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ATMOSPHERIC DEPOSITION AND SOIL SOLUTION WORKING RING TEST 2002

Laboratory ring-test for deposition and soil solution sample analyses between the countries participating in the ICP Forests level II monitoring programme

December 2002







Some photos from the workshop held in Fontainebleau, France, on 17-19 June 2002



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SUMMARY

The task of the first working ring test carried out under the Expert Panel on Deposition and the ad hoc Working Group on Soil Solution of the ICP Forests was to improve the overall analytical quality of the laboratories, with the final aim to increase the comparability and reliability of the data produced. This ring test is one further step in the harmonisation process of all ring tests carried out with the Expert Panels on Foliar Analysis and Soil within the framework of the ad hoc Working Group on Quality Assurance of ICP-Forests. The aim of the ad hoc group is to increase, through the harmonisation of QA/QC procedures, the comparability of the data at the European level. Identification of the main analytical problems and the following discussion should provide the laboratories with the means of solving any problems, if necessary with the direct help or advice of selected laboratories participating in the project. Fifty nine laboratories participated in the 2002 Working Ring Test, performed using 9 natural samples (2 open-field, bulk deposition, 4 throughfall, I stemflow and 2 soil solution samples), I synthetic sample simulating the composition and concentration of atmospheric deposition, and 4 synthetic samples for a detailed check of conductivity and alkalinity measurements. The concentrations of most of the natural samples were low (range 67-380 μ eq l⁻¹, conductivity range 11-36 μ S cm⁻¹), with the highest concentration of 2159 μ eq l⁻¹ and conductivity of 141 μ S cm⁻¹ in the case of sample WAT-5. The chemical variables to be analysed, in addition to pH and conductivity, were the concentrations of the major ions (i.e. Ca, Mg, Na, K, NH₄, SO₄, NO₃, Cl, alkalinity), total nitrogen, DOC, PO₄ and total P, total S, Si, and the metals AI, Fe, Mn, Cu and Zn. Several laboratories did not perform the analyses for alkalinity and total nitrogen, nor for DOC. This was despite the fact that, according to the Manual of Deposition Measurements and Sub-Manual on Soil Solution Collection and Analysis (ICP Forests, 1998), alkalinity (if the median annual pH is >5) and total nitrogen are mandatory variables for deposition samples, and DOC is a mandatory variable for soil solution samples.

The present inter-comparison exercise highlights that the measurement of low alkalinity values (below 50 μ eq l^{-1}) is an extremely demanding procedure. The results of several other interlaboratory exercises have confirmed this, and it is clearly a general analytical problem. The errors arising in the measurement of low alkalinity values are largely systematic. Reliable results are obtained only with those methods that extrapolate the inflection point in the acid titration, e.g. Gran titration, and two end point titration. An alternative procedure is to correct the results obtained by one end point titration with respect to the value of the end point (29 and 47 μ eq l⁻¹ to be subtracted from the results obtained by titration to 4.5 and 4.3, respectively). Systematic errors become less important for alkalinity values higher then 100 - 200 µeq I⁻¹. Other variables that had poorly comparable results were total nitrogen, phosphate and total phosphorous, and metals. As the different analytical methods used were taken into account when comparing the results, this made it possible to identify the less reliable methods. These include relatively outdated methods such as turbidimetry or nephelometry for the determination of sulphate, silver nitrate titration for chloride, Kieldhal digestion for the determination of ammonium+amino nitrogen, and colorimetric titration for alkalinity. Further highlighted points were the submission of results using units different from those required (e.g. mg NO₃ l^{-1} instead of mg N-NO₃ l^{-1}), and even the incorrect interpretation of some variables (e.g. Kjeldhal nitrogen assumed to be the same as total nitrogen).

The Youden plots demonstrated that the errors associated with the analyses were mainly systematic, which means that substantial improvements could be achieved through the more extensive adoption of Good Laboratory Practices. Of these practices, it is strongly recommended to check the analysis results for the major ions using the ionic balance, and to make a comparison of the measured and calculated conductivity values. Acceptance criteria for these calculations are presented on the basis of experimental results. A description of the methods used to perform

these checks and an example for Finland are provided on a CD for the laboratories having participated in this working ring test and for their National Focal Centres only. In the case of the major ions, an erroneous result for a single variable is of course sufficient to invalidate the ionic balance. It is therefore important to solve the analytical problems associated with the measurement of low alkalinity values as this analysis proved to be the most common source of errors. These checks should become part of the routine process for validating the results in every laboratory, They should also be performed as soon as the analyses are completed so that, if the checks fail, the analyses can be repeated.

Practical information and recommendations on how to improve the main analytical measurements, presented by selected experts during a workshop meeting held to discuss the results of the ring test (Fontainebleau, 17-18 June 2002), were included in the report.

On the basis of the inter-comparison results, the laboratories participating in the ICP Forests programme are strongly urged to reconsider their laboratory QA procedures in the light of their results and the recommendations of the rapporteurs. Unreliable analytical methods should be changed, and a validation protocol adopted. This, of course, should supplement the other laboratory practices.

Continuation of the working ring test programme appears to be a useful tool for regularly stimulating self criticism, and checking the improvements achieved in the laboratories until a sufficiently reliable QA level for the ICP Forests program has been reached. At the same time it is important to develop collaboration among the laboratories working with the same type of analyses, as this is a useful, cheap and qualified way to improve the performance. This is the task and the challenge of the Working Ring Test and of all the QA/QC activities proposed within the Expert Panel on Deposition and ad hoc Working Group on Soil Solution of the ICP Forests programme.

I.INTRODUCTION

In recent years increasing concern has been raised about the quality and compatibility of the chemical data (e.g. deposition, needle chemistry, soil, soil solution) produced within the framework of the ICP Forests Level II monitoring programme. In order to ensure that the data being collected within the programme are of the highest quality possible, the relevant expert panels are currently implementing quality assurance, quality control and inter-calibration programmes in co-operation with the national laboratories responsible for the chemical analyses. At the 10th meeting of the Forest Soils Expert Panel (Warsaw, 22-23 February, 2001), it was decided to set up a small ad hoc group of experts responsible for improving the quality control of both soil and soil solution analyses performed in the national laboratories. At the "Quality assurance and quality control in laboratories performing the deposition analyses of the Pan-European Programme of Intensive Monitoring of Forest Ecosystems" meeting (JRC ISPRA, 14-16 May, 2001, Rembges and Geiss, 2001), it was decided that France and Finland should organise a Pan-European laboratory ring test that would include both deposition and soil solution samples. Although most of the laboratories actively participate in both national and international ring tests, e.g. the Aquacon-MedBas Project (Subprojects No. 5 Freshwater analysis, No. 6 Acid rain analysis) arranged by Dr. Mosello from the Italian Institute of Hydrology of the National Research Council, there has been some concern about the fact that the samples used in such ring tests do not always correspond to the type of samples analysed within the ICP Forests programme. For instance, both stand throughfall and soil solution samples frequently have relatively high dissolved organic carbon (DOC) concentrations, and in certain areas sea salt (NaCl) concentrations are high. These components can have a considerable effect on the analysis results.

I.I. Aims

The aim of the pilot study was to carry out a laboratory working ring test between the national laboratories participating in the ICP Forests programme, using natural throughfall and soil solution samples covering the range of sea salt, DOC, aluminium (soil solution) and nitrogen and sulphur concentrations that are encountered in the participating countries.

2. IMPLEMENTATION OF THE WORKING RING TEST

2.1. The water samples

Bulk precipitation, stand throughfall, stemflow and soil solution samples were collected in autumn 2001 in France and Finland and delivered to the laboratory of the Rovaniemi Research Station in December 2001. The samples from Finland were kept in a deep freeze, and those from France in a cold room, up until pre-treatment in January 2002. The type and origin of the samples are given in Table 2.1.

2.2. Preparation of the samples

A total of six synthetic samples were prepared. SYN-Ia and SYN-Ib were used for measuring pH and alkalinity, SYN-2a and SYN-2b for electrical conductivity, SYN-3 for determining anions (nitrate, sulphate and chloride), cations (sodium, potassium, magnesium, calcium and ammonium), total nitrogen and dissolved organic carbon (DOC), and SYN-4 for metals and other elements (Al, Cu, Fe, Mn, P, S, Si and Zn).

Sample code	Type of sample	Characteristic	Origin of the sample
WAT-I	Bulk deposition	Low salt site	Fontainebleau, France (CPS 77)
WAT-2	Bulk deposition	Low salt site	Rovaniemi, northern Finland
WAT-3	Throughfall	Coniferous stand (Picea abies)	Northern Alps, France (site EPC 74)
WAT-4	Throughfall	Broadleaved stand (Quercus)	Fontainebleau, France (site CPS 77)
WAT-5	Throughfall	Coniferous stand (Pinus pinaster)	France (site PM 85)
WAT-6	Throughfall	Coniferous stand (Pinus sylvestris)	Southern Finland
WAT-7	Stemflow	Broadleaved stand (Fagus sylvatica)	Southern Cevennes Mountains, France (site HET 30)
WAT-8	Soil solution	Broadleaved stand (Fagus sylvatica)	Southern Cevennes Mountains, France (site HET 30)
WAT-9	Soil solution	Coniferous stand (Pinus sylvestris)	Southern Finland

 Table 2.1. Description of the samples used in the ring test.

Synthetic samples 1, 2 and 3 were prepared by dissolving analysis grade reagents in deionised water and diluting to the desired volume. SYN-4 was prepared by diluting 1000 ppm commercial standard solutions prepared from ampoules with Milli-Q water, and then diluting to the desired volume. SYN-4, which was prepared for determining metals, was acidified with 65% ultrapure nitric acid (5 ml/L)

All the natural samples were filtered over positive pressure through a glass fibre pre-filter (Whatman GF/A) and a membrane filter (Schleicher & Schüll, ME 25, pore size 0.45 μ m) by means of a peristaltic pump. The samples were filtered directly into acid-washed, 100 litre containers fitted with a tap. The samples were analysed immediately after filtration for the relevant parameters.

The samples were dispensed into 250 and 500 ml bottles (HDPE) and kept in a cold room before dispatch. The cleanliness of the sample bottles was tested before use by adding Milli-Q water to randomly chosen bottles. After shaking for one day the pH and electrical conductivity was measured. The bottles were found to be clean.

Two sets of parallel samples were prepared for the different analyses: one (set A) without acidification, and the other (set B) acidified with 65% ultrapure nitric acid (5 ml/L).

2.3. Homogeneity of the samples after filtration

Homogeneity was tested by measuring pH and electrical conductivity, and determining DOC and metals and other elements, on six to ten randomly selected bottles representing each sample. Anions and cations were analysed on the samples in four randomly selected bottles. The relative standard deviation was calculated for all the variables. No variation was found between the randomly selected samples, and they were therefore considered to be homogeneous.

2.4. Stability of the samples

The stability of all the samples to be analysed in the ring test was tested by carrying out the analyses on six occasions during the three-week period following preparation of the samples (overlapping the period when the analyses were to be performed in the participating laboratories). The relative standard deviation was calculated for all the variables, and the composition of the samples was found to have remained stable over the period in question.

Long-term stability was tested by measuring all the parameters (excluding total nitrogen) approximately three months later. The samples were found to have remained relatively stable.

The standard deviations of the analytical methods were determined by measuring the variables ten times during a period of one week, and the relative standard deviation was calculated.

2.5. Dispatch of the samples

The natural and synthetic samples were dispatched to the participating laboratories by DHL Express, who promised delivery within 2-3 days to almost all of the laboratories. The samples were packed in an insulated box containing cold packs in order to keep the samples cool for as long as possible. The box also contained a list of the samples, and the laboratories were asked to check the list against the samples actually in the box, and report (by FAX) about the condition and date of arrival of the samples. Four of the laboratories that received the samples surprisingly <u>did</u> not check the list of samples enclosed in the delivery and FAX confirmation of receipt back to the organizers, even though this was clearly stated on the form. However, they did inform us by e-mail that "some" samples had arrived! This procedure should be an integral part of quality assurance and control in laboratories that regularly receive water samples to be analysed. The organizers needed this information to ensure that delivery had in actual fact been made, and also to obtain feedback information about the condition of the samples. The three boxes of samples sent to laboratories in Russia were not delivered to their final destination due to the excessive customs duties imposed by the customs authorities in St. Petersburg on each delivery. New samples were subsequently personally delivered to the three laboratories by car.

As the samples were relatively sterile (prefiltered through a 0.45µm membrane filter), which will have considerably lengthened their shelflife, the samples are not likely to have suffered from any deterioration during transport within a reasonable period of time. In fact, almost 60% of the samples were received within 3 days of dispatch, and 75% within 5 days (Fig. 2.1.). Three boxes of samples took 7 days to reach the laboratories owing to hold-ups and mistakes attributable to DHL. The excessively long period of 10 days for the samples sent to Cyprus was due to hold-ups at London Airport, and to the fact that Monday Ist of February was a national holiday in Cyprus. The logistical problems involved in sending samples by express delivery to countries in different parts of Europe will be taken into account in the coming ring tests.



Fig. 2.1. The length of time (days) between dispatch and arrival at the participating laboratories.

3. METHODS

3.1. Presentation of the results and numerical calculation

3.1.1. Graphical presentation of the results

The results for each variable and the number of laboratories that used a specific analytical method (bars on the left side) are presented in graphs for the natural (WATI-9) and synthetic (SYNI-4) samples (box-and-whiskers plots) (example in Fig. 3.1). For each sample and each analytical method (acronyms in Table 5.1), the interval between the mean value minus and plus one standard deviation is indicated by the line (all data) and the box (after outlier rejection). The scale on the left axis refers to the number of laboratories (bar plot), while the scale and the unit on the right axis refer to the results.

3.1.2. The Youden plot

The data are also presented graphically using the Youden plot (Youden, 1959; Youden and Steiner, 1975). This procedure uses the data relative to two samples, with concentrations very close to each other and which have been analysed with the same analytical method, that are plotted in a scatter diagram compared to the expected values or, alternatively, the median values of the results. This makes it possible to distinguish between random and systematic errors affecting the results (Fig. 3.2). The diagram is divided into four quadrants by a vertical and a horizontal line representing the expected values for the two samples. In a hypothetical case, when the analysis is affected by random errors only, the results will be spread randomly over the four quadrants. However, the results are usually located in the lower left and the upper right quadrants, forming a characteristic elliptical pattern along the line passing through the origin and the point representing the expected values. This is due to systematic errors that underestimate or overestimate the concentrations in both samples.

The acceptance limit of the results is represented by an ellipse centred at the expected values, i.e. at the intersection of the two straight lines in the diagram. The distance between the centre of

the ellipse and the data point representing the laboratory is a measure of the total error of the results. The distance along the main axis of the ellipse gives the magnitude of the systematic error, while the distance perpendicular to this axis indicates the magnitude of the random error. In conclusion, the location of the data point for a specific laboratory in the Youden plot gives important information about the size and type of analytical error, which assists in identifying the causes of the error.



Fig. 3.1. Example of presentation of the results.

3.1.3. Detection of the outliers, and the z score

Outliers were detected using Grubbs (1969) test, reported in Soakal and Rohlf (1981). The test, which requires more than 25 measurements, is based on the ratio:

Where YI is the suspected outlier, Ymed is the sample mean, and sd is the standard deviation of the sample. A table of significance of G is given by Soakal and Rohlf (1981).

Z scores are computed from the results after the rejection of outliers. This variable permits quantification of the performance of a laboratory, since it gives an estimate of the bias of the result of a laboratory from the mean of the results. It is given by:

$$Z = (YI-Ymed)/sd$$

where YI is the analytical result of the laboratory, Ymed and sd are the mean and standard deviation of the results, respectively, after the rejection of outliers. Alternatively, sd can be substituted with a target value of dispersion, which could be used in successive interlaboratory exercises in order to identify general trends for a laboratory or a group of laboratories. Z indicates the number of times the measured value deviates from the mean, which is considered as

the most reliable value, using I sd as unit. Thus z = 0 means that the laboratory's measured value is the same as the mean; z = 1 (1.5, 2...) the measured value deviates (+ higher, - lower) from the mean by I (1.5, 2...) standard deviation. The z score can be expressed in terms of the probability of the result of a laboratory being included in the distribution of the results around the mean. Assuming that this distribution is normal, 68.3% of the values should fall between ± 1 sd around Ymed (± 1 z score), 95.5% between ± 2 sd (± 2 z scores) etc.



Fig. 3.2. Examples of Youden's plots.

3.1.4. Estimation of the detection and quantification limits for analytical methods

The use of natural samples resulted in problems with some of the variables because the values were too low to be quantified. As a result, it was not possible to perform statistical analyses. In this context we used the definition of limit of detection (LOD) and limit of quantification (LOQ) as given by the ACS Committee on Environmental Improvement (1989). The limit of detection is defined as the lowest concentration of the analyte that the analytical process can reliably detect. The estimation of LOD is based on the relationship between the gross analyte signal St, the field blank Sb, and the variability in the field blank σ_b . LOD can be defined by the extent to which the gross signal exceeds Sb:

$$St - Sb > Kd \sigma_{h}$$

where a value of 3 is assumed for Kd. The quantification of the concentration (amount) of analyte is considered reliable when:

$$St - Sb > Kt \sigma_b$$

where a value of 10 is assumed for Kt.

The values of LOQ were estimated for the most widely used analytical methods, and the values in the individual natural samples (WAT-1...9) that were lower than these threshold values were rejected.

3.2. Validation of the results for major ions

3.2.1. The ionic balance

When the concentrations of all the major ions and the electrical conductivity are measured in a water sample, one important check of the data quality is evaluation of the ionic balance, i.e. comparing the sum of anions and cations, and estimating the electrical conductivity calculated from the concentrations of each ion multiplied by the equivalent ionic conductance. These very simple checks of the internal consistency of the analyses are strongly recommended in order to verify the correctness of the analyses, as well as to detect other possible sources of error, such as incorrect transcription.

The basic assumption in evaluation of the ionic balance is that the determinations of pH, NH_4^+ , Ca^{2+} , Mg^{2+} , Na^+ , K^+ , HCO_3^- , SO_4^{2-} , NO_3^- and Cl^- account, almost completely, for all the ions present in a solution. At pH values higher than 6.5, the hydrogen ion concentration can be ignored. In most cases the F⁻ concentration is negligible in terms of the ionic balance. On the other hand, the ionic balance in water samples can be strongly influenced by the presence of large amounts of organic matter.

The ionic balance test is based on the electro-neutrality of water samples (soil solution, bulk deposition, stand throughfall). The total number of negative and positive charges must be equal. This can be checked using milli (or micro) equivalents per litre (meq l^{-1} or μ eq l^{-1}) as the concentration unit. The constants required to convert the units used in the ring test into μ eq l^{-1} are given in Table 3.1

Table 3.1. Conversion of concentrations from mg $|\cdot|$ to $\mu eq |\cdot|$, and the equivalent conductance at infinite dilution of the individual ions.

	Unit	Factor to µeq I-1	Equivalent conductance at 20°C	Equivalent conductance at 25°C
			S cm² eq ⁻¹	S cm ² eq ⁻¹
pН		I O (6-pH)	315.1	350.0
Ammonium	mg N I-I	71.39	67.0	73.5
Calcium	mg l-I	49.9	54.3	59.5
Magnesium	mg l-I	82.24	48.6	53.1
Sodium	mg l-I	43.48	45.9	50.1
Potassium	mg l-1	25.58	67.0	73.5
Alkalinity	meq I-I	1000	39.4	44.5
Sulphate	mg S I-1	62.37	71.2	80.0
Nitrate	mg N I ⁻¹	71.39	63.6	71.4
Chloride	mg l-I	28.2	68.0	76.4
Fluoride	mg l-I	52.63	49.1	54.4

The limit of acceptable errors varies with the total ionic concentrations and the nature of the solution. With Σ Cat and Σ An indicating the concentrations (meq l⁻¹ or μ eq l⁻¹) of cations and anions, respectively, and Alk the Gran alkalinity:

$$\Sigma \text{ An} = \text{Alk} + [\text{SO}_{4}^{-}] + [\text{NO}_{3}^{-}] + [\text{Cl}_{3}^{-}]$$

$$\Sigma$$
 Cat =[Ca⁺⁺] +[Mg⁺⁺]+ [Na⁺]+ [K⁺]+[NH₄⁺]+[H⁺]

we can define the per cent difference (PD) as:

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

PD thresholds for accepting analytical results are proposed in Table 3.2. In the ring test, alkalinity was assumed to be wholly due to bicarbonate, which is a correct assumption over the pH range 6.0-8.5. Furthermore, in natural clear water samples other substances affecting alkalinity (i.e. organic acids, sulphides, etc.) must be negligible. In the case of stand throughfall or soil solution samples that have relatively high DOC concentrations, on the other hand, much higher PD-values can be expected and do not necessarily indicate analytical errors. The organic matter (i.e. DOC) in such samples acts as anion with varying negative charge. Higher values can indicate a lack of precision in one or more analytical techniques, the omission of important ions, or high DOC concentrations.

3.2.2. Comparison between measured and calculated conductivity

Conductivity is a measure of the ability of an aqueous solution to carry an electric current. It depends on the type and concentrations of ions, and on the temperature of measurement. It is defined as:

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

where G = I/R is the conductance (unit: ohm⁻¹, or siemens; ohm⁻¹ is sometimes written as mho), defined as the reciprocal of resistance (R, unit ohm); A (m²) is the electrode surface area, L (m) is the distance between the measuring electrodes.

In the International System of Units (SI), conductivity is expressed as siemens per meter (S m⁻¹); this unit, as well as the submultiple μ S cm⁻¹, are also used by the IUPAC. In practice the unit μ S cm⁻¹, where I mS m⁻¹ = 10 μ S cm⁻¹ = 10 μ mho cm⁻¹, is also commonly used.

Conductivity depends on the type and concentration (activity) of 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 (u_i , unit: S cm² eq⁻¹). Values of equivalent conductance of the main ions at 20 and 25 °C are presented in table 3.1.

The dependence of conductivity on temperature makes it necessary to use a "reference" temperature, assumed in the ISO standard 7888-1985 and in the ICP Forests program as 25 °C. The variation of equivalent conductance with temperature is not the same for all the ions (e.g. Pungor, 1965), so that the function of conductivity with temperature will depend on the chemical composition of the solution.

The values of correction of conductivity for temperature are therefore a simplification, performed assuming a "standard composition" for surface water (e.g. Rodier, 1984); this can introduce a systematic error in the case of a different chemical composition, as is the case for atmospheric deposition chemistry.

Of course this is also true if the correction is made automatically by the conductivity meter. For this reason it is suggested that the measurement be made as close as possible to 20 $^{\circ}$ C (e.g. in the range 18-22 $^{\circ}$ C).

A careful, precise conductivity measurement is a further means of checking the results of chemical analyses. It is based on a comparison between measured conductivity (CM) and the conductivity calculated (CE) from individual ion concentrations, multiplied by the respective equivalent ionic conductance (λ_i):

$$\mathsf{CE} = \Sigma \lambda_i \mathbf{C}_i$$

The ions are the same as those considered in calculating the ionic balance; the values of λ_i for the different ions at temperatures of 20 and 25 °C are given in Table 3.1. It is assumed that the bicarbonate ion accounts for almost all the alkalinity; this assumption is correct for solutions with pH in the range 6.0 - 8.5.

The percent difference, CD, is given by the ratio:

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

At low ionic strength (below 0.1 meq l^{-1}) of high altitude lakes or atmospheric deposition samples, the discrepancy between measured and calculated conductivity should be no more than 2% (Miles and Yost, 1982).

lonic strength (IS), in meq l^{-1} , can be calculated from the individual ion concentrations as follows:

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

where c_i = concentration of ion i in mg l⁻¹, z_i = absolute value of the charge for ion l, and w_i = gram molecular weight of ion i.

For ionic strengths higher than 0.1 meq l^{-1} , as is the case in most surface water draining from calcareous soils and bedrock, and in most of the throughfall and stemflow samples, a correction of the calculated conductivity can be used, as proposed e.g. by A.P.H.A., A.W.W.A., W.E.F. (1998). The proposed method uses the Davies equation for IS lower than 0.5 meq l^{-1} and for temperatures from 20 and 30 °C, in order to calculate the monovalent ion activity y:

$$y = 10^{(0.5 (IS^{0.5}/(1+IS^{0.5})-0.3 IS))}$$

Finally, the calculated conductivity is obtained as:

$$CE = y^2 * CE$$

CD = 100 * (CE-CM)/CM

The ion balance and conductivity check should be performed immediately after all the analyses have been completed, so that analyses can be repeated if the desired quality threshold is not reached. These threshold values should be defined in relation to the aims of the laboratory and the type of sample. Threshold values proposed for the ICP Forest program are given in Table 3.2.

Table 3.2. Threshold values for checking the analyses on the basis of the ion balance and conductivity.

	IS < 0.1	meq I ⁻¹	0. < S < (0.2 meq l [.] l	IS > 0.2 meq l ⁻¹			
	open field	throughfall stemflow	open field	throughfall stemflow	open field	throughfall stemflow		
Ion balance, PD	± 25%	-	± 10%	-	± 10%	-		
Conductivity, CD	± 15%	± 15%	± 15%	± 15%	± 10%	± 10%		

4. THE LABORATORIES PARTICIPATING IN THE RING TEST

A total of 59 laboratories participated in the ring test:

Austria	Institute of Pollutant Research and Forest Chemistry, Federal Forest Research Centre, Vienna
Belgium	Laboratory of Soil Science, Department of Geology and Soil Science, Gent University, Gent
Belgium	UCL - Unité des Eaux & Forêts, Louvain-la-Neuve
Cyprus	Analytical Laboratories, Department of Agriculture, Nicosia
Czech Republic	Testing Laboratories of Forestry and Game Management Research Institute, Prague
Denmark	Forest Research Laboratory, Danish Centre for Forest, Landscape, and Planning, Hörsholm
Denmark	ATMI, National Environmental Res. Inst, Roskilde
Estonia	Tartu Environmental Research, Tartu
Finland	Rovaniemi Research Station, the Finnish Forest Research Institute, Rovaniemi
France	SGS-Laboratoires Wolff Environnement, Evry Cedex
Germany	Bayerische Landesanstalt für Wald und Forstwirtschaft, Freising
Germany	Ökologische Gutachten und Labor, Berlin
Germany	Institute of Ecology, Soil Science Department, Berlin
Germany	Landesforstamt Eberswalde, Abt. Waldökologie/Labor, Eberswalde
Germany	Forstliche Versuchs- und Forschungsanstalt, Abt. Bodenkunde und Waldernaehrung, Freiburg
Germany	Institute of Soil Science and Forest Nutrition, Göttingen University
Germany	Federal Institute for Geosciences and Natural Resources, Hannover
Germany	LUFA Hessen, Kassel
Germany	Thüringer Landesanstalt fur Landwirtschaft, Jena
Germany	Umweltbundesamt Außenstelle Langen Labor für Experimentelles Monitoring, Langen
Germany	Niedersächsische Forstliche Versuchsanstalt Abt. D, Sachgebiet Umweltanalytik, Göttingen
Germany	Landesumweltamt NRW, Fachbereich 23.2, Recklinghausen
Germany	Landwirtschaftliche Untersuchungs- und Forschungsanstalt der LMS (LUFA Rostock der LMS), Rostock
Germany	Umweltforschungszentrum der Universität des Saarlandes, AG Forst, Saarbrucken
Germany	Analytical Laboratory, Department of Soil science and Plant Nutrition, Saxon State Institute for Forestry, Pirna OT Graupa
Germany	Landesuntersuchungsamt Sachsen-Anhalt, Aussenstelle Halle-Lettin, Halle
Germany	Oekologie-Zentrum, University of Kiel, Kiel
Germany	Landeslabor Schleswig-Hostein, Kiel
Germany	Landwirtschaftliche Untersuchungs- und Forschungsanstalt Speyer, Speyer
Greece	Forest Soils, Forest Research Institute of Athens
Hungary	Dept. of Ecology, Forest Research Institut, Budapest
Ireland	FERG, ERM, Dept. Ag. Faculty UCD, Dublin
Italy	Laboratorio Biologico Provinciale, Laives

Italy	IRSA-CNR Water Research Institute – National Research Council, Brugherio
Italy	Department of Environmental Science, Siena
Italy	CNR Institute of Ecosystem Study, Verbania Pallanza
Latvia	Latvian Hydrometeorological Agency - ICP-IM National Focal Point, Laboratory Department of Latvian Environment Agency, Riga
Lithuania	Forest Soils Laboratory, the Lithuanian Forest Seed and Forest Tree Breeding Centre, Kaunas
Lithuania	Environmental Physics and Chemistry Laboratory, Institute of Physics, Vilnius
Luxemburg	Centre de Recherche Public
The Netherlands	Alterra, Wageningen
The Netherlands	Energieonderzoek Centrum Nederland, Petten
Norway	Norwegian Forest Research Institute, Ås
Poland	Forest Site Department, Forest Research Institute, Raszyn
Portugal	Laboratório de Análise Instrumental, Azores
Portugal	Laboratorio Quimico Agricola Rebelo da Silva (LQARS), Lisbon
Portugal	SAGILAB, Laboratório de Análises Técnicas, Lda., Porto
Russia	State Unitar Enterprise "Water Research and Control Centre", St. Petersburg
Russia	Analytical Forest Soil laboratory of the Forest Research Institute of the Karelian Research Centre, Russian Academy of Sciences, Petrosavodsk
Russia	Laboratory of Nature Investigations, the Scientific Research Centre of Ecological Safety of Russia, attached to Russian Academy of Sciences and the company "VA-Instrument", St. Petersburg
Slovakia	Laboratory of the Department of Forest Environment, Forest Research Institute, Zvolen
Slovenia	Laboratory of Forest Ecology, Department of Forest Ecology, Slovenian Forest Institutute, Ljubljana
Spain	Laboratory of Forest Ecosystems and Agrobiosystems, Department of Environment INIA, Madrid
Spain	Fundación Centro de Estudios Ambientales del Mediterráneo (CEAM), Valencia
Sweden	Swedish Environmental Research Institute, IVL, Gothenburg
Switzerland	Eidg. Forschungsanstalt für Wald, Schnee und Landschaft (WSL/FNP) Zentrallabor, Birmensdorf
United Kingdom	Environmental Research Laboratory, Forest Research Station, Farnham
United Kingdom	Fisheries Research Services Freshwater Laboratory, Pitlochry, Perthshire

5. RESULTS

5.1. Analytical methods used

The list of analytical methods used by the participating laboratories is presented in Table 5.1. Ion chromatography, using chemical suppression of the eluent (IC-CS), is the most widely used technique for sulphate, nitrate and chloride. The most extensively used technique for cations is ICP optical emission spectrometry (ICP-OES), followed by IC-CS and atomic absorption spectrometry (AAS). ICP-OES is used for most of the metal analyses, while the number of methods used in the spectrophotometric determination of ammonium, total N and total P, and for the acidimetric determination of alkalinity, is much higher. The type of method used has been taken into account in the presentation of the results, and in evaluating the results and the number of outliers (see Section 3.1). Some aspects of the performance of the individual methods are discussed in the presentation of the results for the individual chemical variables.

5.2. Chemical characteristics of the samples

The samples used in this exercise (see list in Section 2.1) were natural precipitation samples collected in the open field (WAT-1, -2), under the canopy, i.e. stand throughfall (WAT-3, -4, -5, -6), and a stemflow sample (WAT-7), and two natural soil solutions (WAT-8, -9) and a number of synthetic samples prepared in the laboratory for the measurement of pH and alkalinity (SYN-1a, b), of conductivity (SYN-2a, b) and of the major ions (SYN-3). Metals were determined in all of the natural samples and in synthetic sample SYN-4. The results obtained for the whole set of laboratories, expressed as median values (all results), mean values (after outlier rejection) and the standard deviation (after outlier rejection), are presented in Tables 5.2, 5.3 and 5.4. Values below

the quantification limit of the most commonly used analytical techniques have been omitted in the tables, as well as in the subsequent data analysis.

The ion balance of the samples, based on the mean values of the concentrations, are presented in Figures 5.1 a, b, c. The first figure compares all the samples, natural and synthetic, used in the exercise. The samples were divided on the basis of the ion concentrations: sample WAT-5 (total ion concentration 2159 μ eq l⁻¹) clearly differs from the others (range 67-380 μ eq l⁻¹), because of the higher marine contribution, indicated by the high chloride, sodium and magnesium concentrations. The concentrations of the main ions in samples WAT-2 and WAT-1 (67 and 122 μ eq l⁻¹) are very low, while for WAT-6, 7 and 8 they range between 172 and 242 μ eq l⁻¹. The concentrations in samples WAT-3, 4 and 9 (350-380 μ eq l⁻¹) and in synthetic sample SYN-3 (283 μ eq l⁻¹) are slightly higher.

The DOC concentrations in WAT-1, 2, 7 and 8 are below 5 mg C l^{-1} , slightly above 5 mg C l^{-1} in WAT-9 and SYN-4, and more than 10 mg C l^{-1} in WAT-3, 4, 5 and 6. The phosphate concentrations were below the quantification limit in most of the samples, WAT-6 having the highest mean value (0.088 mg P l^{-1}).

The metal concentrations were below the quantification limit in most of the natural samples, although the values for AI, Mn and Zn in some of the samples could be determined quantifiably. The concentrations in SYN-4 were above the quantification limit.

Chemical	Acronym	Analytical method	Number	
variable			of labs	
pН	LIS	Low ionic strength electrode	16	
	GEN	Not specified	40	
Conductivity	25°	Measurement performed at 25°C	20	
	Corr	Measurement at different temp, and corrected to 25°C	34	
Alkalinity	PT EX 2PF	Potentiometric titration, two end-points	14	
	PT_EX Gran	Potentiometric titration, Gran titration	8	
	PT_1 4.3	Potentiometric titration, one end-point	5	
	PT_1 4.5	Potentiometric titration, one end-point	8	
	CT Met	Colorimetric titration, methyl orange indicator	3	
Sulphate	IC CS	lon chromatography, chemical suppression	39	
	IC WS	Ion chromatography, no suppression	5	
	CF Met	Continuous flow, Ba sulphate excess, methyl thymol	2	
	ICP OES	ICP optical emission spectrometry	2	
Nitrate	SPEC Phe	Spectrophotometry, phenoldisulphonic acid	2	
	CF Cd	Continuous flow, cadmium reduction	7	
	IC CS	Ion chromatography, chemical suppression	38	
	IC WS	Ion chromatography, no suppression	5	
Chloride	IC CS	lon chromatography, chemical suppression	39	
	IC WS	lon chromatography, no suppression	4	
	CF HgFe	Continuous flow, Hg thiocyanate in presence of ferric ion	6	
	TIT_Ag Cr	Silver nitrate titration, potassium chromate indicator	2	
Ca, Mg	AAS	Atomic absorption spectrometry	13	
-	IC CS	Ion chromatography, chemical suppression	14	
	ICP OES	ICP optical emission spectrometry	26	

 Table 5.1. Analytical methods used and the acronyms used in the figures.

Table 5.1. Continuation

Chemical variable	Acronym	Analytical method	Number of labs
Na, K	AAS	Atomic absorption spectrometry	6
	AES	Atomic emission spectrometry	6
		Ion chromatography, chemical suppression	16
		icr optical emission spectrometry	25
Ammonium	SPEC Nes	Spectrophotometry, Nessler	5
	SPEC Phe	Spectrophotometry, indophenol blue	12
	CF GD	Continuous flow, ammonia diffusion	7
	CF Phe	Continuous flow, indophenol blue	13
	IC CS	Ion chromatography, chemical suppression	13
	IC WS	Ion chromatography, no suppression	3
DOC	THIR	Thermal combustion, IR detection	24
	PSH_UV IR	Persulphate and UV oxidation, IR detection	4
	_		
Phosphate	SPEC Mor	Spectrophotometry	12
	CF Mor	Continuous flow,	6
	IC CS	lon chromatography, chemical suppression	11
Total P	ICP OES	ICP optical emission spectrometry	17
	ICP MS	ICP mass spectrophotometry	3
	PSH SPEC Mor	Persulphate oxidation, spectrophotometry molybdate	4
Total Sulphur	ICP OES	ICP optical emission spectrometry	16
	ICP MS	ICP mass spectrophotometry	2
Total Nitrogen	CF Cd	Continuous flow, hydrazine reduction	8
	CF Cu_Hyd	Continuous flow, cadmium reduction	2
	CHML	Chemioluminescence	7
	KJELD	Kjeldahl	6
	SPEC UV220	Spectrophotometry, 220 nm	3
Silica	SPEC Moxr	Spectrophotometry, molybdate and reduction	5
	ICP OES	ICP optical emission spectrometry	12
AI	AAS Flame	Atomic absorption spectrometry, flame	2
	AAS GFA	Atomic absorption spectrometry, graphite furnace	7
	ICP OES	ICP optical emission spectrometry	25
	ICP MS	ICP mass spectrophotometry	5
Cu	AAS Flame	Atomic absorption spectrometry, flame	2
	AAS GFA	Atomic absorption spectrometry, graphite furnace	9
	ICP OES	ICP optical emission spectrometry	14
	ICP MS	ICP mass spectrophotometry	5
Fe	AAS Flame	Atomic absorption spectrometry, flame	2
	AAS GFA	Atomic absorption spectrometry, graphite furnace	7
	ICP OES	ICP optical emission spectrometry	25
	ICP MS	ICP mass spectrophotometry	3

Table 5.1. Continuation

Chemical variable	Acronym	Analytical method	Number of labs
Mn	AAS Flame	Atomic absorption spectrometry, flame	4
	AAS GFA	Atomic absorption spectrometry, graphite furnace	5
	ICP OES	ICP optical emission spectrometry	26
	ICP MS	ICP mass spectrophotometry	4
Zn	AAS Flame	Atomic absorption spectrometry, flame	3
	AAS GFA	Atomic absorption spectrometry, graphite furnace	5
	ICP OES	ICP optical emission spectrometry	21
	ICP MS	ICP mass spectrophotometry	4

Variable		Unit															
			WAT-I	WAT-2	WAT-3	WAT-4	WAT-5	WAT-6	WAT-7	WAT-8	WAT-9	SYN-1a	SYN-Ib	SYN-2a	SYN-2b	SYN-3	SYN-4
pН			5.13	4.71	4.95	5.92	5.32	5.12	5.44	5.91	4.75	7.00	6.65			4.90	
Conductivity		µS cm-I 25 °C	11.8	11.6	31.0	27.2	140.7	16.0	16.0	17.9	36.4			45.0	59.6	28.9	
Alkalinity		mmol I-I	0.013			0.072	0.025	0.023	0.020	0.030		0.254	0.124				
Sulphate	S-SO4	mg S I-1	0.29	0.22	0.63	0.50	2.07	0.40	0.58	0.52	2.96					0.69	
Nitrate	N-NO3	mg N I-I	0.301	0.207	1.117	0.209	0.710	0.108	0.357	0.372	0.022		ĺ			0.320	
Chloride	Cl	mg l-1	0.62	0.35	1.75	1.89	31.90	0.94	1.31	1.38	1.66					1.94	
Calcium	Ca	mg l-1	0.37		1.51	1.46	1.90	0.36	0.55	0.90	1.21		ĺ			0.43	
Magnesium	Mg	mg l-1	0.05		0.24	0.38	2.34	0.15	0.15	0.17	0.55					0.25	
Sodium	Na	mg l-1	0.22	0.18	0.55	0.58	17.47	0.36	0.82	0.64	2.57					0.51	
Potassium	К	mg l-1	0.54		1.83	3.06	2.46	1.99	0.83	1.21	0.11					3.16	
Ammonium	N-NH4	mg N I-I	0.150	0.081	0.490	0.295	0.365	0.034	0.127	0.230	0.014		ĺ			0.479	
Total nitrogen	Tot N	mg N I-I	0.59	0.30	1.94	0.84	1.30	0.38	0.59	0.77	0.51					0.82	
Phosphate	P-PO4	mg P I ⁻¹	0.017			0.021		0.091					ĺ			0.009	
DOC		mg -1	1.00	2.10	10.64	12.16	10.55	12.08	2.31	4.55	7.65					5.81	
	A1	.			25				120	90	250						909
Aluminum	AI	µg I-'			25				138	90	350						809
Copper	Cu	µg I-'			10	14	12			10	40						83
Iron	Fe	µg I-1			19	14	13	100		20	40						210
Manganese	Mn -	µg I-1			31	243	18	103	22	39	11						109
	Zn	µg I-'			25	29	16	16	13	17							99
I otal phosphorus	۲ ۲	mg I-1			0.70	0.031	2.17	0.104	0.50	0.54	2.40						0.79
I otal sulphur	S	mg I-1			0.73	0.61	2.17	0.49	0.58	0.56	3.69						1.97
Silicon	Si	mg I-1								0.26	0.17						0.14

Table 5.2. Median values, all data. Dark grey = concentrations below the quantification limit, light grey = not to be determined.

Variable		Unit															
			WAT-I	WAT-2	WAT-3	WAT-4	WAT-5	WAT-6	WAT-7	WAT-8	WAT-9	SYN-1a	SYN-Ib	SYN-2a	SYN-2b	SYN-3	SYN-4
pН			5.14	4.73	4.96	5.95	5.30	5.16	5.45	5.89	4.77	6.93	6.62			4.92	
Conductivity		µS cm ⁻¹ 25 °C	12.0	11.4	30.5	26.9	138.8	15.7	15.8	17.6	36.3			45.1	59.5	28.5	
Alkalinity		mmol ŀ'	0.02			0.07	0.03	0.02	0.03	0.03		0.24	0.13				
Sulphate	S-SO4	mg S I ⁻¹	0.29	0.22	0.63	0.50	2.06	0.39	0.57	0.52	2.97					0.68	
Nitrate	N-NO3	mg N I-1	0.295	0.202	1.118	0.206	0.712	0.108	0.353	0.371	0.025					0.318	
Chloride	Cl	mg -1	0.62	0.35	1.73	1.97	31.98	0.94	1.31	1.39	1.64					1.94	
Calcium	Ca	mg -1	0.37		1.50	1.48	1.91	0.37	0.53	0.89	1.20					0.43	
Magnesium	Mg	mg -1	0.05		0.24	0.38	2.34	0.15	0.15	0.17	0.55					0.25	
Sodium	Na	mg l-1	0.22	0.18	0.55	0.58	17.25	0.36	0.81	0.62	2.56					0.51	
Potassium	К	mg -1	0.53		1.82	3.04	2.46	1.97	0.81	1.20	0.11					3.10	
Ammonium	N-NH4	mg N I ⁻¹	0.144	0.077	0.498	0.289	0.384	0.029	0.126	0.230	0.016					0.468	
Total nitrogen	Tot N	mg N I-I	0.62	0.32	1.95	0.89	1.33	0.38	0.60	0.78	0.53					0.84	
Phosphate	P-PO4	mg P I-I	0.021			0.024		0.088								0.008	
DOC		mg -1	1.07	1.96	10.52	12.17	10.30	11.88	2.29	4.41	7.70					5.73	
Aluminum	AI	µg -1			25				137	88	353						800
Copper	Cu	µg I-1								10							83
Iron	Fe	µg -1			20	16	14				39						217
Manganese	Mn	µg -1			31	244	18	105	22	39	11						109
Zinc	Zn	µg -1			24	31	16	16	12	16							99
Total phosphorus	Р	mg l-1				0.064		0.101									0.786
Total sulphur	S	mg l-1			0.74	0.62	2.21	0.48	0.59	0.55	3.63						1.96
Silicon	Si	mg l-1								0.22	0.15						0.12

Table 5.3. Mean values after removal of outliers. Dark grey = concentrations below the quantification limit, Light grey = not to be determined.

Variable																
		WAT-I	WAT-2	WAT-3	WAT-4	WAT-5	WAT-6	WAT-7	WAT-8	WAT-9	SYN-1a	SYN-Ib	SYN-2a	SYN-2b	SYN-3	SYN-4
pН		0.20	0.08	0.16	0.17	0.17	0.16	0.19	0.18	0.09	0.18	0.16			0.11	
Conductivity		2.63	1.10	1.92	1.94	9.71	1.51	1.63	1.60	2.56			2.75	3.61	1.98	
Alkalinity		0.02			0.03	0.02	0.02	0.02	0.02	ns	0.06	0.05				
Sulphate	S-SO4	0.03	0.04	0.04	0.06	0.07	0.03	0.03	0.05	0.24					0.04	
Nitrate	N-NO3	0.05	0.03	0.06	0.02	0.03	0.02	0.02	0.03	0.03					0.02	
Chloride	CI	0.15	0.09	0.26	0.44	1.56	0.09	0.13	0.16	0.15					0.15	
Calcium	Ca	0.04		0.14	0.22	0.22	0.09	0.09	0.10	0.11					0.06	
Magnesium	Mg	0.02		0.02	0.04	0.15	0.02	0.02	0.02	0.03					0.03	
Sodium	Na	0.05	0.05	0.10	0.10	1.20	0.06	0.09	0.09	0.18					0.07	
Potassium	К	0.06		0.17	0.28	0.14	0.20	0.09	0.14	0.03					0.29	
Ammonium	N-NH4	0.02	0.01	0.09	0.06	0.09	0.01	0.02	0.02	0.01					0.08	
Total nitrogen	Tot N	0.19	0.13	0.10	0.17	0.25	0.11	0.18	0.13	0.21					0.09	
Phosphate	P-PO4	0.01			0.02		0.02								0.01	
DOC		0.48	0.57	1.04	1.31	0.92	1.01	0.34	0.44	0.51					0.46	
Aluminum	AI			4.4				30.4	8.8	47.9						58.40
Copper	Cu								1.0	ns						7.35
Iron	Fe			8.8	8.3	5.1	ns	ns	ns	4.2						27.49
Manganese	Mn			1.8	15.9	2.4	12.6	3.3	2.7	0.9						5.56
Zinc	Zn			4.0	10.6	3.6	4.3	1.5	2.9							15.74
Total phosphorus	Р				0.1		0.0									0.07
 Total sulphur	S			0.1	0.0	0.1	0.0	0.0	0.0	0.3						0.21
Silicon	Si								0.1	0.1						0.06

Table 5.4. Standard deviations after removal of outliers. Dark grey = concentrations below the quantification limit, light grey = not to be determined.



Fig. 5.1. lonic balances of the samples.

5.3. Overall performance of the laboratories

Before discussing in detail the results obtained for the different chemical variables, there are some aspects related to the different types of solution and analytical methods used that can have a bearing on the results (Table 5.5). The table highlights the relatively high number of values below the quantification limit of some of the variables, particularly metals, phosphate and total phosphate. This was mainly due to the fact that natural deposition and soil solution samples were selected for the ring test. The characteristics of the solutions are indicated by the range of variation of the median and mean values, before and after the removal of outliers. The individual solutions are described in detail in Tables 5.2, 5.3 and 5.4. Another feature apparent from Table 5.5 is the low number of laboratories that determined some of the variables, e.g. total nitrogen, DOC and alkalinity. This is surprising considering that they are mandatory under specific conditions for the analysis of either deposition or soil solution samples.

Table 5.5 also shows the proportion of measurements falling in different percent classes around the mean values. Two different intervals were applied, the first one for pH, conductivity, major ions and metals (within 10%, 10-20%, 20-30%, >30%), and the second for alkalinity, phosphate and total phosphate (within 30%, 30-50%, 50-100%, outside 100%). The difference between the groups of intervals clearly demonstrates the different precision obtained for the results of the second group of variables.

Variables	>QL	<ql< th=""><th><ql< th=""><th colspan="2" rowspan="2">Range median values</th><th colspan="2" rowspan="2">Range of mean values, outliers included</th><th colspan="2" rowspan="2">Range of mean values outliers excluded</th><th rowspan="2">Outliers No.</th><th rowspan="2">Outliers %</th><th rowspan="2">% results within ±10%</th><th colspan="3">% results</th></ql<></th></ql<>	<ql< th=""><th colspan="2" rowspan="2">Range median values</th><th colspan="2" rowspan="2">Range of mean values, outliers included</th><th colspan="2" rowspan="2">Range of mean values outliers excluded</th><th rowspan="2">Outliers No.</th><th rowspan="2">Outliers %</th><th rowspan="2">% results within ±10%</th><th colspan="3">% results</th></ql<>	Range median values		Range of mean values, outliers included		Range of mean values outliers excluded		Outliers No.	Outliers %	% results within ±10%	% results		
	No.	No.	%										10-20%	20-30%	> 30%
				Min	Max	Min	Max	Min	Max						
рH	682	0	0	4.71	7.00	4.73	6.93	4.73	6.93	21	3	64	15	9	11
' Conductivity	645	0	0	11.55	141	12	139	11	139	23	4	75	17	3	4
, Sulphate	519	I	0	0.22	2.96	0.25	3.03	0.22	2.97	63	12	73	11	4	13
Nitrate	504	44	8	0.02	1.12	0.06	1.19	0.02	1.12	61	12	61	13	5	21
Chloride	547	3	I	0.35	31.90	0.60	31.19	0.35	31.98	48	9	67	15	4	14
Calcium	533	26	5	0.04	1.90	0.12	1.91	0.07	1.91	44	8	61	14	8	16
Magnesium	526	33	6	0.02	2.34	0.03	2.31	0.02	2.34	26	5	66	17	5	12
Sodium	548	П	2	0.18	17.47	0.20	16.90	0.18	17.25	25	5	60	20	9	12
Potassium	539	33	6	0.03	3.16	0.19	3.18	0.03	3.10	39	7	63	17	5	15
Ammonium	499	48	9	0.01	0.49	0.03	0.53	0.02	0.50	41	8	50	15	8	27
Total N	308	15	5	0.30	1.94	0.37	1.91	0.32	1.95	20	6	51	16	6	26
DOC	305	8	3	1.00	12.16	2.10	13.17	1.07	12.17	36	12	55	19	7	19
Aluminium	288	73	21	2.95	809	26	794	3	800	25	9	47	21	11	21
Copper	221	92	30	I	83	1.01	89	0.75	83	22	10	34	12	11	43
Iron	287	98	26	5	210	14.47	210	5.83	217	33	11	36	12	9	43
Manganese	350	42	11	I	243	4.53	230	0.90	244	42	12	66	9	3	22
Zinc	285	34	11	3	99	4.63	96	3.94	99	16	6	45	20	14	21
Total S	174	16	8	0.22	3.69	0.32	4.13	0.22	3.63	22	13	65	17	5	12
Silicon	59	2	3	0.14	0.26	0.12	0.22	0.12	0.22	0	0	33	31	2	34
-												% results		% results	
												within ±30%	30-50%	50-100%	>100%
Alkalinity	353	56	15	0.00	0.25	0.00	0.26	0.00	0.24	8	2	29	9	40	22
Phosphate	180	179	50	0.00	0.09	0.02	0.25	0.00	0.09	30	17	27	14	24	36
Total P	I 40	137	49	0.01	0.79	0.03	1.09	0.01	0.79	23	16	50	7	12	32

 Table 5.5. Number of measurements above and below the quantification limit (QL) and summary.

For the major ions, apart from ammonium, the proportion of results within $\pm 10\%$ of the mean value ranges from 60 to 73%, with the highest value for sulphate and the lowest for sodium. For ammonium 50% of the values were within $\pm 10\%$, while 27% of the values are outside 30% of the mean. On the other hand, for these variables the proportion of values outside the range of $\pm 30\%$ was between 12 and 27%, and the proportion of outliers ranged from 5 (magnesium, sodium) to 12% (nitrate, sulphate).

Alkalinity, which was assumed to be mainly bicarbonate, gave the poorest results for the ions present in solution: only about 36% of the values were in the range of \pm 50%, while the values within 50-100% and outside \pm 100% were 40 and 22%, respectively.

5.4. pH and conductivity

The difference between measurements performed with low ionic strength electrodes (LIS) and other types of electrode (GEN) were checked in the results (Fig. 5.2, see annex). No relevant differences were found as regards either the mean values or the dispersion of the results; the apparently higher range of results for the second type of electrode (i.e. GEN) was due to the higher number of labs using this type of electrode (40 vs. 16 labs). The Youden plots show the prevalence of systematic over random errors; about one quarter to one third of the measurements are outside the range of ± 0.2 pH units.

The difference between conductivity measurements performed at 25°C and those made at a different temperature and then corrected to 25°C are compared in Fig. 5.3 (see annex). There were no significant differences between the two sets of data. The dispersion of the values was relatively high, as demonstrated by the results for sample WAT-5. The Youden plots also showed that several values are outside the range of $\pm 20\%$ of the median values for samples with a low ionic strength. On the other hand, the range of $\pm 20\%$ for samples with a higher conductivity appears to be too wide. For sample SYN-2a, which was prepared as a check sample for conductivity, it was $\pm 10-15 \ \mu\text{S cm}^{-1}$, which is in fact too high in relation to the analytical accuracy attainable with normal equipment, as well as for using the conductivity results as a check of the reliability of the analytical results for the major ion.

5.5. Alkalinity

The alkalinity measurements were one of the most critical of the analyses considered, both as regards missing results and of the associated dispersion and errors. If we exclude samples WAT-2, -3 and -9, the values of which were below the quantification limit (assumed to be 10 μ eg l⁻¹), then the proportion of missing measurements was between 30 and 60% of the maximum total number, with the highest proportion of missing values for those samples with the lowest alkalinity values. The proportion of missing values was 30% for samples SYN-1a and -1b, which were prepared for the measurement of alkalinity and therefore had relatively high values (230 and 130 μ eq l⁻¹, Table 5.3, see annex). The plot of the results (Fig. 5.4, see annex) was made using the results obtained with five different analytical techniques, all based on acidimetric titration: Gran's titration, two end-points, one end point, pH 4.3 and 4.5 separately, and colorimetric determination of the end point using methyl orange. There was a large dispersion of the values, which was even more accentuated in the case of one end point and colorimetric titration. The general trend was always towards overestimation of the results. The Youden plots showed that, even when we apply an acceptance range of $\pm 50\%$ of the expected value, most of the results for samples with the lowest ionic strength are outside this range. Similar results have been obtained in other inter-comparison exercises (e.g. Mosello et al. 1998, 1999, 2002), and reflect the difficulties inherent in measuring low alkalinity values. On the other hand, the results at higher alkalinity values showed a clear

improvement: the mean values for samples SYN-Ia and -Ib do not differ significantly between the five analytical techniques used, although there was very high dispersion in the case of colorimetric titration (Fig. 5.4, see annex).

The poor comparability of the results was partly due to random errors, as was evident from the large variation in the results for even the same technique, and partly to the systematic errors specific for each technique. Alkalinity is defined as the amount of acid needed to neutralise the bases present in a solution. These bases are primarily bicarbonate in freshwater or precipitation, as well as hydroxyl ions at pH values above 8.0, sulphide and nonionic compounds such as calcite or certain organic compounds. The critical feature is the definition and determination of the equivalent point, i.e. the point at which it is assumed that all the bases have been neutralised. If we assume that the main base in solution is bicarbonate, then the equivalent point is the inflection point of the titration curve between bicarbonate and carbonic acid + carbon dioxide (Stumm and Morgan 1981). This value depends on the CO_2 concentration in solution at this point, which is a function of the total concentration of the carbonate system. Consequently, the equivalence point of the alkalinity titration depends on the alkalinity to be determined (Kramer et al. 1986). However, it ranges between pH values 5.0-5.6. In general, the direct determination of the inflection point is difficult and not precise; for this reason the best results are given by those methods that evaluate, by means of extrapolation, the inflection point, such as Gran's titration or the two end-points titration. The one end-point titration (employing an end point of pH 4.3 or 4.5), even in the absence of random errors, inevitably overestimate alkalinity, i.e. the amount of acid necessary to decrease the pH from 5.0-5.6 (bicarbonate inflection point) to 4.5 or 4.3. These systematic errors are equivalent to 32 and 50 μ eq l⁻¹ respectively, i.e. of the same order of magnitude as the low alkalinity values present in atmospheric deposition (Marchetto et al. 1997). Correction of the results may substantially improve the results. In the case of colorimetric determination of the end point, the type of dye used and the pH of the colour change are both critical factors; in this case, of course, the dispersion of the results increases as a result of other factors such as the sensitivity of the eyes to detect the colour change and the amount of extra acid needed to produce the change.

For the reasons given above, as well as because of the importance of alkalinity in determining the ion balance of deposition samples, more care is needed in the measurement of alkalinity and in deciding which analytical techniques are to be used.

5.6. Sulphate, nitrate, chloride

These variables were mainly determined using IC with chemical suppression. In the case of sulphate, 39 laboratories used this technique, while 5 other labs used IC without suppression. The other two techniques, continuous flow methyl thymol (CF Met) and ICP OES, were used by 2 laboratories each. Although statistical comparisons cannot be made on these data, the mean results of the first three techniques gave comparable mean results (Fig. 5.5, see annex). In the case of nitrate, in addition to IC (38 and 5 labs with and without suppression, respectively), 7 labs used CF cadmium reduction and 2 spectrophotometric determination with phenoldisulphonic acid. The mean values of the results (Fig. 5.6, see annex) for IC CS and CF Cd were comparable, but the range of variation was much higher for the CF Cd results. Chloride (Fig. 5.7, see annex) was measured by IC CS and IC WS (39 and 4 labs, respectively), CF with Hg thiocyanide in the presence of ferric ion (CF HgFe, 6 labs) and silver nitrate titration (TIT Ag Cr, 2 labs). The results for IC and CF HgFe were comparable, but the variation in the CF HgFe technique was higher than that in IC. On the other hand, the two titration techniques with silver nitrate gave unacceptably high results. The Youden plots of sulphate, nitrate and chloride showed a prevalence of systematic errors and there were several values exceeding the target range of $\pm 20\%$ of the median values. In the case of nitrate, as well as ammonium, preliminary problems were detected in the data submissions as several labs reported their results as mg NO₃ l^{-1} , instead of mg N l^{-1} as requested in

the form. This difference is appreciable in the case of nitrate because of the high NO_3 :N ratio (4.42:1), and was clearly evident as outlier values caused by the use of the wrong units. The case for ammonium is not as clear because the ratio NH_4 :N is 1.29:1. Attention should be paid to the problem of using incorrect units in data submission in exercises of this sort, as well as of course in the submission of annual monitoring data for deposition and soil solution chemistry within the ICP Forests program.

5.7. Calcium, magnesium, sodium and potassium

ICP OES was the technique most widely used for the analysis of these ions, followed by IC and AAS (Figs. 5.8, 5.9, 5.10 and 5.11, see annex). Close to 60% of the results fell within the $\pm 10\%$ interval, with slight differences between the four cations; the number of outliers and values outside the $\pm 30\%$ interval were slightly higher for calcium (8 and 15%, respectively) than for the other three ions (5-7 and 11-12 %). According to the Youden plots, the errors were mainly systematic for Ca, Na and K, while the results for Mg also included a large random error component. As regards the differences between the individual analytical techniques, the values for Ca determined by IC-CS in some of the samples had surprisingly higher deviation. In the case of potassium the larger range of variation was given by AAS, while for sodium and magnesium there were no clear trends between the analytical technique used.

5.8. Ammonium

Two basic types of analytical methods were used for ammonium: spectrophotometric determination using either Nessler reagent or the blue indophenol reaction, and ion chromatography. There was large dispersion around the mean values (Fig. 5.12, see annex), especially in the case of spectrophotometric determination with the Nessler reagent. However, this analytical technique is no longer used as a standard method because it involves the use of mercury and there are disposal problems. Only 62% of the results were within the \pm 20% range; 22% of the results were outside the \pm 30% range, and 8% outliers. More attention should be paid to this variable as ammonium is an important component of deposition.

5.9. Phosphate, total phosphorus

Neither phosphate nor total phosphorus are mandatory in the monitoring of deposition and soil solution in the ICP Forests program. The analyses were performed by a relatively low number of laboratories (36 and 28 out of 59 for PO_4 and total phosphorus, respectively), and the values for many of the natural samples were below the quantification limit. Relatively few of the laboratories used the same analytical technique (Figs. 5.13 and 5.14, see annex). Phosphate was mainly determined by spectrophotometry and IC. There was wide scatter in the results, and a large component of random errors. The number of comparable results for total phosphorus was only 25. There was a large range of variation, particularly for the results obtained by ICP-MS.

5.10. Dissolved organic carbon (DOC)

The analytical methods used were thermal combustion and IR detection of the carbon dioxide formed (THIR, 24 labs) and persulphate and UV oxidation and IR detection (PSH_UV IR, 4 labs). The two methods gave comparable results, 73% of the results falling within \pm 20% of the mean values and 18% outside the range of \pm 30%, including 12% of outliers (Fig. 5.15, see annex).

5.11. Total nitrogen

Although total nitrogen is a mandatory variable in throughfall and stemflow samples, only 26 of the 59 laboratories performed this determination (Fig. 5.16, see annex). Five main analytical methods were used: determination by continuous flow as nitrite after wet oxidation to nitrate, followed by reduction with Cd (CF_Cd, 8 labs) or after reduction with copper and hydrazine (CF Cu_Hydr, 2 labs), chemioluminescence (CHLM, 7 labs), Kjeldahl digestion (KJELD, 6 labs) and spectrophotometric determination as nitrate at 220 nm, after wet oxidation (SPEC UV220, 3 labs). There was large dispersion of the results for both the CHML and Kjeldahl determinations, while the results for CF_Cd show a higher comparability. Altogether the values were within \pm 20% of the mean in 65% of the cases, 25% of the results were outside the \pm 30% limit. The Youden plots indicated a prevalence of systematic errors (Fig 5.16, see annex). Discussion of the results during an *ad hoc* meeting indicated that there is some misunderstanding concerning the meaning of total nitrogen: Kjeldahl nitrogen is a measure of amino nitrogen and ammonium only, and the nitrate and nitrite concentrations must be determined separately and added in order to obtain a correct value for total nitrogen,. These separate analysis increase the overall error of the final N value.

5.12. Total sulphur

Most of the determinations were performed by ICP optical emission spectrophotometry (ICP OES, 16 labs), while only two labs used ICP mass spectroscopy (ICP MS). The results for ICP OES were in good agreement, while the two values obtained with ICP MS were not comparable (Fig. 5.17, see annex). The dispersion of the results was relatively low, as 76% were within \pm 20% of the mean values. Of course total S does not necessarily coincide with sulphate, as total S also includes organic S.

5.13. Silicon

The analyses were performed by spectrophotometry using the molybdate reaction (SPEC Moxr, 5 labs), and by ICP OES (12 labs). There was large scatter in the case of spectrophotometric determination, and a systematic difference between the two techniques (Fig. 5.18, see annex). On the other hand, spectrophotometric determination measures only the silicon reactive to molybdate, while in the case of ICP most of the silicon is measured. The Youden plot showed large dispersion, with a prevalence of systematic errors.

5.14. Aluminium, iron, manganese, copper and zinc

The number of labs that reported values ranged from 30 for Cu to 39 out of 59 labs for Al (Figs. 5.19-5.23, see annex). The analytical technique most widely used was ICP OES (14-25 labs), followed by AAS with graphite furnace (AAS GFA, 5-9 labs) and ICP MS (3-5 labs); only a small number of laboratories used flame AAS (2-4 labs). In general, the performance of ICP OES was good for these five elements and, when the number of results was sufficient to make a comparison, there were no systematic differences among the four techniques. The poorest results were obtained for Cu (only 35% of the results within \pm 20% of the mean values), and the most reliable for manganese and zinc. The proportion of results exceeding \pm 30% of the mean were close to 30% for Cu and Fe, and close to 20% for Mn and Zn.

6. DISCUSSION

6.1. Ionic balance

The ion balance check could only be made for those laboratories that analysed all the major anions (bicarbonate, sulphate, nitrate, chloride) and cations (hydrogen ions, ammonium, calcium, magnesium, sodium and potassium). The proportion of missing values of the major anions and cations was less than 10% in most of the samples, while the number of missing values for alkalinity (i.e. bicarbonate) was higher than 50-60% for samples with alkalinity values below 50 µeq/l, and about 30% for values higher than 50 µeg/l. As the total ion concentration in deposition samples can be less than 100-150 μ eq/l, an alkalinity value of 50 μ eq/l is therefore very important in the ion balance. For example, the ion concentrations of samples WAT-1, -2, -6, -7 and -8 ranged between 67 and 240 µeg/l (see Section 5.2). As the contribution of bicarbonate to the ion balance is negligible for samples with a pH of below 5.0, this somewhat improved the situation for laboratories that had not measured alkalinity. Despite this, the number of laboratories for which an ion balance could be calculated was still very low, ranging from 12-25% for the samples with a low ionic concentration to 66% for SYN-3, which had a medium-high ion concentration. The ion balance was poorly satisfied for most of the laboratories. The PD values (see Section 3.2 for definition), are given in Table 6.1. Samples WAT-3, -4, -5 and -6 had systematically higher cation excesses than WAT-1, -2, -7 and -8. This is partly due to the higher concentrations of organic anions in the first set of samples (DOC values 10,64-12,08 mg C l^{-1}) than in the second set (1,00-4,55 mg C I^{-1} , Table 5.2). This is typically the case in throughfall, stemflow and soil solution samples.

	Samples	Samples
	VVAI-1, -2,	VVA I -3, - 4 ,
	-7 and -8	-5 and -6
Min.	-70	-76
10%	-37	0
25%	-16	10
50%	0	22
75%	14	36
90%	27	55
Max.	144	96
No. of samples	97	123

Table 6.1. PD values for the samples with low DOC (open field bulk deposition) and high DOC (throughfall and soil solutions) concentrations.

The total concentrations of anions and of cations are plotted separately in Fig. 6.1 for samples with low and high ion concentrations. The data show high dispersion. The systematic deviation of the total cations and anions in WAT-3, a sample with a high level of organic acids (DOC 10.6 mg l^{-1}), is high compared with that for WAT-2 (DOC 2,1 mg l^{-1}).



Fig. 6.1. Plot of anion and cations concentrations for samples with low (left) and high (right) ion concentrations.



Fig. 6.2. Plot of measured and calculated conductivity for samples with low (left) and high (right) ion concentrations.

6.2. Comparison between measured and calculated conductivity

The number of laboratories for which measured and calculated conductivity could be compared was also relatively low and varied between the samples. The contribution of alkalinity was not taken into account in the calculated conductivity in order to increase the number of comparisons. The overall results are presented in Table 6.2, in which the deviation between the measured and calculated value is expressed as per cent of the measured value.

The comparison of measured and calculated conductivity in Fig. 6.2 fits the 1:1 line relatively well in the case of WAT-5, even though there is high dispersion of the results. The calculated conductivity for WAT-1 was higher than the measured values in most of the cases. This is due to the general tendency to overestimate low concentrations of ions as a result of sample contamination and the poor sensitivity of the analytical methods used.
The relatively good results obtained for WAT-5 indicate that the conductivity test is suitable for use even for samples with high DOC concentrations, where the ion balance check is not usually successful. This is due to the low contribution to conductivity of organic compounds. It is therefore recommended that a conductivity check be used for throughfall, stemflow and soil water samples.

Sample	WAT-I	WAT-2	WAT-3	WAT-4	WAT-5	WAT-6	WAT-7	WAT-8
Number of calculated values	37	23	44	42	44	32	42	43
median value (µS/cm 25 °C)	12.0	11.9	31.1	27.4	140.8	16.0	16.2	17.9
% of data within ± 10%	41	48	61	38	82	31	62	60
% of data within ± 20%	76	78	89	71	95	78	81	88
% of data within ± 30%	84	91	93	90	100	91	90	93
% of data outside ± 30%	16	9	7	10	0	9	10	7

 Table 6.2. Comparison between measured and calculated conductivity.

6.3. Methods which gave unsatisfactory results

The identification of unreliable methods is difficult because it is usually impossible to distinguish between the "non reliability" of the method (e.g. interference from other compounds, complex formation, lack of commercial standards etc.) from the incorrect application of the method by one or more laboratories. Certainly the fact that several laboratories which use the same analytical method also had a high number of outlying results is at least partially indicative of the problems inherent to the methods. In many cases the problem lies in the low concentrations of the deposition samples; the analytical error is obviously higher as the quantification limit is approached (see Section 3.1.4.). Another important point is that it was not possible to perform statistical analyses for a specific analytical method when the number of reported values was low; these cases are indicated by a question mark in the table. For the above reasons, the list of methods that gave unsatisfactory results (Table 6.3) does not necessarily mean that the methods are analytically incorrect; the point is that they require more attention from the laboratories that have adopted them.

Table 6.3. Analytical methods that gave unsatisfactory results.

Alkalinity	Colorimetric detection of the end point
(low values)	One end-point titration without correction
Sulphate	ICP-OES, CF Met (?)
Chloride	AgNO3 titration, chromate indicator
Ammonium	Nessler spectrophotometric method
Potassium	AAS (?)
Total nitrogen	Spectrophotometric UV 220 nm
	Chemioluminescence, Kjeldahl digestion
Al, Fe,	ICP MS (?)
Total P, Total S	ICP MS (?)

On the basis of other inter-comparison exercises and the chemical principles underlying the reactions, we can conclude that these methods are not suitable, at least at low concentrations, for determining the respective variables in natural deposition and soil solution samples. This does not apply at present to the methods indicated by a question mark. Laboratories using these techniques should try alternative methods. Both unreliable methods and alternatives have already been discussed in the presentation of the results (see Section 5).

6.4. Comparison with previous exercises

Most of the laboratories participating in the ICP Forests program took part in the intercomparison exercises in 1997, 1998 and 2000 within the framework of the AQUACON-MedBas Project, jointly carried out by the Joint Research Centre of the European Union, Ispra (Italy) and the C.N.R. Institute of Ecosystem Study (former CNR Istituto Italiano Idrobiologia), Verbania Pallanza (Italy). The type of samples covered by these inter-comparisons were acid rain (1997, 1998) and freshwater (2000). The methods used for the preparation of the synthetic samples and the overall results are reported in detail by Mosello et. al. (1998, 1999, 2002). Separate reports on the performance of the ICP Forests laboratories were also produced in connection with the 1997 and 1998 inter-comparison. The results of the three inter-comparisons are compared with those of the present exercise in Table 6.4. The number of determinations was much higher in the present exercise (analysis of ten samples) than in the 1997, 1998 and 2000 inter-comparisons (two samples). Only one of the two samples (the one with the lowest ion concentrations) was considered to be comparable, based on the conductivity values, with the samples analysed in the working ring test.

	Number of determinations			Proportion of values								
				± 20% outside the expected value, %			Proportion of outliers, %					
	1997	1998	2000	2002	1997	1998	2000	2002	1997	1998	2000	2002
pН	38	48	41	682	5	4	12	11	5	10	0	3
Conductivity	39	46	40	645	5	0	0	8	5	7	3	4
Alkalinity	28	39	32	353	24	28	0	45	10	18	13	3
Sulphate	40	50	40	519	10	0	0	16	5	6	3	12
Nitrate	40	48	40	504	15	2	0	20	5	10	10	12
Chloride	40	48	40	547	15	13	28	18	10	13	5	9
Calcium	39	48	42	533	26	21	2	20	5	10	2	8
Magnesium	39	49	42	526	10	10	0	13	5	6	5	5
Sodium	38	48	41	548	24	31	0	20	3	6	0	5
Potassium	38	48	41	539	13	19	10	13	13	6	2	7
Ammonium	38	49	35	499	11	4	31	29	0	8	17	8
Total N	-	-	25	308	-	-	12	31	-	-	8	6

Table 6.4. Comparison between the performances of the present (2002) and previous intercomparison of the ICP Forests laboratories.

The performance of the laboratories is expressed as a percentage of the results outside the \pm 20% range of the expected values and as a percentage of outliers. Comparison of the results of the four inter-comparisons shows that the results of the 2002 working ring test were slightly poorer than those obtained in previous exercises, even though the comparison is restricted to the 1997

and 1998 samples that had lower or similar ion concentrations. Even though rather many laboratories (about 40%) participated for the first time in the 2002 exercise, we can conclude that participation in the inter-comparison exercises is, as such, not sufficient to improve the analytical quality if it is not linked to other actions. These actions should include a detailed discussion of the results during meetings and in each laboratory in order to highlight the main critical aspects in terms of the variables (e.g. alkalinity and total nitrogen in this exercise) and the weak point of each laboratory. A statistical approach may help in quantifying the reason for deviations from the mean values, e.g. by means of the Z score. The discussion should concentrate more on laboratory practices and problems than on statistics.

7. RECOMMENDATIONS OF THE RAPPORTEURS

The following recommendations are the results of presentations given by selected experts in the workshop held in Fontainebleau on 17-19 June 2002, and are highly applicable to the discussion of the results of the working ring test.

7.1. pH measurement

(Rosario Mosello, C.N.R. Institute of Ecosystem Study, Verbania Pallanza, Italy)

Calibration:

- It must be carried out with two buffer solutions, the pH values of which cover the range of pH values expected in the samples;
- The temperature and stirring (or not stirring) conditions must be the same for the buffer solutions and for the samples;
- This can be done at weekly intervals if the pH meter is not turned off after each batch of measurements, and if other conditions (e.g. temperature, voltage) are kept constant;
- Read and follow carefully the instructions given in the pH meter manual for calibration.

Measurement:

- The electrodes must be rinsed with the sample solution between measurements in order to prevent contamination;
- Initial agitation of the sample for at least one minute is suggested; the following measurement may be made on the stirred or quiescent sample;
- Stabilisation of the reading should be achieved within 5-10 minutes. A longer stabilisation time indicates either problems with the electrode or that the solution has not become stabilised with the gas present in the laboratory atmosphere;
- The use of low flow (GLF) or high flow (GHF) glass electrodes seems unimportant. Good quality and maintenance of the pH electrode is more relevant;
- Different equipment (electrodes) must be used for clean and dirty samples. Avoid the use of pH electrodes designed for meat or cheese.

Maintenance:

- The electrode must be stored as indicated by the manufacturer, normally in 3M KCI. Do not use de-ionised water or buffer solutions;
- Follow carefully the instructions for the maintenance of the solution inside the electrode.

General:

- Do not measure conductivity or perform cation or anion determinations on the same solution on which pH has been measured;
- Several books and papers are available on pH measurement, and guidelines for correct measurement are given in most of the analysis handbooks. These includes A.P.H.A., A.W.W.A., W.E.F., (1998); Linnett, (1970); Westcott, (1988).

7.2. Alkalinity measurement

(Rosario Mosello, C.N.R. Institute of Ecosystem Study, Verbania Pallanza, Italy)

- The alkalinity of a water sample is its acid-neutralising capacity. It is a measure of an aggregate property of the solution and can be interpreted in terms of specific substances only when the chemical composition of the sample is known;
- Alkalinity is the sum of all the titratable bases in the sample;
- Alkalinity is determined by means of an acidimetric titration;
- The measured value may vary significantly according to
 - the end-point pH used, and
 - the technique used to detect the end-point;
- The measurement of low values of alkalinity are reliable if:
 - the following analytical methods are used:
 - Gran titration;
 - two end point titration;
 - titration at pH 4.5 (or 4.3) and correction for the extra acid added;

	рН	H ⁺ concentration	Correction to be applied to the alkalinity concentration
Real cut-off point	5.5-5.7	≈ 2-3 µeq/l	
One end point to	4.5	32 µeq/l	29 μeq/l
One end point to	4.3	50 μeq/l	47 μeq/l

- o ordinary analytical quality control procedures are applied, e.g.
 - normal maintenance of the titrator and electrodes;
 - periodic checks of the acid concentration;
 - use of quality control charts.

For more details, see Marchetto et al., 1997.

7.3. Conductivity

(Rosario Mosello, C.N.R. Institute of Ecosystem Study, Verbania Pallanza, Italy)

- Conductivity is a master variable for the quality control of chemical analyses. It is a rapid measurement that gives valuable information on the nature of the water sample, primarily the solute concentrations;

- The type of errors made in the measurement of conductivity are typically systematic, due to poor calibration of the equipment; random errors may be due to a lack of care in rinsing the electrodes;
- Conductivity is strongly dependent on the temperature of the sample. The reference temperature is 25 °C. Many instruments are equipped with temperature compensation devices. Such instruments should be calibrated strictly in accordance with the manufacturer's instructions. If the instrument does not have automatic compensation for temperature, correction factors must be used. Such tables are available in most water analysis standards and manuals (see below);
- A small systematic error is introduced when either automatic or manual corrections are used, as the correction factors apply to water samples with the chemical characteristics of surface water (e.g. Ca>Mg>Na>K, and HCO₃>SO₄>Cl>NO₃). The chemical characteristics of bulk deposition, stand throughfall and soil solution are usually different from the above;
- In order to minimise this error, measuremnts should be performed in a range of $\pm 2^{\circ}$ C from the reference temperature;
- The calibration of the equipment should be regularly checked every six months using KCI solutions, as indicated in the main water analysis texts (e.g. ISO 7888-1985; A.P.H.A, AWWA & WEF 1995).

7.4. ICP and AAS-flame determinations

(Nils König, Niedersächsische Forstliche Versuchsanstalt Göttingen, Germany)

7.4.1. ICP

Calibration/blank:

- Generally the calibration curve is linear over 5-6 decades. As a general rule it is usually sufficient to carry out a 2-point calibration that has to be verified with an independent control sample;
- It is important to check the purity of the blank (Attention! The use of glassware may release sodium);
- Depending on the measuring time, a control sample should be measured every 10 to 20 samples in order to maintain drift and carry-over control.

Automatic sampler/carry-over:

- The use of an automatic sampler can cause contamination of samples and standards as the containers in the sampler are open for a considerable period of time. Carry-over from the preceding samples into blanks may also occur. These problems can be minimized by covering the sampler, and by frequent replacement of the blank solution;
- The rinse time (with rinsing solution) has to be sufficient to avoid carry-over between samples. For achieving equilibrium in the mixing chamber and in the plasma, the suction time of the sample has to be sufficient.

Matrix/addition of acid:

- The standards should be adjusted to correspond to the matrix of the samples. This is especially important for standards containing only one element in trace amounts;
- All samples and standards have to be acidified consistently (0.5 3 ml of concentrated $HNO_3/100$ ml sample).

Background correction:

- Background correction is normally necessary. To set the points for the background correction, all possible interfering elements have to be tested and taken into account.

Inter-element correction (IEC):

- Inter element-correction interferences, caused by line overlay, can be minimised by numerical means. Exact determination of the correction factors for the type of line overlay is necessary.

Internal standard:

- The use of internal standards is normally helpful. Problems caused by oscillations of the plasma and the physical influence of the sample matrix can be compensated to a large extent. The different behaviour of atom lines and ion lines has to be taken into account;
- The sample may not contain the element used for the internal standard. The same amount of internal standard solution has to be added to all the samples and standard solutions. This can normally be automated.

Radial or axial plasma:

- The sensitivity can be increased ten times by using axial plasma;
- Because of ionisation effects, the measurement of alkaline elements is very problematic; these interferences can be reduced by adding an ionisation buffer.

<u>Ultrasonic nebulizer (USN):</u>

- The use of an USN can increase the sensitivity 2-5 times.
- The USN is highly sensitive to matrix influences. Matrix homogenisation by the addition of e.g. CsCl leads to clearly better results.

Selection of wavelengths

	Wavelength proposed	
Element	by DIN EN ISO11885	Remarks
	(additional)	
Ca	317.93	Sensitive, ionisation buffer important with axial plasma
	315.89	
Mg	285.21	Interference only with a high matrix
	279.08	(Fe interference at 285,21)
	(279.55)	
Na	589.59	Not very sensitive, very difficult with axial plasma, ionisation buffer important
K	766.49	Not very sensitive, very difficult with axial plasma; ionisation buffer important
AI	396.15	Contamination problems in the low concentration range
	167.02	(OH interference at 308,22)
	(308.22)	
	(237.31)	
Mn	257.61	An acid admixture important for low concentrations in order to minimise memory effects
Fe	259.94	An acid admixture important for low concentrations in order to minimise memory effects
	238.20	
Cu	327.39	Problems with USN, influence of matrix and acid concentration, alkaline or earth alkaline-
	324.75	additive important (e.g. Cs or Ca), (Fe interference at 324,75), (OH interference at 324,75, but
		can be minimised by using USN)
Zn	206.20	Contamination problems (Fe interference at 213,86)
	213.86	
Р	213.62	Not very sensitive
	178.29	
S	182.04	Problems with USN, influence of matrix
	180.67	

7.4.2. AAS-flame

Calibration/blank:

- Normally the calibration curve is linear over 2-3 decades. Hence a multipoint calibration (3-5 points), which also includes a non-linear range, is reasonable. However, this has to be verified using an independent control sample;
- It is important to check the purity of the blank (Attention! The use of glassware may release Na);
- In order to control the drift of the measurement a control sample should be measured every 15-30 samples (depending on the element and burner type).

Automatic sampler/carry over:

- The use of an automatic sampler can cause carry over from samples into the blank solutions. This problem can be minimised by frequent replacement of the blank solution.

Matrix/additives:

- The standards should be adjusted to correspond to the matrix of the samples.
- For the measurement of some elements additives are necessary in order to avoid ionisation interference and oxide formation.

Background correction:

- Measuring of the background is normally not necessary for water samples.

Burner/gas:

- An air/acetylene flame or a N_2O /acetylene flame and a corresponding burner are used for a number of elements (see following table).

Selection of wavelength

Element	Wavelength	Remarks
Ca	422.7	Small slit (interference NO)
		Flame: N2O/Ac (if using a reducing air/Ac flame, then a La additive is needed)
Mg	285.2	Very sensitive at 285.2, burner crosswise possible at 285,2
	(202.5)	
Na	589.0	Contamination problems
	(589.6)	Cs additive important
К	766.4	No problems
	(769.9)	Cs additive important
AI	309.3	Not very sensitive
		Flame: N2O/Ac (the correct stoichiometry of the flame is important)
		Adjustment of the burner important
		Cs additive important
Mn	279.5	No problems
Fe	248.3	No problems in water samples
		Small slit needed (many interferences)
Cu	324.7	No problems
Zn	213.8	No problems
Р		
S		

7.5. Dissolved organic carbon (DOC)

(Nicholas Clarke, Norwegian Forest Research Institute, Høgskoleveien 12, N-1432 Ås, Norway)

In natural waters, total organic carbon (TOC) is the sum of particulate and dissolved organic carbon. Dissolved organic carbon (DOC) is operationally defined, usually as organic carbon that passes through a 0.45 μ m membrane filter. Cellulose acetate or nitrate filters should not be used for this purpose due to contamination or adsorption problems. Glass fibre filters are preferable.

Although the discussion below concerns DOC, much of it applies to TOC as well.

Organic carbon is most often determined after oxidation to CO_2 using combustion, an oxidant such as persulphate, UV or other high-energy radiation, or a combination of some of these. If only UV radiation with oxygen as oxidant is used, underestimates of the DOC concentration may be obtained in the presence of humic substances. A variety of methods are used for detection, including infrared spectrometry, titration and flame ionization detection after reduction to methane. Always follow the instrument manufacturer's instructions.

For the determination of DOC, dissolved inorganic carbon (DIC) must be either removed by purging the acidified (for example with phosphoric acid) sample with a gas which is free from CO_2 and organic compounds, or determined and subtracted from the total dissolved carbon. If acidification followed by purging is used, care should be taken as volatile organic compounds may also be lost. After acidification, the CO_2 is removed by blowing a stream of pure carbon-free inert gas through the system for at least 5 minutes.

Carbon is ubiquitous in nature, so reagents, water, and glassware cannot be completely cleaned of it. Method interferences (positive bias) may be caused by contaminants in the carrier gas, dilution water, reagents, glassware, or other sample processing hardware (for example a homogenization device). All of these materials must be routinely demonstrated to be free from interference under the conditions of analysis by running reagent blanks.

Plastic bottles can bleed carbon into water samples, especially when they are new, or when they are used for low-level samples (less than 200 ppb C). Any new bottles (especially plastic) should ideally be filled with clean water for a period of several days or boiled in water for a few hours before use.

The use of high purity or purified reagents and gases helps to minimise interference problems. It is very important to use ultra-pure water with a carbon filter or boiled distilled water just before preparing stock and standard solutions, in order to remove dissolved CO_2 . The stock solution should not be kept too long (about one week). For most DOC instruments a correction for DOC (due to dissolved CO_2) in the dilution water used for calibration standards is necessary, especially for standards below 10 ppm C. The carbon in the blank should only be subtracted from standards and not from samples.

For calibration, standard solutions are most often potassium hydrogen phthalate for total dissolved carbon and sodium bicarbonate for dissolved inorganic carbon. The DOC concentration should be within the working range of the calibration. If necessary the sample can be diluted.

Sample DOC below about 50 ppb C can be affected by atmospheric exposure. In these cases, sampling bottles should be kept closed whenever possible, and autosampler vials should be equipped with septa for needle piercing by the autosampler.

7.6. Spectrophotometric determination and flow systems

(Frank Symossek, Sächsische Landesanstalt für Forsten, Graupa, Germany)

<u>General Remarks</u>

Samples to be analysed by spectrophotometric methods should not be influenced by turbidity or sample colour. The problems associated with turbid or coloured samples can be eliminated in a number of ways:

- Make sure that all the samples are free from particles by means of centrifugation or filtration prior to the analysis;
- The colour can be removed from solutions by means of sorptive materials (e.g. C18) or dialysis. Dialysis can be performed statically in dialysis tubes or dynamically by means of a dialysis membrane in a flow cell with an upper and top stream (usually a component of CFA Systems);
- Colour compensation can also be employed, most frequently in manually performed spectrophotometric measurements. The zero point of the photometer is adjusted with a sample containing all the components of the colorimetric method but without the colour reagent. Repeated measurement of the same sample with the colour reagent results gives an absorption measurement that is not affected by the colour of the sample.

The linearity of the working range for spectrophotometric methods is typically given over I decade of concentration. Absorption intensity is influenced by the length of the optical path, the concentration ratio between sample and colouring reagent, the temperature of the measured solution, and the reaction time between the addition of the colour reagent to the sample solution and the start of the absorption measurement.

All measurements can be performed in manual mode or in flow systems (SFA or FIA).

The advantages of a flow system are:

- The measurements can be made in an automated system with high sample throughput;
- All conditions (volume dosage, temperature and colour development time) are well reproducible because they are controlled by the system conditions;
- Sample preparation procedures (dialysis, thermo-, UV- and peroxide dissolution, reduction reaction prior to colour development) are fully integratable;
- Detection can be performed as absorption measurement (increasing or decreasing) or based on potentiometry (ISE).

Selectivity and sensitivity of photometric and flow system methods are rather high. In some cases problems can occur.

Reagents

All reagents should be of "analytical grade". Check solution stability with respect to the solubility of salts (non-saturated solutions). Store the reagent solutions in a cool dark place, and degas the reagent solutions prior to analysis by stirring, He-degassing or membrane filtration (under pressure).

Calibration

Starting the daily analysis with a new calibration should be performed using at least five calibration standards per working range; this should be verified by means of an independent control sample.

Check precision and stability of photometers and flow systems by replicate measurement of calibration or verification standards every $15^{th}-20^{th}$ sample. Some instruments have the ability to perform automatic drift correction by replicated measurements of standards after a predefined number of samples.

Parameter	Method	Remarks
Sulphate	Ba/Ca Methyl- Thymol blue	2-channel method, absolute simultaneous flow of the Ba and Ca channel is required. The signal is obtained as the absorption difference between the two channels. As no dialysis pre-treatment is possible, there is no membrane available for good SO ₄ diffusion. High concentrations of cations cause problems.
Nitrate	Sulphanilamide Cd or hydrazinium reduction	High concentrations of Fe, Cu and other metals cause problems in analysis - add EDTA to the buffer solution to prevent problems. When a Cd reduction column is used, take care that the column is completely degassed and avoid drying out of the Cd granules.
Chloride	Hg-Fe-SCN potentiometry	Bromide and iodide cause interference at concentrations exceeding 30mg/l. Sulphide ions also interfere. Take care that Hg-containing waste solution are completely collected and recycled in
		accordance with environmental regulations.
Ammonium	Indophenol blue Gas Diffusion	High amino acid concentrations increase the measured ammonium concentration. High Mg concentrations cause precipitation of Mg(OH)2 - add sodium citrate to solve the problem.
Total N	Sulphanilamide	After oxidation, detection of total N as nitrate.
	Cd or hydrazinium reduction	High concentrations of Fe, Cu and other metals cause problems in analysis - add EDTA to the buffer solution to prevent this problem.
		Use calibration standards containing NH4 and NO3 components.
Phosphate	Molybdenum blue	Reducing components can interfere. Silicates cause problems - the same molybdenum-blue complex is formed.
Silicon	Molybdenum blue	Reducing components can interfere. Phosphates cause problems - the same molybdenum- blue complex is formed.

Remarks about photometric and flow methods

7.7. Ion Chromatography

(Claude Hennequin, SGS-Laboratoires WOLFF-Environnement, 91031 Evry, France)

lon chromatography (IC) is a well-established analytical technique that is widely used in analytical laboratories. Although, in theory, all the ionic species can be determined by this technique, there are some limitations and differences in the individual applications.

From a technical point of view, conductimetry is the basis of the non-selective universal detector. However, non-selectivity represents a drawback because the conductivity of the eluent must be reduced in order to improve the peak signal:noise ratio. This can be achieved by two techniques: IC with chemical suppression (IC-CS), and IC without suppression (IC-WS). The IC-CS technique was used by about 85% of the laboratories participating in the ring test.

In practice, there are no major differences between the results obtained with IC-CS and with IC-WS (no bias, same typical standard deviation).

The ions determined by this technique can be divided into three groups:

- Anions (chloride, nitrate and sulphate)
- Cations
- Phosphate

Anions: chloride, nitrate and sulphate

This is the oldest and most developed application (about 85 % of the laboratories used IC for these anions).

According to the Youden plots, the precision for these ions is good, because only 10-15 % of the results of the individual laboratories are located noticeably outside the 20% limit. The results for some of the laboratories indicated a systematic bias (calibration problems?).

The scattering of the points in the plots for chloride, sulphate and nitrate, is different. For chloride there is random scattering within the 20% limit, but the values for nitrate tend to follow a straight line, indicating a systematic bias. The results of a few laboratories (2-3) are clearly randomly located.

Cations

In the case of cations there is strong competition with spectrophotometric techniques, because only 15 laboratories determined cations by IC, whereas 37-39 used IC for anions.

For ammonium, the plot of SYN-3 against WAT-3 shows some random spreading, but this is absent for WAT-7 against WAT-1. This may be due to the fact that the ammonium concentrations in SYN-3 and WAT-4 are higher.

Phosphate

Only 5 to 6 laboratories used IC for the determination of phosphate. As there are no specific drawbacks with IC in the determination of this ion, the main reason for this is probably due to the low concentration (around 0.05 mg P/I) of the samples, which is close to the typical limit of quantification ($\cong 0.03$ mg/I).

The standard deviations for the results obtained by IC are in the same range as those for the other techniques; the manual spectrometric techniques gave slightly lower standard deviations. However, the phosphate concentration in these samples is low and no technique is sufficiently robust in this range.

In conclusion, the use of IC is recommended for the analysis of inorganic ionic species. However, "recommended" does not necessarily mean "the best".

<u>Advantages</u>

- One technique can be used, but the use of two ICs is recommended if both anions and cations are to be analysed.
- Small sample volumes required, which means that low precipitation events can be analysed successfully.
- Up to eight ions can be analysed in the same run.

<u>Disadvantages</u>

- Expensive equipment.
- High running costs (columns, vials etc.).

The final decision lies with the laboratory, because none of the techniques are clearly superior.

<u>General</u>

- Take care to avoid contamination during preparation of the samples: the perspiration on one's fingers contains appreciable amounts of NaCl. This is a common problem, but often forgotten.

<u>Methods</u>

- Use a known standard (e.g. CEN, ISO ...)
- Follow the recommendations of the supplier and consult with other users concerning specific problems and techniques.
- Analytical columns are expensive and easily damaged or destroyed: always use a precolumn.

Practical experience

- Separation of the Na and NH_4 peaks has to be improved. Because NH_4 elutes after the Na peak, some columns reduce the tailing (e.g. CS16 for Dionex)
- An increase in the inlet pressure is usually due to the clogging of the inlet frit. Never try to clean it, but discard it and replace with a new one.
- The connecting tubes and sampling loop of some equipment can adsorb and release Ca ions: this is often indicated by unusually high Ca controls. If the problem is not due to the quality of the eluent, replace the injection loop and, if the problem persists, the tubing inlet to the detector.
- Care should be taken when analysing anions and cations on the same system, as the individual eluents are usually incompatible. The system should be carefully rinsed and tested.

Additional recommendations concerning IC measurements resulting from the AQUACON intercomparison exercises (Mosello et al. 2000, 2002):

<u>Calibration</u>

- For Cl⁻, NO₃⁻, SO₄²⁻and NH₄⁺ we recommend quadratic calibrations in the range of two orders of magnitude, obtained using at least five standards, two of which should be at the limits of the measurement interval.
- For Cl⁻, NO_3^{-} , SO_4^{2-} and NH_4^{+} linear calibrations should only be in the range of one order of magnitude, using at least three standards corresponding to the limits and the centre of the measurement interval.
- For Na⁺, K⁺, Mg²⁺ and Ca²⁺ linear calibrations (with at least three standards) up to two orders of magnitude may be used.
- The standards used in calibration must cover the values of the samples analysed.

<u>Measurement</u>

- Calibrate and analyse the samples only when the instrument is stable (after one hour's operating time at least).

- After the initial calibration, a new calibration or a control standard measurement should be performed every 20-30 samples more frequent calibrations do not appear to be necessary.
- End the batch of analysed samples with a complete calibration compare it with the previous one in order to check for any drift.
- Analyse every day at least one sample of ultrapure water (blank) and at least one control chart sample.

<u>General</u>

- We advise using the autosampler to optimise the analysis time and to programme the analysis of batches of samples including calibration, blank, control chart, 20-30 samples, calibration or control standard, 20-30 samples etc. The use of manual injections does not seem to affect the quality of the analyses.
- Two injections per sample or standard are not essential. However, the main causes of errors are to be found in incorrect calibration, contamination during the handling of samples and standards etc.
- When analysing samples with a low ionic content, it is advisable to use injection loops of 50 μl or more.
- Careful quality control must be designed specifically for ion chromatography analyses, even when using external quality controls (certified reference materials) to limit the occurrence of systematic errors.

8. CONCLUSIONS AND RECOMMENDATIONS

The first working ring test initiated within the EU/ICP Forests Expert Panels on Deposition (EPD) and Working Group on Soil Solution of the Expert Panel on Soil was a complete success because practically all the laboratories engaged in analysing deposition or soil solution within the intensive forest monitoring programme participated.

It is important to mention that the word "working ring test" (WRT) was not used neutrally. It should indicate to any participant that this test "only" means (1) to have as far as possible regular feedback of the performance of each lab, (2) to give those labs with poor analytical performance the possibility to improve their QA/QC procedures according to the numerous existing guidelines and standards, and (3) to see the results of their QA/QC work at the next WRT. Hopefully within 2-3 years the overall performance of the labs will have improved to such an extent that the difference between the laboratory with the lowest value and that with the highest value for each parameter will have been reduced to an acceptable level.

This working ring test has used strict criteria for calculating the performance of the laboratories that are comparable to those used by international inter-laboratory circuits. Nevertheless, the WRT is "only" one of the means available to the expert panels to achieve a common goal. In this respect, no judgement is made on the performances of the individual laboratories, and it is left to each laboratory, depending on their financial and personnel resources, to make the necessary improvements for the next WRT.

After this, the first WRT, it would be useful to organise help for those laboratories with the poorest performances. Hopefully, within the next few months, we will be able to find sufficient labs willing to offer help to those labs requiring help.

As far as the analytical and technical aspects of the WRT are concerned, the results have identified the most critical analytical methods and highlighted the need for efforts to improve laboratory performances and analytical quality. Before considering the results, it is important to focus on the role that inter-comparison exercises should play within the laboratory practices. In general, the analytical procedures of a laboratory should be performed as part of codified rules and methodologies with respect to equipment maintenance, the selection and checking of chemical reagents, the checking of de-ionised water and cleanliness of the plastic and glassware, the use of blanks and control charts, the selection of analytical methods reliable for the type of samples to be analysed, and several other aspects generally referred to as in-laboratory Good Laboratory Practices (GLP). These procedures should be coupled with intra-laboratory activities, such as inter-comparison exercises and the use of certified materials, which are essential in identifying systematic errors and basic failures in the methods. Only a correct and balanced coupling of in-and within-laboratory activities can assure the optimal performance of the laboratory.

Within the framework of in-laboratory GLP, some quality checking of the major ions concentrations is possible and recommended, using chemical and physico-chemical properties such as the ion balance and comparison between measured and calculated conductivity (see Sections 3.2, 6.1, 6.2). The results of this inter-comparison have shown that the ion balance is not strictly applicable when the concentration of organic compounds is high (e.g. DOC> 5 mg l⁻¹), or when the analysed ions do not represent most of those present in the samples. In such conditions a comparison between measured and calculated conductivity should be used. Thresholds of acceptance for the differences between total cations and anions, and measured and calculated conductivity, are given in Table 3.4. The reasons why results do not correspond to the expected standard are not necessarily analytical errors: the chemistry of the sample may be different from those of previous events, or other types of error (e.g. transcription of results) may occur. However, if these limits are exceeded, the analyses must be repeated.

Other empirical relationships between ions, e.g. between conductivity and the sum of cations or sum of anions, may help in identifying "strange" results. The validation procedure should also consider the ratio between sodium and chloride concentrations, whose ratio is normally close to those of marine water (Cl/Na = 0,86 on a molar or equivalent basis). The ratio remains relatively constant in throughfall and stemflow samples, as the uptake or release from vegetation is negligible. In soil solution samples in areas with low NaCl deposition, however, this is not necessarily the case. Strong deviation from the marine ratio must be confirmed by a second analysis and, if confirmed, the causes should be identified.

An example of data validation applied using open field and throughfall concentrations is given on the enclosed CD for all laboratories having participated in this working ring test and their National Focal Centers.

One limit of these procedures is that a strong systematic error for one of the ion concentrations is enough to nullify the information from the tests. The present inter-comparison exercise highlights that the measurement of low alkalinity values (below 50 μ eq l⁻¹) is extremely critical. This is in agreement with the results of several other inter-laboratory exercises (Mosello et al. 1998, 1999) and can be assumed to be a general analytical problem. The errors arising at low alkalinity values are largely systematic and they have been discussed in Section 5.5. Reliable results are obtained only with those methods that extrapolate the inflection point in the acid titration, e.g. Gran titration, and two end-point titration. One alternative is correction of the results obtained by one end-point titration in relation to the value of the end point (29 and 47 μ eq l⁻¹ to be subtracted from results obtained by titration to 4.5 and 4.3, respectively). Systematic errors become less important for alkalinity values higher then 100-200 μ eq l⁻¹, i.e. in the range of values in samples SYN-1a and -1b (254 and 124 μ eq l⁻¹), which were explicitly prepared for determining

alkalinity. However, the point is that alkalinity in atmospheric deposition is low, generally below 50 μ eq l⁻¹ and, at the same time, these values are important in the ion balance because of the low ion concentration of most of the samples.

The identification of unreliable analytical methods for other analytes in deposition and soil solution was made difficult by the low number of laboratories performing these analyses, which made it impossible to perform a statistical analysis. On the other hand, a list of unreliable methods has been drawn up by taking into account also the results of other exercises for deposition samples (see Table 6.3), and alternative techniques are suggested. The problematic methods mainly include those that have become somewhat outdated, such as turbidimetry or nephelometry for the determination of sulphate, silver nitrate titration for chloride, Kjeldhal digestion for the determination of ammonium+amino nitrogen, and colorimetric titration for alkalinity.

The laboratories participating in the ICP Forests Programme are strongly invited to reconsider their in-laboratory QA in the light of the results of this inter-comparison and the recommendations of the rapporteurs. Unreliable analytical methods should be changed and a validation protocol adopted. Of course this is not substitution, but should be included in addition to the other in-laboratory practices.

Continuation of the WRT programme appears to be a useful tool to stimulate self criticism and to check the improvements of laboratories from one year to another until a sufficiently reliable QA level has been achieved for the ICP Forests programme. At the same time it is important to develop collaboration between the laboratories engaged in the same type of analyses as this is a useful, cheap and qualified way to improve the performance. This is the task and the challenge of the Working Ring Test and of all the QA/QC activities proposed within the Expert Panels on Deposition and the Working Group on Soil Solution of the ICP Forests programme.

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10. ANNEXES

10.1. Results by parameter

(C.N.R. Institute of Ecosystem Study, Verbania Pallanza, Italy)



Fig. 5.2. The results and Youden plots of the pH measurements.



Fig. 5.3. The results and Youden plots of the conductivity measurements.



Fig. 5.4. The results and Youden plots of the alkalinity determinations.



Fig. 5.5. The results and Youden plots of the sulphate determinations.



Fig. 5.6. The results and Youden plots of the nitrate determinations.



Fig. 5.7. The results and Youden plots of the chloride determinations.



Fig. 5.7. Continuation.



Fig. 5.8. The results and Youden plots of the calcium determinations.



Fig. 5.9. The results and Youden plots of the magnesium determinations.



Fig. 5.10. The results and Youden plots of the sodium determinations.



Fig. 5.10. Continuation.



Fig. 5.11. The results and Youden plots of the potassium determinations.



Fig. 5.12. The results and Youden plots of the ammonium determinations.



Fig. 5.12. Continuation.



Fig. 5.13. The results and Youden plots of the phosphate determinations.



Fig. 5.14. The results and Youden plots of the total phosphorus determinations.



Fig. 5.15. The results and Youden plots of the DOC determinations.



Fig. 5.16. The results and Youden plots of the total nitrogen determinations.



Fig. 5.17. The results and Youden plots of the total sulphur determinations.



Fig. 5.18. The results and Youden plots of the silicon determinations.


Fig. 5.19. The results and Youden plots of the aluminium determinations.



Fig. 5.20. The results and Youden plots of the iron determinations.



Fig. 5.21. The results and Youden plots of the copper determinations.



Fig. 5.22. The results and Youden plots of the manganese determinations.



Fig. 5.23. The results and Youden plots of the zinc determinations.

10.2. Raw data on CD

Only the participating laboratories and their National Focal Centres will be provided by a CD containing not only all the analytical results of all laboratories by laboratory code, but also the nominative results for each laboratory. This way all laboratories can use the data for their different working processes and QA/QC adaptation.

10.3. Example of Excel file with validation of results

A detailed example for the validation of the Finish results is given for water samples 2 and 3 on the CD sent with this report to the participating laboratories and their National Focal Centres only.

10.4. Captions of figures

Fig. 2.1. The length of time (days) between dispatch and arrival at the participating laboratories.

Fig. 3.1. Example of presentation of the results.

Fig. 3.2. Examples of Youden's plots.

Fig. 5.1. Ionic balances of the samples.

Fig. 5.2. The results and Youden plots of the pH measurements.

Fig. 5.3. The results and Youden plots of the conductivity measurements.

Fig. 5.4. The results and Youden plots of the alkalinity determinations.

Fig. 5.5. The results and Youden plots of the sulphate determinations.

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