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ATMOSPHERIC DEPOSITION AND SOIL SOLUTION WORKING RING TEST 2009

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EU/Life+ Project LIFE07 ENV/D/000218
FutMon "Further Development and Implementation of an EU-level Forest Monitoring System"

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

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FutMon "Further Development and Implementation of an EU-level Forest Monitoring System"

TABLE OF CONTENTS

SUMMARY

A 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.

Four natural atmospheric deposition and soil solution samples and 4 synthetic solutions were distributed to 44 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 16% 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.

Some of the analytical methods used by individual laboratories were found to be unsuitable for the samples included in this WRT, and therefore also for the routine analysis of atmospheric deposition and soil solution samples in European forests. These methods included outdated methods, such as turbidimetry or nephelometry for the determination of sulphate, silver nitrate titration and ion selective electrode for chloride, Kjeldahl digestion for the determination of ammonium and organic nitrogen, and colorimetric titrations for alkalinity.

A detailed discussion of the determination of total alkalinity is also given in the report because this variable was associated with the most analytical problems.

ACKNOWLEDGMENTS

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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.

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

Two WRTs for deposition and soil solution chemistry have already been carried out, one in 2002 (EU co-funding) and one in 2005 (co-financed by the EU/Forest Focus programme), 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).

The main purpose of the two 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.

Two WRTs are planned within the FutMon Project, one in 2009 and one in 2010. All the laboratories co-funded under FutMon must participate in both WRTs, and any laboratory which does not reach a minimum data quality must submit a re-qualification report, outlining the analytical problems encountered and the solutions adopted, and then submit new results. The qualification reports are reported in Appendix B.

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 defining tolerable limits, less stringent limits were adopted by the WG on QA/QC for samples with lower concentrations.

FutMon laboratories with more than 50% of their results lying outside the tolerable limits values have to requalify.

In this report we identify the most critical analytical methods and highlight the need for efforts to improve laboratory performances and analytical quality. We also provide guidelines for quality assurance and control and for data validation.

Finally, the report includes a detailed discussion will on the determination of alkalinity, which appeared to be the most problematic analytical technique in this WRT.

1.1. Aims

The aims of the FutMon WRT 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.

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 (co-chairperson of the ICP Forests Expert Panel on Soil, leader of FutMon action C1-SS-10 (FI));
- Anna Kowalska;
- Rosario Mosello;
- Gabriele Tartari;
- Aldo Marchetto (leader of FutMon action C1-Water-40 (IT)).

Registration for the WRT was open until March 7th, 2009, and the samples were sent out in March. The deadline for submitting the results was fixed as May 9th, 2009.

All the laboratories received a qualification report on August 18th. Where appropriate, certain laboratories were informed about the need for carrying out the re-qualification procedure, the deadline for which was fixed as September 30th, 2009.

This draft report will be distributed at the beginning of October, and discussed at a meeting of the heads of the laboratories in Warsaw, October 12-13th, 2009.

The final report will be published before the end of 2009.

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 futher 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:

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

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

$$\text{AR\%} = \pm\, 0.5 * \text{IQR} * 100 / \text{Median}$$

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

$$\text{AR}_{\text{pH}} = \pm\, 0.5 * \text{IQR}$$

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 µS 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 µeq 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

3.1. The water samples

Four natural samples, consisting of throughfall (Samples 1 and 2) and soil solution (Samples 3 and 4), and 4 synthetic samples for the determination of alkalinity (SYN 5 and 6), and DOC and Total N (SYN 7 and 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 DOC, TDN and alkalinity on bottles representing each sample (see Section 3.2). The relative standard deviation was calculated for the four variables. No statistically significant variation was found between the selected samples, and the samples were therefore considered to be fully homogeneous.

The standard deviation of the analyses of the six samples are reported in Table 3.1. The values also include measurement errors.

Parameter	Sample 1	Sample 2	Sample 3	Sample 4	SYN 5	SYN 6	SYN 7	SYN 8
DOC	5.3%	3.2%	0.6%	1.8%	-	-	0.4%	0.2%
TDN	1.2%	1.5%	2.7%	1.8%	-	-	2.8%	3.5%
Alkalinity	-	-	-	-	3.2%	1.9%		

The measurement errors, determined from the standard deviation of three replicate analyses on the same sample, are given in Table 3.2:

Parameter	Sample 1	Sample 2	Sample 3	Sample 4	SYN 5	SYN 6	SYN 7	SYN 8
DOC	1.3%	0.4%	0.2%	0.3%	-	-	0.8%	0.2%
TDN	0.3%	0.2%	2.2%	1.0%	-	-	0.5%	0.1%
Alkalinity	-	-	-	-	1.1%	1.1%		

3.4. Stability of the samples

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

The relative standard deviation was calculated for all the variables, and the composition of the samples remained in most case within 50% of the tolerable limits.

The analyses were carried out independently for the whole period in three laboratories: at METLA, in Finland, at CNR-ISE in Italy, and in triplicate at NW-FVA in Germany. The results of the latter are shown in Fig. 3.1.

Most of the variability is within 20-30% of the tolerable limits for the whole period of analysis, and only a few samples drifted outside 50% of the tolerable limit. A single variable and samples shifted out of the tolerable limit at the end of the sixth month, namely ammonium at very low level in sample S4, rich in organic matter. This value did not concern the results presented in this report, as all the analysis were performed before May 9th, but it was considered when evaluating requalification results.

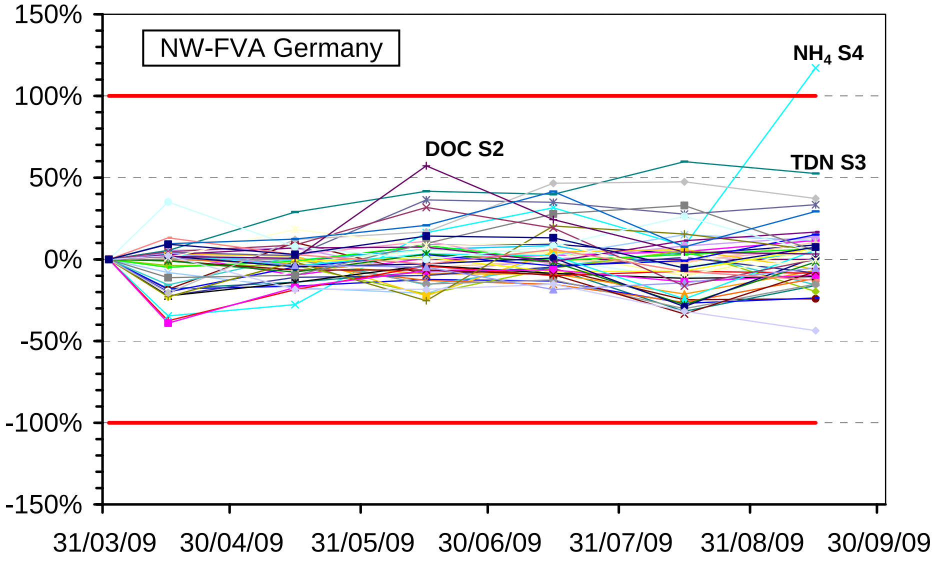


Fig. 3.1. Variations in the concentration of the WRT samples, expressed in percentage of the tolerable limit for each sample and variable.

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.

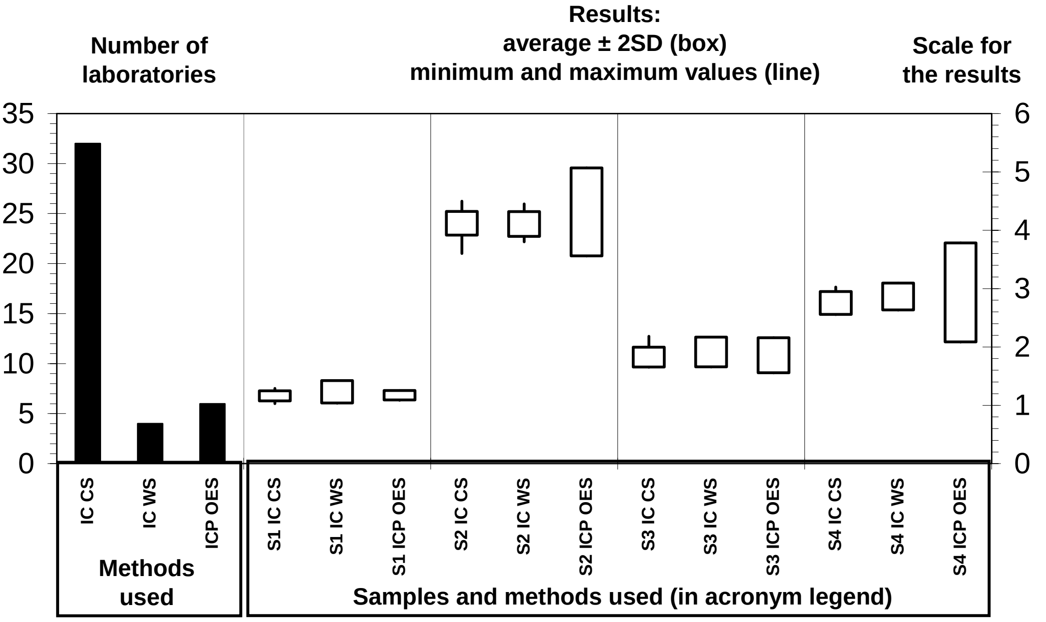


Fig. 4.1. Example showing presentation of the results. The number of laboratories using each analytical method is indicated by the bars on the left, with the scale on the left side of the plot.
The box-and-whiskers graphs on the right, with their own scale on the right side of the plot, show the ±2-standard-deviation 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 $\pm$ 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;

- 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.

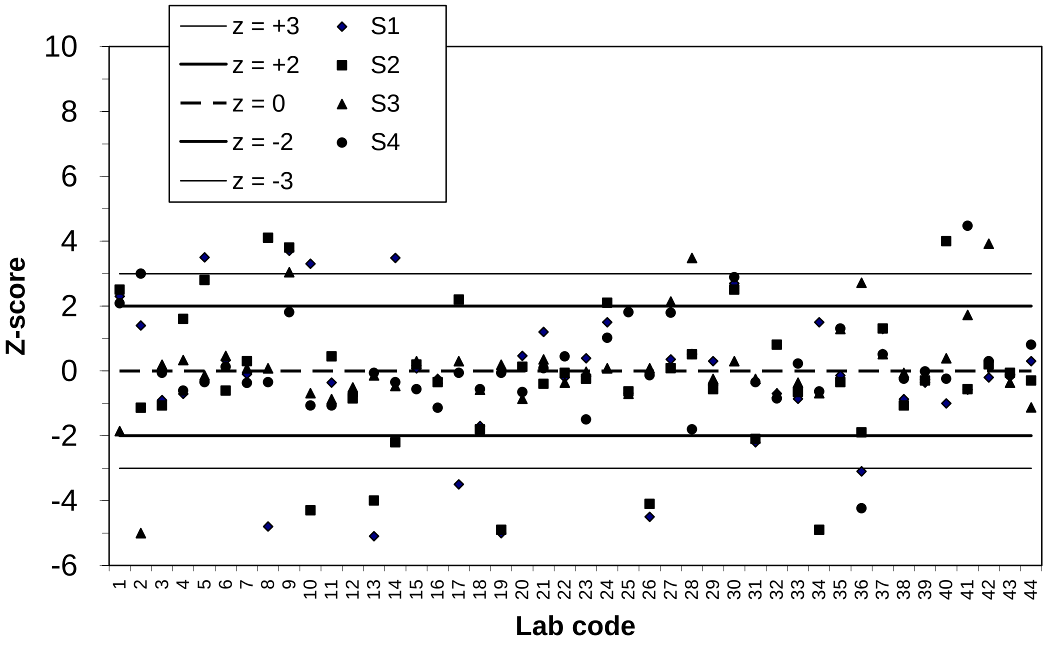


Fig. 4.2. Example of a *z*-score plot.

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.

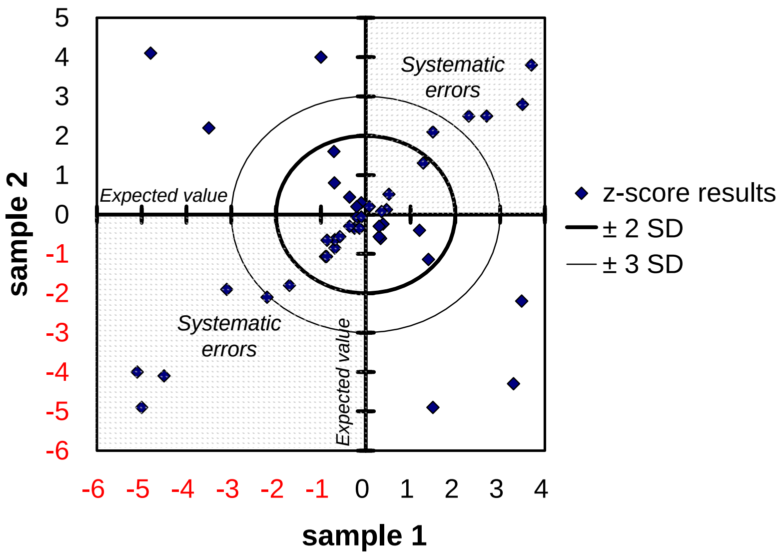


Fig. 4.3. Examples of Youden's plot, with prevailing systematic errors. The data are plotted in z-scores, so that the (robust) mean values line on the axes and the units are imposed standard deviations. The legends on the axes refer to the sample names (Tabs 3.1 and 3.2), while the ellipses indicate 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 $\mu S\ cm^{-1}$, where $1\ mS\ m^{-1} = 10\ \mu S\ cm^{-1} = 10\ \mu mho\ cm^{-1}$, 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_∞) 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:

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

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 44 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
France	SGS MULTILAB, Courcouronnes
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	Hessisches Landeslabor - Abt. VI , Kassel
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	24
	GEN	Not specified	20
Conductivity	25°	Measurement performed at 25°C	25
	Corr	Measurement at different temperature, corrected to 25°C	19
Calcium	AAS	Atomic absorption spectrometry	6
	IC CS	Ion chromatography, chemical suppression	10
	IC WS	Ion chromatography, no suppression	3
	ICP OES	ICP optical emission spectrometry	22
Magnesium	AAS	Atomic absorption spectrometry	6
	IC CS	Ion chromatography, chemical suppression	10
	IC WS	Ion chromatography, no suppression	3
	ICP OES	ICP optical emission spectrometry	21
	ICP MS	ICP mass spectrometry	3
Sodium	AES	Atomic emission spectrometry	4
	IC CS	Ion chromatography, chemical suppression	10
	IC WS	Ion chromatography, no suppression	4
	ICP OES	ICP optical emission spectrometry	21

Chemical variable	**Acronym**	**Analytical method**	**Number of labs**
Potassium	AES	Atomic emission spectrometry	5
	IC CS	Ion chromatography, chemical suppression	10
	IC WS	Ion chromatography, no suppression	4
	ICP OES	ICP optical emission spectrometry	21
Ammonium	SPEC Phe	Spectrophotometry, indophenol blue	7
	CF GD	Continuous flow, ammonia diffusion	10
	CF Phe	Continuous flow, indophenol blue	10
	IC CS	Ion chromatography, chemical suppression	9
	IC WS	Ion chromatography, no suppression	3
Sulphate	IC CS	Ion chromatography, chemical suppression	32
	IC WS	Ion chromatography, no suppression	4
	ICP OES	ICP optical emission spectrometry	6
Nitrate	IC CS	Ion chromatography, chemical suppression	30
	IC WS	Ion chromatography, no suppression	7
Chloride	IC CS	Ion chromatography, chemical suppression	32
	IC WS	Ion chromatography, no suppression	3
	CF HgFe	Continuous flow, Hg thiocyanate in presence of Fe^{++}	4
	CT Hg	Colorimetric titration, Hg nitrate with diphenylcarbazone	3
Alkalinity		Potentiometric titration with extrapolation of the equivalence point:	
	PT_EX 2PF	two end-points	15
	PT_EX Gran	Gran method	6
	PT_1 4.3	end-point at pH=4.3	5
	PT_1 4.5	end-point at pH=4.5	8
TDN	CF Cd	Continuous flow analysis	6
	CHML	Chemioluminescence	17
	KJELD	Kjeldahl digestion	6
	PSOH CF Cd	Persulphate digestion ($K_2S_2O_8$ + NaOH) and continuous flow analysis	5
DOC	THIR	Thermal combustion, IR detection	32
	PSH_UV IR	Persulphate and UV oxidation, IR detection	5

6.2. Expected results

The samples used in the WRT (described in Section 3.1) were natural precipitation samples collected under the canopy within a tree stand, i.e. stand throughfall (samples 1 and 2) and soil solution (samples 3 and 4). Four synthetic samples were also prepared in the laboratory for the measurement of pH and alkalinity (SYN 5, SYN 6), and of TDN and DOC (SYN 6 and SYN 7).

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 throughfall in Europe. The high concentration of DOC in Sample 4 should be noted: the colour of the sample can cause some problems in spectrophotometric determination.

The measured values of pH in samples SYN 5 and SYN 6 are not reported in Table 6.2, nor in the following discussion, because the procedure for calculating the robust average converged into a value that was very different from the median value and outside the cluster of the data results. These values were not used for laboratory qualification, either.

In the case of DOC, we report the results for all the six samples in which it should have been determined. However, for the purpose of laboratory qualification, only samples SYN 7 and SYN 8 were used in case the organic matter in samples 1-4 had degraded during the course of the WRT.. However, the stability tests indicated that only modest degradation had occurred, so the results of the six samples are discussed here.

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

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

Parameter	**unit**	**S1**	**S2**	**S3**	**S4**	**SYN5**	**SYN6**	**SYN7**	**SYN8**
pH	mg L^{-1}	4.76	5.82	5.27	4.84				
Conductivity (at 25°C)	µS cm^{-1}	29.0	85.4	24.1	62.7				
Calcium	mg L^{-1}	0.090	0.39	1.06	6.05				
Magnesium	mg L^{-1}	0.043	0.16	0.41	1.60				
Sodium	mg L^{-1}	0.35	1.01	1.63	2.59				
Potassium	mg L^{-1}	2.46	9.79	0.44	1.73				
Ammonium	mg N L^{-1}	0.83	3.71	0.02	0.16				
Sulphate	mg S L^{-1}	1.16	4.12	1.82	2.78				
Nitrate	mg N L^{-1}	1.11	3.53	0.15	0.05				
Chloride	mg L^{-1}	0.42	1.52	0.87	2.52				
Alkalinity	µeq L^{-1}					33.0	79.4		
TDN	mg L^{-1}	2.01	7.59	0.39	1.59			2.19	14.6
DOC	mg L^{-1}	1.62	8.03	7.00	60.4			5.79	52.8

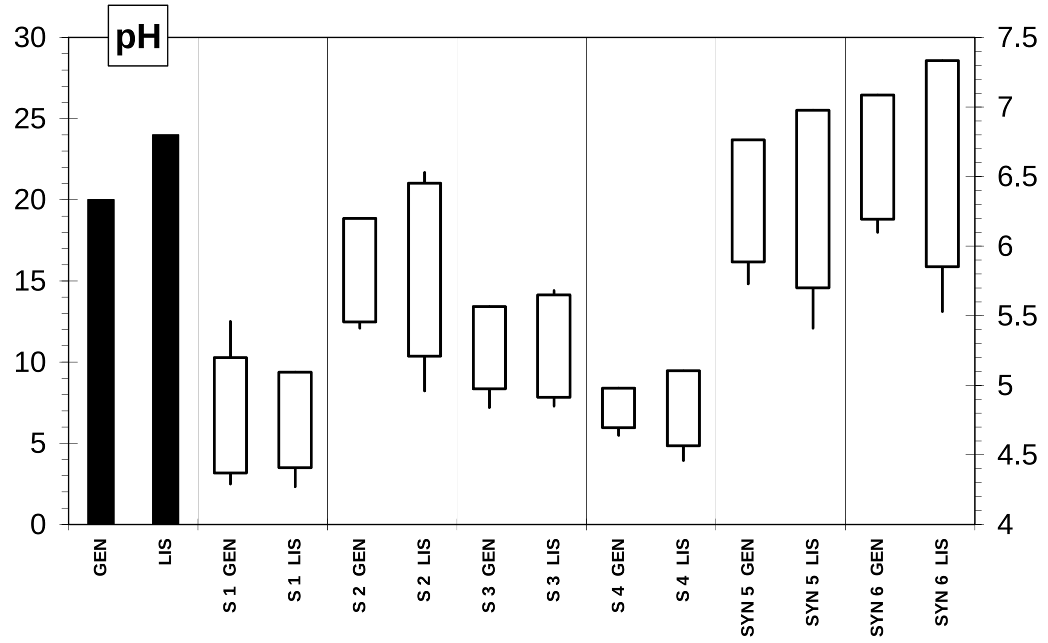
6.3. Overall performance of the laboratories

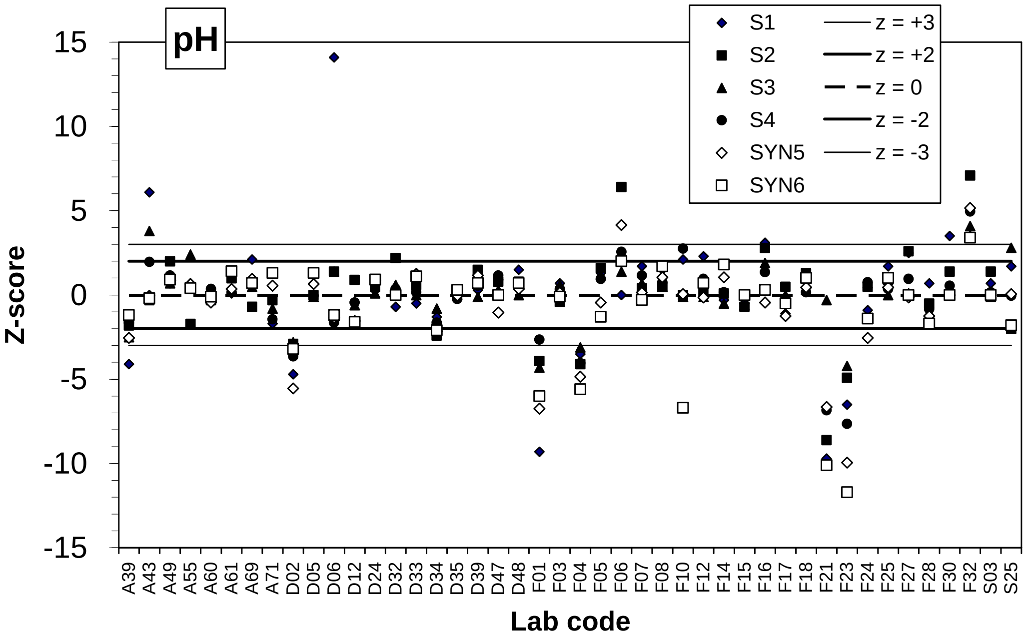
Less than 6% of the samples were not analyzed for most of the mandatory variables. The proportion increases to 11-16% in the case of TDN, DOC and aluminium. These percentages are lower than those reported in the previous WRTs (Mosello *et al.* 2002, Marchetto *et al.* 2006), but they are surprisingly high when we consider that the analysis of these variables is mandatory under certain conditions for deposition and/or soil solution samples.

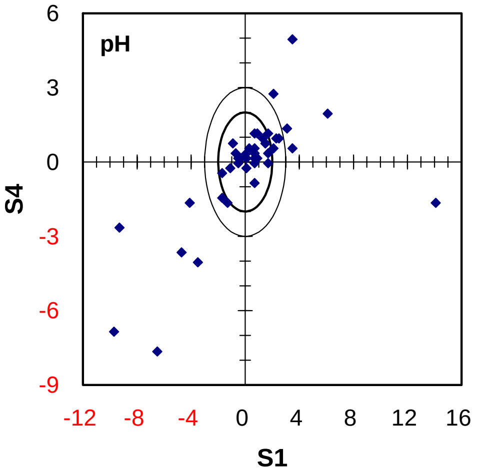
Table 6.3 also shows the proportion of measurements that fell within the tolerable limits given in Table 2.1. For most of the variables the proportion of results falling within the acceptance range is more than 71%, with the highest value for sodium and the lowest for calcium and TDN. On the other hand, the proportion of values outside the tolerable limit for alkalinity is 36%.

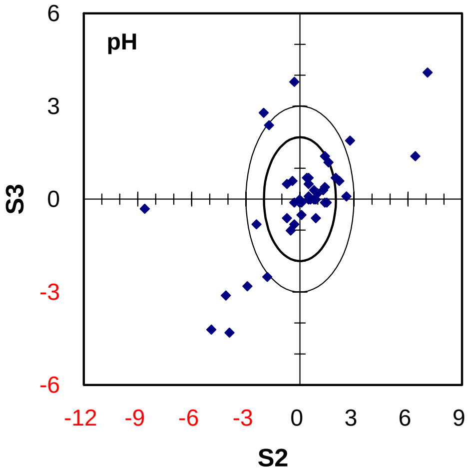
Table 6.3 – Quality performance of the laboratory set for each mandatory variable: TL = tolerable limit (see chapter 2), LOQ = limit of quantitation.

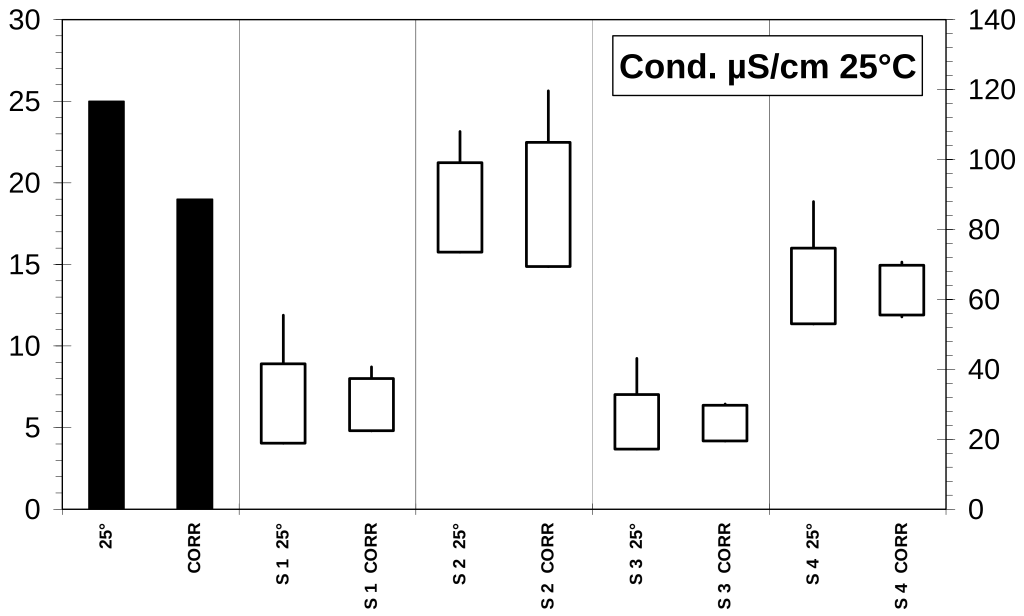
Parameter	Within TL	Outside TL	Not measured	Below LOQ
pH	77%	23%	0%	0%
Conductivity	84%	16%	0%	0%
Calcium	71%	23%	2%	4%
Magnesium	82%	12%	6%	0%
Sodium	89%	9%	2%	0%
Potassium	85%	12%	2%	1%
Ammonium	65%	26%	0%	9%
Sulphate	88%	10%	2%	0%
Nitrate	86%	12%	0%	2%
Chloride	82%	8%	2%	7%
Alkalinity	54%	36%	3%	7%
TDN	71%	13%	16%	0%
DOC	72%	17%	11%	0%
Total	78%	16%	4%	2%

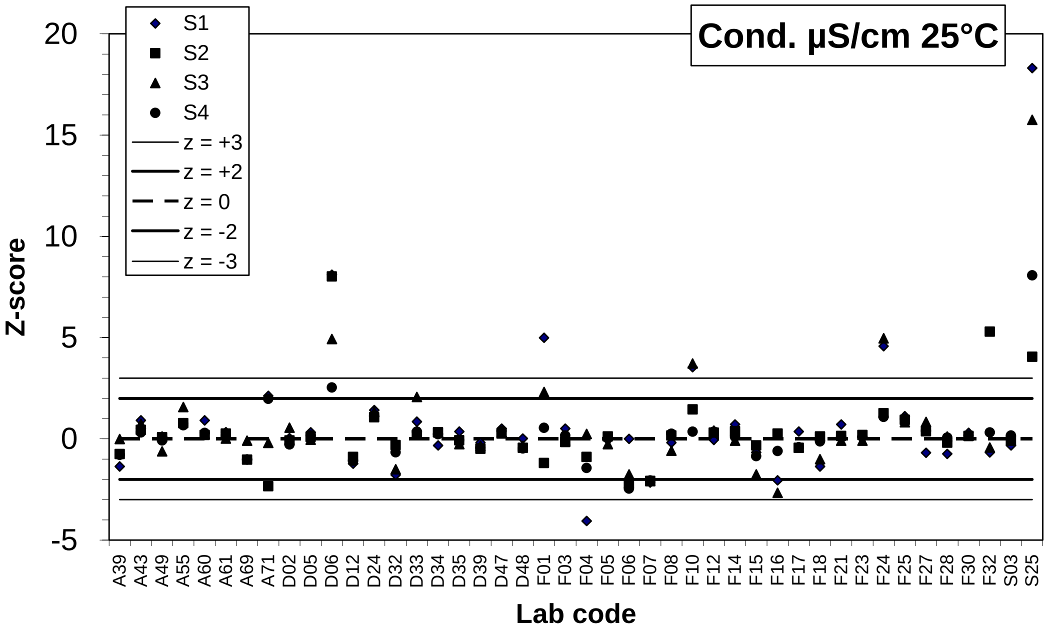

pH
30
25
20
15
10
5
0
7.5
7
6.5
6
5.5
5
4.5
4
GEN
LIS
S 1 GEN
S 1 LIS
S 2 GEN
S 2 LIS
S 3 GEN
S 3 LIS
S 4 GEN
S 4 LIS
SYN 5 GEN
SYN 5 LIS
SYN 6 GEN
SYN 6 LIS

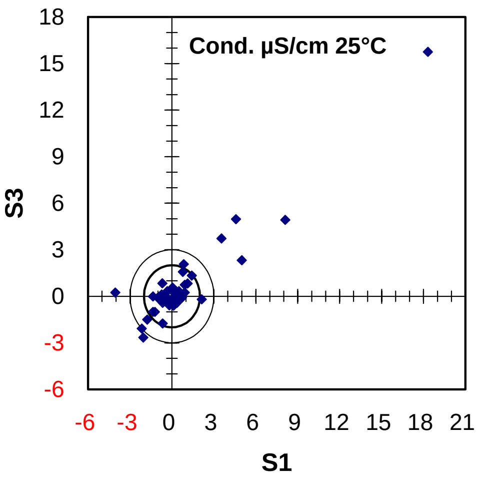

pH
S1
S2
S3
S4
SYN5
SYN6
z = +3
z = +2
z = 0
z = -2
z = -3
15
10
5
0
-5
-10
-15
Z-score
A39 A43 A49 A55 A60 A61 A69 A71 D02 D05 D06 D12 D24 D32 D33 D34 D35 D39 D47 D48 F01 F03 F04 F05 F06 F07 F08 F10 F12 F14 F15 F16 F17 F18 F21 F23 F24 F25 F27 F28 F30 F32 S03 S25
Lab code

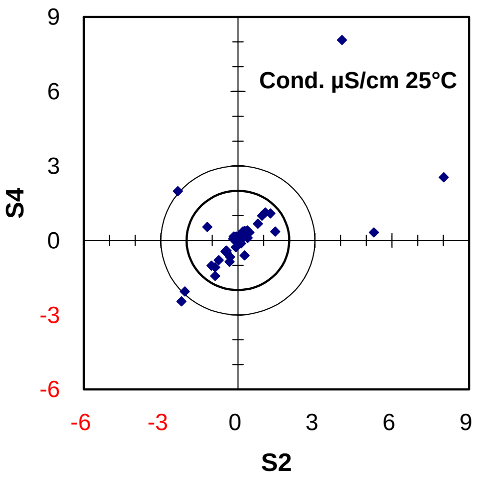

pH
6
3
0
-3
-6
-9
S4
-12
-8
-4
0
4
8
12
16
S1

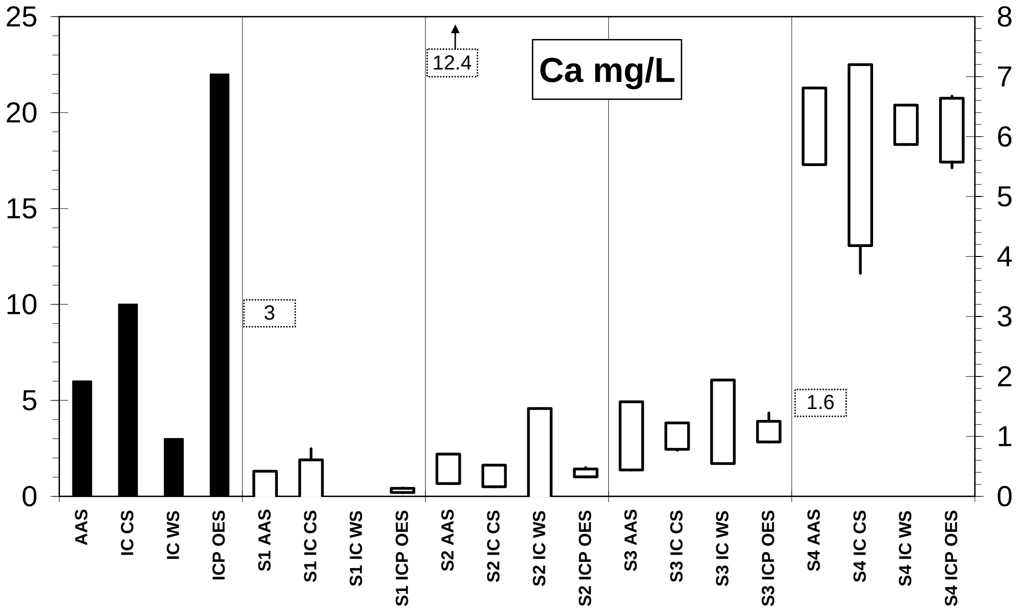

pH
6
3
0
-3
-6
S3
-12
-9
-6
-3
0
3
6
9
S2

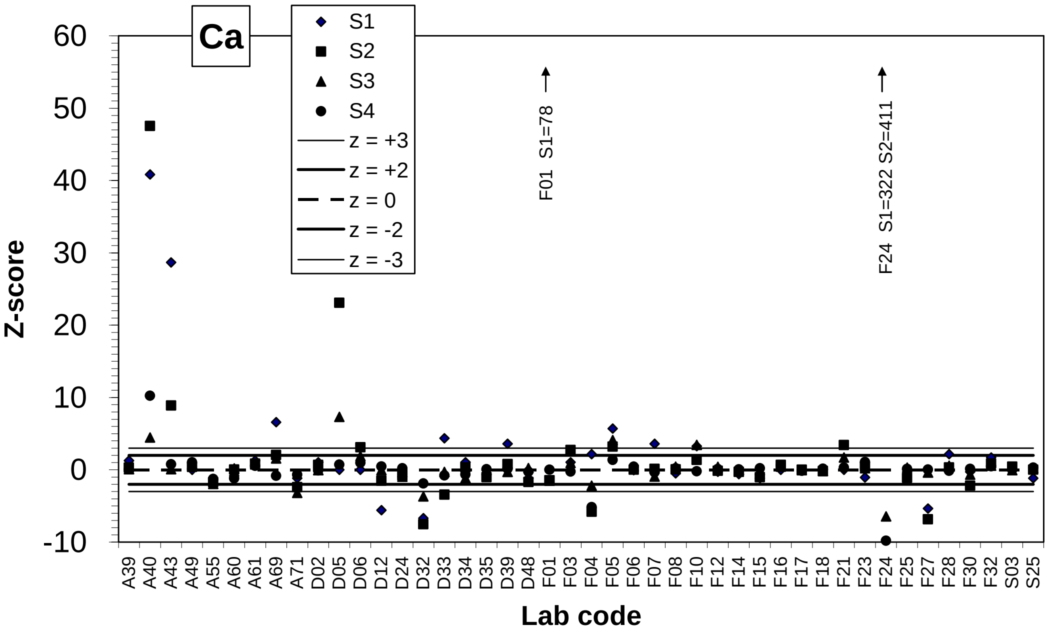

Cond. µS/cm 25°C
30
25
20
15
10
5
0
140
120
100
80
60
40
20
0
25°
CORR
S 1 25°
S 1 CORR
S 2 25°
S 2 CORR
S 3 25°
S 3 CORR
S 4 25°
S 4 CORR


Cond. µS/cm 25°C
S1
S2
S3
S4
z = +3
z = +2
z = 0
z = -2
z = -3
Z-score
20
15
10
5
0
-5
A39
A43
A49
A55
A60
A61
A69
A71
D02
D05
D06
D12
D24
D32
D33
D34
D35
D39
D47
D48
F01
F03
F04
F05
F06
F07
F08
F10
F12
F14
F15
F16
F17
F18
F21
F23
F24
F25
F27
F28
F30
F32
S03
S25
Lab code


Cond. µS/cm 25°C
S3
18
15
12
9
6
3
0
-3
-6
-6
-3
0
3
6
9
12
15
18
21
S1


Cond. µS/cm 25°C
S4
9
6
3
0
-3
-6
-6
-3
0
3
6
9
S2


Ca mg/L
25
20
15
10
5
0
8
7
6
5
4
3
2
1
0
3
12.4
1.6
AAS
IC CS
IC WS
ICP OES
S1 AAS
S1 IC CS
S1 IC WS
S1 ICP OES
S2 AAS
S2 IC CS
S2 IC WS
S2 ICP OES
S3 AAS
S3 IC CS
S3 IC WS
S3 ICP OES
S4 AAS
S4 IC CS
S4 IC WS
S4 ICP OES


Ca
S1
S2
S3
S4
z = +3
z = +2
z = 0
z = -2
z = -3
Z-score
60
50
40
30
20
10
0
-10
F01 S1=78
F24 S1=322 S2=411
A39
A40
A43
A49
A55
A60
A61
A69
A71
D02
D05
D06
D12
D24
D32
D33
D34
D35
D39
D48
F01
F03
F04
F05
F06
F07
F08
F10
F12
F14
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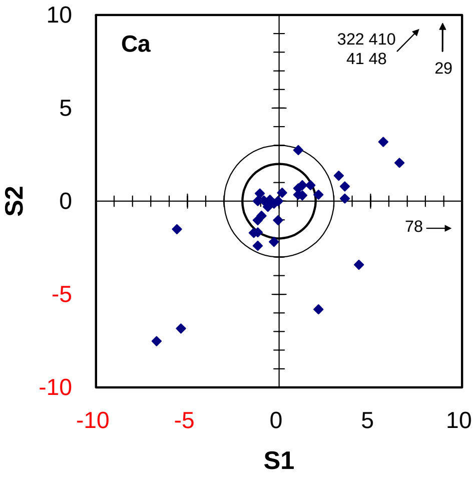
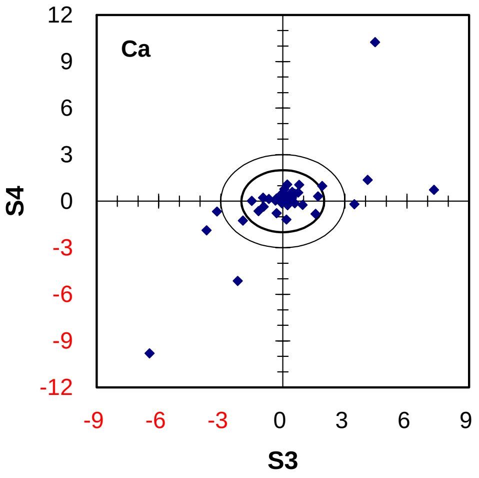
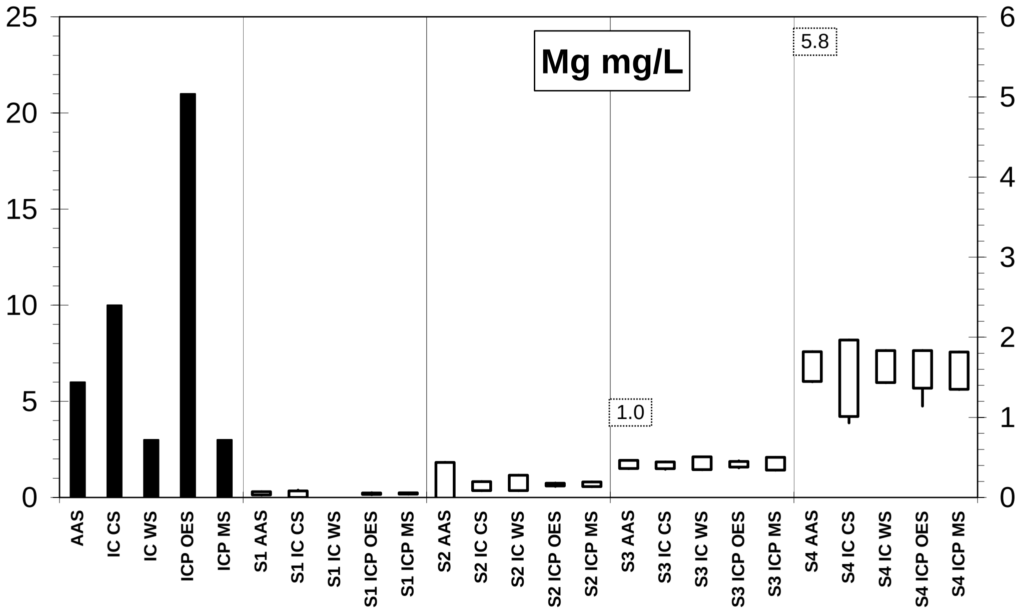
F30
F32
S03
S25
Lab code


Ca
322 410
41 48
29
78
10
5
0
-5
-10
S2
-10
-5
0
5
10
S1


Ca
12
9
6
3
0
-3
-6
-9
-12
S4
-9
-6
-3
0
3
6
9
S3


Mg mg/L
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1.0
25
20
15
10
5
0
6
5
4
3
2
1
0
AAS
IC CS
IC WS
ICP OES
ICP MS
S1 AAS
S1 IC CS
S1 IC WS
S1 ICP OES
S1 ICP MS
S2 AAS
S2 IC CS
S2 IC WS
S2 ICP OES
S2 ICP MS
S3 AAS
S3 IC CS
S3 IC WS
S3 ICP OES
S3 ICP MS
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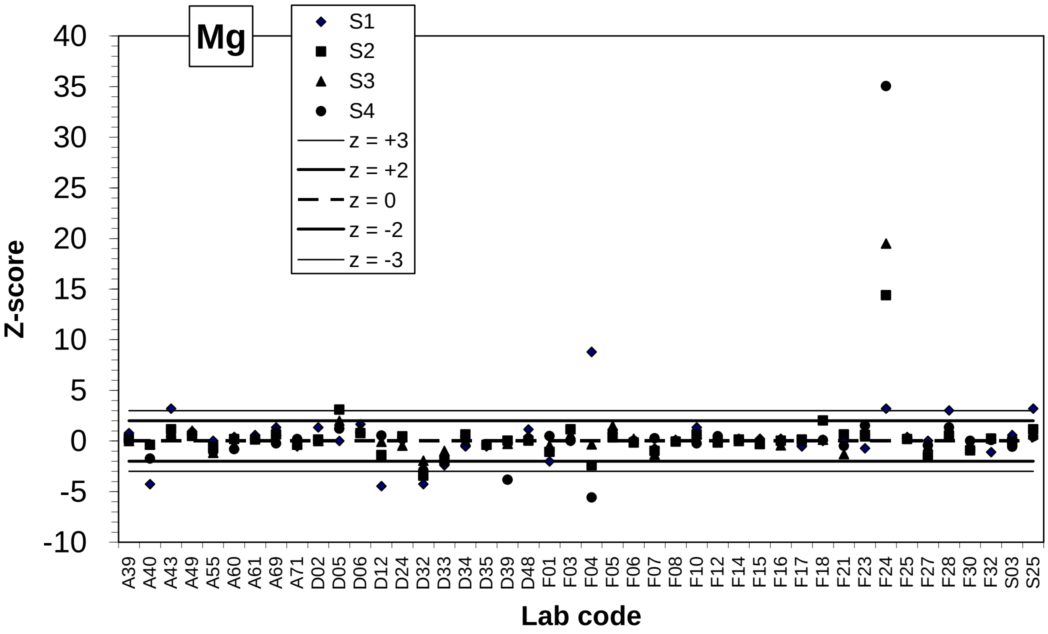
S4 IC WS
S4 ICP OES
S4 ICP MS


Mg
◆ S1
■ S2
▲ S3
● S4
z = +3
z = +2
z = 0
z = -2
z = -3
Z-score
40
35
30
25
20
15
10
5
0
-5
-10
A39
A40
A43
A49
A55
A60
A61
A69
A71
D02
D05
D06
D12
D24
D32
D33
D34
D35
D39
D48
F01
F03
F04
F05
F06
F07
F08
F10
F12
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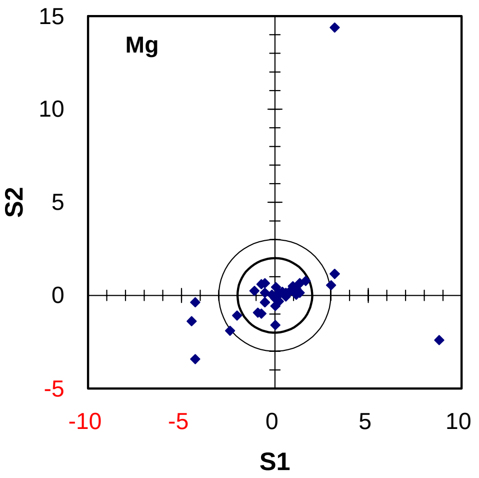
F30
F32
S03
S25
Lab code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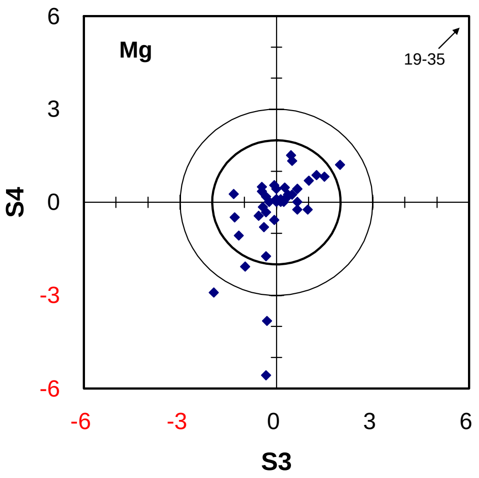
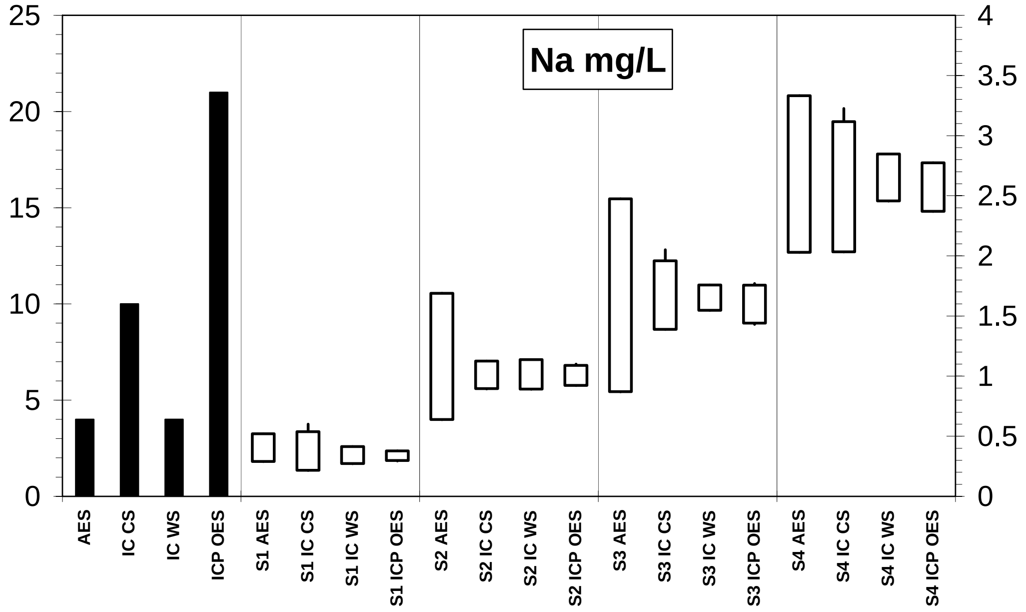
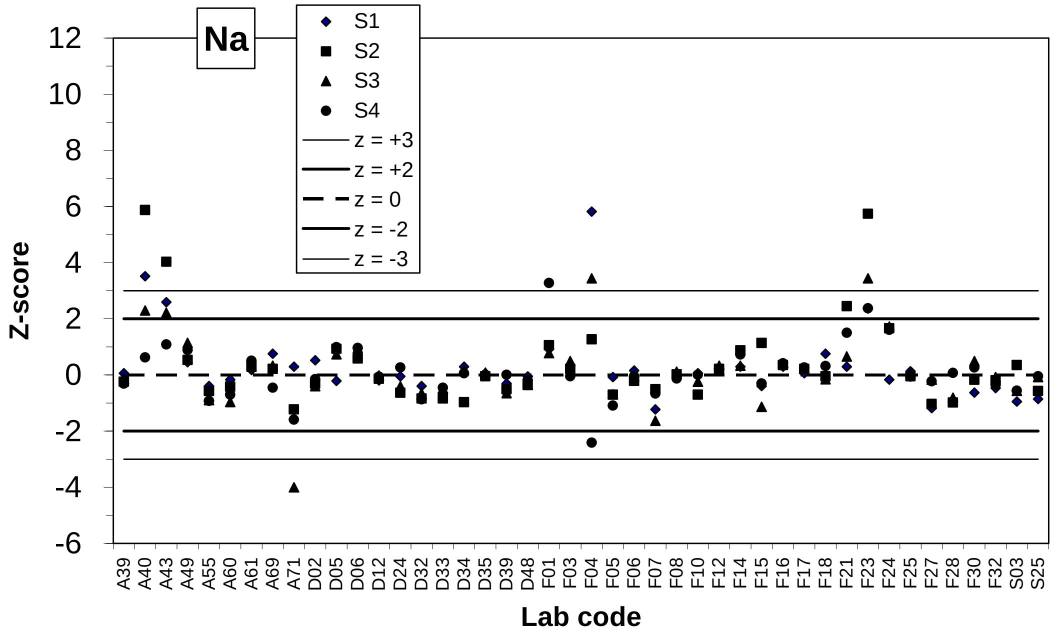
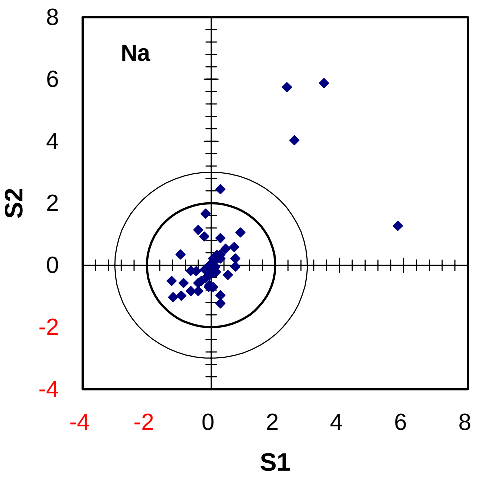
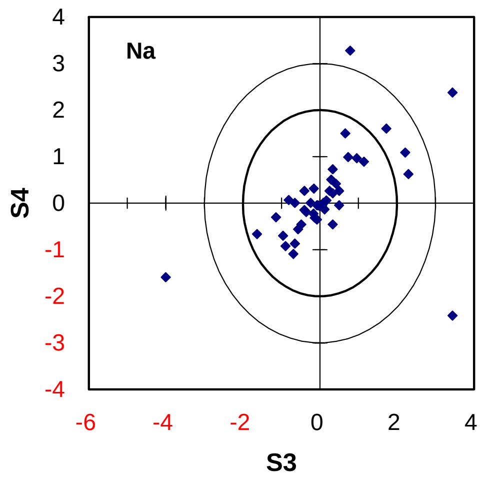
S2
15
10
5
0
-5
-10
-5
0
5
10
S1

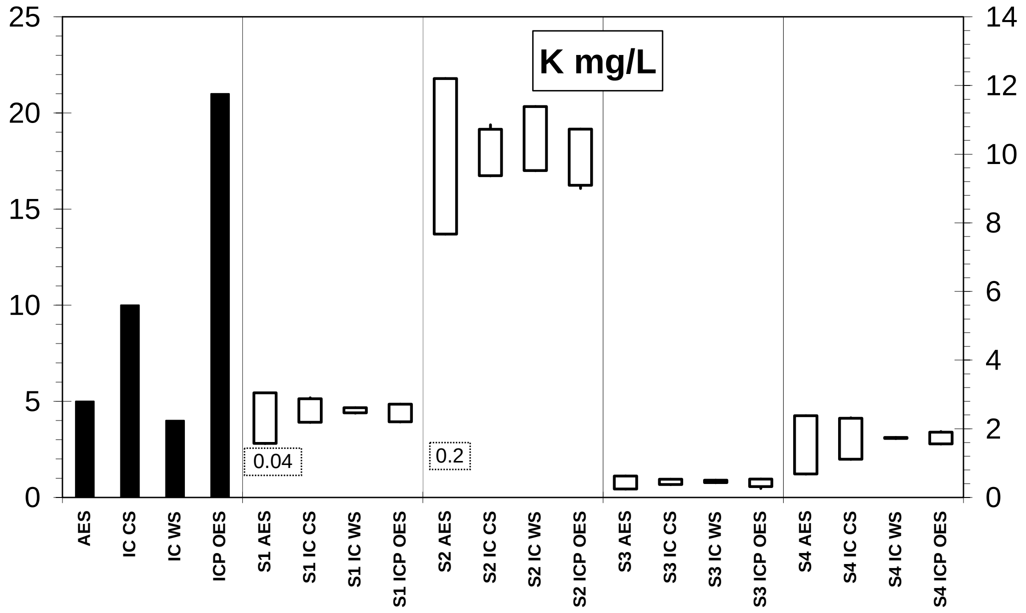

Mg
19-35
S4
6
3
0
-3
-6
-6
-3
0
3
6
S3

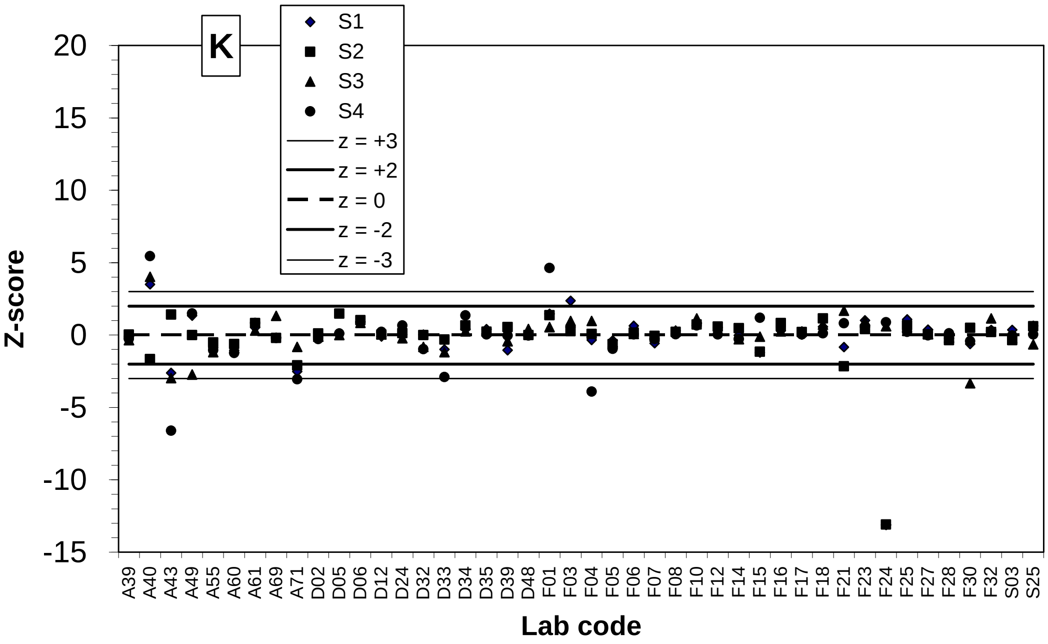

Na mg/L
25
20
15
10
5
0
4
3.5
3
2.5
2
1.5
1
0.5
0
AES
IC CS
IC WS
ICP OES
S1 AES
S1 IC CS
S1 IC WS
S1 ICP OES
S2 AES
S2 IC CS
S2 IC WS
S2 ICP OES
S3 AES
S3 IC CS
S3 IC WS
S3 ICP OES
S4 AES
S4 IC CS
S4 IC WS
S4 ICP OES

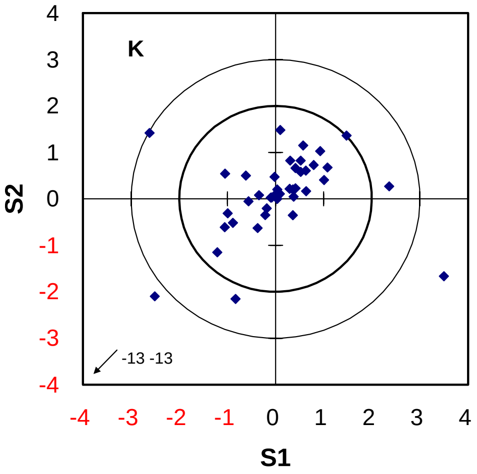

Na
◆ S1
■ S2
▲ S3
● S4
z = +3
z = +2
z = 0
z = -2
z = -3
Z-score
12
10
8
6
4
2
0
-2
-4
-6
A39
A40
A43
A49
A55
A60
A61
A69
A71
D02
D05
D06
D12
D24
D32
D33
D34
D35
D39
D48
F01
F03
F04
F05
F06
F07
F08
F10
F12
F14
F15
F16
F17
F18
F21
F23
F24
F25
F27
F28
F30
F32
S03
S25
Lab code

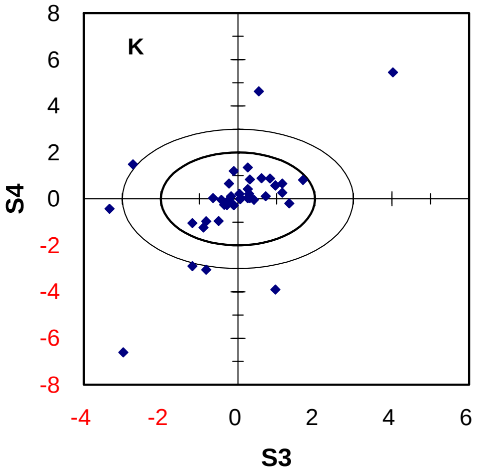

Na
S2
8
6
4
2
0
-2
-4
-4
-2
0
2
4
6
8
S1

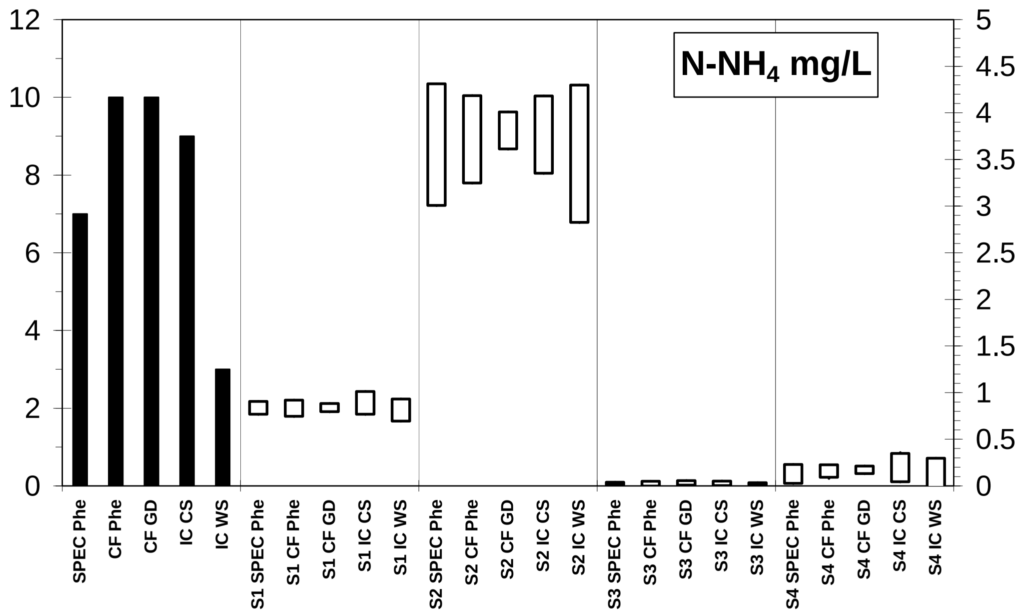

Na
S4
4
3
2
1
0
-1
-2
-3
-4
-6
-4
-2
0
2
4
S3

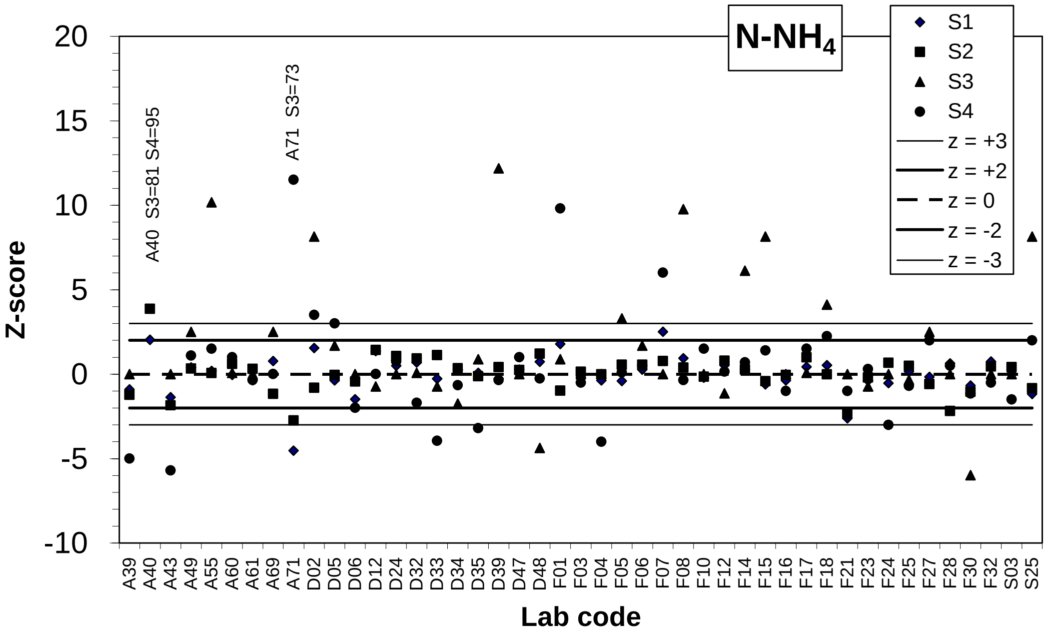

K mg/L
25
20
15
10
5
0
14
12
10
8
6
4
2
0
0.04
0.2
AES
IC CS
IC WS
ICP OES
S1 AES
S1 IC CS
S1 IC WS
S1 ICP OES
S2 AES
S2 IC CS
S2 IC WS
S2 ICP OES
S3 AES
S3 IC CS
S3 IC WS
S3 ICP OES
S4 AES
S4 IC CS
S4 IC WS
S4 ICP OES

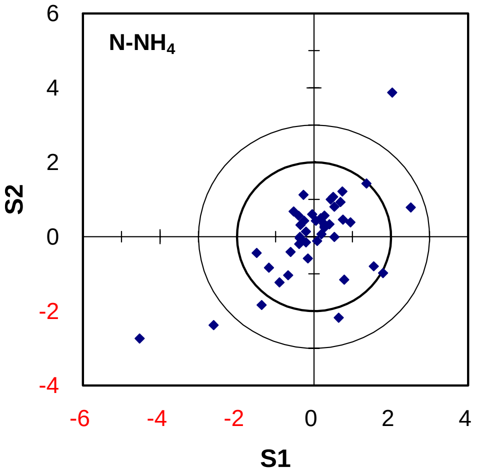

K
S1
S2
S3
S4
z = +3
z = +2
z = 0
z = -2
z = -3
Z-score
20
15
10
5
0
-5
-10
-15
A39
A40
A43
A49
A55
A60
A61
A69
A71
D02
D05
D06
D12
D24
D32
D33
D34
D35
D39
D48
F01
F03
F04
F05
F06
F07
F08
F10
F12
F14
F15
F16
F17
F18
F21
F23
F24
F25
F27
F28
F30
F32
S03
S25
Lab code

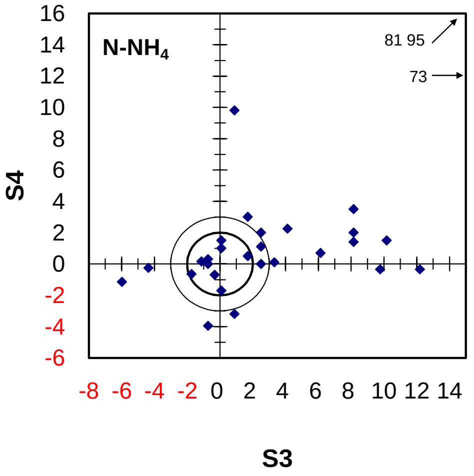

K
S2
S1
4
3
2
1
0
-1
-2
-3
-4
-4
-3
-2
-1
0
1
2
3
4
-13 -13

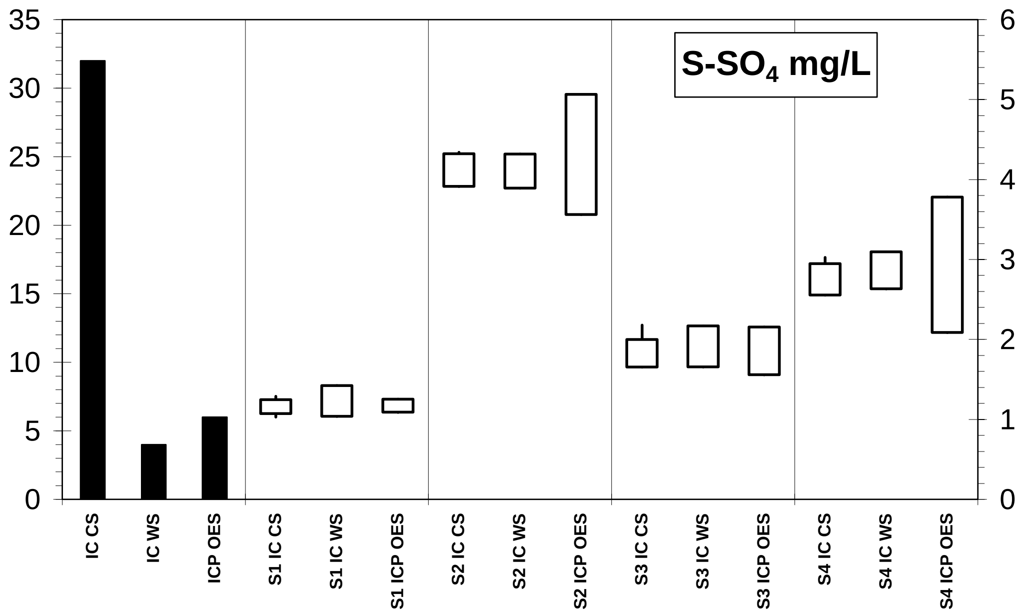

K
S4
S3
8
6
4
2
0
-2
-4
-6
-8
-4
-2
0
2
4
6

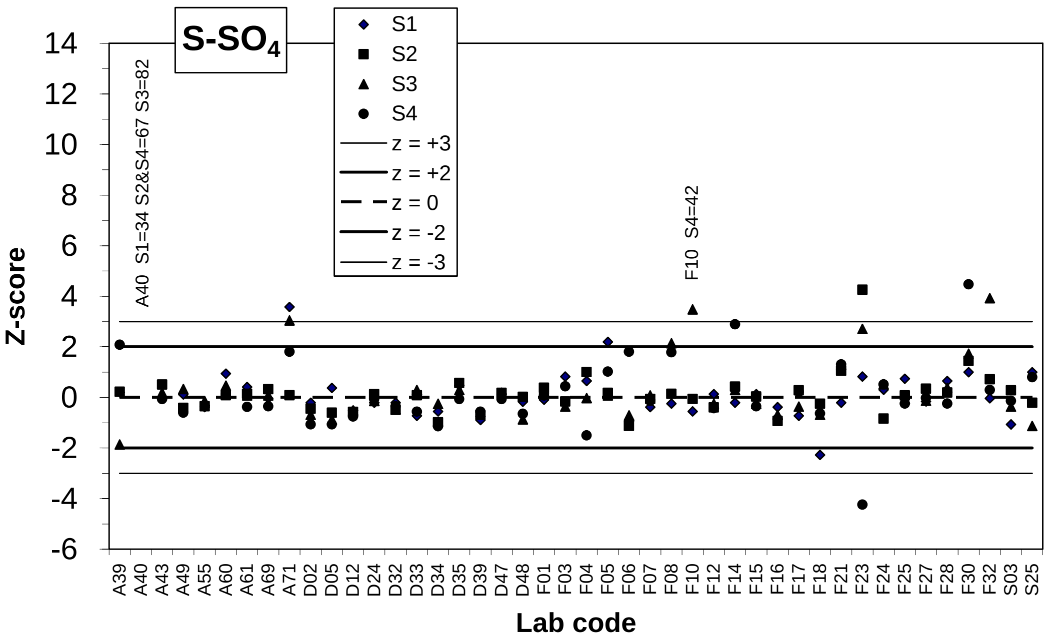

N-NH4 mg/L
12
10
8
6
4
2
0
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
SPEC Phe
CF Phe
CF GD
IC CS
IC WS
S1 SPEC Phe
S1 CF Phe
S1 CF GD
S1 IC CS
S1 IC WS
S2 SPEC Phe
S2 CF Phe
S2 CF GD
S2 IC CS
S2 IC WS
S3 SPEC Phe
S3 CF Phe
S3 CF GD
S3 IC CS
S3 IC WS
S4 SPEC Phe
S4 CF Phe
S4 CF GD
S4 IC CS
S4 IC WS

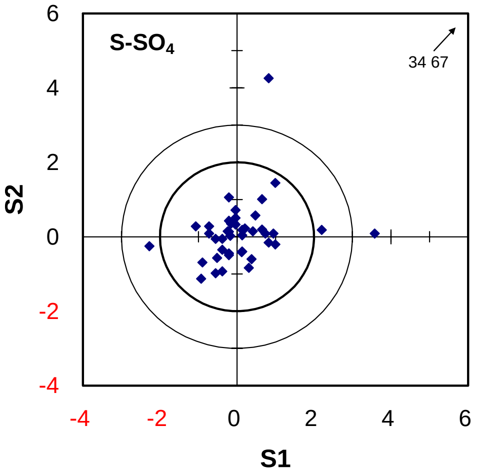

N-NH4
◆ S1
■ S2
▲ S3
● S4
z = +3
z = +2
z = 0
z = -2
z = -3
Z-score
20
15
10
5
0
-5
-10
A40 S3=81 S4=95
A71 S3=73
A39
A40
A43
A49
A55
A60
A61
A69
A71
D02
D05
D06
D12
D24
D32
D33
D34
D35
D39
D47
D48
F01
F03
F04
F05
F06
F07
F08
F10
F12
F14
F15
F16
F17
F18
F21
F23
F24
F25
F27
F28
F30
F32
S03
S25
Lab code

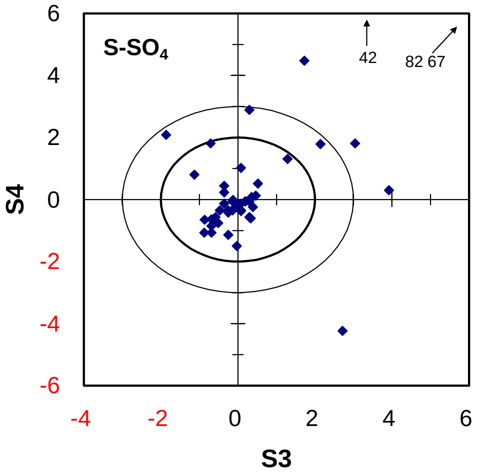

N-NH4
S2
6
4
2
0
-2
-4
-6
-4
-2
0
2
4
S1

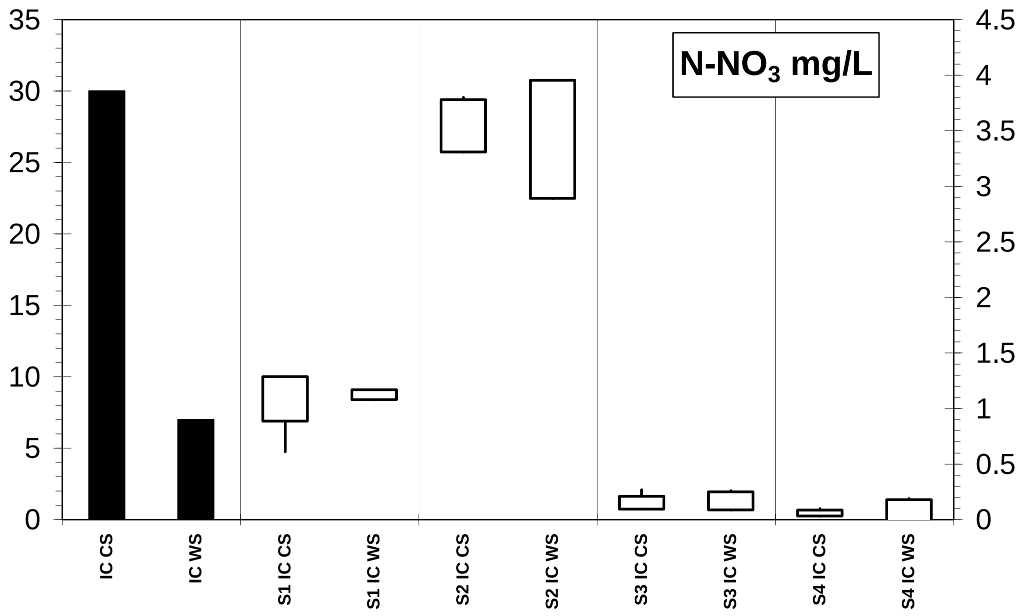

N-NH4
81 95
73
S4
16
14
12
10
8
6
4
2
0
-2
-4
-6
-8
-6
-4
-2
0
2
4
6
8
10
12
14
S3

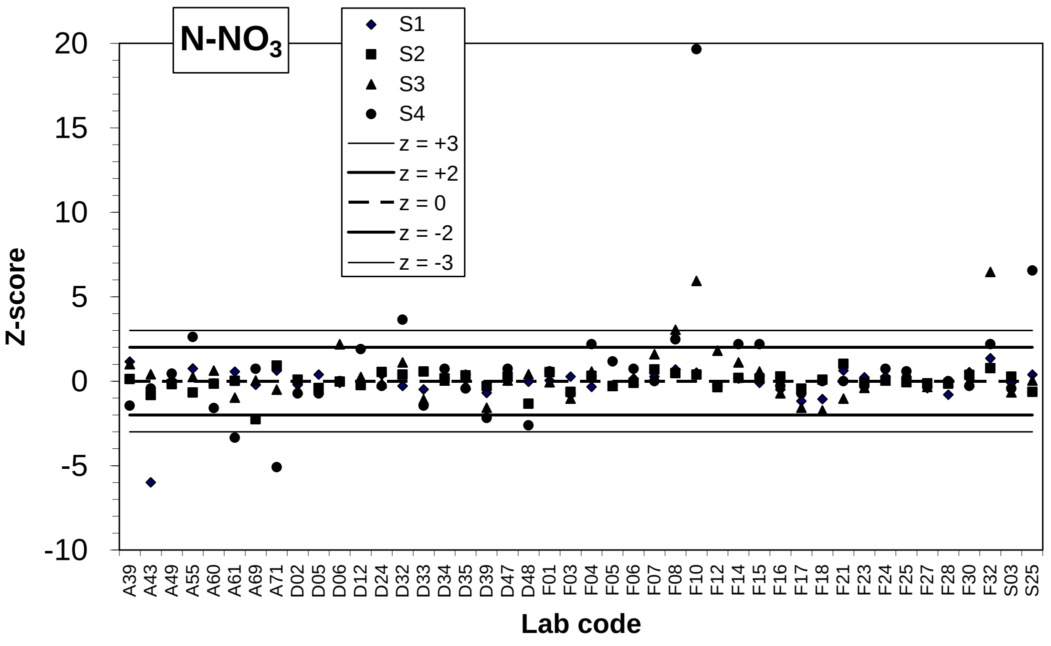

S-SO$_4$ mg/L
35
30
25
20
15
10
5
0
6
5
4
3
2
1
0
IC CS
IC WS
ICP OES
S1 IC CS
S1 IC WS
S1 ICP OES
S2 IC CS
S2 IC WS
S2 ICP OES
S3 IC CS
S3 IC WS
S3 ICP OES
S4 IC CS
S4 IC WS
S4 ICP OES

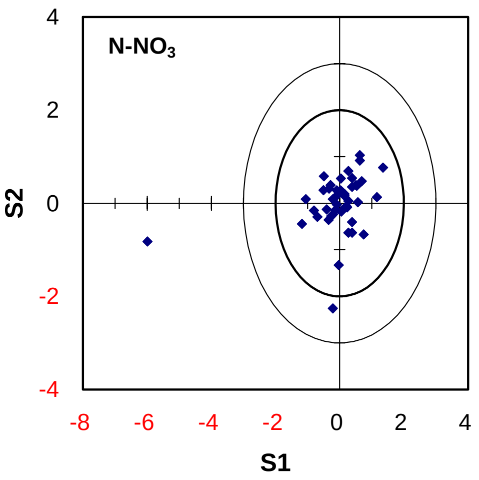

S-SO$_4$
◆ S1
■ S2
▲ S3
● S4
z = +3
z = +2
z = 0
z = -2
z = -3
A40 S1=34 S2&S4=67 S3=82
F10 S4=42
Z-score
14
12
10
8
6
4
2
0
-2
-4
-6
A39
A40
A43
A49
A55
A60
A61
A69
A71
D02
D05
D12
D24
D32
D33
D34
D35
D39
D47
D48
F01
F03
F04
F05
F06
F07
F08
F10
F12
F14
F15
F16
F17
F18
F21
F23
F24
F25
F27
F28
F30
F32
S03
S25
Lab code

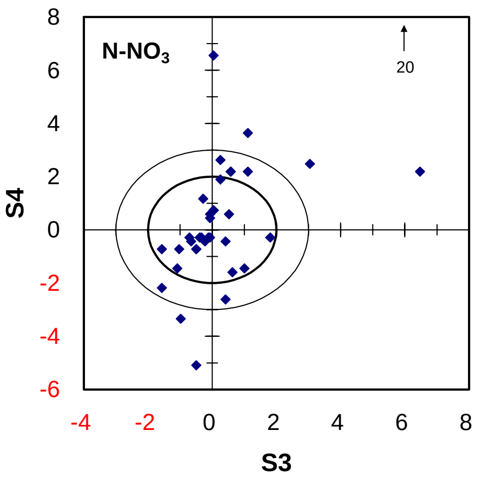

S-SO$_4$
34 67
S2
6
4
2
0
-2
-4
-4
-2
0
2
4
6
S1

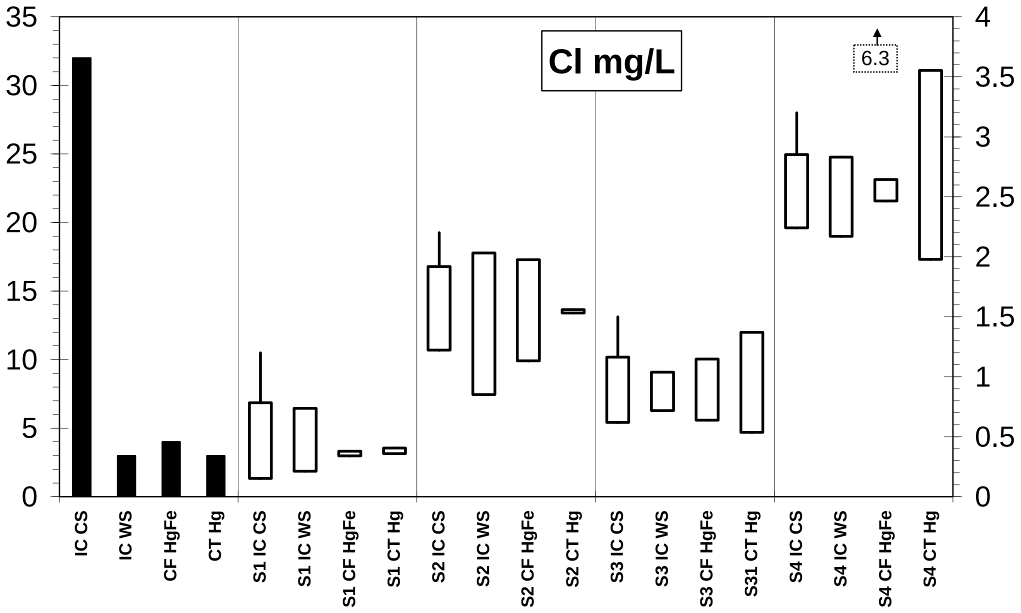

S-SO$_4$
42
82 67
S4
6
4
2
0
-2
-4
-6
-4
-2
0
2
4
6
S3

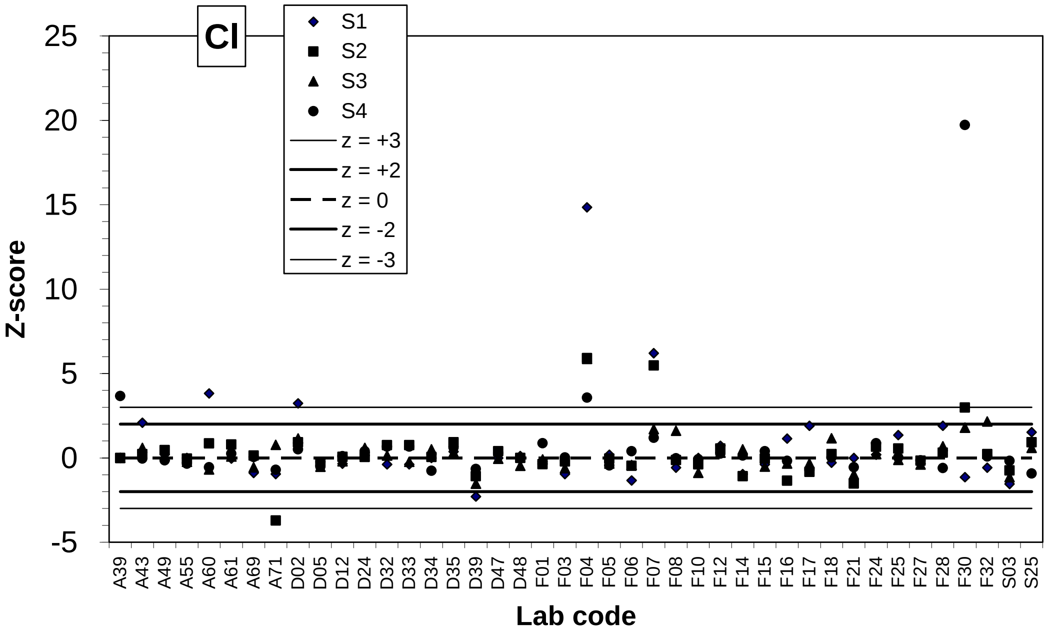

N-NO$_3$ mg/L
35
30
25
20
15
10
5
0
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
IC CS
IC WS
S1 IC CS
S1 IC WS
S2 IC CS
S2 IC WS
S3 IC CS
S3 IC WS
S4 IC CS
S4 IC WS

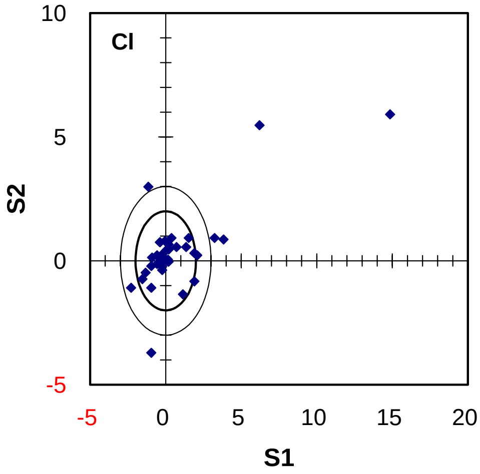

N-NO$_3$
S1
S2
S3
S4
z = +3
z = +2
z = 0
z = -2
z = -3
Z-score
20
15
10
5
0
-5
-10
A39 A43 A49 A55 A60 A61 A69 A71 D02 D05 D06 D12 D24 D32 D33 D34 D35 D39 D47 D48 F01 F03 F04 F05 F06 F07 F08 F10 F12 F14 F15 F16 F17 F18 F21 F23 F24 F25 F27 F28 F30 F32 S03 S25
Lab code

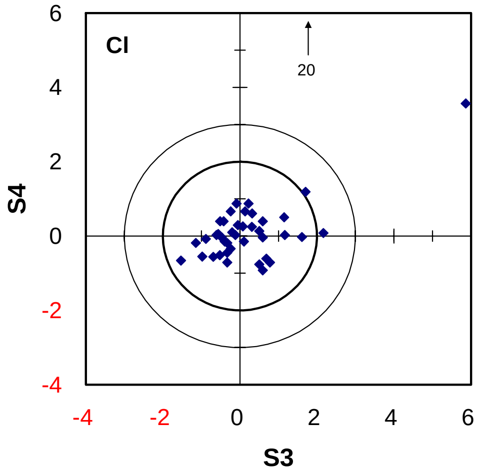

N-NO$_3$
4
2
0
-2
-4
S2
-8
-6
-4
-2
0
2
4
S1

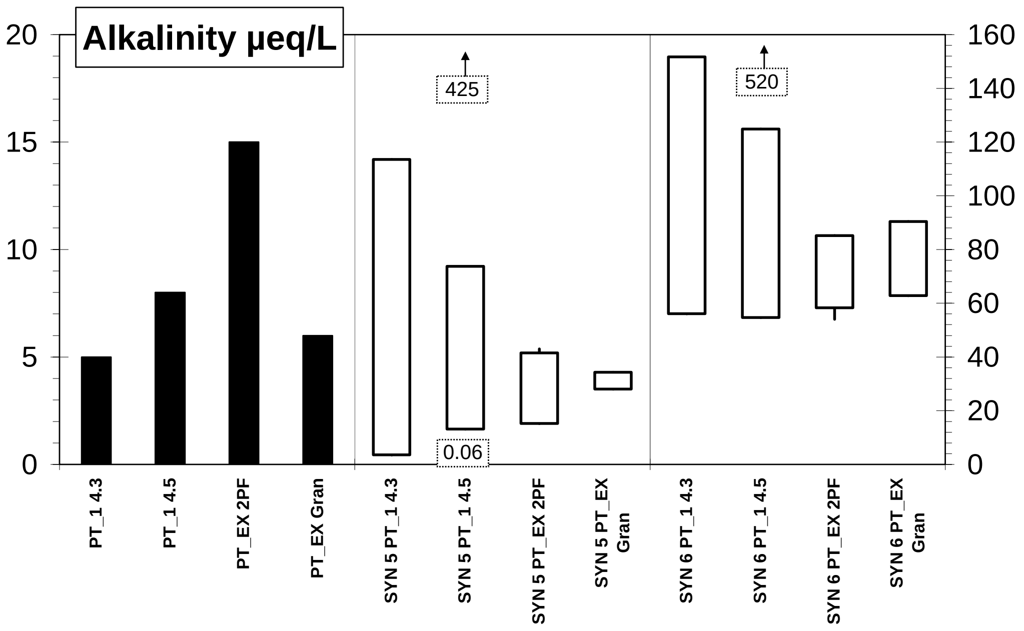

N-NO$_3$
20
8
6
4
2
0
-2
-4
-6
S4
-4
-2
0
2
4
6
8
S3

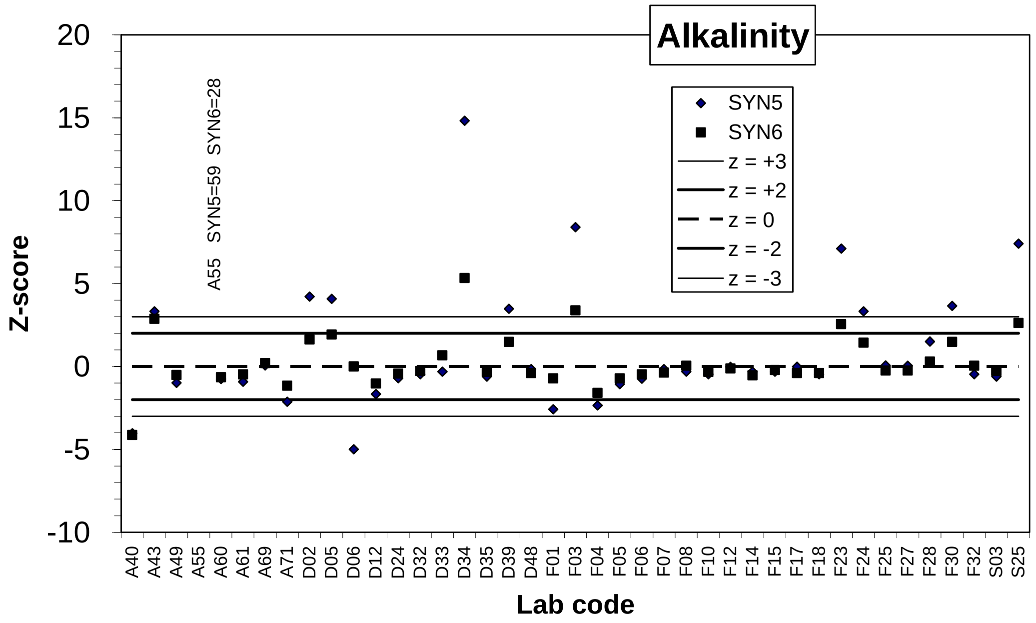

Cl mg/L
6.3
35
30
25
20
15
10
5
0
4
3.5
3
2.5
2
1.5
1
0.5
0
IC CS
IC WS
CF HgFe
CT Hg
S1 IC CS
S1 IC WS
S1 CF HgFe
S1 CT Hg
S2 IC CS
S2 IC WS
S2 CF HgFe
S2 CT Hg
S3 IC CS
S3 IC WS
S3 CF HgFe
S31 CT Hg
S4 IC CS
S4 IC WS
S4 CF HgFe
S4 CT Hg

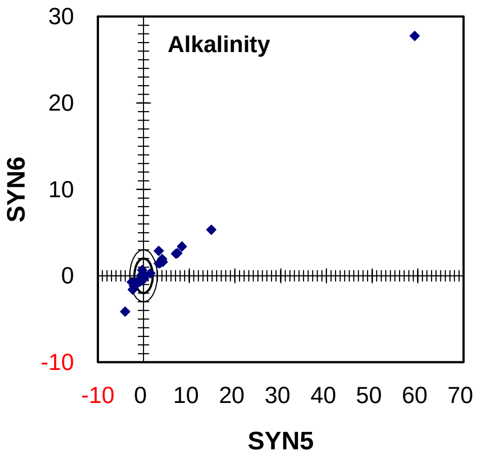

Cl
S1
S2
S3
S4
z = +3
z = +2
z = 0
z = -2
z = -3
Z-score
25
20
15
10
5
0
-5
A39
A43
A49
A55
A60
A61
A69
A71
D02
D05
D12
D24
D32
D33
D34
D35
D39
D47
D48
F01
F03
F04
F05
F06
F07
F08
F10
F12
F14
F15
F16
F17
F18
F21
F24
F25
F27
F28
F30
F32
S03
S25
Lab code

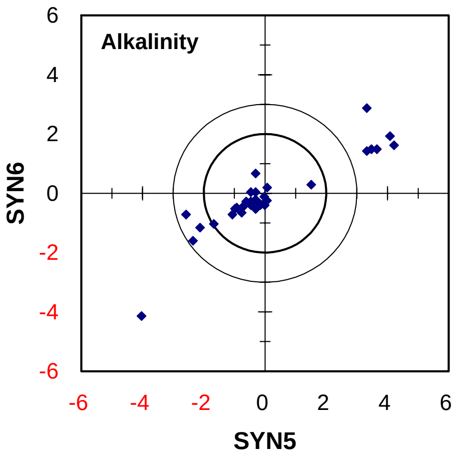

Cl
10
5
0
-5
S2
-5
0
5
10
15
20
S1

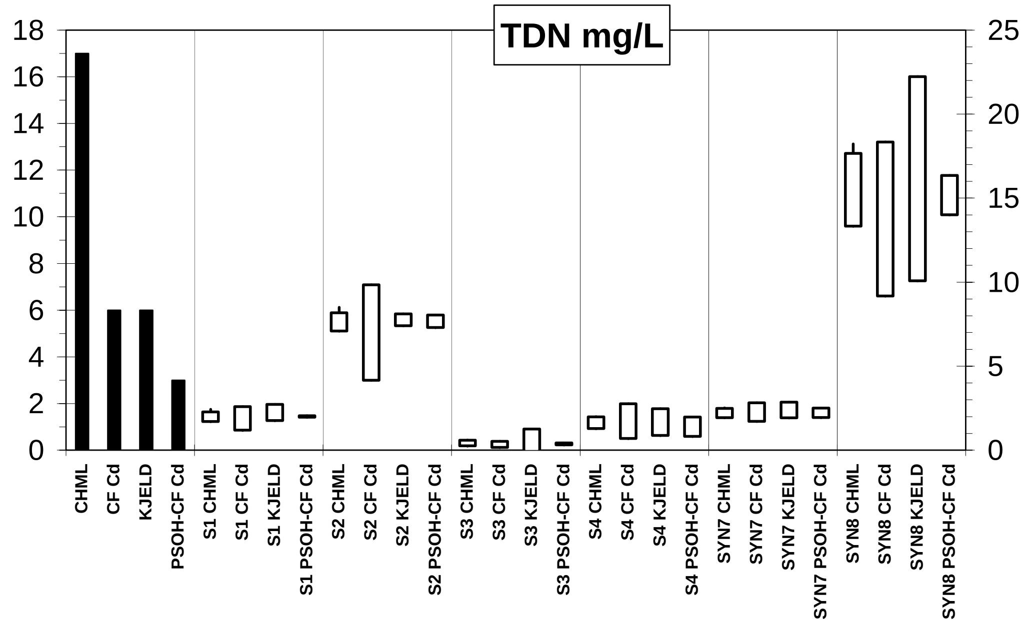

Cl
20
6
4
2
0
-2
-4
S4
-4
-2
0
2
4
6
S3

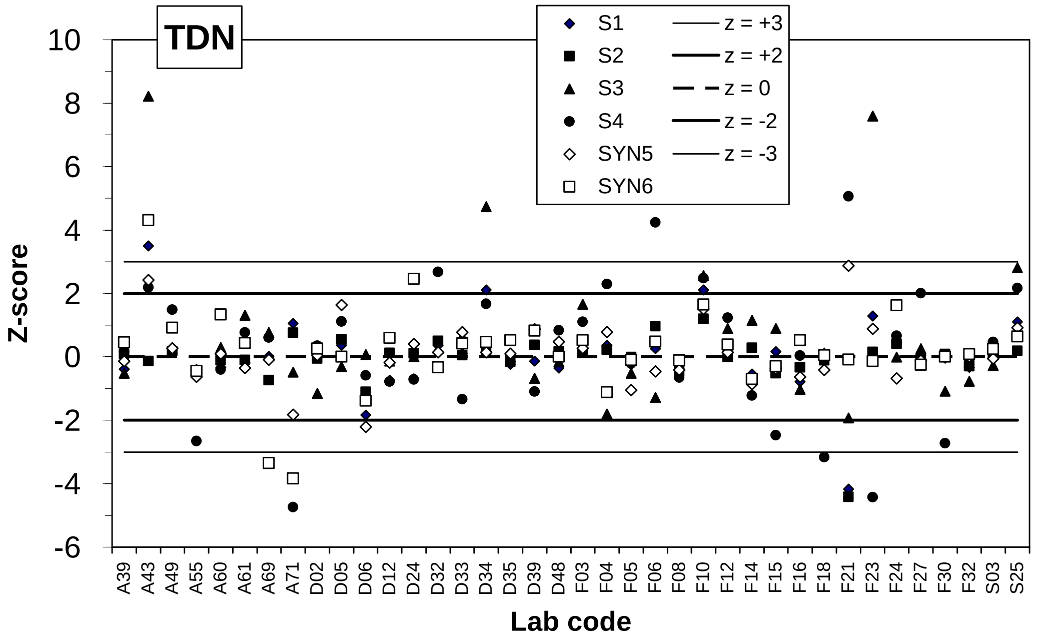

Alkalinity µeq/L
20
15
10
5
0
160
140
120
100
80
60
40
20
0
425
520
0.06
PT_1 4.3
PT_1 4.5
PT_EX 2PF
PT_EX Gran
SYN 5 PT_1 4.3
SYN 5 PT_1 4.5
SYN 5 PT_EX 2PF
SYN 5 PT_EX Gran
SYN 6 PT_1 4.3
SYN 6 PT_1 4.5
SYN 6 PT_EX 2PF
SYN 6 PT_EX Gran

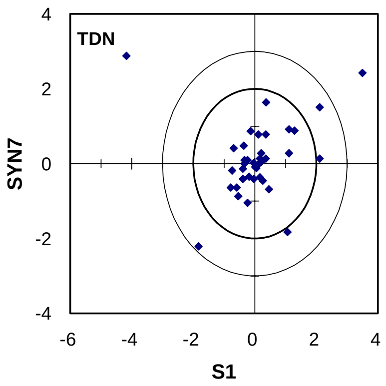

Alkalinity
Z-score
20
15
10
5
0
-5
-10
A55 SYN5=59 SYN6=28
SYN5
SYN6
z = +3
z = +2
z = 0
z = -2
z = -3
A40
A43
A49
A55
A60
A61
A69
A71
D02
D05
D06
D12
D24
D32
D33
D34
D35
D39
D48
F01
F03
F04
F05
F06
F07
F08
F10
F12
F14
F15
F17
F18
F23
F24
F25
F27
F28
F30
F32
S03
S25
Lab code

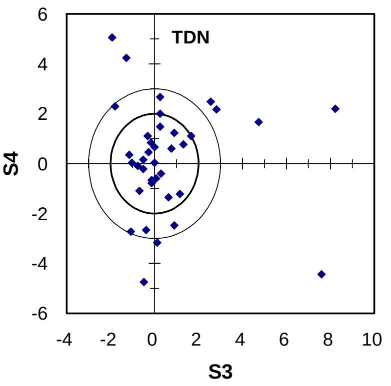

Alkalinity
SYN6
30
20
10
0
-10
-10
0
10
20
30
40
50
60
70
SYN5

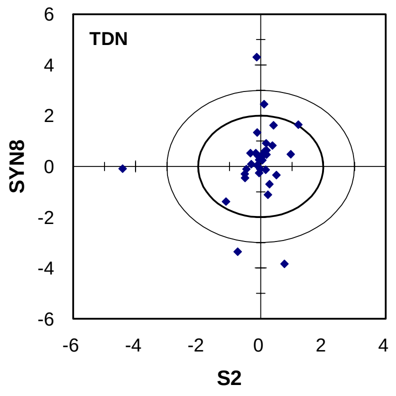

Alkalinity
SYN6
6
4
2
0
-2
-4
-6
-6
-4
-2
0
2
4
6
SYN5

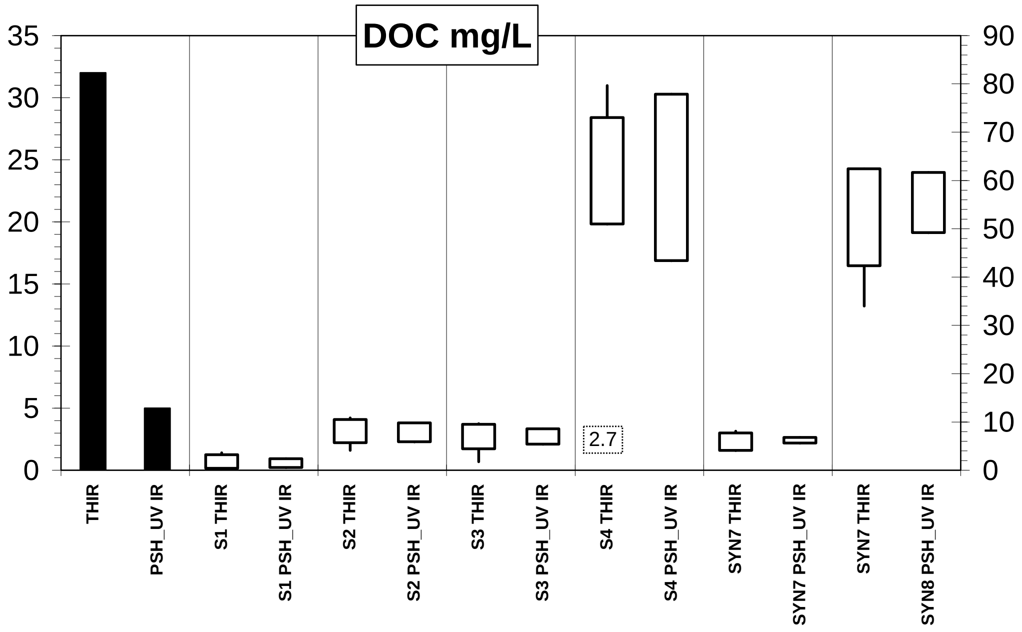

TDN mg/L
18
16
14
12
10
8
6
4
2
0
25
20
15
10
5
0
CHML
CF Cd
KJELD
PSOH-CF Cd
S1 CHML
S1 CF Cd
S1 KJELD
S1 PSOH-CF Cd
S2 CHML
S2 CF Cd
S2 KJELD
S2 PSOH-CF Cd
S3 CHML
S3 CF Cd
S3 KJELD
S3 PSOH-CF Cd
S4 CHML
S4 CF Cd
S4 KJELD
S4 PSOH-CF Cd
SYN7 CHML
SYN7 CF Cd
SYN7 KJELD
SYN7 PSOH-CF Cd
SYN8 CHML
SYN8 CF Cd
SYN8 KJELD
SYN8 PSOH-CF Cd

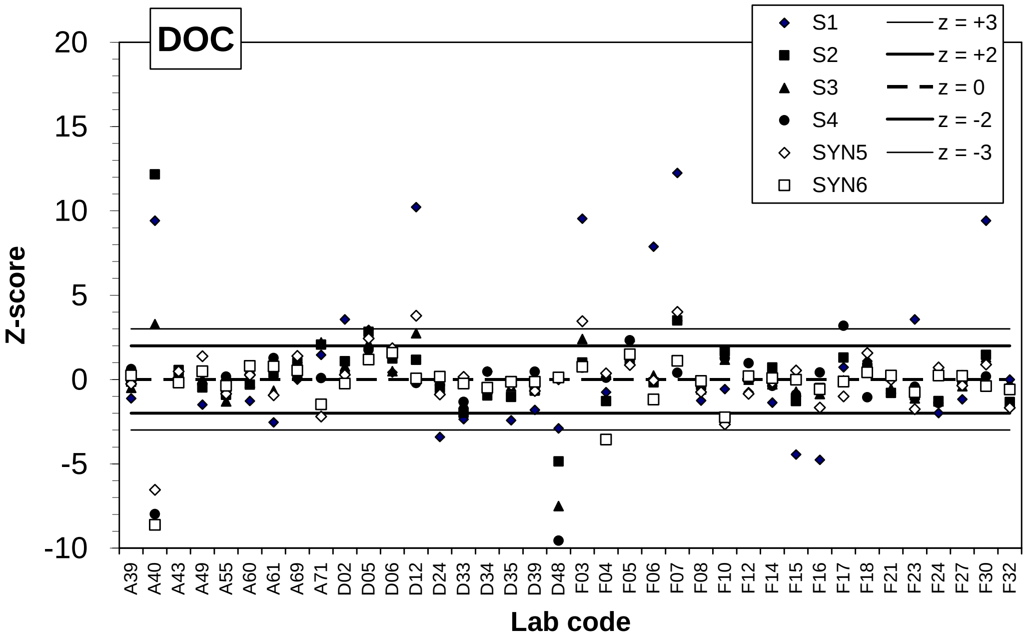

TDN
10
8
6
4
2
0
-2
-4
-6
Z-score
◆ S1
■ S2
▲ S3
● S4
◇ SYN5
□ SYN6
z = +3
z = +2
z = 0
z = -2
z = -3
A39
A43
A49
A55
A60
A61
A69
A71
D02
D05
D06
D12
D24
D32
D33
D34
D35
D39
D48
F03
F04
F05
F06
F08
F10
F12
F14
F15
F16
F18
F21
F23
F24
F27
F30
F32
S03
S25
Lab code

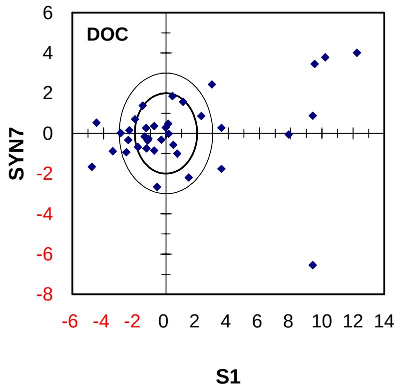

TDN
4
2
0
-2
-4
SYN7
-6
-4
-2
0
2
4
S1


TDN
6
4
2
0
-2
-4
-6
S4
-4
-2
0
2
4
6
8
10
S3


TDN
6
4
2
0
-2
-4
-6
SYN8
-6
-4
-2
0
2
4
S2


DOC mg/L
35
30
25
20
15
10
5
0
90
80
70
60
50
40
30
20
10
0
2.7
THIR
PSH_UV IR
S1 THIR
S1 PSH_UV IR
S2 THIR
S2 PSH_UV IR
S3 THIR
S3 PSH_UV IR
S4 THIR
S4 PSH_UV IR
SYN7 THIR
SYN7 PSH_UV IR
SYN7 THIR
SYN8 PSH_UV IR


DOC
Z-score
20
15
10
5
0
-5
-10
S1
S2
S3
S4
SYN5
SYN6
z = +3
z = +2
z = 0
z = -2
z = -3
A39
A40
A43
A49
A55
A60
A61
A69
A71
D02
D05
D06
D12
D24
D33
D34
D35
D39
D48
F03
F04
F05
F06
F07
F08
F10
F12
F14
F15
F16
F17
F18
F21
F23
F24
F27
F30
F32
Lab code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-2
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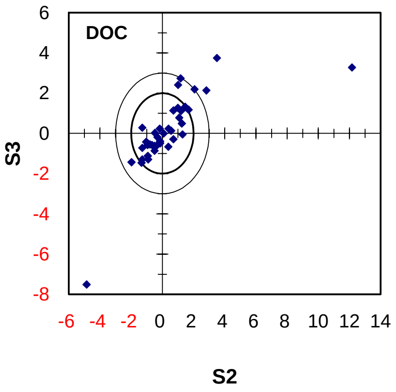
12
14
S1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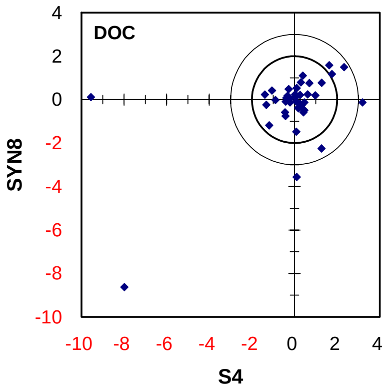
S2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-4
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-8
-10
-10
-8
-6
-4
-2
0
2
4
S4

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. The relatively small proportion of results within the tolerable limit (75%) shows that more attention should be paid to this determination.

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 82% 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 $\mu S\ cm^{-1}$ 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 a Ca and Mg concentration of below 1 mg/L, and one sample with a K and Na 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 80% of the results fell within the tolerable limits, with better results for Na and K. Apart from AES which had greater dispersion of the results, 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 covered a wide range, between 0.04 and 3.7 mg N L^{-1}. Sample 3 had a very low concentration, which caused difficulties to most of the laboratories: 16 laboratories reported that the value was below their limit of quantitation, and less than 50% of the reported results fell within the tolerable limit. Sample 4, which had a relatively high DOC concentration, also gave some analytical problem, and 30% of the results fell outside the tolerable limit. For this sample the colour of the DOC-rich water may have caused interferences in spectrophotometric methods.

In contrast, the results for sample 1 and 2 were very good, with more than 90% of the results within the tolerable limit.

This determination was performed using a number of different methods, primarily continuous flow analysis (20 labs), IC (12 labs), spectrophotometric determination (7 labs).

6.8. Sulphate

Most of the laboratories measured sulphate by IC, either with (32 cases) or without (4 cases) chemical suppression of the eluent. Six 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 (88%) fell within the acceptance range.

6.9. Nitrate

The range of nitrate concentration in the WRT was broad, between 0.06 and 3.53 mg N L^{-1}. As in the case for sulphate, most of the laboratories measured nitrate by IC, with (30 cases) or without (7 cases) chemical suppression of the eluent.

In the case of sample 4, which had a very low nitrate concentration, four laboratories reported values below the limit of quantitation, and 35% of the results fell outside the tolerable limit. However, the results for all the other samples were very good, with 93% of the samples within the tolerable limit.

6.10. Chloride

The concentration of chloride in the WRT samples (0.4-2.5 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 35 laboratories which measured chloride by IC had results that were comparable with the other methods. A relatively high number of results were reported to be below the limit of quantitation (7%) by labs using both continuous flow analysis and argentometric titration. However, some other laboratories using the same techniques obtained results within the tolerable limit.

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 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 30 laboratories reported alkalinity values for samples 1 and/or 4.

Taking into account the fact that the synthetic samples were explicitly intended for determining alkalinity, more than 45% of the data were missing or fell outside the tolerable limit.

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 or 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 38 of the 44 laboratories, mainly by chemoluminescence. The nitrogen concentration in the analysed samples covered a wide range, from 0.4 to 15 mg L^{-1}. The plot of the results clearly shows that chemoluminiscence and continuous flow analyses give comparable results, while data dispersion for the Kjeldahl method is slightly higher. Surprisingly, most of the results outside the tolerable limit were related to sample 4, which had a relatively very high concentration.

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 38 laboratories out of the 45. Most of them (32) measured DOC by thermal combustion and IR detection of the carbon dioxide formed (THIR, 27 labs).

The two most used methods gave similar results over a wide range of concentrations (1.6 to 60 mg L^{-1}), but a number of results fell outside the tolerable limit. This was especially the case for sample 1, which had a DOC concentration of 1.6 mg L^{-1}.

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.

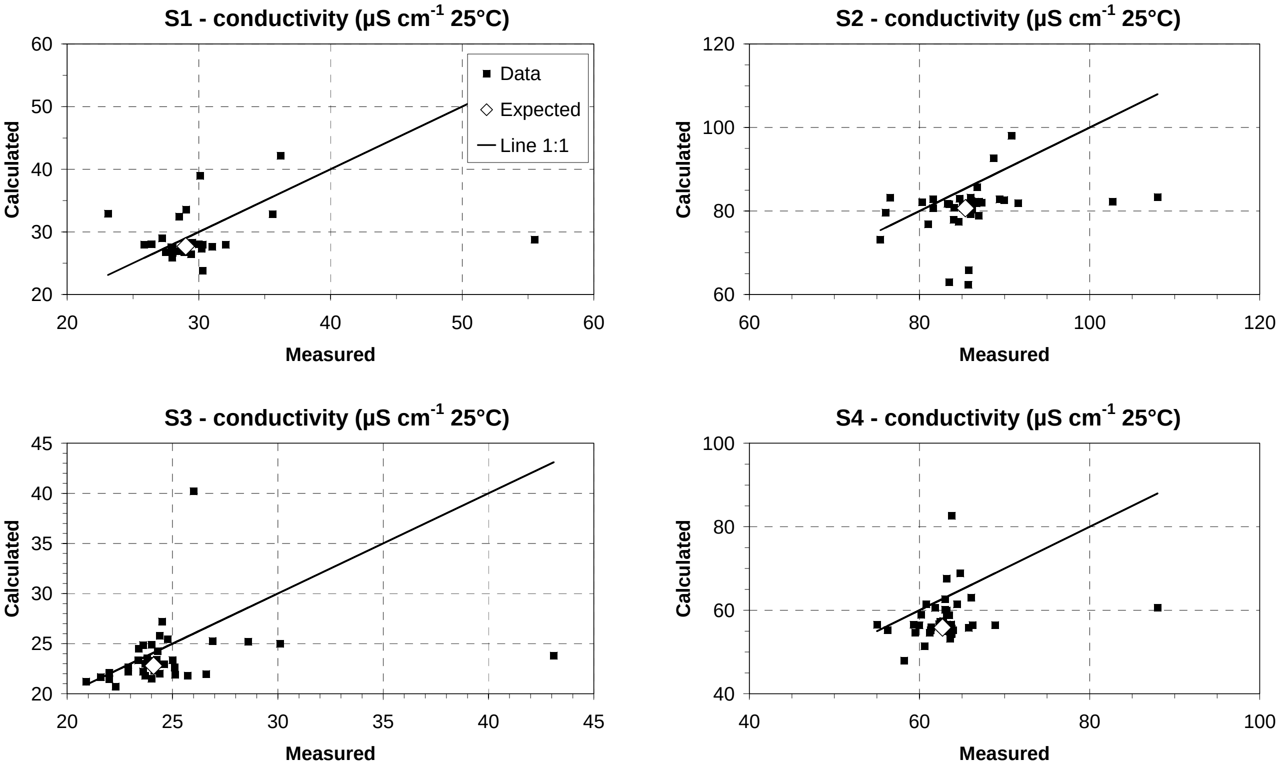

Fig 7.1 Comparison between the measured and calculated conductivity in all the natural samples of the WRT.

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 relevant number of analyses do not satisfy the test: 27% of the samples for which the test could be performed. Sample 1 was associated with a relatively large number of missing data owing to the very low concentrations of some ions, while a relatively high number of labs did not pass the test for sample 4, which had a high DOC concentration, probably due to problems in the ammonium analysis.

Table 7.1 Results of the conductivity check on the results submitted for samples 1-4.

Sample	Incomplete analysis set	Passed	Not passed
1	13	22	10
2	5	31	3
3	7	35	9
4	3	23	19

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.

The conductivity test, if applied when analyses were complete, would have led to the detection of 36% of the data outside the tolerable limit for pH, conductivity and major ions. Considering the results for these variables in whole set of submitted data, 28% of the data outside the tolerable limit are part of analyses which would not have passed the test, 50% of analyses which would have passed the test and 22% of incomplete analyses.

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. However, samples 1-3 would have passed the check on the basis of the expected results. 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.

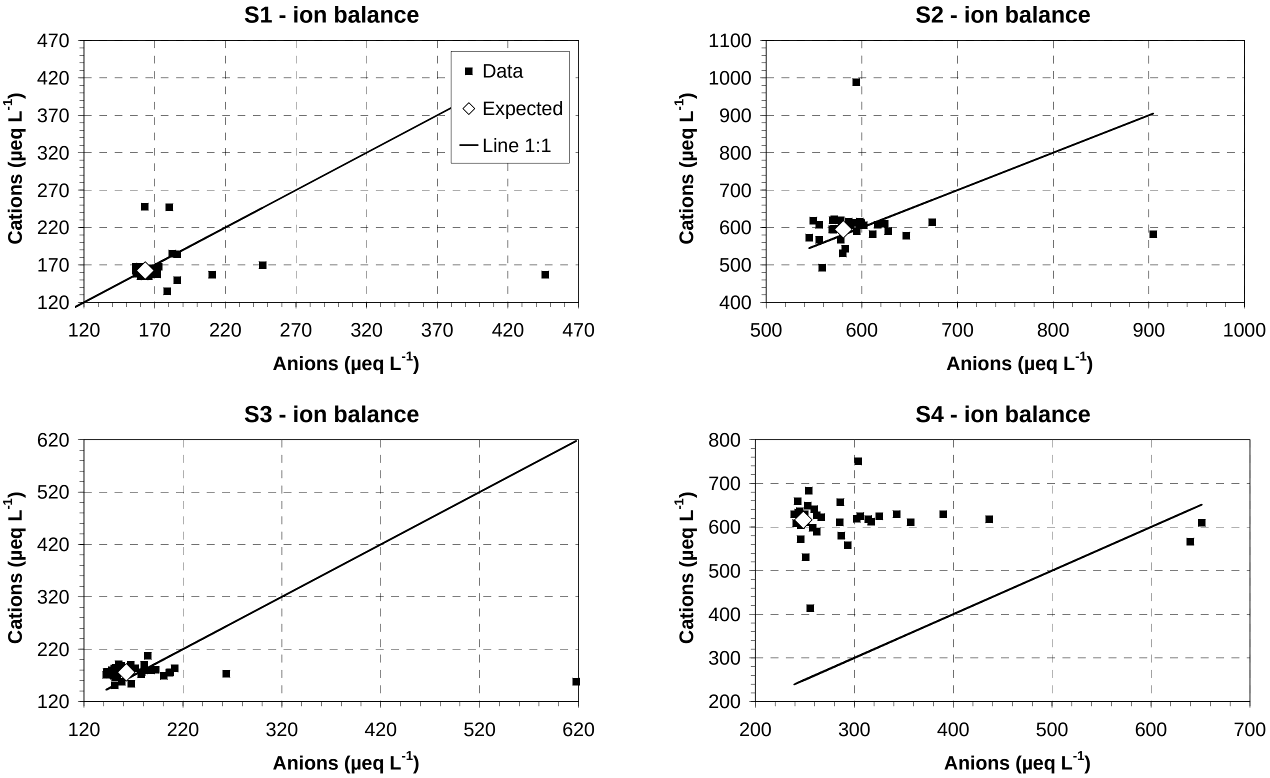

Fig 7.2. Comparison between the cation and anion total concentration in all the natural samples in the WRT.

8. COMPARISON WITH PREVIOUS WRTs

The results of this WRT can be compared with those of two previous exercises involving laboratories working on deposition and soil solutions in European Forests (Mosello et al. 2002, Marchetto et al. 2006). To make the comparison possible, the number of data meeting the data quality objectives (DQOs) for the three exercises was re-calculated, on the basis of the tolerable limits defined in chapter 2.2. The comparison is shown in fig. 8.1.

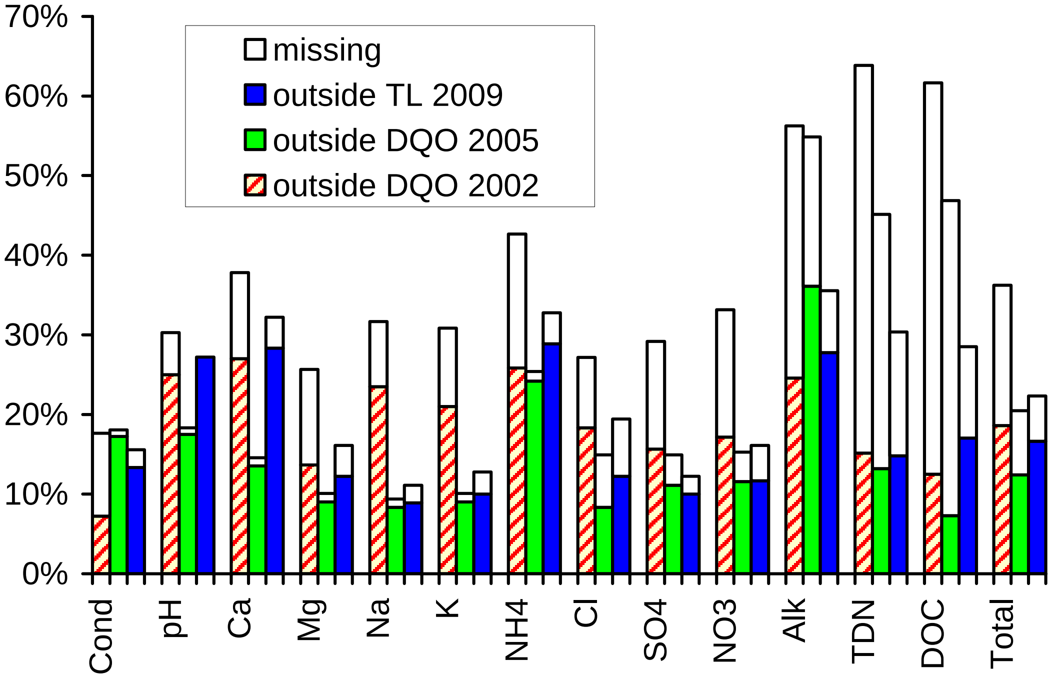

Fig. 8.1 Comparison of the number of missing data and of data outside the tolerable limits in the three WRTs carried out on for deposition and soil analyses in European forests.

The most evident difference among the three exercises, is the strong reduction in the number of missing results, in particular for DOC, alkalinity and DTN, mainly due to the contractual obligation for laboratories participating to the FutMon project to analyse all mandatory parameters.

However, there is an evident decrease in the number of results outside the DQOs for nitrate and sulphate, the most important variables related to atmospheric pollution. A marked amelioration after the first exercise also emerges in laboratory performance for sodium and potassium.

These results once again emphasise the importance of WRTs in making the laboratories aware of the level of their analytical quality, encouraging them to apply quality assessment and control measures to improve their overall analytical performance.

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 first run within the FutMon Life+ project and the third 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 11% of the total number of determinations. However, 56% 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, calcium, alkalinity and ammonium, though the concentration of ammonium was very low in one of the samples.

The continuation of the WRT programme is 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.

This is the task and the challenge of the Working Ring Test and of all the QA/QC activities carried out within the FutMon project.

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Appendix A: SUBMITTED DATA AND STATISTICS

	pH			
Sample	**1**	**2**	**3**	**4**
number of results above LOQ	44	45	45	45
Average	4.76	5.83	5.27	4.83
Median	4.79	5.86	5.27	4.86
Robust average	4.76	5.82	5.27	4.84
A39	4.55	5.64	5.02	4.76
A40	4.7	5.75	5.2	4.79
A43	5.06	5.79	5.65	4.94
A49	4.79	6.02	5.34	4.9
A55	4.79	5.65	5.51	4.87
A60	4.76	5.79	5.26	4.86
A61	4.76	5.92	5.29	4.85
A69	4.86	5.75	5.32	4.87
A71	4.67	5.79	5.19	4.77
D02	4.52	5.53	4.99	4.66
D05	4.79	5.82	5.26	4.84
D06	5.46	5.96	5.41	4.76
D12	4.67	5.91	5.21	4.82
D24	4.79	5.87	5.28	4.86
D32	4.72	6.04	5.33	4.86
D33	4.73	5.88	5.27	4.85
D34	4.69	5.58	5.19	4.76
D35	4.76	5.82	5.27	4.83
D39	4.77	5.97	5.26	4.87
D47	4.8	5.9	5.3	4.9
D48	4.83	5.9	5.27	4.88
F01	4.29	5.43	4.84	4.71
F03	4.79	5.78	5.33	4.86
F04	4.58	5.41	4.96	4.64
F05	4.82	5.98	5.39	4.89
F06		6.462	5.41	4.97
F07	4.84	5.86	5.34	4.9
F08	4.83	5.87	5.32	4.88
F10	4.86	5.82	5.26	4.98
F12	4.87	5.83	5.26	4.89
F14	4.74	5.83	5.22	4.85
F15	4.73	5.75	5.21	4.84
F16	4.91	6.1	5.46	4.91
F17	4.7	5.87	5.27	4.83
F18	4.8	5.95	5.3	4.85
F21	4.27	4.96	5.24	4.5
F23	4.43	5.33	4.85	4.46
F24	4.71	5.87	5.34	4.88
F25	4.84	5.91	5.27	4.86
F27	4.88	6.08	5.28	4.89
F28	4.79	5.77	5.17	4.8
F30	4.93	5.96	5.31	4.87
F32	4.93	6.53	5.68	5.09
S03	4.79	5.96	5.26	4.85
S25	4.84	5.62	5.55	4.84

	CONDUCTIVITY (µS cm^{-1} at 25 °C)			
Sample	**1**	**2**	**3**	**4**
Number of results above LOQ	43	44	44	44
Average	30.1	86.7	24.8	63.3
Median	29.1	86.0	24.0	63.2
Robust average	29.0	85.4	24.1	62.7
A39	27	82.2	24.1	60.2
A40				
A43	30.3	87.3	25	63.7
A49	29.14	85.75	23.37	62.44
A55	30.1	88.7	26	64.8
A60	30.3	86.2	24.4	63.6
A61	29.46	86.5	24.13	63.2
A69	27.5	81	24	59.5
A71	32.05	75.4	23.87	68.9
D02	29.03	85.05	24.78	61.83
D05	29.45	85.8	24.07	63.2
D06	40.72	119.61	30.05	70.66
D12	27.2	81.6	22.9	59.3
D24	31.02	89.95	25.72	66.23
D32	26.4	84.1	22.3	60.6
D33	30.2	86.2	26.6	63.8
D34	28.5	86.8	24.5	63.4
D35	29.5	85.1	23.8	62.5
D39	28.7	83.3	23.7	61.3
D47	29.7	86.5	24.5	63.9
D48	29	83.5	23.7	61.2
F01	36.2	80.3	26.9	64.4
F03	29.7	84.7	24	63.2
F04	23.1	81.6	24.4	58.2
F05	28.9	85.9	23.8	62.8
F06		76	22	55
F07	25.85	76.55	21.6	56.25
F08	28.7	86.1	23.4	63.5
F10	34.1	91.6	28.6	63.8
F12	28.9	86.7	24.6	63.8
F14	30	87	24	63
F15	28	84	22	60
F16	26	86.5	20.9	60.8
F17	29.5	83.5	23.6	61.4
F18	27	85.9	22.9	62.3
F21	30	86	24	63
F23	29.1	86.2	24	63
F24	35.6	90.8	30.1	66.1
F25	30.6	89.4	25.1	65.8
F27	27.98	86.98	25.12	63.95
F28	27.9	84.6	24.25	62.9
F30	29.4	86	24.3	63.2
F32	28	108	23.6	63.7
S03	28.5	85.1	24	63.2
S25	55.5	102.7	43.1	88

	CALCIUM (mg L^{-1})			
Sample	**1**	**2**	**3**	**4**
Number of results above LOQ	37	44	44	44
Average	0.208	0.704	1.077	6.025
Median	0.092	0.393	1.070	6.097
Robust average	0.090	0.390	1.064	6.051
A39	0.102	0.399	1.07	6.078
A40	0.46	1.78	1.42	10.7
A43	0.35	0.65	1.07	6.4
A49		0.401	1.127	6.529
A55	0.078	0.34	0.91	5.48
A60	0.083	0.391	1.078	5.515
A61	0.102	0.415	1.123	6.302
A69	0.15	0.45	1.19	5.68
A71	0.08	0.32	0.81	5.75
D02	0.1	0.41	1.06	6.01
D05		1.065	1.647	6.381
D06		0.4812	1.216	6.493
D12	0.04	0.346	1.06	6.267
D24	0.0818	0.367	0.988	6.15
D32	0.03	0.17	0.77	5.2
D33	0.13	0.29	1.04	5.7
D34	0.1	0.4	0.97	5.76
D35	0.09	0.36	1.06	6.09
D39	0.123	0.413	1.04	6.13
D47				
D48	0.08	0.341	1.082	5.932
F01	0.795	0.348	0.944	6.06
F03	0.1	0.47	1.14	5.94
F04	0.11	0.22	0.89	3.72
F05	0.142	0.483	1.391	6.672
F06	0.09	0.39	1.1	6.25
F07	0.123	0.394	0.99	5.89
F08	0.086	0.392	1.099	6.147
F10	0.12	0.43	1.34	5.96
F12	0.088	0.386	1.097	6.103
F14	0.085	0.381	1.06	6.08
F15	0.08	0.36	1.06	6.15
F16		0.41	1.1	6.32
F17	0.09	0.39	1.06	5.99
F18		0.385	1.05	6.13
F21		0.49	1.2	6.19
F23	0.081	0.402	1.081	6.54
F24	3	12.4	0.55	1.6
F25		0.358	1.089	6.118
F27	0.042	0.19	1.035	6.071
F28	0.11	0.4	1.11	5.99
F30	0.088	0.326	1.01	6.114
F32	0.106	0.415	1.11	6.27
S03	0.092	0.403	1.06	6.07
S25	0.08	0.39	1.08	6.19

	MAGNESIUM (mg L^{-1})			
Sample	**1**	**2**	**3**	**4**
Number of results above LOQ	40	44	44	44
Average	0.0443	0.164	0.425	1.669
Median	0.0436	0.160	0.410	1.610
Robust average	0.0428	0.157	0.410	1.598
A39	0.047	0.161	0.41	1.609
A40	0.02	0.15	0.4	1.39
A43	0.06	0.18	0.43	1.65
A49	0.048	0.167	0.441	1.682
A55	0.043	0.146	0.374	1.47
A60	0.045	0.161	0.398	1.502
A61	0.046	0.16	0.42	1.617
A69	0.05	0.17	0.44	1.57
A71	0.04	0.15	0.4	1.62
D02	0.05	0.16	0.41	1.61
D05		0.218	0.471	1.743
D06	0.0517	0.1725	0.4484	1.703
D12	0.019	0.13	0.408	1.664
D24	0.0432	0.166	0.396	1.64
D32	0.02	0.09	0.35	1.25
D33	0.03	0.12	0.38	1.35
D34	0.04	0.17	0.41	1.65
D35	0.04	0.15	0.4	1.56
D39	0.042	0.158	0.401	1.14
D47				
D48	0.049	0.158	0.425	1.628
F01	0.032	0.136	0.396	1.658
F03		0.18	0.43	1.6
F04	0.09	0.11	0.4	0.93
F05	0.049	0.164	0.456	1.697
F06	0.043	0.154	0.417	1.6
F07	0.039	0.138	0.369	1.63
F08	0.043	0.156	0.414	1.6
F10	0.05	0.17	0.43	1.57
F12	0.043	0.154	0.418	1.655
F14	0.044	0.16	0.41	1.61
F15	0.044	0.151	0.403	1.6
F16	0.044	0.158	0.397	1.58
F17	0.04	0.16	0.41	1.6
F18		0.197	0.414	1.61
F21		0.17	0.37	1.54
F23	0.039	0.169	0.424	1.78
F24	0.06	0.44	1.01	5.8
F25	0.045	0.161	0.421	1.628
F27	0.043	0.126	0.393	1.546
F28	0.059	0.168	0.425	1.758
F30	0.038	0.139	0.403	1.601
F32	0.037	0.162	0.418	1.61
S03	0.046	0.156	0.408	1.53
S25	0.06	0.18	0.43	1.65

	SODIUM (mg L^{-1})			
Sample	**1**	**2**	**3**	**4**
Number of results above LOQ	44	44	44	44
Average	0.359	1.041	1.647	2.610
Median	0.350	1.010	1.631	2.585
Robust average	0.347	1.013	1.629	2.589
A39	0.35	0.995	1.613	2.528
A40	0.5	1.46	1.91	2.71
A43	0.46	1.32	1.9	2.8
A49	0.367	1.054	1.769	2.762
A55	0.33	0.97	1.52	2.41
A60	0.34	0.982	1.512	2.453
A61	0.355	1.039	1.665	2.687
A69	0.38	1.03	1.67	2.5
A71	0.36	0.92	1.14	2.28
D02	0.37	0.99	1.58	2.56
D05	0.338	1.084	1.719	2.781
D06	0.3786	1.058	1.746	2.776
D12	0.339	1.003	1.627	2.578
D24	0.345	0.965	1.58	2.64
D32	0.33	0.95	1.55	2.42
D33	0.32	0.95	1.57	2.5
D34	0.36	0.94	1.65	2.6
D35	0.35	1.01	1.64	2.59
D39	0.334	0.975	1.55	2.59
D47				
D48	0.345	0.989	1.586	2.552
F01	0.387	1.094	1.725	3.225
F03	0.36	1.03	1.69	2.58
F04	0.6	1.11	2.05	2.12
F05	0.344	0.96	1.545	2.377
F06	0.354	0.997	1.622	2.58
F07	0.294	0.975	1.43	2.46
F08	0.346	1.015	1.644	2.563
F10	0.35	0.96	1.6	2.59
F12	0.356	1.03	1.67	2.63
F14	0.36	1.08	1.67	2.73
F15	0.33	1.1	1.49	2.53
F16	0.36	1.04	1.68	2.67
F17	0.35	1.03	1.66	2.64
F18	0.38	1.01	1.61	2.65
F21	0.36	1.2	1.71	2.88
F23	0.45	1.45	2.05	3.05
F24	0.34	1.14	1.84	2.9
F25	0.353	1.01	1.636	2.578
F27	0.296	0.935	1.609	2.545
F28	0.307	0.939	1.53	2.602
F30	0.32	1	1.69	2.64
F32	0.327	0.999	1.62	2.52
S03	0.306	1.04	1.56	2.48
S25	0.31	0.97	1.62	2.58

	POTASSIUM (mg L^{-1})			
Sample	**1**	**2**	**3**	**4**
Number of results above LOQ	44	41	43	44
Average	2.429	9.676	0.447	1.723
Median	2.481	9.972	0.450	1.730
Robust average	2.464	9.786	0.443	1.725
A39	2.449	9.872	0.426	1.692
A40	3.11	8.62	0.67	2.43
A43	1.98	10.9	0.28	0.87
A49	2.712		0.294	1.918
A55	2.3	9.47	0.38	1.59
A60	2.269	9.399	0.396	1.566
A61	2.56	10.46	0.463	1.833
A69	2.43	9.7	0.52	1.7
A71	2	8.3	0.4	1.33
D02	2.48	9.93	0.44	1.69
D05	2.482			1.738
D06	2.635	10.61	0.4922	1.839
D12	2.445	9.87	0.448	1.754
D24	2.47	9.95	0.433	1.81
D32	2.47	9.85	0.4	1.6
D33	2.28	9.62	0.38	1.35
D34	2.54	10.34	0.46	1.9
D35	2.54	10.02	0.46	1.73
D39	2.27	10.25	0.422	1.72
D47				
D48	2.502		0.469	1.72
F01	2.736	10.858	0.476	2.324
F03	2.9	10.05	0.5	1.8
F04	2.4	9.91	0.5	1.22
F05	2.395	9.387	0.418	1.602
F06	2.581	9.972	0.45	1.73
F07	2.36	9.81	0.44	1.69
F08	2.518	10.01	0.463	1.732
F10	2.61	10.39	0.51	1.81
F12	2.56	10.28	0.463	1.73
F14	2.46	10.2	0.43	1.69
F15	2.24	9	0.44	1.88
F16	2.52	10.46	0.46	1.78
F17	2.47	10	0.46	1.73
F18	2.57	10.7	0.486	1.74
F21	2.31	8.26	0.54	1.83
F23	2.65	10.15	0.5	1.8
F24	0.04	0.18	0.48	1.84
F25	2.663	10.35	0.462	1.753
F27	2.533	9.886	0.449	1.723
F28	2.424	9.593	0.436	1.74
F30	2.35	10.22	0.26	1.67
F32	2.53	10	0.51	1.76
S03	2.53	9.59	0.433	1.72
S25	2.58	10.3	0.41	1.73

	AMMONIUM (mg N L^{-1})			
Sample	**1**	**2**	**3**	**4**
Number of results above LOQ	45	45	29	45
Average	0.834	3.72	0.039	0.209
Median	0.838	3.78	0.024	0.162
Robust average	0.833	3.71	0.020	0.160
A39	0.777	3.37		0.06
A40	0.96	4.79	0.22	2.06
A43	0.748	3.2		0.046
A49	0.858	3.805	0.026	0.182
A55	0.845	3.73	0.045	0.19
A60	0.83	3.88	0.02	0.18
A61	0.811	3.799		0.153
A69	0.882	3.39	0.026	0.16
A71	0.55	2.95	0.2	0.39
D02	0.93	3.49	0.04	0.23
D05	0.81	3.7	0.024	0.22
D06	0.74	3.59		0.12
D12	0.918	4.11	0.018	0.16
D24	0.864	4.01		0.175
D32	0.876	3.971	0.02	0.126
D33	0.816	4.025	0.018	0.081
D34	0.849	3.81	0.0155	0.147
D35	0.838	3.68	0.022	0.096
D39	0.817	3.83	0.05	0.153
D47	0.85	3.78		0.18
D48	0.879	4.05	0.009	0.155
F01	0.945	3.44	0.022	0.356
F03	0.82	3.75		0.15
F04	0.81	3.71		0.08
F05	0.808	3.869	0.028	0.162
F06	0.85	3.87	0.024	0.17
F07	0.99	3.93		0.28
F08	0.892	3.819	0.044	0.153
F10	0.82	3.67		0.19
F12	0.866	3.936	0.017	0.163
F14	0.85	3.79	0.035	0.174
F15	0.795	3.597	0.04	0.188
F16	0.81	3.7		0.14
F17	0.86	3.99	0.02	0.19
F18	0.866	3.71	0.03	0.205
F21	0.67	3.05		0.14
F23	0.809	3.657	0.018	0.166
F24	0.8	3.9		0.1
F25	0.844	3.85	0.019	0.146
F27	0.823	3.549	0.026	0.2
F28	0.873	3.106		0.17
F30	0.791	3.423	0.005	0.137
F32	0.88	3.84		0.15
S03	0.836	3.83		0.13
S25	0.76	3.48	0.04	0.2

	SULPHATE (mg S L^{-1})			
Sample	**1**	**2**	**3**	**4**
Number of results above LOQ	44	44	44	44
Average	1.212	4.455	2.015	3.133
Median	1.160	4.140	1.825	2.765
Robust average	1.162	4.122	1.823	2.778
A39	1.174	4.168	1.653	3.068
A40	3.15	17.8	9.3	12.15
A43	1.16	4.226	1.84	2.77
A49	1.169	4.037	1.853	2.694
A55	1.14	4.05	1.81	2.73
A60	1.217	4.14	1.865	2.796
A61	1.186	4.152	1.83	2.727
A69	1.16	4.19	1.83	2.73
A71	1.37	4.14	2.1	3.03
D02	1.15	4.03	1.76	2.63
D05	1.184	3.998	1.743	2.63
D06				
D12	1.132	4.005	1.776	2.673
D24	1.15	4.15	1.81	2.77
D32	1.15	4.02	1.78	2.73
D33	1.12	4.14	1.85	2.7
D34	1.13	3.92	1.8	2.62
D35	1.19	4.24	1.85	2.77
D39	1.11	3.98	1.77	2.7
D47	1.17	4.16	1.84	2.77
D48	1.152	4.127	1.744	2.688
F01	1.157	4.201	1.855	2.789
F03	1.21	4.09	1.79	2.84
F04	1.2	4.33	1.82	2.57
F05	1.29	4.16	1.83	2.92
F06	1.108	3.89	1.758	3.03
F07	1.14	4.11	1.83	2.76
F08	1.148	4.152	2.018	3.027
F10	1.13	4.11	2.14	8.61
F12	1.17	4.04	1.8	2.72
F14	1.15	4.21	1.85	3.18
F15	1.17	4.13	1.8	2.73
F16	1.14	3.93	1.76	2.66
F17	1.12	4.18	1.79	2.81
F18	1.03	4.07	1.76	2.69
F21	1.15	4.34	1.94	2.96
F23	1.21	5	2.07	2.19
F24	1.18	3.95	1.87	2.85
F25	1.205	4.139	1.817	2.745
F27	1.153	4.194	1.811	2.776
F28	1.2	4.162	1.858	2.745
F30	1.22	4.42	1.98	3.4
F32	1.16	4.27	2.18	2.82
S03	1.1	4.18	1.79	2.76
S25	1.22	4.08	1.72	2.89

	NITRATE (mg N L^{-1})			
Sample	**1**	**2**	**3**	**4**
Number of results above LOQ	44	44	44	39
Average	1.102	3.526	0.155	0.060
Median	1.111	3.545	0.150	0.053
Robust average	1.108	3.527	0.149	0.054
A39	1.204	3.562	0.168	0.045
A40				
A43	0.61	3.31	0.157	0.052
A49	1.112	3.48	0.148	0.058
A55	1.17	3.35	0.154	0.073
A60	1.097	3.488	0.161	0.044
A61	1.155	3.533	0.131	0.032
A69	1.09	2.93	0.15	0.06
A71	1.16	3.77	0.14	0.02
D02	1.09	3.55	0.14	0.05
D05	1.14	3.42	0.14	0.05
D06	1.1	3.52	0.19	
D12	1.091	3.465	0.154	0.068
D24	1.14	3.67	0.147	0.053
D32	1.084	3.63	0.17	0.08
D33	1.067	3.68	0.129	0.045
D34	1.12	3.57	0.15	0.06
D35	1.14	3.62	0.145	0.052
D39	1.05	3.45	0.12	0.04
D47	1.11	3.6	0.15	0.06
D48	1.105	3.176	0.157	0.037
F01	1.111	3.668	0.148	0.059
F03	1.13	3.36	0.13	0.05
F04	1.08	3.61	0.16	0.07
F05	1.086	3.454	0.144	0.063
F06	1.12	3.5	0.15	0.06
F07	1.13	3.71	0.179	
F08	1.165	3.652	0.206	0.072
F10	1.15	3.63	0.26	0.19
F12	1.079	3.433	0.183	0.053
F14	1.12	3.58	0.17	0.07
F15	1.1	3.57	0.16	0.07
F16	1.066	3.601	0.136	0.053
F17	1.01	3.41	0.12	0.05
F18	1.02	3.55	0.117	
F21	1.16	3.8	0.13	
F23	1.127	3.504	0.142	0.053
F24	1.13	3.54	0.15	0.06
F25	1.126	3.509	0.159	0.059
F27	1.074	3.492	0.143	0.053
F28	1.041	3.486	0.148	
F30	1.152	3.626	0.148	0.053
F32	1.22	3.73	0.27	0.07
S03	1.1	3.6	0.137	0.052
S25	1.14	3.36	0.15	0.1

	CHLORIDE (mg L^{-1})			
Sample	**1**	**2**	**3**	**4**
Number of results above LOQ	39	41	41	42
Average	0.455	1.557	0.892	2.647
Median	0.420	1.531	0.869	2.530
Robust average	0.420	1.524	0.866	2.525
A39				3.22
A40				
A43	0.53	1.55	0.93	2.518
A49	0.431	1.577	0.877	2.497
A55	0.42	1.52	0.84	2.46
A60	0.621	1.623	0.791	2.419
A61	0.418	1.616	0.874	2.574
A69	0.373	1.54	0.805	2.535
A71	0.37	1.1	0.95	2.39
D02	0.59	1.63	0.99	2.62
D05	0.408	1.498	0.809	2.427
D06				
D12	0.402	1.531	0.844	2.544
D24	0.428	1.53	0.93	2.6
D32	0.4	1.61	0.88	2.65
D33	0.4	1.61	0.84	2.65
D34	0.42	1.53	0.92	2.38
D35	0.44	1.63	0.9	2.64
D39	0.3	1.4	0.7	2.4
D47	0.42	1.57	0.86	2.58
D48	0.426	1.524	0.815	2.517
F01	0.408	1.482	0.856	2.69
F03	0.37	1.5	0.8	2.53
F04	1.2	2.2	1.5	3.2
F05	0.43	1.52	0.83	2.44
F06	0.35	1.47	0.82	2.6
F07	0.746	2.15	1.05	2.75
F08	0.39	1.51	1.04	2.52
F10		1.48	0.77	2.51
F12	0.458	1.588	0.899	2.572
F14	0.37	1.4	0.92	2.55
F15	0.4	1.52	0.81	2.6
F16	0.48	1.37	0.83	2.49
F17	0.52	1.43	0.83	2.39
F18	0.405	1.55	0.992	2.53
F21		1.35	0.76	2.42
F23				
F24	0.43	1.6	0.89	2.69
F25	0.491	1.588	0.853	2.53
F27	0.402	1.505	0.823	2.497
F28	0.52	1.56	0.94	2.41
F30	0.36	1.866	1.06	6.259
F32	0.39	1.55	1.1	2.54
S03	0.339	1.44	0.742	2.49
S25	0.5	1.63	0.93	2.35

	ALKALINITY (µeq L^{-1})	
Sample	**SYN5**	**SYN6**
number of results above LOQ	41	40
average	48	94
median	31	75
robust average	33	79
A39		
A40	6.4	13.7
A43	55	125
A49	26.55	71.13
A55	425	520
A60	28	69
A61	26.93	71.73
A69	33.5	82.5
A71	19	61
D02	60.9	105.1
D05	60	110
D06	0.064	
D12	22	63
D24	28.4	72.5
D32	30	75
D33	31	90
D34	131	164
D35	29	74
D39	56	103
D47		
D48	32	73
F01	16	68
F03	88.5	133.1
F04	17.5	54
F05	26	68
F06	28.2	71.8
F07	32	73.6
F08	31	80
F10	30	74
F12	32.9	77.5
F14	31	71
F15	31	76
F16		
F17	33	73
F18	30	73
F21		
F23	80	120
F24	55	102
F25	33.49	75.453
F27	33.34	75.34
F28	43	84
F30	57.2	103
F32	30	80
S03	29	75
S25	82	121

	TOTAL DISSOLVED NITROGEN (mg L^{-1})					
Sample	**1**	**2**	**3**	**4**	**SYN7**	**SYN8**
Number of results above LOQ	38	38	37	38	38	35
Average	2.024	7.542	0.436	1.621	2.215	14.92
Median	2.014	7.643	0.390	1.635	2.197	15.20
Robust average	2.008	7.589	0.390	1.594	2.190	14.63
A39	1.93	7.66	0.35	1.62	2.16	15.29
A40						
A43	2.71	7.488	1.032	1.944	2.72	20.93
A49	2.05	7.72	0.41	1.83	2.25	15.97
A55	1.89	7.21	0.36	1.17	2.05	13.97
A60	1.94	7.5	0.413	1.53	2.21	16.59
A61	1.97	7.513	0.493	1.717	2.113	15.26
A69	2.01	7.03	0.45	1.69	2.17	9.72
A71	2.220836	8.1668	0.352538	0.838323	1.79	9.01
D02	2.05	7.55	0.3	1.65	2.2	15
D05	2.081	8.007	0.366	1.771	2.548	
D06	1.64	6.748	0.396	1.5	1.706	12.61
D12	1.86	7.68	0.38	1.47	2.15	15.5
D24	1.87	7.67		1.48	2.28	18.22
D32	2.08	7.97	0.41	2.02	2.22	14.14
D33	2.03	7.63	0.44	1.38	2.36	15.25
D34	2.43	7.73	0.76	1.86	2.22	15.32
D35	1.96	7.47	0.39	1.6	2.21	15.4
D39	1.98	7.87	0.337	1.42	2.38	15.83
D47						
D48	1.936	7.711	0.378	1.728	2.294	
F01						
F03	2.23	7.68	0.52	1.77	2.25	15.4
F04	2.08	7.76	0.25	1.96	2.36	13
F05	1.96	7.58	0.35	1.56	1.96	14.49
F06	2.06	8.32	0.29	2.27	2.09	15.33
F07						
F08	1.93	7.24	0.38	1.49	2.1	14.47
F10	2.43	8.5	0.59	1.99	2.52	17.04
F12	2.04	7.58	0.46	1.79	2.22	15.2
F14	1.9	7.8	0.48	1.4	2	13.6
F15	2.04	7.2	0.46	1.2	2.11	14.2
F16	1.85	7.34	0.31	1.6	2.05	15.39
F17						
F18	2	7.5	0.4	1.09	2.1	14.7
F21	1.17	4.24	0.24	2.4	2.82	14.5
F23	2.267	7.707	0.983	0.888	2.383	14.43
F24	2.1	7.9	0.39	1.7	2.04	17
F25						
F27	2.018	7.55	0.41	1.913	2.164	14.255
F28						
F30	2	7.656	0.306	1.16	2.194	
F32	1.94	7.36	0.33	1.58	2.19	14.76
S03	2.023	7.624	0.369	1.668	2.179	14.99
S25	2.23	7.73	0.61	1.94	2.39	15.56

	DISSOLVED ORGANIC CARBON (mg L^{-1})					
Sample	**1**	**2**	**3**	**4**	**SYN7**	**SYN8**
Number of results above LOQ	37	40	40	40	40	40
Average	1.793	8.304	7.060	59.1	5.794	51.4
Median	1.575	7.917	6.921	61.0	5.770	52.9
Robust average	1.622	8.031	7.003	60.4	5.790	52.8
A39	1.44	7.92	6.66	64.12	5.64	54.07
A40	3.15	17.8	9.3	12.15	2	7.25
A43	1.646	8.481	7.098	61.97	6.072	51.785
A49	1.38	7.65	7.02	58.72	6.59	55.33
A55		7.3	6.1	61.4	5.3	50.8
A60	1.416	7.781	6.873	62.21	5.946	56.98
A61	1.21	8.34	6.54	68.1	5.25	56.87
A69		8.83	7.89	61	6.6	55.6
A71	1.86	9.69	8.54	60.89	4.52	44.99
D02	2.2	8.9	7.55	62.5	5.95	51.5
D05	2.1	10.3	8.5	71	7.2	59
D06	1.69	9.032	7.35	70.21	6.864	61.15
D12	3.28	8.97	8.92	59.1	7.98	53.1
D24	1.07	7.63	6.57	58.4	5.28	53.7
D32						
D33	1.24	6.44	6	52.4	5.88	51.5
D34	1.7	7.27	6.6	63.2	5.46	50.2
D35	1.23	7.2	6.71	59.1	5.6	52.1
D39	1.33	7.5	6.6	63.2	5.4	52.1
D47						
D48	1.152	4.127	1.744	2.688	5.8	53.4
F01						
F03	3.17	8.84	8.69	64.6	7.79	56.8
F04	1.5	7	7.2	61	6	34
F05	1.99	9	7.79	74.44	6.29	60.69
F06	2.9	7.9	7.17	53.2	5.76	46.52
F07	3.61	10.84	9.63	62.77	8.11	58.6
F08	1.42	7.76	6.59	57.9	5.36	52.3
F10	1.53	9.38	7.83	68.05	4.25	40.93
F12	1.5	8.1	7	66.3	5.3	53.8
F14	1.4	8.6	6.8	58.1	5.7	53.2
F15	0.9	7	6.5	55	6.1	52.7
F16	0.85	7.63	6.4	62.93	4.83	49.71
F17	1.74	9.07	6.97	79.66	5.21	52.11
F18	1.8	8.6	7.8	54	6.7	55
F21	1.65	7.39	6.62	60.6	5.78	54.05
F23	2.2	7.28	6.22	57.84	4.77	48.8
F24	1.3	7	6.1	52	6.2	54
F25						
F27	1.432	7.913	6.729	61.96	5.587	53.93
F28						
F30	3.15	9.2	7.93	61.52	6.3	50.69
F32		6.96	5.98	57.7	4.82	49.7
S03	1.575	7.197	6.709	60.79	5.611	53.48
S25	1.62	8.35	7.17	60.8	5.96	52.36

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

NP*: not passed, values reported below limit of quantitation

Lab code	pH	Cond.	Ca	Mg	Na	K	NH_4	SO_4	NO_3	Cl	Alk	TDN	DOC	Requalification
A39	ok	ok	ok	ok	ok	ok	ok	ok	ok	NP*	NP*	ok	ok	
A40	ok	NM	NP	ok	NP	NP	NP	NP	NM	NM	NP	NM	NP	
A43	ok	ok	ok	ok	NP	NP	ok	ok	ok	ok	NP	NP	ok	passed§ 30/11/09
A49	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	
A55	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	NP	ok	ok	
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	ok	ok	ok	
A71	ok	ok	ok	ok	ok	ok	NP	ok	ok	ok	ok	ok	ok	passed§ 10/08/09
D02	NP	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	passed§ 11/09/09
D05	ok	ok	NP	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	
D06	ok	NP	ok	ok	ok	ok	ok	NM	ok	NM	NP	ok	ok	
D12	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	
D24	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	
D32	ok	ok	NP	NP	ok	ok	ok	ok	ok	ok	ok	ok	NM	
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	NP	ok	ok	
D35	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	
D39	ok	ok	ok	NP	ok	ok	ok	ok	ok	ok	ok	ok	ok	
D47	ok	ok	NM	NM	NM	NM	ok	ok	ok	ok	NM	NM	NM	
D48	ok	ok	ok	ok	ok	ok	ok	NP	ok	ok	ok	ok	ok	passed^{+} 18/05/09
F01	NP	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	NM	NM	passed§ 22/09/09
F03	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	NP	ok	ok	passed^{+} 25/08/09
F04	NP	ok	NP	NP	NP	ok	ok	ok	ok	NP	ok	ok	ok	

passed§: analytical problem, solved and detailed report sent
passed^{+}: wrong units

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	NP	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	passed§ 26/06/09
F06	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	
F07	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	NM	ok	
F08	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	
F10	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	
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	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	NP*	ok	ok	passed§ 04/06/09
F17	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	NM	ok	passed§ 24/11/09
F18	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	
F21	NP	ok	ok	ok	ok	ok	ok	ok	ok	ok	NP*	ok	ok	
F23	ok	ok	ok	ok	NP	ok	ok	NP	ok	NP*	NP	ok	ok	passed§ 29/06/09 (for Na, Cl, Alk)
F24	ok	ok	NP	NP	ok	ok	ok	ok	ok	ok	ok	ok	ok	passed§§ 24/11/09
F25	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	NM	NM	passed* 29/06/09
F27	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	
F28	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	NM	NM	passed§ 30/09/09
F30	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	ok	
F32	NP	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	NP	ok	ok	ok	ok	ok	ok	ok	ok	NP	ok	ok	

passed*: instrument out of service, determination delayed and test passed
passed§: analytical problem, solved and detailed report sent
passed§§: analytical problem, no detail given