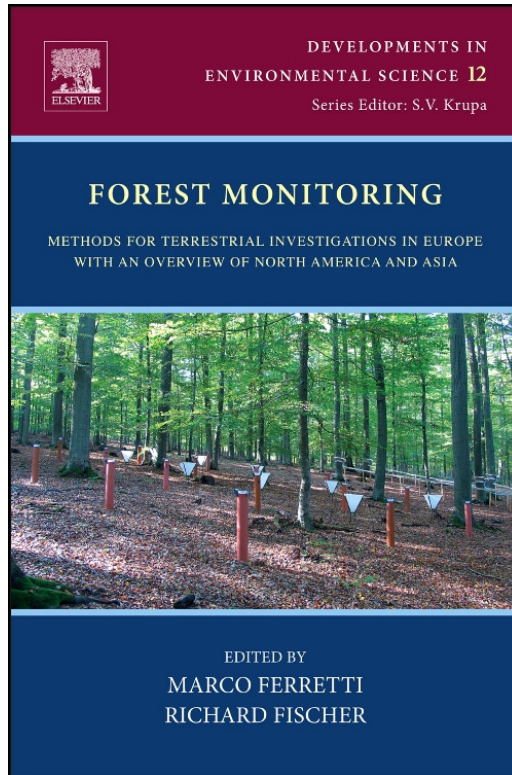


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Data Quality in Laboratories: Methods and Results for Soil, Foliar, and Water Chemical Analyses

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22.1 INTRODUCTION

Chemical analyses are an essential part of forest ecosystem monitoring activities that entail the determination of nutrient and pollutant fluxes in forest ecosystems (De Vries et al., 2003; Fischer et al., 2007; Fürst et al., 2003; Schaub, 2009). The value of chemical data depends to a great extent on the quality of the analytical work provided by the laboratories involved in the monitoring (Durrant Houston and Hiederer, 2009; Ferretti et al., 2009). To maximize the spatial and temporal comparability of monitoring data over time, every effort must be taken to ensure accuracy of the analytical measurements. This has been done in forest monitoring in Europe within the International Co-operative Programme on Assessment and Monitoring of Air Pollution Effects on Forests (ICP Forests). In this context, different expert panels and groups have developed a comprehensive Quality Assurance (QA) and Quality Control (QC) program for the participating laboratories over the past two decades (König et al., 2010a). As part of this drive to improve the inter- and intra-comparability of analytical data, the laboratories have participated in a number of interlaboratory calibration exercises (otherwise known as ring tests) and held extensive discussions on harmonizing and improving the use of analytical methodology and QA/QC procedures (Cools and De Vos, 2008, 2010a, b; Cools et al., 2004; Fürst, 2011; Marchetto et al., 2011).

This chapter presents an overview of the QA/QC criteria that have been devised for the relevant fields of analytical chemistry in international forest monitoring in Europe, including the analysis of atmospheric deposition, soil solution, soil, foliage, and litterfall samples. Additional information on the quality checks and reference standards used, ring tests, and QC results is also provided.

22.2 COMPONENTS OF A LABORATORY QA PROGRAM

The QA program in each laboratory should be based on three pillars:

1. the use of harmonized, well-defined and documented analytical methods;
2. an internal QC program;
3. an external QC program coordinated by the monitoring program organizers.

To obtain comparable results for a range of sample matrices originating from forests across Europe, all laboratories must use similar analytical methods. Therefore, one of the first steps in the development of a QC standard is the selection of harmonized reference methods, the avoidance of unsuitable analytical procedures, and the publishing of the reference methods in a manual (ICP Forests, 2010).

Another important part of an internal QC program is the use of different reference materials (RMs) to ensure accuracy of analytical results. The variation and the quality of the analytical results of these RMs have to be controlled with the use of control charts.

Finally, a key part is the validation of the analytical data to confirm its correctness and exclude the risk of errors. A wide range of data consistency checks can be used depending on the type of matrix analyzed and based on the relationship between the chemical components and/or chemical and physical properties of the samples.

Ring tests are an integral part of any external QC program. Such interlaboratory calibration exercises carried out on a periodic basis enable the assessment of a laboratory's performance in relation to the other participating laboratories. In addition, information on the comparability of the data produced by the different laboratories can be obtained. The performance of the implemented analytical QA/QC program can be evaluated through the use of quality indicators.

22.3 REFERENCE METHODS

To ensure comparability of analytical results for a range of sample matrices originating from forests across Europe, all laboratories participating in the monitoring program are required to use similar, well-tested analytical methods. Therefore, one of the first steps in the development of a QC standard has to be the evaluation and selection of harmonized reference methods.

Within the ICP Forests, a list of analytical extraction and digestion methods was selected after a detailed assessment of ring tests results for a range of variables in different matrices and their use recommended (Clarke et al., 2010; Cools and de Vos, 2010a, b; Nieminen, 2011; Rautio et al., 2010). These procedures were either EN (from the CEN, the European Committee for Standardization) or ISO (the International Organization for Standardization) testing protocols or modified versions of these methods that were routinely employed by the participating laboratories. Only a few non-EN/ISO methods were selected: they were, however, regularly tested in several ring tests and considered the most appropriate for the analysis of the variable under review.

For the determination of variables in acidic, salt extract, or water solutions, a list of EN and ISO methods were also suggested (see Clarke et al., 2010; Cools and de Vos, 2010a, b; Nieminen, 2011; Rautio et al., 2010). Each laboratory was free to select from an approved list of quantification procedures that was compatible with the laboratory's expertise and instrumentation availability. Arising from the results of early ring tests, some of the analytical

methods were identified as producing unreliable results and, as a consequence, excluded from the list of approved procedures. As some analytical procedures are only usable at higher concentration ranges, limits of quantification (LOQ) were introduced for each variable, which limited the laboratories use of such methods.

22.4 CONTROL CHARTS

Control charts are important and useful tools for the internal QC in the laboratory. They monitor the within-laboratory reproducibility (degree of agreement between measurements conducted on replicate specimens by different people within the same laboratory) and repeatability (variation in measurements taken by instrument on the same item and under the same conditions) of a variable over a long-term time-scale. The laboratory runs control samples together with true samples in an analytical batch. Immediately after the run is completed, the control values are plotted on a control chart and checked. There are various types of control chart available (for details, see [International Organization for Standardization, 1993](#)). The most commonly used control charts are the mean chart for laboratory control standards and the blank chart for background or reagent blank results to monitor contamination during different steps of the sample handling. Control charts can also be used for method validation and comparison, estimation of measurement uncertainty, detection limits, 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 [Internal Quality Control—Handbook for Chemical Laboratories, Nordtest report TR 569 \(2007\)](#).

22.5 REFERENCE MATERIALS

To ensure analytical data remains within an acceptable precision and accuracy, the use of control charts for each variable and matrix are essential. In order to produce these control charts, reference material (RM) is necessary. A distinction is made between common RM and certified reference material (CRM). An RM is a material or substance, sufficiently homogeneous and stable with respect to one or more specified properties, which has been established to be fit for its intended use in a measurement process ([International Organization for Standardization, 2008](#)). A prime example of such material would be the surplus sample material left over after the completion of a ring test or a local reference material (LRM).

A CRM is an RM that is characterized by a metrologically valid procedure for one or more specified properties, accompanied by a certificate that provides the value of the specified property, its associated uncertainty, and a statement of metrological traceability ([International Organization for Standardization, 2008](#)). There are two types of CRM available: calibrants

and matrix CRMs. Calibrants are pure standards used for calibrating instruments. These are usually produced by commercial producers. Matrix CRMs contain analytes in a sample (e.g., trace elements in plant material). Due to the difficulty in its production and value assignment, these are usually produced by national or transnational institutes like the American National Institute of Standards and Technology, the German Bundesanstalt für Materialforschung und—prüfung, and the European Institute for Reference Materials and Measurements. RMs are available in a range of types and prices. CRMs are expensive and should be used only when really needed, for example, for calibration, method validation, measurement verification, evaluating measurement uncertainty ([Handbook for Calculation of Measurement Uncertainty in Environmental Laboratories, Nordtest Report 537, 2003](#)), and for training purposes. In many cases, however, the concentrations are not within the ranges encountered in daily practice.

LRMs are, in many cases, easier to acquire and are often not as expensive as CRMs. They are usually issued by national laboratories and are extremely useful for ensuring laboratory quality within a country. 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 variables. These LRMs are extremely important for QA/QC activities because laboratories must use matrix-matched control samples of known stability to demonstrate internal consistency of analysis over time, through the use of control charts.

22.5.1 RM for Water (Deposition and Soil Solution) Analysis

One common approach is to use “natural” samples as LRMs that are preserved with stabilizing agents (such as low concentrations of chloroform). It is necessary to ensure that their use does not cause interferences in the analytical methods for the variables of interest or have an adverse effect on other analyses 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 control standards within the analytical range of the method, that is, low–medium and medium–high concentrations. The stability of LRMs should be tested noting that the stability for individual ion species may vary over time. Before a LRM can be used, the method has to be initially validated with a CRM. The LRM should be used, together with the CRM or a ring test sample, to determine the conventional true value. Another approach to the production of a water LRM is to dissolve inorganic salts in demineralized water in the concentration range comparable to deposition samples (otherwise known as “synthetic rain” LRM). Dissolved organic carbon (DOC) in a stable form can be included in the LRM as suggested by [Allan \(2004\)](#). Alternatively, bottled water with low ionic content can be used as a “synthetic rain” LRM, to which appropriate additional analytes can be added, such as ammonium and DOC.

22.5.2 RM for Foliar Analysis

The matrix properties and the analyte concentrations of the RM should be in the range of those of the samples collected by the monitoring program. As there is only a limited number of certified forest-tree foliage RM available worldwide, agricultural plant material with similar matrix and analyte concentrations, for example, flour, hay, cabbage, olive leaves, apple leaves, can be used as an acceptable substitute. Samples used for ring tests can also be used as RM in method validation. For example, the Forest Foliar Co-ordination Centre of the ICP Forests in Austria offers this material (see www.ffcc.at, accessed on September 2012). One good cheap method for producing a high quality LRM is to prepare a large amount of foliage material for use as a ring test sample (more information on the Website <http://bfw.ac.at/rz/bfwcms.web?dok=9193>, accessed on September 2012). After the ring test, the element concentrations of the sample are well known. The advantage for the laboratory is to have a large amount of RM with (i) a similar concentration ranges as encountered with routine samples and (ii) a mean concentration of known accuracy.

22.5.3 RM for Soil Analysis

For soil analysis, especially for extraction methods, a large amount of sample is needed. Therefore, expensive CRM cannot be used in routine analyses. To produce high quality LRM, several large (10–50 kg) samples from one site (organic and mineral, preferably by horizon) should be taken. All the sampled material has to be dried and homogenized several times to ensure a uniform sample. After splitting or riffing each sample into several parts, it has to be stored in a cool, dry place. Once the LRM is prepared, a test run should be performed with correctly calibrated equipment. The material should be analyzed in replicate (e.g., 10–15) together with at least one (but preferably more) national or international reference samples (e.g., the FSCC, Forest Soil Co-ordinating Centre of the ICP Forests, soil RM of ICP Forests) for all relevant variables. The absolute accuracy and standard deviation of each variable in the LRM can then be quantified. The results can be used as the basis for producing control charts. The mean concentration of each variable in the LRM is of less importance, but it should be within the same range as that determined in the subsequently analyzed samples.

The production of soil reference samples is an essential prerequisite of international soil monitoring programs, and the FSCC in Belgium has produced a large amount of soil RM for the use during the last European soil survey 2006–2009 (Cools and De Vos, 2008) and more recently during the ICP Forests monitoring activity (König et al., 2010b).

Figure 22.1 compares the organic carbon concentrations measured on FSCC soil RM by 19 laboratories during the second European forest soil survey over a period of 18 months. In this survey, one central laboratory (CL)

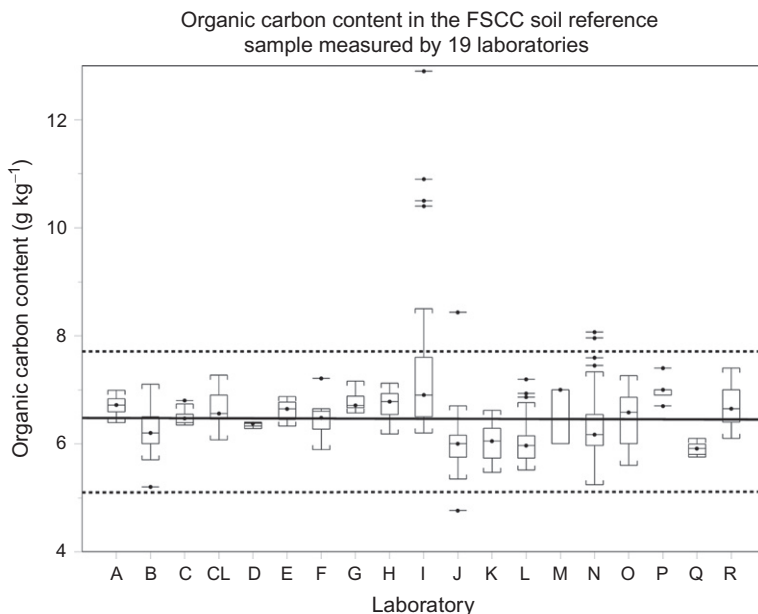


FIGURE 22.1 The organic carbon content in the FSCC soil reference sample measured by 19 laboratories (A–R, CL=central lab) participating in the BioSoil project. The continuous line indicates the reference concentration of 6.4 g kg^{-1} ; the dashed line indicates a range of 20% around this reference concentration. The boxplots show the median values for each laboratory together with their interquartile range (so the range between 25% and 75% of the reported values). Whiskers are drawn to the nearest value not beyond 1.5 times the interquartile range from the quartiles. Values outside this range are considered as outliers.

analyzed a subset of 10% of all the samples collected in the survey. By accepting a deviance of 20% from the general accepted mean value (6.4 g kg^{-1}), the median values of all the laboratories remain within this range. On the other hand, laboratories I, J, and N showed a number of outliers, necessitating the stopping of the analysis, investigation, and correction of the identified source of variability, before continuing with the analyses. The CL, laboratories C, E, F, O, and R measured OC contents centered around the reference value. Although laboratory Q showed low within-laboratory variability, it systematically measured values below the reference value. Laboratory I showed poor within-laboratory and between-laboratory reproducibility as its median value is 0.5 g kg^{-1} above the general mean. In addition, Figure 22.1 shows that laboratories B, J, K, L, and N measured systematically below the reference value by $0.4\text{--}0.6 \text{ g kg}^{-1}$. These over- and underestimations should be taken into account when interpreting and comparing the survey results at the European level.

The results of the other elements analyzed on the FSCC soil RM are reported in Table 22.1. The variance consists of two components: the

TABLE 22.1 Results of the FSCC Soil Reference Material Analyzed by 19 Laboratories over an 18-Month Analysis Period

Variable	Unit	Mean	Stdev. within	Gen. stdev.	Between-laboratory variance (%)	Within laboratory variance (%)	CV (%)
Particle size: clay	%	41.2	1.416	3.228	80.76	19.24	7.8
Particle size: silt	%	48.6	1.677	3.332	74.68	25.32	6.9
Particle size: sand	%	9.5	0.747	1.802	82.84	17.16	19.0
pH (CaCl ₂)		3.84	0.040	0.083	76.36	23.64	1.1
pH (H ₂ O)		4.24	0.045	0.081	69.23	30.77	1.9
Organic carbon	g kg ⁻¹	6.4	0.373	0.554	54.68	45.32	8.7
Total N	g kg ⁻¹	0.4	0.042	0.099	82.24	17.76	22.6
Exchangeable acidity	cmol + kg ⁻¹	3.21	0.225	0.464	76.53	23.47	14.5
Exchangeable Al	cmol + kg ⁻¹	2.85	0.121	0.369	89.17	10.83	13.0
Exchangeable Ca	cmol + kg ⁻¹	0.10	0.021	0.035	64.88	35.12	34.2
Exchangeable Fe	cmol + kg ⁻¹	0.10	0.012	0.020	64.42	35.58	18.9
Exchangeable K	cmol + kg ⁻¹	0.06	0.007	0.025	92.43	7.565	42.7
Exchangeable Mg	cmol + kg ⁻¹	0.04	0.007	0.020	88.48	11.52	50.7
Exchangeable Mn	cmol + kg ⁻¹	0.03	0.003	0.003	-4.53	104.53	10.2
Exchangeable Na	cmol + kg ⁻¹	0.03	0.006	0.015	83.82	16.18	54.1
Free H ⁺	cmol + kg ⁻¹	0.16	0.051	0.080	59.23	40.77	49.9

Extractable P	mg kg ⁻¹	105.4	5.81	20.30	91.8	8.2	19.3
Extractable K	mg kg ⁻¹	1640.5	129.8	302.2	81.6	18.4	18.4
Extractable Ca	mg kg ⁻¹	353.6	52.4	140.8	86.1	13.9	39.8
Extractable Mg	mg kg ⁻¹	1348.2	58.4	74.6	38.8	61.2	5.5
Extractable S	mg kg ⁻¹	76.1	4.28	8.91	76.9	23.1	11.7
Extractable Na	mg kg ⁻¹	39.0	8.17	24.78	89.1	10.9	63.5
Extractable Al	mg kg ⁻¹	9017.1	522.3	875.2	64.4	35.6	9.7
Extractable Fe	mg kg ⁻¹	11,609.8	366.7	889.0	83.0	17.0	7.7
Extractable Mn	mg kg ⁻¹	112.9	5.69	12.38	78.9	21.1	11.0
Extractable Cu	mg kg ⁻¹	3.9	0.42	1.79	94.5	5.5	45.5
Extractable Pb	mg kg ⁻¹	7.3	0.78	3.41	94.8	5.2	46.8
Extractable Ni	mg kg ⁻¹	4.0	0.44	2.33	96.4	3.6	58.5
Extractable Cr	mg kg ⁻¹	22.0	1.74	2.61	55.6	44.4	11.9
Extractable Zn	mg kg ⁻¹	20.2	1.29	1.86	52.3	47.7	9.2
Extractable Cd	mg kg ⁻¹	0.027	0.014	0.037	85.4	14.6	136.4
Extractable Hg	mg kg ⁻¹	0.029	0.003	0.005	54.6	45.4	16.7
Reactive Al	mg kg ⁻¹	1317.0	57.2	128.1	80.0	20.0	9.7
Reactive Fe	mg kg ⁻¹	2764.0	123.9	174.6	49.6	50.4	6.3

within-laboratory variance and the between-laboratory variance. For most elements, the between-laboratory variance is larger than the within-laboratory variance. Furthermore, for some elements in [Table 22.1](#), the coefficient of variation (CV%) is very high, especially at low concentration ranges.

22.6 VALIDATION OF ANALYTICAL DATA

For the validation of analytical data in the laboratory, there is a wide range of data consistency checks that can be used depending on the type of matrix analyzed and based on the relationship between the chemical components and/or chemical and physical properties of the samples.

22.6.1 Validation Procedures for Water Analysis

The analytes in deposition, soil water, and soil extract samples are mainly in ionic form. This enables the use of at least two checks on the consistency of each analysis: the calculation of the ion balance and the comparison of the measured conductivity with the conductivity calculated from the sum of all ion concentration ([Mosello et al., 2005](#); [Stumm and Morgan, 1996](#)). Another consistency test, which is only valid for atmospheric deposition samples, uses the ratio between the Na^+ and Cl^- concentrations, which should normally be relatively close to the value in seawater ([Mosello et al., 2005](#)). A further check is based on the relationship between the different forms of nitrogen analyzed. All these checks are described below. Examples of the application of these checks on datasets from different sites in Europe have been reported by [Mosello et al. \(2005, 2008\)](#).

22.6.1.1 Ion Balance

The ion balance is based on the equivalent concentration of anions (ΣAn) versus the concentration of cations (ΣCat). A general form, valid for open field deposition, throughfall, stemflow, and soil solution, also includes organic anions (Org^-) and metals (Met) such as Fe, Mn, or Al.

$$\Sigma\text{Cat} = [\text{Ca}^{2+}] + [\text{Mg}^{2+}] + [\text{Na}^+] + [\text{K}^+] + [\text{NH}_4^+] + [\text{H}^+] + \Sigma\text{Met} \quad (22.1)$$

$$\Sigma\text{An} = [\text{HCO}_3^-] + [\text{SO}_4^{2-}] + [\text{NO}_3^-] + [\text{Cl}^-] + [\text{PO}_4^{3-}] + [\text{Org}^-] \quad (22.2)$$

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

Ion balance calculation is straightforward in open field deposition samples, where DOC and metal concentration are usually negligible. In this case, formulas can be rewritten as

$$\Sigma\text{Cat} = [\text{Ca}^{2+}] + [\text{Mg}^{2+}] + [\text{Na}^+] + [\text{K}^+] + [\text{NH}_4^+] + [\text{H}^+] \quad (22.3)$$

$$\Sigma\text{An} = [\text{HCO}_3^-] + [\text{SO}_4^{2-}] + [\text{NO}_3^-] + [\text{Cl}^-] + [\text{PO}_4^{3-}] \quad (22.4)$$

On the other hand, in deposition samples with a DOC concentration greater than 5 mg L^{-1} and soil solution containing both DOC and metals,

the estimation of the their ionic fraction becomes important and the determination of the ion balance more complicated. To evaluate the effect of DOC on the ion balance of deposition and soil solution samples, Mosello et al. (2008) assessed about 6000 chemical analyses of open field, throughfall, and stemflow samples carried out in eight different laboratories, in order 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 (Cl^- concentration), and throughfall samples were collected under the canopies of different tree species. The regression coefficients were calculated using the following equation:

$$\Sigma\text{Cat} - \Sigma\text{An} = \beta_1\text{DOC} + \beta_0 \quad (22.5)$$

Regression coefficients were not significant for open field samples, probably because of the high error associated with the measurement of very low DOC concentrations. In contrast, the regression coefficients were highly significant ($p < 0.001$) for throughfall and stemflow samples. In the next step, the charge contribution of DOC was determined as:

$$[\text{Org}^-] = \beta_1\text{DOC} + \beta_0 \quad (22.6)$$

where $[\text{Org}^-]$ expressed in $\mu\text{equiv.L}^{-1}$ is the ionic contribution of DOC. Regression coefficients reported in Table 22.2 were validated using an independent set of data.

In soil solution samples, relatively high concentration of metals (mainly Al, Fe, Mn) are usually found. Their species (e.g., Al^{3+} , $\text{Al}(\text{OH})^{2+}$, $\text{Al}(\text{OH})_2^+$, Fe^{3+} , $\text{Fe}(\text{OH})^{2+}$, $\text{Fe}(\text{OH})_2^+$), their oxidation state, the presence of metal complexes with DOC (e.g., DOC-Fe, DOC-Al, DOC-Mn) are very variable. For example, iron complexed with organic matter can occur in both oxidized (Fe^{3+}) and reduced (Fe^{2+}) forms, and the reduced forms can exist under oxidizing conditions when complexed with organic matter (Clarke and Danielsson, 1995). In calculating the ion balance in such a matrix, account must be taken of the metals, their species, and their complexes with DOC:

$$\Sigma\text{Met} = \Sigma\text{Met}(\text{inorg}) + \Sigma\text{Met}(\text{from DOC complexes}) \quad (22.7)$$

TABLE 22.2 Statistics of the Regression for Determining DOC Contribution to the Ion Balance

Coefficients	Units	Broadleaves		Conifers <i>THR</i>	Soil solution <i>SS</i>
		<i>THR</i>	<i>STF</i>		
β_1	$\mu\text{equiv. (mg C)}^{-1}$	6.80	5.04	4.17	8.64
β_0	$\mu\text{equiv. L}^{-1}$	-12.32	-6.67	-5.01	0

THR, throughfall; *STF*, stemflow; *SS*, soil solution.

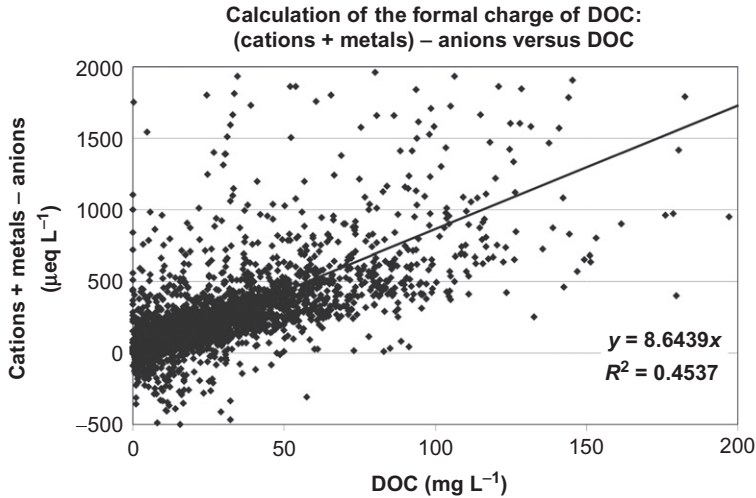


FIGURE 22.2 Calculation of the formal charge of DOC in 6140 soil solution samples from five countries (Germany, Finland, France, Norway, and the United Kingdom).

$$\begin{aligned} \Sigma \text{Met}(\text{inorg}) = & \text{Al}^{3+} + \text{Al}(\text{OH})^{2+} + \text{Al}(\text{OH})_2^+ + \text{Fe}^{3+} + \text{Fe}(\text{OH})^{2+} + \text{Fe}(\text{OH})_2^+ \\ & + \text{Mn}^{2+} + \text{Mn}(\text{OH})^+ (\text{and other inorganic species}) \end{aligned} \quad (22.8)$$

$$\Sigma \text{Met}(\text{from DOC complexes}) = \text{Al-DOC} + \text{Fe-DOC} + \text{Mn-DOC} \quad (22.9)$$

In a study conducted by the ICP Forests Working Group on QA/QC in Laboratories, 6140 soil solution samples—analyzed by laboratories from five 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 charge factor β_1 . The samples cover a wide range of geographical and climatic conditions. The results are shown in [Figure 22.2](#).

When the calculated β_1 was included in the ion balances of these soil solution samples, 64% of the samples had equal ion balances (within $\pm 10\%$). Without this DOC correction of the ion balance, only 30% of the samples had equal ion balances. Better results would probably be obtained by calculating a separate charge factor for specific countries or for similar plots. In fact, the chemical composition of DOC varies with depth along 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. A further approximation comes from the calculation of $[\text{HCO}_3^-]$ from total alkalinity (Gran's alkalinity) in relation to pH, assuming that total alkalinity is determined only by inorganic carbon species, protons, and hydroxide:

$$\text{TAlk} = -[\text{H}^+] + [\text{OH}^-] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \quad (22.10)$$

This definition is not completely correct in the case of high organic-carbon concentrations ($\text{DOC} > 5 \text{ mg L}^{-1}$), and in the presence of metals (e.g., Al, Fe, Mn) that may contribute to alkalinity.

Considering the increasing analytical error at lower concentration and the approximations introduced in calculating $[\text{Org}^-]$ and ΣMet , the limit of acceptable errors should vary according to the total ionic concentration and the type of solution. The percentage difference (PD) is defined as

$$\text{PD} = 100(\Sigma\text{Cat} - \Sigma\text{An})/[0.5(\Sigma\text{Cat} + \Sigma\text{An})] \quad (22.11)$$

The limits adopted within ICP Forests are given in Table 22.3, while the applicability of the ion balance test is summarized in Table 22.4. If the threshold values of these checks are exceeded, the analyses should be repeated.

TABLE 22.3 Acceptance Threshold Values in Data Validation Based on Ion Balance (PD) and Conductivity (CD)

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

TABLE 22.4 Applicability of the Validation Tests for Different Types of Solution

Test	Ion balance			Conductivity		Na/Cl ratio	N test
	No	DOC	DOC+Met	No	Met		
Correction	No	DOC	DOC+Met	No	Met		
Sample type							
Bulk open field	Y	Y	Y	Y	Y	Y	Y
Wet only	Y	Y	Y	Y	Y	Y	Y
Throughfall	N	Y	Y	Y	Y	Y	Y
Stemflow	N	Y	Y	Y	Y	Y	Y
Soil water	N	N	Y	N	Y	N	Y
Surface water	*	Y	Y	Y	Y	N	Y

* if $\text{DOC} < 5 \text{ mg L}^{-1}$.

If the result is confirmed but the threshold values are still exceeded, then the results can be accepted.

22.6.1.2 Conductivity

Conductivity is a measure of the ability of an aqueous solution to carry an electric current, and depends on the type and activity of the individual ions and on the temperature at which conductivity is measured. The activity of the ions in ideal conditions and at infinite dilution is equal to their concentrations, and the conductivity of the solution can be obtained by multiplying the equivalent ionic conductance λ_i of each ion by its concentrations (c_i):

$$CE = \sum \lambda_i c_i \quad (22.12)$$

The ions used in the conductivity calculations are the same as those used in calculating the ion balance. Careful, precise conductivity measurement is then an additional way of checking the results of chemical analyses: the percentage difference (CD) between estimated and measured conductivity (CM), is given by the ratio:

$$CD = 100(CE - CM)/CM \quad (22.13)$$

The limits for CD adopted in the ICP Forests are given in [Table 22.3](#). At low ionic strength (below $100 \mu\text{equiv.L}^{-1}$) in deposition samples, the discrepancy between measured and calculated conductivity should be not more than 2% ([Miles and Yost, 1982](#)). At an ionic strength higher than $100 \mu\text{equiv.L}^{-1}$ (approximately at conductivity higher than 10 mS m^{-1}), differences between ion activity and concentration become relevant. CE should then be corrected. The correction procedure needs first the calculation of the ionic strength (Is) (mequiv.L^{-1}) from the individual ion concentrations as follows:

$$Is = 0.5 \sum c_i z_i^2 / w_i \quad (22.14)$$

where z_i , absolute value of the charge for the i th ion; w_i , molecular weight of the i th ion.

For conductivity values ranging between 100 and $500 \mu\text{equiv.L}^{-1}$, Davies correction can be used, as proposed, for example, by [Stumm and Morgan \(1996\)](#) and [American Public Health Association et al. \(2005\)](#):

$$CE_{\text{corr}} = y^2 CE = y^2 \sum \lambda_i c_i \quad (22.15)$$

where:

$$y = 10^{-0.5 \left(\frac{\sqrt{Is}}{1 + \sqrt{Is}} - 0.3Is \right)} \quad (22.16)$$

This test can also be used for solutions with DOC greater than 5 mg L^{-1} , as throughfall and stemflow samples, because dissolved organic matter does

not contribute significantly to conductivity. A plot of measured and calculated conductivity is useful in the routine checking of a set of analyses. Departure of the results from linearity indicates the probable presence of analytical errors.

22.6.1.3 Na/Cl Ratio

In many parts of Europe, sea salt is a major contributor of sodium and chloride ions in deposition. As a result, the ratio between the two ions is similar to that of sea salt even in parts of Europe situated far from the sea (Mosello et al., 2005). In general, if the ratio (Na^+/Cl^-), calculated by expressing the concentrations on a molar basis, falls outside the range 0.5–1.5, the analytical quality in the measurement of low concentrations of sodium and chloride should be checked. In some areas, other sources of Cl^- and/or Na^+ can be present, for example, because of anthropogenic activities. In this case, the Na^+/Cl^- ratio might be different from that of sea salt and the test cannot be used. However, it is necessary to carefully evaluate if local sources are actually present or if the differences are due to systematic errors in the analyses.

22.6.1.4 N Balance

The test is based on the fact that total dissolved nitrogen (DTN) concentration must be higher than the sum of nitrate (N-NO_3), ammonium (N-NH_4), and nitrite (N-NO_2) concentrations. As the measurement of nitrite is not of priority, and is generally negligible in deposition samples, the following relationship should be verified, within the limits of analytical errors and whatever unit is used:

$$[\text{N-NO}_3] + [\text{N-NH}_4] \leq [\text{DTN}] \quad (22.17)$$

If the relationship does not hold true, then the determination of one of the forms of nitrogen must be erroneous. However, if dissolved organic nitrogen (DON) is very low, DTN may be approximately equal to $\text{NO}_3\text{-N} + \text{NH}_4\text{-N}$. In this case, random analytical errors may result in DTN values slightly lower than the sum of $[\text{NO}_3\text{-N}]$ and $[\text{NH}_4\text{-N}]$, without signaling any major problem with the analyses.

22.6.1.5 Phosphorus Contamination

If bird droppings contaminate the precipitation sample, the chemical composition of the sample (e.g., concentrations of PO_4^{3-} , K^+ , NH_4^+ , and H^+) 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 with chemical analysis.

22.6.2 Validation Procedures for Soil

Two quality check procedures are recommended: plausible range checks and cross-checks.

22.6.2.1 Plausible Variable Ranges

Plausible ranges have been defined separately for organic and mineral soil samples (Table 22.5). Values outside this range may occur, but they need to be validated, for example, by checking the analytical equipment and method, dilution factor, reported unit, sample characteristics, and signs of contamination. Reanalysis may be necessary when no obvious deviations are found in order to ensure that the results are correct. Generally, the lower limit of the min.–max. range depends on the LOQ, which, in turn, is determined by the instrument, method, and dilution factor employed. Table 22.5 shows the median LOQ reported during the European forest soil survey (2006–2009) (De Vos and Cools, 2011). The maximum value of the plausible range is determined by the 97.5 percentile values of the current values in the soil database. Methodology and data evaluation procedures can be found in De Vos and Cools (2011). As it encompasses all the European soil types, this range is relatively broad. For many variables, national plausible ranges will be narrower due to the restricted set of soil and humus types and their local characteristics. Therefore, it is important that each laboratory develops its local plausible ranges specifically for soil samples originating from a region or country.

22.6.2.2 Cross-Checks Between Soil Variables

Because different variables are determined on the same soil sample and many soil variables are autocorrelated, cross-checking is a valuable tool for detecting erroneous analytical results. For example, soils 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 (EA). Simple cross-checks have been developed for easy verification and detection of erroneous results (Table 22.6).

22.6.2.2.1 pH

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⁻¹ 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 considering measurement uncertainty, 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-units, with pH (CaCl₂) always less

TABLE 22.5 Plausible Ranges for Organic and Mineral Forest Soil Samples at the European Level (The Number of Decimal Places Indicates the Required Precision for Reporting)

Variable	Unit	Organic layer sample			Mineral soil sample		
		<i>LOQ</i>	<i>Min.</i>	<i>Max.</i>	<i>LOQ</i>	<i>Min.</i>	<i>Max.</i>
Moisture content	%wt	0.1	<0.1	10	0.1	<0.1	10
Particle size: clay	%wt	–	–	–	0.5	0.5	51.3
Particle size: silt	%wt	–	–	–	0.5	1.5	73.0
Particle size: sand	%wt	–	–	–	0.5	4.0	100
Bulk density	kg m ⁻³	–	50	800	–	380	1800
pH (CaCl ₂)	–	–	2.6	6.9	–	2.9	7.7
pH (H ₂ O)	–	–	3.3	6.9	–	3.7	8.4
CaCO ₃	g kg ⁻¹	3	0	360	3	0	660
Organic carbon	g kg ⁻¹	1.2	93.0	590.0	1.2	0.4	150.0
Total N	g kg ⁻¹	0.5	4.3	32.0	0.1	0.05	10.0
Free H ⁺	cmol ⁺ kg ⁻¹	0.1	0.10	17.50	0.1	<0.10	3
Exchangeable acidity	cmol ⁺ kg ⁻¹	0.1	0.05	22.50	0.1	0.05	11.8
Exchangeable K	cmol ⁺ kg ⁻¹	0.03	0.01	5.3	0.03	0.006	1.3
Exchangeable Ca	cmol ⁺ kg ⁻¹	0.03	0.17	146.00	0.03	0.005	47.00
Exchangeable Mg	cmol ⁺ kg ⁻¹	0.03	0.19	21.50	0.03	0.002	7.15

Continued

TABLE 22.5 Plausible Ranges for Organic and Mineral Forest Soil Samples at the European Level (The Number of Decimal Places Indicates the Required Precision for Reporting)—Cont'd

Variable	Unit	Organic layer sample			Mineral soil sample		
		<i>LOQ</i>	<i>Min.</i>	<i>Max.</i>	<i>LOQ</i>	<i>Min.</i>	<i>Max.</i>
Exchangeable Na	cmol ⁺ kg ⁻¹	0.03	0.005	2.35	0.03	0.002	0.45
Exchangeable Al	cmol ⁺ kg ⁻¹	0.02	0.002	16.60	0.02	0.018	9.00
Exchangeable Fe	cmol ⁺ kg ⁻¹	0.02	0.0001	5.20	0.02	0.0004	0.70
Exchangeable Mn	cmol ⁺ kg ⁻¹	0.02	0.0005	5.70	0.02	0.001	0.70
Extractable P	mg kg ⁻¹	35	80.0	2100.0	35	35.0	1320.0
Extractable K	mg kg ⁻¹	80	4.0	5900.0	80	100.0	9250.0
Extractable Ca	mg kg ⁻¹	50	210.0	50,000.0	50	20	140,000.0
Extractable Mg	mg kg ⁻¹	35	120.0	7600.0	35	75.0	30,500.0
Extractable S	mg kg ⁻¹	20	460.0	6750.0	20	10.0	1100.0
Extractable Na	mg kg ⁻¹	20	4.0	540.0	20	12.0	650.0
Extractable Al	mg kg ⁻¹	10	140.0	26,000.0	10	1100.0	55,250.0
Extractable Fe	mg kg ⁻¹	10	140.0	42,500.0	10	880.0	62500.0
Extractable Mn	mg kg ⁻¹	2	0.8	3600.0	2	8.0	1950.0
Extractable Cu	mg kg ⁻¹	1	0.2	75.0	1	0.3	55.0
Extractable Pb	mg kg ⁻¹	2.5	0.03	245.0	2.5	1.0	110.0

Extractable Ni	mg kg ⁻¹	1	0.06	45.0	1	0.5	80.0
Extractable Cr	mg kg ⁻¹	1	0.1	95.0	1	1.0	80.0
Extractable Zn	mg kg ⁻¹	2	0.8	300.0	2	2.5	165.0
Extractable Cd	mg kg ⁻¹	0.5	<0.01	2.2	0.5	<0.01	2.5
Extractable Hg	mg kg ⁻¹	0.03	<0.01	1.65	0.03	0.02	2.25
Total K	mg kg ⁻¹	80	50.0	25,000.0	80	2000	50,000
Total Ca	mg kg ⁻¹	50	50.0	65,000.0	50	350.0	200,000.0
Total Mg	mg kg ⁻¹	35	100.0	42,000.0	35	180.0	42,000.0
Total Na	mg kg ⁻¹	20	<20.0	15,000.0	20	400.0	20,000.0
Total Al	mg kg ⁻¹	10	100.0	50,000	10	4000.0	100,000
Total Fe	mg kg ⁻¹	10	100.0	25,000.0	10	700.0	65,000.0
Total Mn	mg kg ⁻¹	2	20.0	3500.0	2	15.0	2000.0
Reactive Al	mg kg ⁻¹	50	90	12,500	50	170	10,300
Reactive Fe	mg kg ⁻¹	50	170	40,000	50	100	13,000

TABLE 22.6 Algorithms for Cross-Checks Between Soil Variables Measured on European Forest Soil Samples

Soil variables	Algorithm	
pH	$0 < [\text{pH}(\text{H}_2\text{O}) - \text{pH}(\text{CaCl}_2)] \leq 1.2$	
Carbon and carbonates	$[\text{C}_{\text{CaCO}_3} + \text{TOC}] \leq \text{TC}$ with $\text{C}_{\text{CaCO}_3} = \text{CaCO}_3 \times 0.12$ and $\text{C}_{\text{CaCO}_3} \approx \text{TIC}$	
Extractable and total elements	Extractable element \leq total element (for K, Ca, Mg, Na, Al, Fe, and Mn)	
Reactive and total elements	Reactive Fe \leq total Fe Reactive Al \leq total Al	
Exchangeable and extractable elements	$(\text{K}_{\text{exch}} \times 391) \leq \text{extractable K}$ $(\text{Ca}_{\text{exch}} \times 200) \leq \text{extractable Ca}$ $(\text{Mg}_{\text{exch}} \times 122) \leq \text{extractable Mg}$ $(\text{Na}_{\text{exch}} \times 230) \leq \text{extractable Na}$ $(\text{Al}_{\text{exch}} \times 89) \leq \text{extractable Al}$ $(\text{Fe}_{\text{exch}} \times 186) \leq \text{extractable Fe}$ $(\text{Mn}_{\text{exch}} \times 274) \leq \text{extractable Mn}$	
Free H ⁺ and exchangeable acidity	Free H ⁺ < EA $\text{EA} \approx \text{Al}_{\text{exch}} + \text{Fe}_{\text{exch}} + \text{Mn}_{\text{exch}} + \text{free H}^+$	
Particle size fractions	$\Sigma[\text{clay}(\%), \text{silt}(\%), \text{sand}(\%)] = 100\%$	
	Organic samples ($>200 \text{ g kg}^{-1} \text{ TOC}$)	Mineral soil samples
pH and carbonates	If $\text{pH}(\text{CaCl}_2) < 6.0$, then $\text{CaCO}_3 < 3 \text{ g kg}^{-1}$ (=LOQ)	If $\text{pH}(\text{H}_2\text{O}) < 5$ or if $\text{pH}(\text{CaCl}_2) < 5.5$, then $\text{CaCO}_3 < 3 \text{ g kg}^{-1}$ (=LOQ)
C:N ratio	$5 < \text{C:N ratio} < 100$	$3 < \text{C:N ratio} < 75$
C:P ratio	$100 < \text{C:P ratio} < 2500$	$8 < \text{C:P ratio} < 750$
C:S ratio	$20 < \text{C:S ratio} < 1000$	–

or equal to $\text{pH}(\text{H}_2\text{O})$. Note that in peat samples, the difference between both pH measurements may be higher, up to 1.5 pH-units.

22.6.2.2.2 Carbon

The total carbon content is measured by dry combustion using a total analyzer ([International Organization for Standardization, 1995](#)). In general, total organic carbon (TOC) is obtained by subtracting total inorganic carbon (TIC) from total carbon. Inorganic carbon can be estimated from the carbonate measurement ([International Organization for Standardization, 1994](#)) using a calcimeter

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

22.6.2.2.3 pH-Carbonate

The routinely determination of carbonate in soil samples with low pH values is a waste of time and resources. This can be minimized by carrying out a pH measurement which will determine whether carbonates are present and require to be analyzed. Therefore, if $\text{pH}(\text{CaCl}_2) > 6$, quantifiable amounts of carbonate are most likely present in the soil sample.

22.6.2.2.4 C:N, C:P, and C:S Ratios

Most of the nitrogen and phosphorus 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. Note that for peat soils, the C:P ratio may be greater than 2500. The C:S ratio varies within specific ranges for organic samples only.

22.6.2.2.5 Extractable Versus Total Element

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).

22.6.2.2.6 Reactive Fe and Al

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

22.6.2.2.7 Exchangeable Elements Versus Aqua Regia Extractable Elements

The elements bound to the cation exchange complex in the soil are also readily extracted using aqua regia. Therefore, the concentration of exchangeable cations should always be lower than their aqua regia extractable concentration. A conversion factor is needed to convert from $\text{cmol}(+) \text{ kg}^{-1}$ to mg kg^{-1} . In general, the ratio between an exchangeable element and the same extracted element is higher in organic matrices than in mineral soil.

22.6.2.2.8 Free H^+ and Exchangeable Acidity

Two checks can be applied to free H^+ and exchangeable acidity (EA). For mineral soil samples, free H^+ is usually $< 60\%$ of the EA.

22.6.2.2.9 Particle Size Fraction Sum

A further check is to report the proportion of sand, silt, and clay fractions in mineral soil samples as fractions of the fine earth (0–2 mm fraction) after applying a correction for the dispersing agent. So the sum of the three fractions should be 100%. The mass of the three fractions should equal the weight of the fine earth, minus the weight of carbonate and organic matter which have been removed.

22.6.3 Validation Procedure for Foliar and Litterfall Samples

In comparison to the quality checks for the analytical results on soil, deposition, and soil solution samples, devising robust procedures for checking foliage and litterfall analytical data is relatively difficult. In unpolluted areas, the concentration range of certain analytes in foliage is usually small compared with that in other matrices, and so most of the results are plausible. Correlations between elements in foliage could possibly be used for checking analytical results, but this is only suitable in cases where the sample plots are adjacent to each other and have similar soil characteristics and tree species. As a result, this is probably not a useful procedure for checking the results at the large scale, for example, for a European-wide survey.

22.6.3.1 Plausible Ranges: Foliar

A list of plausible ranges for the element concentrations in foliage was set up based on the foliage data available from past surveys. The 5th and the 95th percentile limits for each tree species were calculated. In [Table 22.7](#), these limits are given for some of the most prominent tree species in Europe (for the full list, see [Rautio et al., 2010](#)). Results falling outside these limits must be checked and, if necessary, be reanalyzed. [Stefan et al. \(1997\)](#) clearly showed that element concentrations in foliage vary considerably in different parts of Europe. There is the need to calculate plausible ranges for, for example, each country/tree species/laboratory using their own results. This would result in narrower limits that may help in detecting nonplausible analytical data.

22.6.3.2 Plausible Ranges: Litterfall

Developing tolerable limits for litterfall chemistry is a more difficult task than that for foliage. After the collection, litterfall is sorted into different fractions, in general two (foliar and nonfoliar) or three (foliage, wood, and fruit cones/seeds) (see [Chapter 14](#)). Litterfall can be analyzed either as a pooled sample or per fraction. As a result, the plausible ranges of element concentrations in litterfall are greater than for foliage. Since foliage is an important fraction in litter, plausible ranges for selected tree species and based on expert experience are given in [Table 22.8](#). Plausible ranges for the nonfoliar fraction in litterfall have yet to be determined.

TABLE 22.7 Plausible Ranges of Element Concentrations in the Foliage of Different Tree Species Calculated from the ICP Forests Level II Datasets (Indicative Values in Grey)

Tree species	Limit	N (mg g ⁻¹)	S (mg g ⁻¹)	P (mg g ⁻¹)	Ca (mg g ⁻¹)	Mg (mg g ⁻¹)	K (mg g ⁻¹)	C (g kg ⁻¹)	Zn (µg g ⁻¹)	Mn (µg g ⁻¹)	Fe (µg g ⁻¹)	Cu (µg g ⁻¹)	Pb (µg g ⁻¹)	Cd (ng g ⁻¹)	B (µg g ⁻¹)	
<i>Fagus sylvatica</i>	C	Low	20.41	1.26	0.89	3.44	0.65	4.81	450	17.0	127	62.0	5.67	–	50	9.1
		High	29.22	2.12	1.86	14.77	2.50	11.14	550	54.2	2902	177.9	12.18	6.79	462	40.0
<i>Quercus ilex</i>	C	Low	11.95	0.81	0.69	4.00	0.76	3.42	450	12.7	278	73.1	4.00	–	–	21.7
		High	17.24	1.41	1.22	10.32	2.62	8.46	550	41.0	5385	716.9	7.00	–	–	–
<i>Quercus petraea</i>	C	Low	19.75	1.24	0.90	4.12	1.06	5.86	450	11.0	905	60.4	5.39	–	24	5.5
		High	29.84	2.01	1.85	10.46	2.26	11.16	550	25.0	4209	149.2	11.64	–	–	–
<i>Quercus robur</i>	C	Low	20.31	1.36	0.97	3.33	1.09	5.80	450	14.0	219	63.8	5.50	0.14	40	23.4
		High	30.69	2.21	2.55	12.26	2.85	12.64	550	50.0	2820	232.8	14.10	17.99	183	54.8
<i>Abies alba</i>	C	Low	11.55	0.79	0.95	3.50	0.68	4.29	470	22.0	185	20.6	2.31	–	48	15.5
		High	16.16	1.69	2.23	11.71	1.90	8.48	570	45.0	2510	85.2	5.89	–	–	–
	C+1	Low	11.67	0.95	0.86	4.19	0.37	3.97	470	20.0	250	32.0	2.00	–	56	14.4
		High	16.46	1.79	2.21	16.39	1.70	7.57	570	47.5	5241	121.0	6.45	–	–	–
<i>Picea abies</i>	C	Low	10.39	0.70	1.01	1.83	0.66	3.65	470	16.0	165	22.0	1.41	–	–	7.2
		High	16.68	1.31	2.10	7.01	1.56	8.36	570	47.0	1739	91.2	5.94	2.92	226	29.4
	C+1	Low	9.47	0.69	0.81	2.26	0.44	3.41	470	12.0	198	26.7	0.94	–	–	6.2
		High	15.97	1.34	1.82	9.77	1.51	7.05	570	51.8	2376	118.1	7.07	5.24	169	32.9

Continued

TABLE 22.7 Plausible Ranges of Element Concentrations in the Foliage of Different Tree Species Calculated from the ICP Forests Level II Datasets (Indicative Values in Grey)—Cont'd

Tree species	Limit	N (mg g ⁻¹)	S (mg g ⁻¹)	P (mg g ⁻¹)	Ca (mg g ⁻¹)	Mg (mg g ⁻¹)	K (mg g ⁻¹)	C (g kg ⁻¹)	Zn (µg g ⁻¹)	Mn (µg g ⁻¹)	Fe (µg g ⁻¹)	Cu (µg g ⁻¹)	Pb (µg g ⁻¹)	Cd (ng g ⁻¹)	B (µg g ⁻¹)	
<i>Pinus sylvestris</i>	C	Low	11.40	0.75	1.11	1.61	0.64	3.77	470	32.0	172	18.3	2.28	–	50	9.2
		High	20.41	1.56	2.06	4.61	1.31	7.27	570	77.6	912	139.0	7.70	3.94	447	30.5
	C+1	Low	10.94	0.77	1.00	2.57	0.50	3.51	470	31.5	222	28.0	1.96	0.14	60	7.4
		High	19.38	1.61	1.88	6.71	1.18	6.52	570	96.0	1332	170.5	6.88	5.59	507	33.9
<i>Pseudo- tsuga menzi- esii</i>	C	Low	13.54	1.00	1.00	1.98	1.02	5.17	470	15.0	159	43.0	2.72	–	141	30.9
		High	22.71	1.80	1.70	5.91	2.10	8.96	570	45.3	1661	129.4	5.95	–	–	–
	C+1	Low	13.55	0.99	0.71	3.09	1.14	2.97	470	14.0	444	57.9	2.91	–	–	–
		High	29.23	2.18	1.45	9.64	2.73	7.30	570	–	155	279.2	–	–	–	–

C, current year needles or leaves; C+1, second (current + 1) year needles.

TABLE 22.8 Plausible Ranges of Element Concentrations in the Foliar Litter of Different Tree Species

Tree species	Limit	N (mg g ⁻¹)	S (mg g ⁻¹)	P (mg g ⁻¹)	Ca (mg g ⁻¹)	Mg (mg g ⁻¹)	K (mg g ⁻¹)	C (g kg ⁻¹)	Zn (μg g ⁻¹)	Mn (μg g ⁻¹)	Fe (μg g ⁻¹)	Cu (μg g ⁻¹)	B (μg g ⁻¹)
<i>Betula pendula</i>	Low	7.30	–	0.20	5.00	1.00	0.30	290	105	600	45	6	–
	High	21.00	–	1.20	12.50	2.00	1.40	330	170	3000	300	19	38
<i>Castanea sativa</i>	Low	9.00	–	0.20	4.50	1.40	0.20	390	35	700	–	5	–
	High	13.00	–	0.70	10.50	2.00	0.55	420	45	2500	90	13	100
<i>Fagus sylvatica</i>	Low	9.00	1.00	0.50	4.00	0.80	2.00	460	25	650	70	4	2
	High	19.00	2.20	1.90	17.00	2.00	8.00	510	35	1600	140	7	40
<i>Fraxinus excelsior</i>	Low	12.00	–	0.75	20.00	2.00	0.40	470	15	110	120	7	–
	High	18.00	–	1.50	25.00	3.50	1.40	470	20	200	200	9	50
<i>Quercus frainetto</i>	Low	8.00	1.10	1.10	14.00	1.20	4.50	–	–	–	–	–	–
	High	11.70	1.10	1.30	18.30	1.40	5.20	–	–	–	–	–	–
<i>Quercus petraea</i>	Low	8.00	–	0.30	7.00	1.30	2.00	460	14	700	50	5	–
	High	12.00	–	0.60	10.00	2.00	4.00	510	25	1700	200	8	35
<i>Quercus robur</i>	Low	10.00	0.85	0.82	5.00	1.00	4.00	460	15	1000	90	6	7
	High	19.00	1.70	2.00	13.00	2.00	8.00	510	25	1200	150	7	35
<i>Abies cephalonica</i>	Low	8.00	–	–	11.00	1.00	2.70	–	–	–	–	–	–
	High	13.00	–	–	24.00	1.50	8.30	–	–	–	–	–	–

Continued

TABLE 22.8 Plausible Ranges of Element Concentrations in the Foliar Litter of Different Tree Species—Cont'd

Tree species	Limit	N	S	P	Ca	Mg	K	C	Zn	Mn	Fe	Cu	B
		(mg g ⁻¹)	(mg g ⁻¹)	(mg g ⁻¹)	(mg g ⁻¹)	(mg g ⁻¹)	(mg g ⁻¹)	(g kg ⁻¹)	(μg g ⁻¹)	(μg g ⁻¹)	(μg g ⁻¹)	(μg g ⁻¹)	(μg g ⁻¹)
<i>Picea abies</i>	Low	6.50	1.00	0.60	2.50	0.70	1.00	–	–	–	–	–	–
	High	12.60	1.50	1.20	16.00	2.20	4.20	520	–	–	–	–	–
<i>Picea sitchensis</i>	Low	6.00	1.00	0.60	4.00	0.60	1.50	440	15	250	40	2	–
	High	13.00	1.10	1.10	11.00	1.00	3.00	530	35	1400	120	4	35
<i>Pinus sylvestris</i>	Low	5.00	0.62	0.40	2.00	0.50	1.00	490	20	180	35	2	–
	High	10.00	0.62	0.80	11.00	0.80	3.00	530	45	800	150	5	45

22.7 INTERLABORATORY QA

Beside QA and good laboratory practice within each laboratory, a continuous exchange of analytical expertise between laboratories cooperating in the same monitoring network is very beneficial. For example, within the ICP Forests, a Working Group QA/QC in Laboratories was established. While the main activity of this group remains the running of regular ring tests and the production of qualification reports, great importance is also given to the exchange of analytical expertise, methods, information about instruments, and practical help among the cooperating laboratories.

22.7.1 Ring Tests

Conducting interlaboratory ring tests is an excellent tool for improving the quality of the analytical results produced by the participating laboratories. There are the combined benefits of improved expertise in using harmonized analytical methods as well as the use of the remaining ring test sample material as RM for subsequent analyses. Within the ICP Forests, for example, the participation in ring tests is required for all participating laboratories. Foliar, water, and soil ring tests conducted on an annual, 2-, and 3-year basis, respectively, form the basis of the quality program (Cools and De Vos, 2010a; Cools et al., 2003, 2006, 2007; Fürst, 2004, 2005, 2006, 2007, 2008, 2009, 2010, 2011; Marchetto et al., 2006, 2009, 2010, 2011; Mosello et al., 2002). Prior to the dispatch of the ring test samples to the laboratories, the samples are checked for homogeneity and, in the case of water samples, are stabilized (i.e., by means of filtration through a 0.45- μm membrane filter). Ring test samples are packed in nonbreakable containers, and water samples are kept cool during transportation. In the case of water samples, it is necessary to set a time period for completion of analysis. This avoids chemical/biological changes in the samples, which, in turn, would lead to differences in the analytical results. The analysis of four to six ring test samples, representing different concentrations of the individual elements, permit the identification of analytical trends for each participating laboratory. This facilitates the detection of possible analytical errors and variation in analytical results arising from the use of different analytical methods. Clear instructions about the standard treatment of the samples and the analytical methods to be followed are given to all participants. This includes sample preparation such as sieving or grinding, digestion or extraction, and determination of element concentrations. By applying a predefined method coding system, the effects of different methods on the results of the ring test can be investigated. As the laboratories are analyzing the ring test samples as a part of their regular sample batch analysis, a direct assessment of the analytical performance can be made.

Once analysis is completed, the participating laboratories submit their results to the ring test organizers. Within the ICP Forests monitoring programme, a Web

interface is used for registration, data collection, and standard evaluation of the ring tests (more information on the Website <http://bfw.ac.at/rz/bfwcms.web?dok=8897>, accessed on September 2012). The initial step in the evaluation of ring test results is the elimination of outliers (Deutsches Institut für Normung, 2005). The outlier-free mean value for each element/sample and the laboratory mean value are then calculated, and these results are compared with the tolerable limits. Depending on the element concentration, tolerable limits for low and high concentrations were used. For a given laboratory, analysis for a particular variable will pass if the laboratory mean value is within the tolerable range (outlier-free mean value \pm the tolerable limit). Furthermore, to avoid the use of methods not sensitive enough for the detection of particular variables, a limit for the highest acceptable LOQ was fixed for each element. The LOQ reported by the laboratory is checked against the maximum acceptable LOQ.

22.7.2 Tolerable Limits

The use of tolerable limits is essential when comparing results from different laboratories (De Vos, 2008). The tolerable limits need to be greater than the laboratory's acceptable precision (within-laboratory repeatability) because they must also include a variance component due to differences between the laboratories. The selection of the tolerable limits should consider that excessively broad acceptance thresholds are of little use for ensuring good data quality, while too strict threshold, that are frequently exceeded, are ignored. The proposed values are the result of a reiterative process lasting more than 5 years. It needs to be verified on a continuous basis in practice and if needed, amended. Arising from this process, the use of different tolerable limits for "low" or "high" concentrations was recommended. The proposed tolerable limits for water, soil, and foliar ring tests at high and low concentrations (if needed) are listed in the Tables 22.9–22.11.

22.7.3 Qualification Reports

It is essential to provide a feedback about the quality achieved. For example, all laboratories participating in the ICP Forests receive a qualification report after taking part in a ring test. In this report, information is provided on the variables that were analyzed (or not) by the laboratory and whether qualification criteria for each variable were met. The qualification criterion states that $\geq 50\%$ of the results of all ring test samples for a particular variable must be within the appropriate tolerable limit. Laboratories who have failed the ring test for a particular variable have the opportunity to requalify by reanalyzing the ring test samples. The laboratories have to report the new results to the organizers of the ring test together with a report on the analytical instrumentation, weight factors, dilution factors, and the reasons behind their poor results in the previous ring test. The ring test organizers will audit the report from the laboratory. Once the reason(s) for the analytical error has been

TABLE 22.9 Tolerable Limits (TL) and Maximum Acceptable Limit of Quantification (LOQ_{max}) for Deposition and Soil Solution Variables

Variable	Unit	Conc. range low		Conc. range high		LOQ_{max}
		Conc. level	TL (%)	Conc. level	TL (%)	
pH	pH units	>5.0	± 0.2 pH units	<5.0	± 0.1 pH units	–
Conductivity	$\mu S\ cm^{-1}$	<10	± 20	>10	± 10	5
Calcium	$mg\ L^{-1}$	<0.25	± 20	>0.25	± 15	0.2
Magnesium	$mg\ L^{-1}$	<0.25	± 25	>0.25	± 15	0.1
Sodium	$mg\ L^{-1}$	<0.50	± 25	>0.50	± 15	0.1
Potassium	$mg\ L^{-1}$	<0.50	± 25	>0.5	± 15	0.08
Ammonium	$mg\ N\ L^{-1}$	<0.25	± 25	>0.25	± 15	0.08
Sulfate	$mg\ S\ L^{-1}$	<1.0	± 20	>1.0	± 10	0.1
Nitrate	$mg\ N\ L^{-1}$	<0.5	± 25	>0.5	± 15	0.08
Chloride	$mg\ L^{-1}$	<1.5	± 25	>1.5	± 15	0.2
Alkalinity	$\mu equiv.\ L^{-1}$	<100	± 40	>100	± 25	10
Total dissolved nitrogen	$mg\ L^{-1}$	<0.5	± 40	>0.50	± 20	0.5
Dissolved organic carbon	$mg\ L^{-1}$	<1.0	± 30	>1.0	± 20	1
Others (metals)	$mg\ L^{-1}$	–	–	–	± 20	–
Phosphorus	$mg\ L^{-1}$	–	–	–	–	0.1

correctly identified and the results of the second submission are within the tolerable limits, the laboratory will receive a requalification report.

The results of the ring tests are integrated in the central database (see Chapter 23). This means that poor ring test results for a particular variable will be known and can be used as a criterion to reject data before being used in evaluations at, for example, the European level. Laboratories with unacceptable results in ring tests will be invited to participate in an assistance program organized by the WG on QA/QC in Laboratories. Close cooperation between these laboratories and laboratories counterparts with good laboratory practices is considered to be an effective way of improving laboratory proficiency. When determining the scope for assistance, it is necessary to take into account the results of the ring test, the state of implementation of a laboratory quality program, and the analytical methods used in the laboratory in question.

TABLE 22.10 Tolerable Limits (TL) and Maximum Acceptable Limit of Quantification (LOQ_{max}) of Mandatory and Optional Foliage and Litterfall Parameters

Variable	Unit	Conc. range low		Conc. range high		LOQ_{max}
		Conc. level	TL (%)	Conc. level	TL (%)	
Nitrogen	mg g ⁻¹	≤5.0	±15	>5.0	±10	2
Sulfur	mg g ⁻¹	≤0.50	±20	>0.50	±15	0.3
Phosphorus	mg g ⁻¹	≤0.50	±15	>0.50	±10	0.3
Calcium	mg g ⁻¹	≤3.0	±15	>3.0	±10	0.5
Magnesium	mg g ⁻¹	≤0.50	±15	>0.50	±10	0.3
Potassium	mg g ⁻¹	≤1.0	±15	>1.0	±10	0.5
Carbon	g 100 g ⁻¹	–	–	–	±5	10
Zinc	μg g ⁻¹	≤20	±20	>20	±15	5
Manganese	μg g ⁻¹	≤20	±20	>20	±15	5
Iron	μg g ⁻¹	≤20	±30	>20	±20	5
Copper	μg g ⁻¹	–	–	–	±20	1
Lead	μg g ⁻¹	≤0.50	±40	>0.50	±30	0.5
Cadmium	ng g ⁻¹	–	–	–	±30	50
Boron	μg g ⁻¹	≤5.0	±30	>5.0	±20	1

Results of ring tests are periodically reviewed in order to assess and, where necessary, optimize analytical quality. Up to now, 6 soil, 5 water, and 14 foliar ring tests have been organized as part of the European forest monitoring program since 1998. The results of these ring tests and the consequent improvement in quality over time in the laboratories can be easily observed (König et al., 2010a). For water samples, the percentage of results exceeding tolerable limits has been reduced over eight years time period from 20–60% to 5–30% (Figure 22.3). A similar trend can be observed over the last four soil ring tests in Figure 22.4, where the CV% for the results of all participants for the selected variable decreased over 7 years from 15–65% to 10–35%. In the case of the foliar ring tests (Figure 22.5), the improvement of results stabilized in 2005, where 3–10% results exceeded tolerable limits, a level that would be difficult to improve upon further.

The comparability and quality of the soil analyses is lower than for water and foliar analysis, and this is confirmed by the soil ring tests. Nevertheless, there is room for improvement with regard to water analyses. Therefore, the

TABLE 22.11 Interlaboratory Tolerable Limits (TL) for Soil Variables Expressed as a Percentage of the Cleaned Mean (De Vos, 2008)

Variable	Unit	Conc. range low		Conc. range high	
		Conc. level	TL (%)	Conc. level	TL (%)
Moisture content	%	≤1.0	±25	>1.0	±15
Clay content	%	≤10.0	±50	>10.0	±35
Silt content	%	≤20.0	±45	>20.0	±30
Sand content	%	≤30.0	±45	>30.0	±25
pH (H ₂ O) and pH (CaCl ₂)	pH units	–	–	2.0–8.0	±5
Carbonate	g kg ⁻¹	≤50	±130	>50	±40
Organic carbon	g kg ⁻¹	≤25	±20	>25	±15
Total nitrogen	g kg ⁻¹	≤1.5	±30	>1.5	±10
Free H ⁺	cmol ⁺ kg ⁻¹	0.02–1.20	±100	0.02–1.20	±100
Exchangeable acidity	cmol ⁺ kg ⁻¹	≤1.00	±90	>1.00	±35
Exchangeable K	cmol ⁺ kg ⁻¹	≤0.10	±45	>0.10	±30
Exchangeable Ca	cmol ⁺ kg ⁻¹	≤1.50	±65	>1.50	±20
Exchangeable Mg	cmol ⁺ kg ⁻¹	≤0.25	±50	>0.25	±20
Exchangeable Na	cmol ⁺ kg ⁻¹	0.01–0.14	±80	0.01–0.14	±80
Exchangeable Al	cmol ⁺ kg ⁻¹	≤0.50	±105	>0.50	±30
Exchangeable Fe	cmol ⁺ kg ⁻¹	≤0.02	±140	>0.02	±50
Exchangeable Mn	cmol ⁺ kg ⁻¹	≤0.03	±45	>0.03	±25
Extractable P	mg kg ⁻¹	≤150	±45	>150	±20
Extractable K	mg kg ⁻¹	≤500	±60	>500	±40
Extractable Ca	mg kg ⁻¹	≤500	±70	>500	±30
Extractable Mg	mg kg ⁻¹	≤500	±60	>500	±15
Extractable S	mg kg ⁻¹	–	–	35–1300	±35
Extractable Na	mg kg ⁻¹	≤75.0	±65	>75.0	±50
Extractable Al	mg kg ⁻¹	≤2500	±50	>2500	±20
Extractable Fe	mg kg ⁻¹	≤2500	±40	>2500	±15
Extractable Mn	mg kg ⁻¹	≤150	±30	>150	±15

Continued

TABLE 22.11 Interlaboratory Tolerable Limits (TL) for Soil Variables Expressed as a Percentage of the Cleaned Mean (De Vos, 2008)—Cont'd

Variable	Unit	Conc. range low		Conc. range high	
		Conc. level	TL (%)	Conc. level	TL (%)
Extractable Cu	mg kg ⁻¹	≤5	±40	>5	±15
Extractable Pb	mg kg ⁻¹	–	–	3–70	±30
Extractable Ni	mg kg ⁻¹	≤10	±40	>10	±15
Extractable Cr	mg kg ⁻¹	≤10	±40	>10	±25
Extractable Zn	mg kg ⁻¹	≤20	±40	>20	±20
Extractable Cd	mg kg ⁻¹	≤0.25	±100	>0.25	±55
Extractable Hg	mg kg ⁻¹	0–0.16	±75	0–0.16	±75
Total K	mg kg ⁻¹	≤7500	±15	>7500	±10
Total Ca	mg kg ⁻¹	≤1500	±20	>1500	±15
Total Mg	mg kg ⁻¹	≤1000	±60	>1000	±10
Total Na	mg kg ⁻¹	≤1500	±20	>1500	±10
Total Al	mg kg ⁻¹	≤20,000	±35	>20,000	±10
Total Fe	mg kg ⁻¹	≤7000	±20	>7000	±10
Total Mn	mg kg ⁻¹	≤200	±25	>200	±10
Reactive Al	mg kg ⁻¹	≤750	±30	>750	±15
Reactive Fe	mg kg ⁻¹	≤1000	±30	>1000	±15

holding of regular ring tests is still an important impetus in driving and maintaining analytical performance in the ICP Forests programme.

22.8 QUALITY INDICATORS

The evaluation and tracking of laboratory quality over time is best captured by using quality indicators. Properly defined indicators deliver quantitative, measurable, and interpretative information on the overall quality system applied by the laboratories within the monitoring program. Three indicators were selected within ICP Forests:

1. the percentage of the results of a ring test within tolerable limits;
2. the percentage of the results of a ring test with a precision within 10% (not applicable to water ring tests);
3. the mean percentage of variables where control charts are used.

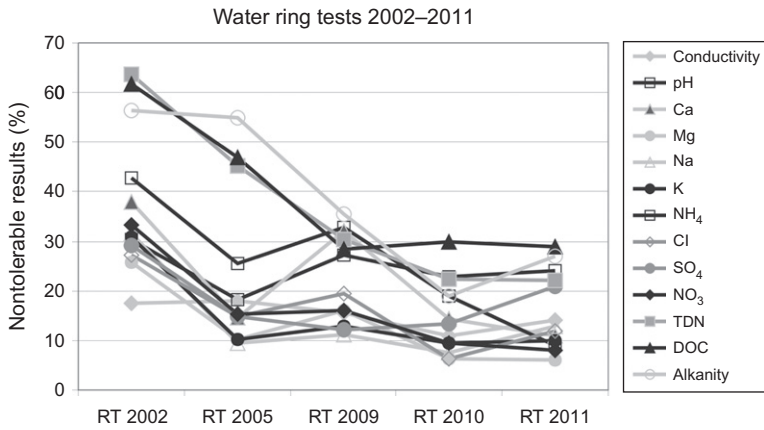


FIGURE 22.3 The change of the nontolerable results of the ICP Forests/FutMon water ring tests (RT) 2002–2011 with time for selected variables (Marchetto et al., 2006, 2009, 2010, 2011; Mosello et al., 2002).

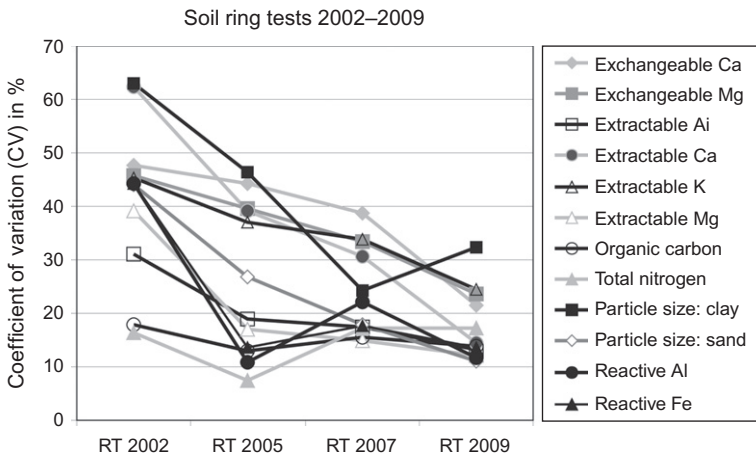


FIGURE 22.4 The change of the coefficient of variation (CV, in %) with time for selected soil parameters in the ICP Forests soil ring tests (RT) 1997–2009 (Cools and De Vos, 2010a; Cools et al., 2003, 2006, 2007).

22.8.1 Percentage Ring Test Results Within Tolerable Limits

In each ring test, the number of results within the tolerable limits for all mandatory parameter is expressed as a fraction of the total number of possible results. Where results are missing, they will be counted as outside the tolerable limits. It is expected that the percentage of results within the tolerable limits should increase as the laboratories analytical expertise improves over time. Over the past 10 years, results within the tolerable limits were ca. 85% for

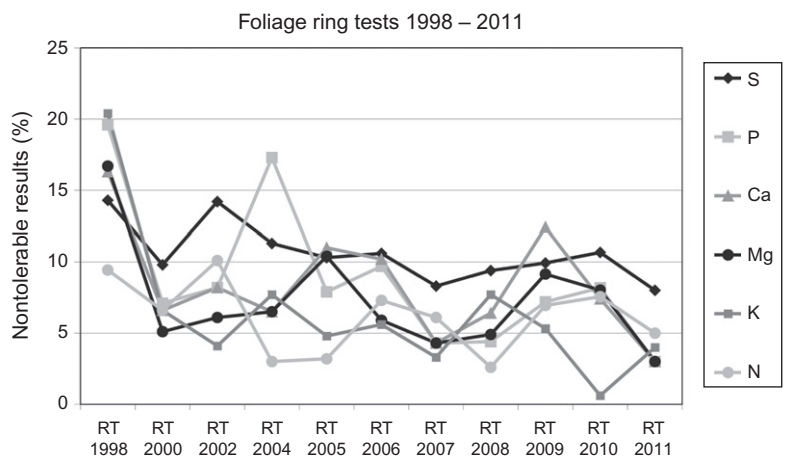


FIGURE 22.5 The change of the nontolerable results of the ICP Forests/FutMon foliar ring tests (RT) 1998–2011 with time for selected variables (Fürst 2004, 2005, 2006, 2007, 2008, 2009, 2010, 2011).

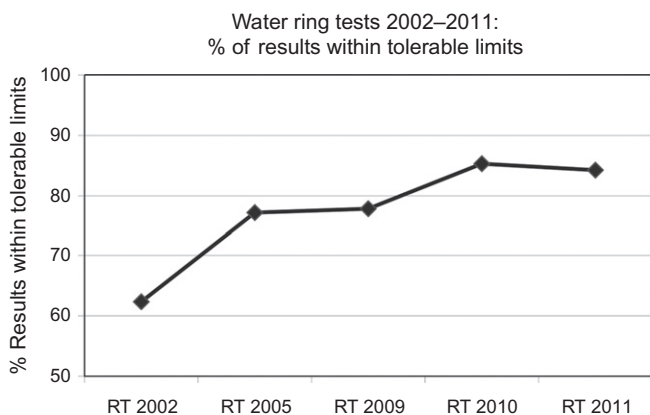


FIGURE 22.6 Frequency (%) of results within the tolerable limits of the ICP Forests/FutMon water ring tests (RT) 2002–2011 for all evaluated variables.

water ring tests and ca. 93% for foliar ring tests (see Figures 22.6 and 22.7). For the last soil ring test 2009, 82% of the submitted results for mandatory parameters were within tolerable limits.

22.8.2 Percentage Ring Test Results Within 10% Precision Level

Normally, the precision (i.e., a measure of agreement between replicate measurements of a specific variable within a laboratory, expressed as % relative standard deviation) should be within 10%. In ring tests, with the exception

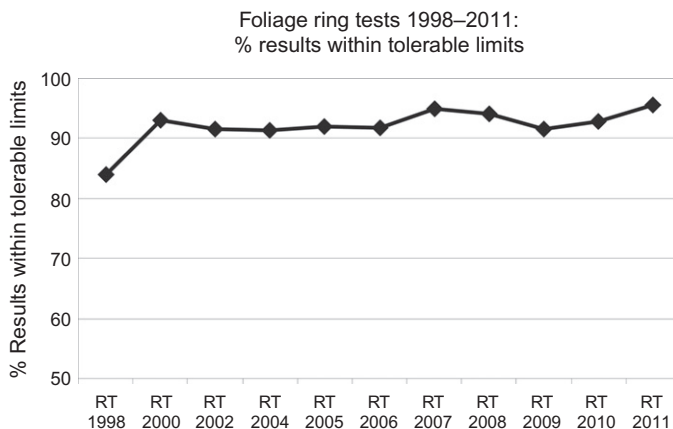


FIGURE 22.7 Frequency of results within the tolerable limits of the ICP Forests/FutMon foliar ring tests (RT) 1998–2010 for all evaluated variables.

of water samples, each sample typically has to be analyzed three or four times. Therefore, the precision for each variable analyzed can be calculated. Furthermore, the overall precision of analysis for the variables analyzed in a sample (or batch of samples) can then be determined. Ideally, 90–100% of all variables analyzed should have a precision within 10%, and this figure should become constant over time.

22.8.3 Mean Percentage of Variables with Control Charts

The percentage of variables where laboratories use control charts was implemented as a quality indicator to foster the use of control charts for all variables and all matrices. All laboratories submit together with the analytical data an annual quality report, including the mean and the standard deviation of regularly measured RMs (CRM or LRM) for each parameter in each matrix. From this report, the percentage of variables where control charts are used can be calculated for each laboratory. The mean percentage of all laboratories using control charts will be an indicator of improved laboratory QC and should get close to 100% over the next years. Within the ICP Forests, for example, the percentage of variables with control charts for foliar analysis reached 92–94% between 2008 and 2011.

22.9 QUALITY REPORTS

In monitoring programs, a large amount of analytical data is collected annually and prepared for storage into databases. To provide information on the quality of that data, a quality report is necessary. For example, such a quality report is provided at the time the analytical data are submitted to the ICP

Forests database (see Chapter 23). The link between quality data and actual data is ensured by the quality report containing information related to the submitted dataset: lab ID code, detection method (using similar codes as to the ring test reports) and LOQ for each variable, mean and relative standard deviation (%) from control charts for each variable, ID of the ring test in which the laboratory participated at the time of data processing, the percentage of results within tolerable limits for each variable in the ring test, and information on passing the requalification procedure (yes/no). The quality report forms are part of the data submission forms defined in the ICP Forests.

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REFERENCES

- Allan, M.A., 2004. World Meteorological Organization. Manual for the GAW Precipitation Chemistry Programme Global Atmosphere Watch. Guidelines, Data Quality Objectives and Standard Operating Procedures. WMO TD No. 1251.
- American Public Health Association (APHA), The American Water Works Association (AWWA), The Water Environment Federation (WEF), 2005. Standard Methods for the Examination of Water and Wastewater, twenty-first ed. American Public Health Association, Washington.
- Clarke, N., Danielsson, L.-G., 1995. The simultaneous speciation of aluminium and iron in a flow-injection system. *Anal. Chim. Acta* 306, 5–20.
- Clarke, N., Wu, Y., Strand, L.T., 2007. Dissolved organic carbon concentrations in four Norway spruce stands of different ages. *Plant Soil* 299, 275–285.
- Clarke, N., Zindra, D., Ulrich, E., et al., 2010. Sampling and analysis of deposition. Manual part XIV. In: Manual on Methods and Criteria for Harmonized Sampling, Assessment, Monitoring and Analysis of the Effects of Air Pollution on Forests. UNECE ICP Forests, Hamburg. ISBN: 978-3-926301-03-1. <http://www.icp-forests.org/Manual.htm>.
- Cools, N., De Vos, B., 2008. The FSCC Soil Reference Material. Supporting Study of the EU Forest Focus BioSoil Demonstration Project. INBO.IR.2008.49. Research Institute for Nature and Forest, Brussels.
- Cools, N., De Vos, B., 2010a. 6th FSCC Interlaboratory Comparison 2009. INBO.R.2010. Forest Soil Coordinating Centre, Research Institute for Nature and Forest, Geraardsbergen, Belgium.
- Cools, N., De Vos, B., 2010b. Sampling and analysis of soil. Manual Part X. In: Manual on Methods and Criteria for Harmonized Sampling, Assessment, Monitoring and Analysis of the Effects of Air Pollution on Forests. UNECE ICP Forests, Hamburg. ISBN:978-3-926301-03-1 <http://www.icp-forests.org/Manual.htm>.
- Cools, N., Delanote, V., De Vos, B., et al., 2003. Quality Assurance and Quality Control in Forest Soil Analysis: 3rd FSCC Interlaboratory Comparison. Forest Soil Coordinating Centre, Institute for Forestry and Game Management, Geraardsbergen, Belgium.
- Cools, N., Delanote, V., Scheldeman, X., et al., 2004. Quality assurance and quality control in forest soil analyses: a comparison between European soil laboratories. *Accred. Qual. Assur.* 9, 688–694.

- Cools, N., Verschelde, P., Quataert, P., et al., 2006. Quality Assurance and Quality Control in Forest Soil Analysis: 4th FSCC Interlaboratory Comparison. INBO.R.2006.6. Forest Soil Coordinating Centre, Research Institute for Nature and Forest, Geraardsbergen, Belgium.
- Cools, N., Mikkelsen, J.H., De Vos, B., 2007. Quality Assurance and Quality Control in Forest Soil Analysis: 5th FSCC Interlaboratory Comparison. INBO.R.2007.46. Forest Soil Coordinating Centre, Research Institute for Nature and Forest, Geraardsbergen, Belgium.
- De Vos, B., 2008. Tolerable Limits for Interlaboratory Forest Soil Ring Tests. FSCC Supporting study of the EU Forest Focus Demonstration Project BioSoil. INBO.IR.2008.43. Research Institute for Nature and Forest, Brussels.
- De Vos, B., Cools, N., 2011. Second European forest soil report. Volume I: results of the BioSoil soil survey. INBO.R.2011.35. Research Institute for Nature and Forests, Brussels.
- De Vries, W., Vel, E., Reinds, G.J., Deelstra, H., et al., 2003. Intensive monitoring of forest ecosystems in Europe: 1. Objectives, set-up and evaluation strategy. *Forest Ecol. Manage.* 174, 77–95.
- Deutsches Institut für Normung, 2005. DIN 38402-42: Deutsche Einheitsverfahren zur Wasser-, Abwasser- und Schlammuntersuchung—Allgemeine Angaben (Gruppe A). Teil 42: Ringversuche zur Verfahrensvalidierung. Auswertung (A 42).
- Durrant Houston, T., Hiederer, R., 2009. Applying quality assurance procedures to environmental monitoring data: a case study. *J. Environ. Monit.* 11, 774–781.
- Erismann, J.W., Möls, H., Fonteijn, P., et al., 2003. Field intercomparison of precipitation measurements performed within the framework of the Pan European Intensive Monitoring Program of ICP Forest. *Environ. Pollut.* 125, 139–155.
- Ferretti, M., König, N., Rautio, P., Sase, H., 2009. Quality assurance (QA) in international forest monitoring programmes: activity, problems and perspectives from East Asia and Europe. *Ann. For. Sci.* 66, 403–414.
- Fischer, R., Mues, V., Ulrich, E., et al., 2007. Monitoring of atmospheric deposition in European forests and an overview on its implication on forest condition. *Appl. Geochem.* 22, 1129–1139.
- Fürst, A., 2004. 6th Needle/Leaf Interlaboratory Comparison Test 2003/2004. Austrian Federal Office and Research Centre for Forests, Vienna/Austria. ISBN: 3-901347-46-1.
- Fürst, A., 2005. 7th Needle/Leaf Interlaboratory Comparison Test 2004/2005. Austrian Federal Research and Training Centre for Forests, Natural Hazards and Landscape, Vienna/Austria. ISBN: 3-901347-52-1.
- Fürst, A., 2006. 8th Needle/Leaf Interlaboratory Comparison Test 2005/2006. Austrian Federal Research and Training Centre for Forests, Natural Hazards and Landscape, Vienna/Austria. ISBN: 3-901347-60-7.
- Fürst, A., 2007. 9th Needle/Leaf Interlaboratory Comparison Test 2006/2007. Austrian Federal Research and Training Centre for Forests, Natural Hazards and Landscape, Vienna/Austria. ISBN: 978-3-901347-66-5.
- Fürst, A., 2008. 10th Needle/Leaf Interlaboratory Comparison Test 2007/2008. Austrian Federal Research and Training Centre for Forests, Natural Hazards and Landscape, Vienna/Austria. ISBN: 978-3-901347-73-3.
- Fürst, A., 2009. 11th Needle/Leaf Interlaboratory Comparison Test 2008/2009. Austrian Federal Research and Training Centre for Forests, Natural Hazards and Landscape, Vienna/Austria. ISBN: 978-3-901347-79-5.
- Fürst, A., 2010. 12th Needle/Leaf Interlaboratory Comparison Test 2009/2010. Austrian Federal Research and Training Centre for Forests, Natural Hazards and Landscape, Vienna/Austria. ISBN: 978-3-901347-89-4.

- Fürst, A., 2011. 13th Needle/Leaf Interlaboratory Comparison Test 2010/2011. Austrian Federal Research and Training Centre for Forests, Natural Hazards and Landscape, Vienna/Austria. ISBN: 978-3-902762-03-0.
- Fürst, A., Smidt, S., Herman, F., 2003. Monitoring the impact of sulphur with the Austrian Bioindicator Grid. *Environ. Pollut.* 12, 13–19.
- Handbook for Calculation of Measurement Uncertainty in Environmental Laboratories. (Nordtest report TR 537, 2003). ISSN 0283-7234 (Approved 2003–05).
- ICP Forests, 2010. Manual on Methods and Criteria for Harmonized Sampling, Assessment, Monitoring and Analysis of the Effects of Air Pollution on Forests. UNECE ICP Forests, Hamburg. ISBN: 978-3-926301-03-1. <http://www.icp-forests.org/Manual.htm>.
- Internal Quality Control—Handbook for Chemical Laboratories. (Nordtest report TR 569, 2007). ISSN 0283–7234/3rd ed. (Approved 2007–03).
- International Organization for Standardization, 1993. ISO 8258: Shewhart Control Charts. Geneva, Switzerland. www.iso.ch.
- International Organization for Standardization, 1994. ISO 10693: Soil Quality—Determination of Carbonate Content—Volumetric Method. Geneva, Switzerland. 7 p. www.iso.ch.
- International Organization for Standardization, 1995. ISO 10694: Soil Quality—Determination of Organic and Total Carbon After Dry Combustion (Elementary Analysis). Geneva, Switzerland, 7 p. www.iso.ch.
- International Organization for Standardization, 2008. ISO Guide 30, Amd 1:2008: Terms and Definitions Used in Connection with Reference Materials—Amendment 1: Revision of Definitions for Reference Material and Certified Reference Material. Geneva, Switzerland. www.iso.org.
- König, N., Cools, N., Derome, J., et al., 2010. Quality Improvement of the Laboratories of the ICP Forests Program and the FutMon Project. Working Papers of the Finnish Research Institute 180, 35.
- König, N., Kowalska, A., Brunialti, G., et al., 2010b. Quality assurance and control in laboratories. Manual Part XVI. In: Manual on Methods and Criteria for Harmonized Sampling, Assessment, Monitoring and Analysis of the Effects of Air Pollution on Forests. UNECE ICP Forests, Hamburg. ISBN: 978-3-926301-03-1. <http://www.icp-forests.org/Manual.htm>.
- Marchetto, A., Mosello, R., Tartari, G., et al., 2006. Atmospheric deposition and soil solution Working Ring Test 2005. E.U. Technical Report, Fontainebleau, France.
- Marchetto, A., Mosello, R., Tartari, G., et al., 2009. Atmospheric deposition and soil solution, Working Ring Test 2009. Laboratory ring test for deposition and soil solution sample analyses for the laboratories participating in the EU/Life+ FutMon Project. Report CNR-ISE, 04–09.
- Marchetto, A., Mosello, R., Tartari, G., et al., 2010. Atmospheric Deposition and soil solution Working Ring Test 2010. Laboratory ring test for deposition and soil solution sample analyses for the laboratories participating in the EU/Life+ FutMon Project. Report CNR-ISE, 05.10.
- Marchetto, A., Mosello, R., Tartari, G., et al., 2011. Atmospheric deposition and soil solution Working Ring Test 2011. Laboratory ring test for deposition and soil solution sample analyses for the laboratories participating in the EU/Life+ FutMon Project. Report CNR-ISE, 06.11.
- Miles, L.J., Yost, K.J., 1982. Quality analysis of USGS precipitation chemistry data for New York. *Atmos. Environ.* 16, 2889–2898.
- Mosello, R., Derome, J., Derome, K., et al., 2002. Atmospheric deposition and soil solution Working Ring Test 2002. E.U. Technical Report, Fontainebleau, France.

- Mosello, R., Amoriello, M., Amoriello, T., et al., 2005. Validation of chemical analyses of atmospheric deposition in forested European sites. *J. Limnol.* 64, 93–102.
- Mosello, R., Amoriello, T., Benham, S., et al., 2008. Validation of chemical analyses of atmospheric deposition on forested sites in Europe: 2. DOC concentration as an estimator of the organic ion charge. *J. Limnol.* 67, 1–15.
- Nieminen, T.M., (Ed.), 2011. Soil solution collection and analysis. Manual Part XI. In: Manual on Methods and Criteria for Harmonized Sampling, Assessment, Monitoring and Analysis of the Effects of Air Pollution on Forests. UNECE ICP Forests, Hamburg. ISBN: 978-3-926301-03-1. <http://www.icp-forests.org/Manual.htm>.
- Rautio, P., Fürst, A., Stefan, K., et al., 2010. Sampling and analysis of needles and leaves. Manual Part XII. In: Manual on Methods and Criteria for Harmonized Sampling, Assessment, Monitoring and Analysis of the Effects of Air Pollution on Forests. UNECE ICP Forests, Hamburg. ISBN: 978-3-926301-03-1. <http://www.icp-forests.org/Manual.htm>.
- Schaub, M., 2009. Future monitoring and research needs for forest ecosystems in a changing environment: an introduction. *iForest* 2, 54–55.
- Stefan, K., Fürst, A., Hacker, R., Bartels, U., 1997. Forest Foliar Condition in Europe—Results of Large-Scale Foliar Chemistry Surveys. ISBN: 3-901347-05-4, EC-UN/ECE-FBVA.
- Stumm, W., Morgan, J.J., 1996. *Aquatic Chemistry*. Wiley & Sons, New York.