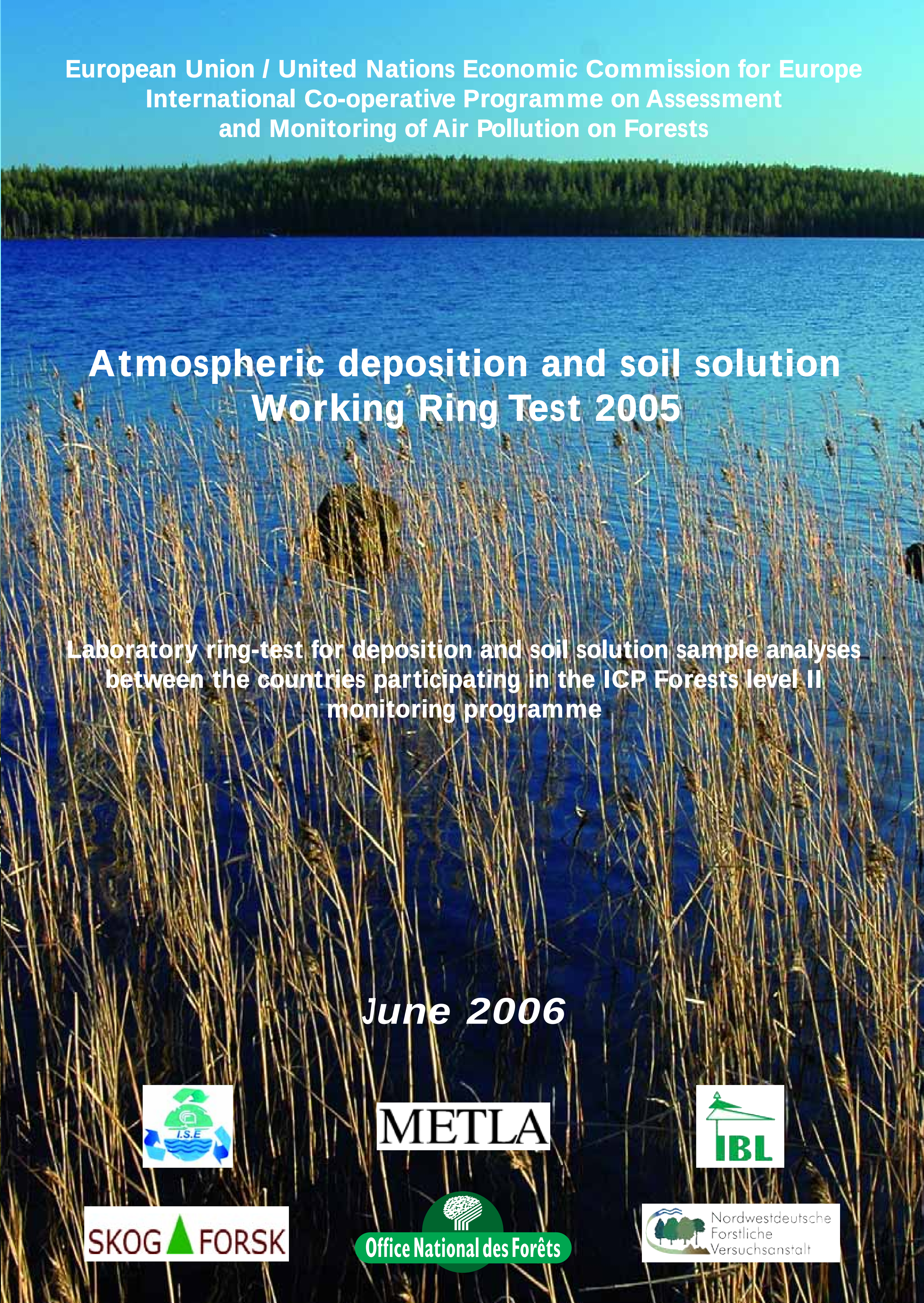

European Union / United Nations Economic Commission for Europe
International Co-operative Programme on Assessment
and Monitoring of Air Pollution on Forests

Atmospheric deposition and soil solution Working Ring Test 2005

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

June 2006

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Working Ring Test 2005

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SUMMARY

A Working Ring Test (WRT) was organised in the framework of EU Regulation (EC) No 2152/2003 (“Forest Focus”) and of the UN/ECE Program “ICP Forests” in order to evaluate the overall performance of the laboratories monitoring atmospheric deposition and soil solution in European Forests, and to verify the improvement in analytical quality resulting from the QA/QC work carried out in the laboratories which participated in a previous WRT.

Seven natural samples of atmospheric deposition and soil solutions and 6 synthetic solutions were distributed to 52 laboratories, which analysed them using their routine method for the following variables: pH, conductivity, calcium, magnesium, sodium, potassium, ammonium, sulphate, nitrate, chloride, total alkalinity, phosphate, total dissolved nitrogen, dissolved organic carbon, aluminium, copper, iron, manganese, zinc, total phosphorus, total sulphur and silica.

A Data Quality Objective (DQO) was defined for each variable, based on the results of the previous WRT, comparison with the DQOs of other international networks, and the importance of the variable in deposition and soil solution monitoring.

It emerged that 38% of the results do not meet the DQO, indicating for which variables and in which laboratories improvement in analytical performance is needed. The results of the exercise clearly show that the use of data check procedures such as those described in the *ICP Forests manual for sampling and analysis of atmospheric deposition* would reveal the presence of inaccurate or outlying results, and would greatly improve the overall performance of the laboratories.

Some analytical methods were found to be unsuitable for the samples used in this WRT and for atmospheric deposition samples in European forests; these include outdated methods, such as turbidimetry or nephelometry for the determination of sulphate, silver nitrate titration and ion selective electrode for chloride, Kjeldahl digestion for the determination of ammonium and organic nitrogen, and colorimetric titrations for alkalinity.

A detailed discussion of the analyses of total dissolved nitrogen, dissolved organic carbon and total alkalinity is also provided, as these were the variables giving rise to most of the analytical difficulties encountered.

Finally, a comparison between the results of this WRT and those of the previous exercise showed that the analytical performance of the laboratories participating in both WRTs improved following the adoption of QA/QC procedures.

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This work was partially funded by the European Union through the Forest Focus European Regulation No. 2152/2003, and by the Finnish Forest Research Institute (Finland), the Italian National Forest Service under the National Programme for Monitoring of Forest Ecosystems (CONECOFOR, Italy), the Norwegian Ministry of Agriculture and Food and the Ministry of the Environment, the Lower Saxon Forest Research Institut (Niedersächsische Forstliche Versuchsanstalt Göttingen, Germany) and the French National Forest Board (Office National des Forêts, France).

1. INTRODUCTION

The first Working Ring Test (WRT) initiated within the ICP Forests Expert Panels on Deposition (EPD) and Soil Solution was carried out in 2002 and it was attended by practically all the laboratories engaged in analysing deposition or soil solution within the intensive forest monitoring programme (Mosello *et al.* 2002). The WRT was intended to give to each laboratory a feedback of its performance and the possibility to improve their procedures for Quality Assurance and Quality Control (QA/QC) according to the numerous existing guidelines and standards.

In 2003, a Working Group on Quality Assurance/Quality Control (WG on QA/QC) for the analyses of atmospheric deposition and soil soluiton was created within the EDP. The WG on QA/QC operated in the updating of the *ICP Forests manual for sampling and analysis of atmospheric deposition* (Lövblad *et al.* 2004) and in promoting practices for the validation of chemical results, e.g. through the check of ion balance, and the comparison between measured and calculated conductivity (Mosello *et al.* 2005)

In the same year, the Parliament and the Council of the European Union adopted the Regulation (EC) No 2152/2003 (“Forest Focus”) concerning monitoring of forests and environmental interactions in the EU, in order to implement forest monitoring and protection activities. The promotion of harmonised collection, handling and assessment of data, the improvement of data evaluation and of the quality of data and information gathered are among the objectives of Forest Focus.

Considering that the WG on QA/QC and Forest focus share the common aim to improve data quality, it was decided to organize a common WRT, which would be part of both programs.

This second WRT is aimed to evaluate again the overall performance of the set of laboratories monitoring atmospheric deposition and soil solution in European Forests, but it will also allow to acknowledge the results of the QA/QC work carried out in the laboratories which participated to the first WRT, verifying the improvement in the analytical quality consequent to the identification and resolution of analytical problems.

As for the previous exercise, this WRT is one of the means available to the expert panels to achieve a common quality 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 to its QA/QC protocol.

However, in this second WRT we introduced Data Quality Objectives for each variable, based on previous international experience and on the results of the first WRT. These Data Quality Objectives should be intended as a compromise between the goals of the deposition and soil analysis within the ICP-Forests and the improvement in QA/QC which can be attended at a reasonable effort and cost.

As for the first WRT, in this report we will show the most critical analytical methods and highlight the need for efforts to improve laboratory performances and analytical quality, and we will provide guidelines for quality assurance and control and for data validation.

Finally, a detailed discussion will also be reserved to the analysis of total dissolved nitrogen, alkalinity and dissolved organic carbon (DOC), because they appeared the most problematic analyses in the previous WRT.

1.1. Aims

The aim of this second WRT were defined during the QA/QC group meeting of the ICP-Forêsts/EU Expert Panel on Deposition, held on 11-12 April in Göttingen as follows:

- to test the performances of the national laboratories participating in the ICP Forests programme, using natural throughfall and soil solution samples covering the range of acidity, sea salt, DOC, aluminium (soil solution), nitrogen and sulphur concentrations that are encountered in the participating countries;
- to identify for each ion a Data Quality Objective (DQO);
- to reiterate the strong recommendation of the use of the validation of single analyses, and to evaluate if the introduction of QA/QC procedures has led to improvements in the WRT results;
- to evaluate the performances of ICPF labs as a whole, to be used to detect trends in comparison with the first WRT and the future test, in relation to DQOs;
- to test in particular any improvement or residual problem in the analysis of total dissolved nitrogen (TDN), dissolved organic carbon (DOC) and total alkalinity (TA), identified as “weak points” in the previous exercise;
- to promote practices for the validation of chemical analyses, through the check of the ion balance and the comparison between measured and calculated conductivity, and
- to identify unreliable analytical methods and to compile of a list of “not permitted” analytical methods.

2. DATA QUALITY OBJECTIVES FOR DEPOSITION MEASUREMENTS IN ICP FORESTS

2.1 Definition of the Data Quality Objectives

To evaluate and maintain the quality of the results obtained in a measurement network, it is very important to define Data Quality Objectives (DQOs), i.e. to define the tolerable uncertainty for the measured data. DQOs are influenced both by the results which can be obtained using adequate analytical techniques and by the precision required by subsequent data elaboration to give reliable results in the framework of the monitoring programme.

In defining the DQOs within a single network, a distinction must be made between laboratory precision, inter-laboratory bias and overall precision.

Laboratory precision can be estimated by each laboratory by making an adequate number of replicate analysis on several samples, covering a concentration range comparable with the values found during monitoring. Although laboratory precision is not covered in this report, it is strongly recommended for each laboratory to estimate and monitor its own precision, so that it can track improvements and weaknesses in its activity.

To obtain an estimate of overall precision which includes both field and laboratory components, two sets of sampling equipment must be operated for at least one year in the same plot. Estimating overall precision is beyond the scope of this WRT.

This WRT gives an estimate of inter-laboratory bias, which assesses the comparability of results obtained in different laboratories. DQOs for this exercise were obtained by combining the results of the first WRT and the requirements of the monitoring programme, in the light of the results obtained by other international networks.

DQO definition is a dynamic process, and the values proposed here are expected to be revised as monitoring networks evolve and the requirements of the monitoring programme change.

2.2. Data Quality Objectives for the second WRT

To identify DQOs, the data collected in the first WRT (Mosello *et al.* 2002) were analysed and the Data Quality Objectives were calculated as follows:

1. for each sample and each parameter above the detection limit, the interquartile range (IQR) of reported concentration was evaluated. This represents the interval including 50% of the reported values:

$$IQR = (75^{th}\text{ percentile} - 25^{th}\text{ percentile})$$

2. an acceptable range (AR) was obtained, by dividing the IQR by the median value and expressing it as a percentage:

$$AR\% = \pm 0.5 * IQR * 100 / Median$$

In the case of pH, because of its logarithmic nature, AR was simply expressed as:

$$AR_{pH} = \pm 0.5 * IQR$$

3. for each parameter, the AR of the 15 samples analysed in the WRT1 were ranked, and the second highest value retained. The highest value was avoided to minimize the probability of this particular range being abnormally larger than the other ranges.

The ARs for all parameters are reported in Table 2.1, and compared with the values obtained in the Global Atmosphere Watch programme of the World Meteorological Organization (Allan 2004) using the same procedures.

The AR data were used to define specific **DQOs** for the various parameters.

In the case of pH and conductivity, the AR of ±0.09 units and ±8% **is** considered satisfactory and were simply rounded to ±0.1 units and ±10%, respectively.

Most of the remaining mandatory parameters showed AR smaller than ±15%, and this value was used, with the following exceptions:

- considering the importance of sulphate deposition in deposition chemistry and the low AR (±6.8%), the DQO for sulphate was set at ±10%;
- in the case of alkalinity, total dissolved nitrogen and DOC, the first WRT **revealed** several weaknesses in their analysis and the AR was calculated as ±70%, ±22% and ±16%, respectively. A DQO of ±15% was considered unrealistic on the basis of present laboratory practice, and it was decided to establish higher DQOs at this stage to help laboratories to improve their performances by aiming for an attainable goal. DQOs were then set at ±25% for alkalinity and ±20% for total dissolved nitrogen and dissolved organic carbon.

The ARs for the other parameters, analysis of which is not mandatory for the ICP Forest Programme, range between ±5 and ±25% (Table 2.1). The latter value is not very significant, as it refers to iron, which was measured at a very low level in four samples only. Considering that these parameters are intended to be optional, and considering the present performances in their analysis, a common DQO was set at ±20%.

Table 2.1 also reports the DQOs used in the EMEP monitoring network (e.g., Uggerud *et al.* 2005), which are very similar to those used in the present test.

Table 2.1 – Data Quality Objectives (DQOs) identified for this WRT (2nd WRT 2005), compared with the laboratory bias measured in the first WRT (WRT1: Mosello et al. 2002), the Global Atmosphere Watch Precipitation Chemistry Programme (GAW: Allan 2004), and with the DQOs used in the EMEP network 2004 intercomparison exercise (Uggerud *et al.* 2005).

Measured parameter	**Acceptable range %**		**Data Quality Objective (DQO)**	**DQO used by EMEP**
	WRT1	**GAW**		
Mandatory parameters				
pH	± 0.09 units	± 0.07 units	± 0.1 units	± 0.1 units
Conductivity	± 8%	± 7%	± 10%	± 15%
Calcium	± 7%	± 15%	± 15%	± 15%
Magnesium	± 7%	± 10%	± 15%	± 15%
Sodium	± 11%	± 10%	± 15%	± 15%
Potassium	± 7%	± 20%	± 15%	± 15%
Ammonium	± 12%	± 7%	± 15%	± 15%
Sulphate	± 7%	± 7%	± 10%	± 10%
Nitrate	± 11%	± 7%	± 15%	± 10%
Chloride	± 8%	± 10%	± 15%	± 15%
Aluminium	± 9%	-	± 15%	-
Alkalinity	± 70%	± 25%	± 25%	-
TDN	± 22%	-	± 20%	-
DOC	± 16%	-	± 20%	-
Other parameters				
Copper	± 5%	-	± 20%	-
Iron	± 25%	-	± 20%	-
Manganese	± 5%	-	± 20%	-
Silica	± 16%	-	± 20%	-
Phosphorus	± 10%	-	± 20%	-
Total Sulphur	± 6%	-	± 20%	-
Zinc	± 10%	-	± 20%	-
Others	-	-	± 20%	-

3. IMPLEMENTATION OF THE WORKING RING TEST

3.1. The water samples

Bulk precipitation, stand throughfall, stemflow and soil solution samples were collected in Germany and Finland in autumn 2004 and in France in winter 2005, and delivered to the laboratory of the Rovaniemi Research Station in early spring 2005. The samples were prepared in April 2005. The type and origin of the samples are given in Table 3.1.

Table 3.1. Description of the natural samples used in the ring test.

Sample code	**Type of sample**	**Characteristic**	**Origin of the sample**
WAT-1	Bulk deposition	Low N & S	Germany
WAT-2	Bulk deposition	Low N & S	France
WAT-3	Throughfall	High N & S, high NaCl	Germany
WAT-4	Throughfall	High NaCl, high DOC	France
WAT-5	Throughfall	Low NaCl, low N & S	Finland
WAT-6	Soil solution	Medium DOC	Finland
WAT-7	Soil solution	High DOC	Finland

A number of synthetic samples (SYN-1…4) were also prepared and included in the ring test (Table 3.2)

Table 3.2. Description of the synthetic samples used in the ring test.

Sample code	Analyses
SYN-1a and 1b	pH and alkalinity only
SYN-2a and 2b	Electrical conductivity only
SYN-3	All analyses, but not alkalinity
SYN-4	Elements (e.g. metals) only

3.2. Preparation of the samples

A total of six synthetic samples were prepared. SYN-1a and SYN-1b 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. Table 3.2).

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 µm) 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, 500 and 1000 ml bottles (HDPE) and kept in a cold room before dispatch. Every tenth bottle was reserved for homogeneity and stability determinations.

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).

3.3. Homogeneity of the samples after filtration

Homogeneity was tested by measuring pH and electrical conductivity, and determining DOC and total nitrogen, on bottles representing each sample (see Section 3.2). The relative standard deviation was calculated for the four variables. No statistically significant variation was found between the selected samples, and the samples were therefore considered to be fully homogeneous.

3.4. Stability of the samples

The stability of the natural samples was tested by analysing the samples, for all the parameters to be determined in the ring test, several times during the following ten-week period (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 inside the instrument dispersion.

3.5. Dispatch of the samples

The natural and synthetic samples were dispatched to the participating laboratories by the Finnish Postal Service, 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. Six of the laboratories that received the samples surprisingly did 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 eventually 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. Five boxes of samples were sent to laboratories in Russia by other means (primarily transported by Russian colleagues returning back to Russia by train), and there were therefore variable time gaps between dispatch and receipt – these laboratories are not taken into account in Fig. 3.1.

As the samples were relatively sterile (prefiltered through a 0.45 µm membrane filter), which will have considerably lengthened their shelf-life, the samples are not likely to have suffered from any deterioration during transport within a reasonable period of time. In fact, 80% of the samples were received within 2 days of dispatch (Fig. 3.1). One box of samples took 8 days to reach the laboratory in Cyprus owing to the long distance and hold-ups at the different central sorting depots.

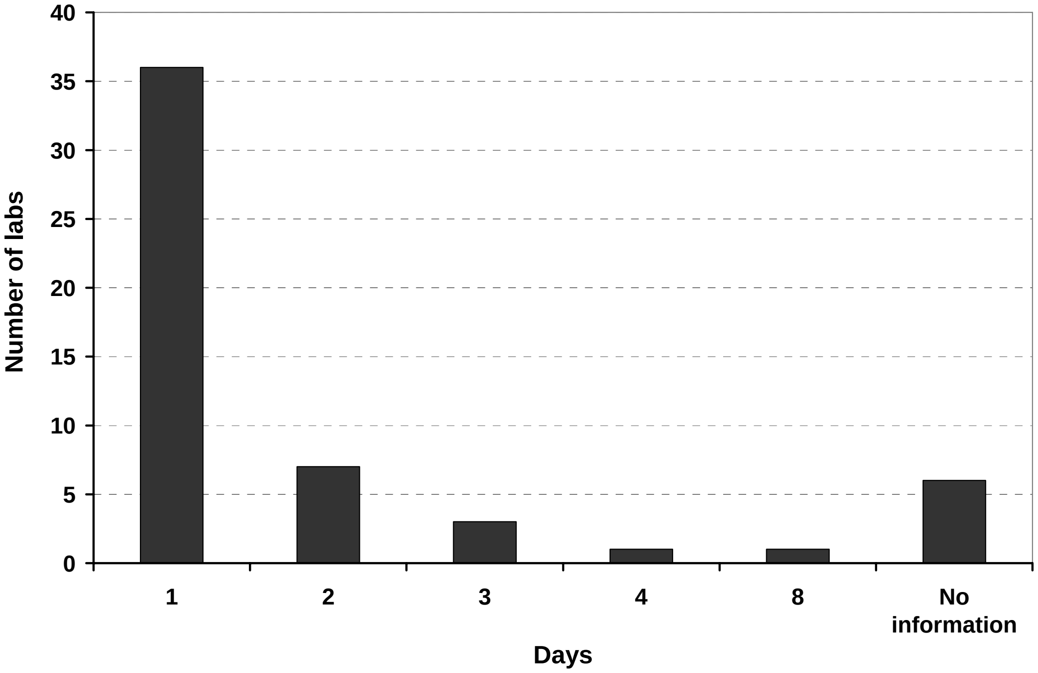


Fig. 3.1. Time between dispatch and arrival at the participating laboratories, and the number of laboratories not acknowledging receipt of the samples.

4. METHODS

4.1 Presentation of the results and numerical calculation

4.1.1. Graphical presentation of the results

The results for each variable (box-and-whiskers plots on the right side) and the number of laboratories that used a specific analytical method (bars on the left side) are presented in graphs for the natural (WAT1-9) and synthetic (SYN1-4) samples (example in Fig. 4.1). For each sample and each analytical method (acronyms in Table 6.1), the range between the mean value ± 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 (box-and-whiskers plots). As standard deviation cannot be calculated for less than three data, methods used by one or two laboratories are not included in the plots.

4.1.2. 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. 4.2). 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.

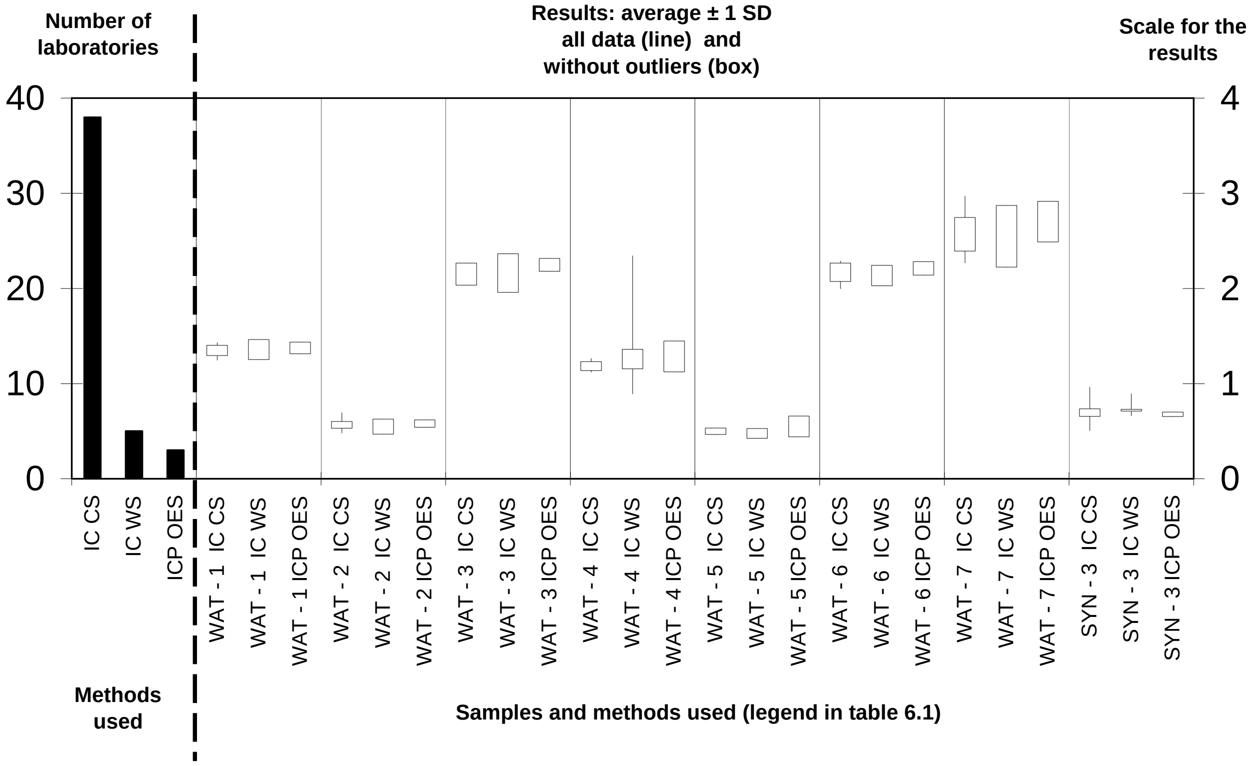


Fig. 4.1. Example of presentation of the results. The number of laboratories using each analytical method is indicated by the bars on the left, with the scale on the left side of the plot.
The box-and-whiskers graphs on the right, with their own scale on the right side of the plot, show the ±1-standard-deviation range around the mean, before (line) and after (box) outlier rejection.

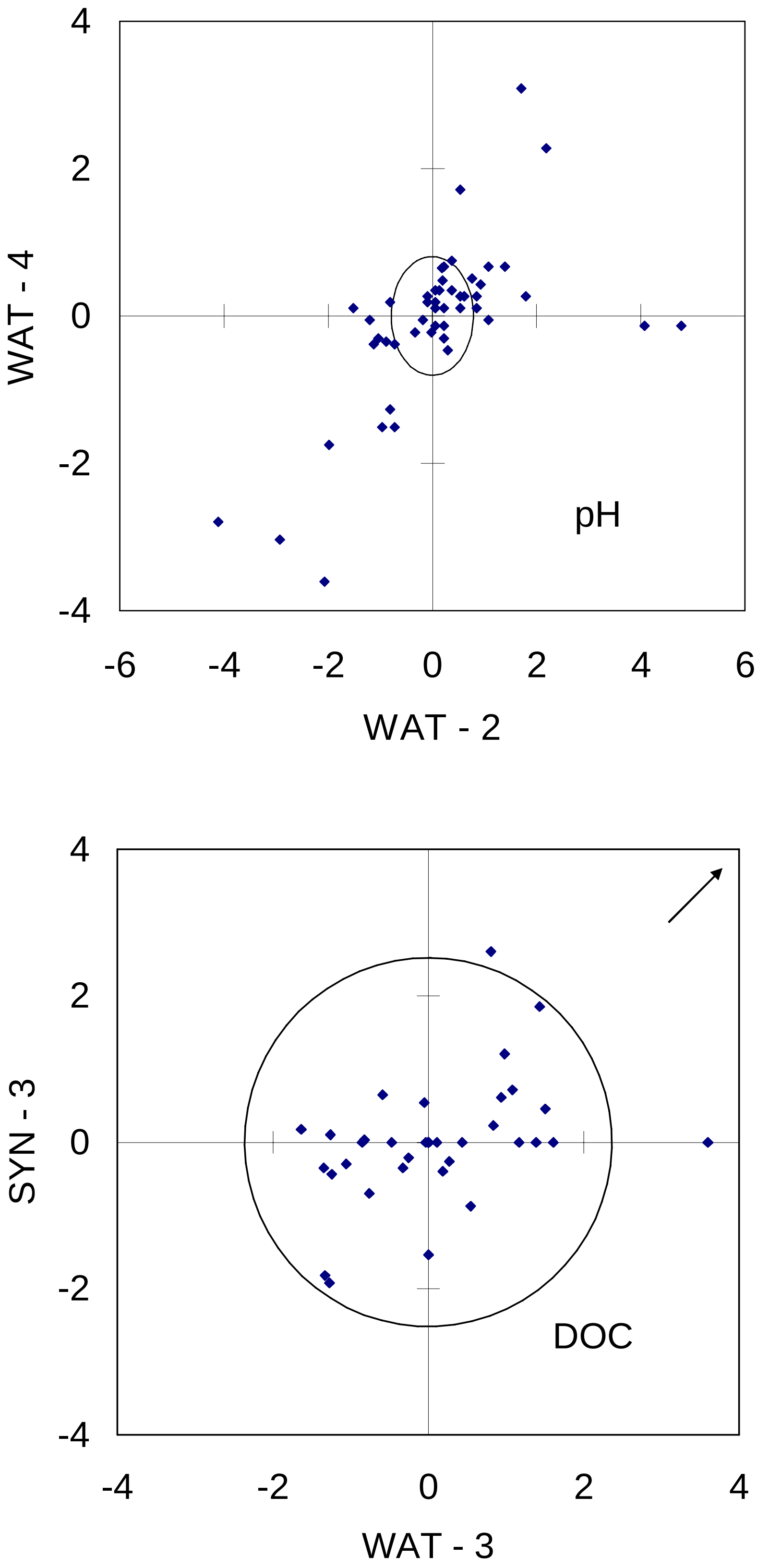


Fig. 4.2. Examples of Youden's plots, with prevailing systematic (top) and random (bottom) errors. The data are plotted in *z*-scores, so that the mean values lie on the axes and the units are standard deviations. The legends on the axes refer to the sample names (Tabs 3.1 and 3.2), while the ellipses indicate the DQOs (Table. 2.1). The arrow points to results outside the axes range.

4.1.3. Outlier detection and z-scores calculation

According to ISO 5725-5 (1998) and ISO/FDS 13528 (2005), 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:

$$G = (Y_i - Y_{average})/s$$

where Y_i is the suspected outlier, $Y_{average}$ is the sample mean, and s is the standard deviation of the sample. A table of significance of G is given by Soakal and Rohlf (1981).

For each laboratory, parameter and sample, a *z*-score is computed from the results after the outliers rejection. This score gives an index of the performance of a laboratory in relation to the network performance, since it gives an estimate of the bias of the result of that laboratory from the mean of the results. It is given by:

$$z = (Y_i - Y_{average})/s$$

where Y_i is the analytical result of the laboratory, $Y_{average}$ and s are the mean and standard deviation of the results after the rejection of outliers.

In this formulation, z indicates the number of times the measured value deviates from the mean, which is considered as the most reliable value, using the standard deviation as unit. Thus $z = 0$ means that the laboratory's measured value is the same as the mean; $z = 1$ means the measured value is 1 standard deviation higher than the mean, $z = -2$ means that the measured value is 2 standard deviations lower than the mean, and so on.

The *z*-score can also 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 *z*-scores should fall within -1 and +1, while 95.5% of them should lie between -2 and +2.

The above cannot be used to compare the performance of the same laboratory between different exercises, because if the global performance of the laboratories participating to the exercise will improve, then the *z*-score would be higher for the same bias. For the same reason, it cannot be used for a global evaluation of the performance of the set of laboratories, as the distribution of *z*-score for non-outlier results would be always the same.

Having defined the Data Quality Objectives, we can use an improved score (z'), in which s is substituted with a the target value of dispersion:

$$z' = (Y_i - Y_{average})/\mathrm{DQO}$$

Assuming that the DQOs will not change, this score can be used in successive interlaboratory exercises in order to identify general trends for a laboratory or a group of laboratories, or even the whole laboratory set. In fact, z' indicates the number of times the measured value deviates from the mean, which is considered as the most reliable value, using the DQO as unit. Thus $z = 0$ means that the laboratory's measured value is the same as the mean, and z'-scores lying between -1 and 1 will mean that the laboratory has met the Data Quality Objective.

As in the first WRT we used the first formulation of the *z*-score (Mosello *et al.* 2002), and considering that the Data Quality Objective for same variables (as alkalinity and total nitrogen) may be set more restrictive in the next exercise(s), we decided not to use for this second WRT the improved definition of *z* and to compare the performance of the laboratories on the basis of the number of outliers and missing data, and the percentage of data meeting the Data Quality Objective.

4.1.4. 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. To detect and exclude those data, 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 lowest detectable analyte signal S_d, the field blank S_b, and the variability in the field blank σ_b. LOD can be defined as the analyte concentration which give a gross signal exceeding S_b by K_d units of σ_b.

At LOD,

$$S_d = S_b + K_d \sigma_b$$

where a value of 3 is assumed for K_d.

For the estimation of LOQ, the quantification (numerical estimation of the amount) of the concentration of the analyte is considered reliable if the corresponding gross signal (S_q) is:

$$S_q = S_b + K_t \sigma_b$$

where a value of 10 is assumed for K_t so that at least one figure of the result is significant.

The values of LOQ and LOD depend on the specific analytical method used. After having evaluated them for the most widely used analytical methods, we decided to define some cutoff value, as the values for which it is no more possible to reliably quantify any substance with the methods commonly used by the laboratories participating in this WRT.

Then the parameters whose mean value in any sample used in this WRT was lower than the specific cutoff value for that variable were not included in the elaboration for that sample.

4.2. Validation of the results for major ions

4.2.1 The ionic balance

When the concentrations of all the major ions and the electrical conductivity of the solution are measured in a water sample, data quality can be checked through the correctness of the ionic balance, i.e. comparing the sum of anions and cations, and estimation of 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 µeq L^{-1}) as the concentration unit. The constants required to convert the units used in the ring test into µeq L^{-1} are given in Table 4.1

Table 4.1. Conversion of concentrations from mg L^{-1} to µeq L^{-1}, and the equivalent conductance at infinite dilution of the individual ions.

	Unit	**Factor to µeq L^{-1}**	**Equivalent conductance at 20°C** S cm^2 eq^{-1}	**Equivalent conductance at 25°C** S cm^2 eq^{-1}
pH		$10^{(6-pH)}$	315.1	350.0
Calcium	mg L^{-1}	49.9	54.3	59.5
Magnesium	mg L^{-1}	82.24	48.6	53.1
Sodium	mg L^{-1}	43.48	45.9	50.1
Potassium	mg L^{-1}	25.28	67.0	73.5
Ammonium	mg N L^{-1}	71.39	67.0	73.5
Sulphate	mg S L^{-1}	62.37	71.2	80.0
Nitrate	mg N L^{-1}	71.39	63.6	71.4
Chloride	mg L^{-1}	28.2	68.0	76.4
Alkalinity	meq L^{-1}	1000	39.4	44.5
Fluoride	mg L^{-1}	52.63	49.1	54.4

The limit of acceptable errors varies with the total ionic concentrations and the nature of the solution. With ΣCat and ΣAn indicating the concentrations (meq L^{-1} or µeq L^{-1}) of cations and anions, respectively, and Alk the Gran alkalinity:

$$\Sigma \text{ An} = \text{Alk} + [SO^{--}_4] + [NO_3^-] + [Cl^-]$$

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

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

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

PD thresholds for accepting analytical results are proposed in Table 4.2. In this WRT , 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, PD values much higher than those listed in table 4.1. can be expected and do not necessarily indicate analytical errors. The organic matter (i.e. DOC) in such samples acts as an anion with varying negative charge.

In samples with low DOC content, however, values of PD higher than those reported in Table 4.2 can indicate a lack of precision in one or more analytical techniques, the omission of important ions, or high DOC concentrations.

4.2.2. Comparison between measured and calculated conductivity

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

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

where $G = 1/R$ 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 (m^2) 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}). In practice the unit µS cm^{-1}, where 1 mS m^{-1} = 10 µS cm^{-1}= 10 µmho 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 cm^2 eq^{-1}). Values of equivalent conductance of the main ions at 20 and 25 °C are presented in table 4.1.

The conductivity calculated (CE_∞) from individual ion concentrations, multiplied by the respective equivalent ionic conductance (u_i)

$$CE_\infty = \Sigma\ u_i\ C_i$$

It is assumed that the bicarbonate ion accounts for almost all the alkalinity; this assumption is correct for solutions with pH in the ranging from 6.0 to 8.5.

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 25 °C.

To compare calculated conductivity (CE) to the measured value (CM), the percent difference, CD, may be defined as the ratio:

$$CD_{\infty} = 100 * |(CE - CM)|/CM$$

At the low ionic strength (below 0.1 meq L^{-1}) of open field atmospheric deposition samples, the discrepancy between measured and calculated conductivity should be no more than 2% (Miles & Yost, 1982). At higher concentration, as 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), based on ionic strength.

Ionic 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 I, and w_i = gram molecular weight of ion i.

The correction became relevant at ionic strengths higher than 0.1 meq L^{-1}, and 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:

$$\mathrm{Log}_{10}\, y = 0.5\ (IS^{0.5}/(1+IS^{0.5})-0.3\ IS)$$

The calculated conductivity, used for calculation of PD, is then obtained as:

$$CE = y^2\ CE_{\infty}$$

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 in the *ICP Forests manual for sampling and analysis of atmospheric deposition* (Lövblad *et al.* 2004) are given in Table 4.2.

Table 4.2. Threshold values for checking the analyses on the basis of the ion balance and conductivity at 25 °C.

Sample conductivity	below 10 µS cm^{-1}		between 10 and 20 µS cm^{-1}		above 20 µS cm^{-1}	
Sample type	open field	throughfall stemflow soil solution	open field	throughfall stemflow soil solution	open field	throughfall stemflow soil solution
Ion balance, PD	± 20%	-	± 20%	-	± 10%	-
Conductivity, CD	± 30%	± 30%	± 20%	± 20%	± 10%	± 10%

5. LABORATORIES PARTICIPATING IN THE WORKING RING TEST

A total of 52 laboratories participated in the second WRT, 44 of which had participated in the first WRT, too. A list is reported in table 5.1.

Table 5.1. List of the laboratories participating in the second WRT.
WRT1 = participating in the first WRT.

Country	Laboratory denomination	WRT1
Austria	Federal Research and Training Centre for Forest, Natural Hazards and Landscape, Vienna	yes
Belgium	Laboratory of Soil Science - Gent University, Gent	yes
Belgium	Unité des Eaux et Forêts, Université catholique de Louvain, Louvain-la-Neuve	yes
Bulgaria	Executive Environment Agency, Sofia	no
Cyprus	Analytical Laboratories Section, Department of Agriculture, Nicosia	yes
Czech Republic	Forestry and Game Management Res. Inst., Testing Laboratory, Praha 5 – Zbraslav	yes
Denmark	Forest & Landscape Denmark, Hørsholm	yes
Denmark	NERI, Department of Atmospheric Environment, Roskilde	yes
Estonia	Tartu Environmental Research Ltd, Tartu	yes
Finland	Finnish Forest Research Institute, Rovaniemi Research Station, Rovaniemi	yes
France	SGS Multilab, Courcouronnes	yes
Germany	Bayerische Landesanstalt fuer Wald und Forstwirtschaft, Freising	yes
Germany	Ecology Centre, University Kiel, Kiel	yes
Germany	Forstliche Versuchs- und Forschungsanstalt Baden-Württ. Abt. B+U, Freiburg	yes
Germany	Hessisches Landeslabor - Abt. VI -, Kassel	yes
Germany	Landesamt fuer Umweltschutz, Saarbrücken	no
Germany	Landesforstanstalt Eberswalde, Eberswalde	yes
Germany	Landesforstpräsidium Abt.III Ref.31 Bodenkunde/Monitoringlabor, Pirna Graupa	yes
Germany	Landeslabor Brandenburg, Cottbus	no
Germany	Landesumweltamt NRW, Essen	no
Germany	LLG Sachsen-Anhalt, Standort Halle-Lettin, Halle	yes
Germany	LUFA Rostock der LMS, Rostock	yes
Germany	LUFA Speyer, Speyer	yes
Germany	Niedersächsische Forstliche Versuchsanstalt, Göttingen	yes
Germany	Thueringer Landesanstalt fuer Landwirtschaft, Jena	yes
Greece	Forest Lands and Biogeochemistry, Athens	yes
Hungary	Ecological Laboratory of the Forest Research Institute, Budapest	yes
Ireland	Coillte Research Laboratory, Co. Wicklow	yes
Italy	Water Research Institute (IRSA-CNR), Brugherio	yes
Italy	CNR - ISE Institute of Ecosystem Study, Verbania Pallanza	yes
Italy	Laboratorio Biologico APPA-BZ, Laives	yes
Italy	Soil Science and Plant Nutrition Department - University of Florence	no

Table 5.1 – continued.

Country	Laboratory denomination	WRT1
Latvia	Latvian Environment, Geology and Meteorology Agency, Environmental Laboratory, Jurmala	yes
Lithuania	Agrochemical Centre of Lithuanian Institute of Agriculture, Kaunas	yes
the Netherlands	Chemical and Biological Laboratory Wageningen University, Wageningen	yes
the Netherlands	Energieonderzoek Centrum Nederland, Petten	yes
Norway	Norwegian Forest Research Institute, Ås	yes
Poland	Forest Research Institute, Laboratory of Forest Environment Chemistry, Warsaw	yes
Portugal	Laboratório de Análise Instrumental, Angra do Heroísmo (Açores)	yes
Portugal	Laboratory of Agricultural Chemistry Rebelo da Silva (LQARS), Lisboa	yes
Russia	«ECOANALYT» Ecoanalytical laboratory , Syktyvkar	no
Russia	Biological Institute SPbSU, Sankt-Petersburg	yes
Russia	Chemical Analytical Centre of Soil Science Faculty, Moscow State University, Moscow	no
Russia	Laboratory of Terrestrial Ecosystems, Apatity	no
Russia	St-Petersburg Scientific Research Center for Ecological Safety RAS, St-Petersburg	yes
Slovakia	Central Forest Laboratory, Forest Research Institute, Zvolen, Zvolen	yes
Slovenija	Laboratory for Forest Ecology, Slovenian Forestry Institute, Ljubljana	yes
Spain	Fundación Centro de Estudios Ambientales del Mediterraneo (CEAM), Paterna	yes
Spain	Laboratory of Forest Ecosystems, Madrid	yes
Sweden	IVL Svenska Miljöinstitutet AB, Göteborg	yes
Switzerland	WSL, Birmensdorf	yes
United Kingdom	Forest Research, Wrecclesham	yes

6. RESULTS

6.1. Analytical methods used

The list of analytical methods used by the participating laboratories is presented in Table 6.1.

Ion chromatography, using chemical suppression of the eluent (IC-CS), is the most widely used technique for sulphate, nitrate, chloride and phosphate.

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 also the most used method for metal analyses and for total phosphorus.

The analyses of ammonium and total dissolved nitrogen have mainly been performed by spectrophotometry or continuous flow analysis, and those of alkalinity by acid titration with potentiometric detection of the end point(s).

The analytical 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 4.1). Some aspects of the performance of the individual methods are discussed in the presentation of the results for the individual chemical variables.

6.2. Chemical characteristics of the samples

The samples used in this exercise (described in Section 3.1) were natural precipitation samples collected in the open field (WAT-1, WAT-2), under the canopy, i.e. stand throughfall (WAT-3, WAT-4, and WAT-5), and two natural soil solutions (WAT-6, WAT-7). A number of synthetic samples were also prepared in the laboratory for the measurement of pH and alkalinity (SYN-1a, SYN-1b), of conductivity (SYN-2A, SYN-2B), of the major ions (SYN-3) and of metals (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 6.2, 6.3 and 6.4. Values below the cutoff value (obtained from the quantification limit of the most commonly used analytical techniques, see chapter 4.1.4) have been omitted in the tables, as well as in the subsequent data analysis.

Sample ionic concentrations range between 218 and 969 µeq L^{-1}, with the highest values in throughfall samples WAT-3 and WAT-4, which show markedly higher contribution of sea-salt, indicated by the high chloride, sodium, sulphate and magnesium concentrations.

The concentrations of the main ions in open field samples are very low, and samples acidity cover the gradient from pH = 4.2 to 6.9.

The DOC concentrations in WAT-1, 2 and 6 are below 5 mg C L^{-1}, but it reaches 37 mg C L^{-1} in soil solution sample WAT-7. The phosphate concentrations were below the quantification limit samples, WAT-6 and SYN-3, and show the highest value (0.2 mg P L^{-1}) in sample WAT-5.

Apart from Al, Mn and Zn, metal concentrations were low, and they fall below the quantification limit of the most common techniques in most of the natural samples. In particular, no value was retained for Cd and Mo, a single value for Co, Ni and Pb and two values for Si.

For what concerns total alkalinity, the ICP Forest protocol prescribe the measurement of this variable for samples with pH higher than 5.0, so that samples WAT-1, WAT-3 and WAT-7 should not have been analyzed. In the case of sample WAT-6, the mean pH value was of 4.94, and the accepted range, assuming a DQO of 0.1 units, extend above 5.0. Nine laboratories measured a pH value higher than this limit and consequently measured alkalinity. Twenty-five further laboratories also did the analysis.

Table 6.1. - Analytical methods used and their acronyms as reported in the figures.

Chemical variable	Acronym	Analytical method	Number of labs
pH	LIS	Low ionic strength electrode	23
	GEN	Not specified	29
Conductivity	25°	Measurement performed at 25°C	16
	Corr	Measurement at different temperature, corrected to 25°C	36
Calcium	AAS	Atomic absorption spectrometry	11
	EDTA	EDTA titration	1
	IC CS	Ion chromatography, chemical suppression	12
	IC WS	Ion chromatography, no suppression	1
	ICP OES	ICP optical emission spectrometry	24
	ICP MS	ICP mass spectrometry	3
Magnesium	AAS	Atomic absorption spectrometry	11
	EDTA	EDTA titration	1
	IC CS	Ion chromatography, chemical suppression	12
	IC WS	Ion chromatography, no suppression	1
	ICP OES	ICP optical emission spectrometry	23
	ICP MS	ICP mass spectrometry	4
Sodium	AAS	Atomic absorption spectrometry	5
	AES	Atomic emission spectrometry	6
	IC CS	Ion chromatography, chemical suppression	12
	ICP OES	ICP optical emission spectrometry	24
	ICP MS	ICP mass spectrometry	3
Potassium	AAS	Atomic absorption spectrometry	6
	AES	Atomic emission spectrometry	5
	IC CS	Ion chromatography, chemical suppression	13
	IC WS	Ion chromatography, no suppression	1
	ICP OES	ICP optical emission spectrometry	23
	ICP MS	ICP mass spectrometry	3
Ammonium	SPEC Nes	Spectrophotometry, Nessler	5
	SPEC Phe	Spectrophotometry, indophenol blue	7
	CF GD	Continuous flow, ammonia diffusion	10
	CF Phe	Continuous flow, indophenol blue	11
	EL	Ion selective electrode	1
	IC CS	Ion chromatography, chemical suppression	10
	IC WS	Ion chromatography, no suppression	4
	CIA	Ion capillary electrophoresis	2
Sulphate	IC CS	Ion chromatography, chemical suppression	38
	IC WS	Ion chromatography, no suppression	5
	CF Met	Continuous flow, Ba sulphate excess, methyl thymol	2
	SPEC Met	Spectrophotometry, Ba sulphate excess, methyl thymol	1
	ICP OES	ICP optical emission spectrometry	3
	TURB	Turbidimetry	2

Table 6.1 - Continued

Chemical variable	Acronym	Analytical method	Number of labs
Nitrate	SPEC Phe	Spectrophotometry, phenoldisulphonic acid	1
	SPEC UV220	Spectrophotometry, UV detection at 220 nm	1
	SPEC Cd	Spectrophotometry, cadmium reduction	1
	CF Cd	Continuous flow, cadmium reduction	6
	CF Cu_Hyd	Continuous flow, copper, hydrazine reduction	1
	IC CS	Ion chromatography, chemical suppression	35
	IC WS	Ion chromatography, no suppression	4
	IV UV220	Ion chromatography, UV detection at 220 nm	1
	CIA	Ion capillary electrophoresis	1
Chloride	IC CS	Ion chromatography, chemical suppression	38
	IC WS	Ion chromatography, no suppression	5
	CIA	Ion capillary electrophoresis	1
	CF HgFe	Continuous flow, Hg thiocyanate in presence of ferric ion	4
	TIT_Ag Cr	Silver nitrate titration, potassium chromate indicator	3
	CT Hg	Colorimetric titration, mercury nitrate with diphenylcarbazone	1
Alkalinity		Potentiometric titration with extrapolation of the equivalence point:	
	PT_EX 2PF	two end-points	13
	PT_EX Gran	Gran method	8
	PT_EX Infl	detection of the inflection point	1
		Potentiometric titration, fixed end-point:	
	PT_1 4.3	end-point at pH=4.3	3
	PT_1 4.5	end-point at pH=4.5	9
	PT_1	other end-point	1
		Colorimetric titration:	
	CT Met	methyl orange indicator	2
	CT Br	bromochresol green indicator	1
	CT Mix	mixed indicator	1
TDN	PSB	Hydrolysis with $K_2S_2O_8$ + H_3BO_3 + NaOH	5
	PSOH	Persulfate digestion ($K_2S_2O_8$ + NaOH)	5
	CHML	Chemioluminescence	15
	KJELD	Kjeldahl digestion	5
	CIA	Ion capillary electrophoresis	2
Silica	SPEC Moxr	Spectrophotometry, oxalic acid, $SnCl_2$ or other reduction	2
	CF Moxr	Continuous flow, oxalic acid, $SnCl_2$ or other reduction	1
	ICP OES	ICP optical emission spectrometry	9
	ICP MS	ICP mass spectrometry	3

Table 6.1 - Continued

Chemical variable	Acronym	Analytical method	Number of labs
Phosphate	SPEC Mor	Spectrophotometry, ammonium molybdate, potassium antimonyl tartrate, ascorbic acid or $SnCl_2$ reduction	10
	SPEC Mov	Spectrophotometry, vanadomolybdophosphoric acid	2
	CF Mor	Continuous flow, ammonium molybdate, potassium antimonyl tartrate, ascorbic acid or $SnCl_2$ reduction	7
	CF Mov	Continuous flow, vanadomolybdophosphoric acid	1
	IC CS	Ion chromatography, chemical suppression	13
	IC WS	Ion chromatography, no suppression	1
	ICP OES	ICP optical emission spectrometry	2
	CIA	Ion capillary electrophoresis	2
DOC	THIR	Thermal combustion, IR detection	27
	PSH_UV IR	Persulphate and UV oxidation, IR detection	3
	SPEC UV320	Spectrophotometry, UV detection at 320 nm	4
	Other		3
Aluminum	AAS Flame	Atomic absorption spectrometry, flame	2
	AAS GFA	Atomic absorption spectrometry, graphite furnace	4
	ICP OES	ICP optical emission spectrometry	22
	ICP MS	ICP mass spectrophotometry	9
Cadmium	AAS Flame	Atomic absorption spectrometry, flame	1
	AAS GFA	Atomic absorption spectrometry, graphite furnace	8
	ICP OES	ICP optical emission spectrometry	11
	ICP MS	ICP mass spectrophotometry	10
	TXRF	Total reflection X-ray fluorescence	1
Cobalt	AAS GFA	Atomic absorption spectrometry, graphite furnace	3
	ICP OES	ICP optical emission spectrometry	8
	ICP MS	ICP mass spectrophotometry	8
	TXRF	Total reflection X-ray fluorescence	1
Copper	AAS Flame	Atomic absorption spectrometry, flame	4
	AAS GFA	Atomic absorption spectrometry, graphite furnace	7
	ICP OES	ICP optical emission spectrometry	14
	ICP MS	ICP mass spectrophotometry	11
	TXRF	Total reflection X-ray fluorescence	1
Iron	AAS Flame	Atomic absorption spectrometry, flame	2
	AAS GFA	Atomic absorption spectrometry, graphite furnace	2
	ICP OES	ICP optical emission spectrometry	24
	ICP MS	ICP mass spectrophotometry	6
	TXRF	Total reflection X-ray fluorescence	1
Mercury	AAS CV	Cold vapor atomic absorption	6
	ICP MS	ICP mass spectrophotometry	1

Table 6.1 - Continued

Chemical variable	Acronym	Analytical method	Number of labs
Manganese	AAS Flame	Atomic absorption spectrometry, flame	6
	AAS GFA	Atomic absorption spectrometry, graphite furnace	1
	ICP OES	ICP optical emission spectrometry	26
	ICP MS	ICP mass spectrophotometry	6
	TXRF	Total reflection X-ray fluorescence	1
	IC WS	Ion chromatography, no suppression	1
Molybdenum	AAS GFA	Atomic absorption spectrometry, graphite furnace	1
	ICP OES	ICP optical emission spectrometry	5
	ICP MS	ICP mass spectrophotometry	8
	TXRF	Total reflection X-ray fluorescence	1
Nickel	AAS Flame	Atomic absorption spectrometry, flame	1
	AAS GFA	Atomic absorption spectrometry, graphite furnace	4
	ICP OES	ICP optical emission spectrometry	11
	ICP MS	ICP mass spectrophotometry	8
	TXRF	Total reflection X-ray fluorescence	1
Lead	AAS Flame	Atomic absorption spectrometry, flame	1
	AAS GFA	Atomic absorption spectrometry, graphite furnace	8
	ICP OES	ICP optical emission spectrometry	10
	ICP MS	ICP mass spectrophotometry	10
	TXRF	Total reflection X-ray fluorescence	1
Zinc	AAS Flame	Atomic absorption spectrometry, flame	5
	AAS GFA	Atomic absorption spectrometry, graphite furnace	2
	ICP OES	ICP optical emission spectrometry	21
	ICP MS	ICP mass spectrophotometry	8
	TXRF	Total reflection X-ray fluorescence	1
Total P	ICP OES	ICP optical emission spectrometry	18
	ICP MS	ICP mass spectrophotometry	2
	SPEC	Persulphate oxidation, spectrophotometry molybdate	4
Total S	ICP OES	ICP optical emission spectrometry	15
	ICP MS	ICP mass spectrophotometry	2

Table 6.2. Median values, after outlier rejection. Dark grey = below the cutoff value (see chapter 4.1.4). Light grey = not to be measured.

Variable		**Unit**	**WAT-1**	**WAT-2**	**WAT-3**	**WAT-4**	**WAT-5**	**WAT-6**	**WAT-7**	**SYN-1a**	**SYN-1b**	**SYN-2a**	**SYN-2b**	**SYN-3**	**SYN4**
pH			4.19	5.14	3.91	5.23	5.49	4.94	4.17	6.96	6.11	░	░	4.85	░
Conductivity		µS cm^{-1} 25 °C	50.3	24.5	111.9	67.3	17	27.6	58.5	░	░	30.3	74.0	34.0	░
Calcium	Ca	mg L^{-1}	0.73	0.25	0.66	0.92	0.40	0.91	2.32	░	░	░	░	0.46	░
Magnesium	Mg	mg L^{-1}	0.19	0.21	0.39	0.57	0.19	0.40	0.67	░	░	░	░	0.19	░
Sodium	Na	mg L^{-1}	0.90	1.67	2.91	5.15	0.73	2.02	1.16	░	░	░	░	0.62	░
Potassium	K	mg L^{-1}	1.56	0.20	3.12	2.68	1.72	0.17	0.82	░	░	░	░	3.61	░
Ammonium	N-NH$_4$	mg N L^{-1}	0.34	0.69	2.20	1.82	0.20	■	0.13	░	░	░	░	0.76	░
Sulphate	S-SO$_4$	mg S L^{-1}	1.36	0.56	2.15	1.19	0.50	2.18	2.59	░	░	░	░	0.69	░
Nitrate	N-NO$_3$	mg N L^{-1}	1.34	0.36	3.53	1.29	0.11	■	■	░	░	░	░	0.33	░
Chloride	Cl	mg L^{-1}	1.45	2.95	5.37	9.08	1.03	1.47	1.34	░	░	░	░	2.65	░
Total alkalinity	T.Alk.	µmol L^{-1}	■	21	■	26	21	■	■	149	39	░	░	░	░
Phosphate	P-PO$_4$	mg P L^{-1}	0.020	0.094	0.52	0.031	0.23	■	0.066	░	░	░	░	■	░
Total dissolved N	TDN	mg N L^{-1}	1.77	1.32	5.98	3.46	0.58	0.18	1.10	░	░	░	░	1.06	░
Dissolved Organic C	DOC	mg L^{-1}	3.02	1.00	8.10	19.6	11.7	4.05	37.8	░	░	░	░	7.20	░
Aluminum	Al	µg L^{-1}	12	13	53	65	38	183	1304	░	░	░	░	░	734
Cadmium	Cd	µg L^{-1}	■	■	■	■	■	■	■	░	░	░	░	░	■
Cobalt	Co	µg L^{-1}	■	■	■	■	■	■	6	░	░	░	░	░	■
Copper	Cu	µg L^{-1}	3	■	2	2	5	■	4	░	░	░	░	░	85
Iron	Fe	µg L^{-1}	10	■	13	21	16	13	333	░	░	░	░	░	180
Mercury	Hg	µg L^{-1}	0.104	■	■	■	■	0.117	0.060	░	░	░	░	░	0.023
Manganese	Mn	µg L^{-1}	146	5	31	60	60	17	166	░	░	░	░	░	100
Molybdenum	Mo	µg L^{-1}	■	■	■	■	■	■	■	░	░	░	░	░	■
Nichel	Ni	µg L^{-1}	■	■	■	■	■	■	6	░	░	░	░	░	■
Lead	Pb	µg L^{-1}	■	■	■	32	■	■	■	░	░	░	░	░	■
Zinc	Zn	µg L^{-1}	19	125	17	43	21	10	42	░	░	░	░	░	87
Total phosphorus	P	mg L^{-1}	■	■	0.180	■	0.091	■	0.051	░	░	░	░	░	0.891
Total sulphur	S	mg L^{-1}	1.37	0.58	2.27	1.33	0.57	2.29	2.90	░	░	░	░	░	1.99
Silica	Si	mg L^{-1}	■	■	■	■	■	0.12	1.06	░	░	░	░	░	■

Table 6.3. Mean values, after outlier rejection. Dark grey = below the cutoff value (see chapter 4.1.4). Light grey = not to be measured.

Variable		**Unit**	**WAT-1**	**WAT-2**	**WAT-3**	**WAT-4**	**WAT-5**	**WAT-6**	**WAT-7**	**SYN-1a**	**SYN1-b**	**SYN-2a**	**SYN-2b**	**SYN-3**	**SYN4**
pH			4.17	5.12	3.90	5.22	5.49	4.92	4.16	6.91	6.09	░	░	4.83	░
Conductivity		µS cm^{-1} 25 °C	49.6	24.3	110.1	66.7	16.8	27.4	58.2	░	░	30.1	73.4	33.5	░
Calcium	Ca	mg L^{-1}	0.73	0.25	0.66	0.92	0.42	0.90	2.30	░	░	░	░	0.45	░
Magnesium	Mg	mg L^{-1}	0.19	0.21	0.39	0.57	0.19	0.40	0.67	░	░	░	░	0.19	░
Sodium	Na	mg L^{-1}	0.91	1.68	2.92	5.17	0.73	2.01	1.16	░	░	░	░	0.62	░
Potassium	K	mg L^{-1}	1.54	0.21	3.10	2.67	1.71	0.17	0.82	░	░	░	░	3.62	░
Ammonium	N-NH_4	mg N L^{-1}	0.34	0.68	2.17	1.81	0.20	■	0.13	░	░	░	░	0.76	░
Sulphate	S-SO_4	mg S L^{-1}	1.35	0.56	2.16	1.20	0.50	2.17	2.58	░	░	░	░	0.70	░
Nitrate	N-NO_3	mg N L^{-1}	1.33	0.41	3.50	1.27	0.11	■	■	░	░	░	░	0.33	░
Chloride	Cl	mg L^{-1}	1.46	2.99	5.41	9.06	1.06	1.50	1.36	░	░	░	░	2.68	░
Total alkalinity	T.Alk.	µmol L^{-1}	■	28	■	37	31	■	■	156	51	░	░	░	░
Phosphate	P-PO_4	mg P L^{-1}	0.020	0.083	0.43	0.03	0.196	■	0.074	░	░	░	░	■	░
Total dissolved N	TDN	mg N L^{-1}	1.76	1.32	5.97	3.49	0.59	0.21	1.07	░	░	░	░	1.06	░
Dissolved Organic C	DOC	mg L^{-1}	3.12	1.14	8.12	19.4	11.4	4.00	37.9	░	░	░	░	7.2	░
Aluminum	Al	µg L^{-1}	15	15	54	66	38	186	1302	░	░	░	░	░	738
Cadmium	Cd	µg L^{-1}	■	■	■	■	■	■	■	░	░	░	░	░	■
Cobalt	Co	µg L^{-1}	■	■	■	■	■	■	6	░	░	░	░	░	■
Copper	Cu	µg L^{-1}	3	■	2	3	5	■	4	░	░	░	░	░	86
Iron	Fe	µg L^{-1}	13	■	15	22	17	14	341	░	░	░	░	░	185
Mercury	Hg	µg L^{-1}	0.104	■	■	■	■	0.117	0.093	░	░	░	░	░	0.023
Manganese	Mn	µg L^{-1}	145	5	31	59	60	17	167	░	░	░	░	░	100
Molybdenum	Mo	µg L^{-1}	■	■	■	■	■	■	■	░	░	░	░	░	■
Nichel	Ni	µg L^{-1}	■	■	■	■	■	■	6	░	░	░	░	░	■
Lead	Pb	µg L^{-1}	■	■	■	32	■	■	■	░	░	░	░	░	■
Zinc	Zn	µg L^{-1}	19	125	18	43	21	11	43	░	░	░	░	░	88
Total phosphorus	P	mg L^{-1}	■	■	0.181	■	0.093	■	0.052	░	░	░	░	░	0.891
Total sulphur	S	mg L^{-1}	1.42	0.61	2.38	1.38	0.61	2.38	3.00	░	░	░	░	░	1.83
Silica	Si	mg L^{-1}	■	■	■	■	■	0.12	0.96	░	░	░	░	░	■

Table 6.4. Standard deviation, after outlier rejection. Dark grey = below the cutoff value (see chapter 4.1.4). Light grey = not to be measured.

Variable		**Unit**	**WAT-1**	**WAT-2**	**WAT-3**	**WAT-4**	**WAT-5**	**WAT-6**	**WAT-7**	**SYN-1a**	**SYN-1b**	**SYN-2a**	**SYN-2b**	**SYN-3**	**SYN4**
pH			0.09	0.13	0.06	0.12	0.16	0.11	0.06	0.15	0.12	░	░	0.12	░
Conductivity		µS cm^{-1} 25 °C	3.7	1.6	7.1	3.9	1.1	1.8	3.9	░	░	1.8	4.4	2.4	░
Calcium	Ca	mg L^{-1}	0.07	0.04	0.05	0.09	0.07	0.10	0.15	░	░	░	░	0.04	░
Magnesium	Mg	mg L^{-1}	0.02	0.02	0.03	0.04	0.02	0.02	0.05	░	░	░	░	0.03	░
Sodium	Na	mg L^{-1}	0.07	0.11	0.15	0.27	0.05	0.18	0.05	░	░	░	░	0.03	░
Potassium	K	mg L^{-1}	0.09	0.04	0.14	0.13	0.12	0.02	0.05	░	░	░	░	0.22	░
Ammonium	$N\text{-}NH_4$	mg N L^{-1}	0.02	0.06	0.17	0.16	0.03	▓	0.03	░	░	░	░	0.06	░
Sulphate	$S\text{-}SO_4$	mg S L^{-1}	0.06	0.05	0.14	0.07	0.04	0.11	0.23	░	░	░	░	0.04	░
Nitrate	$N\text{-}NO_3$	mg N L^{-1}	0.07	0.12	0.22	0.06	0.02	▓	▓	░	░	░	░	0.03	░
Chloride	Cl	mg L^{-1}	0.12	0.28	0.34	0.34	0.13	0.19	0.17	░	░	░	░	0.15	░
Total alkalinity	T.Alk.	µmol L^{-1}	▓	26	▓	31	26	▓	▓	51	27	░	░	░	░
Phosphate	$P\text{-}PO_4$	mg P L^{-1}	0.011	0.033	0.17	0.015	0.084	▓	0.043	░	░	░	░	▓	░
Total dissolved N	TDN	mg N L^{-1}	0.17	0.10	0.23	0.16	0.07	0.08	0.15	░	░	░	░	0.06	░
Dissolved Organic C	DOC	mg L^{-1}	0.52	0.55	0.69	1.40	1.06	0.53	2.83	░	░	░	░	0.57	░
Aluminum	Al	µg L^{-1}	10	5	8	6	6	17	65	░	░	░	░	░	50
Cadmium	Cd	µg L^{-1}	▓	▓	▓	▓	▓	▓	▓	░	░	░	░	░	▓
Cobalt	Co	µg L^{-1}	▓	▓	▓	▓	▓	▓	0.47	░	░	░	░	░	▓
Copper	Cu	µg L^{-1}	1.1	▓	0.8	0.9	1.4	▓	1.3	░	░	░	░	░	7.5
Iron	Fe	µg L^{-1}	5.4	▓	5.9	4.9	4.3	4.9	27	░	░	░	░	░	17
Mercury	Hg	µg L^{-1}	0.09	▓	▓	▓	▓	0.15	0.10	░	░	░	░	░	0.01
Manganese	Mn	µg L^{-1}	10	0.9	2.5	4.1	4.2	1.1	8.9	░	░	░	░	░	5.6
Molybdenum	Mo	µg L^{-1}	▓	▓	▓	▓	▓	▓	▓	░	░	░	░	░	▓
Nichel	Ni	µg L^{-1}	▓	▓	▓	▓	▓	▓	0.6	░	░	░	░	░	▓
Lead	Pb	µg L^{-1}	▓	▓	▓	3.0	▓	▓	▓	░	░	░	░	░	▓
Zinc	Zn	µg L^{-1}	2.1	11	2.1	5.2	2.3	1.6	4.9	░	░	░	░	░	7.5
Total phosphorus	P	mg L^{-1}	▓	▓	0.01	▓	0.01	▓	0.01	░	░	░	░	░	0.04
Total sulphur	S	mg L^{-1}	0.13	0.07	0.22	0.14	0.08	0.25	0.30	░	░	░	░	░	0.52
Silica	Si	mg L^{-1}	▓	▓	▓	▓	▓	0.02	0.31	░	░	░	░	░	▓

6.3. Overall performance of the laboratories

For most mandatory variables, 6 to 12% of the samples were not analyzed. The percentage increases to 40-47% in the case of alkalinity, TDN, DOC and aluminium. These percentages are similar to those found in the previous WRT (Mosello *et al.* 2002), but they are surprisingly high if we consider that the analysis of these variables is mandatory under specific conditions for either deposition or soil solution samples.

Considering the laboratories which participated in both WRTs, the analysis of DOC, TDN and total alkalinity was introduced by 10, 5 and 5 laboratories, respectively. However some labs which reported the values of these variables in 2002 did not perform their analysis in this WRT. They number to 4, 2 and 5, respectively.

Table 6.5 also shows the proportion of measurements falling into the DQOs reported in table 2.1. For the major ions, the proportion of results falling into the acceptance range is higher than 72%, with the highest value for sodium and the lowest for pH. On the other hand, for alkalinity, TDN, DOC and aluminium, the proportion of values outside the DQO ranges between 25 and 51%. Considering that the same variables were not measured by 40% or more of the labs, it is evident that these need special attention.

Considering the results obtained by each laboratory, Fig. 6.1. shows that a relevant number of laboratories measured all variables and produced very few outliers. For more than 50% of the laboratories the sum of missing and outlying results was lower than 12%. On the other hand, in six cases the same sum was higher than 30%, showing that some laboratories need an improvement in their analytical procedure. In a similar way, more than 90% of the results produced by some laboratories met the DQOs, while for some laboratories (including the six above mentioned), more than 50% of the results fall outside the acceptance range. These considerations allowed the WG on QA/QC to identify the laboratories which need to be helped to improve their performances.

Note that in figure 6.1 the laboratories are identified by a number, corresponding to the code included in the file for data transmission, in order to allow each participant to evaluate his or her own performance. However, the numbers do not correspond to the order of the list in table 5.1.

A detailed discussion on alkalinity, DOC and TDN, as well as recommendations on their analysis, are reported in chapter 8 of this report.

Table 6.5 – Quality performance of the laboratory set for each mandatory variable: DQO = Data quality objective (see chapter 2). Mand. = Mandatory for deposition (D) and/or soil solution (S) samples.

Variable	**Mand.**	**No. of Samples to be analyzed**	**Expected no. of analyses**	**Not analysed**	**Reported below detection limit**	**DQO** *(see table 2.1)*	**Within DQO**	**Out of DQO**	**Of which, outliers**
pH	D,S	10	520	6%	0	*0.1 unit*	72%	22%	4%
Conductivity	D	10	520	6%	0	*10%*	84%	10%	3%
Calcium	D,S	8	416	9%	1%	*15%*	81%	10%	5%
Magnesium	D,S	8	416	9%	0	*15%*	83%	8%	7%
Sodium	D	8	416	11%	0	*15%*	85%	4%	7%
Potassium	D,S	8	416	11%	2%	*15%*	82%	7%	7%
Ammonium	D	7	364	10%	1%	*15%*	73%	17%	11%
Sulphate	D,S	8	416	13%	0	*10%*	82%	5%	8%
Nitrate	D,S	6	312	13%	1%	*15%*	79%	8%	5%
Chloride	D	8	416	12%	0	*15%*	78%	10%	10%
Alkalinity	D	4	208	40%	2%	*25%*	25%	35%	2%
TDN	D	8	416	47%	1%	*20%*	47%	6%	6%
DOC	D,S	8	416	44%	1%	*20%*	51%	5%	5%
Aluminium	S	8	416	40%	5%	*15%*	42%	18%	5%

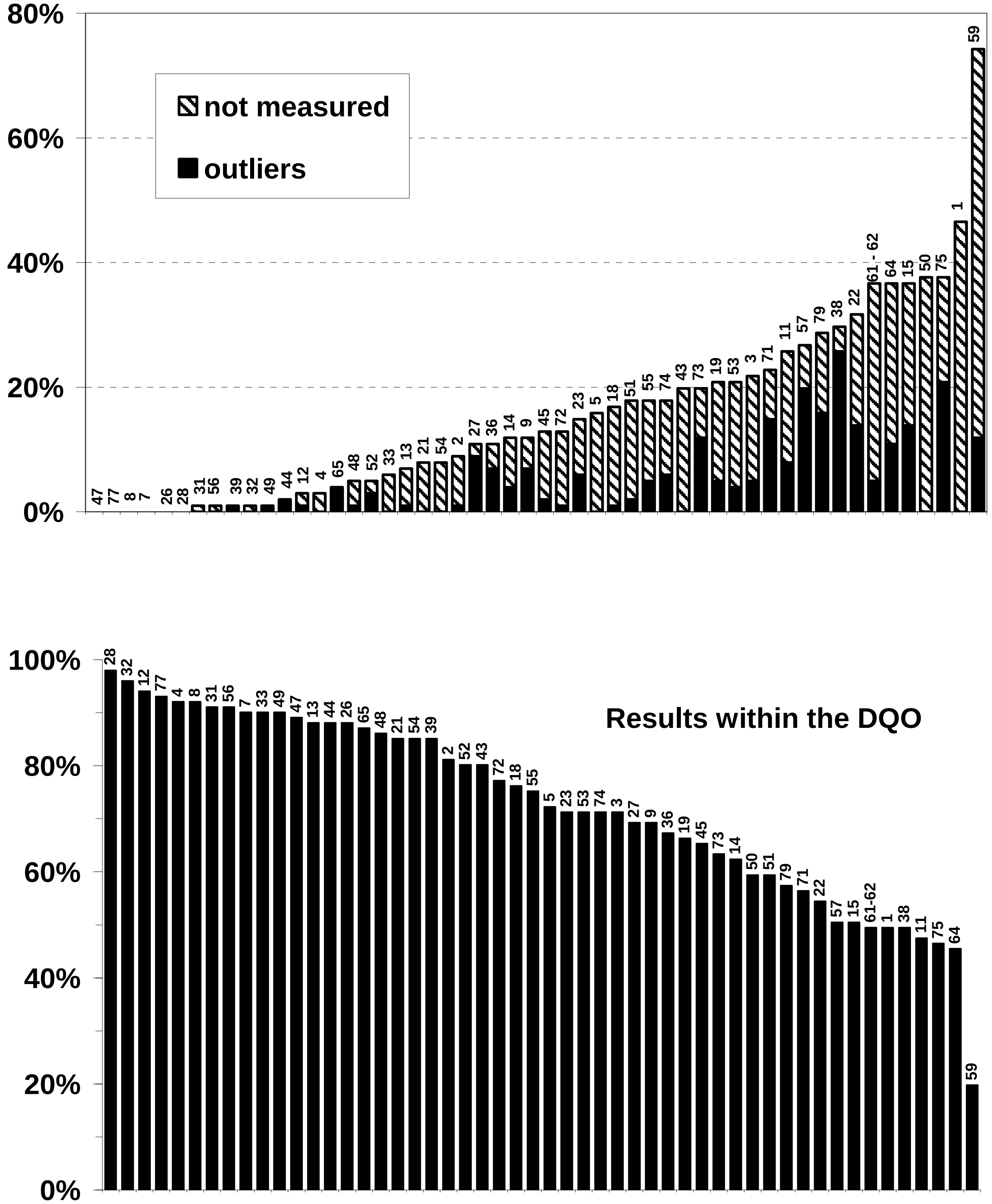


Fig. 6.1. – Percentage of missing or outlying results (top) and of results meeting the DQOs (bottom) submitted by each laboratory. The numbers identifying the laboratories correspond to the code included in the file for data transmission. The laboratories are ordered following decreasing analytical performance, i.e. the increasing number of missing and outlying results, and the decreasing number of results meeting the DQO, respectively.

6.4. pH

The percentage of laboratories using electrodes specific for low ionic strength solutions (LIS) was higher than in the previous WRT, reaching 46% (Fig. 6.2). However no relevant differences were observed between the results obtained with LIS electrodes and other electrodes (GEN), as regards either the mean values or the dispersion of the results. Only in the two synthetic samples with higher pH (SYN-1a and SYN-1b) a very slight difference appears. The Youden plots show the presence of systematic errors in some laboratories, deriving probably by the calibration procedure. The relatively small percentage of results within the DQO (72%) show that more attention should be paid to this analysis.

6.5. Conductivity

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. 6.3. There were no significant differences between the two sets of data. The dispersion of the values was relatively high, but 84% of the data met the DQO. The Youden plots show a very strong prevalence of systematic over random errors. A periodic calibration of the electrodes, using potassium chloride solutions of conductivity ranging from 10 to 500 $\mu S\ cm^{-1}$ is recommended, as well as the check of the temperature correction factor.

6.6. Calcium, magnesium, sodium and potassium

The Ca and Mg concentrations measured in this WRT were relatively low, generally below 1 $mg\ L^{-1}$, while those of Na and K covered a wider range. ICP OES was the technique most widely used for the analysis of these ions, followed by IC, AAS, ICP MS and AES (for Na and K) (Figs 6.4, 6.5, 6.6 and 6.7). A single lab measured Ca and Mg by EDTA titration (not shown in the plots), obtaining good results (but a high LOQ) for Mg and 6 outliers out of 8 results for Ca.

More than 80% of the results fell within the DQO (±15% interval), with slight differences between the four cations. Apart from EDTA titration, no relevant systematic difference was detected among analytical methods, but the precision of the laboratories using ICP MS was markedly lower than for the other methods.

According to the Youden plots, there was a slight prevalence of systematic over random errors, suggesting that the precision of these analyses may still be improved.

6.7. Ammonium

Ammonium concentration covered a wide range, between 0.13 and 2.2 $mg\ L^{-1}$. Sample WAT-6, showed a very low concentration (median of the results 0.03 $mg\ L^{-1}$) and was not considered. The analysis was performed using a relevant number of different methods: continuous flow analysis (21 labs), ion chromatography (14 labs), spectrophotometric determination (12 labs), ion capillary electrophoresis (2 labs, not shown) and ion selective electrode (1 lab, not shown).

The precision was relatively low, with 17% of the results falling outside the DOQ and 11% of outliers. The use of ion selective electrode and of the Nessler reagent for spectrophotometric determination lead to most of the outlying results. The other methods are quite comparable, both in the average and the dispersion of the results (Fig. 6.8).

The Youden plots show a marked dominance of systematic errors. More attention should be paid to this variable as ammonium is an important component of atmospheric deposition in Europe.

In the case of ammonium, as well as nitrate, preliminary problems were detected in the data submissions as some labs reported their results as mg of NH_4 L^{-1}, instead of mg of 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.

6.8. Sulphate

Most of the laboratories measured sulphate by ion chromatography, either with (38 cases) or without (5 cases) chemical suppression of the eluent. Three laboratories used ICP OES, with a correction for organic sulphur, obtained through an empirical relationship between organic carbon and organic sulphur. These three methods led to similar results (Fig. 6.9), with errors mainly due to random factors. In spite of the stricter DQO (±10%), a large number of results (82%) fell into the acceptance range.

Five other labs (not shown in the plot) used different methods, such as turbidimetry and spectrophotometry or continuous flow analysis with $BaSO_4$ excess and methyl thymol, producing results not comparable to the rest of the data (i.e. outliers). In the case of the latter method, one laboratory gave results well comparable with the rest of the WRT participants, while the other laboratory mainly gave outlying results.

6.9. Nitrate

The wide range of nitrate concentration in the WRT spans between 0.11 and 3.53 mg L^{-1}. Samples WAT-6 and WAT-7, showing very low concentrations (median of the results around 0.03 mg L^{-1}), were not considered. As in the case of sulphate, most of the laboratories measured nitrate by ion chromatography, with (35 cases) or without (4 cases) chemical suppression of the eluent, or with UV detection (1 case, not shown), while 7 laboratories used continuous flow analysis, and 4 used other methods, not shown in the plots and listed in table 6.1.

In spite of the large variety of methods used, most of them led to similar results (Fig. 6.10) with 8% of the data lying outside the DQO and 5% of outliers. The only unsatisfactory method was spectrophotometry with direct UV detection at 220 nm, which overestimated most samples producing 3 outliers in a single lab, because of the presence of large amounts of organic compounds in some samples.

Because of these different methods, data comparability is affected by the possible presence of nitrites, like in sample WAT-2. In this case, the results obtained by ion chromatography were distinctly smaller than those obtained with the methods which perform nitrate reduction to nitrite and then obtain nitrate concentration from nitrite determination (i.e. SPEC Cd and CF Cd), leading to the formation of two distinct groups of data.

As reported above, some evident outliers in the submitted data are due to the submission of results as mg of NO_3 L^{-1}, instead of mg of N L^{-1} as requested in the form. We underline again the importance of paying attention to the correct units in data submission both for WRT exercises and for the annual monitoring data.

6.10. Chloride

The concentration of chloride in the WRT samples were relatively high (1-9 mg L^{-1}), representing the values usually found in atmospheric deposition in regions close to the sea, but not covering the range usually measured in more continental areas, like the Alps.

The 43 laboratories which measured sulphate by IC, used the same analytical technique for chloride (Fig. 6.11). Other methods used were ion capillary electrophoresis (1 lab, not shown), continuous flow analysis with $Hg(SCN)_2$ in presence of Fe^{++} (4 labs), $Hg(NO_3)_2$ colorimetric titration with diphenylcarbazone (1 lab, not shown) and $AgNO_3$ titration with K_2CrO_4 indicator (3 labs). Apart the latter methods, which produced 19 outliers out of 24 results, the analytical methods used were comparable.

The Youden plots show a prevalence of systematic errors and there were several values exceeding the target range of ±20% of the median values. This aspect, considering the relatively high concentration of chloride in these samples, and the presence of outlying values produced with the most reliable techniques underline the necessity to pay more attention to the care of the samples to avoid their pollution.

6.11. Alkalinity

The alkalinity measurements were one of the most critical of the analyses considered, as regards both missing results and the associated dispersion and errors. The discussion of the results will be clearer after a brief description of the meaning of alkalinity and of the different way to measure it.

The alkalinity of a water sample is its acid-neutralising capacity, defined as the amount of acid needed to neutralise the bases present in a solution. 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 titrable bases in the sample, and is determined by means of an acidimetric titration. In freshwater or precipitation, these bases are primarily bicarbonate, as well as hydroxyl ions at pH values above 8.0, sulphide and non-ionic 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 & 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.

Alkalinity is always measured by acid titration, but to detect the inflection point, several techniques are used:

1) direct determination of the inflection point, monitoring the pH and plotting the titration curve and its derivative during the titration. This technique, used by a single laboratory in this WRT, is difficult and often not precise at very low alkalinity for the difficulties related to the choice of added volumes and for the slow response of pH electrodes;
2) a titration performed well beyond the end point (e.g. to pH 4 or less), recording a number of pH values and the corresponding added volume of acid. A subsequent extrapolation by least-

squares regressions allow the calculation of the equivalent point (Gran, 1952). The Gran method was used by 8 laboratories;

3) a simplified version of the Gran titration requires only two end-points, at pH 4.5 and 4.2, allowing a simpler calculation of the equivalence point. This is the simplest method to correctly measure alkalinity, and it was used by 13 laboratories;
4) continuing the titration well beyond the end-point, up to pH 4.5 or less. Even if this method assure that all alkalinity is consumed by the added acid, it overestimates alkalinity by the amount of acid necessary to decrease the pH from 5.0-5.6 (bicarbonate inflection point) to the end-point. These systematic errors are equivalent to 32 and 50 μeq L^{-1} for a final pH of 4.5 and 4.3, respectively. These values are 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, but it would be simpler to simply note the added volume and to continue the titration up to pH=4.2 to perform a two end-point titration with better results. Fourteen laboratories used this method, mostly selecting the end-point at pH 4.3;
5) colorimetric determination of the end point, used by four laboratories. In this case the type of dye used and the pH of the colour change are both critical factors; furthermore 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.

A precise understanding of the meaning of alkalinity is necessary to avoid analytical errors. Following the *ICP Forests manual for sampling and analysis of atmospheric deposition* (Lövblad *et al.* 2004), samples with pH lower than 5.0 do not need the measure of alkalinity. In effects its value would be very lower than the LOD.

The ICP Forest protocol prescribes the measurement of this variable for samples with pH higher than 5.0, so that samples WAT-1, WAT-3 and WAT-7 should not have been analyzed.

In the case of sample WAT-6, the mean pH value was 4.94, and the accepted range, assuming a DQO of 0.1 units, extend above 5.0. Nine laboratories measured a pH value higher than this limit and consequently measured alkalinity. Twenty-five further laboratories also did the analysis. Out of the 34 laboratories which measured alkalinity, 20 of them correctly reported "0 μeq L^{-1}", "below the LOD", or negative values, meaning that the sample was actually acid. However, 14 laboratories found alkalinity values ranging from 8 to 110 μeq L^{-1}. Ten of them used colorimetric titration or potentiometric titration to a fixed end-point, techniques which would have justified the detection of 30-50 μeq L^{-1} of alkalinity, but four of them used the Gran method or the titration with two end-points, which should have resulted in negative alkalinity values.

Samples WAT-1, WAT-3 and WAT-7 were even more acid (pH between 3.9 and 4.2), and almost all the laboratories which attempted to analyze their alkalinity reported values below the detection limit, or negative. However one laboratory, using a potentiometric titration with fixed end point at pH=4.3, found 80 and 94 μeq L^{-1} of alkalinity in samples WAT-1 and WAT-3, even if the starting point of the titration was lower or equal to the end point.

Considering the samples with a pH higher than 5.0, for which the analysis of alkalinity would be mandatory, 40% of the data were missing as twenty laboratories did not analyse alkalinity in any sample.

The results obtained through different methods are compared in Fig. 6.12. The plot only shows the results obtained through methods used by more than two laboratories. It is evident that the single end-point titration at pH=4.3 overestimates alkalinity. The other methods give similar results because of the very high dispersion of the data, with relative standard deviations ranging from 32% for the synthetic sample SYN-1a with alkalinity of 149 µeq L^{-1}, to 150% for sample WAT-2 (alkalinity = 21 µeq L^{-1}). In spite of the larger DQO agreed for alkalinity, most of the results still fall outside the acceptance range.

The Youden plots clearly show the strong prevalence of systematic errors, due to both the choice of unsuitable methods and the modality of the titration. Some recommendations for the measurement of alkalinity are reported in chapter 8.

6.12. Total dissolved nitrogen (TDN)

Total dissolved nitrogen, a mandatory variable in throughfall and stemflow samples, was analysed by 32 of the 54 laboratories, only (Fig. 6.13). Fifteen of them used chemoluminescence, five the Kjeldhal method, and two capillary electrophoresis. The last ten laboratories used either ion spectrophotometry or continuous flow analysis after nitrogen oxidation to nitrate by hydrolysis with $K_2S_2O_8$, H_3BO_3 and NaOH (PSB) or by alkaline persulphate digestion ($K_2S_2O_8$ and NaOH, PSOH).

The nitrogen concentration in the analysed samples covers a wide range, from 0.18 to 5.98 mg L^{-1}. From the plot of the results (Fig. 6.13) it clearly appears that chemiluminescence and PSB give comparable results, while in the case of Kjeldahl and PSOH data dispersion is markedly higher, even in the samples with higher concentration. Although the low precision of the Kjeldahl method at these low levels was known, the highly disperse results produced by PSOH, should be noted, probably due to the loss of ammonia in the form of ammoniac because of the high pH of the sample during digestion. A large majority of the results fell within the acceptance range (±20%).

A detailed discussion of the analysis of total dissolved nitrogen, together with an assessment of the analytical techniques, are reported in chapter 8.

6.13. Dissolved organic carbon (DOC)

Dissolved organic carbon is a mandatory variable in the ICP Programme for soil solutions and throughfall deposition samples, but it was measured by only 37 laboratories. Most of them measured DOC by thermal combustion and IR detection of the carbon dioxide formed (THIR, 27 labs), while 3 labs used persulphate and UV oxidation and IR detection (PSH_UV IR) and four labs spectrophotometry, with UV detection at 320 nm. Three labs (not shown in the plot) used oxidation with dichromate, H_2SO_4, and Ag and titration of the residual solution by More salt, and persulphate and UV oxidation followed by conductometry.

Most methods gave similar results (Fig. 6.14), but the spectrophotometric method with detection at 320 nm produced some outlying values and showed a larger dispersion of the results, because of its sensitivity to interferences. Most of the results met the DQO (±20%). Chapter 8 also contains a methodological assessment of DOC analysis.

6.14. Aluminium

The analysis of aluminium is mandatory for soil solutions, and only 37 laboratories performed it, mostly by ICP OES. Other methods used were ICP MS and atomic absorption spectrometry. Two laboratories used AAS Flame, and they analysed only the samples with concentrations higher than 0.7 mg L^{-1}, mostly producing outlying results.

Apart from samples WAT-1 and WAT-2, natural open field deposition samples with very low Al concentration (around 15 µg L^{-1}), the results obtained using different methods were comparable and they mostly met the DQO (Fig. 6.15).

6.15. Phosphate, total phosphorus

Neither phosphate nor total phosphorus are mandatory in the monitoring of deposition and soil solution in the ICP Forests program, but they are used to detect pollution of deposition samples. The analyses of PO_4 and total phosphorus were performed by 24 and 38 laboratories, respectively, and the values for many of the natural samples were below the quantification limit.

Phosphate (Fig. 6.16) was mainly determined by ion chromatography (14 labs), spectrophotometry (12 labs), continuous flow analysis (8 labs), ICP OES (2 labs, not shown) and capillary electrophoresis (2 labs, not shown). The phosphate content in the sample was representative of the values usually found in atmospheric deposition, but it was too low to be correctly analysed by IC or ICP OES. For this reason the results show high dispersion, with standard deviation higher than 40% after outlier rejection, and strong systematic errors.

In the case of total phosphorus (Fig. 6.16), mainly analysed by ICP OES, we considered only the four samples with total P concentration higher than 0.05 mg L^{-1}. At these levels, the methods were comparable, and most of the results fell in the acceptance range of ±20%. Higher dispersion was found for the other samples.

6.16. Total sulphur

Most of the analyses were performed by ICP OES, while ICP-MS was used by two laboratories which overestimated TS concentrations (not shown). Most of data fell within the acceptance range, but the Youden plot (Fig. 6.17) clearly shows the presence of systematic errors.

We recall that total sulphur measured by ICP OES includes both sulphate and organic sulphur, and a correction for the latter is required if TS concentration is intended to give an estimate of sulphate content of atmospheric deposition.

6.17. Silica

Silica was measured in soil solution (WAT-6 and WAT-7) and in one synthetic sample (SYN-4) by 15 laboratories, using ICP OES (9 cases), ICP MS (3 cases), spectrophotometry (2 cases, not shown) and continuous flow analysis (1 case, not shown). The concentrations range between 0.12 and 0.96 mg L^{-1}, and most of the data fell outside the DQO, with clear evidence of systematic errors (Fig. 6.18). A systematic difference between ICP OES and ICP MS is also evident.

6.18. Manganese, zinc, copper and iron.

The number of laboratories reporting an analytical method for performing metal analysis ranged from 7 for Hg to 47 for Mn. The concentrations found in the natural samples used for this WRT were very low, and a number of metal concentrations resulted below the limit of quantification. For example, in the case of Hg, data above quantification limit were reported by 3 labs, only. In this report we will consider Mg, Zn, Cu, Fe.

The most used analytical methods for metal analyses were ICP OES, ICP MS and AAS (Figs. 6.19, 6.20, and 6.21). For all four metals considered here, the results obtained using different analytical methods were well comparable, but the Youden plots clearly show a prevalence of systematic over random errors.

The results for soil solutions (WAT-6 and WAT-7) and for the synthetic sample SYN-4 generally meet the DQOs. For deposition samples, the low concentrations imply higher relative standard deviations, but the results show the overall good analytical quality of these analyses.

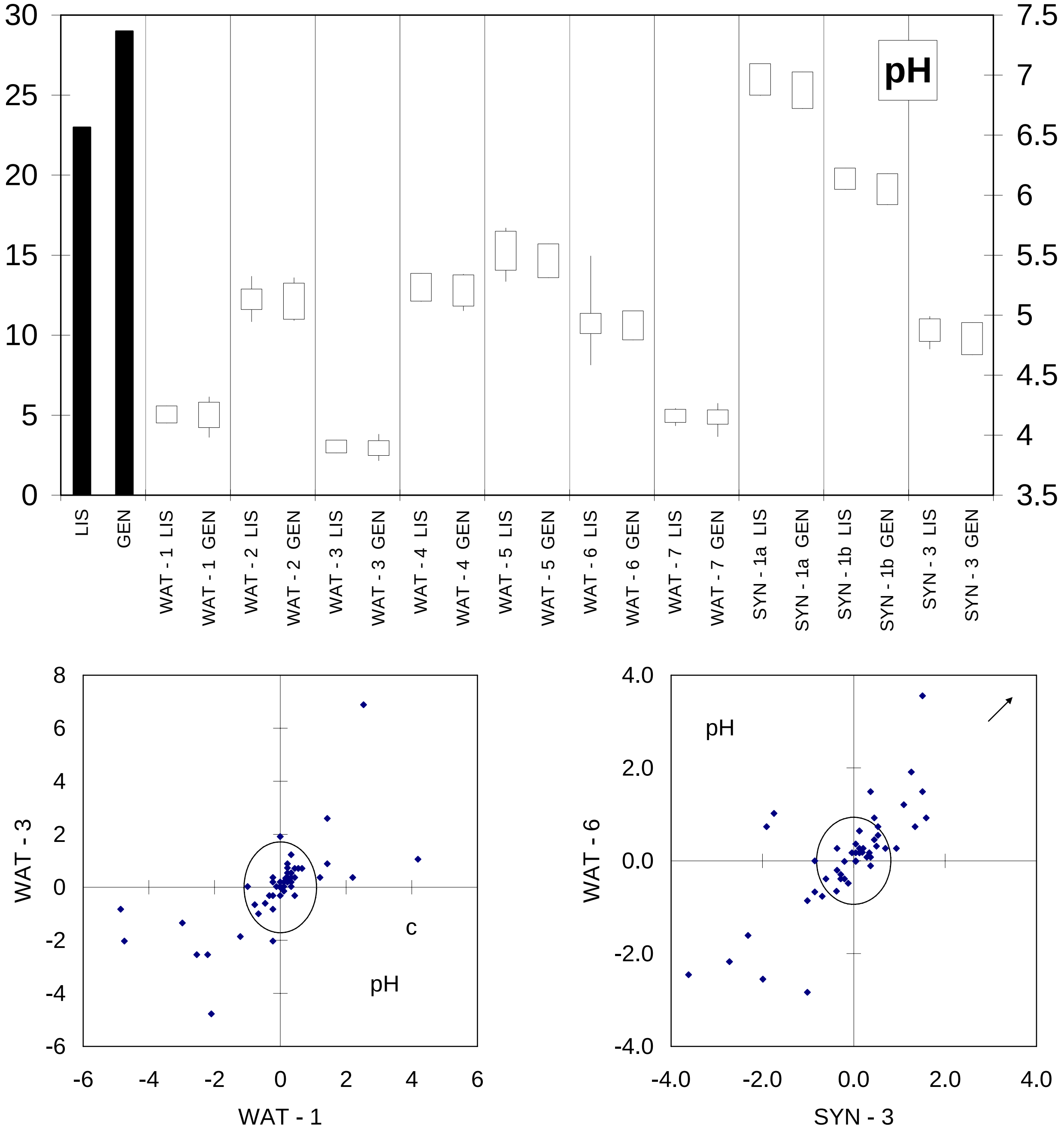


Fig. 6.2 – Results (top) and Youden plots (bottom) for pH.
In the top plot, the number of laboratories using each analytical method is indicated by the bars on the left, with the scale on the left side of the plot. The box-and-whiskers graphs on the right, with their own scale on the right side of the plot, show the ±1-standard-deviation range around the mean, before (line) and after (box) outlier rejection. Method acronyms are listed in Table 6.1.
In the Youden plots, data are plotted in z-scores, so that the mean values lie on the axes and the units are standard deviations. The legends on the axes refer to the sample names (Tabs 3.1 and 3.2), while the ellipses indicate the DQOs (Table. 2.1). The arrow points to results outside the axes range.

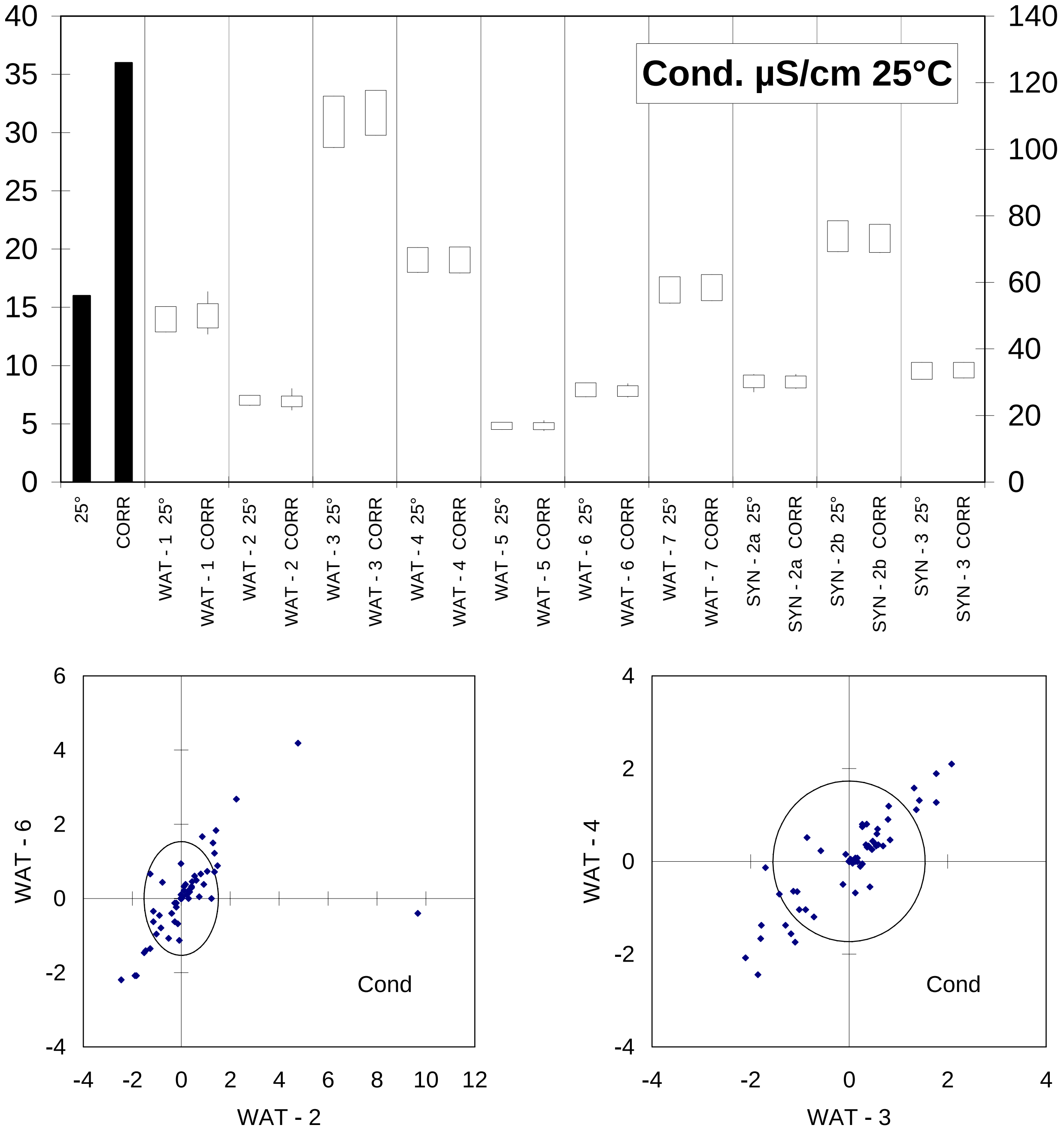


Fig. 6.3 – Results (top) and Youden plots (bottom) for conductivity.
In the top plot, the number of laboratories using each analytical method is indicated by the bars on the left, with the scale on the left side of the plot. The box-and-whiskers graphs on the right, with their own scale on the right side of the plot, show the ±1-standard-deviation range around the mean, before (line) and after (box) outlier rejection. Method acronyms are listed in Table 6.1.
In the Youden plots, data are plotted in z-scores, so that the mean values lie on the axes and the units are standard deviations. The legends on the axes refer to the sample names (Tabs 3.1 and 3.2), while the ellipses indicate the DQOs (Table. 2.1).

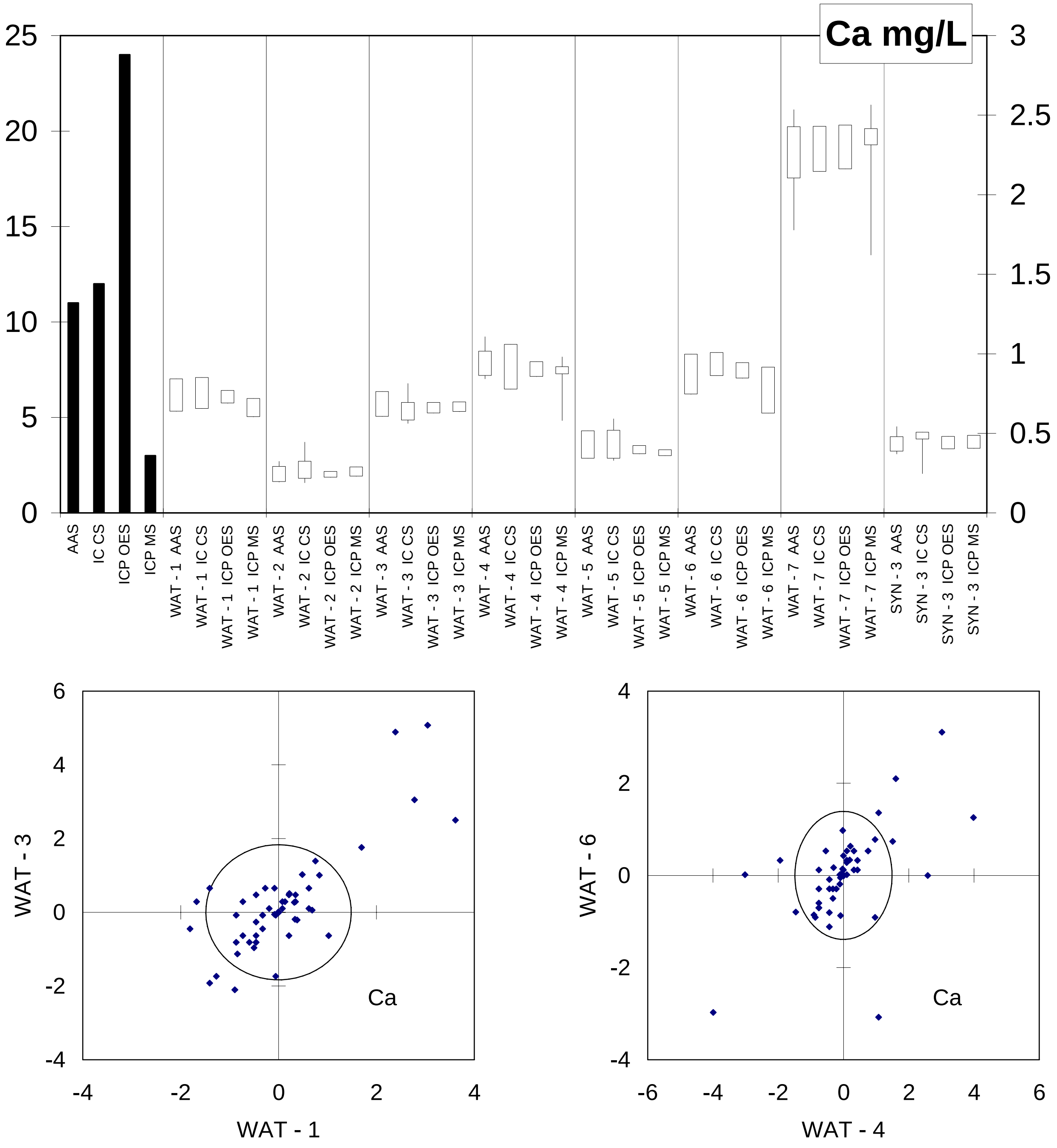


Fig. 6.4 – Results (top) and Youden plots (bottom) for calcium.
In the top plot, the number of laboratories using each analytical method is indicated by the bars on the left, with the scale on the left side of the plot. The box-and-whiskers graphs on the right, with their own scale on the right side of the plot, show the ±1-standard-deviation range around the mean, before (line) and after (box) outlier rejection. Method acronyms are listed in Table 6.1.
In the Youden plots, data are plotted in z-scores, so that the mean values lie on the axes and the units are standard deviations. The legends on the axes refer to the sample names (Tabs 3.1 and 3.2), while the ellipses indicate the DQOs (Table. 2.1).

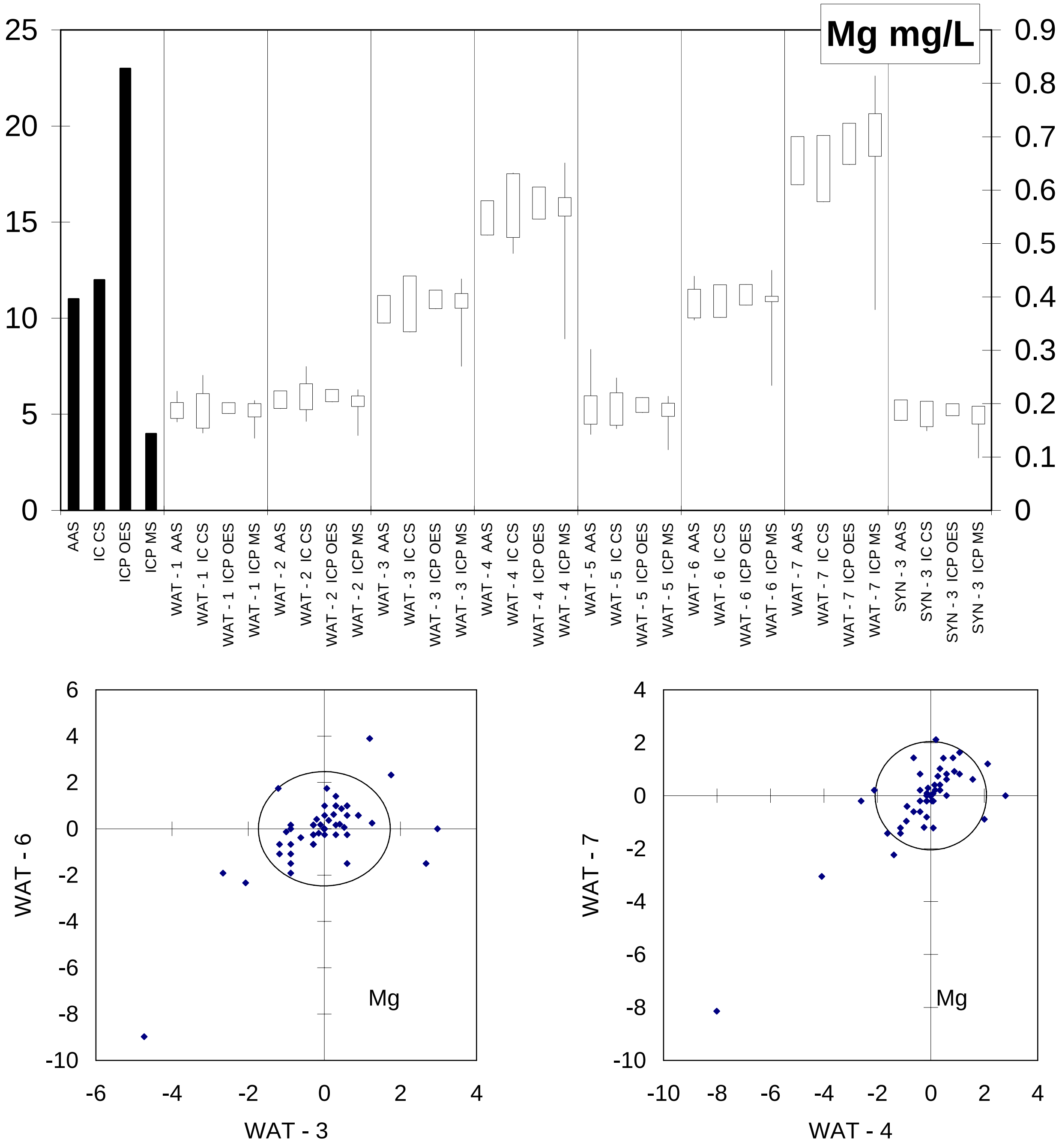


Fig. 6.5 – Results (top) and Youden plots (bottom) for magnesium.
In the top plot, the number of laboratories using each analytical method is indicated by the bars on the left, with the scale on the left side of the plot. The box-and-whiskers graphs on the right, with their own scale on the right side of the plot, show the ±1-standard-deviation range around the mean, before (line) and after (box) outlier rejection. Method acronyms are listed in Table 6.1.
In the Youden plots, data are plotted in z-scores, so that the mean values lie on the axes and the units are standard deviations. The legends on the axes refer to the sample names (Tabs 3.1 and 3.2), while the ellipses indicate the DQOs (Table. 2.1).

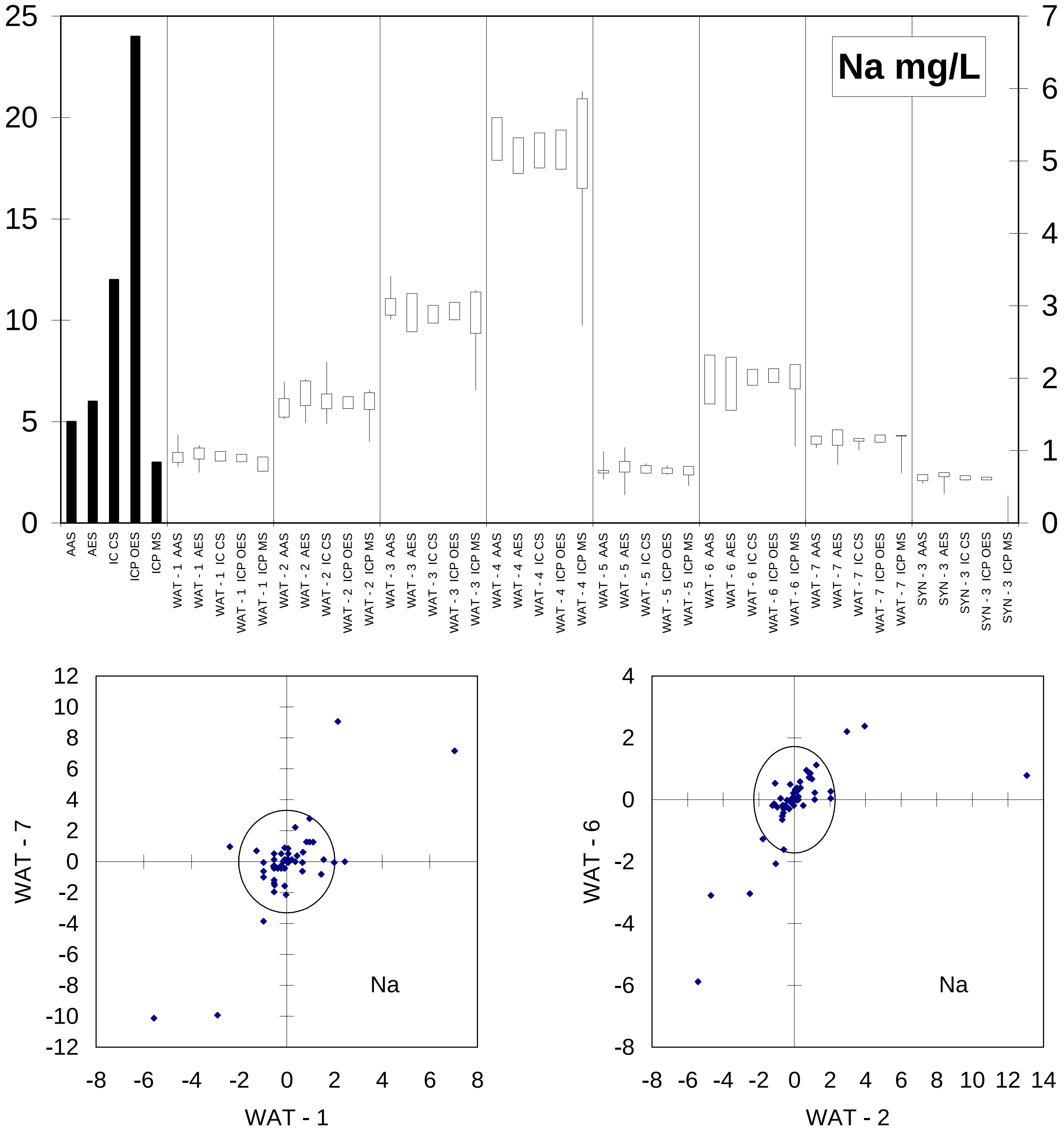


Fig. 6.6 – Results (top) and Youden plots (bottom) for sodium.

In the top plot, the number of laboratories using each analytical method is indicated by the bars on the left, with the scale on the left side of the plot. The box-and-whiskers graphs on the right, with their own scale on the right side of the plot, show the ±1-standard-deviation range around the mean, before (line) and after (box) outlier rejection. Method acronyms are listed in Table 6.1.

In the Youden plots, data are plotted in z-scores, so that the mean values lie on the axes and the units are standard deviations. The legends on the axes refer to the sample names (Tabs 3.1 and 3.2), while the ellipses indicate the DQOs (Table. 2.1).

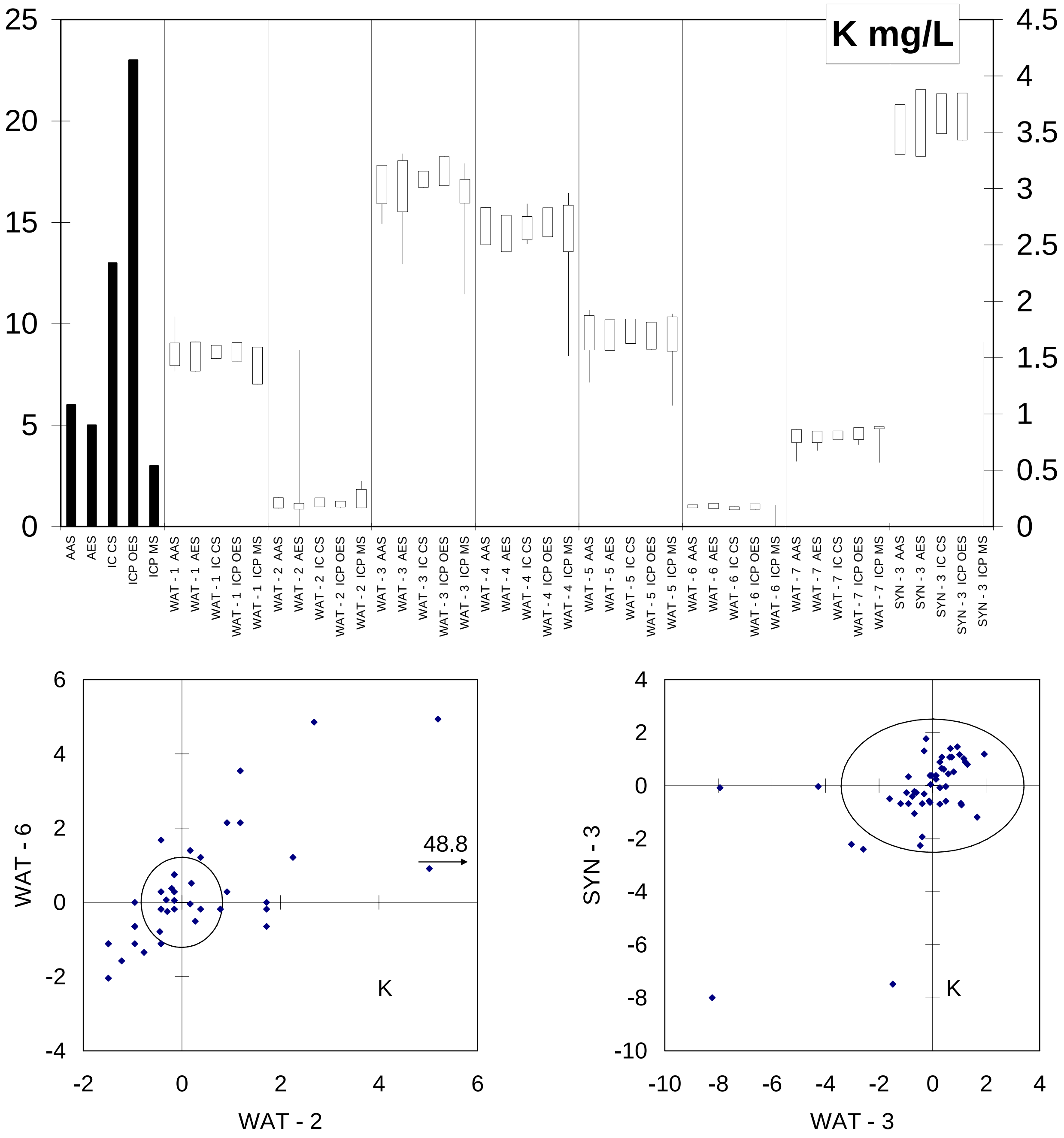


Fig. 6.7 – Results (top) and Youden plots (bottom) for potassium.
In the top plot, the number of laboratories using each analytical method is indicated by the bars on the left, with the scale on the left side of the plot. The box-and-whiskers graphs on the right, with their own scale on the right side of the plot, show the ±1-standard-deviation range around the mean, before (line) and after (box) outlier rejection. Method acronyms are listed in Table 6.1.
In the Youden plots, data are plotted in z-scores, so that the mean values lie on the axes and the units are standard deviations. The legends on the axes refer to the sample names (Tabs 3.1 and 3.2), while the ellipses indicate the DQOs (Table. 2.1). The arrow points to results outside the axes range.

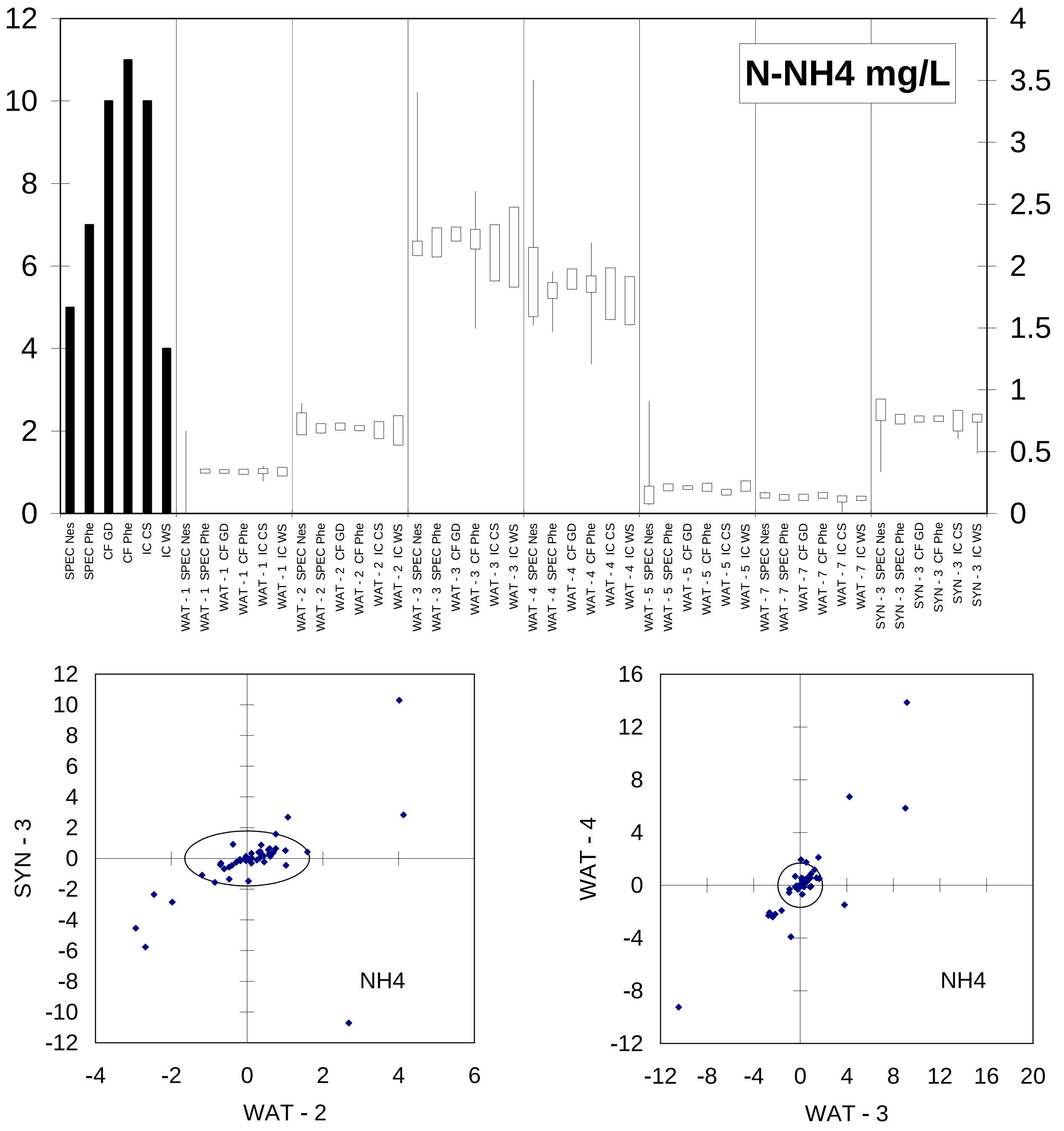


Fig. 6.8 – Results (top) and Youden plots (bottom) for ammonium.
In the top plot, the number of laboratories using each analytical method is indicated by the bars on the left, with the scale on the left side of the plot. The box-and-whiskers graphs on the right, with their own scale on the right side of the plot, show the ±1-standard-deviation range around the mean, before (line) and after (box) outlier rejection. Method acronyms are listed in Table 6.1.
In the Youden plots, data are plotted in z-scores, so that the mean values lie on the axes and the units are standard deviations. The legends on the axes refer to the sample names (Tabs 3.1 and 3.2), while the ellipses indicate the DQOs (Table. 2.1).

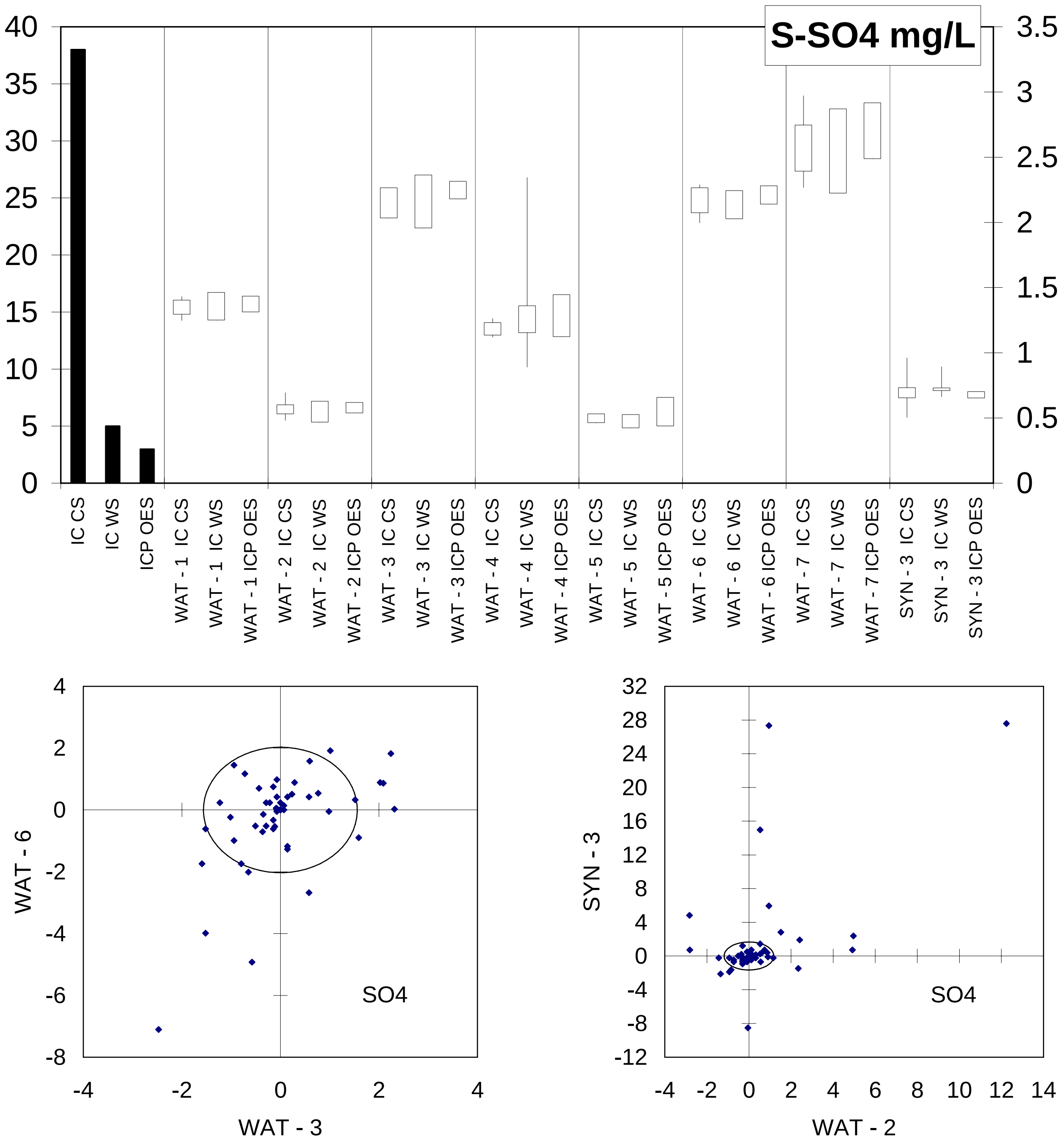


Fig. 6.9 – Results (top) and Youden plots (bottom) for sulphate.

In the top plot, the number of laboratories using each analytical method is indicated by the bars on the left, with the scale on the left side of the plot. The box-and-whiskers graphs on the right, with their own scale on the right side of the plot, show the ±1-standard-deviation range around the mean, before (line) and after (box) outlier rejection. Method acronyms are listed in Table 6.1.

In the Youden plots, data are plotted in z-scores, so that the mean values lie on the axes and the units are standard deviations. The legends on the axes refer to the sample names (Tabs 3.1 and 3.2), while the ellipses indicate the DQOs (Table. 2.1).

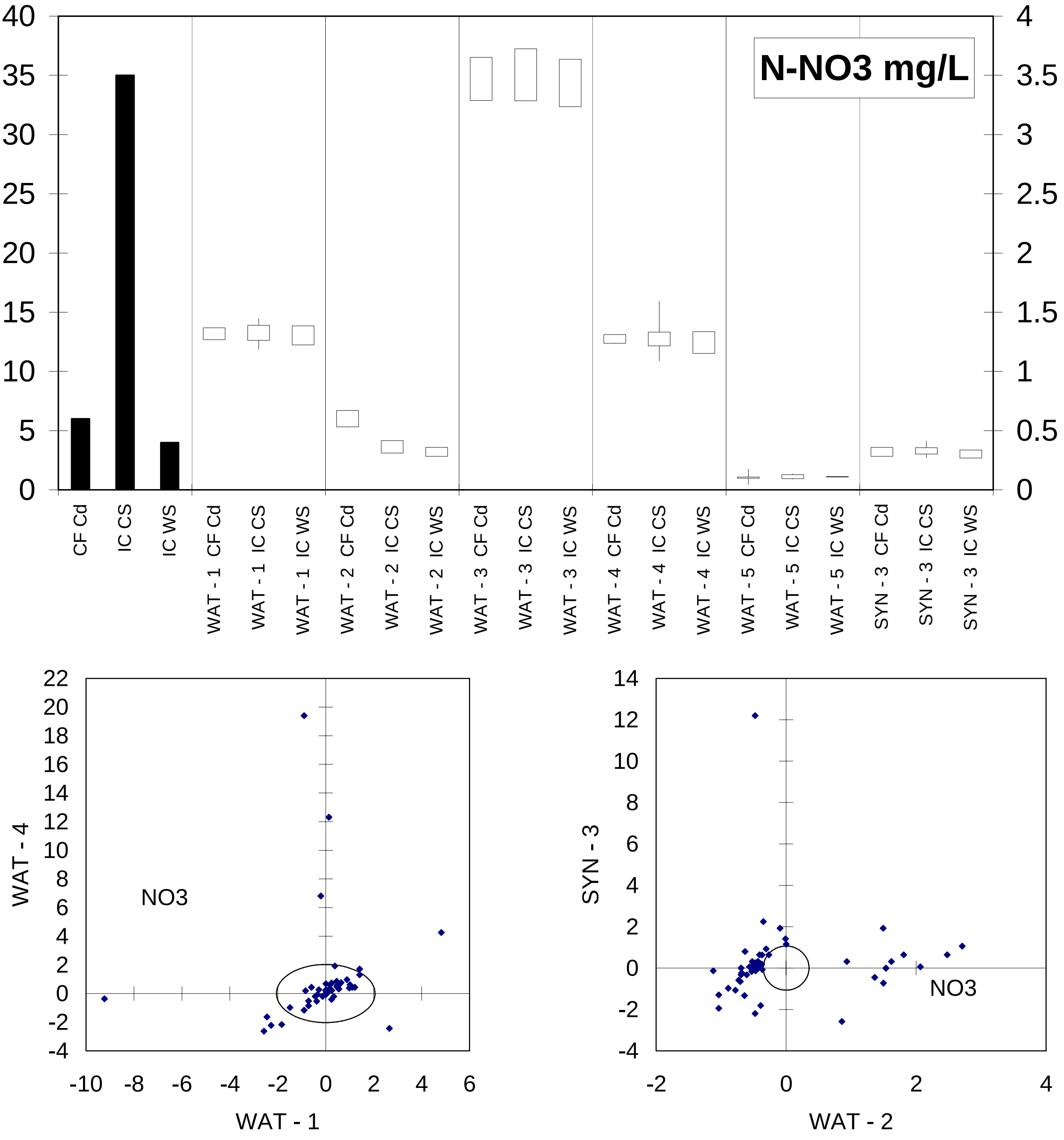


Fig. 6.10 – Results (top) and Youden plots (bottom) for nitrate.
In the top plot, the number of laboratories using each analytical method is indicated by the bars on the left, with the scale on the left side of the plot. The box-and-whiskers graphs on the right, with their own scale on the right side of the plot, show the ±1-standard-deviation range around the mean, before (line) and after (box) outlier rejection. Method acronyms are listed in Table 6.1.
In the Youden plots, data are plotted in z-scores, so that the mean values lie on the axes and the units are standard deviations. The legends on the axes refer to the sample names (Tabs 3.1 and 3.2), while the ellipses indicate the DQOs (Table. 2.1).
For sample WAT-2, note the mean falling between two distinct populations of data (see text)

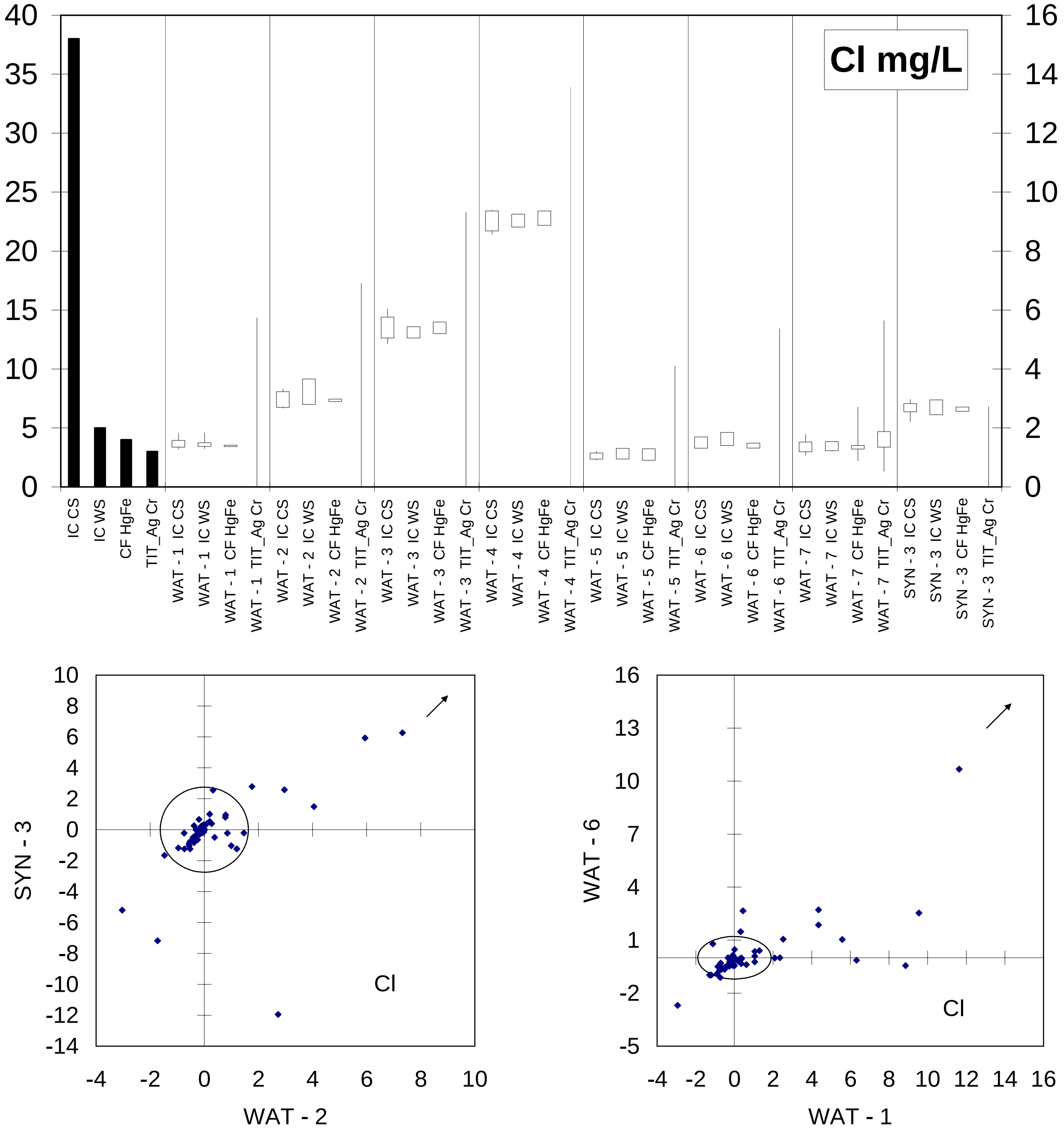


Fig. 6.11 – Results (top) and Youden plots (bottom) for chloride.

In the top plot, the number of laboratories using each analytical method is indicated by the bars on the left, with the scale on the left side of the plot. The box-and-whiskers graphs on the right, with their own scale on the right side of the plot, show the ±1-standard-deviation range around the mean, before (line) and after (box) outlier rejection. Method acronyms are listed in Table 6.1.

In the Youden plots, data are plotted in z-scores, so that the mean values lie on the axes and the units are standard deviations. The legends on the axes refer to the sample names (Tabs 3.1 and 3.2), while the ellipses indicate the DQOs (Table. 2.1). Arrows point to results outside the axes range.

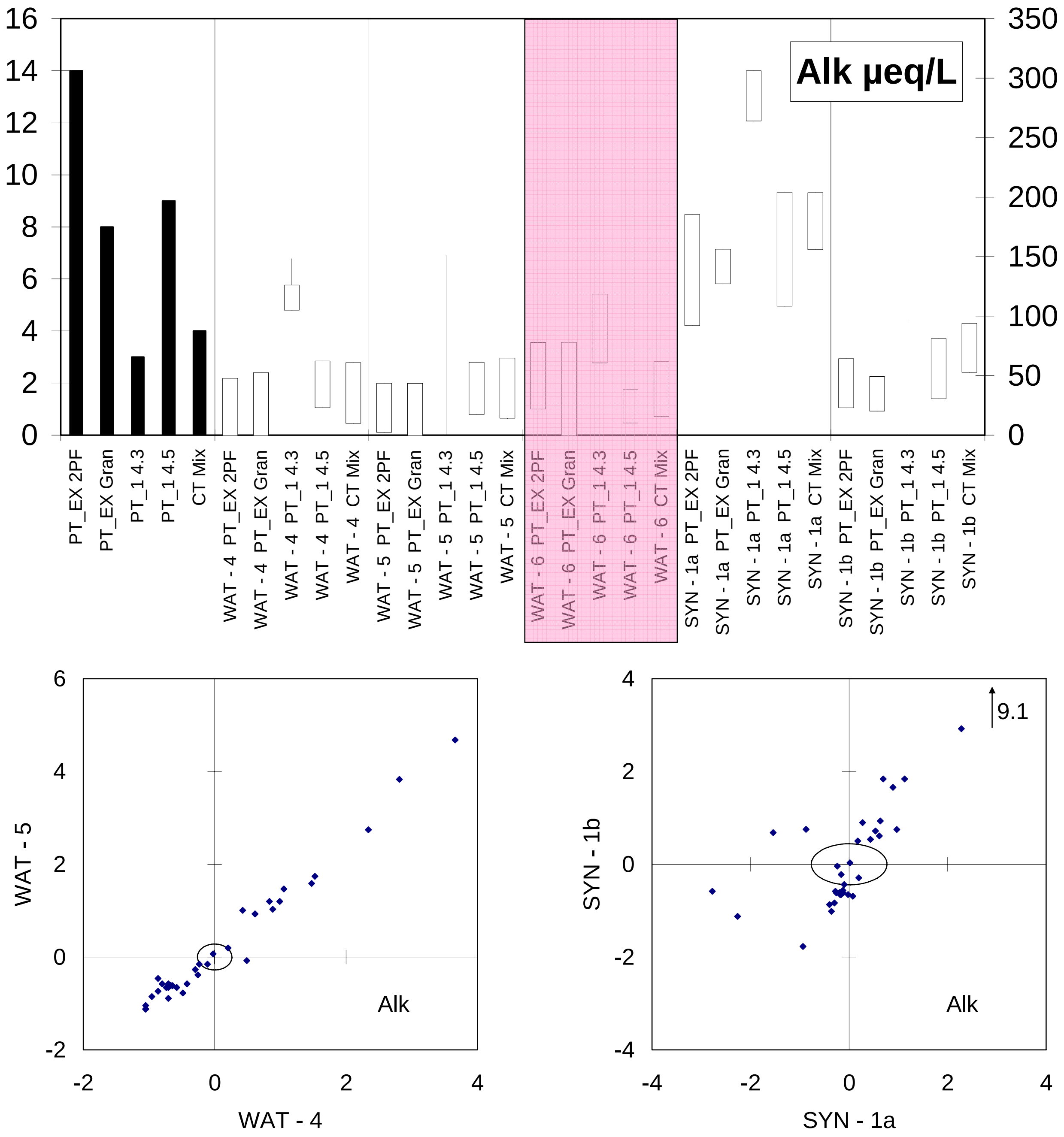


Fig. 6.12 – Results (top) and Youden plots (bottom) for alkalinity. Dashed area shows outlying results obtained for sample WAT-6, with a pH of 4.96 and an expected alkalinity value below the LOD (see text).

In the top plot, the number of laboratories using each analytical method is indicated by the bars on the left, with the scale on the left side of the plot. The box-and-whiskers graphs on the right, with their own scale on the right side of the plot, show the ±1-standard-deviation range around the mean, before (line) and after (box) outlier rejection. Method acronyms are listed in Table 6.1.

In the Youden plots, data are plotted in z-scores, so that the mean values lie on the axes and the units are standard deviations. The legends on the axes refer to the sample names (Tabs 3.1 and 3.2), while the ellipses indicate the DQOs (Table. 2.1). The arrow points to results outside the axes range.

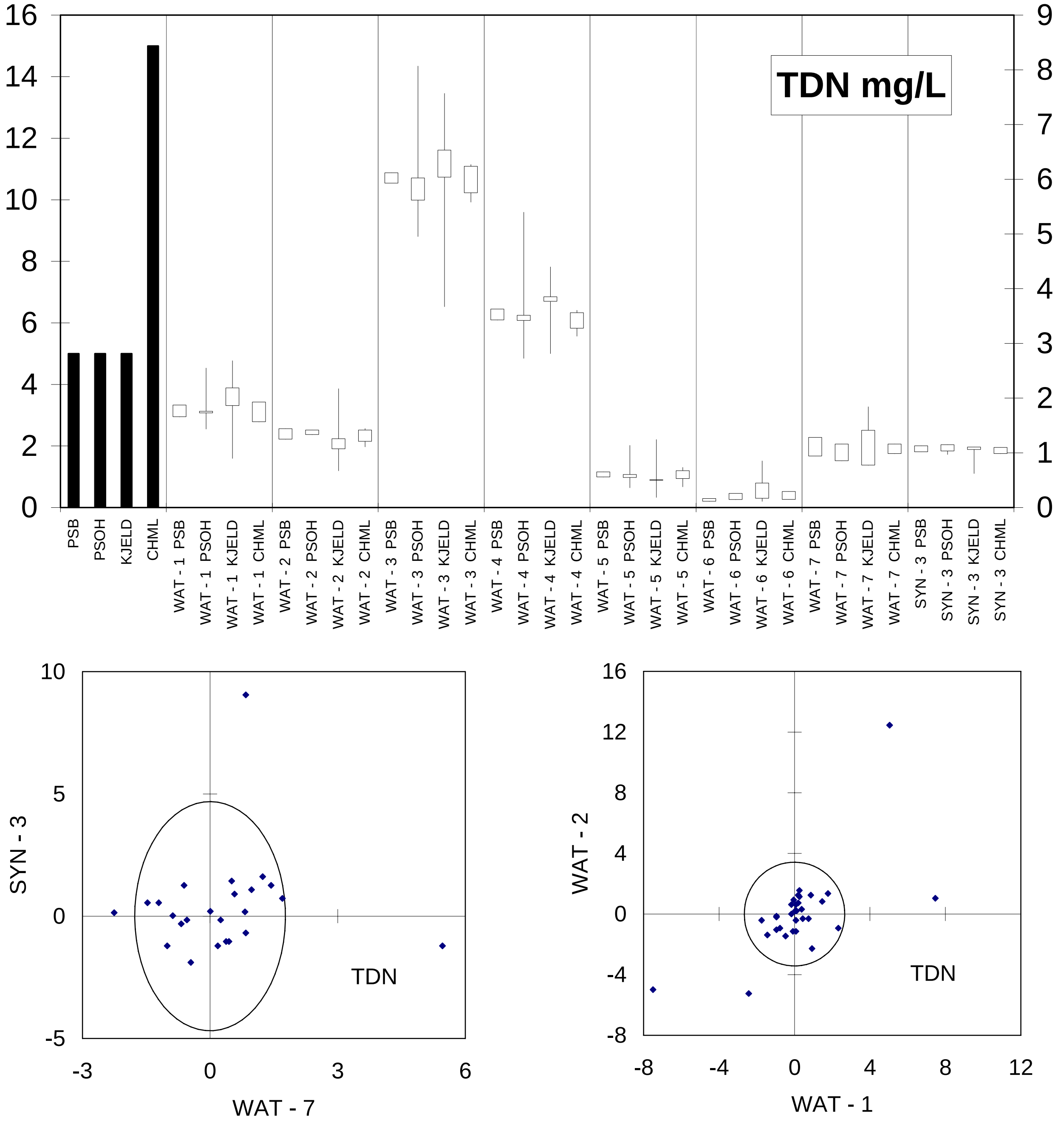


Fig. 6.13 – Results (top) and Youden plots (bottom) for total dissolved nitrogen (TDN).
In the top plot, the number of laboratories using each analytical method is indicated by the bars on the left, with the scale on the left side of the plot. The box-and-whiskers graphs on the right, with their own scale on the right side of the plot, show the ±1-standard-deviation range around the mean, before (line) and after (box) outlier rejection. Method acronyms are listed in Table 6.1.
In the Youden plots, data are plotted in z-scores, so that the mean values lie on the axes and the units are standard deviations. The legends on the axes refer to the sample names (Tabs 3.1 and 3.2), while the ellipses indicate the DQOs (Table. 2.1).

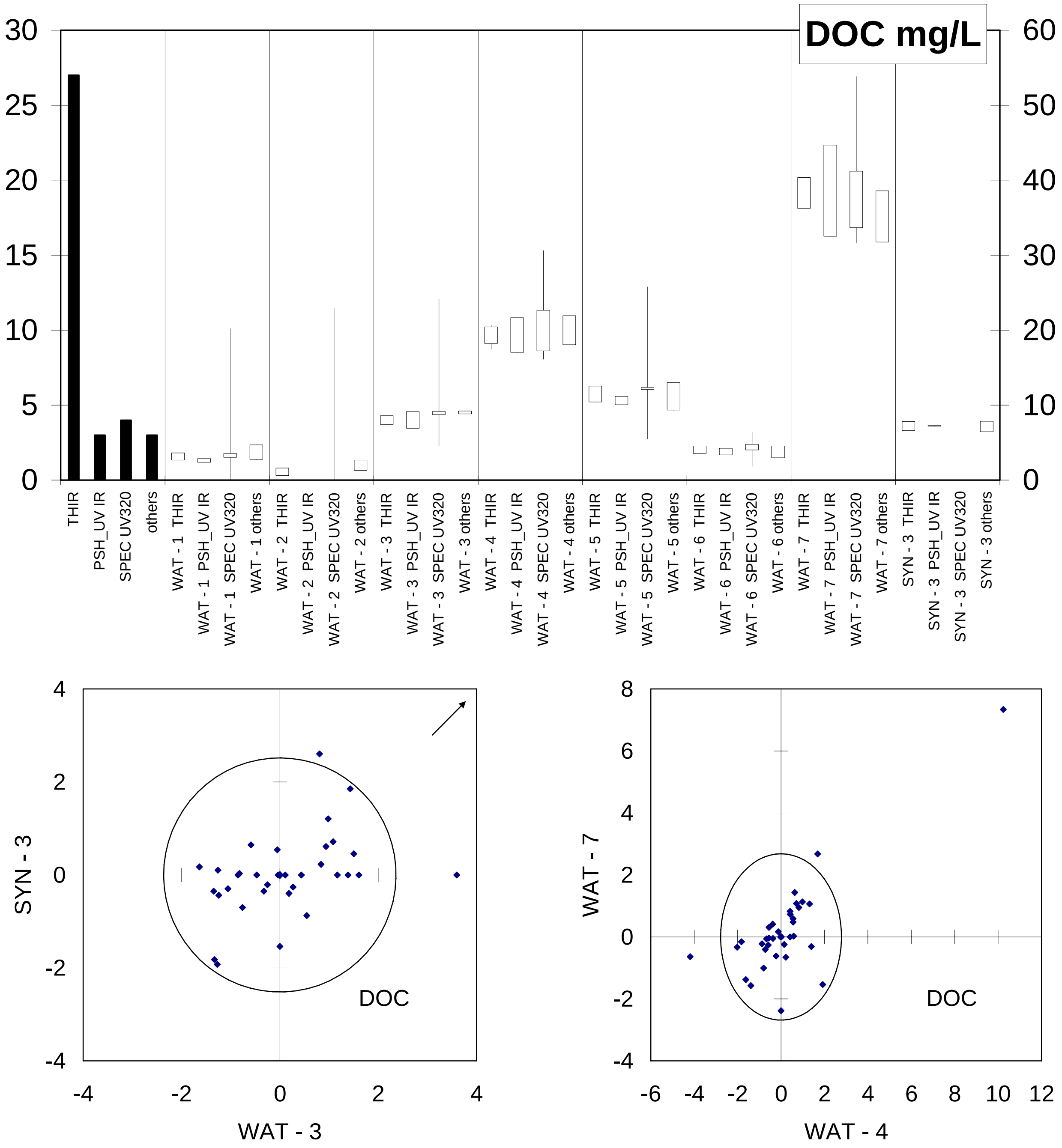


Fig. 6.14 – Results (top) and Youden plots (bottom) for dissolved organic carbon.
In the top plot, the number of laboratories using each analytical method is indicated by the bars on the left, with the scale on the left side of the plot. The box-and-whiskers graphs on the right, with their own scale on the right side of the plot, show the ±1-standard-deviation range around the mean, before (line) and after (box) outlier rejection. Method acronyms are listed in Table 6.1.
In the Youden plots, data are plotted in z-scores, so that the mean values lie on the axes and the units are standard deviations. The legends on the axes refer to the sample names (Tabs 3.1 and 3.2), while the ellipses indicate the DQOs (Table. 2.1). The arrow points to results outside the axes range.

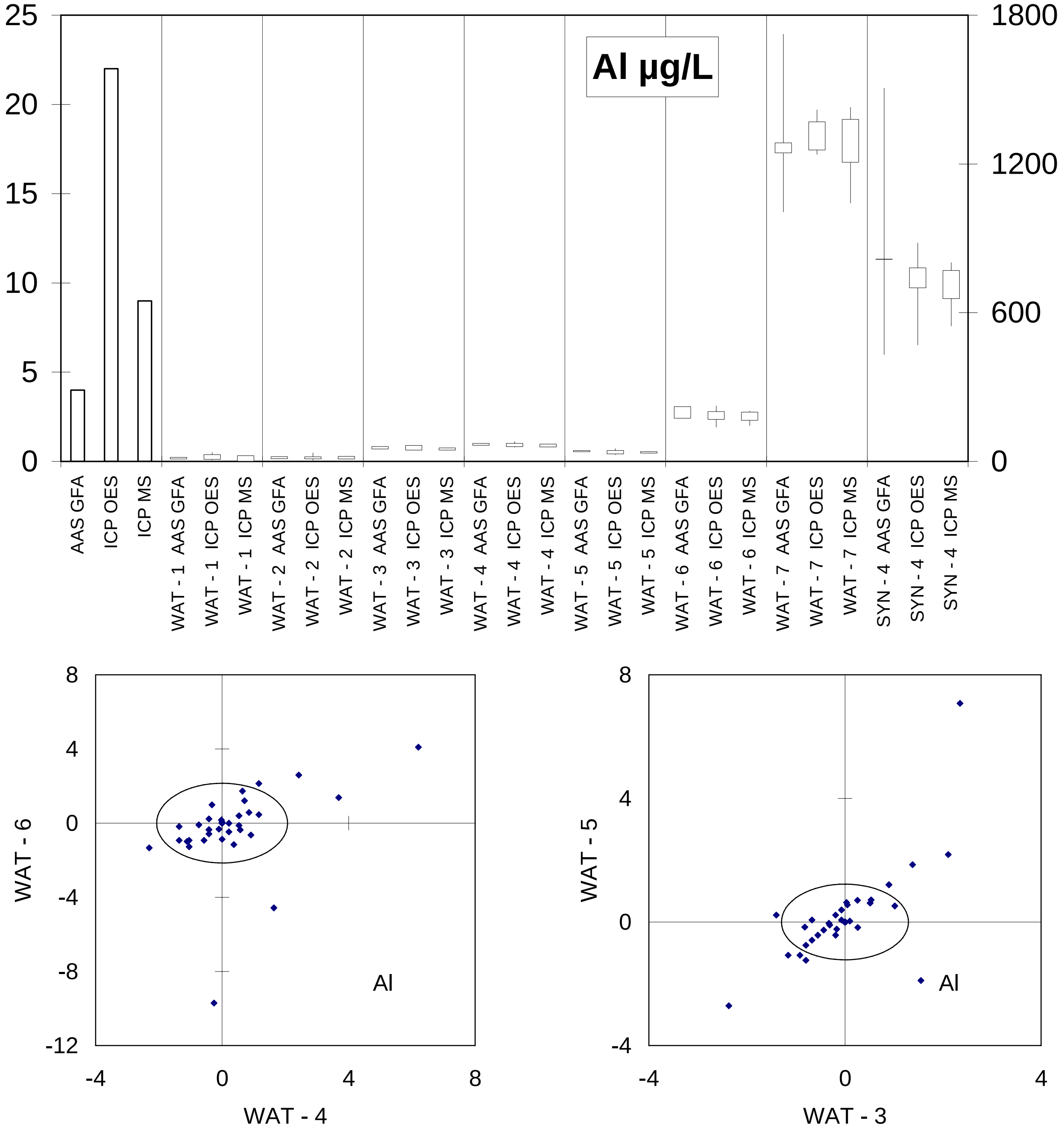
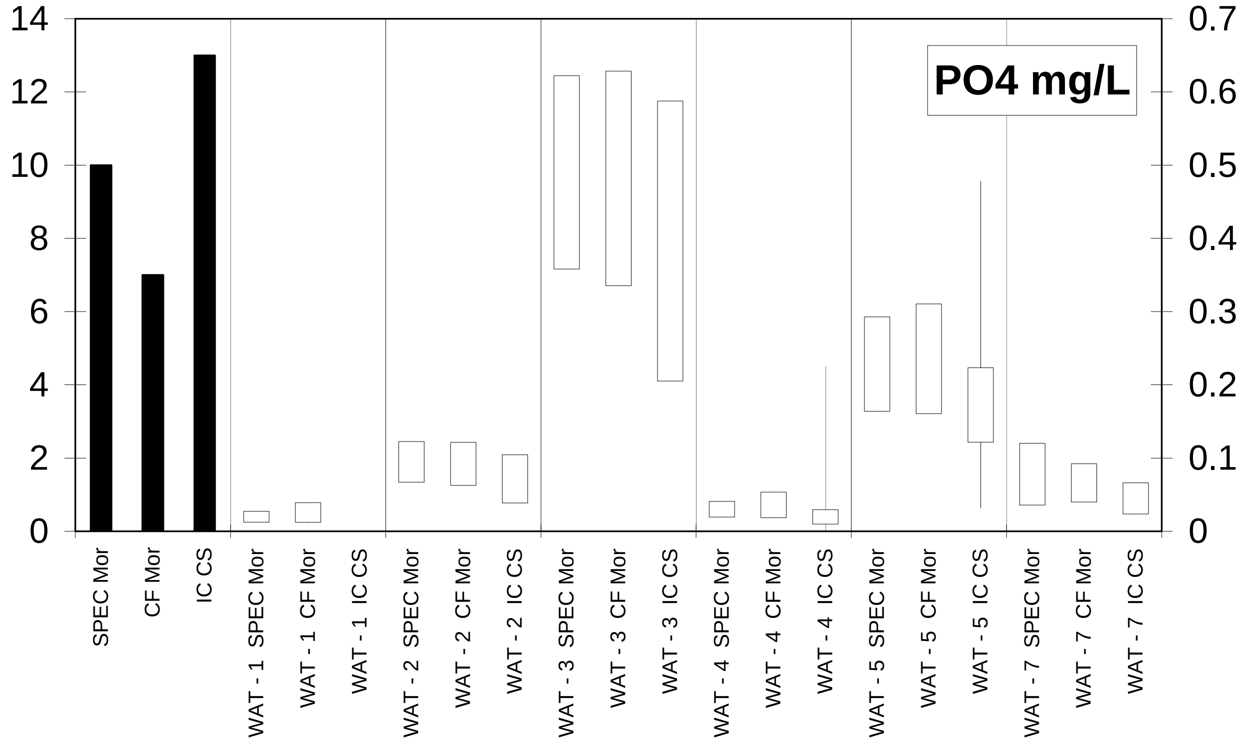


Fig. 6.15 – Results (top) and Youden plots (bottom) for aluminium.

In the top plot, the number of laboratories using each analytical method is indicated by the bars on the left, with the scale on the left side of the plot. The box-and-whiskers graphs on the right, with their own scale on the right side of the plot, show the ±1-standard-deviation range around the mean, before (line) and after (box) outlier rejection. Method acronyms are listed in Table 6.1.

In the Youden plots, data are plotted in z-scores, so that the mean values lie on the axes and the units are standard deviations. The legends on the axes refer to the sample names (Tabs 3.1 and 3.2), while the ellipses indicate the DQOs (Table. 2.1).



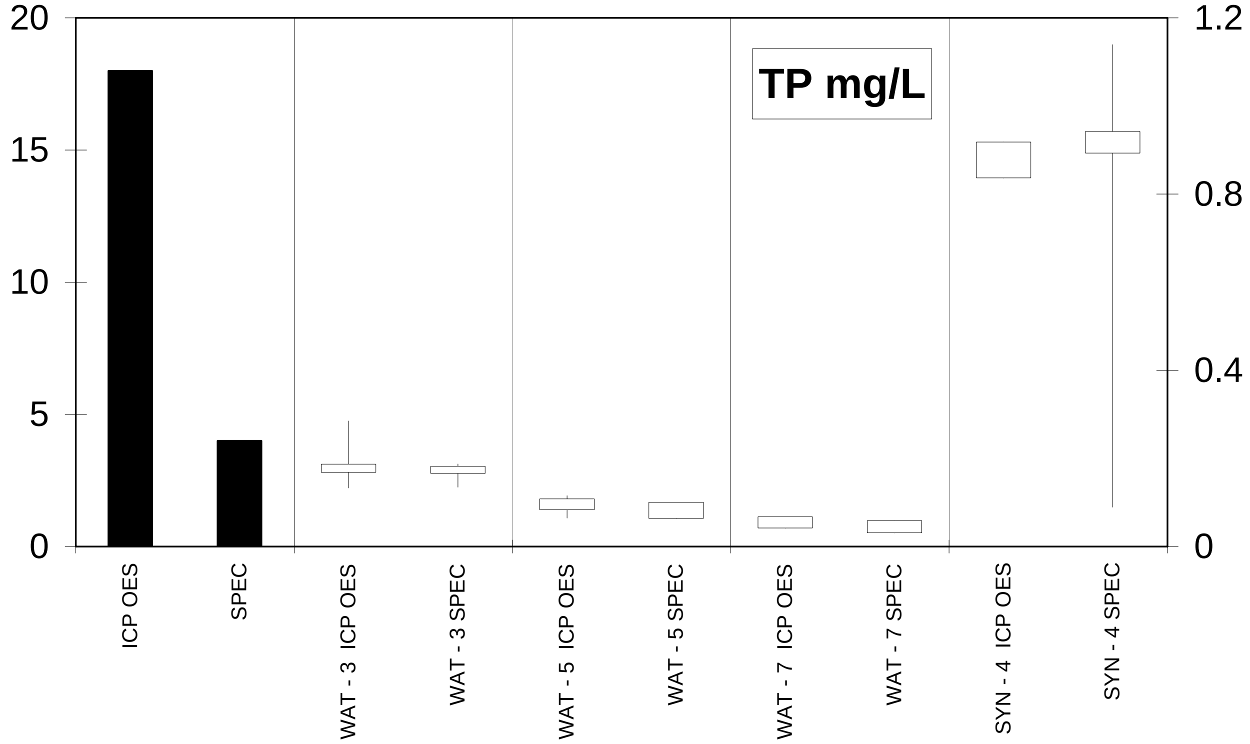


Fig. 6.16 – Results for phosphate (top) and total phosphorus (bottom).
The number of laboratories using each analytical method is indicated by the bars on the left, with the scale on the left side of the plot. The box-and-whiskers graphs on the right, with their own scale on the right side of the plot, show the ±1-standard-deviation range around the mean, before (line) and after (box) outlier rejection. Method acronyms are listed in Table 6.1.

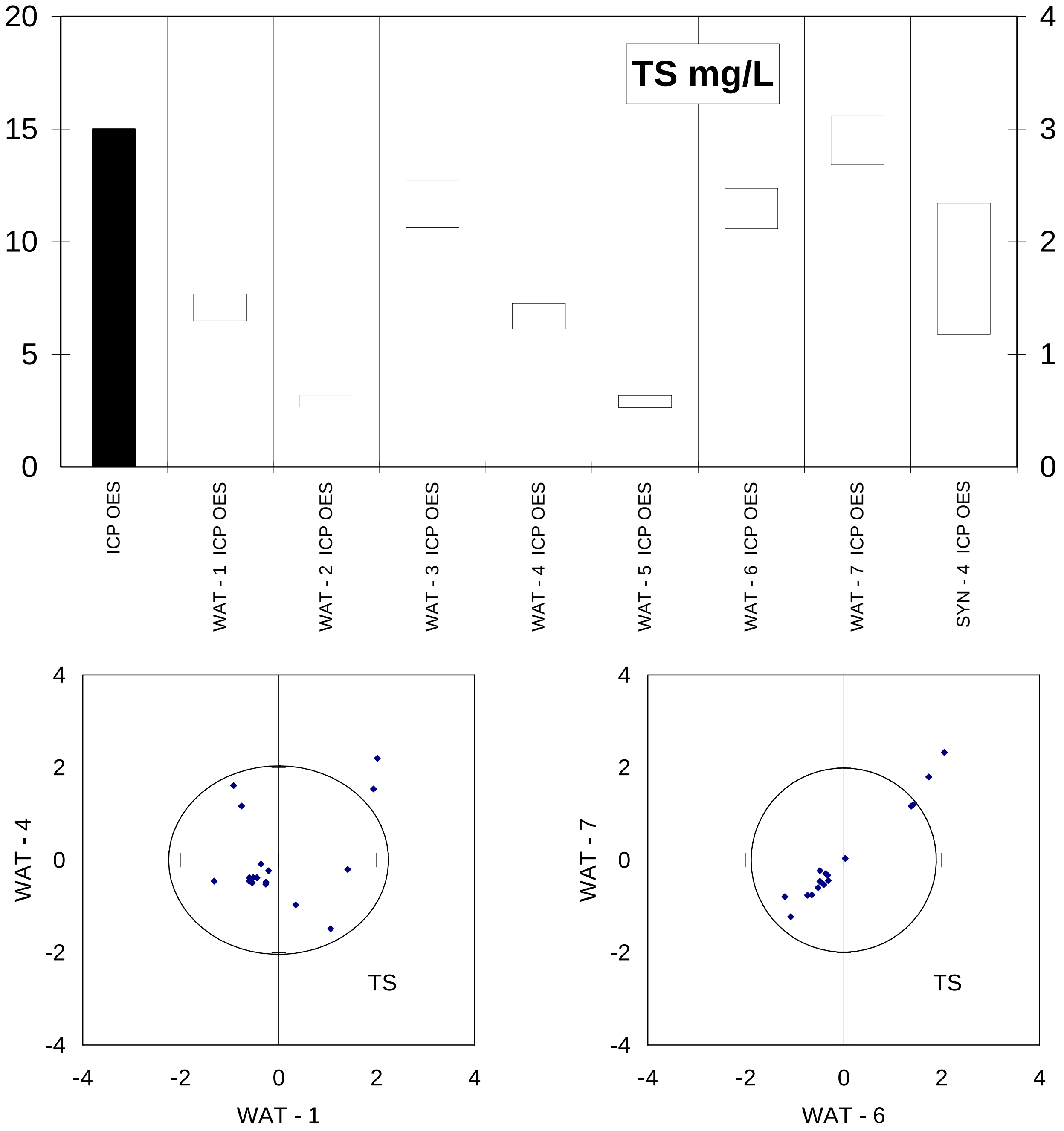
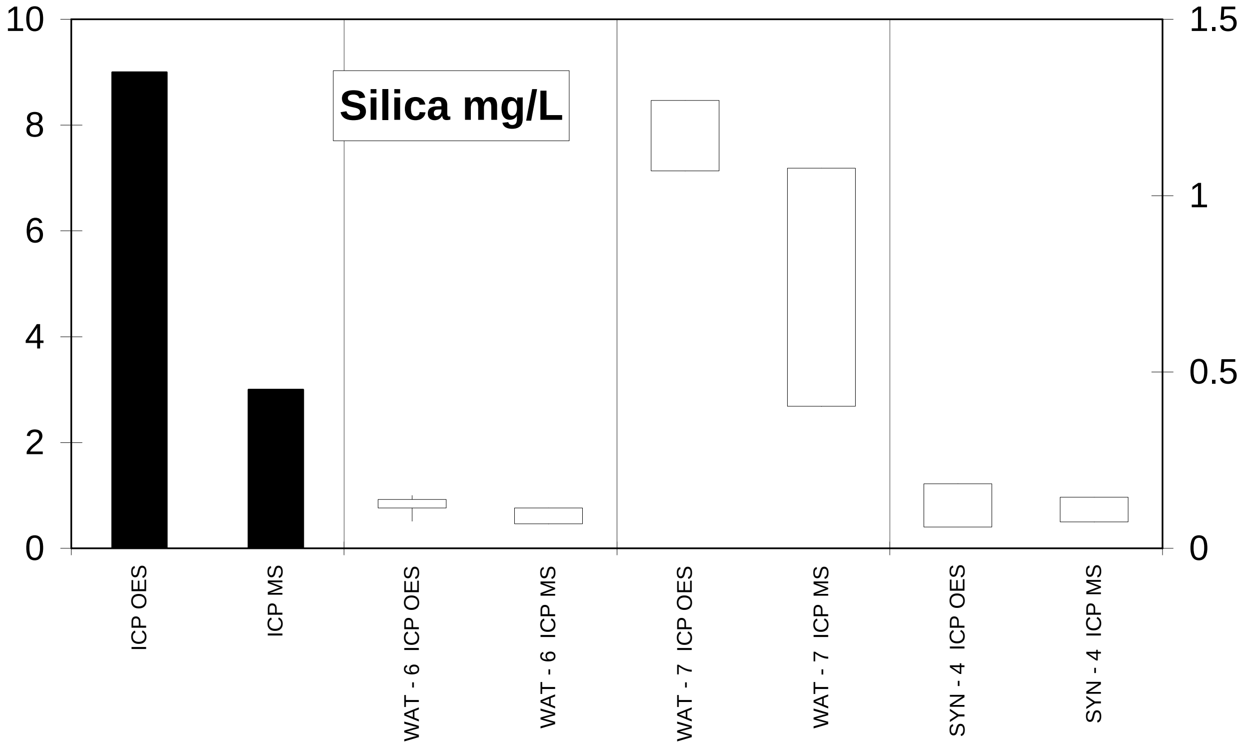


Fig. 6.17 – Results (top) and Youden plots (bottom) for total sulphur.
In the top plot, the number of laboratories using each analytical method is indicated by the bars on the left, with the scale on the left side of the plot. The box-and-whiskers graphs on the right, with their own scale on the right side of the plot, show the ±1-standard-deviation range around the mean, before (line) and after (box) outlier rejection. Method acronyms are listed in Table 6.1.
In the Youden plots, data are plotted in z-scores, so that the mean values lie on the axes and the units are standard deviations. The legends on the axes refer to the sample names (Tabs 3.1 and 3.2), while the ellipses indicate the DQOs (Table. 2.1).



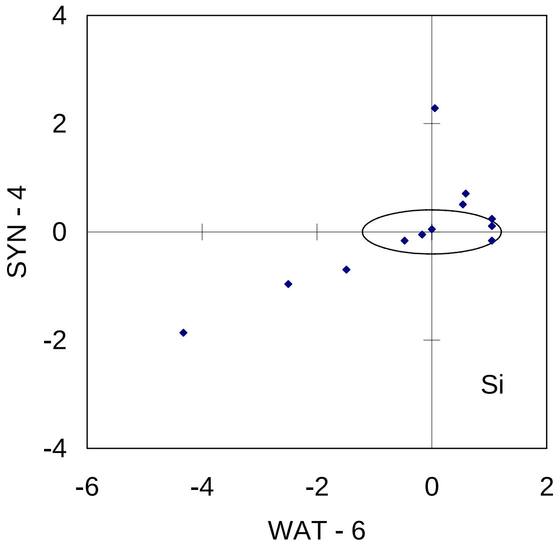


Fig. 6.18 – Results (top) and Youden plot (bottom) for silica.
In the top plot, the number of laboratories using each analytical method is indicated by the bars on the left, with the scale on the left side of the plot. The box-and-whiskers graphs on the right, with their own scale on the right side of the plot, show the ±1-standard-deviation range around the mean, before (line) and after (box) outlier rejection. Method acronyms are listed in Table 6.1.
In the Youden plot, data are plotted in z-scores, so that the mean values lie on the axes and the units are standard deviations. The legends on the axes refer to the sample names (Tabs 3.1 and 3.2), while the ellipses indicate the DQOs (Table. 2.1).

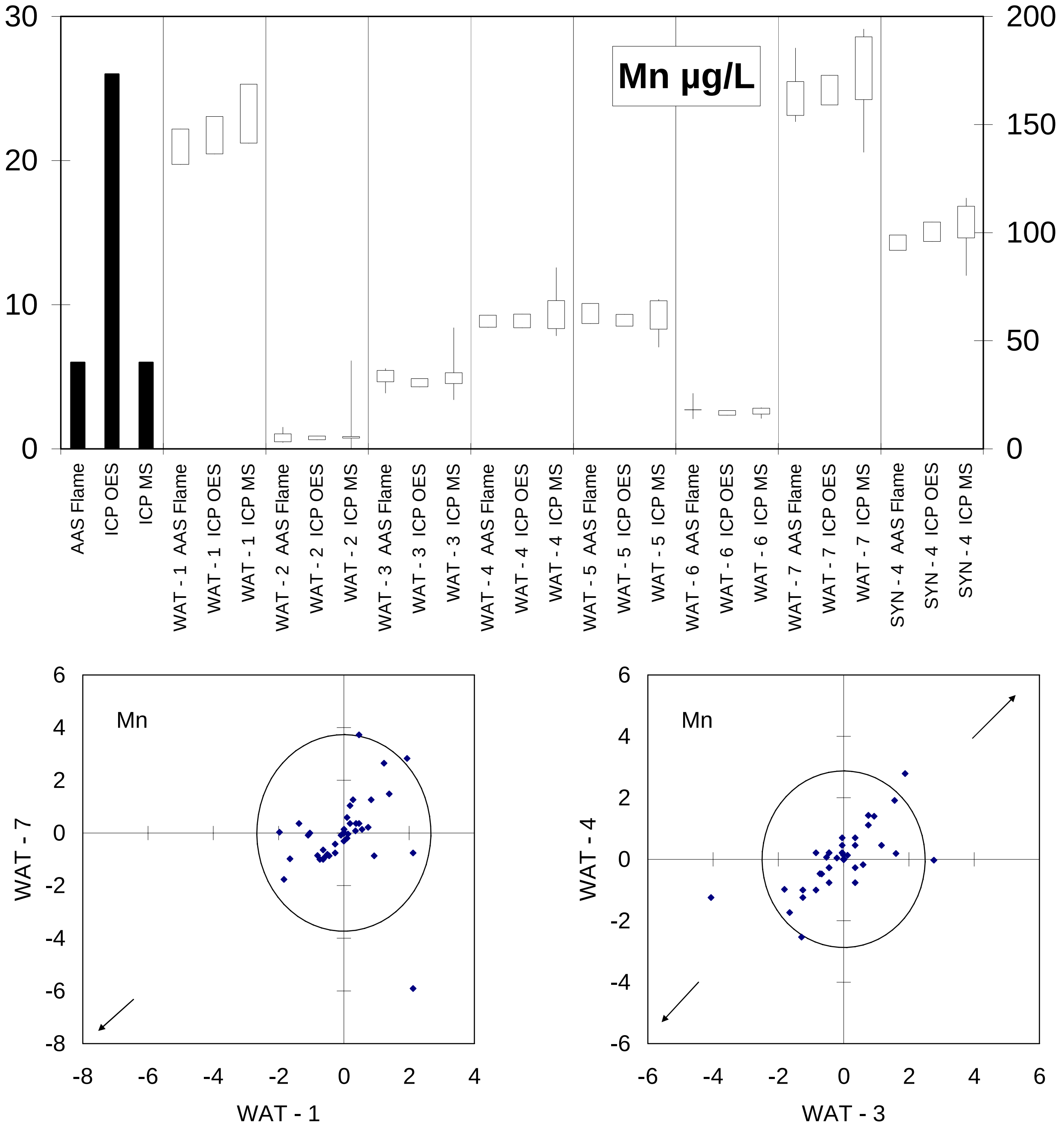


Fig. 6.19 – Results (top) and Youden plots (bottom) for manganese.
In the top plot, the number of laboratories using each analytical method is indicated by the bars on the left, with the scale on the left side of the plot. The box-and-whiskers graphs on the right, with their own scale on the right side of the plot, show the ±1-standard-deviation range around the mean, before (line) and after (box) outlier rejection. Method acronyms are listed in Table 6.1.
In the Youden plots, data are plotted in z-scores, so that the mean values lie on the axes and the units are standard deviations. The legends on the axes refer to the sample names (Tabs 3.1 and 3.2), while the ellipses indicate the DQOs (Table. 2.1). Arrows point to results outside the axes range.

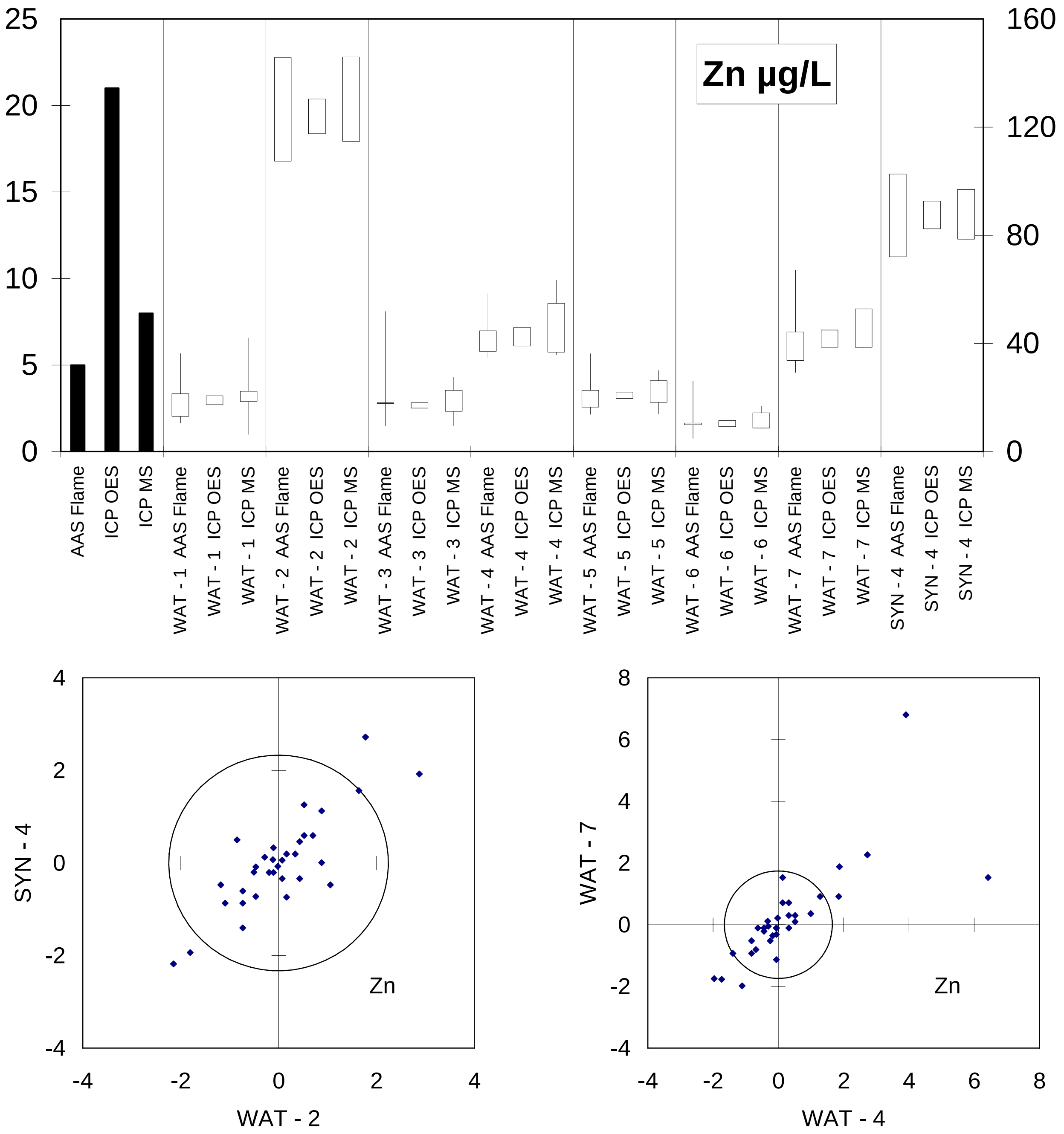
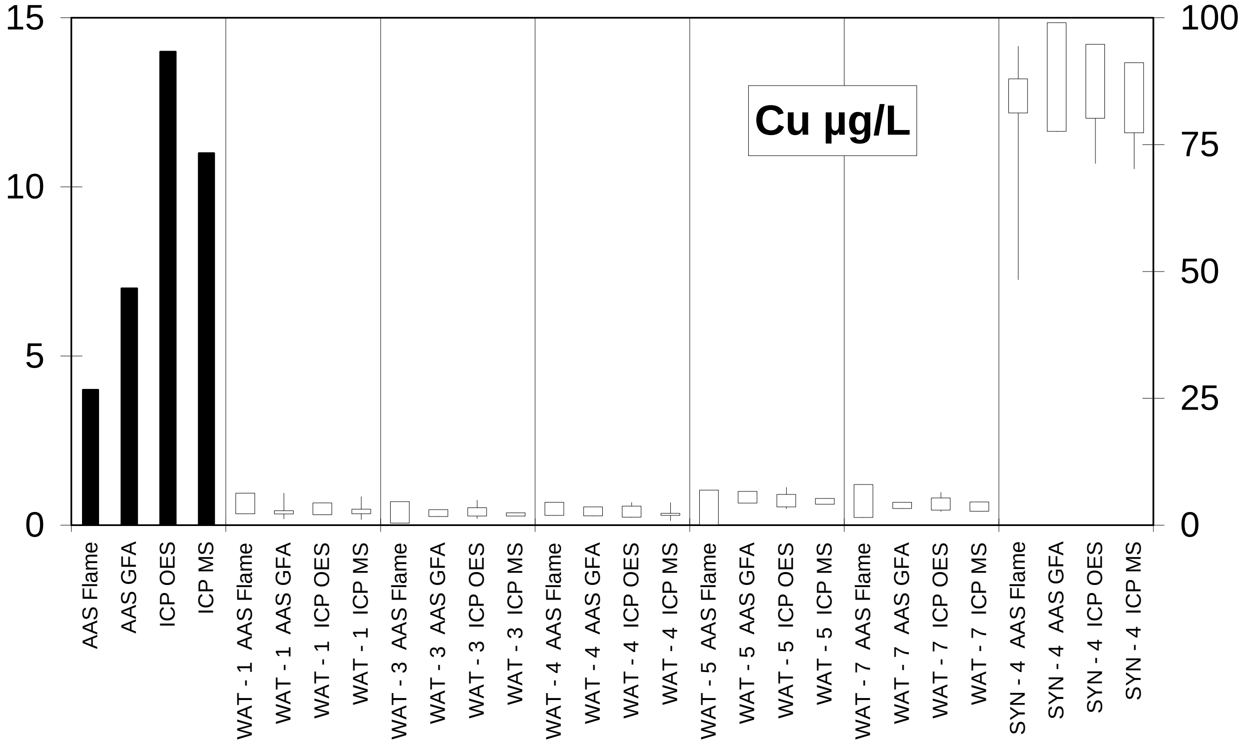


Fig. 6.20 – Results (top) and Youden plots (bottom) for zinc.
In the top plot, the number of laboratories using each analytical method is indicated by the bars on the left, with the scale on the left side of the plot. The box-and-whiskers graphs on the right, with their own scale on the right side of the plot, show the ±1-standard-deviation range around the mean, before (line) and after (box) outlier rejection. Method acronyms are listed in Table 6.1.
In the Youden plots, data are plotted in z-scores, so that the mean values lie on the axes and the units are standard deviations. The legends on the axes refer to the sample names (Tabs 3.1 and 3.2), while the ellipses indicate the DQOs (Table. 2.1). Arrows point to results outside the axes range.



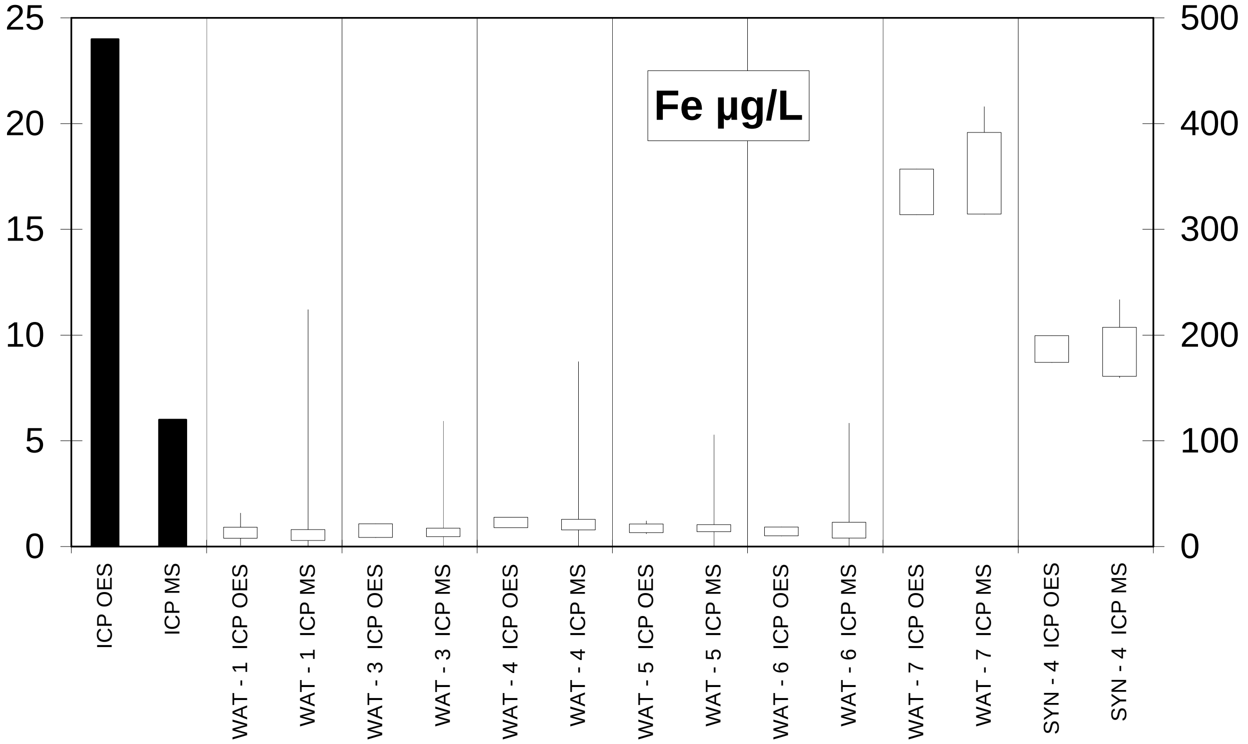


Fig. 6.21 – Results for copper (top) and iron (bottom).
The number of laboratories using each analytical method is indicated by the bars on the left, with the scale on the left side of the plot. The box-and-whiskers graphs on the right, with their own scale on the right side of the plot, show the ±1-standard-deviation range around the mean, before (line) and after (box) outlier rejection. Method acronyms are listed in Table 6.1.

6.19. Use of procedures for Internal Quality Control

A questionnaire was distributed to all laboratories, in order to investigate how many of them use the procedure for Internal Quality Control (IQC) suggested in the *ICP Forests Manual* (Lövblad *et al.* 2004). Table 6.6 gives a summary of the answers to that questionnaire, reporting for each variable how many laboratories use some IQC procedure.

Table 6.6. – Percentage of the laboratories reporting the use of some IQC procedure, for each variable.

IQC procedure reported		pH Cond.	Ca^{2+} Mg^{2+}	Na^+ K^+	NH_4^+	SO_4^{2-}	NO_3^-	Cl^-	TDN	Alk.	DOC	**Total**
No IQC or no answer		49%	40%	42%	48%	39%	37%	39%	75%	50%	56%	**45%**
Control chart, only	C	51%	10%	12%	17%	16%	14%	14%	3%	42%	18%	**20%**
Blank chart, only	B	-	4%	2%	2%	4%	4%	4%	0%	0%	0%	**2%**
Certified reference material, only	R	-	10%	6%	0%	4%	4%	4%	0%	0%	0%	**4%**
Control chart & blank chart	C+B	-	2%	2%	12%	2%	2%	0%	16%	4%	12%	**4%**
Control chart & cert. material	C+R	-	19%	17%	8%	12%	16%	16%	0%	0%	9%	**11%**
Blank chart & cert. ref. material	B+R	-	0%	0%	0%	0%	0%	0%	0%	0%	0%	**0%**
Control chart, blank chart & cert. ref. material	C+B +R	-	15%	19%	13%	24%	24%	24%	6%	4%	6%	**14%**

Most of the laboratories use one or more IQC procedures. Control charts are used in 49% of the cases. Blank charts and certified reference materials are used in 20% and 29% of the cases, respectively, and they are mainly used in conjunction with the other procedures. In particular, in 14% of the cases the three IQC procedures are used together.

Even if only 35 laboratories answered to the questionnaire, it should be noted that the percent of cases in which no IQC procedure is used is still too high, as they can help to improve the quality of the results. Interested readers can find a description of simple and effective IQC procedures in the *ICP Forests manual* (Lövblad *et al.* 2004).

The relation between the use of ICQ procedure and the analytical quality within this exercise is reported in chapter 7.3.

7. DISCUSSION

7.1. Quality check of the analyses

In the *ICP Forests manual for sampling and analysis of atmospheric deposition* (Lövblad *et al.* 2004), the chapter dedicated to deposition analysis contains a detailed procedure for Quality Assurance and Quality Control (QA/QC). The importance of checking analytical results is underlined, and the tests based on ion balance and calculated conductivity are fully described.

During the organisation of this WRT, an MS-Excel data sheet was produced for data transmission and distributed to all participants. It contained all the necessary formulae to perform both tests. Two further tests were also implemented in that file: the third test is based on the ratio Na/Cl, assuming that most of these ions derive from sea spray, so that their ratio should not be far from those found in sea water (0.86), with an accepted range from 0.5 to 1.5. The fourth test simply verifies that the sum of nitrate and ammonium concentration is not larger than the concentration of total dissolved nitrogen, which includes both organic and inorganic forms of nitrogen. The latter includes ammonium, nitrate and other minor compounds, like nitrite.

$$TDN = [N\text{-}NO3] + [N\text{-}NH4] + [N\text{-}org] + [N\text{-}NO2] + \ldots \geq [N\text{-}NO3] + [N\text{-}NH4]$$

A detailed discussion of the four tests, as applied to a set of 7000 results of analyses of atmospheric deposition collected in different European countries is reported by Mosello *et al.* (2005).

It is very important for the quality of the results, that these tests are routinely performed after the analysis of each sample and that the results of the test are used to decide if the analyses can be accepted or the results should be checked for any error or even the analyses should be replicated because of a possible analytical error.

One of the objectives of the Working Group on QA/QC is to assure that the whole quality control procedure, comprising not only these tests, but also control charts, method evaluation and so on, became standard laboratory procedure for the analysis to be included in the ICP Forests data base. The necessity to analyse all the major anions (sulphate, nitrate, chloride, and bicarbonate for samples with pH higher than 5) and cations (hydrogen ions, ammonium, calcium, magnesium, sodium and potassium) in order to perform the tests is also stressed.

For these reasons, it was surprising to note that for 17% of the samples analysed it was not possible to perform the tests because the analyses of one or more of the major ions were not performed.

7.1.1. Ion balance

The *ICP Forests manual for sampling and analysis of atmospheric deposition* (Lövblad *et al.* 2004) suggests to test ion balance for open fields samples, while in soil solutions and in deposition collected in the plot (throughfall and stemflow samples) there is a significant probability to find relevant concentrations of unaccounted ions (such as organic compounds) which would alter the ion balance. For this reason the ionic balance test would be, *a priori,* only performed on samples WAT-1 and WAT-2, which are examples of atmospheric deposition sampled in the open field.

The sum of the expected concentration of cations and anions (i.e. the median value of the results, in µeq L^{-1}) for all the samples are plotted in Figure 7.1. It appears that the points representing four of the samples do not fall on the 1:1 line showing a strong cation excess. The samples concerned are two throughfall samples (WAT-4 and WAT-5), one soil solution sample (WAT-7) and a synthetic sample (SYN-3). All these samples show high DOC concentration (see Table 6.2.), i.e. above 5 mg L^{-1}.

In Fig. 7.2. the sum of the concentration of cations and anions measured by each laboratory are plotted. The results meeting the acceptance criteria for the ion balance test are included between the two lines. The test is required only for open field samples, which are expected to have low DOC values. In this WRT, WAT-1 and WAT-2 were collected in the open field, and the plot show in details the results concerning these two samples The presence of a number of results for which the test is not satisfied is evident for both samples and they represent 40% of the results with complete analysis for which the test is possible.

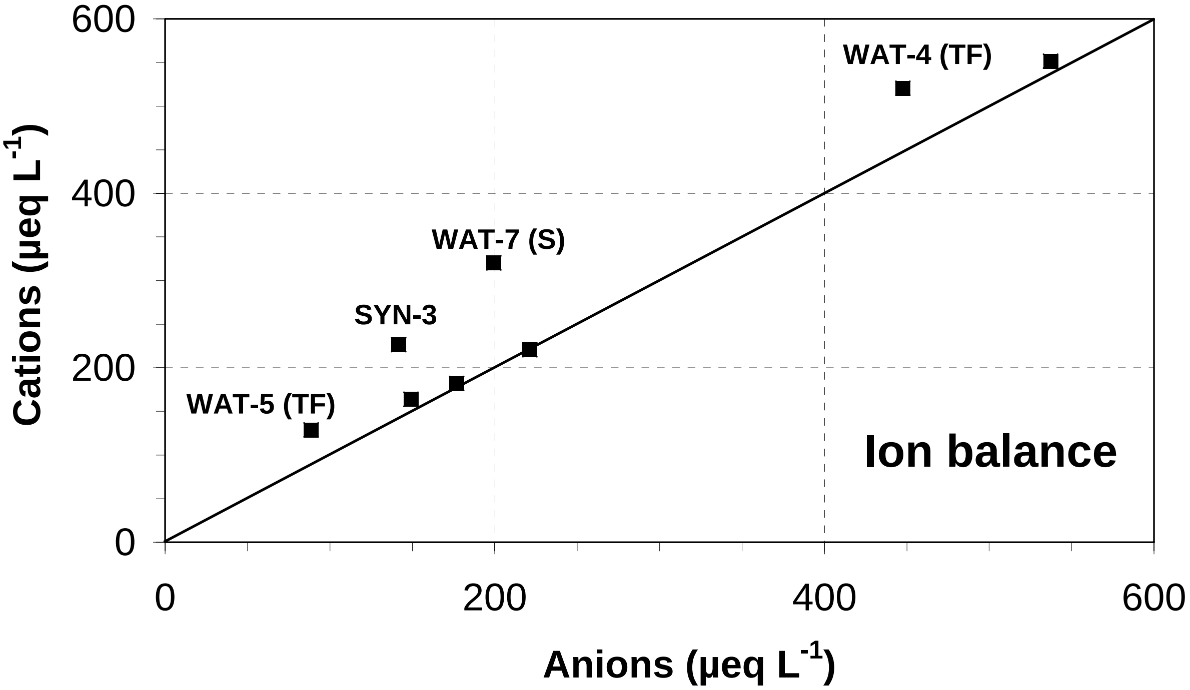


Fig 7.1. Comparison between the sum of the expected concentration (median values) of cations and anions in all the samples used in the WRT.

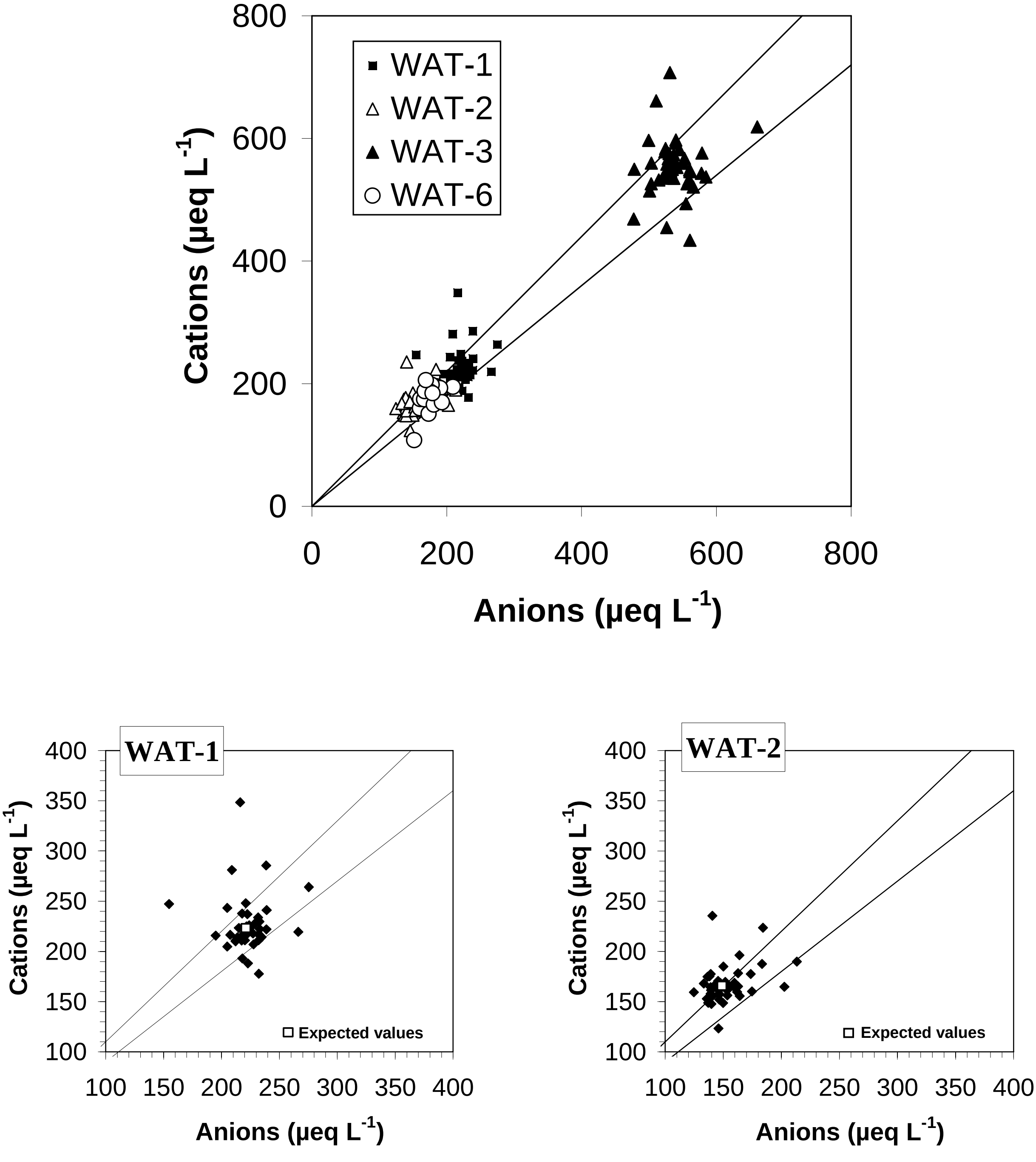


Fig 7.2. Top: comparison between the sum of the measured concentration of cations and anions for all samples in which all major ions were analysed. The data satisfying the quality criteria for ion balance (table 4.2) are comprised between the two lines. The bottom plots represent the open field samples, for which this test is required.

7.1.2. Comparison between measured and calculated conductivity

The requisite for comparing measured and calculated conductivity are the same as for ion balance, i.e. all major ions should be analysed. However, this test is not so sensitive to the presence of organic matter, which generally shows a low conductivity. For this reason, this test is reliable for all samples, including both open field and in-the-plot (throughfall and stemflow) deposition. In this WRT, the analysis of all major ions was required for all WAT samples (WAT-1 to WAT-7) and for one synthetic sample (SYN-3).

In Fig. 7.3 the expected (median) values of measured and calculated conductivity are compared, showing that the test is suitable for all the samples, as the points representing them fall on or close to the 1:1 line.

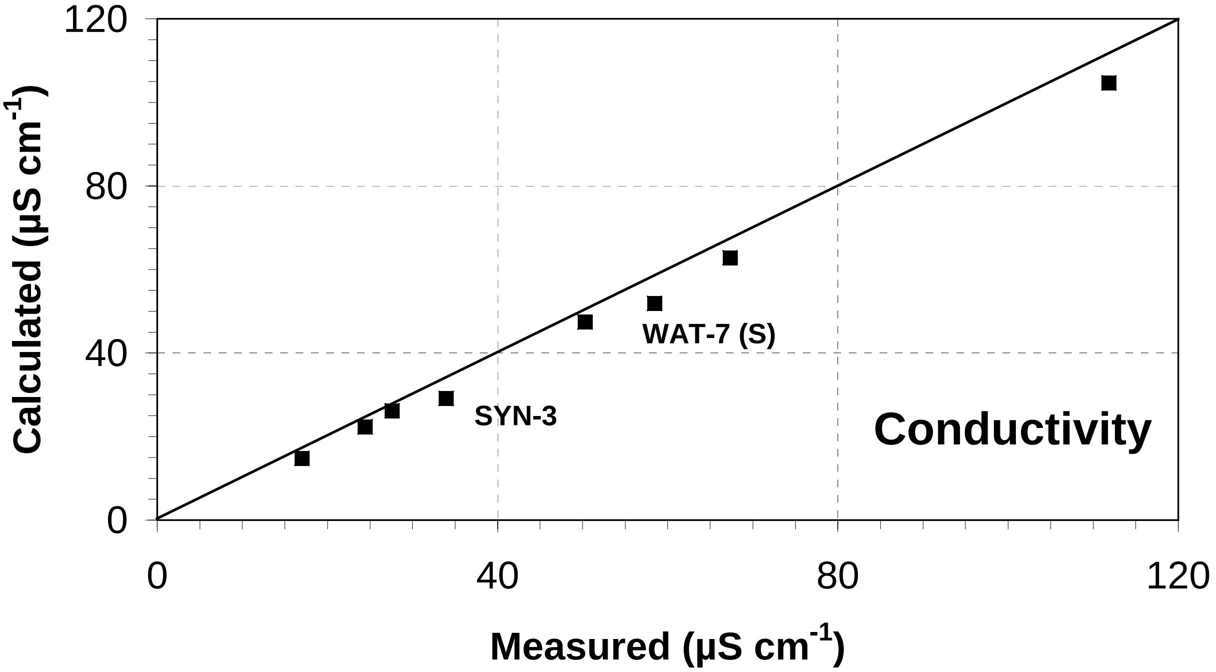


Fig 7.3. Comparison between the expected (median) values of measured and calculated concentration in all the samples used in the WRT (S = soil solution).

In Fig. 7.4. the calculated and measured conductivity are plotted for all samples for which all major ions were analysed. Also in this case, the samples meeting the acceptance criteria for the test are included between the two lines. It is evident that a relevant number of analyses do not satisfy the test. They represent 37% of the samples with complete analysis for which the test is possible. There was no significant difference among the different samples in the percentage of data included in the acceptance range.

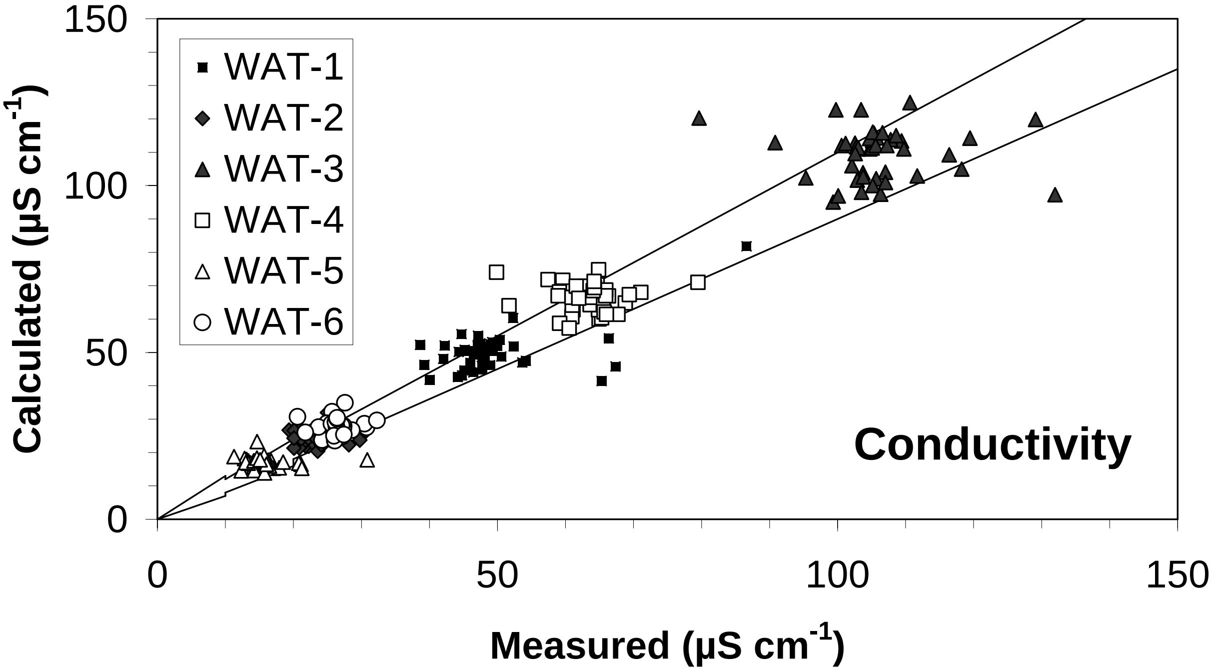


Fig 7.4. Comparison between the measured and calculated conductivity for all the samples in which all major ions were analysed. The data satisfying the quality criteria for the test based on conductivity (table 4.2) are comprised between the two lines.

7.1.3. Ratio Na/Cl

As reported above, in atmospheric deposition, most of the chloride and sodium contents derive from sea salt trapped in sea spray and included in clouds or transported in the air masses. As a consequence, the Na/Cl ratio in deposition samples is usually close to the value normally found in sea salt, around 0.86 for concentration expressed in microequivalent. Figure 7.5 shows in samples deriving from atmospheric deposition, both in the open field (WAT-1 and WAT-2) and on the plot (WAT-3, WAT-4 and WAT-5), this ratio is very close to the value of 0.86. In soil solutions (WAT-6 and WAT-7) as well as in the synthetic sample WAT-3, the ratio is obviously different from this value.

The application of this test to all sodium and chloride concentrations measured in samples originated from atmospheric deposition is shown in Fig. 7.6. Most of the results cluster around the line representing Na/Cl=0.86. A few points fall out of the lines representing the line Na/Cl=0.5 and Na/Cl=1.5 and they would allow the laboratories to detect measurement errors or accidental pollution of the samples. However the test is not sensitive enough to detect most outliers or data outside the acceptance range.

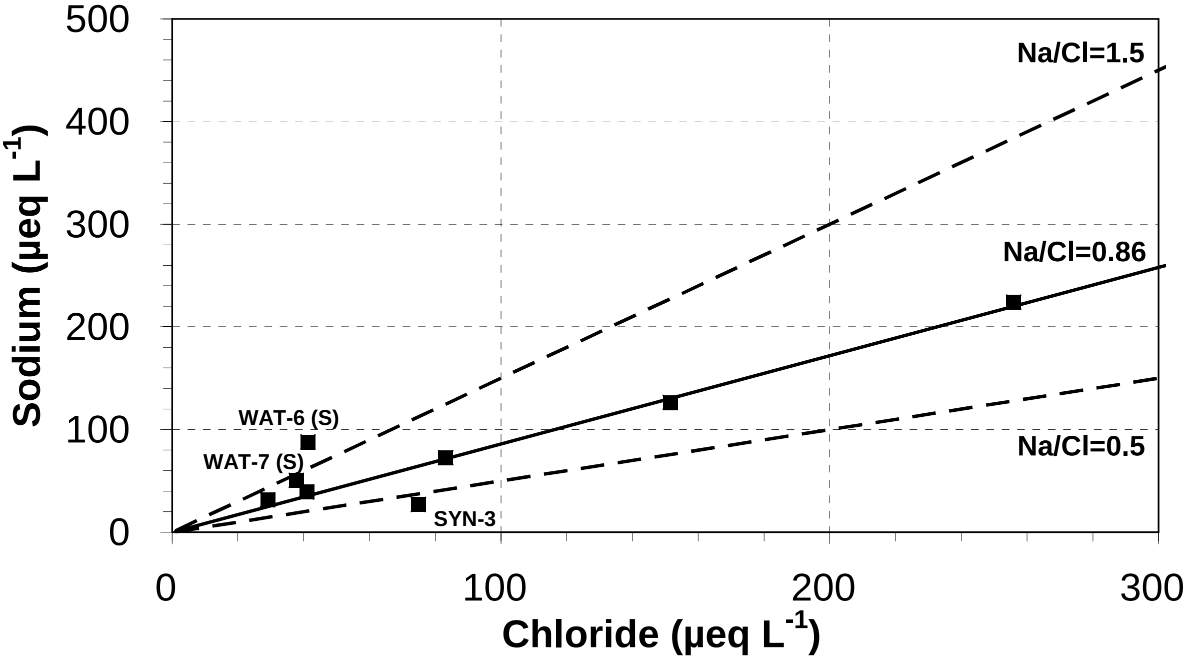


Fig. 7.5 – Sodium and chloride expected concentrations. The lines for some selected Na/Cl ratios are also shown (S = soil solution).

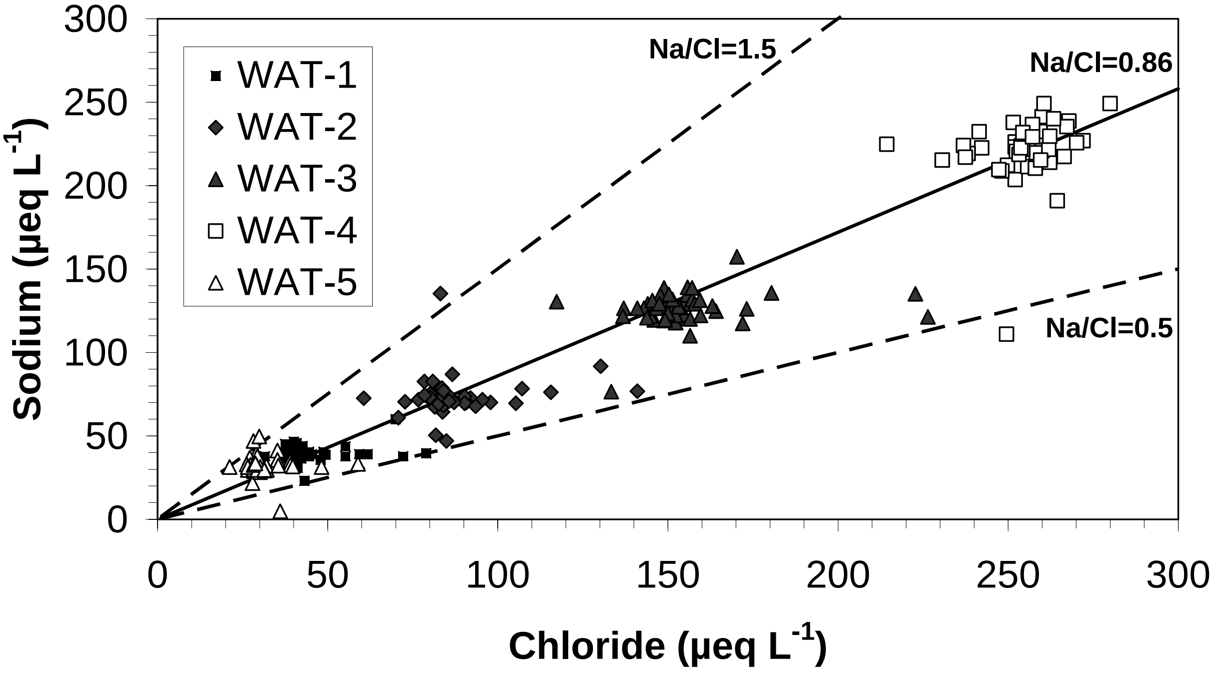


Fig. 7.6 – Sodium and chloride concentration measured by all the laboratories in samples deriving from atmospheric deposition. The lines for some selected Na/Cl ratios are also shown.

7.1.4. Overall considerations regarding quality checks

Following the procedure for Quality Assessment and Quality Control is an important step towards an improvement in the overall quality of the data collected within the ICP Forests programme. For this reason, QA/QC procedures have been or are being adopted for most monitoring programmes.

Tests based on ion balance and on the comparison between calculated and measured conductivity are part of the QA/QC procedures for atmospheric deposition, and the importance of performing them during routine analysis to improve the overall quality of the results cannot be over-emphasised. Analysis of all major ions is required to perform these tests, but these analyses are all mandatory for atmospheric deposition. In the case of soil solution, not all the analyses are mandatory, but the advantage of having a direct test of the reliability of the results should be considered as a way of completing the analysis of all major ions.

Considering only the analysis of the major anions (sulphate, nitrate, chloride, and bicarbonate for samples with pH higher than 5) and cations (hydrogen ions, ammonium, calcium, magnesium, sodium and potassium), 38% of the results submitted for this WRT did not meet the Data Quality Objective (DQO).

It was not possible to make a data check of all the samples, but only of those samples which were analysed for all the major ions, representing 83% of the data set. In this subset, only 21% of the results fell outside the DQOs.

Data checking procedures were included in the file provided for data transfer; these enabled all the participants to perform the test and repeat the analysis in the case of negative results. However, only 52% of the analytical results submitted passed the conductivity test. In the case of samples WAT-1 and WAT-2, for which the ion balance test applied, the percentage of analyses passing the ion balance test and both data checking tests was 50% and 33%, respectively.

It should be noted that the analysis which passed one or both tests contained a smaller percentage of results falling outside the DQO. In particular, 18% of the data which could have been submitted to the conductivity test data check fell outside the DQOs. For the ion balance or both tests, the percentage of results falling outside the DQO was 12% and 11%, respectively.

Table 7.1. – Percentage of samples for which all major ions were analysed , and percentage of the results meeting the data quality objectives.

	% of samples on the whole data set	**% of results outside the DQOs**
Whole data set	-	38%
All major ions analysed (test possible)	83%	21%
Analyses accepted in the conductivity test	52%	18%
Analyses accepted in the ion balance test (open field samples WAT-1 and WAT-2, only)	50%	12%
Analyses accepted in both tests (open field samples WAT-1 and WAT-2, only)	33%	11%

Table 7.1 summarises the results of the data check, showing how the percentage of results falling outside the acceptance range drops dramatically if we consider the samples for which complete analysis was performed, and those satisfying one or both quality tests.

In general terms, these data suggest that more than two thirds of the results not reaching the DQO would have been detected and corrected if the test were routinely performed and the analyses checked or repeated in case of failure at the test.

7.2. Analytical methods that 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.

Another important point is that it is not possible to perform statistical analyses for a specific analytical method when the number of reported values is low. For this reason some methods which could not be evaluated in the previous WRT (Mosello *et al.* 2002), and that were included with a question mark in the list of the analytical methods that gave unsatisfactory results, are now positively evaluated and considered as reliable. They are ICP OES for sulphate, AAS for potassium, chemiluminescence for Total Nitrogen, ICP-MS for Al, Fe.

In the case of total phosphorus, which in the ICP Forests programme is only measured in order to detect accidental sample pollution by bird dropping, it looks as though ICP-MS may be accepted in spite of its low sensitivity.

The continuous flow analysis with $BaSO_4$ excess and methyl thymol was used by two laboratories for the analyses of sulphate, and one of them obtained unsatisfactory results. This method is included in the list with a question mark, as the data are not enough to give a correct evaluation.

For the reasons listed above, the methods reported in table 7.2 are not necessarily incorrect; but they probably require more attention from the laboratories that have adopted them. Apart for the method listed with a question mark, we assume the methods reported in table 7.2 are not suitable, at least at low concentrations, for determining the respective variables in natural deposition and soil solution samples. 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 6).

Table 7.2 - Analytical methods that gave unsatisfactory results.

Analyte	**Methods**
Alkalinity (low values)	Acidimetric titration with colorimetric detection of the end-point Acidimetric titration with single fixed end point without correction
Sulphate	Turbidimetry Spectrophotometry with $BaSO_4$ excess and methyl thymol Continuous flow analysis with $BaSO_4$ excess and methyl thymol (?)
Nitrate (in samples with high DOC)	Spectrophotometry with UV detection at 220 nm
Chloride	$AgNO_3$ titration with K_2CrO_4 indicator
Ca and Mg	EDTA titration
Ammonium	Nessler spectrophotometric method Ion selective electrode
Total Nitrogen	Kjeldahl digestion Alkaline persulphate digestion ($K_2S_2O_8$ and NaOH)
Total Sulphur	ICP MS
Aluminium	AAS Flame
DOC	Spectrophotometry with detection at 320 nm

7.3. Influence of the use of Internal Quality Control procedures on the analytical quality

The relation between the use of IQC procedures and the performance of each laboratory in the WRT is presented graphically in fig. 7.8. The laboratories are arranged from left to right in decreasing order of analytical quality, i.e. in increasing order of missing or outlying results (top plot). The reported use of one or more IQC procedures is shown in the bottom plot.

It emerges clearly that most of the better performing laboratories (on the left) have performed at least one IQC procedure. However, a number of laboratories performing the IQC procedure still produce missing or outlying values, either because they use the procedure for a limited number of analytes, or because the IQC procedures are not sufficiently thorough to allow them to detect their weaknesses, or because the IQC procedures are incorrectly used.

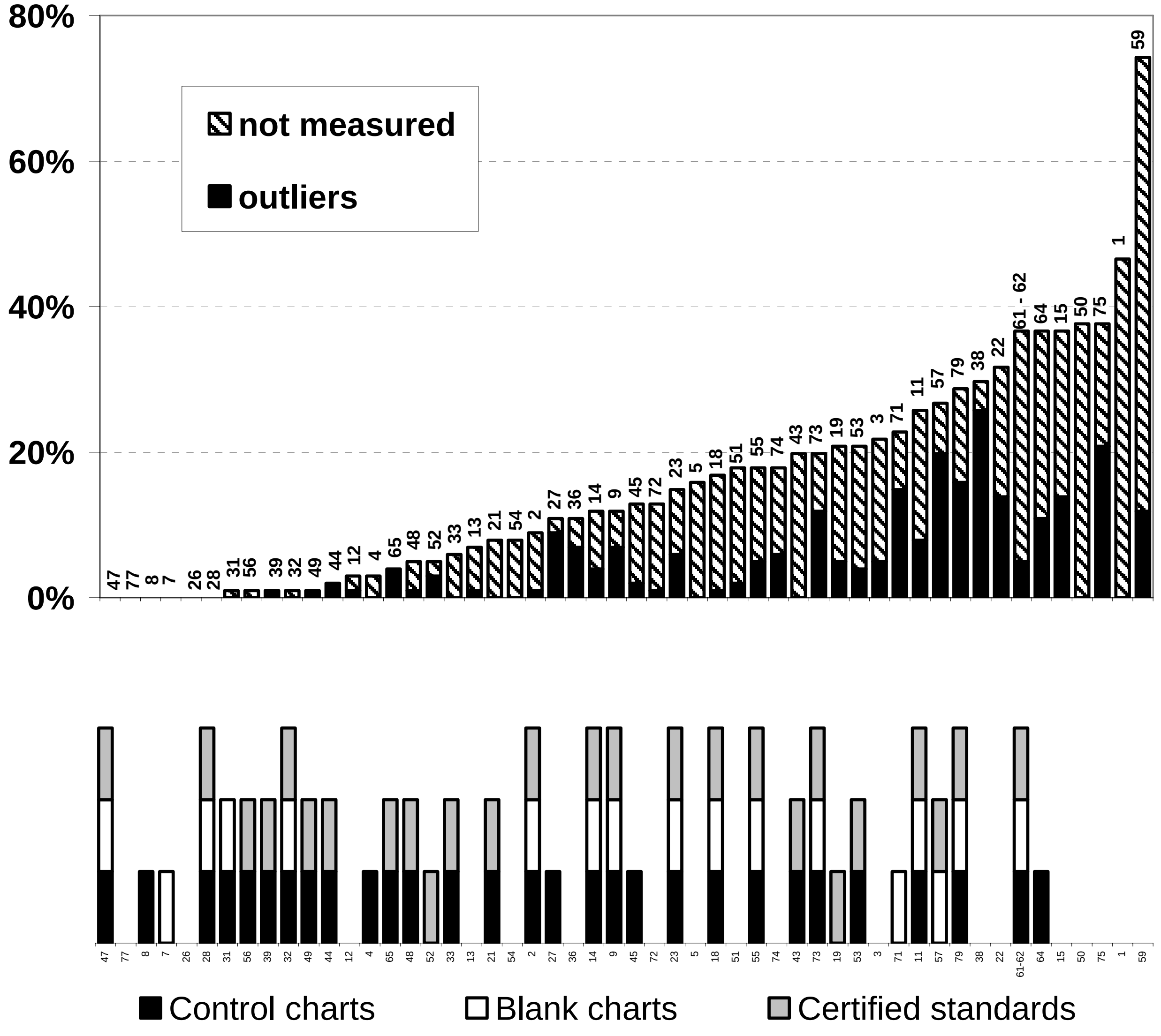


Fig. 7.8. Number of missing or outlying results (top) produced by each laboratory, and reported use of IQC procedures in the same laboratory (bottom). The laboratories are arranged in increasing order of missing and outlying results, i.e. in decreasing order of analytical performance.

To better understand the relation between the analytical performance and the use of IQC procedures, Table 7.3 reports the percentage of outliers produced for each variable by laboratories using no IQC procedure or using the most common combination of procedures, i.e. exclusive use of control charts and combined use of control and blank charts together with certified reference material.

Table 7.3. - Percentage of outliers produced by laboratories using some selected IQC procedures. The numbers in brackets refer to a single laboratory.

Variable	**No IQC, or no answer**	**Control charts only (C)**	**Control charts and certified reference materials (C+R)**	**Control and blank charts, and certified reference materials (C+B+R)**
pH	3%	3%	-	-
Cond	1%	2%	-	-
Ca	2%	10%	0%	8%
Mg	6%	13%	1%	5%
Na	9%	0%	0%	11%
K	8%	4%	3%	3%
Ammonium	10%	3%	0%	5%
Sulphate	6%	9%	2%	8%
Nitrate	3%	2%	0%	4%
Chloride	7%	0%	3%	11%
TDN	11%	*(0%)*	-	6%
Alkalinity	0%	0%	-	*(25%)*
DOC	9%	2%	0%	0%
Total	**6%**	**3%**	**1%**	**7%**

For most of the variables, the use of IQC procedures led to an improvement in analytical quality, revealed by a reduction in the number of outliers produced. This effect is particularly evident in the case of some variables, such as TDN and DOC.

On the other hand, in the case of calcium, sodium and chloride, the number of outliers is comparable between laboratories using none or all of the IQC procedures. It should be noted that these variables are those for which the solutions are more liable to pollution, making the control chart ineffective.

These results should be taken with caution, as some of the laboratories which did not answer the questionnaire may actually use some IQC procedures, but they underline the importance of using both internal and external QC procedures (like the present WRT) to help laboratories assess and improve their analytical quality.

7.4. Comparison with the first WRT

One of the objectives of the WRT is to improve analytical performance in the participating laboratories.

Two synthetic indices are used to evaluate the quality of the results submitted for the WRT and to verify trends in laboratory performance:

- the first index considers the percentage of mandatory results which were not reported, either because they were below the detection limit or because they are not analysed in that laboratory, added to the number of results detected as outliers.
- the second index is the percentage of data meeting the Data Quality Objectives listed in table 2.1.

These two indices give an approximate but valuable indication of the overall performance of the set of laboratories, and they can also be used to monitor improvements in the performance of individual laboratories, assuming that (1) the final goal is for the maximum number of data to fall within the DQOs, (2) a first important result is to reduce the number of outliers and unmeasured data.

In the comparison of the results we purposely decided not to use the *z*-scores. These are frequently used in evaluating the results of intercomparison exercises. While they can give each laboratory a clear understanding of its performance compared to the whole set of participating laboratories, they are not suitable for following a trend in analytical quality, as their value depends on the overall performance of the laboratories. For example, if all the results improve proportionally, the standard deviation also improves and the z-score of each laboratory does not change.

Table 7.4 shows the percentage of missing and outlying results as well as the percentage of results within the DQOs for the two WRTs organized for analyses of atmospheric deposition and soil solution under the ICP Forests Programme. It is evident that the number of results in the acceptance range is quite similar in the two exercises, but the number of missing and outlying values decreased markedly from the first WRT run in 2002 to this WRT, run in 2005. The decrease is more marked if we consider the 47 laboratories which participated in both WRTs.

This comparison shows that increased awareness of the importance of QA/QC procedures and participation in the WRTs have helped the laboratories to improve their overall analytical quality, but at the same time it underlines how essential it is to continue this activity to increase the number of results coming within the DQO.

Table 7.4. Percentage of missing and outlying data and of results lying within the DQO (as defined in table 2.1).

	All laboratories		**Participating in both exercises**	
	WRT 2002	**WRT 2005**	**WRT 2002**	**WRT 2005**
Missing+outliers	15%	9%	11%	7%
missing results	4%	3%	4%	2%
outliers	11%	6%	7%	5%
Meeting the DQO	43%	44%	42%	44%

A similar pattern emerges when we consider the improvement of individual laboratories participating in both WRTs (Fig. 7.7). It is evident that in many laboratories the number of results within the DQOs was much higher in the second exercise than in the first, and that the number of missing and outlying results dropped markedly between the two exercises.

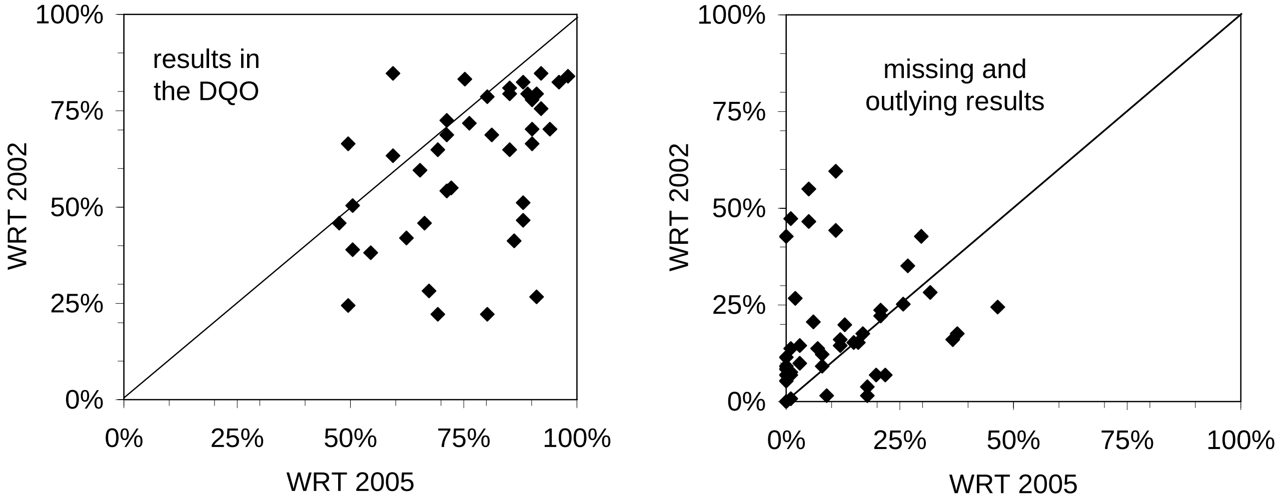


Fig. 7.7 Percent of results falling within the DQOs (left) and percentage of results not submitted or detected as outliers (right) for each laboratory participating in both WRTs.

8. RECOMMENDATIONS

The following recommendations are the results of presentations given by selected experts in the 2nd Workshop on QA/QC in Analysis, during the Combined Meeting of the Expert Panel on Deposition and the Working Group on Soil Solution, held in Rovaniemi (Finland) on 16-20 October 2005, and are highly applicable to the discussion of the results of the WRT.

8.1. Alkalinity measurement

(Rosario Mosello and Gabriele A. Tartari, CNR-ISE Verbania Pallanza, Italy)

8.1.1. Definition of total alkalinity

The alkalinity of a solution is its capacity to neutralise acids, defined as the amount of acid needed to neutralise the bases present in the solution itself. Alkalinity is then the sum of all the bases in the sample, and is determined by means of an acidimetric titration. In freshwater or precipitation, these bases are primarily bicarbonate, as well as hydroxyl ions at pH values above 8.0, sulphide and non-ionic compounds such as calcite or certain organic compounds.

Fig. 8.1. shows the evolution of pH and the concentration of hydrogen ions during an acidimetric titration. The critical point in the titration is the determination of the equivalent point, where it can be 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 & 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), and it ranges between pH 5.0 and 5.6.

To detect the inflection point, it is possible to monitor the pH and to plot the titration curve and its first derivative during the titration. This technique is difficult and often not precise at very low alkalinity because of the difficulties related to the choice of suitable added volumes and for the slow response of pH electrodes.

For this reason some techniques were developed in order to estimate the equivalence point indirectly. The most used are the Gran method and the titration with two fixed end-points, spaced 0.3 pH units, which are described in this chapter.

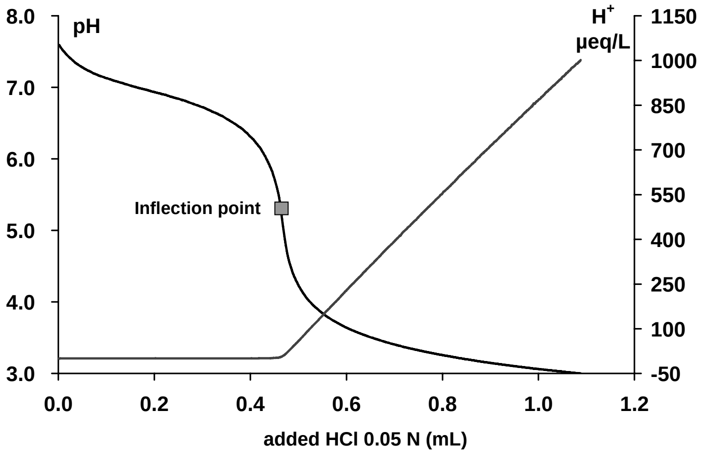


Fig. 8.1. Plot of pH and hydrogen ion concentration during an acidimetric titration.

8.1.2. Two end points titration

This technique requires the continuous reading of pH during titration. Acid (with normality NAc) is added after the equivalence point, decreasing the pH of the solution down to 4.5 (or less), where the titration is stopped (first end point) and the first volume (V_1, in mL) noted. Then acid is added again until the pH decreases of exactly 0.3 units. This is the second end point, and the total volume added (V_2, in mL) is noted again.

A decrease in pH of 0.3 units means a doubling of the hydrogen ion concentration, and simplifies the calculation of alkalinity at the equivalence point, which can be obtained through the following equation:

$$\text{Total alkalinity (meq L}^{-1}\text{)} = \frac{(2V_1 - V_2) \text{ x } N_{Ac} \text{ x } 1000}{\text{Sample volume (mL)}}$$

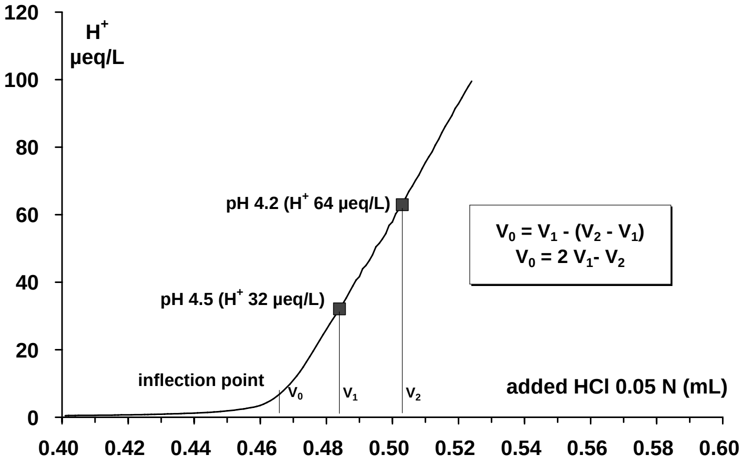


Fig. 8.2. Plot of the concentration of hydrogen ions during the final part of an acidimetric titration, showing the extrapolation to the equivalence point, i.e. the intercept on the x-axis of the straight line passing through the two end points.

8.1.3. The Gran method

It is the most precise technique to measure alkalinity and it is very recommended for low values (Gran 1952).

After adding enough acid to drive the pH down to 4.5 units, a number 4-6 of acid additions (between 10 and 30 µL) are performed and pH is measured. At each point, the following function is calculated:

$$\text{Gran's } F_1 = (\text{sample volume} + \text{added volume}) \text{ x } 10^{-pH}$$

A regression line between Gran F_1 and added volume is then calculated, with an intercept point to the x-axis at the equivalence point V_0.

Total alkalinity is then calculated as follows:

$$\text{Total alkalinity (meq L}^{-1}\text{)} = \frac{V_0 \text{ x } N_{Ac} \text{ x } 1000}{\text{sample volume (mL)}}$$

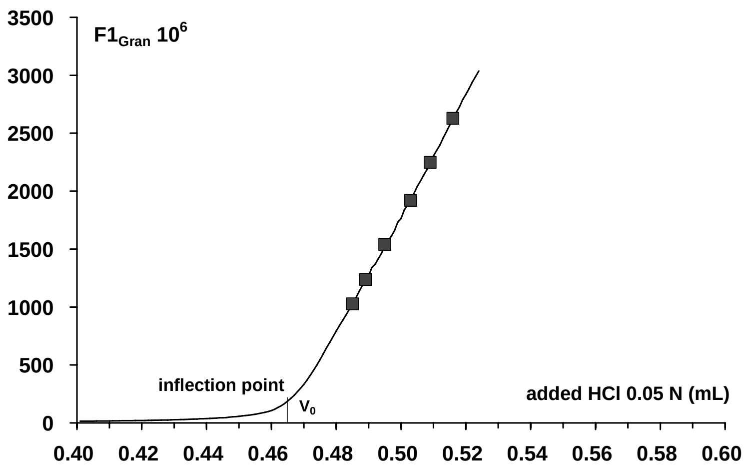


Fig. 8.3. Plot of Gran titration

8.1.3. Suggestions for a correct titration

- Within the alkalinity range 0-5 meq L^{-1}, if the sample volume is around 30-75 mL it is possible to use a titrant acid solution 0.05 N dosed with 2 or 5 mL auto burette.
- Refrigerated samples, and calibration buffers, should be warmed up to 18-24 °C before titration. The pH meter has to be calibrated (pH 7 - 4) before titration, at least weekly.
- It is important to rinse the electrode with de-ionized water before starting the reading.
- Any air bubble in the acid titrant should be eliminated by adequate purging.
- The concentration of the acid should be verified before the first titration, and then at least every two months, measuring samples with known alkalinity (sodium carbonate standards for example).

8.2. Determination of total dissolved nitrogen (TDN) in water samples

(Nils König, Niedersächsische Forstliche Versuchsanstalt Göttingen, Germany)

8.2.1. Definitions:

Total dissolved Nitrogen (TDN) = $NO_3^- + NO_2^- + NH_4^+ + N_{org}$

Dissolved Inorganic Nitrogen (DIN) = $NO_3^- + NO_2^- + NH_4^+$

Dissolved Organic Nitrogen (DON) = $TN - NO_3^- - NO_2^- - NH_4^+$

Kjeldahl Nitrogen $N_{kjel} = NH_4^+ + N_{org}$

Total Dissolved Nitrogen $= N_{kjel} + NO_3^- + NO_2^-$

8.2.2. Determination methods:

always 2 steps:

1. digestion of the organic matter, which contains nitrogen, to NH_4^+, NO_3^- or NO
2. determination of $NO_3^-/NH_4^+/NO$

8.2.2.1. Digestion methods:

1. determination of N_{kjel} with Kjeldahl-digestion

reactions:

Kjeldahl- digestion: $2(NH_2)_2CO + H_2SO_4 \Rightarrow (NH_4)_2SO_4 + 2\ CO_2$

(temp. 360 °C)

Kjeldahl- distillation: $(NH_4)_2SO_4 + NaOH \Rightarrow NaHSO_4 + 2\ NH_3 + H_2O$

absorption of ammonia: $2NH_3 + H_2SO_4 \Rightarrow (NH_4)_2SO_4$

backtitration of the sulfuric acid: $H_2SO_4 + NaOH \Rightarrow NaHSO_4 + H_2O$

problems:

choice of catalyst: HgO, Se (both very toxic!), $CuSO_4$ /TiO_2

interferences: NO_3^- (may be reduced to NH_4^+ or react with NH_4^+ to N_2/N_2O)

H_2S (from organic sulphur) interferes the acidimetry of NH_3

2. determination of TN with Devarda-reduction and Kjeldahl-digestion

reactions:

Devarda-reduction: $NO_3^- + 2\ Al + Zn + 3\ OH^- + 6\ H_2O \Rightarrow NH_3 + 2\ Al(OH)_4^- + Zn(OH)_4^{2-}$

then Kjeldahl digestion

problems:

same as Kjeldahl-digestion

3. peroxodisulfate-digestion with H_3BO_3 and NaOH (Koroleff) (PSB)

reactions:

$(NH_2)_2CO + 8\ S_2O_8^{2-} + 18\ OH^- \Rightarrow 2\ NO_3^- + CO_2 + 16\ SO_4^{2-} + 11\ H_2O$

(temp. 115-120 °C)

problems:

normally no problems, if the concentration of peroxodisulfate is high enough

some organic 5-rings with N are not digested

4. peroxodisulfate-digestion with H_2SO_4 (PSH)

reactions:

$(NH_2)_2CO + 8\ S_2O_8^{2-} + 8\ H_2O \Rightarrow 2\ NO_3^- + HCO_3^- + 16\ HSO_4^- + 3\ H^+$

(temp. 115-120 °C)

problems:

concentration of peroxodisulfate must be high enough

sometimes problems with total oxidation of NH_4^+

some organic pentagonal rings containing N are not digested

5. peroxodisulfate-digestion with NaOH (PSOH)

reactions:

$(NH_2)_2CO + 8\ S_2O_8^{2-} + 18\ OH^- \Rightarrow 2\ NO_3^- + CO_2 + 16\ SO_4^{2-} + 11\ H_2O$

(temp. 115-120 °C)

problems:

possibility of NH_3-loss concerning the high pH

the concentration of peroxodisulfate must be high enough

some organic pentagonal rings containing N are not digested

6. UV-light-digestion

reactions:

$4\ O_2 + UV \Rightarrow 8\ O.$

$(NH_2)_2CO + 2\ OH^- + 8\ O. \Rightarrow 2\ NO_3^- + CO_2 + 3\ H_2O$

problems:

some organic substances are not digested by UV-light

choice of the right UV-lamp

7. combined peroxodisulfate/UV-light-digestion

reactions: see above

problems:

some organic substances are not digested

8. combined peroxodisulfate/microwave-digestion

reactions: see above

problems:

some organic substances are not digested

9. catalytic high temperature combustion to NO (CHML)

reactions:

$2\ (NH_2)_2CO + 7\ O_2$ + catalyst (Pt,CuO, 850°C) => $4\ NO_2 + 4\ H_2O + 2\ CO_2$

$2\ NO_2$ + catalyst (Mo, 350 °C) => $2\ NO + O_2$

problems:

catalyst: the right combination of catalyst and oven temperature (for example Co,Cr, 850°C) has to be chosen

8.2.2.2. Detection methods:

1. NO_3^-:

a. spectrophotometry: UV-detection at 210-220 nm

b. spectrophotometry: Cd-Reduction to NO_2 and detection as diazo-compound

c. spectrophotometry: Cu/Hydrazin-Reduction detection as diazo-compound

d. IC (with and without suppression)

e. Ion capillary electrophoresis (CIA)

2. NH_4^+:

a. NH_3-distillation, acid absorption and back-titration (Kjeldahl)

b. IC (with and without suppression)

c. spectrophotometry: detection as indophenole-blue

3. NO:

a. Chemoluminescence-detection (CHML)

reactions:

$2\ NO + O_3 \Rightarrow 2\ NO_2 + O_2 + hv$

8.2.3. Automated TN-analyser systems:

a. TN-Analyser with catalytic high temperature combustion (A5) and chemoluminescence detection (B3a)

b. Continuous flow analyser with peroxodisulfate- (A2) or combined peroxodisulfate/UV-digestion (A4) and spectrophotometric NO_3^- determination (B1)

8.2.4. Norms

1. N_{kjel} in waters: DIN EN 25663 (Kjeldahl-digestion and distillation)
2. TN in waters: DIN EN ISO 11905-1 or DIN 38409 H-36 (peroxodisulfate CF or FIA)
3. TN in waters: DIN EN ISO 11905-2 or DIN 38409 H-34 (chemoluminescence)
4. TN in Calcium chloride-soil-extracts: DIN ISO 14255 (peroxodisulfate CF or FIA)

8.2.5. Methods recommended for TN as a result of the WRT2

1. TN-Analyser with chemoluminescence detection (CHML)
2. Peroxodisulfate digestion with H_3BO_3 and NaOH (PSB), also in combination with UV-light and in continuous flow systems combined with NO_3^- or UV 220-detection

8.2.6. Methods not recommended as a result of the WRT2

1. Kjeldahl-digestion and distillation of NH_3

8.3 Dissolved organic carbon (DOC) analysis

(Nicholas Clarke, Norwegian Forest Research Institute, Ås, Norway)

In the *ICP Forests Manual*, dissolved organic carbon (DOC) is a mandatory parameter in bulk deposition, throughfall and stemflow.

8.3.1. Effects of filtration

DOC is operationally defined, usually, as organic carbon that passes through a 0.45 µm membrane filter. Other pore sizes are sometimes used. Different pore sizes could give very different results, although this is not always the case (Table 8.1).

Table 8.1. Effects of filter type on DOC (mg/l) from Birkenes, Norway. SW = soil water. F, H and O refer to soil horizons.

Filtration	**SW F**	**SW H**	**SW O**	**Stream**	**Stream**
Filter paper	108.7	52.47	40.10	4.71	5.91
Membrane 1.2 µm	112.3	51.18	37.21		4.50
Membrane 0.45 µm	115.8	52.59	37.91	4.41	4.12
Membrane 0.22 µm	115.4	52.35	37.09		5.03
Membrane 0.05 µm			39.30		4.87

Cellulose acetate or nitrate membrane filters should not be used due to contamination or adsorption problems (Table 8.2). Filter paper may contaminate the sample with NH_4 and organic carbon. Glass fibre filters are preferable. The possible release of organic fibres from the membrane should be tested, and suitable pre-rinsing procedures developed if required.

Table 8.2. Effects of three rounds of filtration with 0.45 µm cellulose acetate/nitrate membrane filters on concentrations of DOC in water samples from Birkenes (mg L^{-1}). F and H refer to soil horizons in the organic layer.

Sample	**DOC**			
	Initial	Round 1	Round 2	Round 3
Soil water H 1	105.5	95.6	87.9	77.9
Soil water H 2	100.3	95.6	88.4	75.6
Soil water F 1	71.2	67.3	59.5	51.8
Soil water F 2	70.0	65.3	61.7	51.6
Stream 1	3.1	3.7	3.7	4.4
Stream 2	3.8	4.2	4.5	4.7

8.3.2. Methods for DOC determination

There are two main groups of methods used for DOC determination:

1. Carbon analyser ISO 8245(1999)
2. Spectrophotometry

No methods are ‘not recommended’ in the ICP Forests manual for sampling and analysis of atmospheric deposition.

8.3.2.1. Carbon analysers

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, underestimation 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 ionisation detection after reduction to methane. There has been some discussion about whether combustion or persulphate oxidation gives the best results, but no conclusion has been reached.

For the determination of DOC, dissolved inorganic carbon must be either removed by purging the acidified (for example with phosphoric acid) sample with a gas that 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.

8.3.2.2. Spectrophotometry

DOC may also be determined by UV absorbance. A typical absorbance spectrum for DOC is shown in Fig. 8.4. At higher wavelengths, absorbance is lower, so care should be taken when measuring in this region.

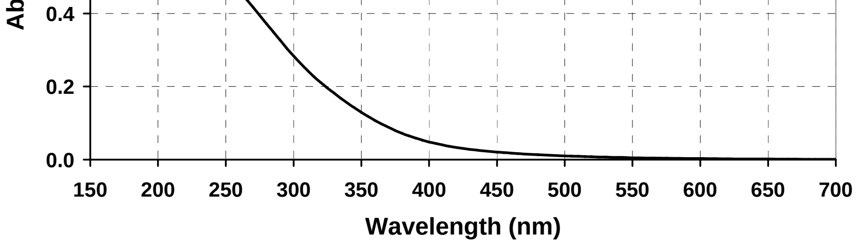


Fig. 8.4. Absorbance spectrum of DOC

Good results have been obtained using a wavelength of 254 nm. This is not the optimal method, but may be used if a carbon analyser is not available. Regression equations are given by Brandstetter *et al.* (1996) for estimation of DOC from the absorbance measurements:

$$\text{DOC (mg L}^{-1}\text{)} = 0.44\ A_{254}\ (\text{m}^{-1}) + 0.9 \text{ for throughfall}$$

$$\text{DOC (mg L}^{-1}\text{)} = 0.86\ A_{254}\ (\text{m}^{-1}) - 11.7 \text{ for stemflow}$$

where: A_{254} = absorbance at 254 nm

For wet deposition, an equation is given by Bartels (1988):

$$\text{DOC (mg L}^{-1}) = 0.46\ A_{254}\ (\text{m}^{-1}) - 0.10$$

Absorbance at 320 nm has often been used in limnology. This wavelength was chosen in order to relate DOC to light attenuation. However, absorbance in this region is not so strong as at 254 nm, which would lead to difficulties in the determination of low concentrations of DOC. This method should not be used for the analysis of deposition or soil water samples within the ICP Forests Programme, as the results of the ring test show it to be unsatisfactory (Table 7.2).

9. CONCLUSIONS AND RECOMMENDATIONS

WRTs are a part of a complex procedure carried out by the WG on QA/QC to assess and improve the analytical quality of the laboratories analysing atmospheric deposition and soil solutions under the ICP Forests Programme. Activities carried out up to now also include revision of the *ICP Forests Manual*, with a procedure for Quality Assessment and Quality Control (QA/QC) assisting specific laboratories to develop their skills and achieve high analytical standards.

This working test is the first run under the Forest Focus regulations of the European Union and the second run by the ICP Forests Expert Panels on Deposition (EPD) and the Working Group on Soil Solution of the Expert Panel on Soil; it saw the participation of most of the laboratories analysing deposition or soil solution within the intensive forest monitoring programme. Of the 54 laboratories included in this WRT, 47 also participated in the previous exercise in 2002.

Like the previous WRT, this test was designed to give to each laboratory feedback on its performance, and to give the labs with poor analytical performance the chance of improving their QA/QC procedures according to the numerous existing guidelines and standards. Furthermore, this second WRT allowed us to directly compare the quality of the data with the previous exercise.

In general, the analytical procedures of a laboratory should be performed under a set of codified rules and methodologies regulating equipment maintenance, the selection and checking of chemical reagents, the checking of de-ionised water and cleanliness of plastic and glassware, the use of blanks and control charts, the selection of reliable analytical methods for the type of samples to be analysed, and a number of other aspects generally referred to as in-laboratory Good Laboratory Practices (GLP). These procedures should be coupled with inter-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 inter-laboratory activities can assure the optimal performance of the laboratory.

Finally, Data Quality Objectives (DQOs) were adopted to indicate if the laboratory performance was adequate in respect of the technical feasibility and objectives of the ICP-Forests Programme. For this reason, the criteria adopted in the present WRT for calculating the performance of the laboratories was on one hand the number of results within the DQOs, and on the other hand the number of values which were detected as outliers, or which were not measured, or which resulted below the quantification limit due to the lack of an adequate method.

The results of the WRT are not intended to be viewed as a criticism of the performances of individual laboratories, or to exclude data from the ICP Forests data base, but to give each laboratory the necessary feedback to understand its weak points and, depending on their financial and personnel resources, to make the necessary improvements.

Some suggestions are included in this report on ways to improve the data QA/QC protocols, and to analyse some problematic variables, such as alkalinity and the concentrations of dissolved organic carbon and total nitrogen.

The results of the present WRT allowed us to identify the most critical analytical methods and to highlight the need for efforts to improve laboratory performance and analytical quality.

However, it was noted that some quality checking of the major ion concentrations, strongly recommended in the *ICP Forests Manual*, can be performed on the basis of chemical and physico-chemical properties such as ion balance and a comparison between measured and calculated conductivity. If routinely performed, these procedures would allow many laboratories to be aware of providing data outside the acceptance range. However, the test should be used carefully, as it is not always analytical errors that lead to unsatisfactory results: 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. If these limits are exceeded, the analyses must be repeated.

The results also showed that the ion balance is not 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. Accordingly, the ion balance is not requested for soil solution samples and for atmospheric deposition in the plot.

Other empirical relationships between ions, e.g. between conductivity and the sum of cations or the sum of anions, may help in identifying anomalous results. The validation procedure should also consider the ratio between sodium and chloride concentrations, whose ratio is normally close to that of sea 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. Any marked deviation from the marine ratio must be confirmed by a second analysis and, if confirmed, the causes should be identified.

One limitation 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 the fact that the measurement of low alkalinity values (below 50 µeq L^{-1}) is extremely critical. This is in agreement with the results of the previous exercise (Mosello *et al.* 2002) and can be assumed to be a general analytical problem. The errors arising at low alkalinity values are largely systematic and are discussed in Section 5.5. Reliable results are obtained only with methods that extrapolate the inflection point in the acid titration, e.g. Gran titration, and two end-point titration. Systematic errors become less important for alkalinity values higher then 100-200 µeq L^{-1}, i.e. in the range of values in samples SYN-1a and -1b (254 and 124 µeq L^{-1}), which were specifically prepared for determining alkalinity. However, the point is that alkalinity in atmospheric deposition is low, generally below 50 µeq L^{-1} but, 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 7.2), 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 and ion selective electrode for chloride, Kjeldahl digestion for the determination of ammonium, and colorimetric titration for alkalinity.

The laboratories participating in the ICP Forests Programme are strongly urged to re-consider their in-laboratory QA in the light of the results of this inter-comparison and the recommendations of the authors of this report. Unreliable analytical methods should be changed and a validation protocol adopted.

The 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 performance. This is the task and the challenge of the WRT and of all the QA/QC activities proposed within the Expert Panels on Deposition and on Soil Solution of the ICP Forests programme.

10. REFERENCES

ACS Committee on Environmental Improvement. 1980. Guidelines for data acquisition and data quality evaluation in environmental chemistry. *Anal. Chem*., 52: 2242-2249.

Allan M.A. (ed). 2004. *Manual for the GAW Precipitation Chemistry Programme. Guidelines, Data Quality Objectives and Standard Operating Procedures.* WMO TD No. 1251: 170 pp.

A.P.H.A., AWWA & WEF. 1998. *Standard methods for the examination of water and wastewater*. 20th ed. American Public Health Association, Washington.

Bartels, U. 1988. Abschätzung der organischen Kohlenstoffeinträge in Waldökosysteme durch Messung der UV-Absorption (254 nm) im Niederschlagswasser. *Z. Pflanzenernähr. Bodenk*. 151: 405-406

Brandstetter A., Sletten R.S., Mentler A. & Wenzel W.W. 1996. Estimating dissolved organic carbon in natural waters by UV absorbance (254 nm*). Z. Pflanzenernähr. Bodenk*. 159: 605-607

Gran, G. 1952. Determination of the equivalence point in potentiometric titration II. *Analyst* 77: 661-671.

Grubbs, F.E. 1969. Procedures for detecting outlying observations in samples. *Technometrics*, 11: 1-21.

I.S.O. 7888 - 1985. *Water quality. Determination of electrical conductivity*. UDC 543.3:541.133. 6 pp.

I.S.O. 8258 - 1991. *Shewhart control charts*.

I.S.O./ TR 13530 - 1997. *Water quality. Guide to analytical quality control for water analysis*.

I.S.O. 8245 – 1999. *Water quality. Gudelines for the determination of total organic carbon (TOC) and dissolved organic carbon (DOC)*.

I.S.O./ IEC 17025 - 2005. *General requirements for the competence of testing and calibration laboratories*.

Kramer, J. R., A.W. Andren, R.A. Smith, A.H. Johnson, R.B. Alexander & G. Oelhert. 1986. Stream sand lakes. In: *Acid deposition: long term trends.* National Academic Press. Washington D.C.: 231-299.

Lövblad, G., R. Mosello, J. Derome, E. Ulrich, K. Derome, N. Clarke, N. König & G.P.J. Draaijers. 2004. Part VI. Sampling and Analysis of Depositino. In: T. Haußmann & M. Lorenz (eds). *Manual on Methods and Criteria for Harmonized Sampling, Assessment, Monitoring and Analysis of the Effects of Air Pollution on Forests.* United Nations Economic Commission for Europe. Convention on Long-range Transboundary Air Pollution, International Co-operative Programme on Assessment and Monitoring of Air Pollution Effects on Forests, 70 pp.

Marchetto, A., M. Bianchi, H. Geiss, H. Muntau, G. Serrini, G. Serrini Lanza, G.A. Tartari & R. Mosello. 1997. Performances of analytical methods for freshwater analysis assessed through intercomparison exercises. I. Total alkalinity. *Mem. Ist. ital. Idrobiol*., 56: 1-13.

Miles, L.J. & K.J. Yost. 1982. Quality analysis of USGS precipitation chemistry data for New York. *Atmosph. Environ*. 16: 2889-2898.

Mosello, R., A. Marchetto, G.A. Tartari, J. Derome, K. Derome, T. Dahlin & E. Ulrich. 2002. *Atmospheric deposition and soil solution. Working Ring Test 2002.* European Union,United Nations Economic Commission for Europe, International Co-operative

Programme on Assessment and Monitoring of Air Pollution on Forests, Fontainebleu, France, 69 pp.

Mosello, R., M. Amoriello, T. Amoriello, S. Arisci, A. Carcano, N. Clarke, J. Derome, K. Derome, N. Koenig, G. Tartari & E. Ulrich. 2005. Validation of chemical analyses of atmospheric deposition in forested European sites. *J. Limnol.* 64: 93-102

Pungor, E. 1965. *Oscillometry and Conductometry*. Pergamon Press.

Rodier, J. 1984. *L'analyse de l'eau*. Dunod. Orleans: 1365 pp.

Soakal, R.R. & F.J. Rohlf. 1981. *Biometry*. Freeman & C. New York. 859 pp.

Stumm, W. & J.J. Morgan. 1981. *Aquatic chemistry*. Wiley and Sons, New York. 780 pp.

Tartari, G.A. & R. Mosello. 1997. Metodologie analitiche e controlli di qualità nel laboratorio chimico dell'Istituto Italiano di Idrobiologia del Consiglio Nazionale delle Ricerche. *Documenta Ist. ital. Idrobiol.*, 60: 160 pp.

Uggerud, H. Th, J. E. Hanssen, J. Schaug & A.G. Hjellbrekke. 2005. *The Twenty-first Intercomparison of Analytical Methods within* EMEP. EMEP/CCC Report 6/2004, NILU, Kjeller, Norway: 82 pp.

Youden, W.J. 1959. Graphical diagnosis of interlaboratory test results. *Industrial Quality Control*, 15-24.

Youden, W.J. & E.H. Steiner. 1975. *Statistical manual of the Association of Official Analytical Chemists. Statistical Techniques for Collaborative Tests*. Arlington.

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