# Tutorial: Analytical Precision − Plotting Thompson and Howarth Charts

Alecos Demetriades and Ariadne Argyraki

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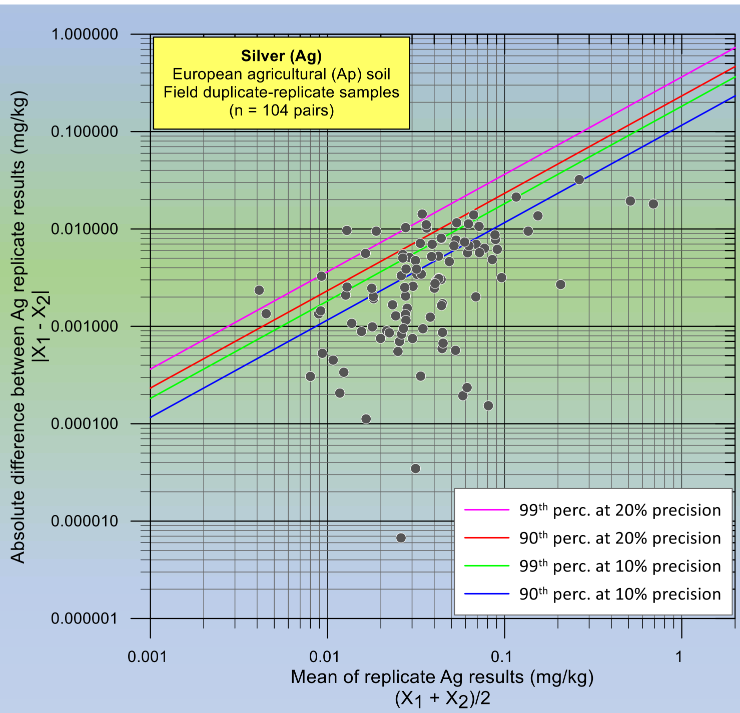


Precision control chart for P = +/-10% and 20% at the 95% confidence level
Control lines at the 90th and 99th percentiles

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Front cover image: Silver (Ag) Thompson and Howarth chart.
Plotted by Alecos Demetriades with Golden Software's Grapher™

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**37 International Geological Congress, Busan, Republic of Korea**
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# Tutorial: Analytical Precision - Plotting Thompson and Howarth Charts with Grapher


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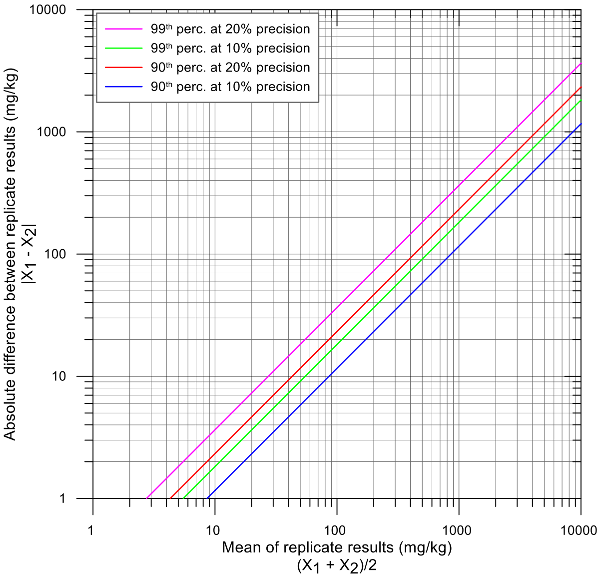
[3] IUGS Commission on Global Geochemical Baselines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## Abstract

Thompson and Howarth developed a graphical method in the 1970s for the visual estimation of analytical precision even for a single duplicate-replicate pair of samples. The mean of the duplicate-replicate pair of samples is plotted against the corresponding absolute difference. A copy of the original precision control chart for replicate results used by the Imperial College Applied Geochemistry Research Group is presented for use in the laboratory and field.

Digital log-log base 10 and linear templates of Thompson and Howarth charts are provided, along with control lines plotted at the 90th and 99th percentiles for 10% and 20% precision at the 95% confidence level. These templates were generated using Golden Software's Grapher™ (version 25). Instructions are provided for preparing the input replicate data set and plotting the results. Worked examples and the interpretation of the plotted results are also included.

**Keywords:** Quality control; Duplicate samples; Replicate samples; Precision; Graph; Statistics; Software; Template

**Requirements:** Microsoft's Excel® and Golden Software's Grapher™ (version 25 or higher) are required to plot the Thompson and Howarth charts. If you do not own these software packages, you need to purchase Microsoft's Office®, and for Grapher™, a fully functional version can be downloaded from the company's website at https://www.goldensoftware.com/products/grapher/. *Golden Software is offering new users a 14-day free trial.*

*Golden Software offers generously discounted licenses for students and educators who use the software in their courses. Academic staff and students are encouraged to learn more by visiting https://www.goldensoftware.com/solutions/education*. This support and encouragement ensure that students and educators have the resources to learn and teach the plotting of Thompson and Howarth charts.

**Note:** This tutorial exercise was designed for the workshop organised at the 37th International Geological Congress in Busan (South Korea) on August 30th and 31st, 2024. The workshop was titled "*International Union of Geological Sciences Manual of Standard Methods for Establishing the Global Geochemical Reference Network*," which is the title of the Manual that the Commission on Global Geochemical Baselines published in 2022.

**Citation:** It is recommended that reference to this instruction manual should be made in the following way:

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# Contents

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## 1. Introduction

Thompson and Howarth (1973, 1976a, b, 1978) and Thompson (1983) described a straightforward graphical method for estimating analytical precision using duplicate-replicate sample pairs (Johnson, 2011, p. 70). This simple method can be applied even to a single duplicate-replicate pair of samples, providing an immediate visual impression of an analytical method's precision.

Researchers interested in the history of the development of Thompson and Howarth charts should read Robert G. Garrett's (2015) freely available article.

The Thompson and Howarth method involves plotting the mean of the replicate sample results against the absolute difference between the two replicate analyses. This graph defines the fitness-for-purpose criteria by the $90^{th}$ and $99^{th}$ percentile lines for 10% and 20% precision (P) at the 95% confidence level. The method is a powerful tool for assessing the precision of analytical techniques, providing a clear visual representation of the data's variability.

The Thompson and Howarth analytical precision charts, which can be plotted using either logarithmic (base 10) or linear axes, are highly practical. They can be easily plotted with a dedicated graph plotting software like Golden Software's Grapher™, empowering researchers with a practical and powerful tool. Reimann *et al.* (2008, 2009, 2011, 2012) give R-generated Thompson and Howarth chart examples, further demonstrating the practicality of these charts in various contexts.

When in the field without a computer, Thompson and Howarth charts can still be plotted on a $\log_{10}$-$\log_{10}$ paper graph using a hand-held calculator to estimate the parameters.

A key point to remember is that precision is estimated only within a batch if the replicate pairs are from the same analytical batch (Fletcher, 1981). This means that the precision estimate only applies to samples analysed together in the same batch and not to samples analysed in different batches. Therefore, it is strongly recommended that the replicate samples be distributed randomly throughout many batches or, even better, in all analytical batches of a project to obtain a comprehensive estimate of the method's precision.

It is noted that all files of this tutorial are included in the 'Thompson&Howarth_charts.zip' file, which needs to be opened. Its contents are:

- The main directory '*Thompson&Howarth_charts*' includes different Grapher™ files (version 25), linear and $\log_{10}$-$\log_{10}$ templates for Grapher™ version 25, and two Excel® Workbooks, and two Subdirectories, which are:
  - '*Master_chart_for_plotting_by_hand*' includes all the necessary files for plotting the 10% precision $\log_{10}$-$\log_{10}$ control chart;
  - '*T&H_references*' includes papers by Thompson and Howarth, and an Excel® workbook with tables from Thompson and Howarth (1978), and
  - T&H templates for earlier versions of Grapher (versions 10 to 15).

## 2. Definitions

The following definitions are taken from Demetriades (2025).

**Routine sample:** This is the sample collected in accordance with the sampling plan of the applied geochemical survey (Fig. 1).

**Duplicate sample:** A '*duplicate sample*' is collected from the same site as the routine sample, but at some distance, in a manner defined by the sampling procedures manual (Fig. 1). This control sample, along with the 'routine sample', both collected from the same site, form a duplicate pair, and give an indication of 'within-site' variability, *i.e.*, sampling variance (Johnson, 2011, p. 64). As it is collected during fieldwork, it is often called a field duplicate sample.

**Replicate sample:** A '*replicate sample*' is made at the field base or laboratory by dividing a collected sample according to a well-defined protocol (Johnson, 2011, p. 64). The replicate pair of samples can be used to identify laboratory errors (Fig. 1). If replicates are made from the pair of duplicate field samples described above, then analysis of variance (ANOVA) can be used to attribute sources of element variability between-sites (geochemical or natural variance), within-sites (sampling or 'at site' variance) and within the laboratory (analytical variance), and to estimate measurement uncertainty. Such samples are also referred to as laboratory duplicates or subsamples. However, the term '*replicate*' is recommended since it clearly distinguishes the field duplicate control sample.

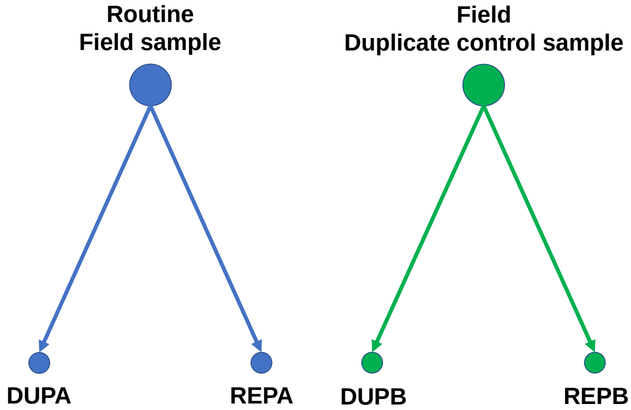



*Figure 1. Diagram showing the relationship between the field duplicate pair (DUPA and DUPB) and the laboratory replicate pair (REPA and REPB). The **DUPA** and **REPA** pair is derived from the splitting of the Routine Field sample and is called the 'Field routine-replicate sample pair', and the **DUPB** and **REPB** pair is derived from the splitting of the Field Duplicate control sample and is called the '**Field duplicate-replicate sample**' pair, the analytical results of which are used for plotting the Thompson and Howarth chart (henceforth, called **duplicate-replicate sample pair**). Slightly modified figure from Johnson (2011, Fig. 5.2, p.64) in Mackovych et al., 2022, Fig. 4.1, p.312. Drawn with Microsoft PowerPoint® by Alecos Demetriades, Hellenic Institute of Geology and Mineral Exploration (IGME) and IUGS Commission on Global Geochemical Baselines (IUGS-CGGB).*

## 3. Plotting Thompson and Howarth charts in the field

Figure 2 displays a 3-cycle versus 4-cycle $\log_{10}$-$\log_{10}$ chart for use in the field. The file is *T&H_10%_precision_control_chart_for_printing.pdf*, and the Golden Software's Grapher™ plot file is *T&H_Master_10%_Precision_log-log_chart.grf*. This particular Grapher™ plot file has the following connected files in Microsoft Excel® format:

- *Precision_1&2&5&10&20&50percent.xls*,
- *Precision_Percentiles_05_to_75.xls*, and
- *Precision_Percentiles_90&99.xls*.

All files are in the subdirectory '*Master_chart_for_plotting_by_hand*'.

## 4. Digital templates of Thompson and Howarth charts

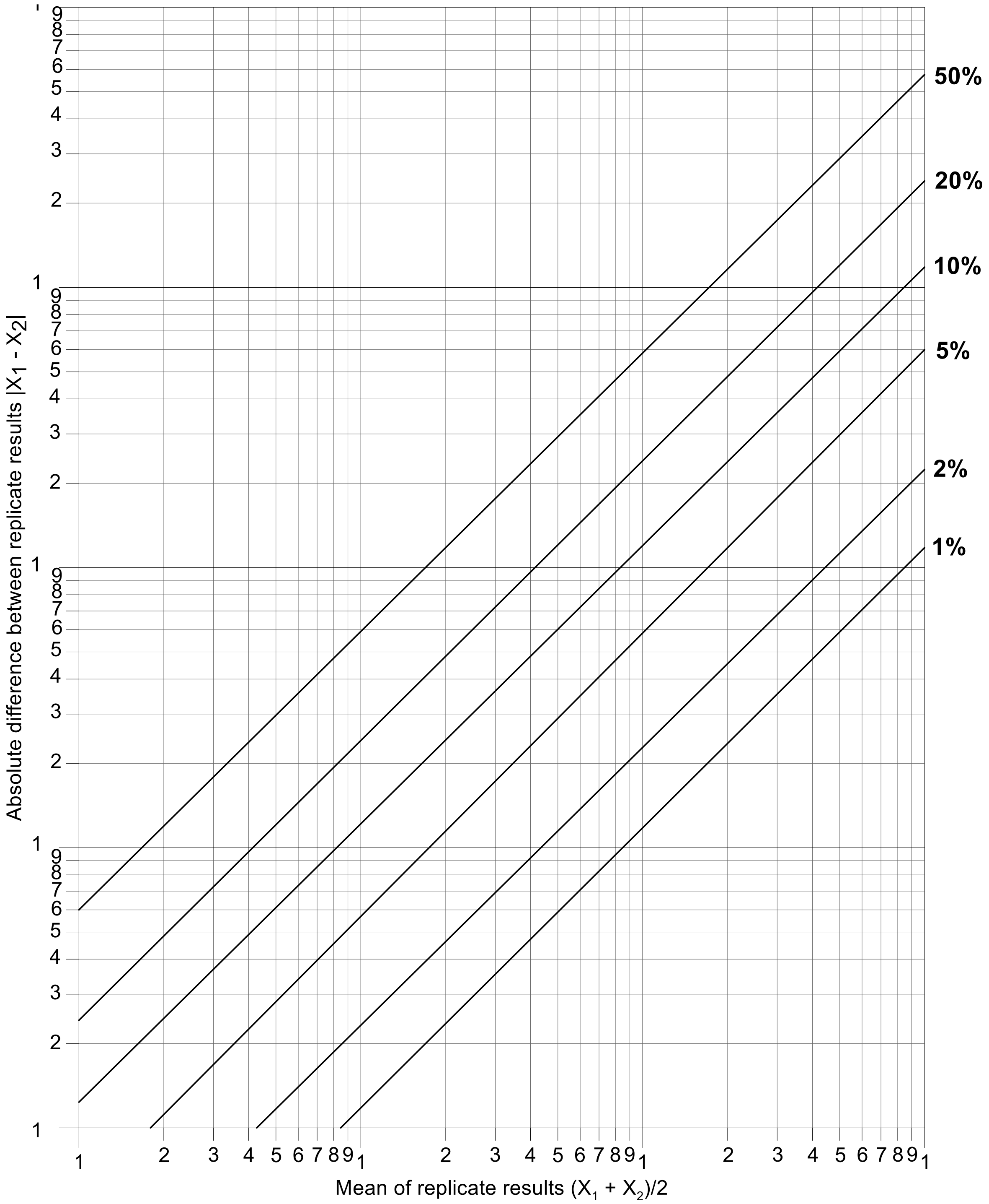
Figures 3 and 4 show digital templates of the $\log_{10}$-$\log_{10}$ and linear Thompson-Howarth charts, respectively, which will be used in the hands-on exercises. They were plotted with Golden Software's Grapher™ (version 25; templates of earlier versions are given). The two files are:

- *T&H_log-log_Precision_chart_template.grf*, and
- *T&H_linear_Precision_chart_template.grf*.

For ±10% and ±20% precision (P) at the 95% confidence level, the following connected Microsoft Excel® file is needed:

- *Plot_90&99perc_at_10&20%precision.xls.*

All files are in the main directory.




PRECISION CONTROL CHART (TYPE 2) FOR REPLICATE RESULTS

In a set of replicate measurements on many samples, 90 per cent of the points will fall below the diagonal appropriate to the precision of the measurements at the 95% confidence limits.

*Figure 2. Template of Thompson and Howarth $log_{10}$-$log_{10}$ precision control chart for use in the field. This precision chart was used by the Applied Geochemistry Research Group at Imperial College (University of London) during the period that John Stuart Webb was Head. It was also used in the M.Sc. course in 'Mining Geology and Mineral Exploration' at the University of Leicester when Clifford Henry James, a Ph.D. student of J.S. Webb, was lecturing (1973-1976). Plotted with Golden Software's Grapher™.*

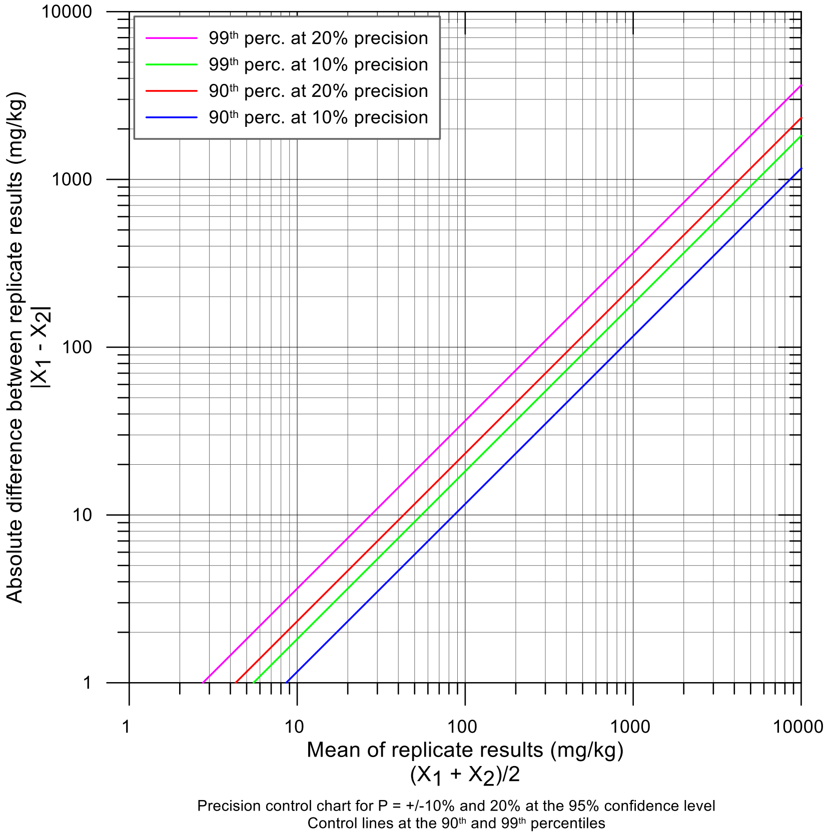



*Figure 3. Template of the digital file of Thompson and Howarth $log_{10}$-$log_{10}$ precision control chart for use with [Golden Software's Grapher](#)™.*

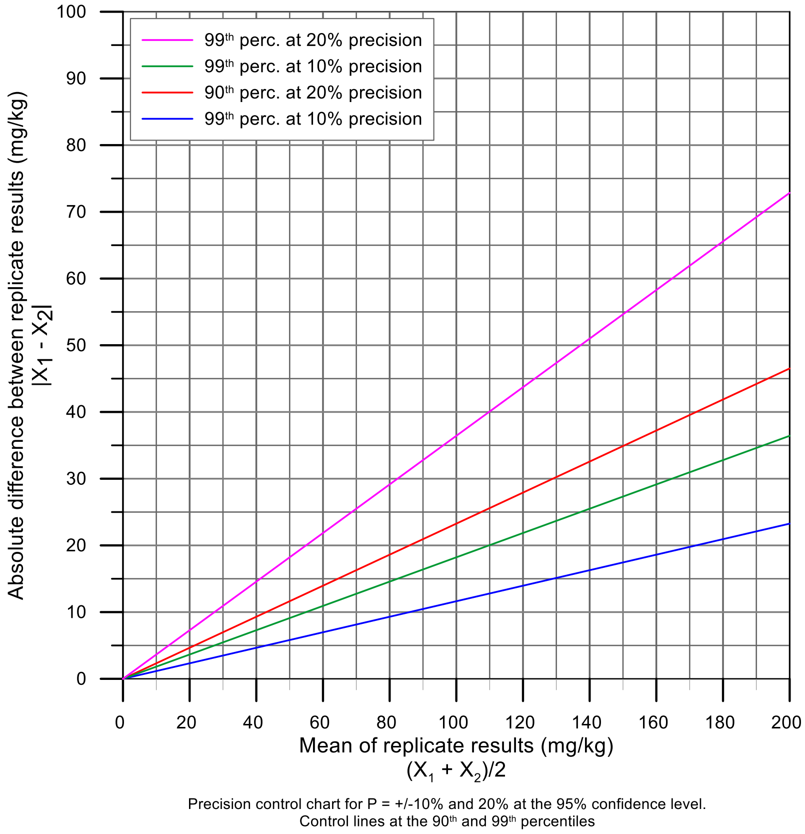



*Figure 4. Template of the digital file of Thompson and Howarth linear precision control chart for use with [Golden Software's Grapher](#)™.*

## 5. Preparing Grapher™ for plotting Thompson and Howarth charts

Figure 5 shows the procedure that should be followed to customise the 'Quick Access Toolbar' with the commands needed to be performed directly; the procedure is explained in the figure caption.

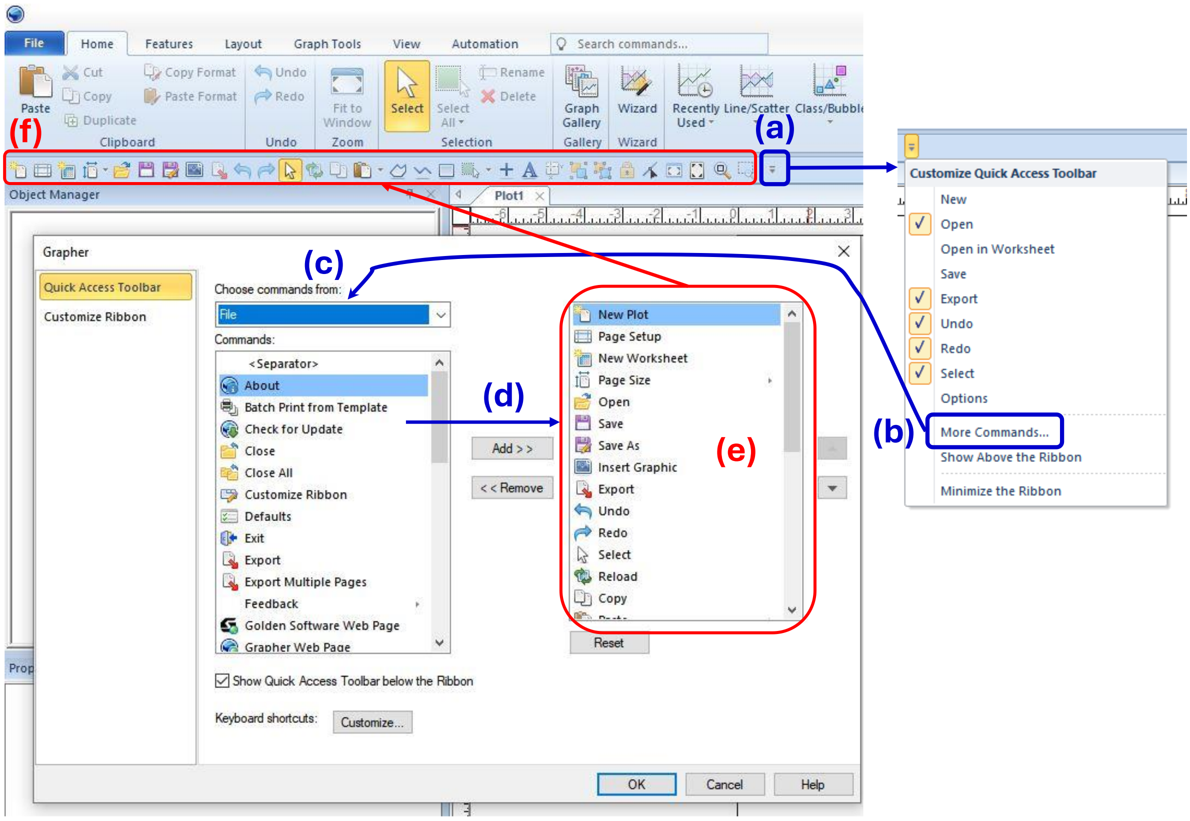



*Figure 5. Customising [Golden Software's Grapher]™ Quick Access Tool Bar (by default, the Quick Access Toolbar is located at the top of the ribbon, not below it as shown in this figure; however, there is an option to relocate it to below the ribbon): (a) This is the [Grapher]™ button ( ) that activates the Quick Access Tool when clicked with the left mouse button; (b) from the small dropdown window select 'More Commands…' activating (c) the 'Quick Access Toolbar' window from which different commands 'Choose commands from:' can be selected, and (d) transferred to the selection window (e). Upon selecting the necessary commands, 'OK' is clicked with the left mouse button, and all selected commands are transferred to (f) the 'Quick Access Tool Bar'.*

## 6. Plotting Thompson and Howarth charts with Golden Software's Grapher™

### 6.1. Preparing the input analytical replicates data set

The replicate data set from the EuroGeoSurveys Geochemistry Expert Group's project with the acronym GEMAS (**GE**ochemical **M**apping of **A**gricultural and grazing land **S**oil; Reimann *et al.*, 2014) will be used. The name of the Microsoft Excel® workbook is: '*GEMAS_AP_replicate_results.xls*', which includes three worksheets:

(i) '*Replicate_results_field-duplica*',
(ii) '*Original_Replicate_Analyses'*, and
(iii) '*Reference*'.

The original replicate analyses are organised in columns and should be kept intact. Table 1 shows part of the '*Replicate_results_field-duplica*' worksheet where the original (B1) and replicate analysis (B2) of the randomly collected field duplicate samples and the calculation of the Mean and absolute Difference (Diff) are shown.

*Table 1. Organisation of the GEMAS replicate analyses of the randomly collected field duplicate samples, and calculation of their mean and absolute difference in Microsoft Excel®. The replicate sample pairs with the codes B1 and B2 correspond to the* ***DUPB*** *and* ***REPB*** *pair, respectively, of the '****Field duplicate-replicate sample****' pair of Figure 1.*

| M | N | O | P | Q | R | S | T |
|---|---|---|---|---|---|---|---|
| Ag_B1 | Ag_B2 | Ag_Mean | Ag_Diff | Al_B1 | Al_B2 | Al_Mean | Al_Diff |
| 0.025988847 | 0.025995571 | 0.025992209 | 0.000006724 | 12771.56494 | 14089.07471 | 13430.319825000 | 1317.509770000 |
| 0.0424942 | 0.039564136 | 0.041029168 | 0.002930064 | 5442.576294 | 4613.745171 | 5028.160732500 | 828.831123000 |
| 0.205824512 | 0.208513541 | 0.207169027 | 0.002689029 | 25104.2749 | 24777.65625 | 24940.965575000 | 326.618650000 |
| 0.005286274 | 0.002936629 | 0.004111452 | 0.002349645 | 4097.570831 | 3786.238878 | 3941.904854500 | 311.331953000 |
| 0.049331263 | 0.057011723 | 0.053171493 | 0.007680460 | 25643.30078 | 26892.18506 | 26267.742920000 | 1248.884280000 |
| 0.052513912 | 0.053080905 | 0.052797409 | 0.000566993 | 12065.38086 | 11982.14355 | 12023.762205000 | 83.237310000 |

## 6.2. Worked examples

### 6.2.1. Using the log-log base 10 Thompson and Howarth template

The procedure is described below:

(i) Open in Golden Software's Grapher™ the file '*T&H_log-log_Precision_chart_template.grf*';
(ii) Use the '*Fit to Window Zoom*' command (marked in fuchsia colour girdle) to enlarge the imported template by clicking on it with the left mouse button (Fig. 6); the enlargement can be seen in Figure 7.

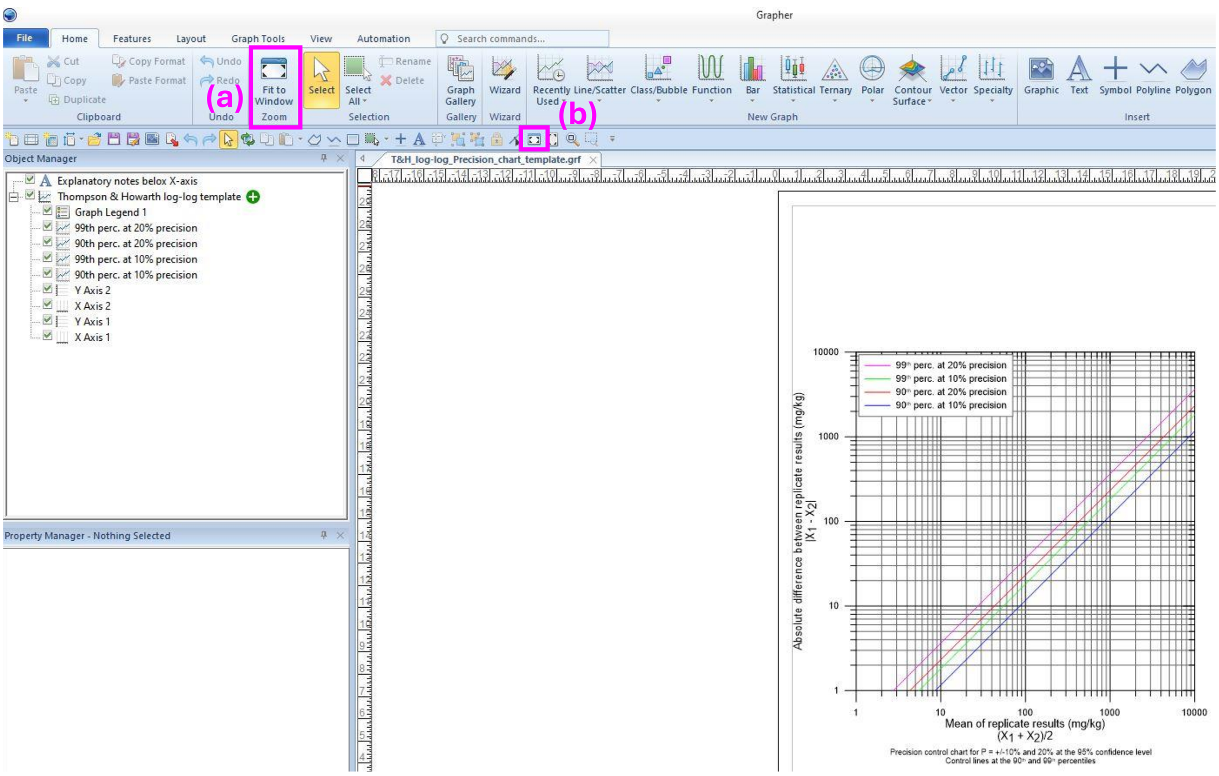



*Figure 6. The opened template is enlarged by using the command 'Fit to Window Zoom' with a left mouse click; there are two options, either* ***(a)*** *or* ***(b)****, that can be used.*

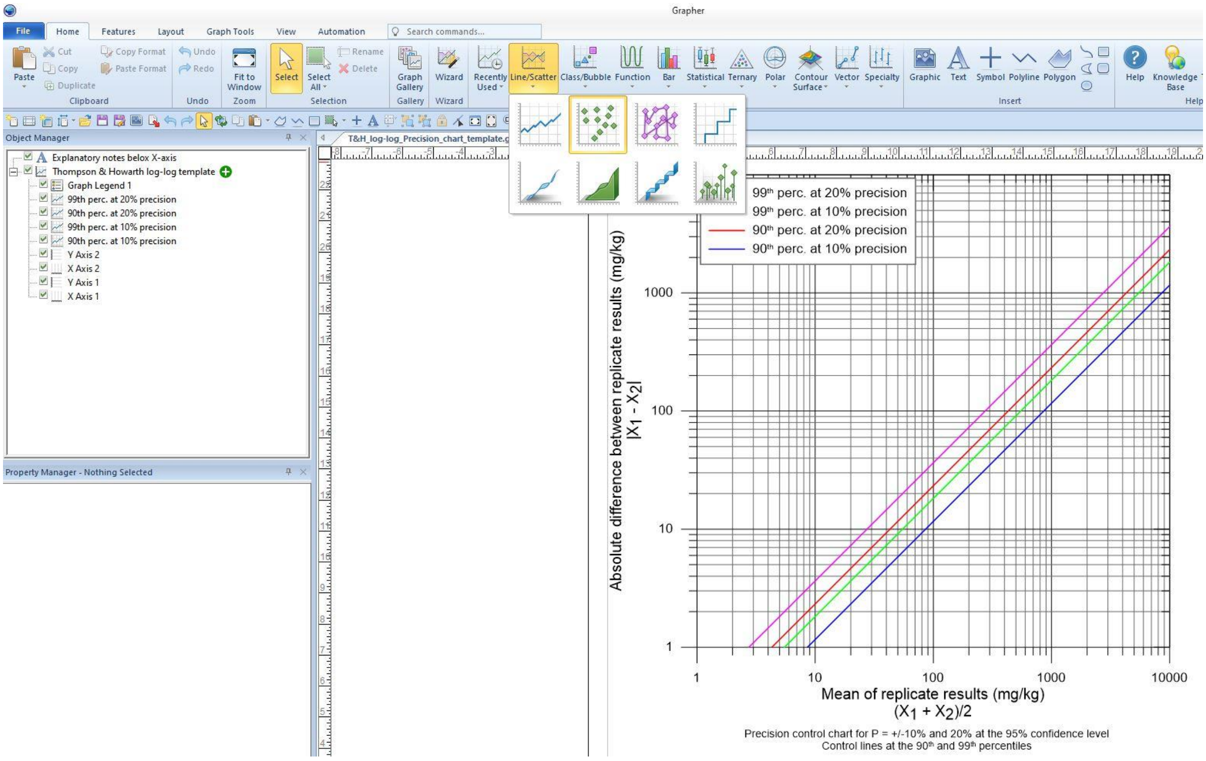



*Figure 7. Enlarged graph. Select with a left mouse click the 'Line/Scatter' group of graphs, and with a second left mouse click, the point scatter plot option is selected.*

(iii) Select the '*Line/Scatter*' option and then '*Scatter*' plot with a left mouse click (Fig. 7).

(iv) A floating dialogue called '*Open Worksheet*' appears; select the file '*GEMAS_Ap_replicate_results.xls*', and click '*Open*' with the left mouse button (Fig. 8).

(v) A small window appears on the screen '*XLS Import options*', and shows that the Microsoft Excel® Workbook consists of 3 Worksheets, *i.e.*, '*Replicate_results_of_field-dupl*', '*Original_Replicate_Analyses*', and '*Reference*' (Fig. 9).

(vi) Select the Worksheet '*Replicate_results_of_field-dupl*' with a left mouse click, and a line with '*blue dots*' appears over the graph (Fig. 10). On the left-hand side of the screen, the '*Object Manager*' window displays the properties of the imported data set (Fig. 10), *i.e.*, Graph 2 and the plotted data set '*ID_B2*' (marked with a fuchsia colour girdle). Below in the '*Property Manager*' window, the details of the '*ID_B2*' variable are shown, *i.e.*, X variable in Column A: ID_B1, and Y variable in Column B: ID_B2 (marked with a fuchsia colour girdle – Fig. 11) – these are the names of the Worksheet identifier columns. What is needed now is to select the studied element's '*Mean*' and '*Absolute Difference*'.

(vii) Select and click the small sign 'v' of the X variable with the left mouse button. A drop-down menu appears, and by scrolling down in Column O, the '*Ag_Mean*' is selected. Repeat the process by clicking on the small sign 'v' of the Y variable to select the corresponding value, the '*Ag_Diff*' (difference), and in Figure 12, the graph of Mean versus Absolute Difference of the Ag replicate results is displayed.

(viii) The next step is to move the variable pair of '*Ag_Diff*' from '*Graph 1*' to the main template of the '*Thompson and Howarth chart*' (Fig. 13). Upon moving the variable pair of '*Ag_Diff*', a drop-down window appears asking us to "*Choose Axes for Plot 'Ag_Diff'*". Click '*OK*' with the left mouse button.

(ix) The blue dots of the Ag replicates are outside the plot window and, thus, not visible, but they are registered in the legend (Fig. 14). Their disappearance is because of the high values of the X and Y axes, which must be changed. They are somewhere in the plotting space because of the legend entry '••• Ag_Diff'. Hence, the minimum and maximum values are extracted from the Excel® worksheet, which are:

| | Ag_Mean | Ag_Diff |
|---|---|---|
| Minimum | 0.004111452 | 0.000006724 |
| Maximum | 0.691519561 | 0.032132449 |

Graph 2 is no longer needed and is deleted by selecting it with a left mouse click, and with a right mouse click, a drop-down menu appears and '*Delete*' is selected with a left mouse click (or after marking it is removed with the keyboard's '*Delete*' button).

(x) The minimum and maximum values of the X-axis are 0.004 and 1 mg/kg Ag, and the corresponding Y-axis values are 0.000006 and 0.05 mg/kg Ag, respectively. Upon changing the X-Y parameters, the Ag replicate values are displayed within the plotting space of the chart (Fig. 15). However, the control lines disappeared from the screen because their minimum and maximum values are outside the current X-Y limits and must also be changed. Further, the minimum and maximum values of '*X Axis 2*' and '*Y Axis 2*' must be changed. The '••• Ag_Diff' entry in the legend is no longer needed and is removed by selecting '*Graph Legend 1*', and in the '*Property Manager – Graph Legend 1*', choose '*Entries*', and select '*Edit*' with a left mouse click. A small dialogue window appears, '*Reorder/Select Legend Entries*', where all legend entries are displayed; remove the tick from the '*Ag_Diff*' entry with a left mouse click, and press '*OK*'.

(xi) The minimum and maximum values of each control line (Fig. 16):

- $90^{th}$ perc. at 10% precision
- $99^{th}$ perc. at 10% precision
- $90^{th}$ perc. at 20% precision
- $99^{th}$ perc. at 20% precision

are changed by using, after selecting each control line, '*Data Limits*' and the option '*Clipping*' and ticking the entry '*Draw plot to clipping limit'*, followed by entering the minimum and maximum values of the X and Y axes for each control line in turn (see above).

(xii) The Ag symbol is added to the titles of the X and Y axes, and the legend is moved to the bottom right corner of the chart (Fig. 17).

(xiii) The following finishing touches are made: the thickness of the X-Y and minor lines is changed to make them more visible, *i.e.*, mark the X and Y lines in turn and select in the properties window '*Line*' and '*Width*' and change to 0.03 cm (Fig. 17).

(xiv) Final touches are made (Fig. 17):

(a) changes to the range of the X and Y axes;
(b) formatting the values of the X and Y axes;
(c) changing the colour of the dots from pale blue to black (Fig. 18);
(d) adding a title box at the top left corner, and
(e) adding sample numbers above the $90^{th}$ percentile at 20% precision to check the reason for their poor precision.

In the title box, the entry '*Field duplicate-replicate samples*' shows that the replicate samples used for plotting the Thompson and Howarth chart come from splitting the field duplicate samples. If the routine samples were split and analysed, then the entry should be '*Field routine-replicate samples*'.

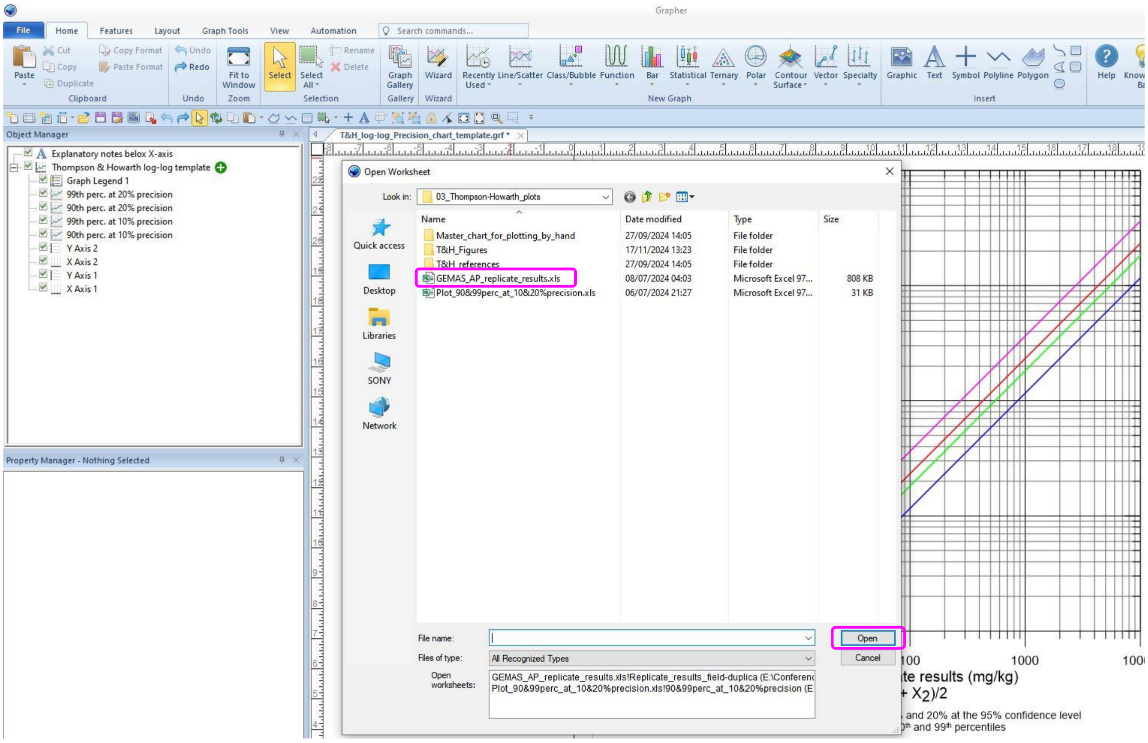



*Figure 8. Select with a left mouse click the 'GEMAS_AP_replicate_results.xls', and then click the 'Open' file command.*

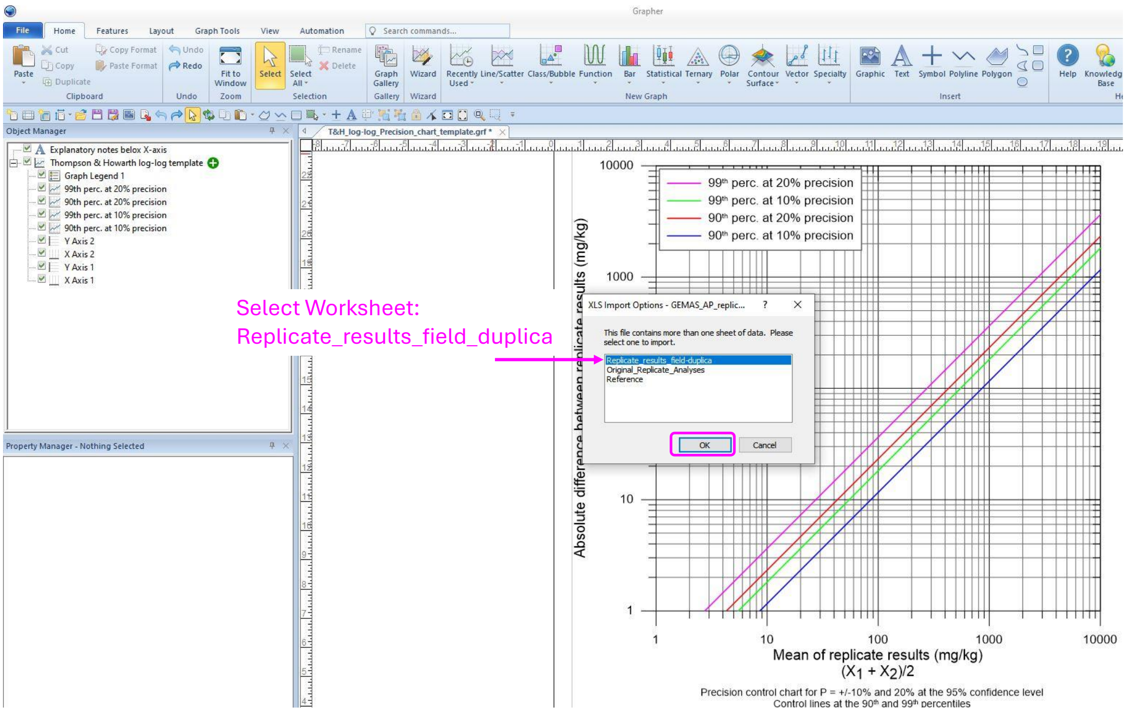



*Figure 9. Select with a left mouse click the 'GEMAS_AP_replicate_results.xls', and afterwards click on the 'Open' file command with a left mouse click.*

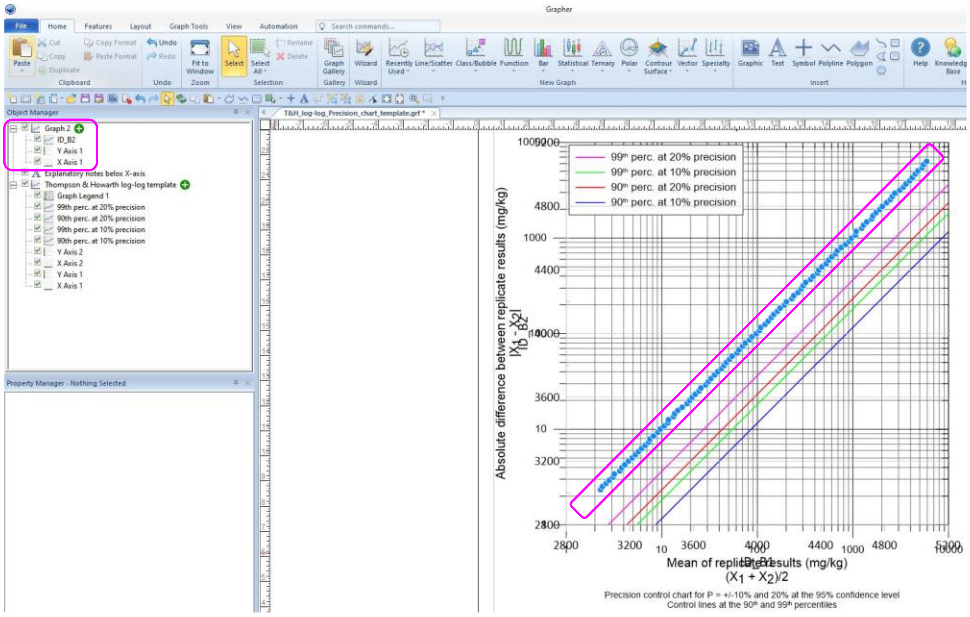



*Figure 10. Select with a left mouse click the ‘GEMAS_AP_replicate_results.xls’, and then click the ‘Open’ file command. It is noted that on top of the template’s X-axis name, ID_B1 is superimposed.*

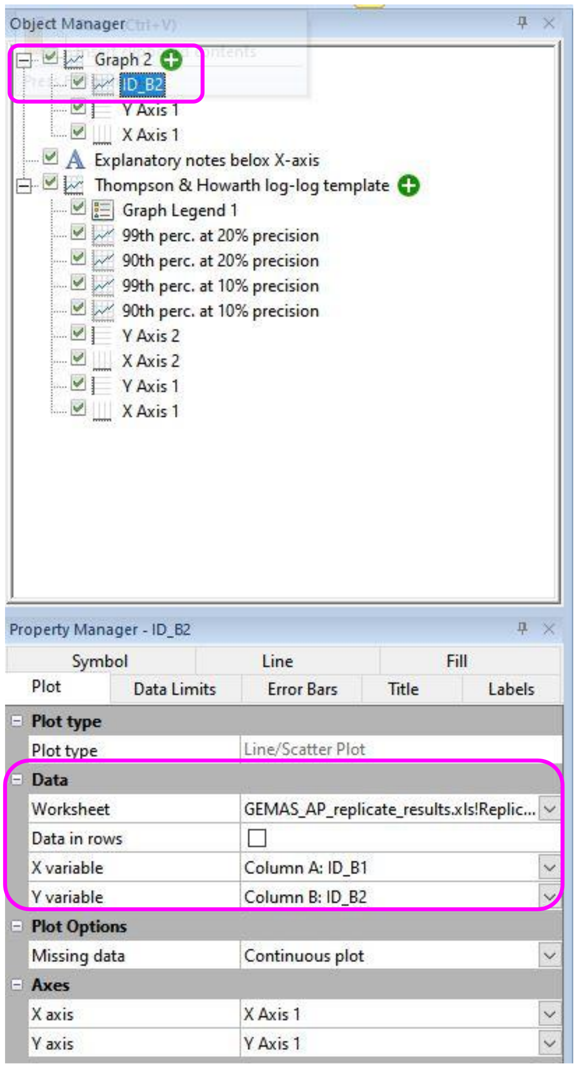



*Figure 11. Select with a left mouse click the ‘GEMAS_AP_replicate_results.xls’, and then click the ‘Open’ file command.*

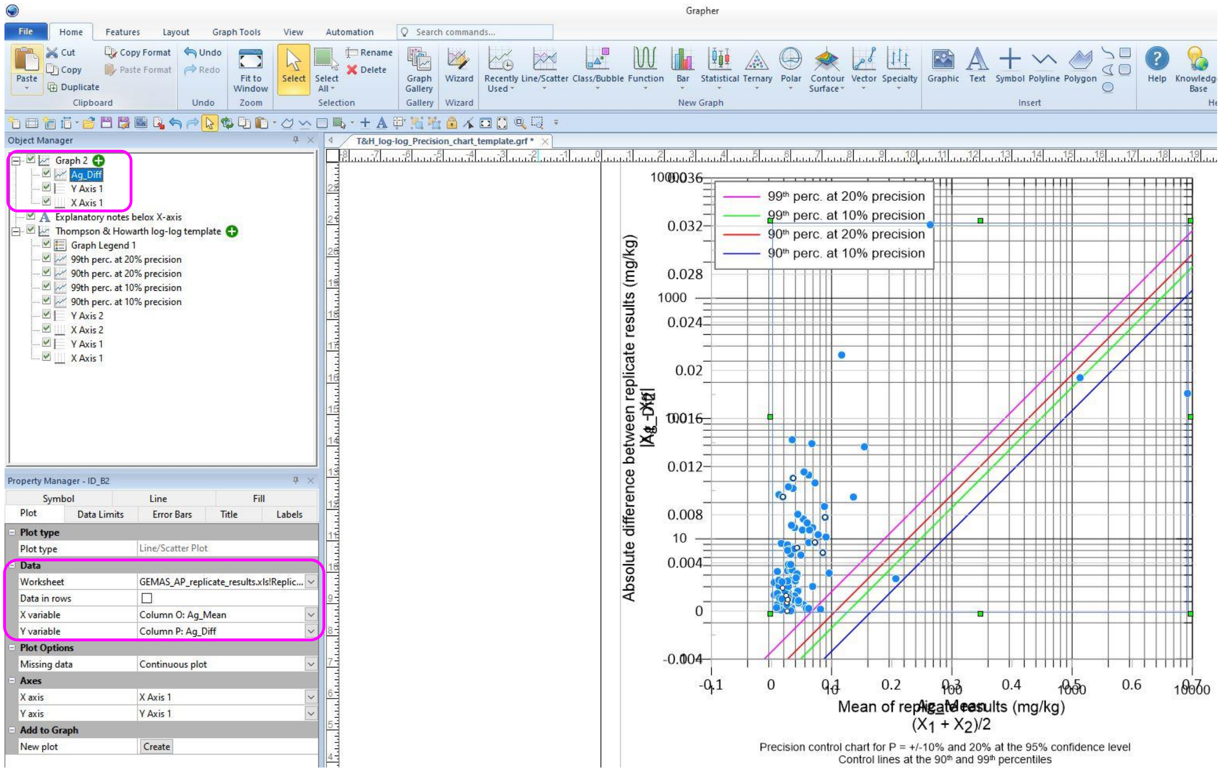


*Figure 12. The graph of Mean versus Absolute Difference of the Ag replicate results is displayed. It is noted that on top of the template's X and Y axes names, Ag_Mean and Ag_Diff are superimposed; this also applies to Figures 13 and 14.*

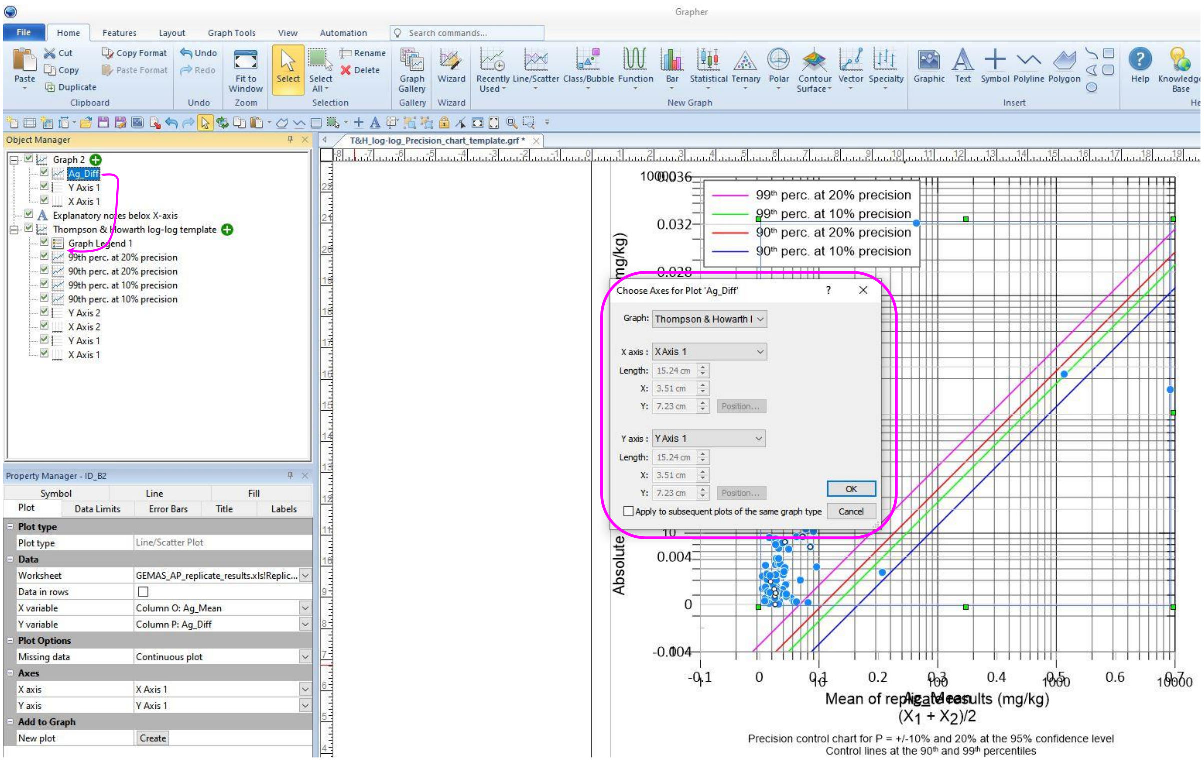


*Figure 13. The Ag chart (Ag_Diff) is moved to the main Thompson and Howarth log-log chart, and a drop-down window appears with a question to "Choose Axes for Plot 'Ag_Diff'"; click 'OK' with the left mouse button.*

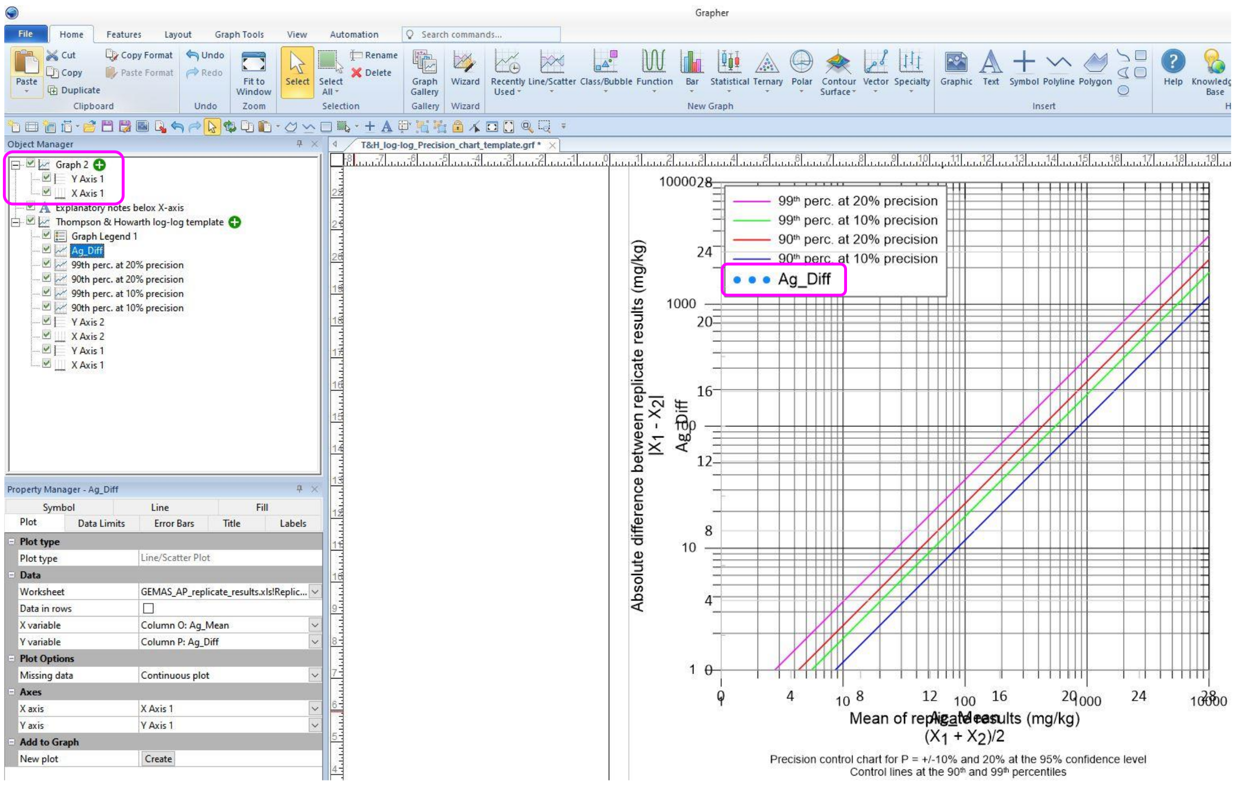


*Figure 14. After moving the Ag replicate pairs (Ag_Diff) to the main Thompson and Howarth log-log chart, and selecting the plot axes (Fig. 11), the blue dots of the Ag replicate pairs disappear from the chart. Since Graph 2 is no longer needed, delete it by marking it and then pressing the command 'Delete'.*

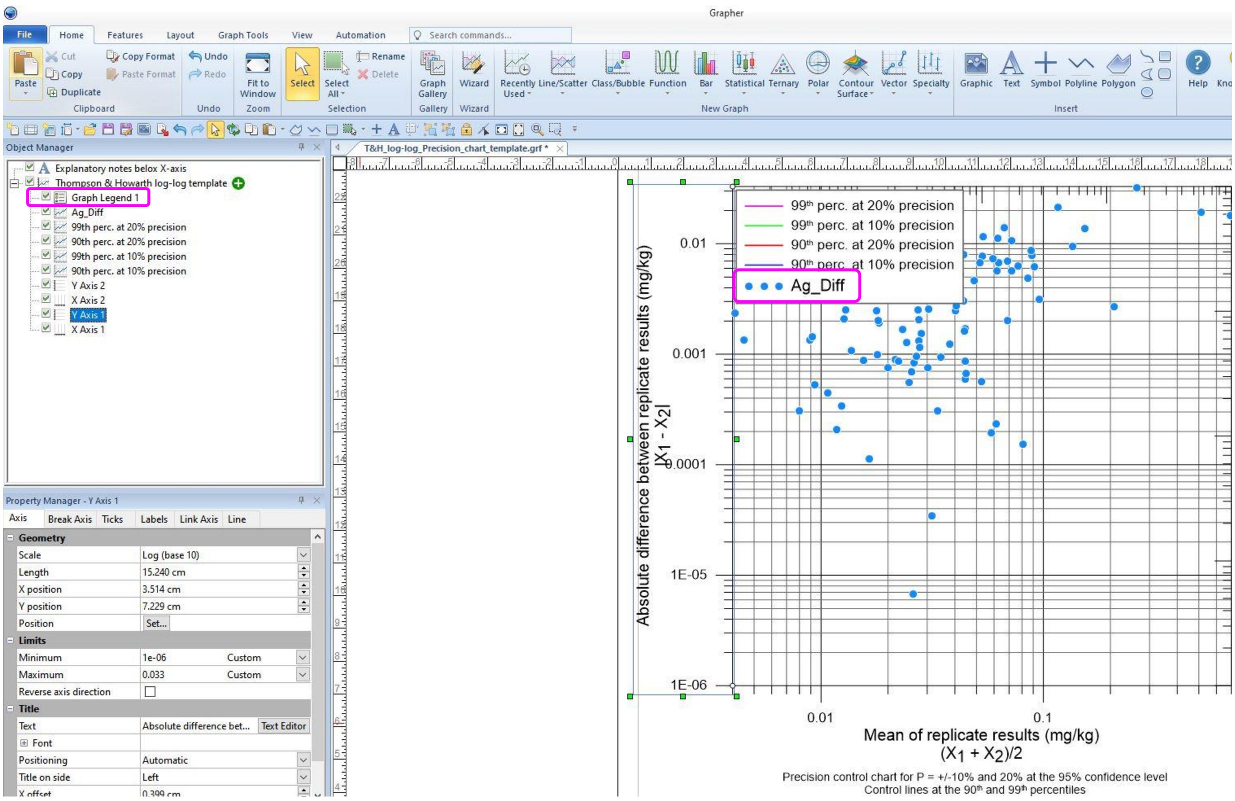


*Figure 15. After changing the minimum and maximum values of the X and Y axes, the Ag replicate pairs appear within the plotting space of the Thompson and Howarth log-log chart. The entry '••• Ag_Diff' is removed from the legend box.*

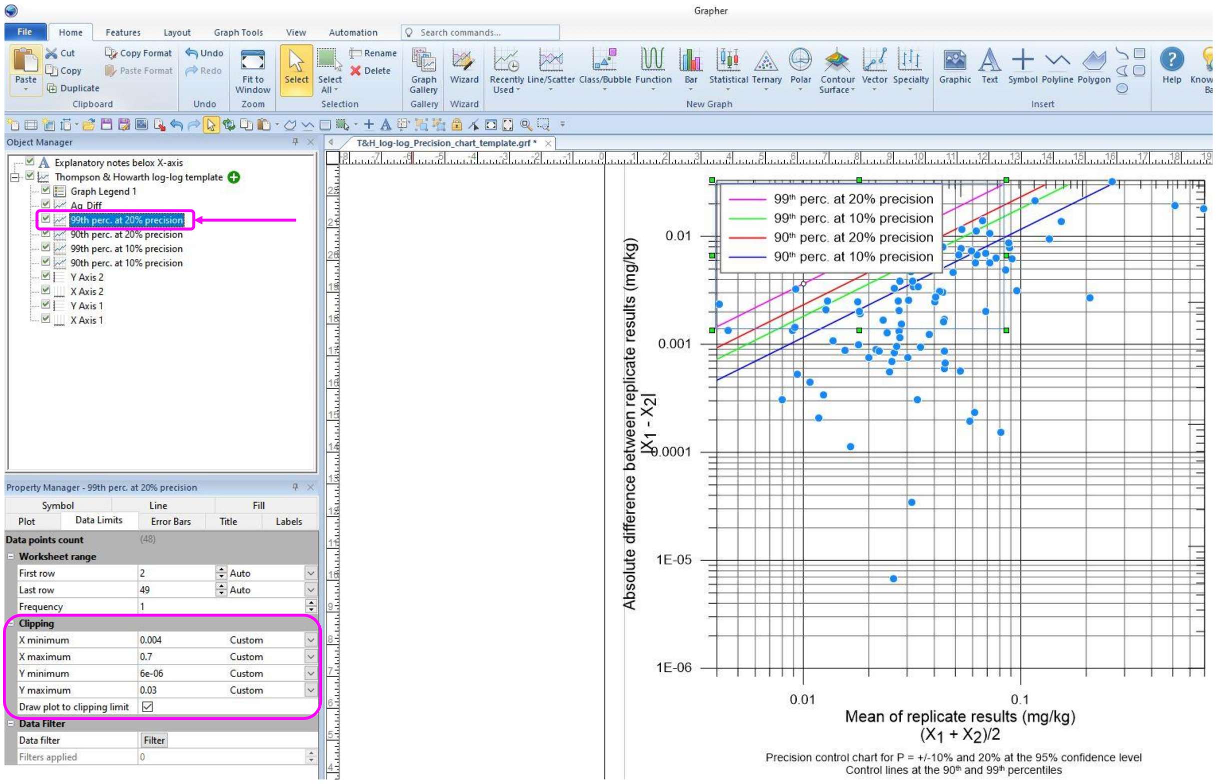


*Figure 16. After changing the minimum and maximum values of the four control lines, they appear within the plotting area of the Thompson and Howarth $log_{10}$-$log_{10}$ chart.*

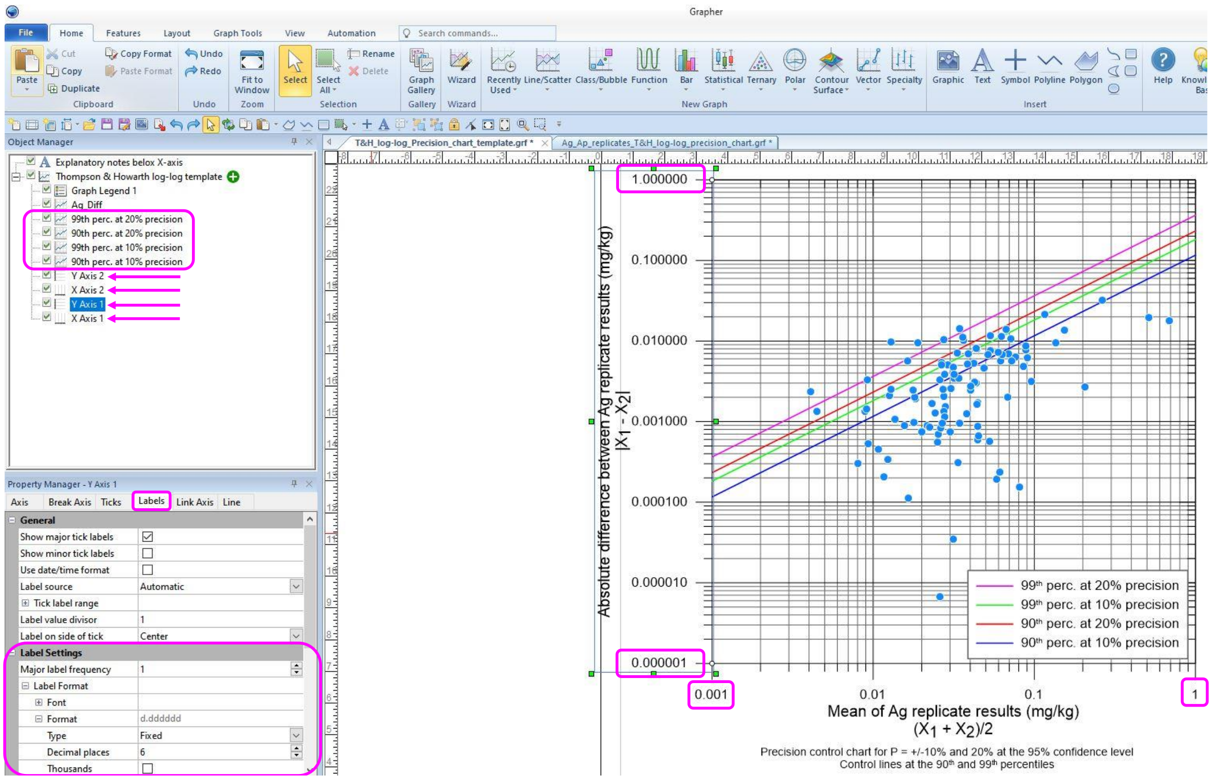


*Figure 17. Final touches to the chart: (a) Minimum and maximum limits of X1-X2 and Y1-Y2 axes changed; (b) limits of the precision lines changed, and (c) the decimal places of the Y-axis changed by selecting 'Labels' in the Property Manager, and selecting 'Type' and assigning 'Fixed' and then 'Decimal places' to 6.*

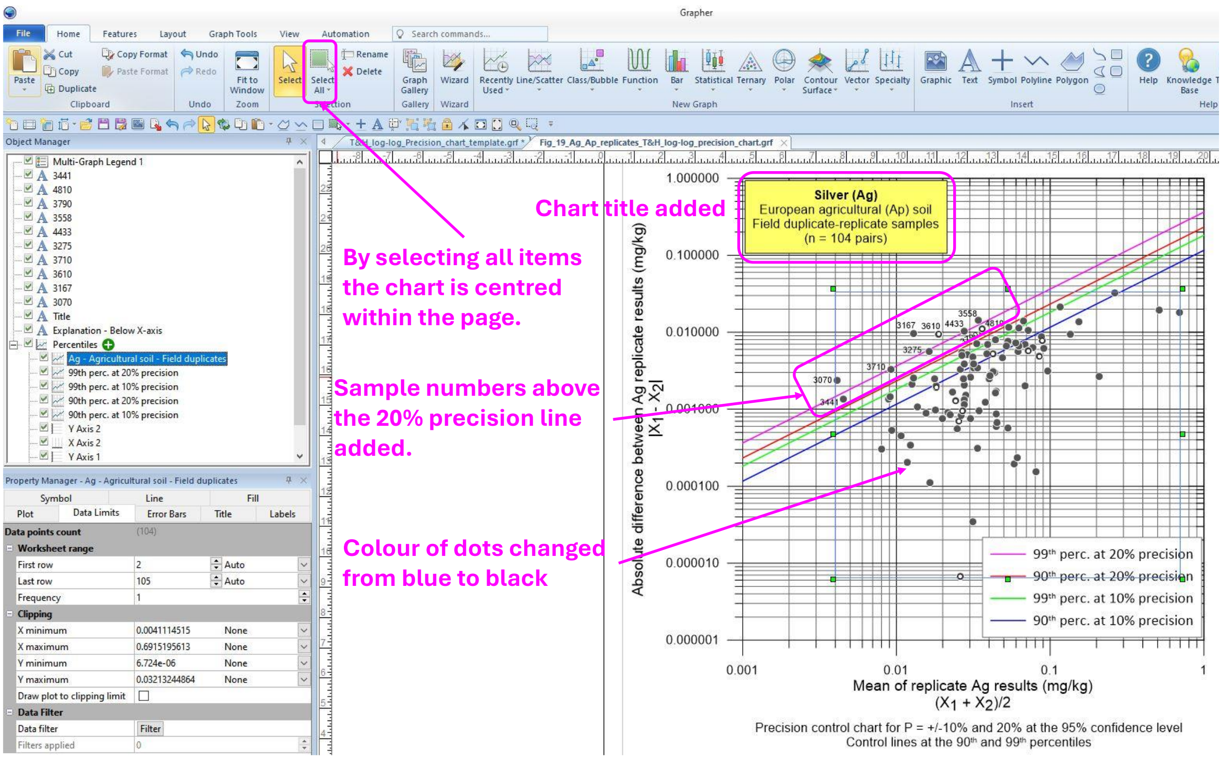



*Figure 18. Annotated figure showing all the changes made.*

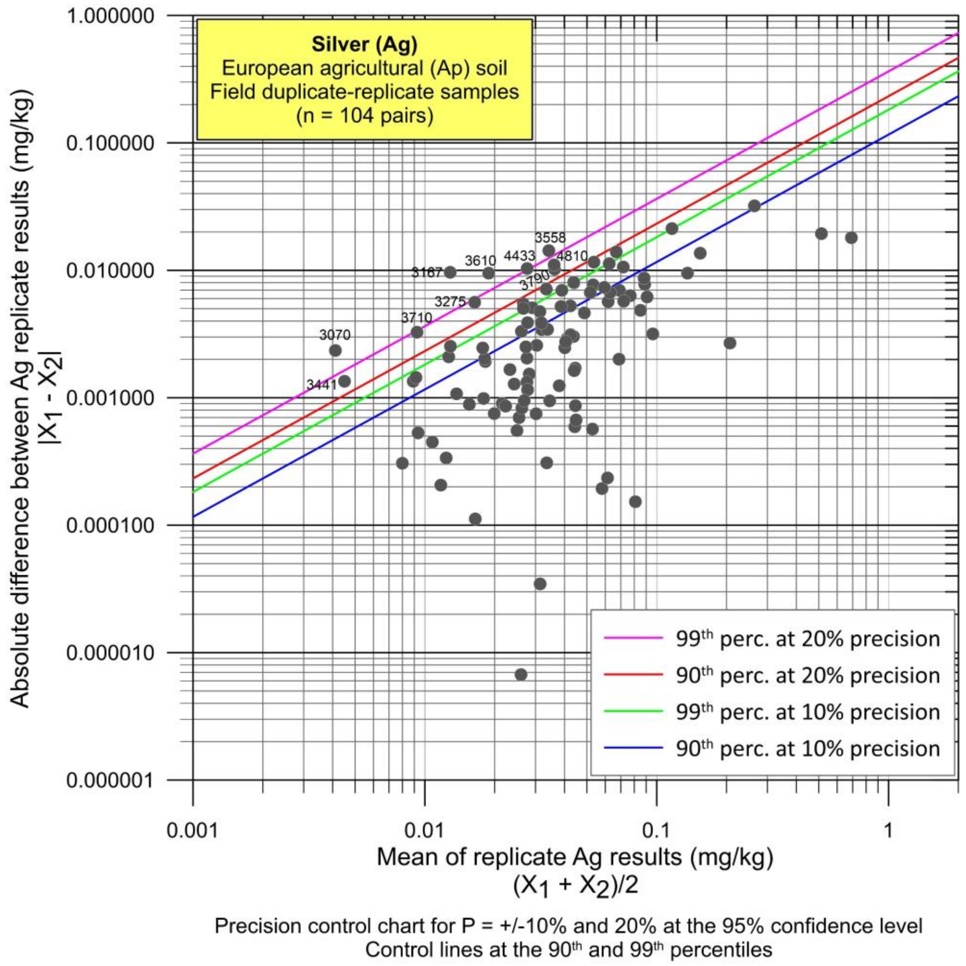



*Figure 19. Final Thompson and Howarth $log_{10}$-$log_{10}$ chart of Ag for inclusion in a report or publication.*

### 6.2.2. Using the linear Thompson and Howarth template

Instead of using the $\log_{10}$-$\log_{10}$ Thompson and Howarth template to plot the replicated analytical data, the linear template can be used (Fig. 3) by following the stepwise procedure described in Section §6.2.1 (p.10).

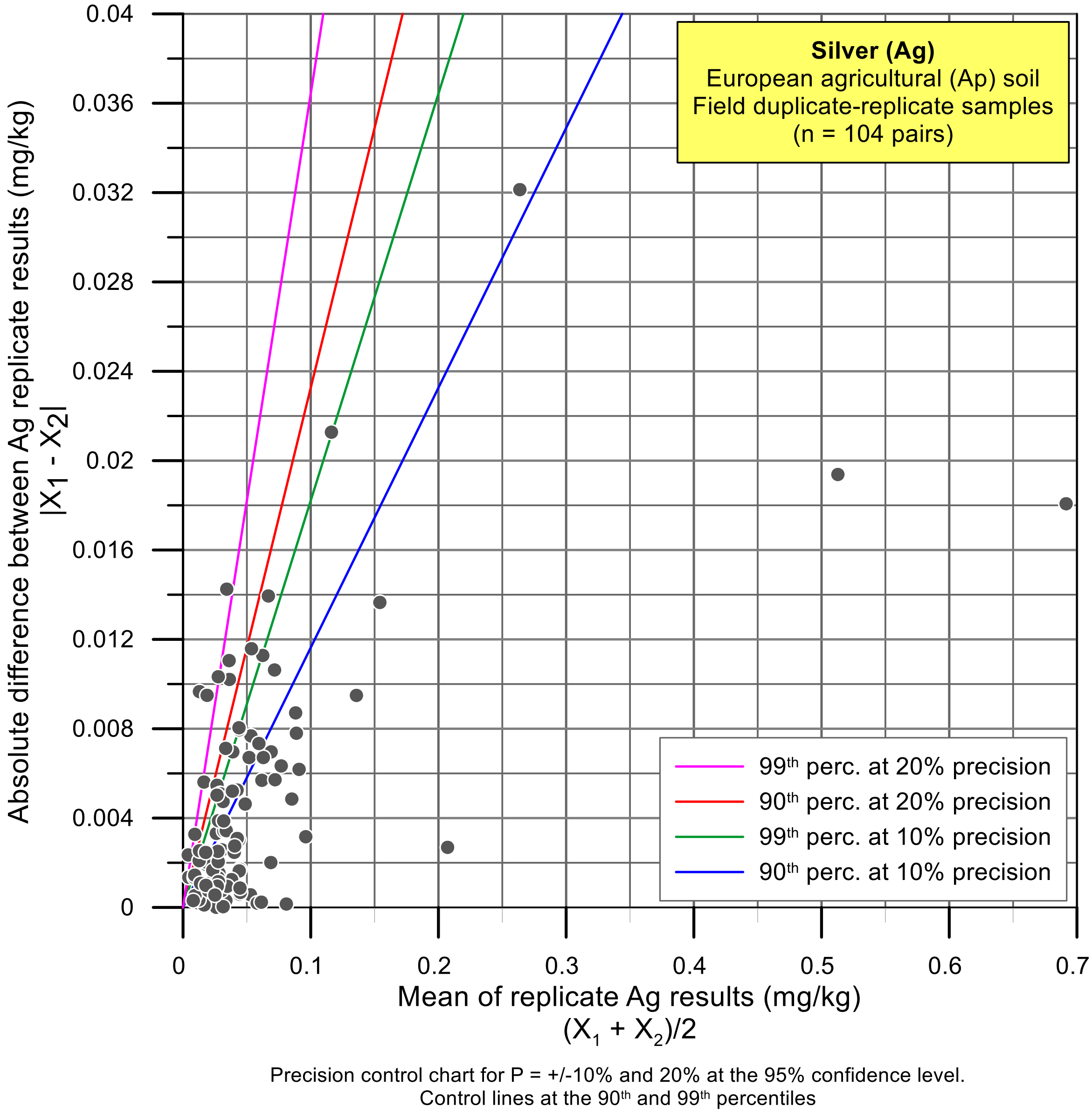



*Figure 20. Final Thompson and Howarth linear chart of Ag for inclusion in a report or publication.*

## 7. Interpretation of Thompson and Howarth charts

As you have seen, no statistical equations are used in the aforementioned graphical process. If you would like to study the statistical theory, the papers by Thompson and Howarth (1973, 1976a, b, 1978), Fletcher (1981), and Thompson (1983) should be consulted.

The combination most useful for precision control is that of the 90$^{th}$ and 99$^{th}$ percentiles, which enables the analyst and applied geochemist to show at once whether the data set conforms to the arbitrary standard and whether any points present probably belong to a different population from the remainder (*i.e.*, gross errors).

According to Thompson and Howarth (1973), in a set of replicate measurements, 90% or 99% of the points will fall below the percentile diagonal appropriate to the precision (±10% or ±20%) of the measurements at the 95% confidence limit.

Consider Figure 19, which shows a set of Ag replicate agricultural soil (Ap) results from the EuroGeoSurveys Geochemistry Expert Group's project with the acronym GEMAS (**GE**ochemical **M**apping of **A**gricultural and grazing land **S**oil). Let us simplify the Thompson and Howarth chart by considering the ±20% precision at the 95% confidence level by removing the ±10% precision control lines (Fig. 21). The distribution of Ag replicate results has the following characteristics for the ±20% precision at the 95% confidence level:

- 99 samples out of 104 are below the 99th percentile of the ±20% precision (theoretically, 103 samples should be below the 99th percentile line), and
- 95 samples out of 104 are below the 90th percentile of the ±20% precision (theoretically, 94 samples should be below the 90th percentile line).

Since the actual and theoretical results are not significantly different, the precision of the Ag analytical replicate data is judged to be consistent with a precision of ±20% at the 95% confidence level.

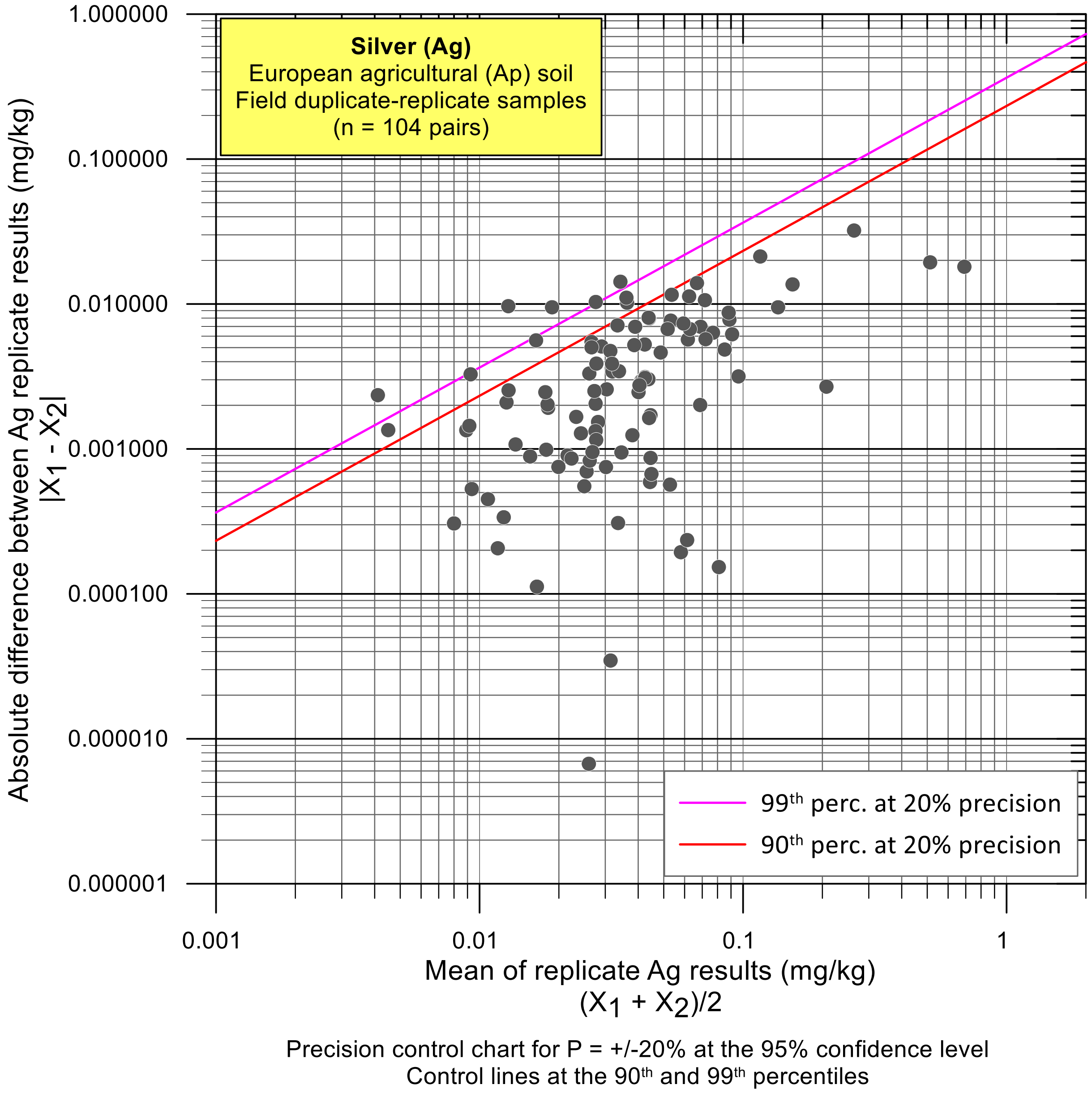



*Figure 21. Thompson and Howarth $log_{10}$-$log_{10}$ chart of Ag for ±20% precision at the 95% confidence level with control lines at the 90th and 99th percentiles.*

Figure 22 shows the Thompson and Howarth chart of Ag by selecting this time the ±10% precision lines at the 95% confidence level and deselecting the ±20% precision control lines. The distribution of Ag replicate results has the following features for the ±10% precision at the 95% confidence level:

- 88 samples out of 104 are below the 99th percentile of the 10% precision (theoretically, 103 samples should be below the 99th percentile line), and
- 68 samples out of 104 are below the 90th percentile of the 10% precision (theoretically, 94 samples should be below the 90th percentile line).

Since the difference between the actual and theoretical results is quite different, the precision of the Ag analytical results is judged to be almost certainly worse than ±10% at the 95% confidence level. It is concluded, therefore, that the precision of the Ag analytical results is close to ±20% at the 95% confidence level.

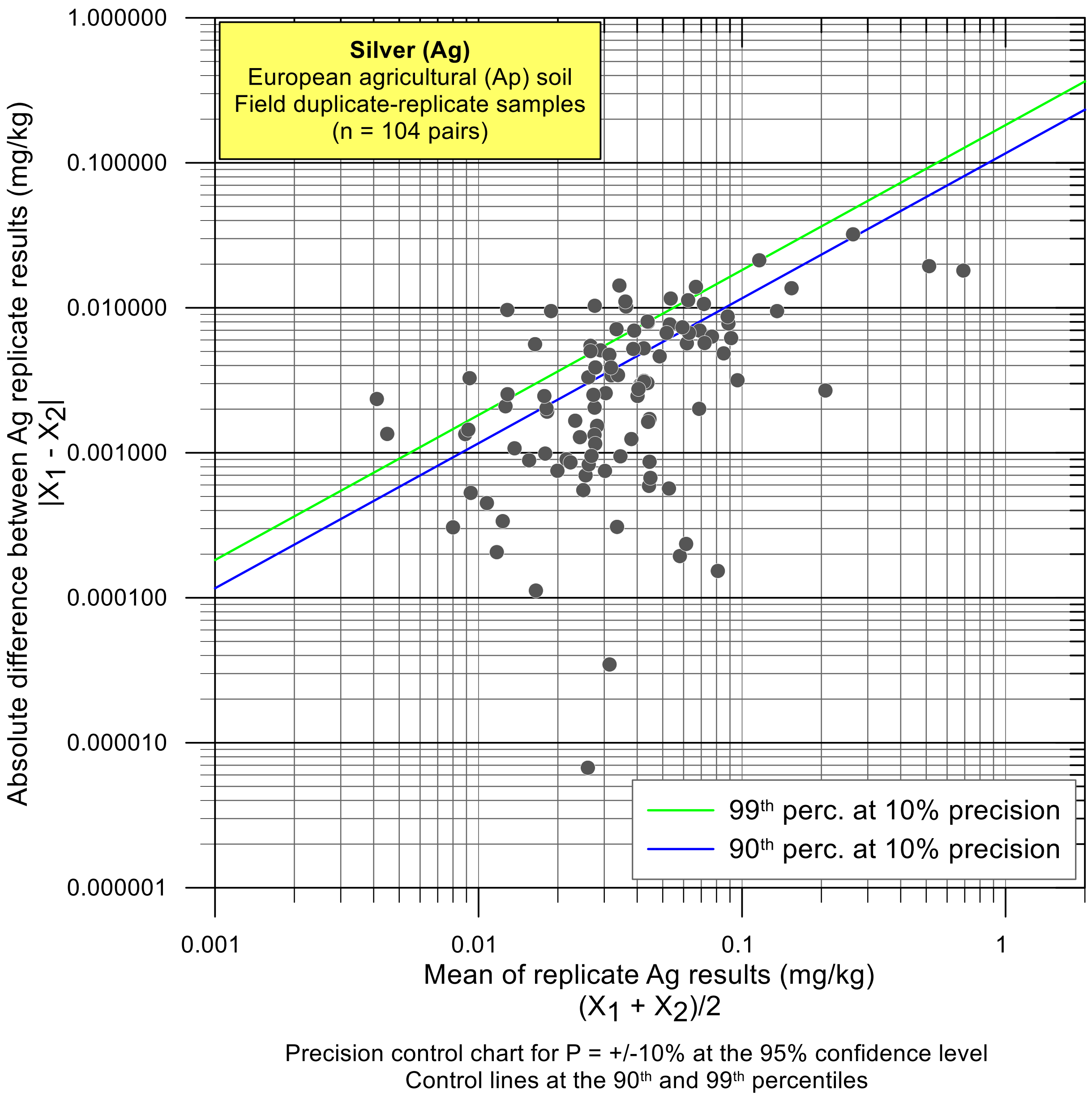



*Figure 22. Thompson and Howarth $\log_{10}$-$\log_{10}$ chart of Ag for ±10% precision at the 95% confidence level with control lines at the 90th and 99th percentiles.*

Below are two additional examples of Thompson and Howarth log-log charts. The first shows the Cu field duplicate-replicate analytical results (Fig. 23), where most samples fall below the 90$^{th}$ percentile of the ±10% precision (n = 94). Therefore, the results are judged to be consistent with a precision of ±10% at the 95% confidence level.

The second example displays the Ge field duplicate-replicate analytical results (Fig. 24), where 15 out of 104 samples fall below the 90$^{th}$ percentile control line at ±10% precision at the 95% confidence level, suggesting that the precision is poor, and, therefore, the quality of the data is unacceptable.

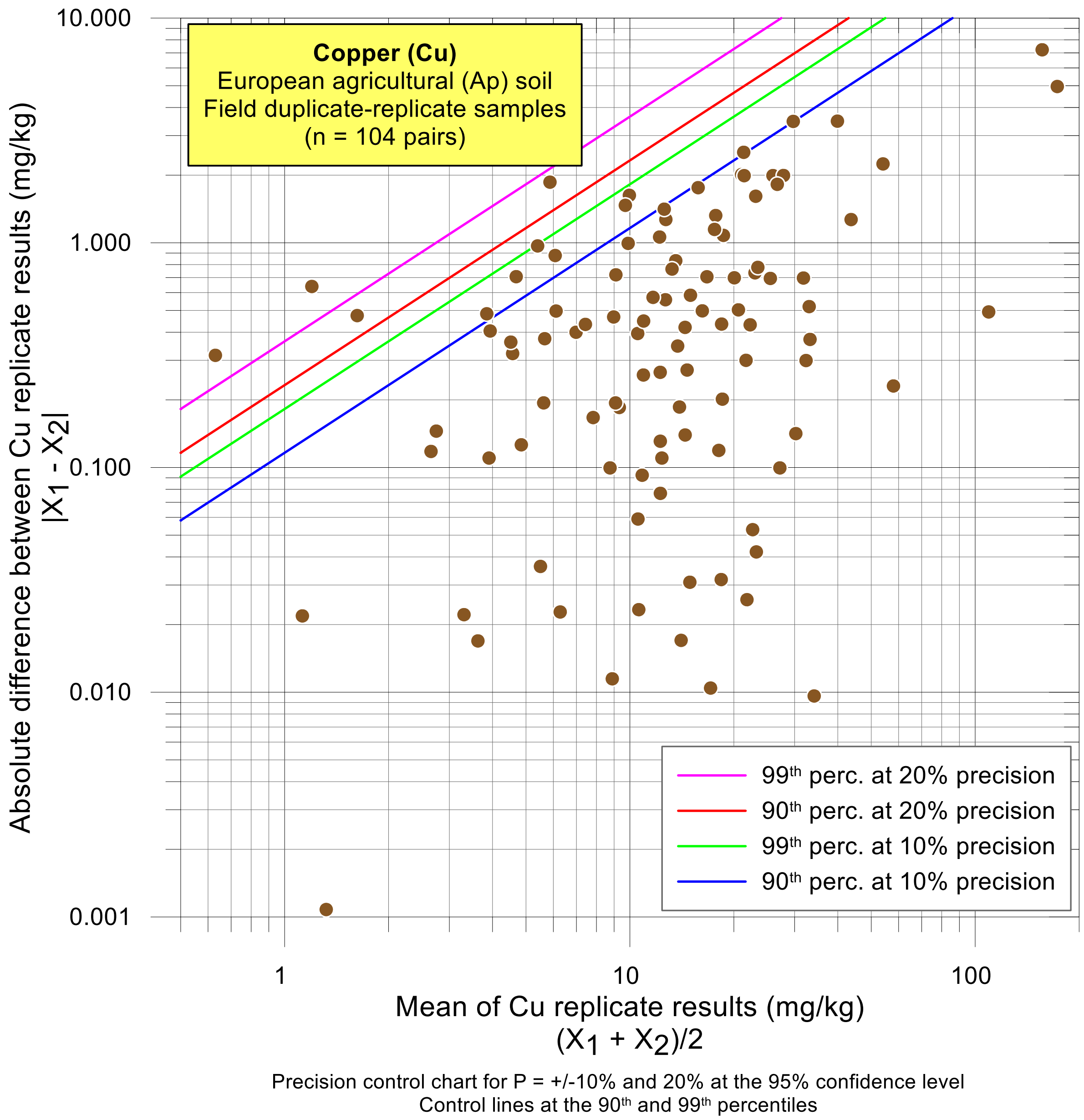



*Figure 23. Thompson and Howarth $log_{10}$-$log_{10}$ chart of Cu for ±10% and 20% precision at the 95% confidence level with control lines at the 90$^{th}$ and 99$^{th}$ percentiles.*

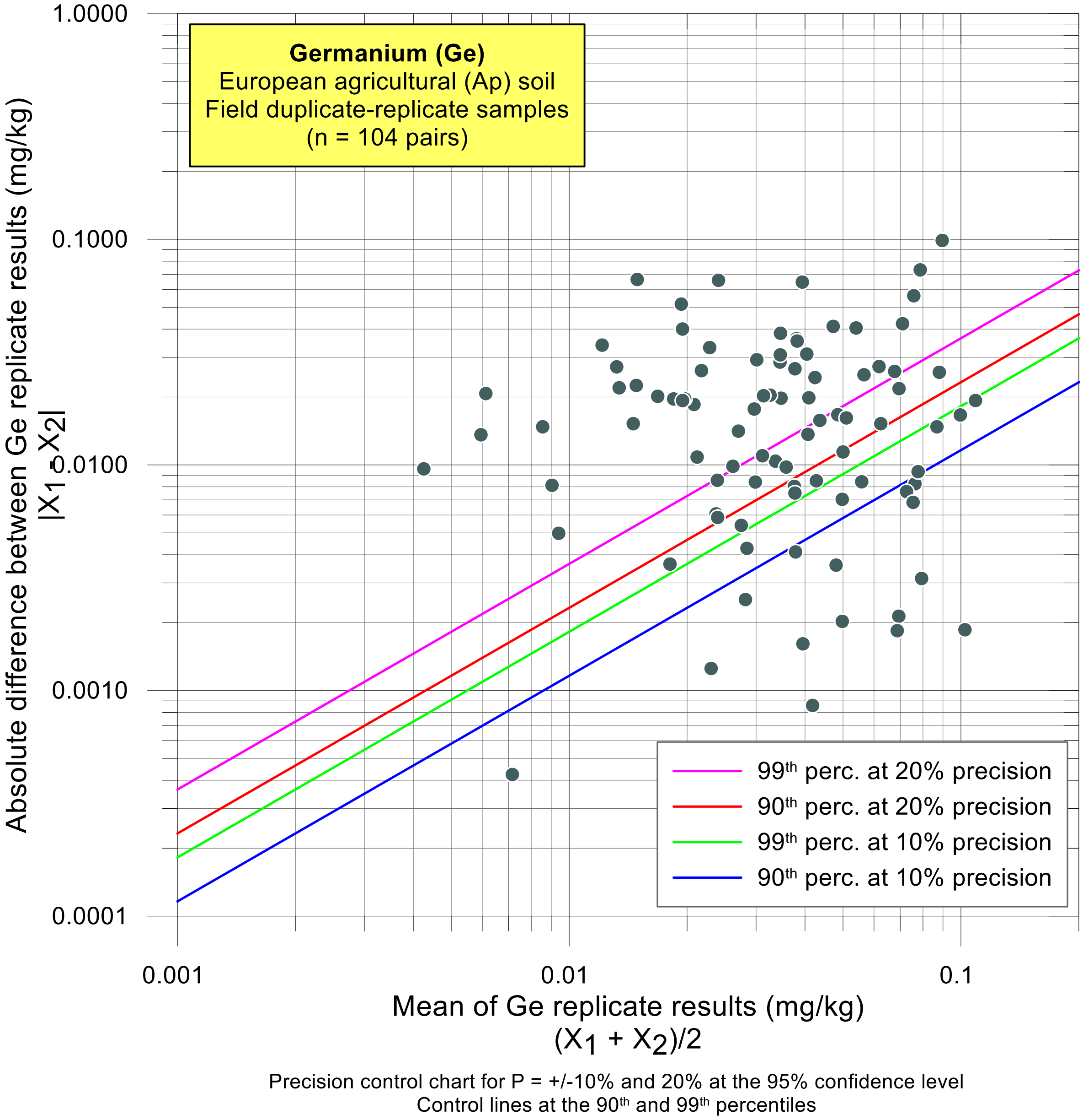



*Figure 24. Thompson and Howarth $log_{10}$-$log_{10}$ chart of Ge for ±10% and 20% precision at the 95% confidence level with control lines at the $90^{th}$ and $99^{th}$ percentiles.*

It is strongly recommended that the evaluation of the GEMAS project's *aqua regia* quality control results be studied (Reimann *et al*., 2009). In this report, you will find other helpful information for evaluating analytical results besides the linear Thompson and Howarth charts. It is also recommended to study the other two GEMAS project's quality control reports, because there is useful information about handling analytical problems (Reimann *et al*., 2011, 2012).

## Acknowledgements


The workshop entitled "*International Union of Geological Sciences Manual of Standard Methods for Establishing the Global Geochemical Reference Network*" was held on the $30^{th}$ and $31^{st}$ of August 2024 during the $37^{th}$ International Geological Conference in Busan (South Korea). It was co-sponsored by the International Union of Geological Sciences and the Association of Applied Geochemists, and both organisations are thanked for their generosity. Drew Dudley and the Golden Software management are thanked for the *free, gratis* renewal of the first author's personal annual Grapher™ licence. Rachel VanOsdol (Customer Success Engineer, Golden

Software Support) and Philippe Négrel (Chairperson of the EuroGeoSurveys Geochemistry Expert Group) are thanked for their review and constructive comments, which improved the quality of this tutorial.

## Supplementary material

The following material is in the '***Thompson&Howarth_charts.zip***' file:

- Fig_2.4_p30_in_Fletcher-1981_Analytical_Methods_in_Geochemical_Prospecting.grf
- Fig_19_Final_Ag_Ap_replicates_T&H_log-log_precision_chart.grf
- Fig_20_Ag_Ap_replicates_T&H_linear_Precision_chart_template.grf
- Fig_21_Ag_Ap_replicates_T&H_log-log_20%_precision_chart.grf
- Fig_22_Ag_Ap_replicates_T&H_log-log_10%_precision_chart.grf
- Fig_23_Cu_T&H_log-log_Precision_chart.grf
- Fig_24_Ge_Ap_replicates_T&H_log-log_precision_chart.grf
- GEMAS_AP_replicate_results.xls
- Plot_90&99perc_at_10&20%precision.xls
- T&H_linear_Precision_chart_template_25.grf
- T&H_log-log_Precision_chart_template_25.grf

**Directory 1: Master-chart-for_plotting_by_hand:-**

- Precision_1&2&5&10&20&50percent.xls
- Precision_Percentiles_05_to_75.xls
- Precision_Percentiles_90&99.xls
- T&H_10%_precision_control_chart_for_printing.pdf
- T&H_Master_10%_Precision_log-log_chart_25.grf

**Directory 2: T&H_references:-**

- Thompson_&_Howarth_1973_Rapid_estimation_and_control_of_precision_by_duplicate_determinations.pdf
- Thompson_&_Howarth_1976_Duplicate_analysis_in_geochemical_practice_I.pdf
- Thompson_&_Howarth_1978_A_new_approach_to_the_estimation_of_analytical_precision_JGE_v9(1)_p23-30.pdf
- Thompson_&_Howarth_1978_Anal_Precision_Tables_1&2.xls

**Directory 3: T&H templates for earlier versions of Grapher™**

In this directory, there are Thompson and Howarth templates of earlier versions of Grapher™, namely, versions 10 to 15, for users who do not have newer versions:

- T&H_linear_Precision_chart_template_10.grf
- T&H_linear_Precision_chart_template_11.grf
- T&H_linear_Precision_chart_template_12.grf
- T&H_linear_Precision_chart_template_13.grf
- T&H_linear_Precision_chart_template_14.grf
- T&H_linear_Precision_chart_template_15.grf
- T&H_log-log_Precision_chart_template_10.grf
- T&H_log-log_Precision_chart_template_11.grf
- T&H_log-log_Precision_chart_template_12.grf
- T&H_log-log_Precision_chart_template_13.grf
- T&H_log-log_Precision_chart_template_14.grf
- T&H_log-log_Precision_chart_template_15.grf

*It is, however, strongly recommended that you upgrade to the latest version of Golden Software's Grapher™ to stay ahead with cutting-edge features and dedicated customer support.*

## References

Note: All hyperlinks were checked on the 29th of May 2025.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## Further reading

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Thompson and Howarth developed a graphical method in the 1970s for visual estimation of analytical precision even for a single duplicate-replicate pair of samples.

The mean of the duplicate-replicate pair of samples is plotted against the corresponding absolute difference.

A copy of the original precision control chart for replicate results used by the Imperial College Applied Geochemistry Research Group is presented for use in the laboratory and field.

Digital log-log base 10 and linear templates of Thompson and Howarth charts are provided with control lines plotted at the 90$^{th}$ and 99$^{th}$ percentile for 10% and 20% precision at the 95% confidence level.  These were generated with Golden Software's Grapher™ (version 25).

Instructions are given for preparing the input replicates data set and plotting the results.

Worked examples and the interpretation of plotted results are provided.

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of the Earth's Land Surface