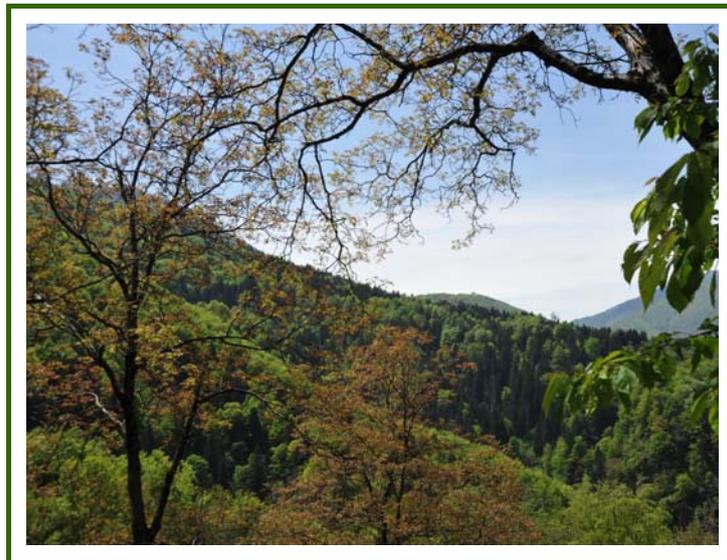Consiglio Nazionale delle Ricerche

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ATMOSPHERIC DEPOSITION AND SOIL SOLUTION WORKING RING TEST 2010

2010

Atmospheric Deposition and Soil Solution Working Ring Test 2010

Laboratory ring test for deposition and soil solution sample analyses for the laboratories participating in the EU/Life+ FutMon Project

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SUMMARY

A second Working Ring Test (WRT) was organised within the framework of the EU/Life+ FutMon Project ("Further Development and Implementation of an EU-level Forest Monitoring System", LIFE07 ENV/D/000218), to evaluate the overall performance of the laboratories responsible for analysing atmospheric deposition and soil solution samples in European forests, and to verify improvements in the analytical quality resulting from the QA/QC work carried out in the laboratories which participated in previous WRTs organized in the framework of the UN/ECE ICP Forests Monitoring Programme.

The WRT was carried out in accordance with International ISO and ILAG guide proficiency test both for sample preparation and numerical elaboration of the results.

Five natural atmospheric deposition and soil solution samples and 3 synthetic solutions were distributed to 42 laboratories for analysis using their routine methods for the following variables: pH, conductivity, calcium, magnesium, sodium, potassium, ammonium, sulphate, nitrate, chloride, total alkalinity, total dissolved nitrogen (TDN), dissolved organic carbon (DOC).

Two tolerable limits were defined for each variable on the basis of the measured value, the results of previous WRTs, a comparison with the Data Quality Objectives of other international networks, and the importance of the variable in deposition and soil solution monitoring.

In the ring test 12% of the results from all the laboratories did not fall within the tolerable limits. This enabled us to identify those variables and laboratories for which improvements in analytical performance are required. The results of the exercise clearly show that the use of data check procedures, as described in the *ICP Forests manual for sampling and analysis of atmospheric deposition*, makes it possible to detect the presence of inaccurate or outlying results, and would therefore greatly improve the overall performance of the laboratories.

A discussion of the improvement of the results in this WRT compared to the previous WRTs is also included, showing a relevant improvent for several variables and underlining the importance of participating to these exercises for the overall analytical quality of the monitoring network.

ACKNOWLEDGMENTS

1. INTRODUCTION

Working Ring Tests (WRTs) represent an essential part of the data quality assurance and control procedures in the FutMon Project. They are organized for almost all of the monitoring activities and the participation of laboratories funded by the project is mandatory. Previous activities carried out since 2002 with funding provided under the EU monitoring programmes (e.g. Forest Focus), in cooperation with the ICP Forests Expert Panels on Deposition (EPD) and Soil Solution, showed that the participation of laboratories in WRTs and the adoption of regular quality assurance procedures in each laboratory can help in substantially improving data comparability in the Level II network.

Three WRTs for deposition and soil solution chemistry have already been carried out, one in 2002 (EU co-funding), one in 2005 (co-financed by the EU/Forest Focus programme), and the last in 2009 (funded by the LIFE+ FutMon project) with most of the laboratories engaged in analysing deposition or soil solution within the intensive forest monitoring programme participating (Mosello *et al.* 2002, Marchetto *et al.* 2006, 2009).

The main purpose of the WRTs was to provide each laboratory with feedback on its performance and the opportunity of improving their procedures for Quality Assurance and Quality Control (QA/QC) according to the numerous existing guidelines and standards.

Data Quality Objectives were introduced for the first time during the second WRT (Marchetto *et al.* 2006), based on previous experience in international ring tests and on the results of the first WRT. These Data Quality Objectives were intended as a compromise between the goals of the deposition and soil analysis carried out within the forest monitoring programmes and the improvement in QA/QC that can be achieved at a reasonable effort and cost.

In the FutMon project, the purpose of this action is to improve the overall quality of the analytical network, making mandatory, for the first time, the participation of all FutMon laboratories to the Working Ring Test, and a re-qualification procedure for laboratories not reaching a minimum data quality.

The aims of the FutMon WRTs were:
- to test the performances of the national laboratories participating in FutMon and in the ICP Forests programme, using natural throughfall and soil solution samples covering the typical range of acidity, sea salt, DOC, nitrogen and sulphur concentrations that are encountered in the participating countries;
- to evaluate the overall performance of the FutMon and ICP Forests laboratories;
- to verify whether there have been any improvements in the analysis of total dissolved nitrogen (TDN), dissolved organic carbon (DOC) and total alkalinity (TA), which were found to be "weak points" in previous exercises;
- to promote chemical analysis validation practices, through the use of the ion balance check and a comparison between measured and calculated conductivity.

Two WRTs were planned within the FutMon Project, one in 2009 and one in 2010. All the laboratories co-funded under FutMon must have participated in both WRTs, and any laboratory with more than 50% of the results lying outside the tolerable limits values have to requalify.

This report represent deliverable QA-Water10 and the final report of action C1-Water-40 and follow a previous report detailing the Working Ring Test carried out in 2009.

In this report we discuss the results of the second FutMon WRT and the improvement in the analytical quality obtained through the participation to the previous WRTs, showing the overall reduction of the number of data falling outside the data quality objective and of the laboratories not reporting mandatory variables.

2. TOLERABLE LIMITS

2.1 Defining the tolerable limits

To evaluate and maintain the quality of the results obtained in a monitoring network, it is very important to define the tolerable uncertainty in the measured data. Tolerable limits are influenced both by the results that can be obtained using appropriate analytical techniques and by the precision required in data elaboration in order to produce reliable results for the monitoring programme.

When defining the tolerable limits within a specific monitoring network, it is necessary to distinguish between laboratory precision, inter-laboratory bias and overall precision.

Laboratory precision can be estimated by each laboratory by performing a suitable number of replicate analyses on several samples that cover the concentration range encountered in the monitoring programme. Although laboratory precision is not covered in this report, it is strongly recommended that each laboratory estimate and monitor its own precision, in order to track improvements and weaknesses in its analytical work.

This WRT allows the estimation of inter-laboratory bias, which is an estimate of the comparability of the results obtained in different laboratories. Tolerable limits were obtained for the FutMon network by combining the results of the first WRT and the requirements of the monitoring programme, in the light of results obtained by other international networks.

Determination of tolerable limits is a dynamic process, and the values proposed here will most probably be revised in accordance with the evolution and future needs of the monitoring programme.

2.2. Tolerable limits

The tolerable limits were agreed on during the meeting of the Working Group on QA/QC in Laboratories, held in Florence (Italy) on April 15, 2008, and are based on the data collected in a previous WRT (Mosello *et al.* 2002) and verified in a further test (Marchetto *et al.* 2006). They take into account the fact that the tolerable limits should be less stringent for values closer to the limit of quantitation.

The tolerable limits were calculated as follows:

1. The interquartile range (IQR) of the reported concentration was evaluated for each sample and each parameter above the limit of quantitation. It represents the interval that includes 50% of the reported values:

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

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

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

Because pH has a logarithmic scale, the AR for pH was simply expressed as:

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

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

The AR for all the parameters were then compared with the values obtained in the Global Atmosphere Watch programme of the World Meteorological Organization (Allan 2004) using the same procedures, and used to define tolerable limits specific for the individual parameters.

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

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

- a tolerable limit of ±10% was set for sulphate because of its importance in deposition and soil solution chemistry and its low AR (±6.8%),

- in the case of alkalinity, total dissolved nitrogen (TDN) and dissolved organic carbon (DOC), the first WRT identified several problems in the analysis of these parameters and their AR values were ±70%, ±22% and ±16%, respectively. A tolerable limit of ±15% was considered not realistic on the basis of current laboratory practice, and it was decided to apply larger tolerable limits at this stage in order to help laboratories to gradually improve their performance. The tolerable limits were set at ±25% for alkalinity and ±20% for total dissolved nitrogen (TDN) and dissolved organic carbon (DOC).

The ARs for the parameters which are not mandatory in the monitoring programmes range between ±5 and ±25%. The latter value is not very important because it is for iron, which was present at only very low concentrations in the four natural samples. As these parameters are optional and there are still problems with their analysis, a common tolerable limit was set at ±20%.

Laboratories not meeting the tolerable limits for more than 50% of the determinations of the same analyte had to re-qualify by submitting a report in which they outlined the analytical problems encountered and the solutions adopted, and then submit new results..

Table 2.1 – Tolerable limits agreed on during the meeting of the Working Group on QA/QC in Laboratories, held in Florence (Italy) on April 15, 2008.

Parameter	Threshold mg/L	> Threshold	< Threshold
pH	5.0	± 0.2 u.	± 0.1 u.
Conductivity	10 $\mu S\ cm^{-1}$	± 10%	± 20%
Ca	0.25 $mg\ L^{-1}$	± 15%	± 20%
Mg	0.25 $mg\ L^{-1}$	± 15%	± 25%
Na	0.5 $mg\ L^{-1}$	± 15%	± 25%
K	0.5 $mg\ L^{-1}$	± 15%	± 25%
$N-NH_4$	0.25 $mg\ L^{-1}$	± 15%	± 25%
$S-SO_4$	1 $mg\ L^{-1}$	± 10%	± 20%
$N-NO_3$	0.5 $mg\ L^{-1}$	± 15%	± 25%
Cl	1.5 $mg\ L^{-1}$	± 15%	± 25%
Alkalinity	100 $\mu eq\ L^{-1}$	± 25%	± 40%
TDN	0.5 $mg\ L^{-1}$	± 20%	± 40%
DOC	1 $mg\ L^{-1}$	± 20%	± 30%

3. IMPLEMENTATION OF THE WORKING RING TEST

The WRT was carried out in accordance with ISO/IEC 43-1 and 43-2 (1997), ISO 5725 (1998), ISO/IEC 17025 (2005), ISO 13528 (2005), ISO/IEC DIS 17043 (2008) and ILAG-G13:08 (2007), the only exception being the NFCs of the associated beneficiaries of the FutMon Project, as well as of ICP Forests countries, and the working group on QA/QC will know the codes of the individual laboratories. Only the Lab IDs are given in this report.

According to the above-mentioned standards, a working group should be established for each inter-comparison exercise. The working group for this ring test consisted of:

- Nils König, chairperson of the ICP Forests Quality Assurance and Quality Control in the Laboratories working group, leader of FutMon action C1-QALAB-30 (NWD);
- Nicholas Clarke, chairperson of the ICP Forests Expert Panel on Deposition;
- Kirsti Derome;
- John Derome†;
- Anna Kowalska, co-chair of the ICP Forests QA/QC in Labs working group;
- Rosario Mosello;
- Gabriele Tartari;
- Aldo Marchetto, leader of FutMon action C1-Water-40 (IT).

Registration for the WRT was open until February 19th, 2010, and the samples were sent out in February. The deadline for submitting the results was fixed as April 16th, 2010.

All the laboratories received a qualification report on May 24th. Where appropriate, certain laboratories were informed about the need for carrying out the re-qualification procedure, the deadline for which was fixed as August 31th, 2010.

3.1. The water samples

Five natural samples, consisting of bulk precipitation (sample 1), throughfall (Samples 2 and 3) and soil solution (Samples 4 and 5), and 3 synthetic samples for the determination of alkalinity (SYN 6-8), were sent to the participating laboratories.

3.2. Preparation of the samples

All the synthetic samples were prepared by dissolving analysis grade reagents in deionised water and diluting them to the required volume.

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

3.3. Homogeneity of the samples after filtration

Homogeneity was tested by determining TDN and alkalinity on ten bottles representing each sample. The relative standard deviation was calculated, and it resulted to be lower than 3% for most samples (Table 3.1). No statistically significant variation was found between the selected samples, and the samples were therefore considered to be fully homogeneous.

Table 3.1 – Relative standard deviation of the analyses of ten bottle for each sample.

Parameter	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	SYN 6	SYN 7	SYN 8
TDN	1.5%	2.7%	0.7%	1.6%	0.8%	-	-	-
Alkalinity	-	-	-	-	-	4.0%	1.6%	1.0%

3.4. Stability of the samples

The stability of the samples was tested by analysing them, for all the parameters to be determined in the ring test, five times during the following 6-month period, overlapping the period when the analyses were to be performed in the participating laboratories and the requalification window.

The analyses were carried out in triplicate at Northwest Forest Research Station (NW-FVA), Göttingen, Germany. The results are shown in Fig. 3.1.

Most of the variability is within 50% of the tolerable limits for the whole period of analysis, and only a two samples drifted outside 50% of the tolerable limits. However, some variables, namely DOC in sample 1 and ammonia in sample 5, showed a different behaviour and a higher variability.

The first did not show a regular drift, but a marked variability between different dates. The latter, on the contrary, started to drift in May and the concentration of ammonium increased regularly during the Summer. This drift did not affect the results presented in this report, as all the analysis were performed before April 16th, but it was considered when evaluating requalification results.

In the case of DOC, the results summitted for sample 1 often falled outside the tolerable limits. However, this fact was not influent in determining the qualification of any laboratory. In the following discussion, DOC results from sample 1 will not be used.
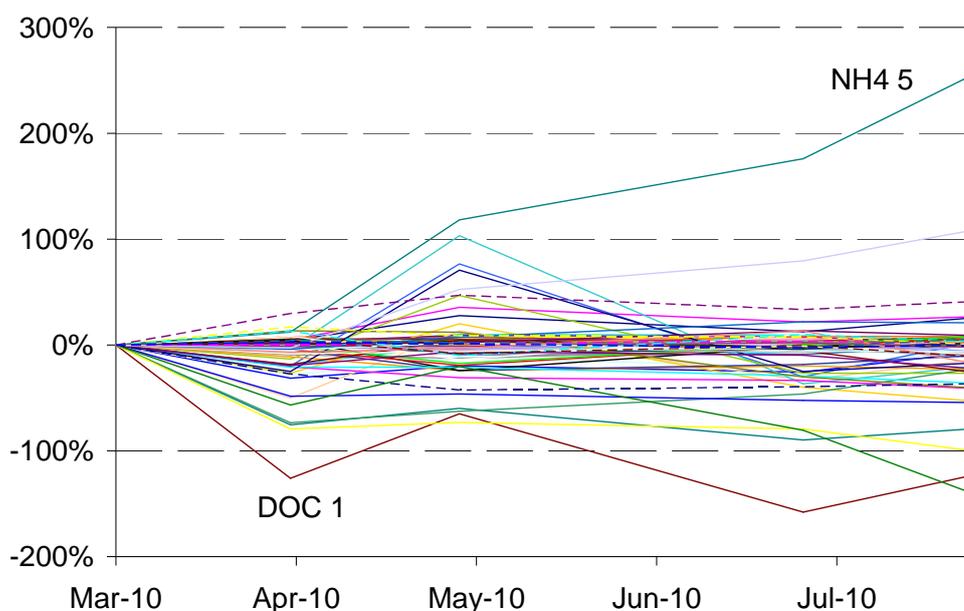

Fig. 3.1. Variations in the concentration of the WRT samples, expressed in percentage of the tolerable limit for each sample and variable.

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 each sample (example in Fig. 4.1). The tolerable limits for each sample and for each analytical method (acronyms given in Table 6.1), are indicated by the box and the full range of the submitted data by the line. The scale on the left axis refers to the number of laboratories (black bar), 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 observations, methods used by one or two laboratories are not included in the plots.
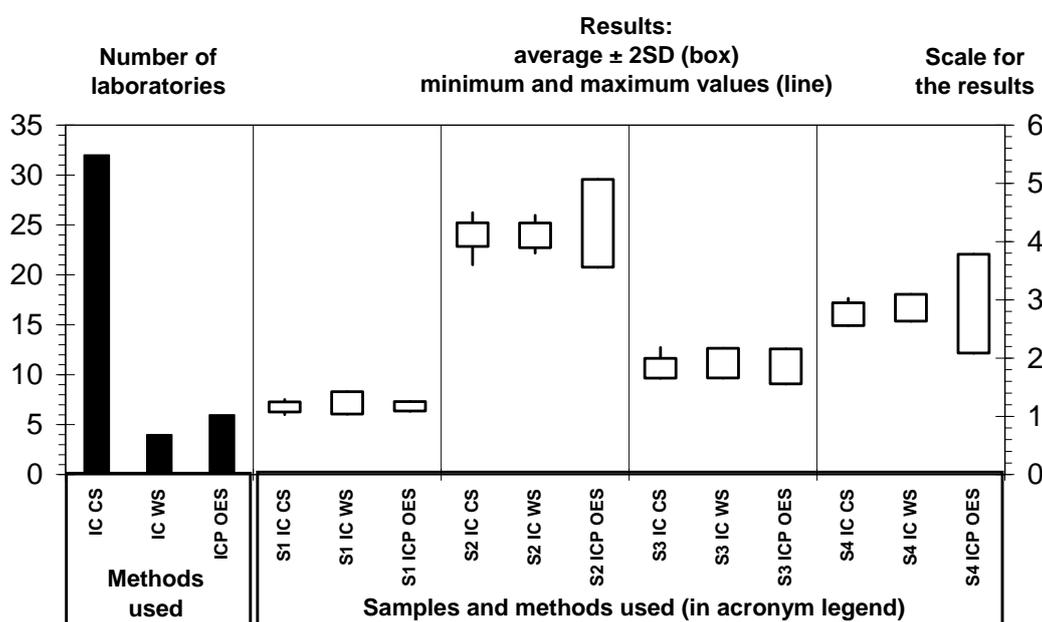
Fig. 4.1. Example showing presentation of the results. The number of laboratories using each analytical method is indicated by the bars on the left, with the scale on the left side of the plot.
The box-and-whiskers graphs on the right, with their own scale on the right side of the plot, show the ±2-standard-deviation range around the robust average (the box) and the full range of the results (the vertical line).

4.1.2. The z-scores plot

The results for each laboratory and for each sample are shown in terms of the z-scores based on an imposed standard deviation equal to half the tolerable limits in Fig. 4.2. The expected values are then represented by a z-score equal to zero, while the tolerable limits extends from -2 to +2 (bold line). The thinner line indicates a z-score of ± 3.

According to ISO rules (Thompson *et al.* 2006), robust statistics from consensus of participants are to be used in order to obtain unbiased estimates of the central value and of the dispersion of the data. The robust mean and standard deviation were iteratively calculated as follows:

- the preliminary "robust mean" was set equal to the median of the submitted data;

- the preliminary "standard deviation" was set at 1,483 times the median of the absolute (unsigned) differences between submitted data and their median;

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- all data lying outside the range of ± 1,5 preliminary robust standard deviations from the preliminary robust average were changed to these values

- the last point was repeated until the robust average and standard deviation converged to a fixed value.

A z-score is computed from the results after outlier rejection for each laboratory, parameter and sample. This score provides an index of the performance of a laboratory in relation to that of the other laboratories in a monitoring programme. It is given by:

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

where Y_i is the analytical result of the laboratory, $Y_{average}$ and s_{imp} are the robust average and the imposed standard deviation, i.e. one half the tolerable limits, respectively.

In this formulation, z is fixed as a function of the tolerable limits so that the z-score can be used to compare the performance of the same laboratory between different ring tests. In fact, if the z-score is calculated using the standard deviation of the submitted data (or its robust equivalent), and the global performance of the laboratories participating in the ring test improve, then the z-score will be higher for the same bias.

Assuming that the tolerable limits do not change, this score can be used in successive inter-laboratory ring tests in order to identify general trends for a laboratory or a group of laboratories, or even the whole set of laboratories. 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 tolerable limit 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 mean that the laboratory has met the tolerable limits.

In the z-score plot, the codes of the laboratories are in alphabetical ordered along the horizontal axis, allowing each laboratory to make a rapid comparison between its own results and the overall performance of all the laboratories.
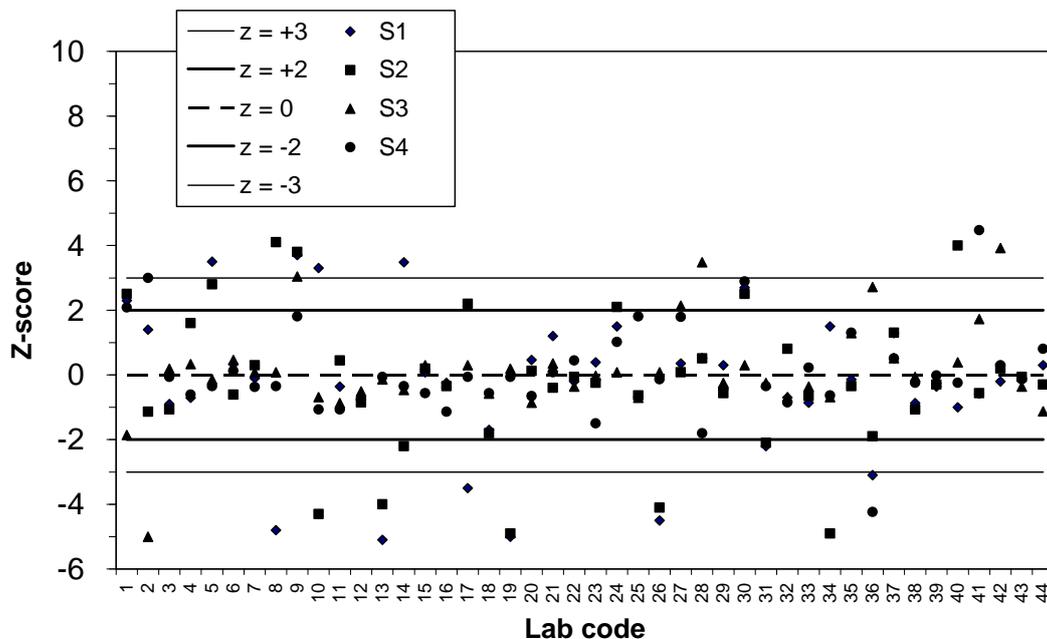

Fig. 4.2. Example of a z-score plot.

4.1.3. 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, which very similar concentrations and which have been analysed with the same analytical method. The data are plotted in a scatter diagram compared to the expected values, in this case the robust average of the submitted data. This makes it possible to determine whether random or systematic errors are affecting the results (Fig. 4.3). The diagram is divided into four quadrants by a vertical and a horizontal line representing the expected values for the two samples.

Also in this case, the axes are rescaled in the z-scores on the basis of an imposed standard deviation, so that the expected values are always represented by a z-score equal to zero, while the tolerable limit extends from -2 to +2.

In a hypothetical case, if 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, due to systematic errors that underestimate or overestimate the concentrations in both samples.

The tolerable limit is represented by the bold ellipse centred on the expected values, i.e. at the intersection of the two straight lines in the diagram, and extending along both axes from -2 to +2. The thinner ellipse indicates the $\pm$ 3 imposed standard deviations. 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.
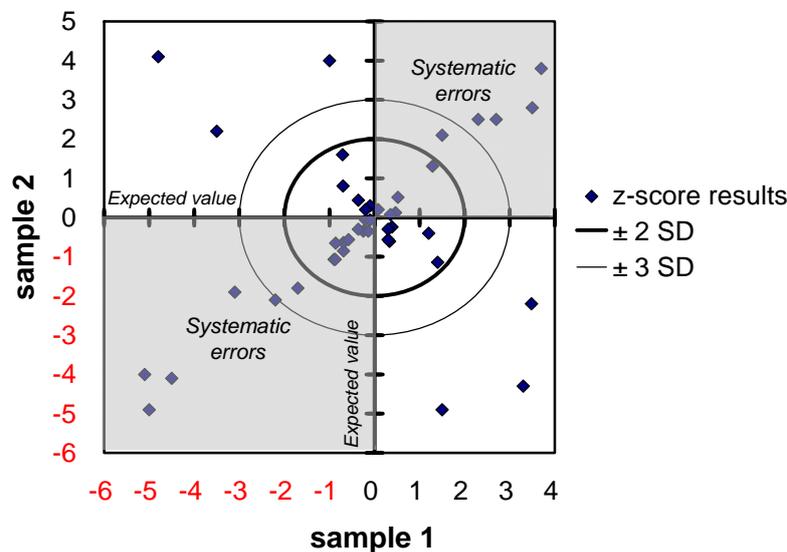

Fig. 4.3. Examples of Youden's plot, with prevailing systematic errors. The data are plotted in *z*-scores, so that the (robust) mean values line on the axes and the units are imposed standard deviations. The legends on the axes refer to the sample names (Tabs 3.1 and 3.2), while the ellipses indicate the tolerable limits (Table. 2.1). The arrow points to results outside the axes range.

4.2. Validation of the results for major ions

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 by means of the ion balance, i.e. by comparing the equivalent sum of anions and cations, and by estimating the electrical conductivity calculated from the concentrations of each ion multiplied by the equivalent ionic conductance.

These very simple checks of the internal consistency of the analyses are strongly recommended in order to verify the correctness of the analyses, as well as to detect other possible sources of error, such as incorrect transcription.

4.2.1 The ion balance

The basic assumption in the ion balance check is that the determination of pH, NH_4^+, Ca^{2+}, Mg^{2+}, Na^+, K^+, HCO_3^-, SO_4^{2-}, NO_3^- and Cl^- accounts, almost completely, for all the ions present in a solution. At pH values higher than 6.5, however, the hydrogen ion concentration can be ignored. In water samples with high concentrations of DOC a specific correction can be done (Mosello *et al.* 2008).

The ion balance check is based on the electro-neutrality of water samples (soil solution, bulk deposition, stand throughfall). The total number of negative and positive charges in a solution must be equal. This can be checked by converting the concentration values for the individual ions into the unit milli- (or micro-) equivalent per litre (meq L^{-1} or µeq L^{-1}). 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

The limit of acceptable errors varies according to the total ionic concentration 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:

$$\Sigma \, An = Alk + [SO^-_4] + [NO_3^- \ ] + [Cl^-]$$

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

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

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

Proposed PD thresholds for accepting analytical results are given 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. In bulk deposition samples the presence of other substances that affect alkalinity (e.g. organic acids, sulphides etc.) will be negligible. Stand throughfall or soil solution samples which have relatively high DOC concentrations, on the other hand, will usually have much higher PD values than those listed in Table 4.1. As such, this does not necessarily indicate analytical errors. Much of the dissolved organic matter (i.e. DOC) in such samples are weak acids, and they therefore acts as an anion with varying negative charge.

In samples with a low DOC concentration, however, PD values higher than those given in Table 4.2 will indicate a lack of precision in one or more analytical techniques or the omission of important ions.

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 the 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 the resistance (R, unit ohm), A (m^2) is the electrode surface area, and L (m) is the distance between the 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 the ions in solution; the capacity of a single ion to transport an electric current is given in standard conditions and in ideal conditions of infinite dilution by the equivalent ionic conductance (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 is calculated (CE$_\infty$) 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 ions account for almost all of the alkalinity; this assumption is correct for solutions with a pH in the range from 6.0 to 8.5.

The dependence of conductivity on temperature makes it necessary to use a "reference" temperature, which in the ISO standard 7888-1985 and in the monitoring programmes is 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 on temperature will depend on the chemical composition of the solution.

The temperature correction values for conductivity 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, such as is the case for 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 percentage difference, CD, is be defined as the ratio:

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

At the low ionic strength (below 0.1 meq L^{-1}) of bulk deposition samples, the discrepancy between measured and calculated conductivity should be no more than 2% (Miles & Yost, 1982). At higher ionic concentrations, such as in most of the throughfall, stemflow and soil solution samples, the calculated conductivity can be corrected, as proposed e.g. by A.P.H.A., A.W.W.A., W.E.F. (1998), on the basis of the ionic strength.

Ionic strength (IS), in meq L^{-1}, is 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
   w_i = gram molecular weight of ion i

The correction becomes relevant at ionic strengths higher than 0.1 meq L^{-1}, and uses the Davies equation for ionic strengths lower than 0.5 meq L^{-1} and for temperatures from 20 and 30 °C, in order to calculate the monovalent ion activity y:

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

The calculated conductivity, used for calculating 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 the 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. The threshold values proposed in the *ICP Forests manual for sampling and analysis of atmospheric deposition* are given in Table 4.2.

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

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 42 laboratories participated in this WRT. A list is reported in table 5.1.

Table 5.1. List of the laboratories participating in the WRT.

Austria	Federal Research and Training Centre for Forest, Natural Hazards and Landscape, Vienna
Belgium	Research Institute for Nature and Forest, Louvain-la-Neuve
Bulgaria	Executive Agency for the Environment, Sofia
Bulgaria	Executive Environment Agency, Varna
Cyprus	Department of Agriculture, Nicosia
Czech Rep.	Forestry and Game Management Res. Inst., Jiloviste
Estonia	Tartu Environmental Research Ltd, Tartu
Finland	Finnish Forest Research Institute, Rovaniemi Research Unit, Rovaniemi
Germany	Bayerische Landesanstalt fuer Wald und Forstwirtschaft, Freising
Germany	Ecology Centre, University Kiel
Germany	Fachhochschule Eberswalde
Germany	Forstliche Versuchs- und Forschungsanstalt Baden-Württ. Abt. B+U, Freiburg
Germany	Landesamt fuer Umwelt- und Arbeitsschutz, Saarbrucken
Germany	LUFA Rostock der LMS, Rostock
Germany	LUFA Speyer
Germany	Nordwestdeutsche Forstliche Versuchsanstalt, Gottingen
Germany	North Rhine Westphalia State Agency for Nature, Environment and Consumer Protection (LANUV NRW), Dusseldorf
Germany	Staatsbetrieb Sachsenforst, Referat 43 Standortserkundung, Bodenmonitoring, Labor Pirna
Germany	Zentrallabor der Thüringer Landesanstalt für Landwirtschaft, Jena
Greece	Forest Research Institute of Athens
Hungary	Forest Research Institute, HungaryCo., Budapest
Ireland	Coillte Research Laboratory, Wicklow
Italy	Institute of Ecosystem Study (CNR-ISE), Verbania Pallanza
Italy	Laboratorio Biologico APPA-BZ,Laives
Italy	Soil Science and Plant Nutrition Department - University of Florence
Italy	Water Research Institute (IRSA-CNR), Brugherio
Latvia	LSFRI Silava, Salaspils
Lithuania	Lithuanian Institute of Agriculture, Kaunas
Netherlands	Wageningen University, Wageningen
Norway	Norwegian Forest and Landscape Institute, Ås
Poland	Forest Research Institute, Raszyn
Romania	Forest Research Station Campulung, Campulung Moldovenesc
Russia	INEP, Apatity
Russia	Institut of Biology, Syktyvkar
Russia	Laboratory of Soil Science and Microbiology, Petrozavodosk
Slovakia	Central forest laboratory, Zvolen
Slovenija	Slovenian Forestry Institute, Ljubljana
Spain	INIA, Madrid
Sweden	Aquatic Sciences and Assessment, Upssala
Sweden	IVL, Gothenburg
Switzerland	WSL, Birmensdorf
UK	Forest Research, Wrecclesham

6. RESULTS

6.1. Analytical methods used

The list of analytical methods, which were used by at least three 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 inductively coupled plasma 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 TDN have mainly been performed by spectrophotometry or continuous flow analysis, and 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 analytical methods are discussed in connection with the results for the individual chemical parameters.

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	21
	GEN	Not specified	21
Conductivity	25°	Measurement performed at 25°C	23
	Corr	Measurement at different temperature, corrected to 25°C	19
Calcium	AAS	Atomic absorption spectrometry	9
	IC CS	Ion chromatography, chemical suppression	8
	IC WS	Ion chromatography, no suppression	3
	ICP OES	ICP optical emission spectrometry	20
	ICP MS	ICP mass spectrometry	2
Magnesium	AAS	Atomic absorption spectrometry	9
	IC CS	Ion chromatography, chemical suppression	8
	IC WS	Ion chromatography, no suppression	3
	ICP OES	ICP optical emission spectrometry	20
	ICP MS	ICP mass spectrometry	2
Sodium	AAS	Atomic absorption spectrometry	6
	AES	Atomic emission spectrometry	2
	IC CS	Ion chromatography, chemical suppression	8
	IC WS	Ion chromatography, no suppression	3
	ICP OES	ICP optical emission spectrometry	21
	ICP MS	ICP mass spectrometry	2

Chemical variable	Acronym	Analytical method	Number of labs
Potassium	AAS	Atomic absorption spectrometry	6
	AES	Atomic emission spectrometry	2
	IC CS	Ion chromatography, chemical suppression	8
	IC WS	Ion chromatography, no suppression	3
	ICP OES	ICP optical emission spectrometry	21
	ICP MS	ICP mass spectrometry	2
Ammonium	SPEC Phe	Spectrophotometry, indophenol blue	9
	CF Phe	Continuous flow, indophenol blue	11
	CF GD	Continuous flow, ammonia diffusion	9
	IC CS	Ion chromatography, chemical suppression	7
	IC WS	Ion chromatography, no suppression	4
	SPEC Nes	Spectrophotometry, Nessler	1
Sulphate	IC CS	Ion chromatography, chemical suppression	33
	IC WS	Ion chromatography, no suppression	3
	ICP OES	ICP optical emission spectrometry	4
	CF Met	Continuous flow, Ba chloranylate excess, methyl thymol	1
	SPEC Th	Spectrophotometry, Ba chloranylate, thorin	1
Nitrate	IC CS	Ion chromatography, chemical suppression	29
	IC UV	Ion chromatography, UV detector	1
	IC WS	Ion chromatography, no suppression	3
	CF Cd	Continuous flow, cadmium reduction	7
	CF Cu_Hyd	Continuous flow, copper, hydrazine reduction	1
	SPEC Cd	Spectrophotometry, cadmium reduction	1
Chloride	IC CS	Ion chromatography, chemical suppression	32
	IC WS	Ion chromatography, no suppression	4
	CF HgFe	Continuous flow, Hg thiocyanate in presence of Fe^{++}	4
	CT Hg	Colorimetric titration, Hg nitrate with diphenylcarbazone	2
Alkalinity		Potentiometric titration with extrapolation of the equivalence point:	
	PT_EX 2PF	two end-points	17
	PT_EX Gran	Gran method	6
	PT_EX Infl	detection of the inflection point	1
	COND	Conductometric titration	1
		Potentiometric titration, fixed end-point:	
	PT_1 4.3	end-point at pH=4.3	4
	PT_1 4.4	end-point at pH=4.4	1
	PT_1 4.5	end-point at pH=4.5	8

Chemical variable	Acronym	Analytical method	Number of labs
TDN	CHML	Chemiluminescence	18
	CF Cd	Continuous flow analysis	6
	KJELD	Kjeldahl digestion	8
	PSB-SPEC UV220	Hydrolysis with K2S2O8 + H3BO3 + NaOH and spectrophotometry UV detection at 220 nm	3
	PSOH CF Cd	Persulphate digestion ($K_2S_2O_8$ + NaOH) and continuous flow analysis	1
	IC CS	Ion chromatography, chemical suppression	1
DOC	THIR	Thermal combustion, IR detection	37
Phosphate	IC CS	Ion chromatography, chemical suppression	5
	CF Mor	Continuous flow, ammonium molybdate, potassium antimonyl tartrate, ascorbic acid or $SnCl_2$ reduction	10
	SPEC Mor	Spectrophotometry, ammonium molybdate, potassium antimonyl tartrate, ascorbic acid or $SnCl_2$ reduction	8
	ICP OES	ICP optical emission spectrometry	1

6.2. Expected results

The samples used in the WRT (described in Section 3.1) were natural precipitation samples collected in the opn field (sample 1) and under the canopy within a tree stand, i.e. stand throughfall (samples 2 and 3) and soil solution (samples 4 and 5). Three synthetic samples were also prepared in the laboratory for the measurement of alkalinity (SYN 5, SYN 6 and SYN 8).

The consensus values were estimated using the robust average, as described in chapter 4, and they are presented in Table 6.2 and verified using the software Tool4PT Pro Cortez & Mermayde version 1.06.10 2009.

The chemical composition of the natural samples reflected the typical composition of deposition, throughfall and soil solution in Europe.

In the case of DOC and ammonium, we report the results for all the five samples in which it should have been determined. However, for the purpose of laboratory qualification and requalification, sample 1 and 5 (respectively) were never relevant.

Medians and averages are reported in Appendix A, together with the submitted data.

The table also contains phosphorus data. The submission of those results was not requested, but was the determination was performed by several laboratories.

Table 6.2 – Expected results from robust averages of the results of the WRT.

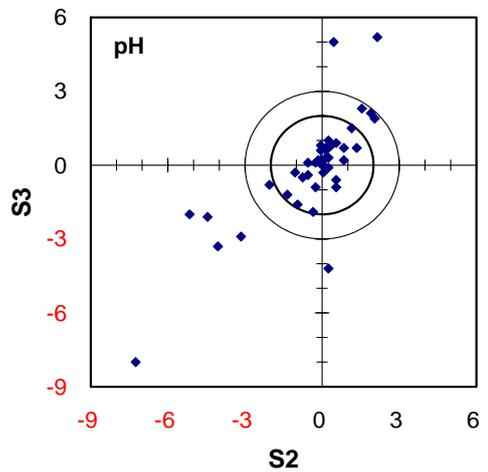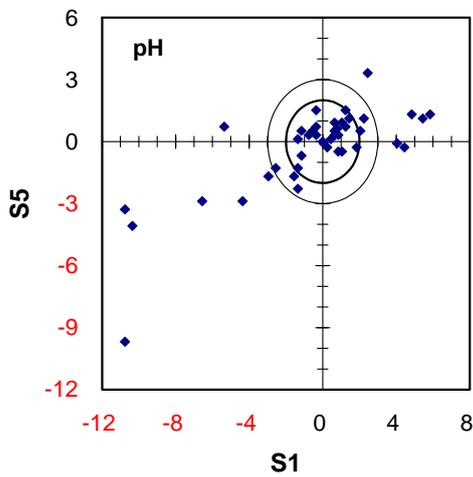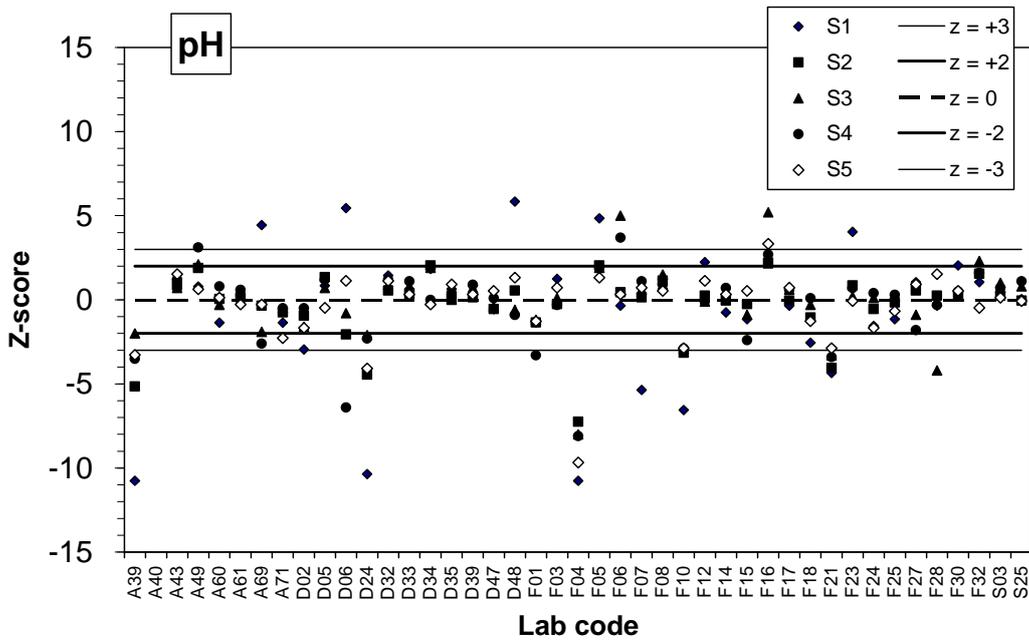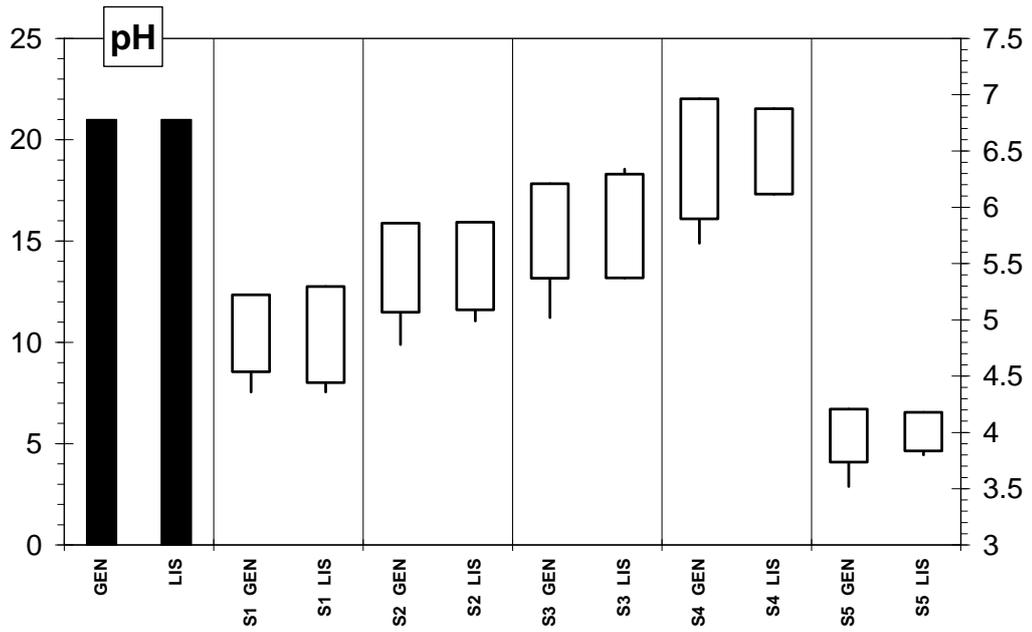| Parameter	unit	S1	S2	S3	S4	S5	SYN6	SYN7	SYN8
pH	mg L^{-1}	4.90	5.51	5.82	6.49	4.00			
Conductivity (at 25°C)	μS cm^{-1}	10.6	18.1	100.0	52.8	115.6			
Calcium	mg L^{-1}	0.20	0.51	1.31	2.27	4.48			
Magnesium	mg L^{-1}	0.05	0.23	1.34	1.06	1.68			
Sodium	mg L^{-1}	0.27	0.76	11.38	4.60	4.59			
Potassium	mg L^{-1}	0.14	1.9	3.55	0.46	1.70			
Ammonium	mg N L^{-1}	0.09	0.08	0.47	0.44	0.34			
Sulphate	mg S L^{-1}	0.31	0.63	1.44	2.28	4.18			
Nitrate	mg N L^{-1}	0.21	0.12	0.38	0.46	2.35			
Chloride	mg L^{-1}	0.40	1.04	21.61	5.33	5.77			
Alkalinity	μeq L^{-1}	0	25	36	87	0	35	78	141
TDN	mg L^{-1}	0.39	0.52	1.27	1.21	3.98			
DOC	mg L^{-1}	1.09	10.93	13.50	8.23	48.77			
Phosphate	mg P L^{-1}		0.041			0.020			

6.3. Overall performance of the laboratories

All samples were analyzed for most of the mandatory variables. However, 5-10% of the samples were not analyzed for TDN, DOC and alkalinity. These percentages are lower than those reported in the previous WRTs (Mosello *et al.* 2002, Marchetto *et al.* 2006, 2009), but they are still high when we consider that the analysis of these variables is mandatory under certain conditions for deposition and/or soil solution samples. In the case of alkalinity, laboratory analysing soil solution and not deposition samples are not required to perform the determination of alkalinity.

Table 6.3 also shows the proportion of measurements that fell within the tolerable limits given in Table 2.1. For most of the variables the proportion of results falling within the acceptance range is more than 77%, with the highest value for magnesium and chloride and the lowest for pH and TDN. On the other hand, the proportion of values outside the tolerable limit for alkalinity is 18%.

Table 6.3 – Quality performance of the laboratory set for each mandatory variable: TL = tolerable limit (see chapter 2), LOQ = limit of quantitation.

Parameter	Within TL	Outside TL	Not measured	Below LOQ
pH	77.1%	22.9%	0	0
Conductivity	89.0%	11.0%	0	0
Calcium	85.7%	13.8%	0	0.5%
Magnesium	93.8%	5.7%	0	0.5%
Sodium	91.9%	7.6%	0	0.5%
Potassium	90.5%	8.6%	0	1.0%
Ammonium	81.0%	16.2%	0	2.8%
Sulphate	86.7%	12.9%	0	0.5%
Nitrate	90.5%	8.5%	0	1.0%
Chloride	93.8%	5.7%	0	0.5%
Alkalinity	70.2%	18.3%	10.1%	1.4%
TDN	77.6%	16.2%	4.8%	1.4%
DOC (samples 2-5)	89.3%	5.4%	4.9%	0.5%
Total	85.6%	12.0%	2.0%	0.4%

Mg mg/L

Magnesium

Magnesium

Magnesium

22

Na mg/L

Sodium

Z-score

Lab code

Sodium

Sodium

K mg/L

Potassium

Z-score

Lab code

Potassium

Potassium

N-NH4 mg/L

Ammonium

Ammonium

Ammonium

S-SO4 mg/L

Sulphate

Z-score

Lab code

Ammonium

Sulphate

Alkalinity

TDN mg/L

TDN

DOC mg/L

DOC

DOC

DOC

32

P-PO4 mg/L

Phosphate

Phosphate
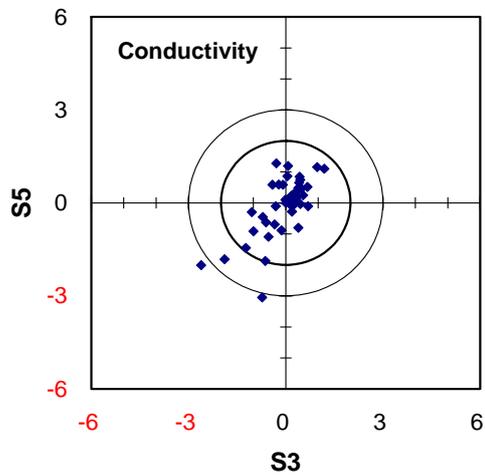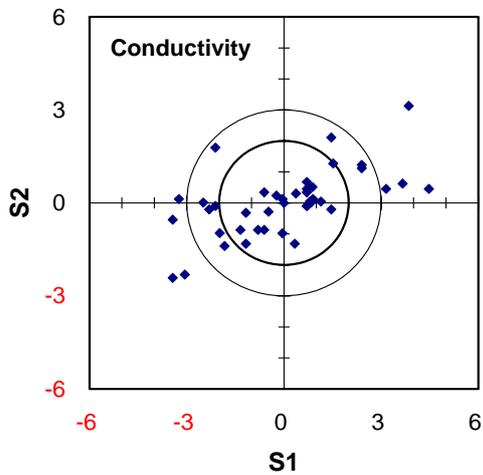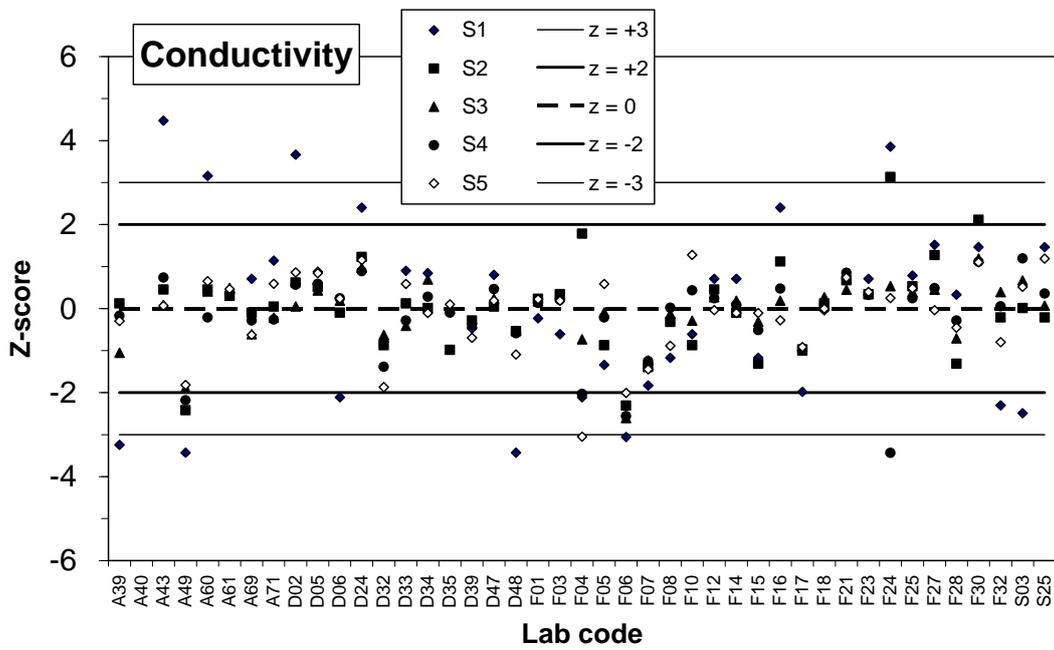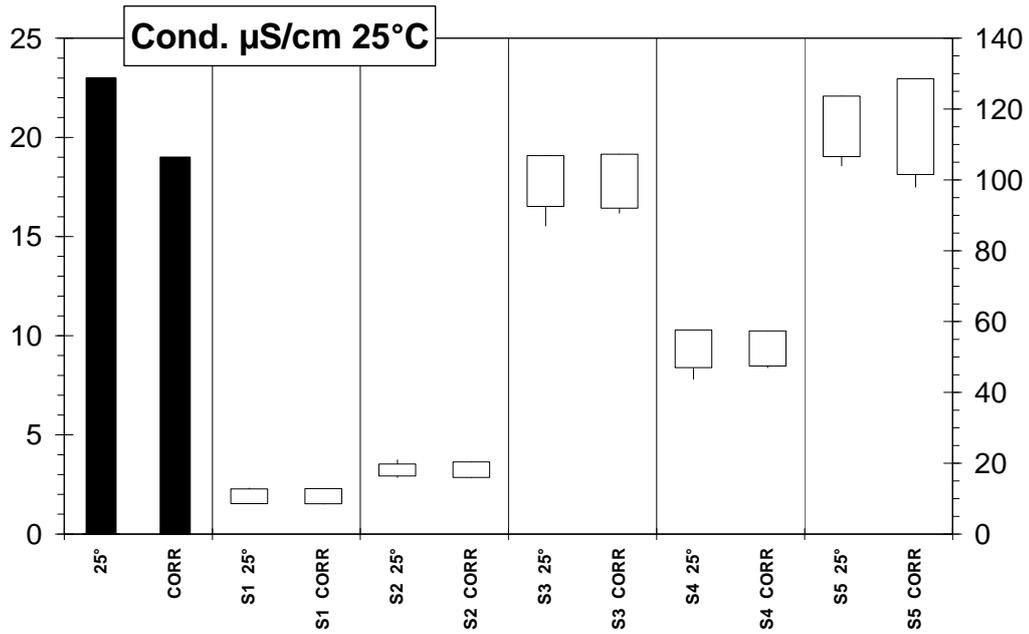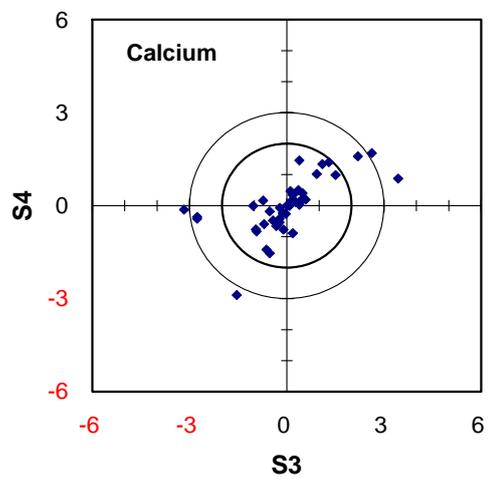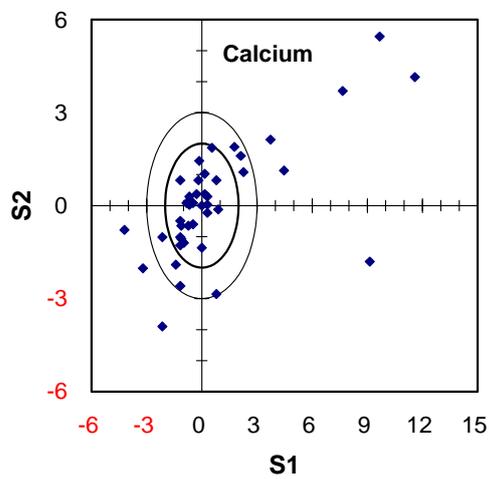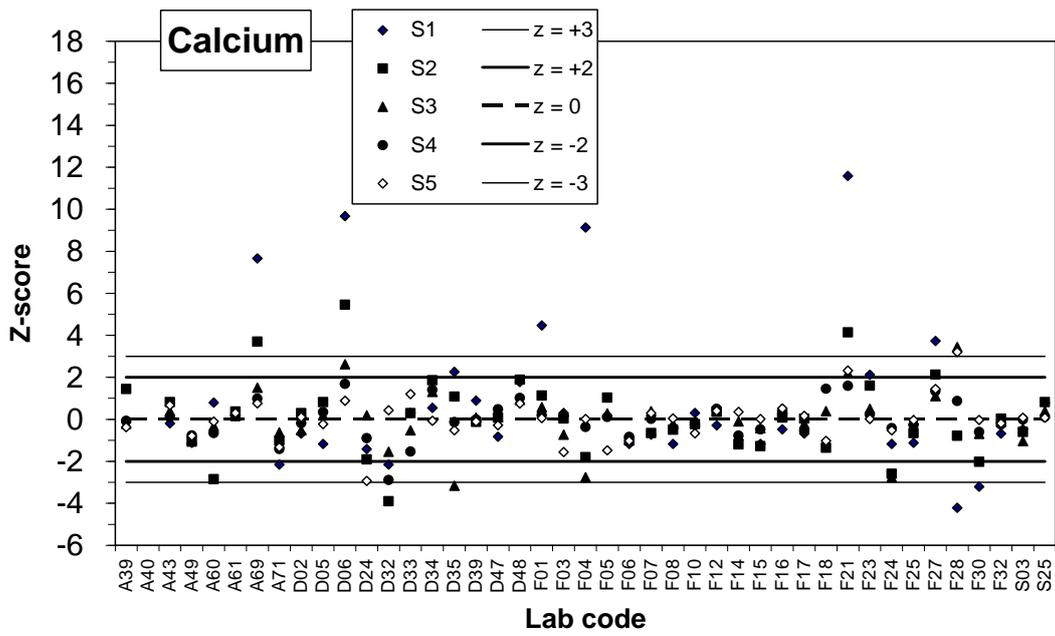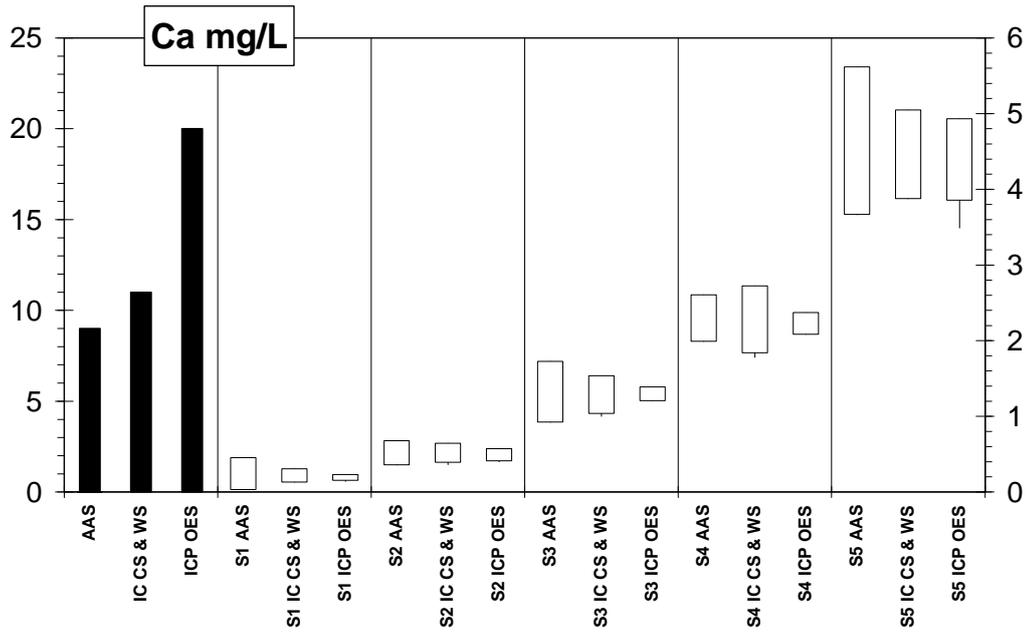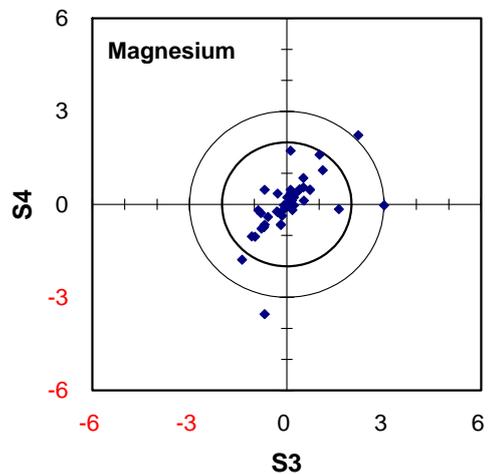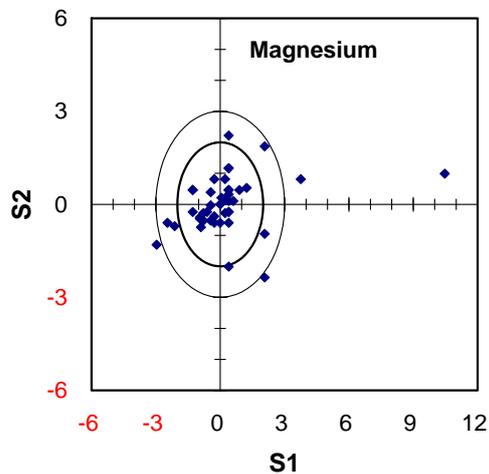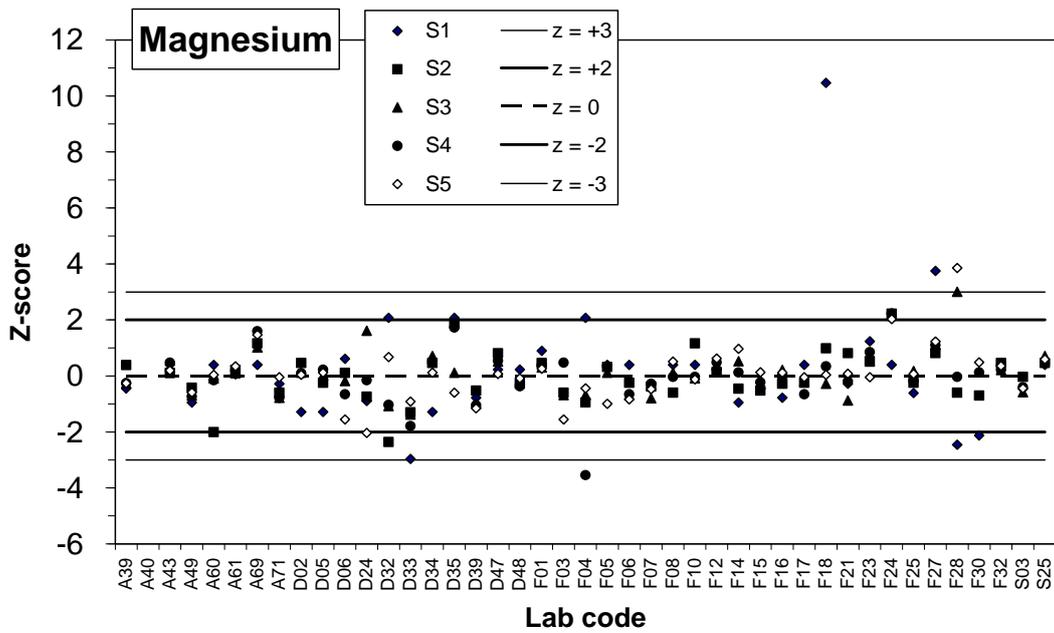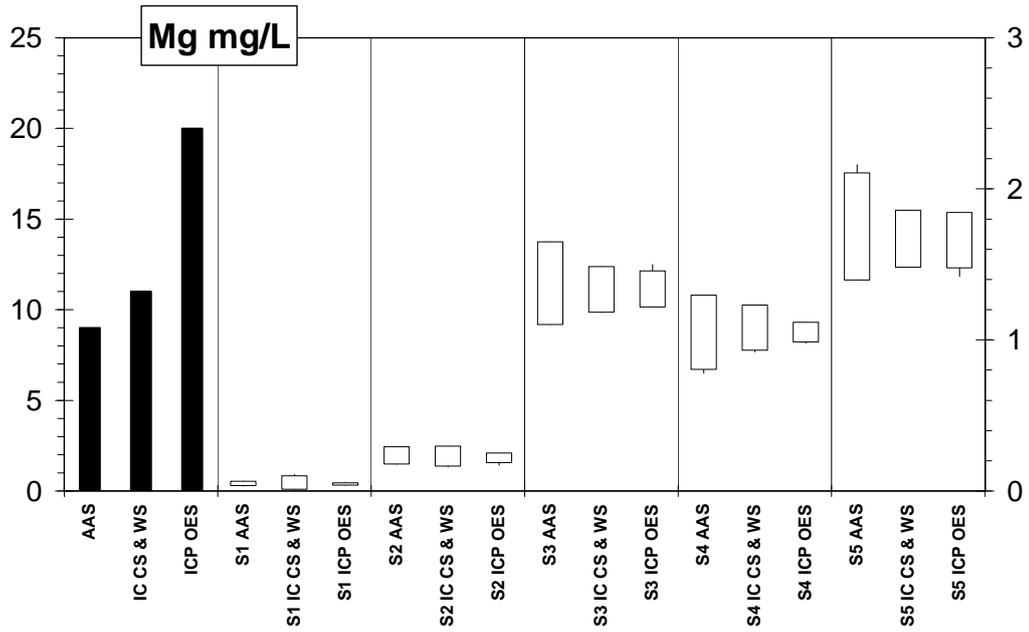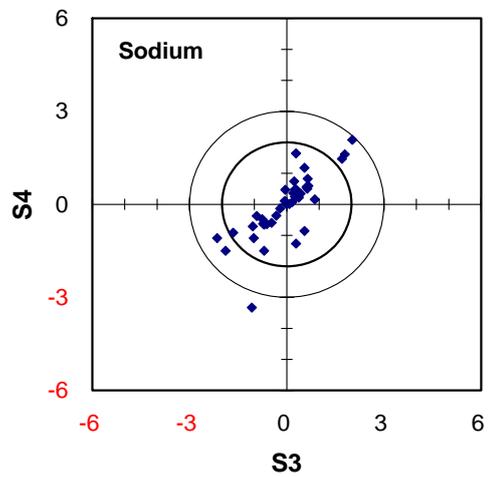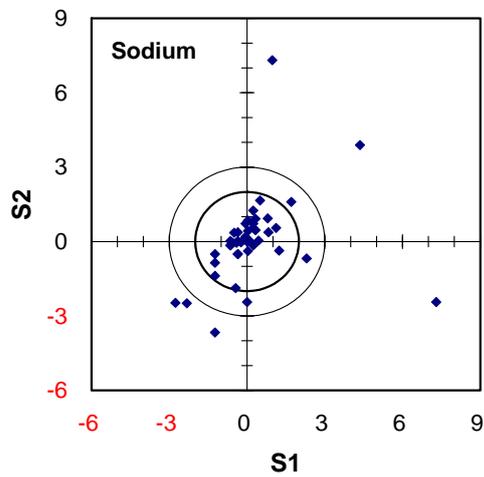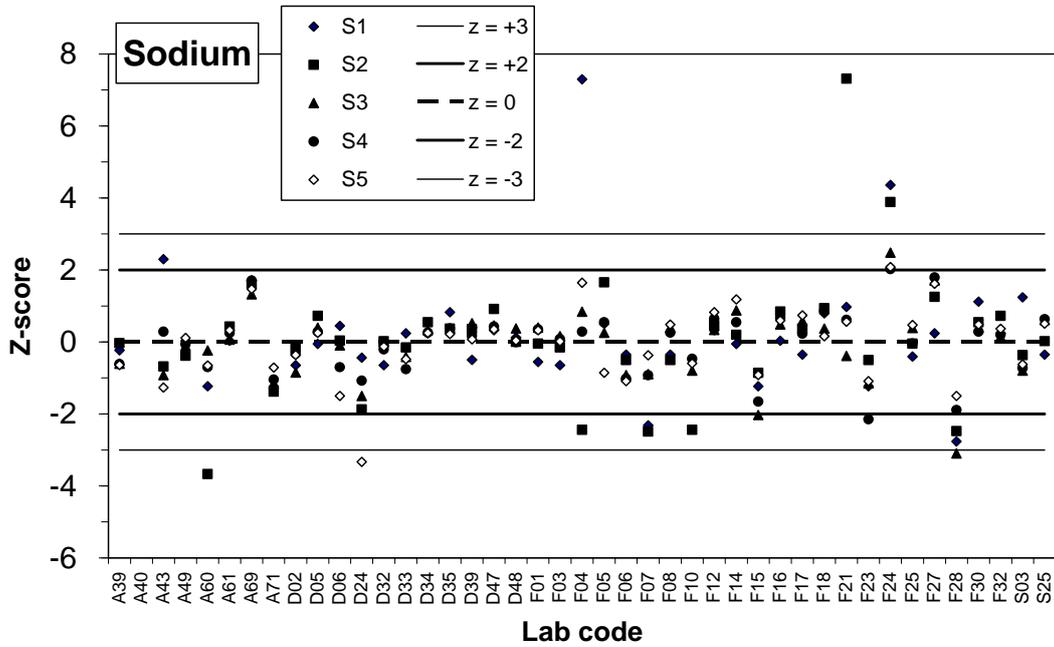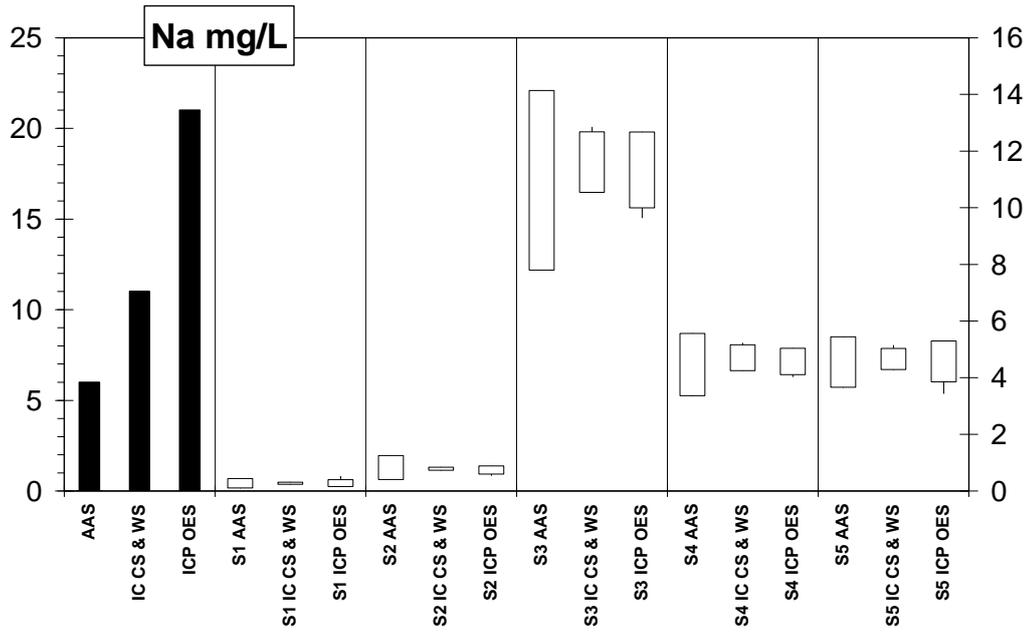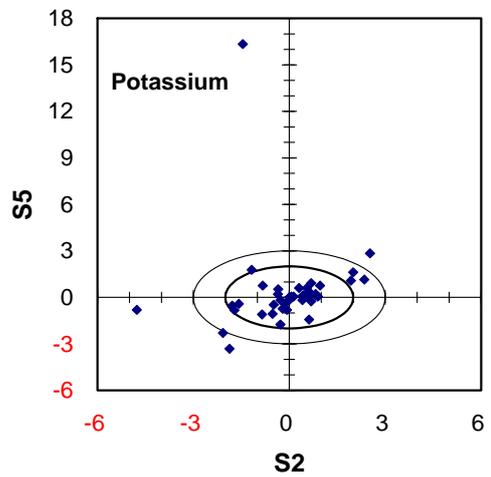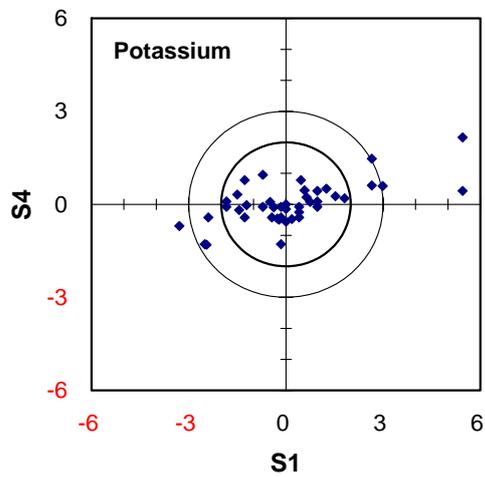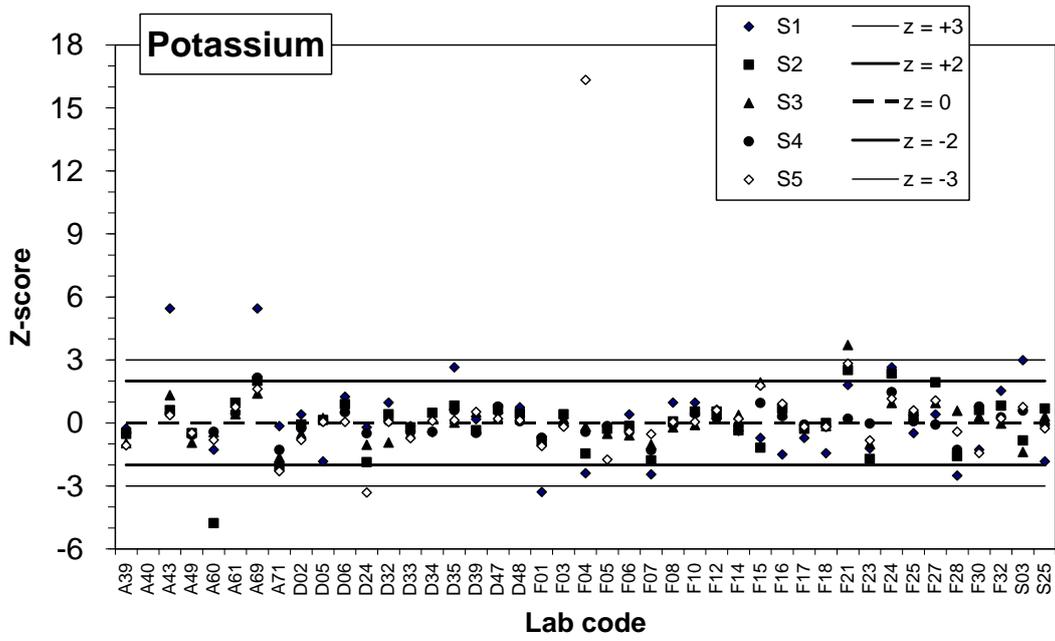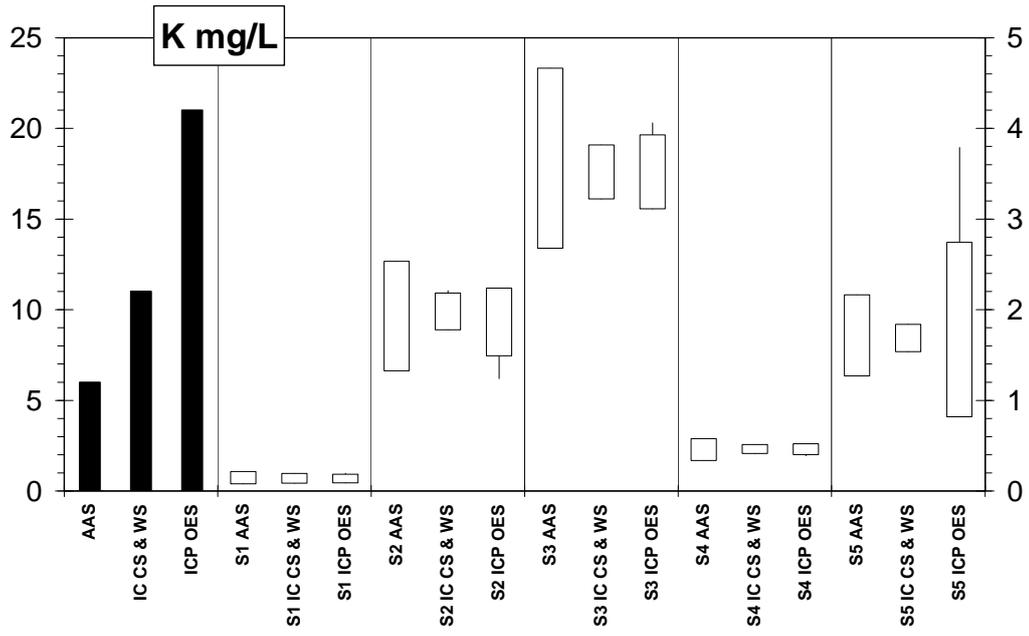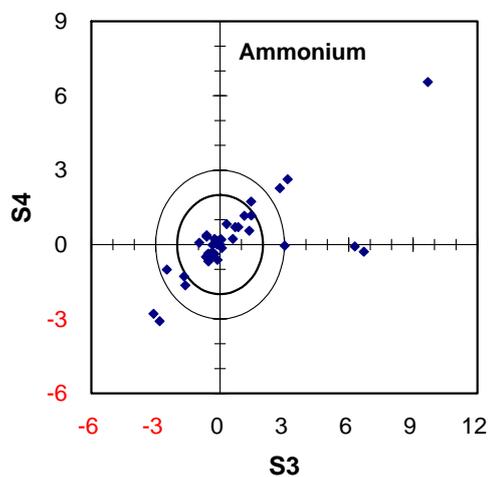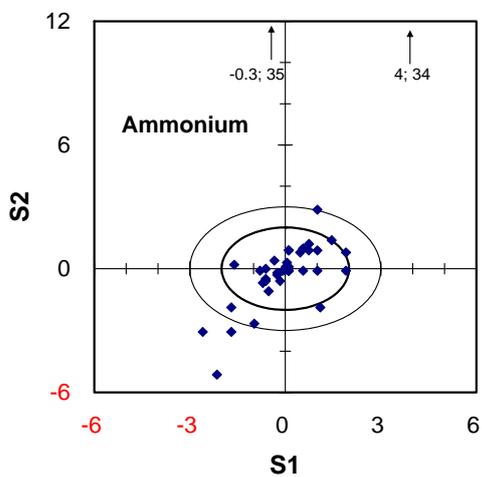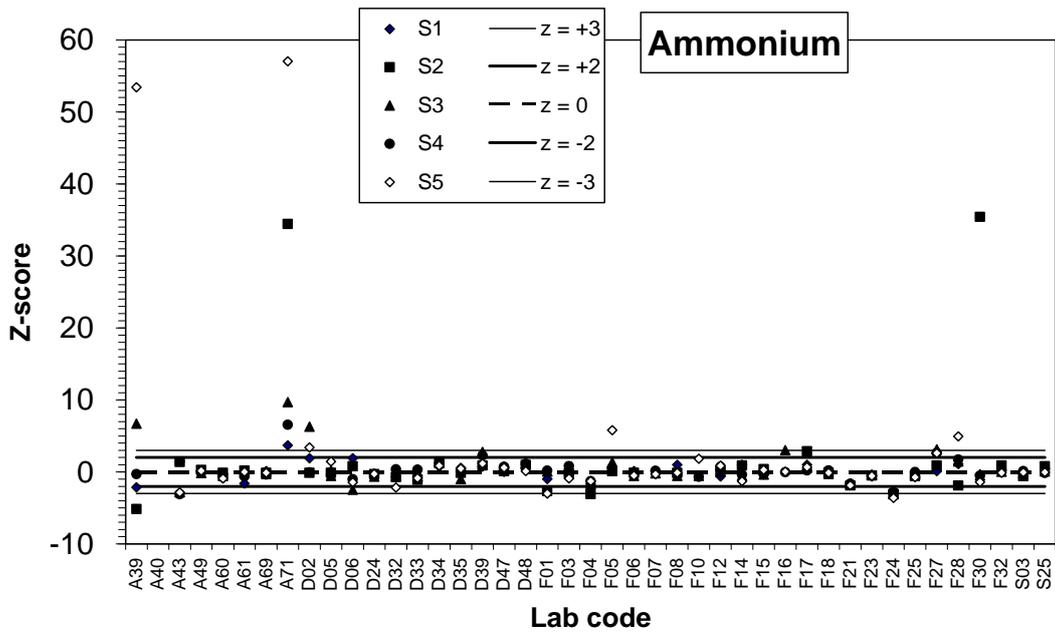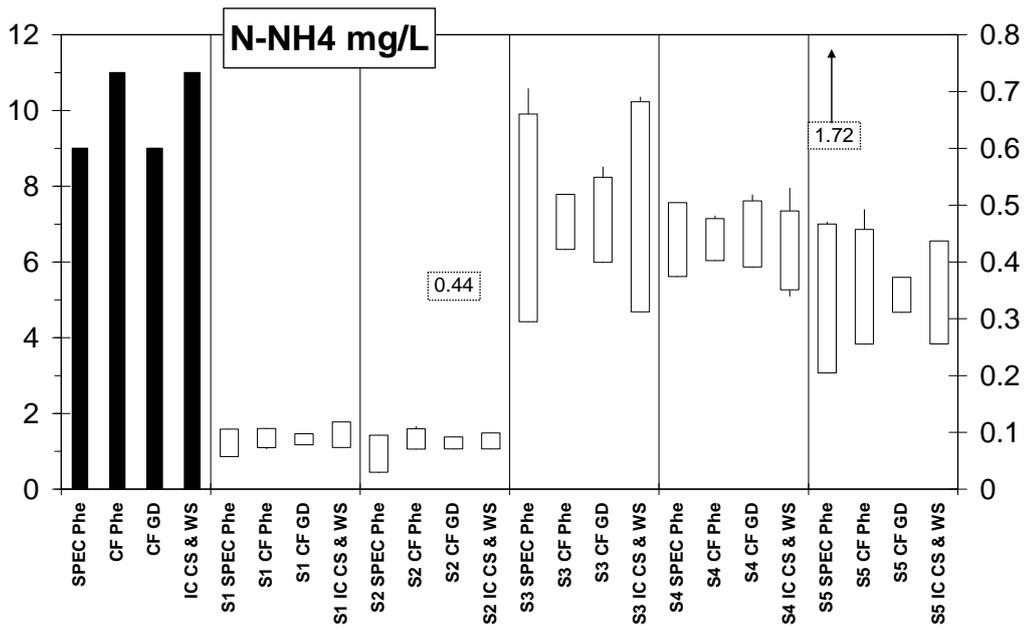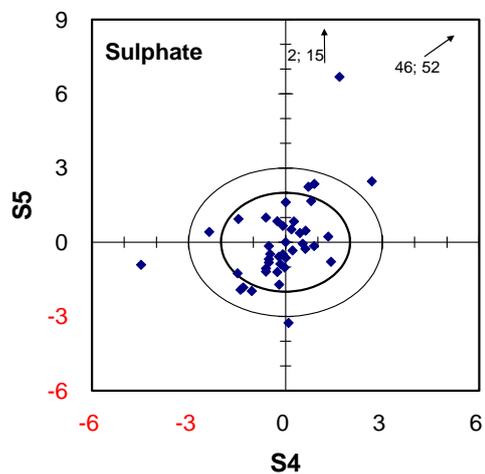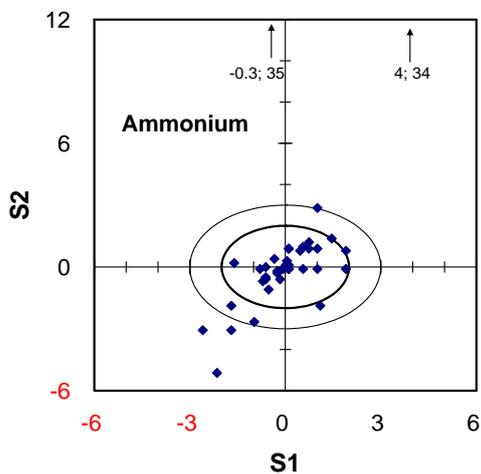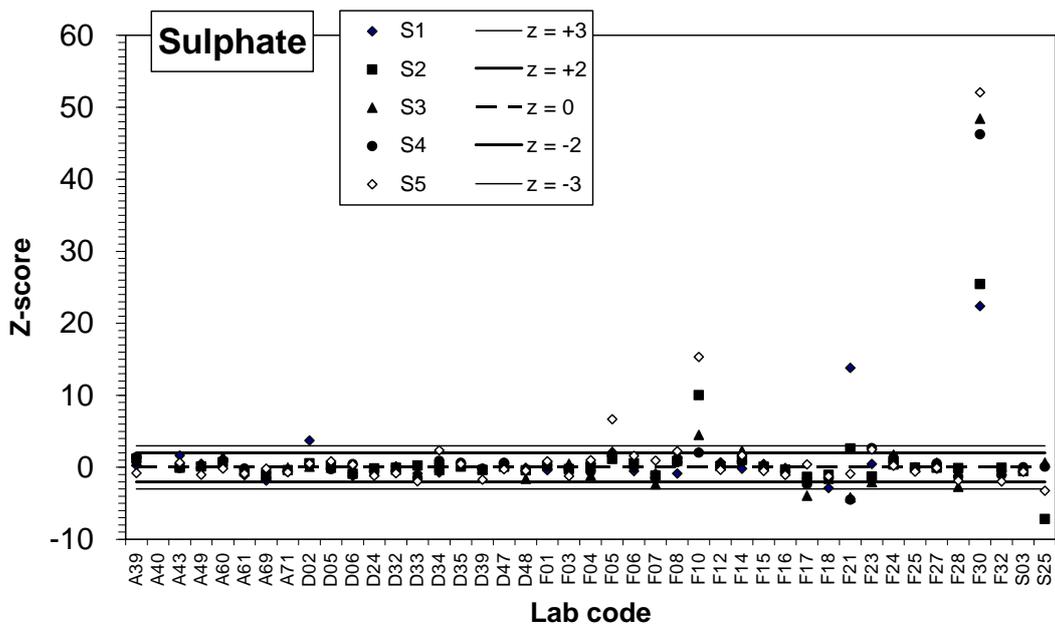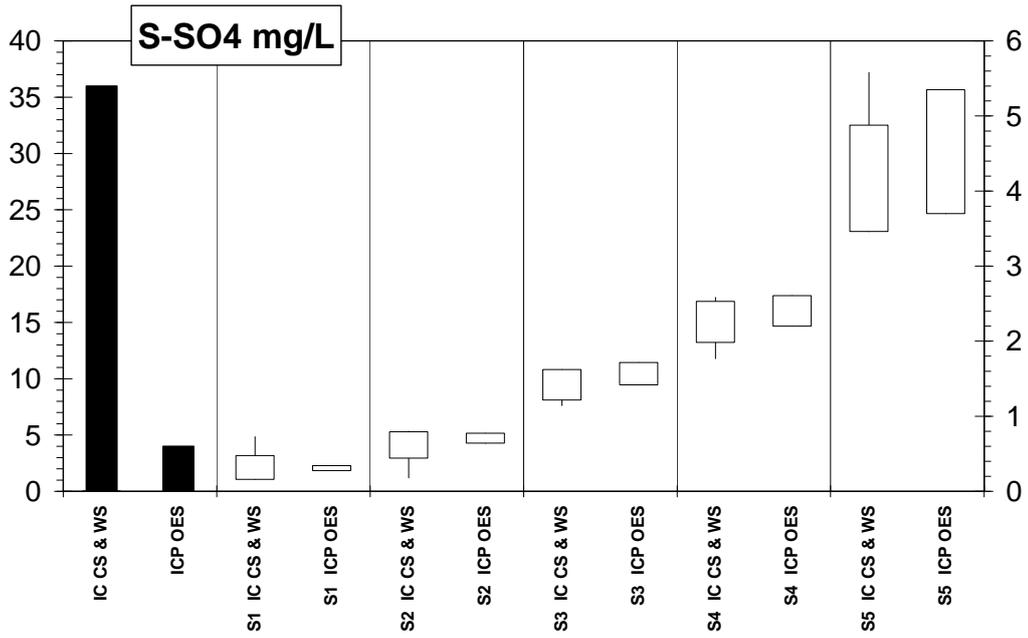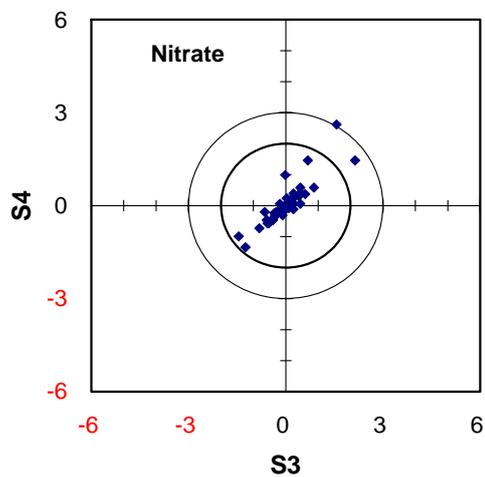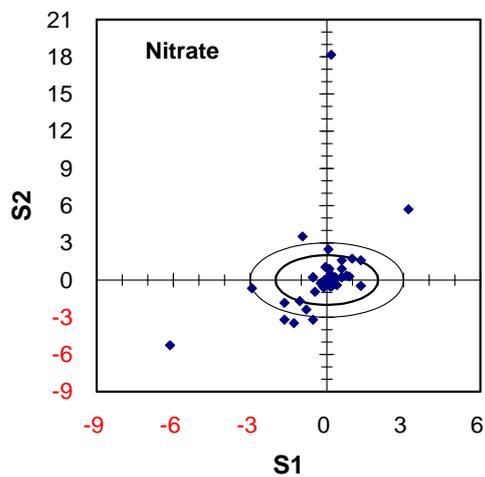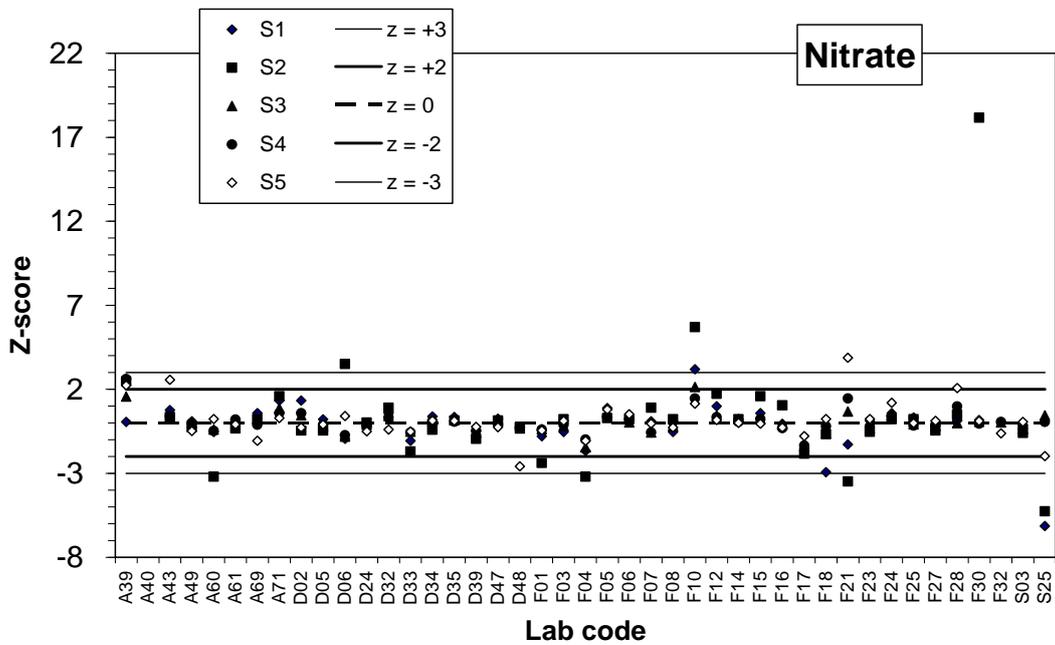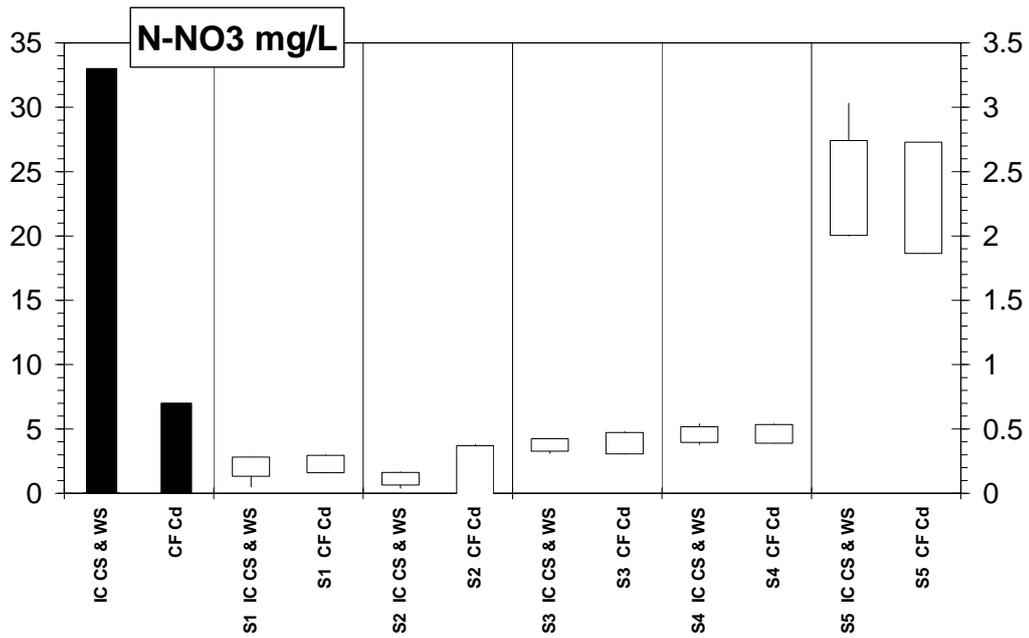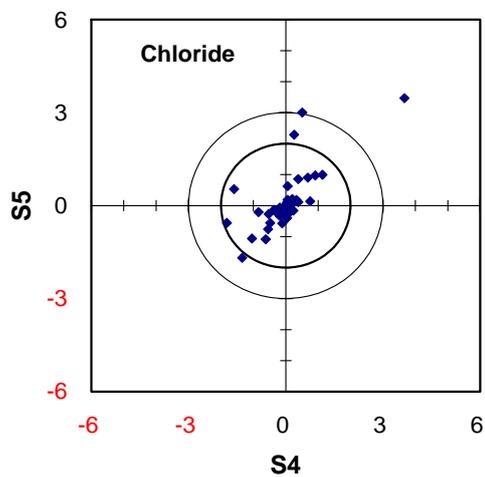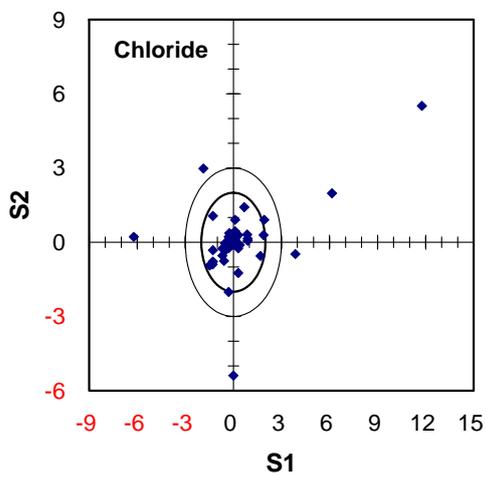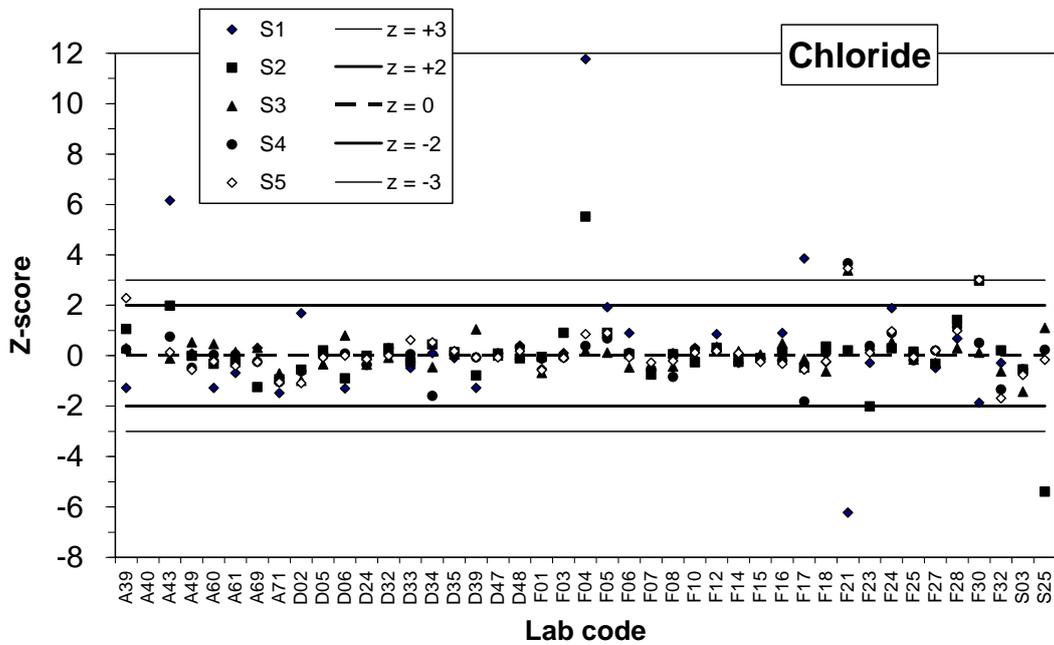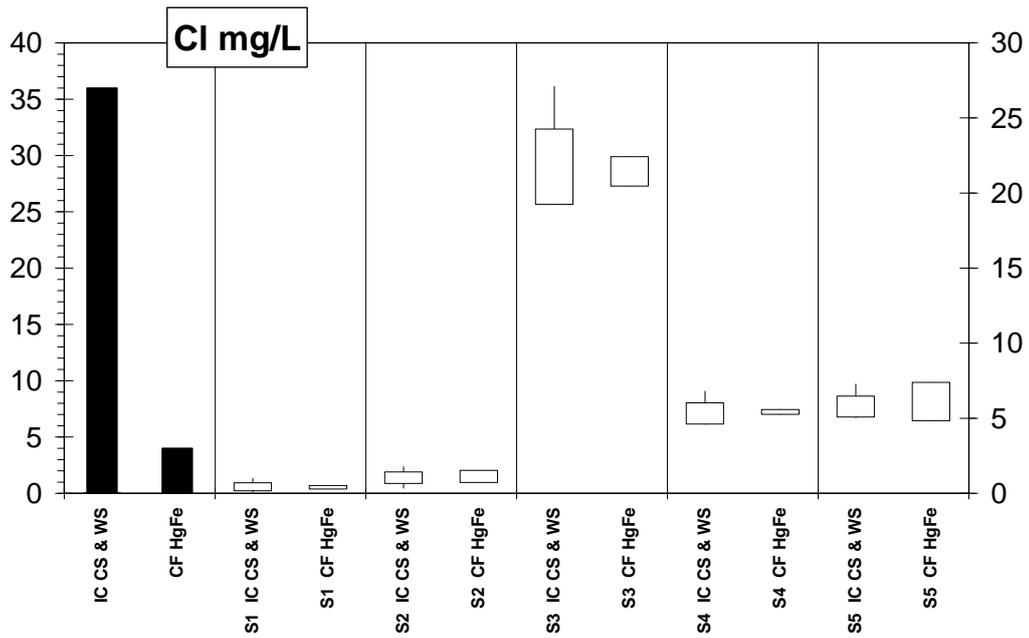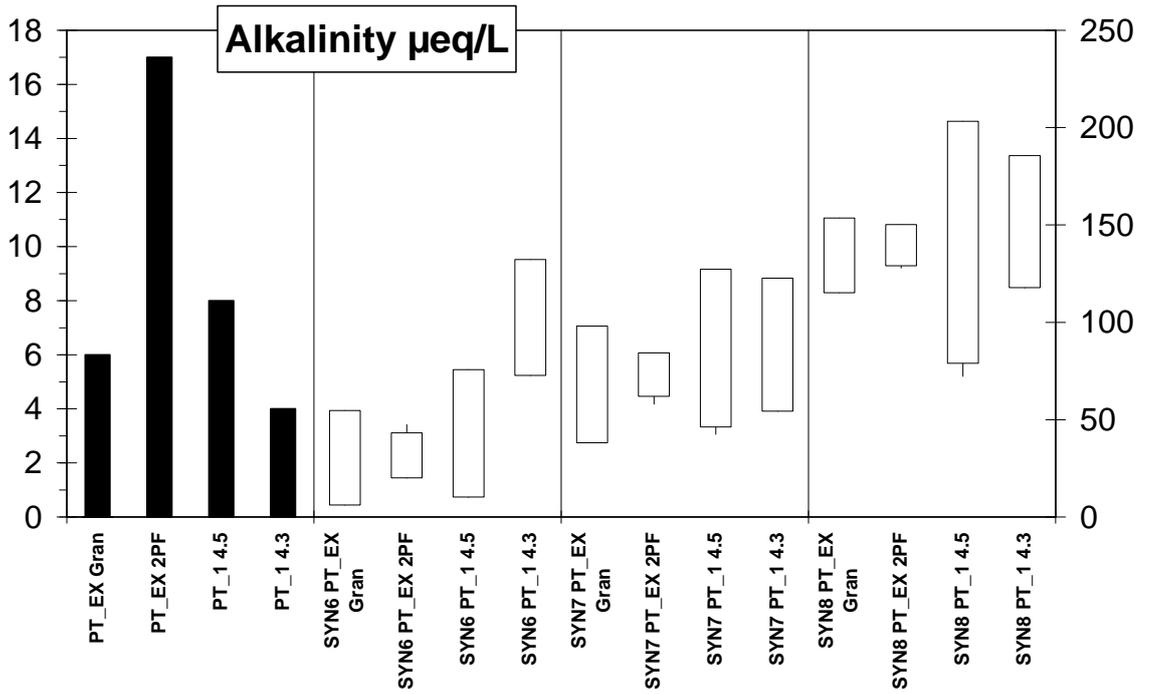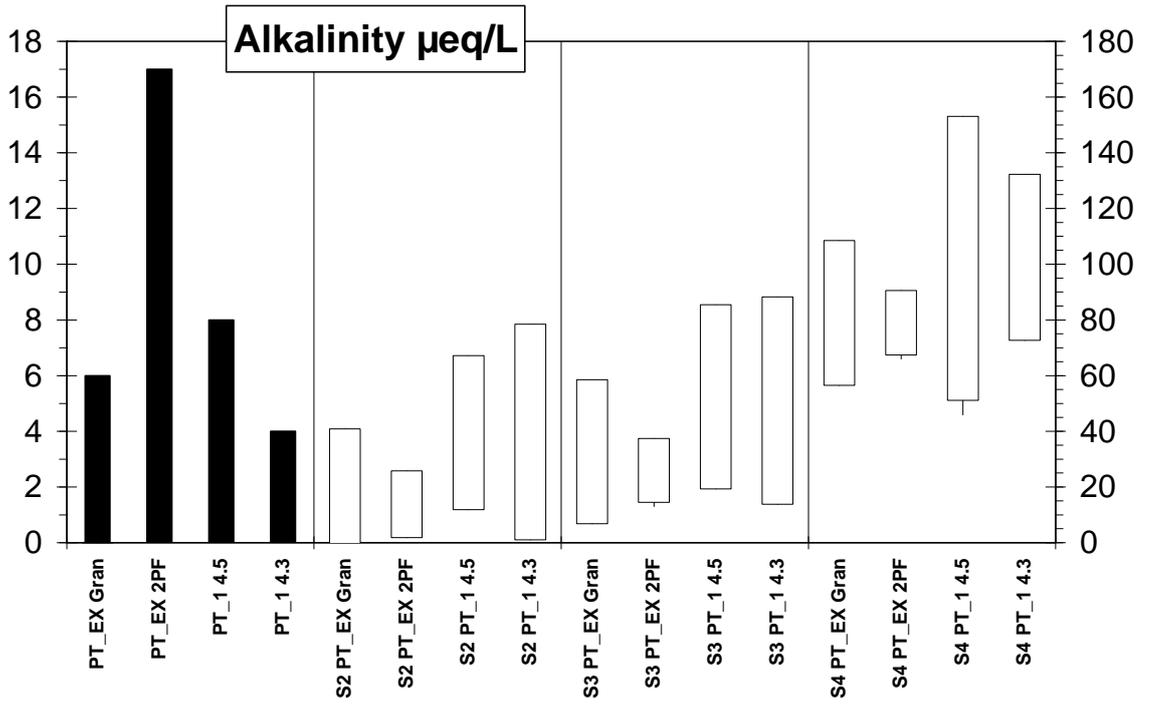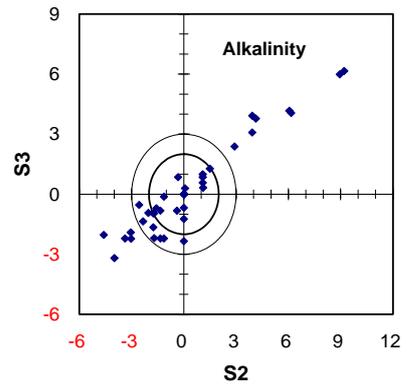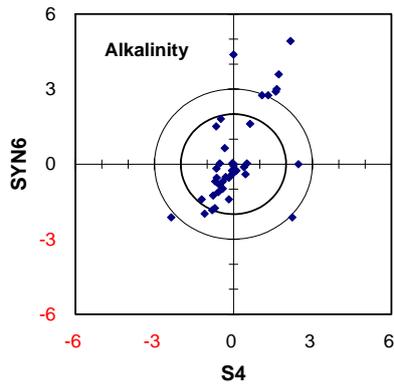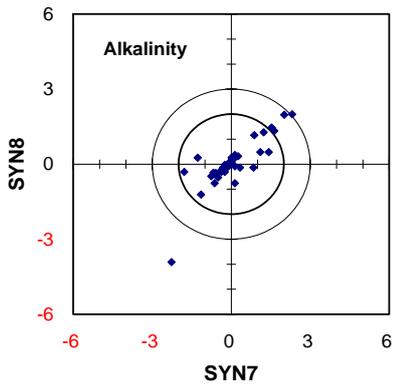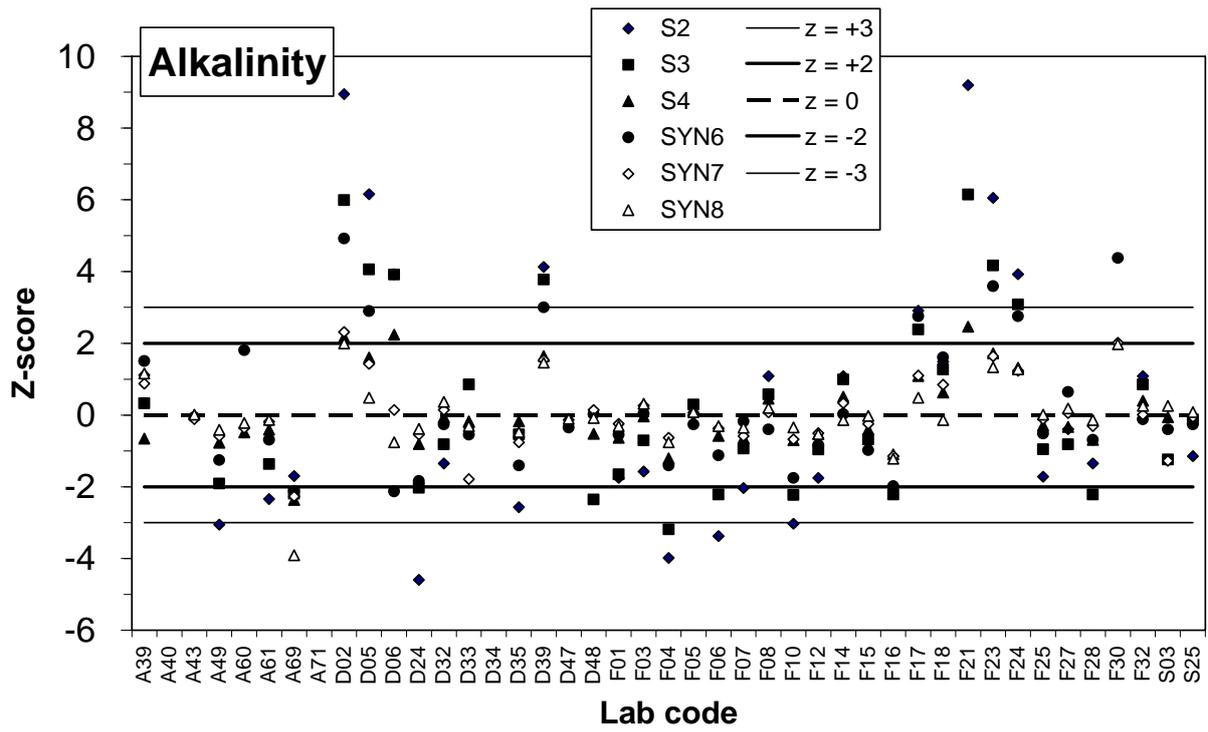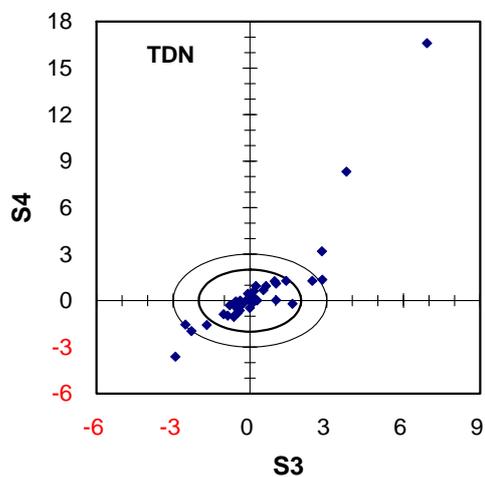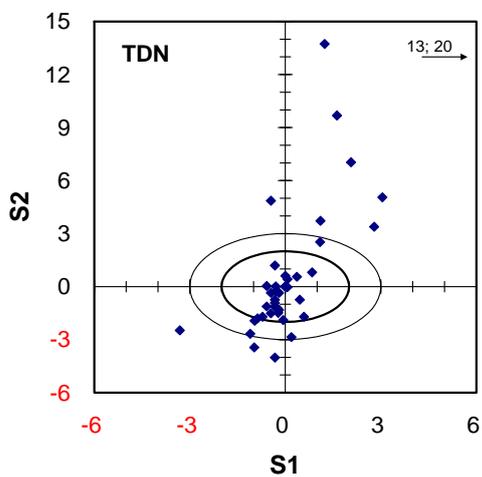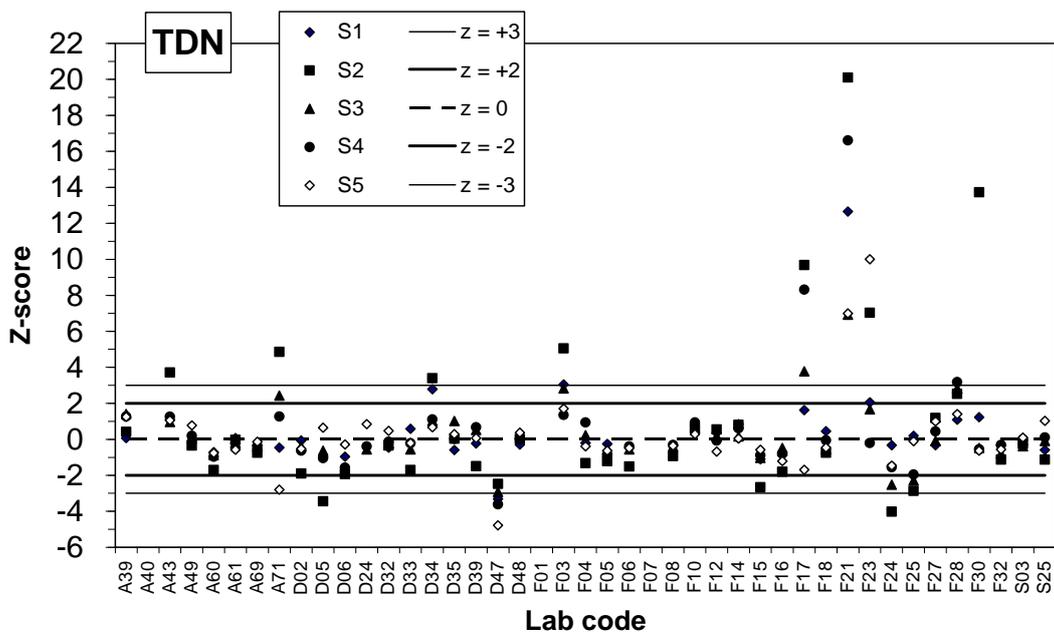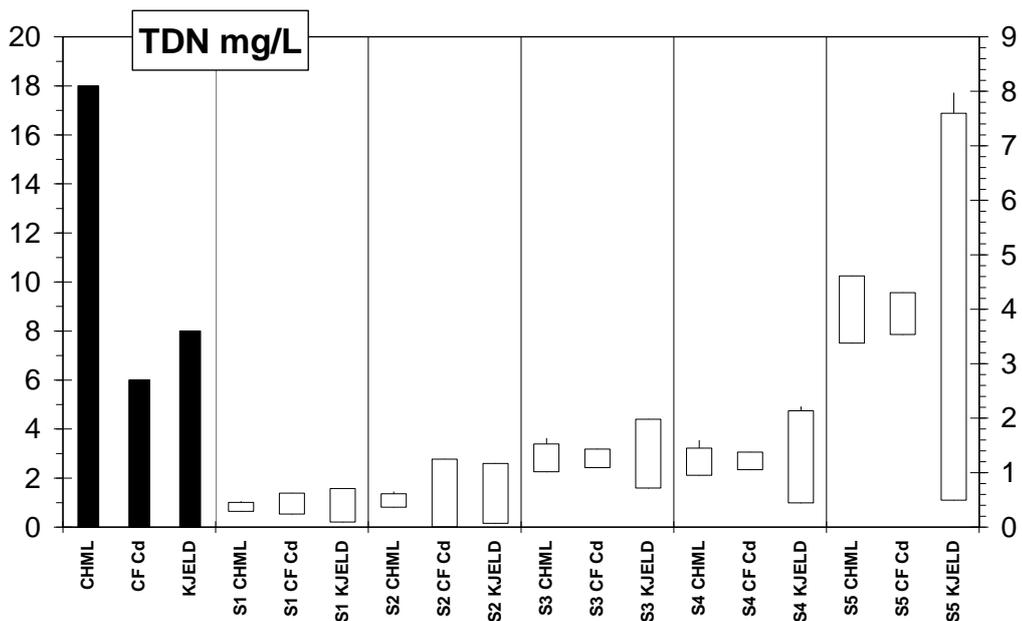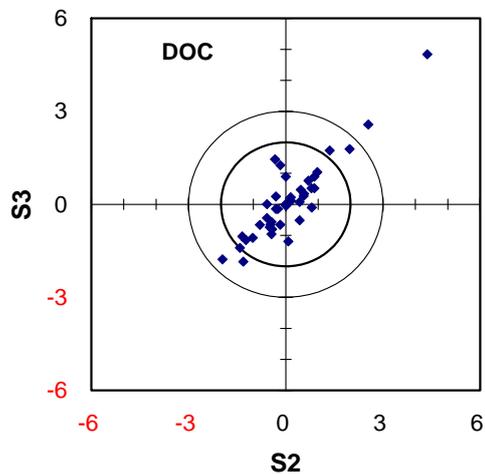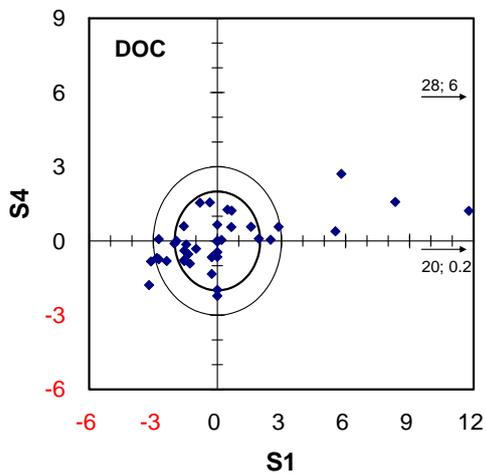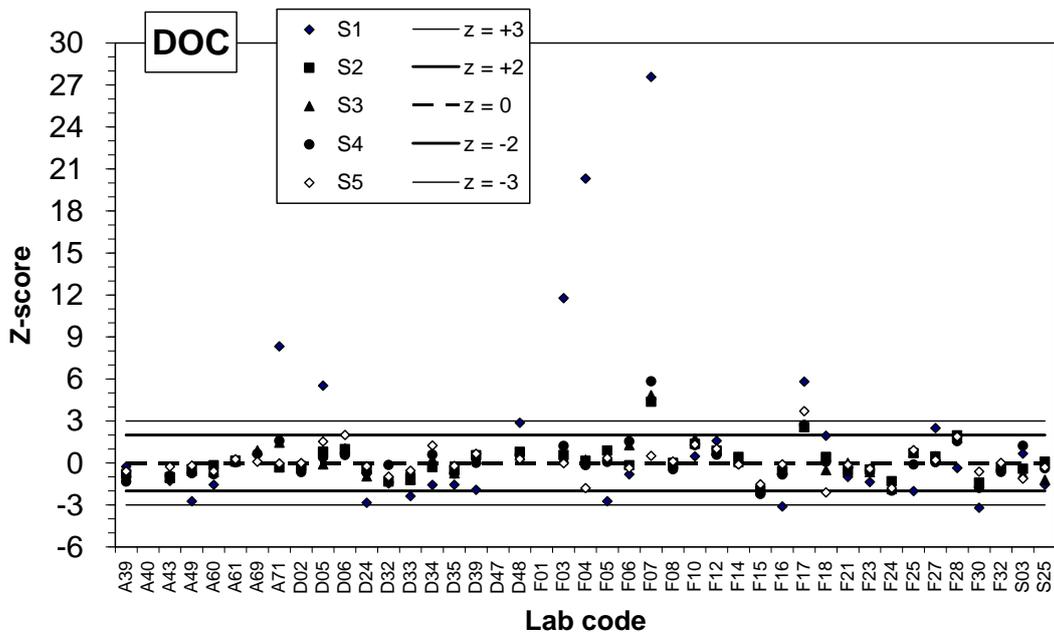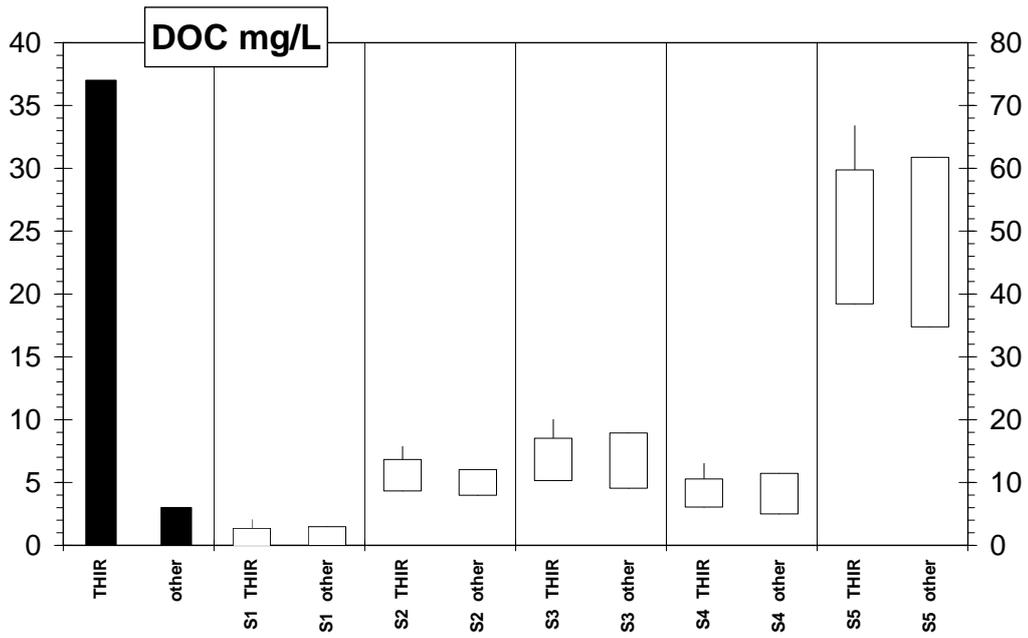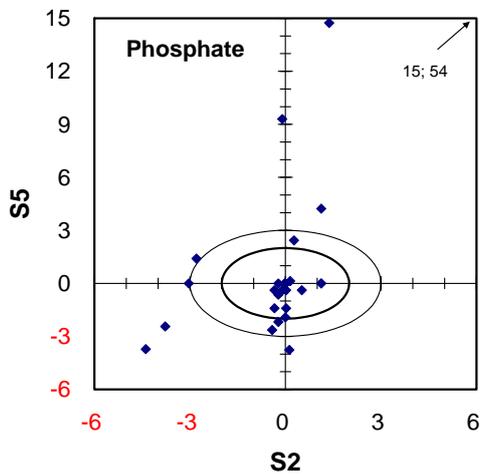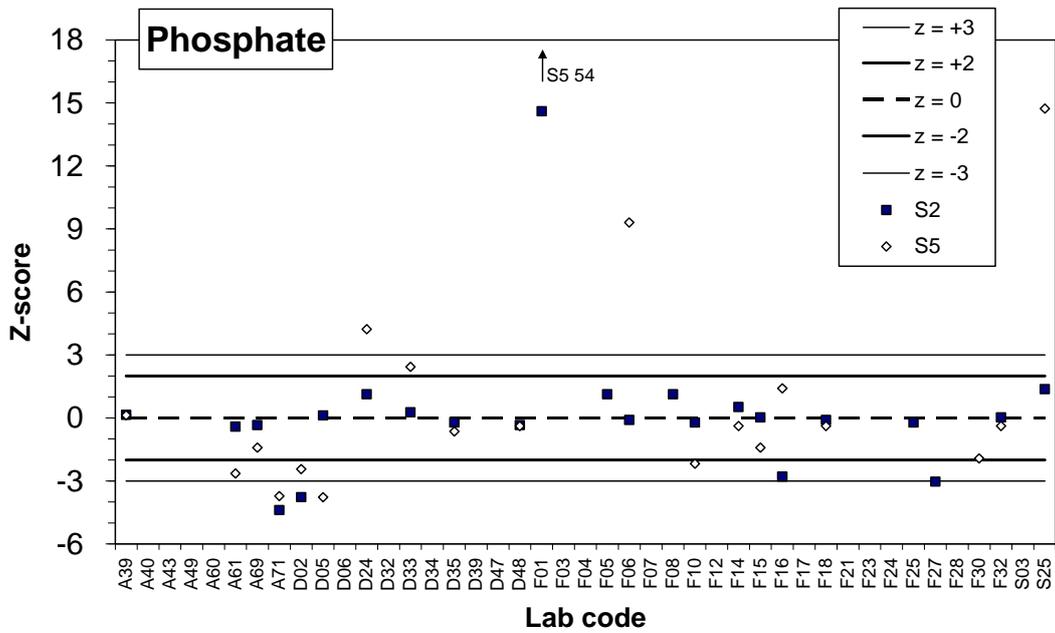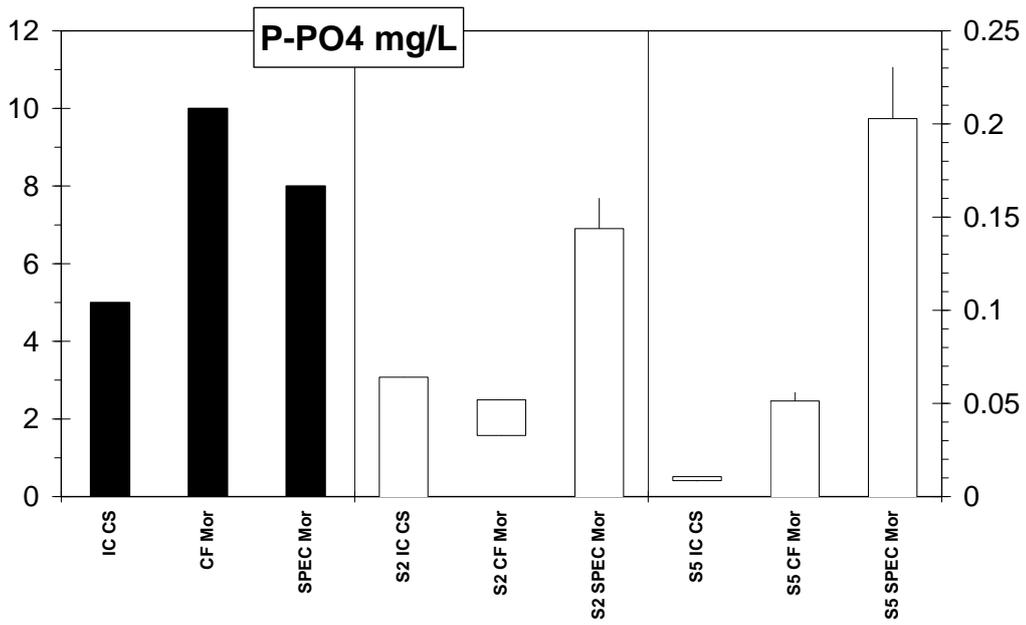
6.4. pH

Most of the laboratories used electrodes specific for low ionic strength solutions (LIS), but no significant differences were found between the results obtained with LIS electrodes and other electrodes (GEN) as regards either the mean values or the dispersion of the results. The Youden plots show the presence of systematic errors in some laboratories, most probably due to their calibration procedure and electrode performance, even for acid samples. The relatively small proportion of results within the tolerable limit (77%) shows that more attention should be paid to this determination, apparently simple.

6.5. Conductivity

There were no significant differences between the conductivity measurements performed at 25°C and those made at a different temperature and then corrected to 25°C. The dispersion of the values was relatively high, but 89% of the data met the tolerable limit. The Youden plots show a strong prevalence of systematic over random errors. Periodic calibration of the electrodes, using potassium chloride solutions of conductivity ranging from 10 to 500 μS cm^{-1} is recommended, as well as a check of the temperature correction factor.

6.6. Calcium, magnesium, sodium and potassium

The concentration of base cations measured in this WRT covered a wider range, with two samples with Ca, Mg, Na or K concentration of below 1 mg/L. ICP OES was the technique most widely used for the analysis of these cations, followed by IC, AAS, ICP MS and AES (for Na and K).

About 85-92% of the results fell within the tolerable limits, with better results for Mg, Na and K. The different analytical techniques gave comparable results. Some of the outliers occurred when AAS was used.

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

6.7. Ammonium

The ammonium concentration were low, between 0.08 and 0.47 mg N L^{-1}. Sample 1 and 2 had very low concentration, but the number of values reported below detection limit was very low.

In general, more than 80% of the results within the tolerable limit, but some results were far from the consensus value.

This determination was performed using a number of different methods, primarily continuous flow analysis, IC , spectrophotometric determination.

In the stability test, the concentration of sample 5 showed a marked drift after the end of the exercise, so that this sample was not used for requalification.

6.8. Sulphate

Most of the laboratories measured sulphate by IC, either with (33 cases) or without (3 cases) chemical suppression of the eluent. Four laboratories used ICP OES, with a correction for organic sulphur, obtained through an empirical relationship between organic carbon and organic sulphur. These three methods gave similar results, with the errors mainly due to random factors. In spite of the stricter tolerable limit (±10%), a large number of results (87%) fell within the acceptance range.

In one case, results were expressed in a wrong unit.

6.9. Nitrate

The range of nitrate concentration in the WRT was broad, between 0.12 and 2.35 mg N L^{-1}. As in the case for sulphate, most of the laboratories measured nitrate by IC. One lab reported values below detection limit for samples 1 and 2, the concentration of which was not so low to be difficult to analyse.

6.10. Chloride

The concentration of chloride in the WRT samples (0.5-5 mg L^{-1}) covered the range of the values usually found in atmospheric deposition in regions close to the sea, as well as in more continental areas.

The 36 laboratories which measured chloride by IC had results that were comparable with the other methods.

The Youden plots show a prevalence of systematic errors. This, combined with the relatively high concentration of chloride in these samples, as well as the occurrence of outlying values with the most reliable analytical techniques, highlights the necessity to pay more attention to the avoidance of sample contamination.

6.11. Alkalinity

Alkalinity determination was still one of the most critical analyses as regards both missing results and the problem of dispersion and errors. Discussion of the results will be facilitated by first giving a brief description of the meaning of alkalinity and of the different ways 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 the aggregate property of a 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 of 5.0-5.6.

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

1) direct determination of the inflection point, by monitoring the pH and plotting the titration curve and its derivative during the titration. This technique, used by only one laboratory in this WRT, is difficult and often not precise at very low alkalinity owing to problems related to the choice of volume additions and to the slow response of pH electrodes;

2) a titration performed well beyond the end point (e.g. to pH 4 or less), by recording a number of pH values and the corresponding added volume of acid. Subsequent extrapolation by the least-

squares regression method allows 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, thus making it simpler to calculate 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 ensures that all the 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, most of them selecting an end-point at pH 4.3;

5) colorimetric determination of the end point was used by four laboratories. In this case the type of indicator 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. In accordance with the *ICP Forests manual for sampling and analysis of atmospheric deposition*, samples with a pH lower than 5.0 do not need to be measured for alkalinity.

Despite the fact that the manual states that samples with a pH higher than 5.0 should not be measured, about 9 laboratories reported positive alkalinity values for samples 1 (pH=4.9) and one for sample 5 (pH=4.0). For sample 1, two of these 9 laboratories also reported pH values higher than 5, and the measurement of alkalinity was the justified.

The results obtained with the different methods are compared in the plot, which only shows the results obtained with methods used by more than two laboratories. It is evident that the single end-point titration at pH = 4.3 to 4.5 can largely overestimate alkalinity. However, the manual clearly states that these techniques should not be used, unless a correction for their bias is used.

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.

6.12. Total dissolved nitrogen (TDN)

Total dissolved nitrogen, which is a mandatory parameter in throughfall and stemflow samples, was analysed by 42 of the 44 laboratories, mainly by chemiluminescence. The nitrogen concentration in the analysed samples covered a wide range, from 0.4 to 4 mg L^{-1}. The plot of the results clearly shows that chemiluminescence and continuous flow analyses give comparable results, while data dispersion for the Kjeldahl method is markedly higher, even at the higher levels.

6.13. Dissolved organic carbon (DOC)

Dissolved organic carbon is a mandatory variable in the monitoring programmes for soil solution and throughfall samples, but it was measured by only 40 laboratories out of 45, most of them (37) using thermal combustion and IR detection of the carbon dioxide formed.

This method resulted very reliable, and 90% of the results fell within the tolerable limit, if we consider samples 2 to 5. In the case of sample 1 (open field deposition with low DOC content),

it was not used in the discussion of the results, as it resulted not enough stable during the stability test.

7. QUALITY CHECK OF THE ANALYSES

In the *ICP Forests manual for sampling and analysis of atmospheric deposition*, the chapter dealing with chemical analysis of the samples 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.

A detailed discussion of the four tests, as applied to a set of 7000 analysis results on deposition samples collected in different European countries can be found in Mosello *et al.* (2005). The effect of high DOC concentration on the quality check is discussed by Mosello *et al.* (2008).

It is very important for the quality of the results to ensure that these tests are performed routinely after the analysis of each sample, and that the results of the test are used to decide whether the analyses can be accepted or whether the results should be checked for specific errors or even repeat the analyses.

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 etc., become standard laboratory procedure for the results of analyses to be submitted and stored in the monitoring programmes' data bases. The necessity to analyse all the major anions (sulphate, nitrate, chloride, and bicarbonate (i.e. alkalinity) for samples with a pH higher than 5) and cations (hydrogen ions (i.e. pH), ammonium, calcium, magnesium, sodium and potassium) in order to be able to perform the tests is also stressed.

The *ICP Forests manual for sampling and analysis of atmospheric deposition* recommends carrying out the ion balance test on bulk deposition (open field) samples. In the case of soil solution, throughfall and stemflow samples, however, it is highly likely that there will be a so-called "anion deficiency". This is primarily due to the presence of organic compounds anions, which should in fact be taken into account when performing the ion balance check. For this reason, the ion balance test should not have been (*a priori*) performed on samples 1 and 4.

However, the test comparing measured and calculated conductivity is not so sensitive to the presence of organic matter, which generally possesses a low conductivity. For this reason, this test is reliable for all types of natural sample (bulk deposition, throughfall, stemflow, soil solution). In this WRT, the analysis of all major ions was required for all the natural samples (1 to 4), and the conductivity quality check could have been performed.
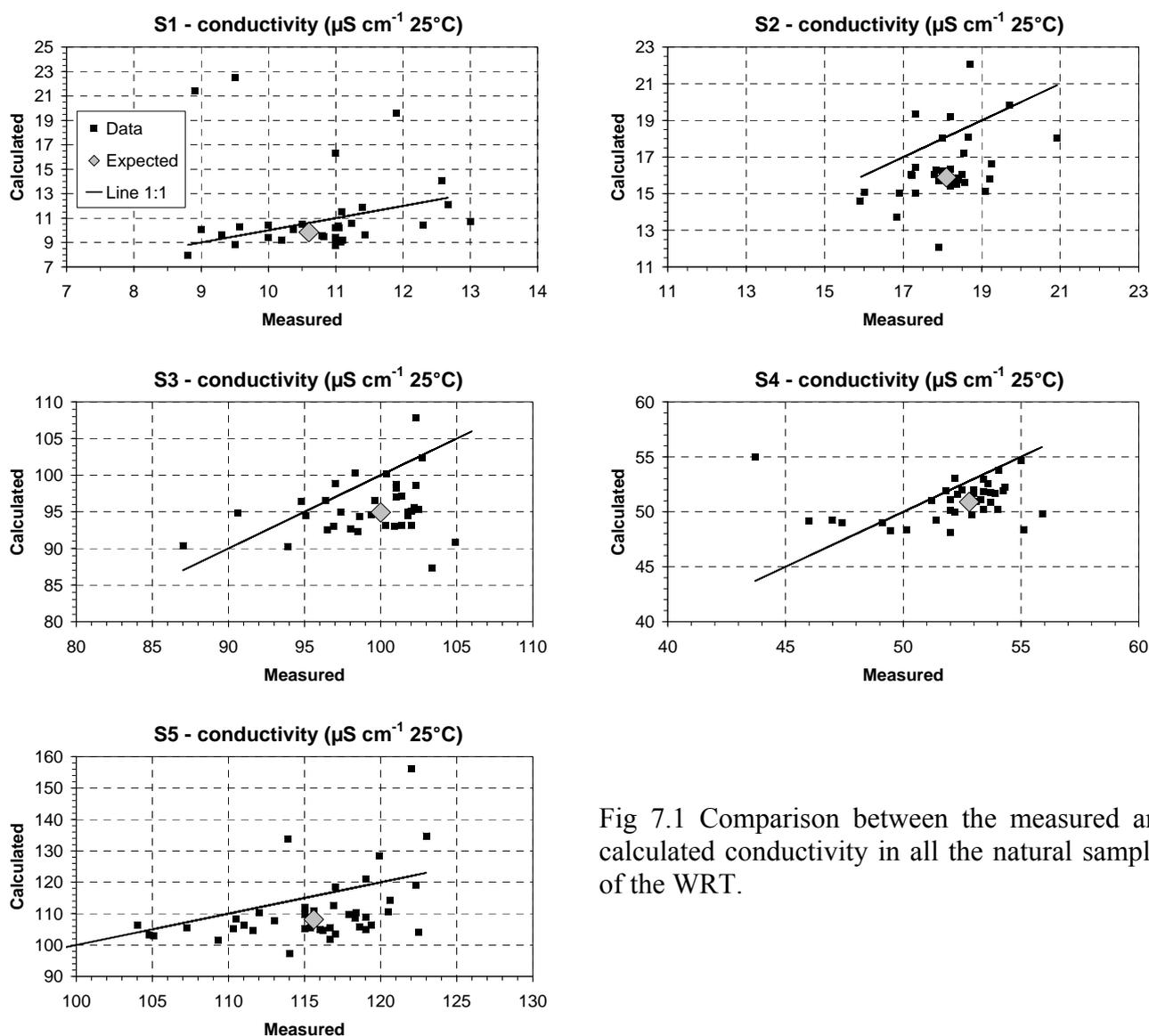
Fig 7.1 Comparison between the measured and calculated conductivity in all the natural samples of the WRT.

The calculated and measured conductivity are plotted for all samples for which all major ions were analysed in Fig. 7.1. Samples meeting the acceptance criterion for the test line close to the 1:1 line. It is evident that a number of analyses do not satisfy the test: 14% of the samples for which the test could be performed. This percentage is still relevant, considering that the conductivity check is reported as a mandatory quality control procedure in the ICP Forests manual. However the number of analyses not passing the conductivity check is markedly smaller than in the previous WRT (27%, Marchetto et al. 2009).

Table 7.1 Results of the conductivity check on the results submitted for samples 1-5.

Sample	Incomplete analysis set	Passed	Not passed
S1	9	28	5
S2	13	27	2
S3	6	34	2
S4	5	34	3
S5	0	32	10

Complying with the procedure for Quality Assessment and Quality Control is an important step towards improving the overall quality of the data collected within the monitoring programmes.

The tests based on ion balance and on the comparison between calculated and measured conductivity are part of the QA/QC procedures for deposition and soil solution analyses, and it is necessary to again underline the importance of performing them during the routine analysis work.

In order to be able to perform these tests it is necessary to analyse all the major ions. In fact all of them are mandatory for deposition samples. In the case of soil solution samples however, not all the analyses are mandatory, but the manual does recommend that all major ions should be analysed in order to be able to carry out these quality checks.

These results indicate that the data quality check procedure can help to improve the overall quality of the results, but the conductivity test alone cannot be considered as the whole solution. It should be combined with other tests, such as the check of the ion balance when possible, the test on the Na:Cl ratio, the comparison of total and inorganic forms of N, and with regular QA/QC procedures such as use of control charts and blank charts.

The check based on ion balance is not recommended for throughfall and soil solution samples with a relatively high DOC concentration. In effect, only sample 1 would have passed the check on the basis of the expected results. As clearly shown in fig. 7.2., a large number of laboratories submitted results that did not pass the ion balance check, and it would have been useful for them to know that some of the results were outside the tolerable limit.
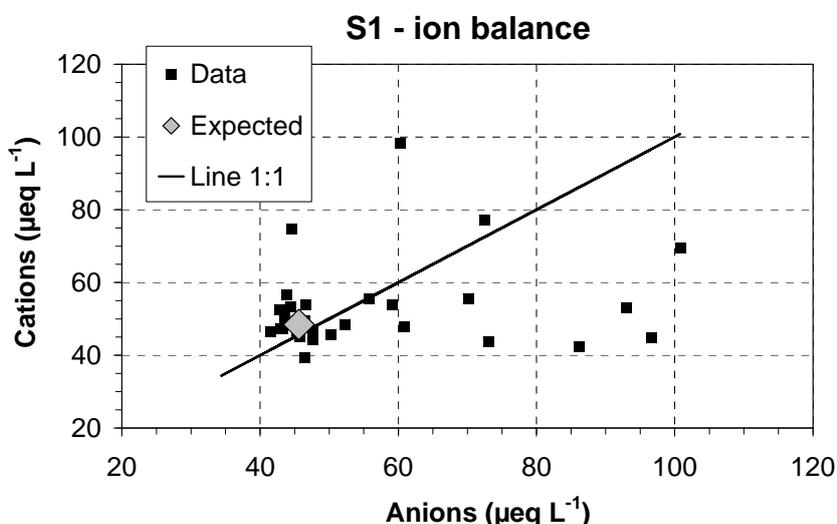
Fig 7.2. Comparison between the cation and anion total concentration in all the natural samples in the WRT.

8. COMPARISON WITH PREVIOUS WRTs

The improvement in the overall analytical performance of the network can be shown in figure 8.1.

In the case of pH and conductivity, the quality of the results was relatively good, and the improvement, in particular in the case of conductivity, is evident but slight.

For main cations and anions, the largest improvement was found after the first ICP Forests WRT, in 2002, when most the laboratories were able to test their performance, to identify their analytical problems and to found solutions for improving the overall quality of the results. The increase in the number of non-tolerable results in the third WRT is accidental, related to the very low concentration found in one sample.

The case of the most problematic variables, namely alkalinity, DOC and TDN, was different. For these variables, the number of non-tolerable results was decreasing constantly from one WRT to the following, and during this forth WRT the percentage of tolerable results begins to be comparable to that obtained for the other variables.
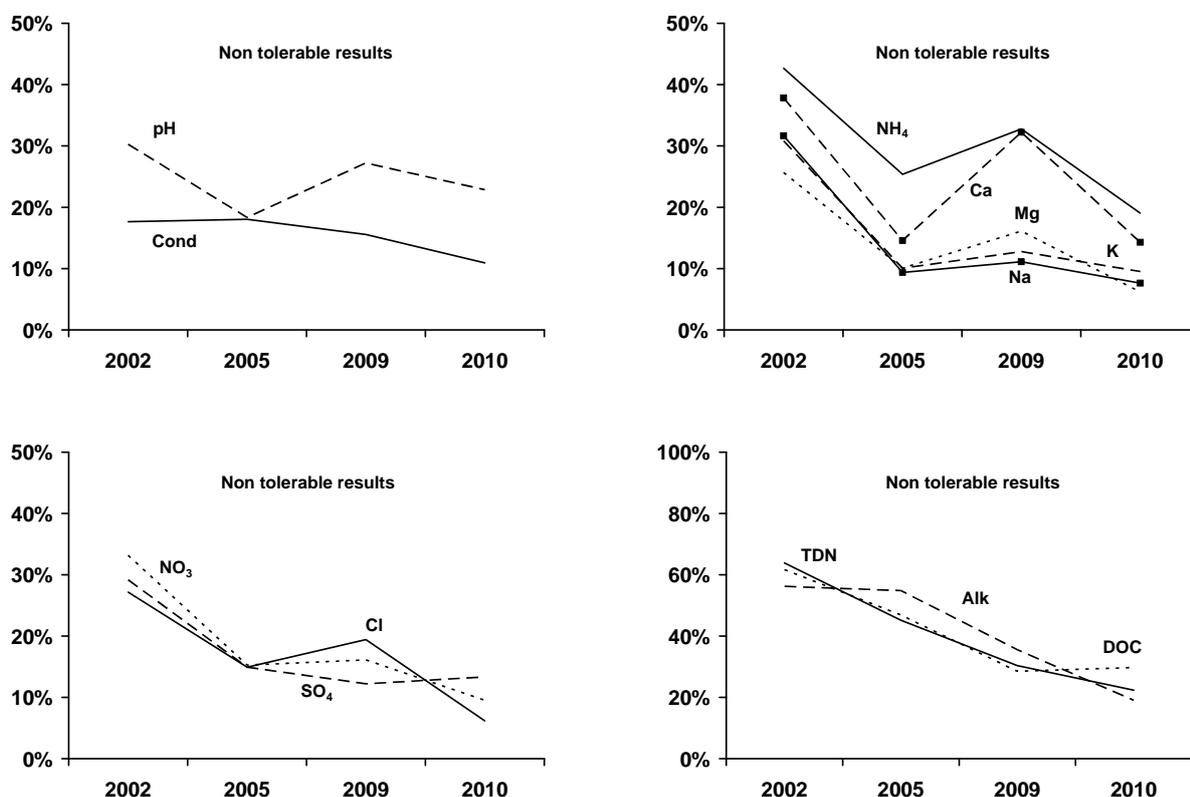
Fig. 8.1 Comparison of the number of missing data and of data outside the tolerable limits in the three WRTs carried out on for deposition and soil analyses in European forests.

9. CONCLUSIONS

Working Ring Tests are part of a complex procedure aimed at improving the analytical quality of the laboratories analysing atmospheric deposition and soil solutions within the FutMon project. This activity also includes revision of the Forest Monitoring Protocols and assistance to specific laboratories to develop their abilities and reach high analytical standards.

This working test is the second run within the FutMon Life+ project and the fourth involving most of the laboratories analysing deposition or soil solution in European forests.

The test was intended to give each laboratory feedback on its performance, but also to enable the FutMon coordination centre to evaluate the overall analytical quality in the FutMon monitoring network, and to directly compare the quality of the results with the previous exercise, highlighting the results of the QA/QC work performed on the basis of the results of the previous exercise.

Within the FutMon project, participation in WRTs is mandatory, with results being used to identify analytical difficulties and if necessary to exclude data from the central data base. However, the main aim of the WRT is to give each laboratory the feedback required to understand its weak points and make the relevant improvements.

The results also showed that analytical problems can be identified through simple checks on the data, and that if all the laboratories had performed the suggested checks, most of the outlying results would have been detected.

The laboratories participating in the exercise received a preliminary report and were invited to carry out a requalification procedure, identifying their analytical problems and if necessary analysing the samples again to check the improvement in their techniques. Each laboratory and each FutMon associated beneficiary received a report detailing the results of the WRT and of the requalification procedure. However, the report referred to the laboratories by their codes only, to keep their identities confidential.

Laboratories were asked to requalify if more than 50% of the results for a given variable were outside the tolerable limit or missing. This was the case for only 13% of the total number of determinations. However, 55% of the labs were requested to requalify for at least one variable. The variables which gave the highest percentage of results outside the tolerable limits were pH, total nitrogen, ammonium and alkalinity.

The WRT programme was included in the FutMon project as a tool to stimulate self-criticism and to check the improvements made by laboratories from one year to another until a sufficiently reliable QA level has been achieved. At the same time, the project includes regular meetings between the heads of the laboratories, with the aim of enhancing collaboration between laboratories engaged in the same type of analyses. We see this as a useful, cost-effective and professional way to improve the analytical performance of the network as a whole.

The comparison of the results of this WRT with the results of the previous WRTs carried out during and before the FutMon project clearly shows that the goal of an overall amelioration of the analytical performance of the laboratories was attained.

10. REFERENCES

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.

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

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.

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

Marchetto, A., R. Mosello, G. Tartari, J. Derome, K. Derome, P. Sorsa, N. König, N. Clarke, E. Ulrich & A. Kowalska. 2006. *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*. Office National des forets, Département Recherche. Fontainebleau, France. 85 pp.

Marchetto A., R. Mosello, G. Tartari, J. Derome, K. Derome, N. König, N. Clarke and A Kowalska. 2009. *Atmospheric Deposition and Soil Solution Working Ring Test 2009. Laboratory ring test for deposition and soil solution sample analyses for the laboratories participating in the EU/Life+ FutMon Project*. Report CNR ISE 04.09. 59 pp

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

Mosello, R., J. Derome, K. Derome, E. Ulrich, T. Dahlin, A. Marchetto & G. Tartari. 2002. *Atmospheric deposition and soil solution Working Ring Test 2002. Laboratory ring-test for deposition and soil solution sample analyses between the countries participating in the ICP Forests level II monitoring programme*. Office National des forets, Département Recherche. Fontainebleau, France. 69 pp.

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

Mosello, R., T. Amoriello, S. Benham, N. Clarke, J. Derome, K. Derome, G. Genouw, N. König, A. Orru, G.A. Tartari, A. Thimonier, E. Ulrich & A.J. Lindroos. 2008. Valitation of chemical analyses of atmospheric deposition on forested sites in Europe: 2. DOC concentration as an estimator of the organic ion charge. *J. Limnol.*, 67: 1-14.

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

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

Thompson M., S.L.R. Ellison & R. Wood. 2006. The international harmonized protocol for the proficiency testing of analytical chemistry laboratories (IUPAC Technical Report). *Pure Appl. Chem.*, 78, 1: 145-196.

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

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

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

Appendix A: SUBMITTED DATA AND STATISTICS

Sample	pH				
	1	2	3	4	5
number of data above LOQ	42	42	42	42	42
average	4.87	5.47	5.81	6.46	3.99
median	4.92	5.52	5.84	6.53	4.02
robust average	4.90	5.51	5.82	6.49	4.00
A39	4.36	4.99	5.62	6.14	3.84
A43	4.96	5.59	5.89	6.61	4.08
A49	4.94	5.70	6.03	6.80	4.04
A60	4.83	5.51	5.79	6.57	4.01
A61	4.91	5.52	5.85	6.55	3.99
A69	5.12	5.47	5.63	6.23	3.99
A71	4.83	5.43	5.77	6.44	3.89
D02	4.75	5.41	5.66	6.44	3.92
D05	4.94	5.64	5.89	6.61	3.98
D06	5.17	5.30	5.74	5.85	4.06
D24	4.38	5.06	5.61	6.26	3.80
D32	4.97	5.56	5.91	6.61	4.06
D33	4.93	5.54	5.90	6.60	4.02
D34	4.99	5.71	6.01	6.49	3.99
D35	4.93	5.51	5.82	6.53	4.05
D39	4.94	5.52	5.89	6.58	4.02
D47	4.87	5.45	5.78	6.50	4.03
D48	5.19	5.56	5.76	6.40	4.07
F01	4.83	5.37	5.70	6.16	3.94
F03	4.96	5.48	5.83	6.46	4.04
F04	4.36	4.78	5.02	5.68	3.52
F05	5.14	5.71	6.01	6.69	4.07
F06	4.88	5.55	6.32	6.86	4.02
F07	4.63	5.52	5.88	6.60	4.04
F08	4.93	5.62	5.97	6.58	4.03
F10	4.57	5.19	5.53	6.20	3.86
F12	5.01	5.53	5.81	6.48	4.06
F14	4.86	5.50	5.84	6.56	4.02
F15	4.84	5.48	5.73	6.25	4.03
F16	5.02	5.72	6.34	6.76	4.17
F17	4.88	5.50	5.88	6.55	4.04
F18	4.77	5.40	5.79	6.50	3.94
F21	4.68	5.10	5.49	6.15	3.86
F23	5.10	5.59	5.84	6.56	4.00
F24	4.82	5.45	5.83	6.53	3.92
F25	4.84	5.49	5.84	6.52	3.97
F27	4.95	5.56	5.73	6.31	4.05
F28	4.88	5.53	5.40	6.46	4.08
F30	5.00	5.53	5.85	6.54	4.03
F32	4.95	5.66	6.05	6.65	3.98
S03	4.92	5.53	5.92	6.56	4.01
S25	4.90	5.50	5.90	6.60	4.00

	Conductivity (at 25° C)				
Sample	1	2	3	4	5
number of data above LOQ	42	42	42	42	42
average	10.64	18.11	99.7	52.34	115.1
median	10.81	18.13	100.7	53.00	116.1
robust average	10.62	18.09	100.0	52.75	115.6
A39	8.90	18.20	94.8	52.30	113.9
A43	13.00	18.50	100.5	54.70	116.0
A49	8.80	15.90	90.6	47.00	105.1
A60	12.30	18.50	102.1	52.20	119.4
A61	10.82	18.36	102.5	53.70	118.3
A69	11.00	18.00	97.0	52.00	112.0
A71	11.23	18.13	99.0	52.06	119.0
D02	12.57	18.65	100.3	54.25	120.6
D05	11.09	18.55	102.2	54.30	120.5
D06	9.50	18.00	101.0	53.40	117.0
D24	11.90	19.20	104.9	55.10	122.3
D32	10.20	17.30	96.9	49.10	104.8
D33	11.10	18.20	98.0	52.00	119.0
D34	11.07	18.10	103.5	53.50	115.0
D35	10.60	17.20	100.0	52.50	116.2
D39	10.37	17.83	98.3	51.80	111.6
D47	11.05	18.13	101.2	53.98	116.7
D48	8.80	17.60	97.4	51.20	109.3
F01	10.50	18.30	100.9	53.10	116.9
F03	10.30	18.40	101.8	53.30	116.7
F04	9.50	19.70	96.4	47.40	98.0
F05	9.91	17.30	99.6	52.20	119.0
F06	9.00	16.00	87.0	46.00	104.0
F07	9.65	16.83	93.9	49.45	107.3
F08	10.00	17.80	99.4	52.80	110.5
F10	10.30	17.30	98.6	53.90	123.0
F12	11.00	18.50	101.4	53.40	115.4
F14	11.00	18.00	101.0	53.00	115.0
F15	10.00	16.90	98.5	51.40	115.0
F16	11.90	19.10	101.0	54.00	114.0
F17	9.57	17.21	95.1	50.12	110.3
F18	10.60	18.20	101.4	53.00	115.6
F21	11.00	18.70	102.3	55.00	119.9
F23	11.00	18.40	101.8	53.60	117.9
F24	12.67	20.92	102.7	43.70	117.1
F25	11.04	18.57	102.0	53.40	118.4
F27	11.43	19.24	102.3	54.04	115.4
F28	10.80	16.90	96.5	52.00	113.0
F30	11.40	20.00	106.0	55.70	122.0
F32	9.40	17.90	102.0	52.90	111.0
S03	9.30	18.10	103.4	55.90	118.6
S25	11.40	17.90	100.4	53.70	122.5

Sample	Calcium				
	1	2	3	4	5
number of data above LOQ	41	42	42	42	42
average	0.22	0.51	1.31	2.27	4.48
median	0.20	0.51	1.31	2.27	4.48
robust average	0.20	0.51	1.31	2.27	4.48
A39	0.20	0.56	1.29	2.26	4.35
A43	0.20	0.54	1.35	2.29	4.70
A49	0.18	0.47	1.22	2.14	4.21
A60	0.22	0.40	1.28	2.16	4.44
A61	0.21	0.52	1.33	2.30	4.58
A69	0.36	0.65	1.46	2.44	4.73
A71	0.16	0.47	1.25	2.03	4.03
D02	0.19	0.52	1.26	2.24	4.51
D05	0.18	0.54	1.33	2.33	4.40
D06	0.40	0.72	1.57	2.56	4.77
D24	0.18	0.44	1.33	2.12	3.49
D32	0.16	0.36	1.16	1.78	4.62
D33	0.21	0.52	1.26	2.01	4.88
D34	0.22	0.58	1.44	2.51	4.45
D35	0.25	0.55	1.00	2.25	4.30
D39	0.22	0.50	1.32	2.27	4.44
D47	0.19	0.51	1.32	2.35	4.38
D48	0.24	0.58	1.40	2.45	4.73
F01	0.30	0.55	1.37	2.31	4.50
F03	0.21	0.51	1.24	2.30	3.95
F04	0.39	0.44	1.04	2.21	4.48
F05	0.21	0.55	1.34	2.29	3.98
F06	0.18	0.47	1.22	2.13	4.13
F07	0.19	0.48	1.35	2.28	4.57
F08	0.18	0.49	1.29	2.20	4.49
F10	0.21	0.50	1.30	2.23	4.25
F12	0.20	0.52	1.35	2.36	4.61
F14	0.18	0.46	1.30	2.14	4.59
F15	0.18	0.46	1.27	2.19	4.48
F16	0.19	0.51	1.36	2.34	4.65
F17	0.19	0.51	1.29	2.18	4.53
F18		0.46	1.35	2.52	4.13
F21	0.44	0.67	1.53	2.54	5.25
F23	0.25	0.57	1.36	2.31	4.48
F24	0.18	0.41	1.04	2.20	4.30
F25	0.18	0.48	1.31	2.23	4.46
F27	0.28	0.59	1.42	2.50	4.96
F28	0.12	0.48	1.65	2.42	5.55
F30	0.14	0.43	1.24	2.17	4.47
F32	0.19	0.51	1.30	2.23	4.41
S03	0.19	0.49	1.21	2.27	4.50
S25	0.22	0.54	1.35	2.29	4.50

| | Magnesium | | | | |
Sample	1	2	3	4	5
number of data above LOQ	41	42	42	42	42
average	0.049	0.227	1.35	1.06	1.68
median	0.049	0.223	1.35	1.06	1.68
robust average	0.048	0.227	1.34	1.06	1.68
A39	0.045	0.238	1.31	1.04	1.64
A43	0.050	0.230	1.35	1.10	1.70
A49	0.042	0.215	1.27	1.00	1.60
A60	0.050	0.170	1.33	1.05	1.68
A61	0.048	0.233	1.35	1.08	1.72
A69	0.050	0.260	1.44	1.19	1.86
A71	0.046	0.210	1.26	1.00	1.67
D02	0.040	0.240	1.35	1.07	1.68
D05	0.040	0.220	1.34	1.08	1.69
D06	0.051	0.230	1.32	1.01	1.48
D24	0.042	0.206	1.50	1.05	1.42
D32	0.060	0.160	1.23	0.98	1.76
D33	0.030	0.190	1.20	0.92	1.56
D34	0.040	0.240	1.41	1.10	1.69
D35	0.060	0.280	1.35	1.20	1.60
D39	0.043	0.212	1.24	0.98	1.53
D47	0.049	0.250	1.39	1.11	1.68
D48	0.049	0.219	1.32	1.03	1.67
F01	0.053	0.240	1.37	1.09	1.71
F03		0.210	1.27	1.10	1.48
F04	0.060	0.200	1.27	0.78	1.62
F05	0.050	0.236	1.35	1.09	1.55
F06	0.050	0.220	1.27	1.01	1.57
F07	0.046	0.216	1.26	1.04	1.62
F08	0.050	0.210	1.35	1.06	1.74
F10	0.050	0.260	1.33	1.06	1.66
F12	0.049	0.231	1.38	1.10	1.75
F14	0.042	0.214	1.39	1.07	1.80
F15	0.045	0.212	1.31	1.04	1.69
F16	0.043	0.219	1.36	1.06	1.69
F17	0.050	0.220	1.32	1.01	1.67
F18	0.110	0.255	1.31	1.09	1.68
F21	0.046	0.250	1.25	1.05	1.69
F23	0.055	0.242	1.39	1.13	1.67
F24	0.050	0.290	1.56	1.24	1.93
F25	0.044	0.220	1.36	1.05	1.68
F27	0.070	0.250	1.45	1.15	1.83
F28	0.033	0.210	1.64	1.06	2.16
F30	0.035	0.207	1.35	1.07	1.74
F32	0.050	0.240	1.36	1.08	1.72
S03	0.045	0.226	1.28	1.03	1.62
S25	0.050	0.240	1.41	1.10	1.75

	Sodium				
Sample	**1**	**2**	**3**	**4**	**5**
number of data above LOQ	41	42	42	42	42
average	0.278	0.762	11.35	4.60	4.58
median	0.273	0.760	11.56	4.68	4.63
robust average	0.272	0.759	11.38	4.60	4.59
A39	0.264	0.757	10.87	4.39	4.37
A43	0.350	0.720	10.60	4.70	4.15
A49	0.273	0.737	11.29	4.58	4.62
A60	0.230	0.550	11.18	4.36	4.36
A61	0.273	0.783	11.43	4.69	4.70
A69	0.330	0.850	12.51	5.19	5.09
A71	0.230	0.680	10.39	4.24	4.34
D02	0.250	0.750	10.66	4.49	4.46
D05	0.270	0.800	11.72	4.70	4.67
D06	0.287	0.761	11.30	4.36	4.07
D24	0.257	0.652	10.10	4.23	3.44
D32	0.250	0.760	11.39	4.53	4.54
D33	0.280	0.750	11.03	4.34	4.42
D34	0.280	0.790	11.66	4.69	4.67
D35	0.300	0.780	11.70	4.73	4.66
D39	0.255	0.779	11.83	4.66	4.61
D47	0.283	0.811	11.77	4.75	4.71
D48	0.276	0.759	11.70	4.60	4.60
F01	0.253	0.756	11.72	4.72	4.70
F03	0.250	0.750	11.52	4.63	4.59
F04	0.520	0.620	12.10	4.70	5.15
F05	0.289	0.853	11.60	4.79	4.29
F06	0.260	0.730	10.60	4.25	4.21
F07	0.193	0.617	10.62	4.28	4.46
F08	0.260	0.730	11.72	4.69	4.75
F10		0.620	10.70	4.44	4.38
F12	0.283	0.785	11.67	4.82	4.87
F14	0.270	0.770	12.13	4.79	4.99
F15	0.230	0.710	9.65	4.03	4.27
F16	0.273	0.807	11.80	4.83	4.79
F17	0.260	0.780	11.88	4.68	4.84
F18	0.299	0.812	11.70	4.90	4.64
F21	0.305	1.175	11.05	4.81	4.78
F23	0.230	0.730	10.40	3.86	4.21
F24	0.420	0.980	13.50	5.30	5.30
F25	0.258	0.756	11.71	4.59	4.75
F27	0.280	0.830	12.84	5.22	5.14
F28	0.178	0.618	8.74	3.95	4.07
F30	0.310	0.790	11.72	4.70	4.75
F32	0.280	0.800	11.50	4.67	4.71
S03	0.314	0.738	10.70	4.35	4.37
S25	0.260	0.760	11.90	4.82	4.76

	Potassium				
Sample	**1**	**2**	**3**	**4**	**5**
number of data above LOQ	40	42	42	42	42
average	0.145	1.92	3.57	0.466	1.75
median	0.140	1.95	3.57	0.460	1.71
robust average	0.143	1.93	3.55	0.465	1.70
A39	0.138	1.86	3.29	0.438	1.57
A43	0.240	2.02	3.90	0.490	1.75
A49		1.86	3.30	0.432	1.64
A60	0.120	1.24	3.43	0.440	1.60
A61	0.153	2.07	3.66	0.491	1.80
A69	0.240	2.22	3.92	0.590	1.91
A71	0.140	1.63	3.11	0.390	1.41
D02	0.150	1.92	3.41	0.450	1.60
D05	0.110	1.95	3.61	0.470	1.71
D06	0.165	2.06	3.73	0.494	1.71
D24	0.139	1.66	3.27	0.436	1.28
D32	0.160	1.99	3.30	0.470	1.71
D33	0.140	1.90	3.41	0.440	1.61
D34	0.135	2.00	3.60	0.440	1.72
D35	0.190	2.05	3.55	0.500	1.72
D39	0.146	1.88	3.68	0.437	1.77
D47	0.151	2.03	3.61	0.510	1.73
D48	0.156	1.99	3.60	0.469	1.72
F01	0.084	1.81	3.32	0.424	1.56
F03	0.140	1.99	3.60	0.460	1.68
F04	0.100	1.72	3.50	0.440	3.79
F05		1.89	3.41	0.456	1.48
F06	0.150	1.91	3.39	0.440	1.65
F07	0.099	1.67	3.27	0.389	1.64
F08	0.160	1.94	3.49	0.460	1.71
F10	0.160	2.01	3.52	0.490	1.71
F12	0.154	2.01	3.66	0.478	1.78
F14	0.136	1.88	3.65	0.459	1.73
F15	0.130	1.76	4.06	0.520	1.93
F16	0.116	2.03	3.67	0.483	1.82
F17	0.130	1.89	3.52	0.460	1.68
F18	0.117	1.93	3.51	0.454	1.68
F21	0.175	2.30	4.53	0.476	2.07
F23	0.121	1.68	3.28	0.463	1.60
F24	0.190	2.27	3.80	0.550	1.85
F25	0.134	1.98	3.70	0.469	1.78
F27	0.150	2.21	3.80	0.460	1.84
F28	0.098	1.70	3.70	0.390	1.65
F30	0.120	2.02	3.63	0.510	1.52
F32	0.170	2.05	3.54	0.480	1.73
S03	0.196	1.81	3.18	0.499	1.80
S25	0.110	2.03	3.63	0.460	1.67

Sample	Ammonium				
	1	2	3	4	5
number of data above LOQ	39	39	42	42	42
average	0.09	0.10	0.49	0.45	0.41
median	0.09	0.08	0.46	0.44	0.34
robust average	0.09	0.08	0.47	0.44	0.34
A39	0.07	0.03	0.71	0.43	1.72
A43	0.11	0.10	0.37	0.34	0.27
A49	0.09	0.08	0.46	0.44	0.35
A60	0.08	0.08	0.45	0.43	0.32
A61	0.07	0.08	0.47	0.42	0.34
A69	0.09	0.08	0.46	0.43	0.34
A71	0.13	0.43	0.81	0.66	1.81
D02	0.11	0.08	0.69	0.44	0.43
D05	0.09	0.08	0.45	0.43	0.38
D06	0.11	0.09	0.38	0.41	0.31
D24	0.09	0.08	0.45	0.43	0.34
D32	0.08	0.07	0.45	0.46	0.29
D33	0.08	0.07	0.45	0.45	0.32
D34	0.10	0.09	0.52	0.48	0.37
D35	0.10	0.08	0.44	0.45	0.36
D39	0.10	0.09	0.57	0.52	0.37
D47	0.09	0.08	0.49	0.47	0.36
D48	0.10	0.09	0.51	0.48	0.35
F01	0.08	0.05	0.47	0.45	0.27
F03	0.09	0.08	0.48	0.47	0.32
F04	0.07	0.05	0.41	0.40	0.31
F05	0.09	0.08	0.52	0.46	0.49
F06	0.09	0.08	0.45	0.43	0.33
F07			0.46	0.45	0.34
F08	0.10	0.08	0.45	0.43	0.34
F10			0.45	0.42	0.39
F12	0.08	0.08	0.50	0.47	0.37
F14	0.10	0.09	0.45	0.43	0.31
F15	0.09	0.09	0.46	0.43	0.35
F16			0.58	0.44	0.34
F17	0.10	0.11	0.49	0.45	0.36
F18	0.09	0.08	0.46	0.45	0.34
F21	0.07	0.06	0.41	0.39	0.30
F23	0.08	0.08	0.46	0.43	0.33
F24	0.06	0.05	0.36	0.35	0.25
F25	0.08	0.08	0.46	0.44	0.32
F27	0.09	0.09	0.58	0.53	0.41
F28	0.10	0.06	0.52	0.50	0.47
F30	0.09	0.44	0.45	0.43	0.31
F32	0.09	0.09	0.47	0.45	0.34
S03	0.09	0.08	0.46	0.45	0.34
S25	0.09	0.09	0.47	0.44	0.34

	Chloride				
sample	1	2	3	4	5
number of data above LOQ	41	42	42	42	42
average	0.42	1.05	21.71	5.33	5.83
median	0.41	1.05	21.68	5.35	5.74
robust average	0.40	1.04	21.61	5.33	5.77
A39	0.34	1.18	22.10	5.43	6.76
A43	0.72	1.30	21.43	5.63	5.83
A49	0.41	1.04	22.47	5.14	5.53
A60	0.34	1.00	22.37	5.34	5.67
A61	0.37	1.01	21.86	5.34	5.60
A69	0.42	0.88	22.12	5.23	5.66
A71	0.33	0.92	20.47	4.91	5.31
D02	0.49	0.97	20.00	5.08	5.30
D05	0.41	1.07	21.06	5.32	5.74
D06	0.34	0.93	22.90	5.36	5.77
D24	0.39	1.04	21.04	5.18	5.71
D32	0.42	1.08	21.48	5.35	5.77
D33	0.38	1.01	21.50	5.35	6.04
D34	0.41	1.10	20.88	4.69	6.00
D35	0.40	1.06	21.70	5.35	5.85
D39	0.34	0.94	23.30	5.30	5.74
D47	0.41	1.05	21.63	5.36	5.74
D48	0.43	1.03	21.66	5.46	5.85
F01	0.38	1.04	20.50	5.28	5.52
F03	0.41	1.16	21.70	5.30	5.73
F04	1.00	1.76	21.90	5.48	6.14
F05	0.50	1.16	21.80	5.60	6.16
F06	0.45	1.05	20.86	5.37	5.74
F07	0.38	0.94	20.99	5.12	5.65
F08	0.41	1.05	20.92	4.99	5.68
F10	0.42	1.01	21.21	5.43	5.82
F12	0.45	1.08	22.19	5.40	5.85
F14	0.39	1.01	21.90	5.34	5.81
F15	0.40	1.03	21.69	5.28	5.66
F16	0.45	1.06	22.40	5.25	5.63
F17	0.60	0.98	21.40	4.60	5.53
F18	0.39	1.09	20.60	5.37	5.67
F21	0.09	1.07	27.10	6.79	7.27
F23	0.39	0.78	22.25	5.48	5.82
F24	0.50	1.08	22.50	5.69	6.19
F25	0.41	1.06	21.38	5.25	5.74
F27	0.38	1.00	21.16	5.41	5.86
F28	0.44	1.23	22.10	5.78	6.20
F30	0.31	1.43	21.80	5.53	7.07
F32	0.39	1.07	20.60	4.79	5.04
S03	0.37	0.97	19.30	5.11	5.44
S25		0.34	23.40	5.42	5.70

Sample	Nitrate				
	1	2	3	4	5
number of data above LOQ	41	41	42	42	42
average	0.211	0.122	0.380	0.460	2.37
median	0.218	0.119	0.379	0.455	2.35
robust average	0.214	0.117	0.379	0.457	2.35
A39	0.216	0.153	0.453	0.606	2.74
A43	0.235	0.122	0.390	0.479	2.80
A49	0.217	0.113	0.378	0.456	2.26
A60	0.200	0.070	0.360	0.430	2.39
A61	0.218	0.112	0.387	0.468	2.33
A69	0.230	0.120	0.390	0.450	2.16
A71	0.250	0.140	0.420	0.490	2.40
D02	0.250	0.110	0.400	0.490	2.30
D05	0.220	0.110	0.370	0.450	2.33
D06	0.189	0.168	0.340	0.415	2.42
D24	0.212	0.117	0.374	0.444	2.26
D32	0.230	0.130	0.398	0.475	2.28
D33	0.186	0.092	0.354	0.424	2.26
D34	0.225	0.111	0.384	0.463	2.37
D35	0.224	0.119	0.387	0.461	2.37
D39	0.202	0.103	0.351	0.430	2.31
D47	0.221	0.119	0.383	0.452	2.30
D48	0.208	0.113	0.363	0.439	1.89
F01	0.193	0.082	0.361	0.434	2.27
F03	0.200	0.120	0.370	0.450	2.37
F04	0.170	0.070	0.310	0.400	2.16
F05	0.238	0.121	0.407	0.478	2.49
F06	0.220	0.120	0.380	0.470	2.44
F07	0.217	0.130	0.352	0.424	2.34
F08	0.200	0.120	0.370	0.460	2.30
F10	0.300	0.200	0.480	0.540	2.55
F12	0.241	0.142	0.399	0.476	2.38
F14	0.220	0.120	0.390	0.460	2.35
F15	0.230	0.140	0.390	0.470	2.34
F16	0.213	0.132	0.374	0.439	2.30
F17	0.170	0.090	0.320	0.380	2.21
F18	0.136	0.107	0.348	0.445	2.39
F21	0.180	0.066	0.411	0.540	3.03
F23	0.218	0.109	0.364	0.444	2.39
F24	0.230	0.120	0.400	0.480	2.56
F25	0.223	0.120	0.375	0.448	2.35
F27	0.210	0.110	0.370	0.450	2.37
F28	0.218	0.124	0.378	0.513	2.71
F30	0.219	0.382	0.382	0.454	2.37
F32			0.380	0.460	2.24
S03	0.211	0.108	0.362	0.443	2.36
S25	0.050	0.040	0.400	0.460	2.00

	Sulphate				
sample	1	2	3	4	5
number of data above LOQ	41	42	42	42	42
average	0.332	0.677	1.52	2.40	4.52
median	0.304	0.633	1.44	2.27	4.14
robust average	0.306	0.635	1.44	2.28	4.18
A39	0.314	0.710	1.50	2.44	4.02
A43	0.356	0.630	1.46	2.27	4.32
A49	0.321	0.642	1.47	2.28	3.97
A60	0.340	0.680	1.55	2.38	4.15
A61	0.272	0.598	1.42	2.26	4.00
A69	0.250	0.550	1.38	2.22	4.15
A71	0.290	0.610	1.44	2.22	4.04
D02	0.420	0.670	1.45	2.30	4.29
D05	0.310	0.650	1.44	2.25	4.36
D06	0.269	0.578	1.43	2.33	4.26
D24	0.296	0.626	1.40	2.21	3.93
D32	0.310	0.630	1.42	2.22	4.01
D33	0.280	0.650	1.37	2.12	3.78
D34	0.284	0.634	1.42	2.38	4.67
D35	0.310	0.640	1.48	2.35	4.28
D39	0.298	0.612	1.43	2.26	3.82
D47	0.307	0.639	1.48	2.35	4.13
D48	0.304	0.608	1.33	2.23	4.08
F01	0.294	0.649	1.47	2.31	4.36
F03	0.310	0.620	1.48	2.25	3.93
F04	0.320	0.640	1.36	2.21	4.39
F05	0.370	0.707	1.60	2.47	5.58
F06	0.290	0.670	1.50	2.28	4.52
F07	0.279	0.562	1.27	2.11	4.38
F08	0.280	0.690	1.58	2.36	4.65
F10	0.370	1.270	1.77	2.51	7.39
F12	0.327	0.645	1.47	2.30	4.11
F14	0.300	0.700	1.61	2.37	4.53
F15	0.320	0.640	1.46	2.27	4.08
F16	0.303	0.614	1.41	2.21	3.96
F17	0.260	0.550	1.16	2.01	4.27
F18	0.218	0.569	1.33	2.11	3.92
F21	0.728	0.801	1.14	1.77	3.99
F23	0.320	0.554	1.30	2.58	4.70
F24	0.330	0.660	1.57	2.43	4.23
F25	0.305	0.632	1.45	2.26	4.06
F27	0.300	0.630	1.49	2.34	4.17
F28	0.296	0.627	1.25	2.13	3.80
F30	0.990	2.250	4.94	7.55	15.07
F32	0.290	0.630	1.41	2.16	3.77
S03	0.289	0.602	1.44	2.28	4.05
S25		0.180	1.49	2.29	3.50

	Total Nitrogen				
Sample	1	2	3	4	5
number of data above LOQ	38	39	40	40	40
average	0.415	0.569	1.30	1.27	4.08
median	0.367	0.500	1.25	1.19	3.94
robust average	0.385	0.518	1.27	1.21	3.98
A39	0.390	0.540	1.45	1.36	4.48
A43	0.470	0.711	1.39	1.36	4.41
A49	0.370	0.500	1.29	1.23	4.29
A60	0.330	0.430	1.16	1.09	3.68
A61	0.390	0.517	1.27	1.15	3.75
A69	0.360	0.480	1.22	1.16	3.93
A71	0.350	0.770	1.58	1.36	2.87
D02	0.380	0.420	1.22	1.13	3.77
D05	0.310	0.340	1.19	1.08	4.24
D06	0.311	0.418	1.06	1.02	3.87
D24			1.20	1.16	4.32
D32	0.350	0.500	1.24	1.19	4.17
D33	0.430	0.430	1.20	1.18	3.90
D34	0.600	0.694	1.40	1.34	4.25
D35	0.340	0.520	1.40	1.21	4.10
D39	0.368	0.441	1.34	1.29	4.01
D47	0.130	0.390	0.90	0.77	2.08
D48	0.362	0.519	1.31	1.21	4.13
F01					
F03	0.620	0.780	1.63	1.37	4.66
F04	0.370	0.450	1.30	1.32	3.83
F05	0.365	0.455	1.20	1.10	3.73
F06	0.350	0.440	1.20	1.16	3.79
F07					
F08	0.360	0.470	1.22	1.17	3.84
F10		0.550	1.35	1.32	4.10
F12	0.413	0.547	1.29	1.20	3.71
F14	0.450	0.560	1.29	1.28	4.00
F15	0.300	0.380	1.14	1.10	3.75
F16	0.318	0.425	1.21	1.11	3.50
F17	0.510	1.020	1.75	2.21	3.31
F18	0.420	0.480	1.20	1.20	3.80
F21	1.360	1.560	2.15	3.21	6.77
F23	0.544	0.883	1.48	1.18	7.97
F24	0.360	0.310	0.95	1.02	3.40
F25	0.400	0.370	0.98	0.97	3.94
F27	0.360	0.580	1.26	1.26	4.38
F28	0.469	0.649	1.63	1.59	4.54
F30	0.480	1.230	1.21	1.14	3.73
F32	0.360	0.460	1.17	1.17	3.76
S03	0.363	0.505	1.22	1.21	4.02
S25	0.340	0.460	1.26	1.22	4.39

Sample	Dissolved Organic Carbon				
	1	2	3	4	5
number of data above LOQ	34	39	40	40	40
average	1.27	11.0	13.6	8.32	49.0
median	1.03	10.8	13.5	8.17	48.5
robust average	1.09	10.9	13.5	8.23	48.8
A39	1.06	10.1	12.6	7.13	45.9
A43	0.95	9.8	12.0	7.48	47.5
A49	0.79	10.5	12.7	7.62	47.9
A60	0.92	10.8	12.6	7.56	45.9
A61	1.11	11.1	13.7	8.26	50.1
A69			14.7	8.77	49.2
A71	2.00	10.6	15.5	9.53	48.6
D02	1.06	10.7	13.3	7.69	48.8
D05	1.69	11.8	13.4	8.55	56.2
D06	1.16	12.0	14.9	8.69	58.5
D24	0.78	10.5	12.2	7.66	47.6
D32	0.93	9.5	12.1	8.11	44.0
D33	0.83	9.6	11.9	7.56	46.1
D34	0.92	10.6	13.8	8.72	54.8
D35	0.92	10.4	12.5	7.60	47.7
D39	0.88	11.5	13.9	8.23	52.0
D47					
D48	1.40	11.8	14.2	8.70	50.1
F01					
F03	2.37	11.6	14.0	9.23	48.7
F04	3.30	11.1	13.8	8.10	40.0
F05	0.79	11.9	14.2	8.29	50.5
F06	1.00	10.8	15.2	9.50	47.0
F07	4.09	15.7	20.0	13.03	51.2
F08		10.9	13.4	7.86	49.3
F10	1.14	12.4	15.8	9.27	55.2
F12	1.26	11.9	14.7	8.70	53.7
F14		11.4	13.6	8.20	48.2
F15		8.8	11.1	6.40	41.3
F16	0.75	10.3	12.9	7.55	48.3
F17	1.72	13.7	17.0	10.46	66.8
F18	1.30	11.4	12.8	8.30	38.5
F21	0.98	10.3	13.5	7.97	48.1
F23	0.94	10.4	12.6	7.79	46.7
F24		9.5	11.0	6.60	40.0
F25	0.87	11.7	14.5	8.14	53.3
F27	1.36	11.4	14.1	8.27	49.8
F28	1.05	13.1	15.9	9.51	58.0
F30	0.74	9.4	11.6	6.76	45.8
F32		10.6	13.3	7.70	48.8
S03	1.16	10.5	12.4	9.24	43.3
S25	0.92	11.0	11.9	7.91	47.3

			Alkalinity			
Sample	**2**	**3**	**4**	**6**	**7**	**8**
number of data above LOQ	33	36	37	39	39	39
average	26.4	37.3	88.3	36.2	78.3	141.9
median	19.0	30.9	84.0	33.0	76.1	140.0
robust average	24.6	35.9	87.0	34.8	77.8	141.5
A39	30.1	38.2	75.6	45.3	91.5	162.0
A43				34.4	76.1	141.6
A49	9.6	22.2	73.6	26.1	68.7	134.1
A60			78.7	47.4	72.2	137.5
A61	13.1	26.1	80.0	30.0	74.9	139.1
A69	16.3	20.2	45.9	20.0	42.5	72.3
A71						
D02	68.8	78.9	124.8	69.1	113.9	176.8
D05	55.0	65.0	115.0	55.0	100.0	150.0
D06	44.0	64.0	126.0	20.0	80.0	128.0
D24	2.0	21.3	73.0	22.0	69.3	134.7
D32	18.0	30.0	86.0	33.0	80.0	148.0
D33	23.0	42.0	84.0	31.0	50.0	136.0
D34						
D35	12.0	32.0	84.0	25.0	66.0	133.0
D39	45.0	63.0	115.7	55.7	101.7	167.3
D47				32.4	75.7	139.5
D48		19.0	78.0	35.0	80.0	140.0
F01	16.0	24.0	76.0	31.0	74.0	136.0
F03	16.9	30.8	86.4	35.1	81.9	147.0
F04	5.0	13.0	66.0	25.0	68.0	128.0
F05	25.0	38.0	89.0	33.0	78.0	143.0
F06	8.0	20.0	77.0	27.0	72.0	136.0
F07	14.6	29.2	75.8	33.6	68.7	135.2
F08	30.0	40.0	95.0	32.0	79.0	145.0
F10	9.7	19.9	74.8	22.6	67.3	135.4
F12	16.0	29.0	78.0	29.0	70.0	132.0
F14	30.0	43.0	96.0	35.0	83.0	139.0
F15		31.0	80.0	28.0	74.0	141.0
F16	19.0	20.0	68.0	21.0	60.0	120.0
F17	39.0	53.0	106.0	54.0	95.0	150.0
F18	32.0	45.0	98.0	46.0	91.0	139.0
F21	70.0	80.0	130.0			
F23	54.5	65.8	117.0	59.8	103.3	165.0
F24	44.0	58.0	110.0	54.0	97.0	164.0
F25	16.2	29.0	82.0	31.2	76.1	141.7
F27	22.7	30.0	81.3	39.3	78.7	144.7
F28	18.0	20.0	75.0	30.0	73.0	139.0
F30				65.3	109.2	176.4
F32	30.0	42.0	94.0	34.0	78.0	146.0
S03		27.0	86.0	32.0	58.0	146.0
S25	19.0	35.0	87.0	33.0	77.0	143.0

	Phosphate	
Sample	2	5
number of data above LOQ	23	20
average	0.042	0.032
median	0.040	0.018
robust average	0.041	0.020
A39	0.042	0.020
A43		
A49		
A60		
A61	0.037	0.009
A69	0.038	0.014
A71	0.005	0.005
D02	0.010	0.010
D05	0.042	0.005
D06		
D24	0.050	0.036
D32		
D33	0.043	0.029
D34		
D35	0.039	0.017
D39		
D47		
D48	0.038	0.018
F01	0.160	0.230
F03		
F04		
F05	0.050	
F06	0.040	0.056
F07		
F08	0.050	
F10	0.039	0.011
F12		
F14	0.045	0.018
F15	0.041	0.014
F16	0.018	0.025
F17		
F18	0.040	0.018
F21		
F23		
F24		
F25	0.039	
F27	0.016	
F28		
F30		0.012
F32	0.041	0.018
S03		
S25	0.052	0.077

Appendix B. RESULTS OF THE QUALIFICATION PROCEDURE

ok: test passed (at least 50% of the results within the tolerable limits)

NM: not measured

NP: not passed

Lab code	pH	Cond.	Ca	Mg	Na	K	NH$_4$	SO$_4$	NO$_3$	Cl	Alk	TDN	DOC	Requalification
A39	NP	ok	ok	ok	ok	ok	NP	ok	NP	ok	ok	ok	ok	not performed
A43	ok	ok	ok	ok	ok	ok	NP	ok	ok	ok	ok	ok	ok	passed
A49	ok	NP	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	passed
A60	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	
A61	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	
A69	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	NP	ok	ok	passed
A71	ok	ok	ok	ok	ok	ok	NP	ok	ok	ok	NM	NP	ok	passed NH$_4$ TDN not perf. Alk
D02	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	NP	ok	ok	passed
D05	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	
D06	ok	ok	NP	ok	ok	ok	ok	ok	ok	ok	NP	ok	ok	passed
D24	NP	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	passed
D32	ok	ok	NP	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	passed
D33	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	
D34	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	NM	ok	ok	not performed: soil solution lab
D35	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	
D39	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	
D47	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	NP	NM	not passed
D48	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	
F01	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	NM	NM	not performed: instruments not available
F03	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	NP	ok	passed
F04	NP	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	passed

ok: test passed (at least 50% of the results within the tolerable limits)

NM: not measured

NP: not passed

Lab code	pH	Cond.	Ca	Mg	Na	K	NH$_4$	SO$_4$	NO$_3$	Cl	Alk	TDN	DOC	Requalification
F05	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	
F06	ok	NP	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	passed
F07	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	NM	NP	passed
F08	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	
F10	NP	ok	ok	ok	ok	ok	ok	NP	NP	ok	ok	ok	ok	passed
F12	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	
F14	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	
F15	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	
F16	NP	ok	ok	ok	ok	ok	NP	ok	ok	ok	ok	ok	ok	passed
F17	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	NP	NP	passed
F18	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	
F21	NP	ok	NP	ok	ok	NP	ok	NP	ok	NP	NP	NP	ok	not performed: TDN, Alk passed: others
F23	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	
F24	ok	NP	ok	NP	NP	ok	NP	ok	ok	ok	ok	ok	ok	passed
F25	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	
F27	NP	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	passed
F28	ok	ok	NP	NP	NP	ok	NP	ok	ok	ok	ok	ok	ok	passed
F30	ok	ok	ok	ok	ok	ok	ok	NP	ok	ok	NP	ok	ok	passed: Alk not passed: SO$_4$
F32	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	
S03	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	
S25	ok	ok	ok	ok	ok	ok	ok	NP	ok	ok	ok	ok	ok	passed