

Test Group Summary Report

C24 Aryloxy Acid Pesticides in Water

June 2024 PT Round

Issued: July 30, 2024

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1.0 The Proficiency Testing Report

The Proficiency Testing Report consists of two parts.

- *PTC Proficiency Testing Report:* This report contains participant-specific data and other confidential information. This report is emailed to participants at the end of the PT round.
- *Test Group Summary Report:* A Test Group Summary Report is created for each quantified test group at the end of the PT round. These reports contain more detailed information on the round than is found in the participant-specific PTC Proficiency Testing Report. These reports do not contain any confidential information and are made available on the PTC web site.

2.0 Definitions

The participant-specific PTC Proficiency Testing Report contains some terms that new participants may not be familiar with.

<i>Code:</i>	The registration code that is unique to each analyte that a participant is registered for.
<i>App:</i>	If a participant is accredited by CALA, this three-digit number is the appendix number that the accredited method is assigned to.
<i>N:</i>	The number of participants results that were used to calculate the summary statistics. This excludes qualified data (e.g., <) and any results that were flagged as outliers.
<i>Assigned:</i>	The Assigned Value is the robust mean of the reported results, outliers excluded. This is often referred to as the “target” value.
<i>±u:</i>	The uncertainty of the assigned value.
<i>Reported:</i>	The result reported by the participant.
<i>s:</i>	The Standard Deviation of Proficiency Assessment (SDPA). This value is used to determine the acceptance limits for the PT evaluation.
<i>z-Score:</i>	A value assigned to each reported result that is a measure of the degree to which it deviates from the Assigned Value.
<i>Score:</i>	The composite score of the four results reported for each analyte. It is normalized to a score out of 100.
<i>Bias:</i>	A flag assigned if bias is detected using the re-scaled z-score procedure.

3.0 Scoring System

Participant performance is evaluated for each proficiency testing sample by a quantitative method that is consistent with ISO/IEC 17043 - *Conformity assessment- General requirements for the competence of proficiency testing providers*, the *International Harmonized Protocol for Proficiency Testing of (Chemical) Analytical Laboratories*(2006), and ISO 13528:2015 *Statistical methods for use in proficiency testing by interlaboratory comparisons*.

The following is a brief description of the evaluation procedure used by PTC. The detailed evaluation procedure is described in PROC09 – PT Evaluation *Procedure*, which is available on the PTC website (www.PTCCanada.org).

3.1 HOMOGENEITY AND STABILITY ASSESSMENT

Homogeneity and stability are assessed using participant data. Regression analysis is performed on reported result against order of sample production (Homogeneity) and reported result against date of analysis (Stability). If the slope is significantly different than zero for either then the Standard Deviation of Proficiency Assessment (s) is increased to minimize the impact.

3.2 THE Z SCORE

A "z-score" is calculated for each reported result as follows:

$$z - Score = \frac{(x - \bar{X})}{SDPA}$$

where: x = participant result;
 \bar{X} = the Assigned Value;
SDPA = the Standard Deviation for Proficiency Assessment.

The assigned value \bar{X} is generally estimated from the inter-laboratory Robust mean after outliers due to obvious gross errors (e.g., reported in wrong units) have been removed.

The Standard Deviation for Proficiency Assessment, s, is determined as follows:

- The inter-laboratory Robust standard deviation ($Stdev_{rob}$) is calculated using reported results, obvious outliers removed;
- The regression equation standard deviation ($Stdev_{reg}$) is estimated from regression equations derived from previous studies (see PROC11- *PT Regression Equations* for details);
- The SDPA is the higher of $Stdev_{rob}$ and $Stdev_{reg}$;
- When a laboratory reports its detection limit, s will be estimated using a pooled variance procedure that uses both the inter-laboratory data and the reported detection limit.

3.2 COMPOSITE (PT) SCORE

Since each PT round involves four or two separate samples of distinct concentration for each test, it is necessary to calculate a composite PT score for each test to determine overall performance. The composite score is calculated by first averaging the absolute z-scores for the four results and then calculating a final score as $100 + (-15 \times \text{avg } |z|)$.

Acceptable PT Scores equal or exceed 70.

3.3 IDENTIFYING BIAS

The proficiency testing report provides flags for bias. These are determined using the re-scaled z-score procedure.

$$RSZ = \frac{\sum z}{\sqrt{N}}$$

where z = the z- score
 N = the number of samples

Flags are assigned for each test group/parameter combination as follows:

$RSZ \geq -2$ and ≤ 2	no flag assigned
$RSZ > 2$	H (High)
$RSZ > 3$	VH (Very High)
$RSZ < -2$	L (LOW)
$RSZ < -3$	VL (Very Low)

3.4 DEVIATIONS FROM EVALUATION PROCEDURE

Other than changes to the Standard Deviation of Proficiency Assessment due to homogeneity or stability flags, any deviation from the published evaluation procedure is described on the cover page(s) of the final *PTC Proficiency Testing Report*.

4.0 PT Round Specific Data Summary

The following pages provide more detailed information about the PT round indicated in the cover page of this report than is found in the participant-specific PTC Proficiency Testing Report. The graphical representations and the statistical summaries are based upon the data after outliers have been removed.

4.1 SUMMARY STATISTICS

In addition to some of the statistics found in the customer reports, this table includes additional summary statistics such as Median, different measures of dispersion, the number of outliers removed, the number of results in the Questionable range ($|z|$ between 2 and 3) and the Unacceptable range ($z > 3$), and whether a data set was flagged for Homogeneity or Stability. This section also includes sorted scatter plots of the data for each sample.

4.2 z- SCORE PLOTS¹

The z-scores for each sample are ranked in increasing order and plotted. When the data is normally distributed, the plot should show a slight sigmoidal curve, with an equal number of points above zero as below. Each bar in these plots is colour-coded to indicate the analytical method used by the participant.

4.3 KERNEL DENSITY PLOTS

Kernel density plots are generated for each data set. These plots are a graphical way to represent the overall data distribution and are used to visualize possible deviations from normality and unimodality.

4.4 STABILITY AND HOMOGENEITY PLOTS

Plots of reported result against analysis date, and reported result against order of bottling are displayed, along with the regression line. These regression analyses are used to determine if the SDPA should be adjusted due to homogeneity or stability.

4.5 BOX-AND-WHISKER PLOTS

Box-and-Whisker plots are another way to display the distribution of the data. The box denotes the first and third quartile and the whiskers are the 5th and 95th percentile.

4.6 HISTORIC COMPARISON PLOT

The Historic Comparison Plot is a plot of robust mean against robust standard deviation for the previous ten PT rounds as well as the current PT round. This plot can be used to identify possible changes in the sample formulation.

¹ For some reports, the colour coding for methods is not being displayed properly.

2,4,5-TRICHLOROPHENOXYACETIC ACID

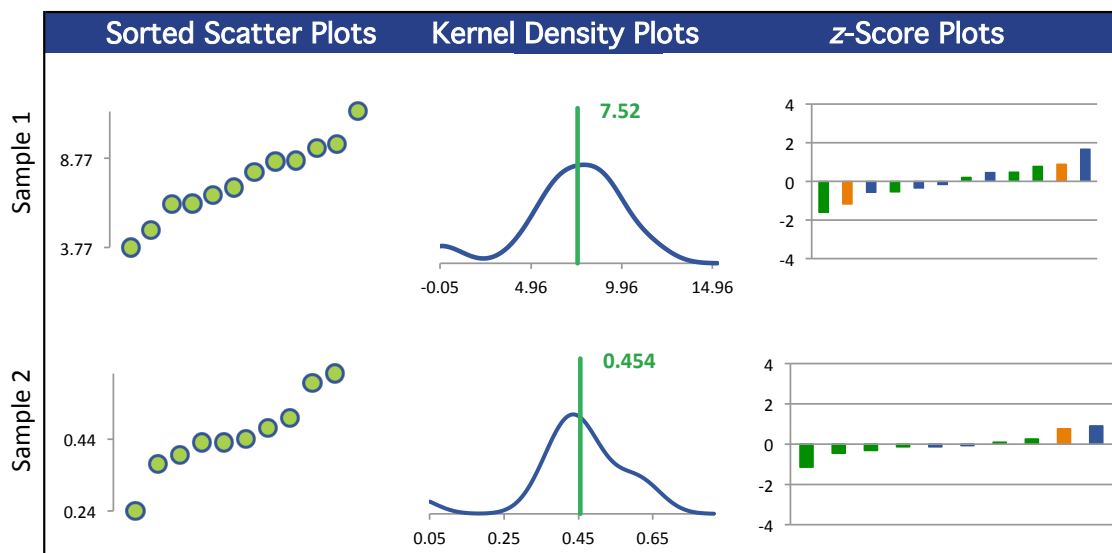
Summary Statistics

Statistic	C24-1	C24-2	C24-3	C24-4
N	12	10	12	12
Median $\mu\text{g/L}$	7.57	0.435	3.39	4.77
Robust Mean $\mu\text{g/L}$	7.52	0.454	3.38	4.80
U $\mu\text{g/L}$	0.841	0.0455	0.372	0.494
Robust Standard Deviation $\mu\text{g/L}$	2.33	0.115	1.03	1.37
Regression Standard Deviation $\mu\text{g/L}$	1.91	0.187	0.901	1.25
Stability Flag				
Homogeneity Flag				
Standard Deviation Used (SDPA) $\mu\text{g/L}$	2.33	0.187	1.03	1.37
Outliers	0	0	0	0
$ z > 3.0$	0	0	0	0
$2 < z < 3$	0	0	2	0

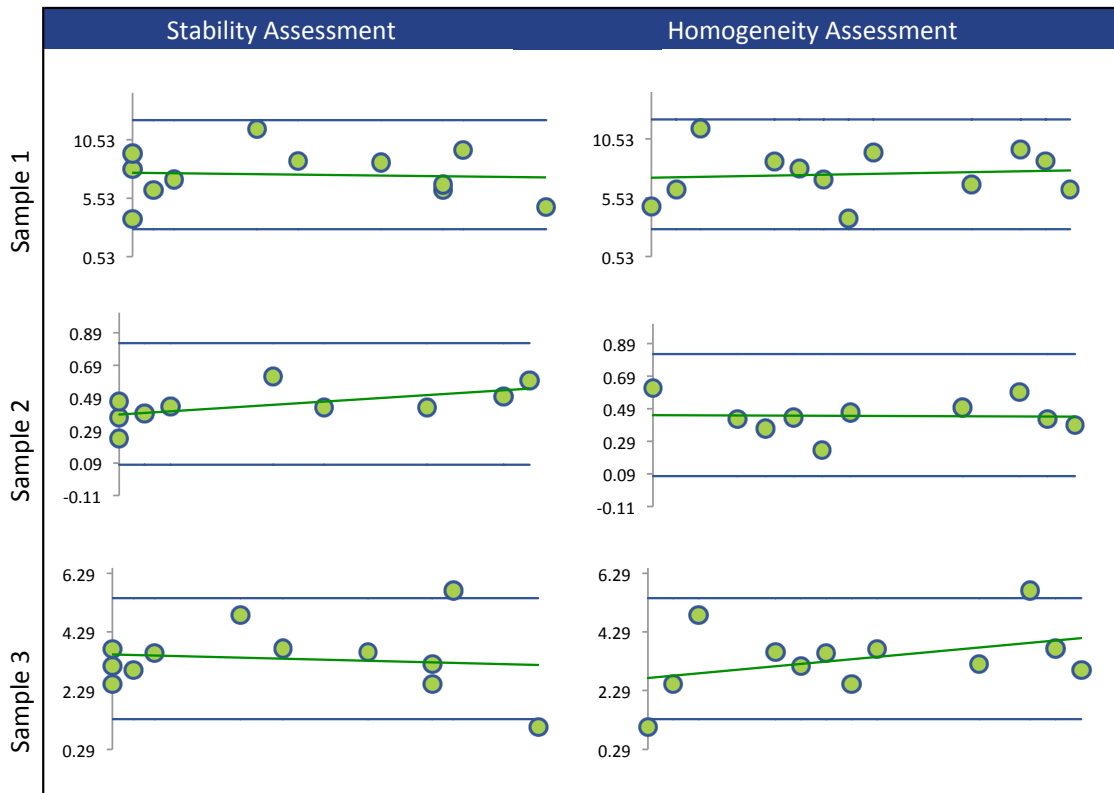
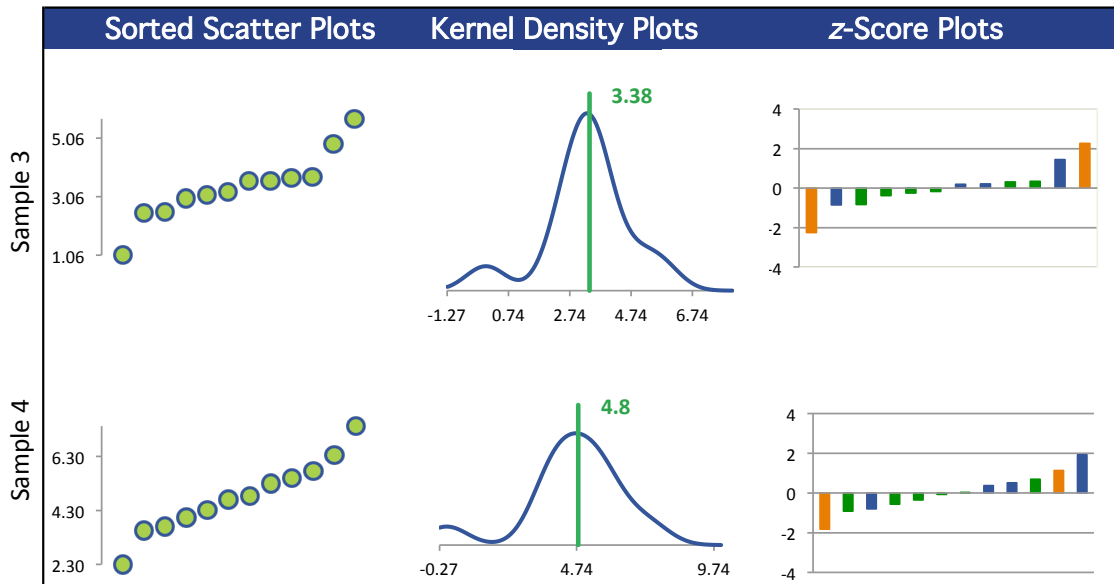
Methods Used

Method	C24-1	C24-2	C24-3	C24-4
LC-MS/MS (Blue)	5	5	5	5
GC/ECD (Red)	2	1	2	2
GC/MS (Green)	4	3	4	4
HPLC (Orange)	1	1	1	1

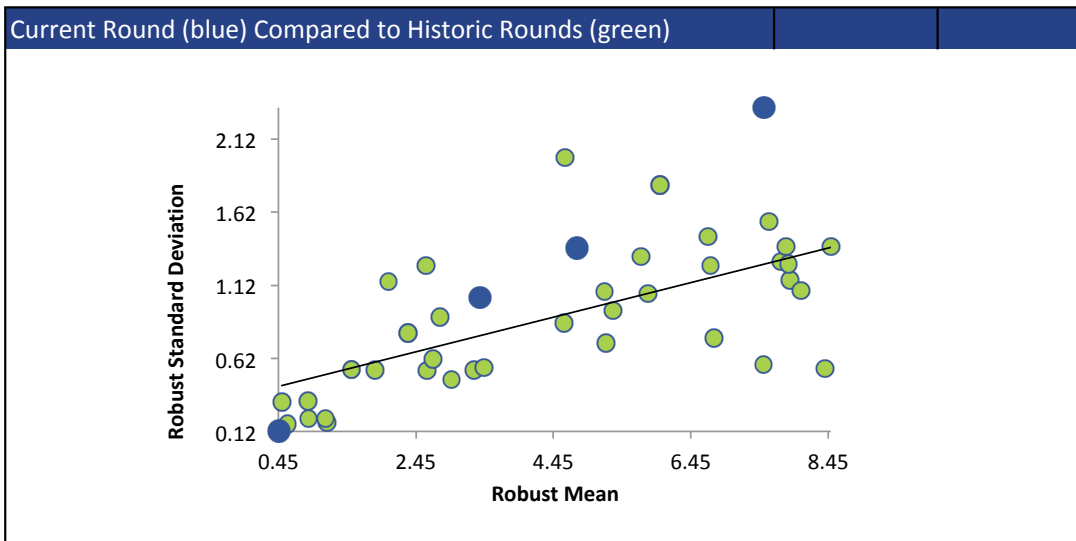
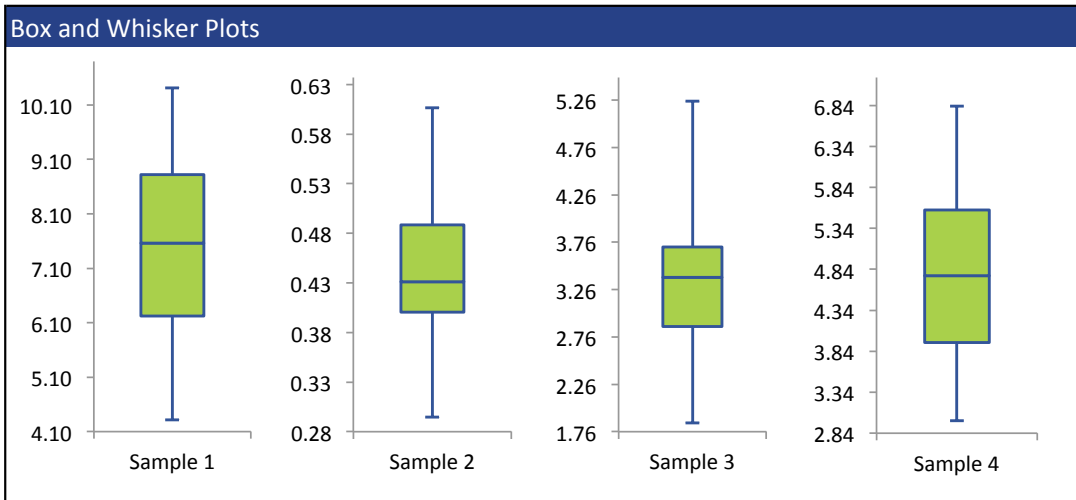
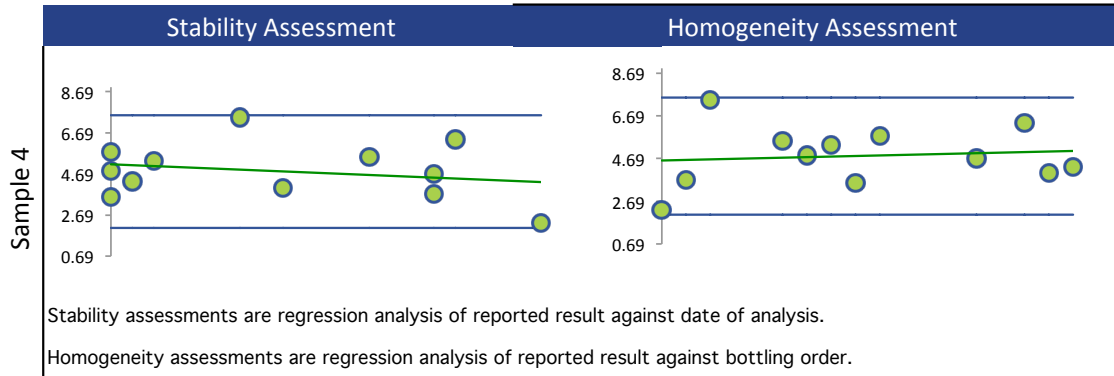
All summary stats and the plots below are based on the data excluding any flagged outliers



2,4,5-TRICHLOROPHENOXYACETIC ACID



2,4,5-TRICHLOROPHENOXYACETIC ACID



2,4-DICHLOROPHENOXYACETIC ACID

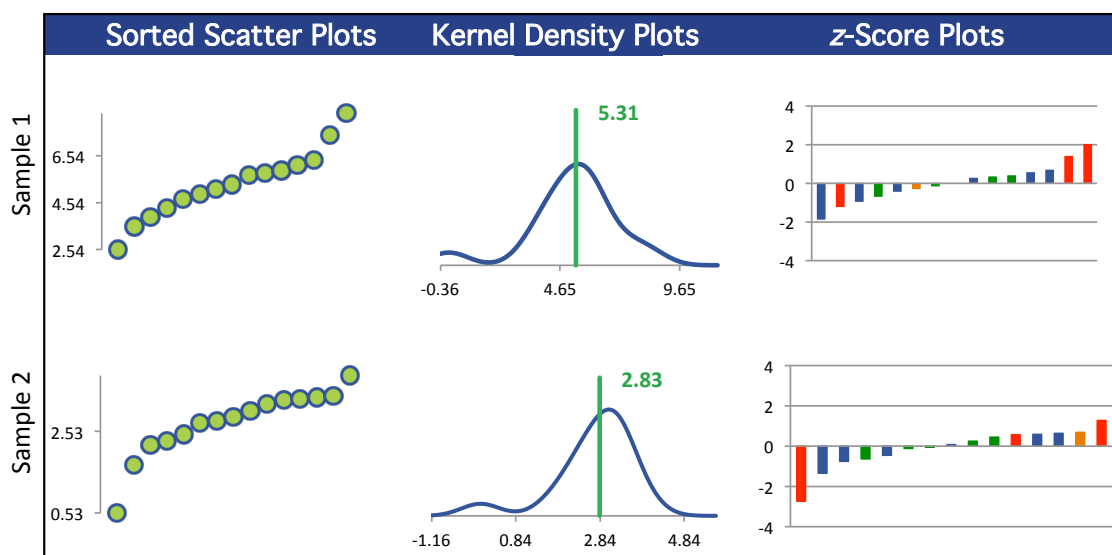
Summary Statistics

Statistic	C24-1	C24-2	C24-3	C24-4
N	15	15	15	15
Median $\mu\text{g/L}$	5.31	2.89	1.37	7.23
Robust Mean $\mu\text{g/L}$	5.31	2.83	1.42	6.92
U $\mu\text{g/L}$	0.471	0.229	0.128	0.455
Robust Standard Deviation $\mu\text{g/L}$	1.46	0.710	0.396	1.41
Regression Standard Deviation $\mu\text{g/L}$	1.50	0.844	0.474	1.92
Stability Flag				
Homogeneity Flag				
Standard Deviation Used (SDPA) $\mu\text{g/L}$	1.50	0.844	0.474	1.92
Outliers	0	0	0	0
$ z > 3.0$	0	0	0	0
$2 < z < 3$	1	1	2	0

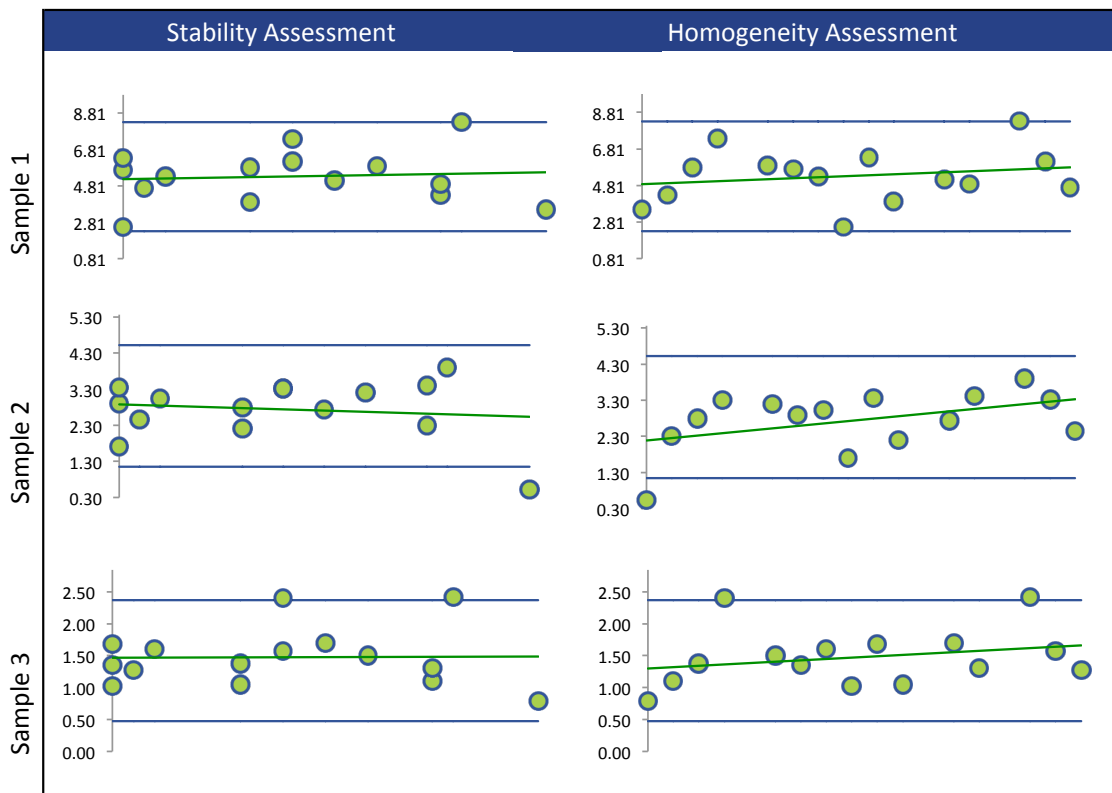
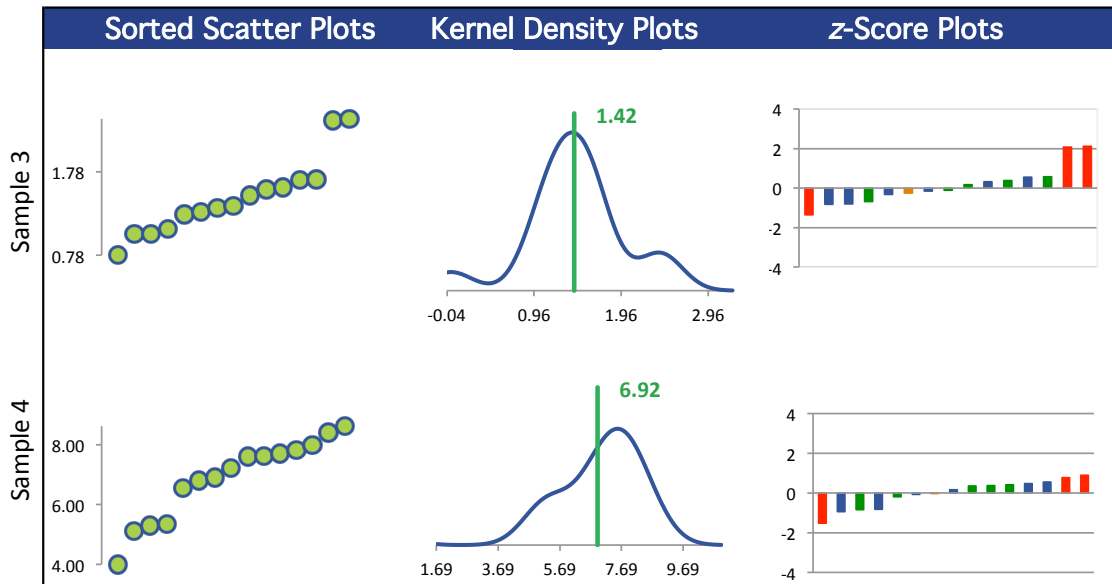
Methods Used

Method	C24-1	C24-2	C24-3	C24-4
LC-MS/MS (Blue)	6	6	6	6
GC/ECD (Red)	3	3	3	3
GC/MS (Green)	5	5	5	5
HPLC (Orange)	1	1	1	1

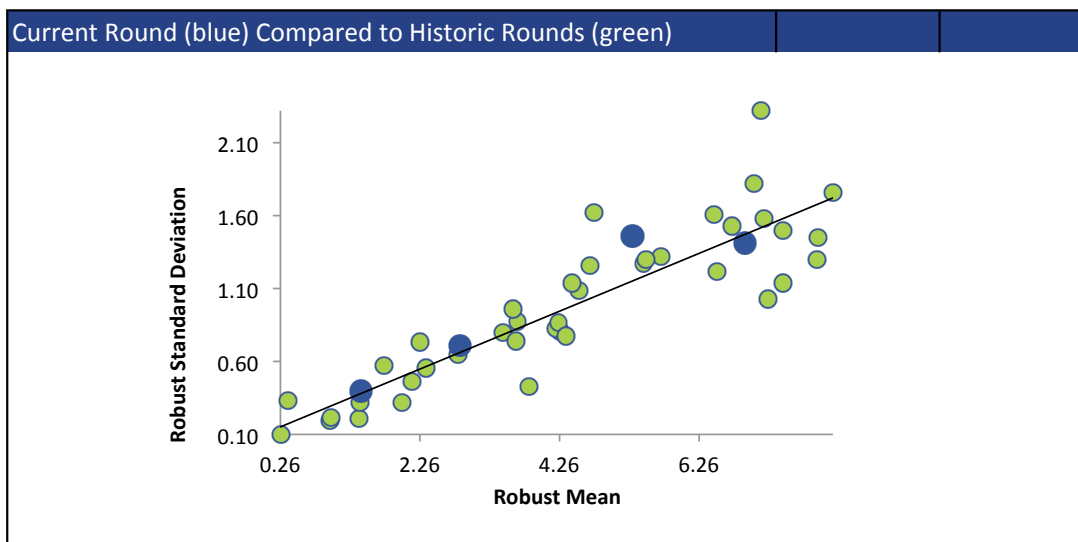
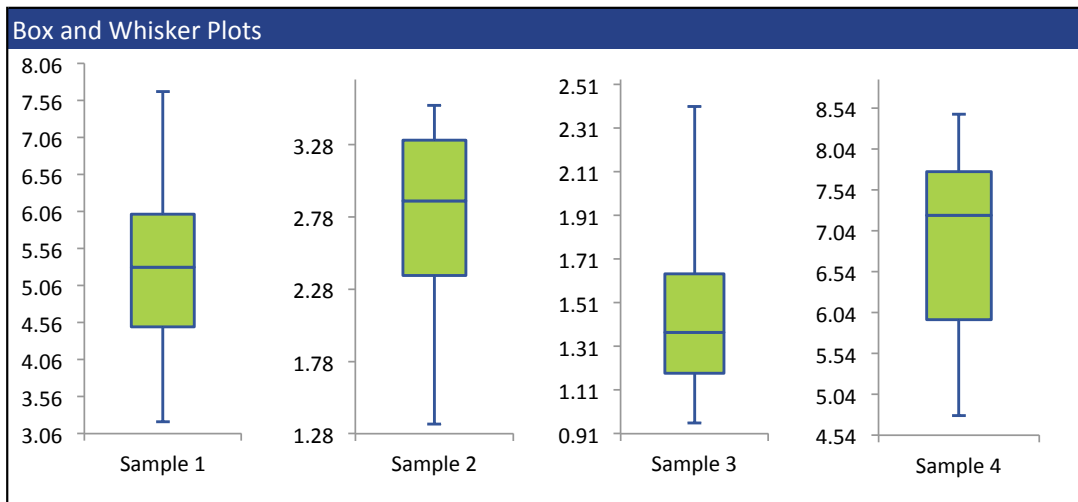
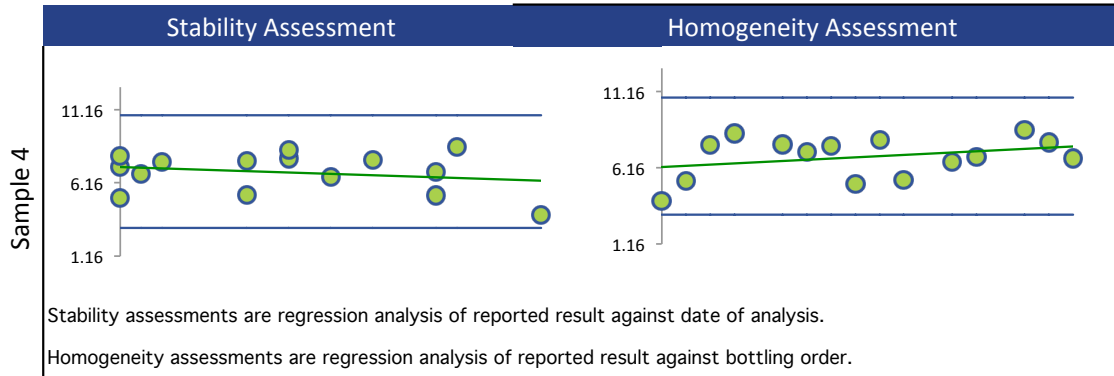
All summary stats and the plots below are based on the data excluding any flagged outliers



2,4-DICHLOROPHENOXYACETIC ACID



2,4-DICHLOROPHENOXYACETIC ACID



BROMOXYNIL

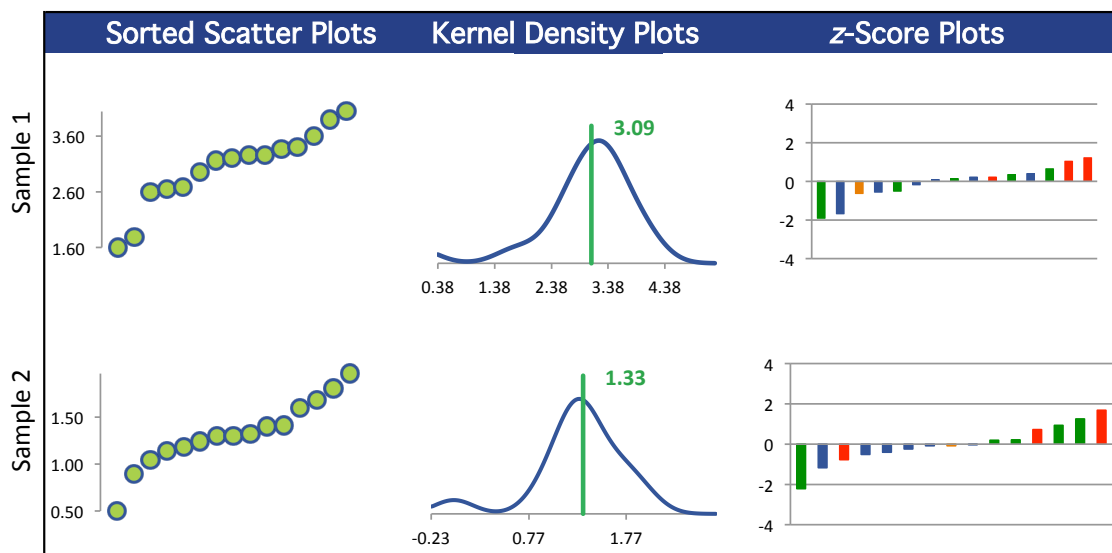
Summary Statistics

Statistic	C24-1	C24-2	C24-3	C24-4
N	15	15	15	14
Median $\mu\text{g/L}$	3.20	1.30	3.81	1.82
Robust Mean $\mu\text{g/L}$	3.09	1.33	3.79	1.89
U $\mu\text{g/L}$	0.209	0.112	0.260	0.127
Robust Standard Deviation $\mu\text{g/L}$	0.649	0.348	0.805	0.379
Regression Standard Deviation $\mu\text{g/L}$	0.780	0.376	0.943	0.505
Stability Flag				
Homogeneity Flag				
Standard Deviation Used (SDPA) $\mu\text{g/L}$	0.780	0.376	0.943	0.505
Outliers	0	0	0	0
$ z > 3.0$	0	0	0	0
$2 < z < 3$	0	1	0	1

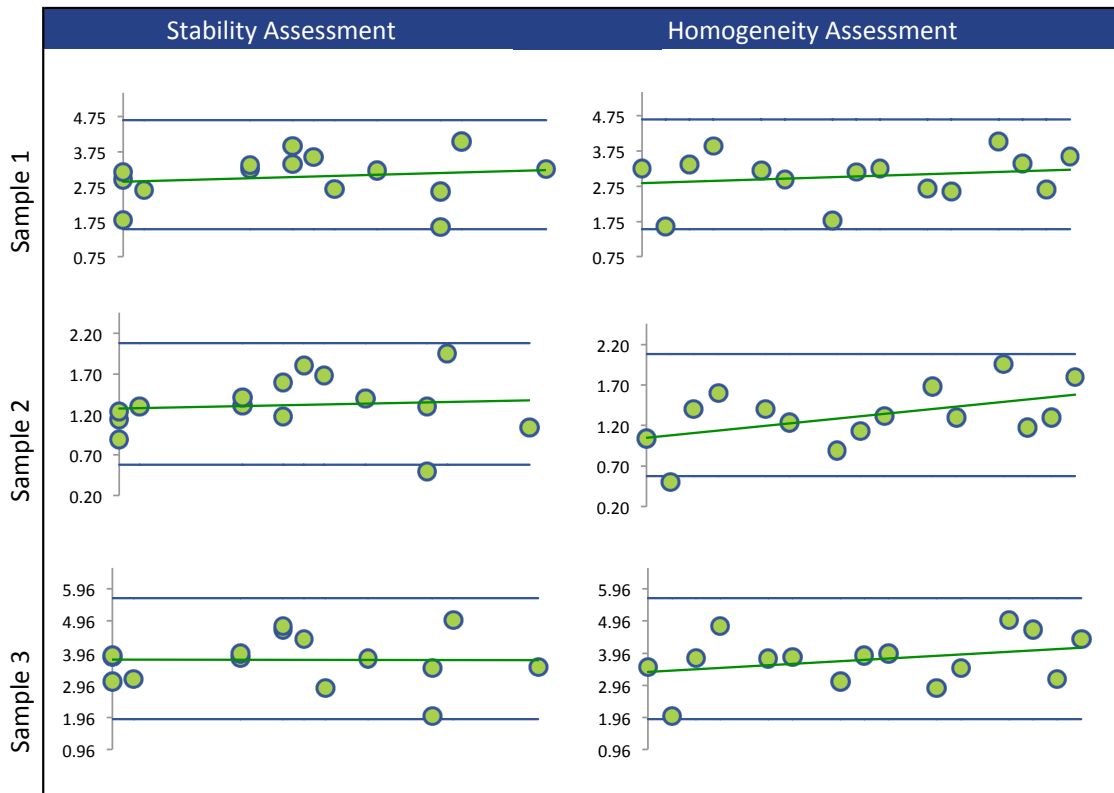
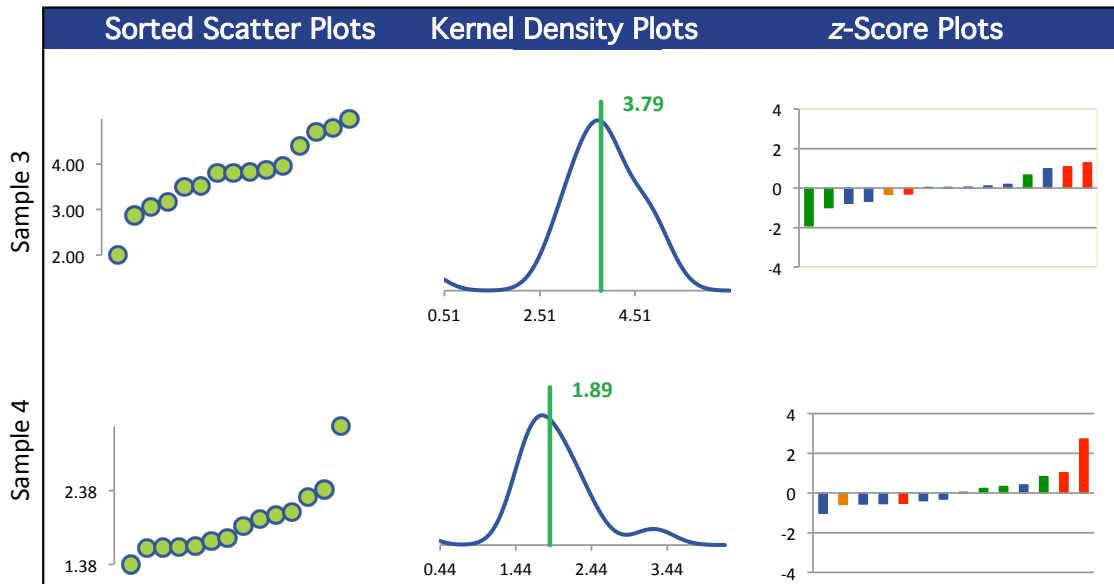
Methods Used

Method	C24-1	C24-2	C24-3	C24-4
GC/MS (Blue)	5	5	5	4
LC-MS/MS (Red)	6	6	6	6
HPLC (Green)	1	1	1	1
GC/ECD (Orange)	3	3	3	3

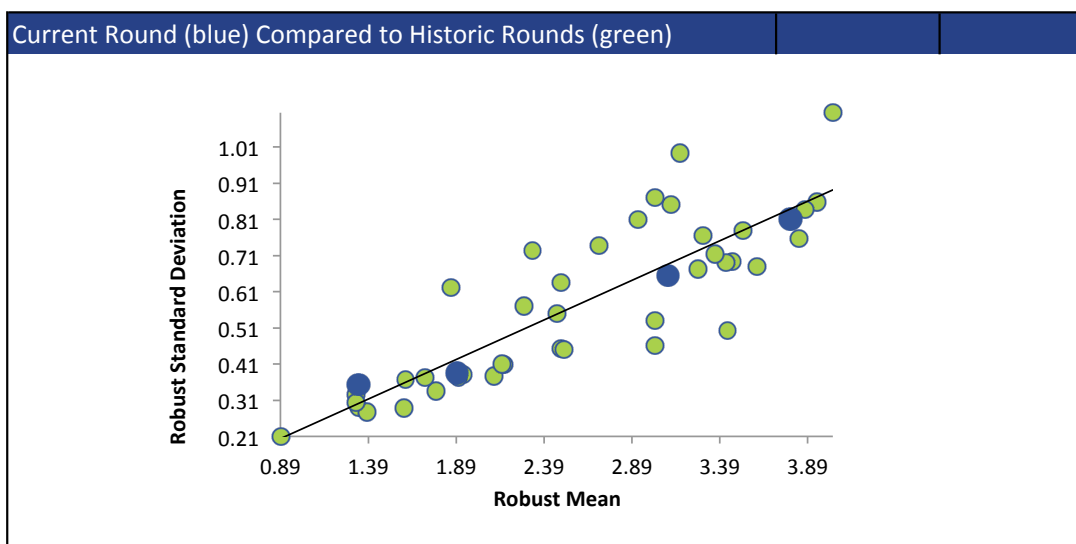
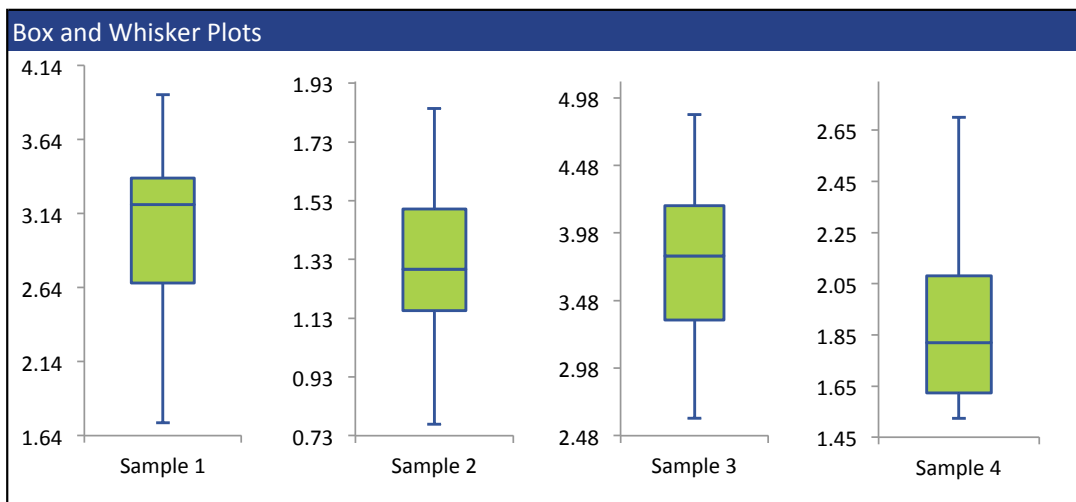
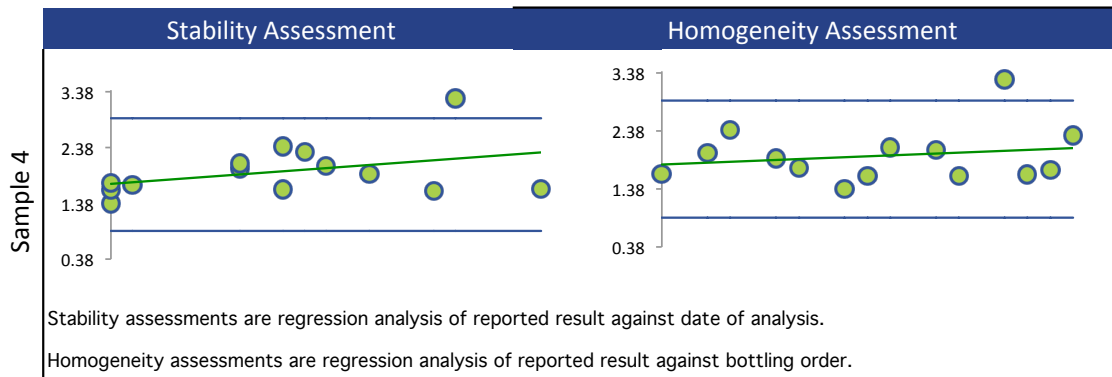
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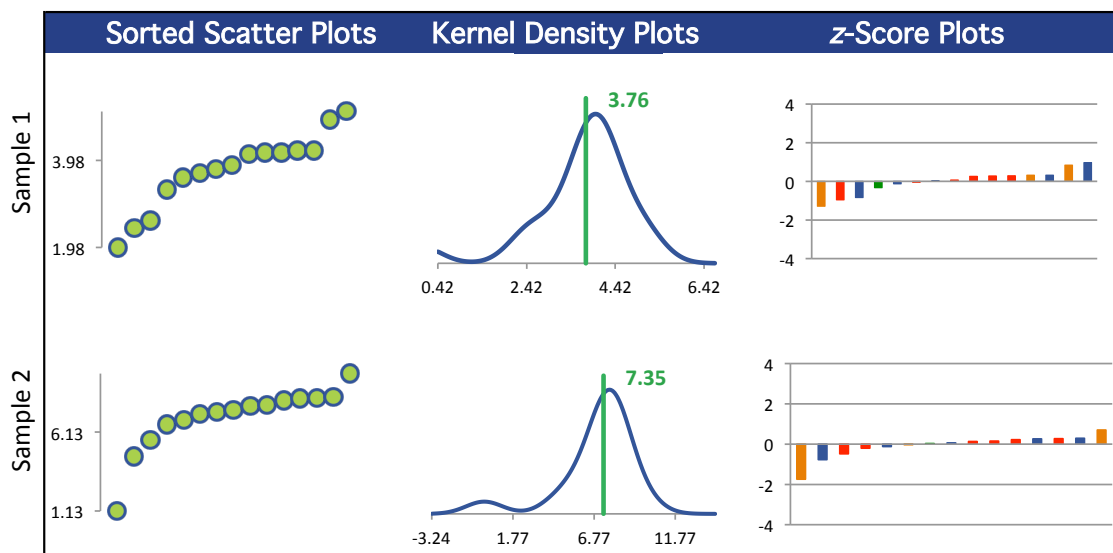
Summary Statistics

Statistic	C24-1	C24-2	C24-3	C24-4
N	15	15	15	15
Median $\mu\text{g/L}$	3.86	7.55	5.80	1.79
Robust Mean $\mu\text{g/L}$	3.76	7.35	5.57	1.73
U $\mu\text{g/L}$	0.297	0.439	0.368	0.118
Robust Standard Deviation $\mu\text{g/L}$	0.921	1.36	1.14	0.365
Regression Standard Deviation $\mu\text{g/L}$	1.10	2.14	1.63	0.512
Stability Flag				
Homogeneity Flag	Homogeneity	Homogeneity	Homogeneity	Homogeneity
Standard Deviation Used (SDPA) $\mu\text{g/L}$	1.38	3.58	3.02	0.790
Outliers	0	0	0	0
$ z > 3.0$	0	0	0	0
$2 < z < 3$	0	0	0	0

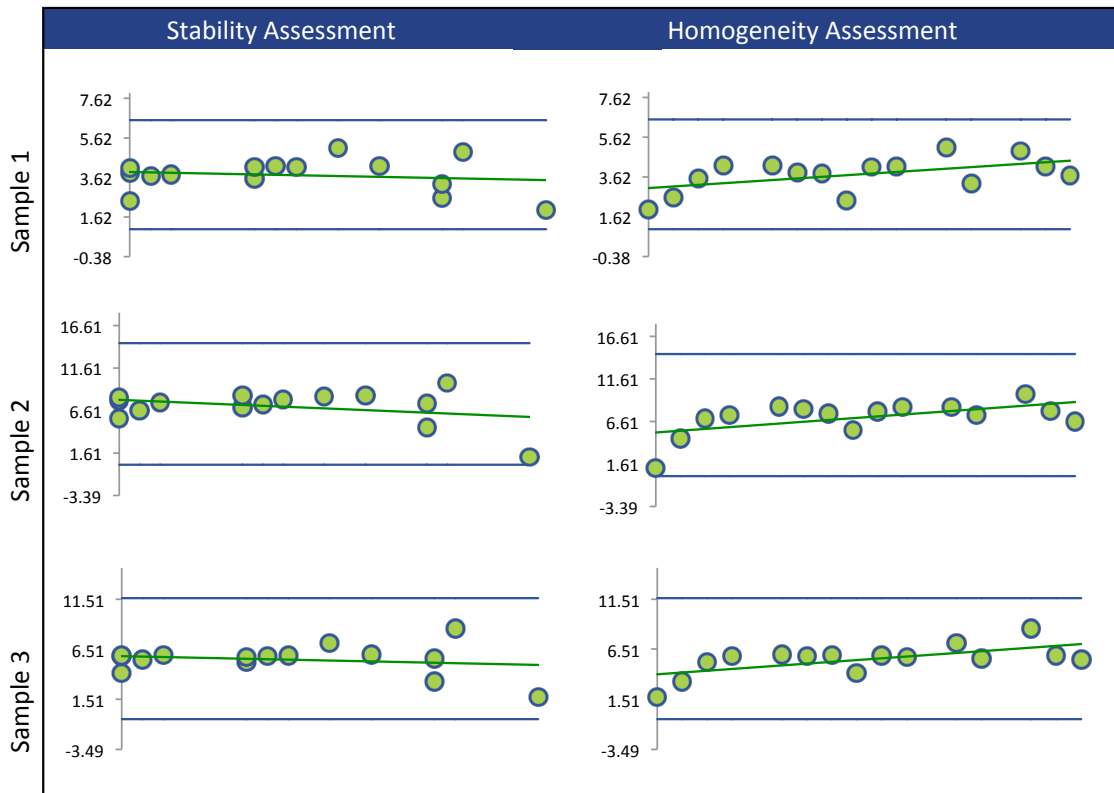
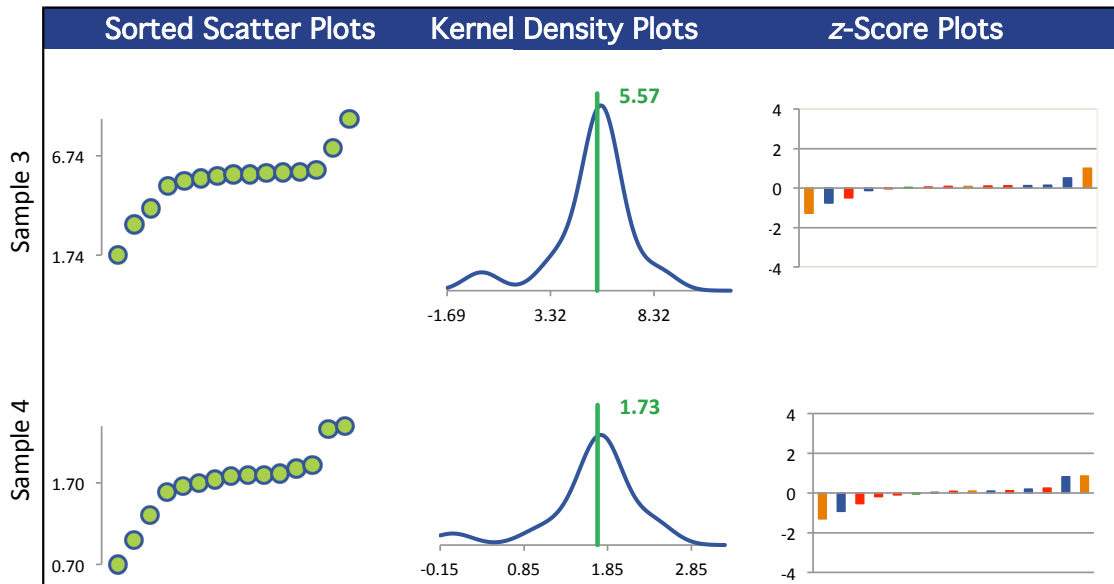
Methods Used

Method	C24-1	C24-2	C24-3	C24-4
GC/ECD (Blue)	3	3	3	3
LC-MS/MS (Red)	6	6	6	6
GC/MS (Green)	5	5	5	5
HPLC (Orange)	1	1	1	1

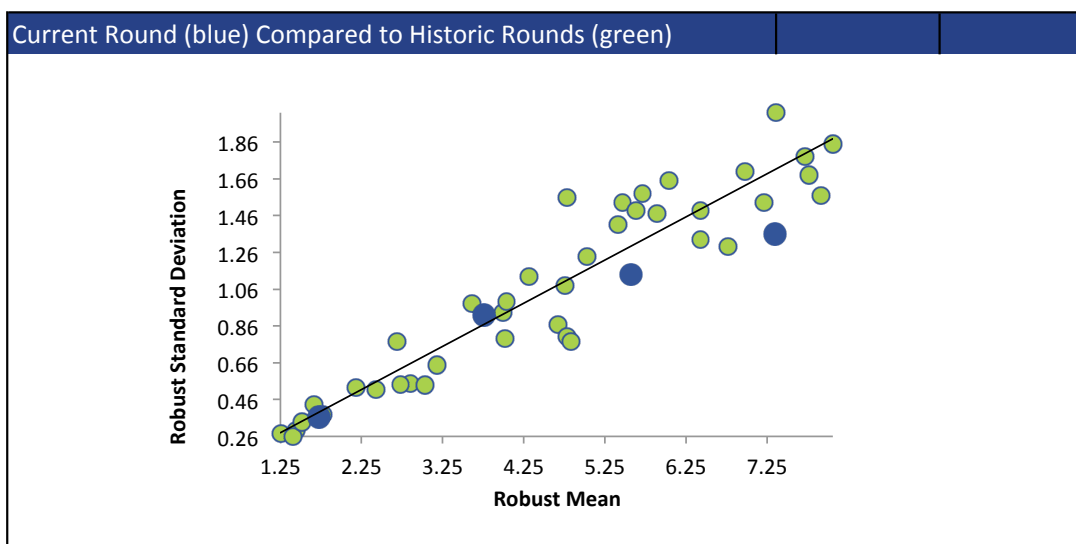
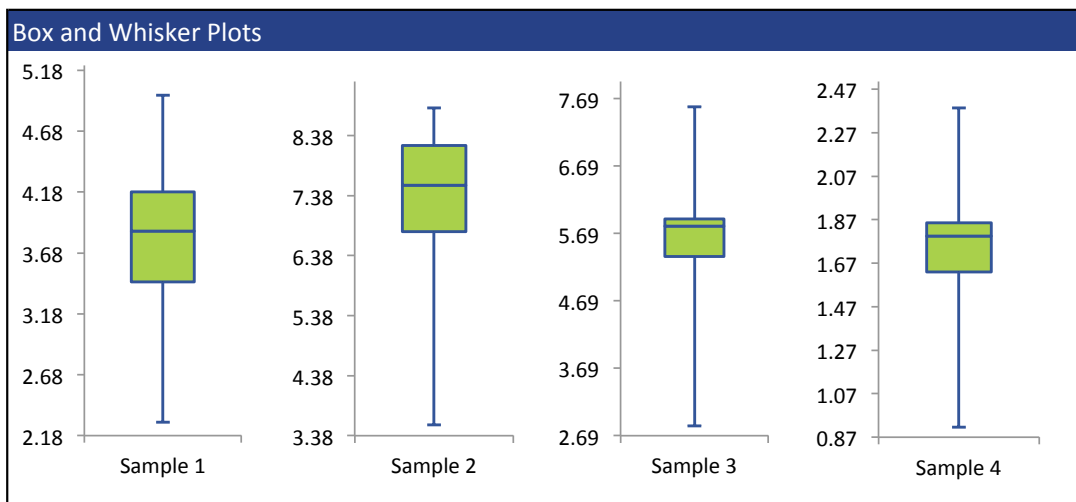
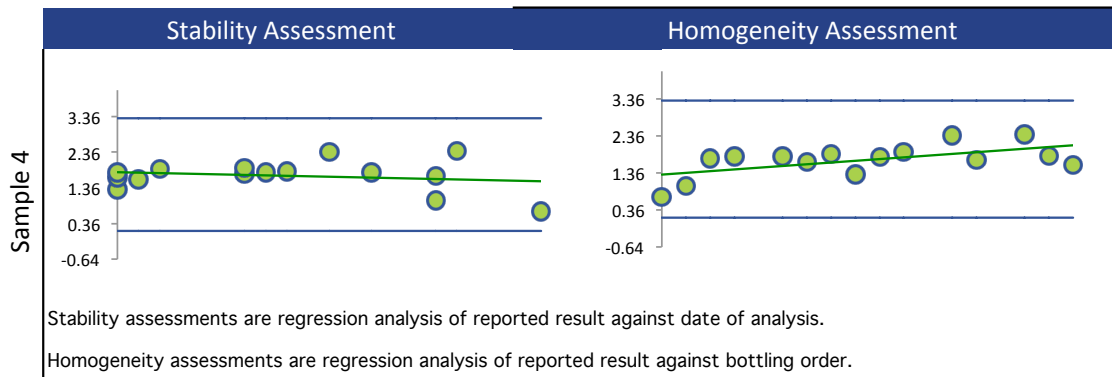
All summary stats and the plots below are based on the data excluding any flagged outliers



DICAMBA



DICAMBA



DICLOFOP-METHYL (AS FREE ACID)

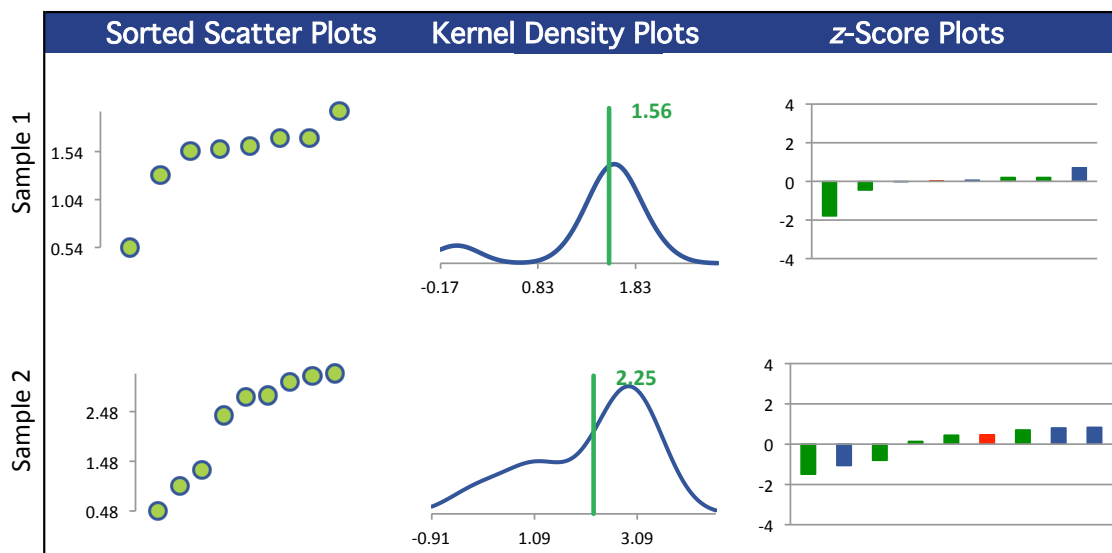
Summary Statistics

Statistic	C24-1	C24-2	C24-3	C24-4
N	8	9	9	8
Median $\mu\text{g/L}$	1.59	2.77	3.70	0.780
Robust Mean $\mu\text{g/L}$	1.56	2.25	3.32	0.765
U $\mu\text{g/L}$	0.126	0.496	0.663	0.100
Robust Standard Deviation $\mu\text{g/L}$	0.285	1.19	1.59	0.227
Regression Standard Deviation $\mu\text{g/L}$	0.566	0.817	1.20	0.278
Stability Flag				
Homogeneity Flag				
Standard Deviation Used (SDPA) $\mu\text{g/L}$	0.566	1.19	1.59	0.278
Outliers	0	0	0	0
$ z > 3.0$	0	0	0	0
$2 < z < 3$	0	0	0	0

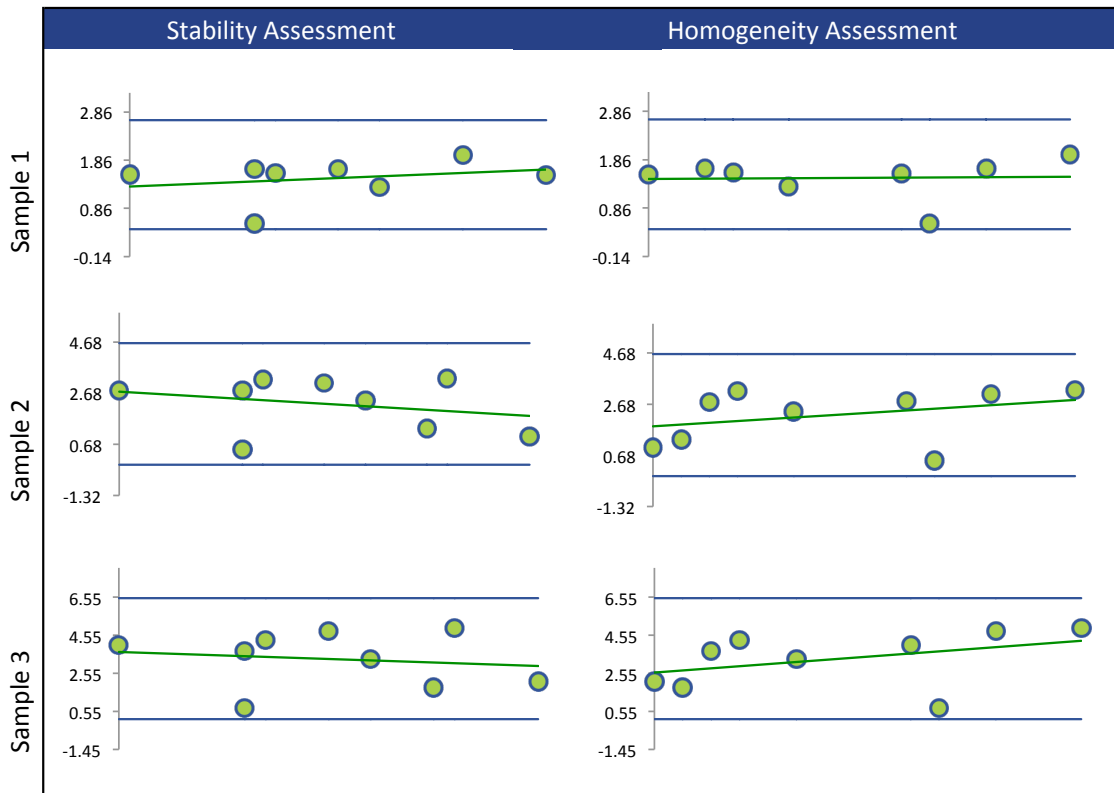
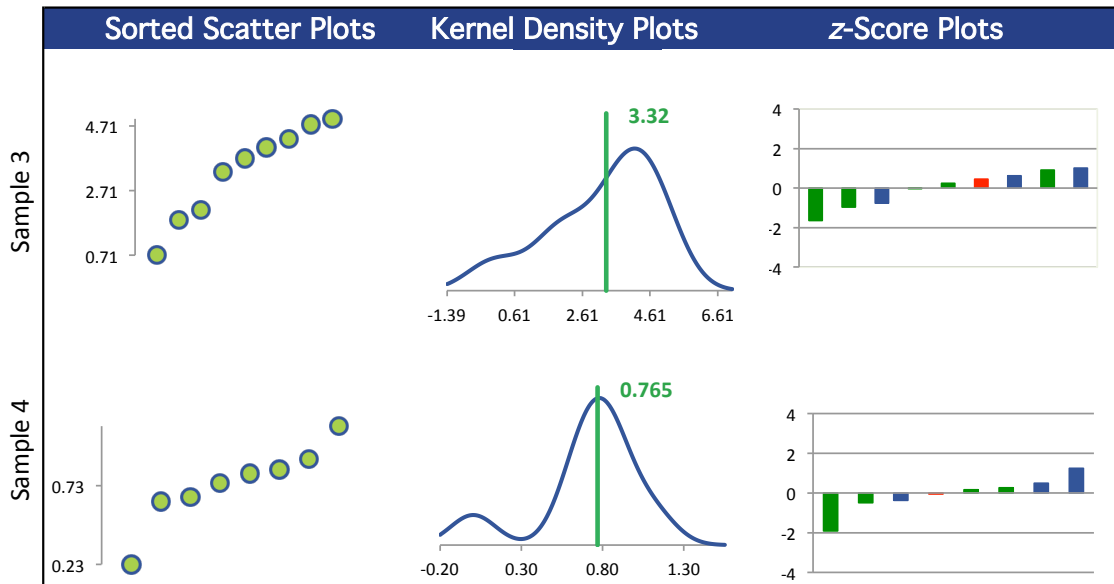
Methods Used

Method	C24-1	C24-2	C24-3	C24-4
GC/MS (Blue)	4	5	5	4
GC/ECD (Red)	3	3	3	3
LC-MS/MS (Green)	1	1	1	1

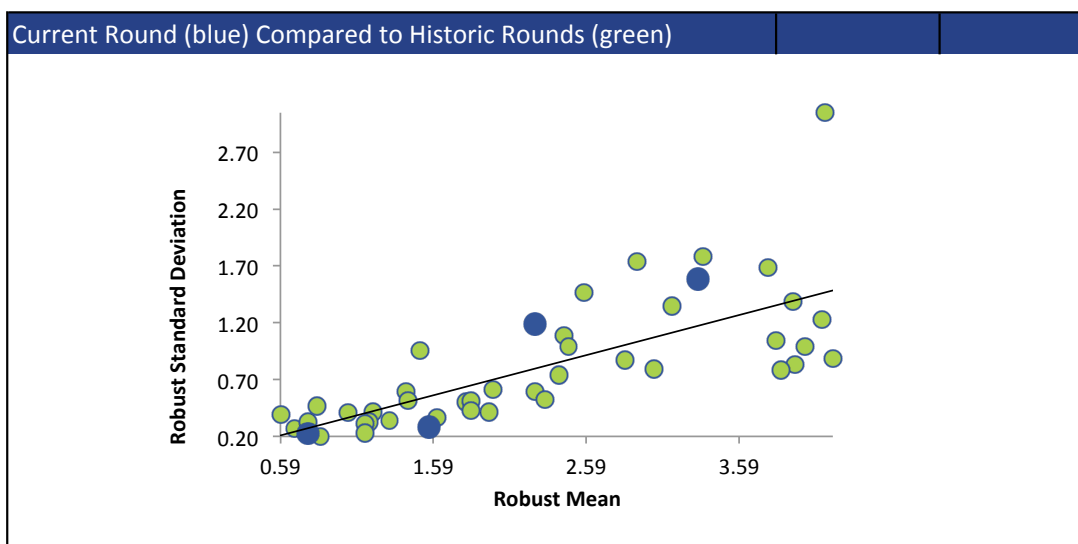
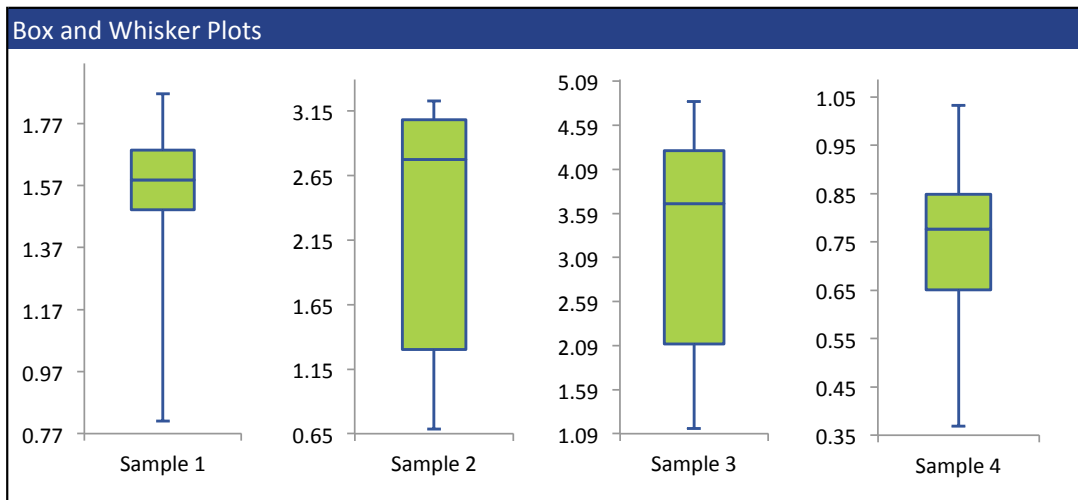
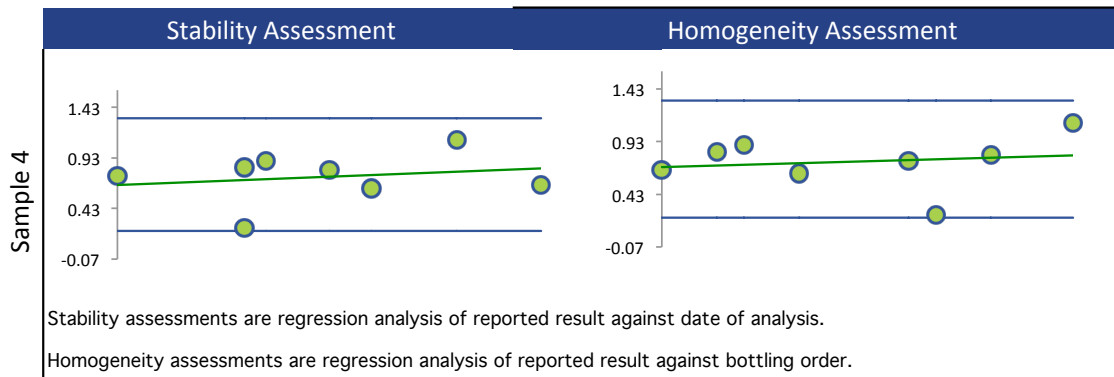
All summary stats and the plots below are based on the data excluding any flagged outliers



DICLOFOP-METHYL (AS FREE ACID)



DICLOFOP-METHYL (AS FREE ACID)



DINOSEB

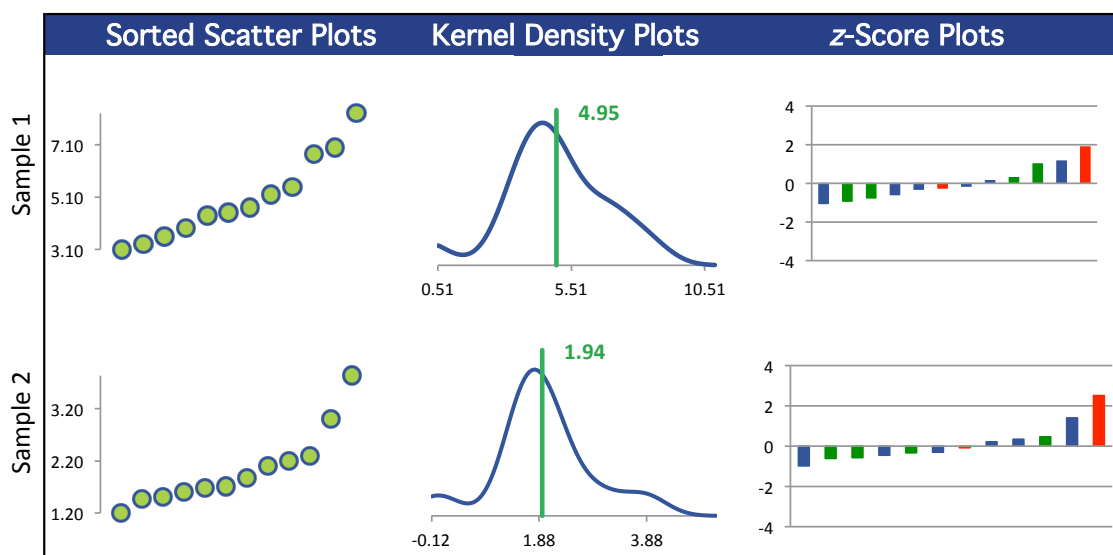
Summary Statistics

Statistic	C24-1	C24-2	C24-3	C24-4
N	12	12	12	12
Median $\mu\text{g/L}$	4.60	1.80	2.73	6.37
Robust Mean $\mu\text{g/L}$	4.95	1.94	2.87	6.84
U $\mu\text{g/L}$	0.599	0.212	0.302	0.678
Robust Standard Deviation $\mu\text{g/L}$	1.66	0.588	0.838	1.88
Regression Standard Deviation $\mu\text{g/L}$	1.77	0.756	1.07	2.42
Stability Flag				
Homogeneity Flag			Homogeneity	
Standard Deviation Used (SDPA) $\mu\text{g/L}$	1.77	0.756	1.54	2.42
Outliers	0	0	0	0
$ z > 3.0$	0	0	0	0
$2 < z < 3$	0	1	0	0

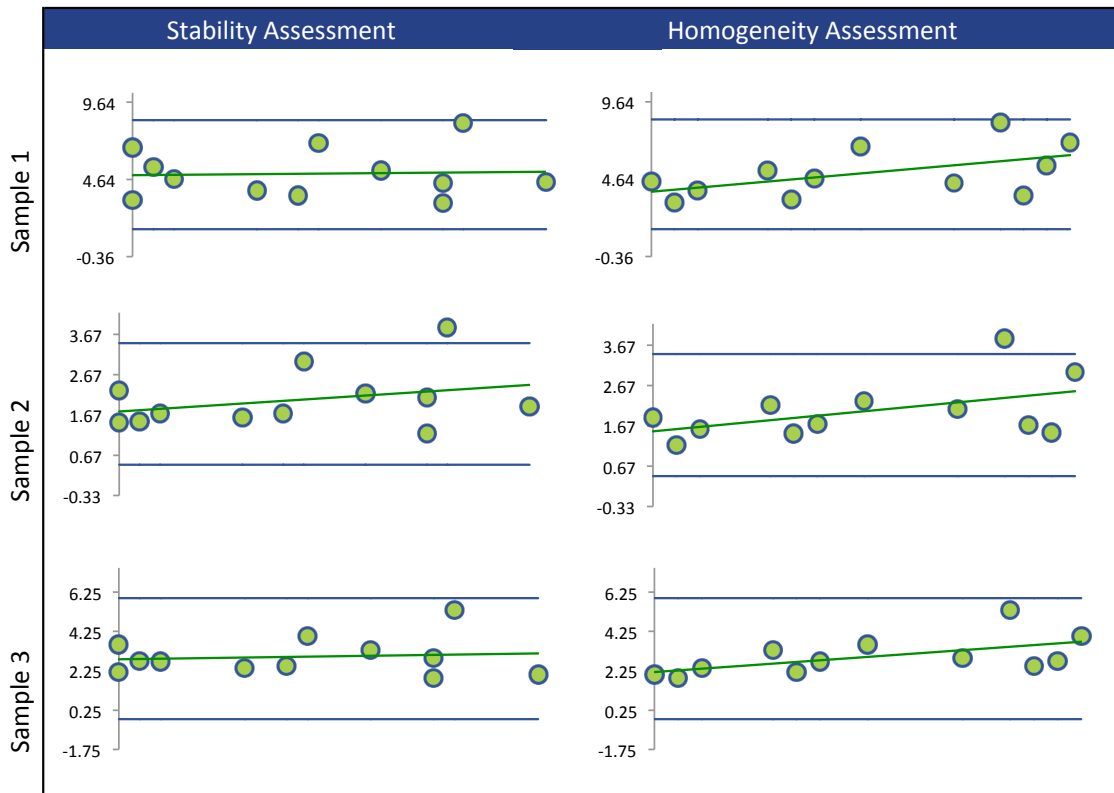
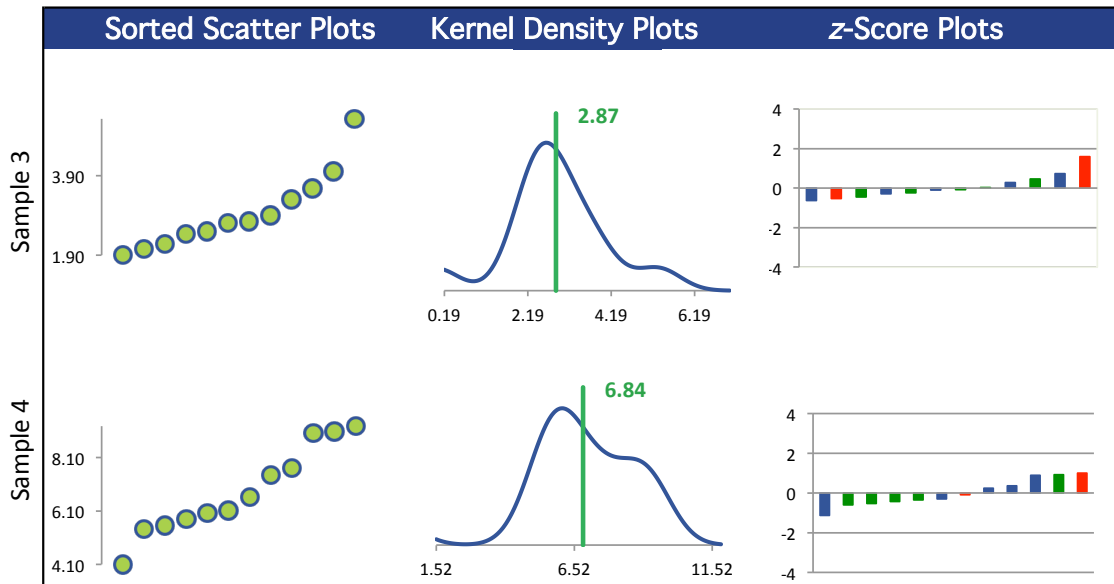
Methods Used

Method	C24-1	C24-2	C24-3	C24-4
GC/MS (Blue)	5	5	5	5
LC-MS/MS (Red)	4	4	4	4
HPLC (Green)	1	1	1	1
GC/ECD (Orange)	2	2	2	2

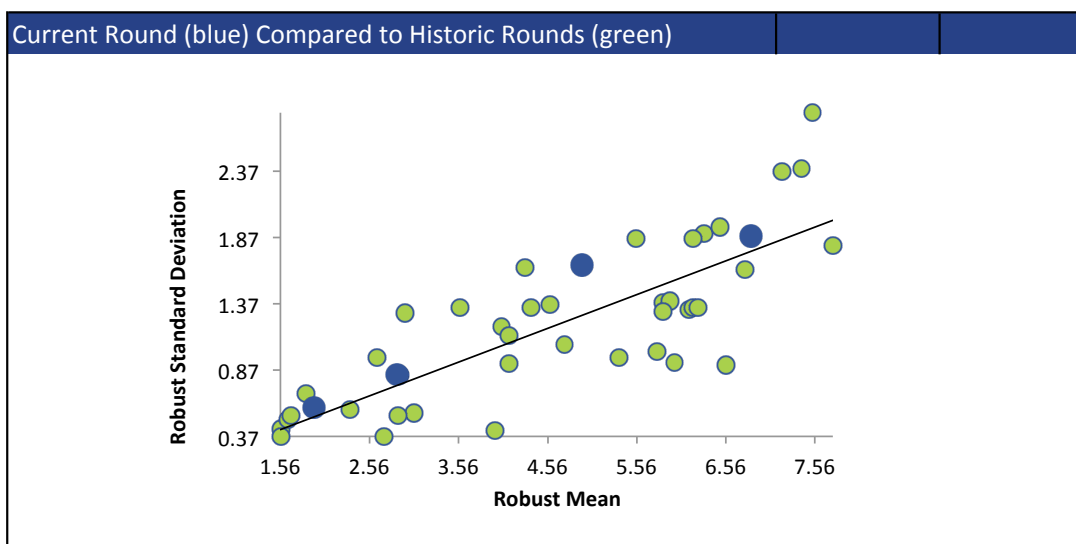
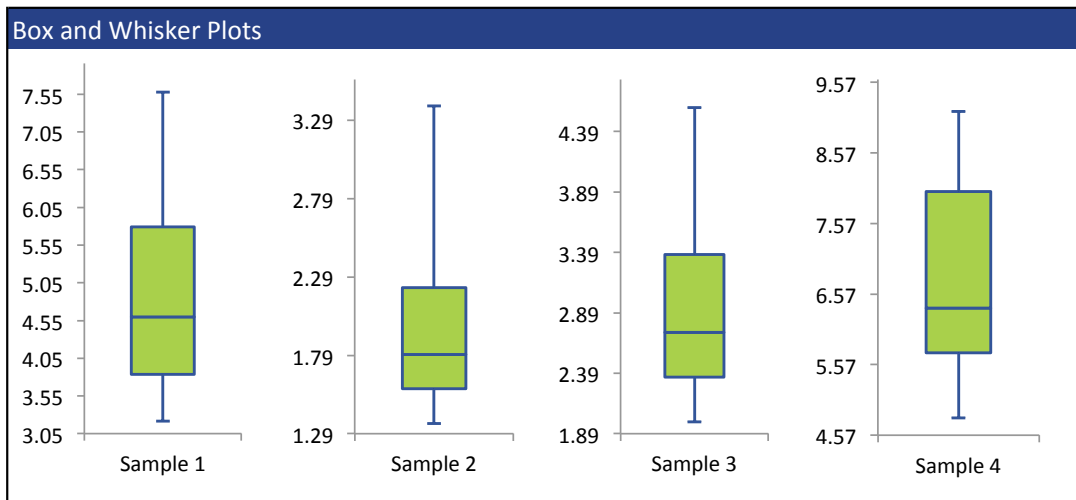
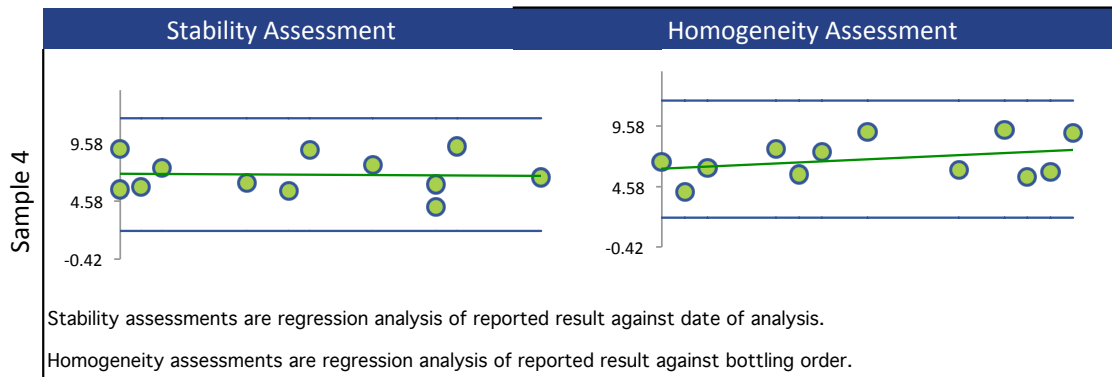
All summary stats and the plots below are based on the data excluding any flagged outliers



DINOSEB



DINOSEB



PICLORAM

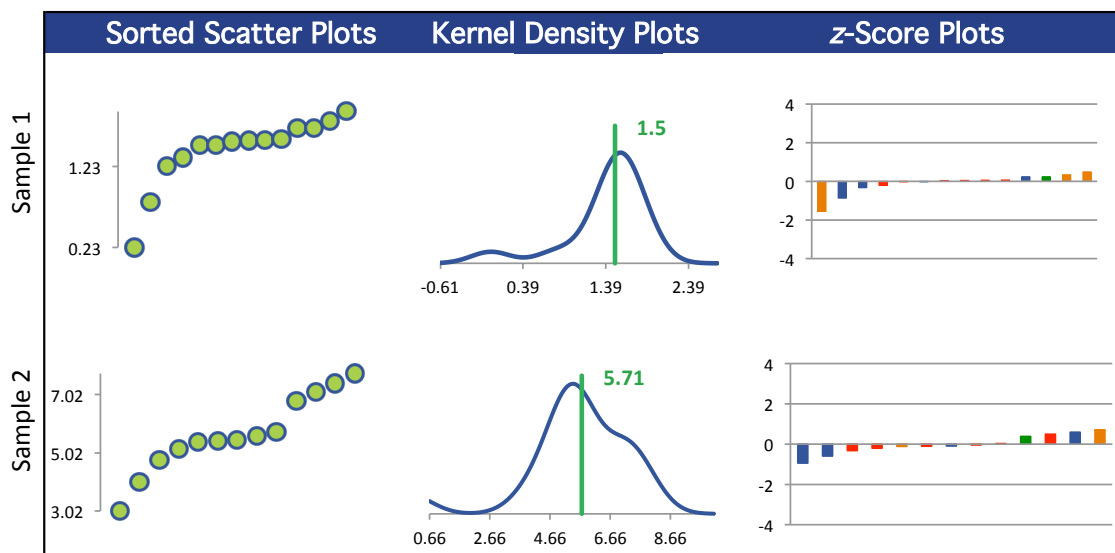
Summary Statistics

Statistic	C24-1	C24-2	C24-3	C24-4
N	14	13	15	14
Median $\mu\text{g/L}$	1.54	5.46	7.56	2.42
Robust Mean $\mu\text{g/L}$	1.50	5.71	7.11	2.37
U $\mu\text{g/L}$	0.0929	0.492	0.729	0.170
Robust Standard Deviation $\mu\text{g/L}$	0.278	1.42	2.26	0.508
Regression Standard Deviation $\mu\text{g/L}$	0.817	2.85	3.52	1.24
Stability Flag				
Homogeneity Flag				
Standard Deviation Used (SDPA) $\mu\text{g/L}$	0.817	2.85	3.52	1.24
Outliers	0	0	0	0
$ z > 3.0$	0	0	0	0
$2 < z < 3$	0	0	0	0

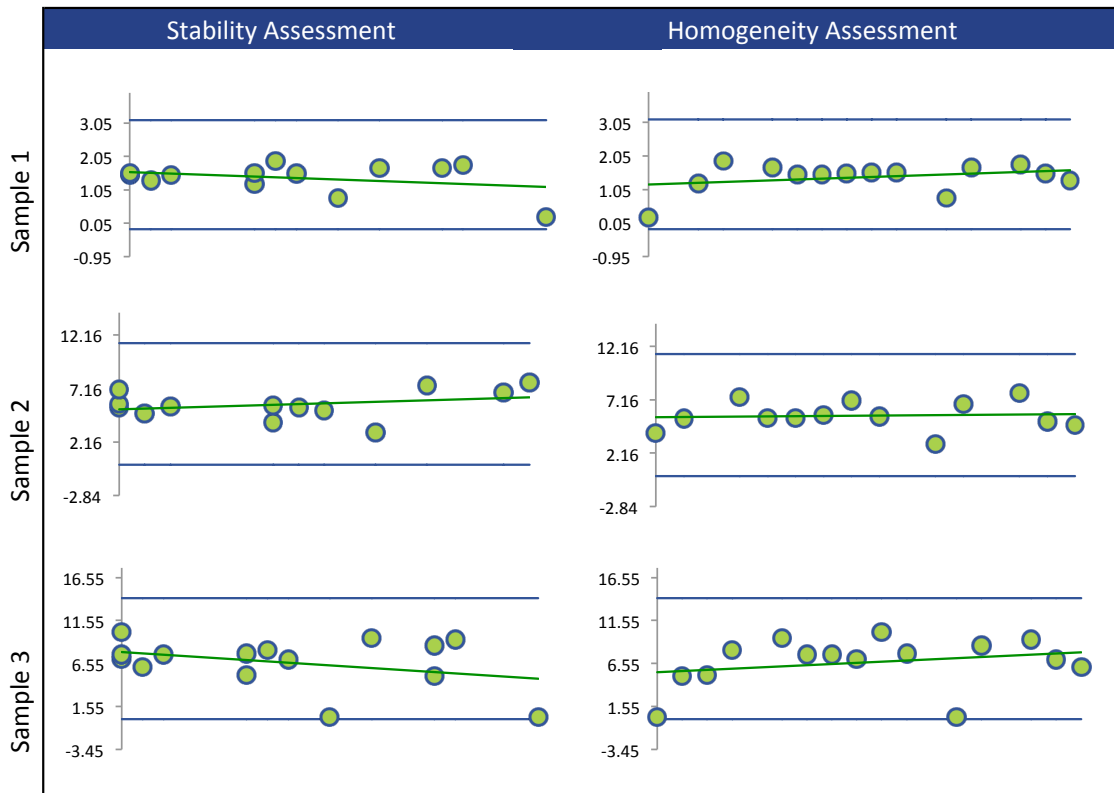
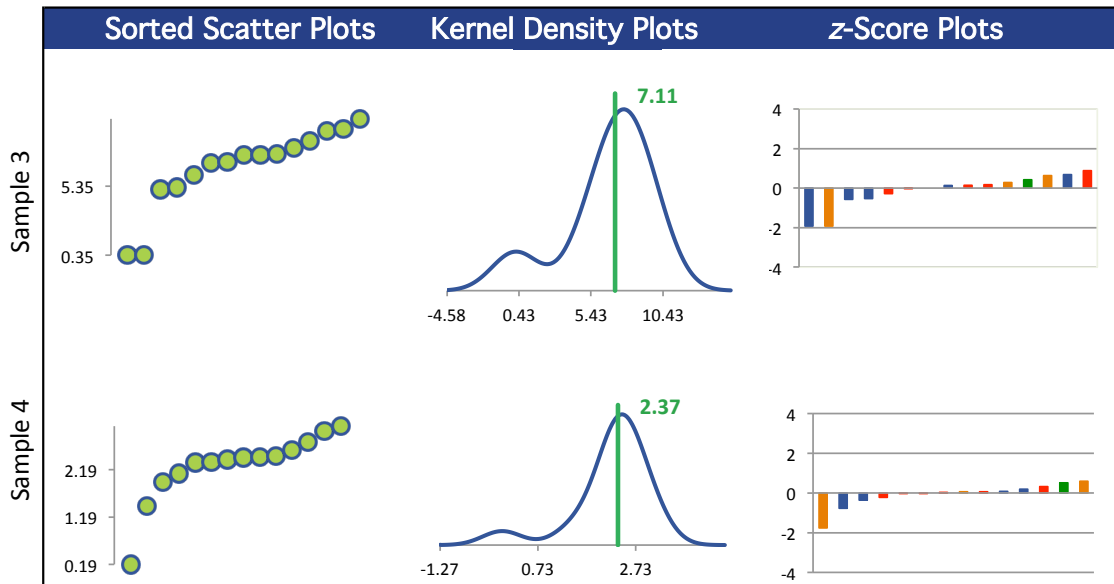
Methods Used

Method	C24-1	C24-2	C24-3	C24-4
GC/ECD (Blue)	3	2	3	3
GC/MS (Red)	4	4	5	4
LC-MS/MS (Green)	6	6	6	6
HPLC (Orange)	1	1	1	1

All summary stats and the plots below are based on the data excluding any flagged outliers



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