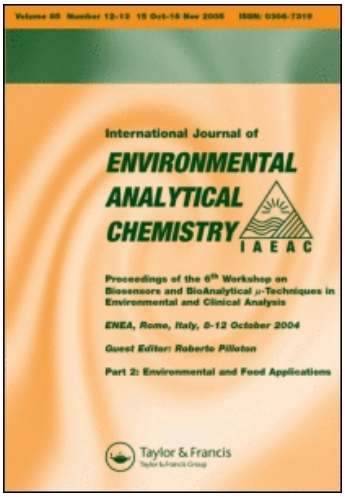

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An Interlaboratory Comparison of a Standardised EDTA Extraction Procedure for the Analysis of Available Trace Elements in Two Quality Control Soils

A. R. Crosland[a]; S. P. McGrath[a]; P. W. Lane[b]
[a] Soil Science, AFRC Institute of Arable Crops Research, Rothamsted Experimental Station, Harpenden, Herts, U.K. [b] Statistics Departments, AFRC Institute of Arable Crops Research, Harpenden, Herts, U.K.

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AN INTERLABORATORY COMPARISON OF A STANDARDISED EDTA EXTRACTION PROCEDURE FOR THE ANALYSIS OF AVAILABLE TRACE ELEMENTS IN TWO QUALITY CONTROL SOILS

A.R. CROSLAND*, S.P. McGRATH* and P.W. LANE†

**Soil Science and †Statistics Departments, AFRC Institute of Arable Crops Research, Rothamsted Experimental Station, Harpenden, Herts AL5 2JQ U.K.*

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A standardised EDTA extraction procedure was tested collaboratively by six laboratories using two in-house reference soils identified as soil A and soil B. The extracts were analysed for Zn, Cu, Pb and Mn by Inductively Coupled Plasma Spectrometry. Concentrations of extractable elements in soil A were generally much lower than those found in soil B. All laboratories produced some extreme outlying results, most of these were produced in soil B. Results for Mn were the most variable, with a range of 63.4-100.3 $\mu g\ g^{-1}$ in soil A and 226.4-415.3 $\mu g\ g^{-1}$ in soil B. In both soils, one laboratory reported high values for Zn and Mn and, one laboratory, for soil B, produced values for all four elements which were consistently low.

If outlying results are ignored, the results from most laboratories were in reasonable agreement for all elements except Mn.

KEY WORDS: Heavy metals, zinc, copper,lead, manganese, ICPAES.

INTRODUCTION

In all analytical processes the application of reliable quality assurance procedures is of paramount importance, and for routine analyses these procedures are well established. An extensive programme of analytical quality assurance was implemented during the analysis of soil samples for the National Soil Inventory of England and Wales (NSI). The NSI project was set up to produce data for a geochemical atlas of soils for England and Wales[1]. The project involved the analysis of almost 6000 soils for 'total' element contents over three years, and for extractable elements over a two year period. This paper discusses only the analyses done using the standardised EDTA extraction procedures adopted by the Agricultural Development and Advisory Service (ADAS)[2] in England and Wales.

In attempting to determine the fraction of nutrient or toxic elements available for uptake by plants and micro-organisms many different reagents have been used[3]. However, it is

recognised that none can truly mimic the processes involved at the soil/root interface and, at best, a correlation with uptake is all that can be achieved.

Although the extraction methods may be chemically rather non-specific, their speed and ease of use make them attractive for routine application for estimation of bio-availability and speciation[4].

EDTA extraction was chosen because of its previous wide application in agricultural science and soil analysis, and the fact that it was a completely standardised method. Furthermore, the method fulfilled the budgetary requirements of the programme and, as a widely used procedure, it enabled comparisons with existing data to be made. This paper presents the results of an interlaboratory calibration exercise designed to assess the effectiveness and reliability of the chosen methodology when under the control of experienced laboratories.

MATERIALS AND METHODS

The soils to be used for quality control were in-house reference materials prepared by two of the participating laboratories. The two soil types were identified as A and B, soil A being a non-humose and B a humose soil. The homogeneity and stability of these soils had been established previously. The soils were air dried and ground to pass a 2 mm sieve. After preparation, the soils were distributed to the six participating laboratories and each laboratory carried out around twelve replicate extractions on each of the soils. In addition, the laboratories supplied blank solution extracts for determination of background trace element levels. The extracts were sent to Rothamsted for analysis by Inductively Coupled Plasma Spectrometry (ICP). In this study, procedures were standardised by weight, and to test the precision and accuracy of the sampling procedures, all laboratories were required to supply actual sample weights taken to achieve the 10 ml volume of soil specified in the published protocol for this method[2].

Extractable trace elements

Zn, Cu, Pb and Mn were extracted by shaking 10 ml of soil with 50 ml of 0.05 $mol l^{-1}$ $(NH_4)_2EDTA$ at pH 7.0 for one hour at 20°C. The extracts were filtered through a Whatman No 2 filter paper and the metals determined by ICP. To minimise systematic instrumental errors the samples were randomized and analysed in duplicate on different days.

Spectrometry

Concentrations of the four elements mentioned above in the EDTA extracts were determined by ICP. The instrument used was an ARL-Fisons 34000 simultaneous multi-channel model that can monitor up to twenty elements in a single solution. Corrections for interference were set after detailed investigation of spectral effects experienced with this instrument[1]. These are applied on-line by the instrument's computer.

Table 1 Variations in the weights of soil (g) taken for extraction using a 10 ml volume sampling vessel.

		A			*B*		
Laboratory	*n*	*range*	*mean*	*cv*	*range*	*mean*	*cv*
1	12	11.4 - 12.1	11.7	1.96	9.8 - 10.2	10.0	1.24
2*	33	12.7 - 13.2	13.0	0.85	9.8 - 10.2	10.1	1.26
3	12	12.6 - 12.9	12.8	0.59	9.8 - 10.2	10.0	1.38
4	10	11.8 - 12.7	12.2	2.47	9.8 - 10.1	10.0	1.01
5	12	12.2 - 12.5	12.4	0.93	9.5 - 10.0	9.7	1.64
6	12	12.2 - 12.5	12.4	0.69	9.9 - 10.2	10.0	0.88
mean		11.4 - 13.2	12.3	3.26	9.5 - 10.2	9.9	1.64

*Laboratory 2 did not supply weights for A and B soils. The weights in the table were obtained from routine NSI extractions and they are not included in the mean.
n = number of replicates

Detection limits

The detection limits are calculated as three times the background standard deviation when aspirating a blank solution. Conventionally, these limits are determined on aqueous standard solutions, but in practice they may bear little relation to the values obtained from dilute soil extracts. In these, much of the analyte signal may arise from interfering components and the accuracy of the interference corrections becomes a limiting factor in determining analytical precision. Interference corrections tend to be additive: corrections applied to one analyte from a range of interfering elements would each make a contribution to the detection limits[5]. For reliable quantification in solution, elemental concentrations should be ten times the detection limit. These values are defined as the lower analytical limit.

RESULTS AND DISCUSSION

Soil weights

The weights of soil taken for extraction using a 10 ml volume sampling vessel are presented in Table 1. For soil A the values ranged from 11.4 to 13.2 g and for soil B from 9.5 to 10.2 g. Clearly, the weights were not well controlled and, if results were expressed on the basis of volume alone, unacceptable discrepancies in elemental concentrations would arise. To eliminate this source of error, all results were calculated on the basis of weight rather than volume although it is recognised that, for agricultural advisory purposes, concentrations of elements extracted by this established method are normally expressed on a volume basis[2].

Background levels of extractable trace elements

The background levels for extractable elements in the blank solutions are presented in Table 2; detectable levels of Zn, Cu and Pb were found in many of the blank solutions. The Zn

Table 2 Mean background concentrations of trace elements in blank extract solutions ($\mu g\ ml^{-1}$).

Laboratory	*n*	*Zn*	*Cu*	*Pb*	*Mn*
1	4	0.038	<DL	0.042	<DL
2	4	<DL	0.067	0.023	<DL
3	8	0.141	0.074	0.039	<DL
4	10	0.021	0.025	0.076	<DL
5	8	<DL	<DL	0.040	<DL
6	8	<DL	0.004	0.035	<DL
DL		0.0027	0.0015	0.050	0.0006

DL = detection limit
lower analytical limit = detection limit × 10

contents in extracts from laboratories 1 and 3 were above the lower analytical limit ($0.027\mu g\ ml^{-1}$). The largest concentrations were in extracts from laboratory 3, with values ranging from 0.048-0.369 $\mu g\ ml^{-1}$ in solution equivalent to 0.243-1.840 $\mu g\ g^{-1}$ in the soil. For Cu, values above the lower analytical limit ($0.015\ \mu g\ ml^{-1}$) were found in extracts from laboratories 2,3 and 4. The highest values were from laboratory 3 with values ranging from 0.021-0.212 $\mu g\ ml^{-1}$ in solution, this is equivalent to 0.106-1.06 $\mu g\ g^{-1}$ in the soil.

Low concentrations of Pb were detected in blank extracts from all laboratories, but none were above the lower analytical limit. Mn was not detected in any of the blanks.

Extractable Zn, Cu, Pb and Mn

The concentrations of extractable Zn, Cu, Pb and Mn in soil A are presented in Figure 1 and for soil B in Figure 2. In each case schematic plots[6] are used to represent the distribution of values for each laboratory. The box represents the interquartile range, and the bar within it is the median. Using the terminology of Tukey[6], the range of outlying results is shown by 'whiskers' which extend up to 1.5 times the interquartile range, with extreme outlier results shown individually beyond that.

Extractable Zn in soil A ranged from 2.9-5.2 $\mu g\ g^{-1}$ with a median value of 3.3 $\mu g\ g^{-1}$ (Figure 1). Most of the outlying values were produced by laboratories 1 and 3; values from laboratory 1 were the most variable and laboratory 3 produced two extreme outliers. If the extreme outliers and results for laboratory 1 were excluded, then 75% of the results would fall within the range of 3.0-3.7 $\mu g\ g^{-1}$. In soil B, the median extractable Zn content was 11.4 $\mu g\ g^{-1}$, with a range of 9.7-13.5 $\mu g\ g^{-1}$ (Figure 2). The highest values were given by laboratory 1 and the lowest by laboratory 5, and within the latter's results, two high values were extreme outliers. If laboratories 1 and 5 were excluded, then the other laboratories would be in good agreement with 75% of their results in the range 10.6-12.9 $\mu g\ g^{-1}$.

In soil A, extractable Cu values ranged from 6.2-7.7 $\mu g\ g^{-1}$ with a median value of $6.8\mu g\ g^{-1}$ (Figure 1). The highest values were given by laboratory 2 and the lowest by laboratory 3. The other laboratories were in good agreement with 75% of their results within the range 6.6-7.3 $\mu g\ g^{-1}$. Overall, in soil B, results ranged from 4.5-6.9$\mu g\ g^{-1}$ (Figure 2), with a median

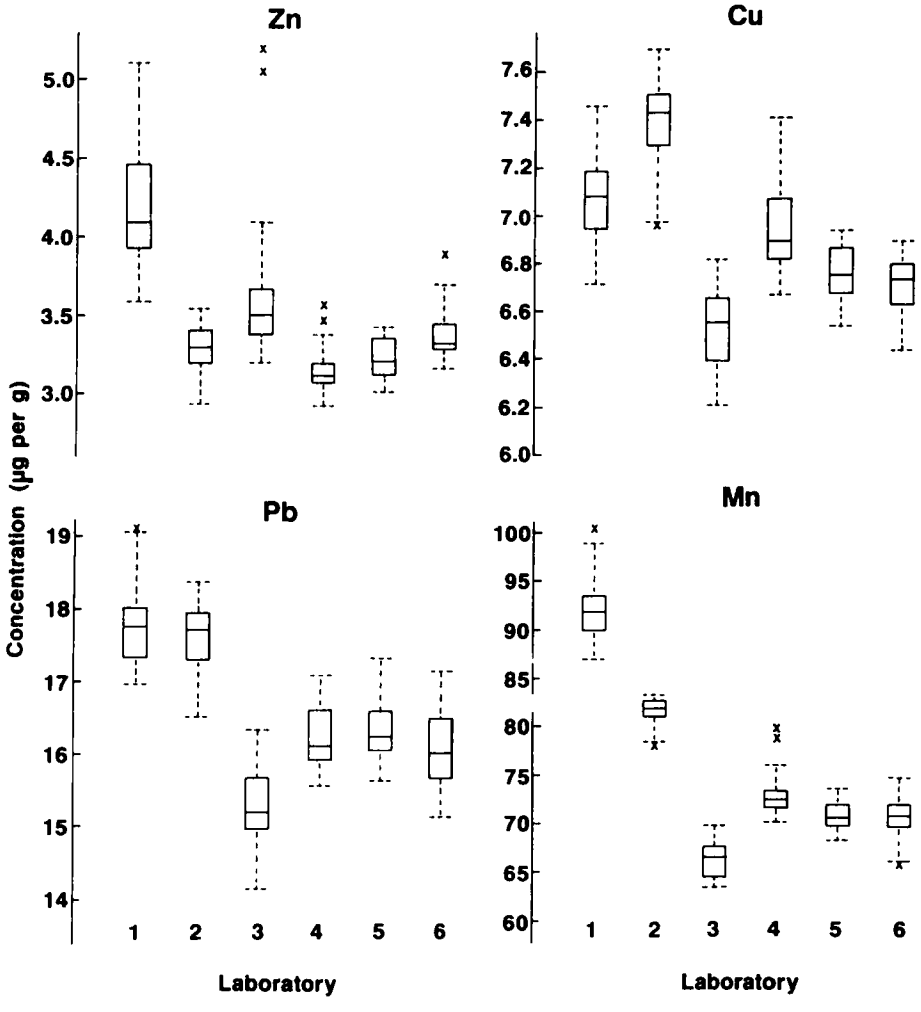

Figure 1 The concentrations of extractable Zn, Cu, Pb and Mn ($\mu g\ g^{-1}$) in soil A measured by the six laboratories. In the schematic plot, the box represents the interquartile range, with an additional line at the median; whiskers extend up to 1.5 times the interquartile range, with more extreme points shown individually.

of 5.5 $\mu g\ g^{-1}$. Extreme outlying results were produced by laboratories 2,3,5 and 6. For soil B results appeared to be less well controlled than for soil A.

In soil A, extractable Pb content ranged from 14.1-19$\mu g\ g^{-1}$ with a median value of 16.4 $\mu g\ g^{-1}$ (Figure 1). As with Zn, laboratories 1 and 3 produced the highest number of outlying results. Of these, only one value from laboratory 1 was an extreme outlier. In soil B, extractable Pb content was much higher at 36.5$\mu g\ g^{-1}$, with values ranging from 31.0-44.1$\mu g\ g^{-1}$; extreme outliers were identified for laboratories 2 and 5. In this soil, the spread of results is much greater than in soil A (Figure 2). This is shown by a range of 13.1 $\mu g\ g^{-1}$ (36% of the median) in soil B compared to 4.9 $\mu g\ g^{-1}$ (30%) in soil A.

The concentration of extractable Mn in soil A was within the range 63.4-100.3 $\mu g\ g^{-1}$,

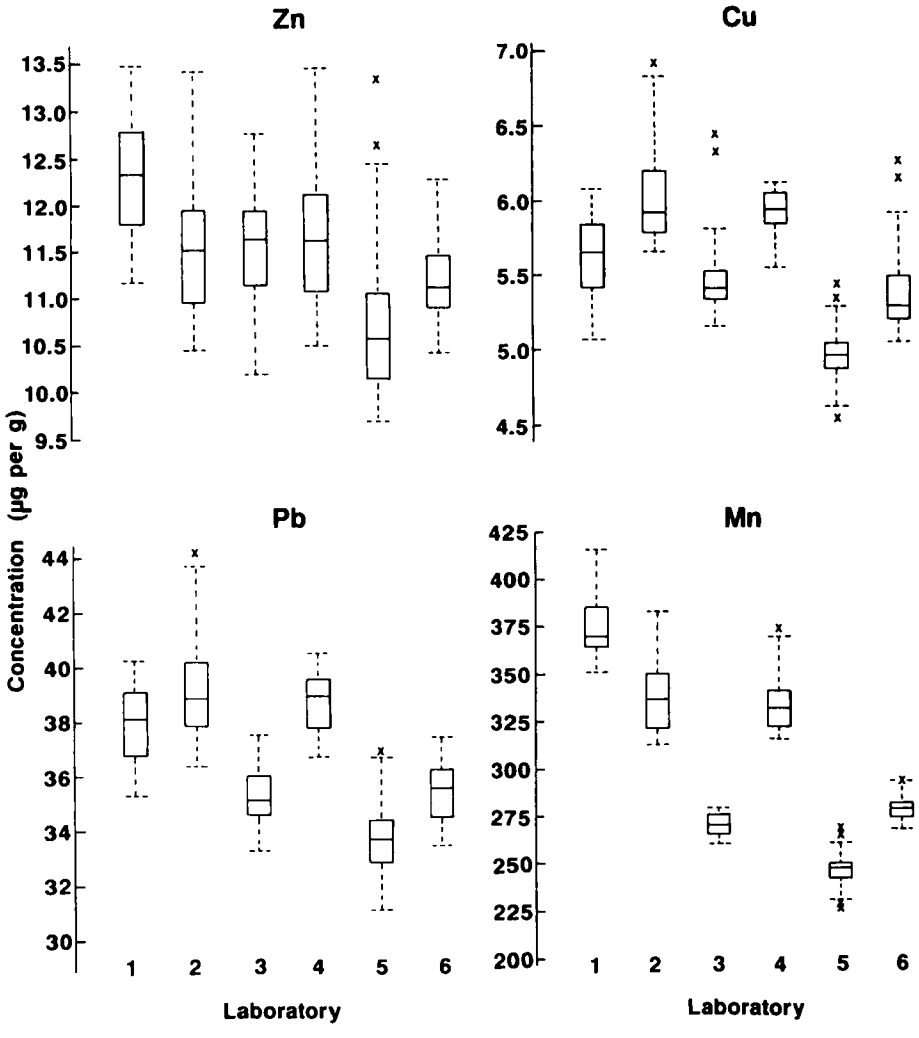

Figure 2 The concentrations of extractable Zn, Cu, Pb and Mn (µg g^{-1}) in soil B measured by the six laboratories. For description of schematic plots refer to Figure 1.

with the highest values from laboratory 1 and the lowest from laboratory 3, a similar trend to that of Pb and Cu (Figure 1). In soil B, the extractable Mn concentrations were much higher, ranging from 226.4-415.3 µg g^{-1}; again the highest and lowest values were reported by laboratories 1 and 5 (Figure 2). Median values for soils A and B were 72.0 and 288.8 µg g^{-1}, respectively. For Mn the range of results in both soils was relatively large and overall agreement between laboratories was poor.

CONCLUSIONS

The concentrations of extractable trace elements found in soil A were generally much lower than in soil B. All laboratories produced some extreme outlying results; there were 12 for soil A and 18 for soil B. This suggests an increase in variability which may be related to soil type or efficiency of the method. Laboratory 1 consistently produced higher results for Zn and Mn in both soils. In soil A, high Zn values were reported for laboratories 1 and 3. An explanation for this may be found by examination of the concentrations of these elements in the blank extracts: both laboratories report high values for Zn. This may be an indication that contamination could have contributed to the higher values obtained. For laboratory 5, the results for all four elements in soil B were consistently low.

If outlying results are ignored, the results from most laboratories were in reasonable agreement for all elements except Mn. When using this method, such variability between laboratories may have to be tolerated for this element.

Some of the differences between laboratories may be related to the way the extraction procedure is applied. Further explanation of these differences would require more detailed information from each participating laboratory or, for example, regulation of pH, temperature, concentration of extractant and time of extraction.

The main objective of this study was to develop an overall view of the performance of the EDTA extraction method. As shown above, there were differences between results determined by analyses done by one laboratory on samples extracted in six regional laboratories. It was decided that the variation was small enough to be acceptable for the countrywide survey in the NSI programme. Additional support for this idea comes from the obvious associations with geochemical features shown in the maps of these results[1]. During the survey, each regional laboratory extracted soils sampled from their local area. There was no evidence of trends associated with the known regions in which the samples were extracted[1].

It is also concluded that when using this method, if even tighter control of results is required, the samples must be both extracted and analysed in one central laboratory. If internationally certified reference soils for EDTA extractable metals are available in future, this would enable a better standardisation of this method in all laboratories involved in these kinds of analyses[7].

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