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Working Group on QA/QC in Laboratories

Quality Assurance and Control in Laboratories

A review of possible quality checks and other forms of assistance

ICP Forests Working Group on QA/QC in Laboratories
Authors: N. Clarke, N. Cools, J. Derome, K. Derome, B. De Vos, A. Fuerst, N. Koenig, A. Kowalska, R. Mosello, G. A. Tartari, E. Ulrich

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0. Introduction

Over the past years considerable efforts have been made to improve the quality of laboratory analyses in the various monitoring programmes within the framework of the ICP Forests programme. The Soil and Soil Solution, Deposition and Foliage and Litterfall expert panels have carried out a number of ring tests and held discussions on quality control. The expert panels' sub-group, 'Working Group on QA/QC in Laboratories', has extended its activities from 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.
This paper presents all the quality control methods that have been devised for the relevant fields of analytical chemistry. The aim is to provide those laboratories carrying out analyses within the ICP Forests programme with a complete overview of the possibilities of applying quality control in their laboratories.

1. Use of reference materials

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 6.4.

Reference materials are available in a range of types and price. CRMs are expensive and should be used only when really needed: **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 quality over the laboratories within a country.
In addition, 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 next chapter)**,** if there is a need to maintain a constant (stable) quality over a longer time scale.

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

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

One alternative 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 (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.

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 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, sometimes has to be used. However, check the sales conditions before ordering –they are given on the webpage.
"Old" ring test samples are also stable enough and extensively analysed for use as reference material in method validation.
(A list of commercially available CRM`s is given in Annex 6.4)
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 utilizes dried, powdered foliage samples from one type of tree and leaf or a homogenized litterfall sample. Removal of the foliage, drying, milling and the first homogenization should be performed in the laboratory. One part (dry weight min. 4-5 kg) should be send to the

FFCC (Contact: alfred.fuerst@bfw.gv.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. The analytical results for this material should be used in the control charts (see next chapter) if it is necessary to have constant (stable) quality over a longer time scale or for calibration, method validation, measurement verification, evaluating measurement uncertainty and for training purposes.

1.3 Reference material for soil analysis

International certified reference material is expensive and should be used only when really needed. In many cases, however, the concentrations are not within the ranges encountered in a specific country/region. (A list of commercially available CRMs is given in Annex 6.4)
National reference material is easier to obtain, is often not as expensive as international ones, and is produced by national laboratories in order to assure quality over the laboratories within a country. The advantage of local reference material is that it can be relatively cheaply prepared by the laboratory in question and is available in sufficient quantity to cover those concentration ranges encountered in normal laboratory work.

a. 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 (e.g. OL/OH horizons, mineral soil: 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 of high concentrations is necessary because the errors are the higher the lower the concentration. 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.
Note: a small standard deviation is good and an indicator of very accurate and precise work, but it is not the primary objective of this QA/QC document.

b. Calibration of local reference material for soils

After the preparation of the LRM, a test run has to be performed with perfectly 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 real 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 last case.

c. Use of local reference material for soils

After successful calibration, a systematic re-sampling 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 analysed real samples. For the solid phase (digestion and analysis) this could be reduced to one LRM per 30 to 50 analysed real samples.

The results of the repeated analysis of the LRM permit evaluation of the stability of the method/equipment over time. It is therefore important that no changes take place in the LRM over time. It is thus strongly recommended that the result of every analysis of the LRM is plotted on a graph over time (see ISO 8258, 1993; see next chapter on Shewhart control charts).

2. Use of control charts

Control charts form an important practical aspect of internal QC in the laboratory. Using reference materials (see Chapter 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 ref. Nordtest report TR 569, 2007.

2.1 Use of control charts for local reference material 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 ± 2s and ± 3s limits for the warning limit (WL) and control limit (CL), respectively (Figure 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±2s (WL) and 99% in the range of X_m±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 propositional 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

corrected. As regards the WL: if two out of three successive points exceed the WL, then an additional sample 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 corrected.

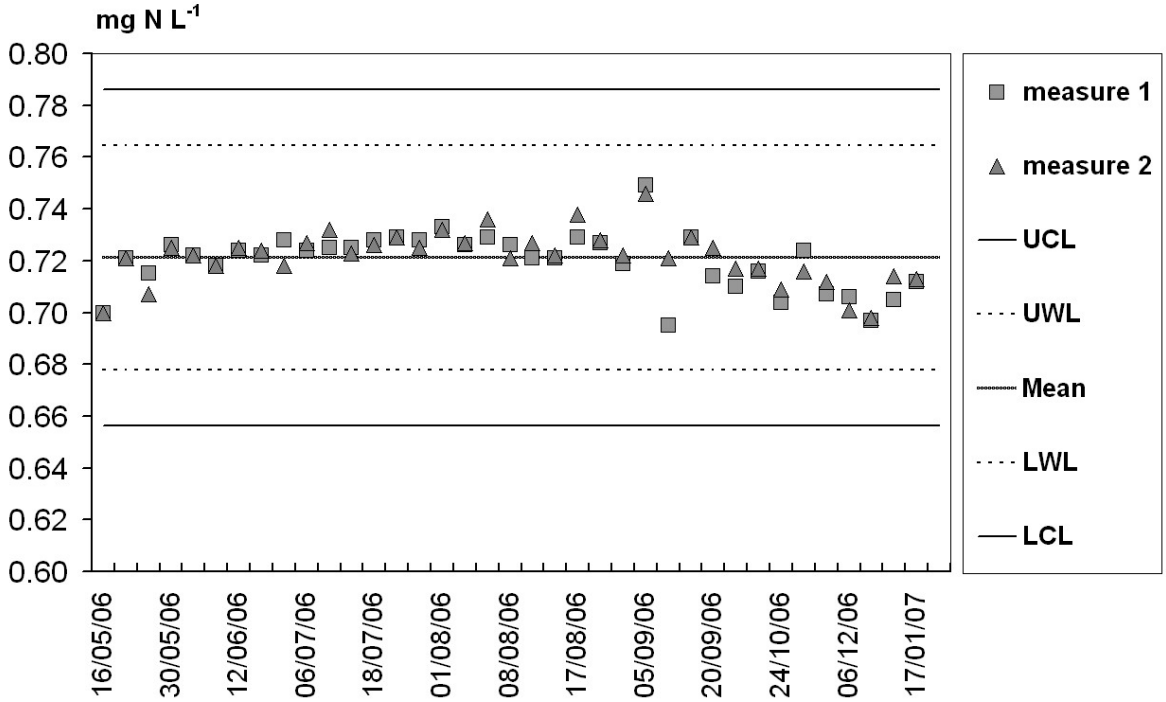

Figure 2.1a: *Example of a control chart for mean concentrations. Mean concentration, LWL, UWL lower, upper warning limit; LCL, UCL lower, upper control limit, calculated on the basis of experience with previous control charts (R.S.D. = 3 %)*

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 %.

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 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.

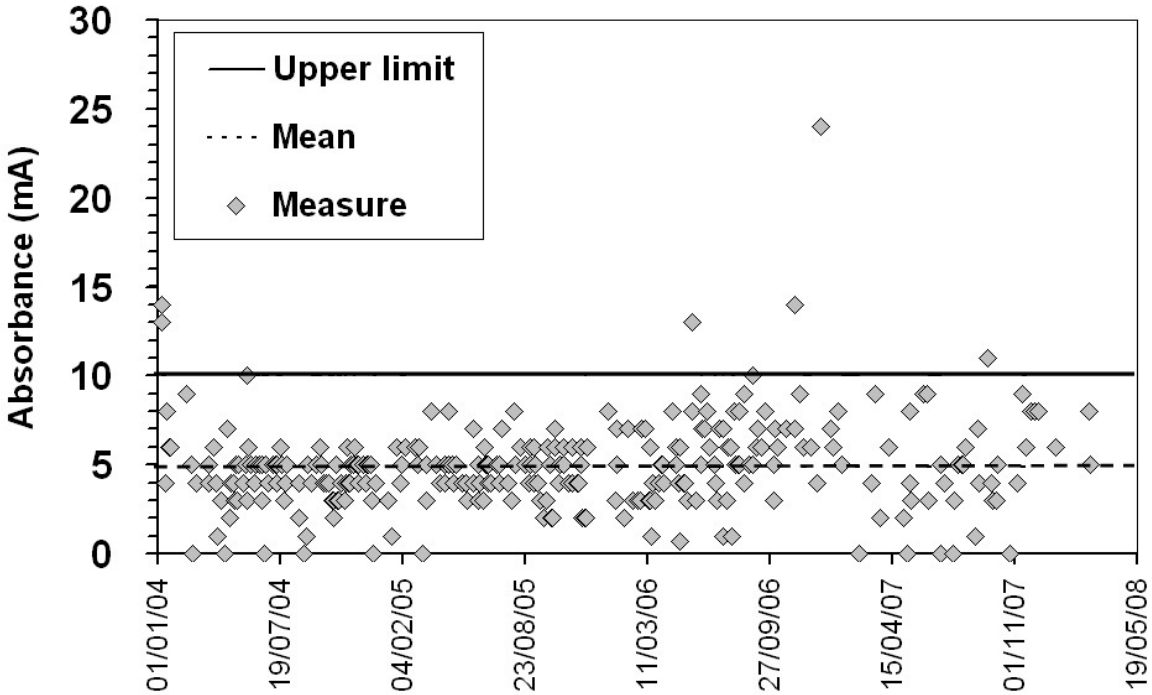

Figure 2.2a: Example of a blank chart

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 Sb:

$$LOD = S_t - S_b \geq K_d\, s_b$$
$$LOQ = S_t - S_b \geq K_q\, s_b$$

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

2.3 Detection and quantification limits

Detection and quantification capabilities are fundamental performance characteristics of any chemical measurement process (Currie, 1999). 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:

$$x_L = x_{bi} + Ks_{bi}$$

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 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 (Thomson 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 (1999), but in practice it is a useful approximation.

Table 2.3.1. IUPAC recommendations for uncertainty associated with limits of detection and quantification (after Thomson et al., 2003).

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

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 worse 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 provide more relevant information than IDLs.
Measurement precision and concentration (or content) are often clearly related, as shown in Figure X. Generally, as the concentration or content of the analyte decreases, the precision for determination, as expressed in the relative standard deviation, gets worse. When empirically precision data are gathered for each concentration or content level, a graph may be constructed as in Figure 2.3.1. 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 solving the RSD values of 30% and 10%, respectively. These limits are indicated on the graph and illustrate clearly that reliable determination of total N in this example is guaranteed for concentrations above the LOQ, whereas determination becomes highly uncertain between the LOD and LOQ.

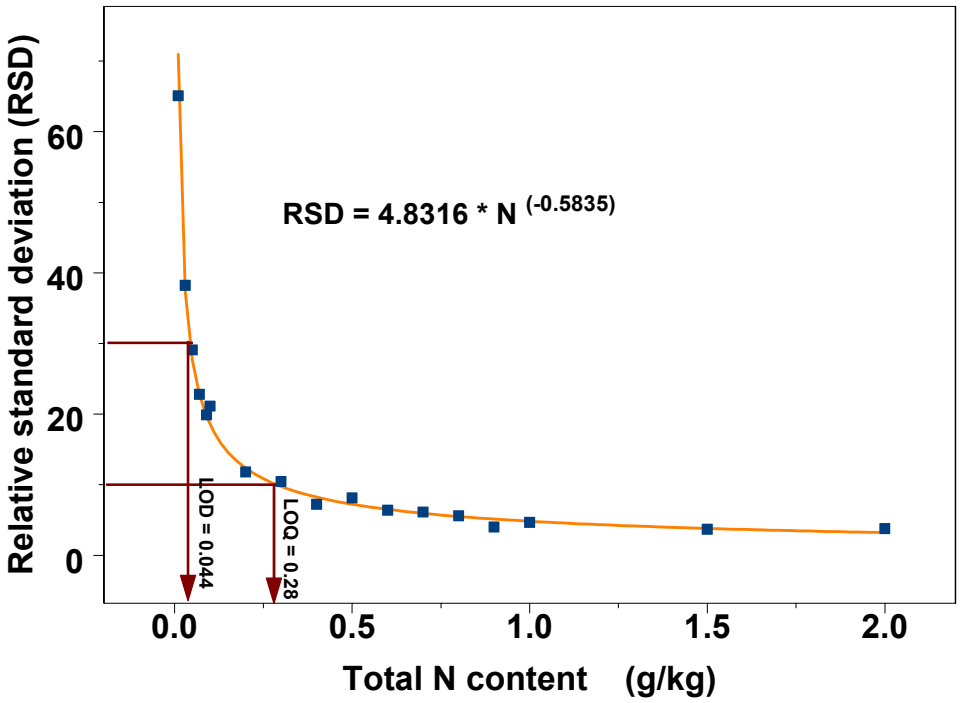

Figure 2.3.1. Relationship between measurement precision (RSD) and N concentration in a test mineral soil sample.

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.

3. Check of analytical results

3.1 Check of analytical results for water samples

The solutes present in deposition and soil water samples and in soil extracts are mainly in ionic form. This enables the use of two checks on the consistency of the results of the analyses performed on individual samples: calculation of the ion balance, and comparison of the measured conductivity and the conductivity calculated from the sum of the contribution of the conductivity 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.
A more detailed explanation of the use of these tests and their incorporation in the analytical QC procedures is given in the ICP Forests manual (UN ECE, 2004, Ulrich et al., 2006). Examples of the application of these checks on sets of data from different sites in Europe have been reported by Mosello et al., 2005.
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 in Annex 6.2.

3.1.1 Ion balance

3.1.1.1 Ion balance without DOC

As prescribed in the ICP Forests manual (UN ECE, 2004, Ulrich et al., 2006), each laboratory performs checks 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 and wet only deposition, throughfall and stemflow) values in order to validate the results.. However, these checks are not always applicable to soil water (SW) samples. 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):

$$\Sigma \text{ Cat} = [Ca^{++}] + [Mg^{++}] + [Na^+] + [K^+] + [NH_4^+] + [H^+]$$

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

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

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

The limits adopted in the ICP Forests/EU Forest Focus programmes are given in Table 3.1.1.1a

Table 3.1.1.1a: Acceptance threshold values in data validation based on ion balance and conductivity (see definition of PD and CD in the text).

Conductivity (25 °C)	PD	CD
<10 µS cm^{-1}	±20%	±30%
<20 µS cm^{-1}	±20%	±20%
>20 µS cm^{-1}	±10%	±10%

The conversion factors required to transform the units used in the ICP Forests Deposition manual (into µeq L^{-1} are given in Table 3.1.1.1b.

Table 3.1.1.1: The conversion factors used in converting the concentrations used in the ICP Forests Deposition Monitoring Programme to µeq L^{-1}, and the values of equivalent ionic conductivity at infinite dilution.

	Unit (ICPF standard)	**Conversion factor to µeq 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	µeq 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:

$$TAlk = -[H^+] + [OH^-] + [HCO_3^-] + [CO_3^{2-}]$$

This definition is not completely correct in the case of high organic carbon concentrations (DOC > 5 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 3.1.1.2 and 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 3.1.1.1c.

Table 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	Y	Y	Y	Y
Stemflow	N	Y	Y	Y	Y
Soil water	N	N	$Y_{(2)}$	N	Y
Surface water	$Y_{(1)}$	Y	Y	N	Y
	(1) If DOC <5 mg C L^{-1} and negligible metal concentrations				
	(2) If metal concentrations are negligible.				

Examples of comparisons between Σ Cat and Σ An are given in Figure 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 in Figure 3.1.1.1b, illustrating the failure of the check in the case of THR and STF samples.

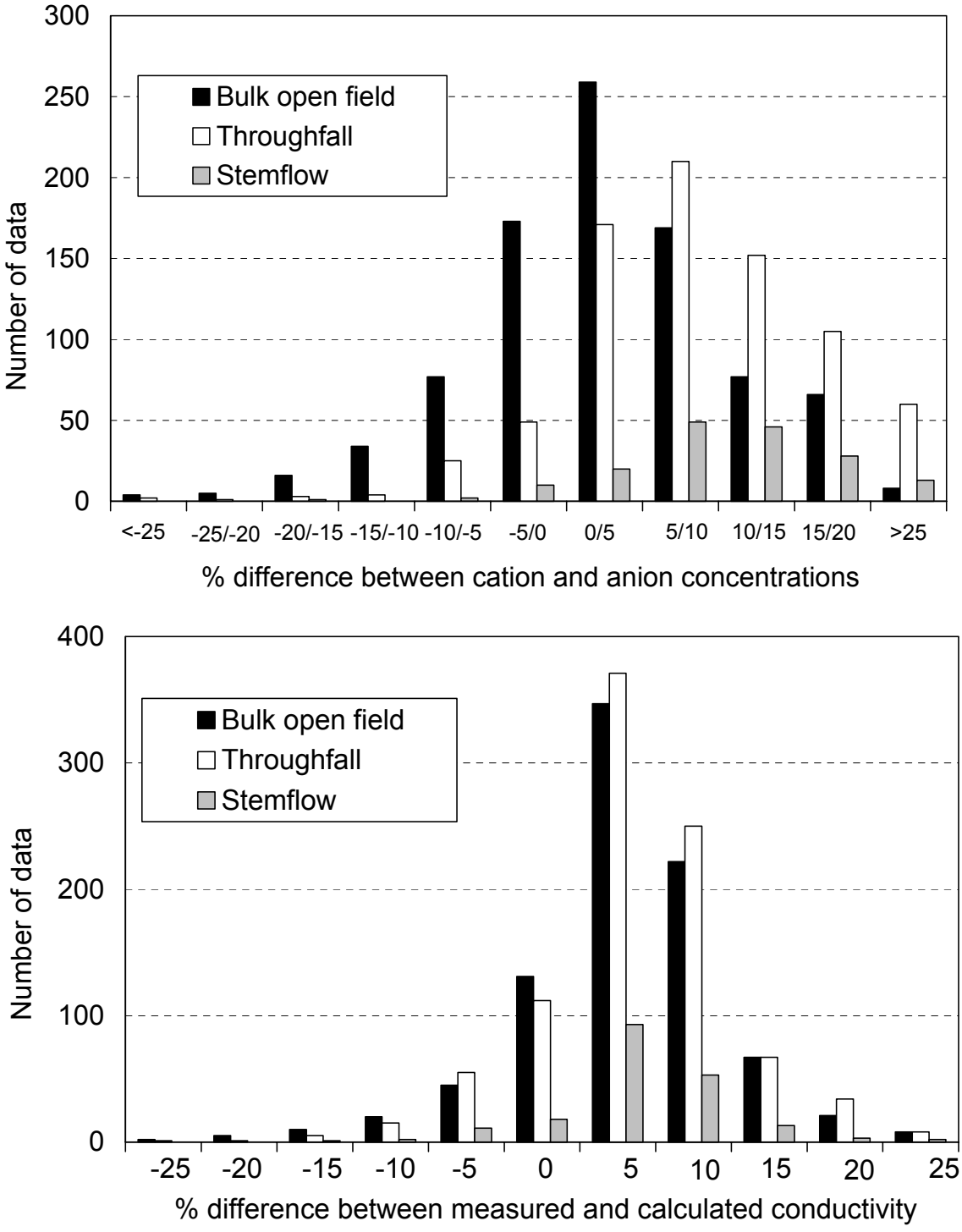

Figure 3.1.1.1a: Departure from zero of the percentage difference between Σ Cat and Σ An (PD), and (below) of the percentage difference between measured and calculated conductivity (CD) for different types of deposition sample.

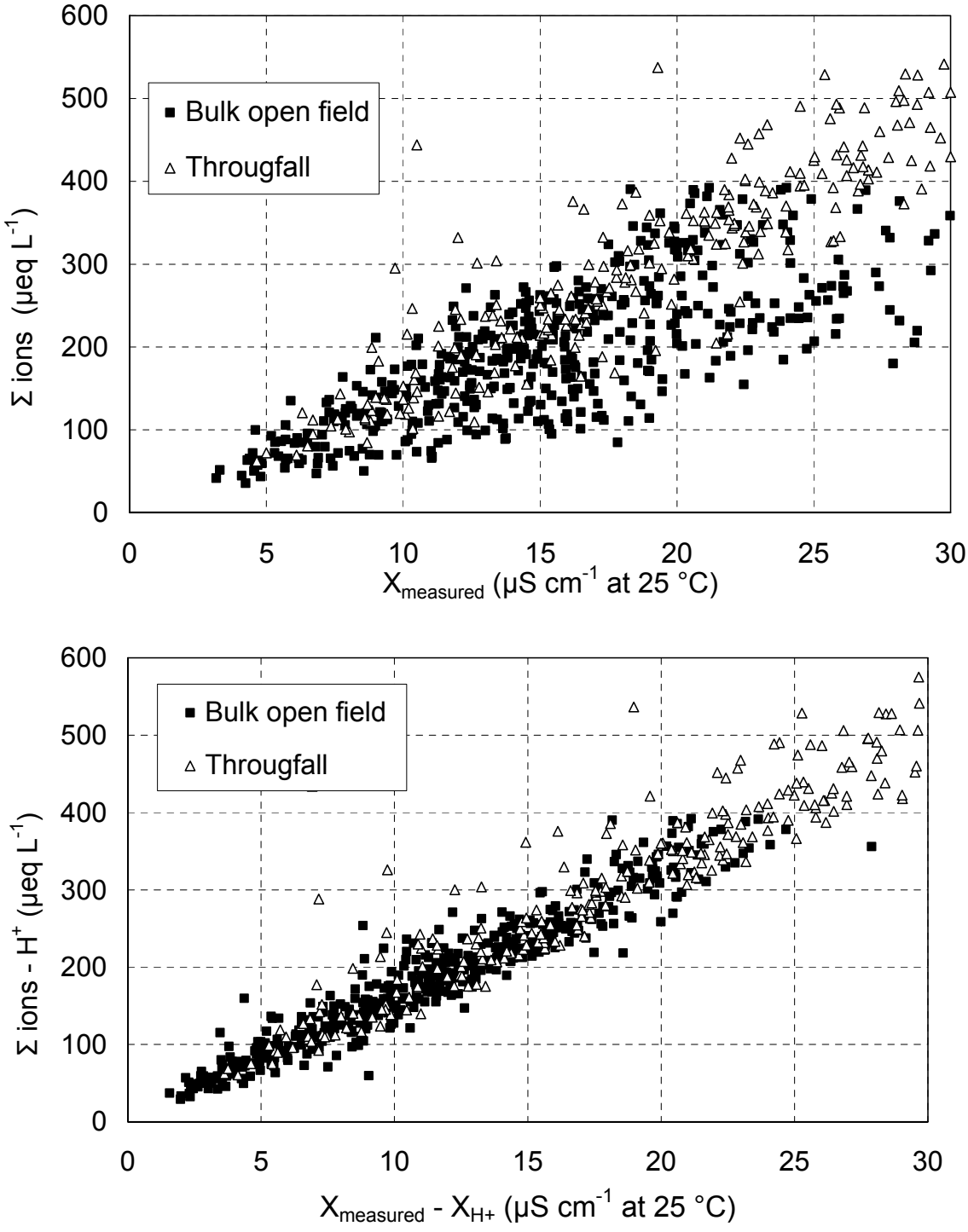

Figure 3.1.1.1b: Examples of the relationships between conductivity and Σ Cat or Σ An, above without the correction for H+ contribution to conductivity, and below with the correction.

3.1.1.2 Ion balance with DOC

Figure 3.1.1.1b 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 Chapters 3.1.1.2 and 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 um 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 δ_0, mg C L^{-1} for DOC, and μeq $(\text{mg C})^{-1}$ for δ_1. 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 $[\text{Org}^-]$ (μeq L^{-1}) is the ionic contribution of DOC. The value of PD was calculated again using the Σ An value including $[\text{Org}^-]$, and evaluated using the threshold values given in Table 3.1.1.1c.
An example of the regression coefficients, β_1 and β_0, as well as the appropriate statistical parameters, are given in Table 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 3.1.1.2a. This evaluation can also be found in the annexed Excel file, which contains examples of analysis validation.

Table 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± σ	u	5.8±0.6	5.6±0.6	5.3±0.5
DOC range	mg C L^{-1}	0-37	1-39	0-40
DOC mean± σ	mg C L^{-1}	8±6	11±7	10±7
∑ Cat range	µeq L^{-1}	37-2736	30-5287	13-2601
∑ Cat mean± σ	µeq L^{-1}	418±321	593±539	316±278
∑ An range	µeq L^{-1}	29-2606	22-5303	10-2584
∑ An mean± σ	µeq L^{-1}	377±304	545±523	279±265
∑ Cat - ∑ An range	µeq L^{-1}	258	263	225
∑ Cat - ∑ An mean± σ	µeq L^{-1}	41±59	48±58	37±41
Slope β_1	µeq (mg C)$^{-1}$	6,8±0,16	5.04±0.25	4.17±0.11
Intercept β_0	µeq L^{-1}	-12,32±1,63	-6.67±3.29	-5.01±1.32
P-value		<0,0001	<0.0001	<0,0001
R^2		0.56	0.4	0.47

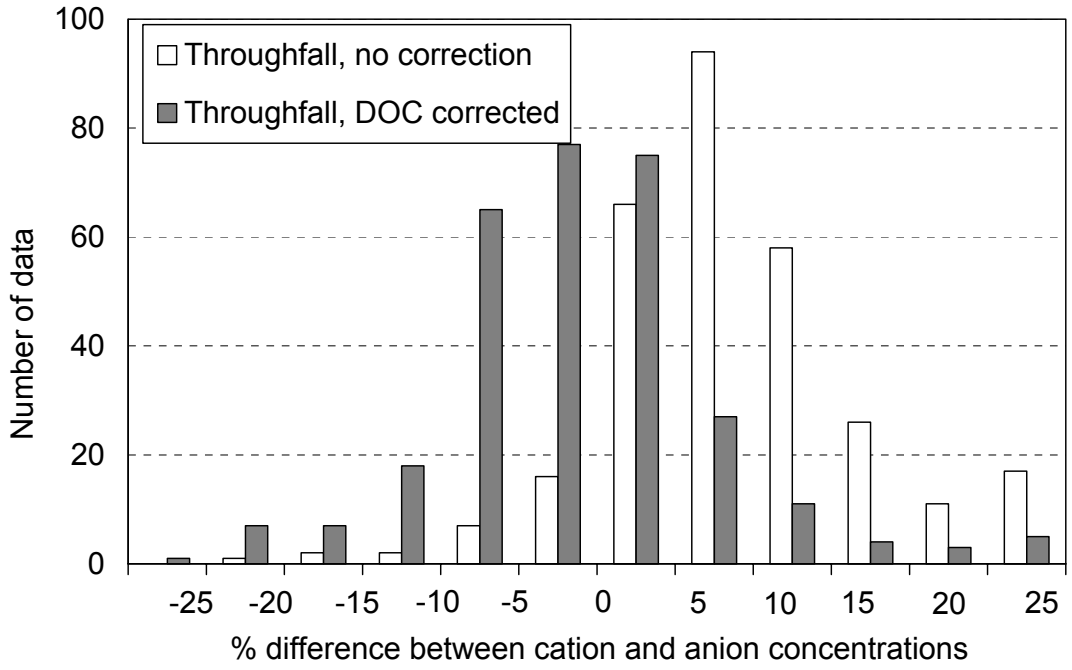

Figure 3.1.1.2a: Departure from zero of the percentage difference between Σ Cat and Σ An (PD, see text) without and with DOC correction.

3.1.1.3 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+}, $Al(OH)^{2+}$,$Al(OH)_2^+$, Fe^{3+}, $Fe(OH)^{2+}$, $Fe(OH)_2^+$), their oxidation state (e.g. Fe^{3+}/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 3.1.1.1) 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 3.1.1.2 for throughfall samples, also has to take into account the metals, their species and their complexes with DOC:

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

where:
Σ Met = Al^{3+} + $Al(OH)^{2+}$ +$Al(OH)_2^+$ + Fe^{3+} + $Fe(OH)^{2+}$ + $Fe(OH)_2^+$ + Mn^{2+} + $Mn(OH)^+$ (and other inorg. species)
Σ Met (from DOC complexes) = Al-DOC + Fe-DOC + Mn-Doc
Σ Org^- (from DOC complexes) = DOC-Fe + DOC-Al + 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 an ongoing study being carried out 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 3.1.1.3a:

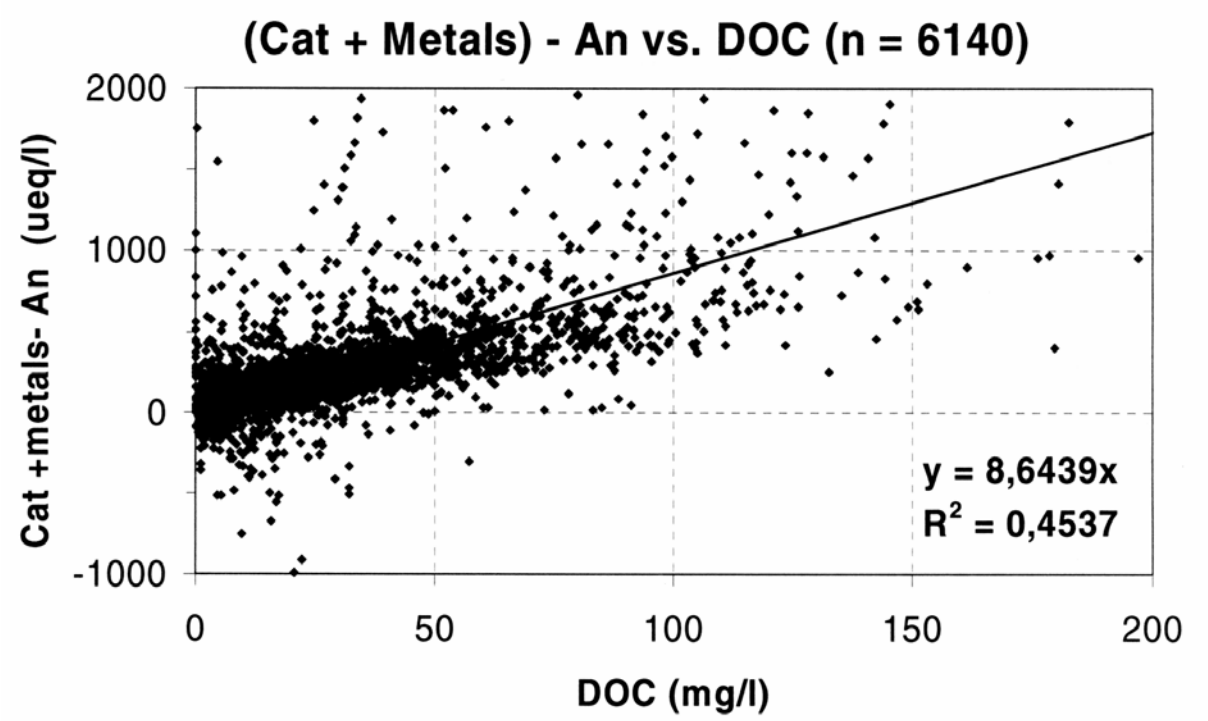

Figure 3.1.1.3a: Calculation of the formal charge of DOC in 6140 soil solution samples from 5 countries (Germany, Finland, France, Norway and the United Kingdom)

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 +/- 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.

3.1.2 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 ohm^{-1} 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 µS cm^{-1}, where 1 mS m^{-1} = 10 µS cm^{-1} = 10 µmho cm^{-1}, is also widely used in practice. The unit adopted in the ICP Forests programme is µS 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: S cm^2 $equivalent^{-1}$).
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)

$$CE = \Sigma \lambda_i c_i$$

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 µeq L^{-1}, λ_i is given as kS cm^2 eq^{-1} in order to obtain the conductivity in µS cm^{-1}. The percentage difference, CD, is given by the ratio:

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

At low ionic strength (below 100 µeq 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 µeq L^{-1} (approximately at conductivity higher than 100 µS cm-1) it is necessary to use activity instead of concentration. This can be done by first calculating the ionic strength (*Is*, meq L^{-1}) from the individual ion concentrations as follows:

$$Is = 0.5 \Sigma c_i z_i^2 / w_i$$

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 µeq L^{-1}, activities must be used instead of concentrations; in the range 100-500 µeq 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):

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

Finally, the corrected conductivity is calculated as:

$$CE_{corr}=y^2 \quad CE= y^2 \ \Sigma \lambda_i c_i$$

Immediate comparison of the measured and calculated conductivity makes it possible to identify single outlier values (see example in the annexed Excel file).
Figure 3.1.1.1a 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, STF. The reason for this is that the DOC (organic matter), 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.

3.1.3 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 (annexed Excel file), samples with a ratio outside the range given below are marked as possible failures, and checks and/or reanalyses should be carried out. The ratio is calculated by expressing the concentrations on a molar (or equivalent) basis.

$$0.5 < (Na/Cl) < 1.5$$

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

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 ($N\text{-}NO_3$), ammonium ($N\text{-}NH_4$) and nitrite ($N\text{-}NO_2$) 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:

$$[N\text{-}NO_3] + [N\text{-}NH_4] < [DTN]$$

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 NO_3-N + NH_4-N. In this case, normal (random) analytical errors may result in a slightly negative value of ([DTN] – ([NO_3-N] + [NH_4-N])), without there being any major problem with the analyses.

3.1.5 Phosphorus concentration as a contamination check

If bird droppings pass into 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.

3.2 Check of analytical results for organic and mineral soil samples

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 checking procedures are recommended: plausible range checks and cross-checks.

3.2.1 Plausible range checks for organic and mineral soil samples

All the mandatory and optional variables for laboratory soil analysis within the ICP Forests programme are listed in Annex I. For each variable, there is a 95 % probability that the analytical result will fall within the plausible min-max range given in Table 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 ICP Forests manual IIIa, Sampling and Analysis of Soil.
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). This is 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 "< X.X", with X.X the LOQ concentration to the required number of decimal places.
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.
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).

table 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.

		Organic sample Plausible range		Mineral soil sample Plausible range	
Parameter	**Unit**	**Min[#]**	**Max**	**Min[#]**	**Max**
Moisture content (air-dry sample)	**%wt**	**< 0.1**	10.0	**< 0.1**	10.0
pH(H_2O)	**-**	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**	5000.00	**< 44.6**	7500.0
Reactive Fe	**mg/kg**	**< 48.4**	5000.00	**< 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).

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.

3.2.2.1. 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 (pH_{H2O}) or 0.01 mol/l calcium chloride (pH_{CaCl2}). The actual pH (pH_{H2O}) and potential pH (pH_{CaCl2}) 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 pH_{CaCl2} always less or equal to pH_{H2O}.

Check algorithm: $\mathbf{0 < [pH_{H2O} - pH_{CaCl2}] \leq 1.2}$

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

3.2.2.2. Carbon check

According to the manual, 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: $\mathbf{[C_{CaCO3}+TOC] \leq TC}$ with $\mathbf{C_{CaCO3} = CaCO_3 \times 0.12}$

and

Check algorithm: $\mathbf{C_{CaCO3} \approx TIC}$

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).

3.2.2.3. 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 pH_{CaCl2} < 6.0 then $CaCO_3$ < 3 g kg^{-1}** (= below LOQ)

For a mineral soil sample:
Check algorithm: **if pH_{H2O} < 5 then $CaCO_3$ < 3 g kg^{-1}** (= below LOQ)
or: if pH_{CaCl2} < 5.5 then $CaCO_3$ < 3 g kg^{-1} (= below LOQ)

Conversely, if pH_{CaCl2} > 6, quantifiable amounts of carbonate are most likely present in the sample.

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 g kg^{-1} TOC):
Check algorithm: **5 < C/N ratio < 100**

For a mineral soil sample:
Check algorithm: **3 < C/N ratio < 75**

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 g kg^{-1} TOC):
Check algorithm: **100 < 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 < C/P ratio < 750**

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 g kg^{-1} TOC):
Check algorithm: **20 < C/S ratio < 1000**

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 ≤ Total element**
for the elements K, Ca, Mg ,Na, Al, Fe and Mn.

3.2.2.8. Reactive Fe and Al check

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

Check algorithm: **Reactive Fe ≤ Total Fe**
Reactive Al ≤ 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.

3.2.2.9. 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 $cmol_{(+)}\ kg^{-1}$ to $mg\ kg^{-1}$.

Check algorithm: $(K_{exch} \times 391) \leq$ Extracted K
Check algorithm: $(Ca_{exch} \times 200) \leq$ Extracted Ca
Check algorithm: $(Mg_{exch} \times 122) \leq$ Extracted Mg
Check algorithm: $(Na_{exch} \times 230) \leq$ Extracted Na
Check algorithm: $(Al_{exch} \times 89) \leq$ Extracted Al
Check algorithm: $(Fe_{exch} \times 186) \leq$ Extracted Fe
Check algorithm: $(Mn_{exch} \times 274) \leq$ Extracted Mn

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

3.2.2.10. 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.

3.2.2.11. Particle size fraction sumcheck

According to the ICP Forests Manual IIIa, 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), 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: **Σ [clay (%), silt (%), sand (%)] = 100 %**

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

3.3 Check of analytical results for foliar and litterfall samples

Compared to the checks for the analytical results on soil, deposition and soil solution samples, devising checks for foliage and litterfall samples is relatively difficult. In unpolluted “background” areas, the concentration range 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.

3.3.1 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

Table 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	Leaf_type*)	Limit	N g/kg	S g/kg	P g/kg	Ca g/kg	Mg g/kg	K g/kg	C g/100g	Zn µg/g	Mn µg/g	Fe µg/g	Cu µg/g	Pb µg/g	Cd ng/g	B µg/g
Fagus sylvatica	0	low	20,41	1,26	0,89	3,44	0,65	4,81	*45*	17	127,2	62	5,67	-	50,3	9,09
	0	high	29,22	2,12	1,86	14,77	2,5	11,14	*55*	54,21	2902	177,9	12,18	6,79	461,5	40,04
Quercus cerris	0	low	12,86	0,91	0,63	4,81	0,98	1,19	*45*	13	509	83	6,89	-	63	15,9
	0	high	30,79	3,24	2,29	16,49	3,24	15,64	*55*	-	-	-	-	-	-	-
Quercus ilex	0	low	11,95	0,81	0,69	4	0,76	3,42	*45*	12,7	277,65	73,1	4	-	-	21,74
	0	high	17,24	1,41	1,22	10,32	2,62	8,46	*55*	41	5384,5	716,9	*7*	-	-	-
Quercus petraea	0	low	19,75	1,24	0,9	4,12	1,06	5,86	*45*	11	905	60,4	5,39	-	24	5,5
	0	high	29,84	2,01	1,85	10,46	2,26	11,16	*55*	25	4208,6	149,2	11,64	-	-	-
Quercus pyrenaica (Q. toza)	0	low	17,85	1,18	1,48	4,6	1,4	3,52	*45*	18	434	81	8,07	-	-	-
	0	high	25,5	2,33	3,12	12,03	3	11,81	*55*	-	-	-	-	-	-	-
Quercus robur (Q. pedunculata)	0	low	20,31	1,36	0,97	3,33	1,09	5,8	*45*	14	218,75	63,8	5,5	0,138	40	23,41
	0	high	30,69	2,21	2,55	12,26	2,85	12,64	*55*	50	2819,7	232,8	14,1	17,993	183,2	54,79
Quercus suber	0	low	11,39	0,85	0,47	4,29	1,22	4,37	*45*	17	291,25	62,15	6,11	-	-	17,5
	0	high	23,09	1,61	1,53	11,02	2,55	9,85	*55*	47	2887,4	621	*20*	-	-	-
Abies alba	0	low	11,55	0,79	0,95	3,5	0,68	4,29	*47*	22	185	20,6	2,31	-	48	15,5
	0	high	16,16	1,69	2,23	11,71	1,9	8,48	*57*	45	2510	85,2	5,89	-	-	-
	1	low	11,67	0,95	0,86	4,19	0,37	3,97	*47*	20	250	32	2	-	56	14,4
	1	high	16,46	1,79	2,21	16,39	1,7	7,57	*57*	47,5	5240,5	120,95	6,45	-	-	-
Picea abies (P. excelsa)	0	low	10,39	0,7	1,01	1,83	0,66	3,65	*47*	16	164,65	22	1,41	-	-	7,2
	0	high	16,68	1,31	2,1	7,01	1,56	8,36	*57*	47	1739,4	91,2	5,94	2,92	226	29,39
	1	low	9,47	0,69	0,81	2,26	0,44	3,41	*47*	12	198,4	26,67	0,94	-	-	6,16
	1	high	15,97	1,34	1,82	9,77	1,51	7,05	*57*	51,83	2376,4	118,05	7,07	5,24	169,05	32,94
Picea sitchensis	0	low	12,67	0,98	1,04	1,21	0,78	5,56	*47*	8,4	147,36	30,54	*0,7*	-	-	6
	0	high	17,61	1,75	2,56	8,02	1,41	10,89	*57*	33,8	1489,1	232,29	5,91	-	-	*42*
	1	low	11,87	0,92	0,84	1,41	0,5	4,62	*47*	9,5	159,72	33,2	*0,7*	-	-	5
	1	high	18,19	1,94	2,43	8,23	1,18	10,05	*57*	29,25	1734	133,32	4,667	-	-	*52*
Pinus contorta	0	low	11,31	0,75	0,98	1,02	0,79	3,56	*47*	-	-	-	-	-	-	-
	0	high	21,51	1,66	1,73	2,7	1,31	6,06	*57*	-	-	-	-	-	-	-
	1	low	13,12	0,87	0,88	1,96	0,75	1,21	*47*	-	-	-	-	-	-	-
	1	high	20,22	*1,7*	1,55	4,41	1,5	6,02	*57*	-	-	-	-	-	-	-
Pinus halepensis	0	low	9,22	0,92	0,8	2,12	1,84	3,2	*47*	23	32	230	-	-	-	-
	0	high	14,28	1,68	1,79	8,04	2,89	8,67	*57*	-	-	-	-	-	-	-
Pinus nigra	0	low	8,42	0,51	0,81	0,97	0,56	3,88	*47*	18,8	60	29,25	1,81	0,56	399	8,9
	0	high	21,18	1,44	1,57	4,42	2,08	8,3	*57*	67,7	1072,4	131	18,08	-	-	-
	1	low	7,97	0,44	0,75	1,17	0,35	3,89	*47*	19	109	69	1,8	0,87	380	8,7
	1	high	23,49	1,93	1,71	6,9	2,06	7,34	*57*	*70*	*1000*	-	-	-	-	-
Pinus pinaster	0	low	6,85	0,61	0,55	0,8	1,01	3,26	*47*	15,6	41,4	22,9	1,697	-	-	15
	0	high	13,71	1,29	1,24	3,8	2,47	7,14	*57*	39	825	578,9	5,03	-	-	-
	1	low	6,25	0,55	0,4	1,09	0,94	2,4	*47*	12,3	35,4	23,3	1,13	-	-	20
	1	high	13,27	1,44	1,38	6,02	2,88	6,86	*57*	36,8	794,1	110,8	4,68	-	-	-
Pinus pinea	0	low	7,51	0,65	0,58	1,53	1,8	3,25	*47*	6	89	44	4,3	-	-	28,5
	0	high	*11,3*	*1,65*	*1,2*	*4,4*	*3*	*6,7*	*57*	-	-	-	-	-	-	-
Pinus sylvestris	0	low	11,4	0,75	1,11	1,61	0,64	3,77	*47*	32	172,05	18,25	2,28	-	50	9,17
	0	high	20,41	1,56	2,06	4,61	1,31	7,27	*57*	77,55	912	138,95	7,7	3,94	446,6	30,49
	1	low	10,94	0,77	1	2,57	0,5	3,51	*47*	31,5	222,05	28	1,96	0,14	60	7,38
	1	high	19,38	1,61	1,88	6,71	1,18	6,52	*57*	96	1331,95	170,5	6,88	5,59	507,2	33,9
Pseudotsuga menziesii	0	low	13,54	1	1	1,98	1,02	5,17	*47*	15	159,3	42,95	2,72	-	141	30,9
	0	high	22,71	1,8	1,7	5,91	2,1	8,96	*57*	45,3	1660,5	129,35	5,95	-	-	-
	1	low	13,55	0,99	0,71	3,09	1,14	2,97	*47*	14	443,6	57,9	2,91	-	-	-
	1	high	29,23	2,18	1,45	9,64	2,73	7,3	*57*	-	155,25	279,2	-	-	-	-

*) Leaf type 0 = needle set 1; Leaf type 1 = needle set 2

(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 3.3.1a). Results falling outside these limits should be checked and, if necessary, be reanalyzed.
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 a 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.

3.3.2 Plausible range check for litterfall

To develop tolerable limits for litterfall is much more difficult than for foliage. Litterfall is sorted in different fractions – in minimum in two, foliar and non-foliar litter. Many countries sort it in three fractions – foliage, wood and fruit coins & seeds. Litterfall is analyzed then as a pooled sample or each fraction is analysed separately.
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 2. Plausible ranges for the non-foliar fraction in litterfall is a project for the future.

Table 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** mg/g	**S** mg/g	**N** mg/g	**P** mg/g	**K** mg/g	**Ca** mg/g	**Mg** mg/g	**Zn** µg/g	**Mn** µg/g	**Fe** µg/g	**Cu** µg/g	**B** 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	low		1.1	8.00	1.10	4.50	14.00	1.20					
(Q. conferta)	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	low	460	0.85	10.00	0.82	4.00	5.00	1.00	15.00	1000	90.0	6	7
(Q. pedunculata)	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	low		1	6.50	0.60	1.00	2.50	0.70					
(P. excelsa)	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

3.4 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.

$$S = \sqrt{\frac{\sum (x_i - \bar{x})^2}{n-1}} \bullet \frac{1}{\sqrt{n}}$$

s = Standard deviation
$\bar{x}$ = Mean value
x = Measured value
n = Replicates

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 (for example during bottling on a sampler) in the

course of a series on the other. If a mistake was found all samples of this batch must be repeated twice.

3.5 Avoidance of contamination

The contamination of samples can occur in the field during sampling, during the transportation of the samples to the laboratory, and during the pre-treatment and analysis of the samples in the laboratory.

3.5.1 Water analyses

Deposition samples can become contaminated already during the sampling period, e.g. as a result of bird droppings, and the laboratory should be informed about signs of any such contamination. 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 one stage that can result in contamination of the samples. 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 by using disposable gloves (non talc), and the use of clean equipment (e.g. glass- and plasticware).
Special care must be taken when filtering the samples, and at least separate plastic tubing (if used) or other 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, and not only with purified water, is recommended. If this is not possible, then an adequate amount of the next sample should be discarded after filtering before taking the sample for the analyses. Contamination 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) and continue with the other types of sample. Attention should also be paid to the different characteristics of the individual sample plots and their specific concentrations.
The material of the filters should be suitable for 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 “abnormal” sample.

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 manual, mineral soil samples should not be milled, but sieved over a 2 mm sieve. These sieves should be clean, with no traces of 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 methods (air extraction equipment) should be used to avoid contamination of other samples or equipment via the air.
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 deionized water and drying before reuse 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.

3.5.3 Foliar and litterfall analyses

There are many possible contamination sources in foliage and litterfall analyses. A short overview is given in Table 3.5.3a.

Table 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
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

4. Interlaboratory 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 experiences and 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.

4.1 Ring tests and ring test limits

4.1.1 Ring tests

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. This is because of the training effect in the use of a method, and because the remaining ring test sample material can be used as reference material in the laboratory up until the next ring tests. If the data (e.g. analytical results) 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). 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 3 to 10 samples or solutions to the participating laboratories, where they are analysed using previously agreed on methods. The results are then returned to the organizers of the ring test.

The ring test samples must be checked for homogeneity and, in the case of water samples, have been stabilized by means of filtration through a 0.45 µm membrane filter, addition of acid or similar procedure. 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 during which the analysis must be carried out. 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 have to develop standard forms or internet-based files so that all the analysis data can be recorded in a standard fashion and used in standardized evaluation programmes for ring tests. It is particularly important to define the units to be used and the required number of decimal places for reporting**.**

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 developed. 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.

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

4.1.2.1 Tolerable limits for water ring tests

Discussions on the results of the two deposition/soil water ring tests highlighted the need for quantification of the acceptable limits of errors among analyses performed in different laboratories. These Data Quality Objectives (DQO) are essential in ensuring the comparability of the results, and to avoid "border effects" in the evaluation of results from different countries. The DQOs need to be higher than the precision in the individual laboratories (when working in accordance with QA/QC criteria) because they include part of the systematic errors that are not included in the precision of the individual laboratories. As is the case for the acceptance values for the validation check of single analyses (Chapter 3.1.6), selection of the DQO 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 soon forgotten. 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 DQOs for „low" or „high" concentrations. However, the results of the next inter-laboratory exercises will show whether this is necessary.
Examples of similar DQOs used in other networks, such as the Global Atmospheric Watch (Allan, 2004) and the EMEP (Uggered et al., 2005) are given in Table 4.1.2.1.
The proposed DQO values for deposition/soil water inter-comparison are listed in Table 4.1.2.2, and are compared with the average of all the samples of the 95% confidence limit of the results obtained in the second ring test exercise (Marchetto et al., 2006), after the exclusion of outliers. These DQOs are intended for general use with samples of average or high concentration.
A second set of DQOs, shown in Table 4.1.2.3, is provided for use with dilute samples, when one or more concentrations are very low, close to the detection limits of the analytical methods, and the expected errors became higher.
It is evident that a significant proportion of the results are still higher than the DQO values, indicating the need for improvements in the performance of the laboratory. On the other hand, many laboratories had values lower than the DQO, clearly indicating that it is possible to remain within these thresholds. The table also highlights a number of analyses that still require a considerable amount of work, such as alkalinity (low values in deposition samples), total

nitrogen and DOC. The analytical problems associated with these determinations were discussion in connection with the two ring tests (Mosello et al., 2002, Marchetto et al., 2006).

Tab. 4.1.2.1: Data Quality Objectives for precipitation and soil water concentrations adopted in other atmospheric deposition networks.

Parameter	Unit	GAW Laboratory Inter-Network Bias	EMEP radii for Youden plot
pH		± 0.07 u. pH	± 0.1 u. pH
Conductivity	µS cm^{-1}	± 7 %	± 10 %
Calcium	mg L^{-1}	± 15 %	± 15 %
Magnesium	mg L^{-1}	± 10 %	± 15 %
Sodium	mg L^{-1}	± 10 %	± 15 %
Potassium	mg L^{-1}	± 20 %	± 15 %
Ammonium	mg N L^{-1}	± 7 %	± 15 %
Sulphate	mg S L^{-1}	± 7 %	± 10 %
Nitrate	mg N L^{-1}	± 7 %	± 15 %
Chloride	mg L^{-1}	± 10 %	± 15 %
Alkalinity	µeq L^{-1}	± 25 %	± 25 %
Total dissolved nitrogen	mg L^{-1}	-	± 20 %
Dissolved organic carbon	mg L^{-1}	-	± 20 %
Other (metals)		-	± 20 %

Tab. 4.1.2.2: Data Quality Objectives proposed for the ICP Forests programme compared with the results of the second ICP Forests/Forest Focus ring test (Marchetto et al., 2006). DQOs valid for relatively high concentrations.

Parameter	for values	DQO	2 s.d.	mean no. of outliers
pH	< 5.0 units	± 0.1 u. pH	0.17 u.	1.6
Conductivity	> 10 $\mu S\ cm^{-1}$	± 10 %	13%	0.7
Calcium	> 0.25 mg L^{-1}	± 15 %	18%	1.7
Magnesium	> 0.25 mg L^{-1}	± 15 %	14%	1.5
Sodium	> 0.5 mg L^{-1}	± 15 %	12%	3.4
Potassium	> 0.5 mg L^{-1}	± 15 %	11%	2.3
Ammonium	> 0.25 mg N L^{-1}	± 15 %	16%	4.3
Sulphate	> 1 mg S L^{-1}	± 10 %	7%	3.8
Nitrate	> 0.5 mg N L^{-1}	± 15 %	10%	1.8
Chloride	> 1.5 mg L^{-1}	± 15 %	11%	5.3
Alkalinity	> 100 $\mu eq\ L^{-1}$	± 25 %	66%	0.0
Total dissolved nitrogen	> 0.5 mg L^{-1}	± 20 %	15%	3.3
Dissolved organic carbon	> 1 mg L^{-1}	± 20 %	20%	1.8
Other (metals)		± 20 %		

Tab. 4.1.2.3: Data Quality Objectives proposed for the ICP Forests programme compared with the results of the second ICP Forests/Forest Focus ring test (Marchetto et al., 2006). DQOs valid for low concentrations.

Parameter	for values	DQO	2 s.d.	mean no. of outliers
pH	**> 5.0 units**	**± 0.2 u. pH**	**0.27 u.**	**1.6**
Conductivity	**< 10 μS cm^{-1}**	**± 20 %**	**-**	**-**
Calcium	**< 0.25 mg L^{-1}**	**± 20 %**	**31%**	**2.5**
Magnesium	**< 0.25 mg L^{-1}**	**± 25 %**	**20%**	**3.5**
Sodium	**< 0.5 mg L^{-1}**	**± 25 %**	**-**	**-**
Potassium	**< 0.5 mg L^{-1}**	**± 25 %**	**30%**	**3.0**
Ammonium	**< 0.25 mg N L^{-1}**	**± 25 %**	**42%**	**4.0**
Sulphate	**< 1 mg S L^{-1}**	**± 20 %**	**11%**	**3.3**
Nitrate	**< 0.5 mg N L^{-1}**	**± 25 %**	**38%**	**2.3**
Chloride	**< 1.5 mg L^{-1}**	**± 25 %**	**22%**	**3.5**
Alkalinity	**< 100 μeq L^{-1}**	**± 40 %**	**161%**	**1.3**
Total dissolved nitrogen	**< 0.5 mg L^{-1}**	**± 40 %**	**51%**	**2.5**
Dissolved organic carbon	**< 1 mg L^{-1}**	**± 30 %**	**98%**	**2.0**

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 (between laboratory variation) and Mandel's k (within-laboratory variation) statistics of the 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 inferred 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 4.1.2.2. In the lower range, the inter-laboratory variation relative to the mean may be as high as 100 %, or even more, whereas in the higher range this variation is much lower. Therefore, tolerable CV's are fixed for both a lower and a higher range for each soil variable. For the N concentration example, the CV_{repr} for the lower range (≤ 1.5 g N kg^{-1} DW) is set to the average of 30 % and for the higher range (> 1.5 g N kg^{-1} DW) to 10% (Fig. 4.1.2.2). For some variables (e.g. pH), no split in a lower and higher range is justified due to the linear relationship of the reproducibility curve.

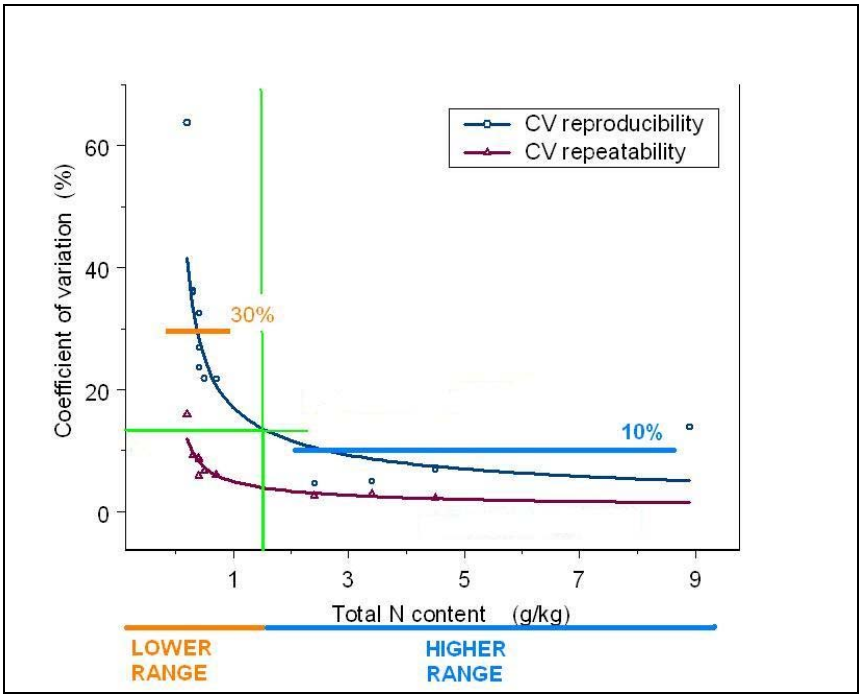

Figure 4.1.2.2: Power curves fitted to the results of total N analysis on the mineral soil samples of earlier FSCC ring tests, and estimation of the lower and higher ranges based on the turning point of the reproducibility curve. Average CV is 30 % and 10 % for the lower and higher range, respectively.

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 ±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.
Tolerable limits can also be inferred for intra-laboratory variation (repeatability). These limits can be used to evaluate within-laboratory repeatability on replicated analyses within the same run.

Table 4.1.2.2a: Tolerable limits for soil moisture content, pH, organic carbon (OC), total nitrogen (TN) and carbonate for inter-laboratory comparison and intra-laboratory performance.

Parameter	Observation Range	Level	Ring Test Tolerable limit (% of mean)	Intra-Laboratory Tolerable limit (% of mean)
Moisture content (%)	lower	≤ 1.0	**± 25**	**± 6**
	higher	> 1.0	**± 15**	**± 4**
pH_{H2O} -	whole	2.0 – 8.0	**± 5**	**± 1**
pH_{CaCl2} -	whole	2.0 – 8.0	**± 5**	**± 1**
OC g kg^{-1}	lower	≤ 25	**± 20**	**± 5**
	higher	> 25	**± 15**	**± 3**
TN g kg^{-1}	lower	≤ 1.5	**± 30**	**± 9**
	higher	> 1.5	**± 10**	**± 3**
Carbonate g kg^{-1}	lower	≤ 50	**± 130**	**± 5**
	higher	> 50	**± 40**	**± 3**

Table 4.1.2.2b. Tolerable limits for soil texture for inter-laboratory comparison and intra-laboratory performance.

Parameter	Observation Range	Level	Ring Test Tolerable limit (% of mean)	Intra-Laboratory Tolerable limit (% of mean)
Clay content %	lower	≤ 10.0	**± 50**	**± 8**
	higher	> 10.0	**± 35**	**± 4**
Silt content %	lower	≤ 20.0	**± 45**	**± 8**
	higher	> 20.0	**± 30**	**± 3**
Sand content %	lower	≤ 30.0	**± 45**	**± 6**
	higher	> 30.0	**± 25**	**± 2**

Table 4.1.2.2c: Tolerable limits for total elements for inter-laboratory comparison and intra-laboratory performance.

Parameter	Observation Range	Level	Ring Test Tolerable limit (% of mean)	Intra-Laboratory Tolerable limit (% of mean)
TotAl mg kg^{-1}	Lower range	≤ 20000	**± 35**	**± 4**
	Higher range	> 20000	**± 5**	**± 1**
TotCa mg kg^{-1}	Lower range	≤ 1500	**± 20**	**± 7**
	Higher range	> 1500	**± 15**	**± 2**
TotFe mg kg^{-1}	Lower range	≤ 7000	**± 20**	**± 5**
	Higher range	> 7000	**± 5**	**± 2**
TotK mg kg^{-1}	Lower range	≤ 7500	**± 15**	**± 3**
	Higher range	> 7500	**± 5**	**± 2**
TotMg mg kg^{-1}	Lower range	≤ 1000	**± 60**	**± 7**
	Higher range	> 1000	**± 5**	**± 2**
TotMn mg kg^{-1}	Lower range	≤ 200	**± 25**	**± 6**
	Higher range	> 200	**± 5**	**± 3**
TotNa mg kg^{-1}	Lower range	≤ 1500	**± 20**	**± 4**
	Higher range	> 1500	**± 5**	**± 2**

Table 4.1.2.2d. Tolerable limits for aqua regia extractable elements for inter-laboratory comparison and intra-laboratory performance.

Parameter	Observation Range	Level	Ring Test Tolerable limit (% of mean)	Intra-Laboratory Tolerable limit (% of mean)
ExtrP mg kg^{-1}	lower	≤ 150	**± 45**	**± 3**
	higher	> 150	**± 20**	**± 3**
ExtrK mg kg^{-1}	lower	≤ 500	**± 60**	**± 6**
	higher	> 500	**± 40**	**± 4**
ExctCa mg kg^{-1}	lower	≤ 500	**± 70**	**± 7**
	higher	> 500	**± 30**	**± 3**
ExctMg mg kg^{-1}	lower	≤ 500	**± 60**	**± 7**
	higher	> 500	**± 15**	**± 3**
ExctrS mg kg^{-1}	whole	35 - 1300	**± 35**	**± 4**
ExtrNa mg kg^{-1}	lower	≤ 75.0	**± 65**	**± 8**
	higher	> 75.0	**± 50**	**± 6**
ExtrAl mg kg^{-1}	lower	≤ 2500	**± 50**	**± 5**
	higher	> 2500	**± 20**	**± 3**
ExtrFe mg kg^{-1}	lower	≤ 2500	**± 40**	**± 4**
	higher	> 2500	**± 15**	**± 3**
ExtrMn mg kg^{-1}	lower	≤ 150	**± 30**	**± 4**
	higher	> 150	**± 15**	**± 4**
ExtrCu mg kg^{-1}	lower	≤ 5	**± 40**	**± 8**
	higher	> 5	**± 15**	**± 4**
ExtrPb mg kg^{-1}	whole	3 - 70	**± 30**	**± 4**
ExtrNi mg kg^{-1}	lower	≤ 10	**± 40**	**± 6**
	higher	> 10	**± 15**	**± 4**
ExtrCr mg kg^{-1}	lower	≤ 10	**± 40**	**± 7**
	higher	> 10	**± 25**	**± 4**
ExtrZn mg kg^{-1}	lower	≤ 20	**± 40**	**± 7**
	higher	> 20	**± 20**	**± 3**
ExtrCd mg kg^{-1}	lower	≤ 0.25	**± 100**	**± 5**
	higher	> 0.25	**± 55**	**± 6**
ExctrHg mg kg^{-1}	whole	0 - 0.16	**± 75**	**± 6**

Table 4.1.2.2e. Tolerable limits for reactive iron and aluminium for inter-laboratory comparison and intra-laboratory performance.

Parameter	Observation Range	Level	Ring Test Tolerable limit (% of mean)	Intra-Laboratory Tolerable limit (% of mean)
Reactive Al mg kg^{-1}	lower	≤ 750	**± 30**	**± 3**
	higher	> 750	**± 15**	**± 3**
Reactive Fe mg kg^{-1}	lower	≤ 1000	**± 30**	**± 4**
	higher	> 1000	**± 15**	**± 3**

Table 4.1.2.2f. Tolerable limits for exchangeable elements and free acidity for inter-laboratory comparison and intra-laboratory performance.

Parameter	Observation Range	Level	Ring Test Tolerable limit (% of mean)	Intra-Laboratory Tolerable limit (% of mean)
Exch Acidity $cmol_{(+)}\ kg^{-1}$	lower	≤ 1.00	**± 90**	**± 9**
	higher	> 1.00	**± 35**	**± 4**
ExchK $cmol_{(+)}\ kg^{-1}$	lower	≤ 0.10	**± 45**	**± 10**
	higher	> 0.10	**± 30**	**± 4**
ExchCa $cmol_{(+)}\ kg^{-1}$	lower	≤ 1.50	**± 65**	**± 12**
	higher	> 1.50	**± 20**	**± 3**
ExchMg $cmol_{(+)}\ kg^{-1}$	lower	≤ 0.25	**± 50**	**± 10**
	higher	> 0.25	**± 20**	**± 2**
ExchNa $cmol_{(+)}\ kg^{-1}$	whole	0.01-0.14	**± 80**	**± 14**
ExchAl $cmol_{(+)}\ kg^{-1}$	lower	≤ 0.50	**± 105**	**± 12**
	higher	> 0.50	**± 30**	**± 4**
ExchFe $cmol_{(+)}\ kg^{-1}$	lower	≤ 0.02	**± 140**	**± 14**
	higher	> 0.02	**± 50**	**± 8**
ExchMn $cmol_{(+)}\ kg^{-1}$	lower	≤ 0.03	**± 45**	**± 7**
	higher	> 0.03	**± 25**	**± 6**
Free H+ $cmol_{(+)}\ kg^{-1}$	whole	0.02-1.20	**± 100**	**± 8**

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. Marked type 1 outliers between the outlier-free maximum and minimum mean value are no longer outliers, and they can be used in further evaluation of the interlaboratory 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. These tolerable limits for foliage samples were adopted by the Forest Foliar Expert Panel at the Meetings in Ås (1994), Vienna (1997), Bonn (1999), Prague (2003) and Madrid (2007).

Table 4.1.2.3a: Tolerable limits for normal concentrations of mandatory and optional elements for (Stefan et al., 2000)

Element	Tolerable deviation from mean in %	Expert Panel-Foliar Meetings where the fixed limits were adopted
N	90-110	6th Meeting - Bonn 1999
S	85-115	10th Meeting – Madrid 2007
P	90-110	10th Meeting – Madrid 2007
Ca	90-110	10th Meeting – Madrid 2007
Mg	90-110	10th Meeting – Madrid 2007
K	90-110	10th Meeting – Madrid 2007
Zn	85-115	8th Meeting - Prague 2003
Mn	85-115	8th Meeting - Prague 2003
Fe	80-120	6th Meeting - Bonn 1999
Cu	80-120	8th Meeting - Prague 2003
Pb	70-130	6th Meeting - Bonn 1999
Cd	70-130	6th Meeting - Bonn 1999
B	80-120	6th Meeting - Bonn 1999
C	95-105	6th Meeting - Bonn 1999

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 normal and low concentrations of all the elements. A proposal for tolerable limits for some elements for low concentrations is given in Table 4.1.2.3a.

Table 4.1.2.3a: Proposed tolerable limits for low concentrations of mandatory and optional elements.

Element	Tolerable deviation from mean in %	For concentrations below
S	80-120	0.5mg/g
P	85-115	0.5mg/g
Mg	85-115	0.5mg/g
Zn	80-120	20µg/g
Mn	80-120	20µg/g
Fe	70-130	20µg/g
Pb	60-140	0.5µg/g

Laboratory results falling inside of these limits can be accepted. Laboratories with values outside these limits need to improve their data quality.

4.2 Exchange of knowledge and experiences with other laboratories

The inter-laboratory comparisons conducted within the framework of the ICP Forests programme 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 ring tests in order to obtain information useful in achieving, maintaining and optimizing their analytical quality.

Laboratories with unacceptable results in ring tests are invited to participate in **assistance program** organized 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 of assistance it is necessary to take into account, in addition to the results of the ring test, the current state of the implementation of a quality programme, and the analytical methods used in the laboratory and described beforehand in a questionnaire filled in by the laboratory in question. The assistance consist of a few days' visit to the laboratory, as well as a return visit, in order to identify easily detectable problems in laboratory organization and/or specific analytical processes.
It is essential that the members of the staff actually involved in the analytical work in participate in the assistance programme.
A list of problems to be solved is drawn up, with the emphasis on problems linked to specific parameters analysed/determined in the ICP Forests programme. The main result of the two visits is a short report on the laboratory's activities, including problems to be solved and suggestions about how this can be achieved. The laboratory is thus provided with knowledge that enables them to make improvements in the quality of their results.

4.2.1 Exchange of know how

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 within and between the WG on QA/QC in Laboratories and te all hlaboratories is ensured through the WG's own **website**. Information about past and ongoing ring tests, Excel files for QA/QC, scientific publications that can be downloaded, analytical info-sheets, contact addresses and useful links are to be found at http://www.icp-forests.org/WGqual_lab.htm .

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 methods used and analytical problems can be quickly and easily identified, and steps taken to rectify the situation.

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6. Annexes

6.1 Definitions and terminology

(this chapter will be part of version 2 of this paper)

6.2 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 3.1). It can be downloaded from the ICP Forests website (www.icp-forests.org/WGqual_lab.htm): click on "excel file for analytical data validation". 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 3.1.1.1) and the **calculated conductivity**, with and without correction for the ion strength (Chapter 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 3.1.1.2. Selection of one the three alternative regression equationss is based on the codes depicting the type of sample and the type of forest cover, as given in Table 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 3.1.3 and 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 (Figures 3.1.1.1a, b).
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).

6.3 Excel worksheet for control charts

The Excel worksheet described in Chapter 6.2 cab be used for creating control charts (paragraph 2.1). It 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.

6.4 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 - Forest 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
1547	plant	peach Leaves		see above
1570a	plant	spinach leaves		see above
1573a	plant	tomato leaves		see above
Sample 2 from the 8th 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 6th needle/leaf inter-laboratory test (ICP Forests)	plant	maple leaves		see above