PROJECT REPORT No. OS44

COMPARISON OF THE PERFORMANCE OF NINE COMMERCIAL LABORATORIES FOR TESTING NITROGEN AND SULPHUR IN PLANTS AND SOIL: A SECOND STUDY

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COMPARISON OF THE PERFORMANCE OF NINE COMMERCIAL LABORATORIES FOR TESTING NITROGEN AND SULPHUR IN PLANTS AND SOIL: A SECOND STUDY

by

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CONTENTS

ABSTRACT

Nine UK laboratories participated in a second inter-laboratory study to evaluate the variability of analysis for concentrations of total Sulphur (S) and Nitrogen (N) in four plant materials, and extractable S in three soil samples. Results for total S varied considerably, with inter-laboratory coefficients of variation (CV's) that ranged from 13.4 to 19.8%. For total N, the results were less variable and laboratories were in reasonable agreement with CV's which ranged from 4.3 to 6.6%. With the soil samples the inter-laboratory variability was even greater, with CV's ranging from 16.7 to 46.2%. The levels of inter-laboratory variability in this second study are similar to that found in the first study and show no improvement. To obtain greater consistency between laboratories, analytical methods need to be more closely controlled. This could be achieved by improved standardisation of methods, wider use of reference materials and regular participation in quality assurance schemes.

1. INTRODUCTION

Sulphur (S) deficiency is widespread in many crops in the UK, including cereals, oilseed rape and grasslands (McGrath *et al.* 1996; Zhao *et al.* 1999). The effects of S deficiency are diverse, ranging from reduced crop yields to changes in the quality of the crop. Visible symptoms of S-deficient plants, such as spindly growth and yellowing of leaves, are similar to those of many other nutrient deficiencies, and therefore not always immediately identifiable (Ceccotti, 1996). However, in wheat leaves, both the number of mesophyll cells and the chlorophyll content of chloroplasts are reduced substantially under conditions of sulphur deficiency (Burke *et al*., 1986). Because S is a major constituent of many essential amino acids, S-deficient cereals show significant changes in the protein composition of the grain. This reduces the nutritional value of animal feeds and results in a loss of baking quality in breadmaking wheat varieties (Randall & Wrigley, 1986; Zhao *et al.* 1999). Changes in the S status of a plant also affect the utilisation of nitrogen (N). As both elements are essential for protein synthesis, when S is deficient, non-protein compounds such as nitrate (NO_3^-) may accumulate within plants. Therefore, if there is insufficient S, N fertilisers will be less efficient and result in the loss of N through leaching.

Sulphur deficiency has only become apparent relatively recently due to a combination of declining S inputs together with increasing S requirements. High atmospheric SO_2 levels prior to the 1980s provided sufficient S through wet precipitation or dry deposition to meet the S requirements of most crops. However, since the beginning of the 1980s, SO_2 emissions in industrialised nations have decreased substantially. In the UK, SO_2 emissions have declined from 6.4 Mt in 1970 to 2 Mt in 1998, a reduction of 70% (Zhao *et al*., 1999). Other European countries have seen even larger decreases. A further decrease in the amount of S has occurred due to changes in fertiliser use, as high-analysis S-free fertilisers have largely replaced low-analysis fertilisers such as ammonium sulphate. In addition to these lower S inputs, higher-yielding crops grown at increased cropping densities remove larger amounts of S from the soil.

To diagnose S deficiency and determine whether S fertiliser applications are necessary, it is imperative that crop tissues and soil samples can be analysed reliably to give estimates of the amount of S present. Decisions on whether to apply fertiliser are based on threshold levels (0.4% and 0.25% for oilseed rape and wheat leaves,

respectively (McGrath *et al.* 1996; Zhao *et al.* 1999). Therefore, over-estimation of the concentration of S could lead to S deficiency not being diagnosed, whereas under-estimation could result in unnecessary fertiliser applications. Compared with other common elements such as N, K (potassium) and P (phosphorous), S is less routinely analysed by laboratories. Analyses therefore need to be tested to make sure that laboratories are providing reliable data. A project done in 1997 (Crosland *et al.* 1998, HGCA Report OS26) compared ten UK laboratories for the analysis of total S and total N in four different plant tissues, and extractable S in two soils. Variability of the data was large; the inter-laboratory CV for total S in plant tissues ranged from 8 – 20 %, and for extractable sulphate in soils the CV was 36 – 45 %. This compares to a CV of less than 6 % in the analysis of total N. The variability in the results between laboratories was not related to the analytical method used. A similar study in the United States (Sterrett *et al*., 1987) also found that inter-laboratory variability in the analysis of S was larger than for other elements. In a selection of six different plant tissues, the inter- laboratory CV's ranged from 18-39%.

Sulphur analysis

Several comprehensive reviews describe in detail the different methods used to analyse S in crops and soils, and discuss the advantages and disadvantages of each one (Blanchar, 1986; Anderson *et al*., 1992; Kowalenko and Van Laerhoven, 1998).

In plant materials, total S or sulphate-S concentration is usually determined, as both can be used as indicators of sulphur deficiency (Zhao and McGrath, 1994). Total S can also be combined with total N measurements to obtain the N: S ratio. In the UK, it was found that the most common methods of total S determination were either ICP (inductively coupled plasma spectroscopy) or turbidimetry (Crosland *et al.* 1998, HGCA report OS26). In general, ICP is more reliable and robust than the turbidimetric method. Apart from S determination, the method of digestion of plant samples can also introduce large errors.

In soils, different extractants result in widely differing amounts of extracted S (Zhao and McGrath, 1994). For this reason, it is advisable that a standard extractant is adopted so that results can be compared accurately between laboratories. Although both extractable inorganic sulphate and total soluble S (inorganic sulphate plus organic S) can be related to plant responses to sulphur deficiency, the latter is usually

measured. This is because total extractable S can be determined using ICP analysis, a method that is precise and more rapid than IC (ion chromatography) analysis, which measures only inorganic sulphate. The majority of UK laboratories were found to use ICP analysis (Crosland *et al*., in press), while most of the others used turbidimetry.

The previous project revealed a large variability between analytical laboratories in the UK in plant and soil S analysis (Crosland *et al*. 1998, HGCA report OS26). The aim of this project was to repeat the inter-laboratory trial to determine if there had been any improvement in the S analysis in both plant tissues and soils in commercial analytical laboratories. Laboratories were asked to analyse four selected plant materials for total S and N and to analyse three soils for extractable S.

2. MATERIALS AND METHODS

Nine laboratories, including IACR-Rothamsted, participated in the study. Four crop materials, sugar beet leaves (PL1), wheat flour (PL2), wheat grain (PL3) and oilseed rape leaves (PL4) were selected for analysis to cover a range of total S and N concentrations. Sample PL2 was a reference material purchased from the Bureau of Analysed Samples (NIST 1567A) with an internationally certified S concentration of 0.165%. The materials PL1, PL3 and PL4 were prepared at Rothamsted; they were dried at 80^{o}C for 24 h and then ground to pass a 0.5 mm sieve. Each was then thoroughly mixed by a process of coning and quartering. To ensure homogeneity of the materials, replicate sub-samples were taken from each bulk sample, which were then analysed for total S and N. Approximately 20 g of each crop material was distributed to the participating laboratories. As a further test of homogeneity, a sub-sample from each crop material was analysed prior to distribution.

Laboratories were instructed to dry the materials at 80^{o}C for 4 h then take five replicate sub-samples from each material and use their routine methods for digestion and analysis. At IACR-Rothamsted, the materials were digested using a mixture of a nitric and perchloric acids (Zhao *et al* 1994), followed by ICP analysis for total S. The instrument was calibrated with a certified standard S solution purchased from Merck. Total N was determined using a combustion analyser (LECO CNS 2000), the instrument was calibrated with standard EDTA purchased from LECO.

Three soils, selected to contain different extractable S concentrations, were prepared at IACR-Rothamsted. Soil SO1 from Rothamsted and soils SO2 and SO3 from Woburn; all three soils were sampled from the top 30-cm of the soil profile. The

soils were air-dried, passed through a 2-mm sieve then thoroughly mixed by coning and quartering. To check for homogeneity, samples of the prepared soils were extracted and analysed at IACR-Rothamsted. Approximately 120 g of each soil was distributed to the laboratories, and as a final check, a sub-sample was analysed from each soil that was sent. For determination of extractable S, laboratories were instructed to carry out five replicate determinations of each soil using KH_2PO_4 extraction (Zhao and McGrath, 1994), extractable S was then determined using the preferred method of each laboratory.

3. RESULTS AND DISCUSSION

Data for total S in all four-crop materials are presented in Figures 1a-1d and plant total N in Figures 2a-2d. Extractable S data for the three soils are presented in Figures 3a-3c. Concentrations are presented on the vertical axis and laboratory code is on the horizontal axis. All laboratories reported five individual values of the repeated analysis of the plant materials and soil samples (L7 had two replicates per sample). The data are presented in the form of box plots, which show the mean value of the replicates as a thick dark line and the median as a thin line within each box. The ends of each box represent 25^{th} to the 75^{th} percentile of replicate data and the two outermost horizontal bars represent the 10^{th} and 90^{th} percentiles. Boxes with a narrower range show tight analytical precision for a laboratory.

3.1 **Total Sulphur in plant materials**

Total S in plant materials was determined in Laboratories L1, L2, L5, L6, L8 and L9 by ICP after acid digestion or ashing with magnesium nitrate. Laboratory 4 used acid digestion followed by precipitation with barium chloride and analysis by atomic absorption spectroscopy. Laboratory L7 used Dumas and the method of analysis used by Laboratory L3 was unknown.

The mean total S concentrations of the four plant samples ranged from 0.08-0.52%. For each plant material the inter-laboratory variability was considerable (Figures 1a-1d and Table 1). In samples PL1, PL2 and PL3 which contained mean S concentrations of 0.28, 0.14 and 0.11%, laboratories reported results which varied by 0.06-0.10% S. In PL4, the sample with the greatest total S concentration and a mean value of 0.42%, results varied by 0.18% S. In PL1 the results tend to fall into two groups, with laboratories (L2, L3, L5, L6 and L9) reporting results with a mean value of 0.31% S, whereas, laboratories (L1, L4, L7 and L8) reported a mean value of 0.25% S. A similar pattern can be seen for the other three plant materials. For example, in the case of PL2, where we have the advantage of knowing the certified value (0.165% ± 0.002), laboratories (L2, L4, L6 and L9) reported an overall mean of 0.16% S with two laboratories (L2 and L6) reporting mean results which fall within the certified range. Laboratories (L1, L3, L5 and L8) reported an overall mean of 0.13% S that is well below the accepted value for this standard. Results from L7 are lower than those of the other laboratories; this may indicate a problem with the analysis. With PL3, laboratories L1, L2, L4, L5, L6 and L9 reported larger values with an overall mean of 0.12% S, and laboratories L3, L7 and L8 reported a mean value of 0.08%S. In material PL4, which has the greatest total S concentration of all the materials, laboratories L2, L4, L5, L6 and L9 reported a larger value of 0.46% S and laboratories L1, L3, L7 and L8 reported an overall mean of 0.37% S. Laboratories L3, L7 and L8 tended to report lower values for total S in all four-plant materials, with the exception of L3 in material PL1.

The inter-laboratory CV's for total S ranged from 13.4 to 19.8%, indicating poor agreement between laboratories. These findings are very similar to those reported in a previous study (Crosland *et al.* 1998, HGCA report OS26), where the CV's ranged from 8.2 to 20.3%. Examination of the methods used show that laboratories use either acid digestion or ashing as the first stage in the analysis. Most

laboratories then measure the total S using ICP. Results suggest that the laboratories which use acid digestion followed by ICP for S measurement, tend to report larger values for total S concentration in plant materials than those using dry ashing procedures. Results from Laboratory L7, which used Dumas, were consistently lower than the results from the other laboratories.

Table 1. Inter-Laboratory CV% for plant material total S and N and soil extractable S

Materials	Inter-Laboratory CV for total S	Inter-Laboratory CV for total N	Inter-Laboratory CV for N:S	Inter-Laboratory CV for extractable S
PL1	13.4	6.6	11.6	
PL2	19.8	5.2	22.4	
PL3	17.3	5.0	20.8	
PL4	13.7	4.3	14.2	
SO1				44.3
SO2				16.7
SO3				46.2

3.2 **Total Nitrogen in plant materials**

For determination of total N, Laboratories L2, L4, L5, L6 and L8 used Kjeldahl and laboratories L1, L7 and L9 used Dumas. The method of analysis used by Laboratory 3 was unknown. In the four plant materials, the concentration of total N ranged from 1.62 to 3.82%. For most plant materials (PL2, PL3 and PL4), the differences between laboratories in the mean values fall within a range of 0.3 to 0.4% N but for PL1, the range is greater, at around 0.5%. The inter-laboratory CV's range from 4.3 to 6 .6% (Figures 2a-d and Table1). These results indicate that the data are quite variable and more so than in the previous study where CV's ranged from 2.7 to 5.4%. In material PL1, mean values for all laboratories apart from L4, are within the range 2.1 to 2.41% N. For plant material PL2, the results tend to fall into two groups, with five laboratories (L1, L3, L5, L6 and L9) reporting a mean value of 2.41% N and the remaining laboratories (L2, L4 L7 and L8) reporting 2.20% N. In PL3, all

laboratories, with the exception of L7, produced mean values which lie within a range of 1.69 to 1.90% N. Again with PL4, the laboratories tend to form two groups, seven laboratories (L1, L3, L5, L6, L7, L8, and L9) produced results with mean values which range from 3.52 to 3.82% N, whereas, mean results from the other two laboratories (L2 and L4) are around 3.4% N. As stated earlier, for the analysis of total N, laboratories used Kjeldahl or Dumas. However, the previous study showed that the inter-laboratory variability did not seem to relate to method of analysis.

3.3 **N: S ratios**

The industry often uses N: S ratios as a diagnostic tool for cereals and grass. This ratio is derived from two independent total N and S measurements, the robustness of which are critical to the reliability of this diagnostic approach. Table 2 shows the N: S ratios that have been calculated for each laboratory from the data obtained in this study. The CV's for total N determinations were reasonable but for total S large and variable. This is reflected in the inter-laboratory CV's for the N: S ratios that ranged from 11.6 to 22.4%. For the four crop materials, around 50% of the laboratories were within 90 to 110% of the median values compared with 40 to 70% in the 1998 study. For PL1 and PL4 the CV's were less than 15% but for PL2 and PL3, the most appropriate sample type for this diagnostic tool (wheat flour and wheat grain) the CVs are unacceptably large at 22.4 and 20.8%. In wheat grain, a ratio of 17:1 is usually considered to be the critical value. From this study, three laboratories would diagnose S deficiency in PL2 and in the case of laboratory L7 this would be severe. The results from the other six laboratories would suggest the opposite. Laboratories that underestimate total S are more likely to generate N: S ratios that tend to indicate sulphur deficiency. In PL3, again three laboratories would diagnose S deficiency, which from the results of laboratory L3 would be severe. The results from other six laboratories suggest the opposite.

Table 2. N: S ratios of the crop materials PL1-4.

Laboratory	PL1(Sugar beet leaf)	PL2 (Wheat flour)	PL3 (Wheat grain)	PL4 (Oilseed rape)
L1	9.4	17.9	17.3	9.4
L2	6.9	13.4	14.5	7.5
L3	7.5	20.2	24.9	10.1
L4	8.0	14.7	14.2	7.5
L5	7.8	18.3	15.2	8.5
L6	7.4	14.9	14.5	7.4
L7	9.6	26.4	18.0	10.4
L8	8.4	17.9	18.5	9.9
L9	7.3	15.0	14.0	7.8
Median	7.8	17.9	15.2	8.5
CV%	11.6	22.4	20.8	14.2

3.4 **Soil extractable sulphur**

The greatest inter-laboratory variability was seen in the results for extractable S analysis (Figures 3a-3c and Table 1). The inter-laboratory CV's for the three soils SO1, SO2 and SO3 were 44.2, 16.7 and 46.2%. In the previous study, the two soils analysed produced results with CV's of 36 and 45%. With the exception of soil SO2, the inter-laboratory CV's are similar with results showing the greatest variability of all the analyses. Laboratories L1, L2, L5, L6, L8 and L9 analysed the extracts by ICP, laboratory L4 used the turbidimetric method and also submitted data for extraction by mono-calcium phosphate (MCP). Laboratory L7 used the Mehlich procedure, data are not included because this method was not the specified procedure.

Where different methods are used it is important that the end user of the data is aware that soil extractable S data may be reported in various ways, for example, as *sulphate sulphur* (SO_4-S) or as *sulphate* (SO_4). When comparing with critical values for diagnostic purposes, it is important to express results on the basis of SO_4-S mg kg^{-1}. This can be achieved by dividing SO_4 mg kg^{-1} by 3; this factor is obtained by dividing the relative molecular mass (RMM) of SO_4 by the RMM of S (96/32). One could also argue that as most laboratories are analysing the extracts by ICP then results should be expressed as S mg kg^{-1} as the technique does not determine SO_4.

For soil SO1, the mean values ranged from 4.8 to 13.0 SO_4-S mg kg^{-1}, four laboratories L1, L6, L8 and L9 were in reasonable agreement, with mean values which ranging from 4.8 to 5.8 mg kg^{-1}. Laboratories L2, L4 and L5 reported much greater values that range from 9.8 to 13.0 mg kg^{-1}. Results from laboratory L4 using the MCP extraction lay between the two groups of laboratories. The mean values for extractable S in soil SO2 ranged from 10.2 to 16.3 mg kg^{-1}. The mean values for six laboratories, which includes the MCP data from laboratory L4 were within the range 10.2 to 14.0 mg kg^{-1}. In soil SO3, the laboratories mean value ranged from 3.2 to 9.4 mg kg-1. Again as in soil SO1, the same four laboratories were in agreement, with mean results, which are within the range 3.2 to 3.5 mg kg^{-1}. The mean results for the other three laboratories including the MCP data from laboratory L4, ranged from 5.2 to 9.4 mg kg^{-1}. Apart from laboratory L4, the methods of measurement used by laboratories was ICP. This suggests that the variability in the results is not related to method used but may relate to the way extractions were performed or the concentration of S in the soil. In soil SO2, the overall agreement between laboratories was more acceptable than in soils SO1 and SO3. The actual S concentration present in the KH_2PO_4 solution based on a soil to solution ratio of 1:5 for soil SO2 would be about 2.5 mg l^{-1}, which was greater than that found in soils SO1 and SO3. From the results of the four laboratories, which were in good agreement, it can be calculated that the solution concentration of S from soil SO1 would have been around 1.0 mg $l^{-1}$and from soil SO3 less than 0.7 mg l^{-1}. These results may indicate that the working detection limits for some of the laboratories ICP instruments are close to the S concentrations in these soil solution extracts. Inter-Laboratory variability seems to increase when the concentrations of extractable S are low.

By taking 6mg S kg^{-1}soil as the critical value, for soil SO1, four laboratories gave results that would lead to the recommendation that fertiliser is applied but three would not. For soil SO2, all laboratories gave results that indicate that the soil S status was adequate, but in the case of soil SO3, five laboratories gave results that lead to a recommendation to apply fertiliser. This includes laboratory L4 using MCP extraction that produces a lower value for S. The other laboratories including L4 (using KH_2PO_4 extraction) produce results which indicate the soil S status to be adequate but the results for L5 are borderline, with a mean value of 6 mg kg^{-1}.

4. CONCLUSIONS AND RECOMMENDATIONS

Analysis of plant total N by all laboratories appears to be reasonably well controlled, but the range of inter-laboratory CV's is slightly larger than that found in the previous study. Total S analysis is variable, and the agreement between laboratories does not appear to have improved since the first inter-laboratory study. For example, with plant material PL2 the certified reference material, five of the laboratories seriously underestimated total S concentration. This suggests that the analytical methods are not well standardised and controlled. Determination of soil extractable S was extremely variable in two of the three soils, and the range of results was considerable. This would create problems in interpretation of data for diagnostic purposes. It is also important to point out that although many of the labs that participated took part in accreditation schemes (e.g. NAMAS, GLP etc), this does not guarantee that the 'correct' results are obtained, for example for the internationally certified plant material.

As a result of this second study, it is appropriate to reiterate the previous recommendations:

1). Laboratories should standardise extraction and digestion procedures.

2). Where possible reference materials should be utilised to ensure that nationally or internationally comparable results are obtained (no reference materials currently exist for soils). Farmers or consultants could include such plant standards in their samples submitted to laboratories, as a check on their performance. However, as these materials are already dried and powdered, they would be obvious and stand out in any batch of samples.

3). Analytical methods must be capable of determining low concentrations of S in soil extracts. Most laboratories are running ICP instruments; the detection limits for S on some manufacturer's instruments can be quite poor. Laboratories should be prepared to supply information on instrument detection limits to the customer.

4). Methods must be calibrated for diagnostic purposes so that results obtained are comparable with those from other methods. Also, soil extractable S data should be expressed as mg S kg^{-1}, especially when the determination is by ICP.

5). Laboratories should assess their analytical performance regularly by participating in schemes such as the International Plant /Soil Analytical Exchange (IPE/ISE) run by Wageningen Agricultural University in the Netherlands. This costs around £500 per year and provides analytical laboratories with sets of four samples on a quarterly

basis. Access in confidence to other laboratory data and information about methods used is also available through the quarterly reports. In this way, problems with the determination of total S in plant material could be quickly identified. Again, if farmers or consultants were in a position to submit these materials, laboratories may have to take steps to produce results that are comparable with others in the industry.

6) IPE/ISE will undertake to produce at cost reference samples for laboratories with reliable consensus values. This could be a way of producing a soil reference for extractable S analysis.

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7. FIGURES

Figures 1a-d. Total S concentration (%) in plant materials PL1, PL2, PL3, and PL4.

Figure 1a

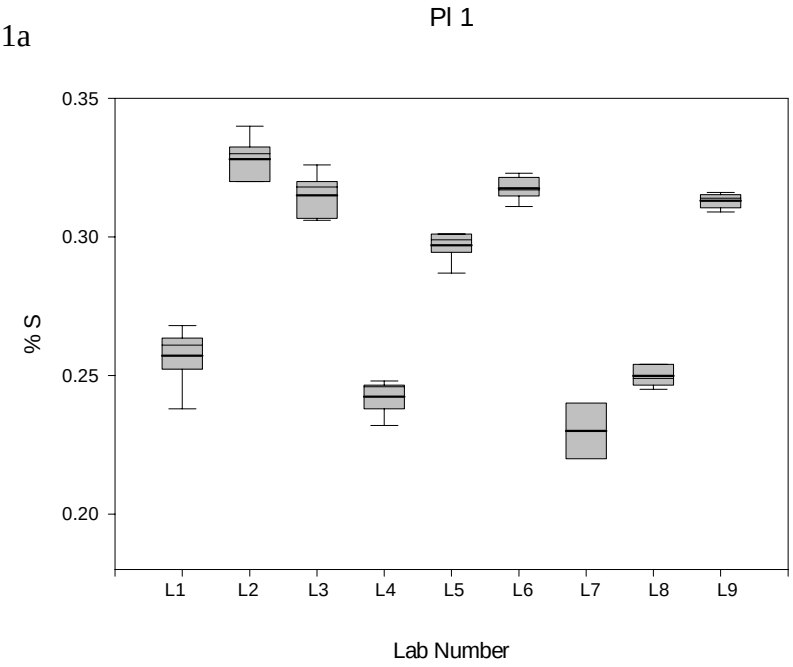
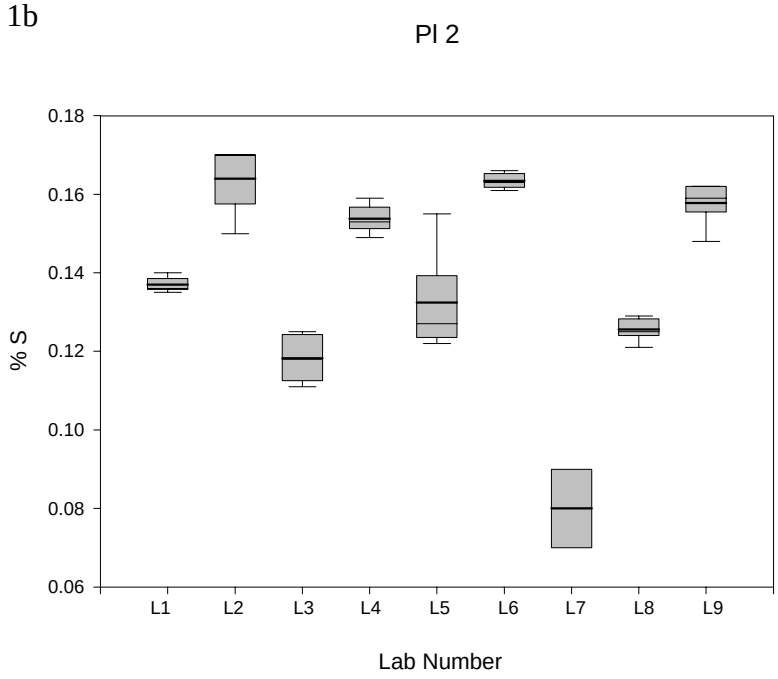


Figure 1b



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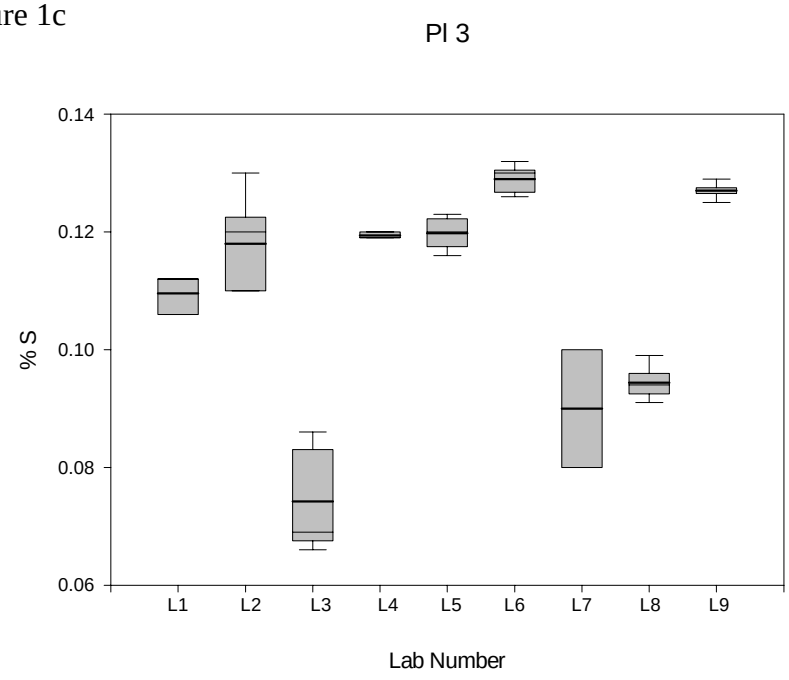

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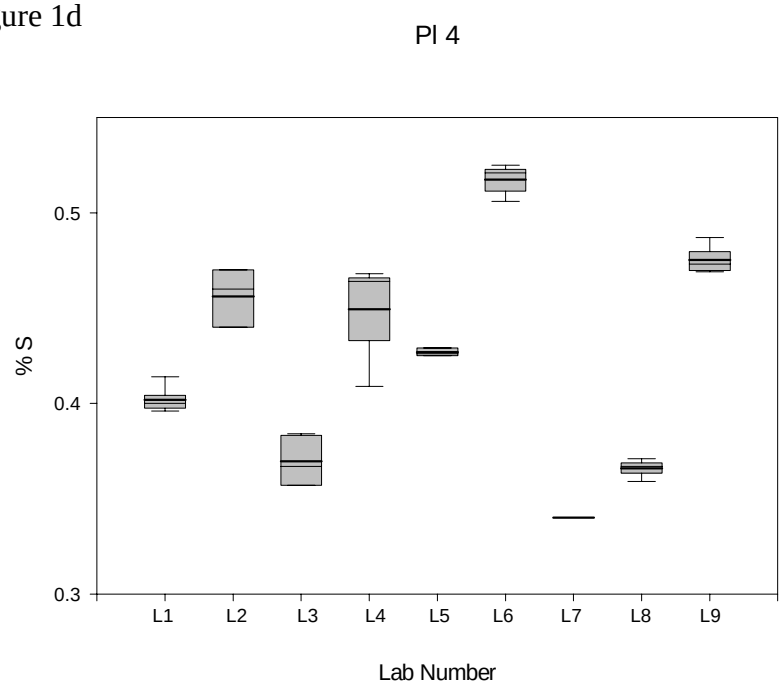
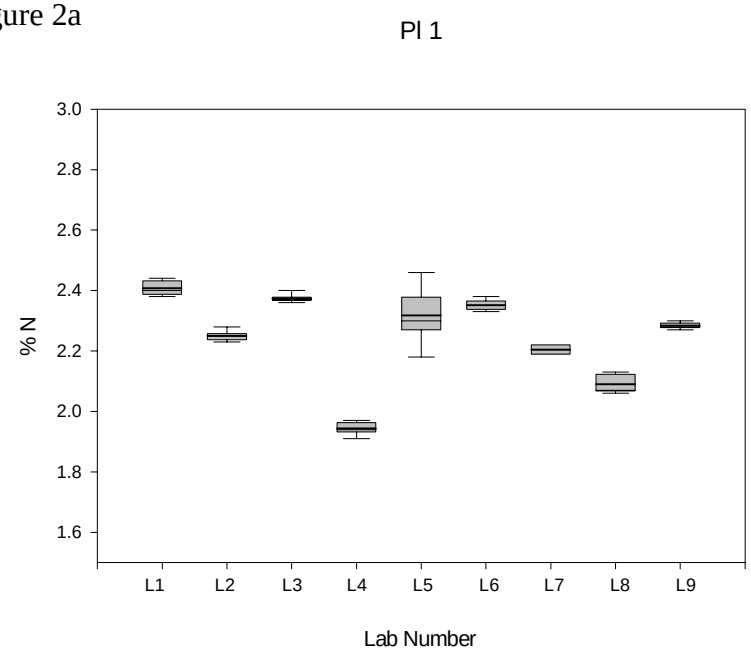


Figure 2a-d. Total N concentration (%) in plant materials PL1, PL2, PL3, and PL4.

Figure 2a



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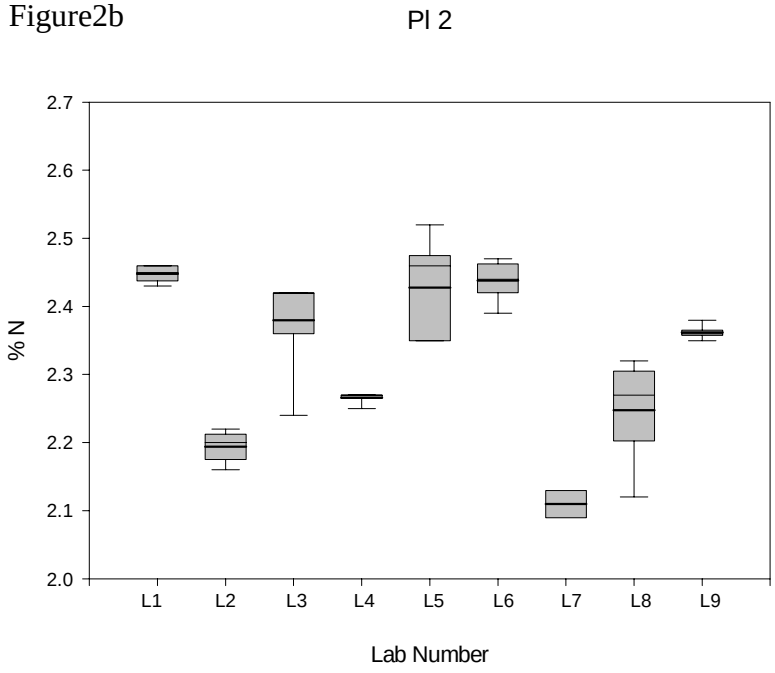

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Figure 2c

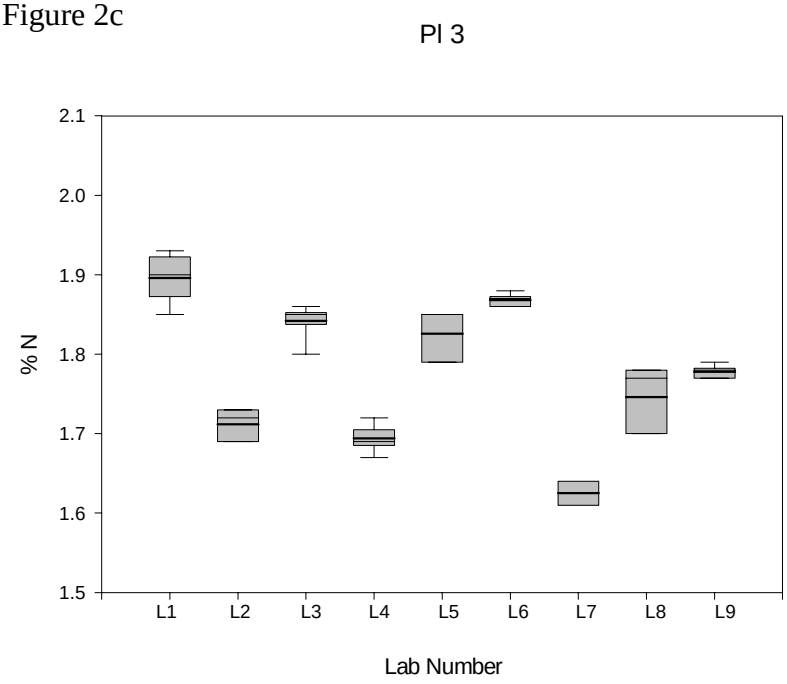
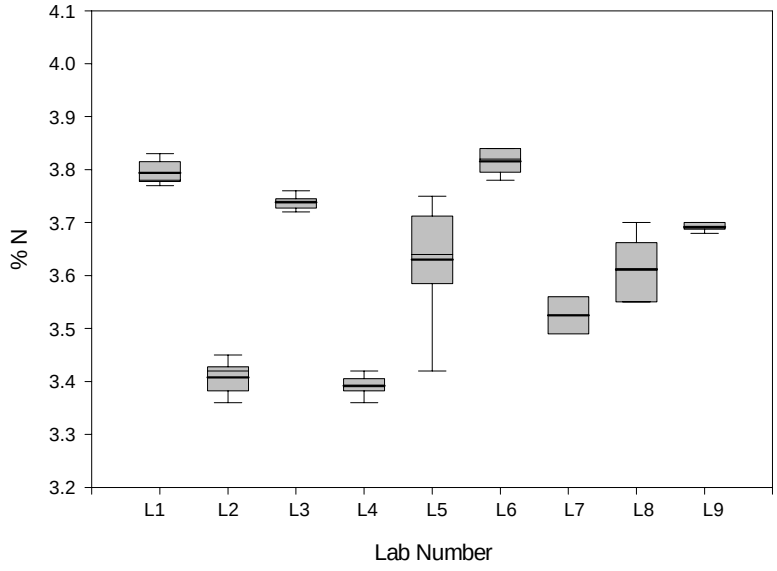


Figure 2d



Figures 3a-c. Extractable S concentration (mg kg^{-1}) in soils SO1, SO2, and SO3.

Figure 3a

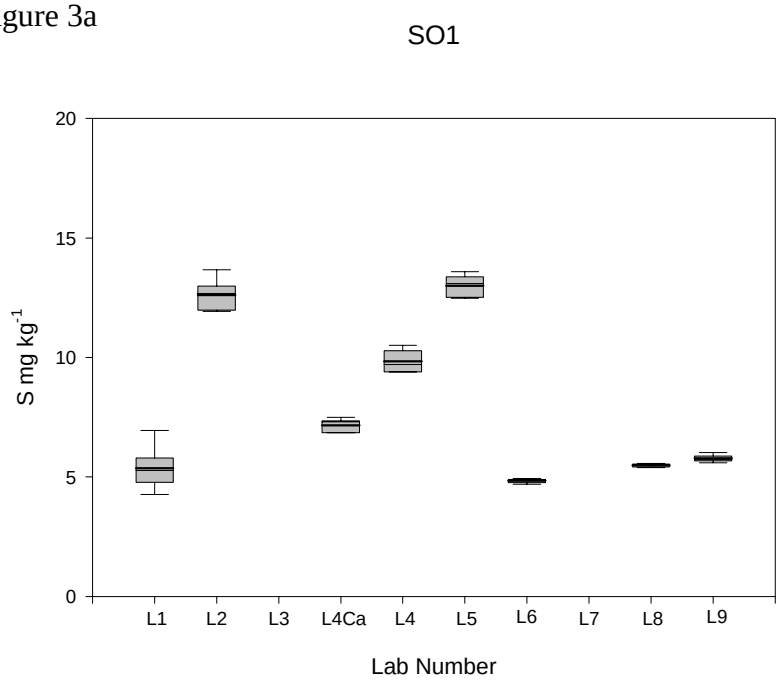


Figure 3b

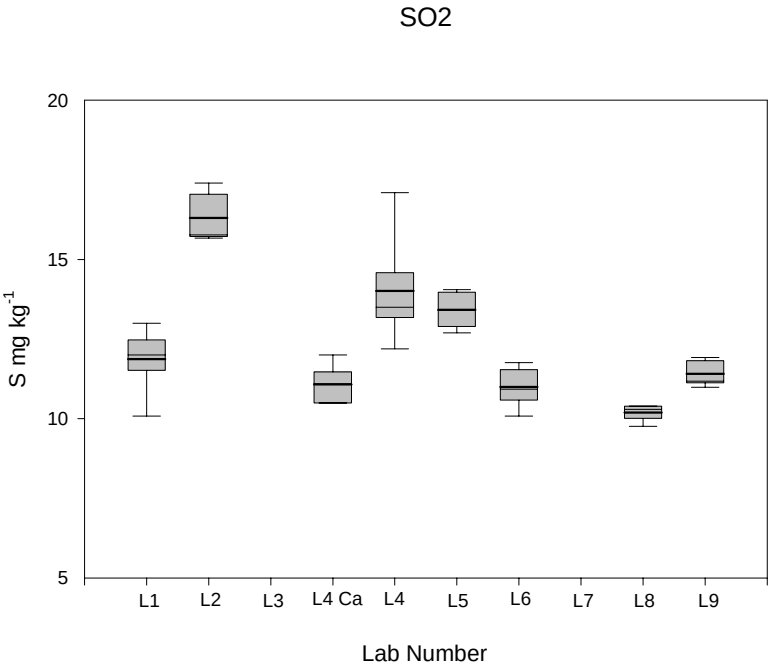


Figure 3c