

# Within site and between site nested analysis of variance (ANOVA) for Geochemical Surveys using MS EXCEL

Internal Report IR/02/043

#### BRITISH GEOLOGICAL SURVEY

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# Within site and between site nested analysis of variance (ANOVA) for Geochemical Surveys using MS EXCEL

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Bibliographical reference

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## Summary

This report describes a method of nested analysis of variance (ANOVA) using a visual basic macro in Microsoft EXCEL 2000. Nested ANOVA analysis is used in geochemical surveys to test the suitability of the sampling and analytical methodology and quantifies the within site and between site variability. If the between site variability is greater than the within site variability then the survey methodology is satisfactory. BGS uses this quality control procedure for its national and international geochemical surveys. However, the restricted availability of specialist statistical software to do nested ANOVA has often resulted in a variety of software packages being used for different projects. This report describes a method of nested ANOVA that can be done using the widely available Microsoft EXCEL. Data input format and result reporting is similar to that used on the Geochemical Baseline Survey of the Environment (G-BASE) Project.

## 1 Introduction

Analysis of variance (ANOVA) is one of several procedures that is used to monitor the quality and representativity of geochemical results. Nested ANOVA analysis done on duplicate and replicate samples can be used to give a quantitative measure of the variability of results within and between sampling sites. For the methods of a geochemical survey results to be considered valid, the variation in results between different sites should be much more than the variation in results from samples collected at the same site.

This is determined by calculating the variance components expressed as a percentage of the total and a summary table of such data is shown in Table 1.

	Variance Component (%)								
	Sites	Duplicates	Replicates	Total					
Ag	2.7193	0.0000	97.2807	100					
As	99.5744	0.2556	0.1700	100					
Ba	99.5641	0.2944	0.1415	100					
Be	95.6789	0.0000	4.3211	100					
Bi	95.4449	0.0000	4.5551	100					
Cd	13.8361	0.0000	86.1639	100					
Со	68.6439	0.0000	31.3561	100					
Cr	99.0051	0.2933	0.7016	100					
Cu	99.0679	0.0921	0.8399	100					
Fe <sub>2</sub> O <sub>3</sub>	98.9610	0.9041	0.1349	100					
Li	98.3441	0.0000	1.6559	100					
MnO	99.0357	0.8001	0.1642	100					
Мо	79.3723	11.9387	8.6890	100					
Nb	99.5499	0.4251	0.0250	100					
Ni	93.1000	0.0000	6.9000	100					
Pb	97.6080	2.1987	0.1934	100					
Sb	90.2153	2.3122	7.4725	100					
Sn	94.0362	0.2867	5.6771	100					
Sr	99.8779	0.0774	0.0447	100					
Te	0.0000	0.0000	100	100					
Th	92.8791	0.0000	7.1209	100					
TiO <sub>2</sub>	98.3582	1.4452	0.1965	100					
U	71.1965	0.1202	28.6833	100					
V	99.0381	0.3177	0.6442	100					
W	88.0914	8.8383	3.0702	100					
Y	96.9617	1.8054	1.2330	100					
Zn	99.4340	0.4571	0.1089	100					
Zr	98.7967	1.0113	0.1920	100					

# Table 1: Summary of nested ANOVA results for a regional geochemical data set from Morocco

The amount of importance we should attach to the ANOVA method depends on how representative the replicate and duplicate sampling is, and to what extent the geochemical data fits in with the ideal statistical models for data distribution. For the UK Regional Geochemical Mapping there are ANOVA samples for one out of every 93 sites sampled and the analysis is done without considering any of the site characteristics (such as catchment lithology). Furthermore, the geochemical data rarely follows the ideal normal population distribution so poly-modal non-normal distributions, with outlying values, will not give strictly valid ANOVA results. Inspection of the ANOVA data beforehand (e.g. plotting cumulative probability plots) will help to establish the applicability of the ANOVA method and may be used to explain high

percentage of variance between samples collected at the same site. Converting the results to  $log_{10}$  will reduce the effect of outlying results.

It should also be noted that although duplicate samples are collected at the same site, this is strictly speaking not true. Two samples cannot be collected from the same point so there will be some variance component because of this. The significance of this will vary with different sample media.

Any discussion of the ANOVA results should take into account these limitations discussed above. Nevertheless, the results can be used to indicate the elements for which geochemical variability between sites is most significant. A good discussion of ANOVA analysis for evaluation of precision requirements for geochemical analysis is given by Ramsey and others (1992). This work recommends that analytical variance should be <4% and duplicate variance <16%. The term nested (sometimes referred to as hierarchical) is used when fewer than all levels of one factor occur within each level of the other factor.

In order to look at "within" site and "between" site variability it is necessary for the data set to contain duplicate and replicate samples. A duplicate sample is a sample that is collected from the same sampling site as an original sample. A replicate is an original sample subdivided in the laboratory. A duplicate sample will therefore indicate sampling variability within a single site whereas a replicate will indicate the variability of the laboratory analysis. For the G-BASE project the replicates are sub-samples of the duplicate samples (see Figure 1) so the nested ANOVA is made up of the results from four samples originating from a single site.



Figure 1: Explanation of the G-BASE method of duplicate and replicate numbering

This report does not cover the theory behind the random nested ANOVA method (see Sinclair, 1983). It is based on an unpublished note by Johnson (1995).

Nested ANOVA is not a simple statistical procedure and methods vary (particularly in data input format) between statistical packages. The G-BASE project has used SAS and MINITAB software but these relatively expensive packages have not generally been available for use in overseas geochemical surveys because of licencing restrictions. It is much more satisfactory to carry out the nested ANOVA in a software package that is universally available. Microsoft Office is a software package widely used and Microsoft EXCEL can be used to do much of the

statistical analysis necessary for regional geochemical surveys (e.g. summary statistics and histograms, Johnson, 2000).

The method described here is therefore widely applicable, particularly for international geochemical surveys where specialist statistical software in the local language is not available. It is a simple procedure to edit the macro to report the summary table with column headings in, say for example, French.

#### 1.1 NESTED ANOVA ANALYSIS BY MICROSOFT EXCEL 2000

Microsoft Excel has "Data Analysis" option from the Tools menu (if installed) that brings up the dialogue shown in Figure 2.

ata Analysis	? >
<u>A</u> nalysis Tools	OK
Anova: Single Factor	
Anova: Two-Factor Without Replication	
Correlation Covariance	Help
Descriptive Statistics	
Exponential Smoothing	
Fourier Analysis	
Histogram	•

#### Figure 2: Microsoft Excel 2000 Data Analysis dialogue box

Nested ANOVA analysis is **not** an option<sup>1</sup> and the data analysis **cannot** be used be performed using this data analysis tool. For nested ANOVA an EXCEL visual basic macro has been written that will reformat and log the raw data, calculate the variance components for each element and create a summary table of the results. The equations and formulae for calculating the variance are based on those presented by Sinclair (1983). A listing of the macro is given in Appendix 1 and is available in a blank workbook file called *nested\_Anova\_blank.xls*<sup>2</sup>.

<sup>&</sup>lt;sup>1</sup> An explanation of the the ANOVA options that are available can be found at <u>http://www.mastep.sjsu.edu/learn/anova.htm</u>

 $<sup>^2</sup>$  For those who have access to the internal BGS server this is available on the corporate shared drive in the G-BASE project directory at : .....gbase/Sample Analysis/

# 2 Procedure for Nested Analysis of Variance using MS EXCEL 2000

The procedure has two stages. Firstly, the data (in a standard format) is copied into an EXCEL workbook containing the "nested-ANOVA" macro. The data input format (see below) is similar to that used for the G-BASE project. Secondly, the macro is run to produce a summary percentage variance table. The macro is currently set to process a data set with a maximum of 4000 control sites and 50 elements. These are merely a check to stop uncontrolled looping and could be increased if necessary.

#### 2.1 DATA FORMAT

Appendix 2 gives an example of the format for the input data. The correct data input format is essential and the following should be used as a checklist prior to actually doing the ANOVA analysis:

- 1) The first cell (A1) should contain a title for the data
- 2) The second row should contain the column headers and these headers will be used in the final summary table. Column one is the site/sample number, column two the control sample description (e.g. DUPA), and subsequent columns the data to be interpreted
- 3) The data records should commence on the third row. **The data should not contain zeros or minus data**.
- 4) Data for each set of control samples (i.e. two duplicates and two replicates) **must be** listed in the order DUPA, REPA, DUPB, and REPB (see Appendix 2)
- 5) The worksheet should be named "Data" and it should be the **only** worksheet in the workbook.

#### 2.2 DOING THE ANOVA ANALYSIS

When the data is correctly set out as described above the actual data processing can commence. This is simply done by running the nested-Anova macro in EXCEL (shortcut key Ctrl+Shift+R).

The macro then does the following:

- 1) The data layout is checked and the user informed as to how many sites and elements will be processed. If the data layout is incorrect the user will be informed or it will be obvious from the "number of sites and elements to be processed" message.
- 2) A new worksheet is created and named after the element being processed
- 3) The four control samples (DUPA, REPA, DUPB and REPB) are reformatted from four rows in a single column to one row of four columns
- 4) The data is log transformed ( $\log_{10}$ )
- 5) The degrees of freedom and various summations as described by Sinclair (1983) are performed and listed on the data sheet. The layout of a worksheet for a single element ANOVA analysis described in Appendix 3

6) The variance component (expressed as a percentage) is taken from each element sheet and placed in a neatly formatted table. This table is placed in a worksheet called "Summary" which is displayed when the macro ends successfully.

Element	Between Site %	Between Sample %	Within Sample %	Total %
MnO	96.03	3.92	0.05	100
FE2O3	96.62	3.36	0.01	100
v	97.85	2.09	0.06	100
Cr	93.46	5.55	0.99	100
Co	94.00	5.62	0.38	100
Ва	97.39	2.56	0.05	100
Ni	95.96	3.83	0.21	100
Cu	98.87	1.08	0.06	100
Zn	92.64	7.34	0.02	100
As	97.87	1.82	0.31	100
Мо	93.59	3.23	3.17	100
Pb	96.51	3.43	0.06	100

#### **Urban Soil Control data**

#### Table 2: Summary table of results from nested ANOVA analysis of control data set

#### 2.3 TESTING THE PROCEDURE

This procedure has been tested using a control data set analysed in SAS and described by Lister (2002). The table of variance components is shown in Table 2 and is consistent with the results obtained by Lister (2002).

### Appendix 1 : Listing of Nested\_Anova macro

Sub Nested\_Anova() ' Macro to do nested ANOVA analysis ' Macro written 18/02/2002 by Chris Johnson ' Keyboard Shortcut: Ctrl+Shift+R 'declare variables Dim Msg, Style, title, Help, Ctxt, Response, MyString Dim myRange As Range Dim c As Object Dim d As Object Dim e As Object Dim Results(1 To 50, 1 To 4) As Single Dim ncols, nrows, replicates, duplicates, nrecords, sites, n, i, k, j As Integer Dim element, listofnames(50) As String Dim tit, site As String 'check name of active sheet which must be "Data" and check that there is only one sheet in the workbook If ActiveSheet.name <> "Data" Or Sheets.Count > 1 Then MsgBox "Program terminated as your currently active sheet is not called Data or you have more than one worksheet in your workbook" Stop End If 'read in title tit = ActiveSheet.Cells(1, 1).Value 'determine size of dataset 'move to first row of data Range("A3:A3").Select Set c = ActiveCell ncols = 0'count the number of colums. Exit if number of columns gets to 50 Do Until IsEmpty(c.Value) ncols = ncols + 1Set c = c.Offset(0, 1)If ncols = 50 Then MsgBox "Program terminated as number of columns greater than 50" Stop End If Loop 'number of elements to be processed is no cols -2 ncols = ncols - 2'move to first row of data Range("A3:A3").Select Set c = ActiveCell nrows = 0'count the number of rows. Exit if number of rows gets to 4000 Do Until IsEmpty(c.Value) nrows = nrows + 1Set c = c.Offset(1, 0)If nrows = 4000 Then

MsgBox "Program terminated as number of rows of data greater than 4000" Stop End If qool Msg = "You have chosen to process " & ncols & " elements and " & nrows / 4 & " sites. Do you want to continue ?" ' Define message. Style = vbYesNo + vbCritical + vbDefaultButton1 ' Define buttons. title = "Parameters selected" ' Define title. Help = "DEMO.HLP" ' Define Help file. Ctxt = 1000 ' Define topic ' context. ' Display message. Response = MsgBox(Msg, Style, title, Help, Ctxt) If Response = vbYes Then ' User chose Yes. MyString = "Yes" ' Perform some action. Else ' User chose No. MyString = "No" ' Perform some action. MsgBox "Processing terminated" End End If 'start processing each element column For n = 1 To ncols Worksheets("Data").Activate 'activate first column in first row of data on data sheet Range("A2:A2").Select 'move to column label Set d = ActiveCell.Offset(0, 1 + n)element = d.Value Set d = d.Offset(1, 0)'add a worksheet and name it after the element being processed Sheets.Add ActiveSheet.name = element 'place lables ActiveSheet.Cells(1, 1).Value = tit ActiveSheet.Cells(2, 1).Value = element ActiveSheet.Cells(3, 1).Value = "Site" ActiveSheet.Cells(3, 2).Value = "DupA" ActiveSheet.Cells(3, 3).Value = "RepA" ActiveSheet.Cells(3, 4).Value = "DupB" ActiveSheet.Cells(3, 5).Value = "RepB" ActiveSheet.Cells(3, 6).Value = "Log10(DupA)" ActiveSheet.Cells(3, 7).Value = "Log10(RepA)" ActiveSheet.Cells(3, 8).Value = "Log10(DupB)" ActiveSheet.Cells(3, 9).Value = "Log10(RepB)" ActiveSheet.Cells(3, 10).Value = "A=DupA+RepA" ActiveSheet.Cells(3, 11).Value = "B=DupB+RepB" ActiveSheet.Cells(3, 12).Value = "C=A+B" ActiveSheet.Cells(3, 13).Value = "Results" 'activate cell for first information Range("A4:A4").Select Set c = ActiveCell For j = 1 To nrows / 4 Set d = d.Offset(0, -(n + 1))c.Value = d.Value

```
Set d = d.Offset(0, 1 + n)
    Set c = c.Offset(0, 1)
       For k = 1 To 4
                With c
                c.Value = d.Value
                Set c = c.Offset(0, 4)
                c.Value = Log10(d.Value)
                Set c = c.Offset(0, -3)
                Set d = d.Offset(1, 0)
                End With
        Next k
        Set c = c.Offset(1, -5)
       Next j
'do calculations
' variable names take on cell reference from Johnson (1995)
nrecords = nrows
duplicates = 2
replicates = 2
sites = nrecords / (duplicates + replicates)
Worksheets(element).Activate
Range("J4:J4").Select
Set e = ActiveCell
                        For j = 0 To (nrows / 4) - 1
                                e.Offset(j, 0).Value = e.Offset(j, -4).Value
+ e.Offset(j, -3).Value
                                e.Offset(j, 1).Value = e.Offset(j, -2).Value
+ e.Offset(j, -1).Value
                                e.Offset(j, 2).Value = e.Offset(j, 0).Value +
e.Offset(j, 1).Value
                        Next j
 Range("M4:M4").Select
 Set e = ActiveCell
 Set myRange = Range(Cells(4, 12), Cells((4 + (sites) - 1), 12))
 e.Value = Application.WorksheetFunction.Sum(myRange)
 Range("M5:M5").Select
 Set e = ActiveCell
 Set myRange = Range(Cells(4, 6), Cells((4 + (sites) - 1), 9))
 e.Value = Application.WorksheetFunction.SumSq(myRange)
 k2 = e.Value
 Range("M6:M6").Select
 Set e = ActiveCell
 Set myRange = Range(Cells(4, 10), Cells((4 + (sites) - 1), 11))
 e.Value = (Application.WorksheetFunction.SumSq(myRange)) / 2
 k3 = e.Value
 Range("M7:M7").Select
 Set e = ActiveCell
 Set myRange = Range(Cells(4, 12), Cells((4 + (sites) - 1), 12))
 e.Value = (Application.WorksheetFunction.SumSq(myRange)) / (2 * 2)
 k4 = e.Value
Range("M8:M8").Select
 Set e = ActiveCell
 Set myRange = Range(Cells(4, 13), Cells(4, 13))
 e.Value = (Application.WorksheetFunction.SumSq(myRange)) / (duplicates *
replicates * (sites))
    k5 = e.Value
'Degrees of Freedom
    ' TOTAL
    q12 = (sites * duplicates * replicates) - 1
```

```
'SITE
    q14 = sites - 1
    'SAMPLE
    q16 = sites * (duplicates - 1)
    'ERROR
    q18 = sites * duplicates * (replicates - 1)
'Sum of squares
    'SITE
    r14 = k4 - k5
    'SAMPLE
    r16 = k3 - r14 - k5
    'ERROR
    r18 = k2 - k5 - r14 - r16
    ' TOTAL
    r12 = r14 + r16 + r18
'Mean of Squares
    'SITE
    s14 = r14 / q14
    'SAMPLE
    s16 = r16 / q16
    'ERROR
    s18 = r18 / q18
    ' TOTAL
    s12 = r12 / q12
'F(calc)
    'SITE
    t14 = s14 / s16
    'SAMPLE
    t16 = s16 / s18
'Variance component
    'SITE
    ul4 = (s14 - s16) / (duplicates * replicates)
    'SAMPLE
    u16 = (s16 - s18) / replicates
    'ERROR
    u18 = s18 / 1
    'TOTAL
    u12 = u14 + u16 + u18
'variance of total
    'SITE
    v14 = (u14 / u12) * 100
    'SAMPLE
    v16 = (u16 / u12) * 100
    'ERROR
    v18 = (u18 / u12) * 100
    ' TOTAL
    v12 = (u12 / u12) * 100
'place all the results in the last column of the current worksheet
Worksheets(element).Activate
Range("n4:n4").Select
Set e = ActiveCell
e.Value = q12
Set e = e.Offset(1, 0)
e.Value = q14
Set e = e.Offset(1, 0)
e.Value = q16
Set e = e.Offset(1, 0)
e.Value = q18
```

Set e = e.Offset(1, 0)e.Value = r12Set e = e.Offset(1, 0)e.Value = r14 Set e = e.Offset(1, 0)e.Value = r16 Set e = e.Offset(1, 0)e.Value = r18 Set e = e.Offset(1, 0)e.Value = s12 Set e = e.Offset(1, 0)e.Value = s14Set e = e.Offset(1, 0)e.Value = s16 Set e = e.Offset(1, 0)e.Value = s18Set e = e.Offset(1, 0)e.Value = t14Set e = e.Offset(1, 0)e.Value = t16Set e = e.Offset(1, 0)e.Value = u12Set e = e.Offset(1, 0)e.Value = u14 Set e = e.Offset(1, 0)e.Value = u16 Set e = e.Offset(1, 0)e.Value = u18 Set e = e.Offset(1, 0)e.Value = v12Set e = e.Offset(1, 0)e.Value = v14 Set e = e.Offset(1, 0)e.Value = v16 Set e = e.Offset(1, 0)e.Value = v18 Set e = e.Offset(1, 0)' Fill array with values. listofnames(n) = element Results(n, 1) = v14Results(n, 2) = v16Results(n, 3) = v18Results(n, 4) = v12Next n 'add a worksheet and name it summary Sheets.Add ActiveSheet.name = "Summary" 'place standard text into summary table Range("al:al").Select Set e = ActiveCell e.Value = tit Set e = e.Offset(2, 0)e.Value = "Element" Set e = e.Offset(0, 1)e.Value = "Between Site %" Set e = e.Offset(0, 1)e.Value = "Between Sample %" Set e = e.Offset(0, 1)

```
e.Value = "Within Sample %"
Set e = e.Offset(0, 1)
e.Value = "Total %"
'fill table with results
Range("a4:a4").Select
Set e = ActiveCell
For i = 1 To ncols
e.Value = listofnames(i)
   For n = 1 To 4
   Set e = e.Offset(0, 1)
   e.Value = Results(i, n)
   Next n
Set e = e.Offset(1, -4)
Next i
'tidy up summary table
    'format numbers to two decimal places
    Columns("B:D").Select
    Selection.NumberFormat = "0.00"
    Rows("3:3").Select
    With Selection.Font
        .name = "Arial"
        .FontStyle = "Bold"
        .Size = 10
        .Strikethrough = False
        .Superscript = False
        .Subscript = False
        .OutlineFont = False
        .Shadow = False
        .Underline = xlUnderlineStyleNone
        .ColorIndex = xlAutomatic
    End With
    'set all text in colum A to be in bold
    Columns("A:A").Select
    With Selection.Font
        .name = "Arial"
        .FontStyle = "Bold"
        .Size = 10
        .Strikethrough = False
        .Superscript = False
        .Subscript = False
        .OutlineFont = False
        .Shadow = False
        .Underline = xlUnderlineStyleNone
        .ColorIndex = xlAutomatic
    End With
    'set column widths
  Columns("B:E").Select
    Selection.ColumnWidth = 12
    With Selection
        .HorizontalAlignment = xlCenter
        .VerticalAlignment = xlBottom
        .WrapText = False
        .Orientation = 0
        .ShrinkToFit = False
        .MergeCells = False
    End With
    'put a border around the table
    Range(Cells(3, 1), Cells(3 + ncols, 5)).Select
    Selection.Borders(xlDiagonalDown).LineStyle = xlNone
    Selection.Borders(xlDiagonalUp).LineStyle = xlNone
```

```
With Selection.Borders(xlEdgeLeft)
      .LineStyle = xlContinuous
      .Weight = xlThin
      .ColorIndex = xlAutomatic
  End With
  With Selection.Borders(xlEdgeTop)
      .LineStyle = xlContinuous
      .Weight = xlThin
      .ColorIndex = xlAutomatic
  End With
 With Selection.Borders(xlEdgeBottom)
      .LineStyle = xlContinuous
      .Weight = xlThin
      .ColorIndex = xlAutomatic
  End With
  With Selection.Borders(xlEdgeRight)
      .LineStyle = xlContinuous
      .Weight = xlThin
      .ColorIndex = xlAutomatic
  End With
  Selection.Borders(xlInsideVertical).LineStyle = xlNone
 Selection.Borders(xlInsideHorizontal).LineStyle = xlNone
  'put a border around the column headings
 Range(Cells(3, 1), Cells(3, 5)).Select
  Selection.Borders(xlDiagonalDown).LineStyle = xlNone
 Selection.Borders(xlDiagonalUp).LineStyle = xlNone
 With Selection.Borders(xlEdgeLeft)
      .LineStyle = xlContinuous
      .Weight = xlThin
      .ColorIndex = xlAutomatic
 End With
 With Selection.Borders(xlEdgeTop)
      .LineStyle = xlContinuous
      .Weight = xlThin
      .ColorIndex = xlAutomatic
  End With
  With Selection.Borders(xlEdgeBottom)
      .LineStyle = xlContinuous
      .Weight = xlThin
      .ColorIndex = xlAutomatic
  End With
  With Selection.Borders(xlEdgeRight)
      .LineStyle = xlContinuous
      .Weight = xlThin
      .ColorIndex = xlAutomatic
  End With
  'set column headings to wrap round
  Rows("3:3").Select
  With Selection
      .VerticalAlignment = xlBottom
      .WrapText = True
      .Orientation = 0
      .AddIndent = False
      .ShrinkToFit = False
      .MergeCells = False
  End With
End Sub
          Static Function Log10(X)
          Log10 = Log(X) / Log(10#)
          End Function
```

# Appendix 2 : Example of data format

This is an example of the data format that is placed in the "Data" worksheet:

Urban Soil Control data

Site	Control	MnO	$FE_2O_3$	V	Cr	Co	Ba	Ni	Cu	Zn	As	Мо	Pb	,
	602276 DUP A	0.059	4.62	2	76	69	16	425	22	16	226	11	1.7	68
	602286 SUB A	0.06	4.59	)	75	74	16	432	22	15	225	12	2.1	68
	602281 DUP B	0.057	4.4		73	69	14	442	19	16	211	10	1.9	51
	602278 SUB B	0.057	4.41		75	71	14	436	20	17	211	10	1.8	52
	602331 DUP A	0.065	4.16	i	130	105	26	603	43	28	52	4	0.1	14
	602377 SUB A	0.066	4.16	5	127	105	26	606	44	29	51	6	0.6	15
	602337 DUP B	0.06	4.26	i	131	104	25	593	41	28	65	6	0.7	20
	602358 SUB B	0.061	4.26	5	131	107	25	592	42	28	64	6	0.7	20
	602404 DUP A	0.067	4.26	;	142	111	24	651	41	31	91	9	0.5	36
	602462 SUB A	0.068	4.23	6	140	111	24	640	39	33	90	9	0.7	36
	602496 DUP B	0.081	4.88		129	101	28	631	40	36	201	8	1.1	56
	602453 SUB B	0.079	4.83	5	126	99	29	623	41	37	202	8	1	57
	602571 DUP A	0.181	4.68		86	79	17	514	24	27	246	11	1.1	104
	602560 SUB A	0.182	4.7	•	83	80	16	515	24	27	245	12	1.5	103
	602566 DUP B	0.136	4.9	)	84	83	18	511	25	26	205	10	1.4	86
	602534 SUB B	0.133	4.94		83	81	17	511	25	27	206	11	1.4	85
	602676 DUP A	0.022	2.57		211	122	16	362	43	87	120	5	1.2	69
	602686 SUB A	0.021	2.56	;	209	123	15	364	44	87	120	5	1.2	70
	602681 DUP B	0.029	2.53	5	217	120	20	401	42	85	178	6	0.7	110
	602678 SUB B	0.029	2.53		218	118	21	405	43	85	178	5	1	110
	602731 DUP A	0.026	2.39	)	66	76	13	103	12	7	65	7	1.8	50
	602777 SUB A	0.024	2.38	5	66	79	13	105	12	7	65	7	1.8	50
	602737 DUP B	0.042	3.39	)	79	85	24	115	18	8	104	11	2.6	70
	602758 SUB B	0.043	3.39	)	82	90	25	126	18	7	104	11	2.2	70

## Appendix 3 : ANOVA results sheet for each element

#### Urban Soil Control data

Pb													
0.1	-								A=DupA +	B=DupB +			
Site	DupA	КерА	DupB	Керв	Log10(DupA)	Log10(RepA)	Log10(DupB)	Log10(RepB)	КерА	Керв	C=A+B	Results	
	68	68	51	52	2 1.832508913	3 1.832508913	1.707570176	1.716003344	3.6650178	3.4235735	7.0885913	387.80245	199 Degrees of freedom - IUIAL
602331	14	15	20	) 20	0 1.146128036	6 1.176091259	1.301029996	1.301029996	2.3222193	2.60206	4.9242793	788.47745	49 Degrees of freedom -SITE
602404	36	36	56	5 57	7 1.556302501	1.556302501	1.748188027	1.755874856	3.112605	3.5040629	6.6166679	788.46646	50 Degrees of freedom -SAMPLE
602571	104	103	86	6 85	5 2.017033339	9 2.012837225	1.934498451	1.929418926	4.0298706	3.8639174	7.8937879	787.82271	100 Degrees of freedom -ERROR
602676	69	70	110	) 110	0 1.838849091	l 1.84509804	2.041392685	2.041392685	3.6839471	4.0827854	7.7667325	751.95368	36.523769 Sum of Squares - TOTAL
602731	50	50	70	) 7(	0 1.698970004	1.698970004	1.84509804	1.84509804	3.39794	3.6901961	7.0881361		35.869022 Sum of Squares - SITE
388131	28	30	27	27	7 1.447158031	1.477121255	1.431363764	1.431363764	2.9242793	2.8627275	5.7870068		0.6437525 Sum of Squares - SAMPLE
388204	63	64	92	2 90	0 1.799340549	9 1.806179974	1.963787827	1.954242509	3.6055205	3.9180303	7.5235509		0.0109947 Sum of Squares - ERROR
388371	113	115	136	5 138	3 2.053078443	3 2.06069784	2.133538908	2.139879086	4.1137763	4.273418	8.3871943		0.1835365 Mean of Squares - TOTAL
388476	155	155	197	200	0 2.190331698	3 2.190331698	2.294466226	2.301029996	4.3806634	4.5954962	8.9761596		0.7320209 Mean of Squares - SITE
388531	494	481	334	4 336	5 2.693726949	2.682145076	2.523746467	2.526339277	5.375872	5.0500857	10.425958		0.012875 Mean of Squares - SAMPLE
388604	79	77	74	1 75	5 1.897627091	1 1.886490725	1.86923172	1.875061263	3.7841178	3.744293	7.5284108		0.0001099 Mean of Squares - ERROR
388704	301	297	209	9 210	) 2.478566496	6 2.472756449	2.320146286	2.322219295	4.9513229	4.6423656	9.5936885		56.855771 <b>F(Calc) - SITE</b>
388876	150	150	118	3 117	7 2.176091259	2.176091259	2.071882007	2.068185862	4.3521825	4.1400679	8.4922504		117.10235 F(Calc) - SAMPLE
388976	1900	1900	1300	) 1300	0 3.278753601	3.278753601	3.113943352	3.113943352	6.5575072	6.2278867	12.785394		0.186279 Variance Component - TOTAL
389004	227	226	353	3 354	4 2.356025857	7 2.354108439	2.547774705	2.549003262	4.7101343	5.096778	9.8069123		0.1797865 Variance Component - SITE
389171	351	349	404	410	0 2.545307116	6 2.542825427	2.606381365	2.612783857	5.0881325	5.2191652	10.307298		0.0063826 Variance Component - SAMPLE
389276	34	35	38	38	3 1.531478917	7 1.544068044	1.579783597	1.579783597	3.075547	3.1595672	6.2351142		0.0001099 Variance Component - ERROR
389331	107	107	172	2 167	7 2.029383778	3 2.029383778	2.235528447	2.222716471	4.0587676	4.4582449	8.5170125		100 % variance - Total
389404	36	36	36	6 34	1.556302501	1.556302501	1.556302501	1.531478917	3.112605	3.0877814	6.2003864		96.514637 % variance - Site
600076	30	32	30	) 3(	) 1.477121255	5 1.505149978	1.477121255	1.477121255	2.9822712	2.9542425	5.9365137		3.4263406 % variance - Sample
600131	27	27	28	3 27	7 1.431363764	1.431363764	1.447158031	1.431363764	2.8627275	2.8785218	5.7412493		0.0590228 % variance - Error
600371	44	44	41	4	1 1.643452676	6 1.643452676	1.612783857	1.612783857	3.2869054	3.2255677	6.5124731		
600476	37	38	33	. ⊤ } 3∠	1 1 568201724	1 1 579783597	1 51851394	1 531478917	3 1479853	3 0499929	6 1979782		
600531	154	156	155	5 156	6 2.187520721	2.1931246	2.1903317	2.1931246	4.380645	4.383456	8.764102		

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