Statistical Analyses and Summary of Analytical Round Robin #4 – a Data Comparability Study

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Samples collected February 8, 2010 from Dauphin Island and Three-Mile Creek, AL by the Alabama Department of Environmental Management
Preserved and split February 9, and shipped February 10, 2010 at the Florida Department of Environmental Protection's Central Laboratory, Tallahassee, FL

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1. **Introduction**

Many groups routinely take measurements in ambient waters of the Gulf of Mexico. However, each group uses slightly different standard operating procedures (SOPs), equipment, and standards, which leads to an unknown amount of variability in the data collected. This lack of data comparability has been the subject of many discussions. The Gulf of Mexico Alliance (GOMA) identified the need to assess this variability and to explore ways to decrease variability in the data values based solely on changes to SOPs. The GOMA initiated its analytical round robin efforts in February 2008 to address this need.

In September 2007, GOMA workshop participants established a core set of analytes (see Table 1 for the analytes analyzed in this round robin and their method of preservation) for adoption by Gulf of Mexico monitoring programs. This forth analytical round robin addresses the variability in analytes among participating Gulf of Mexico laboratories. This report presents information on the collection and methods used to prepare the water for analyses, the results from the laboratories, and the statistical analyses that were conducted to assess the comparability of the data.

Analyte	**Acid preserved**	**0.45-µm filtered**
Chlorophyll a (it is unclear if results are corrected or uncorrected for phaeophytin)	No	No
Biochemical Oxygen Demand	No	No
Carbonaceous Biochemical Oxygen Demand	No	No
Total Nitrite	No	No
Total Kjeldahl Nitrogen	Yes	No
Ammonia	Yes	No
Total Nitrate + Nitrite	Yes	No
Total Phosphorous	Yes	No
Total Organic Carbon	Yes	No
Dissolved Organic Carbon	Yes	Yes
Dissolved Nitrate + Nitrite	Yes	Yes
Dissolved Nitrite	No	Yes
Orthophosphate	No	Yes

Table 1. Core analytes and preservation methods for this round robin.

A total of fifteen laboratories, representing local, state, federal, academic, and private laboratories participated in this round robin. Samples were collected on 8 February 2010 from Dauphin Island and Three-Mile Creek, AL by the Alabama Department of Environmental Management. Sites were selected in an effort to provide one sample that was high in nutrients and another that was low. Field measurements are listed in Table 2.

	Dauphin Island	Three-Mile Creek
Depth (m)	1.0	2.0
Temperature (ºC)	11.8	10.12
pH	7.49	7.67
Dissolved Oxygen (mg/L)	7.71	10.70
Salinity (PSU)	0.11	4.60
Conductivity (mS)	0.224	8.244

Table 2. Field measurements.

The Florida Department of Environmental Protection's Central Laboratory in Tallahassee, FL hosted the round robin event.

For each participating laboratory, samples were split to provide:

- 1 L of unfiltered, unpreserved sample for chlorophyll a (ChlA)
- 1 L of unfiltered, unpreserved sample for biochemical oxygen demand (BOD)
- 1 L of unfiltered, unpreserved sample for carbonaceous biochemical oxygen demand (CBOD)
- 125 mL of unfiltered, unpreserved sample for total nitrite (NO_2)
- 250 mL of unfiltered, acid-preserved sample for total nitrate + nitrite (NO_x) , ammonia (NH_3) , Total Kjeldahl Nitrogen (TKN), total phosphorous (TP), and total organic carbon (TOC)
- 125 mL of 0.45-µm filtered, unpreserved sample for orthophosphate (OP) and dissolved nitrite (DNO_2)
- 125 mL of 0.45-µm filtered, acid-preserved sample for dissolved nitrate + nitrite (DNO_x) and dissolved organic carbon (DOC)

Samples for each bottle type were kept homogenized by constant stirring. Each laboratory received three replicates of each of the above sample types for Dauphin Island, and four replicates for Three-Mile Creek. Samples were kept in a walk-in cooler at 4 ^oC until shipment, and were shipped on ice in coolers on ice.

Laboratories were given approximately six weeks to complete their analyses and provide results. Methods used by participating laboratories were not explored in this round robin.

Laboratories participating in Analytical Round Robin #4:

ADEM_Mob – Alabama Department of Environmental Management, Mobile Laboratory (AL)
ADEM_Mon – Alabama Department of Environmental Management, Montgomery, Field Operations Central Laboratory (AL)
Benchmark – Benchmark EnviroAnalytical, Inc. (FL)
Eastex – Eastex Environmental Laboratory, Inc. (TX)
EPA – U.S. Environmental Protection Agency, Region 4 Laboratory (GA)
EPCHC – Environmental Protection Commission of Hillsborough County (FL)
FDEP – Florida Department of Environmental Protection Central Laboratory, Tallahassee (FL)
FWRI – Florida Fish & Wildlife Conservation Commission, Fish & Wildlife Research Institute, Harmful Algal Blooms (FL)
MDEQ – Mississippi Department of Environmental Quality (MS)
Sanders – Sanders Laboratories, Inc. (FL)
SERC – Florida International University, Southeast Environmental Research Center (FL)
SFWMD – South Florida Water Management District, Water Quality Analysis Division, Chemistry Laboratory (FL)
SWFWMD – Southwest Florida Water Management District, Data Collection Bureau, Chemistry Laboratory (FL)
TCEQ – Texas Commission on Environmental Quality, Houston Laboratory (TX)
USGS – USGS National Water Quality Laboratory (CO)

2. Determining comparability

In all analyses, the actual value reported by the laboratory was used regardless of significant figures, with the exception of those requiring conversion (e.g., µg/L to mg/L). However, data in this report are typically displayed to two or three decimal places. Data values reported by the laboratories are displayed graphically.

Data were analyzed using statistical methods developed by Hoaglin et al (1983) which are used in the U.S. Geological Survey's Standard Reference Samples (SRS) round robins (e.g., Woodworth and Connor 2003). Variability among laboratories was measured by calculating F-pseudosigma, which approximates the standard deviation without the assumption of normal distribution. It is considered a robust statistic because outliers have little influence resulting from a higher breakdown point than that of the mean. The %F-pseudosigma, which is equivalent to % relative standard deviation (%RSD) under normal distributions, was also calculated. In order to evaluate inter-laboratory variability, Z-values were calculated; the average of these was used to rate the laboratories' performance. The absolute Z-values are rated as follows: 0.00 - 0.50 = excellent; 0.51 - 1.00 = good; 1.01 – 1.50 = satisfactory; 1.51 – 2.00 = marginal; and >2.00 = unsatisfactory. Z-values greater than 6 typically are the result of mistakes due to unit conversions, calculation errors, dilution errors, transcription errors (and other typographical errors), etc. (e.g., QUASIMEME 2012). Although this system of rating will be used, it is important to note that, as the group's precision increases, the Z-values can become inflated, making comparable values appear to be non-comparable. These three methods are used when at least seven laboratories report at least three detectable values (i.e., N≥21; roughly a 60% chance of being able to detect a difference in values based on power analysis). In situations where less than 21 values are reported, summary statistics and robust estimators (based on Kaplan-Meier; e.g., Helsel 2012) are provided; no further analyses are performed. In addition, robust estimators are given for analytes with non-values (i.e., data reported or qualified as qualifier codes such as: <, <PQL, BDL, etc.). False negatives are evaluated using the U.S.G.S. SRS method. To be considered a false negative, a result must be reported as a non-value and the detection/quantitation limit must be more than 2 F-pseudosigma below the median.

Outliers are evaluated using a variety of statistical methods, including Mahalanobis D^2, Rosner's test and Dixon's test. For post hoc comparisons (between subjects tests for inter-laboratory comparisons), if only one value was reported, it was combined with the laboratory reporting multiple results whose mean and median were closest to the individual value and whose range of data contained that individual value. Whether statistical assumptions (normality, homoscedasticity, independence, balanced design, etc.) are met or not will guide which statistical tests are employed.

Note: The breakdown point of a statistic is a measure of how many values one would have to change in order to have the statistic change. For the mean, it requires only one extreme outlier to do this. To change the median, at least one-half of all values must become extreme outliers. For example, in a set of five values: 1, 2, 1, 3, and 2, the mean is 1.8 and the median is 2. If the 3 in this set is increased to 300, the mean becomes 61.2; however, the median is still 2.

Note: Within-subjects tests are comparisons of three or more groups. They indicate only that there is a difference among groups, but do not identify which ones or distinguish how they differ. Examples are ANOVA and Kruskal-Wallis. Between-subjects tests are a follow-up to the

within-subjects test (i.e., post hoc). They identify the group(s) that is different and how they differ. These include Gabriel's test, t-tests, Mann-Whitney, and many other pair-wise comparisons. In a comparison of only two groups, the within-subjects test and the between-subjects tests render the same results.

Table 3 lists the analytes and the number of laboratories that analyzed each.

	Dauphin Island		Three-Mile Creek	
Analyte	N laboratories	N values >MDL	N laboratories	N values >MDL
TKN	11	33	11	44
NH_3	14	29	14	56
NO_x	10	30	10	40
NO_2	10	22	10	39
DNO_x	12	35	12	47
DNO_2	11	20	11	43
TP	14	41	14	56
OP	13	33	13	51
TOC	7	21	7	28
DOC	7	21	7	28
ChlA	14	42	14	44
BOD	9	8	9	28
CBOD	9	6	9	23

* More results were reported as above the MDL, but no value was given (i.e., only a qualifier [<PQL, I, etc.] was listed).

Table 3. Analytes of interest for this round robin; the number of laboratories that ran each; and the number of values above a given laboratory's detection limit.

Laboratory identities were concealed by assigning letter designations so that laboratories do not feel judged by their results. Furthermore, in order to maintain anonymity, laboratories are not listed with the analyses they conducted or the number of results they reported. The GOMA round robins are critical in helping achieve data comparability, and serve as a tool for groups to speak freely about what they are and are not comfortable with in their methodology, rather than as a way to grade programs on their results.

3. Results and Discussion

NOTE: After the samples were shipped to the participating laboratories, three laboratories notified the round robin coordinator that they had received non-acidified aliquots that appeared to be acidified. The coordinator notified all participants to check the pH of their samples for verification, and then launched an investigation. A fourth laboratory noted that it received two acidified bottles that should have been unacidified. A total of fifteen bottles containing three analytes, including total nitrite, dissolved nitrite and orthophosphate, from the four laboratories were affected. Ion chromatography showed that the affected bottles were contaminated with hydrochloric acid (HCl) rather than the sulfuric acid used to preserve the samples. The HCl contamination was due to the host laboratory cleaning the tubing used to split the sample with 10% HCl without thoroughly flushing the tubing with sample water prior to filling the bottles. The results from the fifteen bottles are not included in these analyses.

A. Total Kjeldahl Nitrogen. Thirty of the 33 values for Dauphin Island were within acceptable ranges. Lab F reported all three values outside acceptable ranges, each of which were more than a magnitude greater than the other laboratories' values. Two of Lab F's results were statistical outliers (7.0 and 7.7 mg/L). The %F-pseudosigma value was large (greater than 30%), indicating a lack of precision among laboratories. Of the 33 reported values, 55% were within 1 F-pseudosigma and 91% were within 2 F-pseudosigma.

At Three-Mile Creek, 39 of the 44 values were within acceptable ranges. Lab F reported all four values outside of acceptable ranges, and Lab D reported one value outside of acceptable ranges. One of Lab F's results was a statistical outlier (18.3 mg/L). The %F-pseudosigma value was very small (less than 10%), indicating a higher degree of precision at increased analyte concentrations among laboratories. Of the 44 reported values, 66% were within 1 F-pseudosigma and 89% were within 2 F-pseudosigma. At both locations, Lab F's values were re-examined in order to ensure these were not conversion or typographical errors, they were not. It is unclear why this laboratory's results are so much greater than the others. See Figures 1 & 2 for scatter-plots of values obtained by individual laboratories. See Tables 4 - 9 for F-pseudosigma values, summary statistics and inter-laboratory comparisons.

Total Kjeldahl Nitrogen				
Location	**F-pseudosigma**	**% F-pseudosigma**	**Median**	**Range**
Dauphin Island	0.115	30.33%	0.380	7.527
Three-Mile Creek	0.092	6.90%	1.335	17.220

Table 4. F-pseudosigma values for TKN.

TKN

	Dauphin Island				Three-Mile Creek			
Lab ID	N	Lab Median	Range	Mean Z-value	N	Lab Median	Range	Mean Z-value
A	3	0.360	0.040	0.17	4	1.300	0.200	0.73
B	3	0.489	0.316	1.23	4	1.327	0.104	0.36
C	3	0.177	0.014	1.75	4	1.415	0.087	0.87
D	3	0.220	0.040	1.33	4	1.170	0.130	1.93
F	3	7.000	5.300	46.26	4	4.450	14.200	70.54
G	3	0.357	0.032	0.21	4	1.370	0.050	0.35
H	3	0.380	0.000	0.00	4	1.295	0.020	0.46
J	3	0.500	0.050	1.13	4	1.325	0.290	1.30
M	3	0.540	0.100	1.28	4	1.300	0.200	0.73
N	3	0.387	0.013	0.04	4	1.325	0.030	0.14
O	3	0.470	0.020	0.78	4	1.400	0.200	0.90

Table 5. Summary statistics and Z-values by laboratory for TKN.

Descriptives

Total Kjeldahl Nitrogen mg/L

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
A	3	.36000	.020000	.011547	.31032	.40968	.340	.380
B	3	.39833	.176435	.101865	-.03996	.83662	.195	.511
C	3	.17900	.007211	.004163	.16109	.19691	.173	.187
D	3	.22667	.020817	.012019	.17496	.27838	.210	.250
F	3	5.70000	2.879236	1.662328	-1.45242	12.85242	2.400	7.700
G	3	.35567	.016042	.009262	.31582	.39552	.339	.371
H	3	.38000	.000000	.000000	.38000	.38000	.380	.380
J	3	.51000	.026458	.015275	.44428	.57572	.490	.540
M	3	.52667	.051316	.029627	.39919	.65414	.470	.570
N	3	.38167	.007234	.004177	.36370	.39964	.377	.390
O	3	.47000	.010000	.005774	.44516	.49484	.460	.480
Total	33	.86255	1.715826	.298687	.25414	1.47095	.173	7.700

Table 6. Descriptive statistics by laboratory for TKN for Dauphin Island.

Descriptives

Total Kjeldahl Nitrogen mg/L

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
A	4	1.30000	.081650	.040825	1.17008	1.42992	1.200	1.400
B	4	1.31975	.044761	.022381	1.24852	1.39098	1.261	1.365
C	4	1.41475	.035855	.017928	1.35770	1.47180	1.371	1.458
D	4	1.15750	.055603	.027801	1.06902	1.24598	1.080	1.210
F	4	7.82500	6.985401	3.492701	-3.29033	18.94033	4.100	18.300
G	4	1.36750	.022174	.011087	1.33222	1.40278	1.340	1.390
H	4	1.29250	.009574	.004787	1.27727	1.30773	1.280	1.300
J	4	1.34000	.142595	.071297	1.11310	1.56690	1.210	1.500
M	4	1.30000	.081650	.040825	1.17008	1.42992	1.200	1.400
N	4	1.32500	.012910	.006455	1.30446	1.34554	1.310	1.340
O	4	1.39000	.082865	.041433	1.25814	1.52186	1.280	1.480
Total	44	1.91200	2.643765	.398563	1.10822	2.71578	1.080	18.300

Table 7. Descriptive statistics by laboratory for TKN for Three-Mile Creek.

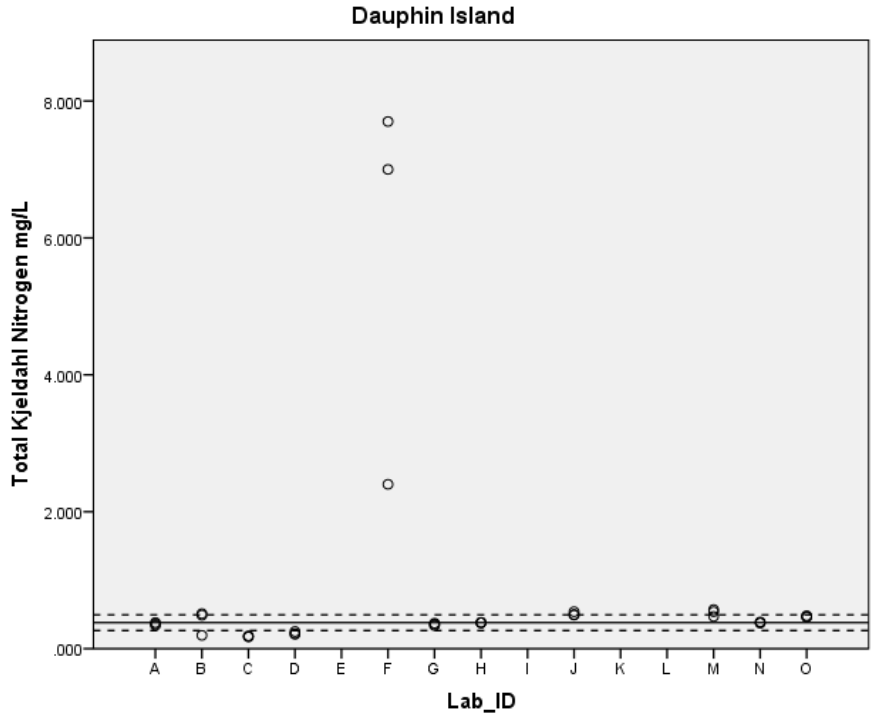

Figure 1. Scatter-plot of TKN values obtained by eleven laboratories for Dauphin Island. The solid line indicates the overall median, and the dashed lines indicate +/- 1 F-pseudosigma.

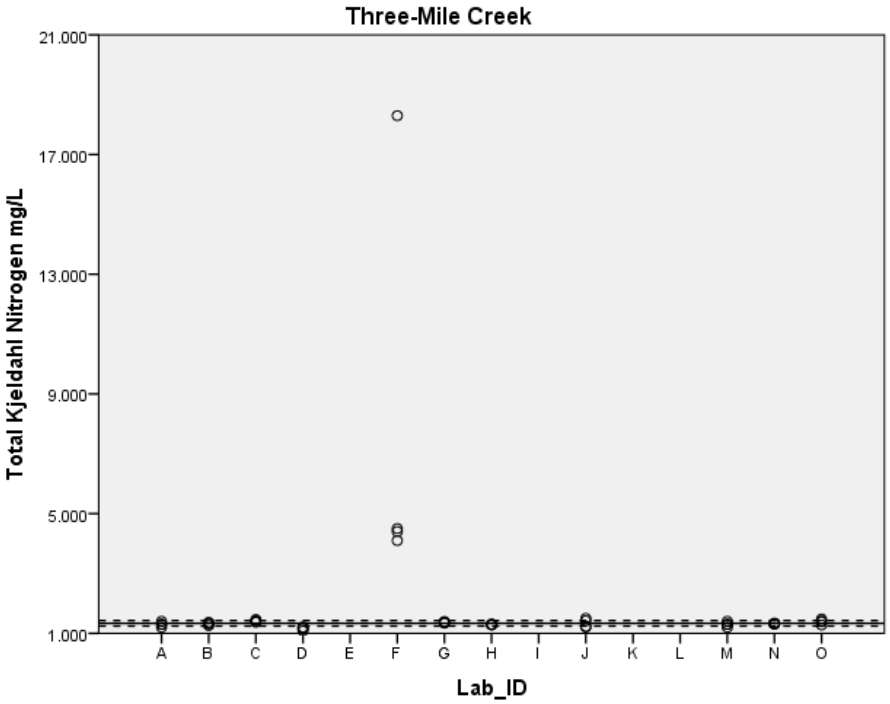

Figure 2. Scatter-plot of TKN values obtained by eleven laboratories for Three-Mile Creek. The solid line indicates the overall median, and the dashed lines indicate +/- 1 F-pseudosigma.

Hypothesis Test Summary

	Null Hypothesis	Test	Sig.	Decision
1	The medians of Total Kjeldahl Nitrogen mg/L are the same across categories of Lab_ID.	Independent-Samples Median Test	.002	Reject the null hypothesis.
2	The distribution of Total Kjeldahl Nitrogen mg/L is the same across categories of Lab_ID.	Independent-Samples Kruskal-Wallis Test	.002	Reject the null hypothesis.

Asymptotic significances are displayed. The significance level is .05.

Homogeneous Subsets based on Total Kjeldahl Nitrogen mg/L

		Subset				
		1	2	3	4	5
Sample[1]	C	2.000				
	D		6.000			
	G		10.000			
	A		12.167	12.167		
	N		15.333	15.333	15.333	
	H		16.500	16.500	16.500	
	B		18.333	18.333	18.333	
	O		21.500	21.500	21.500	
	J			26.500	26.500	26.500
	M				26.667	26.667
	F					32.000
Test Statistic		.[2]	11.717	10.293	10.827	5.535
Sig. (2-sided test)		.	.069	.067	.055	.063
Adjusted Sig. (2-sided test)		.	.106	.120	.098	.212

Homogeneous subsets are based on asymptotic significances. The significance level is .05.

[1]Each cell shows the sample average rank of Total Kjeldahl Nitrogen mg/L.

[2]Unable to compute because the subset contains only one sample.

Table 8. Kruskal-Wallis and post hoc inter-laboratory comparisons for TKN from Dauphin Island.

Hypothesis Test Summary

	Null Hypothesis	Test	Sig.	Decision
1	The medians of Total Kjeldahl Nitrogen mg/L are the same across categories of Lab_ID.	Independent-Samples Median Test	.008	Reject the null hypothesis.
2	The distribution of Total Kjeldahl Nitrogen mg/L is the same across categories of Lab_ID.	Independent-Samples Kruskal-Wallis Test	.002	Reject the null hypothesis.

Asymptotic significances are displayed. The significance level is .05.

Homogeneous Subsets based on Total Kjeldahl Nitrogen mg/L

		Subset		
		1	2	3
Sample[1]	D	3.125		
	H	13.375	13.375	
	A	17.000	17.000	
	M	17.000	17.000	
	B	20.250	20.250	
	N	21.375	21.375	
	J	22.625	22.625	
	G	27.250	27.250	
	O	28.750	28.750	
	C		34.250	
	F			42.500
Test Statistic		15.480	12.478	.[2]
Sig. (2-sided test)		.050	.131	.
Adjusted Sig. (2-sided test)		.061	.158	.

Homogeneous subsets are based on asymptotic significances. The significance level is .05.

[1]Each cell shows the sample average rank of Total Kjeldahl Nitrogen mg/L.

[2]Unable to compute because the subset contains only one sample.

Table 9. Kruskal-Wallis and post hoc inter-laboratory comparisons for TKN from Three-Mile Creek.

B. Ammonia. Twenty-five of the 29 reported values for Dauphin Island were within acceptable ranges. Labs E and O reported two values outside acceptable ranges. Labs B and M reported all three results below the detection limits. Labs F and J reported all three results as below the quantitation limit (PQL), and D reported one result as less than the PQL (i.e., no value was reported; these three labs did not report any results for any analytes that fell between the MDL and PQL; the results are treated as non-detects). The MDLs ranged from 0.0007 to 0.029 mg/L; and the PQLs for Labs D, F, and J ranged from 0.04 to 0.1 mg/L. Of the 42 total results, thirteen were non-values (31%). The %F-pseudosigma value was moderate (between 20 and 30%), indicating a lack of precision among laboratories. Of the 29 reported values, 69% were within 1 F-pseudosigma and 86% were within 2 F-pseudosigma.

At Three-Mile Creek, 48 of the 56 values were within acceptable ranges. Labs E and F reported all four values outside acceptable ranges. The %F-pseudosigma value was very small (less than 10%), indicating a higher degree of precision at increased analyte concentrations among laboratories. Of the 56 reported values, 79% were within 1 F-pseudosigma and 86% were within 2 F-pseudosigma. See Figures 3 & 4 for scatter-plots of values obtained by individual laboratories. See Tables 10 - 15 for F-pseudosigma values, summary statistics and inter-laboratory comparisons.

Ammonia				
	F-pseudosigma	**% F-pseudosigma**	**Median**	**Range**
Dauphin Island	0.013	28.64%	0.044	0.066
Three-Mile Creek	0.055	8.36%	0.663	0.637

Table 10. F-pseudosigma values for ammonia.

NH_3

	Dauphin Island				Three-Mile Creek			
Lab ID	N	Lab Median	Range	Mean Z-value	N	Lab Median	Range	Mean Z-value
A	3	0.046	0.008	0.26	4	0.670	0.020	0.15
B	3	NR	NR	NR	4	0.616	0.008	0.84
C	3	0.040	0.000	0.31	4	0.640	0.005	0.43
D	3*	0.055	0.010	0.85	4	0.660	0.060	0.30
E	3	0.014	0.006	2.13	4	0.907	0.071	4.39
F	3	NR	NR	NR	4	0.350	0.100	5.69
G	3	0.035	0.014	0.59	4	0.667	0.071	0.57
H	3	0.039	0.016	0.64	4	0.676	0.026	0.25
I	3	0.052	0.005	0.69	4	0.672	0.086	0.51
J	3	NR	NR	NR	4	0.715	0.040	0.99
L	3	0.040	0.009	0.33	4	0.682	0.002	0.35
M	3	NR	NR	NR	4	0.610	0.010	1.01
N	3	0.054	0.001	0.79	4	0.703	0.009	0.73
O	3	0.080	0.010	2.51	4	0.615	0.020	0.83

* One non-value reported. NR = all non-values reported.

Table 11. Summary statistics and Z-values by laboratory for ammonia.

Descriptives

Ammonia mg/L

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
A	3	.04533	.004041	.002333	.03529	.05537	.041	.049
C	3	.04000	.000000	.000000	.04000	.04000	.040	.040
D	2	.05500	.007071	.005000	-.00853	.11853	.050	.060
E	3	.01637	.003625	.002093	.00736	.02537	.014	.021
G	3	.03633	.007095	.004096	.01871	.05396	.030	.044
H	3	.03567	.008505	.004910	.01454	.05679	.026	.042
I	3	.05300	.002646	.001528	.04643	.05957	.051	.056
L	3	.03967	.004509	.002603	.02847	.05087	.035	.044
N	3	.05433	.000577	.000333	.05290	.05577	.054	.055
O	3	.07667	.005774	.003333	.06232	.09101	.070	.080
Total	29	.04490	.016085	.002987	.03878	.05102	.014	.080

Table 12. Descriptive statistics by laboratory for ammonia for Dauphin Island.

Descriptives

Ammonia mg/L

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
A	4	.67000	.008165	.004082	.65701	.68299	.660	.680
B	4	.61700	.003830	.001915	.61091	.62309	.614	.622
C	4	.63950	.002082	.001041	.63619	.64281	.637	.642
D	4	.65500	.025166	.012583	.61496	.69504	.620	.680
E	4	.90440	.029658	.014829	.85721	.95160	.866	.937
F	4	.35000	.057735	.028868	.25813	.44187	.300	.400
G	4	.67125	.036746	.018373	.61278	.72972	.640	.711
H	4	.67700	.011431	.005715	.65881	.69519	.665	.691
I	4	.65850	.039854	.019927	.59508	.72192	.602	.688
J	4	.71750	.017078	.008539	.69032	.74468	.700	.740
L	4	.68200	.000816	.000408	.68070	.68330	.681	.683
M	4	.60750	.005000	.002500	.59954	.61546	.600	.610
N	4	.70325	.004031	.002016	.69684	.70966	.699	.708
O	4	.61750	.009574	.004787	.60227	.63273	.610	.630
Total	56	.65503	.112764	.015069	.62483	.68523	.300	.937

Table 13. Descriptive statistics by laboratory for ammonia for Three-Mile Creek.

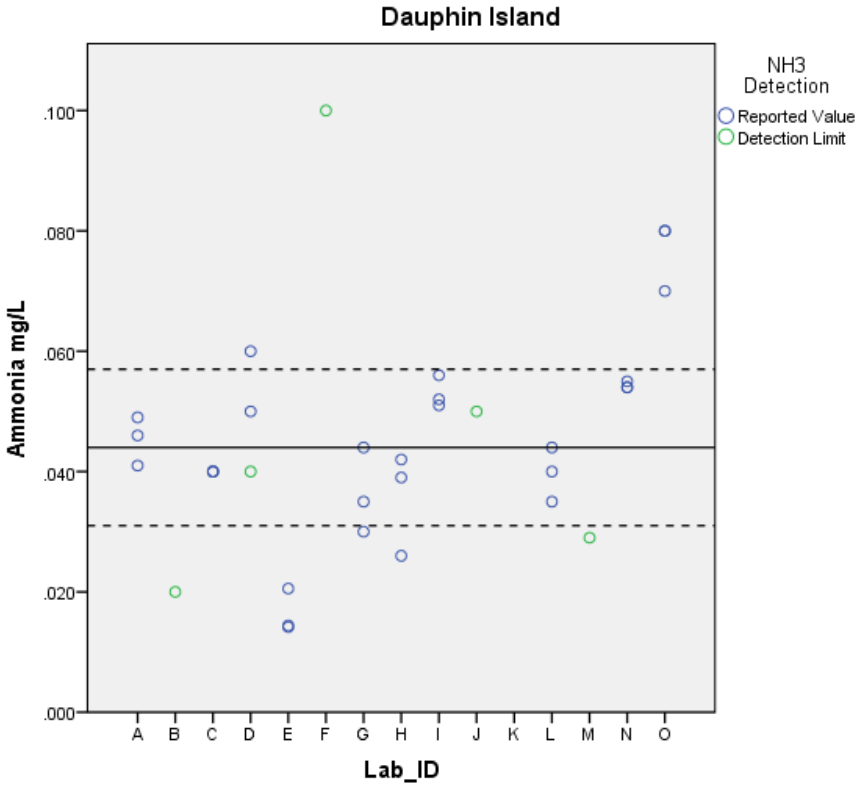

Figure 3. Scatter-plot of ammonia values and detection/quantitation limits obtained by fourteen laboratories for Dauphin Island. The solid line indicates the overall median, and the dashed lines indicate +/- 1 F-pseudosigma.

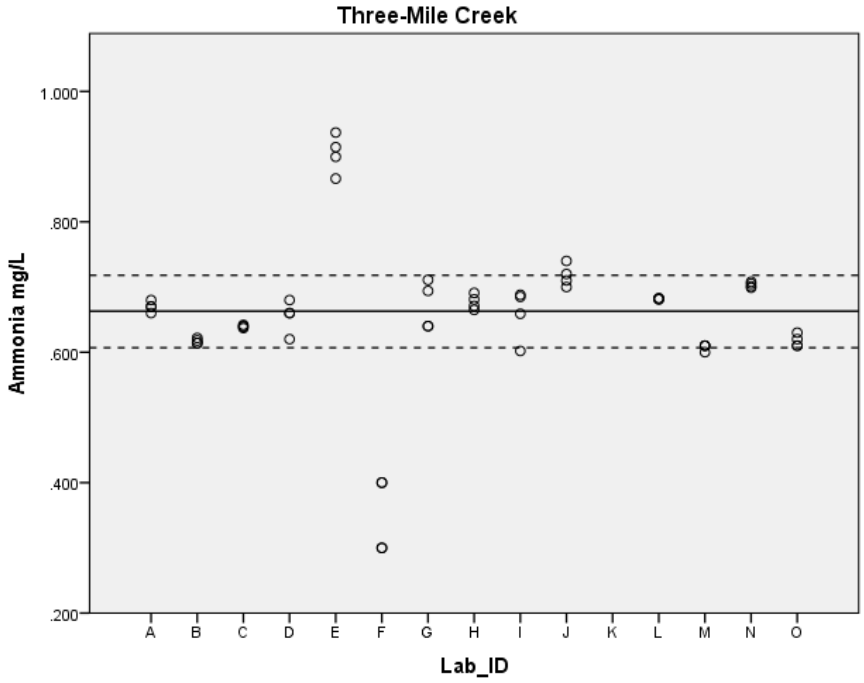

Figure 4. Scatter-plot of ammonia values and detection/quantitation limits obtained by fourteen laboratories for Three-Mile Creek. The solid line indicates the overall median, and the dashed lines indicate +/- 1 F-pseudosigma.

Ammonia mg/L

	Lab ID	N	Subset for alpha = 0.05			
			1	2	3	4
Gabriel[a,b]	E	3	0.01637			
	H	3		0.03567		
	G	3		0.03633		
	L	3		0.03967	0.03967	
	C	3		0.04000	0.04000	
	A	3		0.04533	0.04533	
	I	3			0.05300	
	N	3			0.05433	
	D	2			0.05500	
	O	3				0.07667
	Sig.		1.000	.623	.060	1.000

Means for groups in homogeneous subsets are displayed.
a. Uses Harmonic Mean Sample Size = 2.857.
b. The group sizes are unequal. The harmonic mean of the group sizes is used. Type I error levels are not guaranteed.

Table 14. Post hoc inter-laboratory (between subjects) comparison for ammonia from Dauphin Island.

Hypothesis Test Summary

	Null Hypothesis	Test	Sig.	Decision
1	The medians of Ammonia mg/L are the same across categories of Lab_ID.	Independent-Samples Median Test	.000	Reject the null hypothesis.
2	The distribution of Ammonia mg/L is the same across categories of Lab_ID.	Independent-Samples Kruskal-Wallis Test	.000	Reject the null hypothesis.

Asymptotic significances are displayed. The significance level is .05.

Homogeneous Subsets based on Ammonia mg/L

		Subset							
		1	2	3	4	5	6	7	8
Sample[1]	F	2.500							
	M		8.000						
	O		12.875	12.875					
	B		14.000	14.000	14.000				
	C			21.250	21.250	21.250			
	D			25.750	25.750	25.750	25.750		
	I			28.000	28.000	28.000	28.000		
	A				30.375	30.375	30.375		
	G				34.250	34.250	34.250		
	H					34.625	34.625		
	L					37.375	37.375		
	N						46.250	46.250	
	J							49.250	
	E								54.500
Test Statistic		.[2]	5.521	8.665	10.714	10.201	12.126	2.083	.[2]
Sig. (2-sided test)		.	.063	.070	.057	.116	.059	.149	.
Adjusted Sig. (2-sided test)		.	.263	.184	.129	.219	.115	.677	.

Homogeneous subsets are based on asymptotic significances. The significance level is .05.

[1]Each cell shows the sample average rank of Ammonia mg/L.

[2]Unable to compute because the subset contains only one sample.

Table 15. Kruskal-Wallis and post hoc inter-laboratory comparisons for ammonia from Three-Mile Creek.

C. Total Nitrite + Nitrate. Twenty-four of the 30 reported values for Dauphin Island were within acceptable ranges. Labs F and M reported all three values outside acceptable ranges. Lab F reported one statistical outlier (0.30 mg/L). The %F-pseudosigma value was very small (less than 10%), indicating a high degree of precision among laboratories. Of the 30 reported values, 70% were within 1 F-pseudosigma and 80% were within 2 F-pseudosigma.

At Three-Mile Creek, 33 of the 40 values were within acceptable ranges. Lab M reported all four values outside acceptable ranges, Lab F reported two, and Lab D reported one. Lab M reported two statistical outliers (2.52 and 2.48 mg/L). The %F-pseudosigma value was very small (less than 10%), indicating a high degree of precision among laboratories. Of the 40 reported values, 73% were within 1 F-pseudosigma and 83% were within 2 F-pseudosigma. See Figures 5 & 6 for scatter-plots of values obtained by individual laboratories. See Tables 16 - 21 for F-pseudosigma values, summary statistics and inter-laboratory comparisons.

NO_x				
	F-pseudosigma	**% F-pseudosigma**	**Median**	**Range**
Dauphin Island	0.016	9.27%	0.170	0.160
Three-Mile Creek	0.084	4.60%	1.825	0.900

Table 16. F-pseudosigma values for NO_x.

NO_x

	Dauphin Island				Three-Mile Creek			
Lab ID	N	Lab Median	Range	Mean Z-value	N	Lab Median	Range	Mean Z-value
A	3	0.170	0.000	0.00	4	1.900	0.000	0.89
B	3	0.141	0.001	1.83	4	1.764	0.003	0.73
C	3	0.169	0.001	0.08	4	1.781	0.013	0.52
D	3	0.156	0.002	0.88	4	1.785	0.170	0.77
F	3	0.230	0.090	4.79	4	1.735	0.290	1.49
G	3	0.185	0.005	0.83	4	1.870	0.040	0.42
J	3	0.170	0.000	0.00	4	1.845	0.060	0.30
L	3	0.171	0.020	0.44	4	1.850	0.140	0.57
M	3	0.243	0.016	4.52	4	2.395	0.400	6.34
O	3	0.167	0.004	0.15	4	1.750	0.050	0.86

Table 17. Summary statistics and Z-values by Laboratory for NO_x.

Descriptives

Total $NO_3 + NO_2$ mg/L

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
A	3	.17000	.000000	.000000	.17000	.17000	.170	.170
B	3	.14067	.000577	.000333	.13923	.14210	.140	.141
C	3	.16867	.000577	.000333	.16723	.17010	.168	.169
D	3	.15600	.001000	.000577	.15352	.15848	.155	.157
F	3	.24667	.047258	.027285	.12927	.36406	.210	.300
G	3	.18333	.002887	.001667	.17616	.19050	.180	.185
J	3	.17000	.000000	.000000	.17000	.17000	.170	.170
L	3	.16700	.010583	.006110	.14071	.19329	.155	.175
M	3	.24233	.008021	.004631	.22241	.26226	.234	.250
O	3	.16767	.002082	.001202	.16250	.17284	.166	.170
Total	30	.18123	.036267	.006621	.16769	.19478	.140	.300

Table 18. Descriptive statistics by laboratory for NO_x for Dauphin Island.

Descriptives

Total $NO_3 + NO_2$ mg/L

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
A	4	1.90000	.000000	.000000	1.90000	1.90000	1.900	1.900
B	4	1.76350	.001291	.000645	1.76145	1.76555	1.762	1.765
C	4	1.78125	.006238	.003119	1.77132	1.79118	1.775	1.788
D	4	1.76000	.076158	.038079	1.63882	1.88118	1.650	1.820
F	4	1.75000	.147196	.073598	1.51578	1.98422	1.620	1.910
G	4	1.86000	.020000	.010000	1.82818	1.89182	1.830	1.870
J	4	1.84750	.025000	.012500	1.80772	1.88728	1.820	1.880
L	4	1.82500	.064031	.032016	1.72311	1.92689	1.730	1.870
M	4	2.35750	.182643	.091321	2.06687	2.64813	2.120	2.520
O	4	1.75250	.022174	.011087	1.71722	1.78778	1.730	1.780
Total	40	1.85972	.189336	.029937	1.79917	1.92028	1.620	2.520

Table 19. Descriptive statistics by laboratory for NO_x for Three-Mile Creek.

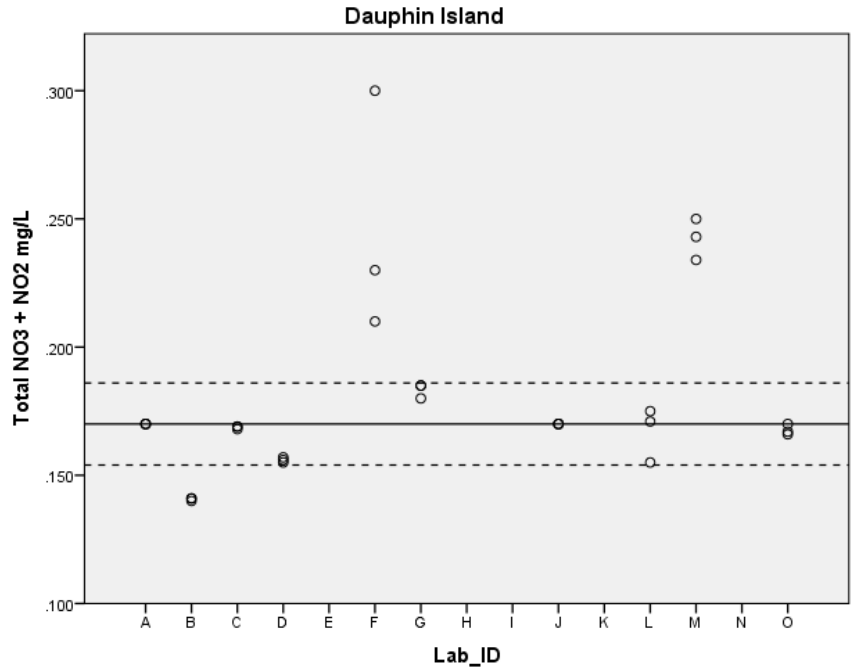

Figure 5. Scatter-plot of NO_x values and detection limits obtained by ten laboratories for Dauphin Island. The solid line indicates the overall median, and the dashed lines indicate +/- 1 F-pseudosigma.

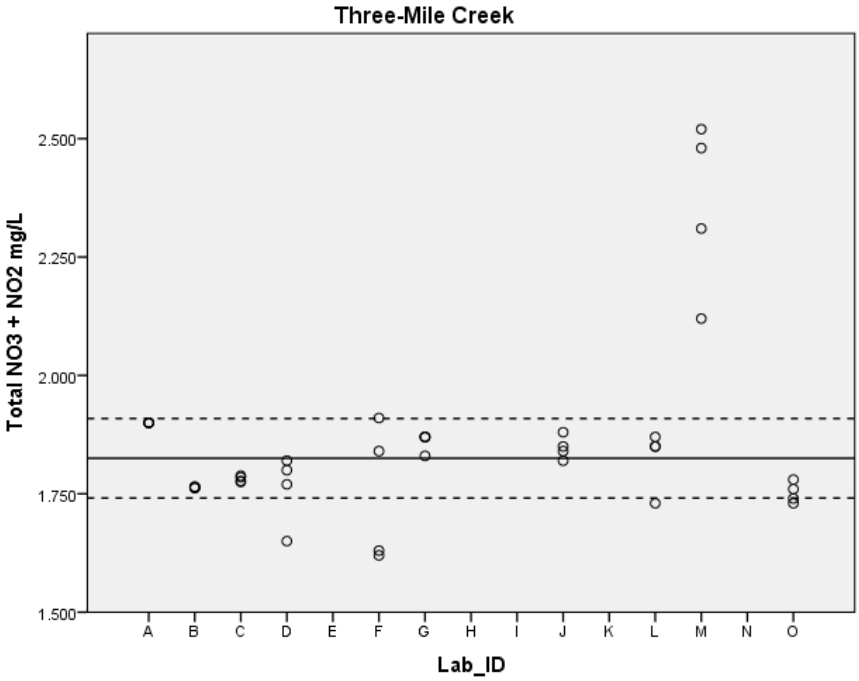

Figure 6. Scatter-plot of NO_x values and detection limits obtained by ten laboratories for Three-Mile Creek. The solid line indicates the overall median, and the dashed lines indicate +/- 1 F-pseudosigma.

Hypothesis Test Summary

	Null Hypothesis	Test	Sig.	Decision
1	The medians of Total NO3 + NO2 mg/L are the same across categories of Lab_ID.	Independent-Samples Median Test	.001	Reject the null hypothesis.
2	The distribution of Total NO3 + NO2 mg/L is the same across categories of Lab_ID.	Independent-Samples Kruskal-Wallis Test	.002	Reject the null hypothesis.

Asymptotic significances are displayed. The significance level is .05.

Homogeneous Subsets based on Total NO_3 + NO_2 mg/L					
		Subset			
		1	2	3	4
Sample[1]	B	2.000			
	D		5.833		
	O		11.000	11.000	
	C		11.000	11.000	
	L		15.167	15.167	
	A		16.000	16.000	
	J		16.000	16.000	
	G			23.000	23.000
	F				27.000
	M				28.000
Test Statistic		.[2]	9.019	10.917	5.647
Sig. (2-sided test)		.	.108	.053	.059
Adjusted Sig. (2-sided test)		.	.174	.087	.185

Homogeneous subsets are based on asymptotic significances. The significance level is .05.

[1]Each cell shows the sample average rank of Total NO_3 + NO_2 mg/L.

[2]Unable to compute because the subset contains only one sample.

Table 20. Kruskal-Wallis and post hoc inter-laboratory comparisons for NO_x from Dauphin Island.

Hypothesis Test Summary

	Null Hypothesis	Test	Sig.	Decision
1	The medians of Total NO3 + NO2 mg/L are the same across categories of Lab_ID.	Independent-Samples Median Test	.000	Reject the null hypothesis.
2	The distribution of Total NO3 + NO2 mg/L is the same across categories of Lab_ID.	Independent-Samples Kruskal-Wallis Test	.001	Reject the null hypothesis.

Asymptotic significances are displayed. The significance level is .05.

Homogeneous Subsets based on Total NO_3 + NO_2 mg/L					
		Subset			
		1	2	3	4
Sample[1]	O	8.125			
	B	9.500	9.500		
	D	13.125	13.125		
	C	15.000	15.000		
	F	15.375	15.375	15.375	
	L	20.750	20.750	20.750	
	J	24.500	24.500	24.500	
	G		26.625	26.625	
	A			33.500	
	M				38.500
Test Statistic		9.961	12.249	7.782	.[2]
Sig. (2-sided test)		.126	.057	.100	.
Adjusted Sig. (2-sided test)		.175	.080	.190	.

Homogeneous subsets are based on asymptotic significances. The significance level is .05.

[1]Each cell shows the sample average rank of Total NO_3 + NO_2 mg/L.

[2]Unable to compute because the subset contains only one sample.

Table 21. Kruskal-Wallis and post hoc inter-laboratory comparisons for NO_x from Three-Mile Creek.

D. Total Nitrite. Eighteen of the 22 reported values for Dauphin Island were within acceptable ranges. Lab E reported all three values outside acceptable ranges, and Lab M reported one. Lab O reported one result below its detection limits. Lab J reported all three results as below the PQL (i.e., no value was reported; the results are treated as non-detects). The MDLs ranged from 0.001 to 0.006 mg/L; and the PQLs for Labs D and J ranged from 0.005 to 0.02 mg/L. The %F-pseudosigma value was large (greater than 30%), indicating a lack of precision among laboratories. Of the 22 reported values, 68% were within 1 F-pseudosigma and 82% were within 2 F-pseudosigma.

At Three-Mile Creek, 37 of the 39 values were within acceptable ranges. Lab D reported two values outside acceptable ranges. Lab O reported one false negative. The %F-pseudosigma value was (less than 20%), indicating a high degree of precision among laboratories. Of the 39 reported values, 69% were within 1 F-pseudosigma and 95% were within 2 F-pseudosigma. See Figures 7 & 8 for scatter-plots of values obtained by individual laboratories. See Tables 22 - 27 for F-pseudosigma values, summary statistics and inter-laboratory comparisons.

NO_2				
	F-pseudosigma	**% F-pseudosigma**	**Median**	**Range**
Dauphin Island	0.006	42.65%	0.015	0.031
Three-Mile Creek	0.007	18.08%	0.041	0.019

Table 22. F-pseudosigma values for NO_2.

NO_2

	Dauphin Island				Three-Mile Creek			
Lab ID	N	Lab Median	Range	Mean Z-value	N	Lab Median	Range	Mean Z-value
A	3	0.014	0.002	0.17	4	0.040	0.001	0.21
B	3	0.019	0.004	0.56	4	0.043	0.003	0.21
C	3	0.013	0.003	0.39	4	0.040	0.002	0.14
D	3	0.021	0.003	1.09	4	0.055	0.002	1.97
F	3	0.030	0.000	2.50	4	0.050	0.010	1.00
G	3	0.015	0.002	0.11	4	0.041	0.001	0.04
J	3	NR	NR	NR	4	0.050	0.000	1.29
L	3	0.012	0.007	0.78	4	0.039	0.002	0.29
M	1	0.037	N/A	3.67	4	0.047	0.003	0.86
O	1	NR	NR	NR	4*	0.039	0.002	0.38

* One or more non-values reported. NR = all non-values reported.

Table 23. Summary statistics and Z-values by Laboratory for NO_2.

Descriptives

Total Nitrite mg/L

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
A	3	.01400	.001000	.000577	.01152	.01648	.013	.015
B	3	.01833	.002082	.001202	.01316	.02350	.016	.020
C	3	.01267	.001528	.000882	.00887	.01646	.011	.014
D	3	.02153	.001498	.000865	.01781	.02525	.020	.023
F	3	.03000	.000000	.000000	.03000	.03000	.030	.030
G	3	.01433	.001155	.000667	.01146	.01720	.013	.015
L	3	.01033	.003786	.002186	.00093	.01974	.006	.013
M	1	.03700	N/A	N/A	N/A	N/A	.037	.037
Total	22	.01821	.007656	.001632	.01481	.02160	.006	.037

Table 24. Descriptive statistics by laboratory for NO_2 for Dauphin Island.

Descriptives

Total Nitrite mg/L

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
A	4	.03950	.000577	.000289	.03858	.04042	.039	.040
B	4	.04200	.001414	.000707	.03975	.04425	.040	.043
C	4	.04000	.000816	.000408	.03870	.04130	.039	.041
D	4	.05480	.001020	.000510	.05318	.05642	.053	.056
F	4	.04750	.005000	.002500	.03954	.05546	.040	.050
G	4	.04075	.000500	.000250	.03995	.04155	.040	.041
J	4	.05000	.000000	.000000	.05000	.05000	.050	.050
L	4	.03900	.000816	.000408	.03770	.04030	.038	.040
M	4	.04700	.001414	.000707	.04475	.04925	.046	.049
O	3	.03833	.001155	.000667	.03546	.04120	.037	.039
Total	39	.04403	.005605	.000897	.04221	.04585	.037	.056

Table 25. Descriptive statistics by laboratory for NO_2 for Three-Mile Creek.

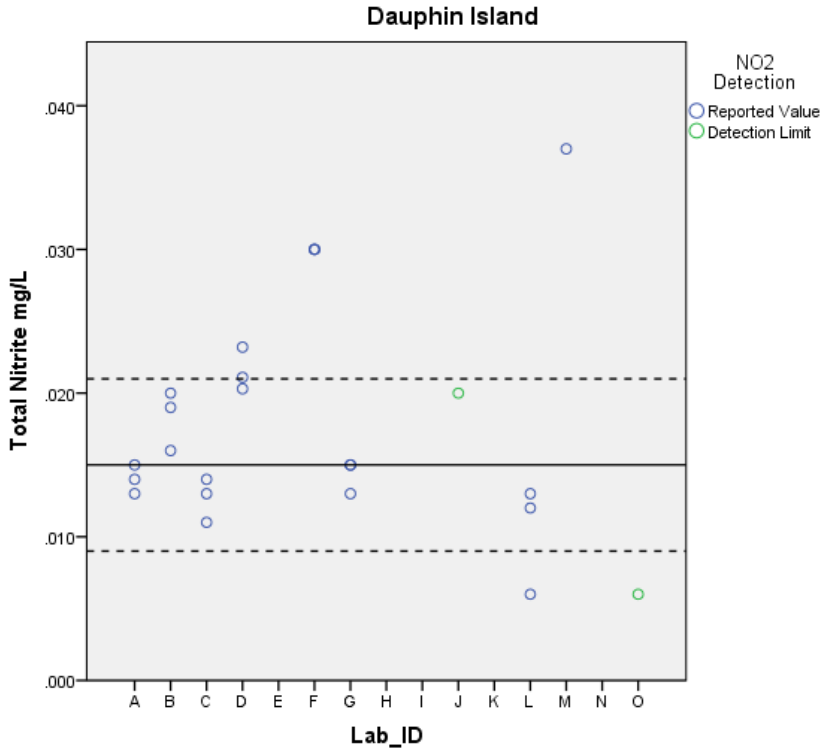

Figure 7. Scatter-plot of NO_2 values and detection limits obtained by ten laboratories for Dauphin Island. The solid line indicates the overall median, and the dashed lines indicate +/- 1 F-pseudosigma.

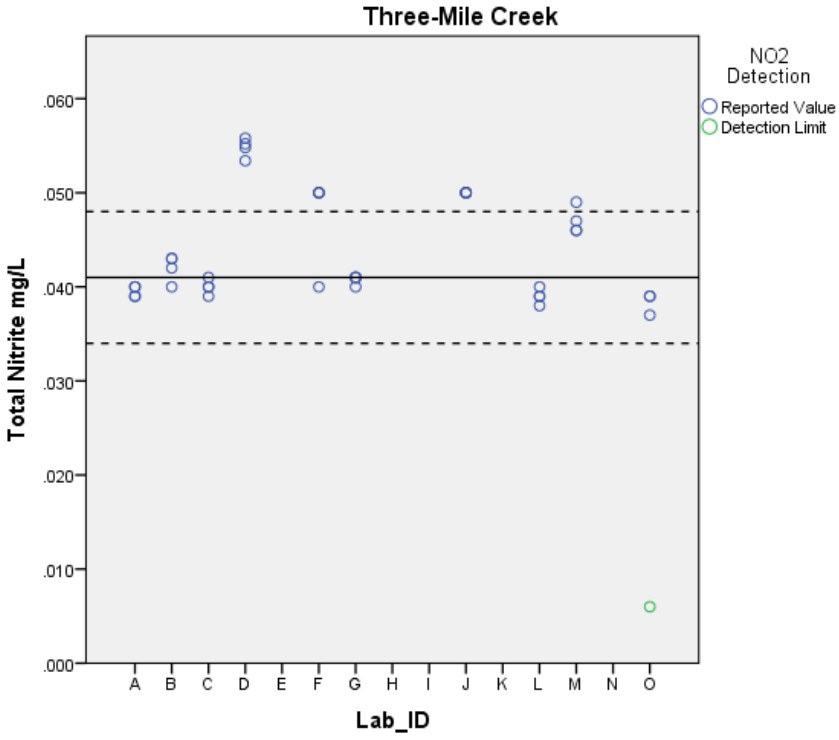

Figure 8. Scatter-plot of NO_2 values and detection limits obtained by ten laboratories for Three-Mile Creek. The solid line indicates the overall median, and the dashed lines indicate +/- 1 F-pseudosigma.

Total Nitrite mg/L

	Lab ID	N	Subset for alpha = 0.05			
			1	2	3	4
Gabriel[a,b]	L	3	.01033			
	C	3	.01267	.01267		
	A	3	.01400	.01400		
	G	3	.01433	.01433		
	B	3		.01833	.01833	
	D	3			.02153	
	F+M	4				.03175
	Sig.		.592	.163	.850	1.000

Means for groups in homogeneous subsets are displayed.
a. Uses Harmonic Mean Sample Size = 3.111.
b. The group sizes are unequal. The harmonic mean of the group sizes is used. Type I error levels are not guaranteed.
Table 26. Post hoc inter-laboratory comparisons for NO_2 from Dauphin Island.

Total Nitrite mg/L

	Lab ID	N	Subset for alpha = 0.05		
			1	2	3
Gabriel[a,b]	O	3	.03833		
	L	4	.03900		
	A	4	.03950		
	C	4	.04000		
	G	4	.04075		
	B	4	.04200		
	M	4		.04700	
	F	4		.04750	
	J	4		.05000	
	D	4			.05480
	Sig.		.300	.655	1.000

Means for groups in homogeneous subsets are displayed.
a. Uses Harmonic Mean Sample Size = 3.871.
b. The group sizes are unequal. The harmonic mean of the group sizes is used. Type I error levels are not guaranteed.
Table 27. Post hoc inter-laboratory comparisons for NO_2 from Three-Mile Creek.

E. Dissolved Nitrite + Nitrate. Twenty-six of the 35 reported values for Dauphin Island were within acceptable ranges. Labs M and O reported all three values outside acceptable ranges, and Labs H, I, and N reported one each outside acceptable ranges. The %F-pseudosigma value was very small (less than 10%), indicating a high degree of precision among laboratories. Of the 35 reported values, 63% were within 1 F-pseudosigma and 74% were within 2 F-pseudosigma.

At Three-Mile Creek, 40 of the 47 values were within acceptable ranges. Lab I reported all four values outside acceptable ranges, and Lab M reported three. The %F-pseudosigma value was very low (less than 10%), indicating a high degree of precision among laboratories. Of the 47 reported values, 66% were within 1 F-pseudosigma and 85% were within 2 F-pseudosigma. See Figures 9 & 10 for scatter-plots of values obtained by individual laboratories. See Tables 28 - 33 for F-pseudosigma values, summary statistics and inter-laboratory comparisons.

DNO_x				
	F-pseudosigma	**% F-pseudosigma**	**Median**	**Range**
Dauphin Island	0.006	3.31%	0.179	0.078
Three-Mile Creek	0.071	3.79%	1.879	0.540

Table 28. F-pseudosigma values for DNO_x.

DNO_x

	Dauphin Island				Three-Mile Creek			
Lab ID	N	Lab Median	Range	Mean Z-value	N	Lab Median	Range	Mean Z-value
A	3	0.180	0.000	0.17	4	1.900	0.000	0.30
B	3	0.179	0.003	0.17	4	1.877	0.019	0.08
C	2	0.190	0.001	1.75	3	1.793	0.036	1.09
D	3	0.174	0.005	0.78	4	1.825	0.030	0.76
G	3	0.179	0.006	0.33	4	1.815	0.070	0.97
H	3	0.178	0.030	1.72	4	1.900	0.050	0.33
I	3	0.184	0.016	1.50	4	2.143	0.065	3.59
J	3	0.170	0.010	1.06	4	1.835	0.050	0.49
L	3	0.176	0.001	0.56	4	1.865	0.050	0.28
M	3	0.224	0.004	7.61	4	2.175	0.340	3.71
N	3	0.173	0.012	1.11	4	1.920	0.180	0.92
O	3	0.164	0.017	3.22	4	1.740	0.030	1.85

Table 29. Summary statistics and Z-values by Laboratory for DNO_x.

Descriptives

Dissolved $NO_3 + NO_2$ mg/L

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
A	3	.18000	.000000	.000000	.18000	.18000	.180	.180
B	3	.17933	.001528	.000882	.17554	.18313	.178	.181
C	2	.18950	.000707	.000500	.18315	.19585	.189	.190
D	3	.17433	.000577	.000333	.17290	.17577	.174	.175
G	3	.18100	.003464	.002000	.17239	.18961	.179	.185
H	3	.16867	.017039	.009838	.12634	.21099	.149	.179
I	3	.18800	.008718	.005033	.16634	.20966	.182	.198
J	3	.17333	.005774	.003333	.15899	.18768	.170	.180
L	3	.17567	.000577	.000333	.17423	.17710	.175	.176
M	3	.22467	.002082	.001202	.21950	.22984	.223	.227
N	3	.17233	.006028	.003480	.15736	.18731	.166	.178
O	3	.15967	.009292	.005364	.13659	.18275	.149	.166
Total	35	.18029	.016743	.002830	.17453	.18604	.149	.227

Table 30. Descriptive statistics by laboratory for DNO_x for Dauphin Island.

Descriptives

Dissolved $NO_3 + NO_2$ mg/L

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
A	4	1.90000	.000000	.000000	1.90000	1.90000	1.900	1.900
B	4	1.87350	.008737	.004368	1.85960	1.88740	1.861	1.880
C	3	1.80167	.019502	.011260	1.75322	1.85011	1.788	1.824
D	4	1.82500	.012910	.006455	1.80446	1.84554	1.810	1.840
G	4	1.81000	.035590	.017795	1.75337	1.86663	1.770	1.840
H	4	1.90250	.020616	.010308	1.86970	1.93530	1.880	1.930
I	4	2.13375	.028652	.014326	2.08816	2.17934	2.092	2.157
J	4	1.84500	.023805	.011902	1.80712	1.88288	1.830	1.880
L	4	1.86500	.023805	.011902	1.82712	1.90288	1.840	1.890
M	4	2.14250	.143846	.071923	1.91361	2.37139	1.940	2.280
N	4	1.88000	.086795	.043397	1.74189	2.01811	1.750	1.930
O	4	1.74750	.015000	.007500	1.72363	1.77137	1.740	1.770
Total	47	1.89583	.127613	.018614	1.85836	1.93330	1.740	2.280

Table 31. Descriptive statistics by laboratory for DNO_x for Three-Mile Creek.

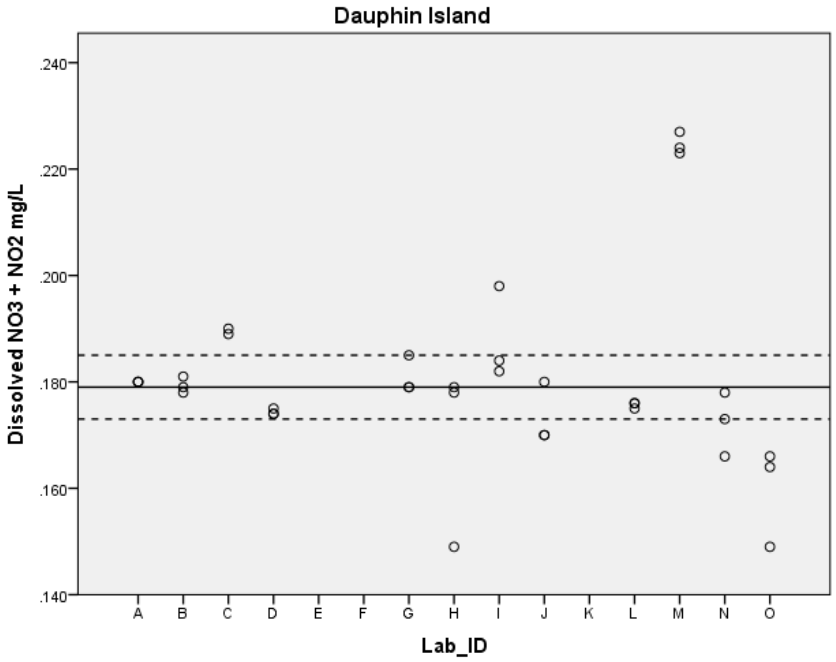

Figure 9. Scatter-plot of DNO_x values obtained by twelve laboratories for Dauphin Island. The solid line indicates the overall median, and the dashed lines indicate +/- 1 F-pseudosigma.

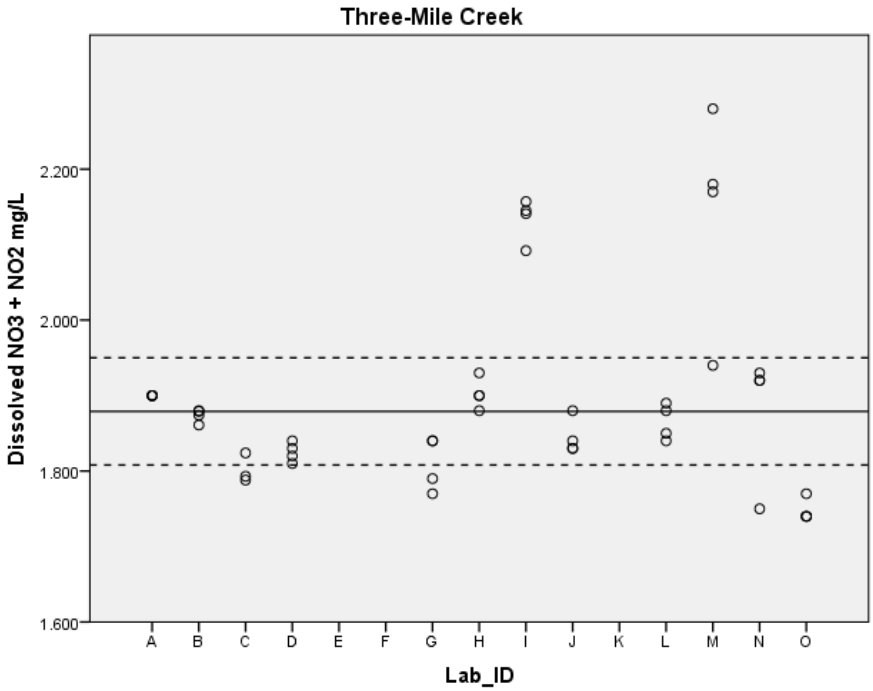

Figure 10. Scatter-plot of DNO_x values obtained by twelve laboratories for Three-Mile Creek. The solid line indicates the overall median, and the dashed lines indicate +/- 1 F-pseudosigma.

Hypothesis Test Summary

	Null Hypothesis	Test	Sig.	Decision
1	The medians of Dissolved NO3 + NO2 mg/L are the same across categories of Lab_ID.	Independent-Samples Median Test	.005	Reject the null hypothesis.
2	The distribution of Dissolved NO3 + NO2 mg/L is the same across categories of Lab_ID.	Independent-Samples Kruskal-Wallis Test	.003	Reject the null hypothesis.

Asymptotic significances are displayed. The significance level is .05.

Homogeneous Subsets based on Dissolved NO_3 + NO_2 mg/L					
		Subset			
		1	2	3	4
Sample[1]	O	3.000			
	N	9.500	9.500		
	D	10.167	10.167		
	J	12.167	12.167		
	H	12.333	12.333		
	L	12.833	12.833		
	B	20.500	20.500	20.500	
	G	22.667	22.667	22.667	
	A		23.500	23.500	
	I			29.000	29.000
	C			30.500	30.500
	M				34.000
Test Statistic		13.726	13.204	8.163	5.139
Sig. (2-sided test)		.056	.067	.086	.077
Adjusted Sig. (2-sided test)		.083	.099	.194	.273

Homogeneous subsets are based on asymptotic significances. The significance level is .05.

[1]Each cell shows the sample average rank of Dissolved NO_3 + NO_2 mg/L.

Table 32. Kruskal-Wallis and nonparametric post hoc inter-laboratory comparisons for DNO_x from Dauphin Island.

Hypothesis Test Summary

	Null Hypothesis	Test	Sig.	Decision
1	The medians of Dissolved NO3 + NO2 mg/L are the same across categories of Lab_ID.	Independent-Samples Median Test	.000	Reject the null hypothesis.
2	The distribution of Dissolved NO3 + NO2 mg/L is the same across categories of Lab_ID.	Independent-Samples Kruskal-Wallis Test	.000	Reject the null hypothesis.

Asymptotic significances are displayed. The significance level is .05.

Homogeneous Subsets based on Dissolved NO_3 + NO_2 mg/L

		Subset					
		1	2	3	4	5	6
Sample[1]	O	2.875					
	C		9.333				
	G		12.375	12.375			
	D		13.250	13.250			
	J		18.125	18.125	18.125		
	L			23.625	23.625	23.625	
	B			23.875	23.875	23.875	
	N			28.875	28.875	28.875	
	A				32.500	32.500	
	H					32.500	
	I						42.500
	M						44.500
Test Statistic		.[2]	4.524	10.168	8.852	8.877	1.333
Sig. (2-sided test)		.	.210	.071	.065	.064	.248
Adjusted Sig. (2-sided test)		.	.507	.136	.149	.147	.819

Homogeneous subsets are based on asymptotic significances. The significance level is .05.

[1]Each cell shows the sample average rank of Dissolved NO_3 + NO_2 mg/L.

[2]Unable to compute because the subset contains only one sample.

Table 33. Kruskal-Wallis test and results of nonparametric pair-wise comparisons of DNO_x by laboratory from Three-Mile Creek.

F. Dissolved Nitrite. Although DNO_2 for Dauphin Island had only 20 reported values (vs. the 21 needed) analyses were run; however, caution should be exercised in interpreting the results due to the lack of power (β~56%). Seventeen of the 20 reported values for Dauphin Island were within acceptable ranges. Lab D reported all three values outside acceptable ranges. Labs B and M reported all results as below detection limits, Lab A reported two, and Labs H and N reported one result below detection limits, each. Lab D reported all three results below the PQL. The MDLs ranged from 0.001 to 0.005 mg/L; and the PQLs for Labs D and J ranged from 0.005 to 0.02 mg/L. Of the 33 total results, thirteen were non-values (39%). The %F-pseudosigma value was very large (nearly 100%), indicating a lack of precision among laboratories (this may be due to the small number of reported values). Of the 20 reported values, 80% were within 1 F-pseudosigma and there were no other values within 2 F-pseudosigma.

At Three-Mile Creek, 43 of the 47 values were within acceptable ranges. Lab D reported all four values outside acceptable ranges. In addition, two of Lab D's results were statistical outliers (both were 0.051 mg/L). The %F-pseudosigma value was very low (less than 10%), indicating a high degree of precision at higher analyte concentrations among laboratories. Of the 47 reported values, 70% were within 1 F-pseudosigma and 91% were within 2 F-pseudosigma. See Figures 11 & 12 for scatter-plots of values obtained by individual laboratories. See Tables 34 - 39 for F-pseudosigma values, summary statistics and inter-laboratory comparisons.

DNO_2				
	F-pseudosigma	**% F-pseudosigma**	**Median**	**Range**
Dauphin Island	0.003	96.37%	0.003	0.011
Three-Mile Creek	0.002	6.01%	0.037	0.017

Table 34. F-pseudosigma values for DNO_2.

DNO_2

Lab ID	Dauphin Island				Three-Mile Creek			
	N	Lab Median	Range	Mean Z-value	N	Lab Median	Range	Mean Z-value
A	3*	0.006	N/A	1.00	4	0.036	0.001	0.63
B	3	NR	NR	NR	4	0.038	0.001	0.38
C	2	0.003	0.000	0.00	3	0.036	0.001	0.67
D	3	0.011	0.003	2.93	4	0.050	0.003	6.38
G	3	0.006	0.000	1.00	4	0.037	0.000	0.00
H	3*	0.003	0.001	0.17	4	0.037	0.002	0.38
I	3	0.003	0.001	0.11	4	0.035	0.001	1.13
J	3	NR	NR	NR	4	0.040	0.000	1.50
L	3	0.005	0.003	0.56	4	0.036	0.001	0.38
M	2	NR	NR	NR	4	0.039	0.001	1.13
N	3*	0.002	0.000	0.25	4	0.037	0.001	0.15

* One or more non-values reported. NR = all non-values reported.

Table 35. Summary statistics and Z-values by Laboratory for DNO_2.

Descriptives

Dissolved Nitrite mg/L

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
A	1	.00600	N/A	N/A	N/A	N/A	.006	.006
C	2	.00300	.000000	.000000	.00300	.00300	.003	.003
D	3	.01180	.001442	.000833	.00822	.01538	.011	.013
G	3	.00600	.000000	.000000	.00600	.00600	.006	.006
H	2	.00250	.000707	.000500	-.00385	.00885	.002	.003
I	3	.00267	.000577	.000333	.00123	.00410	.002	.003
L	3	.00400	.001732	.001000	-.00030	.00830	.002	.005
N	2	.00225	.000071	.000050	.00161	.00289	.002	.002
Total	19	.00499	.003408	.000782	.00335	.00664	.002	.013

Table 36. Descriptive statistics by laboratory for DNO_2 for Dauphin Island.

Descriptives

Dissolved Nitrite mg/L

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
A	4	.03575	.000500	.000250	.03495	.03655	.035	.036
B	4	.03775	.000500	.000250	.03695	.03855	.037	.038
C	3	.03567	.000577	.000333	.03423	.03710	.035	.036
D	4	.04975	.001484	.000742	.04739	.05211	.048	.051
G	4	.03700	.000000	.000000	.03700	.03700	.037	.037
H	4	.03675	.000957	.000479	.03523	.03827	.036	.038
I	4	.03475	.000500	.000250	.03395	.03555	.034	.035
J	4	.04000	.000000	.000000	.04000	.04000	.040	.040
L	4	.03625	.000500	.000250	.03545	.03705	.036	.037
M	4	.03925	.000500	.000250	.03845	.04005	.039	.040
N	4	.03680	.000356	.000178	.03623	.03737	.037	.037
Total	43	.03821	.004065	.000620	.03696	.03946	.034	.051

Table 37. Descriptive statistics by laboratory for DNO_2 for Three-Mile Creek.

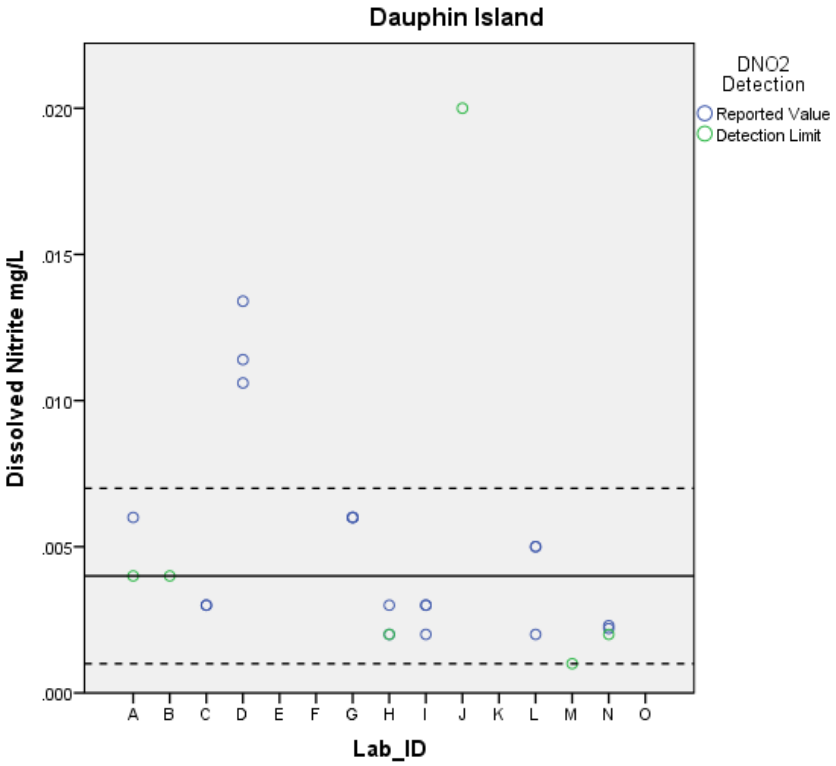

Figure 11. Scatter-plot of DNO_2 values and detection/quantitation limits obtained by eleven laboratories for Dauphin Island. The solid line indicates the overall median, and the dashed lines indicate +/- 1 F-pseudosigma.

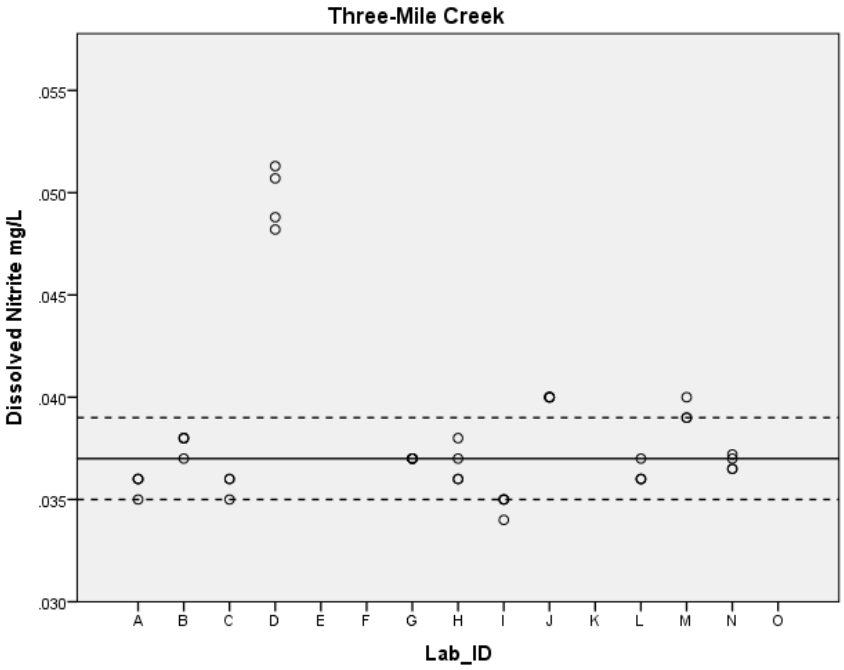

Figure 12. Scatter-plot of DNO_2 values and detection/quantitation limits obtained by eleven laboratories for Dauphin Island. The solid line indicates the overall median, and the dashed lines indicate +/- 1 F-pseudosigma.

Dissolved Nitrite mg/L

	Lab ID	N	Subset for alpha = 0.05		
			1	2	3
Gabriel[a,b]	N	2	.00225		
	H	2	.00250		
	I	3	.00267		
	C	2	.00300	.00300	
	L	3	.00400	.00400	
	G+A	4		.00600	
	D	3			.01180
	Sig.		.615	.072	1.000

Means for groups in homogeneous subsets are displayed.
a. Uses Harmonic Mean Sample Size = 2.545.
b. The group sizes are unequal. The harmonic mean of the group sizes is used.
Type I error levels are not guaranteed.
Table 38. Post hoc inter-laboratory comparisons for DNO_2 for Dauphin Island.

Hypothesis Test Summary

	Null Hypothesis	Test	Sig.	Decision
1	The medians of Dissolved Nitrite mg/L are the same across categories of Lab_ID.	Independent-Samples Median Test	.000	Reject the null hypothesis.
2	The distribution of Dissolved Nitrite mg/L is the same across categories of Lab_ID.	Independent-Samples Kruskal-Wallis Test	.000	Reject the null hypothesis.

Asymptotic significances are displayed. The significance level is .05.

Homogeneous Subsets based on Dissolved Nitrite mg/L

		Subset						
		1	2	3	4	5	6	7
Sample[1]	I	3.250						
	C	9.000	9.000					
	A	9.625	9.625	9.625				
	L		14.250	14.250	14.250			
	H		18.750	18.750	18.750			
	N			21.125	21.125			
	G				22.500			
	B				27.750			
	M					34.000		
	J						37.000	
	D							41.500
Test Statistic		5.315	5.116	7.024	8.925	.[2]	.[2]	.[2]
Sig. (2-sided test)		.070	.163	.071	.063	.	.	.
Adjusted Sig. (2-sided test)		.234	.388	.184	.133	.	.	.

Homogeneous subsets are based on asymptotic significances. The significance level is .05.
[1]Each cell shows the sample average rank of Dissolved Nitrite mg/L.
[2]Unable to compute because the subset contains only one sample.

Table 39. Kruskal-Wallis test and results of nonparametric pair-wise comparisons of DNO_2 by laboratory for Three-Mile Creek.

G. Total Phosphorus. Thirty-seven of the 41 reported values for Dauphin Island were within acceptable ranges. Lab F reported all three values outside acceptable ranges, and Lab G reported one. Lab D had one result reported as below its detection limits; this was determined to be a false negative. The PQL for Lab D was 0.02 mg/L. Lab F reported one statistical outlier (0.192 mg/L). The %F-pseudosigma value was moderate (>20% and <30%), indicating a lack of precision among laboratories. Of the 41 reported values, 63% were within 1 F-pseudosigma and 90% were within 2 F-pseudosigma.

At Three-Mile Creek, 52 of the 56 values were within acceptable ranges. Labs D and F each reported two values outside acceptable ranges. One of Lab F's results was a statistical outlier (0.278). The %F-pseudosigma value was very low (less than 10%), indicating a high degree of precision at higher analyte concentrations among the laboratories. Of the 56 reported values, 71% were within 1 F-pseudosigma and 93% were within 2 F-pseudosigma. See Figures 13 & 14 for scatter-plots of values obtained by individual laboratories. See Tables 40 - 45 for F-pseudosigma values, summary statistics and inter-laboratory comparisons.

Total Phosphorus				
	F-pseudosigma	**% F-pseudosigma**	**Median**	**Range**
Dauphin Island	0.014	25.36%	0.057	0.155
Three-Mile Creek	0.019	9.62%	0.195	0.128

Table 40. F-pseudosigma values for TP.

TP

Lab ID	Dauphin Island				Three-Mile Creek			
	N	Lab Median	Range	Mean Z-value	N	Lab Median	Range	Mean Z-value
A	3	0.057	0.002	0.05	4	0.200	0.000	0.26
B	3	0.055	0.007	0.21	4	0.190	0.001	0.29
C	3	0.061	0.005	0.31	4	0.166	0.003	1.54
D	3*	0.040	0.000	1.21	4	0.155	0.010	2.11
E	3	0.037	0.001	1.40	4	0.159	0.003	1.90
F	3	0.185	0.017	9.07	4	0.227	0.073	2.05
G	3	0.061	0.039	1.02	4	0.212	0.013	0.87
H	3	0.066	0.001	0.67	4	0.198	0.004	0.14
I	3	0.038	0.000	1.36	4	0.183	0.014	0.74
J	3	0.080	0.020	1.17	4	0.200	0.010	0.26
L	3	0.052	0.011	0.43	4	0.191	0.004	0.22
M	3	0.057	0.004	0.10	4	0.210	0.000	0.79
N	3	0.069	0.008	1.03	4	0.211	0.004	0.83
O	3	0.049	0.013	0.55	4	0.191	0.015	0.30

* One non-value reported. NR = All non-values reported.

Table 41. Summary statistics and Z-values by Laboratory for TP.

Descriptives

Total Phosphorus mg/L

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
A	3	.05700	.001000	.000577	.05452	.05948	.056	.058
B	3	.05533	.003512	.002028	.04661	.06406	.052	.059
C	3	.06133	.002517	.001453	.05508	.06758	.059	.064
D	2	.04000	.000000	.000000	.04000	.04000	.040	.040
E	3	.03739	.000460	.000266	.03625	.03853	.037	.038
F	3	.18400	.008544	.004933	.16278	.20522	.175	.192
G	3	.06867	.020599	.011893	.01750	.11984	.053	.092
H	3	.06633	.000577	.000333	.06490	.06777	.066	.067
I	3	.03800	.000000	.000000	.03800	.03800	.038	.038
J	3	.07333	.011547	.006667	.04465	.10202	.060	.080
L	3	.05100	.005568	.003215	.03717	.06483	.045	.056
M	3	.05767	.002082	.001202	.05250	.06284	.056	.060
N	3	.07137	.004291	.002477	.06071	.08203	.069	.076
O	3	.04933	.006506	.003756	.03317	.06550	.043	.056
Total	41	.06567	.036075	.005634	.05428	.07705	.037	.192

Table 42. Descriptive statistics by laboratory for TP from Dauphin Island.

Descriptives

Total Phosphorus mg/L

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
A	4	.20000	.000000	.000000	.20000	.20000	.200	.200
B	4	.18950	.000577	.000289	.18858	.19042	.189	.190
C	4	.16575	.001500	.000750	.16336	.16814	.164	.167
D	4	.15500	.005774	.002887	.14581	.16419	.150	.160
E	4	.15888	.001412	.000706	.15663	.16112	.157	.161
F	4	.23400	.034516	.017258	.17908	.28892	.205	.278
G	4	.21150	.005323	.002661	.20303	.21997	.205	.218
H	4	.19775	.002062	.001031	.19447	.20103	.196	.200
I	4	.18100	.006377	.003189	.17085	.19115	.172	.186
J	4	.19750	.005000	.002500	.18954	.20546	.190	.200
L	4	.19075	.001708	.000854	.18803	.19347	.189	.193
M	4	.21000	.000000	.000000	.21000	.21000	.210	.210
N	4	.21075	.001708	.000854	.20803	.21347	.209	.213
O	4	.19225	.006292	.003146	.18224	.20226	.186	.201
Total	56	.19247	.022975	.003070	.18632	.19863	.150	.278

Table 43. Descriptive statistics by laboratory for TP from Three-Mile Creek.

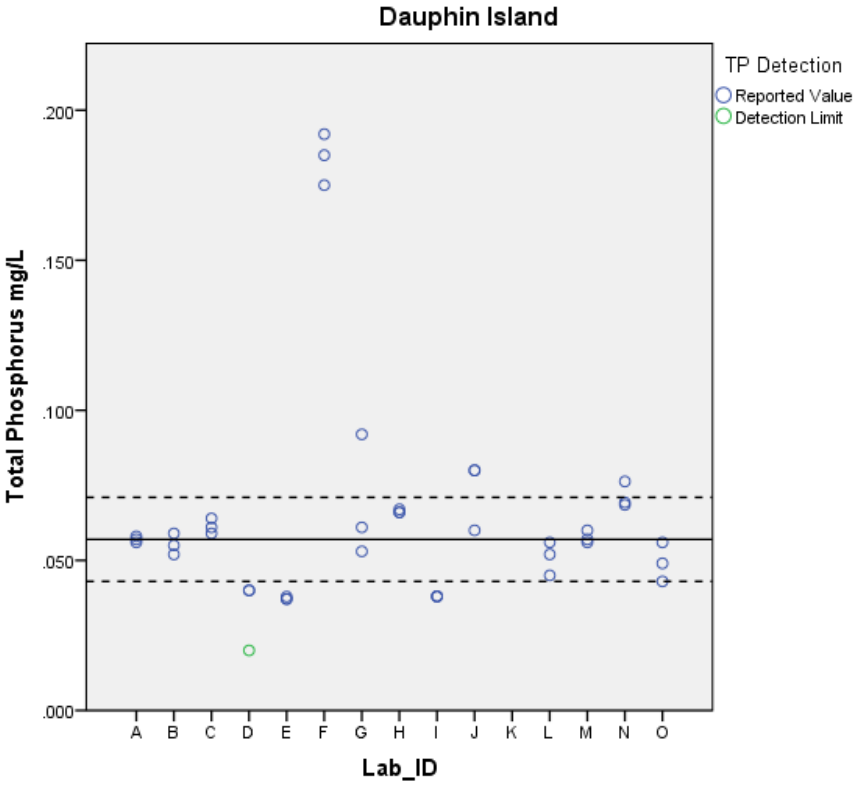

Figure 13. Scatter-plot of TP values and detection/quantitation limits obtained by fourteen laboratories for Dauphin Island. The solid line indicates the overall median, and the dashed lines indicate +/- 1 F-pseudosigma.

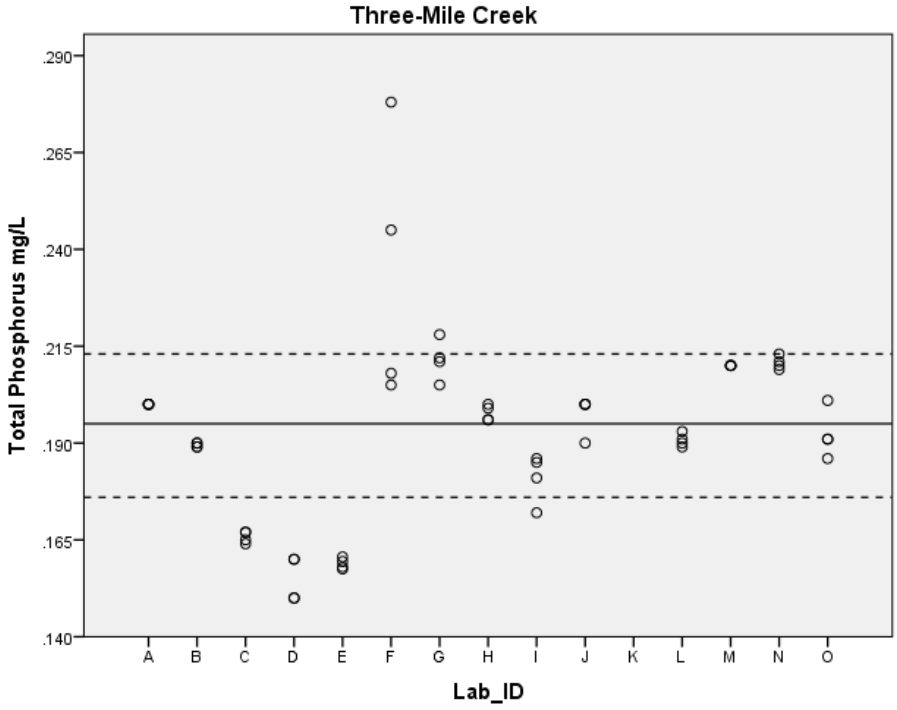

Figure 14. Scatter-plot of TP values obtained by fourteen laboratories for Three-Mile Creek. The solid line indicates the overall median, and the dashed lines indicate +/- 1 F-pseudosigma.

Hypothesis Test Summary

	Null Hypothesis	Test	Sig.	Decision
1	The medians of Total Phosphorus mg/L are the same across categories of Lab_ID.	Independent-Samples Median Test	.004	Reject the null hypothesis.
2	The distribution of Total Phosphorus mg/L is the same across categories of Lab_ID.	Independent-Samples Kruskal-Wallis Test	.001	Reject the null hypothesis.

Asymptotic significances are displayed. The significance level is .05.

Homogeneous Subsets based on Total Phosphorus mg/L

		Subset						
		1	2	3	4	5	6	7
Sample[1]	E	2.000						
	I		5.000					
	D			7.500				
	O			12.500	12.500			
	L			13.333	13.333			
	B			17.000	17.000	17.000		
	A			20.000	20.000	20.000	20.000	
	M			21.167	21.167	21.167	21.167	
	G			26.500	26.500	26.500	26.500	26.500
	C				26.667	26.667	26.667	26.667
	H					31.000	31.000	31.000
	J					32.833	32.833	32.833
	N						34.000	34.000
	F							40.000
Test Statistic		.[2]	.[2]	11.811	11.774	11.776	11.595	10.195
Sig. (2-sided test)		.	.	.066	.067	.067	.072	.070
Adjusted Sig. (2-sided test)		.	.	.128	.130	.130	.138	.156

Homogeneous subsets are based on asymptotic significances. The significance level is .05.

[1]Each cell shows the sample average rank of Total Phosphorus mg/L.

[2]Unable to compute because the subset contains only one sample.

Table 44. Kruskal-Wallis test and results of nonparametric pair-wise comparisons of TP by laboratory for all reported values for Dauphin Island.

Hypothesis Test Summary

	Null Hypothesis	Test	Sig.	Decision
1	The medians of Total Phosphorus mg/L are the same across categories of Lab_ID.	Independent-Samples Median Test	.000	Reject the null hypothesis.
2	The distribution of Total Phosphorus mg/L is the same across categories of Lab_ID.	Independent-Samples Kruskal-Wallis Test	.000	Reject the null hypothesis.

Asymptotic significances are displayed. The significance level is .05.

Homogeneous Subsets based on Total Phosphorus mg/L

		Subset					
		1	2	3	4	5	6
Sample[1]	D	4.000					
	E	5.000					
	C		10.500				
	I			14.625			
	B				20.750		
	L				23.875	23.875	
	O				27.125	27.125	
	H				31.375	31.375	
	J				32.250	32.250	
	A					35.500	
	M						47.000
	N						48.625
	F						48.875
	G						49.500
Test Statistic		.341	.[2]	.[2]	9.022	8.148	.621
Sig. (2-sided test)		.559	.	.	.061	.086	.892
Adjusted Sig. (2-sided test)		.997	.	.	.160	.223	1.000

Homogeneous subsets are based on asymptotic significances. The significance level is .05.

[1]Each cell shows the sample average rank of Total Phosphorus mg/L.

[2]Unable to compute because the subset contains only one sample.

Table 45. Kruskal-Wallis test and results of nonparametric pair-wise comparisons of TP by laboratory for Three-Mile Creek.

H. Orthophosphate. Twenty-eight of the 33 reported values for Dauphin Island were within acceptable ranges. Labs C and J reported two values outside acceptable ranges, and Lab G reported one. Lab F had all three results reported below its quantitation limits, and Lab J had one result reported as below its quantitation limits. The MDLs ranged from 0.00017 to 0.009 mg/L; and the PQLs for Labs D, F, and J ranged from 0.005 to 0.04 mg/L. The %F-pseudosigma value was large (greater than 30%), indicating a lack of precision among laboratories. Of the 33 reported values, 64% were within 1 F-pseudosigma and 85% were within 2 F-pseudosigma.

At Three-Mile Creek, 43 of the 51 values were within acceptable ranges. Lab F reported all four values outside acceptable ranges, Lab G reported three, and Lab J reported one. The %F-pseudosigma value was very low (less than 10%), indicating a high degree of precision at higher analyte concentrations among the laboratories. Of the 51 reported values, 57% were within 1 F-pseudosigma and 84% were within 2 F-pseudosigma. See Figures 15 & 16 for scatter-plots of values obtained by individual laboratories. See Tables 46 - 51 for F-pseudosigma values, summary statistics and inter-laboratory comparisons.

Orthophosphate				
	F-pseudosigma	**% F-pseudosigma**	**Median**	**Range**
Dauphin Island	0.003	31.75%	0.009	0.016
Three-Mile Creek	0.007	7.31%	0.101	0.050

Table 46. F-pseudosigma values for OP.

OP

	Dauphin Island				Three-Mile Creek			
Lab ID	N	Lab Median	Range	Mean Z-value	N	Lab Median	Range	Mean Z-value
A	3	0.012	0.001	0.89	4	0.100	0.000	0.14
B	3	0.013	0.001	1.22	4	0.105	0.000	0.57
C	2	0.020	0.001	3.50	3	0.095	0.001	0.81
D	3	0.005	0.001	1.44	4	0.098	0.003	0.43
E	3	0.009	0.000	0.07	4	0.102	0.001	0.09
F	3	NR	NR	NR	4	0.130	0.010	3.79
G	3	0.013	0.004	1.78	4	0.085	0.005	2.36
H	3	0.009	0.000	0.00	4	0.105	0.002	0.57
I	3	0.009	0.001	0.11	4	0.108	0.005	0.93
J	3*	0.020	0.000	3.67	4	0.090	0.010	1.93
L	3	0.008	0.001	0.22	4	0.102	0.003	0.18
M	2	0.009	0.001	0.17	4	0.093	0.001	1.18
N	3	0.011	0.001	0.77	4	0.110	0.002	1.36

* One non-value reported. NR = All non-values reported.

Table 47. Summary statistics by Laboratory for OP.

Descriptives

Orthophosphate mg/L

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
A	3	.01167	.000577	.000333	.01023	.01310	.011	.012
B	3	.01267	.000577	.000333	.01123	.01410	.012	.013
C	2	.01950	.000707	.000500	.01315	.02585	.019	.020
D	3	.00467	.000577	.000333	.00323	.00610	.004	.005
E	3	.00921	.000117	.000067	.00892	.00950	.009	.009
G	3	.01433	.002309	.001333	.00860	.02007	.013	.017
H	3	.00900	.000000	.000000	.00900	.00900	.009	.009
I	3	.00867	.000577	.000333	.00723	.01010	.008	.009
J	2	.02000	.000000	.000000	.02000	.02000	.020	.020
L	3	.00833	.000577	.000333	.00690	.00977	.008	.009
M	2	.00850	.000707	.000500	.00215	.01485	.008	.009
N	3	.01130	.000361	.000208	.01040	.01220	.011	.012
Total	33	.01108	.004172	.000726	.00960	.01256	.004	.020

Table 48. Descriptive statistics by laboratory for OP for Dauphin Island.

Descriptives

Orthophosphate mg/L

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
A	4	.10000	.000000	.000000	.10000	.10000	.100	.100
B	4	.10500	.000000	.000000	.10500	.10500	.105	.105
C	3	.09533	.000577	.000333	.09390	.09677	.095	.096
D	4	.09800	.001414	.000707	.09575	.10025	.097	.100
E	4	.10163	.000361	.000180	.10105	.10220	.101	.102
F	4	.12750	.005000	.002500	.11954	.13546	.120	.130
G	4	.08450	.002380	.001190	.08071	.08829	.082	.087
H	4	.10500	.000816	.000408	.10370	.10630	.104	.106
I	4	.10750	.002380	.001190	.10371	.11129	.105	.110
J	4	.08750	.005000	.002500	.07954	.09546	.080	.090
L	4	.10225	.001258	.000629	.10025	.10425	.101	.104
M	4	.09275	.000500	.000250	.09195	.09355	.092	.093
N	4	.11050	.001000	.000500	.10891	.11209	.110	.112
Total	51	.10146	.010856	.001520	.09841	.10451	.080	.130

Table 49. Descriptive statistics by laboratory for OP for Three-Mile Creek.

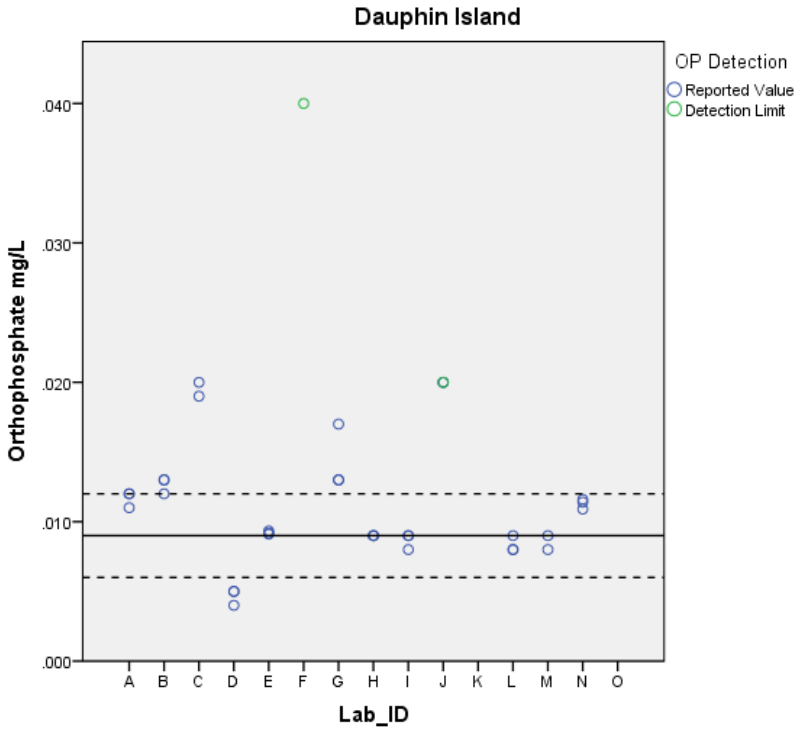

Figure 15. Scatter-plot of OP values and detection/quantitation limits obtained by thirteen laboratories for Dauphin Island. The solid line indicates the overall median, and the dashed lines indicate +/- 1 F-pseudosigma.

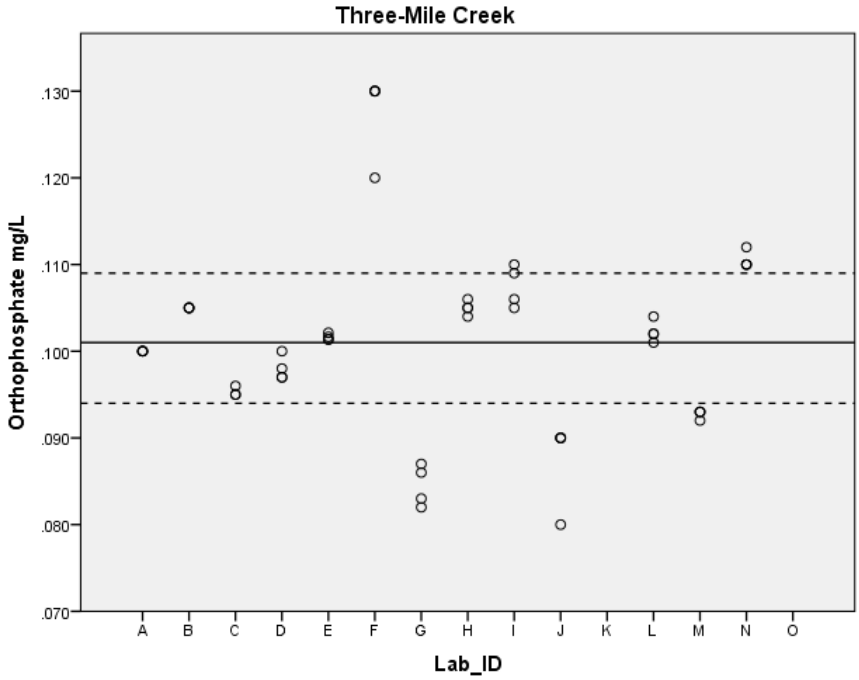

Figure 16. Scatter-plot of OP values obtained by thirteen laboratories for Three-Mile Creek. The solid line indicates the overall median, and the dashed lines indicate +/- 1 F-pseudosigma.

Orthophosphate mg/L

	Lab ID	N	Subset for alpha = 0.05						
			1	2	3	4	5	6	7
Gabriel[a,b]	D	3	.00467						
	L	3		.00833					
	M	2		.00850	.00850				
	I	3		.00867	.00867				
	H	3		.00900	.00900	.00900			
	E	3		.00921	.00921	.00921			
	N	3			.01130	.01130	.01130		
	A	3				.01167	.01167	.01167	
	B	3					.01267	.01267	
	G	3						.01433	
	C	2							.01950
	J	2							.02000
	Sig.		1.000	1.000	.056	.083	.951	.083	1.000

Means for groups in homogeneous subsets are displayed.

a. Uses Harmonic Mean Sample Size = 2.667.

b. The group sizes are unequal. The harmonic mean of the group sizes is used. Type I error levels are not guaranteed.

Table 50. Post hoc inter-laboratory comparisons of all reported values for OP from Dauphin Island.

Hypothesis Test Summary

	Null Hypothesis	Test	Sig.	Decision
1	The medians of Orthophosphate mg/L are the same across categories of Lab_ID.	Independent-Samples Median Test	.000	Reject the null hypothesis.
2	The distribution of Orthophosphate mg/L is the same across categories of Lab_ID.	Independent-Samples Kruskal-Wallis Test	.000	Reject the null hypothesis.

Asymptotic significances are displayed. The significance level is .05.

Homogeneous Subsets based on Orthophosphate mg/L

		Subset								
		1	2	3	4	5	6	7	8	9
Sample[1]	G	3.500								
	J	5.500								
	M		10.500							
	C			14.000						
	D				18.000					
	A					21.000				
	E						27.000			
	L						28.125			
	B							36.000		
	H							36.000		
	I							40.750		
	N								45.125	
	F									49.500
Test Statistic		1.400	.[2]	.[2]	.[2]	.[2]	.337	4.767	.[2]	.[2]
Sig. (2-sided test)		.237	.	.	.	.	.561	.092	.	.
Adjusted Sig. (2-sided test)		.827	.	.	.	.	.995	.342	.	.

Homogeneous subsets are based on asymptotic significances. The significance level is .05.

[1]Each cell shows the sample average rank of Orthophosphate mg/L.

[2]Unable to compute because the subset contains only one sample.

Table 51. Kruskal-Wallis test and results of nonparametric pair-wise comparisons of OP by laboratory for Three-Mile Creek.

I. Total Organic Carbon. Eighteen of the 21 reported values for Dauphin Island were within acceptable ranges. Lab D reported all three values outside acceptable ranges. The %F-pseudosigma value was very low (less than 10%), indicating a high degree of precision among laboratories. Of the 21 reported values, 81% were within 1 F-pseudosigma and 86% were within 2 F-pseudosigma.

At Three-Mile Creek, 24 of the 28 values were within acceptable ranges. Lab D reported all four values outside acceptable ranges. The %F-pseudosigma value was low (between 10 and 20%), indicating a high degree of precision among the laboratories. Of the 28 reported values, 82% were within 1 F-pseudosigma and 86% were within 2 F-pseudosigma. See Figures 17 & 18 for scatter-plots of values obtained by individual laboratories. See Tables 52 - 57 for F-pseudosigma values, summary statistics and inter-laboratory comparisons.

Total Organic Carbon				
	F-pseudosigma	**% F-pseudosigma**	**Median**	**Range**
Dauphin Island	0.297	7.95%	3.730	1.90
Three-Mile Creek	0.734	13.10%	5.600	4.20

Table 52. F-pseudosigma values for TOC.

TOC

	Dauphin Island				Three-Mile Creek			
Lab ID	N	Lab Median	Range	Mean Z-value	N	Lab Median	Range	Mean Z-value
A	3	3.600	0.300	0.48	4	5.850	0.500	0.34
D	3	5.100	0.200	4.61	4	8.950	0.800	4.33
G	3	3.650	0.070	0.24	4	4.900	0.110	0.89
H	3	3.500	0.100	0.66	4	5.600	0.200	0.07
I	3	3.750	0.020	0.04	4	4.985	0.210	0.89
J	3	4.000	0.000	0.91	4	6.000	0.000	0.55
L	3	3.700	0.500	0.59	4	5.400	0.500	0.31

Table 53. Summary statistics and Z-values by Laboratory for TOC.

Descriptives

Total Organic Carbon mg/L

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
A	3	3.6333	.15275	.08819	3.2539	4.0128	3.50	3.80
D	3	5.1000	.10000	.05774	4.8516	5.3484	5.00	5.20
G	3	3.6600	.03606	.02082	3.5704	3.7496	3.63	3.70
H	3	3.5333	.05774	.03333	3.3899	3.6768	3.50	3.60
I	3	3.7433	.01155	.00667	3.7146	3.7720	3.73	3.75
J	3	4.0000	.00000	.00000	4.0000	4.0000	4.00	4.00
L	3	3.6000	.26458	.15275	2.9428	4.2572	3.30	3.80
Total	21	3.8957	.53380	.11649	3.6527	4.1387	3.30	5.20

Table 54. Descriptive statistics by laboratory for TOC for Dauphin Island.

Descriptives

Total Organic Carbon mg/L

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
A	4	5.8500	.23805	.11902	5.4712	6.2288	5.60	6.10
D	4	8.7750	.38622	.19311	8.1604	9.3896	8.20	9.00
G	4	4.9475	.04856	.02428	4.8702	5.0248	4.90	5.01
H	4	5.5500	.10000	.05000	5.3909	5.7091	5.40	5.60
I	4	4.9450	.09950	.04975	4.7867	5.1033	4.80	5.01
J	4	6.0000	.00000	.00000	6.0000	6.0000	6.00	6.00
L	4	5.4750	.22174	.11087	5.1222	5.8278	5.30	5.80
Total	28	5.9346	1.25315	.23682	5.4487	6.4206	4.80	9.00

Table 55. Descriptive statistics by laboratory for TOC for Three-Mile Creek.

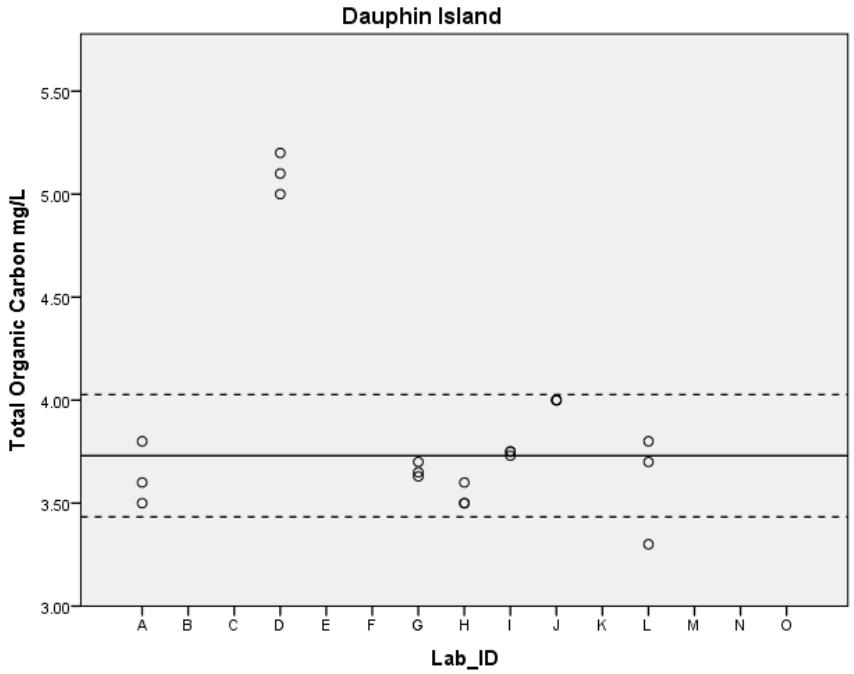

Figure 17. Scatter-plot of TOC values obtained by seven laboratories for Dauphin Island. The solid line indicates the overall median, and the dashed lines indicate +/- 1 F-pseudosigma.

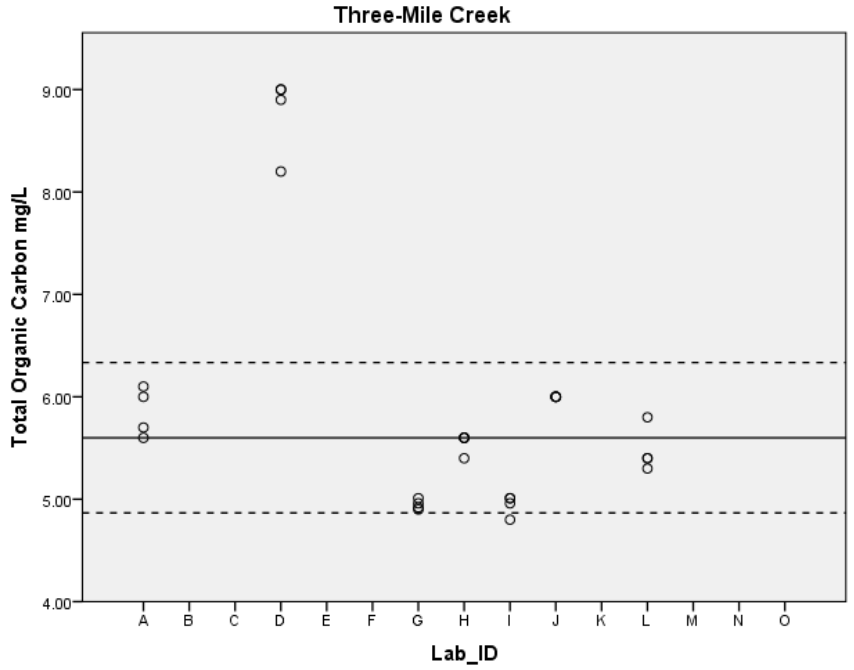

Figure 18. Scatter-plot of TOC values obtained by seven laboratories for Three-Mile Creek. The solid line indicates the overall median, and the dashed lines indicate +/- 1 F-pseudosigma.

Hypothesis Test Summary

	Null Hypothesis	Test	Sig.	Decision
1	The medians of Total Organic Carbon mg/L are the same across categories of Lab_ID.	Independent-Samples Median Test	.043	Reject the null hypothesis.
2	The distribution of Total Organic Carbon mg/L is the same across categories of Lab_ID.	Independent-Samples Kruskal-Wallis Test	.018	Reject the null hypothesis.

Asymptotic significances are displayed. The significance level is .05.

Homogeneous Subsets based on Total Organic Carbon mg/L			
		Subset	
		1	2
Sample[1]	H	3.833	
	A	7.667	
	G	8.167	
	L	8.333	
	I	12.000	
	J	17.000	
	D		20.000
Test Statistic		10.777	.[2]
Sig. (2-sided test)		.056	.
Adjusted Sig. (2-sided test)		.056	.
Homogeneous subsets are based on asymptotic significances. The significance level is .05.			
[1]Each cell shows the sample average rank of Total Organic Carbon mg/L.			
[2]Unable to compute because the subset contains only one sample.			

Table 56. Kruskal-Wallis test and results of nonparametric pair-wise comparisons of TOC by laboratory for Dauphin Island.

Hypothesis Test Summary

	Null Hypothesis	Test	Sig.	Decision
1	The medians of Total Organic Carbon mg/L are the same across categories of Lab_ID.	Independent-Samples Median Test	.001	Reject the null hypothesis.
2	The distribution of Total Organic Carbon mg/L is the same across categories of Lab_ID.	Independent-Samples Kruskal-Wallis Test	.000	Reject the null hypothesis.

Asymptotic significances are displayed. The significance level is .05.

Homogeneous Subsets based on Total Organic Carbon mg/L

		Subset			
		1	2	3	4
Sample[1]	G	4.125			
	I	4.875			
	L		12.250		
	H		13.625		
	A		19.125	19.125	
	J			21.000	
	D				26.500
Test Statistic		.199	5.045	.437	.[2]
Sig. (2-sided test)		.655	.080	.508	.
Adjusted Sig. (2-sided test)		.976	.177	.917	.

Homogeneous subsets are based on asymptotic significances. The significance level is .05.

[1]Each cell shows the sample average rank of Total Organic Carbon mg/L.

[2]Unable to compute because the subset contains only one sample.

Table 57. Kruskal-Wallis test and results of nonparametric pair-wise comparisons of TOC by laboratory for Three-Mile Creek.

J. Dissolved Organic Carbon. Eighteen of the 21 reported values for Dauphin Island were within acceptable ranges. Lab D reported all three values outside acceptable ranges. The %F-pseudosigma value was low (between 10 and 20%), indicating a high degree of precision among laboratories. Of the 21 reported values, 81% were within 1 F-pseudosigma and 86% were within 2 F-pseudosigma.

At Three-Mile Creek, 24 of the 28 values were within acceptable ranges. Lab D reported all four values outside acceptable ranges. The %F-pseudosigma value was very low (less than 10%), indicating a high degree of precision among the laboratories. Of the 28 reported values, 71% were within 1 F-pseudosigma and 86% were within 2 F-pseudosigma. See Figures 19 & 20 for scatter-plots of values obtained by individual laboratories. See Tables 58 - 63 for F-pseudosigma values, summary statistics and inter-laboratory comparisons.

Dissolved Organic Carbon				
	F-pseudosigma	**% F-pseudosigma**	**Median**	**Range**
Dauphin Island	0.463	13.05%	3.55	2.40
Three-Mile Creek	0.313	6.46%	4.85	2.96

Table 58. F-pseudosigma values for DOC.

DOC

	Dauphin Island				Three-Mile Creek			
Lab ID	N	Lab Median	Range	Mean Z-value	N	Lab Median	Range	Mean Z-value
A	3	3.500	0.100	0.18	4	5.100	0.500	0.80
D	3	4.800	0.400	2.84	4	7.200	0.300	7.43
G	3	3.340	0.050	0.48	4	4.500	0.320	1.12
H	3	3.300	0.700	0.90	4	4.700	0.200	0.48
I	3	3.550	0.040	0.03	4	4.620	0.110	0.73
J	3	4.000	0.000	0.97	4	5.000	0.000	0.48
L	3	3.600	0.000	0.11	4	5.000	0.300	0.48

Table 59. Summary statistics and Z-values by Laboratory for DOC.

Descriptives

Dissolved Organic Carbon mg/L

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
A	3	3.46667	.057735	.033333	3.32324	3.61009	3.400	3.500
D	3	4.86667	.208167	.120185	4.34955	5.38378	4.700	5.100
G	3	3.33000	.026458	.015275	3.26428	3.39572	3.300	3.350
H	3	3.13333	.378594	.218581	2.19285	4.07381	2.700	3.400
I	3	3.55667	.020817	.012019	3.50496	3.60838	3.540	3.580
J	3	4.00000	.000000	.000000	4.00000	4.00000	4.000	4.000
L	3	3.60000	.000000	.000000	3.60000	3.60000	3.600	3.600
Total	21	3.70762	.564065	.123089	3.45086	3.96438	2.700	5.100

Table 60. Descriptive statistics by laboratory for DOC from Dauphin Island.

Descriptives

Dissolved Organic Carbon mg/L

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
A	4	5.07500	.262996	.131498	4.65652	5.49348	4.800	5.300
D	4	7.17500	.150000	.075000	6.93632	7.41368	7.000	7.300
G	4	4.50000	.146059	.073030	4.26759	4.73241	4.340	4.660
H	4	4.70000	.081650	.040825	4.57008	4.82992	4.600	4.800
I	4	4.62250	.051235	.025617	4.54097	4.70403	4.570	4.680
J	4	5.00000	.000000	.000000	5.00000	5.00000	5.000	5.000
L	4	4.97500	.125831	.062915	4.77478	5.17522	4.800	5.100
Total	28	5.14964	.874852	.165332	4.81041	5.48888	4.340	7.300

Table 61. Descriptive statistics by laboratory for DOC from Three-Mile Creek.

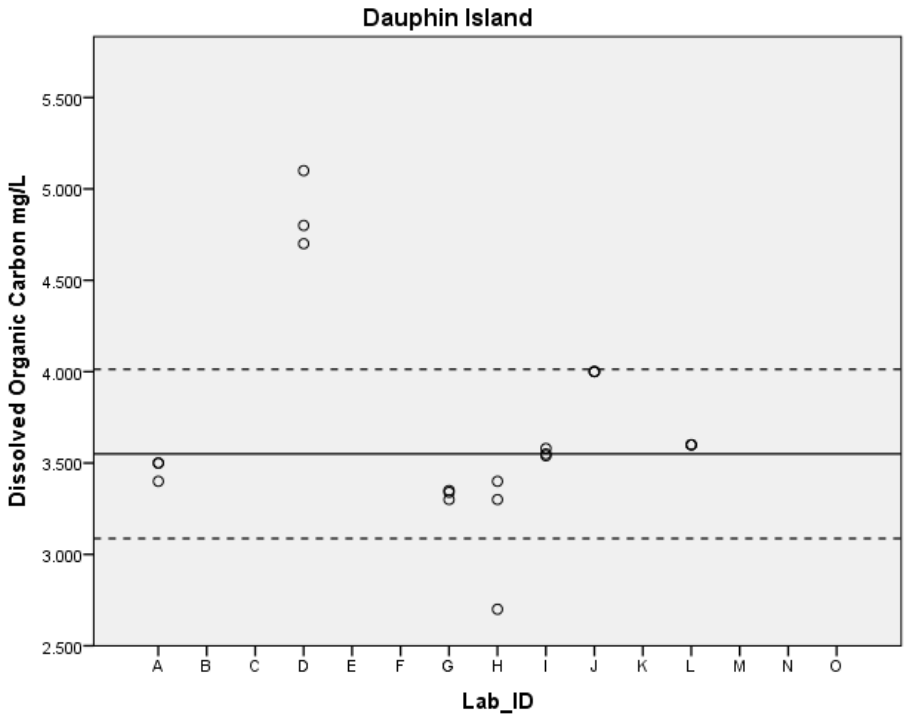

Figure 19. Scatter-plot of DOC values obtained by seven laboratories for Dauphin Island. The solid line indicates the overall median, and the dashed lines indicate +/- 1 F-pseudosigma.

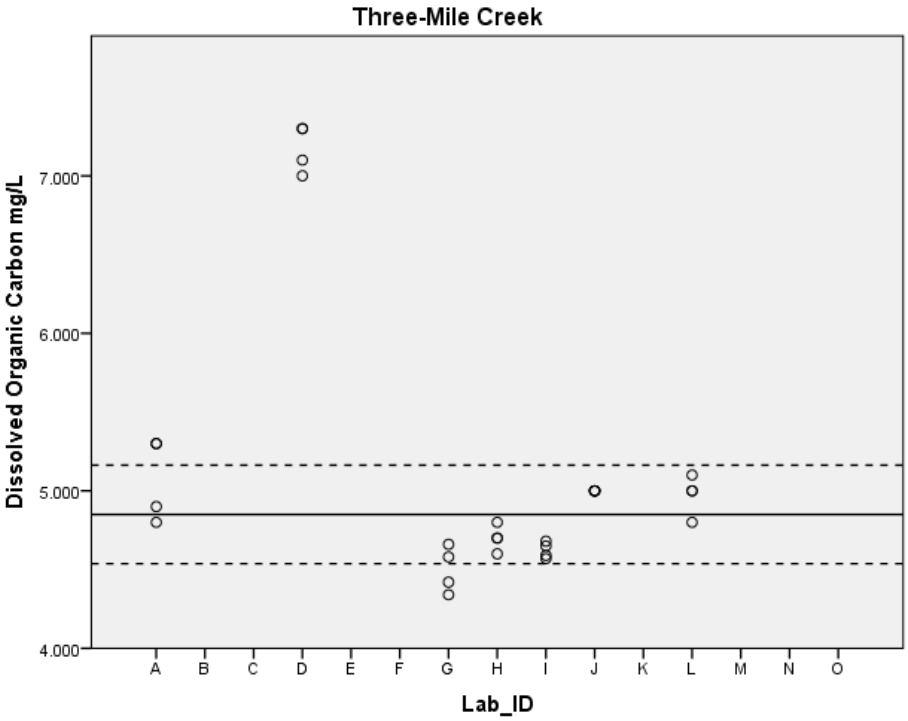

Figure 20. Scatter-plot of DOC values obtained by seven laboratories for Three-Mile Creek. The solid line indicates the overall median, and the dashed lines indicate +/- 1 F-pseudosigma.

Dissolved Organic Carbon mg/L

	Lab ID	N	Subset for alpha = 0.05		
			1	2	3
Gabriel[a]	H	3	3.13333		
	G	3	3.33000		
	A	3	3.46667		
	I	3	3.55667	3.55667	
	L	3	3.60000	3.60000	
	J	3		4.00000	
	D	3			4.86667
	Sig.		.065	.089	1.000

Means for groups in homogeneous subsets are displayed.
a. Uses Harmonic Mean Sample Size = 3.000.
Table 62. Post hoc inter-laboratory comparisons for DOC for Dauphin Island.

Hypothesis Test Summary

	Null Hypothesis	Test	Sig.	Decision
1	The medians of Dissolved Organic Carbon mg/L are the same across categories of Lab_ID.	Independent-Samples Median Test	.001	Reject the null hypothesis.
2	The distribution of Dissolved Organic Carbon mg/L is the same across categories of Lab_ID.	Independent-Samples Kruskal-Wallis Test	.001	Reject the null hypothesis.

Asymptotic significances are displayed. The significance level is .05.

Homogeneous Subsets based on Dissolved Organic Carbon mg/L

		Subset		
		1	2	3
Sample[1]	G	3.750		
	I	6.000		
	H	10.000		
	L		18.000	
	J		18.500	
	A		18.750	
	D			26.500
Test Statistic		5.674	.099	.[2]
Sig. (2-sided test)		.059	.952	.
Adjusted Sig. (2-sided test)		.131	.999	.

Homogeneous subsets are based on asymptotic significances. The significance level is .05.

[1]Each cell shows the sample average rank of Dissolved Organic Carbon mg/L.

[2]Unable to compute because the subset contains only one sample.

Table 63. Kruskal-Wallis test and results of nonparametric pair-wise comparisons of DOC by laboratory for Three-Mile Creek.

K. Chlorophyll a. Thirty-five of the 39 reported values for Dauphin Island were within acceptable ranges. Lab I reported all three values outside acceptable ranges, and Lab M reported one. Lab M reported two false negatives. The %F-pseudosigma value was moderate (between 20 and 30%), indicating a small degree of precision among laboratories. Of the 39 reported values, 74% were within 1 F-pseudosigma and 90% were within 2 F-pseudosigma.

At Three-Mile Creek, 38 of the 44 values were within acceptable ranges. Lab O reported all four values outside acceptable ranges, Labs C and I each reported one. Lab O reported one statistical outlier (3 µg/L), which may be due to rounding. Labs F, J, and M had reported all three results below their detection/quantitation limits. The MDLs for all laboratories ranged from 0.01 to 2.3 µg/L; the PQLs for Labs F, D, and J ranged from 0.1 to 3 µg/L. The %F-pseudosigma value was moderate (between 20 and 30%), indicating a small degree of precision among laboratories. Of the 44reported values, 70% were within 1 F-pseudosigma and 86% were within 2 F-pseudosigma. See Figures 21 & 22 for scatter-plots of values obtained by individual laboratories. See Tables 64 - 69 for F-pseudosigma values, summary statistics and inter-laboratory comparisons.

Chlorophyll a				
	F-pseudosigma	**% F-pseudosigma**	**Median**	**Range**
Dauphin Island	0.890	26.16%	3.400	3.89
Three-Mile Creek	0.361	28.34%	1.275	2.71

Table 64. F-pseudosigma values for ChlA.

ChlA

Lab ID	Dauphin Island				Three-Mile Creek			
	N	Lab Median	Range	Mean Z-value	N	Lab Median	Range	Mean Z-value
A	3	4.000	0.300	0.64	4	1.650	0.300	1.04
B	3	3.200	0.000	0.22	4	1.070	0.530	0.65
C	3	2.900	1.700	0.82	4	1.300	1.200	0.87
D	3	2.800	0.300	0.79	4	1.150	0.100	0.35
E	3	3.510	0.370	0.18	4	1.305	0.300	0.25
F	3*	3.600	0.400	0.22	4	NR	NR	NR
G	3	4.100	0.530	0.66	4	1.815	0.380	1.30
H	3	3.530	1.790	0.72	4	1.505	0.420	0.61
I	3	1.270	0.170	2.45	4	0.840	0.660	1.51
J	3	4.180	0.480	0.79	4	NR	NR	NR
K	3	2.790	0.290	0.66	4	1.185	0.080	0.24
L	3	3.300	0.800	0.34	4	1.200	0.100	0.28
M	3*	1.500	N/A	2.13	4	NR	NR	NR
O	3	5.000	1.000	1.42	4	2.000	1.000	2.70

* One or more non-value reported. NR = All non-values reported.

Table 65. Summary statistics and Z-values by Laboratory for ChlA.

Descriptives

Chlorophyll a µg/L

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
A	3	3.9667	.15275	.08819	3.5872	4.3461	3.80	4.10
B	3	3.2000	.00000	.00000	3.2000	3.2000	3.20	3.20
C	3	3.1333	.87369	.50442	.9630	5.3037	2.40	4.10
D	3	2.7000	.17321	.10000	2.2697	3.1303	2.50	2.80
E	3	3.5200	.18520	.10693	3.0599	3.9801	3.34	3.71
F	2	3.6000	.28284	.20000	1.0588	6.1412	3.40	3.80
G	3	3.9900	.28160	.16258	3.2905	4.6895	3.67	4.20
H	3	3.0467	.98805	.57045	.5922	5.5011	1.91	3.70
I	3	1.2200	.09539	.05508	.9830	1.4570	1.11	1.28
J	3	4.1067	.24826	.14333	3.4900	4.7234	3.83	4.31
K	3	2.8133	.14640	.08452	2.4497	3.1770	2.68	2.97
L	3	3.3667	.40415	.23333	2.3627	4.3706	3.00	3.80
M	1	1.5000	N/A	N/A	N/A	N/A	1.50	1.50
O	3	4.6667	.57735	.33333	3.2324	6.1009	4.00	5.00
Total	39	3.2792	.94625	.15152	2.9725	3.5860	1.11	5.00

Table 66. Descriptive statistics by laboratory for ChlA for Dauphin Island.

Descriptives

Chlorophyll a µg/L

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
A	4	1.6500	.12910	.06455	1.4446	1.8554	1.50	1.80
B	4	1.2025	.26500	.13250	.7808	1.6242	1.07	1.60
C	4	1.3500	.49329	.24664	.5651	2.1349	.80	2.00
D	4	1.1500	.05774	.02887	1.0581	1.2419	1.10	1.20
E	4	1.3625	.14080	.07040	1.1385	1.5865	1.27	1.57
G	4	1.7425	.17746	.08873	1.4601	2.0249	1.48	1.86
H	4	1.4375	.19568	.09784	1.1261	1.7489	1.16	1.58
I	4	.7300	.30496	.15248	.2447	1.2153	.29	.95
K	4	1.1875	.03862	.01931	1.1260	1.2490	1.15	1.23
L	4	1.1750	.05000	.02500	1.0954	1.2546	1.10	1.20
O	4	2.2500	.50000	.25000	1.4544	3.0456	2.00	3.00
Total	44	1.3852	.44503	.06709	1.2499	1.5205	.29	3.00

Table 67. Descriptive statistics by laboratory for ChlA for Three-Mile Creek.

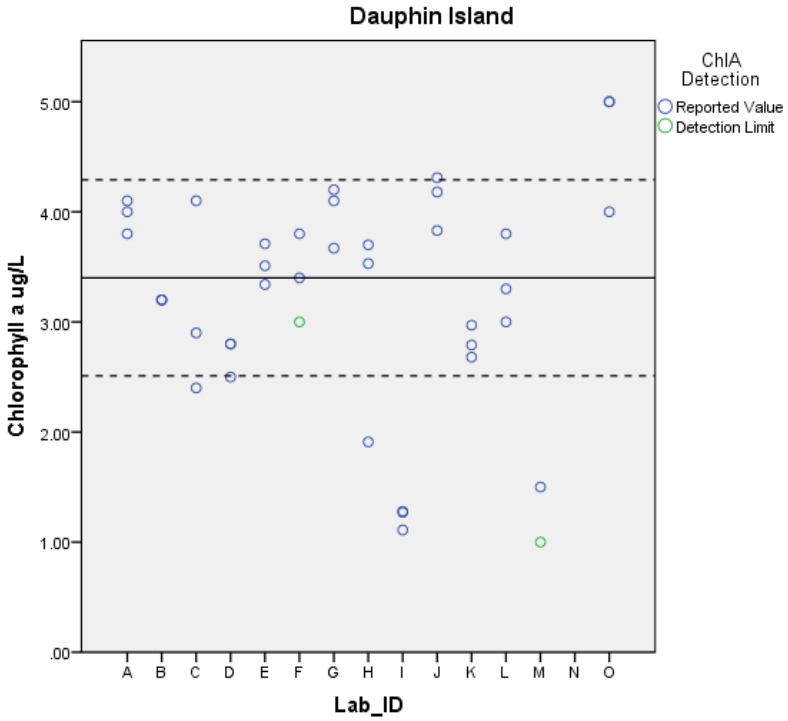

Figure 21. Scatter-plot of ChlA values and detection/quantitation limits obtained by fourteen laboratories for Dauphin Island. The solid line indicates the overall median, and the dashed lines indicate +/- 1 F-pseudosigma.

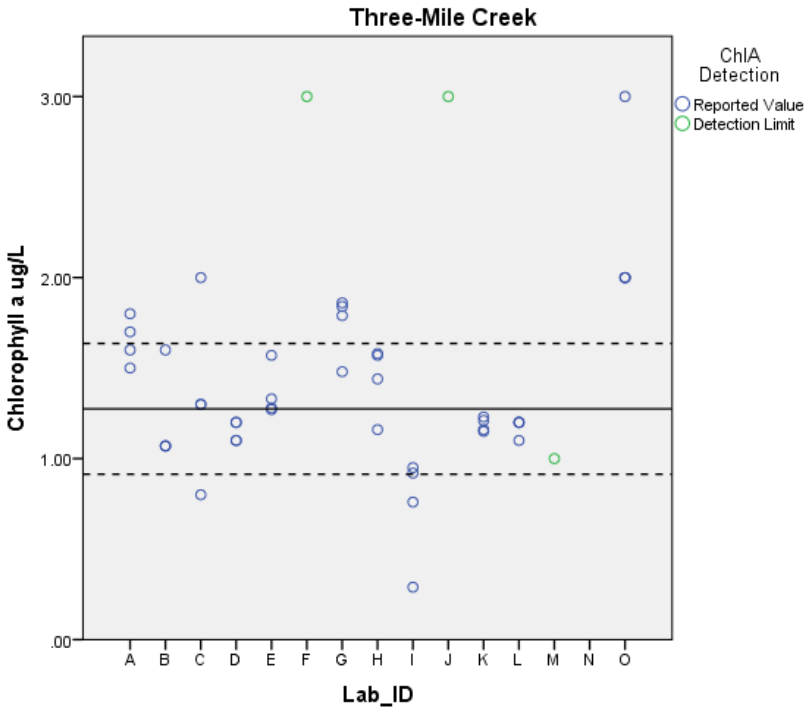

Figure 22. Scatter-plot of ChlA values and detection/quantitation limits obtained by fourteen laboratories for Three-Mile Creek. The solid line indicates the overall median, and the dashed lines indicate +/- 1 F-pseudosigma.

Chlorophyll a µg/L

	Lab ID	N	Subset for alpha = 0.05			
			1	2	3	4
Gabriel[a,b]	I+M	4	1.2900			
	D	3		2.7000		
	K	3		2.8133	2.8133	
	H	3		3.0467	3.0467	
	C	3		3.1333	3.1333	
	B	3		3.2000	3.2000	
	L	3		3.3667	3.3667	3.3667
	E	3		3.5200	3.5200	3.5200
	F	2		3.6000	3.6000	3.6000
	A	3		3.9667	3.9667	3.9667
	G	3		3.9900	3.9900	3.9900
	J	3			4.1067	4.1067
	O	3				4.6667
	Sig.		1.000	.097	.095	.091

Means for groups in homogeneous subsets are displayed.
a. Uses Harmonic Mean Sample Size = 2.943.
b. The group sizes are unequal. The harmonic mean of the group sizes is used. Type I error levels are not guaranteed.

Table 68. Post hoc inter-laboratory comparisons for ChlA for Dauphin Island.

Hypothesis Test Summary

	Null Hypothesis	Test	Sig.	Decision
1	The medians of Chlorophyll a ug/L are the same across categories of Lab_ID.	Independent-Samples Median Test	.000	Reject the null hypothesis.
2	The distribution of Chlorophyll a ug/L is the same across categories of Lab_ID.	Independent-Samples Kruskal-Wallis Test	.000	Reject the null hypothesis.

Asymptotic significances are displayed. The significance level is .05.

Homogeneous Subsets based on Chlorophyll a µg/L						
		Subset				
		1	2	3	4	5
Sample[1]	I	3.000				
	D	13.500	13.500			
	B	13.625	13.625	13.625		
	L	15.250	15.250	15.250		
	K	16.625	16.625	16.625		
	C	23.375	23.375	23.375	23.375	
	E		25.375	25.375	25.375	
	H		25.750	25.750	25.750	
	A			33.625	33.625	
	G				35.250	
	O					42.125
Test Statistic		10.857	9.422	12.473	7.329	.[2]
Sig. (2-sided test)		.054	.151	.052	.119	.
Adjusted Sig. (2-sided test)		.097	.227	.081	.244	.

Homogeneous subsets are based on asymptotic significances. The significance level is .05.

[1]Each cell shows the sample average rank of Chlorophyll a µg/L.

[2]Unable to compute because the subset contains only one sample.

Table 69. Kruskal-Wallis test and results of nonparametric pair-wise comparisons of ChlA by laboratory for all reported values from Three-Mile Creek.

L. Biochemical Oxygen Demand. Eight of the 27 results for Dauphin Island were reported values; the other 70% were reported as qualifiers. None of the detection/quantitation limits that were reported as results were determined to be false negatives. No other analyses were conducted for BOD for Dauphin Island.

At Three-Mile Creek, 27 of the 28 values were within acceptable ranges. Lab A reported the only value outside acceptable ranges. Lab D had all four results reported below its detection/quantitation limits, Lab J had three, and Lab F had one. The MDLs ranged from 0.2 to 2 mg/L; the PQLs for Labs F, D, and J ranged from 2 to 3 mg/L. The %F-pseudosigma value was low (between 10 and 20%), indicating a high degree of precision among laboratories. Of the 28reported values, 64% were within 1 F-pseudosigma and 96% were within 2 F-pseudosigma. See Figures 23 & 24 for scatter-plots of values obtained by individual laboratories. See Tables 70 - 73 for F-pseudosigma values, summary statistics and inter-laboratory comparisons.

Biochemical Oxygen Demand				
	F-pseudosigma	**% F-pseudosigma**	**Median**	**Range**
Dauphin Island	N/A	N/A	0.70	0.41
Three-Mile Creek	0.291	11.64%	2.50	1.30

Table 70. F-pseudosigma values for BOD.

BOD

	Dauphin Island				Three-Mile Creek			
Lab ID	N	Lab Median	Range	Mean Z-value	N	Lab Median	Range	Mean Z-value
A	3*	0.910	0.380	N/A	4	2.800	0.600	1.37
B	3	NR	NR	NR	4	2.400	0.400	0.52
C	3	0.700	0.000	N/A	4	2.400	0.100	0.43
D	3	NR	NR	NR	4	NR	NR	NR
F	3	NR	NR	NR	4*	2.200	0.400	0.80
G	3	0.700	0.030	N/A	4	2.405	0.170	0.31
J	3	NR	NR	NR	4*	3.000	N/A	1.72
M	3	NR	NR	NR	4	2.600	0.100	0.43
O	3	NR	NR	NR	4	2.500	1.000	1.72

* One or more non-value reported. NR = All non-values reported.

Table 71. Summary statistics and Z-values by Laboratory for BOD.

Descriptives

Biochemical Oxygen Demand mg/L

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
A	4	2.9000	.27080	.13540	2.4691	3.3309	2.70	3.30
B	4	2.4500	.19149	.09574	2.1453	2.7547	2.30	2.70
C	4	2.3750	.05000	.02500	2.2954	2.4546	2.30	2.40
F	3	2.2667	.20817	.12019	1.7496	2.7838	2.10	2.50
G	4	2.4100	.07071	.03536	2.2975	2.5225	2.33	2.50
J	1	3.0000	N/A	N/A	N/A	N/A	3.00	3.00
M	4	2.6250	.05000	.02500	2.5454	2.7046	2.60	2.70
O	4	2.5000	.57735	.28868	1.5813	3.4187	2.00	3.00
Total	28	2.5300	.31282	.05912	2.4087	2.6513	2.00	3.30

Table 72. Descriptive statistics by laboratory for BOD from Three-Mile Creek.

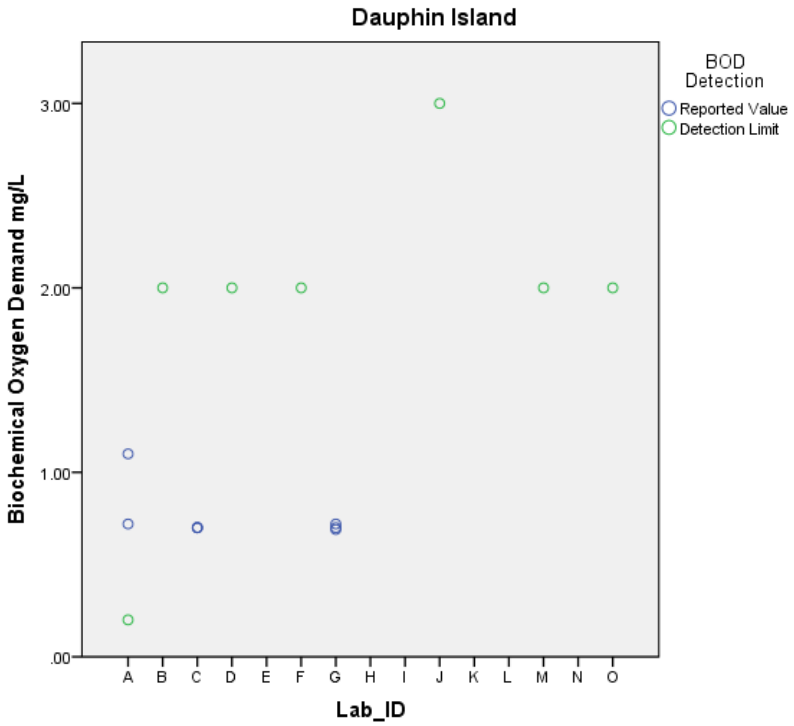

Figure 23. Scatter-plot of BOD values and detection/quantitation limits obtained by nine laboratories for Dauphin Island.

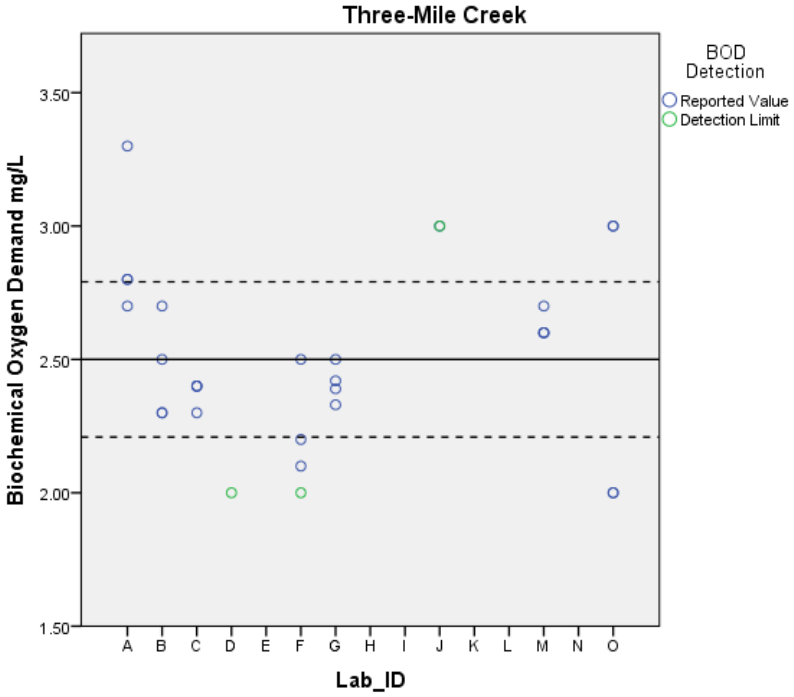

Figure 24. Scatter-plot of BOD values and detection/quantitation limits obtained by nine laboratories for Three-Mile Creek. The solid line indicates the overall median, and the dashed lines indicate +/- 1 F-pseudosigma.

Biochemical Oxygen Demand mg/L

	Lab ID	N	Subset for alpha = 0.05	
			1	2
Gabriel[a,b]	F	3	2.2667	
	C	4	2.3750	2.3750
	G	4	2.4100	2.4100
	B	4	2.4500	2.4500
	O	4	2.5000	2.5000
	M	4	2.6250	2.6250
	A+J	5		2.9200
	Sig.		.697	.144

Means for groups in homogeneous subsets are displayed.
a. Uses Harmonic Mean Sample Size = 3.925.
b. The group sizes are unequal. The harmonic mean of the group sizes is used. Type I error levels are not guaranteed.

Table 73. Post hoc inter-laboratory comparisons for BOD for Three-Mile Creek.

M. Carbonaceous Biochemical Oxygen Demand. Six of the 27 results for Dauphin Island were reported values; the other 78% were reported as qualifiers. None of the detection/quantitation limits that were reported as results were determined to be false negatives. No other analyses were conducted for CBOD for Dauphin Island.

At Three-Mile Creek, 23 of the 24 values were within acceptable ranges. Lab F reported the only value outside acceptable ranges. Labs B, D, and J had all four results reported below their detection/quantitation limits, and Lab O had one. The MDLs ranged from 0.2 to 2 mg/L; the PQLs for Labs F, D, and J ranged from 2 to 3 mg/L. The %F-pseudosigma value was moderate (between 20 and 30%), indicating a small degree of precision among laboratories. Of the 24reported values, 63% were within 1 F-pseudosigma and 96% were within 2 F-pseudosigma. See Figures 25 & 26 for scatter-plots of values obtained by individual laboratories. See Tables 74 - 77 for F-pseudosigma values, summary statistics and inter-laboratory comparisons.

Carbonaceous Biochemical Oxygen Demand				
	F-pseudosigma	**% F-pseudosigma**	**Median**	**Range**
Dauphin Island	N/A	N/A	0.78	0.70
Three-Mile Creek	0.484	24.18%	2.00	2.25

Table 74. F-pseudosigma values for CBOD.

CBOD

	Dauphin Island				Three-Mile Creek			
Lab ID	N	Lab Median	Range	Mean Z-value	N	Lab Median	Range	Mean Z-value
A	3	0.690	0.360	N/A	4	2.200	1.500	0.98
B	3	NR	NR	NR	4	NR	NR	NR
C	3	0.900	0.300	N/A	4	2.050	0.400	0.26
D	3	NR	NR	NR	4	NR	NR	NR
F	3	NR	NR	NR	4	2.600	1.100	1.50
G	3	NR	NR	NR	4	1.330	0.480	1.32
J	3	NR	NR	NR	4	NR	NR	NR
M	3	NR	NR	NR	4	1.750	0.300	0.62
O	3	NR	NR	NR	4*	2.000	0.000	0.00

* One or more non-value reported. NR = All non-values reported.

Table 75. Summary statistics and Z-values by Laboratory for CBOD.

Descriptives

Carbonaceous Biochemical Oxygen Demand mg/L

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
A	4	2.1750	.63443	.31721	1.1655	3.1845	1.40	2.90
C	4	2.0750	.17078	.08539	1.8032	2.3468	1.90	2.30
F	4	2.7250	.53151	.26575	1.8793	3.5707	2.30	3.40
G	4	1.3600	.20050	.10025	1.0410	1.6790	1.15	1.63
M	4	1.7000	.14142	.07071	1.4750	1.9250	1.50	1.80
O	3	2.0000	.00000	.00000	2.0000	2.0000	2.00	2.00
Total	23	2.0061	.54640	.11393	1.7698	2.2424	1.15	3.40

Table 76. Descriptive statistics by laboratory for CBOD for Three-Mile Creek.

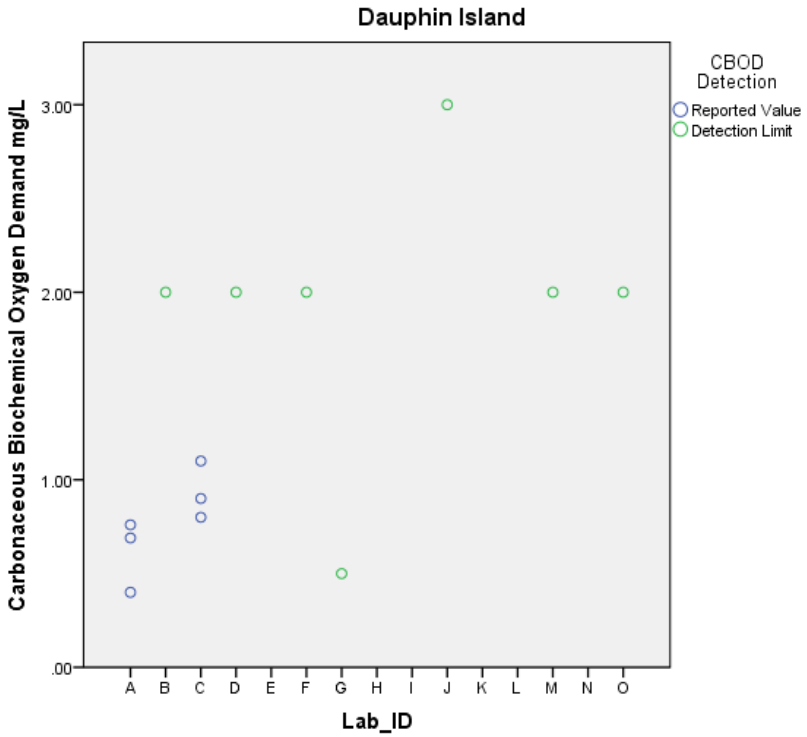

Figure 25. Scatter-plot of CBOD values and detection/quantitation limits obtained by nine laboratories for Dauphin Island.

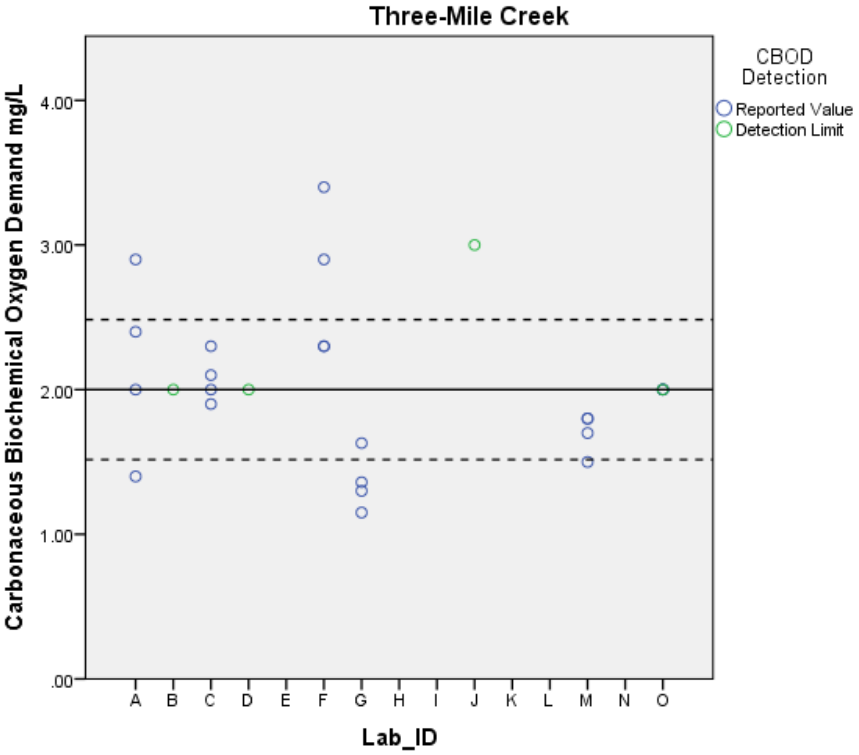

Figure 26. Scatter-plot of CBOD values and detection/quantitation limits obtained by nine laboratories for Three-Mile Creek. The solid line indicates the overall median, and the dashed lines indicate +/- 1 F-pseudosigma.

Carbonaceous Biochemical Oxygen Demand mg/L

	Lab ID	N	Subset for alpha = 0.05	
			1	2
Gabriel[a,b]	G	4	1.3600	
	M	4	1.7000	
	O	3	2.0000	2.0000
	C	4	2.0750	2.0750
	A	4	2.1750	2.1750
	F	4		2.7250
	Sig.		.094	.177

Means for groups in homogeneous subsets are displayed.
a. Uses Harmonic Mean Sample Size = 3.789.
b. The group sizes are unequal. The harmonic mean of the group sizes is used. Type I error levels are not guaranteed.

Table 77. Post hoc inter-laboratory comparisons for CBOD from Three-Mile Creek.

4. Conclusions and Recommendations

Total Kjeldahl Nitrogen: There was little variability among laboratories for total Kjeldahl nitrogen at higher concentrations, but was quite variable at low concentrations. However, values from Lab F were highly variable at both concentrations, and were considerably higher than all other values. Lab F reported two statistical outliers for Dauphin Island and one outlier for Three-Mile Creek. It is unclear why this laboratory's results are higher and more variable than those of the other laboratories. Detection and quantitation limits were not an issue for this analyte.

Ammonia: Ammonia was moderately variable at lower concentrations. At higher concentrations, the variability among results was reduced considerably. Detection and quantitation limits need to be addressed, as roughly one third of the results from Dauphin Island (the low concentration site) were non-values.

Total Nitrite + Nitrate: There was little variability in results for NO_x for both sites. Lab F reported one statistical outlier for Dauphin Island, and Lab M reported two results that were statistical outliers for Three-Mile Creek. In addition, Lab M's results were considerably high for both locations. Detection and quantitation limits were not an issue for this analyte.

Total Nitrite: The variability in results for NO_2 was inversely proportional to the concentration. At the low concentration site, the variability was high, whereas at the high concentration site, it was low. Lab O reported one false negative for Three-Mile Creek. Detection and quantitation limits were not an issue for this analyte.

Dissolved Nitrite + Nitrate: There was little variability in results for DNO_x for both sites. There were no statistical outliers reported for either location; however, Lab M's results were considerably high for both locations, whereas Lab O's values were low for both locations. Detection and quantitation limits were not an issue for this analyte, as no non-values were reported.

Dissolved Nitrite: As with NO_2, the variability in results for DNO_2 was inversely proportional to the concentration. At the low concentration site, the variability was very high, whereas at the high concentration site, it was very low. Lab D reported all of its results for both sites outside of acceptable ranges, and on the high end; this laboratory also reported two statistical outliers for Three-Mile Creek. Detection and quantitation limits need to be addressed, as roughly one third of the results from the low concentration site were non-values.

Total Phosphorus: Results for total phosphorus were somewhat variable; however, at least 90% of the results were within acceptable ranges for either location. Lab F reported one statistical outlier for both sites, and its results tended to be high. Lab D reported one false negative for Dauphin Island. Other than the false negative, detection and quantitation limits were not an issue for this analyte during this round robin.

Orthophosphate: As with NO_2 and DNO_2, the variability in results for OP was inversely proportional to the concentration. At the low concentration site, the variability was high, whereas at the high concentration site, it was low. Labs C and J reported all detected values outside acceptable ranges for Dauphin Island, whereas Lab F reported all values outside acceptable ranges for Three-Mile Creek. There were no statistical outliers for OP at either site. Although very few results were reported as non-values, detection and quantitation limits need to be addressed.

Total Organic Carbon: There was little variability among laboratories, or within laboratories, for TOC. Lab D reported all values outside of acceptable ranges on the high end for both sites; this may be due to an improperly functioning SO_3 scrubber. No values were reported as below detection or quantitation limits for either site.

Dissolved Organic Carbon: As with TOC, there was little variability among laboratories, or within laboratories, for DOC. Lab D reported all values outside of acceptable ranges on the high end for both sites; this may be due to an improperly functioning SO_3 scrubber. No values were reported as below detection or quantitation limits for either site.

Chlorophyll a: Variability among laboratories was moderate for chlorophyll a for both sites. Lab O's reported values tended to be high, which is most likely due to rounding its results. Lab I reported the lowest results at both sites. Of the 98 possible results from both sites, twelve were below detection/quantitation limits. Laboratories need to report if they are analyzing corrected or uncorrected chlorophyll a concentrations, not simply listing it as chlorophyll a.

Biochemical Oxygen Demand and Carbonaceous Biochemical Oxygen Demand: Very few values were reported for BOD and CBOD. Therefore, detection and quantitation limits need to be addressed.

Overall: Overall, the data were quite similar among laboratories; however, a contamination issue at the host laboratory resulted in fewer than optimum number of samples available for analyses. The host laboratory is responsible for minimizing the error and variability associated with preparing samples for the GOMA analytical round robins. In addition, it must follow sampling protocols, including rinsing tubing and equipment thoroughly with sample water prior to splitting the aliquots.

In addition, modifying or standardizing the practices of participating labs could further minimize variability. For example, variability in results could be reduced by laboratories adopting the following practices:

- improve the accuracy in calculating and reporting their detection and quantitation limits;
- revise methods to better quantify their techniques to reduce the amount of variability in the methods employed;
- minimize gross errors due to unit conversions, calculation errors, dilution errors, transcription errors (and other typographical errors), etc. through automation, improved quality control and quality assurance plans;
- report the results for a round robin as the output of the analyses, not as a reporting limit for a database (e.g., report the values out to 2 to 3 decimal places rather than rounding to whole numbers).

Future round robins could address these issues by documenting the methods employed by the participating laboratories to identify and quantify the variability associated with the individual methods.

The greatest challenge to the round robin project and to achieving data comparability in the Gulf is addressing the high number of nutrient, ChlA, BOD, and CBOD results reported as below detection and quantitation limits. In order to adequately monitor water quality in and around the Gulf of Mexico, the detection problem must be resolved. As technology advances,

allowing equipment to gain greater accuracy and precision, the detection limits should come down; in addition, calculations for quantitation limits need to better quantify noise.

We recommend that laboratories that have the capabilities to detect and quantify nutrients within these waters coordinate with laboratories that do not have this ability in order to help them achieve detectable and quantifiable results. It is recommended that future round robins include a greater number of laboratories that conduct analyses around the Gulf and increase the number of analytes of interest in order to better assess comparability around the Gulf and increase the power of statistical analyses. Finally, we recommend that GOMA and its partners obtain funding to facilitate laboratory education and information exchange to address the challenges listed above.

5. References

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GOMA Analytical Round Robin #4 Results – February 10, 2010

Samples collected from the east end of Dauphin Island, Alabama

Where an actual number was given for results listed below the MDL or PQL, the reported number is given. However, when the result was simply listed as less than the MDL or PQL, a U qualifier is listed for below MDL and an I qualifier is listed for below PQL.

Only the laboratories that ran analyses for a particular analyte are listed with that analyte.

Calculations include all reported values.

*** = Less than PQL**

Total Kjeldahl Nitrogen mg/L

	A	B	C	D	F	G	H	J	M	N	O
	0.380	0.195	0.177	0.220	7.000	0.357	0.380	0.490	0.570	0.390	0.470
	0.360	0.489	0.187	0.210	2.400	0.339	0.380	0.500	0.470	0.378	0.460
	0.340	0.511	0.173	0.250	7.700	0.371	0.380	0.540	0.540	0.377	0.480
Average:	**0.360**	**0.398**	**0.179**	**0.227**	**5.700**	**0.356**	**0.380**	**0.510**	**0.527**	**0.382**	**0.470**
Std. Dev.	**0.020**	**0.176**	**0.007**	**0.021**	**2.879**	**0.016**	**0.000**	**0.026**	**0.051**	**0.007**	**0.010**

Ammonia mg/L

	A	B	C	D	E	F	G	H	I	J	L	M	N	O
	0.041	U	0.040	0.050	0.021	U	0.044	0.026	0.056	U	0.044	U	0.054	0.080
	0.049	U	0.040	U	0.014	U	0.030	0.042	0.051	U	0.040	U	0.055	0.070
	0.046	U	0.040	0.060	0.014	U	0.035	0.039	0.052	U	0.035	U	0.054	0.080
Average:	**0.045**		**0.040**	**0.055**	**0.016**		**0.036**	**0.036**	**0.053**		**0.040**		**0.054**	**0.077**
Std. Dev.	**0.004**		**0.000**	**0.007**	**0.004**		**0.007**	**0.009**	**0.003**		**0.005**		**0.001**	**0.006**

Total Nitrite + Nitrate mg/L

	A	B	C	D	F	G	J	L	M	O
	0.170	0.141	0.169	0.157	0.230	0.180	0.170	0.175	0.250	0.167
	0.170	0.140	0.169	0.156	0.210	0.185	0.170	0.171	0.243	0.166
	0.170	0.141	0.168	0.155	0.300	0.185	0.170	0.155	0.234	0.170
Average:	**0.170**	**0.141**	**0.169**	**0.156**	**0.247**	**0.183**	**0.170**	**0.167**	**0.242**	**0.168**
Std. Dev.	**0.000**	**0.001**	**0.001**	**0.001**	**0.047**	**0.003**	**0.000**	**0.011**	**0.008**	**0.002**

Total Nitrite mg/L

	A	B	C*	D	F	G*	J	L*	M	O
	0.014	0.020	0.014	0.023	0.030	0.013	U	0.013	0.037	
	0.015	0.016	0.013	0.021	0.030	0.015	U	0.012		
	0.013	0.019	0.011	0.020	0.030	0.015	U	0.006		U
Average:	**0.014**	**0.018**	**0.013**	**0.021**	**0.030**	**0.014**		**0.010**	**0.037**	
Std. Dev.	**0.001**	**0.002**	**0.002**	**0.002**	**0.000**	**0.001**		**0.004**		

Dissolved Nitrite + Nitrate mg/L

	A	B	C	D	G	H	I	J	L	M	N	O
	0.180	0.181	0.190	0.175	0.179	0.149	0.184	0.170	0.175	0.223	0.178	0.164
	0.180	0.178		0.174	0.185	0.179	0.198	0.170	0.176	0.224	0.173	0.166
	0.180	0.179	0.189	0.174	0.179	0.178	0.182	0.180	0.176	0.227	0.166	0.149
Average:	**0.180**	**0.179**	**0.190**	**0.174**	**0.181**	**0.169**	**0.188**	**0.173**	**0.176**	**0.225**	**0.172**	**0.160**
Std. Dev.	**0.000**	**0.002**	**0.001**	**0.001**	**0.003**	**0.017**	**0.009**	**0.006**	**0.001**	**0.002**	**0.006**	**0.009**

Dissolved Nitrite mg/L

	A*	B	C*	D	G*	H*	I*	J	L*	M	N
	U	U	0.003	0.011	0.006	0.002	0.003	U	0.005		0.002
	U	U		0.011	0.006	0.003	0.002	U	0.005	U	U
	0.006	U	0.003	0.013	0.006	U	0.003	U	0.002		0.002
Average:	**0.006**		**0.003**	**0.012**	**0.006**	**0.003**	**0.003**		**0.004**		**0.002**
Std. Dev.			**0.000**	**0.001**	**0.000**	**0.001**	**0.001**		**0.002**		**0.000**

Total Phosphorus mg/L

	A	B	C*	D	E	F	G	H	I	J	L	M	N	O
	0.057	0.059	0.064	0.040	0.038	0.175	0.053	0.066	0.038	0.080	0.056	0.056	0.076	0.043
	0.058	0.052	0.061	0.040	0.037	0.185	0.061	0.067	0.038	0.060	0.052	0.057	0.069	0.049
	0.056	0.055	0.059	U	0.037	0.192	0.092	0.066	0.038	0.080	0.045	0.060	0.069	0.056
Average:	**0.057**	**0.055**	**0.061**	**0.040**	**0.037**	**0.184**	**0.069**	**0.066**	**0.038**	**0.073**	**0.051**	**0.058**	**0.071**	**0.049**
Std. Dev.	**0.001**	**0.004**	**0.003**	**0.000**	**0.001**	**0.009**	**0.021**	**0.001**	**0.000**	**0.012**	**0.006**	**0.002**	**0.004**	**0.007**

Orthophosphate mg/L

	A	B	C*	D	E	F	G	H	I	J	L*	M	N
	0.012	0.013	0.020	0.005	0.009	U	0.017	0.009	0.009	0.020	0.009	0.009	0.011
	0.011	0.013		0.005	0.009	U	0.013	0.009	0.009	0.020	0.008	0.008	0.011
	0.012	0.012	0.019	0.004	0.009	U	0.013	0.009	0.008	U	0.008		0.012
Average:	**0.012**	**0.013**	**0.020**	**0.005**	**0.009**		**0.014**	**0.009**	**0.009**	**0.020**	**0.008**	**0.009**	**0.011**
Std. Dev.	**0.001**	**0.001**	**0.001**	**0.001**	**0.000**		**0.002**	**0.000**	**0.001**	**0.000**	**0.001**	**0.001**	**0.001**

Total Organic Carbon mg/L

	A*	D	G	H*	I	J	L
	3.500	5.000	3.630	3.600	3.750	4.000	3.800
	3.600	5.200	3.650	3.500	3.730	4.000	3.700
	3.800	5.100	3.700	3.500	3.750	4.000	3.300
Average:	**3.633**	**5.100**	**3.660**	**3.533**	**3.743**	**4.000**	**3.600**
Std. Dev.	**0.153**	**0.100**	**0.036**	**0.058**	**0.012**	**0.000**	**0.265**

Notes **Lab D's high values may be due to positive interference due to SO_3 detection caused by H_2SO_4 preservation. May require an SO_3 scrubber.**

Dissolved Organic Carbon mg/L

	A*	D	G	H*	I	J	L
	3.500	4.700	3.350	2.700	3.540	4.000	3.600
	3.500	4.800	3.340	3.400	3.580	4.000	3.600
	3.400	5.100	3.300	3.300	3.550	4.000	3.600
Average:	**3.467**	**4.867**	**3.330**	**3.133**	**3.557**	**4.000**	**3.600**
Std. Dev.	**0.058**	**0.208**	**0.026**	**0.379**	**0.021**	**0.000**	**0.000**

Notes **Lab D's high values may be due to positive interference due to SO_3 detection caused by H_2SO_4 preservation. May require an SO_3 scrubber.**

Chlorophyll a µg/L

	A	B	C*	D	E	F	G	H	I	J	K	L*	M	O
	4.100	3.200	2.900	2.800	3.510	U	3.670	1.910	1.110	3.830	2.680	3.800	1.500	5.000
	3.800	3.200	4.100	2.500	3.710	3.400	4.100	3.700	1.270	4.180	2.970	3.000	U	5.000
	4.000	3.200	2.400	2.800	3.340	3.800	4.200	3.530	1.280	4.310	2.790	3.300	U	4.000
Average:	**3.967**	**3.200**	**3.133**	**2.700**	**3.520**	**3.600**	**3.990**	**3.047**	**1.220**	**4.107**	**2.813**	**3.367**	**1.500**	**4.667**
Std. Dev.	**0.153**	**0.000**	**0.874**	**0.173**	**0.185**	**0.283**	**0.282**	**0.988**	**0.095**	**0.248**	**0.146**	**0.404**		**0.577**

Biochemical Oxygen Demand mg/L

	A*	B	C	D	F	G*	J	M	O
	U	U	0.700	U	U	0.700	U	U	U
	0.720	U	0.700	U	U	0.720	U	U	U
	1.100	U	0.700	U	U	0.690	U	U	U
Average:	**0.910**		**0.700**			**0.703**			
Std. Dev.	**0.269**		**0.000**			**0.015**			

Carbonaceous Biochemical Oxygen Demand mg/L

	A*	B	C	D	F	G	J	M	O
	0.690	U	0.800	U	U	U	U	U	U
	0.400	U	1.100	U	U	U	U	U	U
	0.760	U	0.900	U	U	U	U	U	U
Average:	**0.617**		**0.933**						
Std. Dev.	**0.191**		**0.153**						

GOMA Analytical Round Robin #4 Results – February 10, 2010

Samples collected from Three-Mile Creek, Alabama

Total Kjeldahl Nitrogen mg/L

	A	B	C	D	F	G	H	J	M	N	O
	1.400	1.341	1.371	1.210	18.300	1.360	1.290	1.500	1.200	1.340	1.410
	1.300	1.365	1.421	1.160	4.400	1.380	1.300	1.230	1.300	1.310	1.390
	1.200	1.261	1.409	1.080	4.500	1.340	1.280	1.210	1.400	1.330	1.480
	1.300	1.312	1.458	1.180	4.100	1.390	1.300	1.420	1.300	1.320	1.280
Average:	**1.300**	**1.320**	**1.415**	**1.158**	**7.825**	**1.368**	**1.293**	**1.340**	**1.300**	**1.325**	**1.390**
Std. Dev.	**0.082**	**0.045**	**0.036**	**0.056**	**6.985**	**0.022**	**0.010**	**0.143**	**0.082**	**0.013**	**0.083**

Ammonia mg/L

	A	B	C	D	E	F	G	H	I	J	L	M	N	O
	0.670	0.614	0.637	0.660	0.937	0.400	0.640	0.665	0.659	0.740	0.683	0.610	0.699	0.630
	0.680	0.618	0.640	0.680	0.915	0.300	0.694	0.671	0.685	0.720	0.682	0.600	0.708	0.620
	0.670	0.622	0.642	0.660	0.900	0.300	0.711	0.681	0.602	0.700	0.681	0.610	0.705	0.610
	0.660	0.614	0.639	0.620	0.866	0.400	0.640	0.691	0.688	0.710	0.682	0.610	0.701	0.610
Average:	**0.670**	**0.617**	**0.640**	**0.655**	**0.905**	**0.350**	**0.671**	**0.677**	**0.659**	**0.718**	**0.682**	**0.608**	**0.703**	**0.618**
Std. Dev.	**0.008**	**0.004**	**0.002**	**0.025**	**0.030**	**0.058**	**0.037**	**0.011**	**0.040**	**0.017**	**0.001**	**0.005**	**0.004**	**0.010**

Total Nitrite + Nitrate mg/L

	A	B	C	D	F	G	J	L	M	O
	1.900	1.764	1.788	1.770	1.910	1.870	1.880	1.850	2.520	1.730
	1.900	1.762	1.785	1.800	1.630	1.870	1.820	1.850	2.480	1.740
	1.900	1.763	1.777	1.820	1.620	1.870	1.840	1.870	2.310	1.760
	1.900	1.765	1.775	1.650	1.840	1.830	1.850	1.730	2.120	1.780
Average:	**1.900**	**1.764**	**1.781**	**1.760**	**1.750**	**1.860**	**1.848**	**1.825**	**2.358**	**1.753**
Std. Dev.	**0.000**	**0.001**	**0.006**	**0.076**	**0.147**	**0.020**	**0.025**	**0.064**	**0.183**	**0.022**

Total Nitrite mg/L

	A	B	C	D	F	G	J	L	M	O
	0.039	0.040	0.040	0.056	0.050	0.040	0.050	0.039	0.046	0.037
	0.040	0.043	0.040	0.055	0.050	0.041	0.050	0.038	0.046	0.039
	0.039	0.043	0.039	0.055	0.040	0.041	0.050	0.040	0.047	U
	0.040	0.042	0.041	0.053	0.050	0.041	0.050	0.039	0.049	0.039
Average:	**0.040**	**0.042**	**0.040**	**0.055**	**0.048**	**0.041**	**0.050**	**0.039**	**0.047**	**0.038**
Std. Dev.	**0.001**	**0.001**	**0.001**	**0.001**	**0.005**	**0.001**	**0.000**	**0.001**	**0.001**	**0.001**

Dissolved Nitrite + Nitrate mg/L

	A	B	C	D	G	H	I	J	L	M	N	O
	1.900	1.861		1.810	1.840	1.880	2.092	1.840	1.840	2.280	1.750	1.770
	1.900	1.874	1.824	1.840	1.840	1.900	2.157	1.880	1.850	2.180	1.920	1.740
	1.900	1.880	1.788	1.830	1.790	1.900	2.141	1.830	1.880	2.170	1.920	1.740
	1.900	1.879	1.793	1.820	1.770	1.930	2.145	1.830	1.890	1.940	1.930	1.740
Average:	**1.900**	**1.874**	**1.802**	**1.825**	**1.810**	**1.903**	**2.134**	**1.845**	**1.865**	**2.143**	**1.880**	**1.748**
Std. Dev.	**0.000**	**0.009**	**0.020**	**0.013**	**0.036**	**0.021**	**0.029**	**0.024**	**0.024**	**0.144**	**0.087**	**0.015**

Dissolved Nitrite mg/L

	A	B	C	D	G	H	I	J	L	M	N
	0.035	0.038		0.051	0.037	0.036	0.034	0.040	0.036	0.039	0.037
	0.036	0.038	0.036	0.051	0.037	0.037	0.035	0.040	0.036	0.040	0.037
	0.036	0.037	0.036	0.048	0.037	0.036	0.035	0.040	0.037	0.039	0.037
	0.036	0.038	0.035	0.049	0.037	0.038	0.035	0.040	0.036	0.039	0.037
Average:	**0.036**	**0.038**	**0.036**	**0.050**	**0.037**	**0.037**	**0.035**	**0.040**	**0.036**	**0.039**	**0.037**
Std. Dev.	**0.000**	**0.001**	**0.001**	**0.002**	**0.000**	**0.001**	**0.001**	**0.000**	**0.001**	**0.001**	**0.000**

Total Phosphorus mg/L

	A	B	C	D	E	F	G	H	I	J	L	M	N	O
	0.200	0.189	0.167	0.160	0.158	0.208	0.218	0.200	0.172	0.190	0.193	0.210	0.211	0.191
	0.200	0.190	0.164	0.150	0.157	0.205	0.205	0.196	0.185	0.200	0.191	0.210	0.201	0.186
	0.200	0.190	0.165	0.160	0.161	0.278	0.212	0.199	0.181	0.200	0.189	0.210	0.213	0.191
	0.200	0.189	0.167	0.150	0.159	0.245	0.211	0.196	0.186	0.200	0.190	0.210	0.210	0.201
Average:	**0.200**	**0.190**	**0.166**	**0.155**	**0.159**	**0.234**	**0.212**	**0.198**	**0.181**	**0.198**	**0.191**	**0.210**	**0.209**	**0.192**
Std. Dev.	**0.000**	**0.001**	**0.002**	**0.006**	**0.002**	**0.035**	**0.005**	**0.002**	**0.006**	**0.005**	**0.002**	**0.000**	**0.005**	**0.006**

Orthophosphate mg/L

	A	B	C	D	E	F	G	H	I	J	L	M	N
	0.100	0.105		0.098	0.101	0.130	0.087	0.105	0.105	0.090	0.102	0.093	0.110
	0.100	0.105	0.095	0.100	0.102	0.120	0.082	0.105	0.110	0.090	0.104	0.092	0.112
	0.100	0.105	0.095	0.097	0.102	0.130	0.083	0.106	0.109	0.080	0.102	0.093	0.110
	0.100	0.105	0.096	0.097	0.101	0.130	0.086	0.104	0.106	0.090	0.101	0.093	0.110
Average:	**0.100**	**0.105**	**0.095**	**0.098**	**0.102**	**0.128**	**0.085**	**0.105**	**0.108**	**0.088**	**0.102**	**0.093**	**0.111**
Std. Dev.	**0.000**	**0.000**	**0.001**	**0.001**	**0.001**	**0.005**	**0.002**	**0.001**	**0.002**	**0.005**	**0.001**	**0.001**	**0.001**

Total Organic Carbon mg/L

	A	D	G	H	I	J	L
	6.000	9.000	4.900	5.400	4.800	6.000	5.300
	5.600	8.900	5.010	5.600	5.010	6.000	5.400
	6.100	9.000	4.920	5.600	4.960	6.000	5.800
	5.700	8.200	4.960	5.600	5.010	6.000	5.400
Average:	**5.850**	**8.775**	**4.948**	**5.550**	**4.945**	**6.000**	**5.475**
Std. Dev.	**0.238**	**0.386**	**0.049**	**0.100**	**0.099**	**0.000**	**0.222**

Notes Lab D's high values may be due to positive interference due to SO_3 detection caused by H_2SO_4 preservation. May require an SO_3 scrubber.

Dissolved Organic Carbon mg/L

	A*	D	G	H	I	J	L
	4.900	7.000	4.420	4.600	4.590	5.000	5.100
	5.300	7.100	4.660	4.800	4.570	5.000	4.800
	5.300	7.300	4.580	4.700	4.680	5.000	5.000
	4.800	7.300	4.340	4.700	4.650	5.000	5.000
Average:	**5.075**	**7.175**	**4.500**	**4.700**	**4.623**	**5.000**	**4.975**
Std. Dev.	**0.263**	**0.150**	**0.146**	**0.082**	**0.051**	**0.000**	**0.126**

Notes Lab D's high values may be due to positive interference due to SO_3 detection caused by H_2SO_4 preservation. May require an SO_3 scrubber.

Chlorophyll a µg/L

	A*	B	C*	D	E	F	G	H	I	J	K	L*	M	O
	1.600	1.070	1.300	1.100	1.330	U	1.840	1.580	0.950	U	1.210	1.200	U	3.000
	1.700	1.070	1.300	1.100	1.570	U	1.480	1.570	0.920	U	1.150	1.200	U	2.000
	1.800	1.600	0.800	1.200	1.270	U	1.860	1.440	0.760	U	1.230	1.100	U	2.000
	1.500	1.070	2.000	1.200	1.280	U	1.790	1.160	0.290	U	1.160	1.200	U	2.000
Average:	**1.650**	**1.203**	**1.350**	**1.150**	**1.363**		**1.743**	**1.438**	**0.730**		**1.188**	**1.175**		**2.250**
Std. Dev.	**0.129**	**0.265**	**0.493**	**0.058**	**0.141**		**0.177**	**0.196**	**0.305**		**0.039**	**0.050**		**0.500**

Notes Lab C reported one value below the MDL.

Biochemical Oxygen Demand mg/L

	A	B	C	D	F	G	J	M	O
	2.700	2.300	2.300	U	2.100	2.420	U	2.600	3.000
	3.300	2.700	2.400	U	U	2.330	U	2.600	2.000
	2.800	2.500	2.400	U	2.200	2.390	3.000	2.700	2.000
	2.800	2.300	2.400	U	2.500	2.500	U	2.600	3.000
Average:	**2.900**	**2.450**	**2.375**		**2.267**	**2.410**	**3.000**	**2.625**	**2.500**
Std. Dev.	**0.271**	**0.191**	**0.050**		**0.208**	**0.071**		**0.050**	**0.577**

Carbonaceous Biochemical Oxygen Demand mg/L									
	A*	**B**	**C**	**D**	**F**	**G***	**J**	**M**	**O**
	1.400	U	2.300	U	3.400	1.300	U	1.500	U
	2.400	U	2.100	U	2.300	1.150	U	1.800	2.000
	2.900	U	2.000	U	2.900	1.360	U	1.700	2.000
	2.000	U	1.900	U	2.300	1.630	U	1.800	2.000
Average:	**2.175**		**2.075**		**2.725**	**1.360**		**1.700**	**2.000**
Std. Dev.	**0.634**		**0.171**		**0.532**	**0.200**		**0.141**	**0.000**

Dauphin Island

	TKN		NH3		NOx		NO2		DNOx		DNO2		TP		OP		TOC		DOC		ChlA		BOD		CBOD	
	Stat.	S.Er.	Stat.	S.Er.	Stat.	S.Er.	Stat.	S.Er.	Stat.	S.Er.	Stat.	S.Er.	Stat.	S.Er.	Stat.	S.Er.	Stat.	S.Er.	Stat.	S.Er.	Stat.	S.Er.	Stat.	S.Er.	Stat.	S.Er.
Descriptives																										
N (Total)	33		42		30		31		35		31		42		37		21		21		42		27		27	
N (> PQL)	33		29		30		18		35		9		38		28		15		15		33		3		3	
N Analyzed	33		29		30		22		35		20		41		33		21		21		39		8		6	
Mean	0.863	0.299	0.045	0.003	0.181	0.007	0.018	0.002	0.180	0.003	0.005	0.001	0.066	0.006	0.011	0.001	3.896	0.116	3.708	0.123	3.279	0.152	0.754	0.050	0.775	0.095
95% CI (LB)	0.254		0.039		0.168		0.015		0.175		0.003		0.054		0.010		3.653		3.451		2.973		0.637		0.531	
95% CI (UB)	1.471		0.051		0.195		0.022		0.186		0.007		0.077		0.013		4.139		3.964		3.586		0.871		1.019	
5% Trimmed	0.536		0.045		0.178		0.018		0.180		0.005		0.060		0.011		3.856		3.685		3.300		0.738		0.778	
Median	0.380		0.044		0.170		0.015		0.179		0.003		0.057		0.009		3.730		3.550		3.400		0.700		0.780	
Variance	2.944		0.000		0.001		0.000		0.000		0.000		0.001		0.000		0.285		0.318		0.895		0.020		0.054	
Std. Dev.	1.716		0.016		0.036		0.008		0.017		0.003		0.036		0.004		0.534		0.564		0.946		0.140		0.232	
Min	0.173		0.014		0.140		0.006		0.149		0.002		0.037		0.004		3.300		2.700		1.110		0.690		0.400	
Max	7.700		0.080		0.300		0.037		0.227		0.013		0.192		0.020		5.200		5.100		5.000		1.100		1.100	
Range	7.527		0.066		0.160		0.031		0.078		0.011		0.155		0.016		1.900		2.400		3.890		0.410		0.700	
IQR	0.155		0.017		0.021		0.009		0.008		0.004		0.020		0.004		0.400		0.625		1.200		0.020		0.330	
Skew	3.625	0.409	0.238	0.434	1.729	0.427	0.987	0.491	1.301	0.398	1.373	0.524	2.711	0.369	0.855	0.409	1.746	0.501	1.143	0.501	-0.664	0.378	2.797	0.752	-0.408	0.845
Kurtosis	12.410	0.798	0.511	0.845	3.040	0.833	0.462	0.953	2.949	0.778	1.089	1.014	7.159	0.724	0.432	0.798	2.076	0.972	1.374	0.972	0.269	0.741	7.865	1.481	1.249	1.741
Huber's ψ	0.406		0.045		0.171		0.016		0.178		0.004		0.058		0.010		3.732		3.562		3.394		0.703		0.787	
Kaplan-Meier (KM) Method																										
Minimum Non-Detect	N/A		0.02		N/A		0.006		N/A		0.001		0.02		0.02		N/A		N/A		1		0.2		0.5	
Maximum Non-Detect	N/A		0.1		N/A		0.02		N/A		0.02		0.02		0.04		N/A		N/A		3		3		3	
Mean	N/A	N/A	0.039	0.003	N/A	N/A	0.017	0.002	N/A	N/A	0.004	0.001	0.065	0.005	0.011	0.001	N/A	N/A	N/A	N/A	3.147	0.162	0.747	0.045	0.650	0.090
SD	N/A		0.018		N/A		0.007		N/A		0.003		0.036		0.004		N/A		N/A		1.032		0.125		0.247	
95% KM UCL	2.164		0.044		0.192		0.020		0.185		0.005		0.089		0.014		4.097		3.920		3.420		0.823		0.804	
Normality																										
Test of Skew	**0.000**		0.563		**0.001**		0.048		**0.003**		**0.013**		**0.000**		**0.040**		**0.002**		**0.028**		0.079		**0.000**		N/A	
Test of Kurtosis	**0.000**		0.420		**0.016**		0.480		**0.014**		0.245		**0.000**		0.453		0.074		0.166		0.556		**0.002**		0.429	
Jarque & Bera	**0.000**		0.858		**0.000**		0.212		**0.000**		0.072		**0.000**		0.157		**0.005**		0.106		0.265		**0.007**		N/A	
Outliers																										
F Crit. (Mahalanobis D2)	8.710		8.370		8.460		7.610		8.870		7.190		9.280		8.710		7.470		7.470		9.150		4.520		3.560	
Mahalanobis D2 Max	15.880		4.760		10.720		6.020		7.780		6.080		12.260		4.570		5.970		6.090		5.260		6.090		2.600	
+ 2 Std. Dev.	4.294		0.077		0.254		0.034		0.214		0.012		0.138		0.019		4.963		4.836		5.172		1.034		1.240	
- 2 Std. Dev.	-2.569		0.013		0.109		0.003		0.147		-0.002		-0.006		0.003		2.828		2.579		1.387		0.473		0.310	
# Outside 2 Std. Dev.	2		2		1		1		3		1		3		3		3		1		3		1		0.000	
+ 2 F-Pseudosigma	0.611		0.069		0.202		0.028		0.191		0.009		0.086		0.015		4.323		4.477		5.179		0.730		1.273	
- 2 F-Pseudosigma	0.149		0.019		0.138		0.002		0.167		-0.003		0.028		0.003		3.137		2.623		1.621		0.670		0.287	
# Outside 2 F-Pseudosigma	3		5		6		4		9		4		4		5		3		3		4		1		0	
# from Boxplots	3		4		5		1		6		2		4		3		3		1		1		1		0	
Homoscedasticity (between laboratories)																										
Levene's	**0.000**		**0.000**		**0.000**		**0.011**		**0.000**		**0.006**		**0.000**		**0.000**		**0.004**		**0.000**		**0.000**		**0.000**		0.594	

Dauphin Island

	TKN		NH3		NOx		NO2		DNOx		DNO2		TP		OP		TOC		DOC		ChlA		BOD		CBOD	
	Stat.	S.Er.	Stat.	S.Er.	Stat.	S.Er.	Stat.	S.Er.	Stat.	S.Er.	Stat.	S.Er.	Stat.	S.Er.	Stat.	S.Er.	Stat.	S.Er.	Stat.	S.Er.	Stat.	S.Er.	Stat.	S.Er.	Stat.	S.Er.
Detection Limits																										
< MDL	0		13		0		4		0		8		1		4		0		0		3		19		21	
% < MDL	0%		31%		0%		13%		0%		26%		2%		11%		0%		0%		7%		70%		78%	
< PQL	0		0		0		9		0		10		3		5		6		6		6		5		3	
% < PQL	0%		31%		0%		42%		0%		58%		10%		24%		29%		29%		21%		89%		89%	
Precision																										
%F-Pseudosigma	30.33%		28.64%		9.27%		42.65%		3.31%		96.37%		25.36%		31.75%		7.95%		13.05%		26.16%		2.12%		31.60%	
%RSD	198.93%		35.86%		20.01%		42.05%		9.29%		126.72%		54.95%		37.82%		13.70%		15.21%		28.86%		18.57%		29.94%	

Bold values are significant p-values at the 0.05 level.

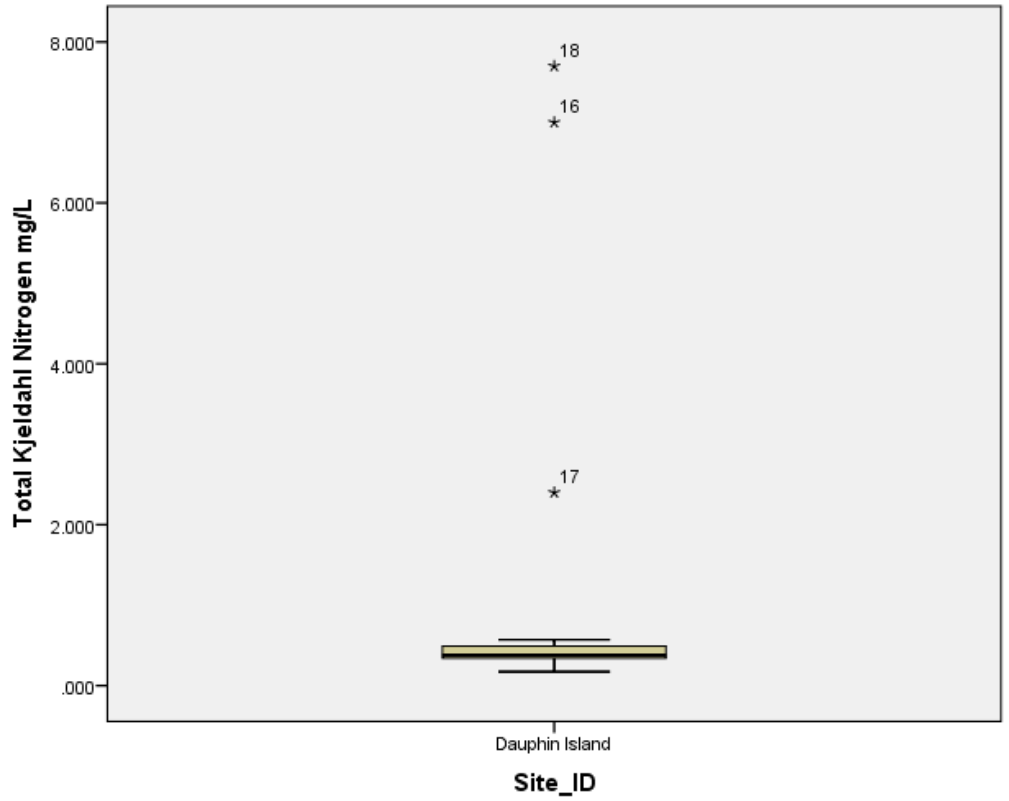
Three-Mile Creek

	TKN		NH3		NOx		NO2		DNOx		DNO2		TP		OP		TOC		DOC		ChlA		BOD		CBOD	
	Stat.	S.Er.	Stat.	S.Er.	Stat.	S.Er.	Stat.	S.Er.	Stat.	S.Er.	Stat.	S.Er.	Stat.	S.Er.	Stat.	S.Er.	Stat.	S.Er.	Stat.	S.Er.	Stat.	S.Er.	Stat.	S.Er.	Stat.	S.Er.
Descriptives																										
N (Total)	44		56		40		40		47		42		56		51		28		28		56		36		36	
N (> PQL)	44		56		40		39		47		42		56		51		28		26		44		28		18	
N Analyzed	44		56		40		39		47		42		56		51		28		28		44		28		24	
Mean	1.912	0.399	0.655	0.015	1.860	0.030	0.044	0.001	1.896	0.019	0.038	0.001	0.192	0.003	0.101	0.002	5.935	0.237	5.150	0.165	1.385	0.067	2.530	0.059	2.006	0.109
95% CI (LB)	1.108		0.625		1.799		0.042		1.858		0.037		0.186		0.098		5.449		4.810		1.250		2.409		1.780	
95% CI (UB)	2.716		0.685		1.920		0.046		1.933		0.039		0.199		0.105		6.421		5.489		1.521		2.651		2.232	
5% Trimmed	1.464		0.659		1.837		0.044		1.886		0.038		0.192		0.101		5.826		5.074		1.372		2.521		1.979	
Median	1.335		0.663		1.825		0.041		1.879		0.037		0.195		0.101		5.600		4.850		1.275		2.500		2.000	
Variance	6.989		0.013		0.036		0.000		0.016		0.000		0.001		0.000		1.570		0.765		0.198		0.098		0.286	
Std. Dev.	2.644		0.113		0.189		0.006		0.128		0.004		0.023		0.011		1.253		0.875		0.445		0.313		0.534	
Min	1.080		0.300		1.620		0.037		1.740		0.034		0.150		0.080		4.800		4.340		0.290		2.000		1.150	
Max	18.300		0.937		2.520		0.056		2.280		0.051		0.278		0.130		9.000		7.300		3.000		3.300		3.400	
Range	17.220		0.637		0.900		0.019		0.540		0.017		0.128		0.050		4.200		2.960		2.710		1.300		2.250	
IQR	0.124		0.075		0.113		0.010		0.096		0.003		0.025		0.010		0.990		0.422		0.490		0.390		0.650	
Skew	5.848	0.357	-0.759	0.319	2.332	0.374	0.732	0.378	1.428	0.347	2.240	0.361	0.618	0.319	0.689	0.333	1.755	0.441	1.865	0.441	0.930	0.357	0.462	0.441	0.801	0.472
Kurtosis	36.320	0.702	3.959	0.628	5.909	0.733	-0.871	0.741	1.546	0.681	4.550	0.709	2.574	0.628	1.358	0.656	2.049	0.858	2.194	0.858	3.184	0.702	0.145	0.858	0.923	0.918
Huber's ψ	1.338		0.660		1.823		0.042		1.871		0.037		0.195		0.101		5.590		4.859		1.331		2.507		1.965	
Kaplan-Meier (KM) Method																										
Minimum Non-Detect	N/A		N/A		N/A		0.006		N/A		N/A		N/A		N/A		N/A		N/A		1		2		2	
Maximum Non-Detect	N/A		N/A		N/A		0.006		N/A		N/A		N/A		N/A		N/A		N/A		3		3		3	
Mean	N/A	N/A	N/A	N/A	N/A	N/A	0.044	0.001	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	1.327	0.067	2.443	0.059	1.873	0.095
SD	N/A		N/A		N/A		0.006		N/A		N/A		N/A		N/A		N/A		N/A		0.454		0.336		0.505	
95% KM UCL	2.582		0.680		1.910		0.048		1.927		0.039		0.198		0.104		6.338		5.431		1.428		2.541		2.035	
Normality																										
Test of Skew	**0.000**		**0.021**		**0.000**		0.056		**0.000**		**0.000**		0.055		**0.042**		**0.001**		**0.000**		**0.013**		0.276		0.089	
Test of Kurtosis	**0.000**		**0.001**		**0.000**		0.111		0.063		**0.001**		**0.009**		0.079		0.057		**0.047**		**0.007**		0.682		0.265	
Jarque & Bera	**0.000**		**0.000**		**0.000**		0.102		**0.000**		**0.000**		**0.001**		**0.040**		**0.000**		**0.000**		**0.000**		0.638		0.286	
Outliers																										
F Crit. (Mahalanobis D2)	9.460		10.070		9.220		9.150		9.630		9.400		10.070		9.840		8.270		8.270		9.460		8.270		7.850	
Mahalanobis D2 Max	38.420		9.910		12.160		4.410		9.060		10.360		13.860		6.910		5.980		6.040		13.170		6.060		6.810	
+ 2 Std. Dev.	7.200		0.881		2.238		0.055		2.151		0.046		0.238		0.123		8.441		6.899		2.275		3.156		3.075	
- 2 Std. Dev.	-3.376		0.430		1.481		0.033		1.641		0.030		0.147		0.080		3.428		3.400		0.495		1.904		0.937	
# Outside 2 Std. Dev.	1		7		3		1		4		4		2		3		3		4		3		1		1	
+ 2 F-Pseudosigma	1.519		0.773		1.993		0.056		2.021		0.041		0.232		0.116		7.068		5.476		1.998		3.082		2.967	
- 2 F-Pseudosigma	1.151		0.552		1.657		0.026		1.737		0.033		0.157		0.087		4.132		4.224		0.552		1.918		1.033	
# Outside 2 F-Pseudosigma	5		8		7		0		7		4		5		8		4		4		6		1		1	
# from Boxplots	5		8		4		0		7		4		2		3		4		4		2		1		1	

Three-Mile Creek

	TKN		NH3		NOx		NO2		DNOx		DNO2		TP		OP		TOC		DOC		ChlA		BOD		CBOD	
	Stat.	S.Er.	Stat.	S.Er.	Stat.	S.Er.	Stat.	S.Er.	Stat.	S.Er.	Stat.	S.Er.	Stat.	S.Er.	Stat.	S.Er.	Stat.	S.Er.	Stat.	S.Er.	Stat.	S.Er.	Stat.	S.Er.	Stat.	S.Er.
Homoscedasticity (between laboratories)																										
Levene's	**0.000**		**0.000**		**0.000**		**0.001**		**0.001**		**0.000**		**0.000**		**0.000**		**0.004**		**0.000**		**0.031**		**0.000**		**0.004**	
Detection Limits																										
< MDL	0		0		0		1		0		0		0		0		0		0		4		8		13	
% < MDL	0%		0%		0%		3%		0%		0%		0%		0%		0%		0%		7%		22%		36%	
< PQL	0		0		0		0		0		0		0		0		0		2		8		0		5	
% < PQL	0%		0%		0%		3%		0%		0%		0%		0%		0%		7%		21%		22%		50%	
Precision																										
%F-Pseudosigma	6.90%		8.36%		4.60%		18.08%		3.79%		6.01%		9.62%		7.31%		13.10%		6.46%		28.34%		11.64%		26.64%	
%RSD	138.27%		17.22%		10.18%		12.72%		6.73%		10.74%		11.94%		10.70%		21.12%		16.99%		32.13%		12.36%		24.18%	

Bold values are significant p-values at the 0.05 level.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Dauphin Island
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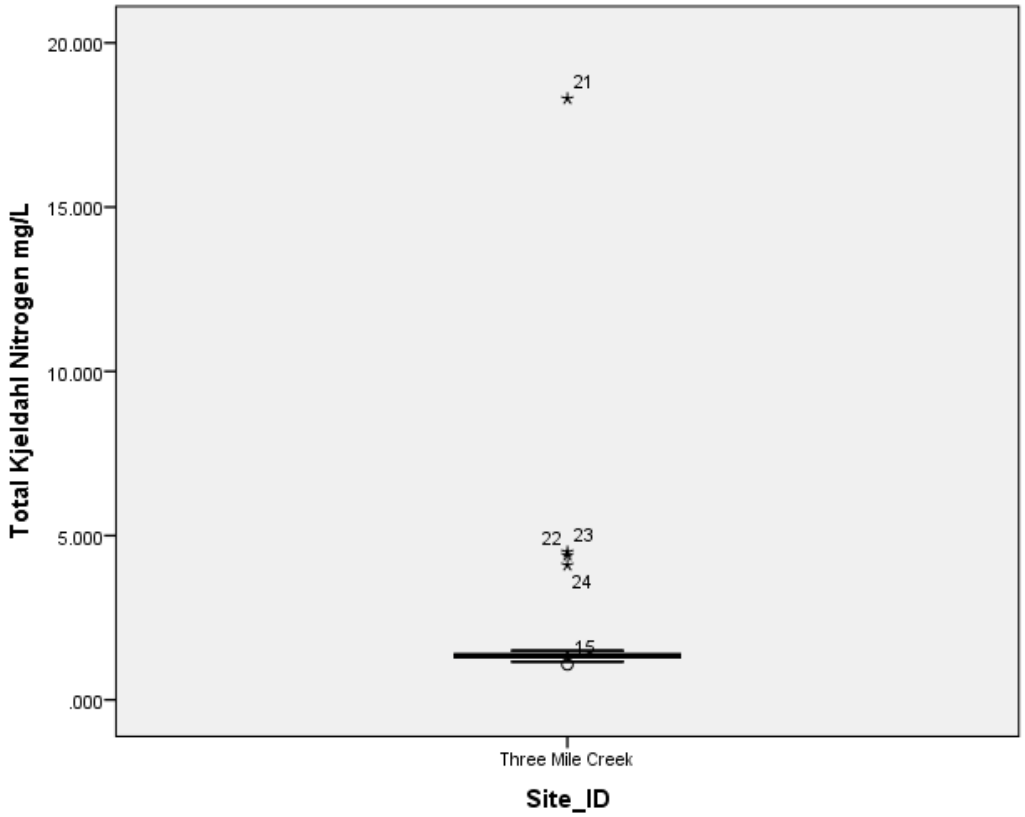
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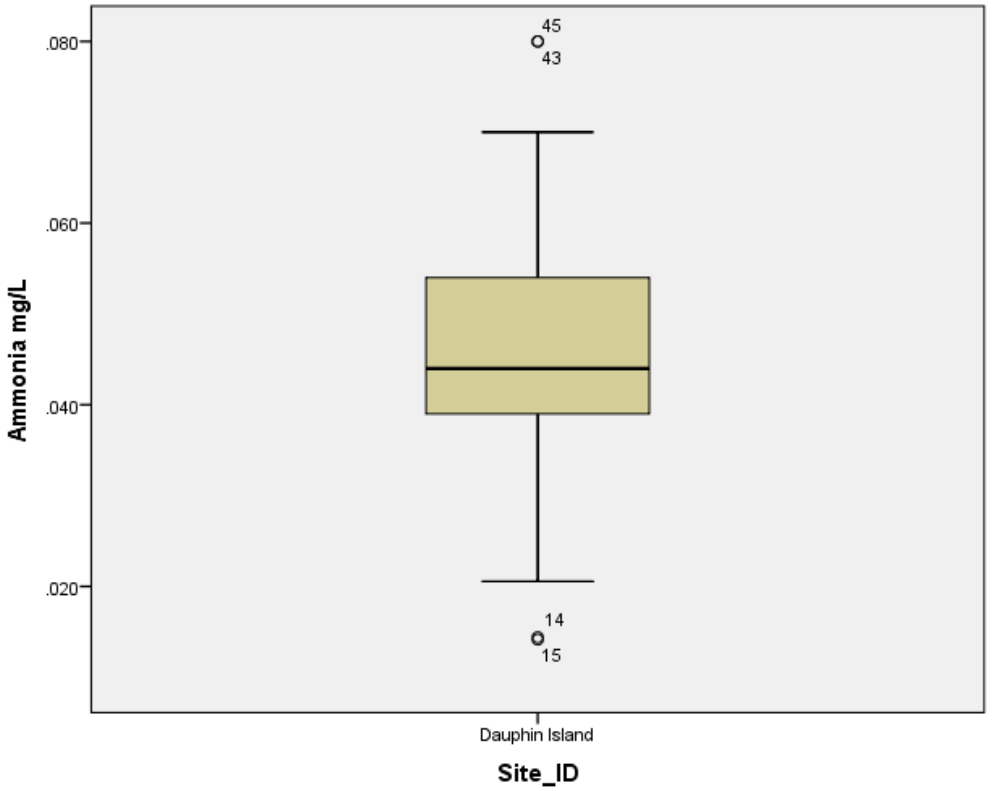
Three Mile Creek
Site_ID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Dauphin Island
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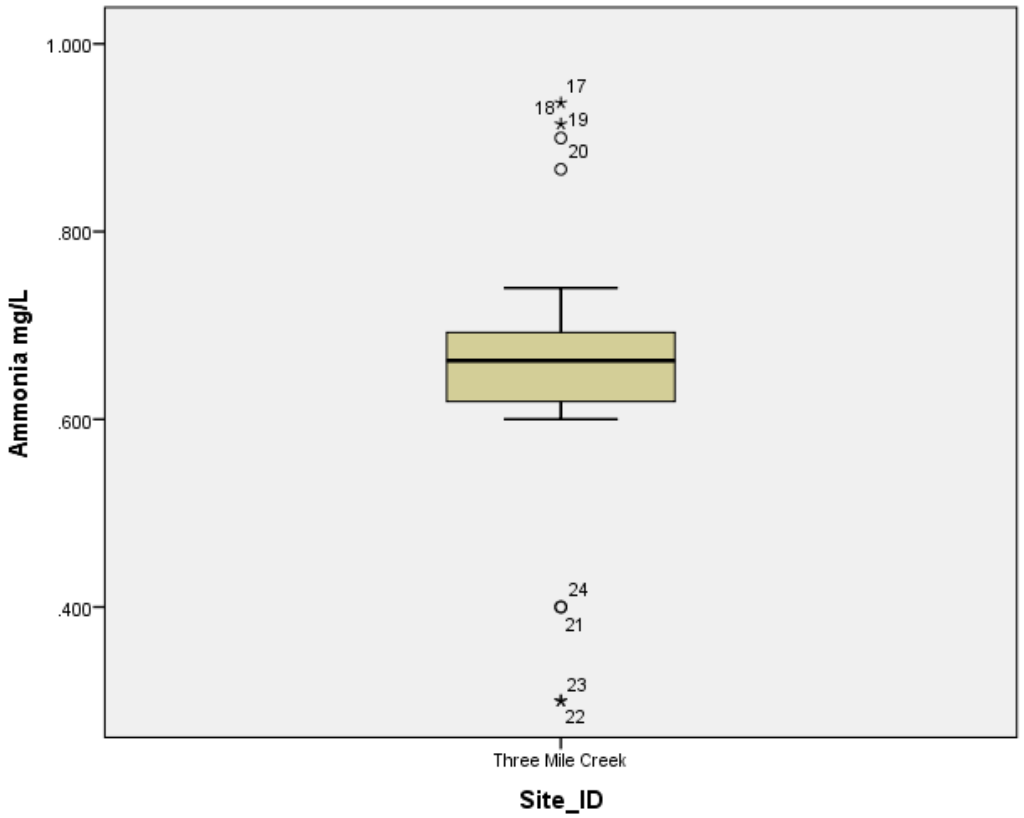
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Ammonia mg/L
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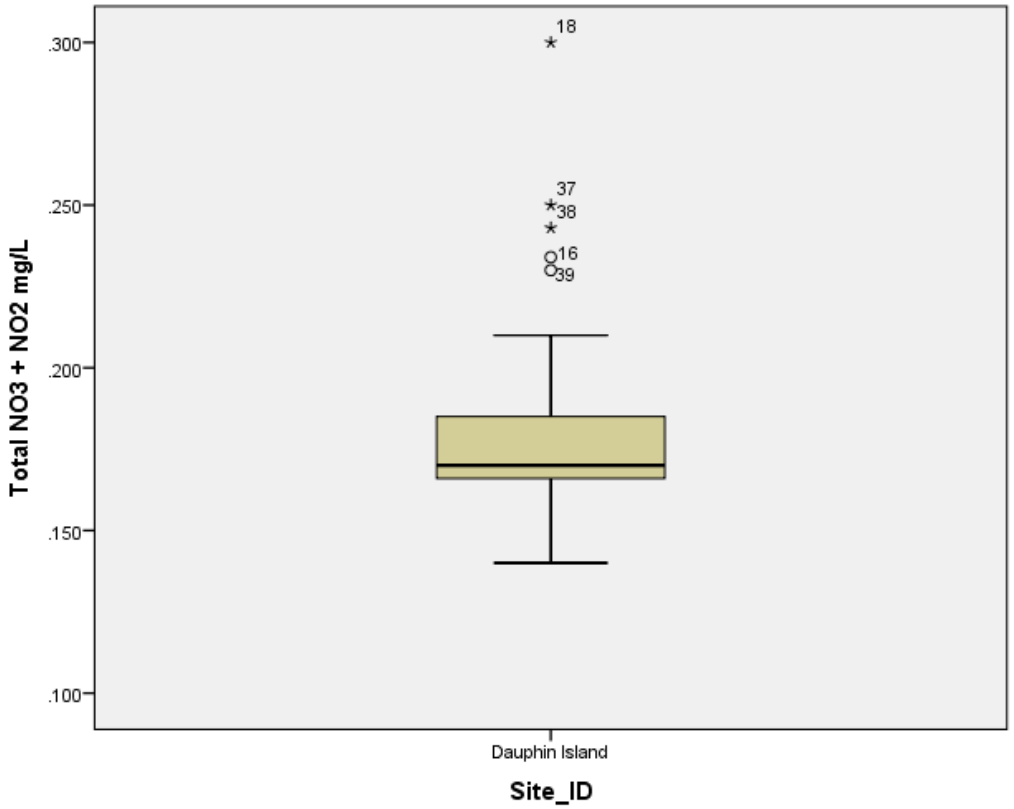
Three Mile Creek
Site_ID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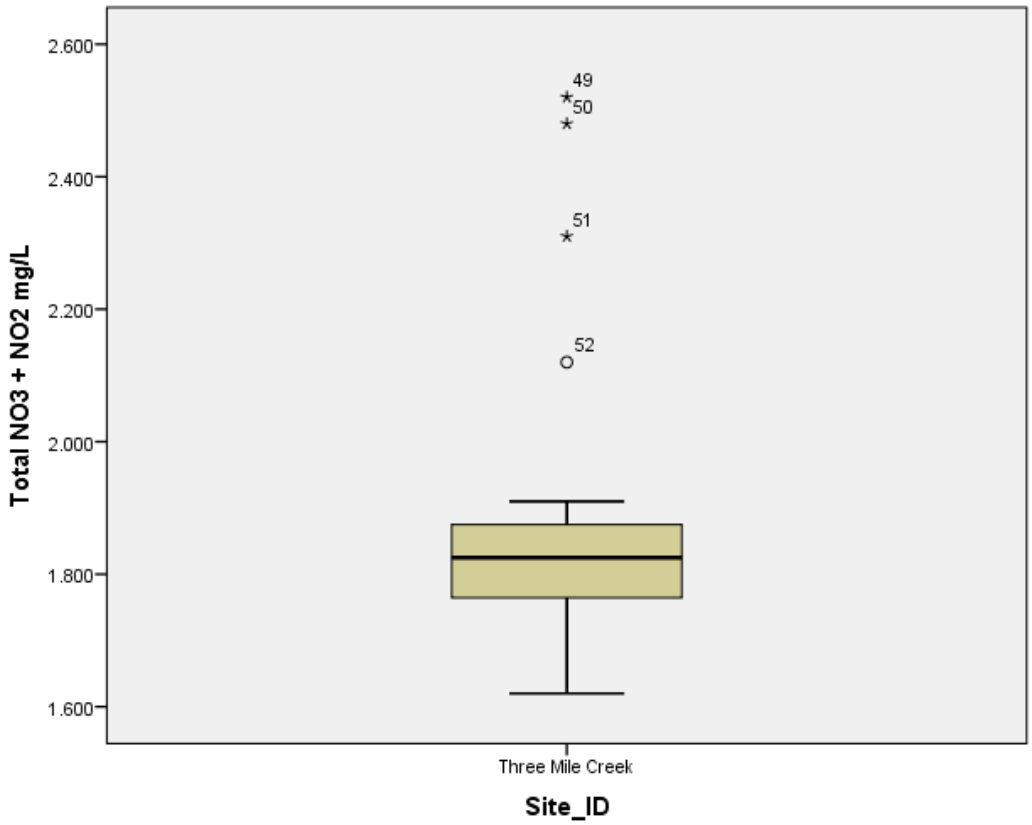
Dauphin Island
Site_ID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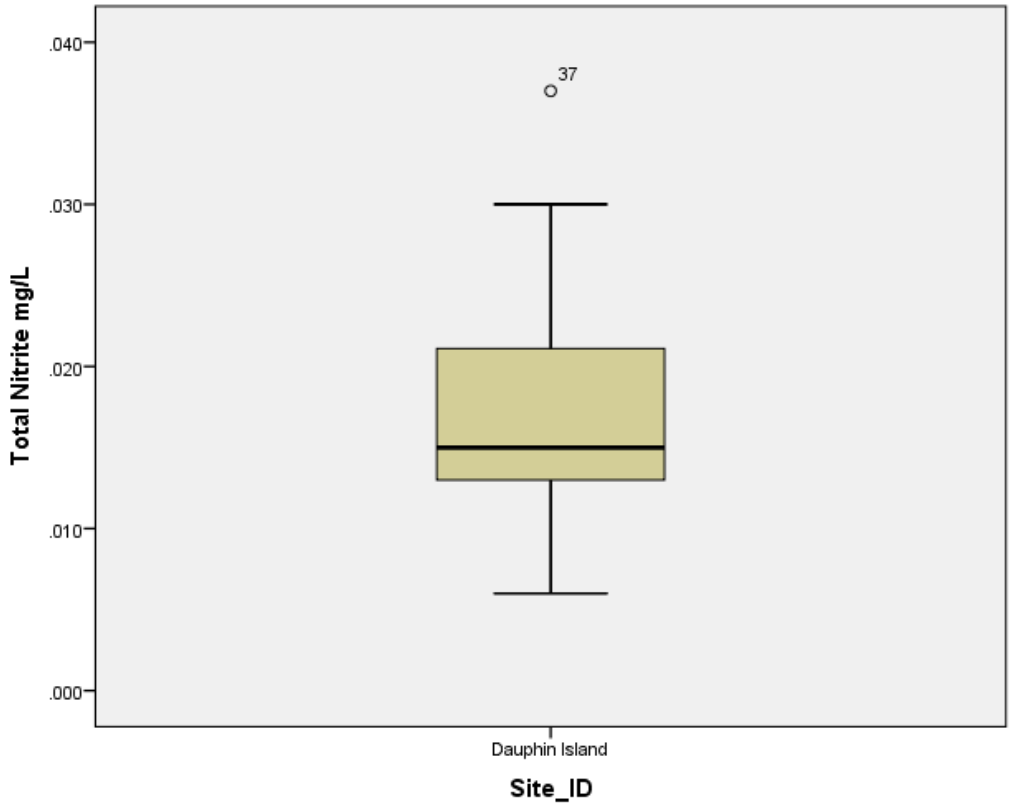
Three Mile Creek
Site_ID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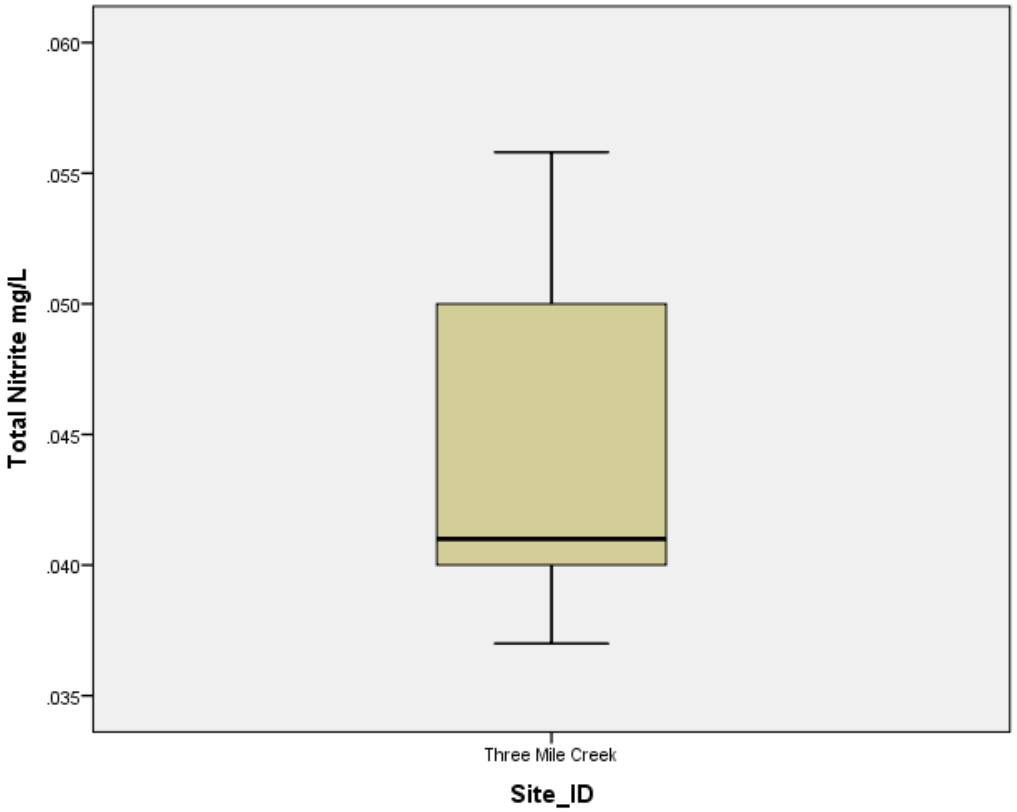
Total Nitrite mg/L
Dauphin Island
Site_ID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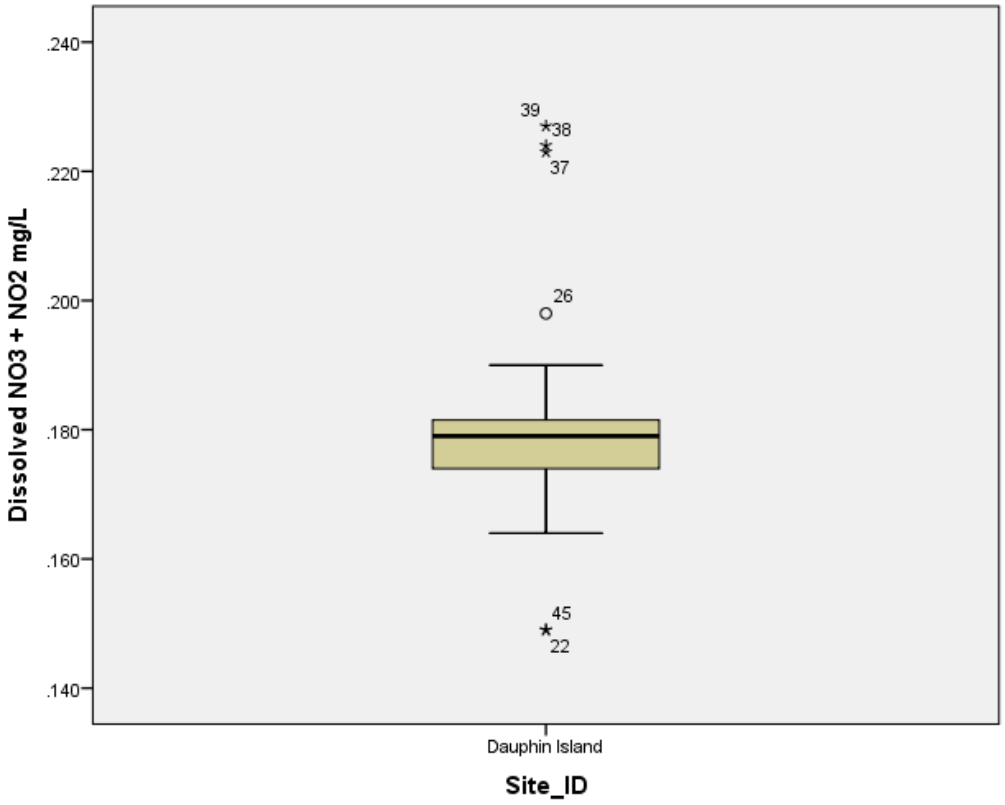
Total Nitrite mg/L
Three Mile Creek
Site_ID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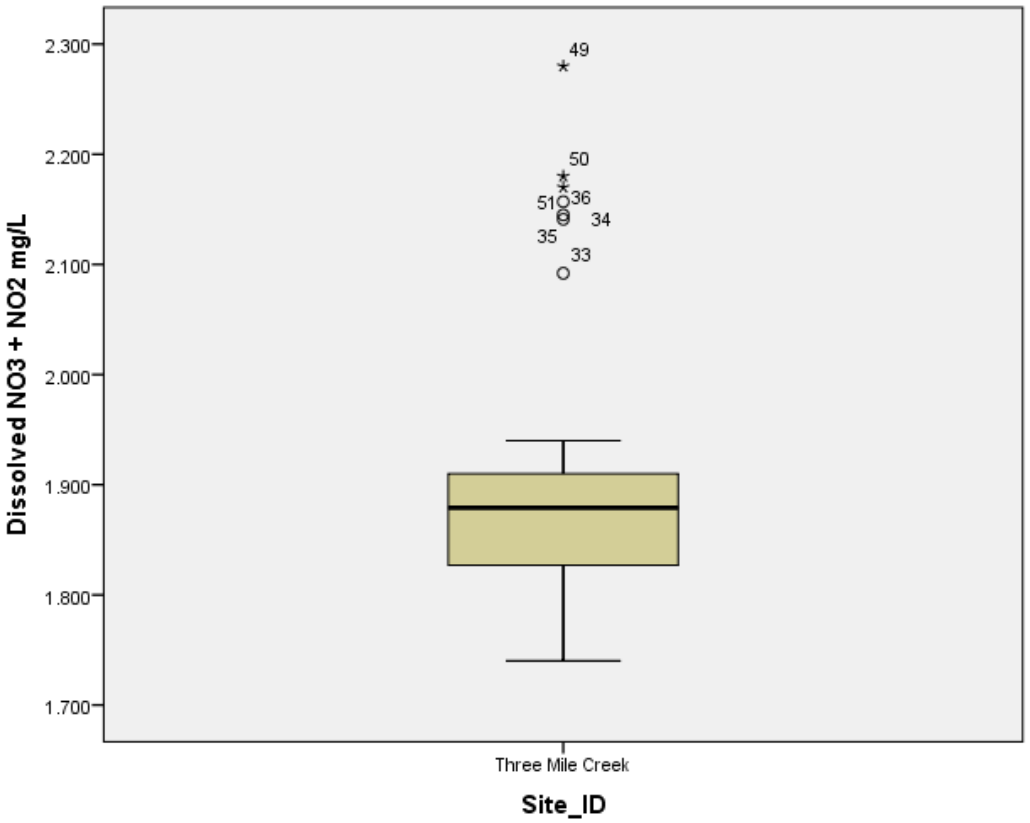
Dauphin Island
Site_ID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2.000
1.900
1.800
1.700
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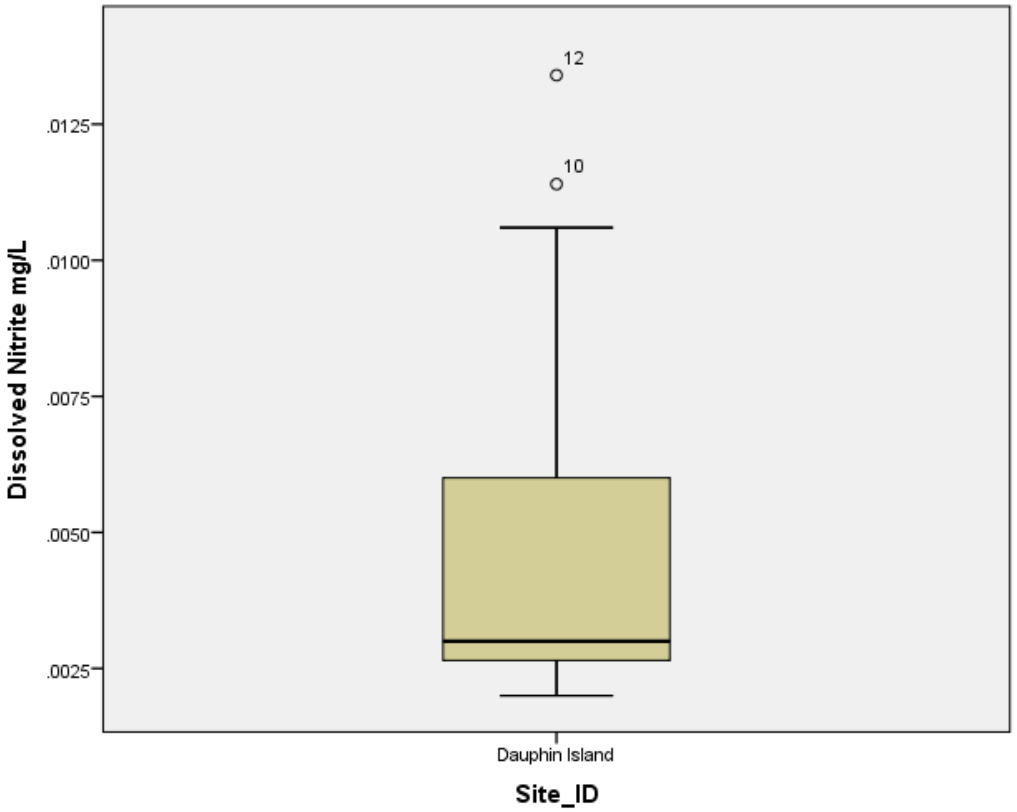
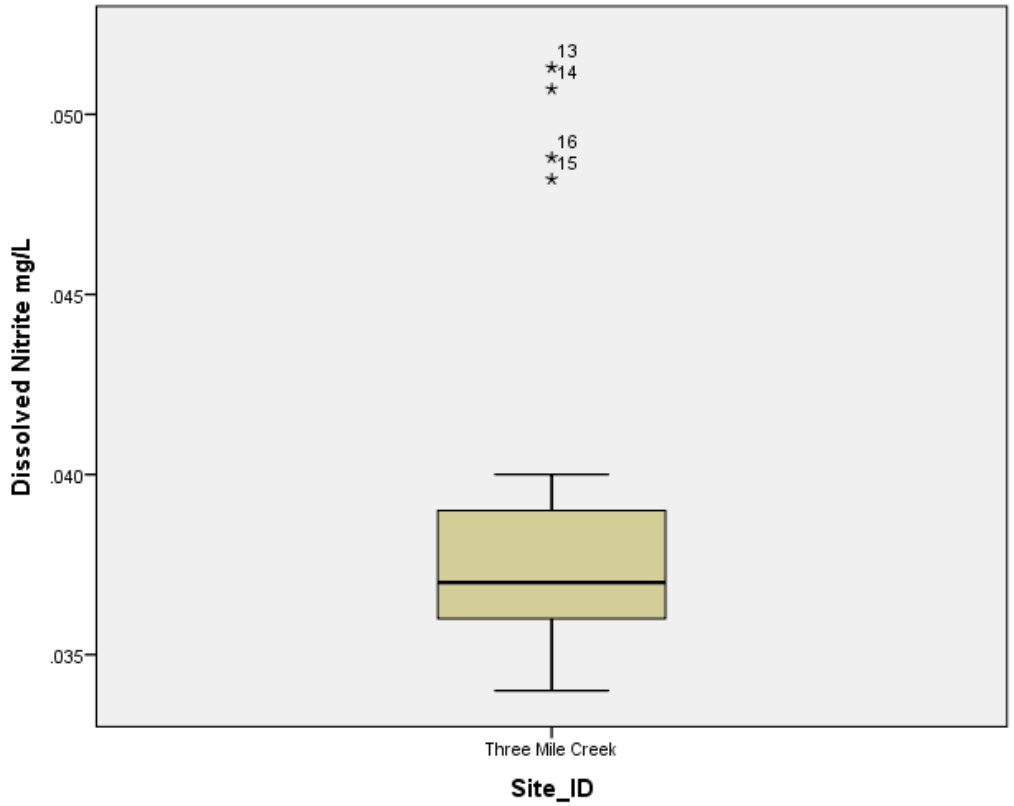
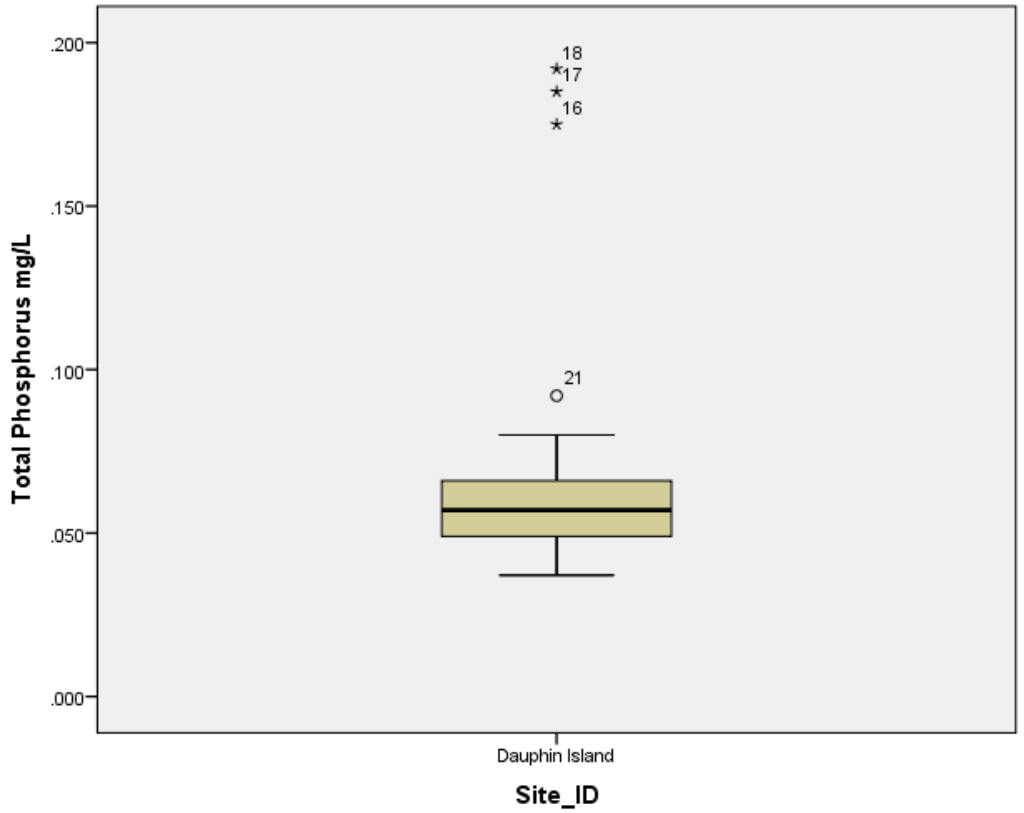
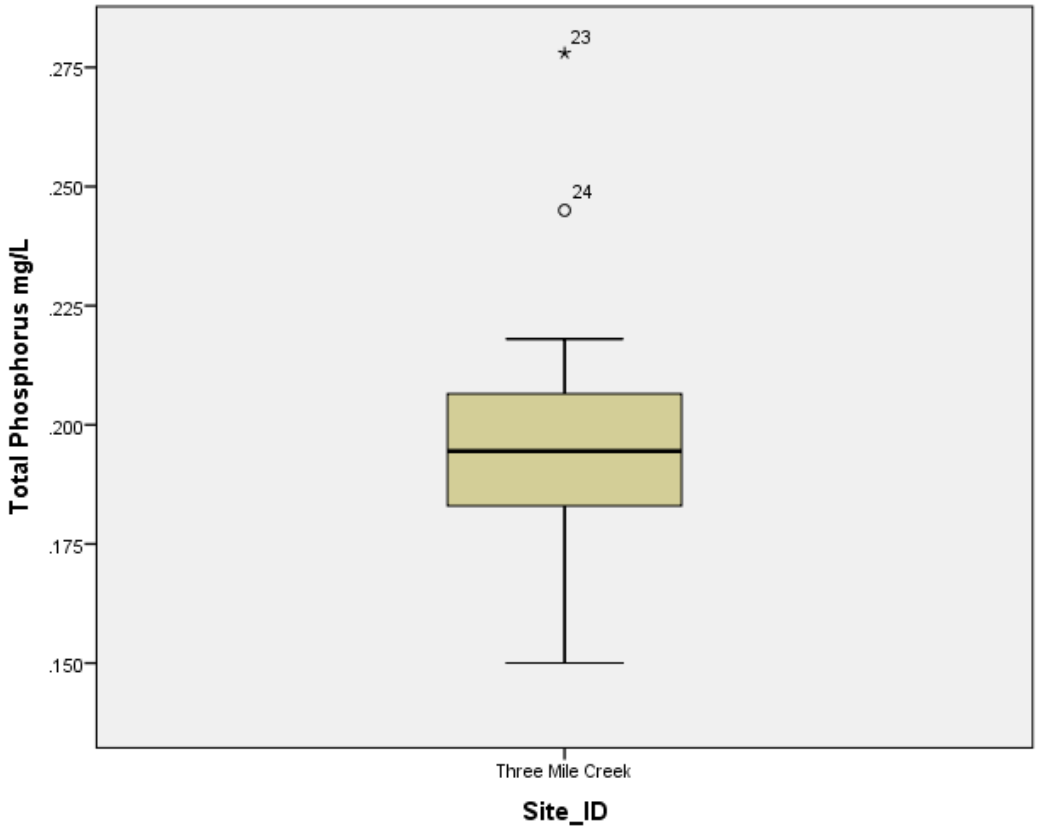
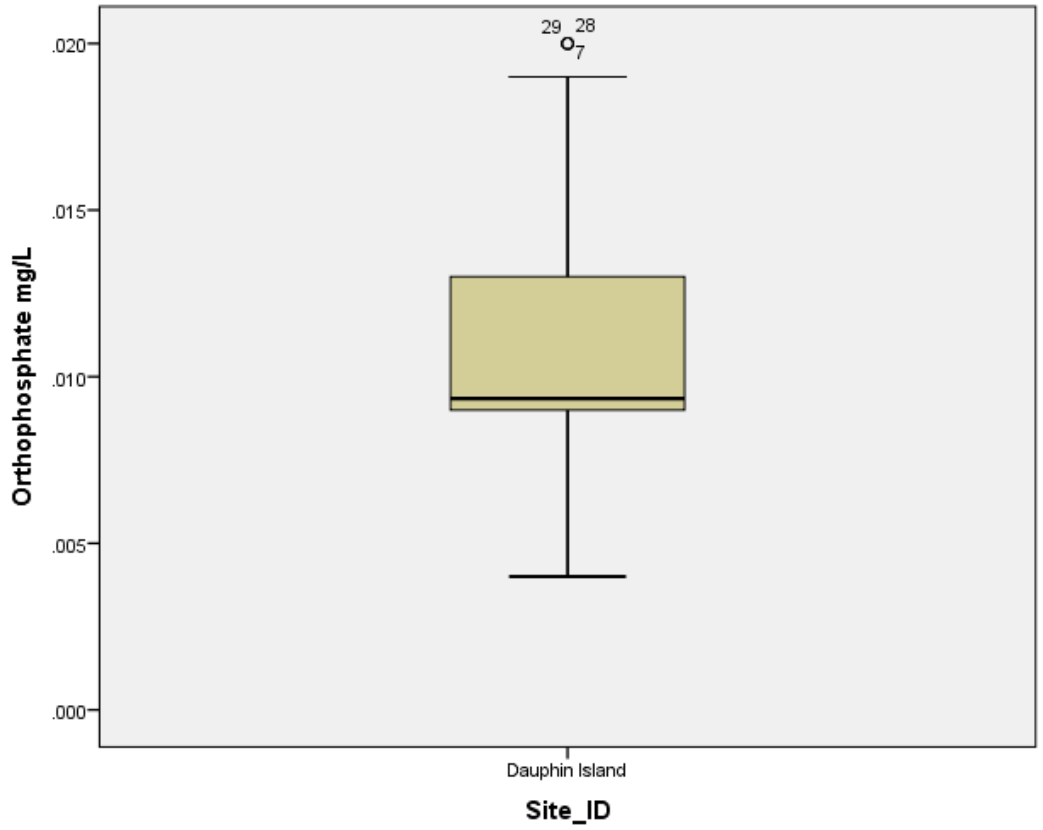
35
33
Three Mile Creek
Site_ID

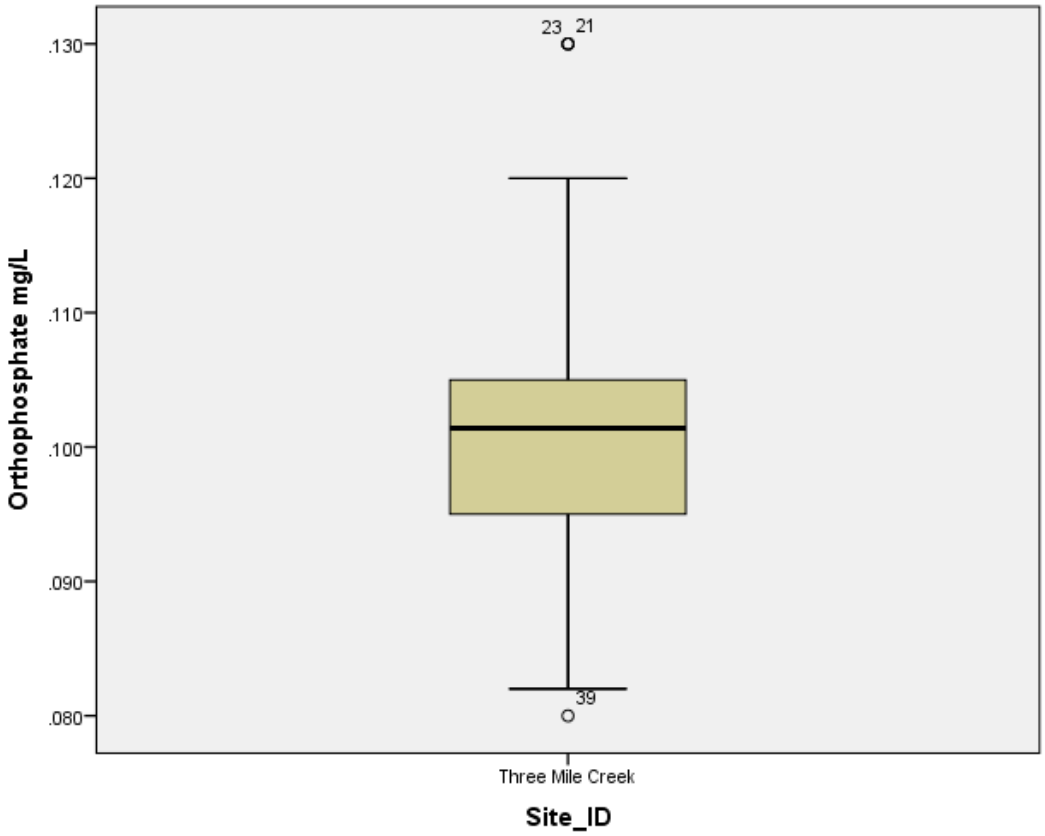

12
10
.0125
.0100
.0075
.0050
.0025
Dissolved Nitrite mg/L
Dauphin Island
Site_ID

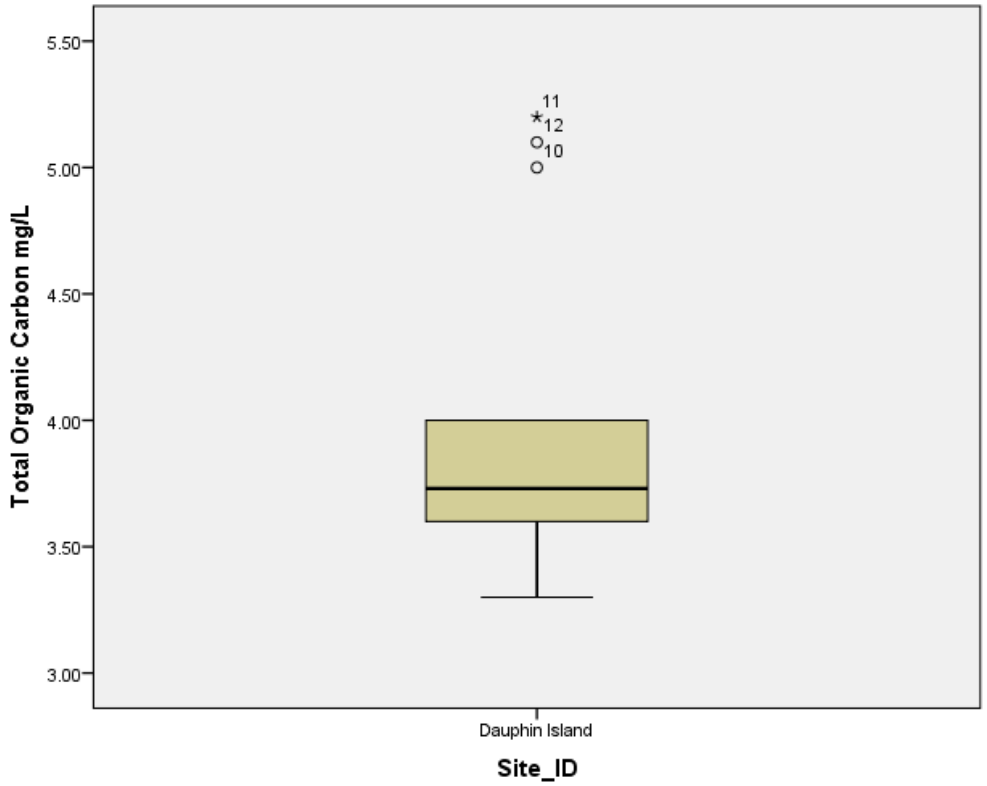

13
14
16
15
.050
.045
.040
.035
Dissolved Nitrite mg/L
Three Mile Creek
Site_ID

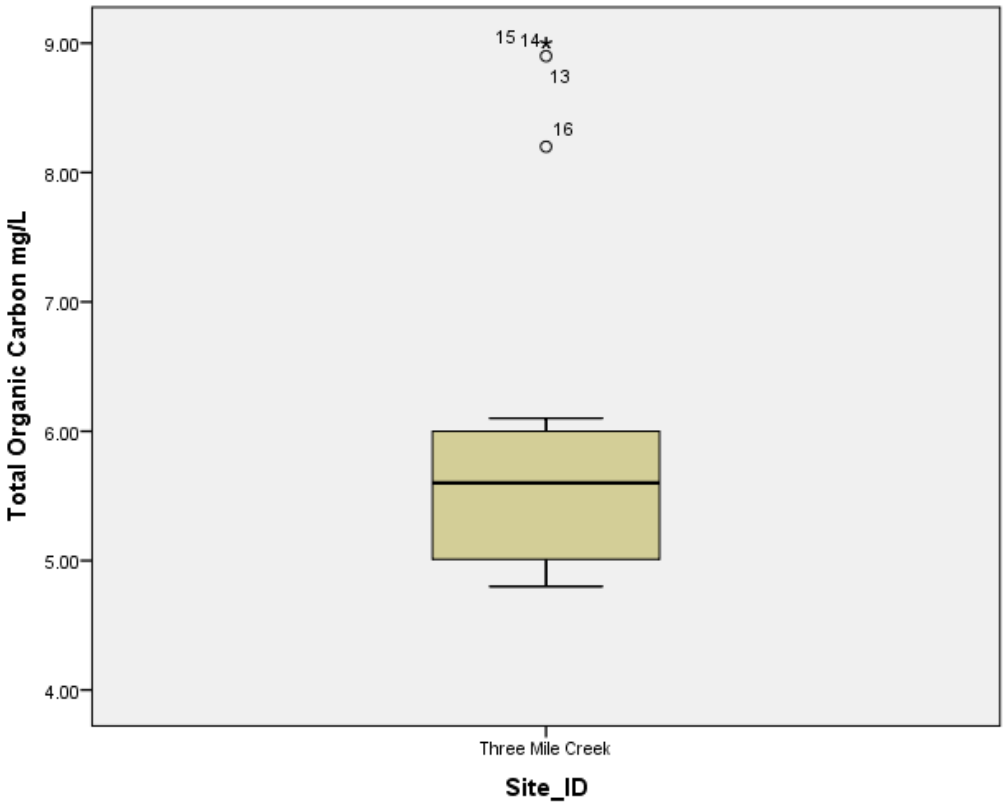

Total Phosphorus mg/L
.200
.150
.100
.050
.000
18
17
16
21
Dauphin Island
Site_ID

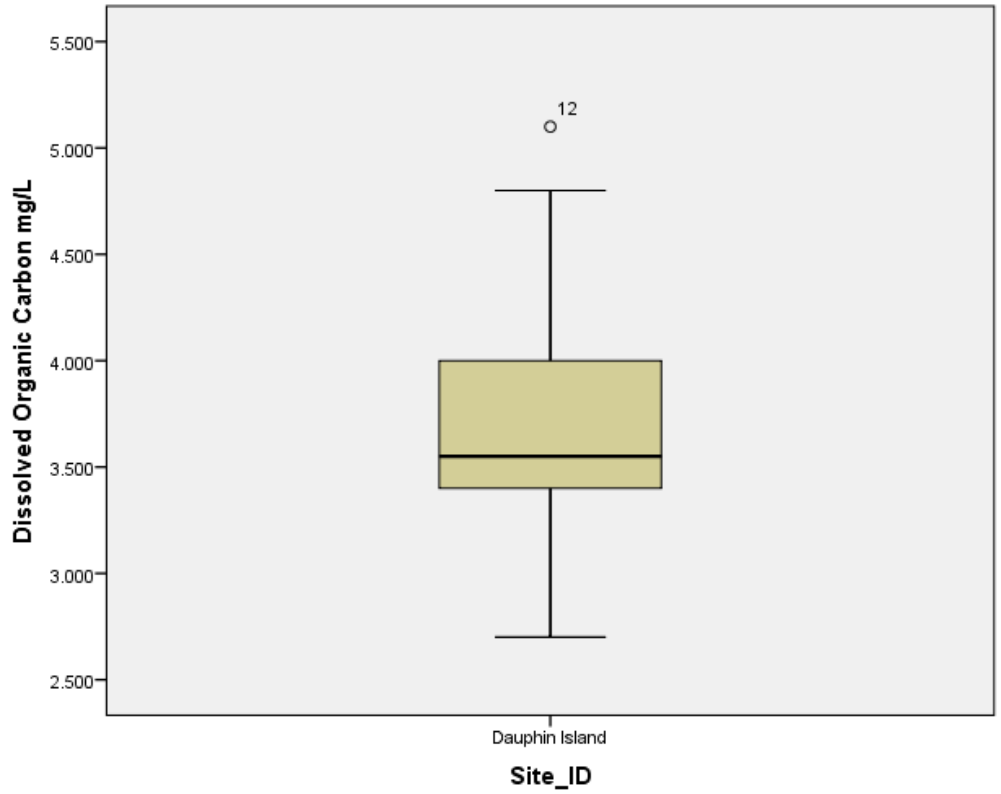

Total Phosphorus mg/L
.275
.250
.225
.200
.175
.150
23
24
Three Mile Creek
Site_ID

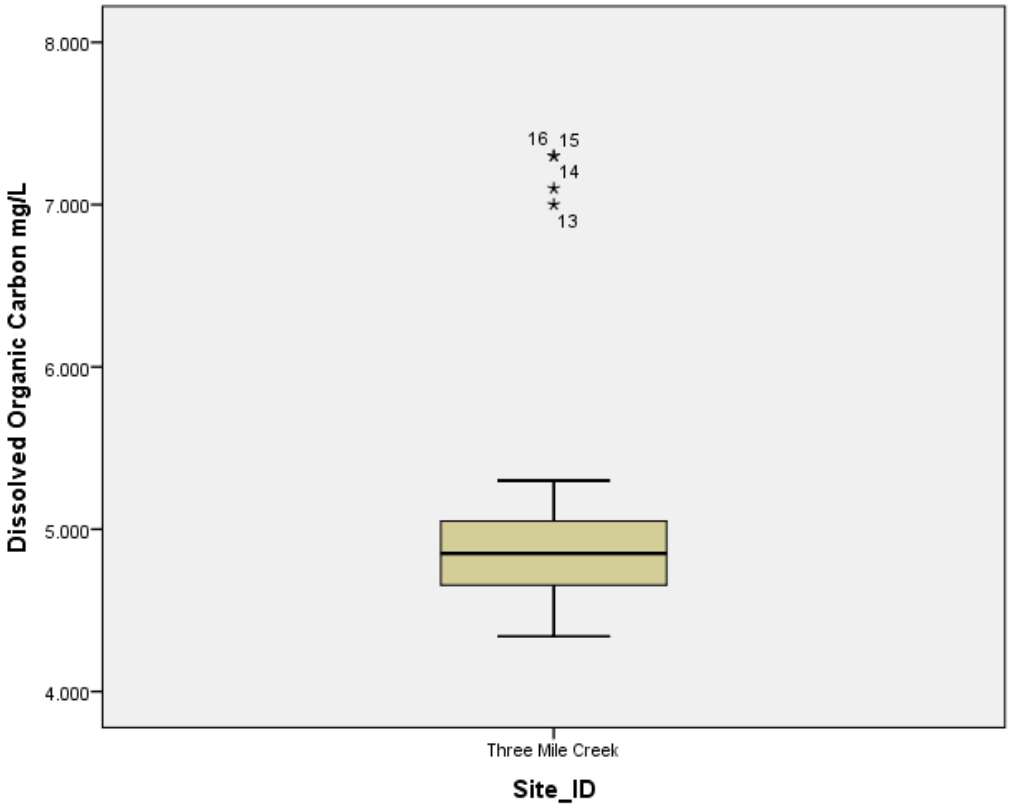

29
28
7
.020
.015
.010
.005
.000
Orthophosphate mg/L
Dauphin Island
Site_ID

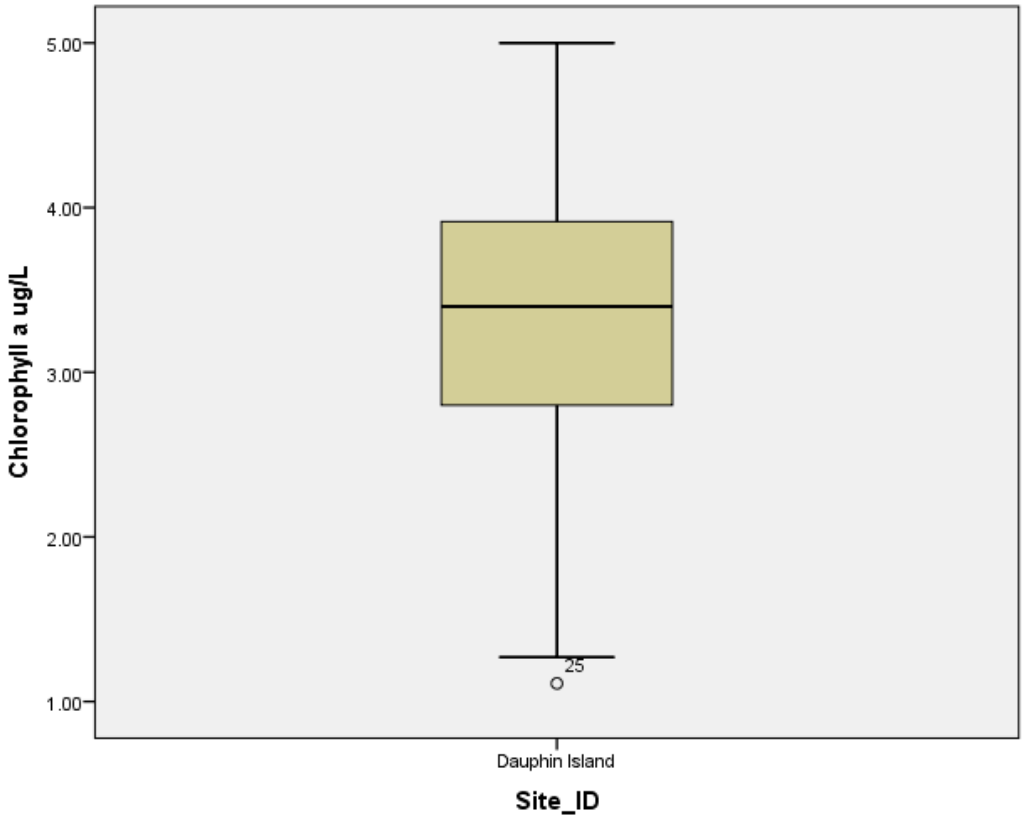

23
21
39
.130
.120
.110
.100
.090
.080
Orthophosphate mg/L
Three Mile Creek
Site_ID

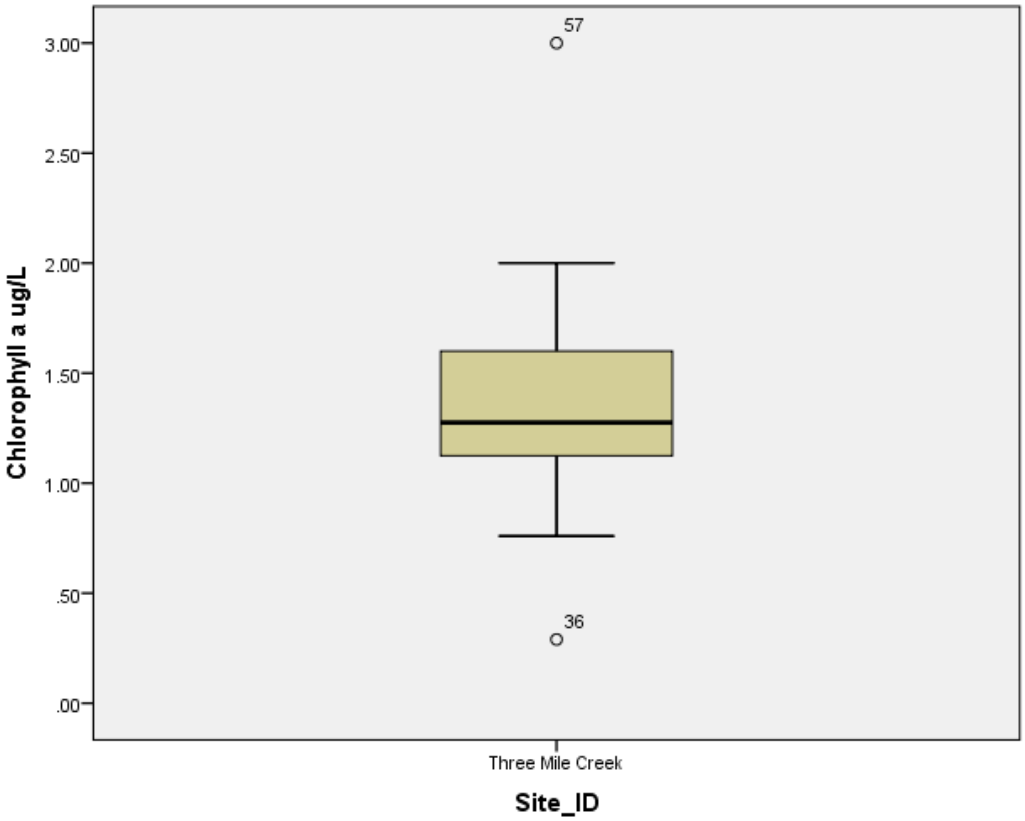

5.50
5.00
4.50
4.00
3.50
3.00
Total Organic Carbon mg/L
11
12
10
Dauphin Island
Site_ID


9.00
8.00
7.00
6.00
5.00
4.00
Total Organic Carbon mg/L
15
14
13
16
Three Mile Creek
Site_ID

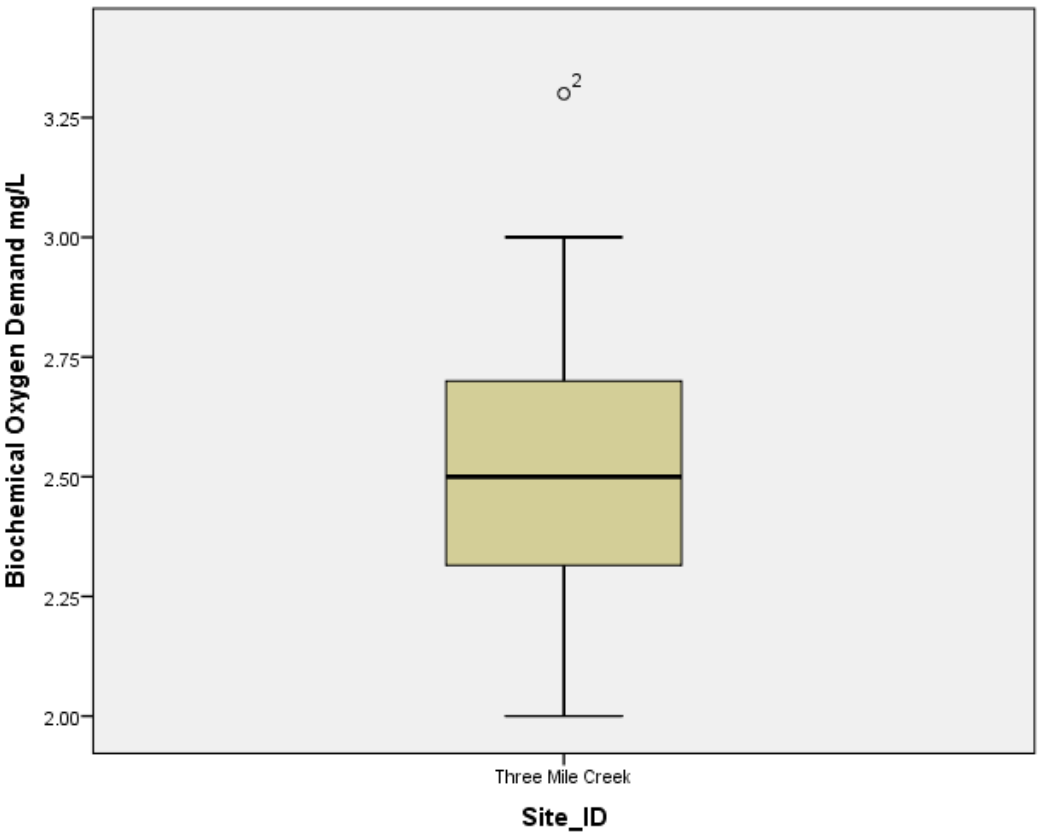

Dissolved Organic Carbon mg/L
5.500
5.000
4.500
4.000
3.500
3.000
2.500
12
Dauphin Island
Site_ID

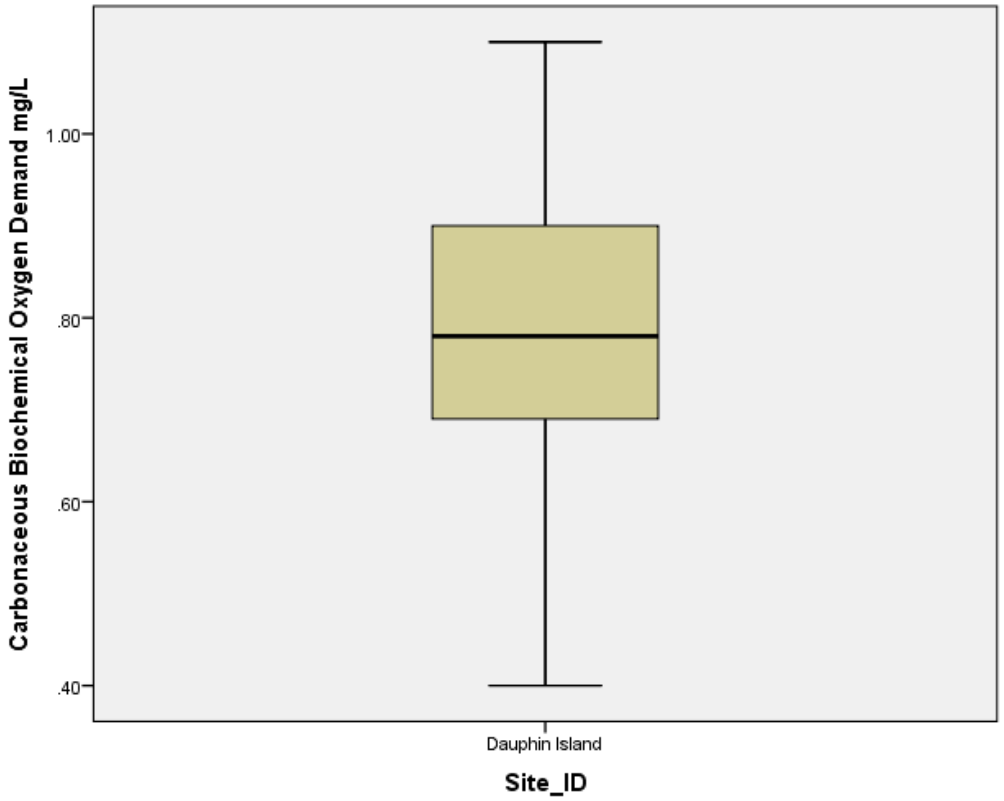

Dissolved Organic Carbon mg/L
8.000
7.000
6.000
5.000
4.000
16
15
14
13
Three Mile Creek
Site_ID

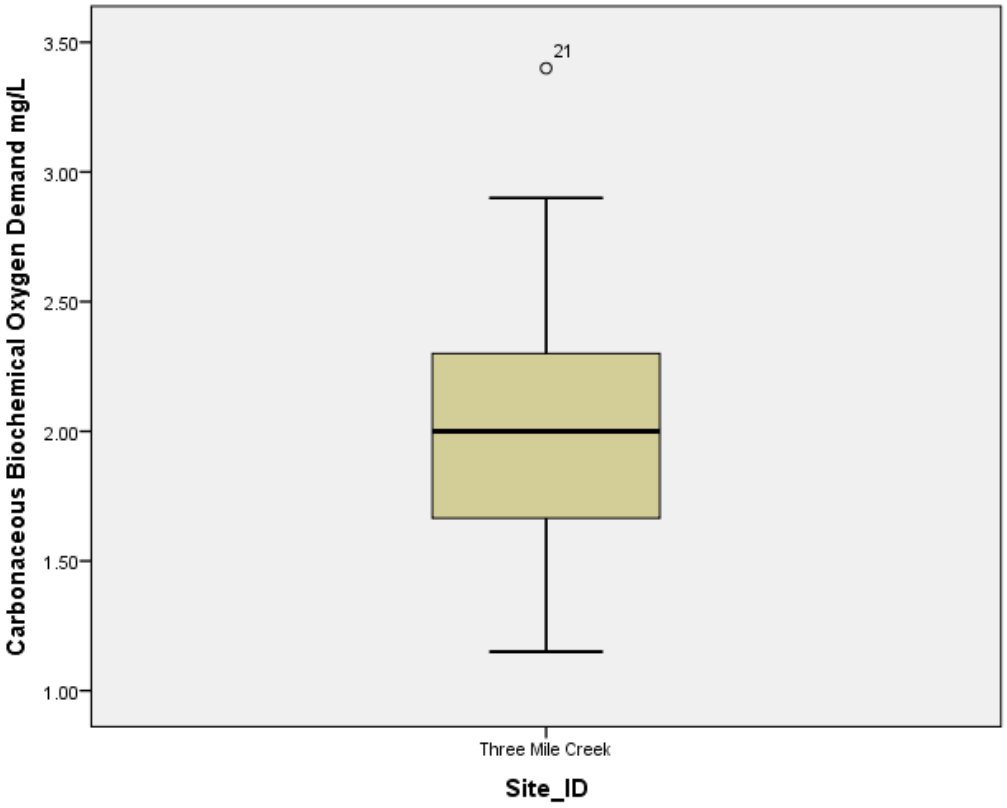

5.00
4.00
3.00
2.00
1.00
Chlorophyll a ug/L
25
Dauphin Island
Site_ID


3.00
2.50
2.00
1.50
1.00
.50
.00
Chlorophyll a ug/L
57
36
Three Mile Creek
Site_ID


Biochemical Oxygen Demand mg/L
1.10
1.00
.90
.80
.70
.60
3
Dauphin Island
Site_ID


Biochemical Oxygen Demand mg/L
3.25
3.00
2.75
2.50
2.25
2.00
2
Three Mile Creek
Site_ID


Carbonaceous Biochemical Oxygen Demand mg/L
1.00
.80
.60
.40
Dauphin Island
Site_ID


Carbonaceous Biochemical Oxygen Demand mg/L
3.50
3.00
2.50
2.00
1.50
1.00
21
Three Mile Creek
Site_ID