control charts, a reference material is necessary.

There are two types of reference material:

- 1 Reference Materials (RM): a material or substance, one or more of whose property values are sufficiently homogeneous and well established to be used for the calibration of an apparatus, the assessment of a measurement method, or for assigning values to materials (ISO Guide 30, 1992)
- 2 Certified Reference Materials (CRM): Reference material, accompanied by a certificate, one or more of whose property values are certified by a procedure, which establishes its traceability to an accurate realisation of the units in which the property values are expressed, and for which each certified value is accompanied by an uncertainty at a stated level of confidence (ISO Guide 30, 1992). The CRM can be of national or international origin. A list of commercially available CRMs is given in Annex 5.3.

Reference materials are available in a range of types and prices. CRMs are expensive and should be used only when really needed: e.g. calibration, method validation, measurement verification, evaluating measurement uncertainty (Nordtest Report 537, 2003), and for training purposes. In many cases, however, the concentrations are not within the ranges encountered in daily practice. National Reference Materials are, in many cases, easier to acquire and are often not as expensive as CRMs. They are usually issued by national laboratories, and are extremely useful for ensuring laboratory quality within a country.

Furthermore, laboratories must use matrix-matched control samples of demonstrated stability to demonstrate internal consistency over time, e.g. through control charts. The analyte concentrations of these samples do not need to be accurately known or traceable. However, traceability would be a bonus. Here, again, CRMs or ring test samples can be used.

The Local Reference Materials (LRMs) are prepared by the laboratory itself for routine use and can be easily and cheaply prepared in large quantities. They can often also be prepared within the concentration ranges for the more important parameters. These LRMs are extremely important for QA/QC activities, mainly for use in **control charts** (see Chapter 3.2), if there is a need to maintain a constant (stable) quality over a longtime scale.

The following reference materials can be used in each field of interest:

3.1.1 Reference material for water analysis (deposition and soil solution)

One common approach is to use natural samples that are preserved with stabilising agents (e.g. low chloroform concentrations), after first ensuring that their use does not cause interferences in the analytical methods or has an adverse effect on other activities performed in the laboratory. The use of natural samples makes it possible to have concentrations close to those normally measured. It is advisable to use two standards for each type of analysis, one of medium-low and one of

medium-high concentrations, in relation to the range normally analysed. The stability of LRMs should be tested; their stability for individual ion species may vary.

One very cheap method for preparing an LRM is to buy mineral water that has chemical characteristics close to the range normally measured. Before you can use an LRM, however, you first have to validate your method with a CRM. You should run your LRM together with the CRM or a ring test sample so as to determine the conventional true value.

For deposition samples, mineral water derived from volcanic bedrock has very similar concentrations. For soil solution samples, a specific type of mineral water has to be selected in accordance with the prevailing soil types in the monitoring network. The advantage of using mineral water is that they are relatively stable over time as long as the bottles of the same batch are stored in a dark place. However, mineral water does not contain dissolved organic carbon (DOC) in a form similar to that occurring in either deposition or soil solution samples.

3.1.2 Reference material for foliar analysis

The matrix properties and the analyte concentrations of the reference material should be similar to those of the samples from the regional/national network. As there is only a limited number of certified forest-tree foliage reference material available worldwide, agricultural plant material with similar matrix and analyte concentrations, e.g. flour, hay, cabbage, olive leaves, apple leaves, can be used as an acceptable substitute. However, check the analyte concentrations before placing the order. (A list of commercially available CRM's is given in Annex 5.3).

"Old" ring test samples are also stable enough and extensively analysed for use as reference material in method validation.

One good cheap method for producing a high quality LRM is to prepare foliage material for use as a ring test sample. In the ring tests, the Forest Foliar Co-ordinating Centre (FFCC) always utilises dried, powdered foliage samples from one type of tree and leaf or a homogenized litterfall sample. Therefore, the laboratory should initially separate the needles/leaves from the branches and dry, mill and homogenise the material (dry weight min. 4-5 kg) prior to dispatch to the FFCC (<http://www.ffcc.at/>)

The FFCC homogenizes the sample again, divides it up and uses it in one of the subsequent ring tests. The advantage for the laboratory is in having a large amount of reference material with a similar element concentration as their normal samples and known accuracy of the mean concentration.

3.1.3 Reference material for soil analysis

3.1.3.1 Preparation of local reference material for soils

Due to the type of soil samples and the nature of the two-step analysis, LRM samples are needed for both the solid phase (to control the quality of digestion) and the liquid phase (to control the quality of the chemical analyses).

- Solid phase:

Take several large (10 to 50 kg) samples from one site (organic and mineral, preferably by horizon). Dry all the sampled material and homogenise the samples several times to ensure a uniform homogeneous sample. Split or riffle each sample into several parts and store in a cool, dry place. It may be worthwhile preparing several sets of the individual soil types and concentration ranges occurring in the country (e.g. one for clay soils in the coastal area with high sea salt concentrations, and one for sandy soil from an inland site).

- Liquid phase:

After digestion of larger amounts of the solid phase LRM, store the solution (liquid phase) in a cool, dark place.

In general, no control with high analyte concentrations is necessary because the errors are normally associated with lower concentrations. Solutions with excessively high concentrations often have to be diluted in order to fit within the ranges for which the analysers have been calibrated.

The amount of LRM has to be large enough to be used for an extended period of time (preferably up to one year). The amount needed annually will depend on the type of analytical equipment and methods used by the laboratory. The sample should be stored in such a way that no or minimal changes occur over time.

3.1.3.2 Calibration of local reference material for soils

After the preparation of the LRM, a test run has to be performed with correctly calibrated equipment. A number of replicates (e.g. 5 for the solid and 30 for the liquid phase) have to be analysed for all relevant parameters, and at least one (but preferably more) national or international reference samples. The absolute accuracy is determined for each parameter on the latter samples. The standard deviation (SD) calculated from the results of analysis of the LRM should be as small as possible. The results of the first test run should be treated according to the ISO standard 8258 (1993, Shewhart control charts). The mean value of the parameters for the LRM is of less importance, but it should be within the same range as the values of the samples that will be subsequently analysed.

Each parameter now has its own SD, which allows evaluation of the parameters and the relevance of the analysis by the method in question. If the SD is significantly larger than the expected values, then the relevance of analysing the parameter by the selected method is low. Other methods/equipment may have to be used to analyse the parameter within an acceptable range.

This procedure should be repeated whenever equipment is changed, important components are replaced, or when temporal trends appear in the results. The absolute values obtained from the national and international reference material are extremely importance in the former case.

3.1.3.3 C. Use of local reference material for soils

After successful calibration, a systematic re-analysis of the LRM (liquid phase) is included in every batch or series of samples. Depending on the number of samples to be analysed and the methods and equipment used, this could be in the range of one LRM per 10 to 30 real samples to be analysed. For the solid phase (digestion and analysis) this could be reduced to one LRM per 30 to 50 samples to be analysed.

The results of the repeated analysis of the LRM permit evaluation of the stability of the method/equipment over time. Therefore, it is strongly recommended to plot on a graph the LRM result of every analysis over time (see ISO 8258, 1993 and Chapter 3.2).

3.2 Use of control charts

Within the ICP-Forests programme the use of control charts for each parameter and matrix is mandatory.

Control charts form an important practical aspect of internal QC in the laboratory. Using reference materials (see Chapter 3.1) the quality of the method can be checked immediately, while control charts are a useful tool for checking the quality and the variation in quality over a longer time scale. The laboratory runs control samples together with the real samples in an analytical batch and,

immediately after the run is completed, the control values are plotted on a control chart. There are various types of control chart available (for details see the ISO 8258, 1993). The most commonly used control charts are the **mean chart** and **range chart** for laboratory control standards, and the **blank chart** for background or reagent blank results.

In addition, the control charts can be used for calibration, method validation and comparison, estimation of measurement uncertainty and limit of detection, checking the drift of equipment, comparison or qualification of laboratory personnel, and evaluation of proficiency tests.

For more information about the use of control charts see Nordtest report TR 569, 2007.

3.2.1 Use of control charts for LRM or laboratory control standards

Means chart (X-chart). The main aim of the means chart is to check the repeatability of the measurements in every batch of analyses. It is constructed from the average and standard deviations of a standard, determined from a solution of one or more analyte(s), or a natural sample, that is sufficiently stabilised to keep the concentrations constant over time for at least 2-4 months. In the case of deposition samples, the choice of preservative (e.g. inorganic acids or chloroform) is determined by the analyte of interest and the conditions under which the analyses are carried out. It is advisable to use more than one control chart, at different concentration levels for each analyte.

The means chart is prepared on the basis of the first 20 to 25 measurements used to calculate the mean concentration (X_m) and the standard deviation (s). These variables are used to evaluate the upper and lower warning levels (UWL, LWL) and the upper and lower control levels (UCL, LCL). It is a common practice to use $\pm 2s$ and $\pm 3s$ limits for the warning limit (WL) and control limit (CL), respectively (Figure 3.2.1a). For variables with a non-normal distribution, transformation to a normal distribution may be necessary.

Assuming that s is correctly estimated, 95% of the measurements should fall within the range of $X_m \pm 2s$ (WL) and 99% in the range of $X_m \pm 3s$ (CL). In long-term routine analyses, on the other hand, UWL and LWL may be chosen by the analyst on the basis of experience with previous control charts or according to specific goals that are to be reached in the analyses.

The means chart can also incorporate a target or nominal value of the analyte in the case of reference material with the reported concentration. The target control limits may also be used, and the laboratory results then be compared with these values.

If measurement uncertainty is determined for an analyte as a part of method validation, this value can be added to a means chart. Measurement uncertainty limits in the chart should lie between the warning and control limits ($2s$ and $3s$), in most case nearer the warning limit. The results of a control sample should not exceed the measurement uncertainty limits and, in the case of a synthetic control sample, they should remain between these limits. A target or nominal value can also be used with the measurement uncertainty limits. Because measurement uncertainty is proportional to the concentration of the analyte, different measurement uncertainty limits should be used for different control charts of the same analyte. With this type of x-chart it is possible to check that the set measurement uncertainty is achievable in the course of time.

Every batch of analyses should include one or more measurements of the standard for the control chart. This measurement is plotted on the control chart: if a measurement exceeds the CL, the analysis must be repeated immediately. If the repeat is within the CL, then the analysis can be continued; if it exceeds the CL, the analysis should be stopped and the problem rectified. In regard to the WL: if two out of three successive points exceed the WL, then an additional standard should be analysed. If the concentration is less than the WL, the analysis can be continued; if it exceeds the WL, then the analysis should be stopped and the problem rectified.

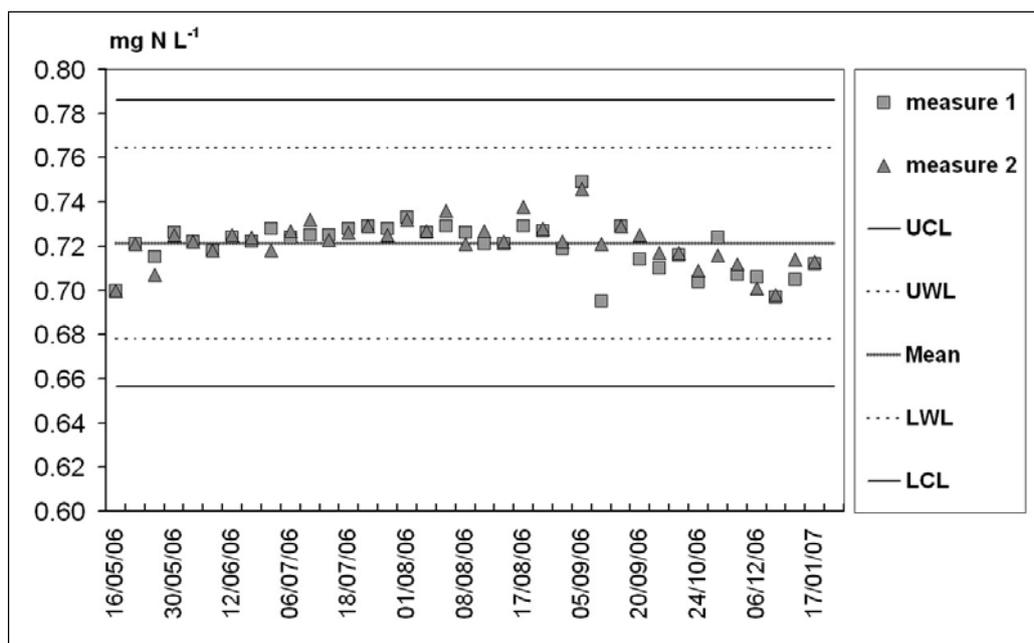


Figure 3.2.1a: Example of a control chart using mean concentrations. Mean concentration, LWL, UWL lower, upper warning limit; LCL, UCL lower, upper control limit, calculated on the basis of experience with previous control charts (R.S.D. = 3 %)

Range chart (R chart). The difference between two (or more) determinations on the same sample can also be described on a graph. This R chart is used for checking the repeatability of the analysis, usually of duplicate determinations. As the range is normally proportional to the sample concentration, it will therefore be more appropriate to use a control chart where the control value is the relative range r %.

3.2.2 Use of control charts for blanks

Blank chart. A blank is defined as a solution of the purest available water that contains all the reagents used for the analysis, but not the analyte. The solution should be subjected to all the steps of the analysis (filtration, digestion, addition of reagents) up until the final measurement. The blank signal then indicates the sum of the analyte released in the different phases of the process, and a check must be made in order to exclude the possibility of occasional contamination. An example of a blank chart is shown in Figure 3.2.2a. The chart makes it possible to compare the blank values obtained in different batches of analyses at different times; an abnormally high blank value indicates the presence of contaminants at some stage of the process. The upper limit of acceptance is chosen by the analyst, either based on a previous set of analyses (e.g. two times the mean values of the blank absorbance) or on the dispersion of values around the mean.

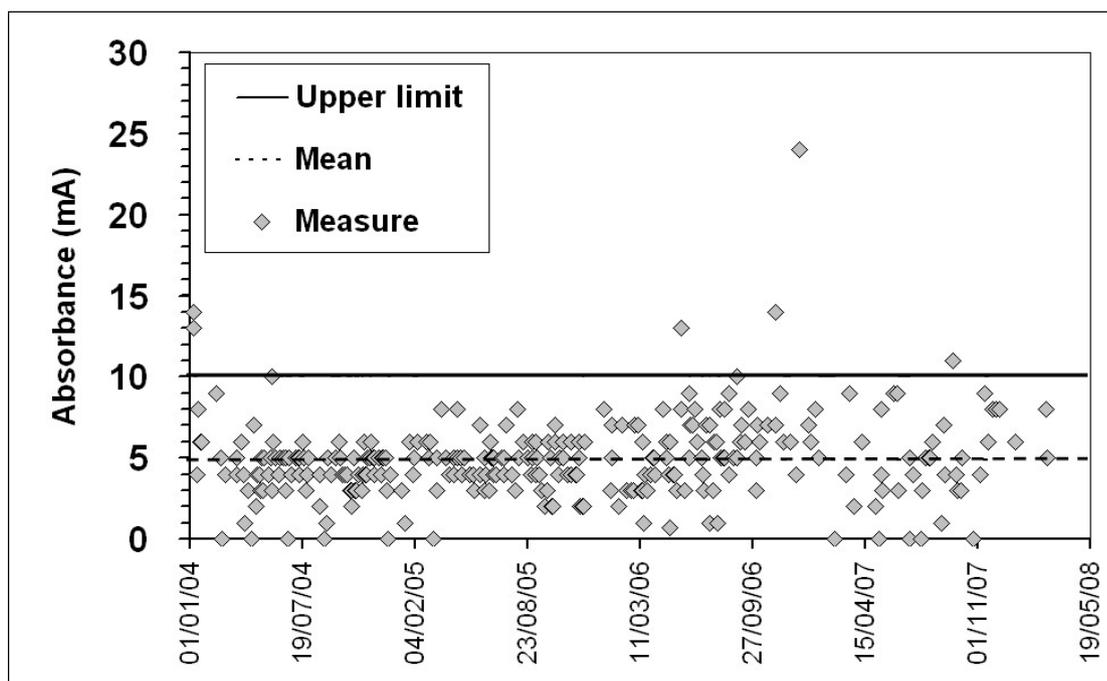


Figure 3.2.2a: Example of a blank chart

The standard deviation (s_b) of the blanks makes it possible to determine the detection limit (LOD) and the quantification limit (LOQ) of the analytical method. The LOD in most instrumental methods is based on the relationship between the gross analyte signal S_t , the field blank S_b , and the variability in the field blank (s_b). The limit of detection and quantification may be defined by the extent to which the gross signal exceeds S_b :

$$\text{LOD} = S_t - S_b \geq K_d s_b$$

$$\text{LOQ} = S_t - S_b \geq K_q s_b$$

Recommended values for K_d and K_q are 3 and 10, respectively (Analytical Methods Committee, 1987, Currie, L.A. 1999b).

3.2.3 Detection and quantification limits

Detection and quantification capabilities are fundamental performance characteristics of any chemical measurement process (Currie, 1999a). For each matrix (soil, water, foliage) and each analytical method, the limit of detection (LOD) and quantification (LOQ) should be determined by each laboratory.

The limit of detection (LOD) is the smallest measure, x_L , that can be detected with reasonable certainty for a given analytical procedure.

The value of x_L is given by the equation:

$$x_L = x_{bi} + K s_{bi}$$

where x_{bi} is the mean of n blank measurements, s_{bi} is the standard deviation of n blank measurements, and K is a numerical factor chosen according to the confidence level desired (IUPAC, 1997). For LOD, this K factor is commonly set at 3 (see also K_d in Chapter 3.2.2). The LOD is the concentration at which we can decide whether an element is present or not. It is the point where we can just distinguish a signal from the background (Thomsen et al., 2003).

It is recommended that the number of blank measurements (n) is higher than 30, preferably determined under within-lab reproducibility conditions (e.g. different operators, different runs on different days).

The limit of quantification (LOQ), also referred to as the quantitation limit, is generally agreed to begin at a concentration equal to 10 standard deviations of the blank ($K_q = 10$). Therefore, LOQ is 3.3 times LOD. Quantitatively, the relative standard deviation (RSD) of repeated measures is 10% at the LOQ, and 33% at the LOD (Thomsen et al., 2003). This is in fact a statistical simplification of the uncertainty problem near the lower measurements limits, as explained by Currie (1999b), but in practice it is a useful approximation.

Table 3.2.3a: IUPAC recommendations for uncertainty associated with limits of detection and quantification (after Thomsen et al., 2003).

		Absolute SD	Relative SD
Limit of detection	LOD	3σ	33%
Limit of quantification	LOQ	10σ	10%

Similar results can also be obtained using the standard deviation of the signal of the lowest calibration standard, instead of the standard deviation of the signal of blank samples. This method should be used in particular when the signal of blank samples is very low, as in the case of ion chromatography. A further possibility is the use of the Hubaux-Vox method for calculating LOD from the error associated to the calibration regression.

A distinction should be made between instrument detection/quantification limits and method (or matrix) detection limits. Generally, instrument detection limits (IDLs) are based on a clean matrix. Method/matrix detection limits (MDL) consider real-life matrices such as soil, organic matter and rainwater. Spectroscopists commonly accept that the MDL can be anywhere from about two to five times greater than the IDL.

Therefore, labs should clearly mention whether the reported limits are instrument or matrix detection limits. In the case of environmental research, MDLs are more meaningful than IDLs.

Measurement precision and concentration (or content) are often clearly related, as shown in Figure 3.2.3a. Generally, as the concentration or content of the analyte decreases, the precision for determination, as expressed in the relative standard deviation increases. When empirically precision data are gathered for each concentration or content level, a graph may be constructed as in Figure 3.2.3a. Each data point represents the RSD of 8 to 20 replicate measurements per level.

When a curve is fitted with a suitable equation (e.g. $y = a x^{-b}$), the limits of detection and quantification may be estimated from this equation by determining the limits at the RSD values of 30% and 10%, respectively. These limits are illustrated in Figure 3.2.3a, whereby total N can be reliably determined in this example at concentrations above the LOQ, whereas determination becomes highly uncertain between the LOD and LOQ. The curve can be constructed using the standard deviation obtained from control charts at different concentration. When the matrix effect is negligible, the standard deviation of the signal of the calibration standards can also be used.

An example of application of the LOD and LOQ estimation method for the determination of carbon by the Walkley-Black method in forest soils can be found in De Vos et al. (2007).

This empirical method is time-consuming and laborious. However, it immediately shows the matrix detection and quantification limits for real-life samples under specific laboratory conditions.

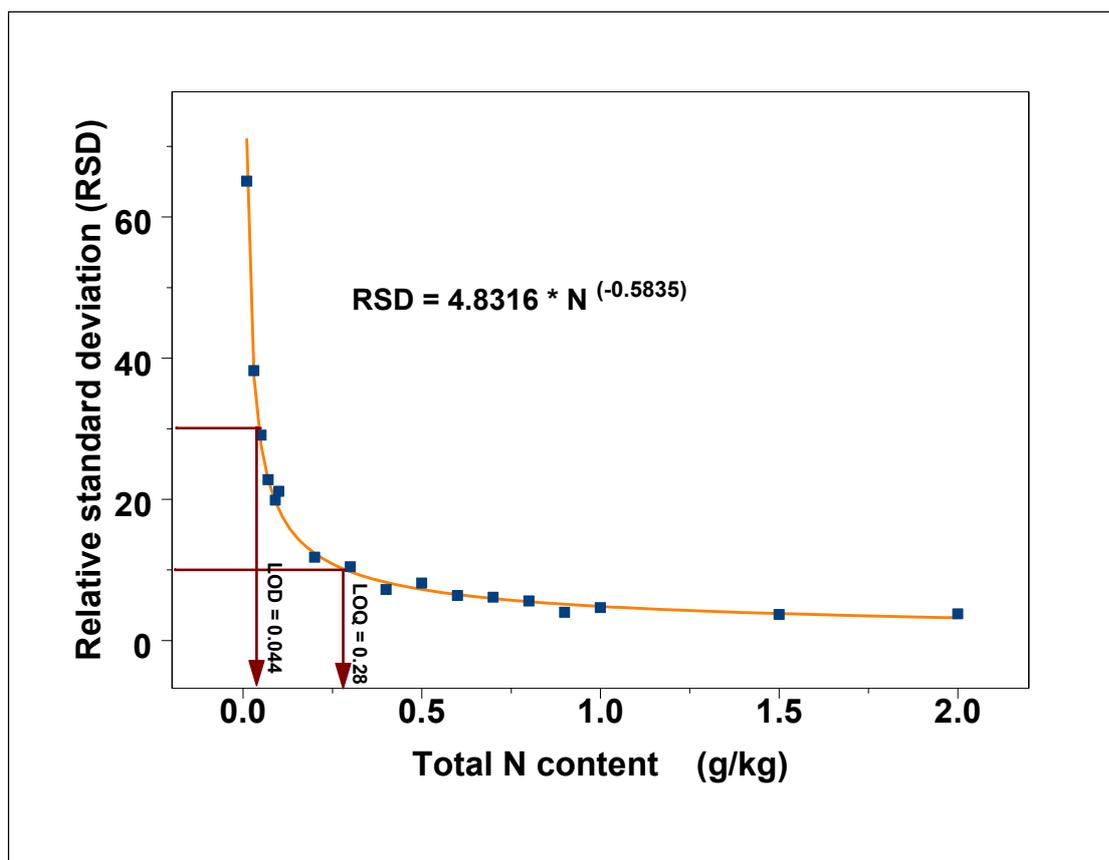


Figure 3.2.3a: Relationship between measurement precision (RSD) and N concentration in a test mineral soil sample

3.3 Checking analytical data

3.3.1 Checking water sample results

The analytes present in deposition and soil water samples and in soil extracts are mainly in ionic form. This enables the use of at least two checks on the consistency of the analysis results obtained for individual samples: i.e. the calculation of the ion balance, and comparison of the measured conductivity with the conductivity calculated from the sum of each ion. A third consistency test, which is only valid for deposition samples, employs the ratio between the Na^+ and Cl^- concentrations, which should normally be relatively close to the value in seawater. A fourth check, aimed at identifying analytical errors, is based on the relationship between the different forms of nitrogen analysed. Other statistical procedures that employ the relationship between the equivalent sum of ions (cations, anions) and conductivity can be applied to the datasets. These are based on the relative similarity of the ratio between certain ions in deposition samples, due to their common origin (e.g. Na^+ and Cl^- from sea spray, SO_4^{2-} and NO_3^- from combustion processes, Ca^{++} and alkalinity from soil dust). However, these methods require a relatively large set of data for the same type of precipitation before they can be applied to the results of single analyses in order to identify outlier values.

Examples of the application of these checks on sets of data from different sites in Europe have been reported by Mosello et al. (2005, 2008).

Most of the calculations needed to use the validation check, starting from concentration values, can be simplified by using a worksheet file similar to the one given on the ICP Forests web site (<http://www.icp-forests.org/DocsQualLab/AnalyticalDataValidation.xls>; see also Chapter 5.1).

3.3.1.1 Ion balance

3.3.1.1.1 Ion balance without DOC

Each laboratory performs checks on the chemical analyses by calculating the ion balance (for bulk open field and wet only deposition) and comparing the measured and calculated conductivity (for bulk open field [BOF] and wet only deposition, throughfall [THF] and stemflow [STF]) values in order to validate the results. However, these checks are not always applicable to soil water samples due to the presence of aluminium and other metals as various ionic species, especially at a pH < 5 (see Chapter 3.3.1.1.3).

If the threshold values of these checks are exceeded, then the analyses must be repeated. If the result is confirmed but the threshold values are still exceeded, then the results must be accepted.

The ion balance is based on the equivalent concentration of anions vs. the concentration of cations (Σ Cat vs. Σ An):

$$\Sigma \text{ Cat} = [\text{Ca}^{++}] + [\text{Mg}^{++}] + [\text{Na}^+] + [\text{K}^+] + [\text{NH}_4^+] + [\text{H}^+]$$

$$\Sigma \text{ An} = [\text{HCO}_3^-] + [\text{SO}_4^{--}] + [\text{NO}_3^-] + [\text{Cl}^-] + [\text{Org}^-]$$

The contribution of fluoride to the ionic balance is normally insignificant.

The limit of acceptable errors varies according to the total ionic concentration and the type of solution. The percentage difference (PD) is defined as:

$$\text{PD} = 100 * (\Sigma \text{ Cat} - \Sigma \text{ An}) / (0.5 * (\Sigma \text{ Cat} + \Sigma \text{ An}))$$

The limits adopted in the ICP Forests/EU Forest Focus programmes are given in Table 3.3.1.1.1°

Table 3.3.1.1.1a: Acceptance threshold values in data validation based on ion balance and conductivity (see definition of CD [the percentage difference between measured and calculated conductivity] in Chapter 3.3.1.2)

Conductivity (25 °C)	PD	CD
<10 $\mu\text{S cm}^{-1}$	$\pm 20\%$	$\pm 30\%$
<20 $\mu\text{S cm}^{-1}$	$\pm 20\%$	$\pm 20\%$
>20 $\mu\text{S cm}^{-1}$	$\pm 10\%$	$\pm 10\%$

The conversion factors required to transform the units used in the ICP Forests Manual Part XIV (Deposition) into $\mu\text{eq L}^{-1}$ are given in Table 3.3.1.1.1b.

Table 3.3.1.1.1b: The conversion factors used in converting the concentrations used in the ICP Forests Deposition Monitoring Programme to $\mu\text{eq L}^{-1}$, and the values of equivalent ionic conductivity at infinite dilution

	Unit (ICPF standard)	Conversion factor to $\mu\text{eq L}^{-1}$	Equivalent conductance at 20°C	Equivalent conductance at 25°C
			kS cm ² eq ⁻¹	kS cm ² eq ⁻¹
pH	Unit	10(6-pH)	0.3151	0.3500
Ammonium	mg N L ⁻¹	71.39	0.0670	0.0735
Calcium	mg L ⁻¹	49.9	0.0543	0.0595
Magnesium	mg L ⁻¹	82.24	0.0486	0.0531
Sodium	mg L ⁻¹	43.48	0.0459	0.0501
Potassium	mg L ⁻¹	25.28	0.0670	0.0735
Alkalinity	$\mu\text{eq L}^{-1}$	1	0.0394	0.0445
Sulphate	mg S L ⁻¹	62.37	0.0712	0.0800
Nitrate	mg N L ⁻¹	71.39	0.0636	0.0714
Chloride	mg L ⁻¹	28.2	0.0680	0.0764

Bicarbonate is calculated from total alkalinity (Gran's alkalinity) in relation to pH, assuming that total alkalinity is determined only by inorganic carbon species, protons and hydroxide:

$$\text{TA} = -[\text{H}^+] + [\text{OH}^-] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$$

This definition is not completely correct in the case of high organic carbon concentrations ($\text{DOC} > 5 \text{ mg C L}^{-1}$), and in the presence of metals (Al, Fe, Mn etc.) that may contribute to alkalinity or to the cation concentrations (see Chapters 3.3.1.1.2 and 3.3.1.1.3). This sets limits on the use of the ion balance check in validating the analyses for certain types of solution, as summarised in Table 3.3.1.1.1c.

Table 3.3.1.1.1c: Applicability of the validation tests for different types of solution

	Ion balance	Ion balance DOC corrected	Conductivity	Na/Cl ratio	N test
Bulk open field	Y	Y	Y	Y	Y
Wet only	Y	Y	Y	Y	Y
Throughfall	N(3)	Y	Y	Y	Y
Stemflow	N(3)	Y	Y	Y	Y
Soil water	N(3)	N(4)	Y(2)	N	Y
Surface water	Y(1)	Y	Y	N	Y

(1) If $\text{DOC} < 5 \text{ mg C L}^{-1}$ and negligible metal concentrations

(2) If metal concentrations are negligible.

(3) see chapter 3.3.1.1.2

(4) see chapter 3.3.1.1.3

Examples of comparisons between ΣCat and ΣAn are given in Figure 3.3.1.1.1a for different types of solution. The departure from zero of the ion balance for different types of deposition sample is shown, illustrating the failure of the check in the case of Throughfall (THR) and Stemflow (STF) samples.

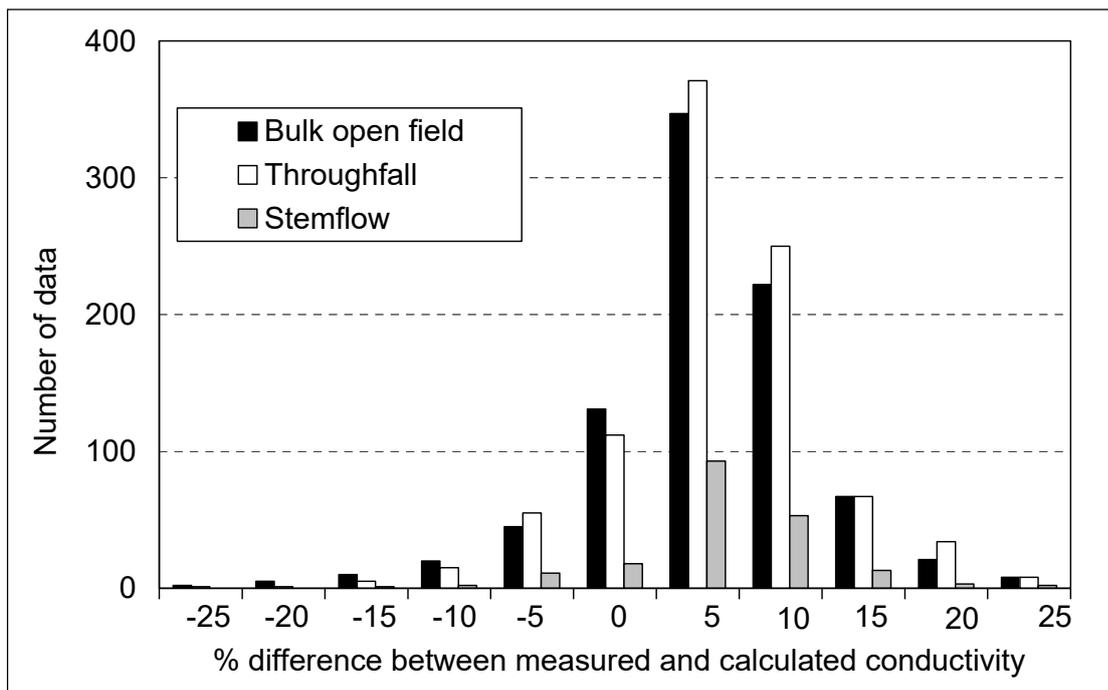
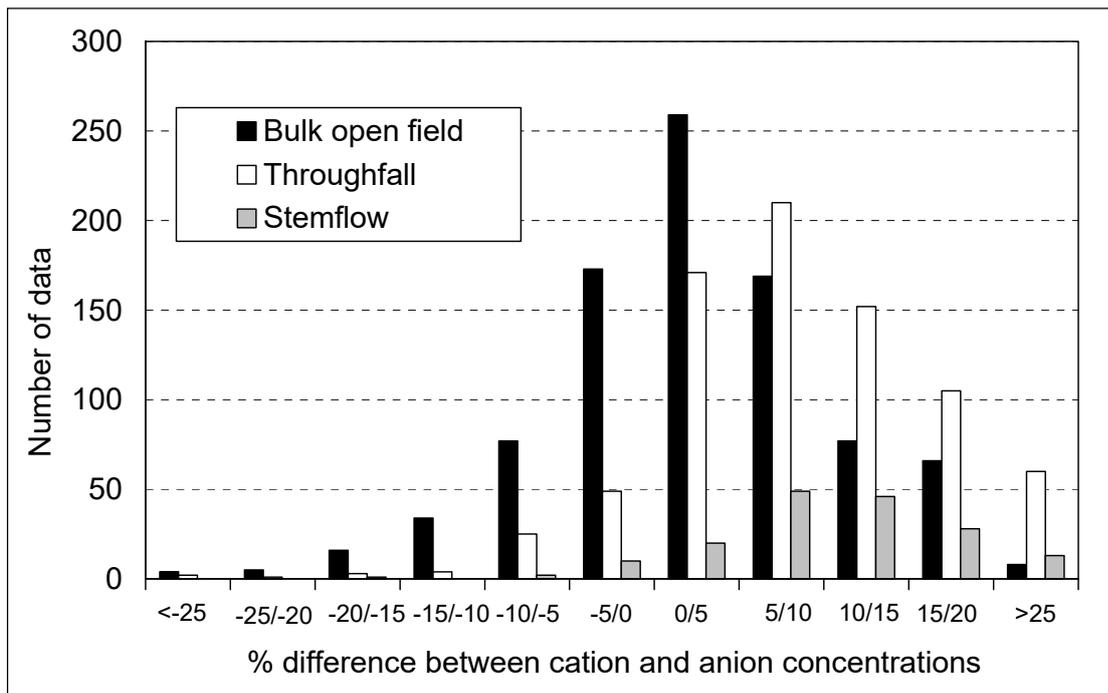


Figure 3.3.1.1.1a: Departure from zeron of the percentage difference between Σ Cat and Σ An (PD) (above), and (below) of the percentage difference between measured and calculated conductivity (CD) for different types of deposition sample

3.3.1.1.2 Ion balance with DOC

Figure 3.3.1.1.1a clearly illustrates the failure of the ion balance check in the case of THR and STF samples. This is also the case for soil water samples (not shown in figure) in which, in addition to high DOC concentrations, elevated concentrations of metals may also be present (see Chapter 3.3.1.1.3).

The ion balance test can be used to evaluate the ionic contribution of DOC (all solutions are filtered through 0.45 µm membrane filters before analysis) (Mosello et al., 2008). This study was carried out as part of the activities of the WG on QA/QC in laboratories regularly performing the chemical analysis of deposition and soil water samples within the framework of the ICP Forests and the EU/Forest Focus Programmes. About 6000 chemical analyses of bulk open field, throughfall and stemflow samples, which contained complete sets of all ion concentrations, alkalinity, conductivity and DOC, carried out in 8 different laboratories, were used to calculate empirical relationships between DOC and the difference between the sum of cations and the sum of anions. The aim was to determine the formal charge per mg of organic C. The samples covered a wide range of geographical and climatic conditions, as well as variables such as the proximity of the sea (chloride concentration) and the type of vegetation for THR and STF.

Regression coefficients were obtained for the data sets from each laboratory, as well as for all the data combined, as follows:

$$\Sigma \text{Cat} - \Sigma \text{An} = \delta_1 \text{DOC} + \delta_0$$

where the units are µeq L⁻¹ for the sum of ions and δ₀, mg C L⁻¹ for DOC, and µeq (mg C)⁻¹ for δ₁. The regressions were not significant for BOF, because of the relatively high error associated with the low DOC concentrations. In contrast, the regressions were statistically highly significant for THR and STF in all the 8 laboratories.

In the next step, the charge contribution of DOC was determined as:

$$[\text{Org}^-] = \beta_1 * \text{DOC} + \beta_0$$

where [Org⁻] (µeq L⁻¹) is the ionic contribution of DOC. The value of PD was calculated again using the Σ An value including [Org⁻], and evaluated using the threshold values given in Table 3.3.1.1.1a.

An example of the regression coefficients, β₁ and β₀, as well as the appropriate statistical parameters, is given in Table 3.3.1.1.2a. The coefficients were further tested using an independent set of data from each laboratory. Comparison of the differences between the individual laboratories and the overall regression coefficients showed that the coefficients were generally applicable for deposition samples, and also suitable for estimating the contribution of organic acids in the ion balance test. This means a considerable improvement in the applicability of the ion balance as a validation criterion for samples with high DOC concentrations. The improvement in the ion balance check in an example data set is shown in Figure 3.3.1.1.2a. This evaluation can also be found in the annexed Excel file (<http://www.icp-forests.org/DocsQualLab/AlyticalDataValidation.xls>; Chapter 5.1), which contains examples of analysis validation.

Table 3.3.1.1.2a: Statistical parameters of the regression equations for determining the DOC contribution to the ion balance. THR = throughfall, STF = stemflow, N = number of samples, σ = standard deviation.

	Units	Broadleaves		Conifers
		THR	STF	THR
N	-	1454	597	1657
pH range	U	4.0 - 7.9	3.8 - 8.1	4.1 - 7.0
pH mean \pm σ	U	5.8 \pm 0.6	5.6 \pm 0.6	5.3 \pm 0.5
DOC range	Mg C L ⁻¹	0-37	1-39	0-40
DOC mean \pm σ	Mg C L ⁻¹	8 \pm 6	11 \pm 7	10 \pm 7
Σ Cat range	μ eq L ⁻¹	37-2736	30-5287	13-2601
Σ Cat mean \pm σ	μ eq L ⁻¹	418 \pm 321	593 \pm 539	316 \pm 278
Σ An range	μ eq L ⁻¹	29-2606	22-5303	10-2584
Σ An mean \pm σ	μ eq L ⁻¹	377 \pm 304	545 \pm 523	279 \pm 265
Σ Cat - Σ An range	μ eq L ⁻¹	258	263	225
Σ Cat - Σ An mean \pm σ	μ eq L ⁻¹	41 \pm 59	48 \pm 58	37 \pm 41
Slope β_1	μ eq (mg C) ⁻¹	6.8 \pm 0.16	5.04 \pm 0.25	4.17 \pm 0.11
Intercept β_0	μ eq L ⁻¹	-12.32 \pm 1.63	-6.67 \pm 3.29	-5.01 \pm 1.32
P-value		<0.0001	<0.0001	<0.0001
R ²		0.56	0.4	0.47

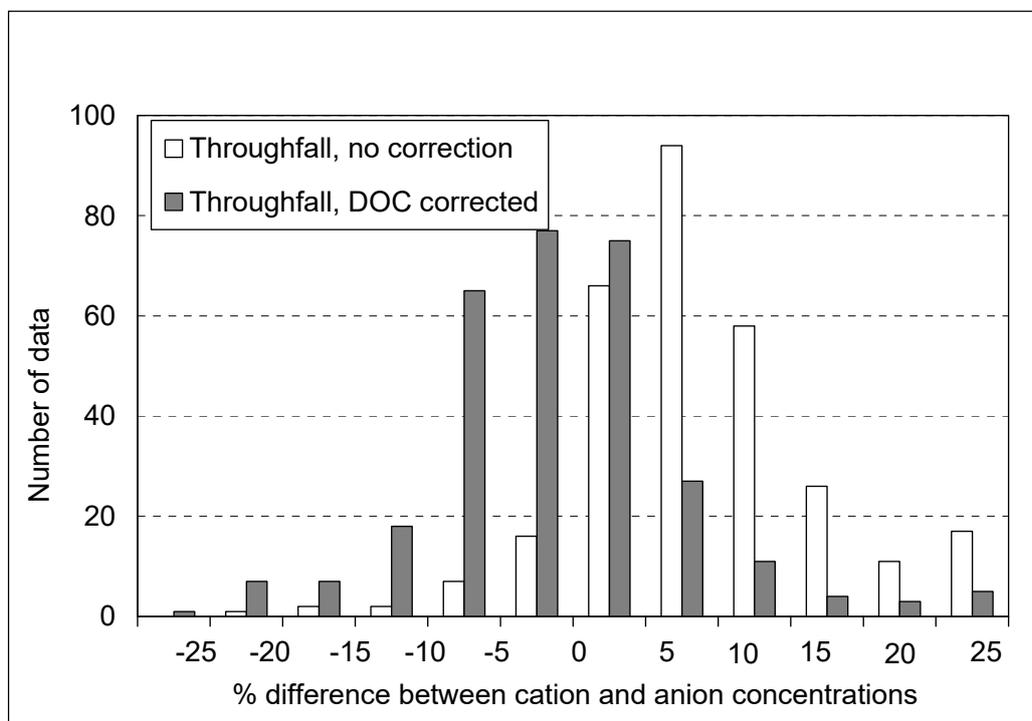


Figure 3.3.1.1.2a: Departure from zero of the percentage difference between Σ Cat and Σ An (PD, see text) without and with DOC correction

3.3.1.1.3 *Ion balance with DOC and metals*

The ion balance for soil water samples is more complicated owing to the presence of metals (e.g. Al, Fe, Mn), their species (e.g. Al^{3+} , $\text{Al}(\text{OH})^{2+}$, $\text{Al}(\text{OH})_2^+$, Fe^{3+} , $\text{Fe}(\text{OH})^{2+}$, $\text{Fe}(\text{OH})_2^+$), their oxidation state (e.g. $\text{Fe}^{3+}/\text{Fe}^{2+}$; iron complexed with organic matter can occur in both oxidised and reduced forms and the reduced forms can exist under oxidising conditions when complexed with organic matter; see e.g. Clarke and Danielsson, 1995) and metal complexes with DOC (e.g. DOC-Fe, DOC-Al, DOC-Mn) in the solution.

The calculation of bicarbonate from total alkalinity (see Chapter 3.3.1.1.1) is not completely correct because it is influenced by the different species of DOC in the solution.

Therefore calculation of the formal charge per mg of organic C from the difference between the sum of cations and the sum of anions, as described in Chapter 3.3.1.1.2 for throughfall samples, also has to take into account the metals, their species and their complexes with DOC:

$$\begin{aligned} \Sigma \text{Cat} + \Sigma \text{Met (all inorg. species)} + \Sigma \text{Met (from DOC complexes)} \\ = \Sigma \text{An} + \Sigma \text{Org}^- \text{ (from DOC complexes)} \end{aligned}$$

where:

$\Sigma \text{Met} = \text{Al}^{3+} + \text{Al}(\text{OH})^{2+} + \text{Al}(\text{OH})_2^+ + \text{Fe}^{3+} + \text{Fe}(\text{OH})^{2+} + \text{Fe}(\text{OH})_2^+ + \text{Mn}^{2+} + \text{Mn}(\text{OH})^+$ (and other inorg. species)

$\Sigma \text{Met (from DOC complexes)} = \text{Al-DOC} + \text{Fe-DOC} + \text{Mn-DOC}$

$\Sigma \text{Org}^- \text{ (from DOC complexes)} = \text{DOC-Fe} + \text{DOC-Al} + \text{DOC-Mn}$

Normally only the total concentrations of the metals and the total concentration of DOC are measured in soil solution samples. Therefore calculation of the formal charge per mg of organic C using the following formula overestimates the formal charge of DOC when the highest possible charge for the metals (Al^{3+} , Fe^{3+} , Mn^{2+}) is used and there is no correction for bicarbonate:

$$\Sigma \text{cat} + \Sigma \text{met}_{\text{total}} - \Sigma \text{an} = \delta_1 \text{DOC}_{\text{total}}$$

In a study conducted by the WG on QA/QC in Laboratories, about 6200 chemical analyses on soil solution samples (complete sets of all ion and total metal concentrations, alkalinity, conductivity and DOC, carried out in the laboratories of 6 countries, were used to calculate empirical relationships between DOC and the difference between the sum of cations and metals and the sum of anions. The aim was to determine the formal charge per mg of organic C. The samples cover a wide range of geographical and climatic conditions. The results are shown in Figure 3.3.1.1.3a:

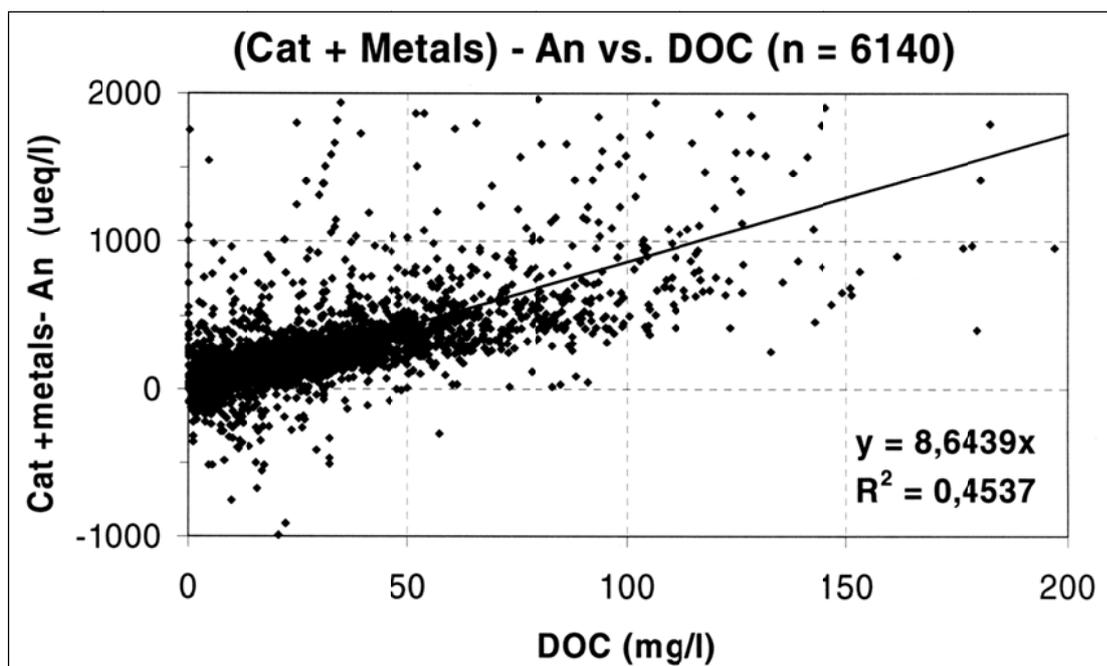


Figure 3.3.1.1.3a: Calculation of the formal charge of DOC in 6140 soil solution samples from 5 countries (Germany, Finland, France, Norway and the United Kingdom)

When the calculated charge factor for DOC was included in the ion balances of these soil solution samples, 64 % of the samples had equal ion balances (within $\pm 10\%$) while only 30 % of the samples had equal ion balances without using the DOC correction.

The results are different in the individual countries and at different pH values. Therefore the charge factor value obtained here can only be used as a first step in the procedure. It would be better to calculate the charge factor for specific countries or for similar types of plot. The chemical composition of DOC varies with depth down the soil profile (e.g. it is more polar at greater depth, Clarke et al., 2007), so the charge factor is also likely to vary with depth.

3.3.1.2 Conductivity check

Conductivity is a measure of the ability of an aqueous solution to carry an electric current. This property depends on the type and concentration of the individual ions and on the temperature at which conductivity is measured. It is defined as:

$$K = G * (L/A)$$

where G = is the conductance (unit: ohm^{-1} or siemens; ohm^{-1} is sometime written as mho), defined as the reciprocal of resistance, A (cm^2) is the electrode surface area, and L (cm) is the distance between the two electrodes. The units of K are $\text{ohm}^{-1} \text{cm}^{-1}$. In the International System of Units (SI), conductivity is expressed as millisiemens per meter (mS m^{-1}); this unit is also used by the IUPAC and accepted as the Nordic standard. The unit $\mu\text{S cm}^{-1}$, where $1 \text{ mS m}^{-1} = 10 \mu\text{S cm}^{-1} = 10 \mu\text{mho cm}^{-1}$, is also widely used in practice. The unit adopted in the ICP Forests programme is $\mu\text{S cm}^{-1}$, and the reference temperature 25 °C.

Conductivity depends on the type and concentration (activity) of the ions in solution; the capacity of a single ion to transport an electric current is given, in standard conditions and in ideal conditions of infinite dilution, by the equivalent ionic conductance (λ_i ; unit: $\text{S cm}^2 \text{equivalent}^{-1}$).

Careful, precise conductivity measurement is an additional way of checking the results of chemical analyses. It is based on comparison between measured conductivity (CM) and the conductivity calculated (CE) from the individual ion concentrations (c_i), multiplied by the respective equivalent ionic conductance (λ_i)

$$CE = \sum \lambda_i c_i$$

The ions used in the conductivity calculations are the same as those used in calculating the ion balance; the values of λ_i for the different ions at temperatures of 20 and 25°C are given in Table 3.1.1.1b. As the concentrations are expressed in $\mu\text{eq L}^{-1}$, λ_i is given as $\text{kS cm}^2 \text{eq}^{-1}$ in order to obtain the conductivity in $\mu\text{S cm}^{-1}$. The percentage difference, CD, is given by the ratio:

$$CD = 100 * (CE - CM) / CM$$

At low ionic strength (below $100 \mu\text{eq L}^{-1}$) in deposition samples, the discrepancy between measured and calculated conductivity should be no more than 2% (Miles & Yost 1982).

At an ionic strength higher than $100 \mu\text{eq L}^{-1}$ (approximately at conductivity higher than $100 \mu\text{S cm}^{-1}$) it is necessary to use activity instead of concentration. This can be done by first calculating the ionic strength (I_s , meq L^{-1}) from the individual ion concentrations as follows:

$$I_s = 0.5 \sum c_i z_i^2 / w_i$$

where:

c_i = concentration of the i -th ion in mg L^{-1} ;

z_i = absolute value of the charge for the i -th ion;

w_i = gram molecular weight of the i -th ion.

For an ionic strength higher than $100 \mu\text{eq L}^{-1}$, activities must be used instead of concentrations; in the range 100 - $500 \mu\text{eq L}^{-1}$ the Davies correction of the activity of each ion can be used, as proposed e.g. by Stumm and Morgan (1981) and A.P.H.A., A.W.W.A., W.E.F. (2005):

$$y = 10^{-0.5 \left(\frac{\sqrt{I_s}}{1 + \sqrt{I_s}} - 0.3 I_s \right)}$$

Finally, the corrected conductivity is calculated as:

$$CE_{\text{corr}} = y^2 CE = y^2 \sum \lambda_i c_i$$

Immediate comparison of the measured and calculated conductivity makes it possible to identify single outlier values (see example in the annexed Excel file).

Figure 3.3.1.1a shows the departure from zero of the CD values for different types of deposition sample. The pattern is different from that for the ion balance: the CD values do not show any great asymmetry for BOF, THR, or STF. The reason for this is that dissolved organic matter (DOM), which causes an imbalance between the cation and anion concentrations, does not contribute significantly to conductivity.

In conclusion, a plot of measured and calculated conductivity is useful in the routine checking of a set of analyses. Departure of the results from linearity suggests the presence of analytical or some other kind of error.

3.3.1.3 Na/Cl ratio check

In many parts of Europe sea salt is a major contributor of sodium and chloride ions in deposition and, as a result, the ratio between the two ions is similar to that of sea salt. This is true even in parts of Europe situated far from the sea, as has been shown from a statistical study conducted on more than 6000 samples covering the area from Scandinavia to South Europe (Mosello et al., 2005). In the validation file

(Chapter 8.1 <http://www.icp-forests.org/DocsQualLab/AnalyticalDataValidation.xls>), samples with a ratio outside the range given below are marked as possible failures, and checks and/or re-analyses should be carried out. The ratio is calculated by expressing the concentrations on a molar (or equivalent) basis.

$$0.5 < (\text{Na}/\text{Cl}) < 1.5$$

If the Na/Cl ratio results systematically fall outside this range, this may be due to poor analytical quality in the measurement of low concentrations of sodium and chloride.

In some localised areas, where there are other sources of Cl and/or Na (e.g. from anthropogenic activities), the Na/Cl ratio might be different from that of sea salt. Where this is suspected, it is recommended to carry out a study to confirm whether this is true or not.

3.3.1.4 N balance check

The test is based on the fact that total dissolved nitrogen (DTN) concentration must be higher than the sum of nitrate (N-NO₃), ammonium (N-NH₄) and nitrite (N-NO₂) concentrations. Although the measurement of nitrite is not mandatory in the ICP Forests programme, the following relationship must be verified, within the limits of analytical errors and whatever unit is used:

$$[\text{N-NO}_3] + [\text{N-NH}_4] < [\text{DTN}]$$

If the relationship does not hold true, then the determination of one of the forms of nitrogen must be erroneous. However, if DON is very low, DTN may be approximately equal to NO₃-N + NH₄-N. In this case, normal (random) analytical errors may result in a slightly negative value of ((DTN) - ((NO₃-N) + [NH₄-N])), without there being any major problem with the analyses.

3.3.1.5 Comparison between measured conductivity and ion concentrations

Samples with similar ionic ratios and different ionic concentrations should show linear correlation between conductivity and the sum of cations and anions. The linearity is valid if the H⁺ concentration is low (i.e. pH higher than 5.0). However, because of the high specific electric conductance of H⁺ (0.35 kS cm² eq⁻¹ at 25 °C, Table 3.3.1.1b), compared to that of the other ions (range 0.044-0.080 kS cm² eq⁻¹), small variations in H⁺ concentrations produce relatively strong variations in conductivity. In these cases, a conductivity value corrected for the contribution of hydrogen ion can be used:

$$C_{\text{H}^+ \text{ correct}} = \text{CM} - \lambda_{\text{H}^+} [\text{H}^+] = \text{CM} - 0.35 * 10^{-\text{pH}}$$

where the conductivities are expressed as μS cm⁻¹ at 25°C and [H⁺] as μeq L⁻¹ (Fig. 3.3.1.5a).

Results diverging from linearity should be carefully checked in order to see whether there have been any mistakes in the analyses or in the data processing, or whether the values of some important ions are missing from the calculation.

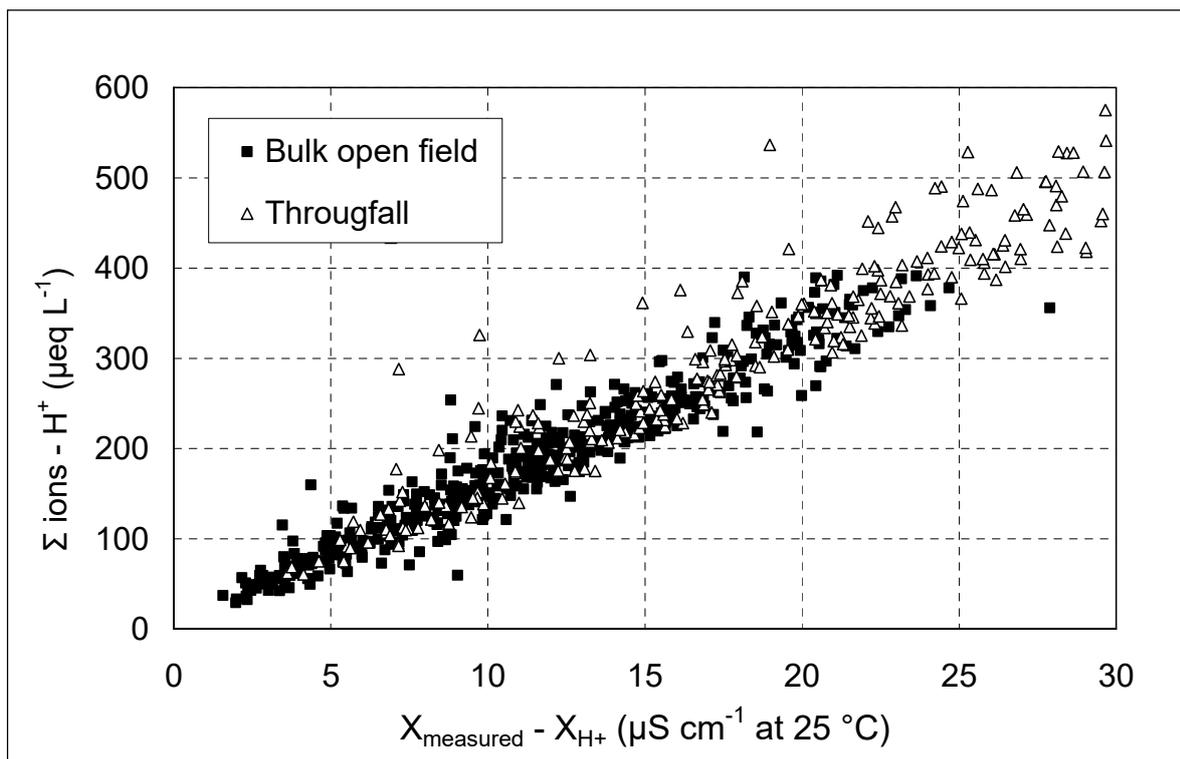
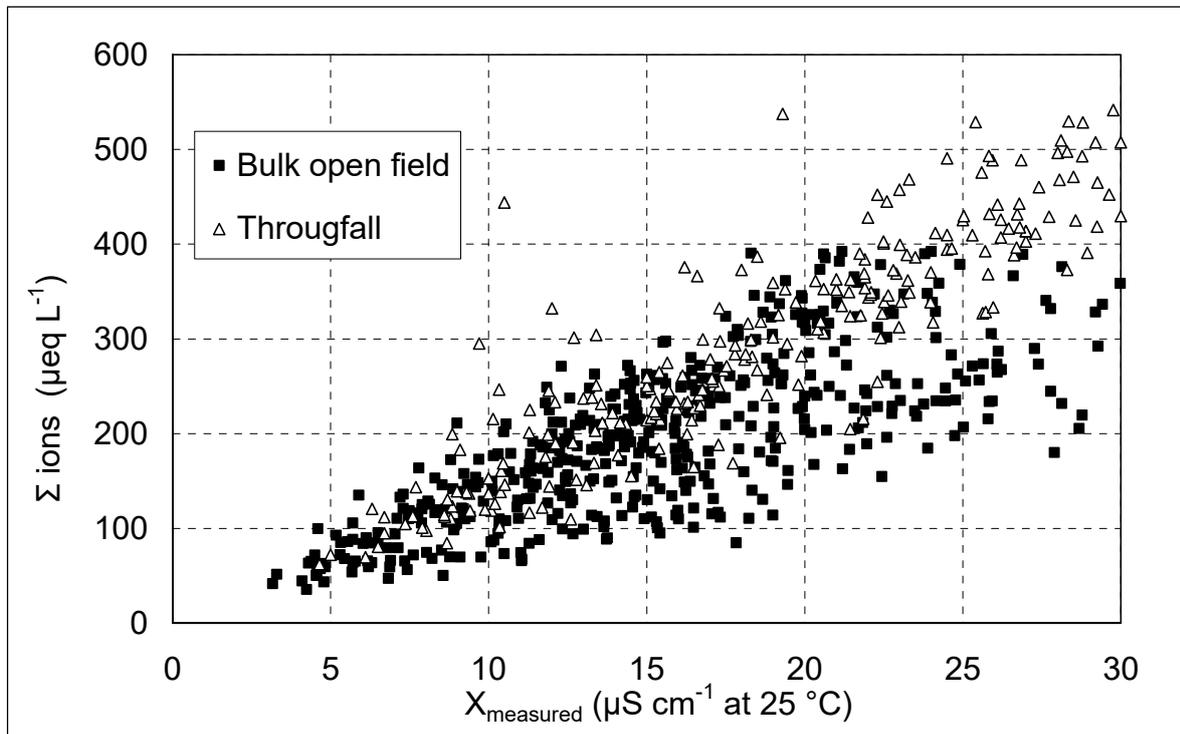


Figure 3.3.1.5a: Examples of the relationships between conductivity and $\Sigma \text{ Cat}$ or $\Sigma \text{ An}$, above without the correction for H^+ contribution to conductivity, and below with the correction

3.3.1.6 Phosphorus concentration as a contamination check

If bird droppings contaminate the precipitation/throughfall/stemflow sample, this will considerably alter the chemical composition of the sample. The concentrations of PO_4^{3-} , K^+ , NH_4^+ and H^+ , for instance, will be affected. A phosphate concentration of 0.25 mg l^{-1} has been suggested as the threshold value for sample contamination by bird droppings (Erisman et al., 2003). Contamination by bird droppings is not always easily visible, so it may sometimes be detected only after the chemical analyses have been performed.

3.3.2 Checking organic and mineral soil samples results

An important step in laboratory QA/QC is to check whether the result of an analysis is within the expected range and that the general relationships between soil variables are valid. Therefore two quality check procedures are recommended: **plausible range checks** and **cross-checks**.

3.3.2.1 Plausible range checks for organic and mineral soil samples

For each variable, there is a 95 % probability that the analytical result will fall within the plausible min-max range given in Table 3.3.2.1a. Values outside this range may occur, but they need to be validated (e.g. checking of equipment and method, dilution factor, reported unit, sample characteristics, signs of contamination). Re-analysis may be necessary when no obvious deviations are found in order to ensure that the results are correct.

Specific plausible ranges have been developed for organic material (forest floor, peat) and mineral soil samples. The number of significant decimal places for each variable is in accordance with the reporting format given in the ICP Forests Manual Part X (Soil Sampling and Analysis).

Generally, the lower limit of the min-max range depends on the limit of quantification (LOQ) which is, in turn, determined by the instrument, method and dilution factor used. Instead of merely mentioning 'LOQ', we have listed the average LOQ values reported by the soil laboratories that participated in the 4th FSCC Ring test (Cools et al., 2006) as this was found to be more informative. Laboratories with lower LOQ values than the average will be able to quantify lower concentrations reliably. However, each laboratory should always report concentrations lower than its LOQ as "-1" and reporting the LOQ concentration to the required number of decimal places in the data quality report.

The maximum value of the plausible range is determined by the maxima (mainly 97.5 percentile values) in the European forest soil condition database (first ICP Forests Level I Soil Survey). Information on the methods and data evaluation can be found in the Forest Soil Condition Report (EC, UN/ECE, 1997). As it encompasses all the European soil types, this range is relatively broad.

Table 3.3.2.1a: Plausible ranges for organic and mineral soil samples at the European level. The number of decimal places indicates the required precision for reporting.

Parameter	Unit	Organic sample		Mineral soil sample	
		Plausible range		Plausible range	
		Min#	Max	Min#	Max
Moisture content (air-dry sample)	%wt	< 0.1	10.0	< 0.1	10.0
pH(H ₂ O)	-	2.0	8.0	2.5	10.0
pH(CaCl ₂)	-	2.0	8.0	2.0	10.0
Organic carbon	g/kg	120.0	580.0	< 1.2	200.0
Total N	g/kg	< 0.5	25.0	< 0.1	20.0
CaCO ₃	g/kg	< 3	850	< 3	850
Particle size: clay	%wt	--	--	< 0.6	80.0
Particle size: silt	%wt	--	--	< 0.4	100.0
Particle size: sand	%wt	--	--	< 0.6	100.0
Aqua regia extractable P	mg/kg	< 32.8	3000.0	< 35.2	10000.0
Aqua regia extractable K	mg/kg	< 74.2	10000.0	< 81.4	40000.0
Aqua regia extractable Ca	mg/kg	< 45.9	100000.0	< 50.0	250000.0
Aqua regia extractable Mg	mg/kg	< 33.3	80000.0	< 38.5	200000.0
Aqua regia extractable S	mg/kg	< 128.6	7500.0	< 134.6	3000.0
Aqua regia extractable Na	mg/kg	< 20.6	3000.0	< 21.1	1000.0
Aqua regia extractable Al	mg/kg	< 76.1	40000.0	< 77.1	50000.0
Aqua regia extractable Fe	mg/kg	< 75.5	50000.0	< 82.6	250000.0
Aqua regia extractable Mn	mg/kg	< 7.2	35000.0	< 7.8	10000.0
Aqua regia extractable Cu	mg/kg	< 1.9	300.0	< 2.0	100.0
Aqua regia extractable Pb	mg/kg	< 2.4	1000.0	< 2.4	500.0
Aqua regia extractable Ni	mg/kg	< 1.5	300.0	< 1.6	150.0
Aqua regia extractable Cr	mg/kg	< 3.3	600.0	< 3.3	150.0
Aqua regia extractable Zn	mg/kg	< 2.0	1000.0	< 2.1	500.0
Aqua regia extractable Cd	mg/kg	< 0.5	18.0	< 0.5	6.0
Aqua regia extractable Hg	mg/kg	< 0.3	4.0	< 0.3	2.0
Exchangeable acidity	cmol+/kg	< 0.23	10.00	< 0.21	8.00
Exchangeable K	cmol+/kg	< 0.23	5.00	< 0.23	2.00
Exchangeable Ca	cmol+/kg	< 0.25	60.00	< 0.22	40.00
Exchangeable Mg	cmol+/kg	< 0.19	15.00	< 0.18	5.00
Exchangeable Na	cmol+/kg	< 0.18	1.50	< 0.17	1.00
Exchangeable Al	cmol+/kg	< 0.22	9.00	< 0.20	8.00
Exchangeable Fe	cmol+/kg	< 0.05	0.70	< 0.04	2.00
Exchangeable Mn	cmol+/kg	< 0.03	6.00	< 0.03	1.50
Free H ⁺	cmol+/kg	< 0.25	10.00	< 0.21	3.00
Total K	mg/kg	< 50.0	10000.0	< 50.0	50000.0
Total Ca	mg/kg	< 20.0	100000.0	< 20.0	500000.0
Total Mg	mg/kg	< 5.0	80000.0	< 5.0	250000.0
Total Na	mg/kg	< 20.0	5000.0	< 20.0	12000.0
Total Al	mg/kg	< 40.0	50000.0	< 40.0	100000.0
Total Fe	mg/kg	< 3.5	60000.0	< 3.5	250000.0
Total Mn	mg/kg	< 0.5	35000.0	< 0.5	15000.0
Reactive Al	mg/kg	< 44.6	5000.0	< 44.6	7500.0
Reactive Fe	mg/kg	< 48.4	5000.0	< 48.4	7500.0

* Values in bold are the average limit of quantification (LOQ) reported by the laboratories (Cools et al., 2006). The syntax is 'less than' LOQ (< LOQ).

For some parameters, national plausible ranges will be narrower due to the restricted set of soil and humus types and their local characteristics. It would be worthwhile developing regional plausible ranges specifically for soil samples originating from the region.

When the analytical data from the soils part of the BioSoil Project become available for elaboration, it will be possible to further develop the plausible ranges on both a European and regional scale.

If the values obtained in the analyses are outside the plausible range, the values should be marked with a flag for further investigation by the head of the laboratory and/or the responsible scientist. The head of the laboratory should be able to make comments in their report on possible reasons for the deviating value(s).

3.3.2.2 Cross-checks between soil variables

Because different parameters are determined on the same soil sample and many soil variables are auto-correlated, cross-checking is a valuable tool for detecting erroneous analytical results. Obviously, soils high with a high organic matter content should have high carbon and (organically bound) nitrogen concentrations. Calcareous soils should have elevated pH values, high exchangeable and total Ca concentrations, but low exchangeable acidity.

Simple cross-checks have been developed for easy verification and detection of erroneous results.

3.3.2.2.1 pH check

The soil reaction of organic and mineral soil material is measured potentiometrically in a suspension of a 1:5 soil:liquid (v/v) mixture of water ($\text{pH}_{\text{H}_2\text{O}}$) or 0.01 mol/l calcium chloride ($\text{pH}_{\text{CaCl}_2}$). The actual pH ($\text{pH}_{\text{H}_2\text{O}}$) and potential pH ($\text{pH}_{\text{CaCl}_2}$) are generally well correlated. Outliers may be detected using simple linear regression.

Theoretically, without taking measurement uncertainty into account, the difference between both pH measurements should be less than 1 pH-unit. In practice, the difference between both pH measurements is generally less than 1.2 pH-unit, with $\text{pH}_{\text{CaCl}_2}$ always less or equal to $\text{pH}_{\text{H}_2\text{O}}$.

Check algorithm: $0 < [\text{pH}_{\text{H}_2\text{O}} - \text{pH}_{\text{CaCl}_2}] \leq 1.2$

Note that for peat soils, the difference between both pH measurements may be higher, up to 1.5 pH-units.

3.3.2.2.2 Carbon check

According to the ICP Forests Manual Part X (Soil sampling and analysis), the recommended method for C determination is dry combustion using a total analyser (ISO 10694, 1995). In general, total organic carbon is obtained by subtracting inorganic carbon (TIC) from total carbon (TC), both of which are determined by the same analyser.

Inorganic carbon can be estimated from the carbonate measurement (ISO 10693, 1994) using a calcimeter (Scheibler unit).

Check algorithm: $[C_{\text{CaCO}_3} + \text{TOC}] \leq \text{TC}$ with $C_{\text{CaCO}_3} = \text{CaCO}_3 \times 0.12$

and

Check algorithm: $C_{\text{CaCO}_3} \approx \text{TIC}$

The latter check cannot be performed if the carbonate concentration is below the LOQ (3 g kg^{-1} carbonate or 0.36 g kg^{-1} TIC).

3.3.2.2.3 pH-Carbonate check

Routinely determining carbonate in soil samples with low pH values is a waste of time and resources. Carrying out a fast, cheap pH measurement can be used to decide whether carbonates are present and carbonate analysis is necessary.

For an organic sample (> 200 g kg^{-1} TOC):

Check algorithm: if $\text{pH}_{\text{CaCl}_2} < 6.0$ then $\text{CaCO}_3 < 3 \text{ g kg}^{-1}$ (= below LOQ)

For a mineral soil sample:

Check algorithm: **if $\text{pH}_{\text{H}_2\text{O}} < 5$ then $\text{CaCO}_3 < 3 \text{ g kg}^{-1}$** (= below LOQ)

or: if $\text{pH}_{\text{CaCl}_2} < 5.5$ then $\text{CaCO}_3 < 3 \text{ g kg}^{-1}$ (= below LOQ)

Conversely, if $\text{pH}_{\text{CaCl}_2} > 6$, quantifiable amounts of carbonate are most likely present in the sample.

3.3.2.2.4 C/N ratio check

Most of the nitrogen in a forest soil sample is organically bound. Carbon and nitrogen are linked through the C/N ratio of organic matter, which varies within a specific range.

For an organic sample ($> 200 \text{ g kg}^{-1}$ TOC):

Check algorithm: **$5 < \text{C/N ratio} < 100$**

For a mineral soil sample:

Check algorithm: **$3 < \text{C/N ratio} < 75$**

3.3.2.2.5 C/P ratio check

Similarly to C/N, the C/P ratio varies within expected ranges for organic and mineral soil samples.

For an organic sample ($> 200 \text{ g kg}^{-1}$ TOC):

Check algorithm: **$100 < \text{C/P ratio} < 2500$**

Note that for peat soils, the C/P ratio may be greater than 2500. In the 5th FSCC soil ring test, the C/P ratio of the peat sample was ca. 4500.

For a mineral soil sample:

Check algorithm: **$8 < \text{C/P ratio} < 750$**

3.3.2.2.6 C/S ratio check

The C/S ratio varies within specific ranges for organic samples only.

For an organic sample ($> 200 \text{ g kg}^{-1}$ TOC):

Check algorithm: **$20 < \text{C/S ratio} < 1000$**

3.3.2.2.7 Extracted/total element check

In both organic and mineral soil samples the concentration of the aqua regia extractable elements K, Ca, Mg, Na, Al, Fe and Mn (pseudo-total extraction) should be less than their total concentrations after complete dissolution (total analysis).

Therefore:

Check algorithm: **Extracted element \leq Total element**

for the elements K, Ca, Mg, Na, Al, Fe and Mn.

3.3.2.2.8 *Reactive Fe and Al check*

Acid oxalate extractable Fe and Al indicate the active (\approx "amorphous") Fe and Al compounds in soils. Their concentration should be less than the total Fe and Al concentration.

Check algorithm:

$$\text{Reactive Fe} \leq \text{Total Fe}$$

$$\text{Reactive Al} \leq \text{Total Al}$$

For mineral soil samples, reactive Fe is usually less than 25 % of the total Fe, and reactive Al less than 10 % of the total Al.

3.3.2.2.9 *Exchangeable element/total element check*

The elements bound to the cation exchange complex in the soil are also readily extracted using Aqua regia. Therefore, the concentration of exchangeable cations should always be lower than their Aqua regia extractable concentration.

A conversion factor is needed to convert from $\text{cmol}_{(+)} \text{kg}^{-1}$ to mg kg^{-1} .

Check algorithm: $(K_{\text{exch}} \times 391) \leq \text{Extracted K}$

Check algorithm: $(Ca_{\text{exch}} \times 200) \leq \text{Extracted Ca}$

Check algorithm: $(Mg_{\text{exch}} \times 122) \leq \text{Extracted Mg}$

Check algorithm: $(Na_{\text{exch}} \times 230) \leq \text{Extracted Na}$

Check algorithm: $(Al_{\text{exch}} \times 89) \leq \text{Extracted Al}$

Check algorithm: $(Fe_{\text{exch}} \times 186) \leq \text{Extracted Fe}$

Check algorithm: $(Mn_{\text{exch}} \times 274) \leq \text{Extracted Mn}$

In general, the ratio between an exchangeable element and the same extracted element is higher in organic matrices than in mineral soil.

3.3.2.2.10 *Free H⁺ and Exchangeable acidity check*

Two checks can be applied to Free H⁺ and Exchangeable acidity (EA).

Check algorithm: **Free H⁺ < EA**

Check algorithm: **EA \approx Al_{exch} + Fe_{exch} + Mn_{exch} + Free H⁺**

For mineral soil samples, Free H⁺ is usually < 60 % of the Exchangeable acidity.

3.3.2.2.11 *Particle size fraction sum check*

According to the ICP Forests Manual Part X (Soil sampling and analysis), laboratories have to report the proportion of sand, silt and clay fractions in mineral soil samples. However, different methods are used for determining each fraction. After shaking with a dispersing agent, sand (63 μm -2 mm) is separated from clay and silt with a 63 μm sieve (wet sieving). The clay (< 2 μm) and silt (2-63 μm) fractions are determined using the standard pipette method (sedimentation).

When correctly applying the Soil manual procedure (SA03) (ICP Forests Manual Part X (Soil sampling and analysis)), which is based on ISO 11277 (1998) and includes the correction for the dispersing agent, the sum of the three fractions should be 100 %. The mass of the three fractions

should equal the weight of the fine earth (0- 2mm fraction), minus the weight of carbonate and organic matter which have been removed.

Check algorithm: $\Sigma [\text{clay (\%)} , \text{silt (\%)} , \text{sand (\%)}] = 100 \%$

Ensure that the clay, silt and sand fractions are reported in the right format as mistakes occur regularly, even in ring tests.

3.3.3 Check of analytical results for foliar and litterfall samples

In comparison to the quality checks for the analytical results on soil, deposition and soil solution samples, devising robust procedures for checking foliage and litterfall analytical data is relatively difficult. In unpolluted areas, the concentration range of analytes in foliage is usually small compared with that in other matrices and so most of the results are plausible.

Correlations between elements in foliage could be one possible tool for checking analytical results, but this is only suitable in cases where the sample plots are located very close to each other and have similar soil characteristics and the same tree species. As a result, this is probably not a useful procedure for checking the results in a European-wide survey.

3.3.3.1 Plausible range check for foliage

In order to provide the laboratories carrying out foliage analyses with support on QA/QC issues, a preliminary list of plausible ranges for the element concentrations in foliage was agreed on at the 4th Expert Panel Meeting in Vienna 1997. However, these limits were very broad (see: http://bfw.ac.at/600/pdf/Minutes_4.pdf).

In order to improve the list and put it on a more sound statistical basis, the Forest Foliar Coordinating Centre removed 5% of the lowest and 5% of the highest results from the European Level I database. 90% of all the submitted

Level I results fell within these limits. As the manual covers a large number of different tree species, it was necessary, in order to obtain sufficient data for meaningful statistical analysis, to group them into the main tree genera (Stefan et al., 1997). The new limits were adopted at the Expert Panel Foliage and Litterfall meeting in Madrid/Spain (2007).

The Joint Research Centre was asked to carry out a statistical evaluation on the submitted Level II results in order to obtain statistical information about the concentration range for different tree species. The 5% and the 95% percentile limits for each tree species were calculated. 90% of the submitted results fell within these limits (see Table 3.3.3.1a). Results falling outside these limits should be checked and, if necessary, be re-analyzed.

The report of the Level I foliage survey (Stefan et al., 1997) clearly shows that element concentrations in foliage vary considerably in different parts of Europe. There is thus a need to calculate these limits for each country/laboratory using their own results. This would result in narrower limits that would provide a more reliable tool for detecting non-plausible results.

Table 3.3.3.1a: Plausible range of element concentrations in the foliage of different tree species calculated from the Level II data sets (indicative values in grey)

Tree species	n	Limit	N	S	P	Ca	Mg	K	C	Zn	Mn	Fe	Cu	Pb	Cd	B
			g/kg	g/kg	g/kg	g/kg	g/kg	g/kg	g/kg	g/kg	µg/g	µg/g	µg/g	µg/g	µg/g	ng/g
<i>Fagus sylvatica</i>	611	low	20.41	1.26	0.89	3.44	0.65	4.81	450	17.0	127	62	5.67	-	50	9.1
		high	29.22	2.12	1.86	14.77	2.50	11.14	550	54.2	2902	178	12.18	6.8	462	40.0
<i>Quercus cerris</i>	37	low	12.86	0.91	0.63	4.81	0.98	1.19	450	13.0	509	83	6.89	-	63	15.9
		high	30.79	3.24	2.29	16.49	3.24	15.64	550	-	-	-	-	-	-	-
<i>Quercus ilex</i>	141	low	11.95	0.81	0.69	4.00	0.76	3.42	450	12.7	278	73	4.00	-	-	21.7
		high	17,24	1,41	1,22	10,32	2,62	8,46	550	41,0	5385	717	7,00	-	-	-
<i>Quercus petraea</i>	268	low	19.75	1.24	0.90	4.12	1.06	5.86	450	11.0	905	60	5.39	-	24	5.5
		high	29.84	2.01	1.85	10.46	2.26	11.16	550	25.0	4209	149	11.64	-	-	-
<i>Quercus pyrenaica</i> (Q. toza)	27	low	17.85	1.18	1.48	4.60	1.40	3.52	450	18.0	434	81	8.07	-	-	-
		high	25,50	2,33	3,12	12,03	3,00	11,81	550	-	-	-	-	-	-	-
<i>Quercus robur</i> (Q. pedunculata)	313	low	20.31	1.36	0.97	3.33	1.09	5.80	450	14.0	219	64	5.50	0.1	40	23.4
		high	30.69	2.21	2.55	12.26	2.85	12.64	550	50.0	2820	233	14.10	18.0	183	54.8
<i>Quercus suber</i>	39	low	11.39	0.85	0.47	4.29	1.22	4.37	450	17.0	291	62	6.11	-	-	17.5
		high	23.09	1.61	1.53	11.02	2.55	9.85	550	47.0	2887	621	20.00	-	-	-
<i>Abies alba</i>	230	low	11.55	0.79	0.95	3.50	0.68	4.29	470	22.0	185	21	2.31	-	48	15.5
		high	16.16	1.69	2.23	11.71	1.90	8.48	570	45.0	2510	85	5.89	-	-	-
		low	11.67	0.95	0.86	4.19	0.37	3.97	470	20.0	250	32	2.00	-	56	14.4
		high	16.46	1.79	2.21	16.39	1.70	7.57	570	47.5	5241	121	6.45	-	-	-
<i>Picea abies</i> (P. excelsa)	1763	low	10.39	0.70	1.01	1.83	0.66	3.65	470	16.0	165	22	1.41	-	-	7.2
		high	16.68	1.31	2.10	7.01	1.56	8.36	570	47.0	1739	91	5.94	2.9	226	29.4
		low	9.47	0.69	0.81	2.26	0.44	3.41	470	12.0	198	27	0.94	-	-	6.2
		high	15.97	1.34	1.82	9.77	1.51	7.05	570	51.8	2376	118	7.07	5.2	169	32.9
<i>Picea sitchensis</i>	108	low	12.67	0.98	1.04	1.21	0.78	5.56	470	8.4	147	31	0.70	-	-	6.0
		high	17.61	1.75	2.56	8.02	1.41	10.89	570	33.8	1489	232	5.91	-	-	42.0
		low	11.87	0.92	0.84	1.41	0.50	4.62	470	9.5	160	33	0.70	-	-	5.0
		high	18.19	1.94	2.43	8.23	1.18	10.05	570	29.3	1734	133	4.67	-	-	52.0
<i>Pinus contorta</i>	40	low	11.31	0.75	0.98	1.02	0.79	3.56	470	-	-	-	-	-	-	-
		high	21.51	1.66	1.73	2.70	1.31	6.06	570	-	-	-	-	-	-	-
		low	13.12	0.87	0.88	1.96	0.75	1.21	470	-	-	-	-	-	-	-
		high	20.22	1.70	1.55	4.41	1.50	6.02	570	-	-	-	-	-	-	-
<i>Pinus halepensis</i>	30	low	9.22	0.92	0.80	2.12	1.84	3.20	470	23.0	32	230	-	-	-	-
		high	14.28	1.68	1.79	8.04	2.89	8.67	570	-	-	-	-	-	-	-
<i>Pinus nigra</i>	81	low	8.42	0.51	0.81	0.97	0.56	3.88	470	18.8	60	29	1.81	0.6	399	8.9
		high	21.18	1.44	1.57	4.42	2.08	8.30	570	67.7	1072	131	18.08	-	-	-
		low	7.97	0.44	0.75	1.17	0.35	3.89	470	19.0	109	69	1.80	0.9	380	8.7
		high	23.49	1.93	1.71	6.90	2.06	7.34	570	70.0	1000	-	-	-	-	-

<i>Pinus pinaster</i>	116	low	6.85	0.61	0.55	0.80	1.01	3.26	470	15.6	41	23	1.70	-	-	15.0
		high	13.71	1.29	1.24	3.80	2.47	7.14	570	39.0	825	579	5.03	-	-	-
		low	6.25	0.55	0.40	1.09	0.94	2.40	470	12.3	35	23	1.13	-	-	20.0
		high	13.27	1.44	1.38	6.02	2.88	6.86	570	36.8	794	111	4.68	-	-	-
<i>Pinus pinea</i>	24	low	7.51	0.65	0.58	1.53	1.80	3.25	470	6.0	89	44	4.30	-	-	28.5
		high	11.30	1.65	1.20	4.40	3.00	6.70	570	-	-	-	-	-	-	-
<i>Pinus sylvestris</i>	1859	low	11.40	0.75	1.11	1.61	0.64	3.77	470	32.0	172	18	2.28	-	50	9.2
		high	20.41	1.56	2.06	4.61	1.31	7.27	570	77.6	912	139	7.70	3.9	447	30.5
		low	10.94	0.77	1.00	2.57	0.50	3.51	470	31.5	222	28	1.96	0.1	60	7.4
		high	19.38	1.61	1.88	6.71	1.18	6.52	570	96.0	1332	171	6.88	5.6	507	33.9
<i>Pseudotsuga menziesii</i>	137	low	13.54	1.00	1.00	1.98	1.02	5.17	470	15.0	159	43	2.72	-	141	30.9
		high	22.71	1.80	1.70	5.91	2.10	8.96	570	45.3	1661	129	5.95	-	-	-
		low	13.55	0.99	0.71	3.09	1.14	2.97	470	14.0	444	58	2.91	-	-	-
		high	29.23	2.18	1.45	9.64	2.73	7.30	570	-	155	279	-	-	-	-

3.3.3.2 Plausible range check for litterfall

Developing tolerable limits for litterfall is a more difficult task than that for foliage. Following collection, litterfall is sorted into different fractions – at a minimum two, foliar and non-foliar litter. Most countries sort the litterfall into three fractions – foliage, wood and fruit cones & seeds. Litterfall can then be analyzed either as a pooled sample or per fraction.

The plausible range of the results of the chemical analysis of litter must be much bigger than for foliage. An important fraction in the litter is the foliar fraction, and for this fraction plausible ranges for selected tree species, based on the expert experience, are given in table 3.3.3.2a. Plausible ranges for the non-foliar fraction in litterfall will need to be determined.

Table 3.3.3.2a: Plausible range of element concentrations in the foliar-litter of different tree species (indicative values in grey)

Tree Species (Foliar litter)	Limit	C	S	N	P	K	Ca	Mg	Zn	Mn	Fe	Cu	B
		mg/g	mg/g	mg/g	mg/g	mg/g	mg/g	mg/g	µg/g	µg/g	µg/g	µg/g	µg/g
Betula pendula	low	290		7.30	0.20	0.30	5.00	1.00	105.00	600	45.0	6	
	high	330		21.00	1.20	1.40	12.50	2.00	170.00	3000	300.0	19	38
Castanea sativa	low	390		9.00	0.20	0.20	4.50	1.40	35.00	700		5	
	high	420		13.00	0.70	0.55	10.50	2.00	45.00	2500	90.0	13	100
Fagus sylvatica	low	460	1	9.00	0.50	2.00	4.00	0.80	25.00	650	70.0	4	2
	high	510	2.2	19.00	1.90	8.00	17.00	2.00	35.00	1600	140.0	7	40
Fraxinus excelsior	low	470		12.00	0.75	0.40	20.00	2.00	15.00	110	120.0	7	
	high	470		18.00	1.50	1.40	25.00	3.50	20.00	200	200.0	9	50
Quercus frainetto (Q. conferta)	low		1.1	8.00	1.10	4.50	14.00	1.20					
	high		1.1	11.70	1.30	5.20	18.30	1.40					
Quercus petraea	low	460		8.00	0.30	2.00	7.00	1.30	14.00	700	50.0	5	
	high	510		12.00	0.60	4.00	10.00	2.00	25.00	1700	200.0	8	35
Quercus robur (Q. pedunculata)	low	460	0.85	10.00	0.82	4.00	5.00	1.00	15.00	1000	90.0	6	7
	high	510	1.7	19.00	2.00	8.00	13.00	2.00	25.00	1200	150.0	7	35
Abies cephalonica	low			8.00		2.70	11.00	1.00					
	high			13.00		8.30	24.00	1.50					
Picea abies (P. excelsa)	low		1	6.50	0.60	1.00	2.50	0.70					
	high	520	1.5	12.60	1.20	4.20	16.00	2.20					
Picea sitchensis	low	440	1	6.00	0.60	1.50	4.00	0.60	15.00	250	40.0	2	
	high	530	1.1	13.00	1.10	3.00	11.00	1.00	35.00	1400	120.0	4	35
Pinus sylvestris	low	490	0.62	5.00	0.40	1.00	2.00	0.50	20.00	180	35.0	2	
	high	530	0.62	10.00	0.80	3.00	11.00	0.80	45.00	800	150.0	5	45

3.3.4 Analyses in duplicate

Performing duplicate analyses represents a very worthwhile quality check. The samples or digestion solutions/extracts are measured twice independently for the individual parameters, the results are compared, and their repeatability determined.

As this is a very time-consuming and expensive procedure when the number of samples is large, it may be sufficient to analyse only part (e.g. 5%) of the samples in duplicate. If this is adopted, 5% of the samples should be randomly selected and analysed again at the end of the batch. Thus, one can check repeatability on the one hand and make sure that samples weren't mistakenly exchanged during the course of the analysis. If a mistake was determined, all samples in the batch will need to be re-analysed in duplicate.

3.3.5 Avoidance of contamination

The contamination of samples can occur at any stage from the field to the final analysis result, including sampling in the field during, transportation to the laboratory, and the pre-treatment and analysis of the samples in the laboratory.

3.3.5.1 Water analyses

As outlined deposition samples can become contaminated during the sampling period, e.g. as a result of bird droppings, and the laboratory should be informed about signs of such contamination (see Chapter 3.3.1.6). The transfer of deposition and soil water samples in the field from the sampling devices to the bottles used for transportation to the laboratory is another stage where contamination of the samples can occur. The best way to avoid this problem is to transport the collection devices (bottles, bags etc.) directly to the laboratory, if possible. The most important point during this step, as well as throughout the whole sample preparation procedure in the laboratory, is to avoid skin contact with the samples by using disposable gloves (non talc), and the use of clean equipment (e.g. glass- and plastic ware).

Special care must be taken when filtering the samples, and at least separate plastic tubing (if used) and/or filtering devices for different types of sample (bulk, throughfall, stem flow, soil solution) should be used. Rinsing the filter capsule or funnel between the samples with the next sample, as well as with purified water, is highly recommended. If this is not possible, then an adequate amount of the next sample should be discarded after filtering before taking a sample for analysis. Control samples (ultra pure water) should be used after every 20 to 30 samples depending on the type of filtering system. It is always recommendable to start working with cleaner samples (e.g. bulk first with low analyte concentrations) and continue with the other types of sample in sequential order. Attention should also be paid to the different characteristics of the individual sample plots and their specific concentrations.

It is important that filters used are appropriate to the analyses to be carried out, e.g. paper filters can affect ammonium and DOC determinations through contamination and the release of paper fibres that of course contain C. In some cases, the opposite may occur: sample loss through adsorption on filters. For the filtration of samples on which DOC is to be determined, glass fibre filters are recommended.

The filters and the amount of ultra pure water needed to rinse off possible contaminants should be tested and checked by using blank charts. The filters should be handled with clean forceps.

One highly recommendable procedure is to use a separate set of bottles for preparing the standard solutions for every single type of analysis. If the pH or conductivity value for a sample is exceptionally high, then it is recommendable to inform the persons carrying out the other analyses (which are usually performed later) about the "atypical" sample.

3.3.5.2 Organic and mineral soil analyses

Samples of organic and mineral soil material need several preparatory steps prior to analysis. Contamination can occur in each of these steps.

Cleanliness of equipment, glass- and plastic-ware, is a prerequisite for avoiding contamination and conforming with good laboratory practice.

Milling and/or sieving is the first step in the pre-treatment of organic and mineral soil samples.

The milling equipment is one possible source of contamination. Metals, especially, may be released through abrasion of the inner compartments or sieves. In the laboratory responsible for preparing the FSCC ring test samples, the use of a hammer-mill system with a titanium rotor and a stainless steel sieve was tested for milling organic samples. Milling resulted in elevated Ni and Cr concentrations of up to 3.6 and 2.2 mg kg⁻¹, respectively, whereas for manual pulverization the increase was below 0.6 mg kg⁻¹ for both metals. Although no systematic contamination was observed, the degree of contamination appeared to be a function of the hardness of the sample material (wood, bark) and the age of the sieve. The use of titanium rotors and sieves is therefore recommended, as well as periodical replacement of the sieves.

According to the ICP Forests Manual Part X (Soil sampling and analysis), mineral soil samples should not be milled, but sieved with a 2 mm sieve. These sieves should be clean, with no traces of rust (i.e. oxidation on their metallic parts). Attention should be paid to ensure that no residues from tools (crusher, pestle, brush, cleaning equipment) end up in the samples as a result of thorough cleaning by brushing or wiping. This also holds true for other equipment (sample divider, mixer, splitter, riffler). When pre-treating silty or clayey soil samples, appropriate ventilation methods (i.e. air extraction equipment) should be used to avoid contamination of other samples or equipment via the air as well as for the health and safety of the laboratory technician.

If a separate container is used to weigh and transfer sub-samples to extraction vessels, then it should be carefully brushed clean between samples to avoid cross-contamination. All glass- and plastic-ware should be cleaned by rinsing with a dilute acid solution or appropriate cleaning agent. Rinsing twice with distilled or de-ionized water and drying before re-use is a common practice.

Ions adsorbed on the inner surfaces of extraction flasks or sample bottles coming into contact with extracts may be a source of contamination for subsequent analyses using the same containers.

Finally, some types of filter paper used for filtration may contain contaminants. Many laboratories encounter problems with Na⁺ or other cations. Careful analysis of blanks and the filter material may indicate problematic elements that enhance the background noise.

3.3.5.3 Foliar and litterfall analyses

There are many possible contamination sources in foliage and litterfall analyses. A short overview is given in Table 3.3.5.3a.

Table 3.3.5.3a: Possible contamination sources in foliage and litterfall analyses for some elements

Element	Possible contamination source
N	NH ₃ from the laboratory air (only if the Kjeldahl method is used), reagents
S	Water (distilled or deionised), reagents
P	Dishwasher (detergent), water (distilled or deionised), reagents
Ca	Soil contamination from sampling, water (distilled or deionised), glassware, reagents
Mg	Soil contamination during sampling, water (distilled or deionised), glassware, reagents
K	Dishwasher (detergent), water (distilled or deionised), glassware, reagents

Element	Possible contamination source
Zn	Soil contamination during sampling, Dishwasher (detergent), water (distilled or deionised), glassware, dust, reagents
Mn	Reagents
Fe	Soil contamination during sampling, water (distilled or deionised), glassware, dust, reagents
Cu	Water (distilled or deionised), glassware, reagents
Pb	Soil contamination during sampling, glassware, dust, reagents
Cd	Soil contamination during sampling, glassware, dust, reagents
B	Water (distilled or deionised), glassware, reagents
Cr, Ni	Instruments made of stainless steel used in sampling, pre-treatment etc.
C	Reagents

3.4 Inter-laboratory quality assurance

In addition to the quality assurance carried out within each laboratory, there are also quality checks and procedures that can be used between different laboratories. These include ring tests, as well as the exchange of expertise and analytical methods employed between laboratories. In the case of international programmes, especially, the use of identical analytical methods and regular ring tests are of particular importance in ensuring comparability and joint evaluation of the data.

3.4.1 Ring tests and ring test limits

3.4.1.1 Ring tests

Within the ICP Forests programme the participation in different ring tests is mandatory for all laboratories which are analysing samples from the ICP-Forests programme.

In order to participate in the ring tests, each laboratory has to register on-line. Information about the registration procedure will be sent to both the NFCs and the responsible person for the ring tests in the laboratory.

A series of inter-laboratory comparison tests is an excellent tool for improving the quality of the data produced by the participating laboratories over time. There are the twin benefits of improved expertise in using harmonised analytical methods as well as the use of the remaining ring test sample material as reference material for subsequent analyses.

In instances where the analytical data generated in environmental monitoring or long-term ecological research programmes are of poor quality, then this may prevent the detection of trends, resulting in delays of up to three decades before they can be identified (Sulkava et al., 2007). To address this issue, tolerable limits for the deviation of the individual test result from the comparison mean value were selected for each variable measured. Results falling outside the tolerable limits indicate problems in the analytical procedure, or more general quality problems in the laboratory. The tolerable limits were set in order to act as a driving force to reduce measurement uncertainty and increase the comparability of results among the participating laboratories. As a result, the tolerable limits have, in some cases, been adjusted downwards in order to maintain their role as a driver for quality improvement as an increasing number of the laboratories meet this quality requirement.

Ring tests should be carried out between the involved laboratories at regular intervals in order to ensure comparability of analytical data. This involves the dispatch of between 3 to 10 samples or solutions to the participating laboratories, where they are analysed using previously agreed analytical methods. The results are then returned to the organizers of the ring test.

Prior to the dispatch of the ring test samples to the participating laboratories, the samples must be checked for homogeneity and, in the case of water samples, have been stabilized (i.e. by means of filtration through a 0.45 µm membrane filter and addition of appropriate acid where required). When mailed to the laboratories, the samples have to be packed in non-breakable flasks, and water samples should be kept cool during transportation.

The analysis of 4 to 6 samples, representing different concentrations of the individual parameters, is the optimum, because only then can clear analytical trends be identified for each participating laboratory. This simplifies the detection of possible analytical mistakes and differences in the methods used.

Particularly in the case of water samples, it is necessary to set a time period for completion of analysis and reporting of results. This avoids chemical/biological changes in the samples which, in turn, would lead to differences in the results.

Care should be taken to agree on standard treatment of the samples and analytical methods. This includes their preparation such as sieving or grinding, digestion or extraction and determination of element concentrations.

The effects of differing methods on the results of the ring test can only be investigated if the methods used are properly documented or a method-code used.

The participating laboratories should carry out the ring tests as a part of their normal laboratory analysis runs so that the functioning of their normal routine activities can be checked.

The organizers of the ring tests should ensure that forms and/or internet-based files are harmonised so that all the analysis data can be recorded in a standard fashion and similar evaluation programmes used. It is particularly important that for reporting purpose the units are defined including the required number of decimal places.

There are a number of computer programmes on the market that comply with standards such as DIN 38402/42 (1984), and these can be used for evaluating the analysis data. Custom-made programmes can also be used. The deviation from the mean value and the coefficient of variation, as well as outliers, must be recorded for each parameter and for each sample.

3.4.1.2 Tolerable limits for ring tests

In order to evaluate the results of ring tests and of the participating laboratories, tolerable deviations from the mean value, expressed as a percentage for each parameter and method, have to be determined. As a rule, the permitted deviations for double-stepped analytical methods (e.g. digestion/extraction and subsequent determination of the element concentration in the solution) are significantly larger than for direct element determination.

All laboratories participating within ICP-Forests monitoring programme will get a qualification report after taking part in a ring test. In this report, information about the analysed and not analysed parameters and the passing of the qualification criteria for each parameter will be listed.

The qualification criterion is that 50 % or more of the results of all ring test samples for a particular parameter must be within the appropriate tolerable limit.

The WG on QC/QA in Laboratories and the various expert panels of the ICP Forests programme have proposed tolerable limits for all samples and parameters. They are described in detail in the following chapters.

Laboratories without qualification for all parameters have the opportunity to requalify by reanalysis of the ring test samples and/or by receiving help through the assistance program for laboratories organized by the Working Group QA/QC in Laboratories. The laboratories have to report the new

results to the organizers of the ring test together with the original reports of the analytical instruments and information about weight factors, dilution factors etc. and information about the reasons for the bad results during the ring test. The ring test organizers then will decide about the report from the laboratory. If the results are within the tolerable limits the laboratory will receive a requalification report.

The results of the ring tests are integrated in the data reports to the EC and PCC and in the data base. This means that the bad ring test results will be known and can be used as a criterion for rejecting the data before being used in evaluations.

When a lab did not qualify and did not make efforts to requalify, the ring test organisers will send a letter to the National Focal Centre and inform them about the consequence that their data possibly cannot be used for evaluations on an European level.

3.4.1.2.1 Tolerable limits for water ring tests

Discussions on the results of the 1st and 2nd Deposition/Soil water ring tests highlighted the requirement for the determination of tolerable limits of acceptable variance amongst the participating laboratories. Thus, the deriving of tolerable limits (also known as data quality objectives (DQO)) are essential in ensuring the comparability of results from different laboratories. The tolerable limits need to be greater than the laboratory's acceptable precision (if adhering to the QA/QC criteria) because they must also include a systematic error contribution. As is the case for determining the acceptance limits for single analyses validation checks (Chapter 3.3.1.1), selection of the tolerable limits should take into account the fact that excessively large acceptance thresholds are of little use for ensuring good data quality, while too strict threshold values that are frequently exceeded are ignored. The proposed set of values is only a preliminary step and it needs to be verified in practice and, if needed, changed. It also may be necessary to use different tolerable limits for "low" or "high" concentrations. However, a review of the results from further inter-laboratory exercises will show whether this is necessary or not.

The proposed tolerable limits values for deposition/soil water inter-comparison at high and low concentrations are listed in Table 3.4.1.2.1, and are compared with the average of all the samples of the 95% confidence limit of the results obtained in the 2nd Ring Test (Marchetto et al., 2006), after the exclusion of outliers.

It is evident that a significant proportion of the results still exceed the proposed tolerable limit values, indicating the need for improvement of performance in some laboratories. On the other hand, many laboratories had values lower than the tolerable limits, clearly indicating that it is possible to remain within these thresholds. The table also highlights a number of analyses where further work is required to improve analytical quality, such as alkalinity (low values in deposition samples), total nitrogen (at low concentrations) and DOC (both at low and high concentrations). The analytical problems associated with these determinations were discussed in detail in the work of Mosello et al., 2002, Marchetto et al., 2006 in relation to findings of the two ring test results.

Table 3.4.1.2.1: Comparing the results of the second ICP Forests/Forest Focus working ring test (Marchetto et al., 2006) with the proposed tolerable limits for deposition/soil water parameters.

Parameter	Conc. Range	Conc. Level	2005 WRT 2 x SD (% of mean except for pH)	Proposed Inter-Laboratory Tolerable limit (% of mean except for pH)
pH units pH	Low	>5.0	± 0.27 u. pH	± 0.2 u. pH
	High	<5.0	± 0.17 u. pH	± 0.1 u. pH
Conductivity $\mu\text{S cm}^{-1}$	Low	<10	-	± 20
	High	>10	± 13	± 10
Calcium mg L^{-1}	Low	<0.25	± 31	± 20
	High	>0.25	± 18	± 15
Magnesium mg L^{-1}	Low	<0.25	± 20	± 25
	High	>0.25	± 14	± 15
Sodium mg L^{-1}	Low	<0.50	-	± 25
	High	>0.50	± 12	± 15
Potassium mg L^{-1}	Low	<0.50	± 30	± 25
	High	>0.5	± 11	± 15
Ammonium mg N L^{-1}	Low	<0.25	± 42	± 25
	High	>0.25	± 16	± 15
Sulphate mg S L^{-1}	Low	<1.0	± 11	± 20
	High	>1.0	± 7	± 10
Nitrate mg N L^{-1}	Low	<0.5	± 38	± 25
	High	>0.5	± 10	± 15
Chloride mg L^{-1}	Low	<1.5	± 22	± 25
	High	>1.5	± 11	± 15
Alkalinity $\mu\text{eq L}^{-1}$	Low	<100	± 161	± 40
	High	>100	± 66	± 25
Total dissolved nitrogen mg L^{-1}	Low	<0.5	± 51	± 40
	High	>0.50	± 15	± 20
Dissolved organic carbon mg L^{-1}	Low	<1.0	± 98	± 30
	High	>1.0	± 20	± 20
Other (metals) mg L^{-1}	Low	-	-	-
	High	-	-	20

3.4.1.2.2 Tolerable limits for soil ring tests

For the inter-laboratory comparison of organic and mineral soil samples, tolerable limits were calculated on the basis of the Mandel's h (a measure for the reproducibility) and Mandel's k (a measure for the repeatability) statistics from earlier FSCC soil ring tests (De Vos, 2008). An explanation of the evaluation methodology for the soil ring tests based on ISO 5725-2 (1994) is given in the FSCC ring test reports (Cools et al., 2003, 2006, 2007).

Tolerable limits for the soil ring tests are determined from the coefficient of variation for laboratory reproducibility (CV_{repr}). For many soil variables, CV_{repr} decreases with increasing concentrations, as shown for total nitrogen in Figure 3.4.1.2.2a. The reproducibility relative to the mean may be as high as 100 %, or even more at low concentrations, whereas there is less variation at higher concentrations. Therefore, tolerable CV's are fixed for both low and high concentrations for each soil variable. In the case of nitrogen, the CV_{repr} for low ($\leq 1.5 \text{ g N kg}^{-1} \text{ DW}$) and high ($> 1.5 \text{ g N kg}^{-1} \text{ DW}$) concentration levels is set at 30% to 10% respectively (Fig. 3.4.1.2.2a). For some variables (e.g.

pH), no distinction in tolerable limits between low and high concentrations is justified due to the linear relationship of the reproducibility curve.

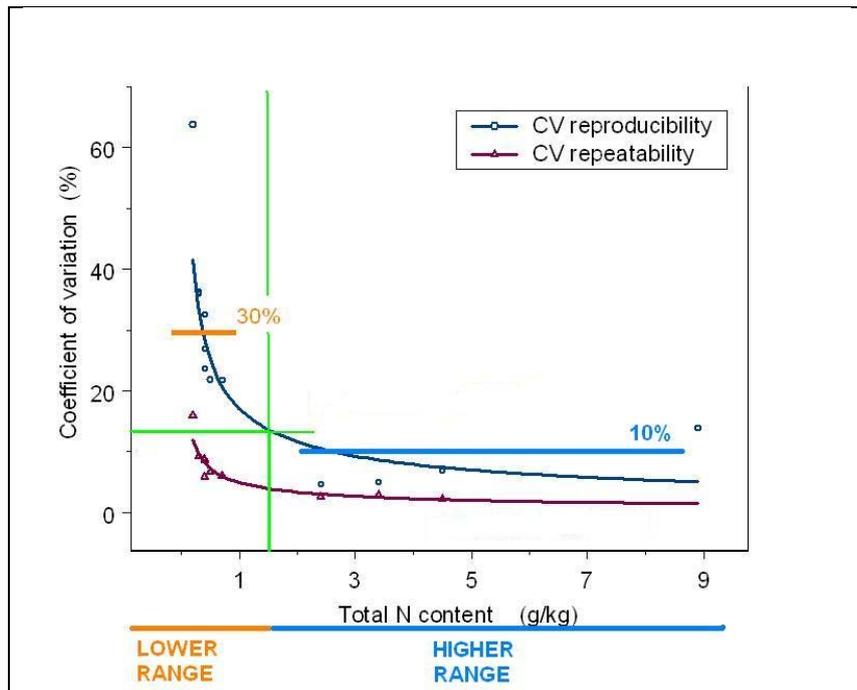


Figure 3.4.1.2.2a: Power curves fitted to the results of total N in mineral soil samples of previous FSCC ring tests. The estimation of the CVs at low and high N concentrations are based on the turning point of the reproducibility curve. Therefore, in this example, the average CV for low and high concentrations of total N in mineral soils is 30 % and 10 % respectively.

Tolerable limits are set using a z-score of 1: the deviation from the mean is equal to the standard deviation (SD). Consequently, tolerable limits equal the average CV_{repr} in the earlier FSCC ring tests, rounded off to the nearest 5 %.

Because the tolerable limits equal $\pm SD$, in theory 68% of the labs should meet this criterion. However, a simulation for the 5th ring test revealed that, on the average, 70-90 % of the laboratories reported results within the tolerable range and 10-30 % failed, depending on the variable in question.

In the future, as laboratory performance improves, these limits will be gradually narrowed using z-scores of less than 1.

The tolerable limits for between laboratory variability for a range of soil parameters are given in Table 3.4.1.2.2.

Table 3.4.1.2.2: Inter-laboratory (i.e. between laboratories) tolerable limits for a range of soil parameters, including moisture content, soil texture, total, aqua regia extractable and exchangeable elements, reactive iron and aluminium and free acidity

Parameter	Conc. Range	Conc. Level	Inter-laboratory Tolerable limit (% of mean)
Moisture content (%)	Low	≤ 1.0	± 25
	High	> 1.0	± 15
pH _{H2O} -	-	2.0 – 8.0	± 5
pH _{CaCl2} -	-	2.0 – 8.0	± 5
OC g kg ⁻¹	Low	≤ 25	± 20
	High	> 25	± 15
TN g kg ⁻¹	Low	≤ 1.5	± 30
	High	> 1.5	± 10
Carbonate g kg ⁻¹	Low	≤ 50	± 130
	High	> 50	± 40
Clay content %	Low	≤ 10.0	± 50
	High	> 10.0	± 35
Silt content %	Low	≤ 20.0	± 45
	High	> 20.0	± 30
Sand content %	Low	≤ 30.0	± 45
	High	> 30.0	± 25
TotAl mg kg ⁻¹	Low	≤ 20000	± 35
	High	> 20000	± 10
TotCa mg kg ⁻¹	Low	≤ 1500	± 20
	High	> 1500	± 15
TotFe mg kg ⁻¹	Low	≤ 7000	± 20
	High	> 7000	± 10
TotK mg kg ⁻¹	Low	≤ 7500	± 15
	High	> 7500	± 10
TotMg mg kg ⁻¹	Low	≤ 1000	± 60
	High	> 1000	± 10
TotMn mg kg ⁻¹	Low	≤ 200	± 25
	High	> 200	± 10
TotNa mg kg ⁻¹	Low	≤ 1500	± 20
	High	> 1500	± 10
ExtrP mg kg ⁻¹	Low	≤ 150	± 45
	High	> 150	± 20
ExtrK mg kg ⁻¹	Low	≤ 500	± 60
	High	> 500	± 40
ExctCa mg kg ⁻¹	Low	≤ 500	± 70
	High	> 500	± 30
ExctMg mg kg ⁻¹	Low	≤ 500	± 60
	High	> 500	± 15
ExctrS mg kg ⁻¹	-	35 - 1300	± 35
ExtrNa mg kg ⁻¹	Low	≤ 75.0	± 65
	High	> 75.0	± 50
ExtrAl mg kg ⁻¹	Low	≤ 2500	± 50
	High	> 2500	± 20
ExtrFe mg kg ⁻¹	Low	≤ 2500	± 40
	High	> 2500	± 15

ExtrMn mg kg ⁻¹	Low	≤ 150	± 30
	High	> 150	± 15
ExtrCu mg kg ⁻¹	Low	≤ 5	± 40
	High	> 5	± 15
ExtrPb mg kg ⁻¹	-	3 - 70	± 30
ExtrNi mg kg ⁻¹	Low	≤ 10	± 40
	High	> 10	± 15
ExtrCr mg kg ⁻¹	Low	≤ 10	± 40
	High	> 10	± 25
ExtrZn mg kg ⁻¹	Low	≤ 20	± 40
	High	> 20	± 20
ExtrCd mg kg ⁻¹	Low	≤ 0.25	± 100
	High	> 0.25	± 55
ExctrHg mg kg ⁻¹	-	0 - 0.16	± 75
Exch Acidity cmol ₍₊₎ kg ⁻¹	Low	≤ 1.00	± 90
	High	> 1.00	± 35
ExchK cmol ₍₊₎ kg ⁻¹	Low	≤ 0.10	± 45
	High	> 0.10	± 30
ExchCa cmol ₍₊₎ kg ⁻¹	Low	≤ 1.50	± 65
	High	> 1.50	± 20
ExchMg cmol ₍₊₎ kg ⁻¹	Low	≤ 0.25	± 50
	High	> 0.25	± 20
ExchNa cmol ₍₊₎ kg ⁻¹	-	0.01-0.14	± 80
ExchAl cmol ₍₊₎ kg ⁻¹	Low	≤ 0.50	± 105
	High	> 0.50	± 30
ExchFe cmol ₍₊₎ kg ⁻¹	Low	≤ 0.02	± 140
	High	> 0.02	± 50
ExchMn cmol ₍₊₎ kg ⁻¹	Low	≤ 0.03	± 45
	High	> 0.03	± 25
Free H ⁺ cmol ₍₊₎ kg ⁻¹	-	0.02-1.20	± 100
Reactive Al mg kg ⁻¹	Low	≤ 750	± 30
	High	> 750	± 15
Reactive Fe mg kg ⁻¹	Low	≤ 1000	± 30
	High	> 1000	± 15

3.4.1.2.3 Tolerable limits for plant (foliar and litterfall) ring tests

The first step in the evaluation procedure of foliage ring tests is the elimination of outliers in the results of the Needle/Leaf interlaboratory comparison test (DIN 38402/42, 1984). This method identifies three types of outlier. The Grubbs test can be used to check the four replicates from each laboratory for outliers (outlier type 1). The next step is to compare the recalculated mean values of each laboratory with the mean value from all the laboratories, as well as with the Grubb test for outliers (outlier type 2). Finally, the recalculated standard deviation from the laboratories must be compared with the total standard deviation (F-test) in order to eliminate laboratories with an excessive standard deviation (outlier type 3). The outlier-free, total mean value and the outlier-free maximum and minimum mean value of all the laboratories can then be calculated. If the initially identified type 1 outliers lie between the calculated outlier-free maximum and minimum mean values then they are no longer considered as outliers, and they can be used in further evaluation of the inter-laboratory comparison test. The last step is to calculate the outlier-free statistical values (Fürst, 2004, 2005, 2006, 2007, 2008).

In the next step an outlier-free mean value for each element/sample and the laboratory mean value and the recovery is calculated, and the results are compared with the tolerable limits given in Table 3.4.1.2.3. These tolerable limits for foliage samples were adopted by the Forest Foliar and Litterfall Expert Panel at the Meetings in Ås (1994), Vienna (1997), Bonn (1999), Prague (2003), Madrid (2007) and Hamburg 2009.

As the concentration range in foliage and in litterfall is usually very small compared with that for soil and deposition matrices, it is not necessary to have different tolerable limits for high and low concentrations of all the elements. Tolerable limits for low concentrations of some elements are given in Table 3.4.1.2.3.

Laboratory results within these limits will be accepted. However, laboratories with values exceeding these limits will need to take measures to improve their data quality.

Table 3.4.1.2.3: Inter-laboratory tolerable limits for high and low concentrations of mandatory and optional foliage and litterfall parameters

Parameter	Conc. Range	Conc. Level	Inter-Laboratory Tolerable limit (% of mean)
N mg g ⁻¹	Low	≤ 5.0	± 15
	High	> 5.0	± 10
S mg g ⁻¹	Low	≤ 0.50	± 20
	High	> 0.50	± 15
P mg g ⁻¹	Low	≤ 0.50	± 15
	High	> 0.50	± 10
Ca mg g ⁻¹	Low	≤ 3.0	± 15
	High	> 3.0	± 10
Mg mg g ⁻¹	Low	≤ 0.50	± 15
	High	> 0.50	± 10
K mg g ⁻¹	Low	≤ 1.0	±15
	High	> 1.0	±10
Zn µg g ⁻¹	Low	≤ 20	± 20
	High	> 20	± 15
Mn µg g ⁻¹	Low	≤ 20	± 20
	High	> 20	± 15
Fe µg g ⁻¹	Low	≤ 20	±30
	High	> 20	±20
Cu µg g ⁻¹	Low	-	±20
	High	-	±20
Pb µg g ⁻¹	Low	≤ 0.50	± 40
	High	> 0.50	± 30
Cd ng g ⁻¹	Low	-	± 30
	High	-	± 30
B µg g ⁻¹	Low	≤ 5.0	± 30
	High	> 5.0	± 20
C g 100g ⁻¹	Low	-	± 5
	High	-	± 5

3.4.2 Exchange of knowledge and expertise amongst laboratories

The inter-laboratory comparisons conducted within the framework of ICP Forests are aimed at testing the proficiency of the laboratories, i.e. evaluating the comparability of the results and, if possible, identifying the main causes of errors. The laboratories must be involved in discussions on the outcome of the ring tests in order to assess and where necessary optimise their analytical quality.

Laboratories with unacceptable results in ring tests will be invited to participate in an assistance programme organised by the WG on QA/QC in Laboratories. Close cooperation between these laboratories and laboratories with good laboratory practices is considered to be an effective way of improving laboratory proficiency.

When determining the scope for assistance, it is necessary to take into account, not only the results of the ring test but the current state of the implementation of a quality programme in the laboratory, as well as the analytical methods used in the laboratory in question. Such information will be ascertained beforehand from a questionnaire that the laboratory will be obliged to complete. The assistance will consist of a few days' visit to the laboratory, as well as a return visit, in order to identify and rectify easily detectable problems in the laboratory organisation and/or specific analytical processes.

It is essential that the members of the staff actually involved in the analytical work participate in the assistance programme.

The initial step of the assistance programme will entail drafting a list of analytical problems, with the emphasis on specific parameters analysed in the ICP Forests monitoring programme. Following from the inter-laboratory exchange visits, a short report will be produced detailing the laboratory's activities, the analytical problems encountered and suggestions about how best they can be remedied. Through this assistance programme, the laboratory will be provided with sufficient information to enable them to make improvements in the quality of their analytical results.

3.4.2.1 Exchange of analytical expertise

All laboratories are strongly invited to share their experience through internal **info-sheets**, developed as an easy tool for the exchange of information among laboratories about studies carried out in the laboratory which otherwise would not be published. The info-sheets are short Word files containing concise information about method comparison, development and implementation of new methods, material tests (e.g. on contamination or adsorption problems), sample pre-treatment, sample storage and technical information. Thus the work performed in one laboratory can help to avoid duplication in others.

The circulation of information between the WG on QA/QC in Laboratories and the participating laboratories is ensured through the WG's own **website**. This information, including details about past and ongoing ring tests, Excel files for QA/QC, downloadable scientific publications, analytical info-sheets, relevant contact addresses and useful links can be found at http://www.icp-forests.org/WGqual_lab.htm.

3.4.2.2 Exchange of samples

The exchange of a limited number of routine samples between two laboratories is a simple and easy way to test the quality and comparability of the methods used. About 20 routine samples should be analysed in each laboratory and the results compared. This ensures that differences in the analytical methods used and problems encountered can be quickly and easily be identified, and steps taken to rectify the situation.

3.5 Quality indicators

The development of the quality over time can be followed by using quality indicators.

While, there are a number of quality indicators that can be used to evaluate the development of the participating laboratories QC/QA programme within ICP Forests, only 3 indicators were ultimately selected:

- Percentage of the results of a ring test within tolerable limits -

- Percentage of the results of a ring test with a precision <10% (not applicable to water ring tests)
- Mean percentage of parameters where laboratories use control charts

The first two of them can be determined from results of the ring tests. The third one must be obtained from laboratories (for example an answer submitted with the ring test results or from the quality report forms).

3.5.1 Percentage of the results of a ring test within tolerable limits

In each ring test, the number of results within the tolerable limits for all mandatory parameter will be related as a percentage to the total number of possible results. Where results are missing, they will be counted as outside the tolerable limit. It is expected that the percentage of results within the tolerable limits should increase as the laboratories analytical expertise improves over time.

3.5.2 Percentage of the results of a ring test with a precision <10%

Normally, the precision (i.e. the repeatability of a result within a laboratory) should be <10 % for all parameters. In ring tests, with the exception of water samples, each sample typically has to be analysed 3 or 4 times. Therefore, where possible, the precision for each parameter can be calculated. The number of times the precision is <10 % can then be determined as a percentage of the total number of results where this calculation could be made.

Ideally, the precision <10 % should be between 90 to 100 % for all parameters analysed and should become constant over time.

3.5.3 Mean percentage of parameters for which laboratories use control charts

Control charts are a useful tool for checking the quality and the variation in quality over time (see Chapter 3.2). For each parameter and each matrix a laboratory has to use control charts. To foster the use of control charts for all parameters, it was decided to use as a quality indicator the percentage of parameters where laboratories use control charts. In future, all laboratories will have to include an annual quality report together with the data submission. In this report (see Chapter 3.6) each laboratory has to submit for each parameter in each matrix, the mean and the standard deviation of regularly measured reference materials (CRM or LRM). From this report, the percentage of parameters where control charts are used can be calculated for each laboratory. The mean percentage of all laboratories using control charts will be an indicator of improved laboratory quality control and should reach 100 % over the next number of years.

3.6 Quality reports

In the ICP Forests monitoring programme, there is little information about the quality of the analytical data submitted each year, by attaching a quality report with the annual data submission, it is possible to link information on the analytical quality to the data in a database. To ensure this linkage, the quality report must have the same base information as the data submission report (e.g. plot No., country code, year, lab code). The quality information parameters which have to be reported are:

- country code
- year
- plot No.
- lab code
- LOQ for each parameter (if needed)

- detection method (coded like in ring test reports) for each parameter,
- ring test No
- % of results within tolerable limits for each parameter
- requalification information (yes/no)
- mean and standard deviation (%) for each parameter from control charts (if a laboratory use more than one control chart for a parameter it has to submit only data from one control chart in a normal concentration range).

The quality report forms are part of the data submission forms (see ICP Forests Manual Part XVII Data submission forms).

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Annex I

Excel worksheet for ion balance (with and without DOC correction), conductivity, N balance and Na/Cl ratio checks.

The Excel worksheet permits different quality checks to be performed, as described in the text (Chapter 3.3.1). It can be downloaded from the ICP Forests website (<http://www.icp-forests.org/DocsQualLab/AnalyticalDataValidation.xls>). It can be used as a tool for validating the results and as a file for data storage, according to the requirements of the operator and the procedure for data handling in the laboratory. The sheet contains green cells in which new data are to be entered using the units given at the top of the column. The units are the same as those in the ICP Forests database, and the correct use of units is essential for all further checking (ion balance, measured/calculated conductivity check etc.) of the results. Information about the type of sample (BOF, THR, STF) and the type of forest cover on the plot (BL = broadleaves, CON = conifers) is required for DOC correction of the ion balance calculation. They are used as strings for the calculations, and therefore they must be entered correctly.

After entering the data in the green cells, the sheet calculates the **ion balance** (in accordance with the method described in Chapter 3.3.1.1.1) and the **calculated conductivity**, with and without correction for the ion strength (Chapter 3.3.1.2). The results of the tests are expressed in the worksheet as OK (test passed) or NO (test not passed) in the columns highlighted in yellow. The **DOC contribution to ion balance** is calculated using the empirical regressions described in Chapter 3.3.1.1.2. Selection of one of the three alternative regression equations is based on the codes depicting the type of sample and the type of forest cover, as given in Table 3.3.1.1.2a.

The principles and validation criteria for the **Na/Cl ratio** and **N forms balance** (i.e. N balance check) are described in Chapters 3.3.1.3 and 3.3.1.4. The **graphs** help in interpreting the results and identifying outliers. There are three graphs in the Excel worksheet: one for the ion balance, one for the comparison between measured and calculated conductivity, and one for the Na/Cl ratio. Other graphs can easily be added by the analysts themselves, e.g. for the comparison between measured conductivity and sum of anions or sum of cations and the conductivity corrected for the contribution of H⁺ and the sum of cations, with H⁺ excluded (Figure 3.3.1.5a).

The Excel worksheet includes a sheet (**notes**) giving the meaning of the acronyms and a summary of the adopted validation criteria.

The theoretical and statistical bases applied in developing the validation criteria for deposition data in the worksheet are based on thousands of full analysis sets provided by different laboratories, and are representative of different forest types and climatic conditions in Europe, ranging from northern Finland to southern Italy. The results of this work have been published in two papers (Mosello et al., 2005, 2008).

Excel worksheet for control charts

The Excel worksheet that can be used for creating control charts (Chapter 3.2.1), can be downloaded from the ICP Forests website (www.icp-forests.org/WGqual_lab.htm): click on "Excel file with instruction and example of control chart use". It also includes instructions on how to use the worksheet.

List of commercially available reference materials

Reference material	Matrix	Type	Comments	Supplier
BCR-408	water	simulated rain water	low concentrations	European Commission, Directorate-General Joint Research Centre Institute for Reference Materials and Measurements Reference Materials Unit Retieseweg 111 B-2440 Geel Belgium E-Mail: jrc-irmm-rm-sales@ec.europa.eu Webpage: www.irmm.jrc.be Order by Fax: +32 (0)14 590 406
BCR-409	water	simulated rain water	high concentrations	see above
BCR-100	plant	beech leaves		see above
BCR-062	plant	Olea europea (olive leaves)		see above
BCR-129	plant	powdered hay		see above
BCR-141R	soil	calcareous loam soil		see above
BCR-142R	soil	light sandy soil		see above
BCR-143R	soil	sewage sludge amended soil	heavy metal pollution	see above
BCR-146R	soil/organic material	sewage sludge of industrial origin	heavy metal pollution	see above
BCR-320	soil	river sediment		see above
FSCC RM1	soil	loamy forest soil	moderate concentrations	ICP Forests Soil Coordinating Centre Gaverstraat 4 9550 Geraardsbergen Belgium
1575a	plant	pine needles		Standard Reference Materials Program, National Institute of Standards and Technology 100 Bureau Drive, Stop 2322 Gaithersburg, MD 20899-2322 USA E-Mail: srminfo@nist.gov Webpage: www.nist.gov/srm Order by Fax: (301) 948-3730
1515	plant	apple Leaves		see above

Reference material	Matrix	Type	Comments	Supplier
1547	plant	peach Leaves		see above
1570a	plant	spinach leaves		see above
1573a	plant	tomato leaves		see above
Sample 2 from the 8 th needle/leaf inter-laboratory test (ICP Forests)	plant	spruce needles		Federal Research and Training Centre for Forests, Natural Hazards and Landscape M. Alfred Fürst Seckendorff-Gudent Weg 8 A-1131 Vienna Austria E-Mail: alfred.fuerst@bfw.gv.at Web: www.ffcc.at Order per fax: +43-1-87838-1250
Sample 4 from the 6 th needle/leaf inter-laboratory test (ICP Forests)	plant	maple leaves		see above

Definitions and terminology

accuracy – the closeness of agreement between a test result and the accepted reference value.

NOTE: The term accuracy, when applied to a set of test results, involves a combination of random components and a common systematic error or bias component. (ISO 3534-1:1993)

bias – a systematic difference or systematic error between an observed value and some measure of the truth. Generally used to describe the inaccuracy of a method relative to a comparative method in a method comparison experiment. (Westgard J.O., 2003)

blank – is defined as the sample without the analyte.

blank determination - an analysis of the sample without the analyte or attribute, or an analysis without the sample e.g. going through all steps of the procedure with the reagents only. (van Reeuwijk and Houba, 1998)

blank chart – a type of control chart used to detect the possibility of occasional contamination with the use of blank.

blind sample - in chemical analysis: a selected sample whose composition is unknown except to the person submitting it; used to test the validity of the measurement process.

or:

a sample with known content of the analyte. The analyst is aware of the possible presence of the blind sample but he does not recognize the material as such. (van Reeuwijk and Houba, 1998)

calibration – operation that, under specified conditions, in a first step, establishes a relation between the quantity values with measurement uncertainties provided by measurement standards and corresponding indications with associated measurement uncertainties and, in a second step, uses this information to establish a relation for obtaining a measurement result from an indication. (VIM:2008)

or:

Process of determining the relation between the output or response of a measuring instrument and the value of the input. Calibration typically involves the use of a measuring standard.

certified reference material (CRM) - a reference material, accompanied by a certificate, one or more of whose property values are certified by a procedure which establishes traceability to an accurate realization of the unit in which the property values are expressed, and for which certified value is accompanied by an uncertainty at a stated level of confidence. (ISO Guide 30:1992)

or:

reference material, accompanied by documentation issued by an authoritative body and providing one or more specified property values with associated uncertainties and traceabilities, using valid procedures. (VIM:2008)

control chart - a graphical method for evaluating whether a testing process is operating within the limits expected from its inherent random variation. (Westgard J.O., 2003)

control levels/limits - the limits on a control chart such that, when data points fall outside them, special causes of variation must be suspected. These are normally three standard deviations either side of the mean.

Note: control limits are calculated, not assigned. They are a statistical point.

There are different formulae for calculating control limits, depending on the different type of control charts being used.

control sample - (sequence - control sample) a sample with an extreme content of the analyte but falling within the working range of the method. It is inserted at random in a batch to verify the correct order of the samples. (van Reeuwijk and Houba, 1998)

conventional true value - value attributed to a particular quantity and accepted, sometimes by convention, as having an uncertainty appropriate for a given purpose. (<http://www.measurementuncertainty.org> - VIM:1993)

or:

quantity value attributed by agreement to a quantity for a given purpose. (VIM:2008)

error - measured quantity value minus a reference quantity value (VIM:2008)

or:

the collective noun for a departure of the result from the true value. (van Reeuwijk and Houba, 1998)

homogeneity - the degree to which items (e.g. tested substance) are similar.

instrument limit of detection (IDL) - the concentration equivalent to a signal, due to the analyte of interest, which is the smallest signal that can be distinguished from background noise by a particular instrument. The IDL should always be below the method detection limit, it is not used for compliance data reporting, but may be used for statistical data analysis and comparing the attributes of different instruments. (Standard Methods, 18th Edition)

interference - artificial increase or decrease in apparent concentration or intensity of an analyte due to the presence of a substance that reacts nonspecifically with either the detecting reagent or the signal itself. (Westgard J.O., 2003)

interlaboratory comparison - organization, performance and evaluation of tests on the same or similar test items by two or more laboratories in accordance with predetermined conditions. (ISO/IEC Guide 43-1:1997)

limit of detection (LOD) - the smallest measure, that can be detected with reasonable certainty for a given analytical procedure. (IUPAC:1997)

or:

measured quantity value, obtained by a given measurement procedure, for which the probability of falsely claiming the absence of a component in a material is β , given a probability α of falsely claiming its presence. (VIM:2008)

or:

the smallest test value that can distinguished from zero. (Westgard J.O., 2003)

or:

the lowest amount of analyte in a sample which can be detected but not quantitated as an exact value. (Westgard J.O., 2003)

limit of quantification (LOQ) – the lowest concentration of an analyte that can be determined with acceptable precision (repeatability) and accuracy under the stated conditions of the test.' (NATA Tech Note #13)

or:

performance characteristic that marks the ability of a CMP to adequately “quantify” an analyte (...) The ability to quantify is generally expressed in terms of the signal or analyte (true) value that will produce estimates having a specified relative standard deviation (RSD), commonly 10%. (IUPAC:1997)

local reference material (LRM) – a material prepared and standardized in a laboratory, used especially for daily control of analytical process.

or:

a local reference sample (in-house) for which one or more property values have been established by the user laboratory, possibly in collaboration with other laboratories. The sample should be sufficiently stable and homogeneous for the properties concerned (van Reeuwijk and Houba, 1998)

matrix - the components of material system, except the analyte. Used to refer to the physical and chemical nature of the specimen, the substances present, and their concentrations. (Westgard J.O., 2003)

mean chart (X-chart) – a control chart used to check the repeatability of the measurements. In this chart the sample means are plotted in order to control the mean value of a variable.

measurement uncertainty – non-negative parameter characterizing the dispersion of the quantity values being attributed to a measurand, based on the information used. (VIM:2008)

(method) validation – verification, where the specified requirements are adequate for an intended use. (VIM:2008)

nominal value - rounded or approximate value of a characterizing quantity of a measuring instrument or measuring system that provides guidance for its appropriate use. (VIM:2008)

outlier - an observation that is numerically distant from the rest of the data.

or:

an observation that lies outside the overall pattern of a distribution. (Moore and McCabe 1999)

or:

discrepant value. Value which do not agree with the pattern of the majority of other values. (Westgard J.O., 2003)

precision – the closeness of agreement between independent test results obtained under prescribed conditions. (ISO 3534-1:1993)

proficiency testing – determination of laboratory testing performance by means of interlaboratory comparisons. (ISO/IEC Guide 2)

quantity - property of a phenomenon, body, or substance, where the property has a magnitude that can be expressed as a number and a reference. (VIM:2008)

random errors - a component of measurement error that in replicate measurements varies in an unpredictable manner. (VIM:2008)

or:

an error that can be positive or negative, the direction and exact magnitude of which cannot be exactly predicted. (Westgard J.O., 2003)

range chart (R-chart) – a type of control chart used to check the repeatability of the analysis, usually of duplicate determinations. In this chart, the sample ranges are plotted in order to control the variability of a variable.

reference material (RM) – a material or substance one or more of whose property values are sufficiently homogeneous and well established to be used for the calibration of an apparatus, the assessment of a measurement method, or for assigning values to materials. (ISO Guide 30:1992)

or:

a secondary reference material or substance, one or more of whose property values are accurately determined by number of laboratories with a stated method), and which values are accompanied by an uncertainty at a stated level of confidence. The origin of the material and the data should be traceable (van Reeuwijk and Houba, 1998)

or:

a material, sufficiently homogeneous and stable with reference to specified properties, which has been established to be fit for its intended use in measurement or in examination of nominal properties. (VIM:2008)

repeatability - precision under repeatability conditions. (ISO 3534-1:1993)

repeatability conditions – conditions where independent test results are obtained with the same method on identical test material in the same laboratory by the same operator using the same equipment within short intervals of time. (ISO 3534-1:1993)

or:

condition of measurement, out of a set of conditions that includes the same measurement procedure, same operators, same measuring system, same operating conditions and same location, and replicate measurements on the same or similar objects over a short period of time. (VIM:2008)

replicate result - the result of replicated measurement. (van Reeuwijk and Houba, 1998)

reproducibility – precision under reproducibility conditions. (ISO 3534-1:1993)

reproducibility conditions – conditions where test results are obtained with the same method on identical material in different laboratories by different operators using different equipment. (ISO 3534-1:1993)

or:

condition of measurement, out of a set of conditions that includes different locations, operators, measuring systems, and replicate measurements on the same or similar objects. (VIM:2008)

stability - in the technical sense in chemistry means thermodynamic stability of a chemical system. Chemical systems might include changes in the phase of matter or a set of chemical reactions.

standard deviation (s) – a statistic that describes the dispersion or spread of a set of measurements about the mean value of a Gaussian or normal distribution. (Westgard J.O., 2003)

systematic error – a component of measurement error that in replicate measurements remains constant or varies in a predictable manner. (VIM:2008)

or:

an error that is always in one direction and is predictable. (Westgard J.O., 2003)

target value – used in proficiency testing to designate the correct value usually estimated by the mean of all participant responses, after removal of outliers, or by the mean established by definitive or reference method. (Westgard J.O., 2003)

test sample - the sample, prepared from the laboratory sample, from which test portions are removed for testing or for analysis. (IUPAC:1997)

traceability- a property of the result of a measurement or the value of a standard whereby it can be related to stated references, usually national or international standards through an unbroken chain of comparison all having stated uncertainties. (Westgard J.O., 2003)

trueness - the closeness of agreement between the average value obtained from a large series of test results and an accepted reference value.

NOTE: The measure of trueness is usually expressed in terms of bias. (ISO 3534-1:1993)

true value - value consistent with the definition of a given particular quantity.

Notes:

- 1) This is a value that would be obtained by a perfect measurement.
- 2) True values are by nature indeterminate.

or:

quantity value consistent with the definition of a quantity. (VIM:2008)

t-value – a statistical value which depends on the number of data and the required confidence. (van Reeuwijk and Houba, 1998)

warning levels/limits – the limits on a control chart, normally set at two standard deviations either side of the mean.

working range - set of values of measurands for which the error of a measuring instrument is intended to lie within specified limits

z-score – statistically: a dimensionless quantity derived by subtracting the population mean from an individual test result and then dividing the difference by the population standard deviation. Often used for individual rating of the proficiency of a laboratory in interlaboratory comparisons.

Following this formulation, the z-score is a function of both the accuracy of the individual test result and the dispersion of the whole set of results, and it can not be used to compare the results of different tests.

Annex II – Minor changes after 2016

Date	Minor change to latest published version in 2016	Affected sections of this document