Memorandum

To: *Stephanie Vaughn, EPA Region 2*
Elizabeth Buckrucker, USACE

From: *Frank Tsang and Scott Kirchner*

Date: *March 3, 2014*

Subject: *2012 Low Resolution Supplemental Coring Split Sample Data Comparison for the Lower Passaic River Study Area*

At the request of the United State Environmental Protection Agency (EPA) and the United States Army Corps of Engineers (USACE), CDM Federal Programs Corporation (CDM Smith) collected oversight split sediment samples as part of the Lower Passaic River (LPR) Restoration Project remedial investigation conducted by the Cooperating Parties Group (CPG). This memorandum presents the comparison of the EPA oversight team's split sample results to the CPG's sample results and discusses the differences in the data pairs. In this document, samples are referred to as either CPG samples or EPA split samples for clarity.

The split sample comparison of the 2012 Low Resolution Supplemental Coring for the Lower Passaic River consisted of 24 sample pairs: 24 split samples were evaluated for dioxins/furans, pesticides, polychlorinated biphenyls (PCBs), and polycyclic aromatic hydrocarbons (PAHs); 18 split samples evaluated for total organic carbon (TOC) and metals; and 22 split samples were evaluated for mercury. All of the EPA and CPG split samples are comparable except the following:

- Dioxins/Furans: 2,3,7,8- tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD), octachlorodibenzofuran (OCDF), and total tetrachlorodibenzo-p-dioxin (total TCDD)
- Pesticides: 4,4'-dichlorodiphenyltrichloroethane (4,4'-DDT) and 2,4'-dichlorodiphenyltrichloroethane (2,4'-DDT)
- PCBs: 3,4,4',5-tetrachlorobiphenyl (PCB 81), 2,3,4,4',5-pentachlorobiphenyl (PCB 114), 2,3',4,4',5-pentachlorobiphenyl (PCB 118), 2',3,4,4',5-pentachlorobiphenyl (PCB 123), 3,3',4,4',5-pentachlorobiphenyl (PCB 126), 2,3,3',4,4',5-hexachlorobiphenyl (PCB 156) plus 2,3,3',4,4',5'-hexachlorobiphenyl (PCB 157), 2,3',4,4',5,5'-hexachlorobiphenyl (PCB 167), and 2,3,3',4,4',5,5'-heptachlorobiphenyl (PCB 189)
- PAHs: anthracene, fluoranthene, and pyrene

Oversight Program

Oversight was conducted in accordance with the Final Quality Assurance Project Plan (QAPP), Addendum No. 9, River Mile 10.9 Characterization for the Lower Passaic River Restoration Project. The split sample program consisted of 24 sediment split samples collected from the study area. Of these, 24 split samples were analyzed for dioxins/furans, pesticides, PCBs, and PAHs and 18 split samples were analyzed for TOC and metals, except mercury where 22 split samples were analyzed. These split samples pairs were compared for each of the analytical methods analyzed.

Data Comparison Methodology

The CPG and EPA split sample data were evaluated for potential differences by plotting selected analytes (Table 1) for the following parameters. For each of the following three plots, data are plotted and evaluated only for the cases where both sample pairs are detected.

- Line Plot: The concentrations measured by both analytical programs for the detected paired samples were plotted against the same axes. The graph depicts the relative magnitudes and patterns of concentrations.
- Bivariate Scatter Plot: CPG sample concentration was plotted as a function of EPA sample concentration for each detected pair. The bivariate scatter plot illustrates the relationship between EPA and CPG data. Also included on the graph is a line which depicts a 1:1 ratio of concentration of EPA and CPG sample. The bivariate plot can be used to identify potential systematic bias when data points fall consistently above or below the 1:1 line.
- Percent Difference Plot: The percent difference (%D) was defined as the difference between concentration for detected data pairs, divided by the concentration of EPA sample (Equation 1).

$$\% D = \frac{(R_{EPA} - R_{CPG})}{(R_{EPA})}(100) \qquad \text{(Equation 1)}$$

  Consequently, a negative %D indicates a CPG result that is higher than the EPA result, while a positive %D indicates a CPG result that is lower than the EPA result. This plot provides a visual indication of the extent of positive and negative differences between the two data pairs. The red dashed lines on the plot correspond to the criteria of 40%D and -67%D. These criteria correspond to 50% relative percent difference (RPD) (the CPG's field duplicate acceptance criterion), converted to %D values. The term of %D is commonly used when one of the two values is known or accepted, whereas RPD is more commonly used when both values are uncertain. The sample data in this graph was represented with the EPA result as the known value and the CPG result as the unknown value.

In addition to the preparation of data comparison plots, the tests described below were also conducted for CPG and EPA data pairs where both results were detected.

- Average Ratio: The ratios of the CPG results to EPA results were calculated for each sample pair. The average ratio and standard deviation were calculated. An average ratio above one indicates that

the CPG results were detected higher than the EPA results, while an average ratio below one indicates that the CPG results were detected lower than the EPA results.

- Percent Difference: The calculated %D values were evaluated against the acceptance criteria of greater than or equal to -67%, or less than or equal to 40% (equivalent to less than or equal to 50% RPD).
- Statistical Test: The statistical tests were performed to calculate *p*-values. The *p*-value is an indicator of the presence of a difference between the data pairs. A *p*-value of less than 0.05 indicates a statistically significant difference between the two data sets.
  - Wilcoxon Signed Rank Test: The Wilcoxon Signed Rank test was used to calculate *p*-values for all detected sample pairs.
  - Paired Prentice-Wilcoxon (PPW) Test: In addition to the standard paired Wilcoxon test conducted on the detected data pairs, a modified version of the test, the PPW test, was also conducted to allow inclusion of the left-censored (nondetected) data pairs. The elimination of data pairs containing nondetected values is essentially equivalent to ignoring potentially substantial information contained within these nondetect-containing data pairs, and may lead to biased results. The PPW test relies on survival analysis computations as detailed in O'Brien and Fleming (1987) and is considered the standard test for the case of censored matched pairs (Helsel 2005).

The data comparison plots are depicted in Figures 1 through 47. Results for the three comparison criteria (average ratio, %D, and statistical test) are presented in Table 1. The numbers of split sample pairs are listed for each compound/group along with the number of pairs which had detected results for both samples. The average ratio of results of CPG sample to those of EPA sample results are reported with the standard deviation of the ratios. The %D results are summarized by reporting the percentage of data pairs that exceeded the acceptance criteria (40% and -67%). Also included are the *p*-values calculated by the Wilcoxon Signed Rank test and the PPW test.

An overall evaluation of the split sample data is based on the result of the three comparison criteria, where each compound has a rating of "Same" or "Different". The data pairs are considered comparable or "Same" if at least two of the three criteria are met. The comparison criteria for each compound are listed below.

- Average Ratio: Average ratio of CPG to EPA results within 0.70 to 1.30.
- Percent Difference: Less than 16% of the data pairs exceed the acceptance criteria of 40 to -67%.
- Statistical Test (Wilcoxon Signed Rank Test and PPW Test): *p*-values greater than or equal to 0.05 are within acceptance limits, indicating there is no significant statistical difference between the data sets.

Results of data comparison of CPG and EPA split samples are summarized below and presented in Table 1 and Figures 1 through 47.

Dioxins/Furans

There were seven dioxin/furan compounds evaluated for the three comparison criteria. The data pairs for three compounds, 2,3,7,8-TCDD, OCDF, and total TCDD, were not comparable (Table 1). From examination of individual sample pairs, the calculated high average ratios were influenced by several high detections which differed greatly between these two data pairs. The majority of detections were within %D criteria as shown in Figures 1 through 7.

Pesticides

The data pairs for all pesticide compounds were comparable, except 2,4'-DDT and 4,4'-DDT. Figures 8 through 15 show the data comparison plots for eight of the pesticide compounds evaluated. More than 16% of the sample pairs exceeded the acceptance criteria between -67% and 40% for both 4,4'-DDT and 2,4'-DDT (Table 1).

Polychlorinated Biphenyls

Eight of the eleven compounds evaluated by the three comparison criteria were found to be different in data pairs (Table1). They are PCB 81, PCB 114, PCB 118, PCB 123, PCB 126, PCB 156 plus PCB 157, PCB 167, and PCB 189. The bivariate plots in Figures 16 through 26 show the predominant high bias of CPG results relative to EPA results. The total PCB results were found to be comparable in contrast to the trend for the individual congeners. The difference in PCB congener results between CPG and EPA data pairs was consistent and could not be attributed to the influence of outliers.

Polycyclic Aromatic Hydrocarbons

There were nine PAH compounds evaluated for the three comparison criteria. The data pairs of six compounds are comparable (Table 1). The three PAHs considered "different" are anthracene, fluoranthene, and pyrene. Figures 27 to 35 show a trend of a low bias of CPG results relative to EPA results.

Total Organic Carbon

The results for TOC were comparable for the two data pairs. The CPG data are usually higher than the EPA data, but all %Ds were within the acceptance criteria (Figure 36). The statistical tests indicated that the data was statistically different, but all other comparison criteria indicated that the data pairs were comparable.

Metals

Split sample data was evaluated for eleven metals, and the results were found to be comparable. The majority of detections were within %D criteria as shown in Figures 37 through 47, except two arsenic, one lead, and two mercury results.

Attachments

Table 1 - 2012 Low Resolution Supplemental Coring Split Sample Data Comparison Summary

Figures 1 through 47: Statistical Plots

a. Line Plots
b. Bivariate Scatter Plots
c. Percent Differences Plots

- Figures 1 through 7: Plots of Dioxin/Furan Concentration
- Figures 8 through 15: Plots of Pesticide Concentration
- Figures 16 through 26: Plots of Polychlorinated Biphenyl Concentration
- Figures 27 through 35: Plots of Polycyclic Aromatic Hydrocarbon Concentration
- Figure 36: Plot of Total Organic Carbon Concentration
- Figures 37 through 47: Plots of Metal Concentration

References

Helsel, D.R. 2005. Nondetects and Data Analysis: Statistics for Censored Environmental Data. Wiley-Interscience.

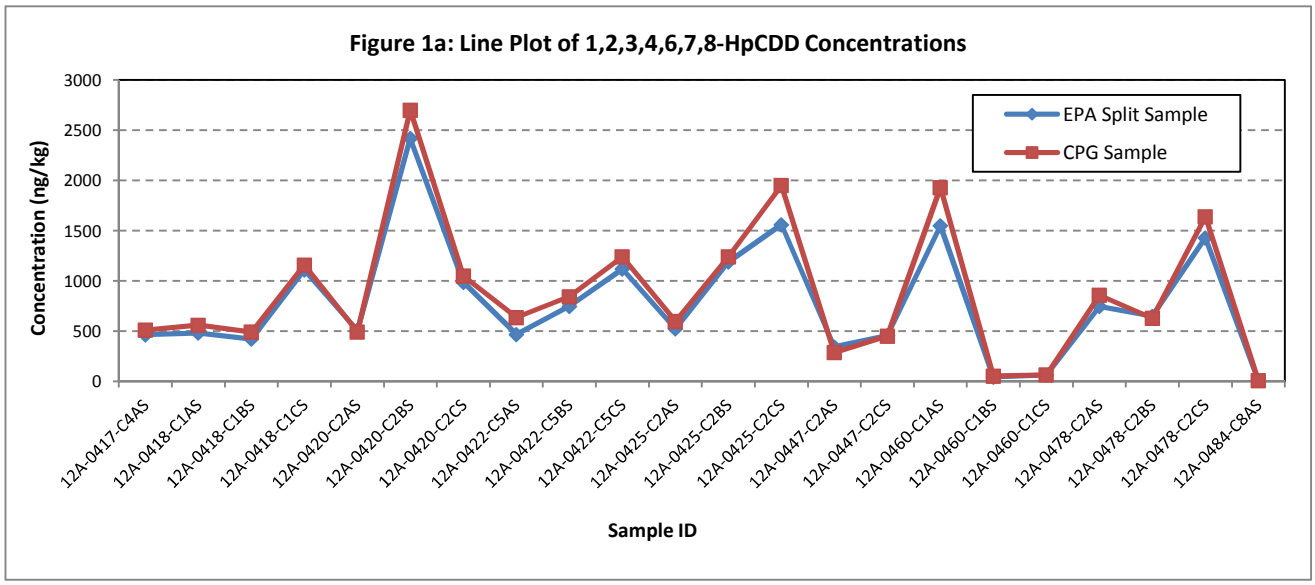
O'Brien, P.C. and T.R. Fleming. 1987. A Paired Prentice-Wilcoxon Test for Censored Paired Data. Biometrics 43: 169-180.

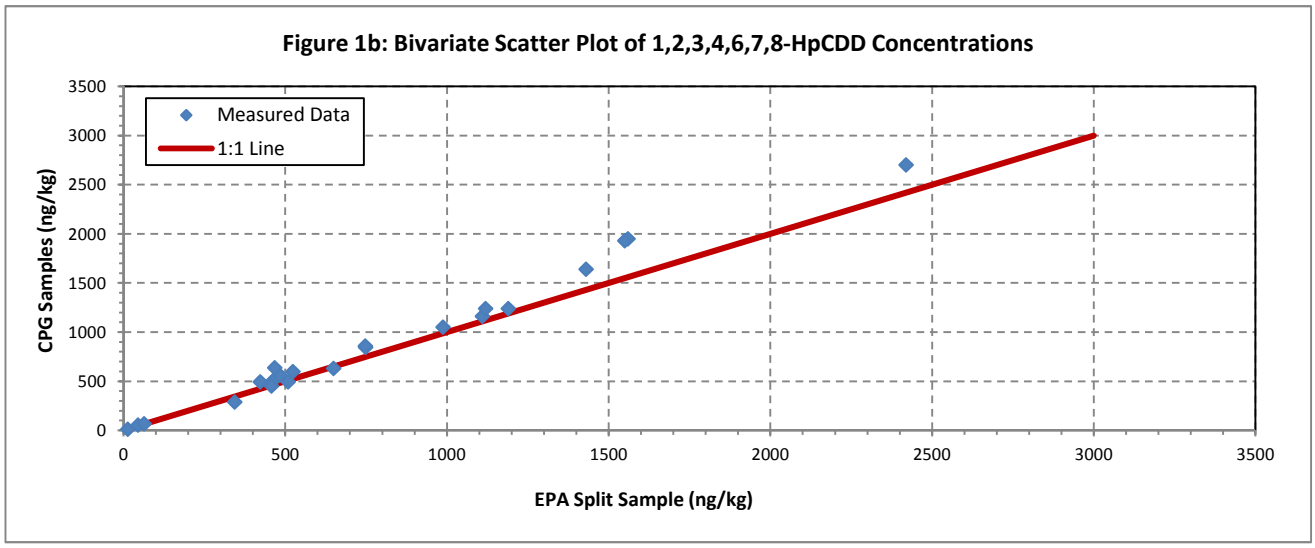
Table 1
2012 Low Resolution Supplemental Coring Split Sample Data Comparison Summary
Lower Passaic River Study Area

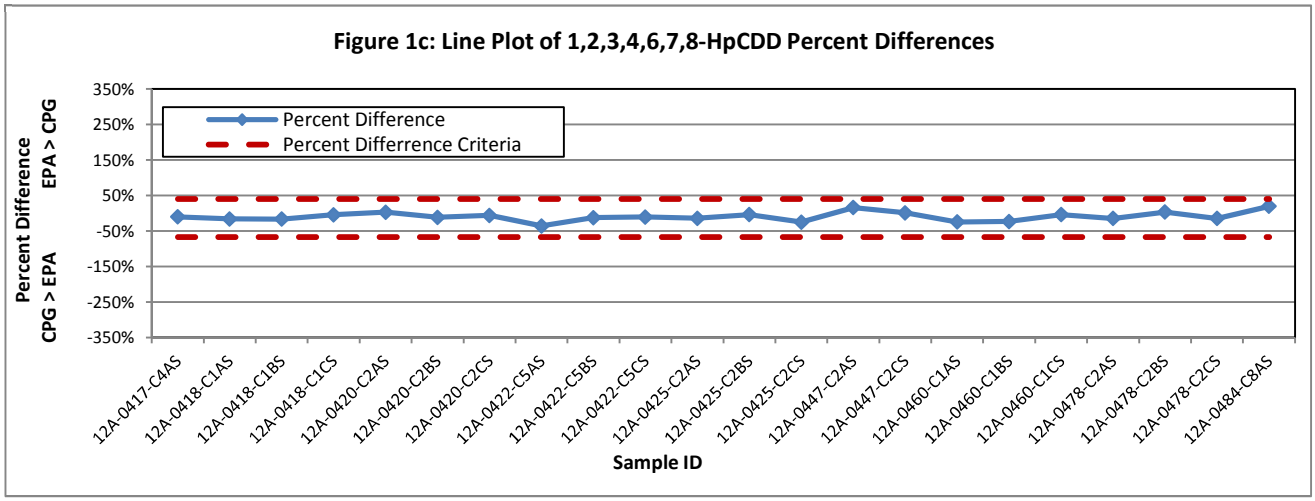
Parameter	Number of Split Sample Pairs	Number of Detected Pairs [1]	Comparison Criteria: Average Ratio of CPG to EPA for Detected Pairs [2]	Comparison Criteria: Percent Difference for Detected Pairs [3] (% outside criteria)	Statistical Test [4]: p-value [5]: Wilcoxon Signed Rank Test for Detected Pairs	Statistical Test [4]: p-value [5]: Paired Prentice-Wilcoxon Test	Statistical Test [4]: Statistical Difference (Yes or No)	Overall Split Sample Comparison (Same or Different) [6]
Dioxins/Furans								
1,2,3,4,6,7,8-HpCDD	24	22	1.09 ± 0.13	0%	**0.001**	**0.004**	**Yes**	Same
1,2,3,4,6,7,8-HpCDF	24	22	1.01 ± 0.3	9%	0.277	0.79	No	Same
2,3,7,8-TCDD	24	23	**1.82 ± 2.98** [7]	**35%**	0.627	0.95	No	**Different**
2,3,7,8-TCDF	24	21	1.05 ± 0.24	5%	0.366	0.925	No	Same
OCDD	24	22	1.02 ± 0.13	0%	0.2	0.135	No	Same
OCDF	24	23	**4.94 ± 19.04** [7]	**17%**	0.205	0.48	No	**Different**
Total TCDD	24	23	**1.71 ± 2.57** [7]	**26%**	0.693	0.706	No	**Different**
Pesticides								
4,4'-DDD	24	21	0.89 ± 0.4	**19%**	0.122	0.391	No	Same
4,4'-DDE	24	21	0.93 ± 0.25	10%	0.149	0.433	No	Same
4,4'-DDT	24	20	1.04 ± 1.46	**60%**	0.151	**0.042**	**Yes**	**Different**
Dieldrin	24	20	0.92 ± 0.26	10%	**0.029**	0.118	**Yes**	Same
beta-Chlordane	24	21	0.92 ± 0.19	10%	**0.037**	0.146	**Yes**	Same
2,4'-DDD	24	21	0.93 ± 0.33	**24%**	0.232	0.413	No	Same
2,4'-DDE	24	20	0.99 ± 0.21	5%	0.433	0.763	No	Same
2,4'-DDT	24	18	0.75 ± 0.4	**44%**	**0.031**	**0.025**	**Yes**	**Different**
Polychlorinated Biphenyls (PCBs)								
PCB 77	24	21	1.21 ± 0.2	0%	**<0.001**	**<0.001**	**Yes**	Same
PCB 81	24	16	**1.44 ± 0.33**	**25%**	**<0.001**	**0.028**	**Yes**	**Different**
PCB 105	24	21	1.29 ± 0.32	10%	**<0.001**	**<0.001**	**Yes**	Same
PCB 114	24	20	**1.32 ± 0.2**	10%	**<0.001**	**<0.001**	**Yes**	**Different**
PCB 118	24	21	**1.31 ± 0.31**	10%	**<0.001**	**<0.001**	**Yes**	**Different**
PCB 123	24	20	**1.41 ± 0.36**	**20%**	**<0.001**	**<0.001**	**Yes**	**Different**
PCB 126	24	18	**1.38 ± 0.44**	6%	**<0.001**	**0.001**	**Yes**	**Different**
PCB 156 + PCB 157	24	21	**1.44 ± 0.59**	**19%**	**<0.001**	**<0.001**	**Yes**	**Different**
PCB 167	24	21	**1.38 ± 0.54**	**19%**	**<0.001**	**0.001**	**Yes**	**Different**
PCB 189	24	20	**1.49 ± 0.85**	**20%**	**<0.001**	**0.006**	**Yes**	**Different**
Total PCB	24	22	1.23 ± 0.32	9%	**<0.001**	**<0.001**	**Yes**	Same
Polycyclic Aromatic Hydrocarbons								
Anthracene	24	22	**0.67 ± 0.13**	**27%**	**<0.001**	**<0.001**	**Yes**	**Different**
Benzo[a]anthracene	24	22	0.82 ± 0.19	5%	**0.001**	**0.002**	**Yes**	Same
Benzo[a]pyrene	24	22	0.89 ± 0.2	5%	**0.002**	**0.014**	**Yes**	Same
Chrysene	24	23	0.97 ± 0.23	4%	0.125	0.367	No	Same
Fluoranthene	24	23	**0.69 ± 0.23**	**30%**	**<0.001**	**<0.001**	**Yes**	**Different**
Indeno[1,2,3-cd]pyrene	24	22	0.76 ± 0.15	5%	**<0.001**	**<0.001**	**Yes**	Same
Naphthalene	24	22	0.82 ± 0.18	14%	**0.001**	**0.001**	**Yes**	Same
Phenanthrene	24	22	0.94 ± 0.28	14%	**0.01**	0.149	**Yes**	Same
Pyrene	24	23	**0.65 ± 0.2**	**30%**	**<0.001**	**<0.001**	**Yes**	**Different**
Total Organic Carbon (TOC)								
TOC	18	16	1.11 ± 0.1	0%	**0.005**	**0.021**	**Yes**	Same
Metals								
Arsenic	18	18	0.82 ± 0.23	11%	**0.048**	**0.002**	**Yes**	Same
Barium	18	18	1.06 ± 0.09	0%	**0.033**	**0.03**	**Yes**	Same
Cadmium	18	16	0.95 ± 0.18	0%	0.798	0.261	No	Same
Chromium	18	18	1.06 ± 0.13	0%	**0.041**	0.099	**Yes**	Same
Cobalt	18	18	1.02 ± 0.14	0%	0.332	0.514	No	Same
Copper	18	18	1.04 ± 0.11	0%	0.064	0.126	No	Same
Iron	18	18	1.03 ± 0.13	0%	0.258	0.371	No	Same
Lead	18	18	1.3 ± 0.16	6%	**<0.001**	**<0.001**	**Yes**	Same
Nickel	18	18	0.93 ± 0.15	0%	0.112	**0.011**	**Yes**	Same
Zinc	18	18	1.15 ± 0.14	0%	**0.001**	**0.002**	**Yes**	Same
Mercury	22	22	**1.31 ± 0.79**	9%	0.417	0.132	No	Same

Notes:
Results outside acceptance criteria are **bolded**
[1] Detected pairs: split samples where both EPA and CPG samples results were detected.
[2] Average ratio criteria: average ratio of CPG to EPA within 0.70 to 1.30. Values shown are average ratio with standard deviation.
[3] Percent difference criteria: no more than 16% of split samples pairs outside of -67 to 40 percent difference range.
[4] Statistical test criteria: p-value greater than or equal to 0.05 indicating there is no significant statistical difference between the data pairs.
[5] Wilcoxon Signed Rank test and Paired Prentice-Wilcoxon test were employed at significance level (p-value) of 0.05.
[6] If there are at least two of the three criteria (average ratio, percent different, and statistical test) are met, the overall split sample comparison would be labeled "same". Otherwise, it would be "different".
[7] Although average ratio is outside of the criterion, the actual average ratio can be within criterion because of the high standard deviation.

Abbreviations:
EPA = United States Environmental Protection Agency
CPG = Cooperating Parties Group
1,2,3,4,6,7,8-HpCDD = 1,2,3,4,6,7,8-heptachlorodibenzo-p-dioxin
1,2,3,4,6,7,8-HpCDF = 1,2,3,4,6,7,8-heptachlorodibenzofuran
2,3,7,8-TCDD = 2,3,7,8-tetrachlorodibenzo-p-dioxin
2,3,7,8-TCDF = 2,3,7,8-tetrachlorodibenzofuran
OCDD = octachlorodibenzo-p-dioxin
OCDF = octachlorodibenzofuran
Total TCDD = total tetrachlorodibenzo-p-dioxin
4,4'-DDD = 4,4'-dichlorodiphenyldichloroethane
4,4'-DDE = 4,4'-dichlorodiphenyldichloroethylene
4,4'-DDT = 4,4'-dichlorodiphenyltrichloroethane
2,4'-DDD = 2,4'-dichlorodiphenyldichloroethane
2,4'-DDE = 2,4'-dichlorodiphenyldichloroethylene
2,4'-DDT = 2,4'-dichlorodiphenyltrichloroethane
PCB 77 = 3,3',4,4'-tetrachlorobiphenyl
PCB 81 = 3,4,4',5-tetrachlorobiphenyl
PCB 105 = 2,3,3',4,4'-pentachlorobiphenyl
PCB 114 = 2,3,4,4',5-pentachlorobiphenyl
PCB 118 = 2,3',4,4',5-pentachlorobiphenyl
PCB 123 = 2',3,4,4',5-pentachlorobiphenyl
PCB 126 = 3,3',4,4',5-pentachlorobiphenyl
PCB 156 = 2,3,3',4,4',5-hexachlorobiphenyl
PCB 157 = 2,3,3',4,4',5'-hexachlorobiphenyl
PCB 167 = 2,3',4,4',5,5'-hexachlorobiphenyl
PCB 189 = 2,3,3',4,4',5,5'-heptachlorobiphenyl







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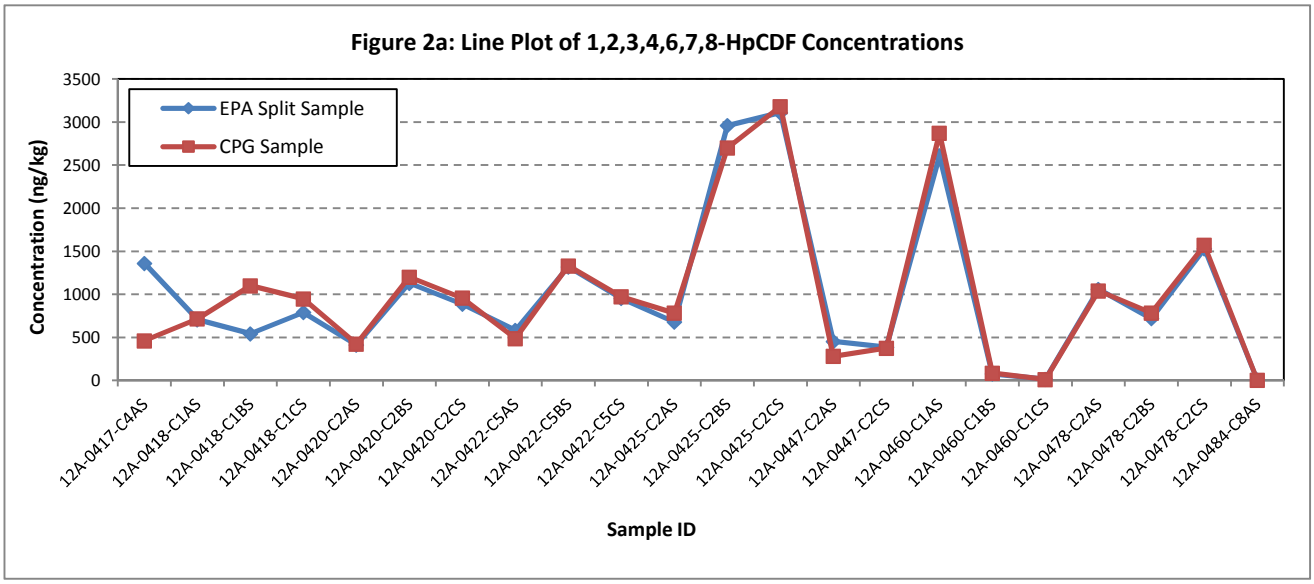
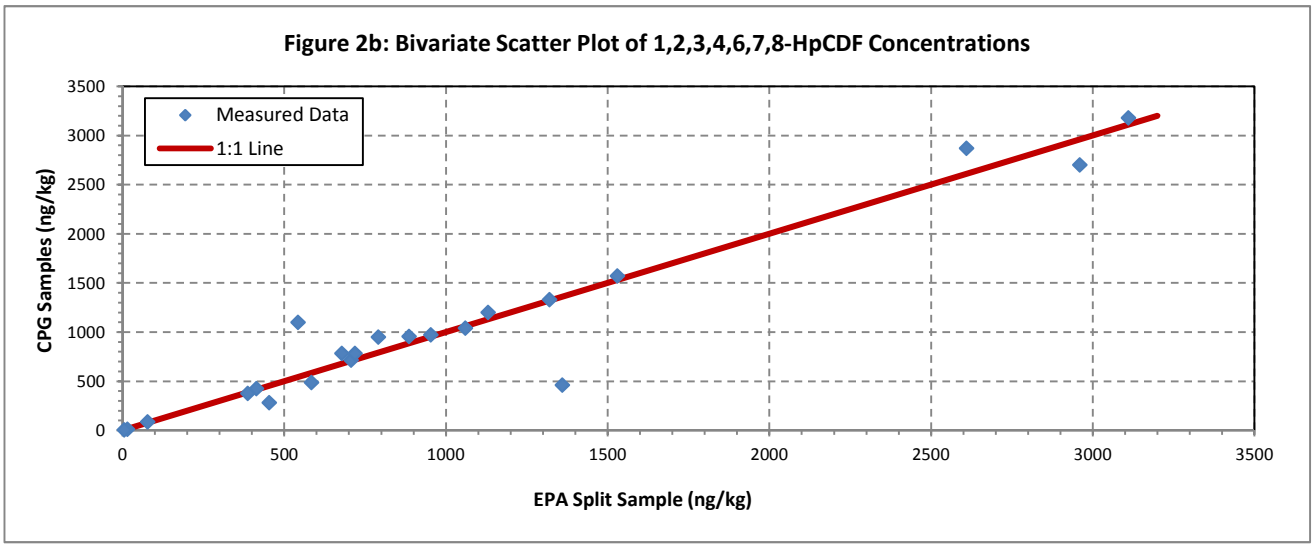
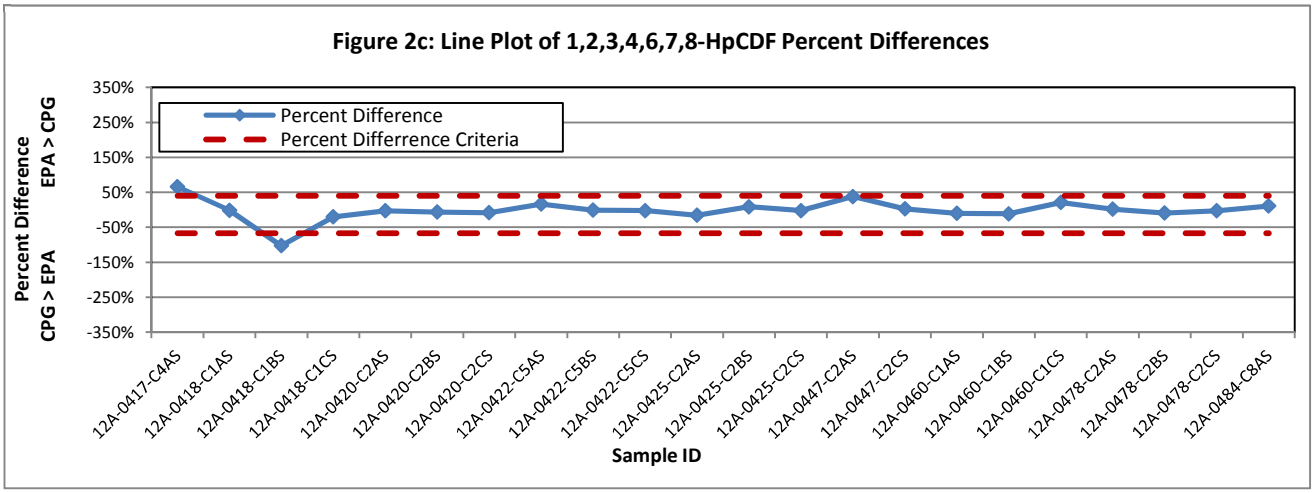
Statistical Plot of Sediment 1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin (1,2,3,4,6,7,8-HpCDD) Concentrations

Figure 1







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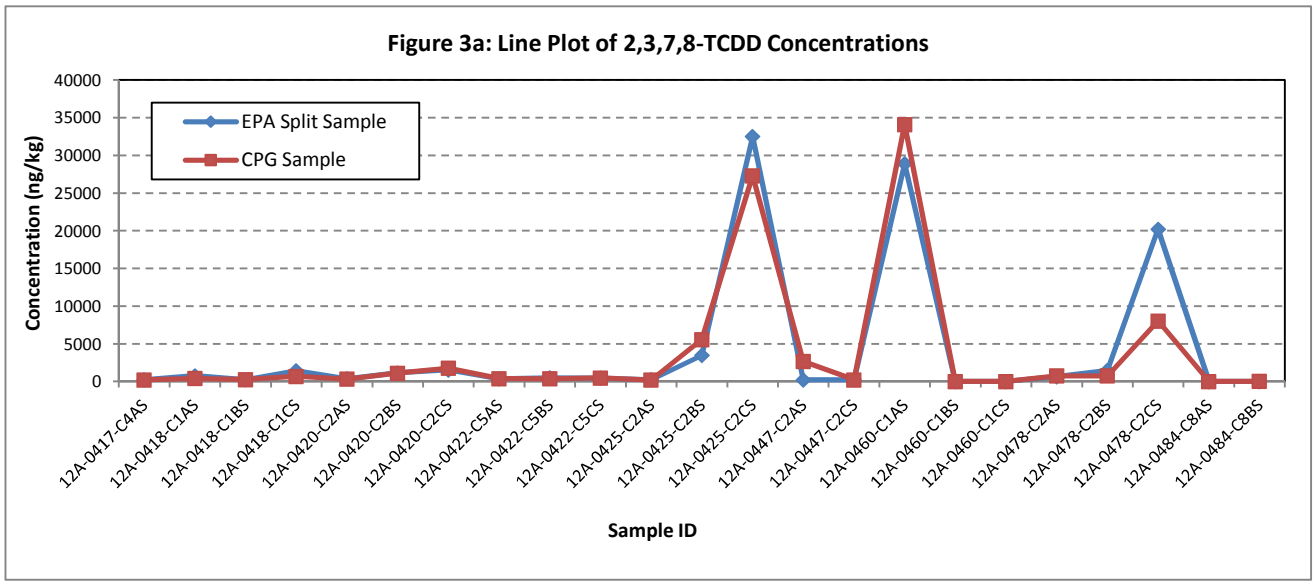
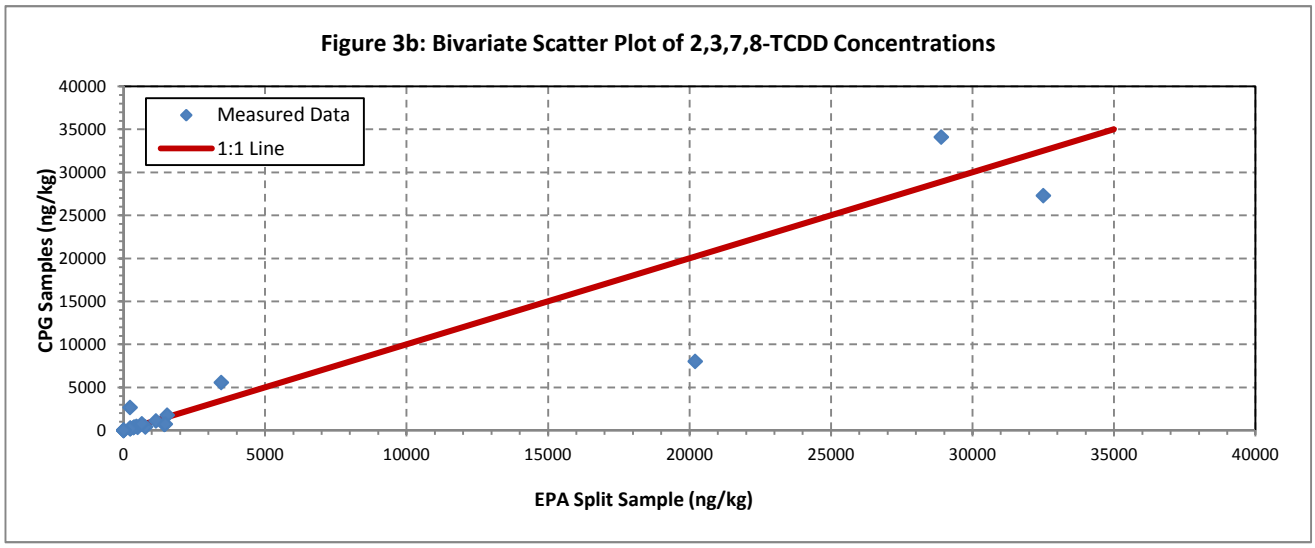
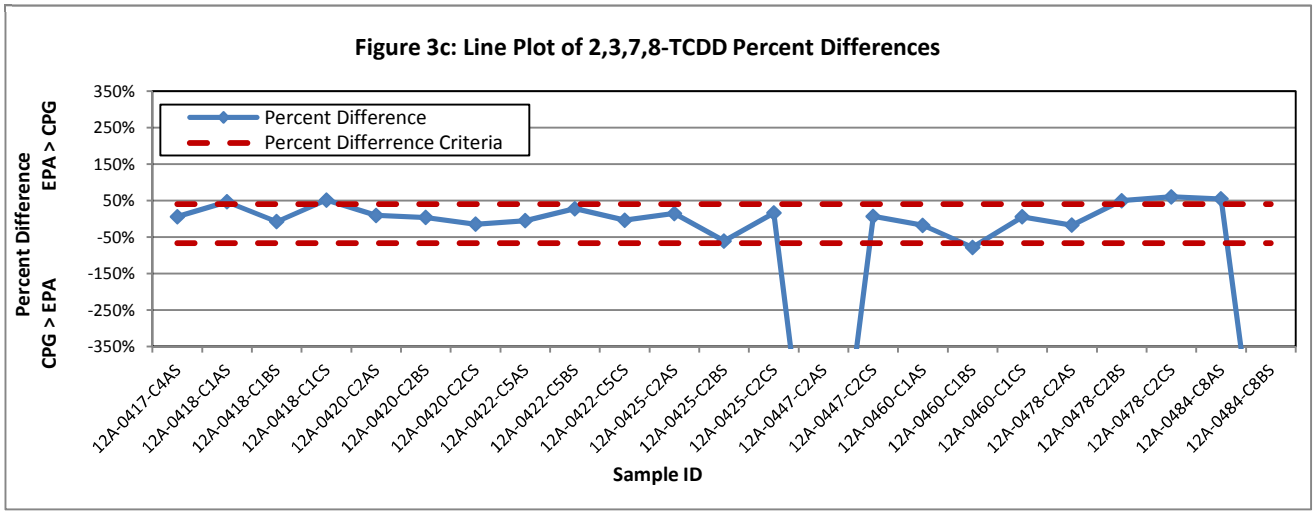
Statistical Plot of Sediment 1,2,3,4,6,7,8-Heptachlorodibenzofuran (1,2,3,4,6,7,8-HpCDF) Concentrations

Figure 2







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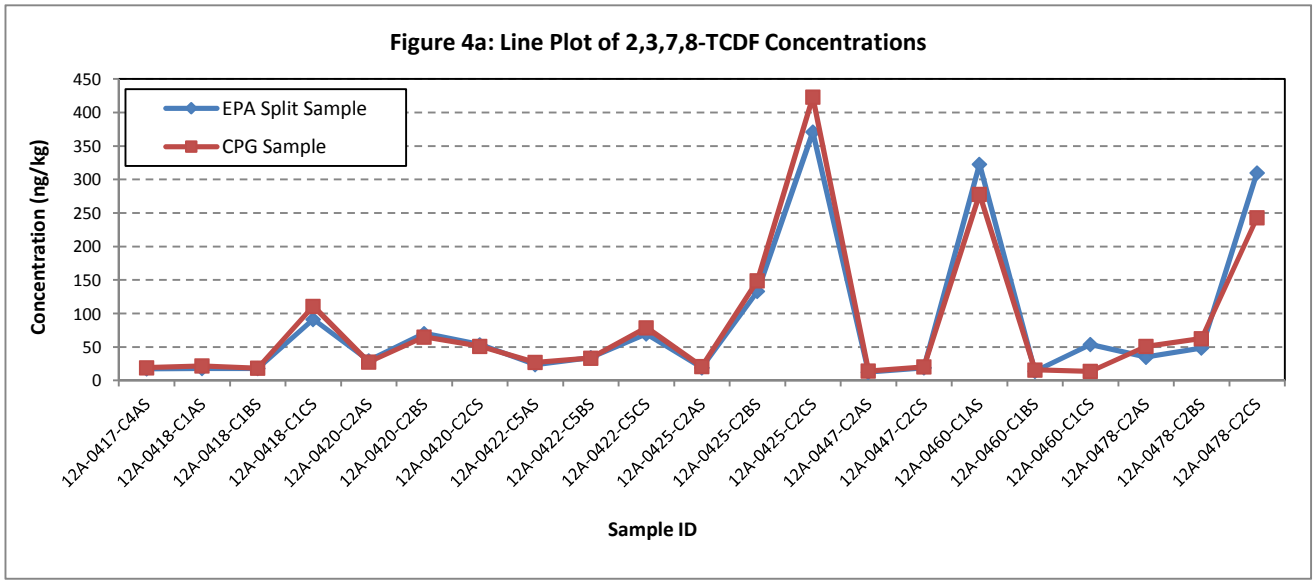
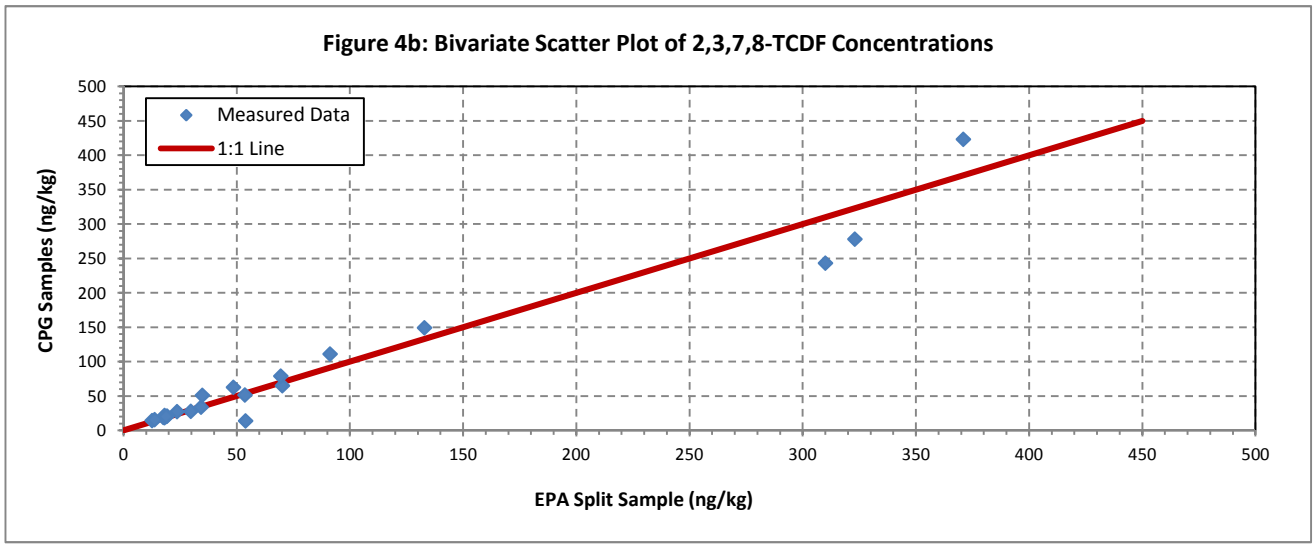
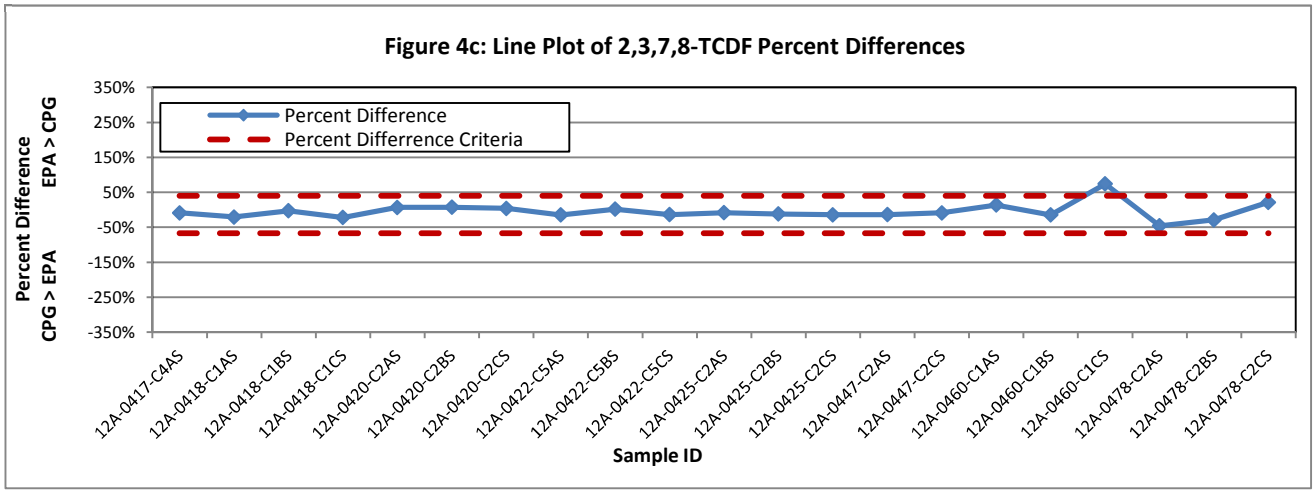
Statistical Plot of Sediment 2,3,7,8-Tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) Concentrations

Figure 3







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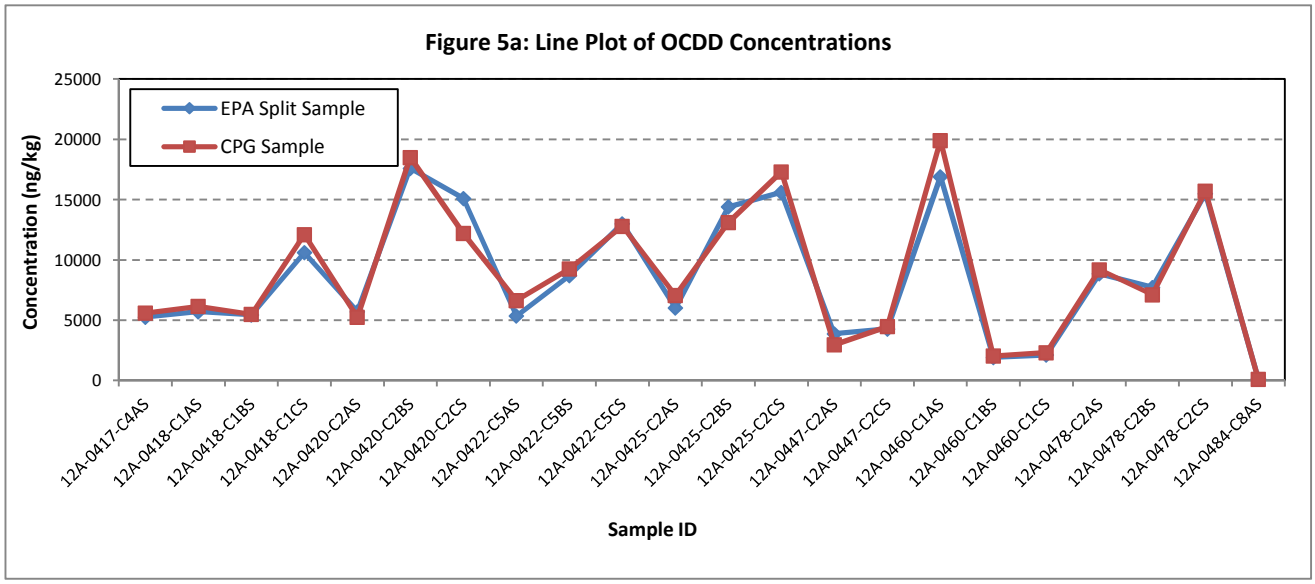
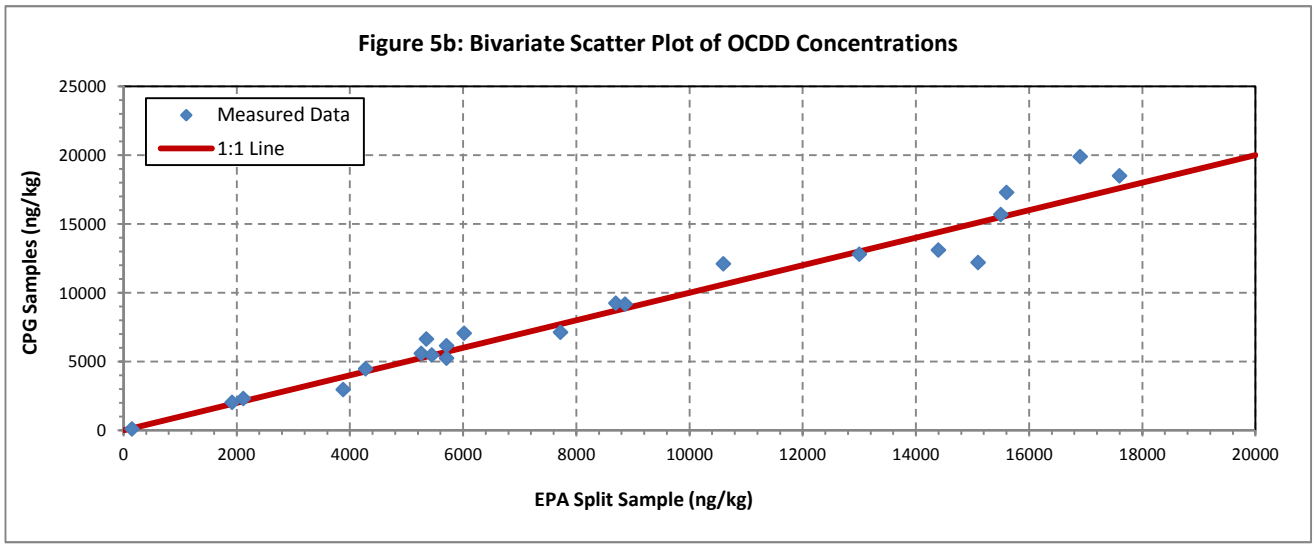
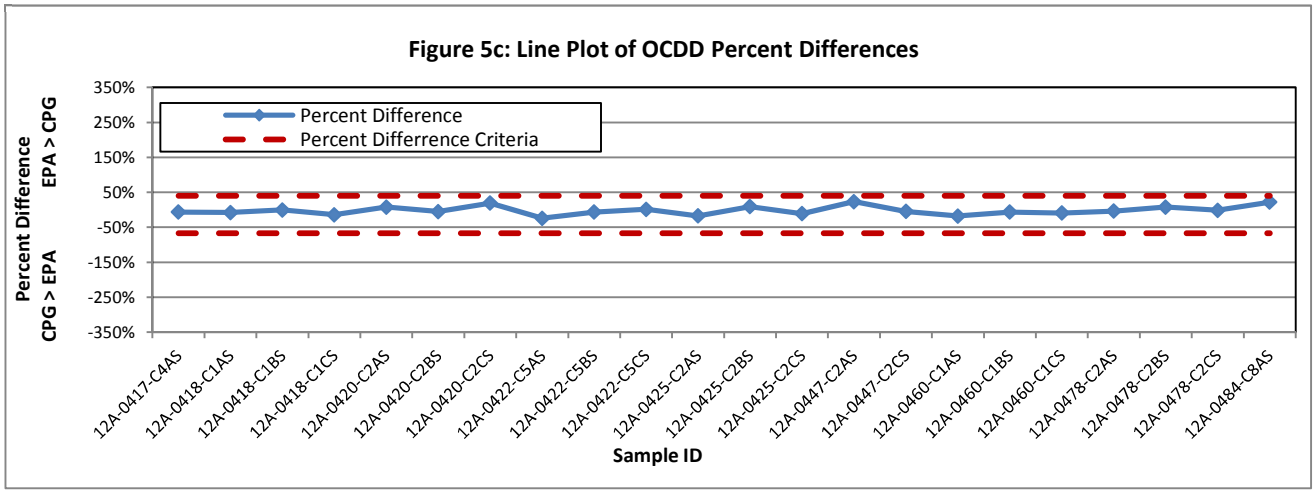
Statistical Plot of Sediment 2,3,7,8-Tetrachlorodibenzofuran (2,3,7,8-TCDF) Concentrations

Figure 4







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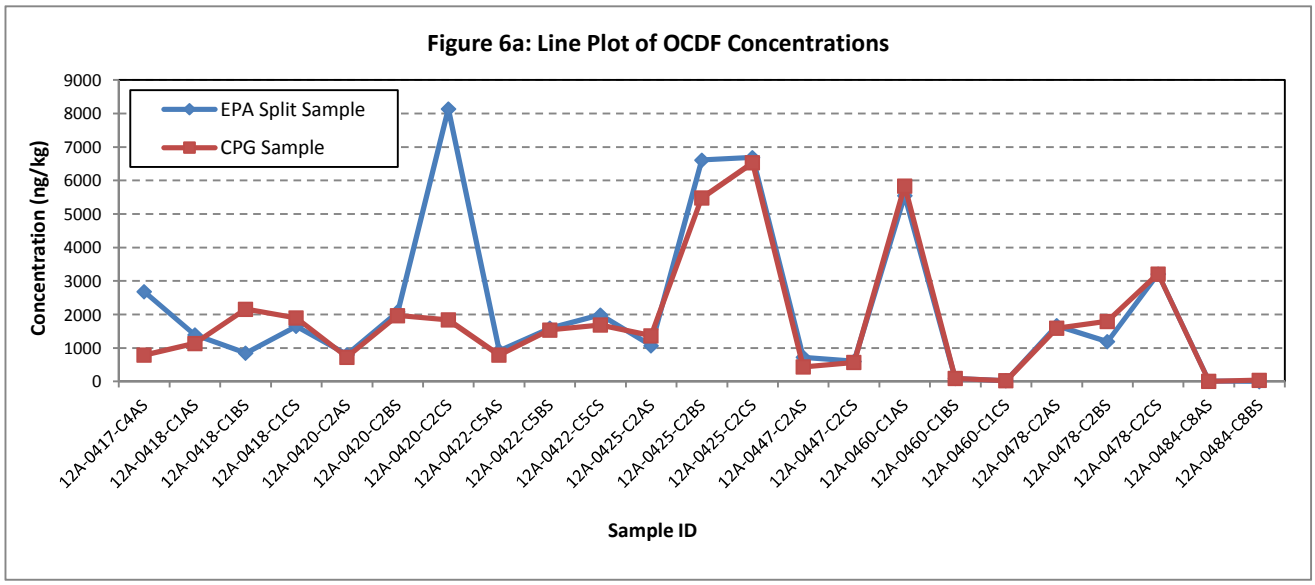
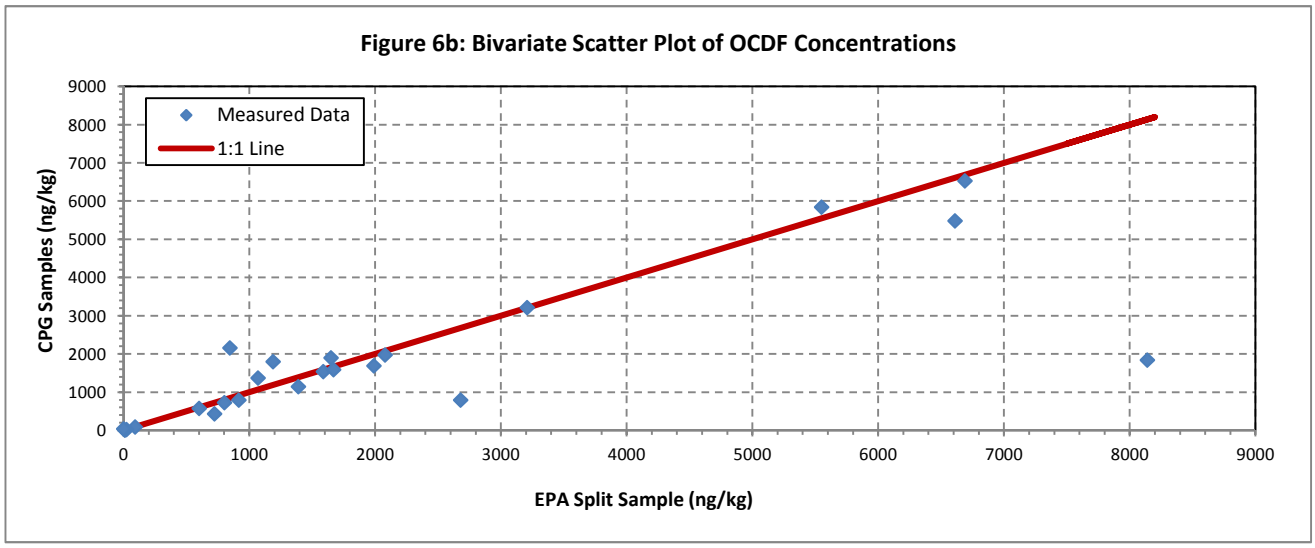
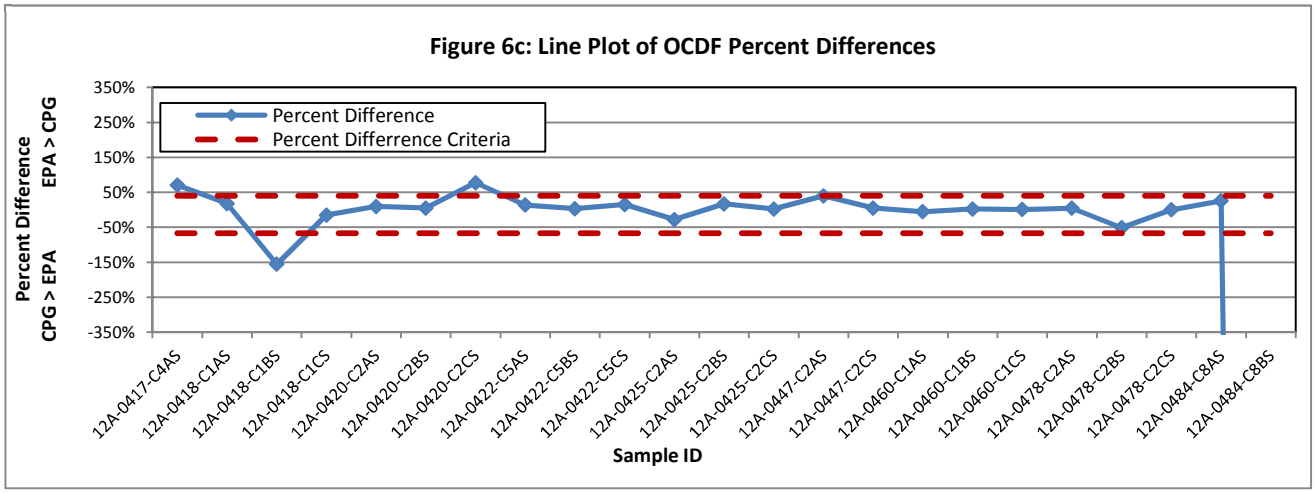
Statistical Plot of Sediment Octachlorodibenzo-p-dioxin (OCDD) Concentrations

Figure 5







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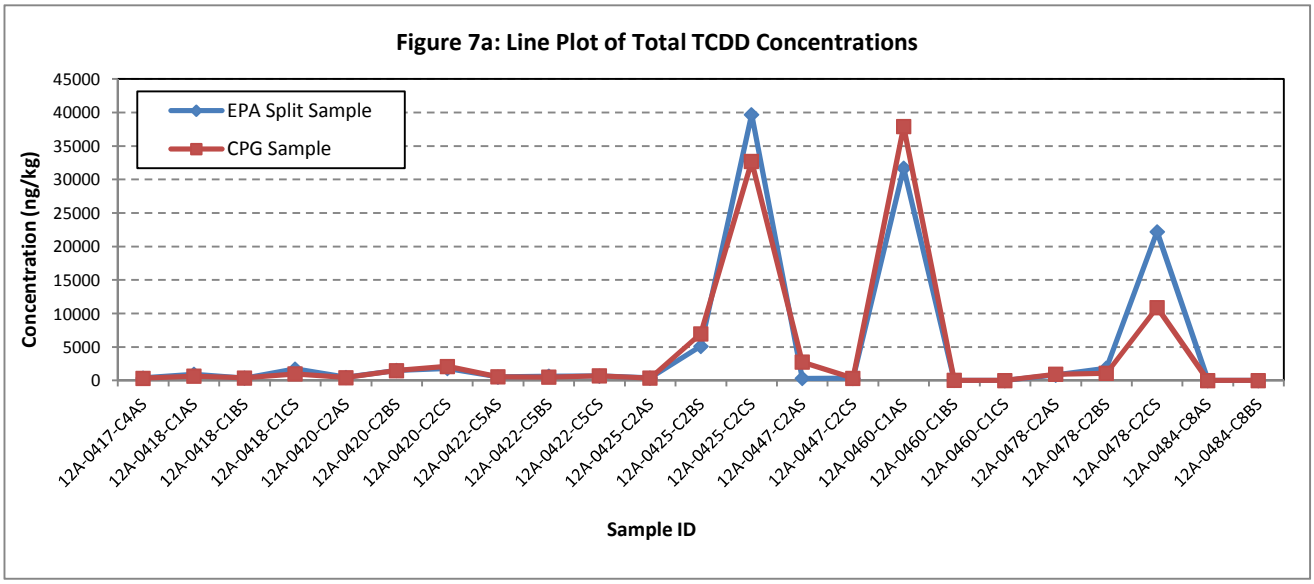
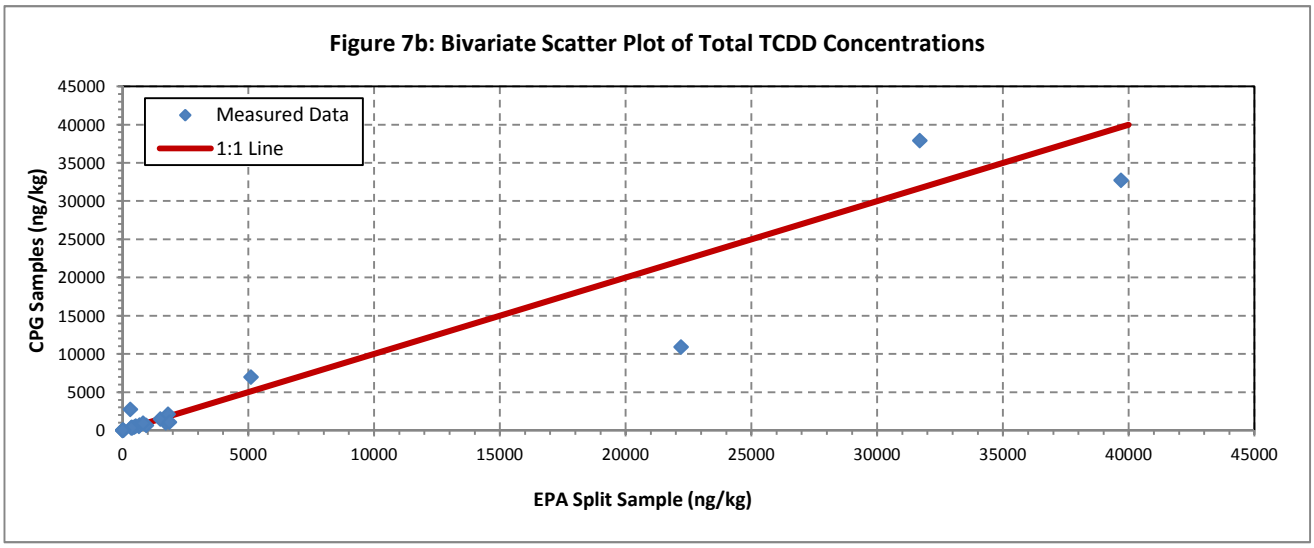
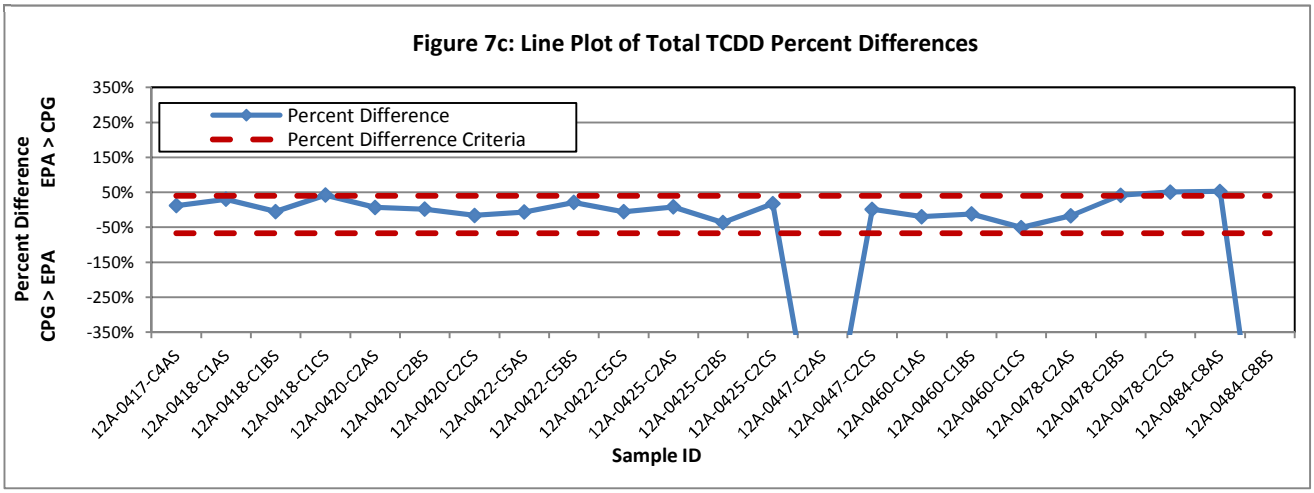
Statistical Plot of Sediment Octachlorodibenzofuran (OCDF) Concentrations

Figure 6







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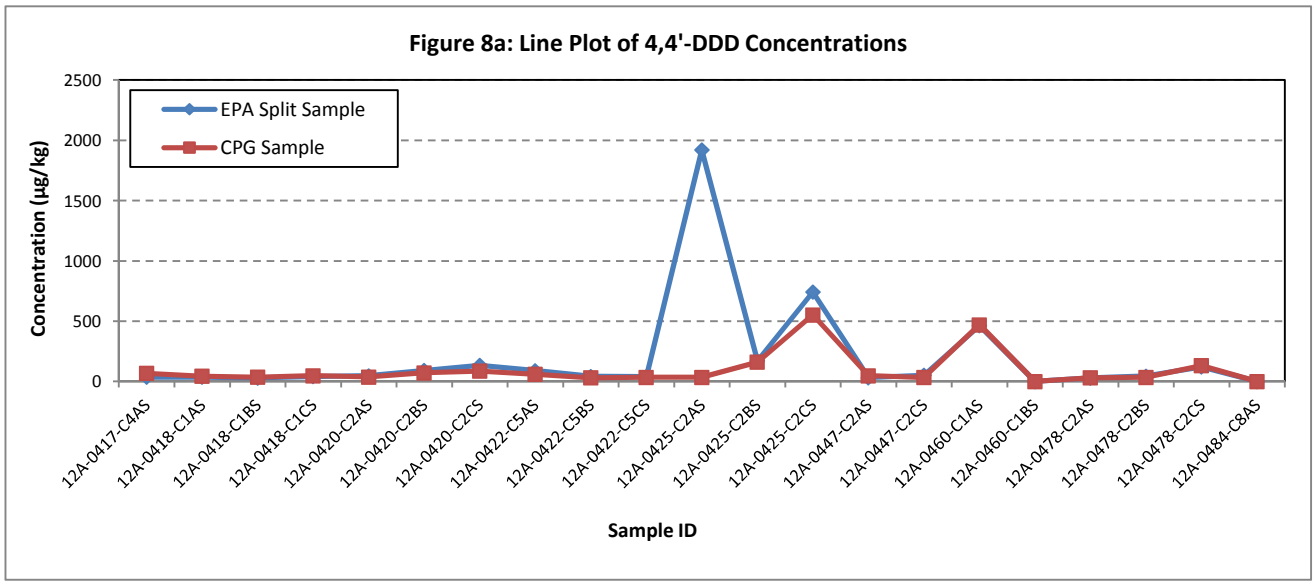
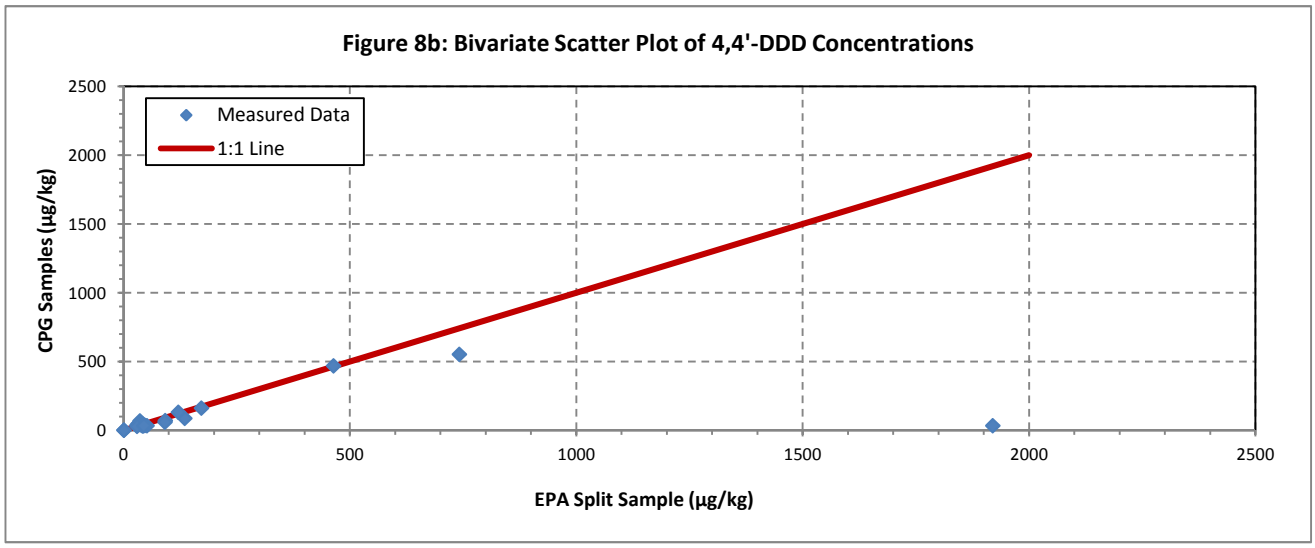
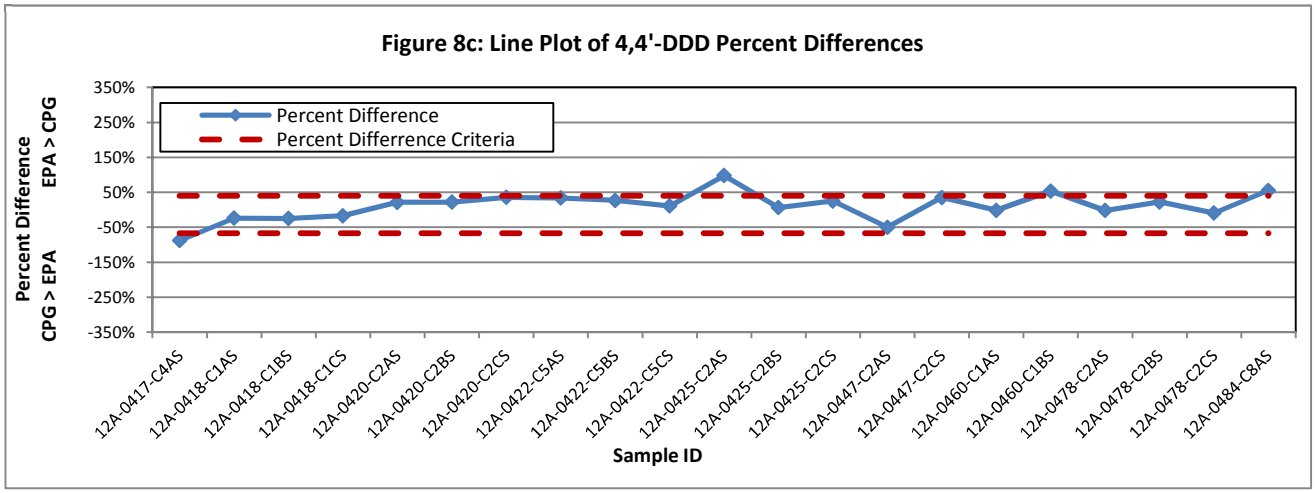
Statistical Plot of Sediment Total Tetrachlorodibenzo-p-dioxin (TCDD) Concentrations

Figure 7







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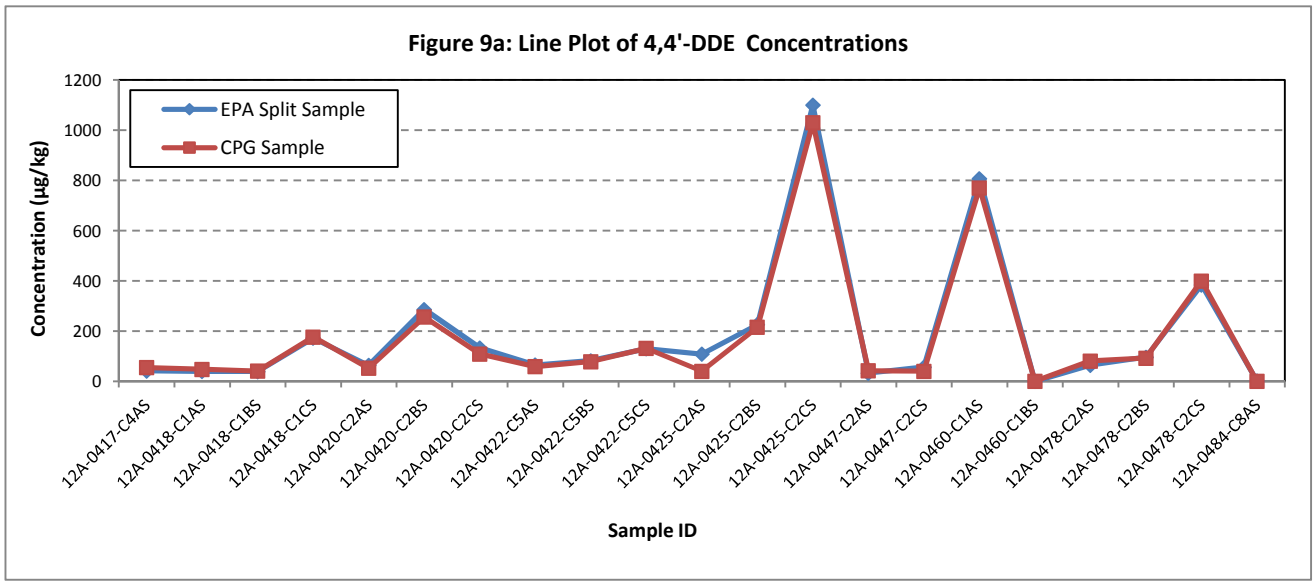
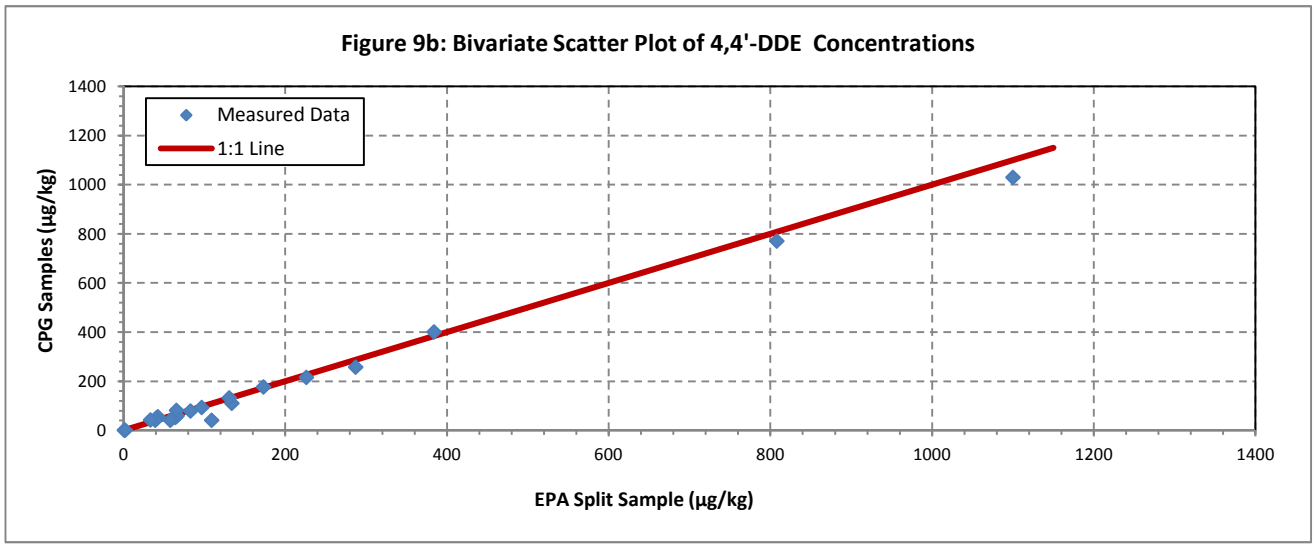
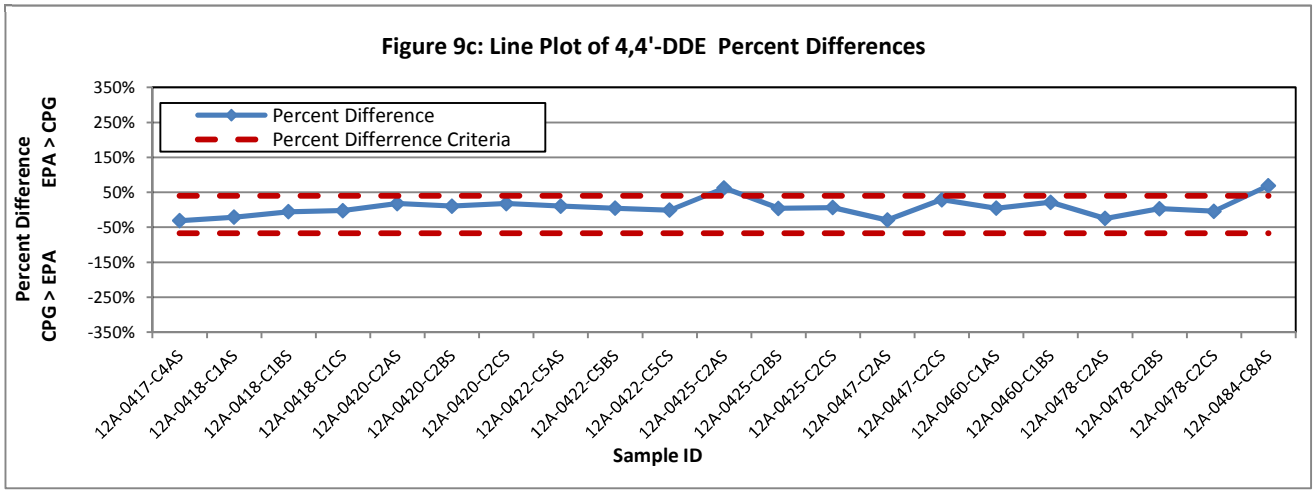
Statistical Plot of Sediment 4,4'-Dichlorodiphenyldichloroethane (4,4'-DDD) Concentrations

Figure 8







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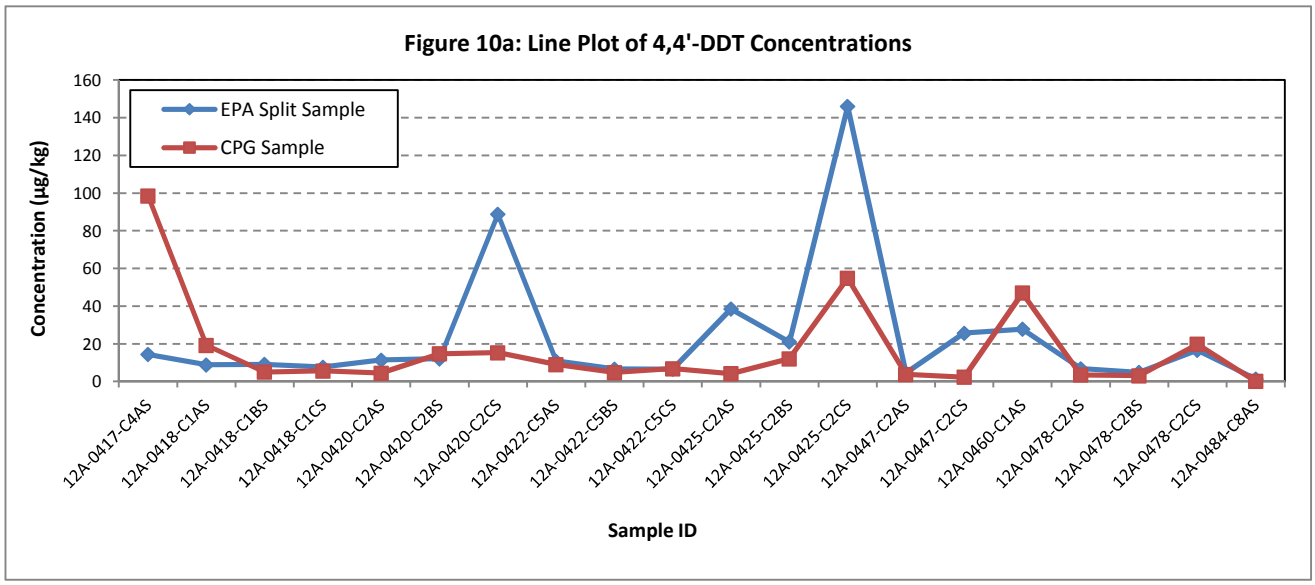
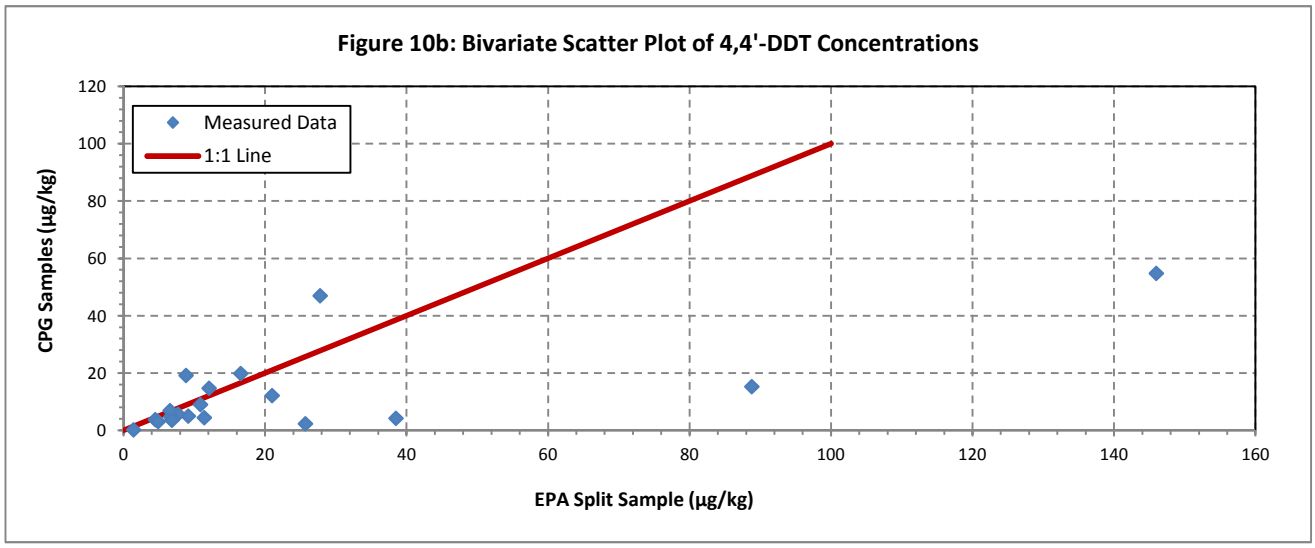
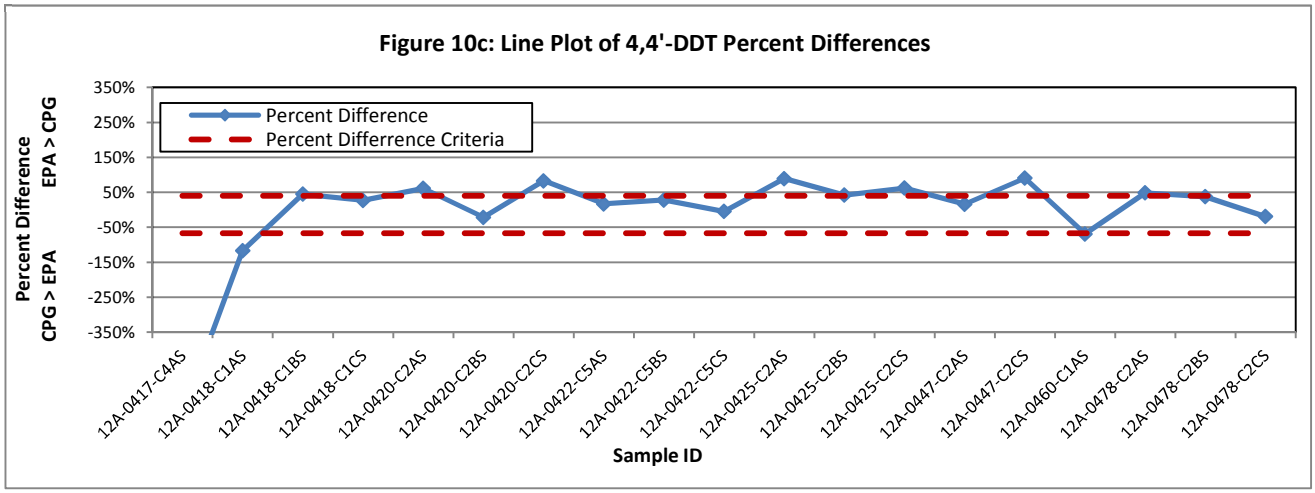
Statistical Plot of Sediment 4,4'-Dichlorodiphenyldichloroethylene (4,4'-DDE) Concentrations

Figure 9







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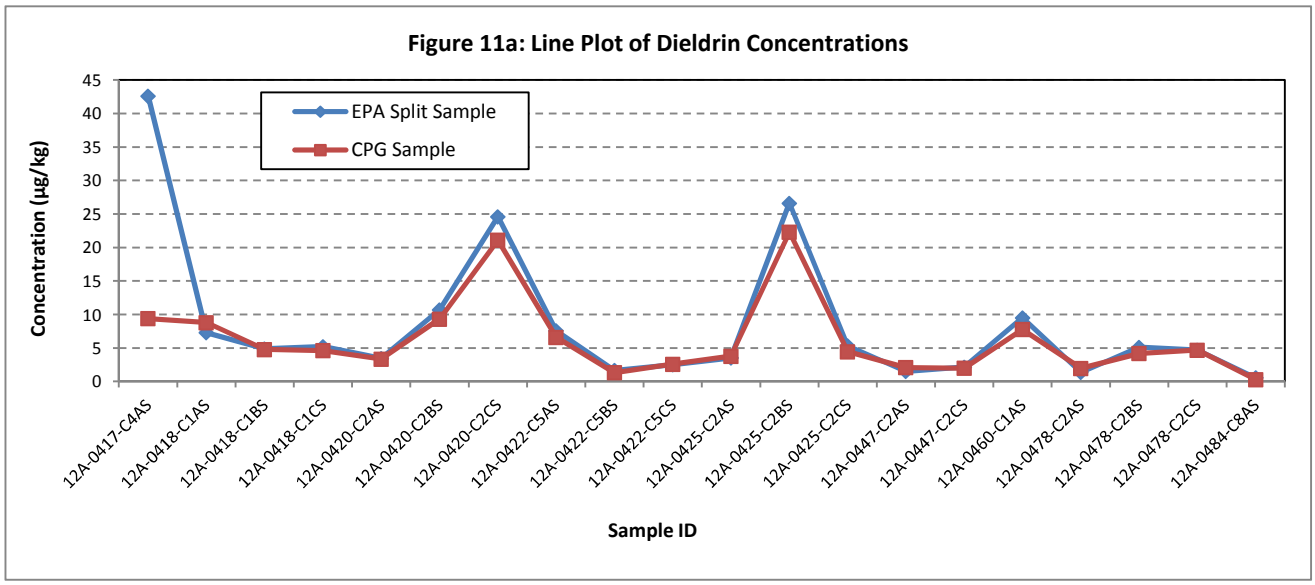
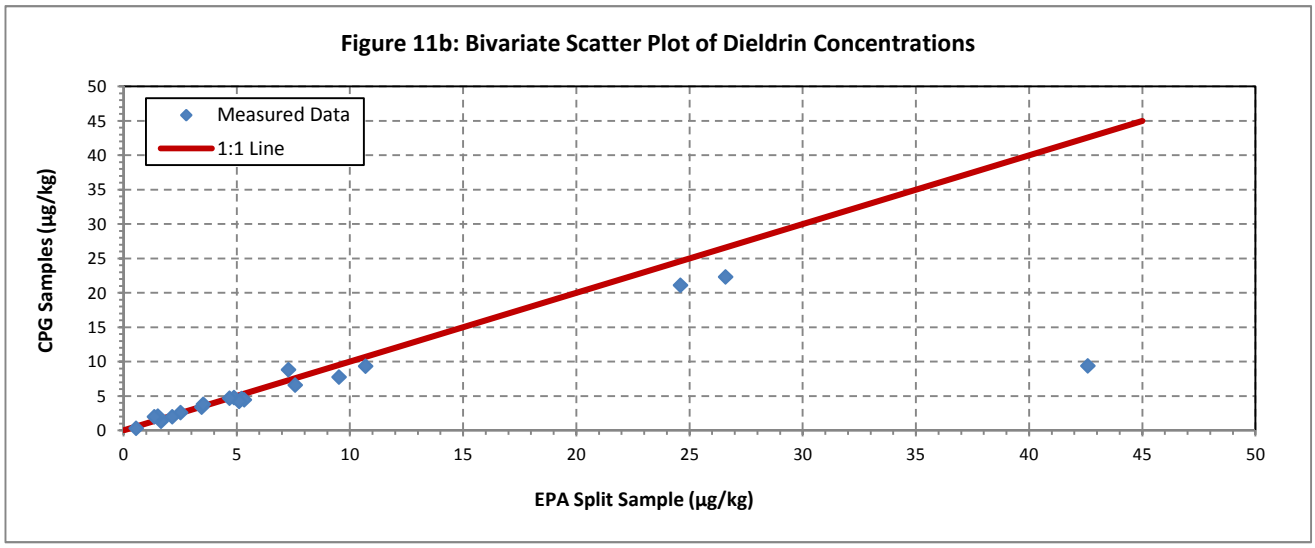
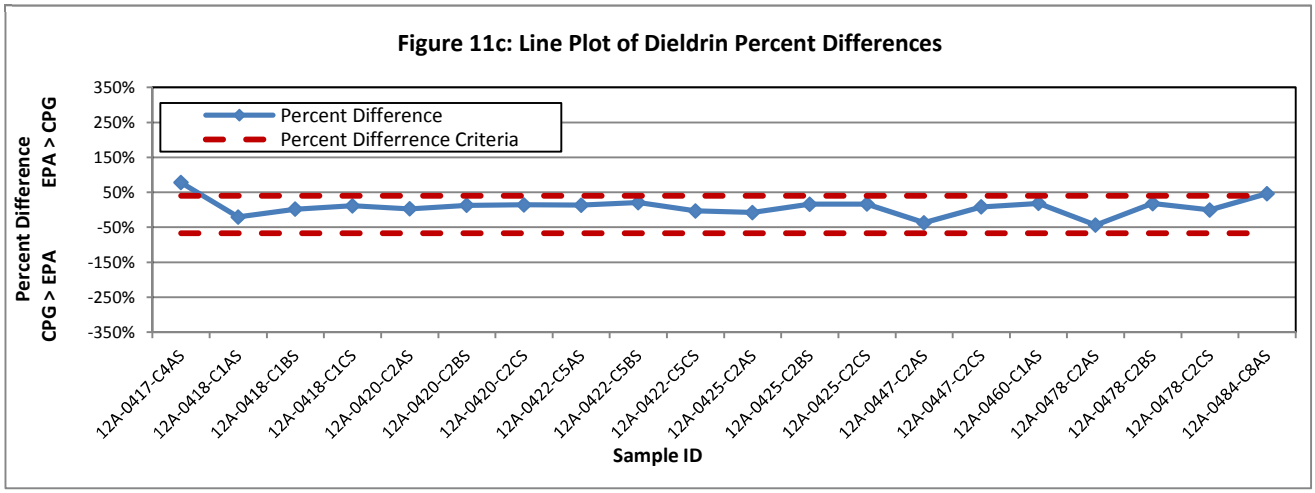
Statistical Plot of Sediment 4,4'-Dichlorodiphenyltrichloroethane (4,4'-DDT) Concentrations

Figure 10







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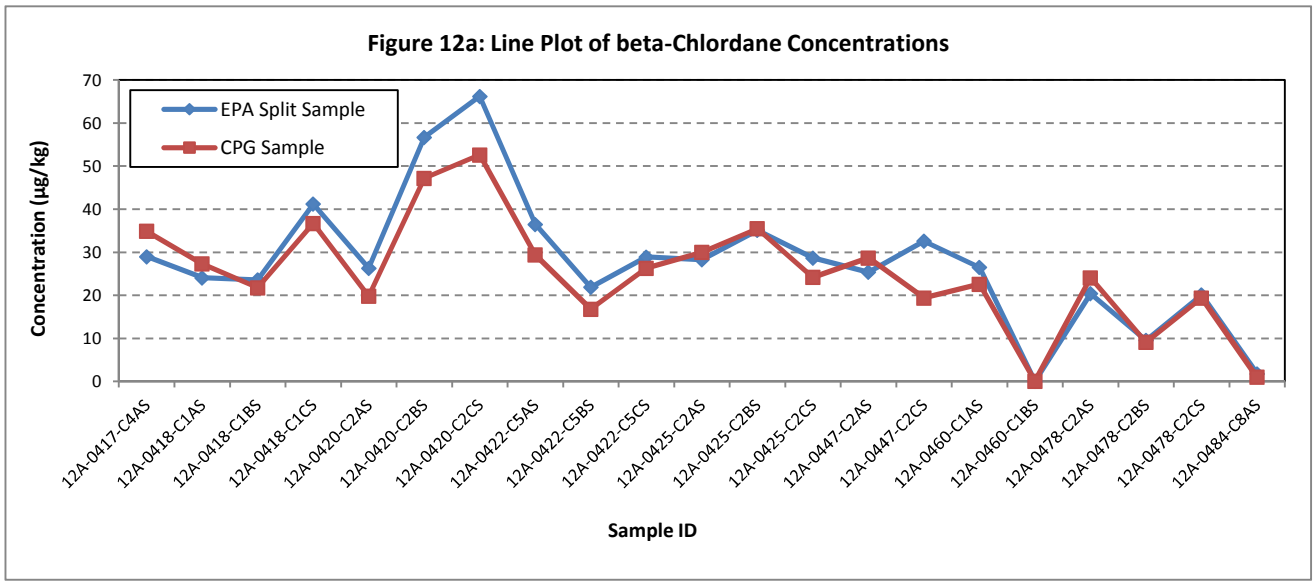
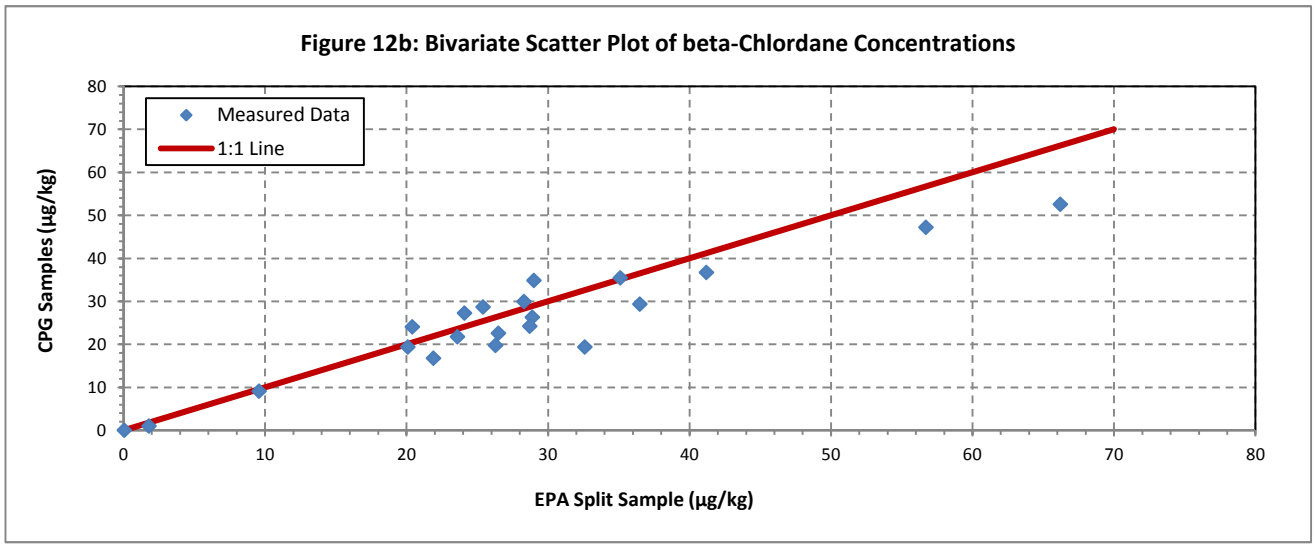
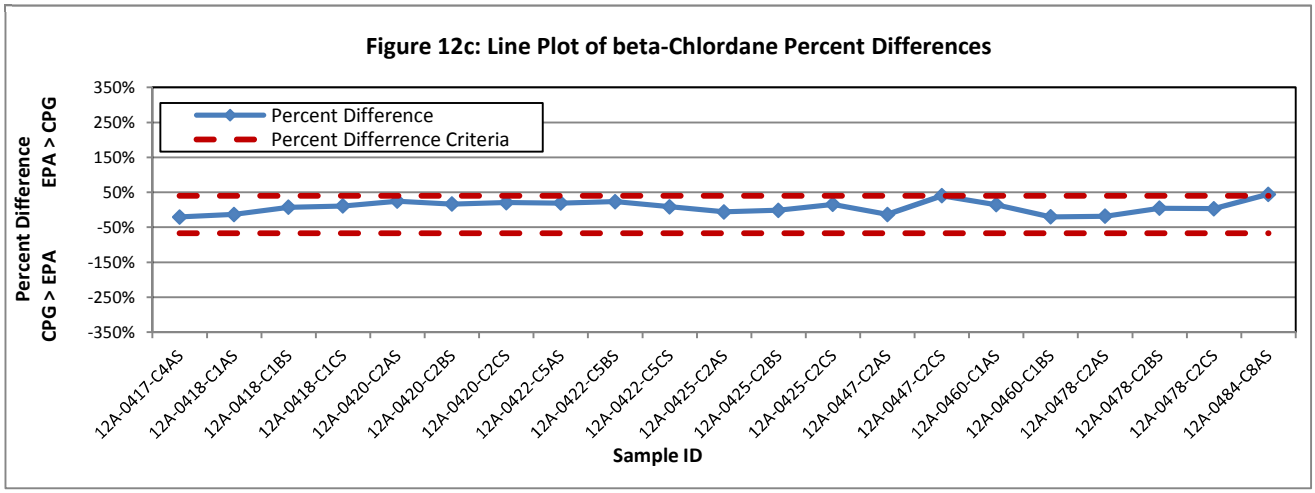
Statistical Plot of Sediment Dieldrin Concentrations

Figure 11







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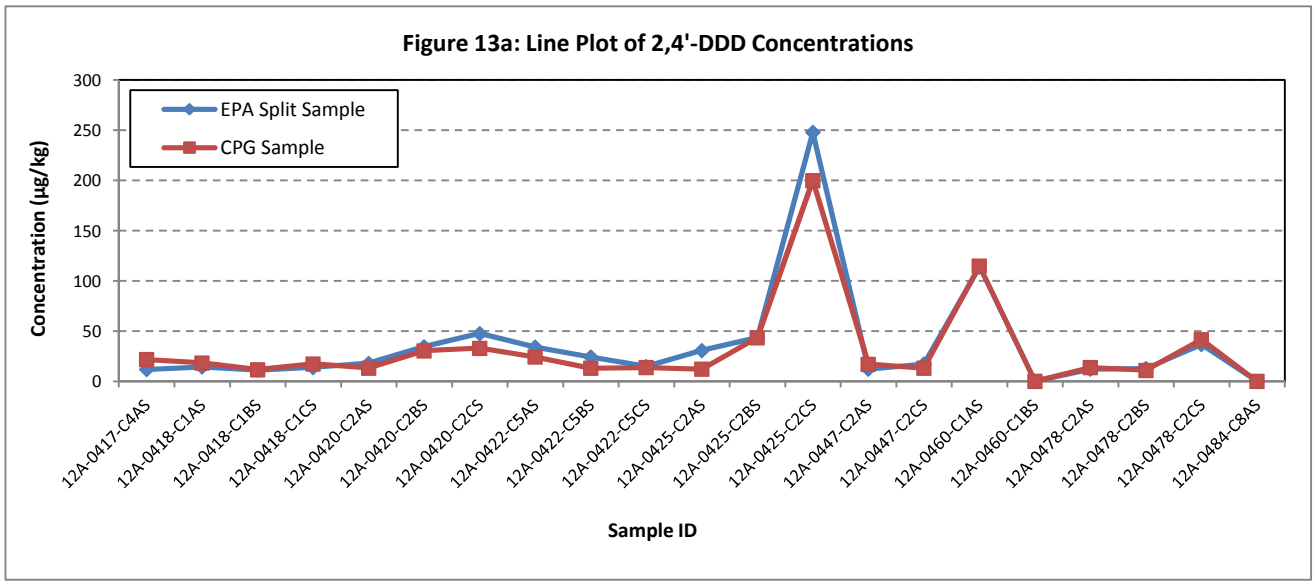
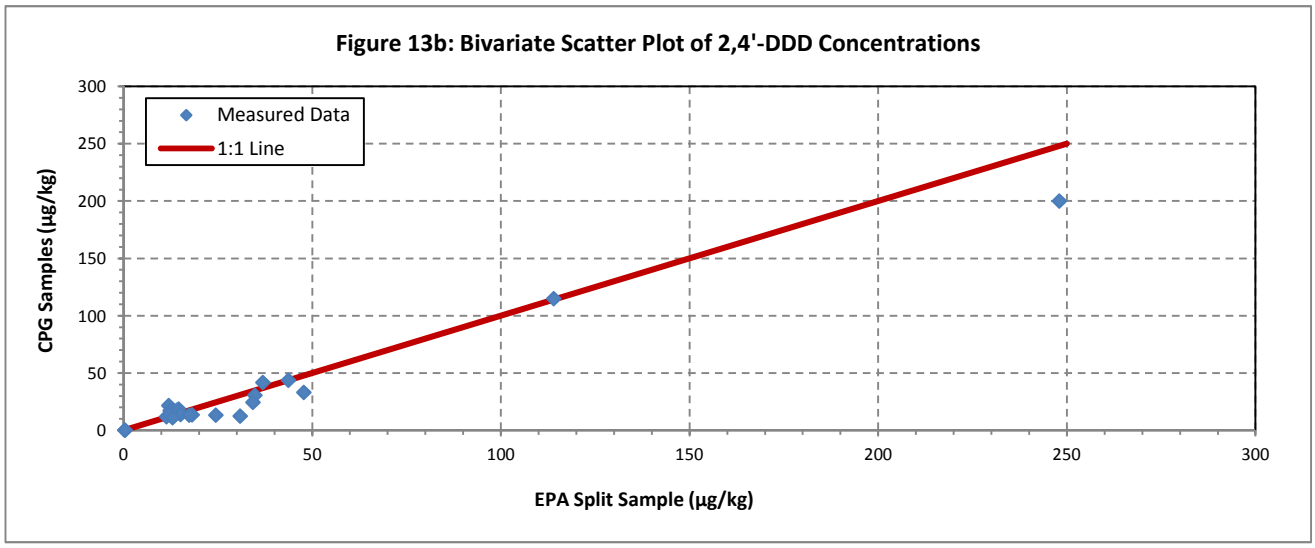
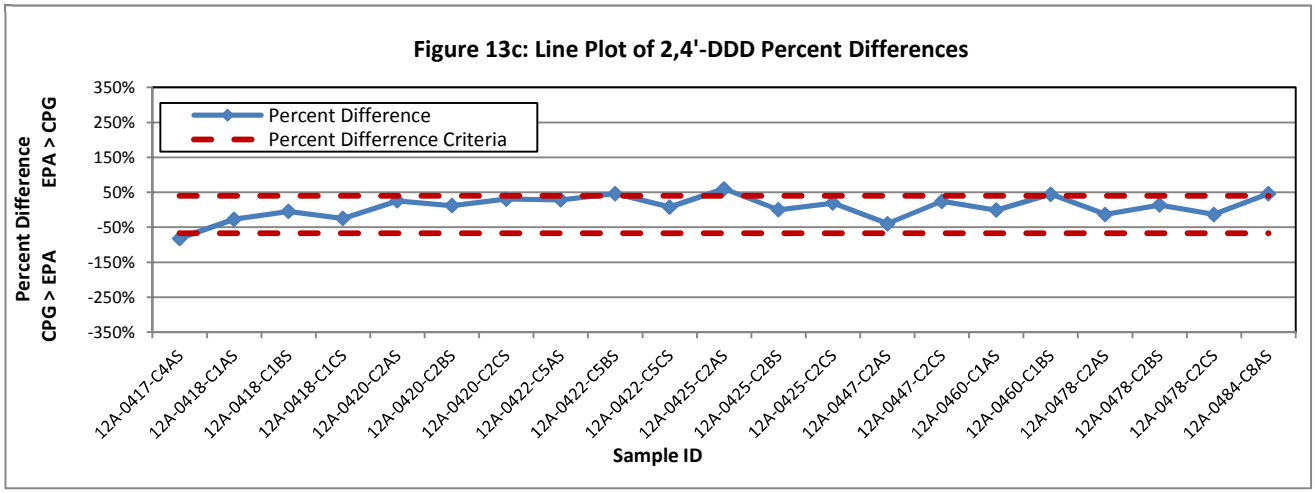
Statistical Plot of Sediment beta-Chlordane Concentrations

Figure 12







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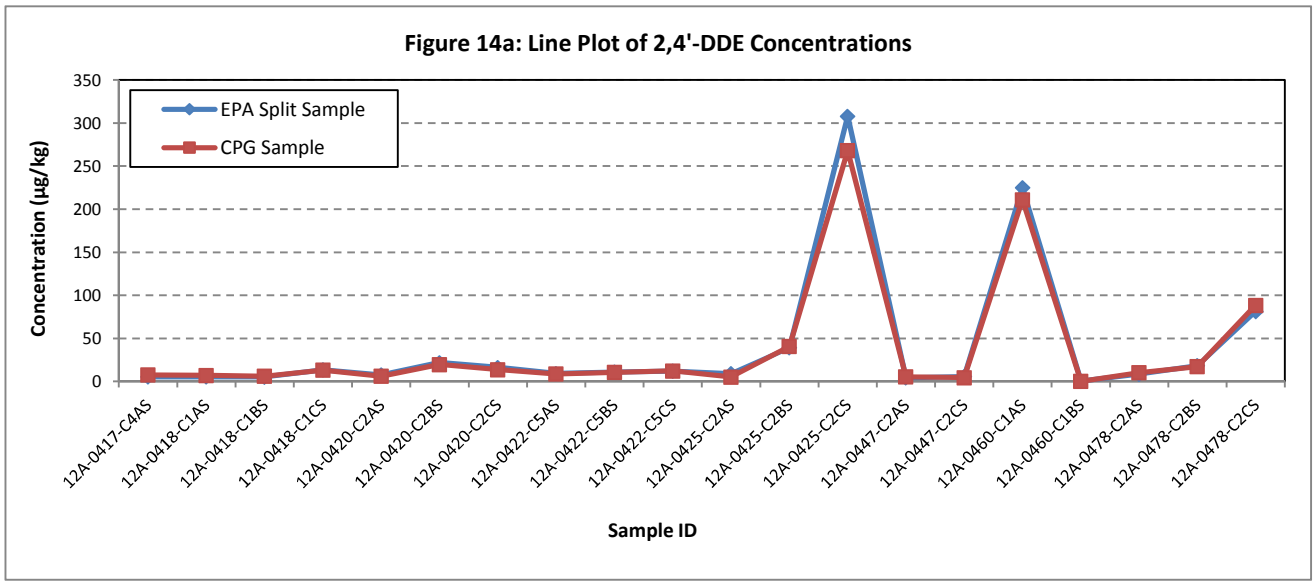
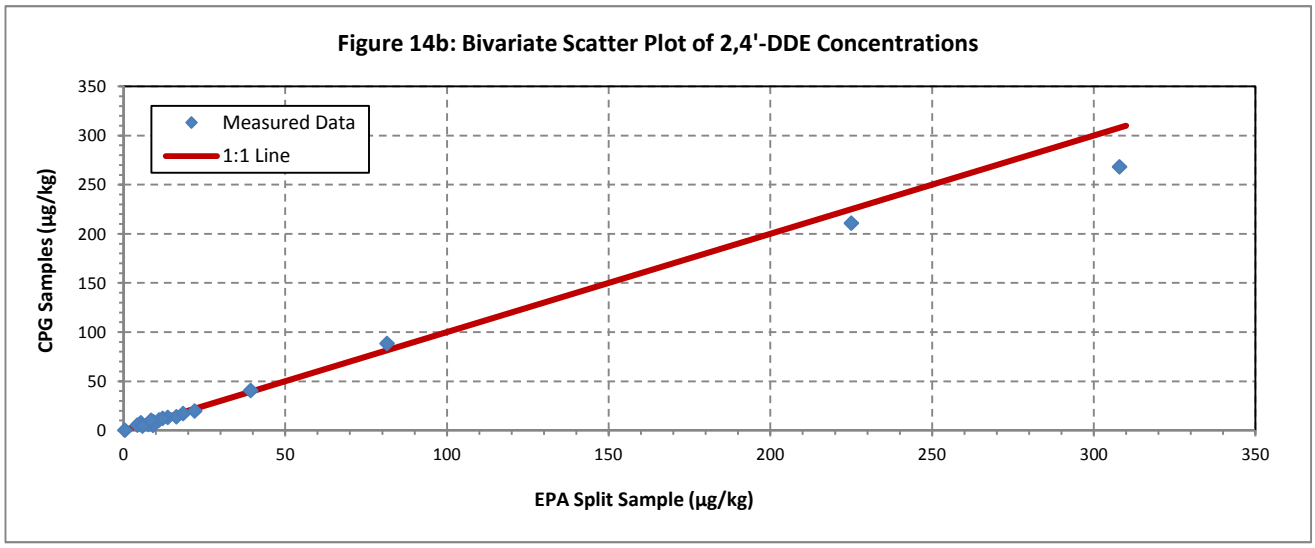
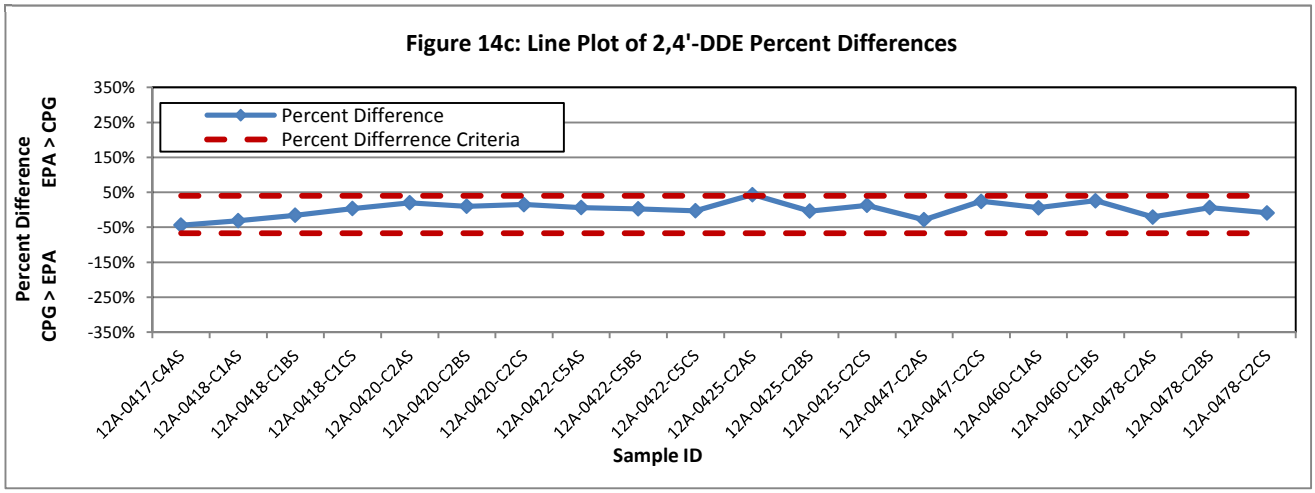
Statistical Plot of Sediment 2,4'-Dichlorodiphenyldichloroethane (2,4'-DDD) Concentrations

Figure 13







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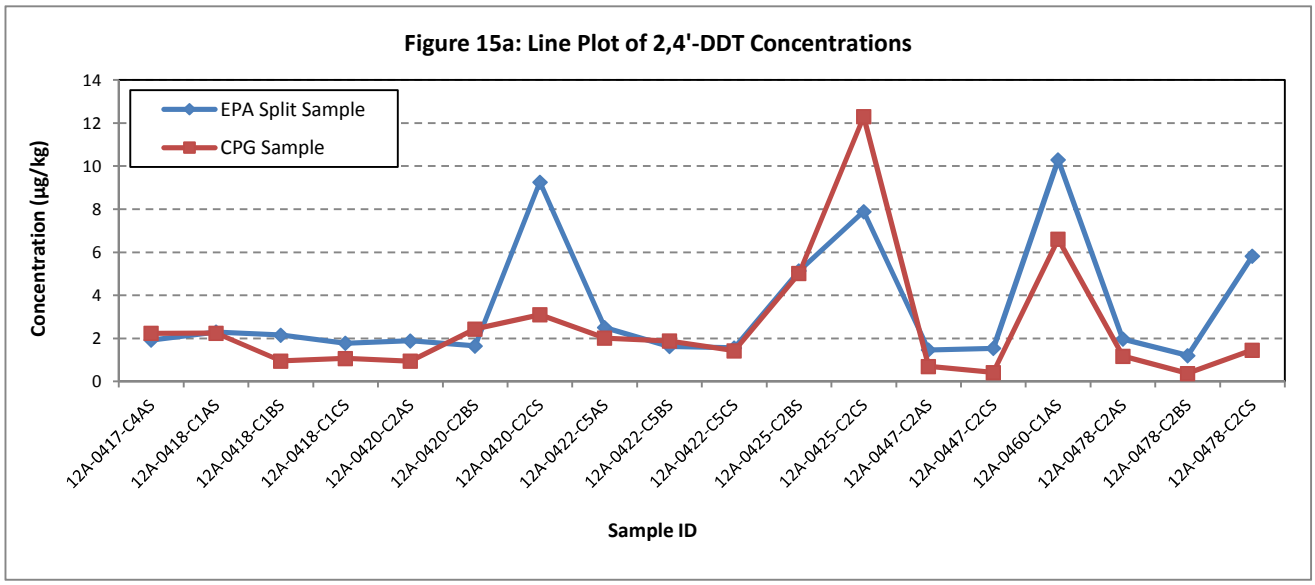
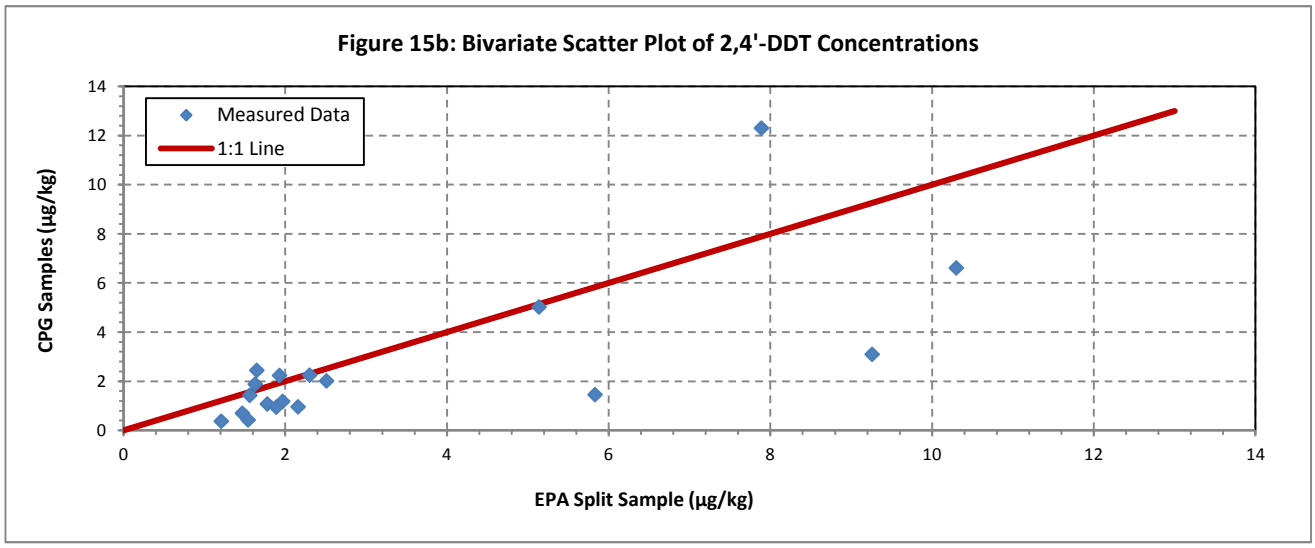
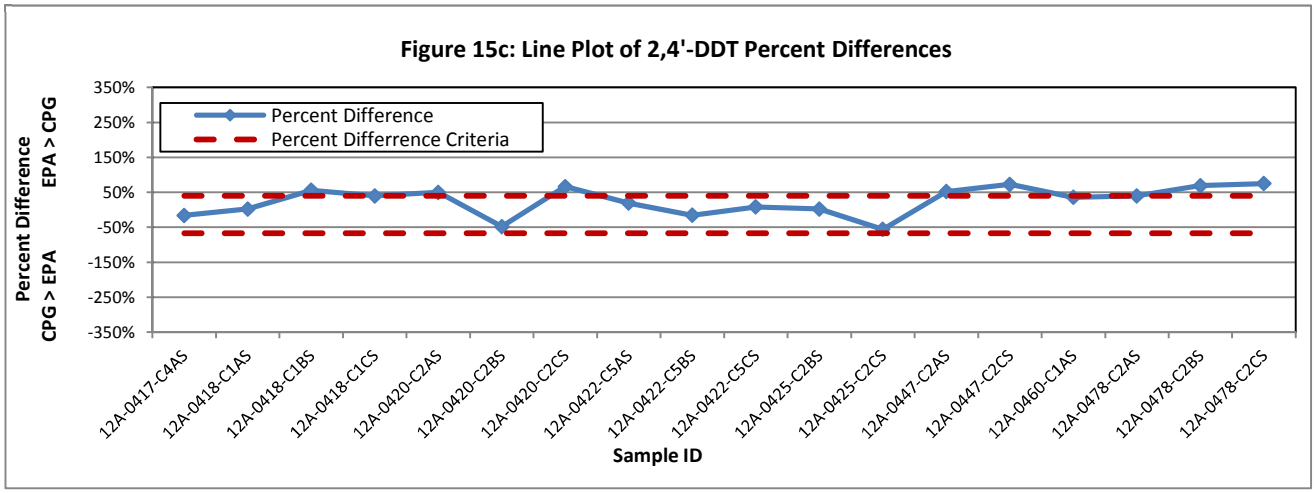
Statistical Plot of Sediment 2,4'-Dichlorodiphenyldichloroethylene (2,4'-DDE) Concentrations

Figure 14







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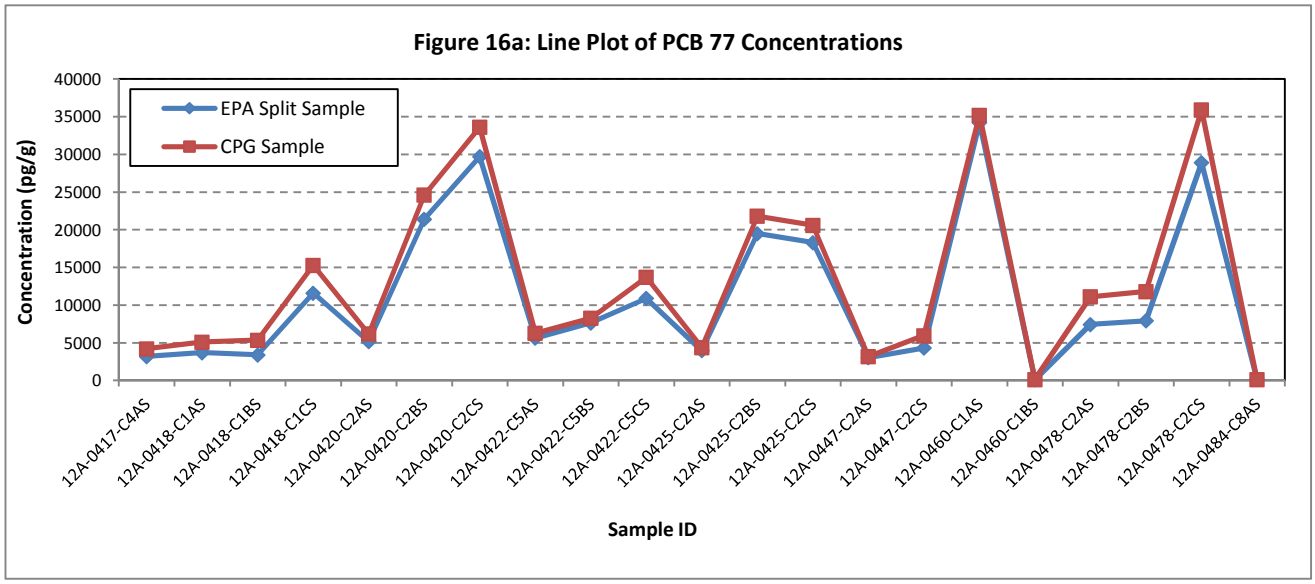
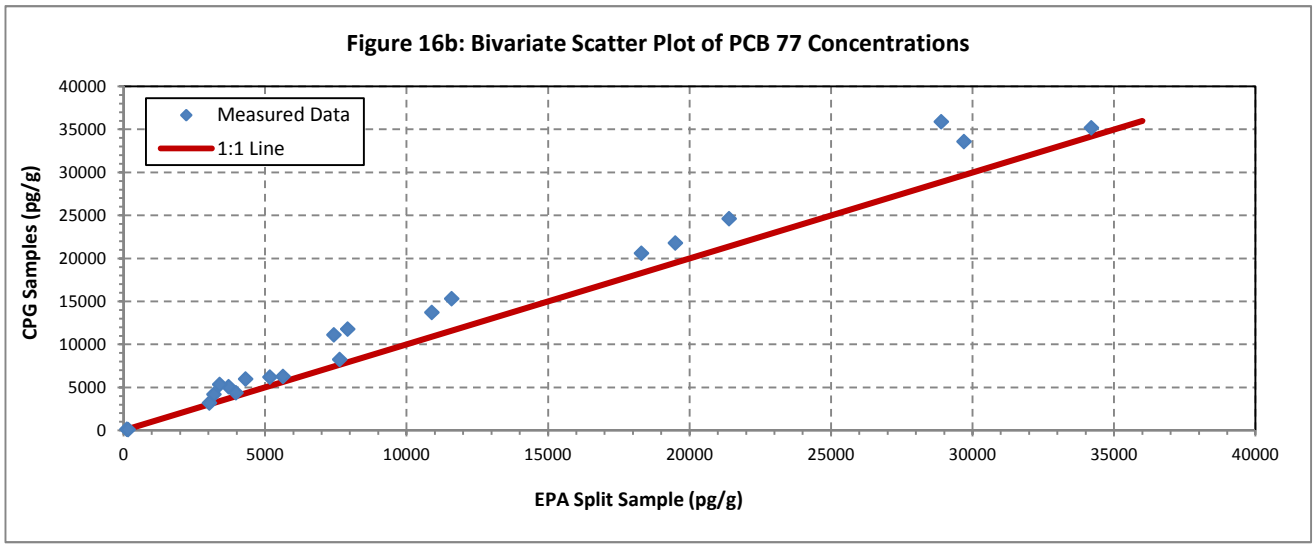
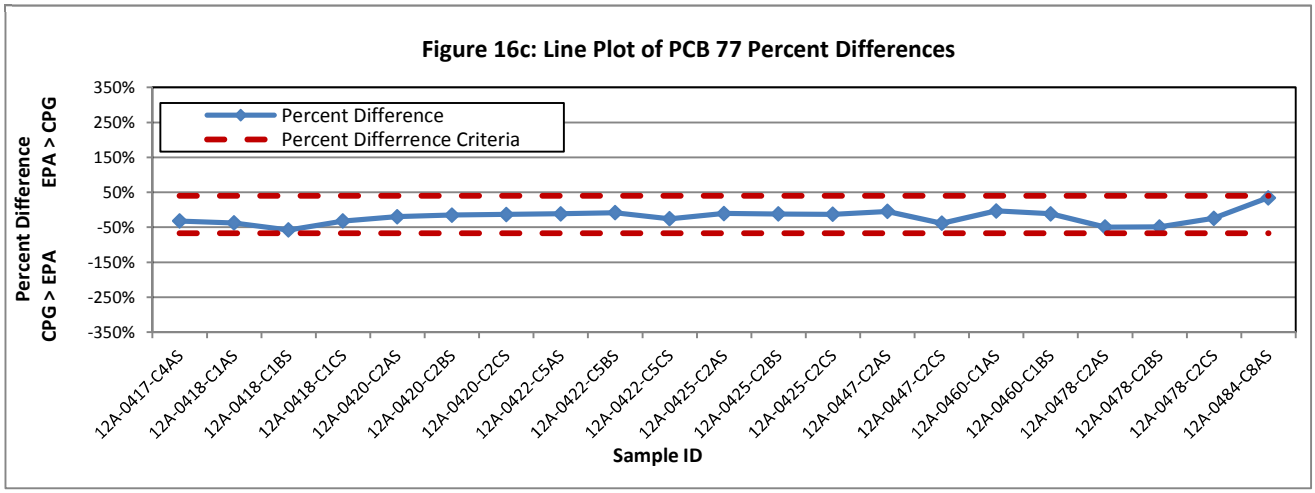
Statistical Plot of Sediment 2,4'-Dichlorodiphenyltrichloroethane (2,4'-DDT) Concentrations

Figure 15







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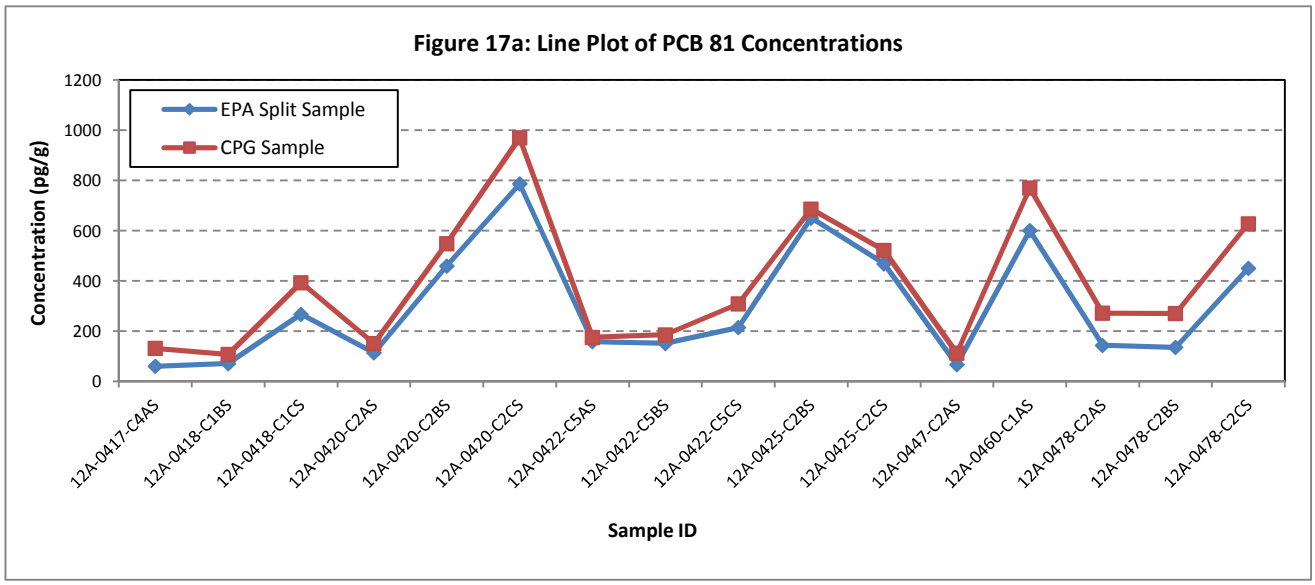
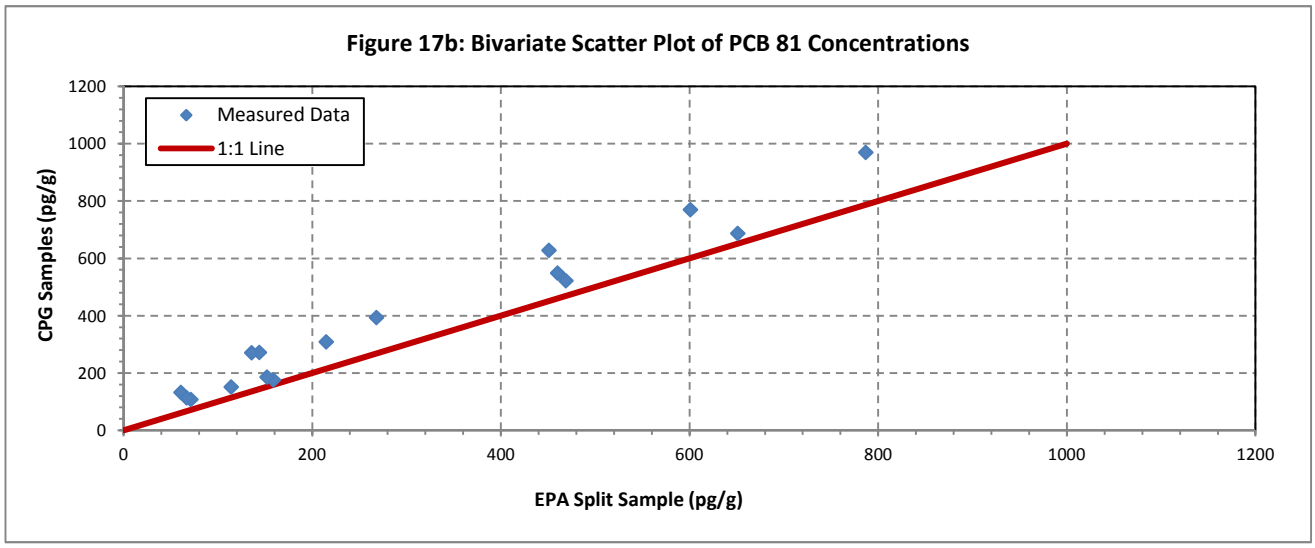
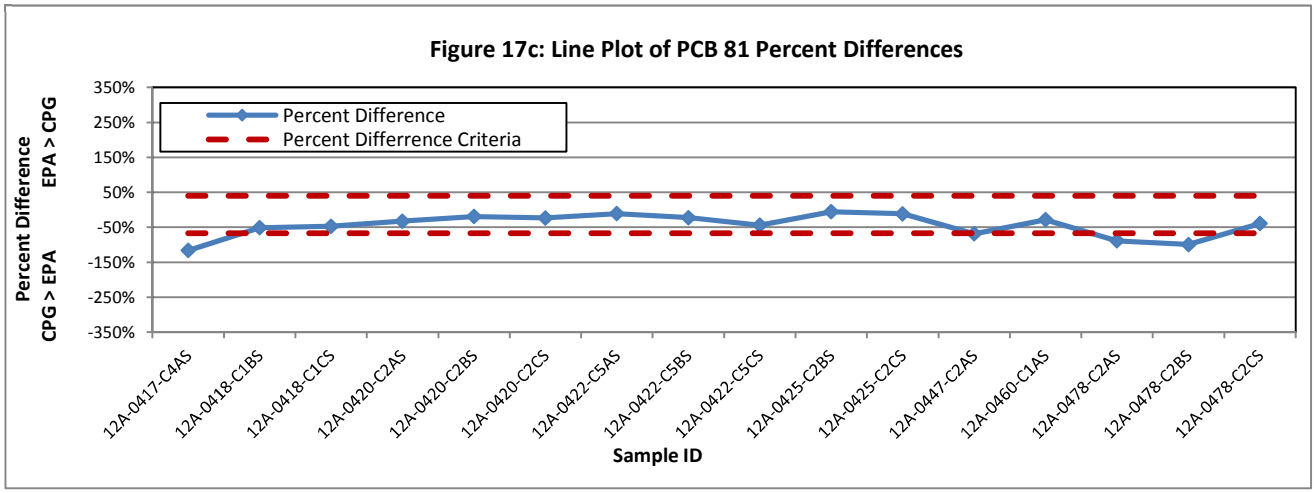
Statistical Plot of Sediment 3,3',4,4'-Tetrachlorobiphenyl (PCB 77) Concentrations

Figure 16







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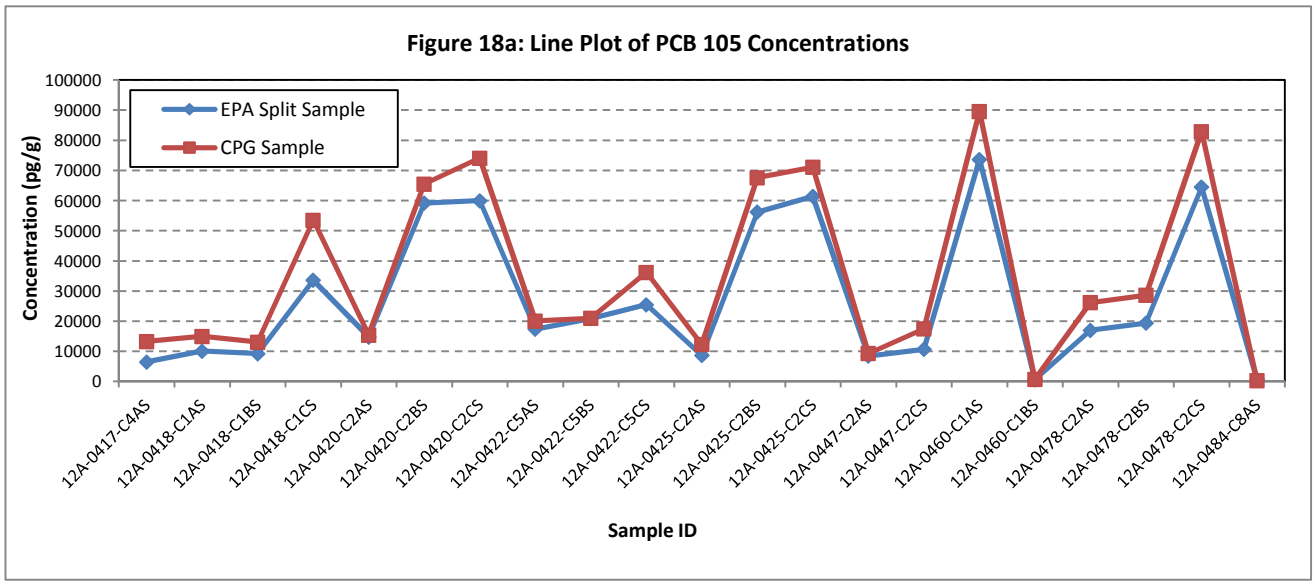
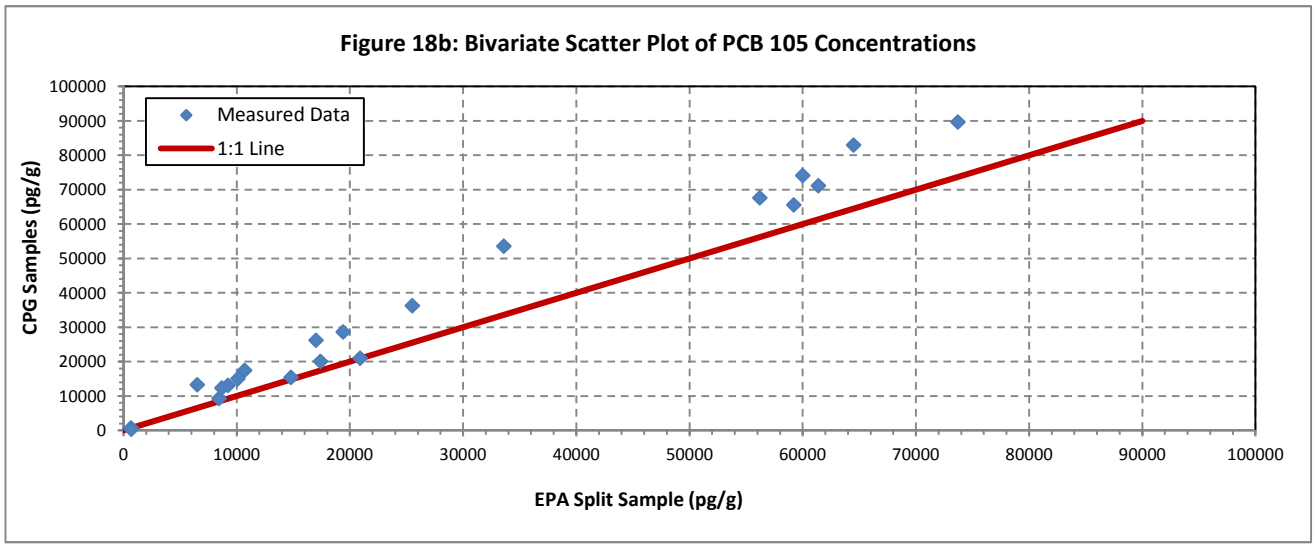
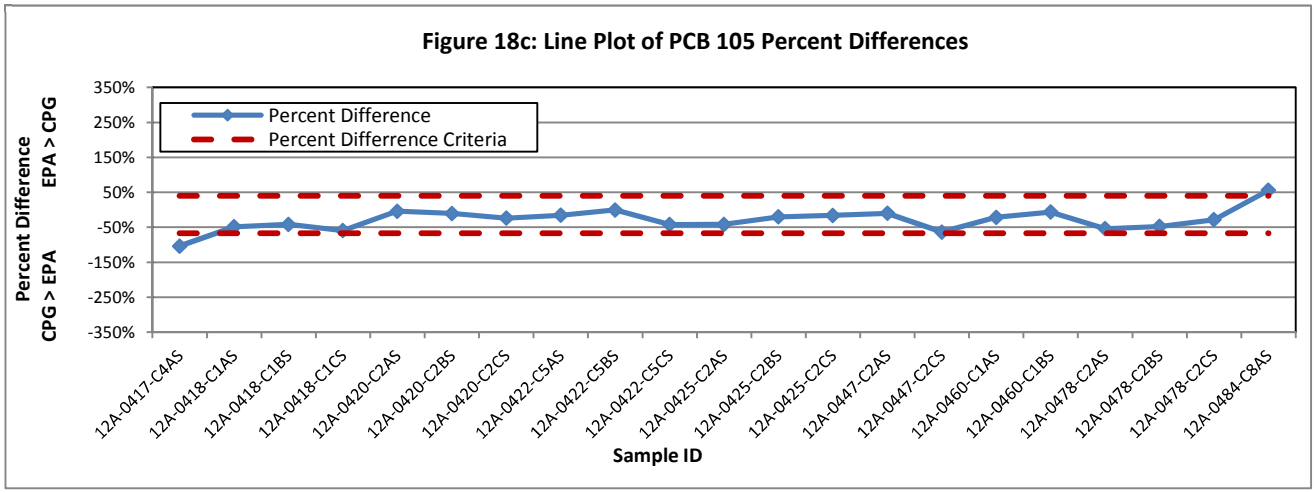
Statistical Plot of Sediment 3,4,4',5-Tetrachlorobiphenyl (PCB 81) Concentrations

Figure 17







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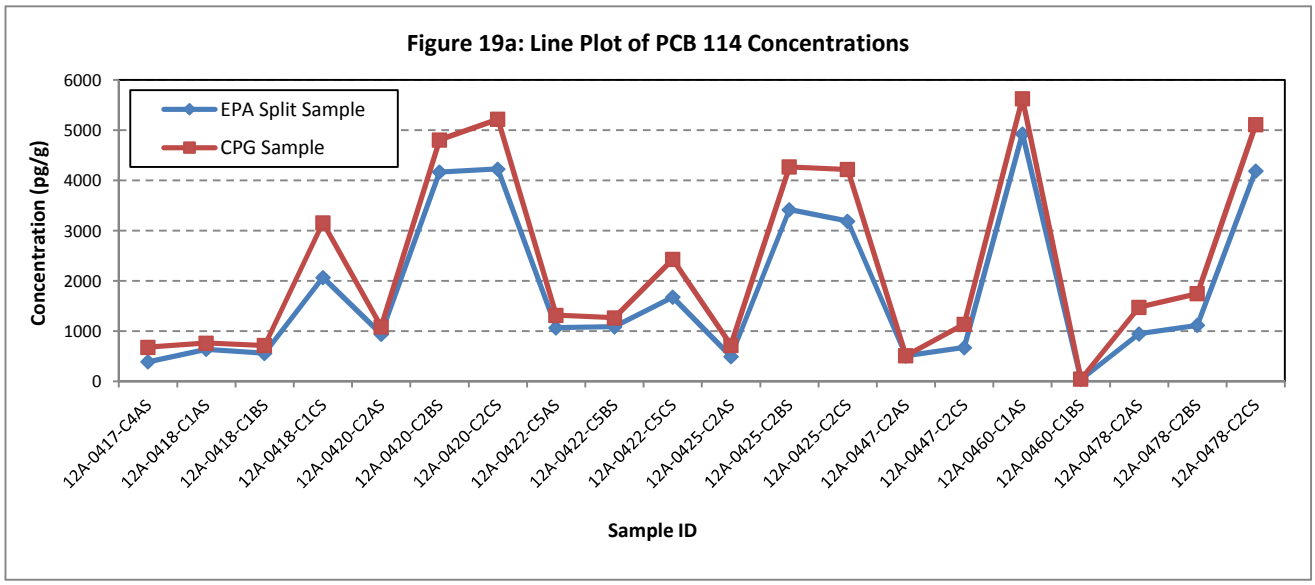
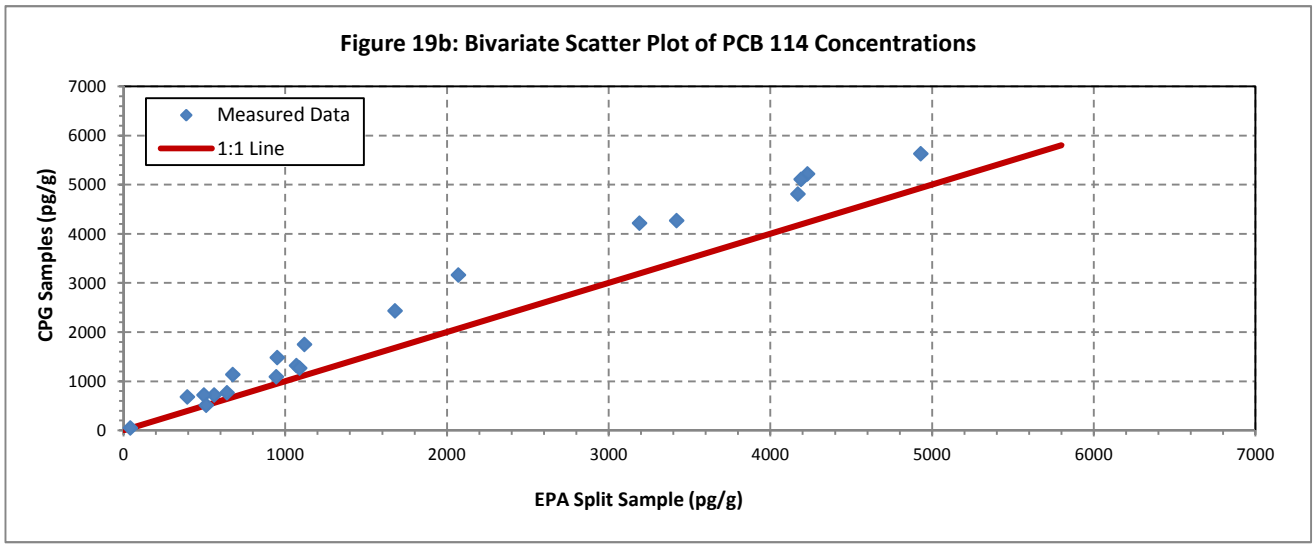
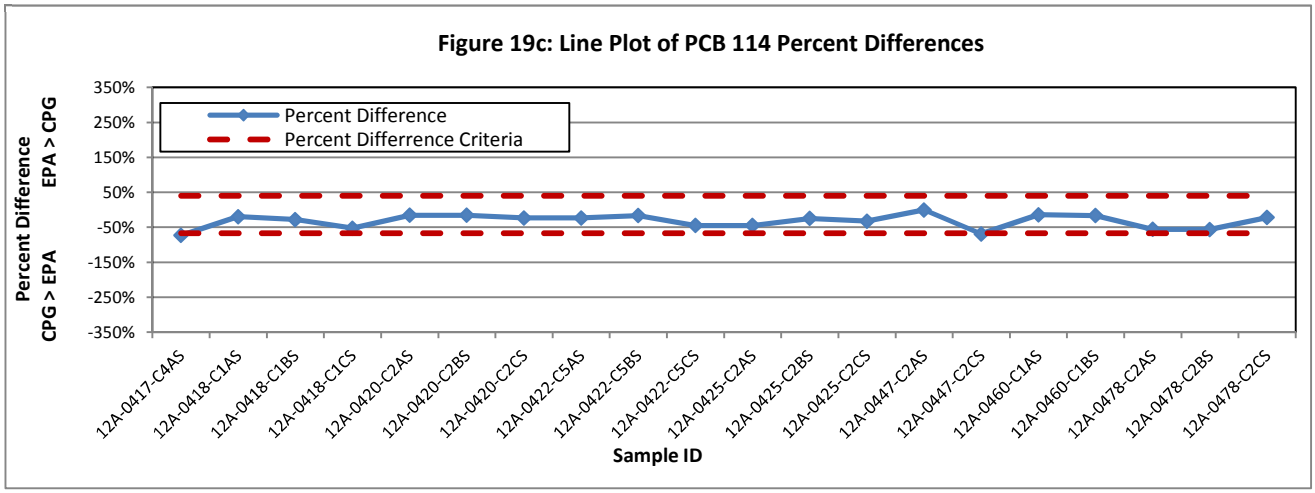
Statistical Plot of Sediment 2,3,3',4,4'-Pentachlorobiphenyl (PCB 105) Concentrations

Figure 18







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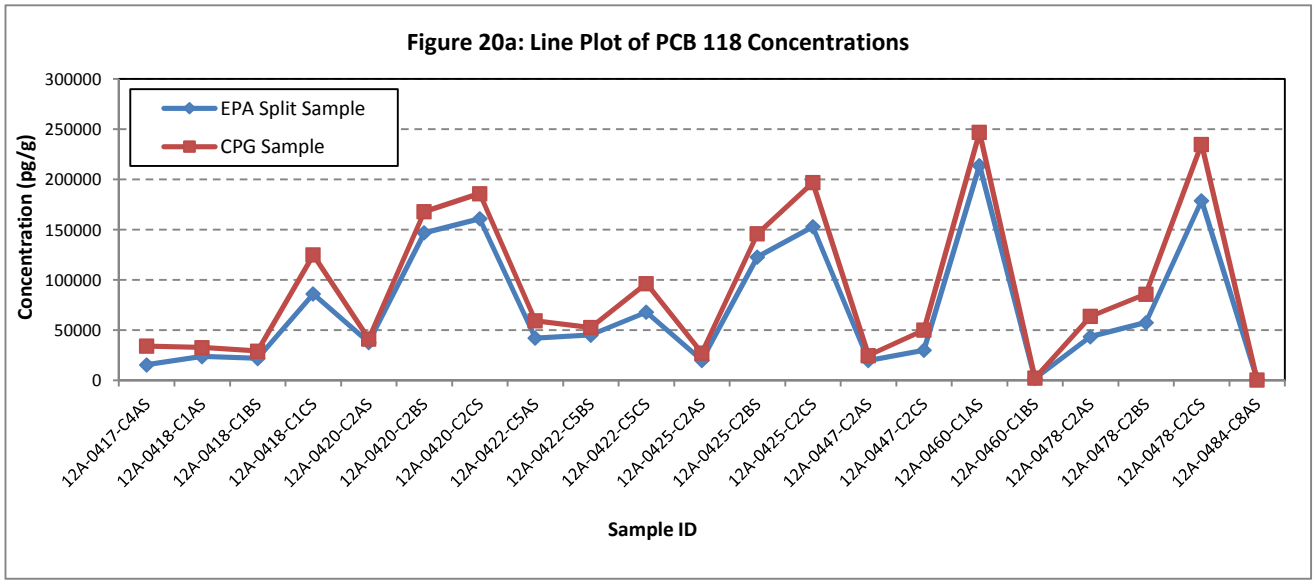
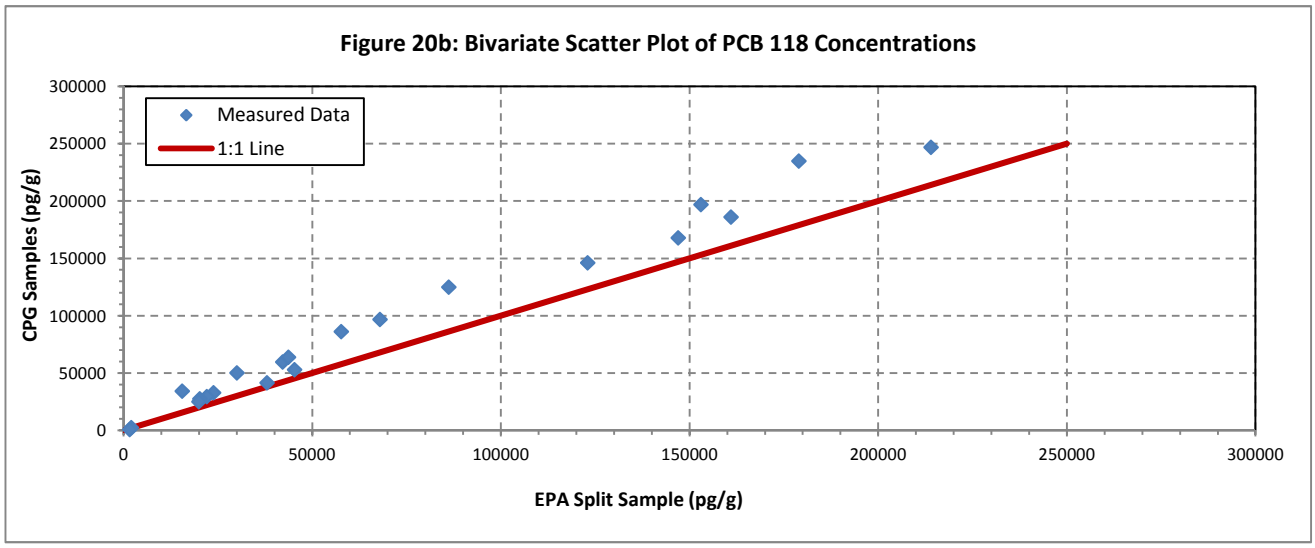
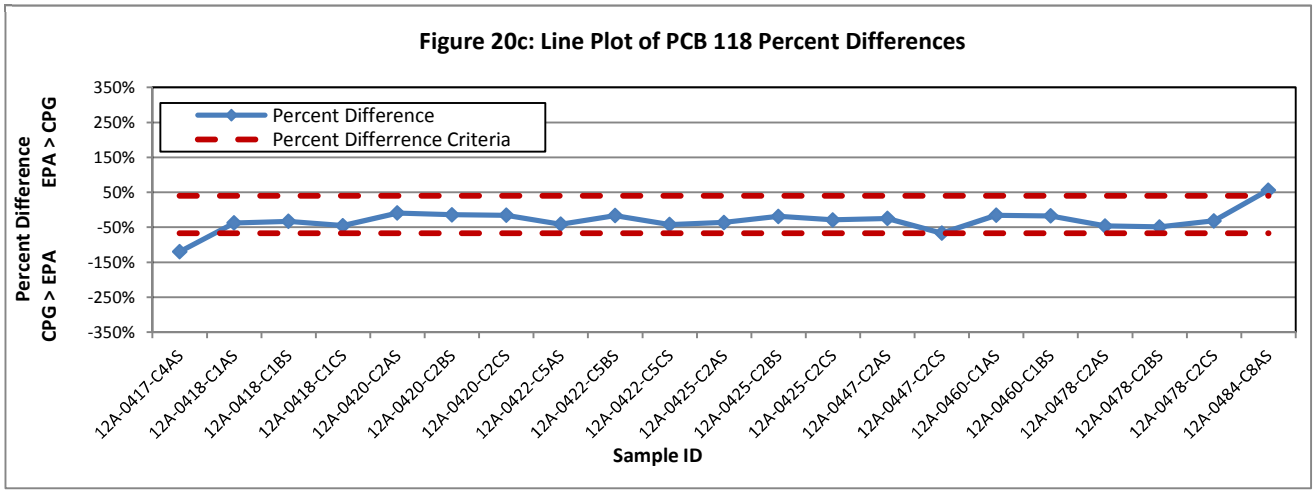
Statistical Plot of Sediment 2,3,4,4',5-Pentachlorobiphenyl (PCB 114) Concentrations

Figure 19







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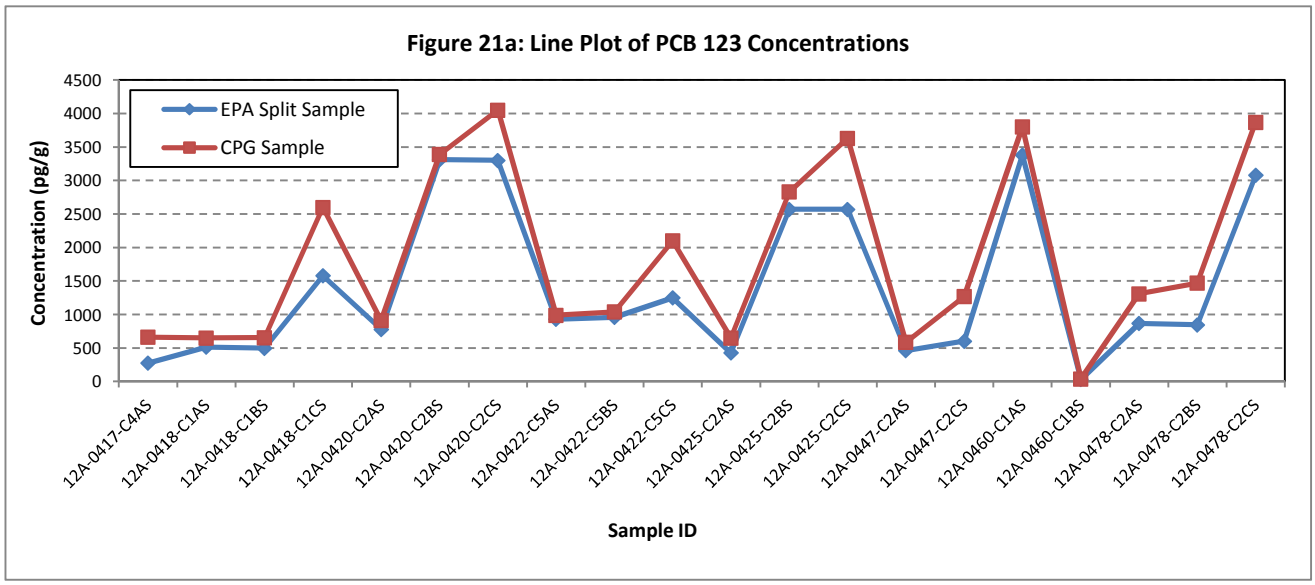
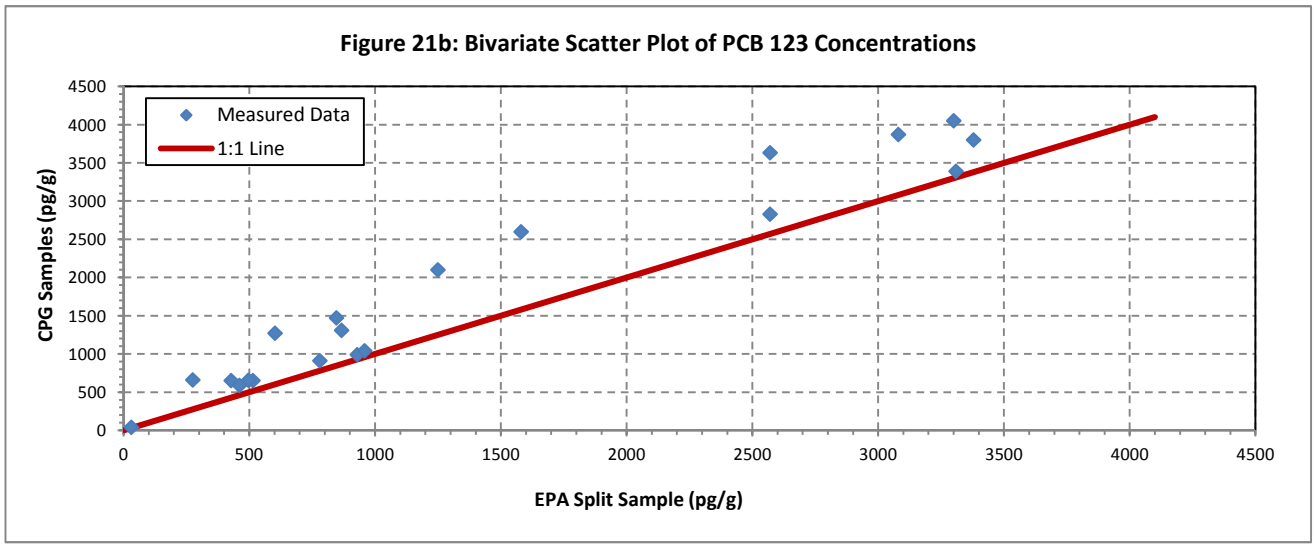
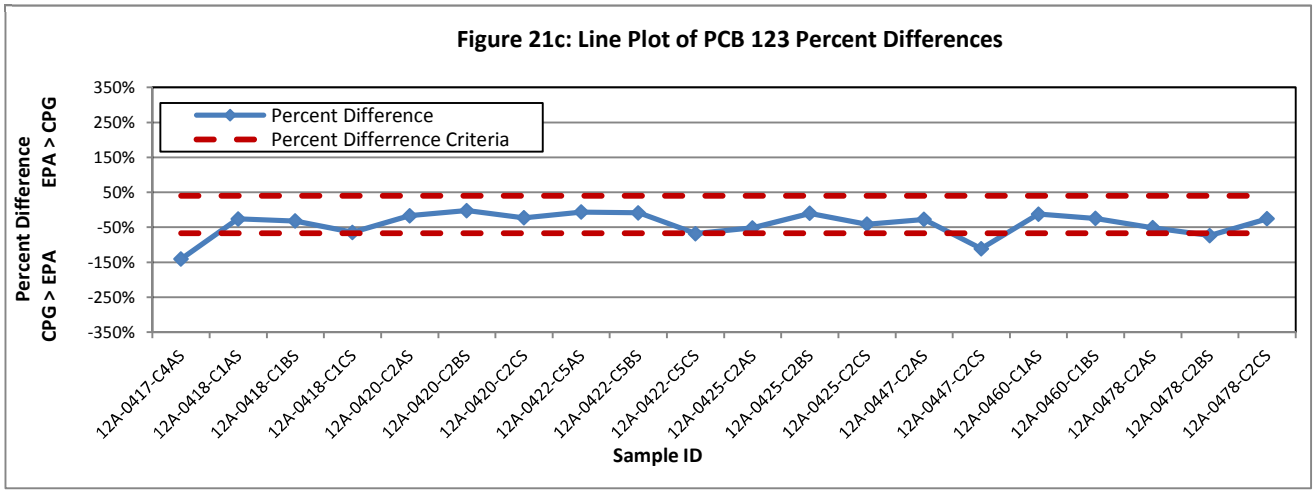
Statistical Plot of Sediment 2,3',4,4',5-Pentachlorobiphenyl (PCB 118) Concentrations

Figure 20







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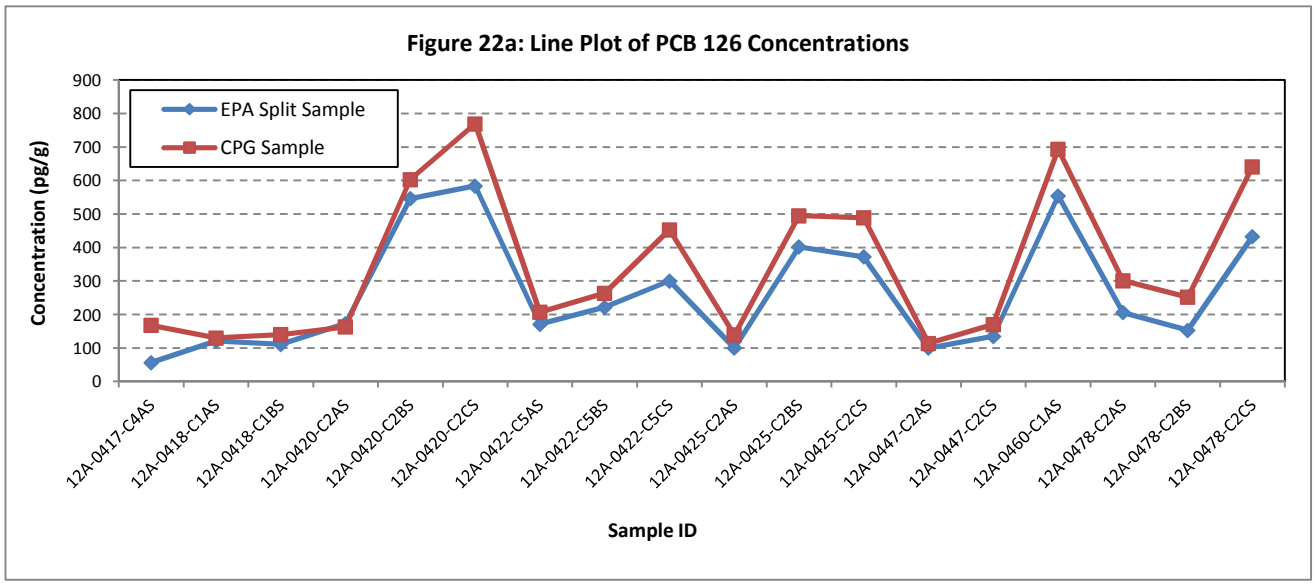
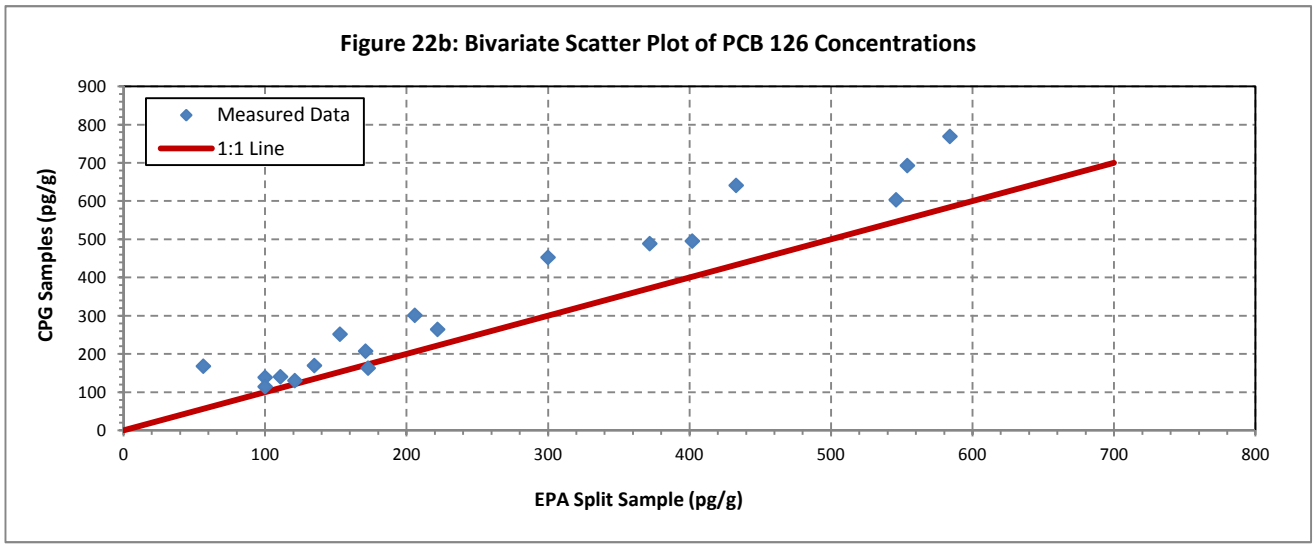
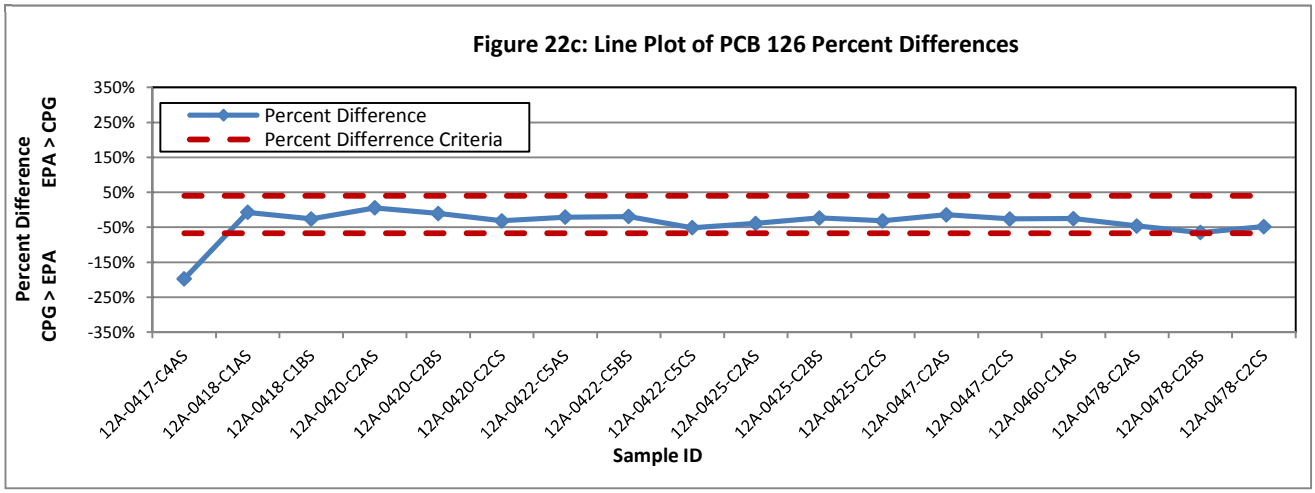
Statistical Plot of Sediment 2,3',4,4',5'-Pentachlorobiphenyl (PCB 123) Concentrations

Figure 21







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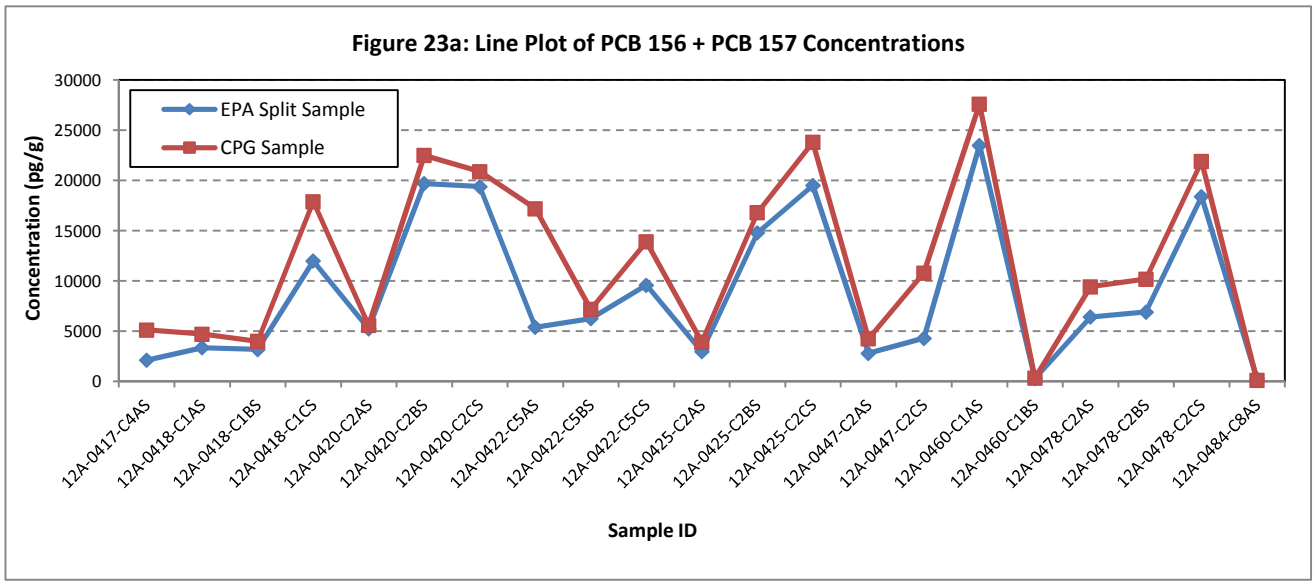
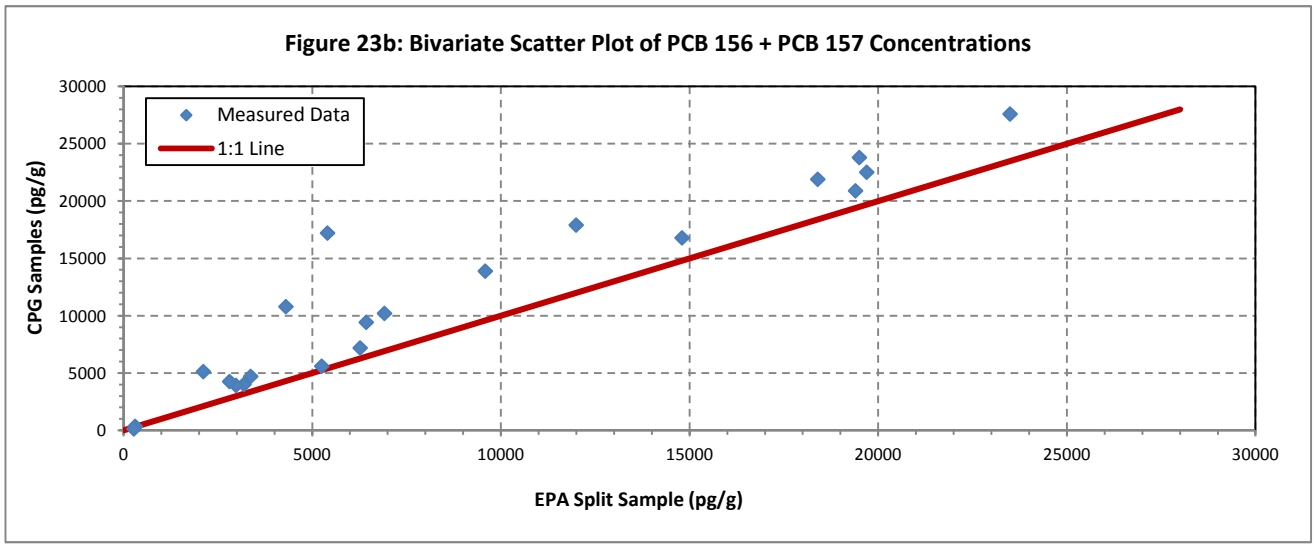
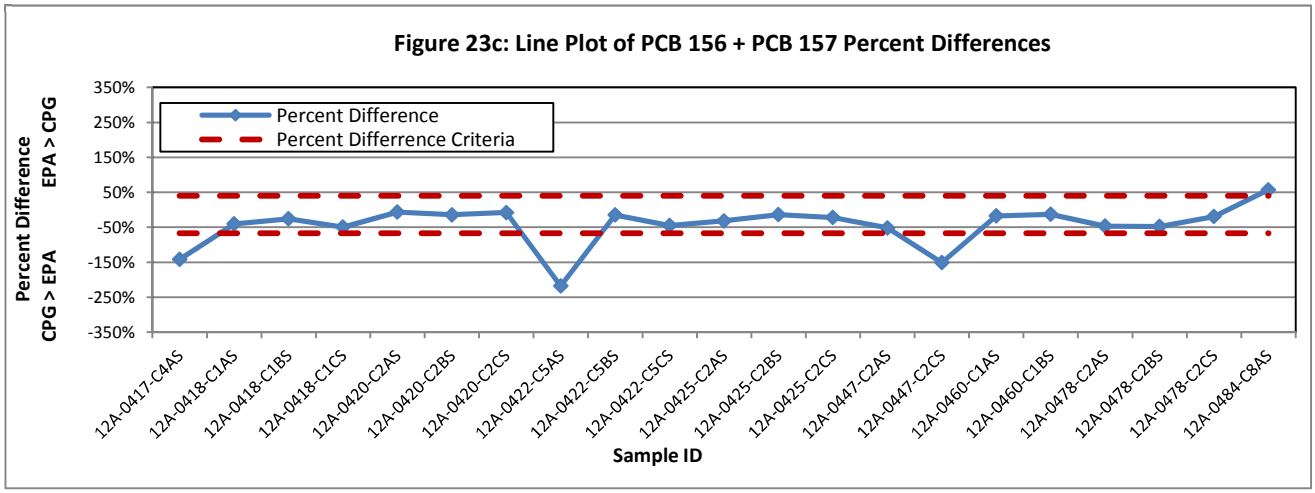
Statistical Plot of Sediment 3,3',4,4',5-Pentachlorobiphenyl (PCB 126) Concentrations

Figure 22







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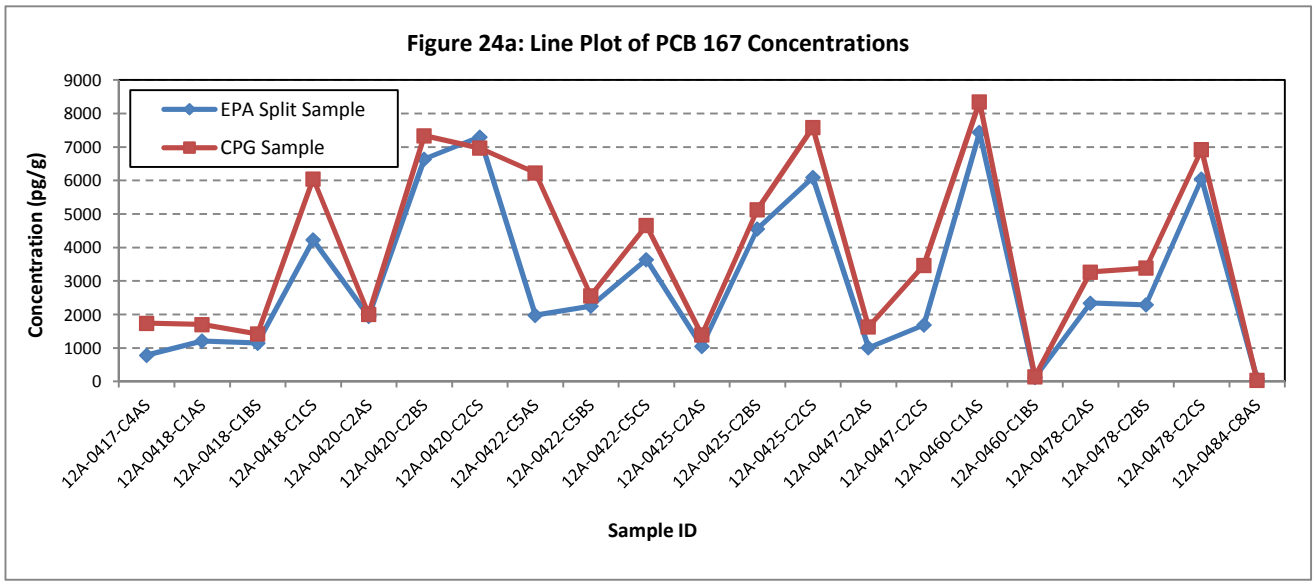
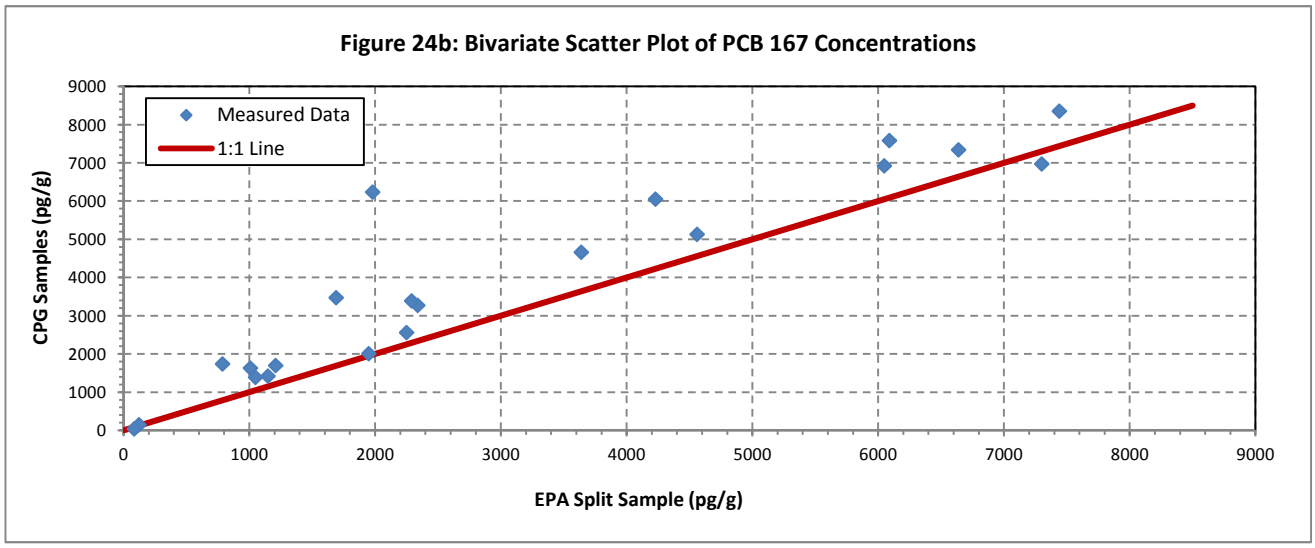
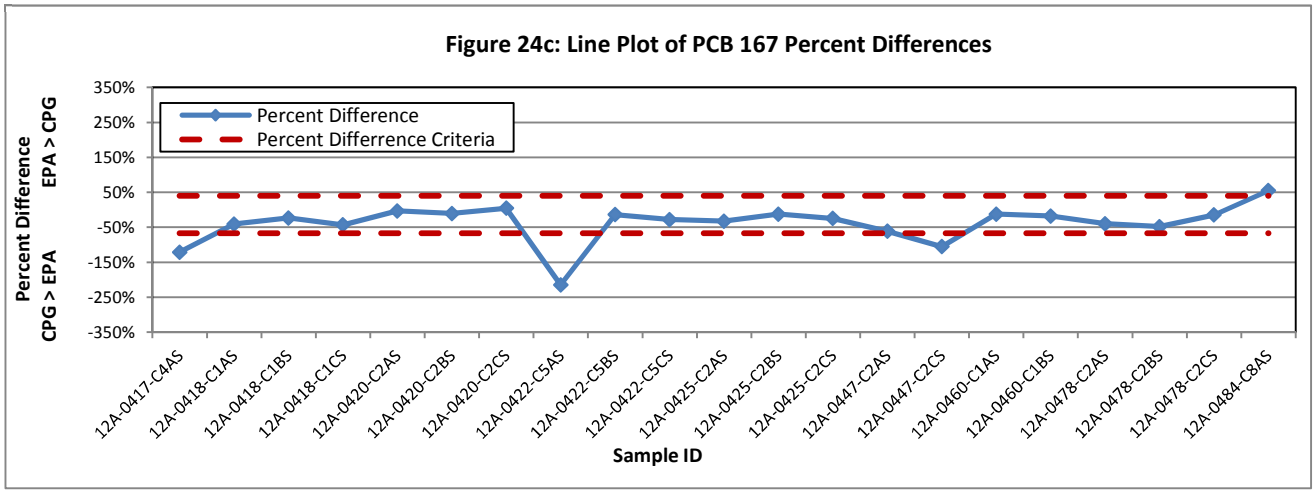
Statistical Plot of Sediment 2,3,3',4,4',5-Hexachlorobiphenyl + 2,3,3',4,4',5'-Hexachlorobiphenyl (PCB 156 + PCB 157) Concentrations

Figure 23







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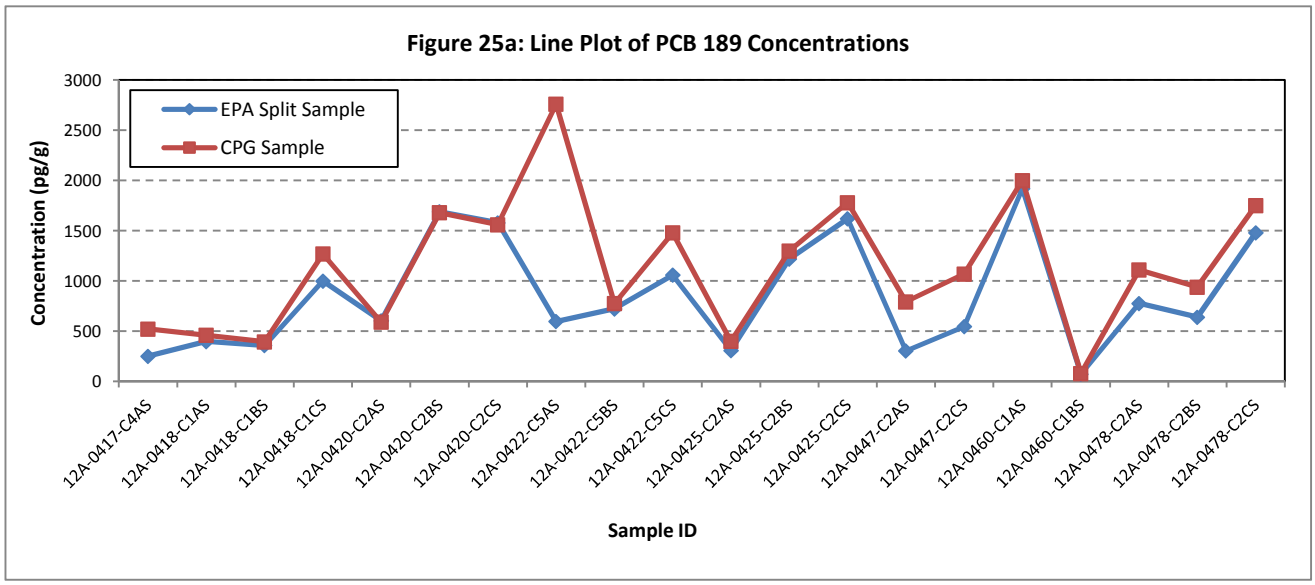
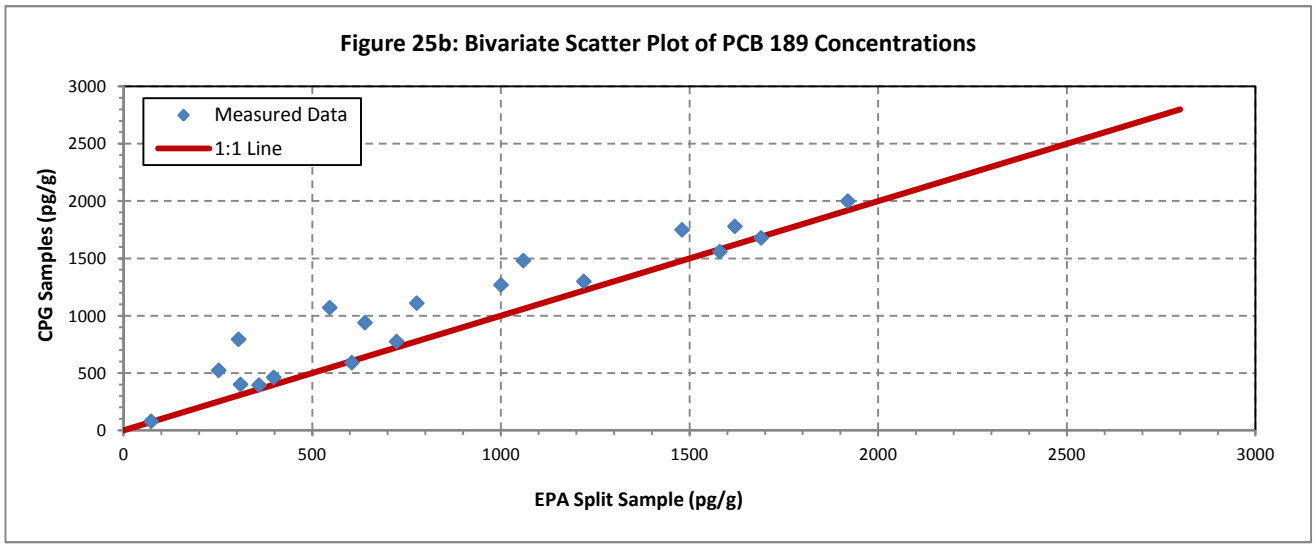
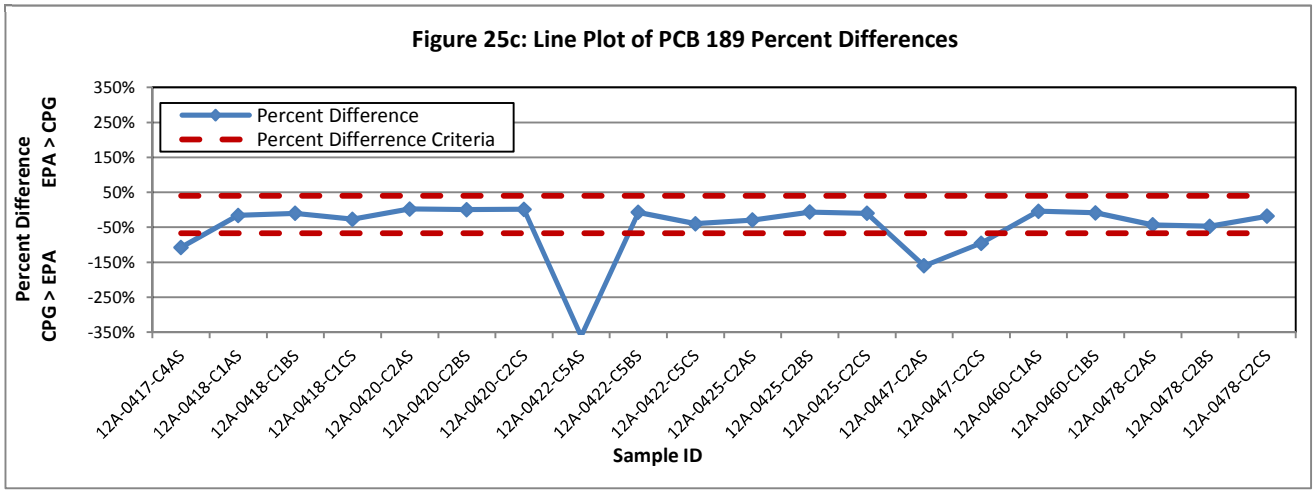
Statistical Plot of Sediment 2,3',4,4',5,5'-Hexachlorobiphenyl (PCB 167) Concentrations

Figure 24







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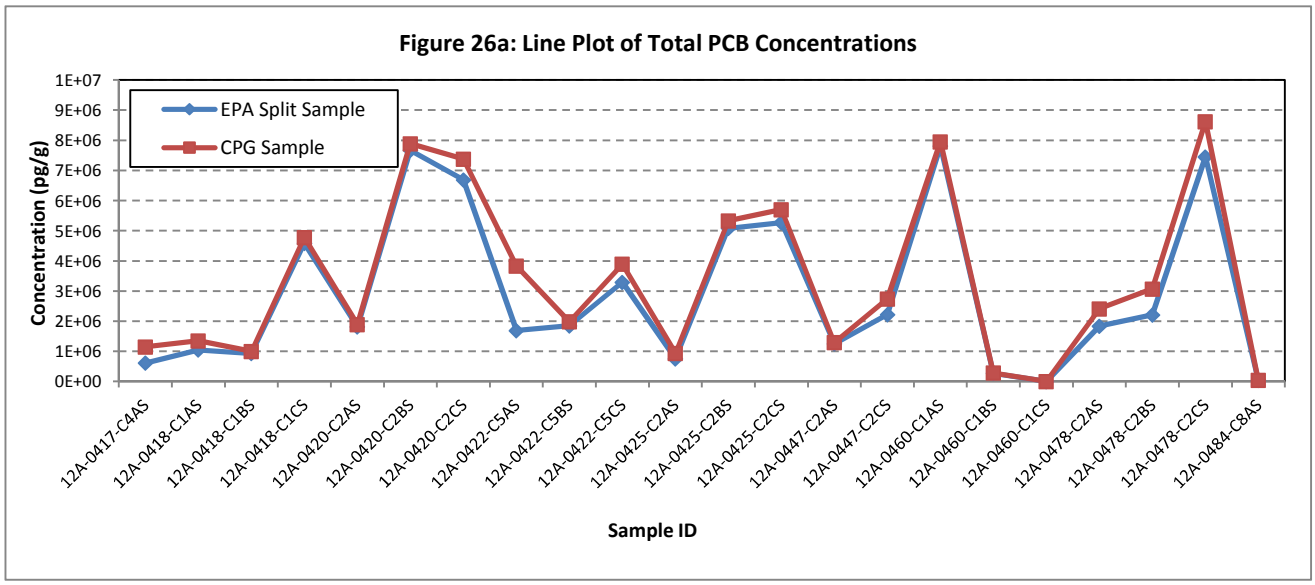
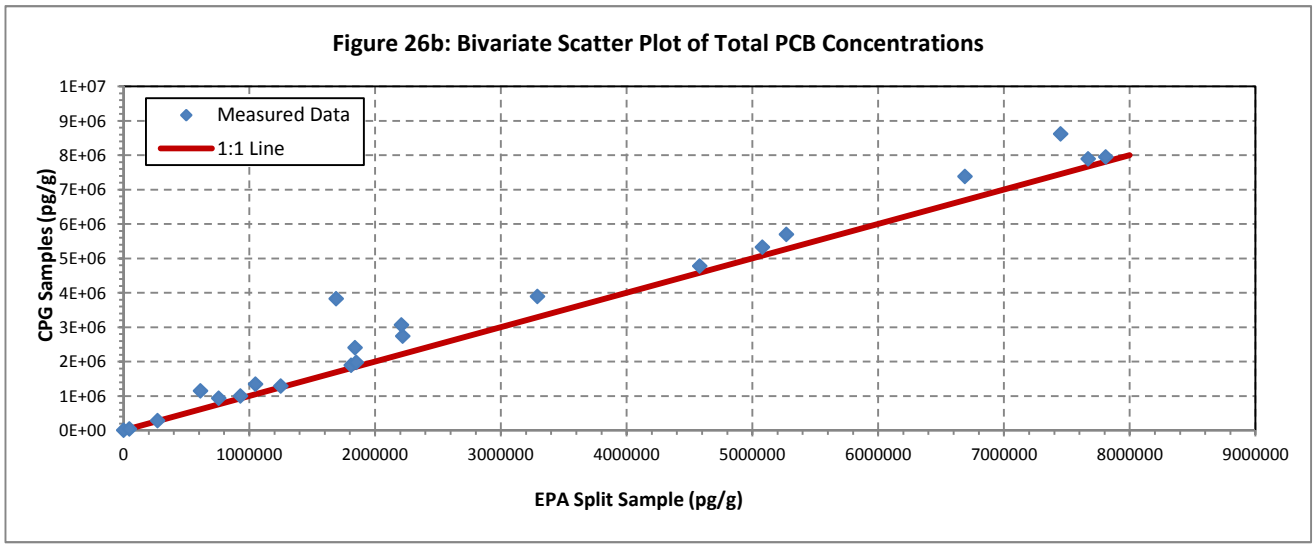
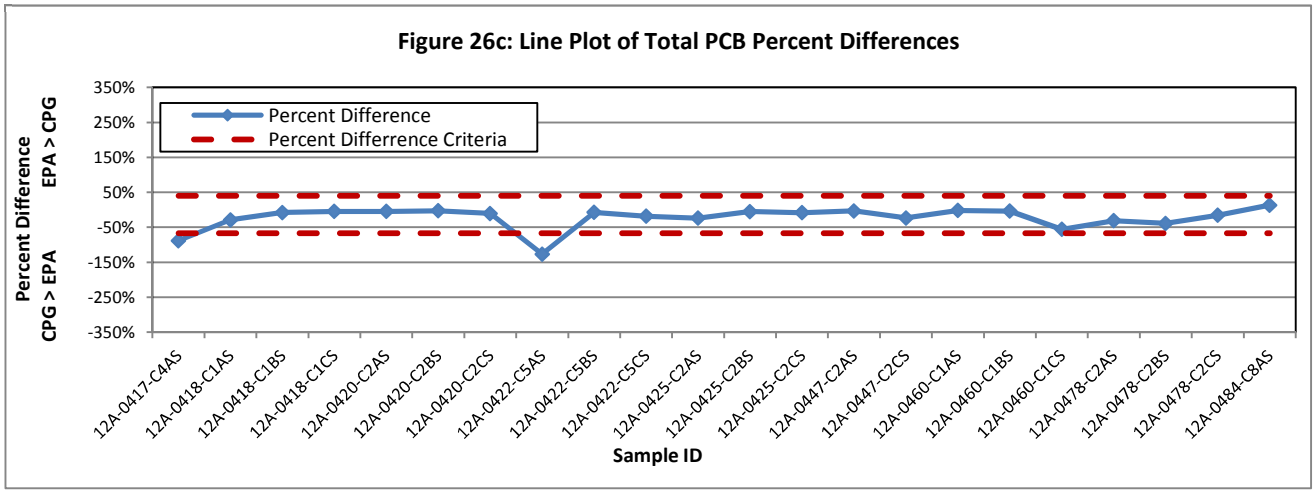
Statistical Plot of Sediment 2,3,3',4,4',5,5'-Heptachlorobiphenyl (PCB 189) Concentrations

Figure 25







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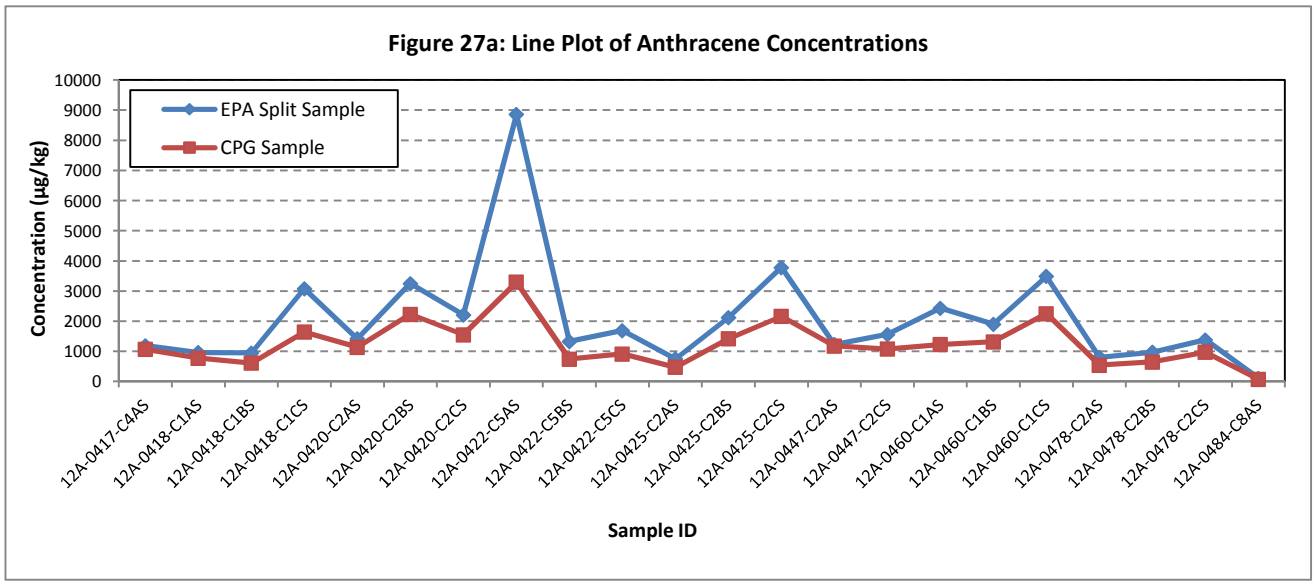
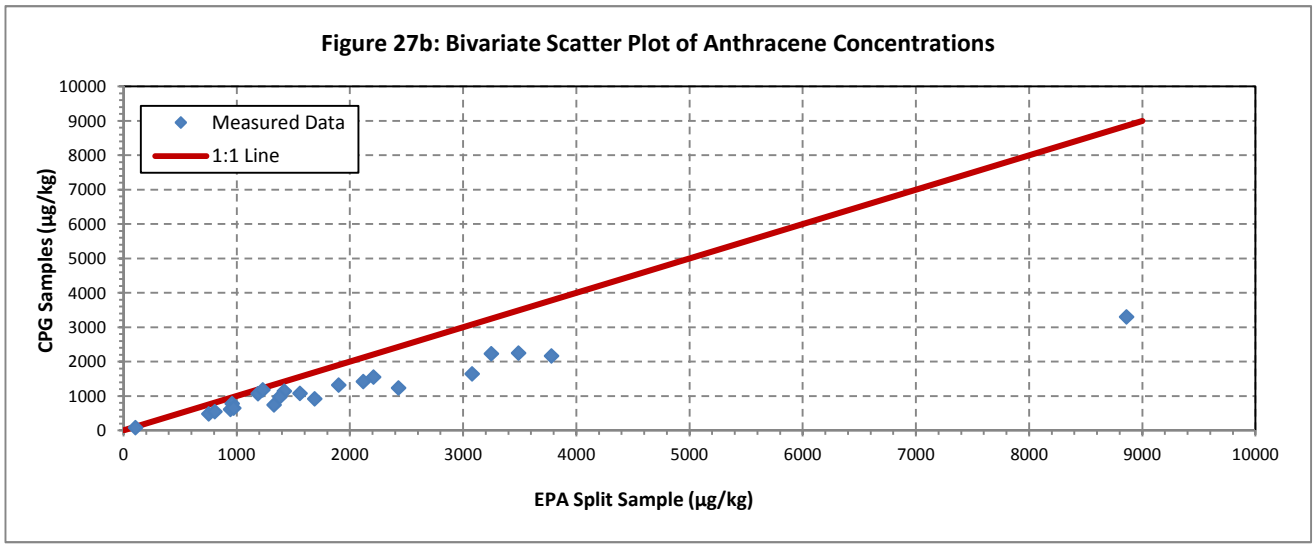
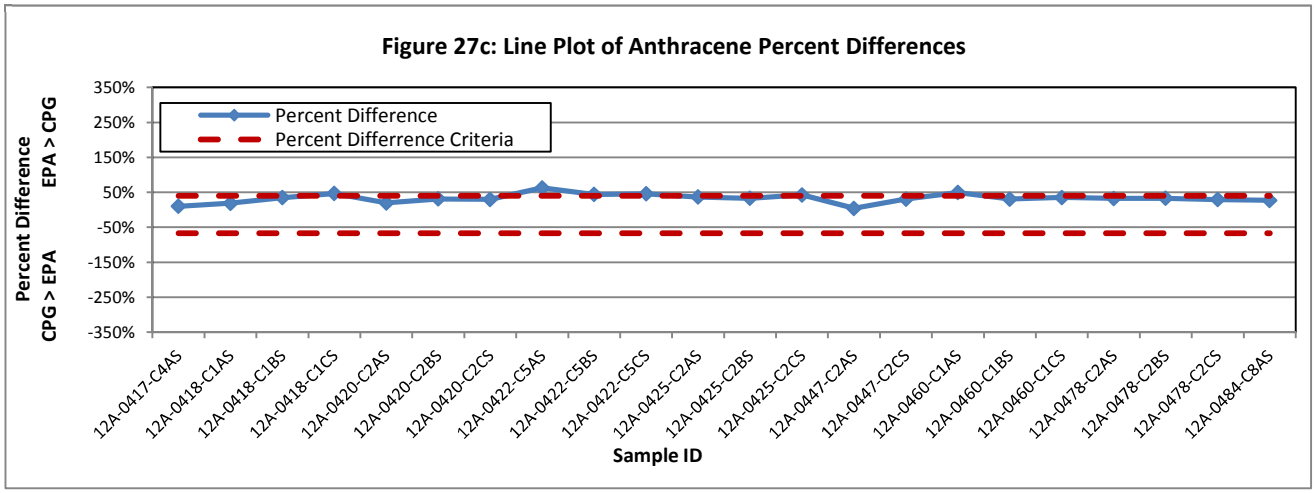
Statistical Plot of Sediment Total Polychlorinated Chlorinated Biphenyl (PCB) Concentrations

Figure 26







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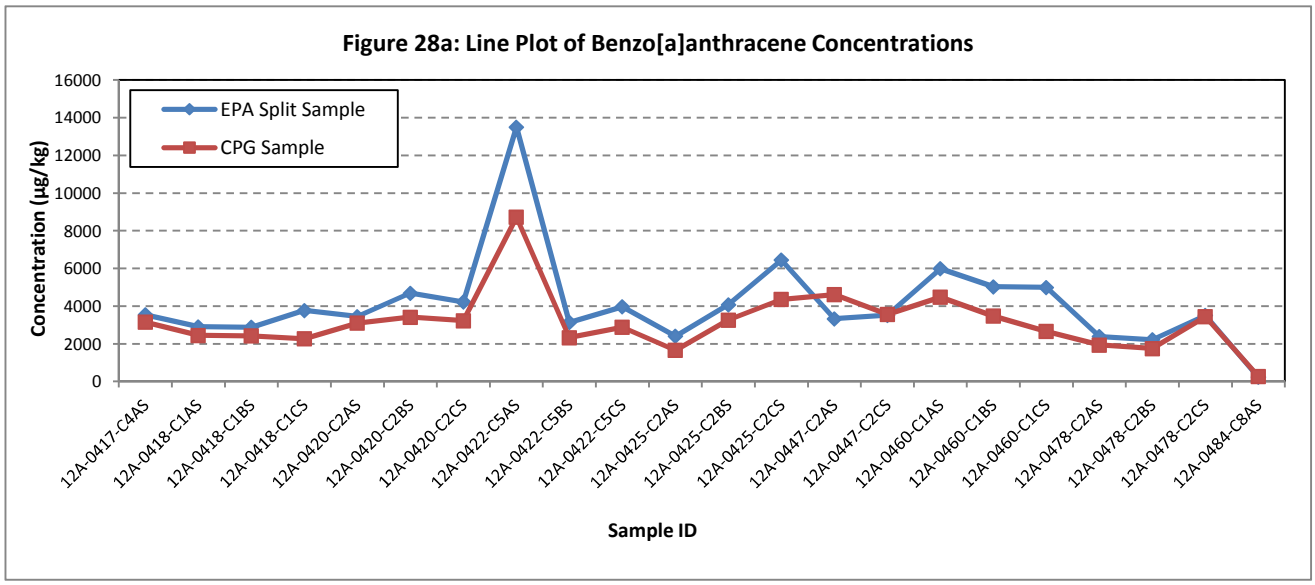
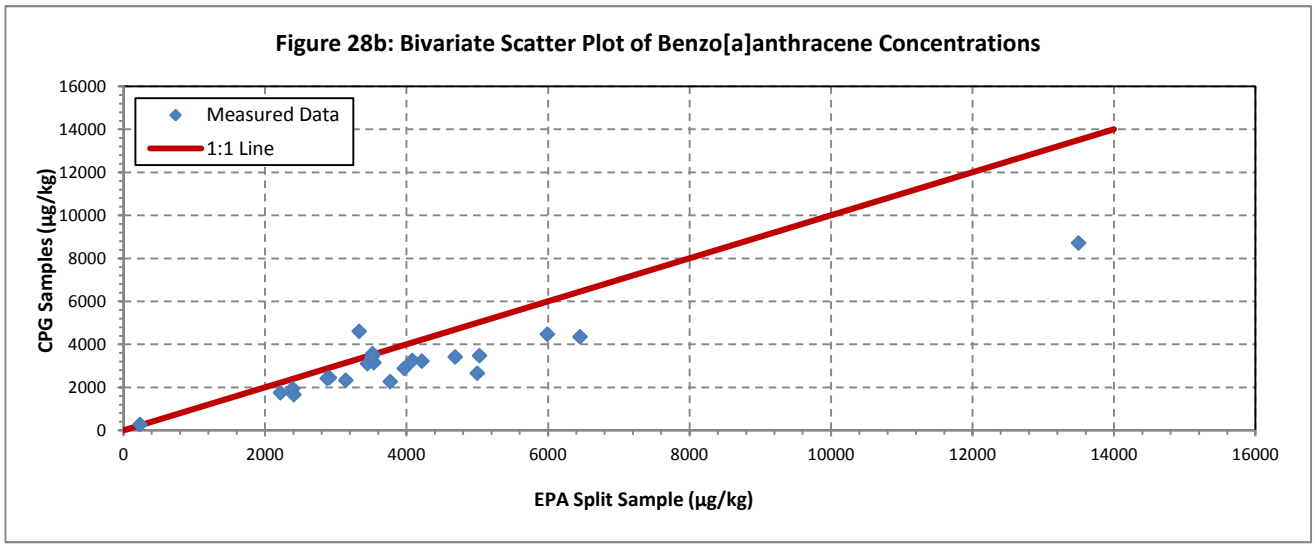
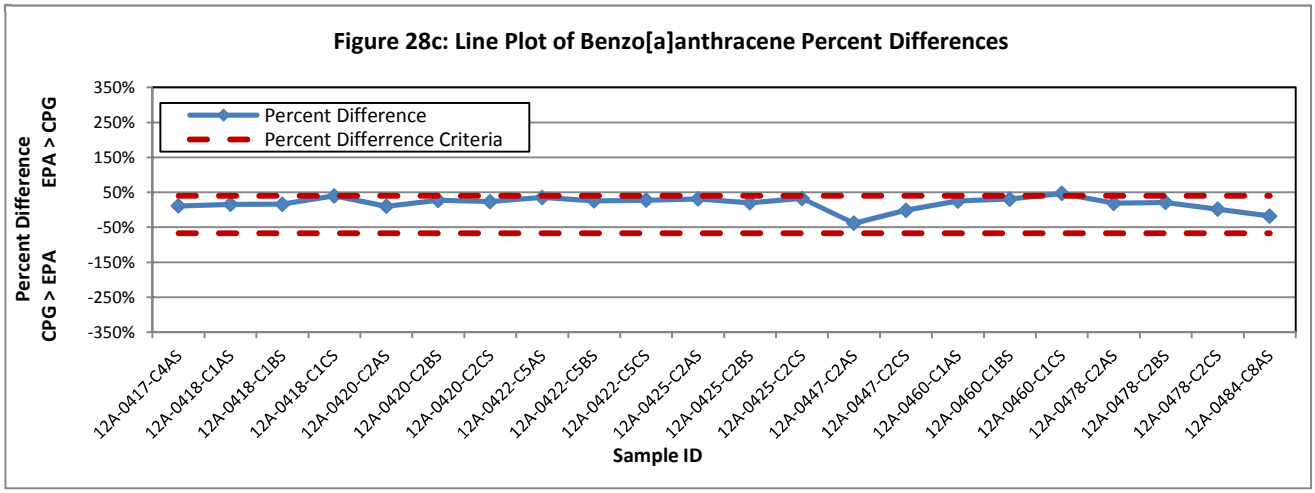
Statistical Plot of Sediment Anthracene Concentrations

Figure 27







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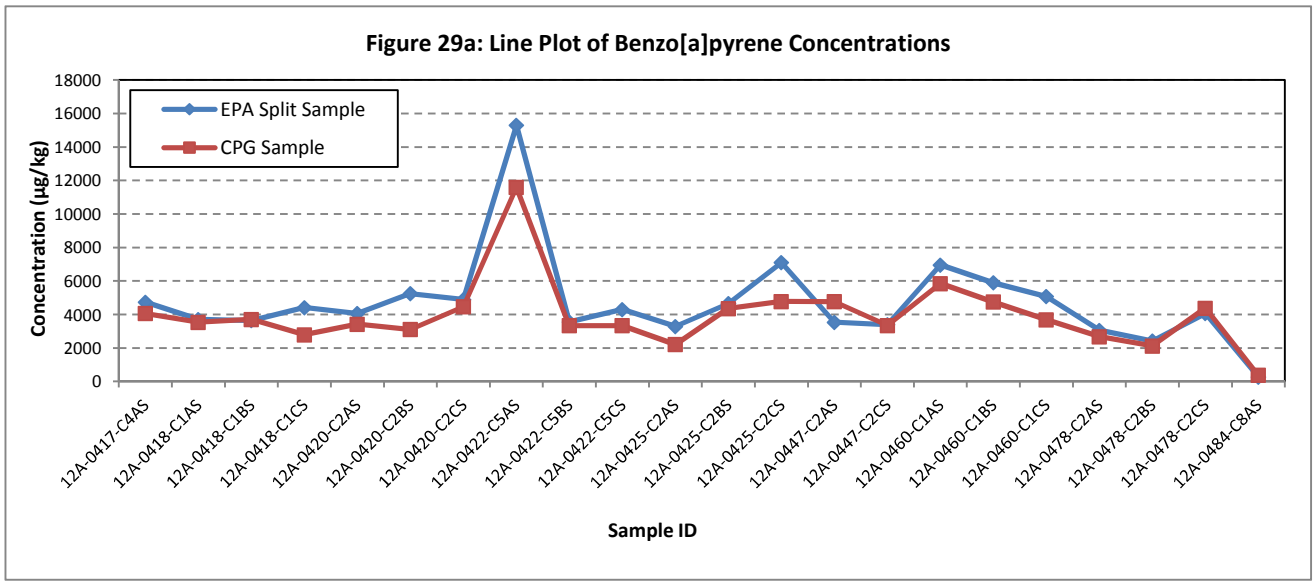
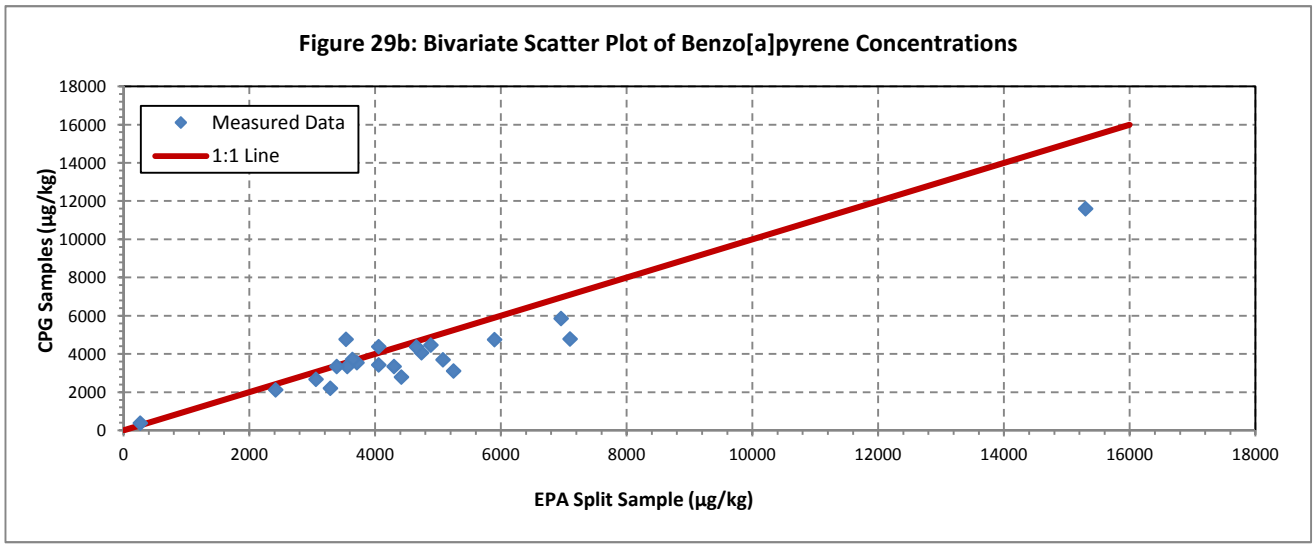
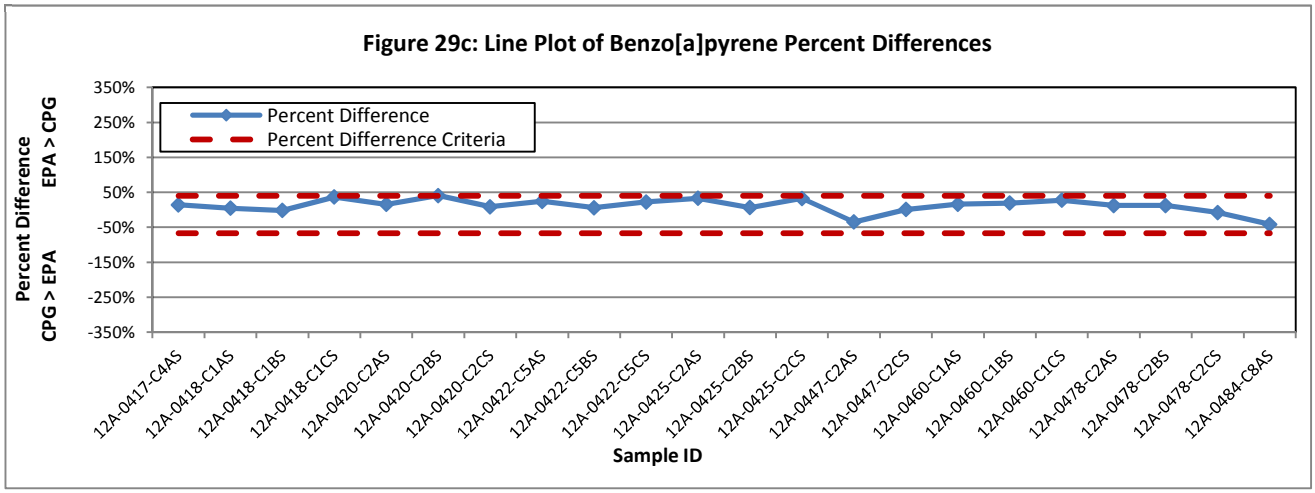
Statistical Plot of Sediment Benzo[a]anthracene Concentrations

Figure 28







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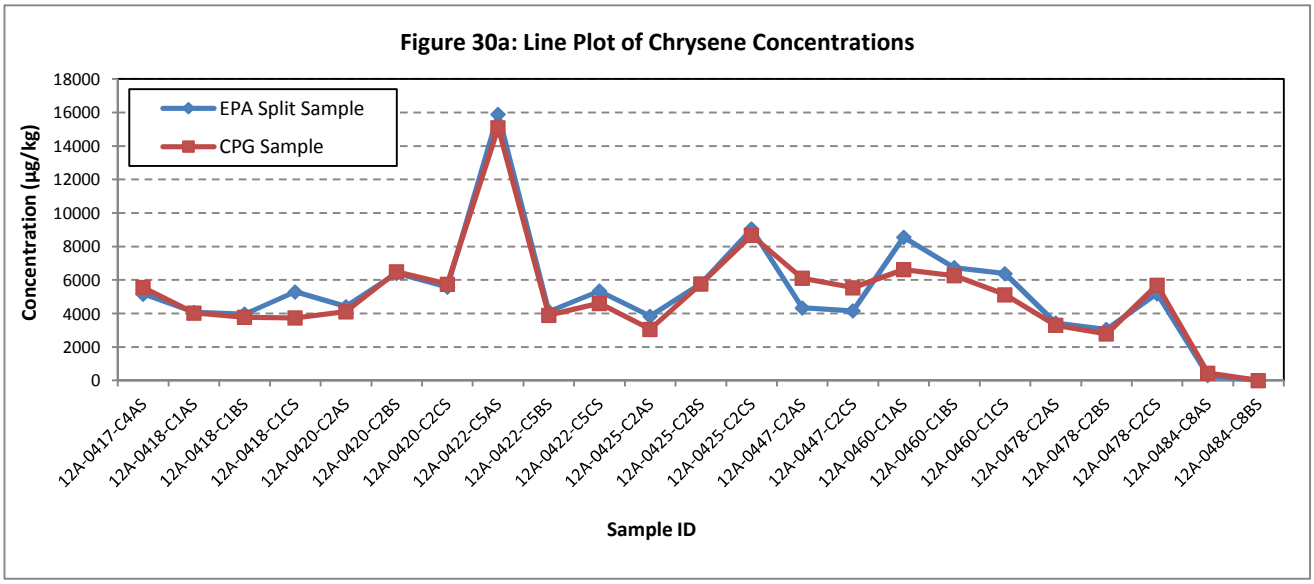
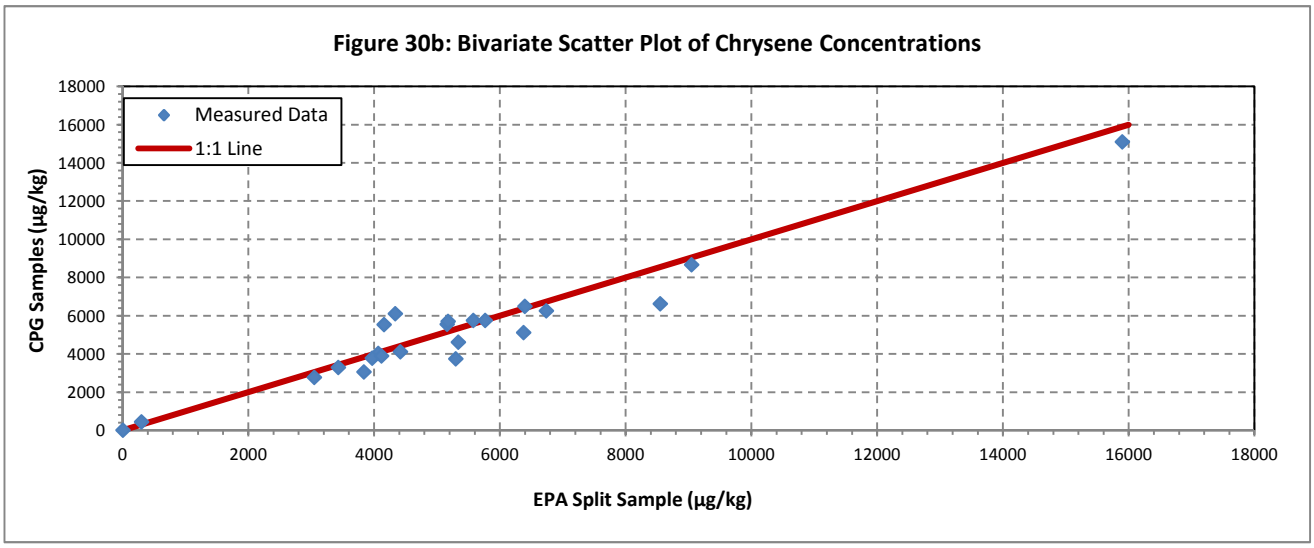
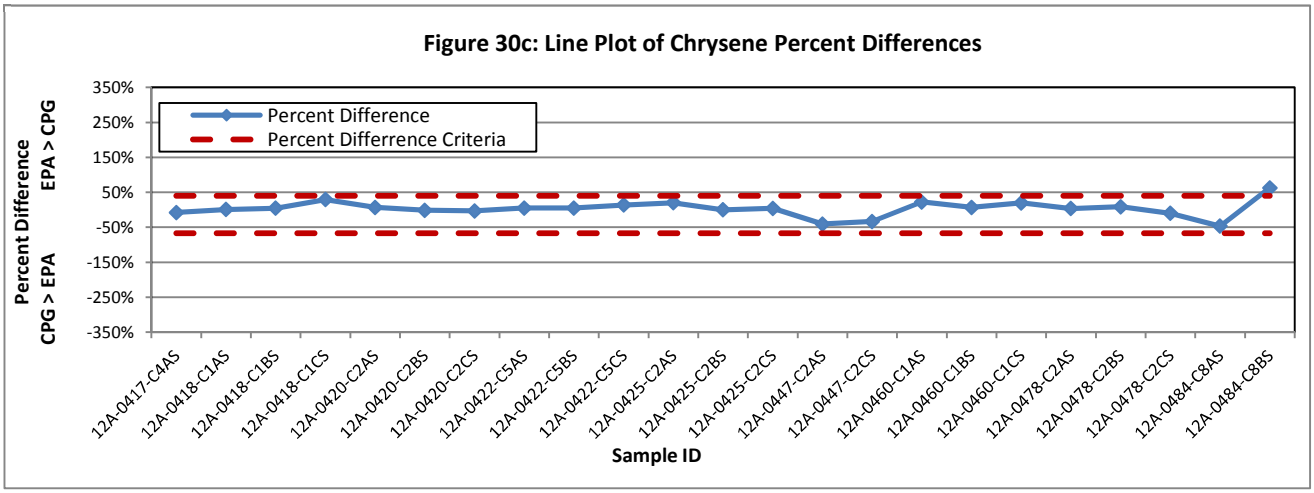
Statistical Plot of Sediment Benzo[a]pyrene Concentrations

Figure 29







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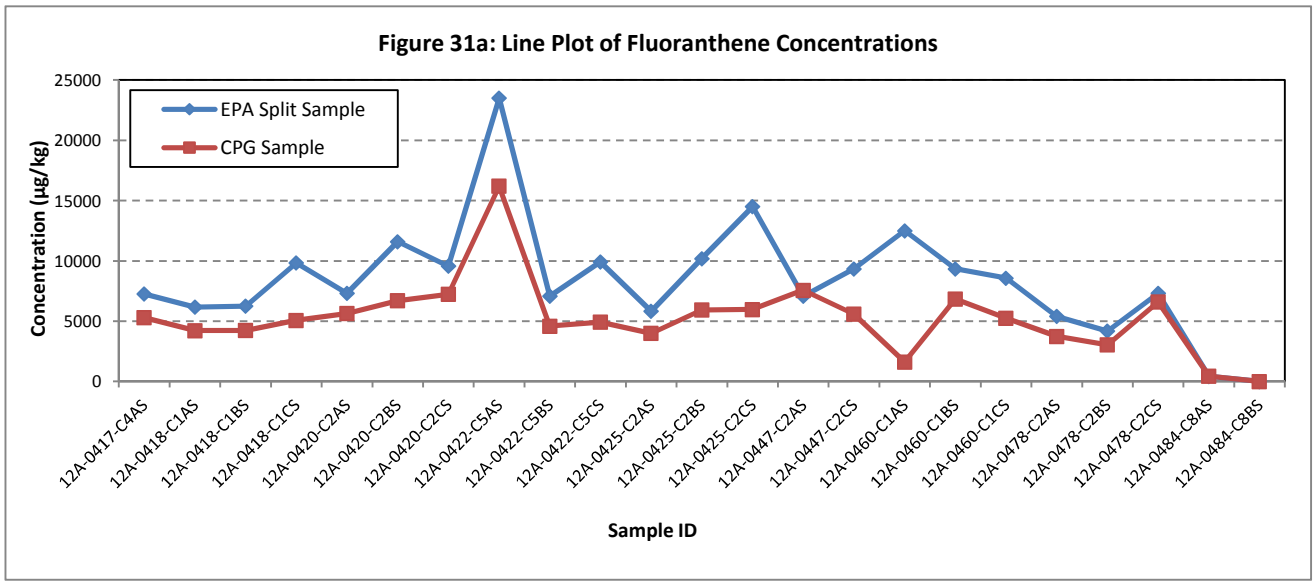
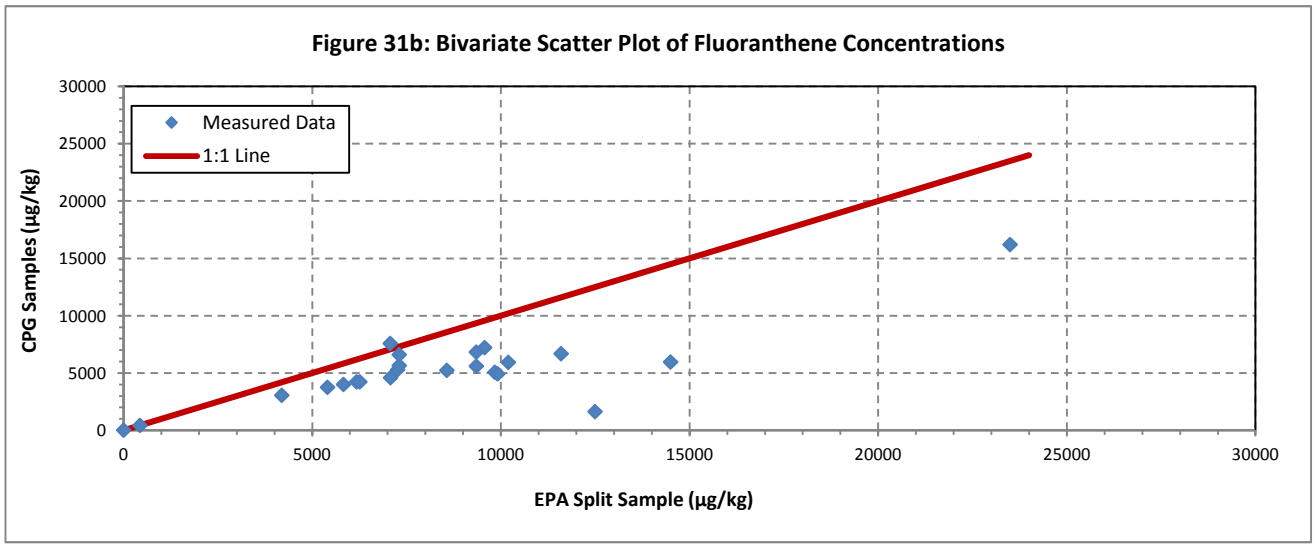
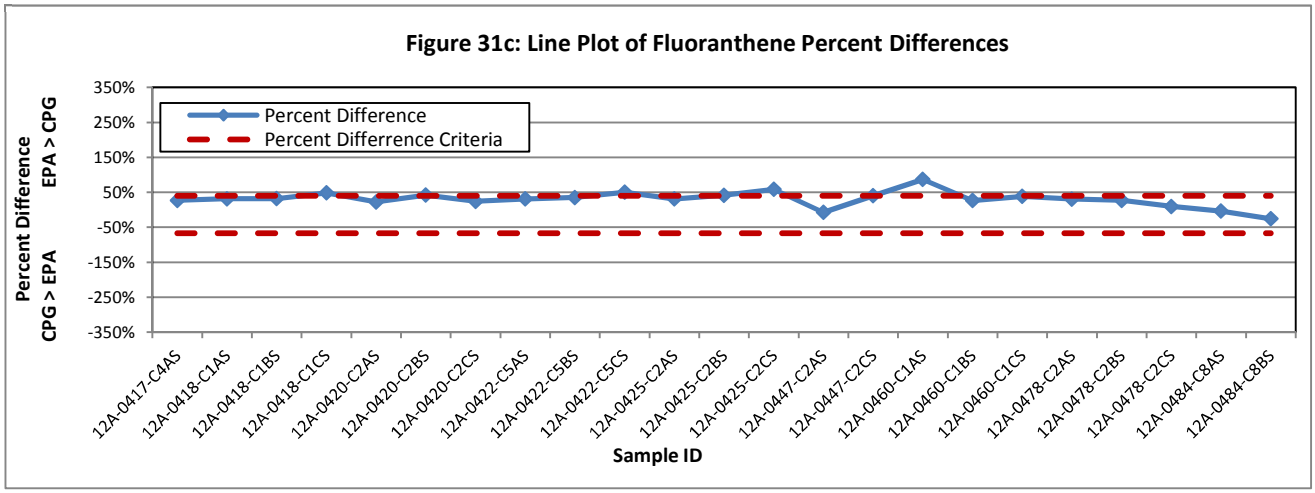
Statistical Plot of Sediment Chrysene Concentrations

Figure 30







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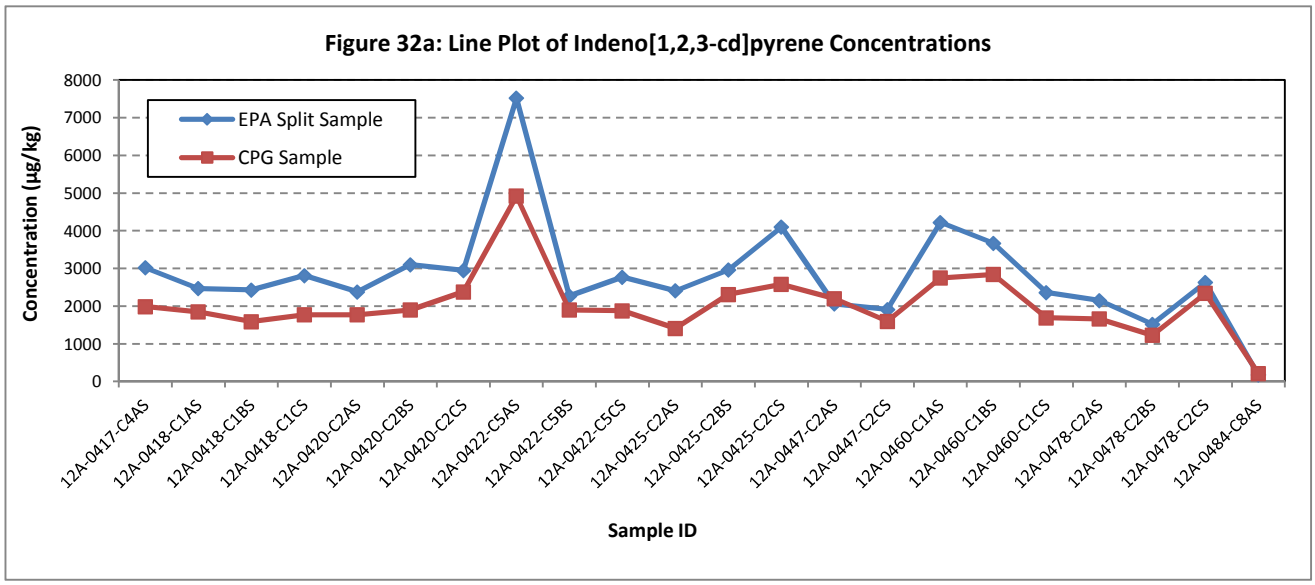
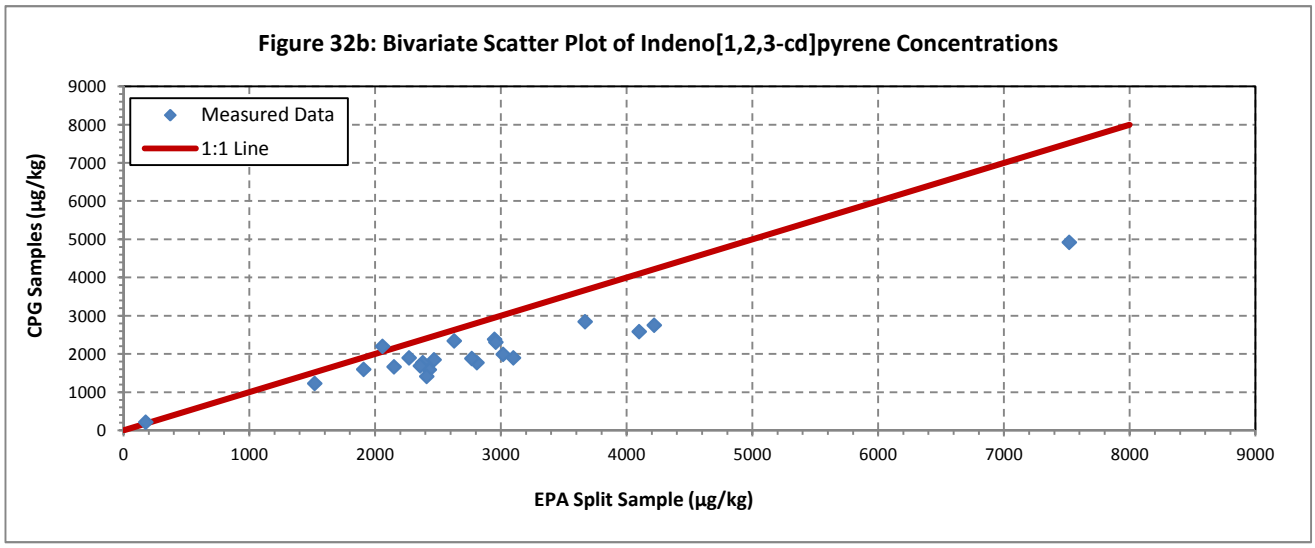
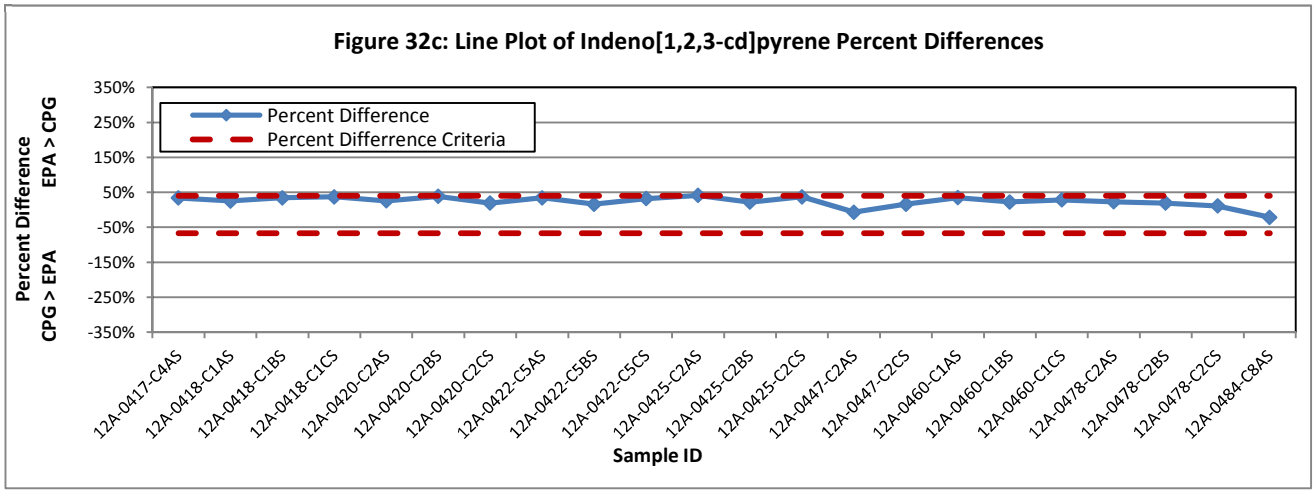
Statistical Plot of Sediment Fluoranthene Concentrations

Figure 31







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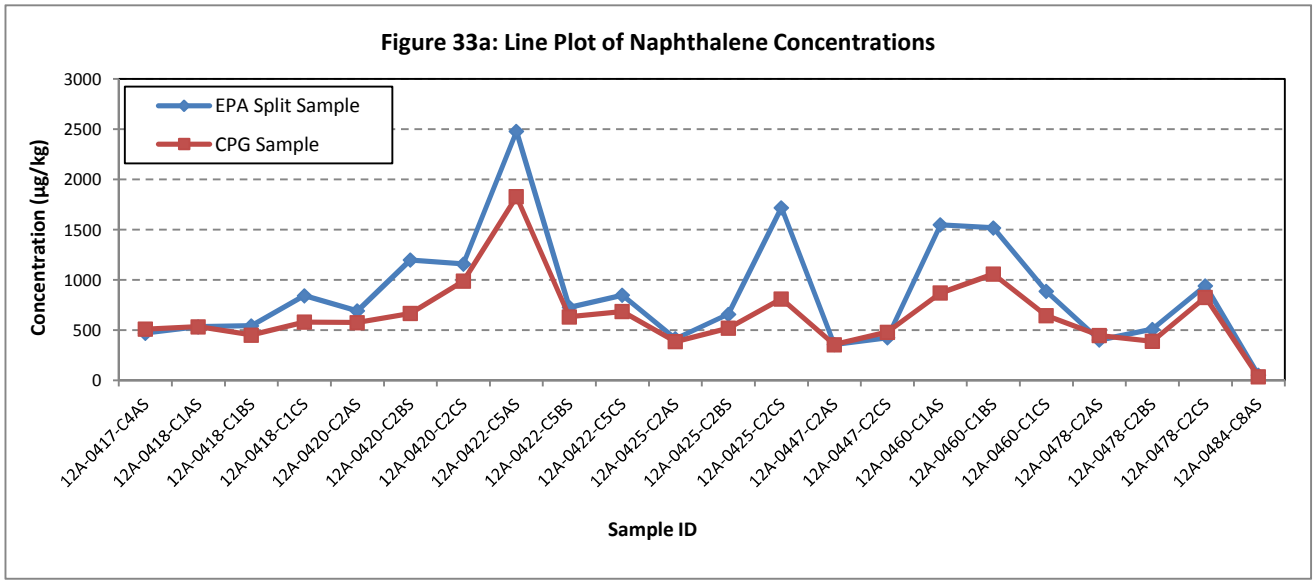
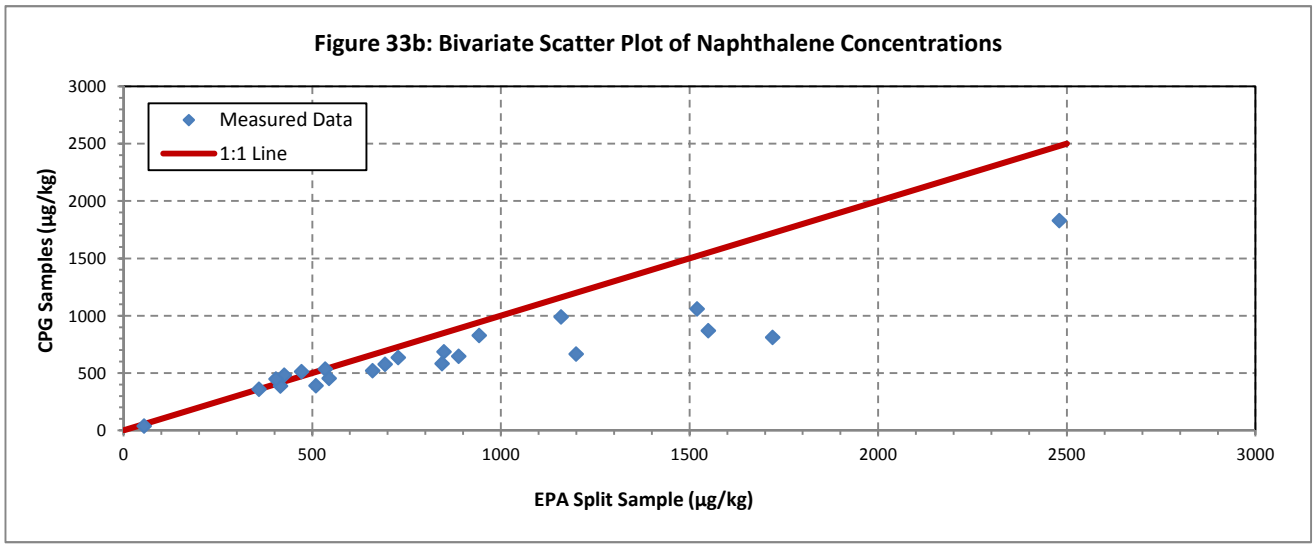
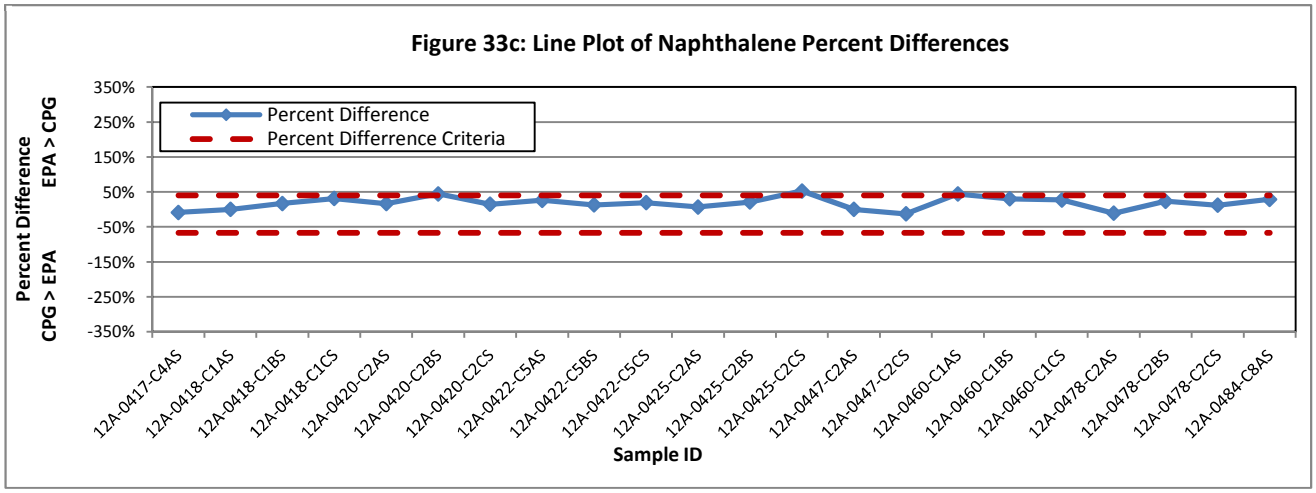
Statistical Plot of Sediment Indeno[1,2,3-cd]pyrene Concentrations

Figure 32







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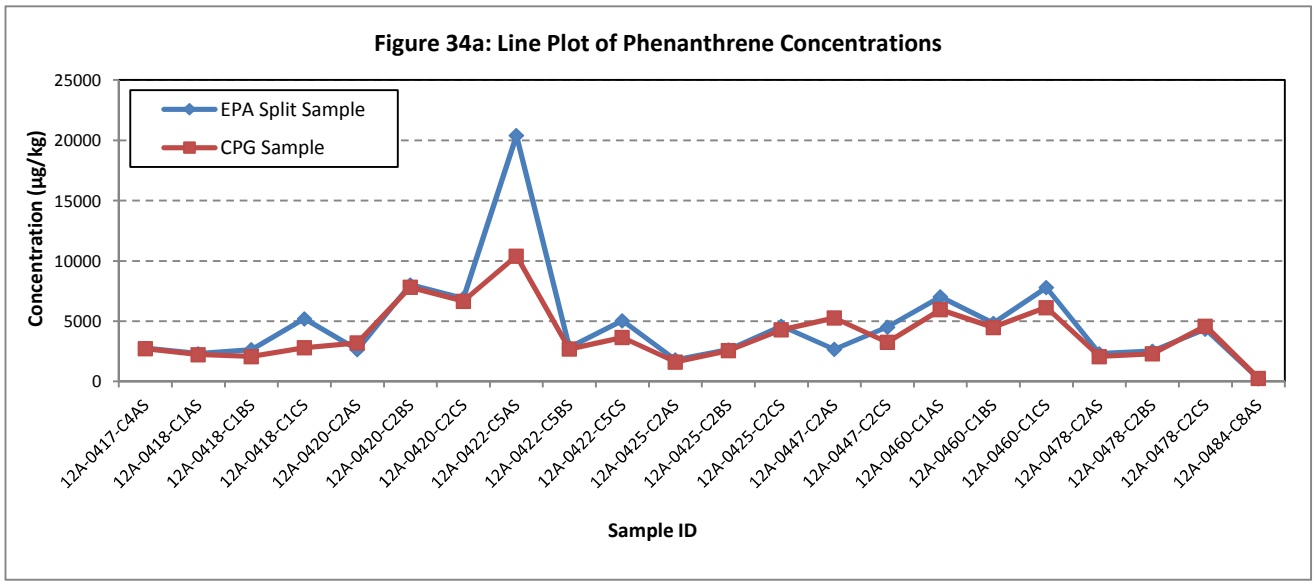
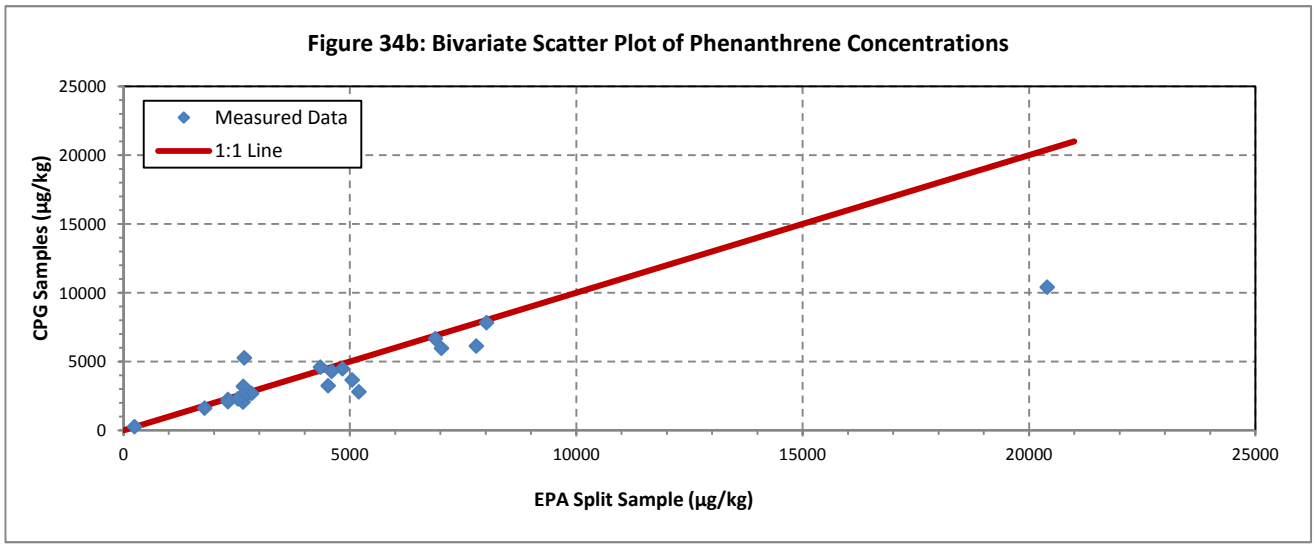
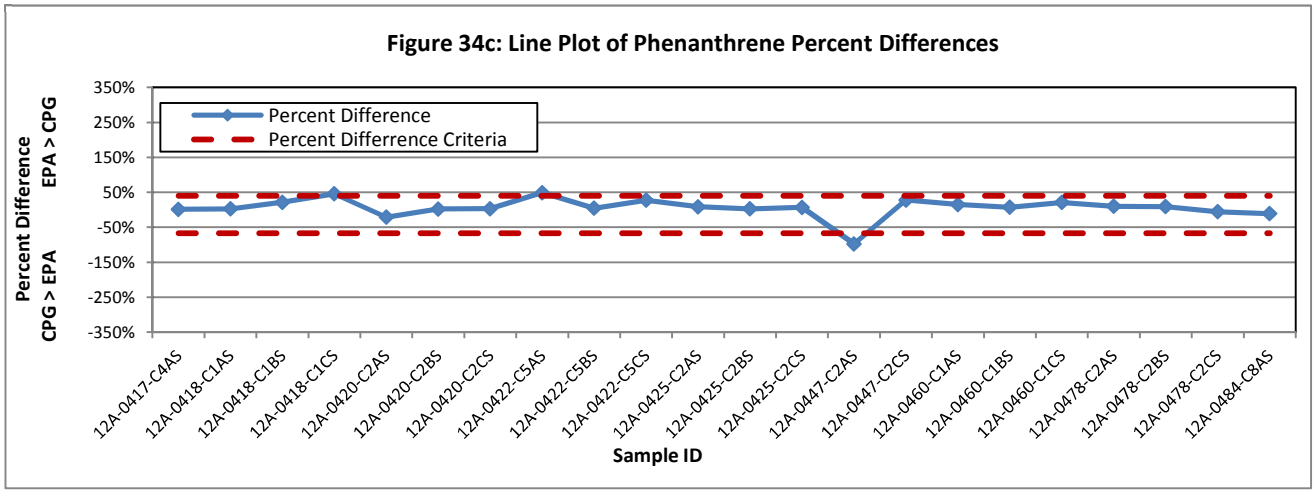
Statistical Plot of Sediment Naphthalene Concentrations

Figure 33







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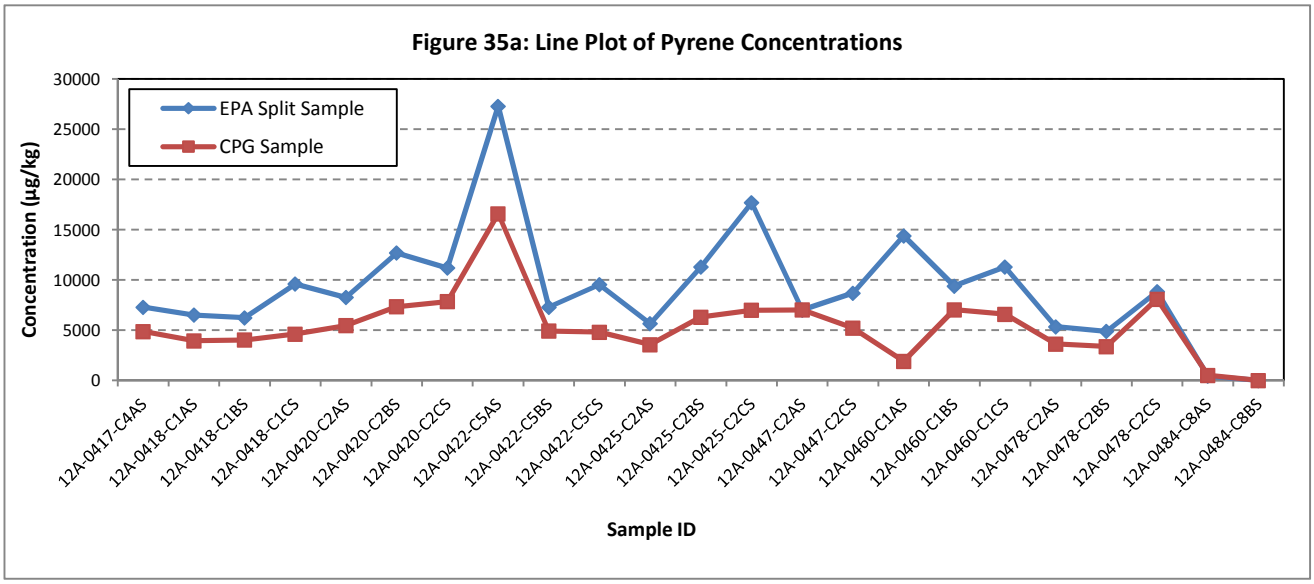
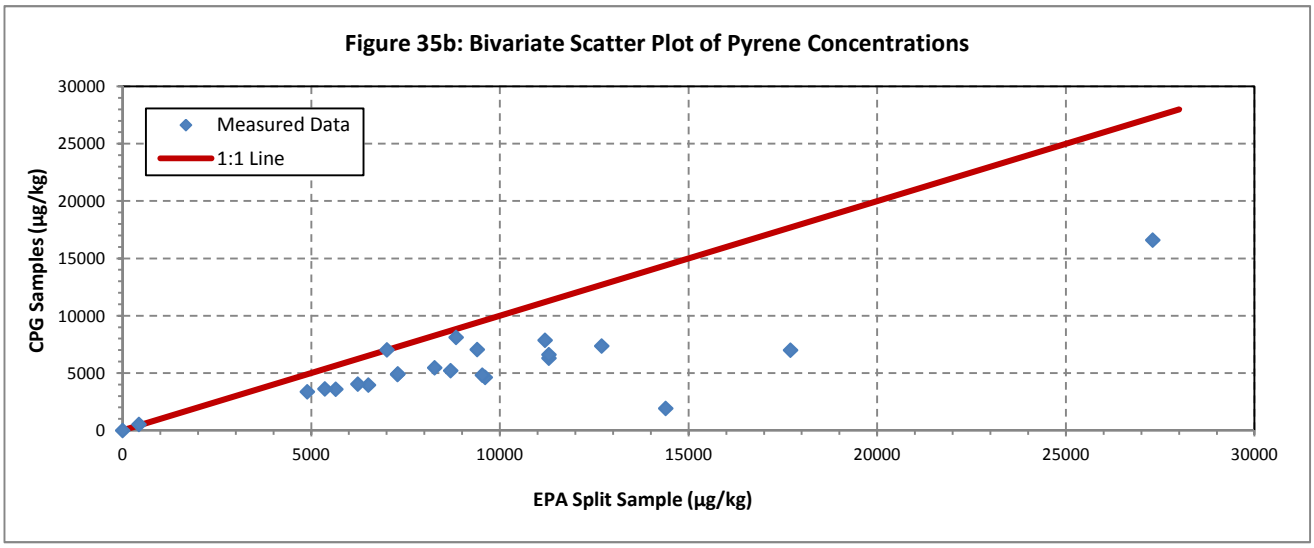
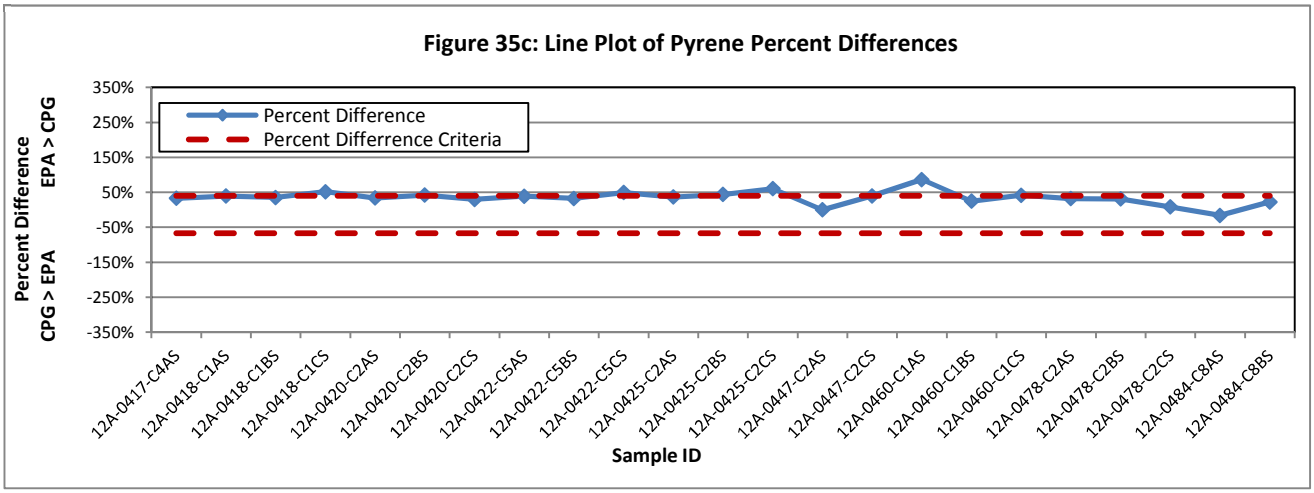
Statistical Plot of Sediment Phenanthrene Concentrations

Figure 34







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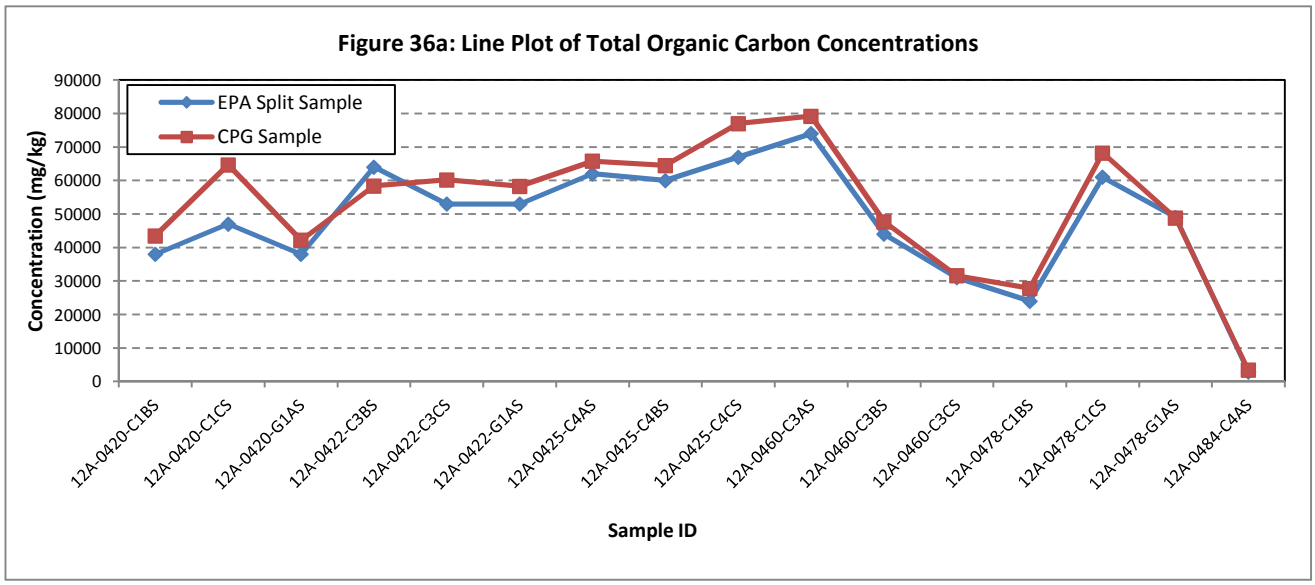
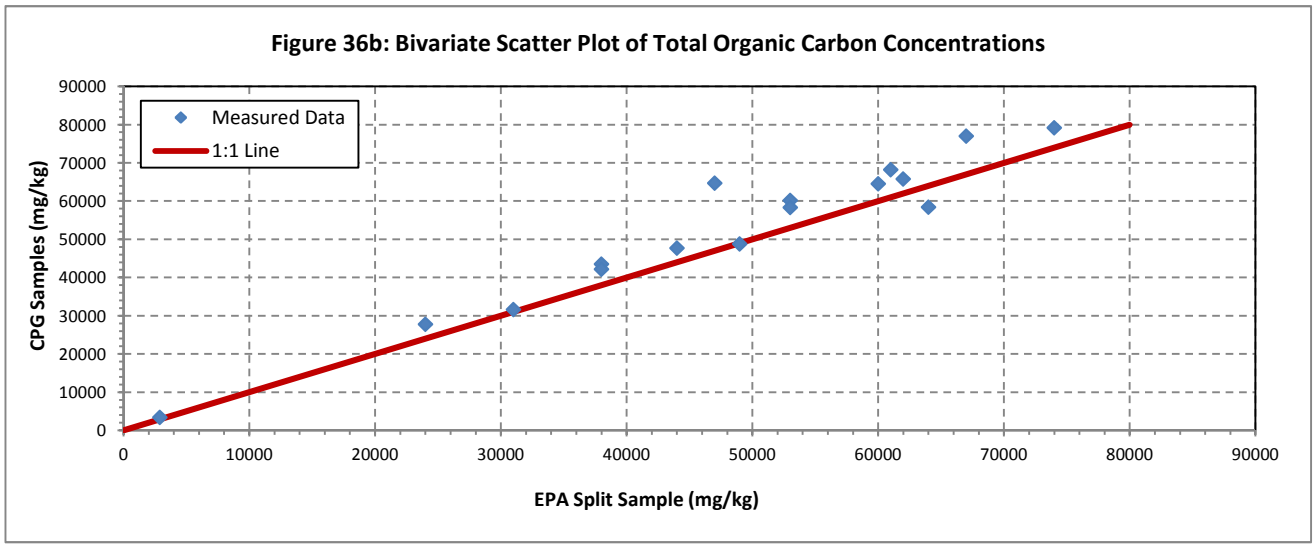
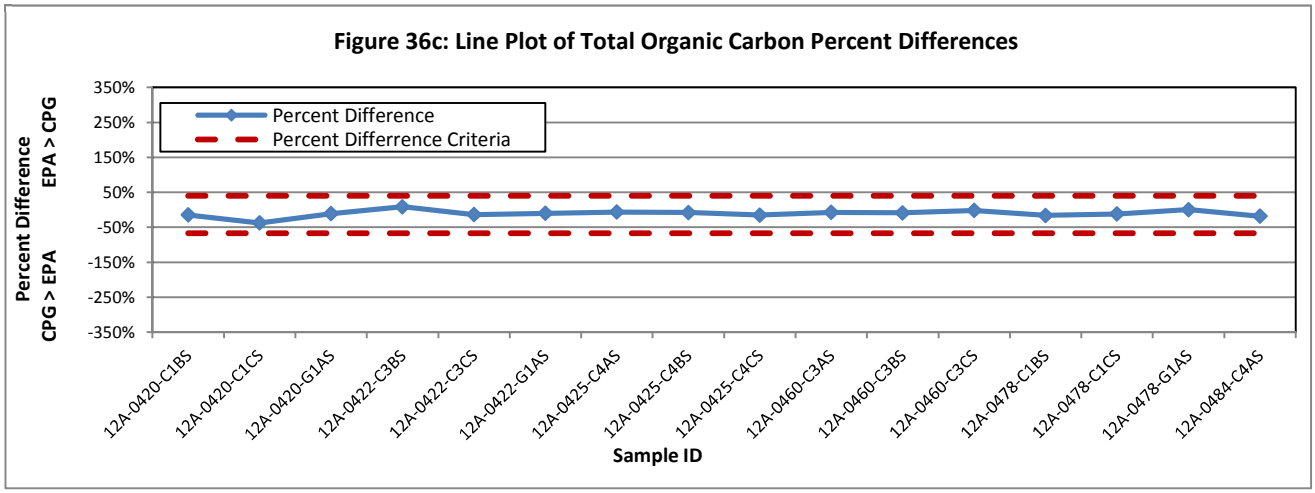
Statistical Plot of Sediment Pyrene Concentrations

Figure 35







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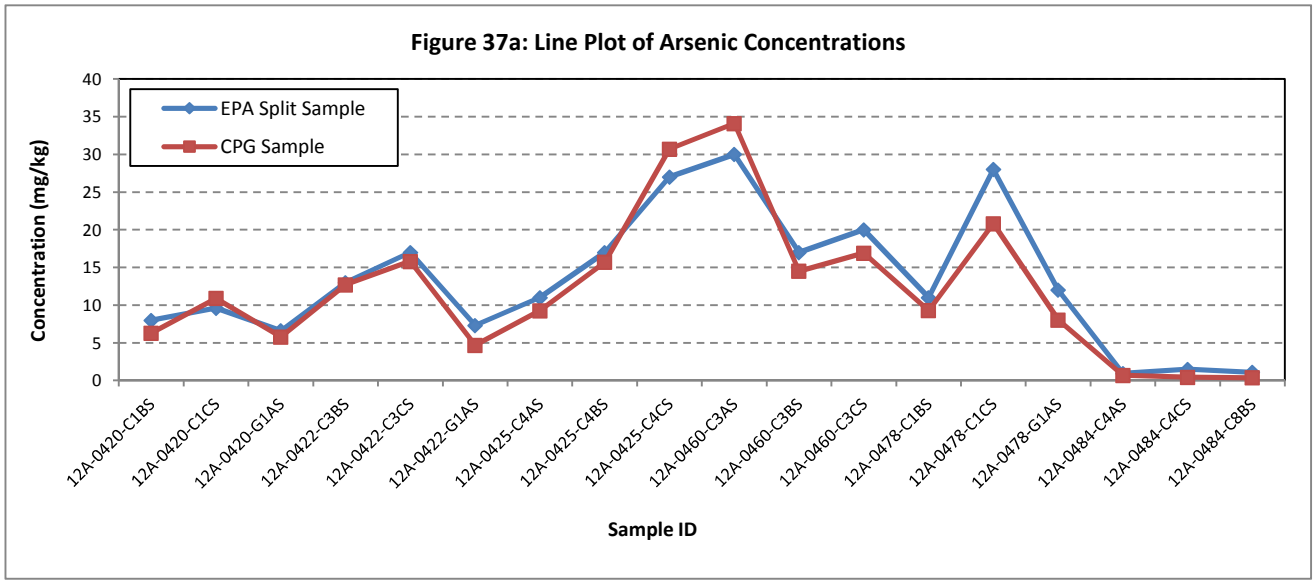
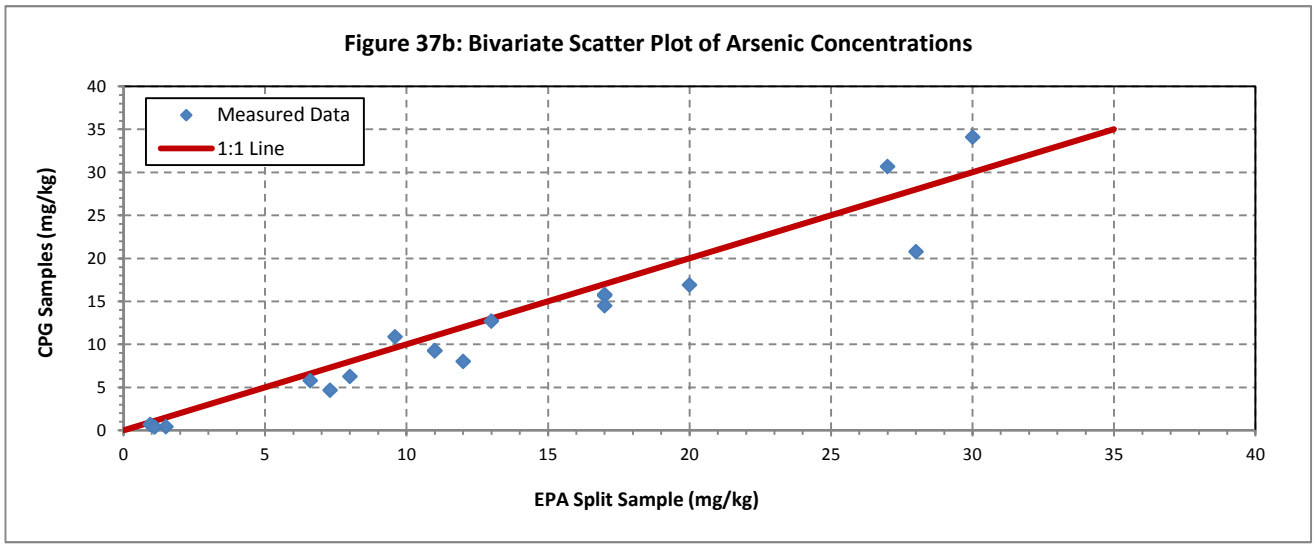
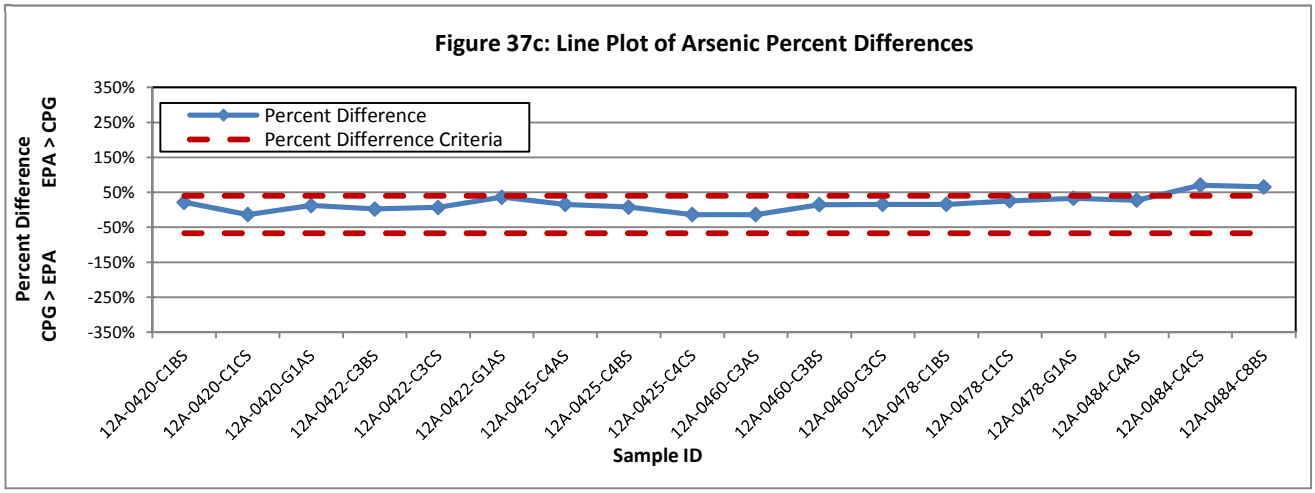
Statistical Plot of Sediment Total Organic Carbon Concentrations

Figure 36







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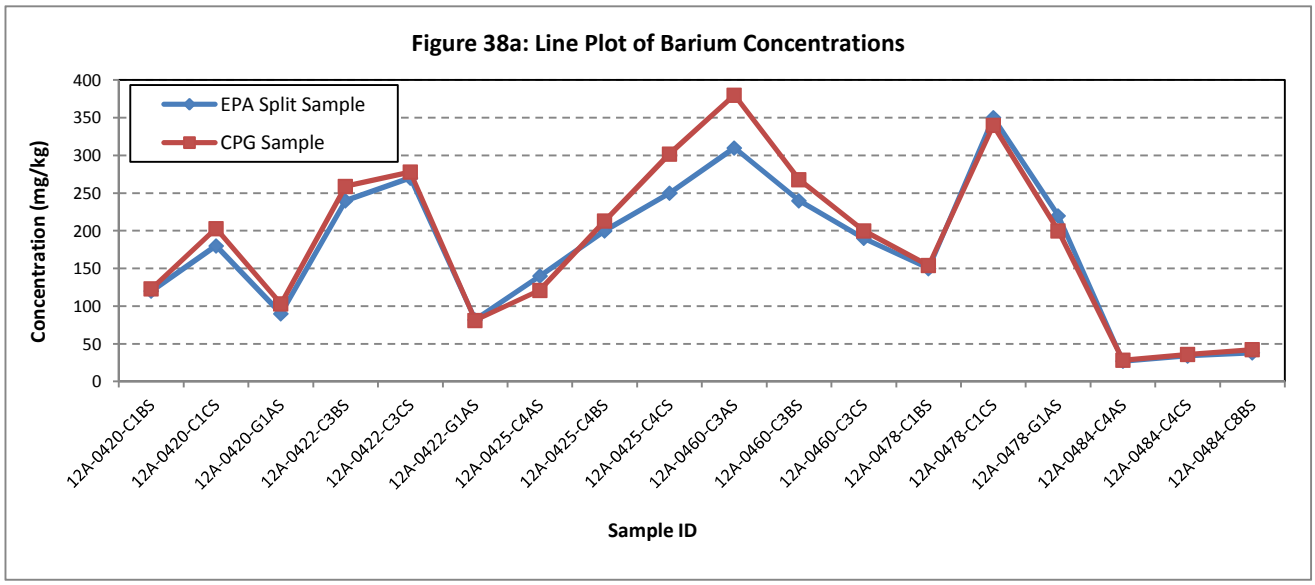
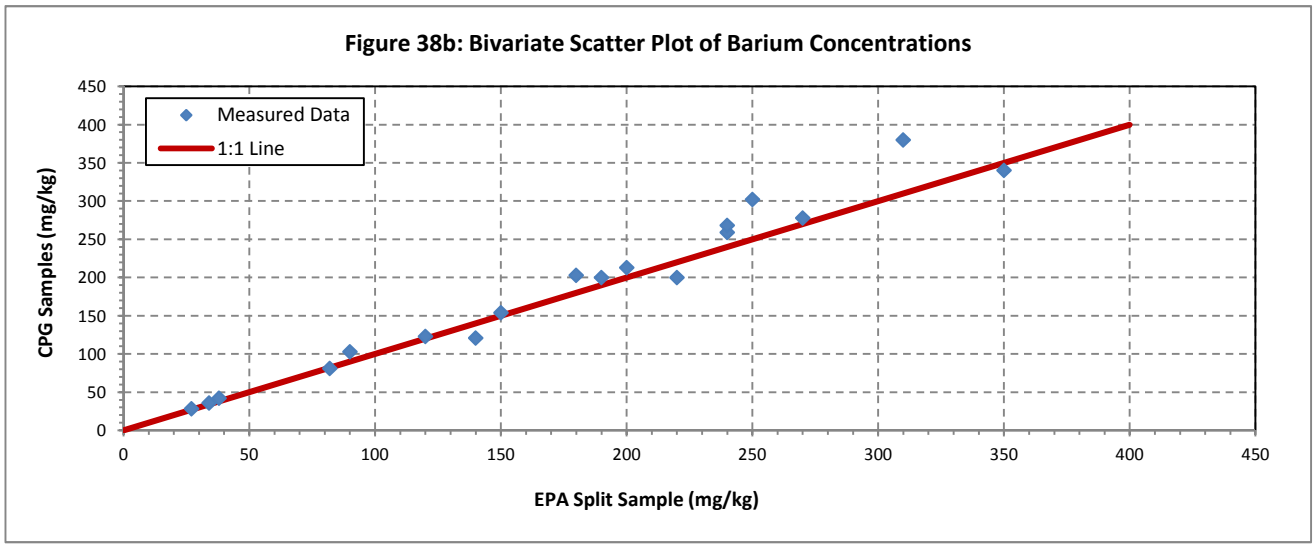
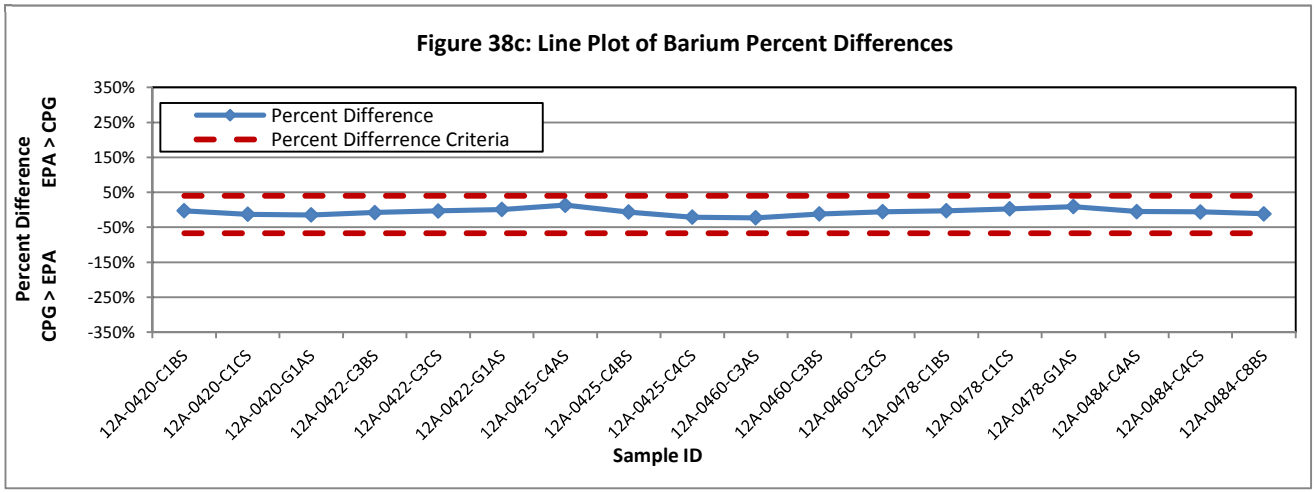
Statistical Plot of Sediment Arsenic Concentrations

Figure 37







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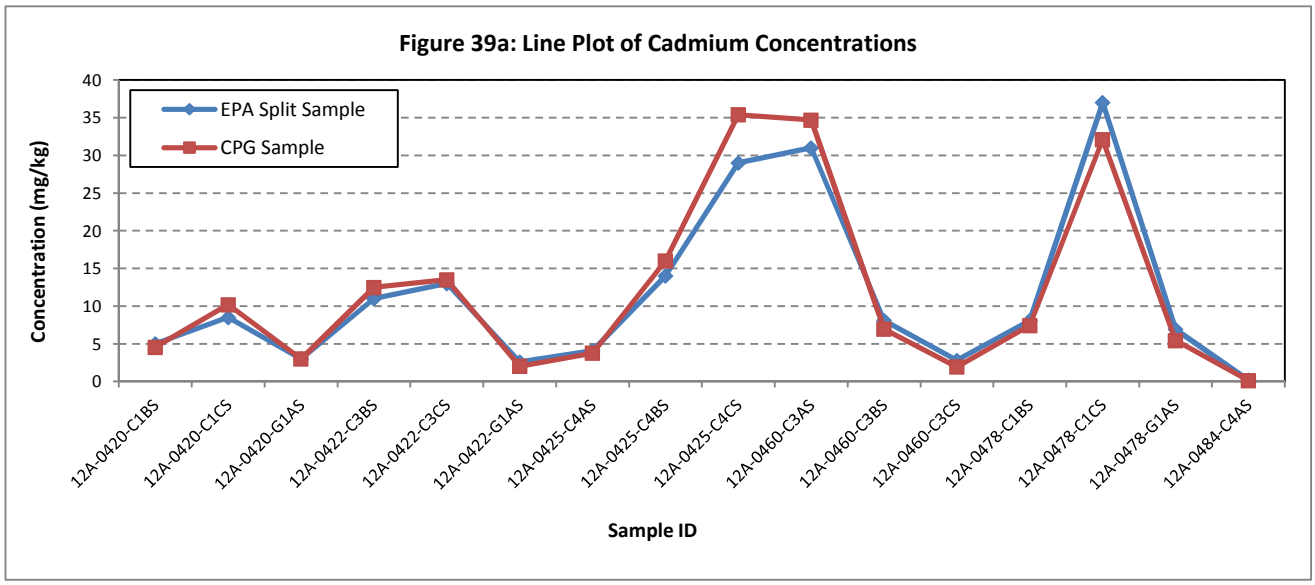
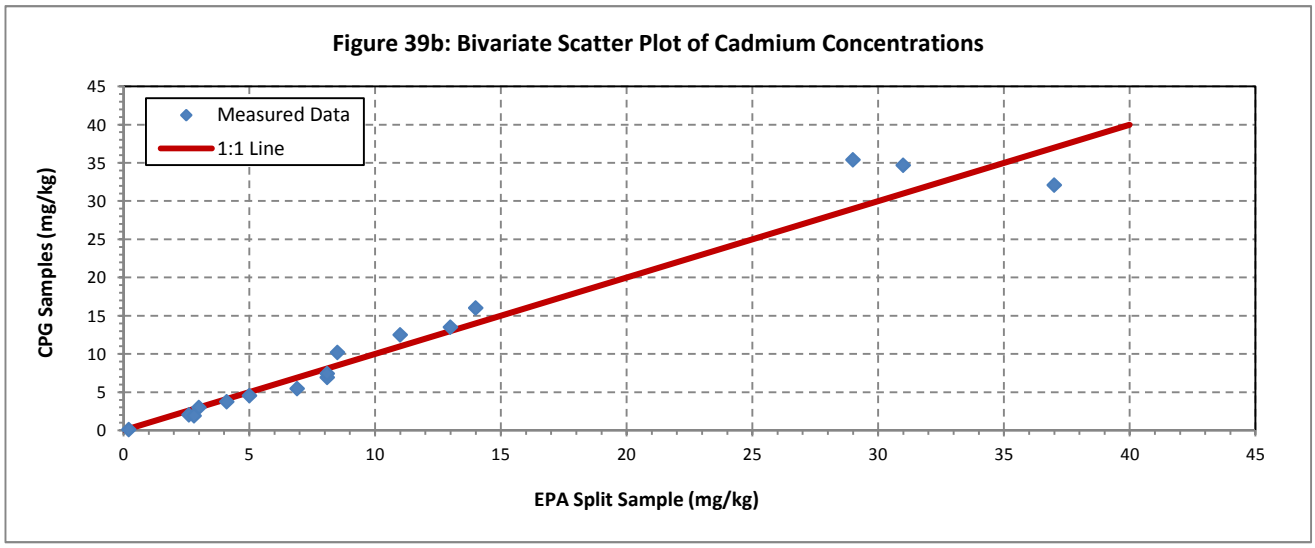
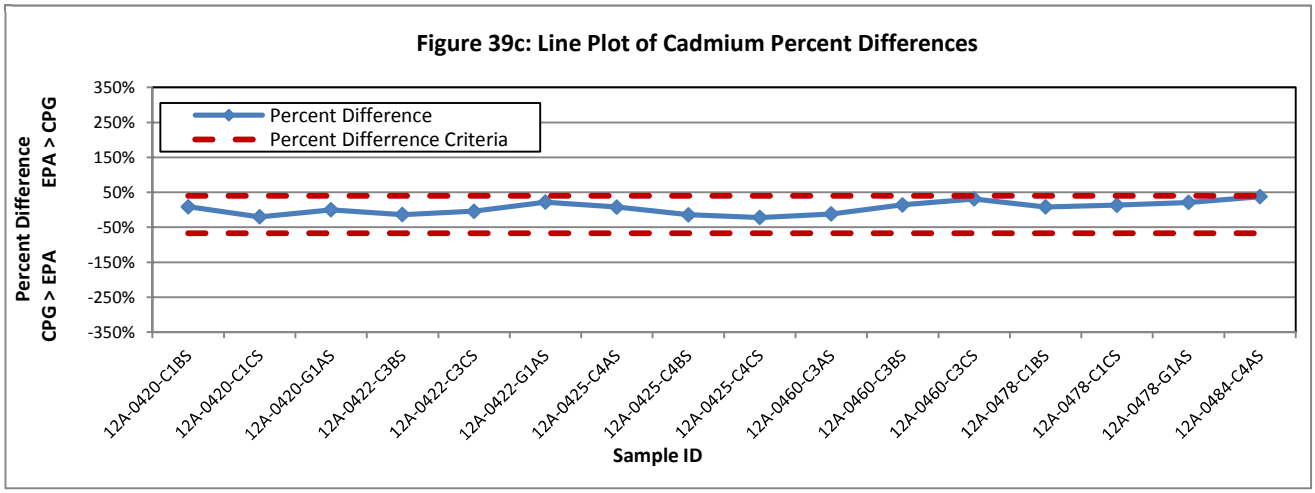
Statistical Plot of Sediment Barium Concentrations

Figure 38







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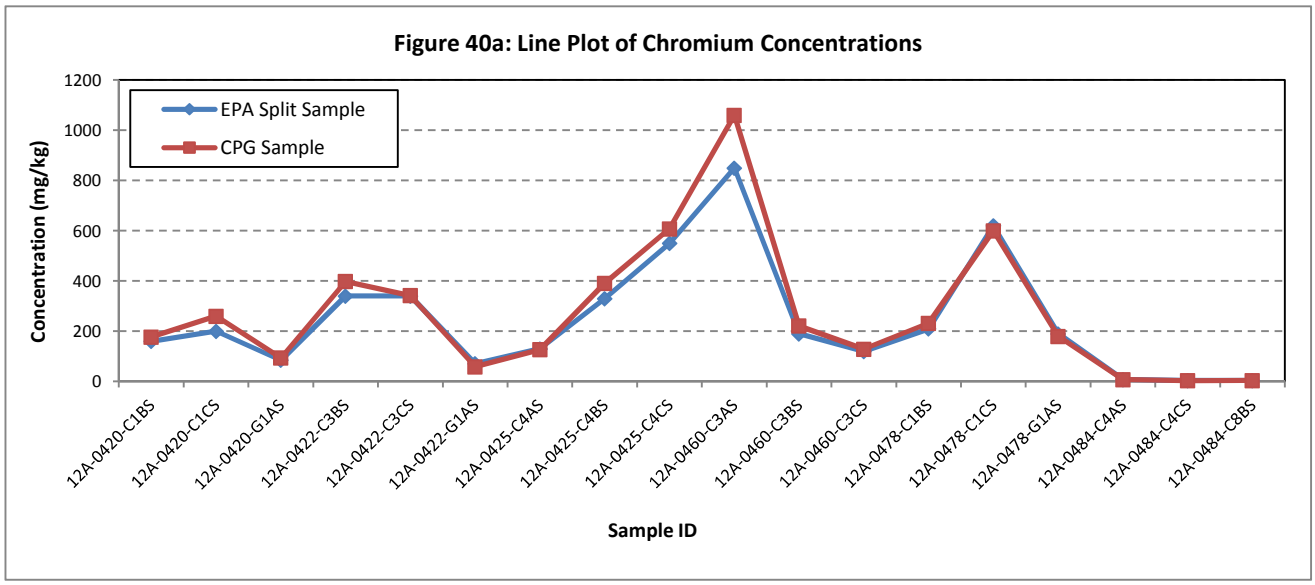
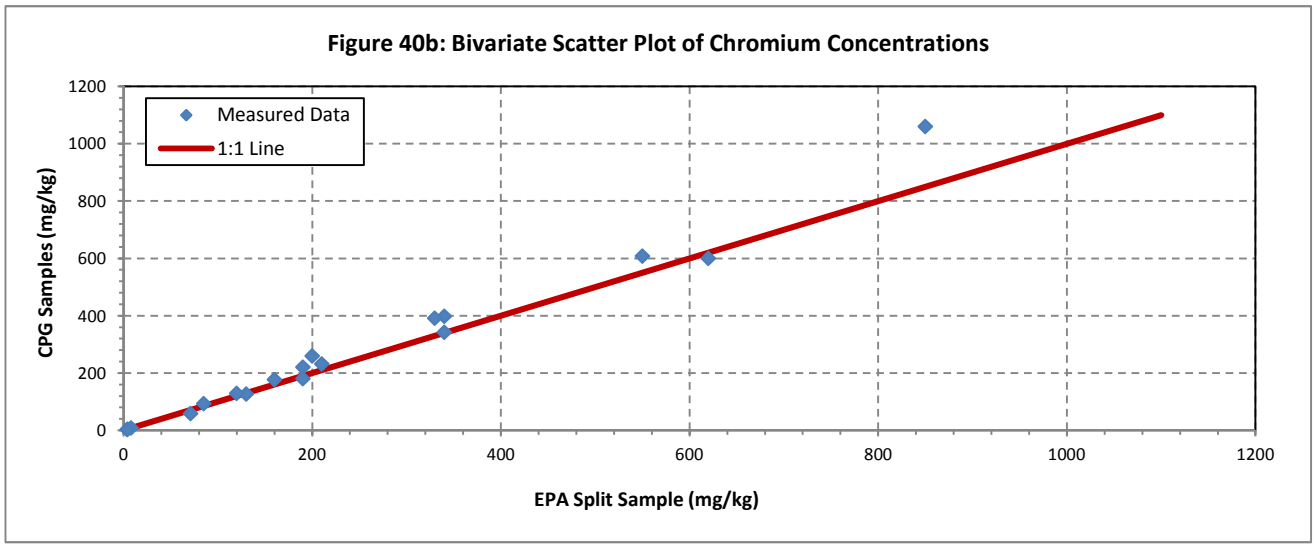
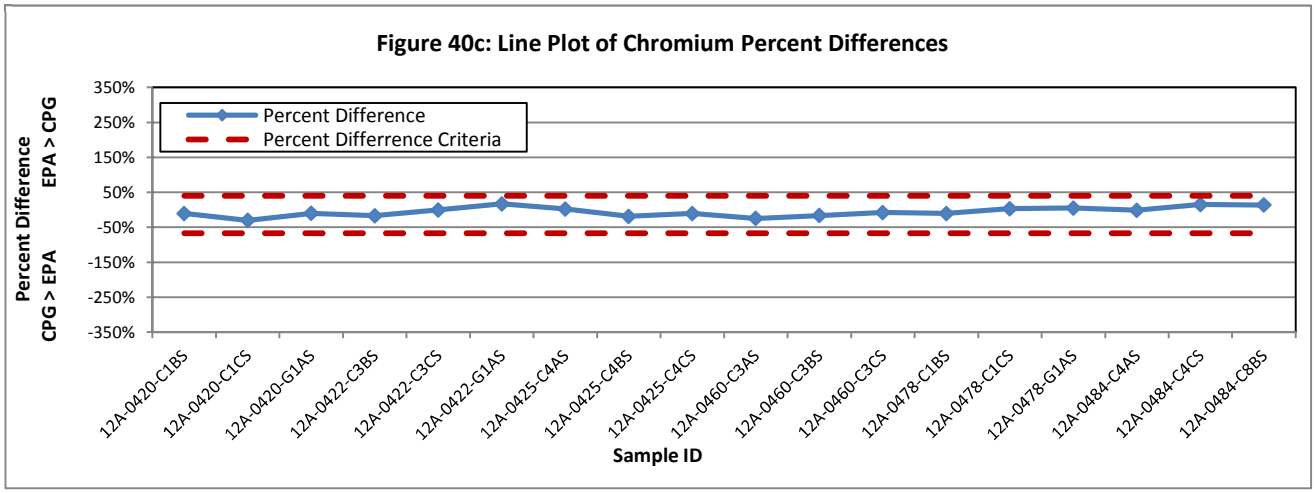
Statistical Plot of Sediment Cadmium Concentrations

Figure 39







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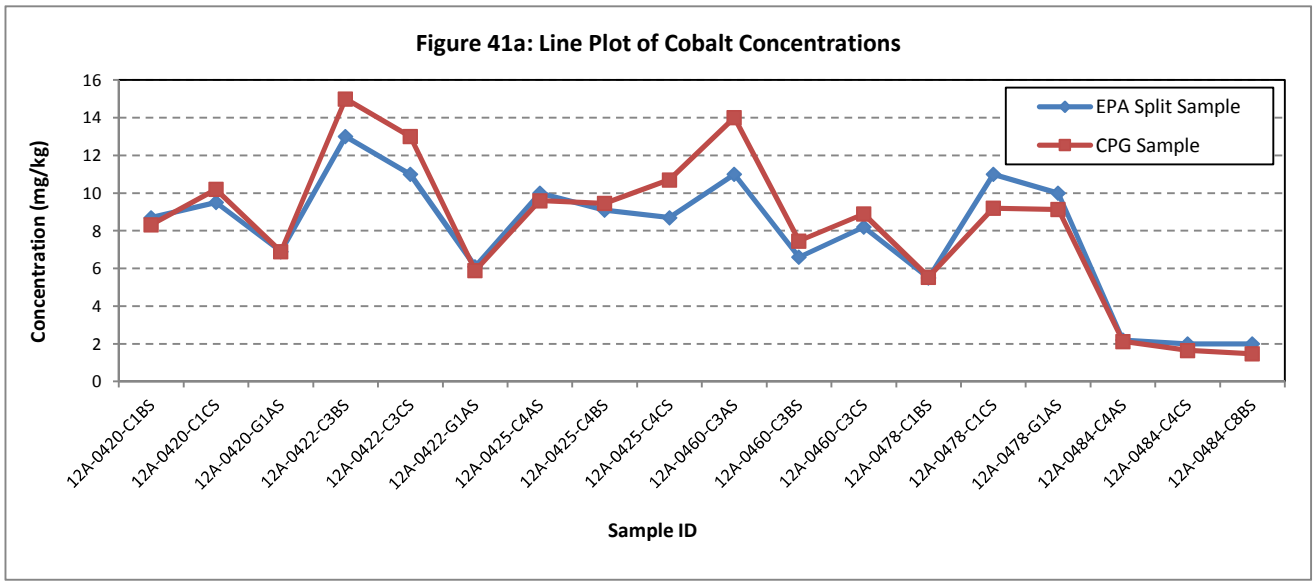
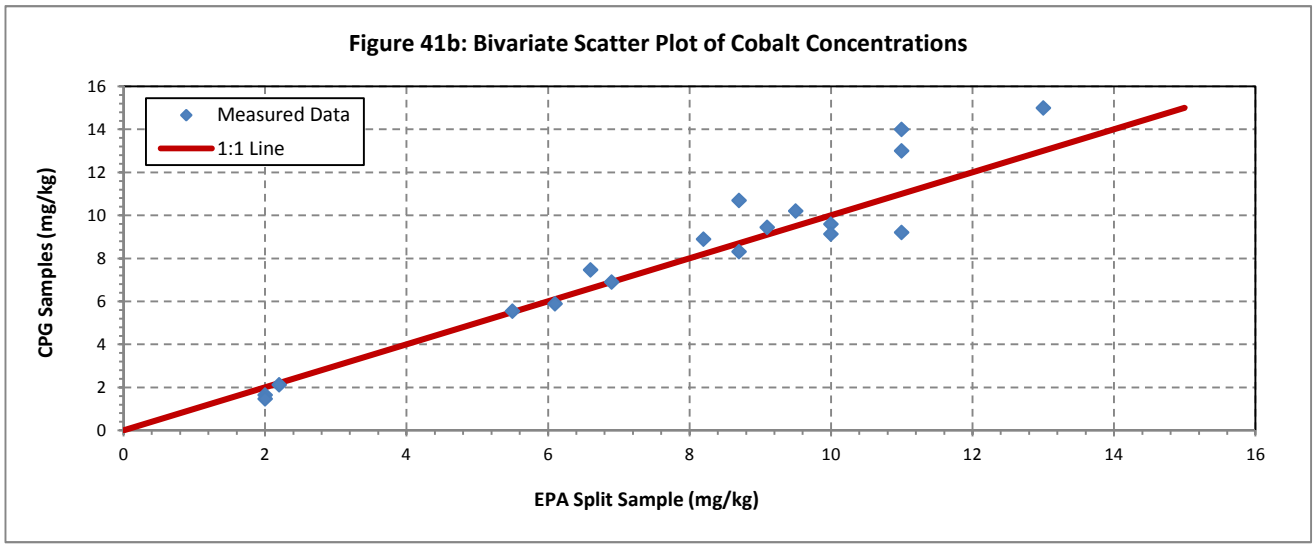
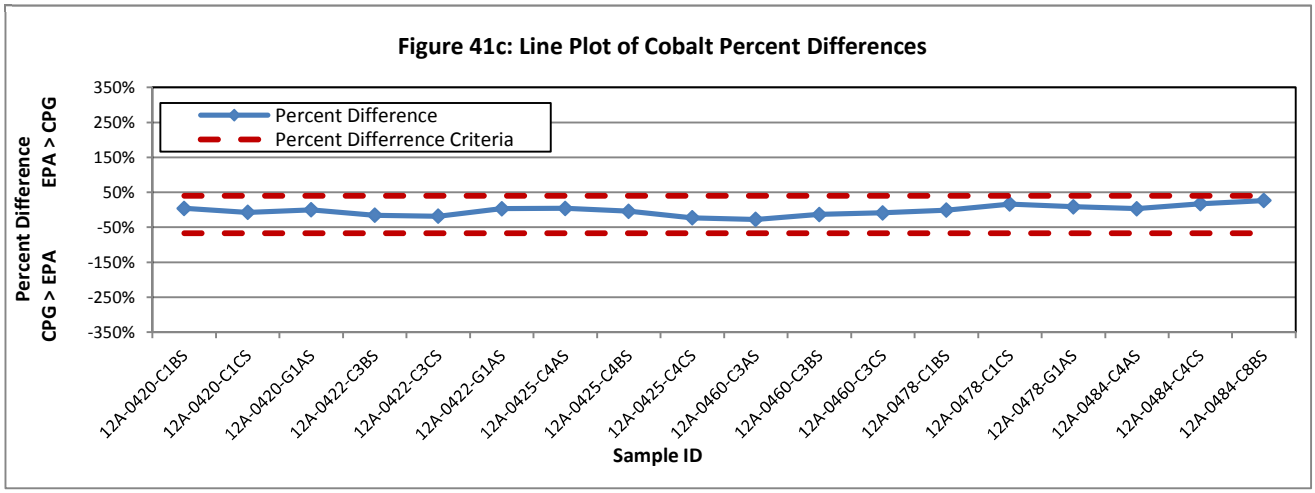
Statistical Plot of Sediment Chromium Concentrations

Figure 40







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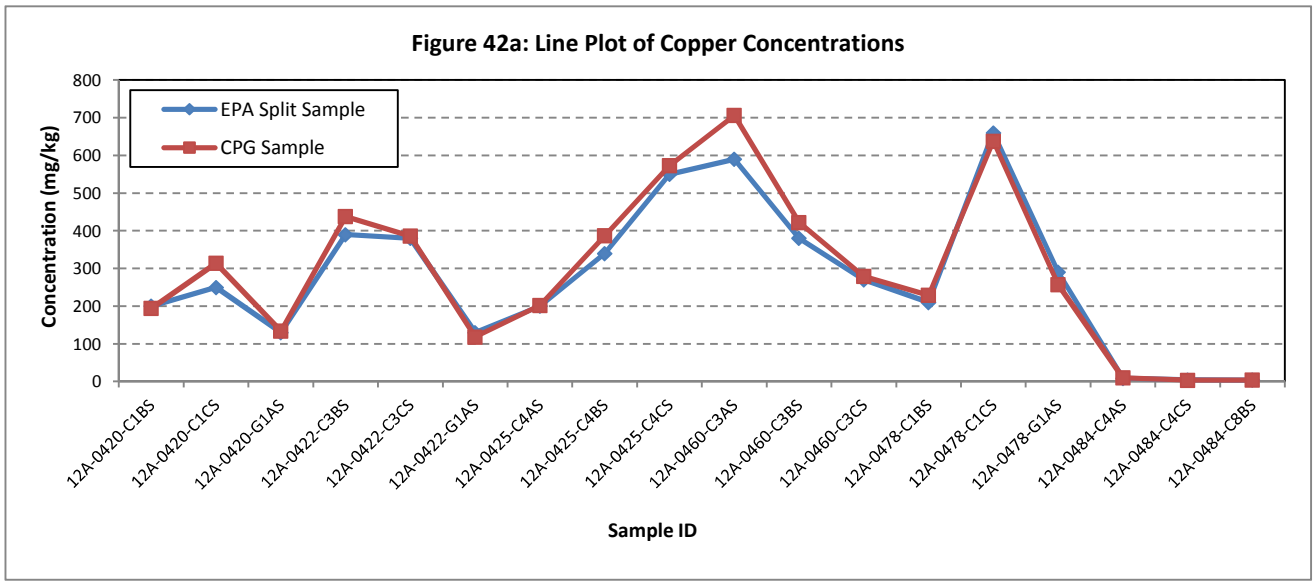
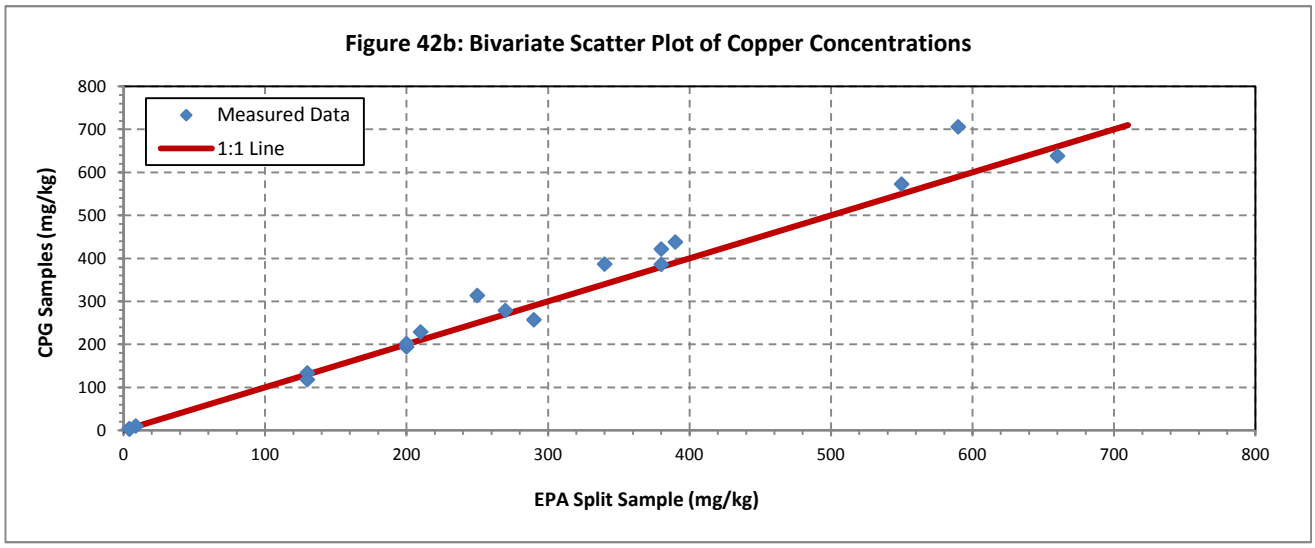
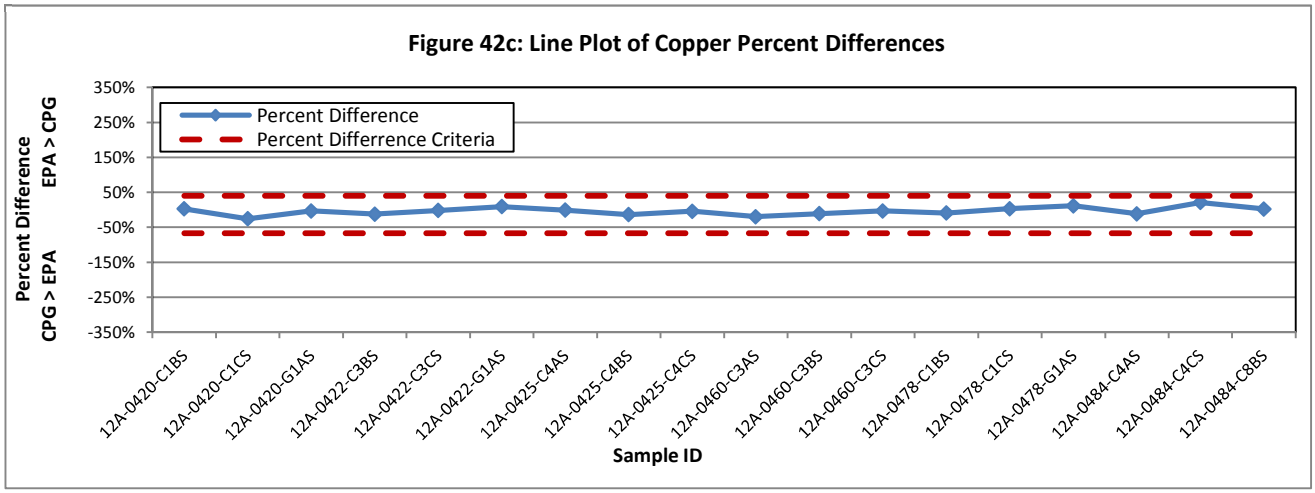
Statistical Plot of Sediment Cobalt Concentrations

Figure 41







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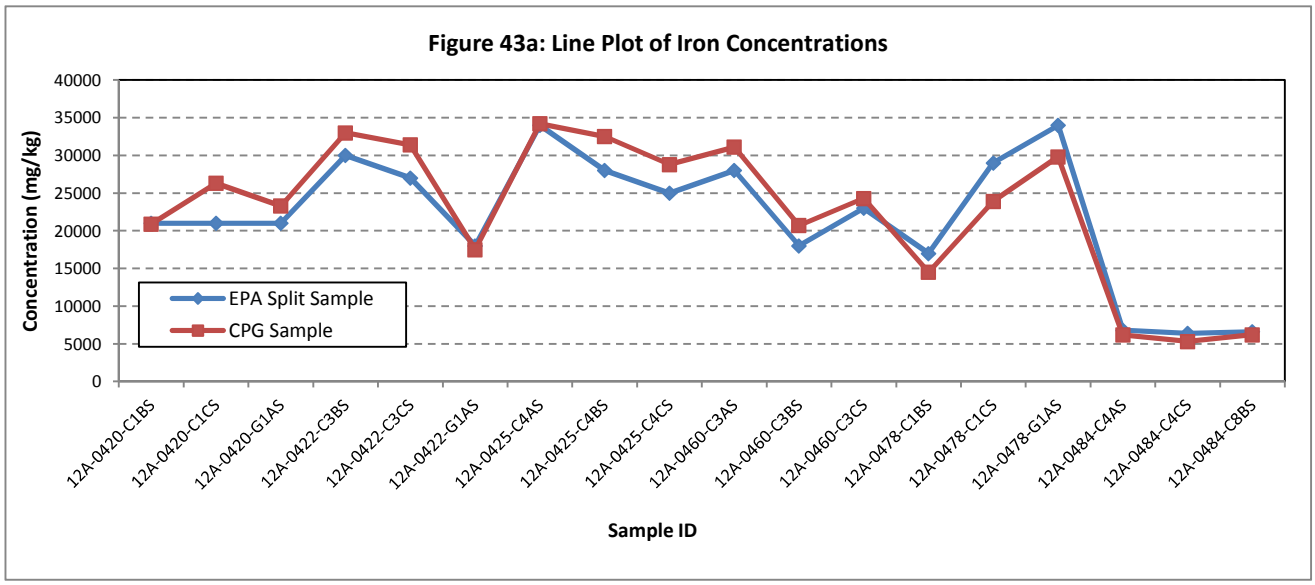
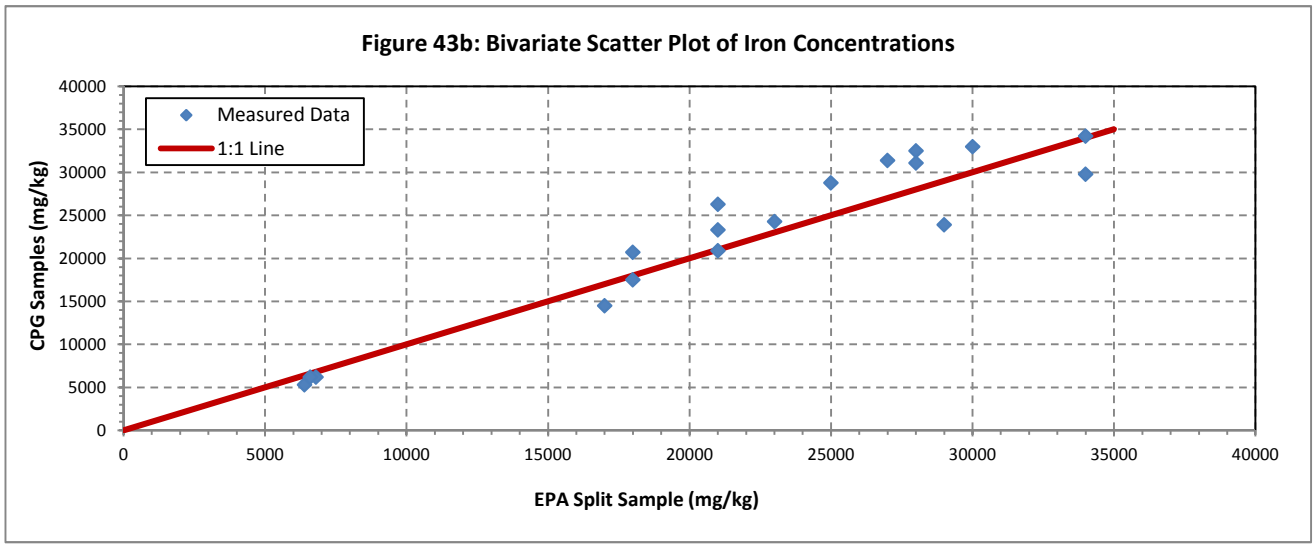
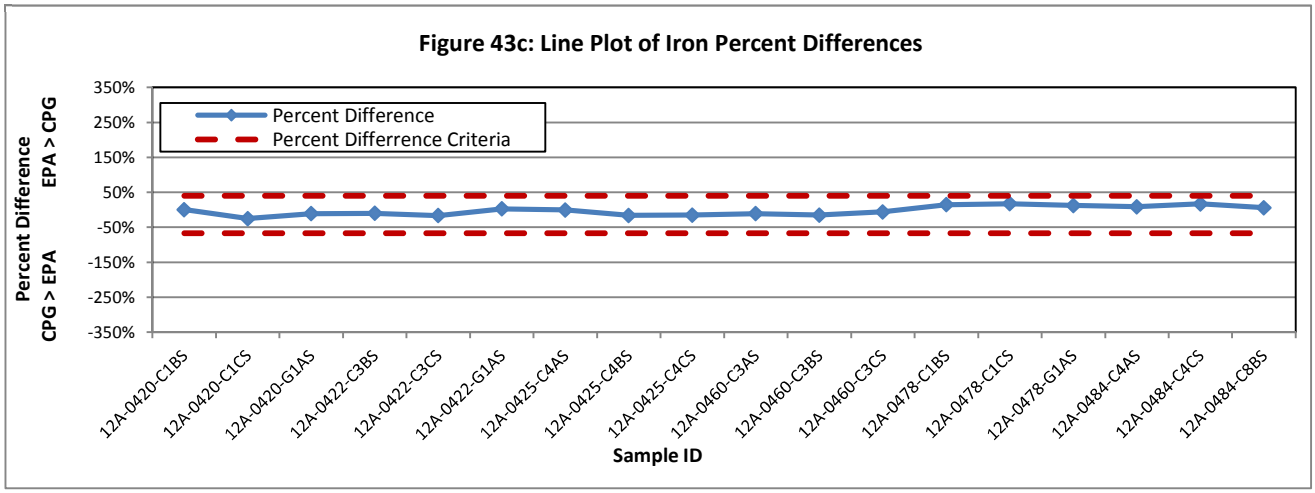
Statistical Plot of Sediment Copper Concentrations

Figure 42







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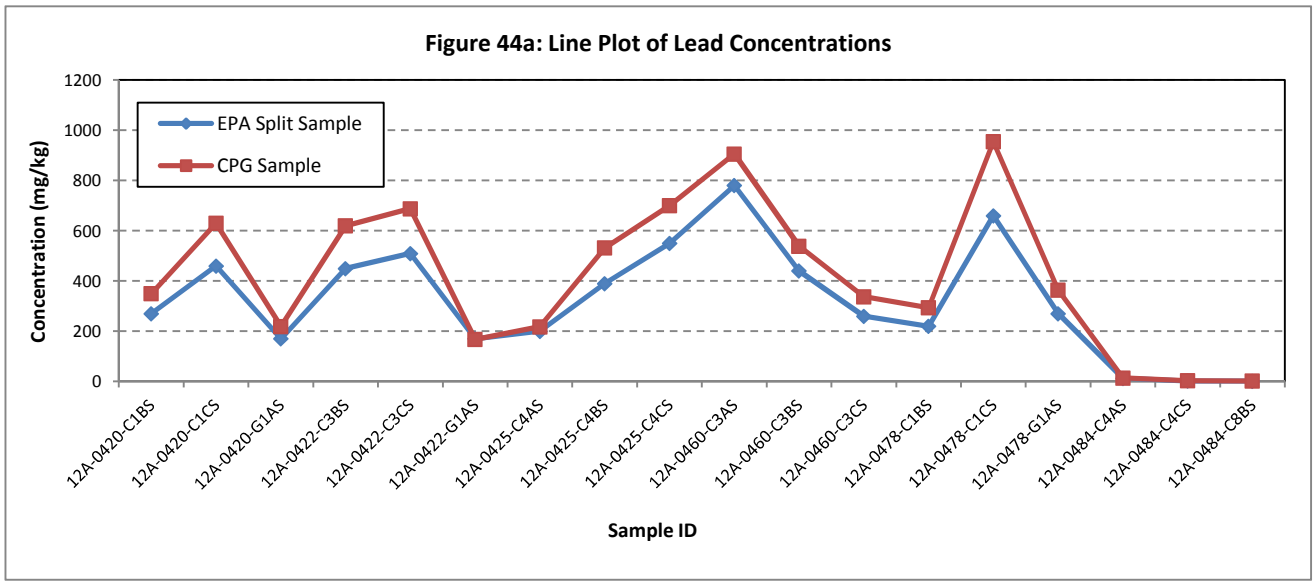
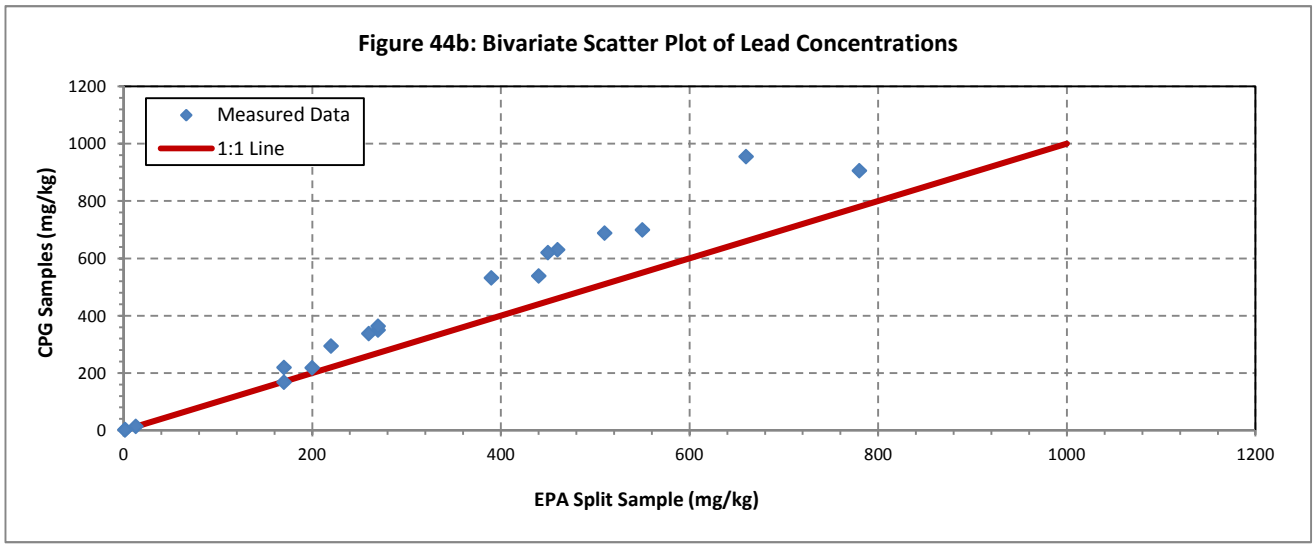
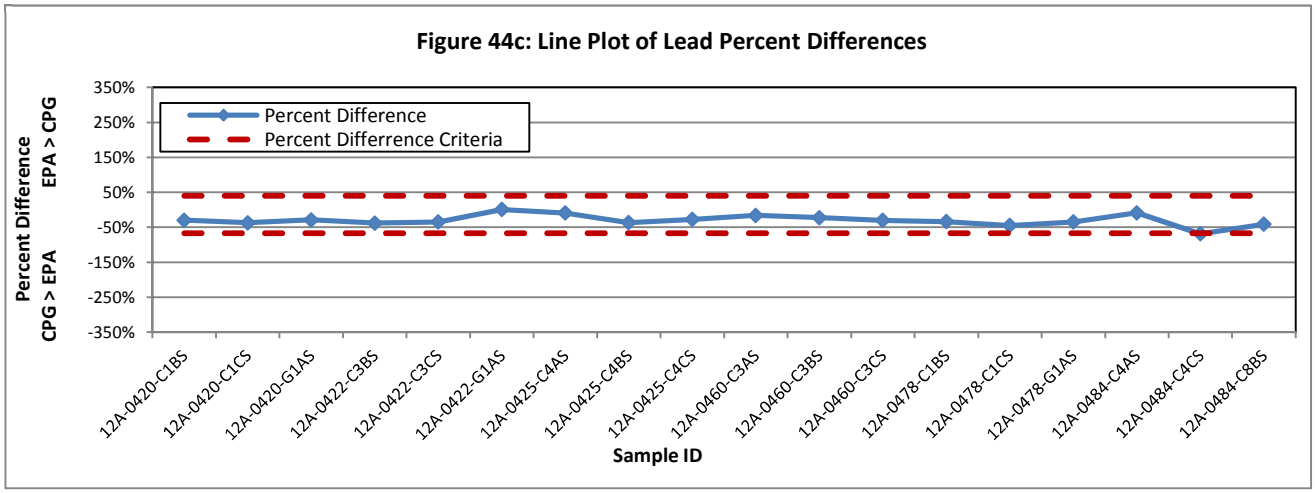
Statistical Plot of Sediment Iron Concentrations

Figure 43







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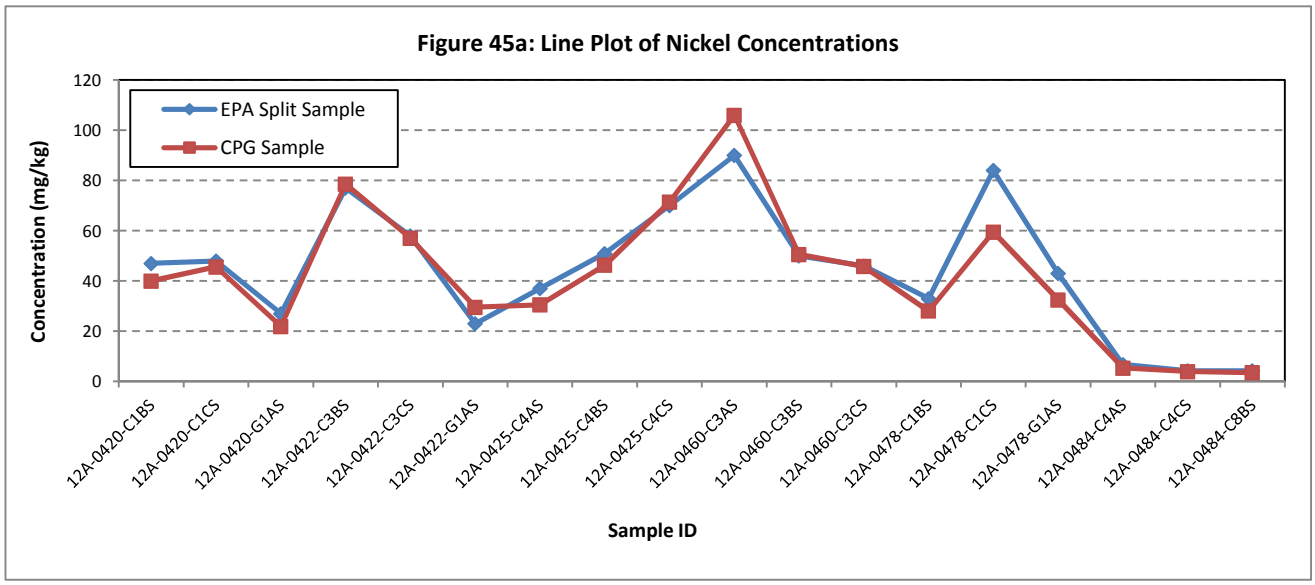
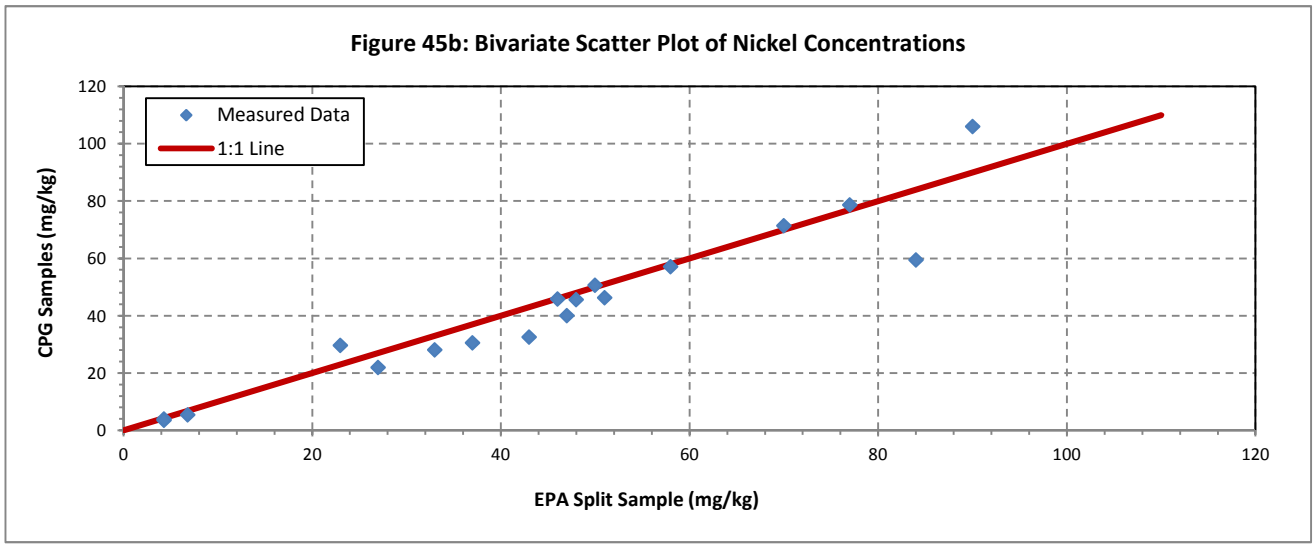
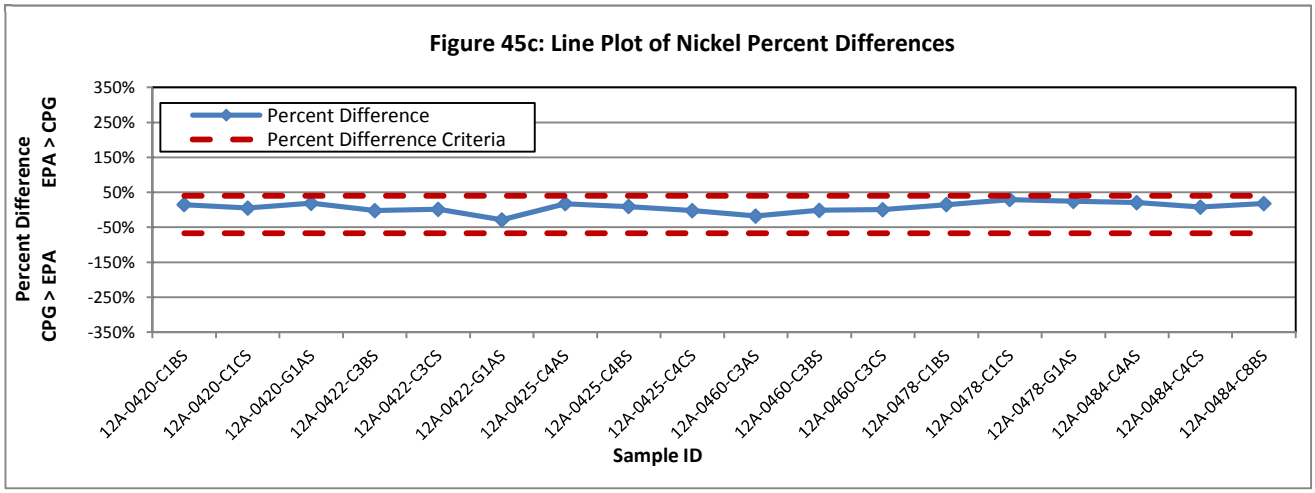
Statistical Plot of Sediment Lead Concentrations

Figure 44







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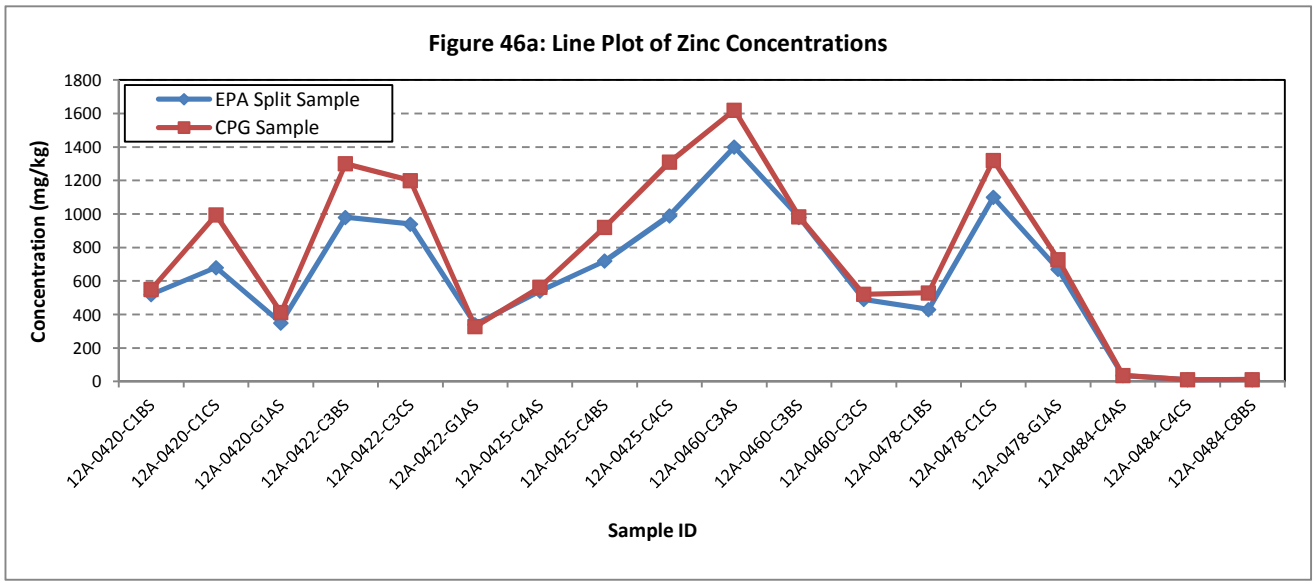
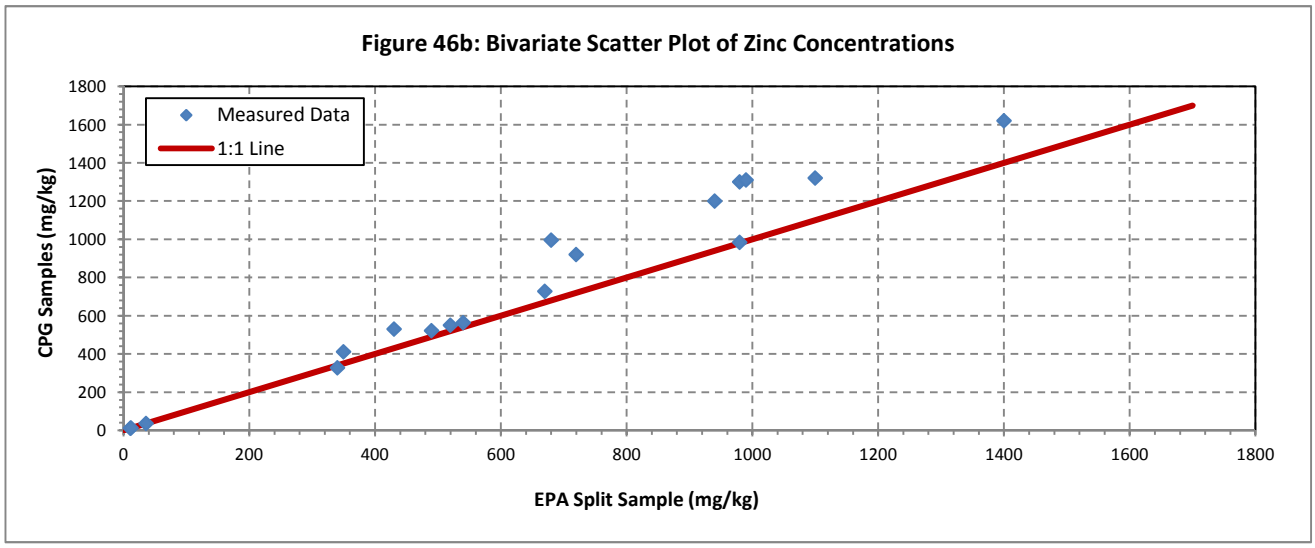
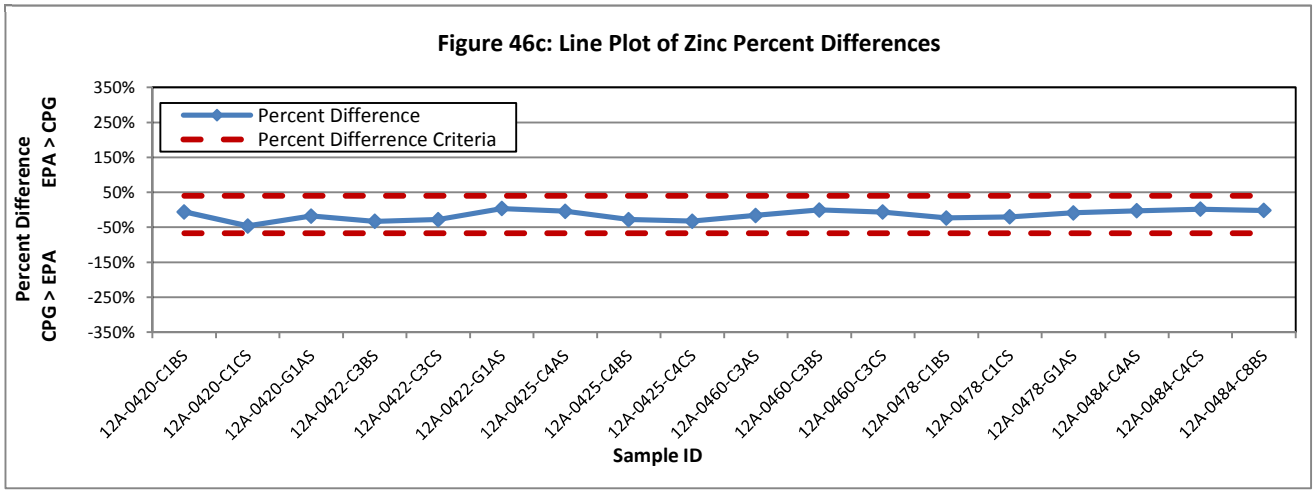
Statistical Plot of Sediment Nickel Concentrations

Figure 45







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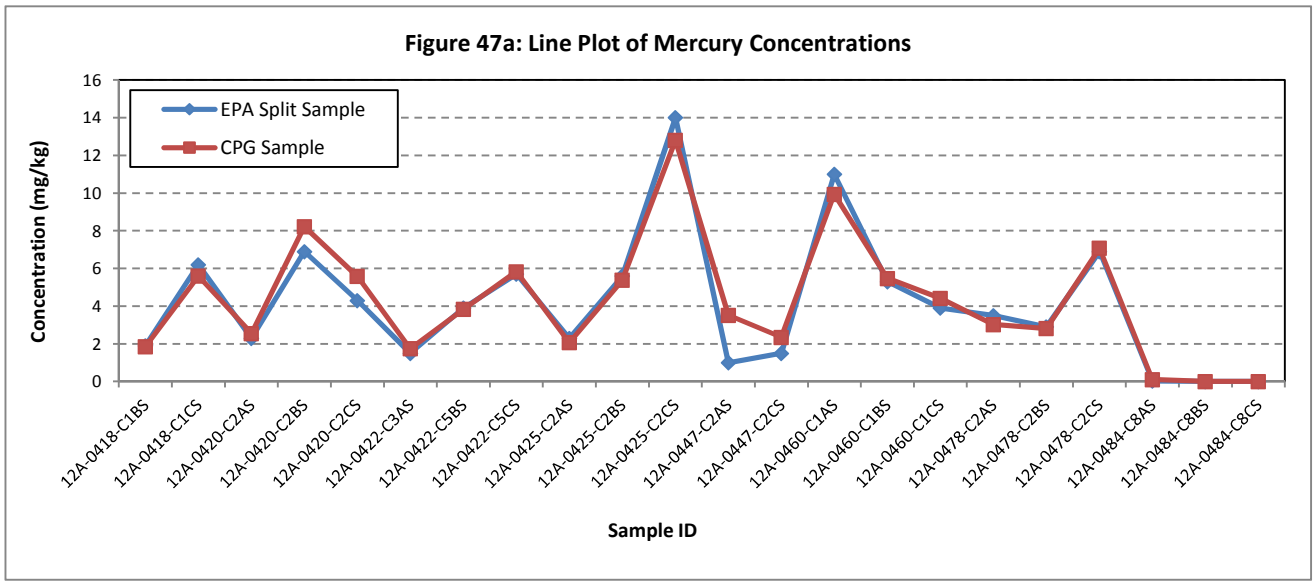
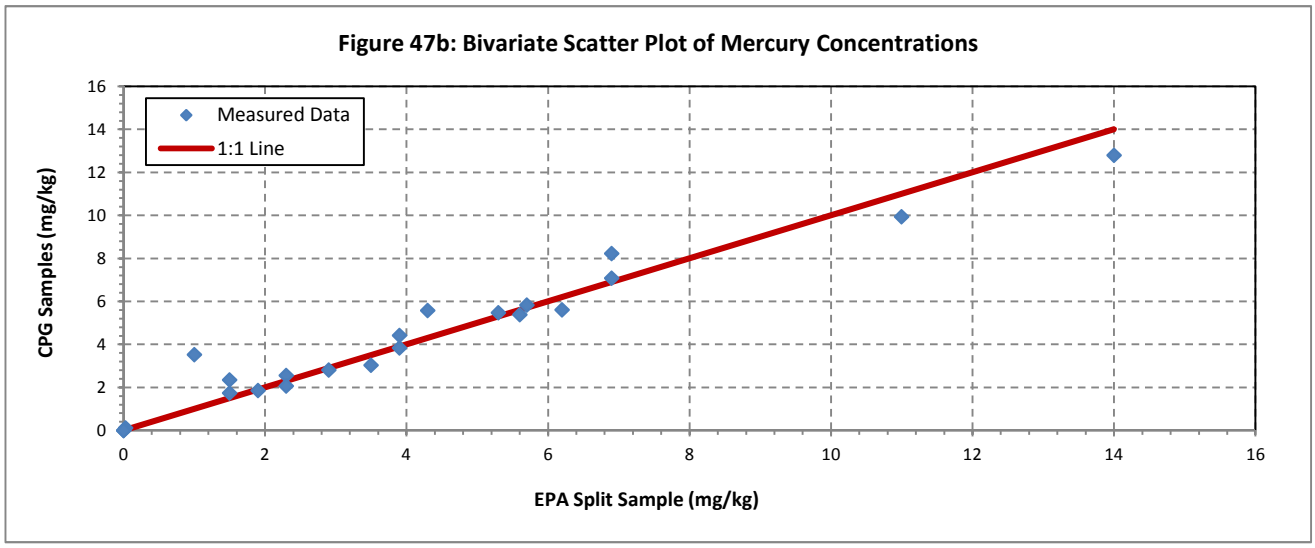
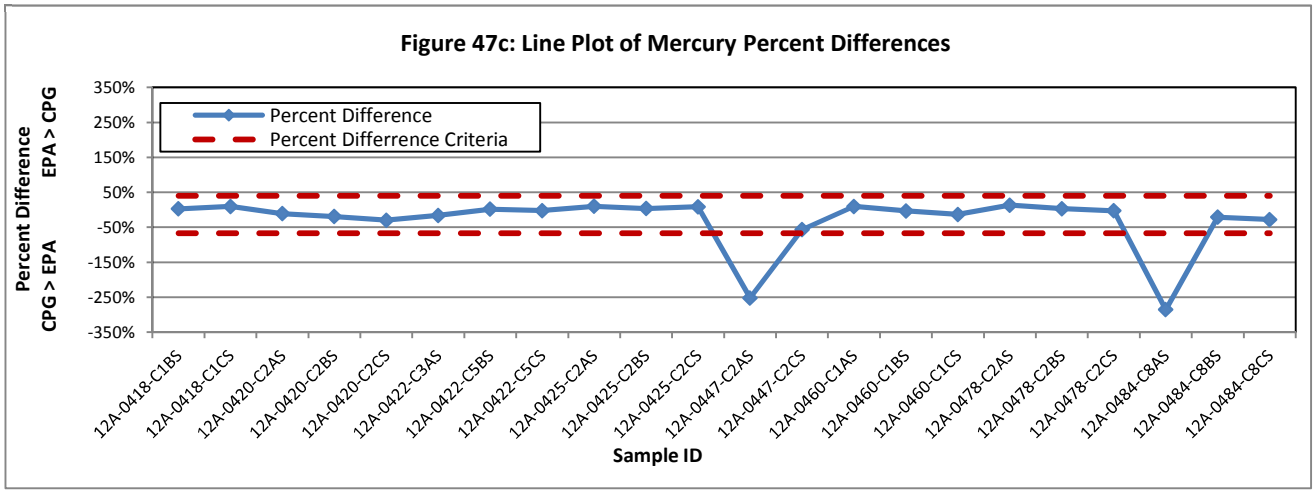
Statistical Plot of Sediment Zinc Concentrations

Figure 46







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Statistical Plot of Sediment Mercury Concentrations

Figure 47