Statistical Analyses and Summary of Analytical Round Robin #5 – a Data Comparability Study

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Samples collected October 18, 2010 from the Florida State University Coastal and Marine Laboratory and Alligator Harbor, FL
Preserved and split October 19, and shipped October 20, 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 fifth analytical round robin addresses the variability in these 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 Kjeldahl Nitrogen	Yes	No
Ammonia	Yes	No
Total Nitrate + Nitrite	Yes	No
Total Phosphorous	Yes	No
Total Organic Carbon	Yes	No
Dissolved Nitrite	No	Yes
Orthophosphate	No	Yes

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

A total of ten laboratories, representing local, state, federal, academic, and private laboratories participated in this round robin. Samples were collected on 18 October 2010 from the Florida State University Coastal and Marine Laboratory (FSU CML) and from Alligator Harbor, FL by Linda Sedlacek and Heather Ritchie. Sites were selected in an effort to provide one sample that was high in nutrients and another low in nutrients. Water was collected from FSU CML using its seawater system which had been unused for months prior and was not flushed before collection. Dead algae were noted in the system, and may elucidate the effects of a significant phaeophytin fraction upon chlorophyll results. Field measurements are listed in Table 2.

	FSU CML	Alligator Harbor
Depth (m)	~2	~0.3
Temperature (ºC)	23.3	23.9
pH	7.66	8.02
Dissolved Oxygen (mg/L)	5.72	7.12
Salinity (PSU)	33.42	32.19
Conductivity (mS)	48.044	46.605

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)
- 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)

Samples for each bottle type were kept homogenized by constant stirring. In an effort to ensure that some values were above the laboratories' detection limits, the FSU CML filtered, unpreserved sample was spiked with orthophosphate (enough to raise the value 0.008 mg/L) and nitrite (enough to raise the value 0.011 mg/L) before splitting; the FSU CML acid-preserved, unfiltered sample was spiked with ammonia (enough to raise the value 0.110 mg/L) before splitting. Each laboratory received three replicates of each of the above sample types for sites. Samples were kept in a walk-in cooler at 4 ^{o}C until shipment, and were shipped on ice in coolers.

Laboratories were given approximately six weeks to complete their analyses and provide results. Many of the methods utilized by participating laboratories involved are considered "equivalent." Table 3 lists the methods used. One of the goals of this, and future round robins, is to test the true equivalency of these methods. We measured "true equivalency" by statistically analyzing the variability in data reported between methods; our analyses required that each laboratory report only values above its detection limit.

TKN	**NH_3**	**Total NO_x**	**Dissolved NO_2**	**TP**	**OP**	**TOC**	**ChlA**	**BOD**	**CBOD**
EPA 351.2	EPA 350.1	EPA 353.2	EPA 353.2	EPA 365.1	EPA 365.1	EPA 415.1	EPA 445.0	SM 5210 B	SM 5210 B
Lachat 10-107-06-2-D	Lachat 10-107-06-1-C	Lachat 10-107-04-1-C	Lachat 10-107-04-1-C	EPA 365.4	Lachat 31-115-01-1-I	SM 5310 B	SM 10200 H		SM 5210 C
USGS I-4515-91	SM 4500 NH_3 G	SM 4500 NO_3 F	SM 4500 NO_2 B	Lachat 10-115-01-1-C	SM 4500 P E	SM 5310 C			
		USGS I-2545-90	USGS I-2540-90		SM 4500 P F				
					USGS I-2601-90				

Table 3. Methods used by laboratories participating in the fifth analytical round robin.

Laboratories participating in Analytical Round Robin #5:

ADEM_Mon – Alabama Department of Environmental Management, Montgomery, Field Operations Central Laboratory (AL)
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)
MDEQ – Mississippi Department of Environmental Quality (MS)
Sanders – Sanders Laboratories, Inc. (FL)
SERC – Florida International University, Southeast Environmental Research Center (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 guides the selection of statistical tests 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, Dunnett's T3, Tukey's Honestly Significant Difference (HSD), Tukey-Kramer 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 4 lists the analytes and the number of laboratories that carried out each.

	FSU CML		Alligator Harbor	
Analyte	N laboratories	N values >MDL	N laboratories	N values >MDL
TKN	7	21	7	21
NH_3	9	27	9	12*
NO_x	8	24	8	7*
DNO_2	9	27	9	6*
TP	9	27	9	26*
OP	9	27	9	6*
TOC	6	18	6	18
ChlA	9	27	9	27
BOD	6	10*	6	15
CBOD	6	7*	6	11*

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

Table 4. 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

A. Total Kjeldahl Nitrogen. Seventeen of the 21 values for FSU CML were within acceptable ranges. Lab E reported two values outside acceptable ranges, and Labs A and I both reported one value outside acceptable ranges. There were no statistical outliers. The %F-pseudosigma value was moderate (between 20 and 30%), indicating a lack of precision among laboratories. Of the 21 reported values, 62% were within 1 F-pseudosigma and 81% were within 2 F-pseudosigma. Method Lachat 10-107-06-2-D was statistically significantly lower than the other methods.

At Alligator Harbor, 16 of the 21 values were within acceptable ranges. Labs E and I reported two values outside acceptable ranges, and Lab G reported one value outside acceptable ranges. The %F-pseudosigma value was small (between 10 and 20%), indicating a high degree of precision among laboratories. Of the 21 reported values, 67% were within 1 F-pseudosigma and 76% were within 2 F-pseudosigma. At both locations, Lab E's values were highly variable, and Lab I's values were higher than most of the other values. There was no statistical difference among methods; however, Lachat 10-107-06-2-D was considerably lower than the other two methods. See Figures 1 – 3 and Table 5 - 11 for scatter-plots of values obtained by individual laboratories, F-pseudosigma values, summary statistics, inter-laboratory comparisons, and method comparisons.

Total Kjeldahl Nitrogen				
	FSU CML			
	F-pseudosigma	**% F-pseudosigma**	**Median**	**Range**
	0.177	20.42%	0.866	1.046
Method	**N**	**Mean**	**Median**	**Range**
EPA 351.2	15	0.987	0.890	0.796
Lachat 10-107-06-2-D	3	0.530	0.540	0.050
USGS I-4515-91	3	0.892	0.900	0.044
	Alligator Harbor			
	F-pseudosigma	**% F-pseudosigma**	**Median**	**Range**
	0.118	15.36%	0.770	0.823
Method	**N**	**Mean**	**Median**	**Range**
EPA 351.2	15	0.789	0.790	0.823
Lachat 10-107-06-2-D	3	0.667	0.660	0.020
USGS I-4515-91	3	0.798	0.812	0.075

Table 5. F-pseudosigma values for TKN.

TKN

	FSU CML				Alligator Harbor			
Lab ID	N	Lab Median	Range	Mean Z-value	N	Lab Median	Range	Mean Z-value
A	3	0.540	0.050	1.90	3	0.660	0.020	0.88
B	3	0.827	0.045	0.21	3	0.744	0.014	0.26
C	3	0.900	0.044	0.15	3	0.812	0.075	0.24
E	3	1.319	0.591	2.30	3	0.791	0.036	0.60
G	3	0.850	0.060	0.05	3	0.770	0.280	0.68
I	3	1.160	0.160	1.74	3	1.090	0.120	2.43
J	3	0.770	0.140	0.35	3	0.800	0.180	0.08

Table 6. 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	.53000	.026458	.015275	.46428	.59572	.500	.550
B	3	.82933	.022591	.013043	.77322	.88545	.808	.853
C	3	.89200	.023065	.013317	.83470	.94930	.866	.910
E	3	1.27333	.298135	.172128	.53273	2.01394	.955	1.546
G	3	.85667	.030551	.017638	.78078	.93256	.830	.890
I	3	1.17333	.080829	.046667	.97254	1.37412	1.100	1.260
J	3	.80333	.075719	.043716	.61524	.99143	.750	.890
Total	21	.90829	.255736	.055806	.79188	1.02470	.500	1.546

Table 7. Descriptive statistics by laboratory for TKN for FSU CML.

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	.66667	.011547	.006667	.63798	.69535	.660	.680
B	3	.73933	.008083	.004667	.71925	.75941	.730	.744
C	3	.79833	.039323	.022703	.70065	.89602	.754	.829
E	3	.69933	.384778	.222152	-.25651	1.65518	.277	1.030
G	3	.69000	.156205	.090185	.30197	1.07803	.510	.790
I	3	1.05667	.066583	.038442	.89126	1.22207	.980	1.100
J	3	.76000	.096437	.055678	.52044	.99956	.650	.830
Total	21	.77290	.186275	.040648	.68811	.85770	.277	1.100

Table 8. Descriptive statistics by laboratory for TKN for Alligator Harbor.

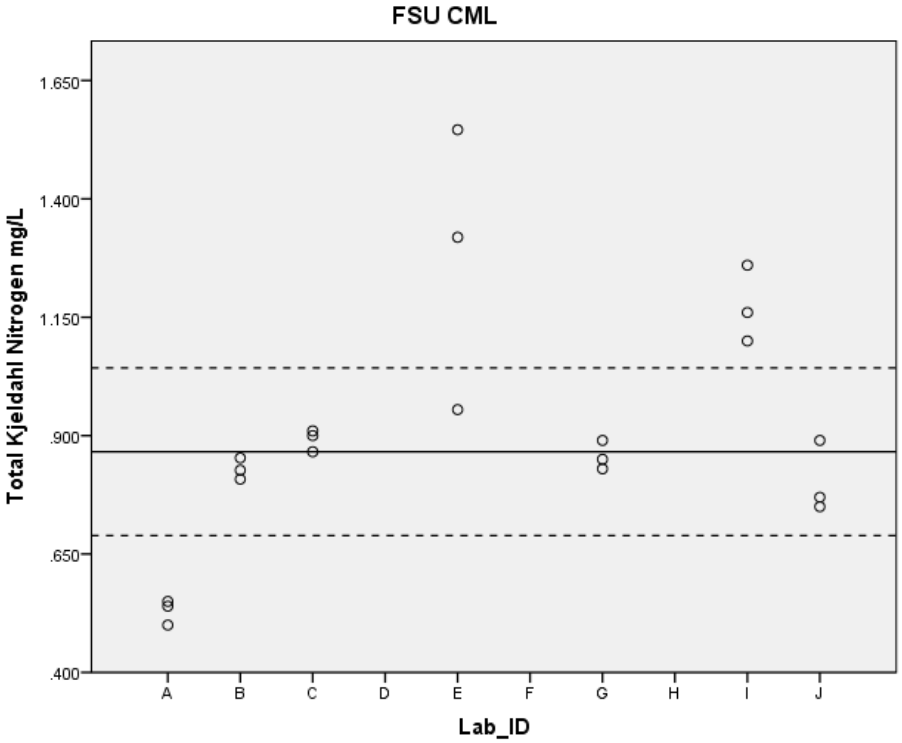


Figure 1. Scatter-plot of TKN values obtained by seven laboratories for FSU CML. The solid line indicates the overall median, and the dashed lines indicate +/- 1 F-pseudosigma.

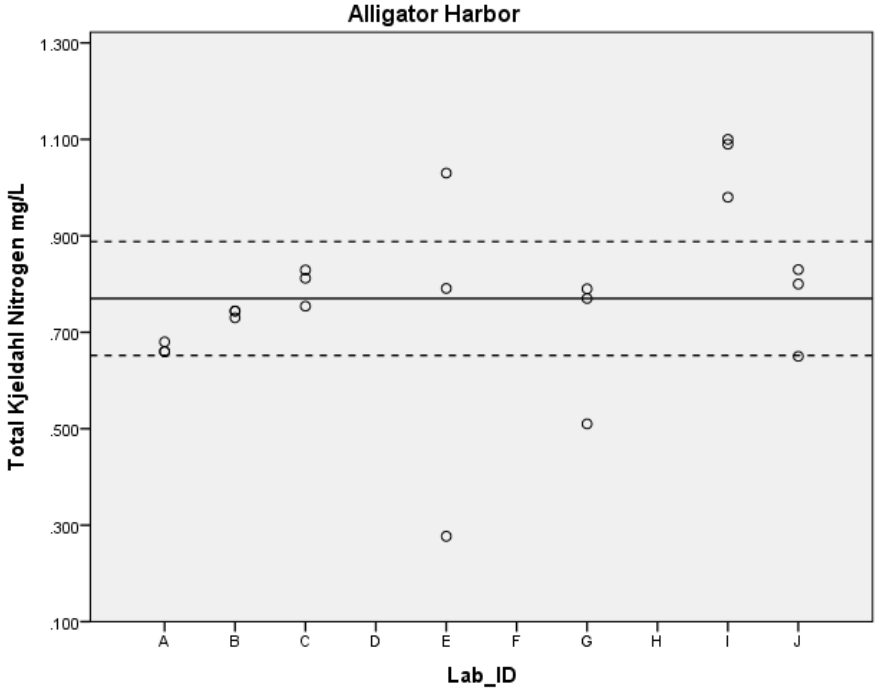


Figure 2. Scatter-plot of TKN values obtained by seven laboratories for Alligator Harbor. The solid line indicates the overall median, and the dashed lines indicate +/- 1 F-pseudosigma.

Hypothesis Test Summary				
	Null Hypothesis	Test	Sig.	Decision
1	The distribution of Total Kjeldahl Nitrogen mg/L is the same across categories of Lab_ID.	Independent-Samples Kruskal-Wallis Test	.007	Reject the null hypothesis.

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

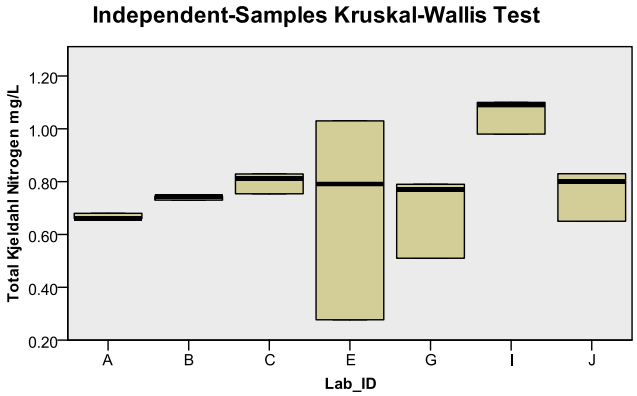
Homogeneous Subsets based on Total Kjeldahl Nitrogen mg/L

		Subset		
		1	2	3
Sample[1]	A	2.000		
	J	7.167	7.167	
	B	7.667	7.667	
	G	9.833	9.833	
	C		13.333	13.333
	I			18.000
	E			19.000
Test Statistic		7.115	5.468	5.600
Sig. (2-sided test)		.068	.141	.061
Adjusted Sig. (2-sided test)		.162	.315	.189

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.

Table 9. Kruskal-Wallis and post hoc inter-laboratory comparisons for TKN from FSU CML.



Total N	21
Test Statistic	10.490
Degrees of Freedom	6
Asymptotic Sig. (2-sided test)	.105

1. The test statistic is adjusted for ties.
2. Multiple comparisons are not performed because the overall test does not show significant differences across samples.

Figure 3. Results of Kruskal-Wallis test of TKN by laboratory for Alligator Harbor.

Multiple Comparisons

Dependent Variable: Total Kjeldahl Nitrogen mg/L

	(I) Method ID	(J) Method ID	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
						Lower Bound	Upper Bound
Dunnett's T[3]	EPA 351.2	Lachat 10-107-06-2-D	.457200*	.062908	.000	.28978	.62462
		USGS I-4515-91	.095200	.062461	.368	-.07135	.26175
	Lachat 10-107-06-2-D	EPA 351.2	-.457200*	.062908	.000	-.62462	-.28978
		USGS I-4515-91	-.362000*	.020265	.000	-.43858	-.28542
	USGS I-4515-91	EPA 351.2	-.095200	.062461	.368	-.26175	.07135
		Lachat 10-107-06-2-D	.362000*	.020265	.000	.28542	.43858

Method ID	N	Subset for alpha = 0.05	
		1	2
Lachat 10-107-06-2-D	3	.53000	
USGS I-4515-91	3		.89200
EPA 351.2	15		.98720

*. The mean difference is significant at the 0.05 level.

Table 10. Post hoc comparisons for TKN values by method for all reported values for FSU CML.

Test of Homogeneity of Variances

Total Kjeldahl Nitrogen mg/L

Levene's Statistic	df1	df2	Sig.
1.912	2	18	.177

ANOVA

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	.040	2	.020	.546	.588
Within Groups	.654	18	.036		
Total	.694	20			

	TKN_ID	N	Subset for alpha = 0.05
			1
Gabriel[a,b]	Lachat 10-107-06-2-D	3	.66667
	EPA 351.2	15	.78907
	USGS I-4515-91	3	.79833
	Sig.		.695

Means for groups in homogeneous subsets are displayed.

a. Uses Harmonic Mean Sample Size = 4.091.

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

Table 11. ANOVA and post hoc comparisons for TKN values by method for all reported values for Alligator Harbor.

B. Ammonia. Fifteen of the 27 reported values for FSU CML were within acceptable ranges. Labs A, C, E, and I reported all values outside acceptable ranges. No values were determined to be statistical outliers; however, Lab I's values were quite high. There were no results that were reported as non-values. The %F-pseudosigma value was moderate (between 20 and 30%), indicating a lack of precision among laboratories. Of the 27 reported values, 56% were within 1 F-pseudosigma; no other values were within 2 F-pseudosigma. Method Lachat 10-107-06-1-J was significantly lower than the other methods.

At Alligator Harbor, twelve of the 27 results were reported values; the other 56% were reported as qualifiers. There were no statistical outliers. The MDLs ranged from 0.0017 to 0.02 mg/L; and the PQLs for Labs A, E, and G ranged from 0.02 to 0.05 mg/L. There were no values reported as less than detection/quantitation limits that were determined to be false negatives. Method EPA 350.1 was the only method to report values. No other analyses were conducted for ammonia for Alligator Harbor. Values reported by Lab I were high for both sites. See Figures 4 & 5 and Tables 12 - 18 for scatter-plots of values obtained by individual laboratories, F-pseudosigma values, summary statistics, inter-laboratory comparisons, and method comparisons.

Ammonia				
	FSU CML			
	F-pseudosigma	**% F-pseudosigma**	**Median**	**Range**
	0.017	21.31%	0.080	0.194
Method	**N**	**Mean**	**Median**	**Range**
EPA 350.1	21	0.099	0.082	0.194
Lachat 10-107-06-1-J	3	0.040	0.040	0.000
SM 4500 NH3 G	3	0.069	0.069	0.005
	Alligator Harbor			
	F-pseudosigma	**% F-pseudosigma**	**Median**	**Range**
	0.082	208.78%	0.770	0.145
Method	**N**	**Mean**	**Median**	**Range**
EPA 350.1	21 (nine non-values)	0.062	0.040	0.145
Lachat 10-107-06-1-J	3	All Non-detect	N/A	N/A
SM 4500 NH3 G	3	All Non-detect	N/A	N/A

Table 12. F-pseudosigma values for ammonia.

NH_3

	FSU CML				Alligator Harbor			
Lab ID	N	Lab Median	Range	Mean Z-value	N	Lab Median	Range	Mean Z-value
A	3	0.040	0.000	2.35	3*	NR	NR	NR
B	3	0.079	0.005	0.08	3	0.020	0.002	N/A
C	3	0.129	0.044	2.84	3	0.061	0.004	N/A
E	3	0.027	0.001	3.14	3*	NR	NR	NR
F	3	0.069	0.005	0.67	3*	NR	NR	NR
G	3	0.070	0.010	0.39	3*	NR	NR	NR
H	3	0.082	0.009	0.22	3	0.016	0.001	N/A
I	3	0.220	0.010	8.04	3	0.150	0.010	N/A
J	3	0.085	0.002	0.29	3*	NR	NR	NR

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

Table 13. Summary statistics and Z-values by laboratory for ammonia.

Ammonia		
Method	**MDL Range**	**PQL Range**
ALL	0.0017 - 0.02	0.012 - 0.05
EPA 350.1	0.003 - 0.02	0.012 - 0.05
Lachat 10-107-06-1-J	0.0017	0.04
SM 4500 NH3 G	0.007	0.028

Table 14. Methods and detection/quantitation limits for NH_3.

Descriptives

Ammonia mg/L

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
A	3	.04000	.000000	.000000	.04000	.04000	.040	.040
B	3	.07867	.002517	.001453	.07242	.08492	.076	.081
C	3	.12833	.003055	.001764	.12074	.13592	.125	.131
E	3	.02667	.000577	.000333	.02523	.02810	.026	.027
F	3	.06867	.002517	.001453	.06242	.07492	.066	.071
G	3	.07333	.005774	.003333	.05899	.08768	.070	.080
H	3	.08367	.004726	.002728	.07193	.09541	.080	.089
I	3	.21667	.005774	.003333	.20232	.23101	.210	.220
J	3	.08500	.001000	.000577	.08252	.08748	.084	.086
Total	27	.08900	.053727	.010340	.06775	.11025	.026	.220

Table 15. Descriptive statistics by laboratory for ammonia for FSU CML.

Descriptives

Ammonia mg/L

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
B	3	.02000	.001000	.000577	.01752	.02248	.019	.021
C	3	.06033	.002082	.001202	.05516	.06550	.058	.062
H	3	.01567	.000577	.000333	.01423	.01710	.015	.016
I	3	.15333	.005774	.003333	.13899	.16768	.150	.160
Total	12	.06233	.057873	.016707	.02556	.09910	.015	.160

Table 16. Descriptive statistics by laboratory for ammonia for Alligator Harbor.

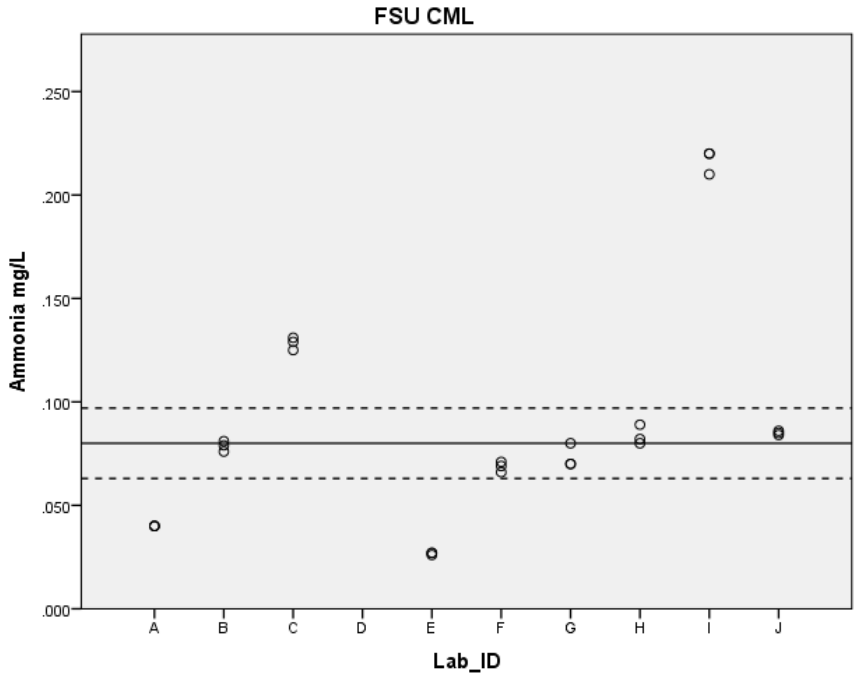


Figure 4. Scatter-plot of ammonia values obtained by nine laboratories for FSU CML. The solid line indicates the overall median, and the dashed lines indicate +/- 1 F-pseudosigma.

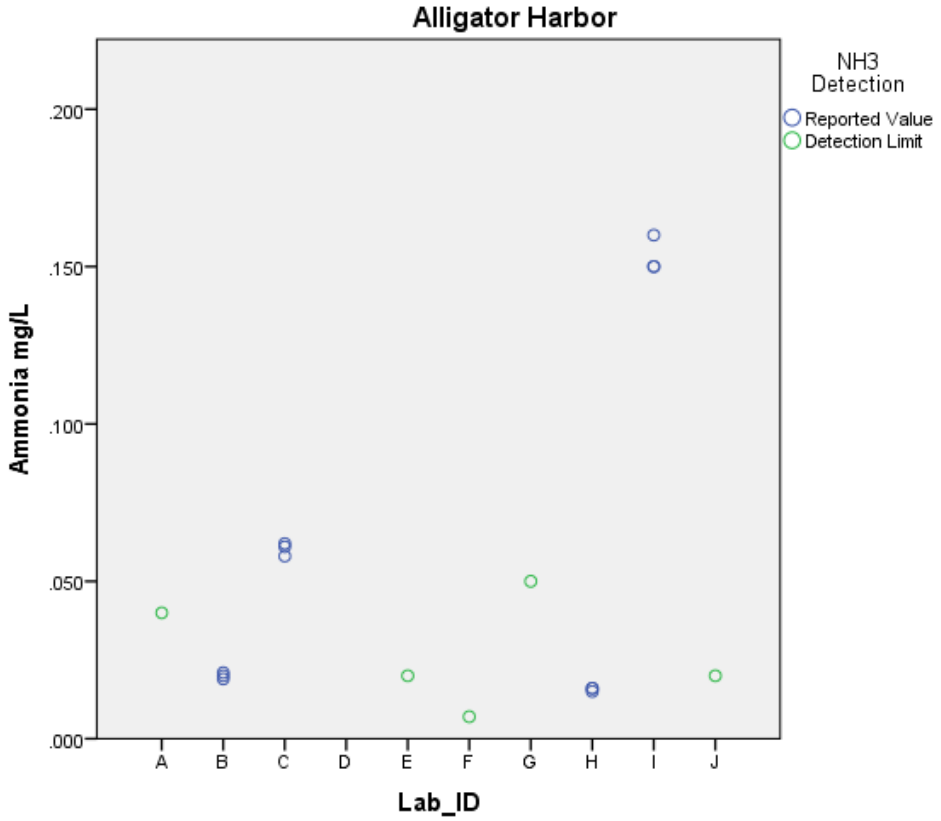


Figure 5. Scatter-plot of ammonia values and detection/quantitation limits obtained by nine laboratories for Alligator Harbor.

Hypothesis Test Summary

	Null Hypothesis	Test	Sig.	Decision
1	The distribution of Ammonia 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 Ammonia mg/L

		Subset					
		1	2	3	4	5	6
Sample[1]	E	2.000					
	A		5.000				
	F			8.667			
	G			11.167	11.167		
	B			13.667	13.667		
	H				17.500	17.500	
	J				19.000	19.000	
	C					23.000	
	I						26.000
Test Statistic		.[2]	.[2]	4.392	7.682	5.600	.[2]
Sig. (2-sided test)		.	.	.111	.053	.061	.
Adjusted Sig. (2-sided test)		.	.	.325	.127	.189	.

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 17. Kruskal-Wallis and post hoc inter-laboratory comparisons for ammonia from FSU CML.

Multiple Comparisons

Dependent Variable: Ammonia mg/L

	(I) Method ID	(J) Method ID	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
						Lower Bound	Upper Bound
Dunnett's T[3]	EPA 350.1	Lachat 10-107-06-1-J	.058905*	.012396	.000	.02675	.09106
		SM 4500 NH3 G	.030238	.012481	.071	-.00207	.06255
	Lachat 10-107-06-1-J	EPA 350.1	-.058905*	.012396	.000	-.09106	-.02675
		SM 4500 NH3 G	-.028667*	.001453	.005	-.03788	-.01945
	SM 4500 NH3 G	EPA 350.1	-.030238	.012481	.071	-.06255	.00207
		Lachat 10-107-06-1-J	.028667*	.001453	.005	.01945	.03788

Method ID	N	Subset for alpha = 0.05	
		1	2
Lachat 10-107-06-1-J	3	.04000	
SM 4500 NH3 G	3		.06867
EPA 350.1	21		.09890

*. The mean difference is significant at the 0.05 level.

Table 18. Post hoc comparisons for ammonia values by method for all reported values for FSU CML.

C. Total Nitrite + Nitrate. Twenty-one of the 24 reported values for FSU CML were within acceptable ranges. Lab E reported all three values outside acceptable ranges, two of which were statistical outliers (0.46 mg/L for both). The %F-pseudosigma value was large (greater than 30%), indicating a lack of precision among laboratories. Of the 24 reported values, 75% were within 1 F-pseudosigma and 88% were within 2 F-pseudosigma. There was no statistical difference among the four methods.

At Alligator Harbor, seven of the 24 results were reported values; the other 71% were reported as qualifiers. There were no statistical outliers. The MDLs ranged from 0.002 to 0.02 mg/L; and the PQLs for Labs A and G ranged from 0.02 to 0.04 mg/L. There were no values reported as less than detection/quantitation limits that were determined to be false negatives. No other analyses were conducted for NO_x for Alligator Harbor, due to the paucity of reported values. See Figures 6 - 8 and Tables 19 – 24 for scatter-plots of values obtained by individual laboratories, F-pseudosigma values, summary statistics, inter-laboratory comparisons, and method comparisons.

NO_x				
	FSU CML			
	F-pseudosigma	**% F-pseudosigma**	**Median**	**Range**
	0.061	37.87%	0.161	0.321
Method	**N**	**Mean**	**Median**	**Range**
EPA 353.2	15	0.200	0.155	0.321
Lachat 10-107-04-1-C	3	0.240	0.240	0.000
SM 4500 N03 F	3	0.180	0.181	0.002
USGS I-2545-90	3	0.162	0.163	0.002
	Alligator Harbor			
	F-pseudosigma	**% F-pseudosigma**	**Median**	**Range**
	0.065	250.90%	0.026	0.098
Method	**N**	**Mean**	**Median**	**Range**
EPA 353.2	15 (eleven non-values)	0.008	0.002	0.024
Lachat 10-107-04-1-C	3	0.090	0.090	0.020
SM 4500 N03 F	3	All Non-detect	N/A	N/A
USGS I-2545-90	3	All Non-detect	N/A	N/A

Table 19. F-pseudosigma values for NO_x.

NO_x

	FSU CML				Alligator Harbor			
Lab ID	N	Lab Median	Range	Mean Z-value	N	Lab Median	Range	Mean Z-value
A	3	0.240	0.000	1.30	3	0.090	0.020	N/A
B	3	0.181	0.002	0.32	3*	NR	NR	NR
C	3	0.163	0.002	0.02	3*	NR	NR	NR
E	3	0.160	0.001	0.02	3	0.002	0.000	N/A
F	3	0.139	0.003	0.34	3*	NR	NR	NR
G	3	0.460	0.160	4.03	3*	NR	NR	NR
I	3	0.155	0.009	0.14	3*	0.026	N/A	N/A
J	3	0.140	0.000	0.34	3*	NR	NR	NR

Table 20. Summary statistics and Z-values by Laboratory for NO_x.

NO_x		
Method	**MDL Range**	**PQL Range**
All	0.002 - 0.02	0.01 - 0.05
EPA 353.2	0.002 - 0.02	0.01 - 0.05
Lachat 10-107-04-1-C	0.0023	0.02
SM 4500 N03 F	0.003	0.012
USGS I-2545-90	0.02	Not Reported

Table 21. Methods and detection/quantitation limits 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	.24000	.000000	.000000	.24000	.24000	.240	.240
B	3	.18033	.001155	.000667	.17746	.18320	.179	.181
C	3	.16233	.001155	.000667	.15946	.16520	.161	.163
E	3	.15967	.000577	.000333	.15823	.16110	.159	.160
F	3	.14000	.001732	.001000	.13570	.14430	.139	.142
G	3	.40667	.092376	.053333	.17719	.63614	.300	.460
I	3	.15267	.004933	.002848	.14041	.16492	.147	.156
J	3	.14000	.000000	.000000	.14000	.14000	.140	.140
Total	24	.19771	.090543	.018482	.15948	.23594	.139	.460

Table 22. Descriptive statistics by laboratory for NO_x for FSU CML.

Descriptives

Total NO3 + NO2 mg/L

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
A	3	.09000	.010000	.005774	.06516	.11484	.080	.100
E	3	.00200	.000000	.000000	.00200	.00200	.002	.002
I	1	.02600	N/A	N/A	N/A	N/A	.026	.026
Total	7	.04314	.045016	.017015	.00151	.08478	.002	.100

Table 23. Descriptive statistics by laboratory for NO_x for Alligator Harbor.

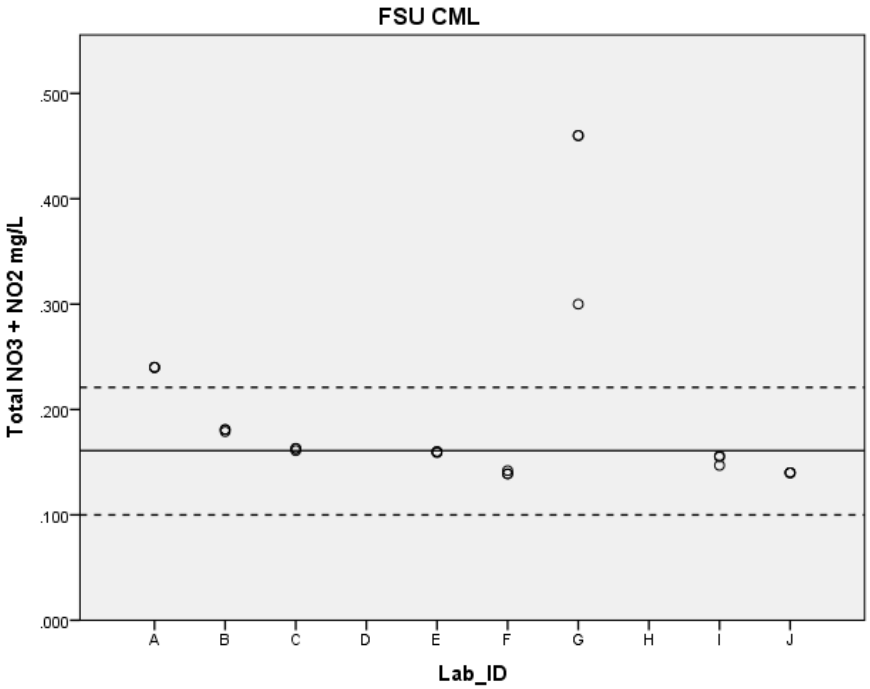


Figure 6. Scatter-plot of NO_x values obtained by eight laboratories for FSU CML. The solid line indicates the overall median, and the dashed lines indicate +/- 1 F-pseudosigma.

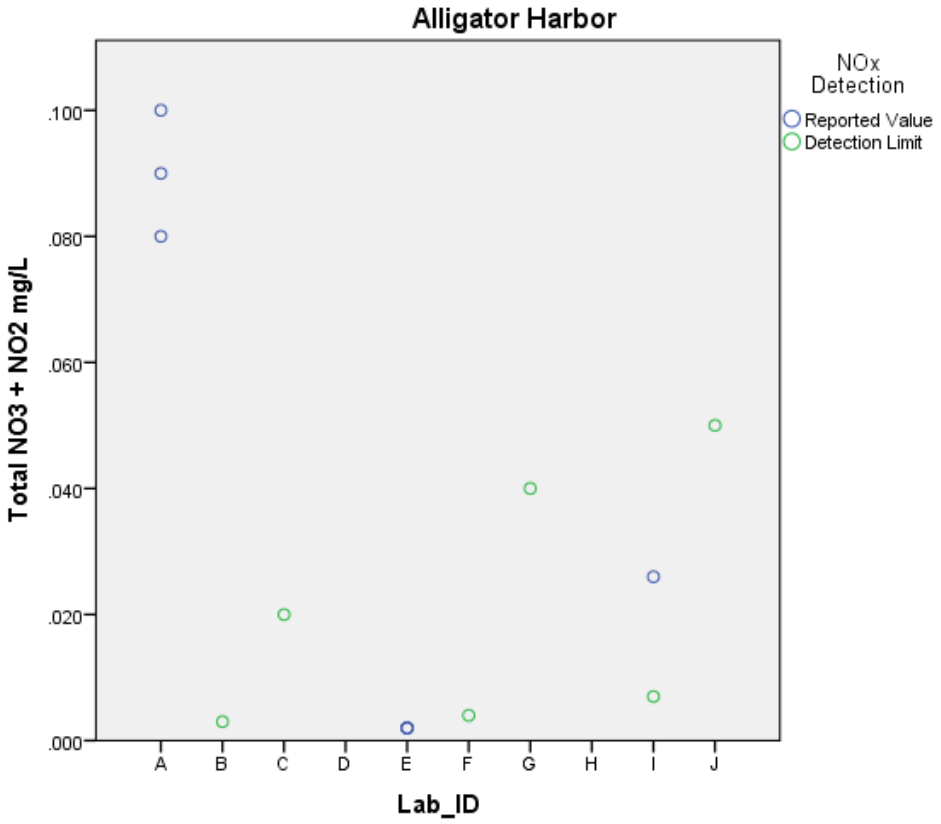
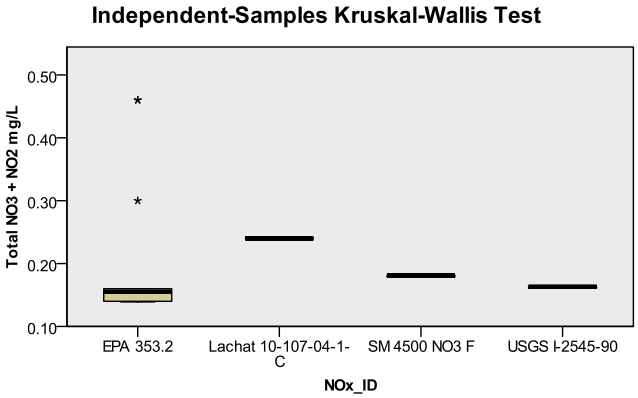


Figure 7. Scatter-plot of NO_x values and detection/quantitation limits obtained by eight laboratories for Alligator Harbor.

Hypothesis Test Summary				
	Null Hypothesis	Test	Sig.	Decision
1	The distribution of Total NO_3 + NO_2 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 NO3 + NO2 mg/L							
		Subset					
		1	2	3	4	5	6
Sample[1]	F	3.000					
	J	4.000					
	I	8.000					
	E		11.000				
	C			14.000			
	B				17.000		
	A					20.000	
	G						23.000
Test Statistic		5.843	.[2]	.[2]	.[2]	.[2]	.[2]
Sig. (2-sided test)		.054	.	.	.	.	.
Adjusted Sig. (2-sided test)		.168	.	.	.	.	.
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 24. Kruskal-Wallis and post hoc inter-laboratory comparisons for NO_x from FSU CML.



Total N	24
Test Statistic	6.951
Degrees of Freedom	3
Asymptotic Sig. (2-sided test)	.073

1. The test statistic is adjusted for ties.
2. Multiple comparisons are not performed because the overall test does not show significant differences across samples.

Figure 8. Results of Kruskal-Wallis method comparisons for NO_x from FSU CML.

D. Dissolved Nitrite. Twenty-four of the 27 reported values for FSU CML were within acceptable ranges. Lab G reported two values outside acceptable ranges, and Lab I reported one. There were no statistical outliers. The %F-pseudosigma value was very small (less than 10%), indicating a high degree of precision among laboratories. Of the 27 reported values, 67% were within 1 F-pseudosigma and 89% were within 2 F-pseudosigma. Results derived from Method SM 4500 NO2 B were statistically lower than results from all other methods; Lachat 10-107-04-1-C results were significantly lower than those from USGS I-2540-90, and EPA 353.2 results were equivalent to both Lachat 10-107-04-1-C and USGS I-2540-90.

At Alligator Harbor, six of the 27 results were reported values; the other 78% were reported as qualifiers. There were no statistical outliers. The MDLs ranged from 0.0003 to 0.004 mg/L; and the PQLs for Labs A and G ranged from 0.005 to 0.02 mg/L. There were no values reported as less than detection/quantitation limits that were determined to be false negatives. Method EPA 353.2 was the only method to report values. No other analyses were conducted for DNO_2 for Alligator Harbor. See Figures 9 & 10 and Tables 25 – 31 for scatter-plots of values obtained by individual laboratories, F-pseudosigma values, summary statistics, inter-laboratory comparisons, and method comparisons.

DNO_2				
	FSU CML			
	F-pseudosigma	**% F-pseudosigma**	**Median**	**Range**
	0.007	6.01%	0.111	0.023
Method	**N**	**Mean**	**Median**	**Range**
EPA 353.2	18	0.115	0.111	0.021
Lachat 10-107-04-1-C	3	0.112	0.113	0.002
SM 4500 N02 B	3	0.108	0.107	0.002
USGS I-2540-90	3	0.119	0.119	0.000
	Alligator Harbor			
	F-pseudosigma	**% F-pseudosigma**	**Median**	**Range**
	0.001	87.86%	0.001	0.002
Method	**N**	**Mean**	**Median**	**Range**
EPA 353.2	18 (twelve non-values)	0.001	0.001	0.002
Lachat 10-107-04-1-C	3	All Non-detect	N/A	N/A
SM 4500 N02 B	3	All Non-detect	N/A	N/A
USGS I-2540-90	3	All Non-detect	N/A	N/A

Table 25. F-pseudosigma values for DNO_2.

DNO_2

	FSU CML				Alligator Harbor			
Lab ID	N	Lab Median	Range	Mean Z-value	N	Lab Median	Range	Mean Z-value
A	3	0.113	0.002	0.19	3*	NR	NR	NR
B	3	0.107	0.002	0.48	3*	NR	NR	NR
C	3	0.119	0.000	1.14	3*	NR	NR	NR
E	3	0.111	0.001	0.05	3	0.002	0.000	N/A
F	3	0.111	0.001	0.05	3*	NR	NR	NR
G	3	0.130	0.010	2.24	3*	NR	NR	NR
H	3	0.110	0.002	0.09	3	0.0004	0.0003	N/A
I	3	0.122	0.004	1.76	3*	NR	NR	NR
J	3	0.110	0.000	0.14	3*	NR	NR	NR

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

Table 26. Summary statistics and Z-values by Laboratory for DNO_2.

DNO_2		
Method	**MDL Range**	**PQL Range**
All	0.0003 - 0.004	0.005 - 0.022
EPA 353.2	0.0003 - 0.004	0.01 - 0.022
Lachat 10-107-04-1-C	0.002	0.005
SM 4500 N02 B	0.002	0.008
USGS I-2540-90	0.001	Not Reported

Table 27. Methods and detection/quantitation limits 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	3	.11233	.001155	.000667	.10946	.11520	.111	.113
B	3	.10767	.001155	.000667	.10480	.11054	.107	.109
C	3	.11900	.000000	.000000	.11900	.11900	.119	.119
E	3	.11133	.000577	.000333	.10990	.11277	.111	.112
F	3	.11067	.000577	.000333	.10923	.11210	.110	.111
G	3	.12667	.005774	.003333	.11232	.14101	.120	.130
H	3	.11040	.001153	.000666	.10754	.11326	.110	.112
I	3	.12333	.002309	.001333	.11760	.12907	.122	.126
J	3	.11000	.000000	.000000	.11000	.11000	.110	.110
Total	27	.11460	.006693	.001288	.11195	.11725	.107	.130

Table 28. Descriptive statistics by laboratory for DNO_2 for FSU CML.

Descriptives

Dissolved Nitrite mg/L

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
E	3	.00200	.000000	.000000	.00200	.00200	.002	.002
H	3	.00050	.000173	.000100	.00007	.00093	.000	.001
Total	6	.00125	.000829	.000338	.00038	.00212	.000	.002

Table 29. Descriptive statistics by laboratory for DNO_2 for Alligator Harbor.

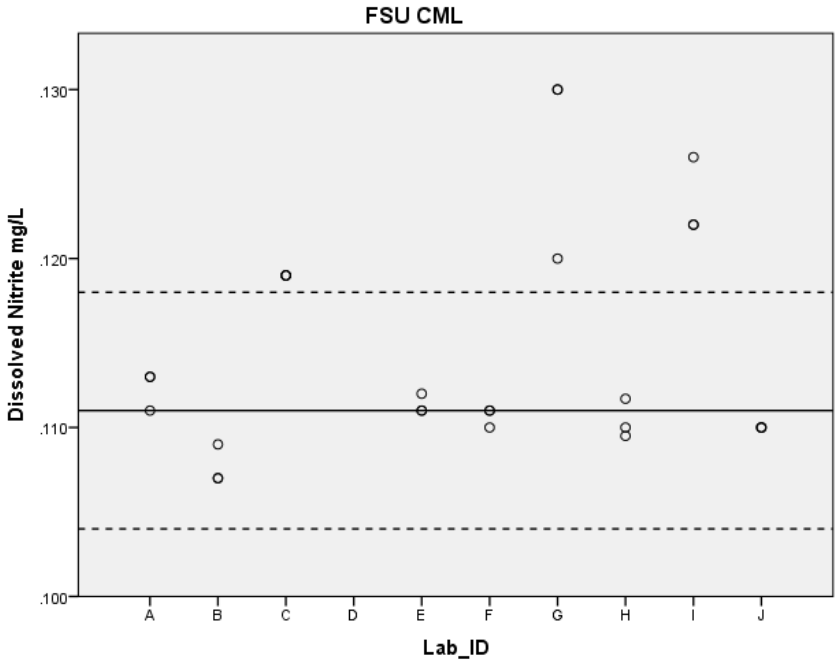


Figure 9. Scatter-plot of DNO_2 values and detection limits obtained by nine laboratories for FSU CML. The solid line indicates the overall median, and the dashed lines indicate +/- 1 F-pseudosigma.

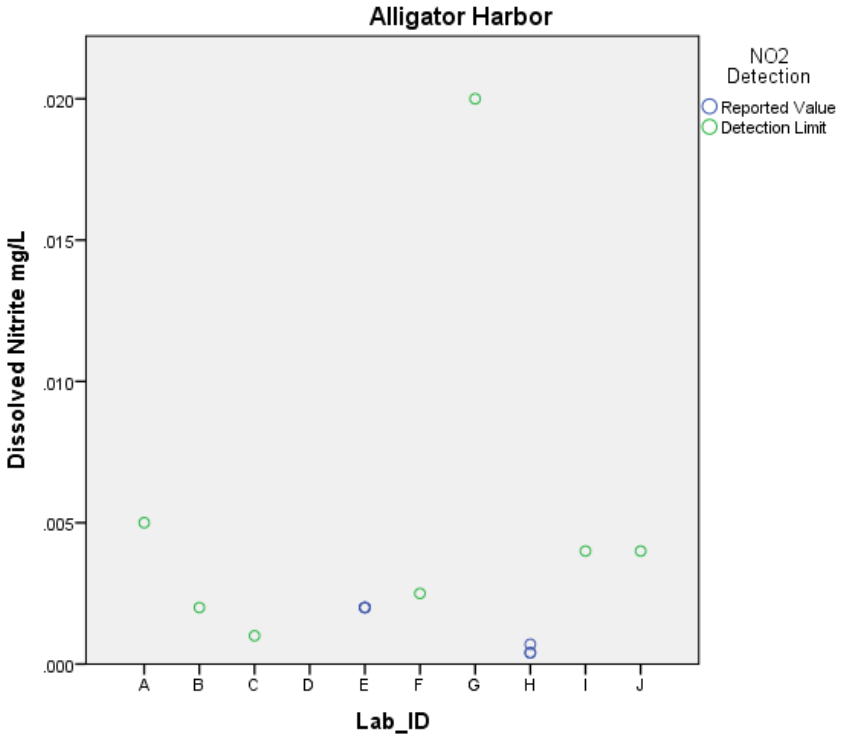


Figure 10. Scatter-plot of NO_2 values and detection limits obtained by nine laboratories for Alligator Harbor.

Dissolved Nitrite mg/L

	Lab_ID	N	Subset for alpha = 0.05		
			1	2	3
Gabriel[a]	B	3	.10767		
	J	3	.11000		
	H	3	.11040		
	F	3	.11067		
	E	3	.11133		
	A	3	.11233		
	C	3		.11900	
	I	3		.12333	.12333
	G	3			.12667
	Sig.		.375	.490	.854

Means for groups in homogeneous subsets are displayed.
a. Uses Harmonic Mean Sample Size = 3.000.
Table 30. Post hoc inter-laboratory comparisons for DNO_2 from FSU CML.

Multiple Comparisons

Dependent Variable: Dissolved Nitrite mg/L

	(I) Method ID	(J) Method ID	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
						Lower Bound	Upper Bound
Dunnett's T3	EPA 353.2	Lachat 10-107-04-1-C	.003067	.001867	.495	-.00237	.00851
		SM 4500 N02 B	.007733*	.001867	.003	.00229	.01317
		USGS I-2540-90	-.003600	.001744	.265	-.00874	.00154
	Lachat 10-107-04-1-C	EPA 353.2	-.003067	.001867	.495	-.00851	.00237
		SM 4500 N02 B	.004667*	.000943	.033	.00055	.00878
		USGS I-2540-90	-.006667*	.000667	.030	-.01176	-.00157
	SM 4500 N02 B	EPA 353.2	-.007733*	.001867	.003	-.01317	-.00229
		Lachat 10-107-04-1-C	-.004667*	.000943	.033	-.00878	-.00055
		USGS I-2540-90	-.011333*	.000667	.010	-.01643	-.00624
	USGS I-2540-90	EPA 353.2	.003600	.001744	.265	-.00154	.00874
		Lachat 10-107-04-1-C	.006667*	.000667	.030	.00157	.01176
		SM 4500 N02 B	.011333*	.000667	.010	.00624	.01643

Method ID	N	Subset for alpha = 0.05		
		1	2	3
SM 4500 N02 B	3	.10767		
Lachat 10-107-04-1-C	3		.11233	
EPA 353.2	18		.11540	.11540
USGS I-2540-90	3			.11900

*. The mean difference is significant at the 0.05 level.
Table 31. Post hoc comparisons for DNO_2 values by method for FSU CML.

E. Total Phosphorus. All of the 27 reported values for FSU CML were within acceptable ranges. There were no outliers or non-values reported. The %F-pseudosigma value was moderate (between 10 and 20%), indicating a high degree of precision among laboratories. Of the 27 reported values, 78% were within 1 F-pseudosigma and 100% were within 2 F-pseudosigma. Method EPA 365.4 was significantly higher than the other two methods.

At Alligator Harbor, 22 of the 26 values were within acceptable ranges. Labs B and I reported two values outside acceptable ranges. Lab G reported the only non-value; however, this was not a false-negative. The %F-pseudosigma value was high (greater than 30%), indicating a lack of precision among laboratories. Of the 26 reported values, 69% were within 1 F-pseudosigma and 85% were within 2 F-pseudosigma. Results derived from Method EPA 365.1 were statistically lower than those from the other two methods. See Figures 11 & 12 and Tables 31 – 38 for scatter-plots of values obtained by individual laboratories, F-pseudosigma values, summary statistics, inter-laboratory comparisons, and method comparisons.

TP				
	FSU CML			
	F-pseudosigma	**% F-pseudosigma**	**Median**	**Range**
	0.030	19.77%	0.150	0.082
Method	**N**	**Mean**	**Median**	**Range**
EPA 365.1	15	0.141	0.141	0.029
EPA 365.4	9	0.189	0.190	0.049
Lachat 10-115-01-1-C	3	0.153	0.150	0.030
	Alligator Harbor			
	F-pseudosigma	**% F-pseudosigma**	**Median**	**Range**
	0.024	54.33%	0.044	0.070
Method	**N**	**Mean**	**Median**	**Range**
EPA 365.1	15	0.039	0.038	0.013
EPA 365.4	9 (one non-value)	0.086	0.093	0.035
Lachat 10-115-01-1-C	3	0.067	0.044	0.070

Table 31. F-pseudosigma values for TP.

TP

	FSU CML				Alligator Harbor			
Lab ID	N	Lab Median	Range	Mean Z-value	N	Lab Median	Range	Mean Z-value
A	3	0.150	0.030	0.11	3	0.070	0.010	0.94
B	3	0.204	0.006	1.82	3	0.094	0.002	2.06
C	3	0.155	0.004	0.12	3	0.038	0.003	0.24
E	3	0.148	0.001	0.06	3	0.036	0.000	0.33
F	3	0.141	0.001	0.31	3	0.036	0.005	0.35
G	3	0.190	0.010	1.22	3*	0.070	0.00	1.08
H	3	0.128	0.018	0.58	3	0.044	0.006	0.03
I	3	0.180	0.028	0.84	3	0.098	0.035	1.90
J	3	0.130	0.000	0.67	3	0.043	0.003	0.06

* One non-value reported.

Table 32. 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	.15333	.015275	.008819	.11539	.19128	.140	.170
B	3	.20467	.003055	.001764	.19708	.21226	.202	.208
C	3	.15367	.002309	.001333	.14793	.15940	.151	.155
E	3	.14833	.000577	.000333	.14690	.14977	.148	.149
F	3	.14067	.000577	.000333	.13923	.14210	.140	.141
G	3	.18667	.005774	.003333	.17232	.20101	.180	.190
H	3	.13267	.009866	.005696	.10816	.15717	.126	.144
I	3	.17533	.014572	.008413	.13914	.21153	.159	.187
J	3	.13000	.000000	.000000	.13000	.13000	.130	.130
Total	27	.15837	.025314	.004872	.14836	.16838	.126	.208

Table 33. Descriptive statistics by laboratory for TP for FSU CML.

Descriptives

Total Phosphorus mg/L

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
A	3	.06667	.005774	.003333	.05232	.08101	.060	.070
B	3	.09333	.001155	.000667	.09046	.09620	.092	.094
C	3	.03833	.001528	.000882	.03454	.04213	.037	.040
E	3	.03600	.000000	.000000	.03600	.03600	.036	.036
F	3	.03567	.002517	.001453	.02942	.04192	.033	.038
G	2	.07000	.000000	.000000	.07000	.07000	.070	.070
H	3	.04333	.003055	.001764	.03574	.05092	.040	.046
I	3	.08967	.018930	.010929	.04264	.13669	.068	.103
J	3	.04267	.001528	.000882	.03887	.04646	.041	.044
Total	26	.05681	.023252	.004560	.04742	.06620	.033	.103

Table 34. Descriptive statistics by laboratory for TP for Alligator Harbor.

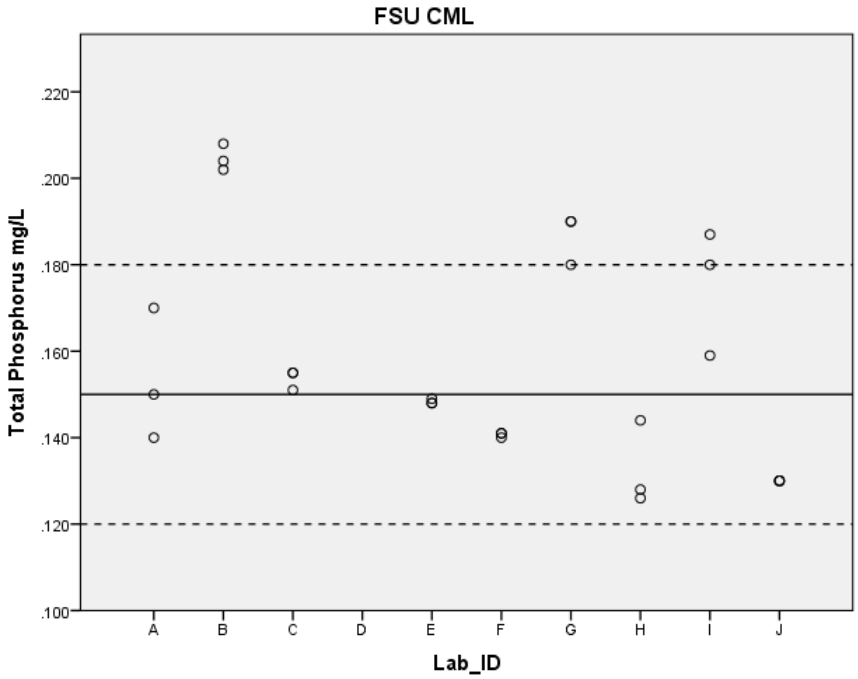


Figure 11. Scatter-plot of TP values obtained by nine laboratories for FSU CML. The solid line indicates the overall median, and the dashed lines indicate +/- 1 F-pseudosigma.

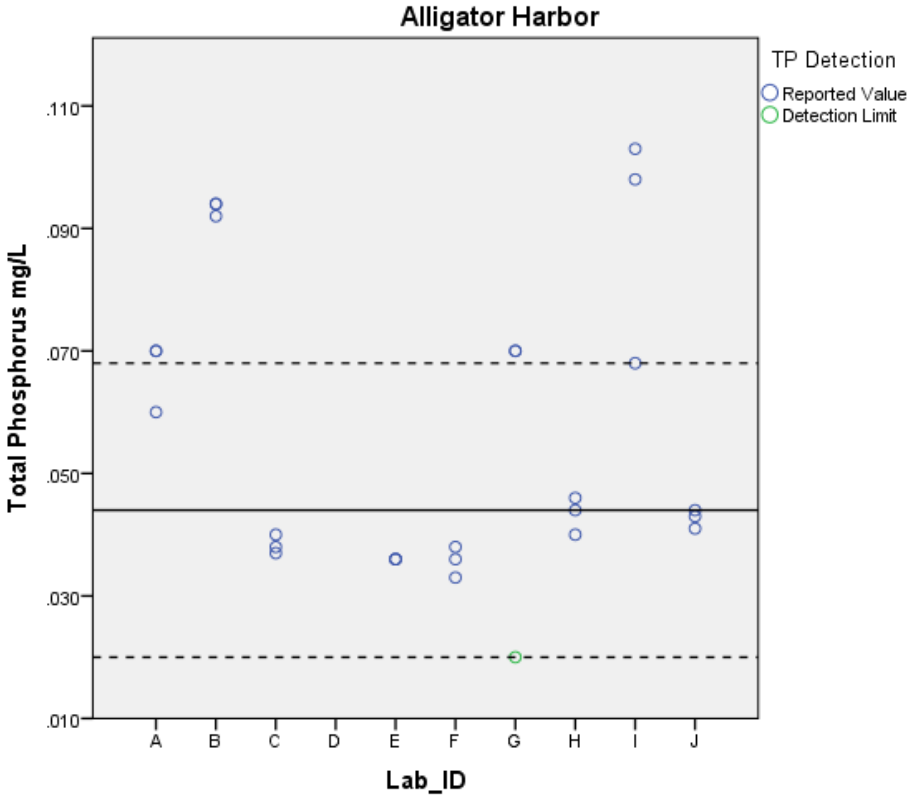


Figure 12. Scatter-plot of TP values and one detection limit obtained by nine laboratories for Alligator Harbor. The solid line indicates the overall median, and the dashed lines indicate +/- 1 F-pseudosigma.

Hypothesis Test Summary				
	Null Hypothesis	Test	Sig.	Decision
1	The distribution of Total Phosphorus 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 Total Phosphorus mg/L

		Subset				
		1	2	3	4	5
Sample[1]	J	4.000				
	H	4.333	4.333			
	F	7.833	7.833			
	E	12.000	12.000	12.000		
	A	13.167	13.167	13.167		
	C		16.000	16.000		
	I			20.167	20.167	
	G				22.500	
	B					26.000
Test Statistic		9.139	9.241	7.256	1.818	.[2]
Sig. (2-sided test)		.058	.055	.064	.178	.
Adjusted Sig. (2-sided test)		.112	.108	.153	.624	.

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 35. Kruskal-Wallis and nonparametric post hoc inter-laboratory comparisons for TP for FSU CML.

Hypothesis Test Summary				
	Null Hypothesis	Test	Sig.	Decision
1	The distribution of Total Phosphorus 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 Total Phosphorus mg/L

		Subset			
		1	2	3	4
Sample[1]	E	3.500			
	F	4.000			
	C	7.667	7.667		
	J		12.167	12.167	
	H		12.667	12.667	12.667
	A			18.333	18.333
	G				19.500
	I				22.667
	B				23.000
Test Statistic		4.183	4.949	5.582	9.467
Sig. (2-sided test)		.123	.084	.061	.050
Adjusted Sig. (2-sided test)		.356	.254	.190	.098

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.

Table 36. Kruskal-Wallis test and results of nonparametric inter-laboratory comparisons of TP for Alligator Harbor.

Total Phosphorus mg/L

Tukey-Kramer[a,b]

Method ID	N	Subset for alpha = 0.05	
		1	2
EPA 365.1	15	.14107	
Lachat 10-115-01-1-C	3	.15333	
EPA 365.4	9		.18889
Sig.		.229	1.000

Means for groups in homogeneous subsets are displayed.
a. Uses Harmonic Mean Sample Size = 5.870.
b. The group sizes are unequal. The harmonic mean of the group sizes is used. Type I error levels are not guaranteed.

Table 37. Post hoc comparisons for TP values by method for FSU CML.

Multiple Comparisons

Dependent Variable: Total Phosphorus mg/L

	(I) Method ID	(J) Method ID	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
						Lower Bound	Upper Bound
Dunnett's T[3]	EPA 365.1	EPA 365.4	-.039578*	.008650	.005	-.06502	-.01413
		Lachat 10-115-01-1-C	-.027467*	.003472	.021	-.04614	-.00879
	EPA 365.4	EPA 365.1	.039578*	.008650	.005	.01413	.06502
		Lachat 10-115-01-1-C	.012111	.009219	.499	-.01411	.03833
	Lachat 10-115-01-1-C	EPA 365.1	.027467*	.003472	.021	.00879	.04614
		EPA 365.4	-.012111	.009219	.499	-.03833	.01411

Method ID	N	Subset for alpha = 0.05	
		1	2
EPA 365.1	15	.03920	
Lachat 10-115-01-1-C	3		.06667
EPA 365.4	9		.07878

*. The mean difference is significant at the 0.05 level.

Table 38. Post hoc comparisons for TP values by method for all reported values for Alligator Harbor.

F. Orthophosphate. Twenty-six of the 27 reported values for FSU CML were within acceptable ranges. Lab A reported the only value outside acceptable ranges; this was a statistical outlier (0.111 mg/L). The %F-pseudosigma value was very low (less than 10%), indicating a high degree of precision among laboratories. Of the 27 reported values, 74% were within 1 F-pseudosigma and 96% were within 2 F-pseudosigma. There was no statistically significant difference between use of methods EPA 365.1, SM 4500 P E and SM 4500 P F, whereas results from USGS I-2601-90 were significantly greater than those using the three previous methods; results obtained from Lachat 10-115-01-1-I were significantly higher than all other methods.

At Alligator Harbor, six of the 27 results were reported values; the other 78% were reported as qualifiers. The MDLs ranged from 0.0019 to 0.009 mg/L; and the PQLs for Labs A and G ranged from 0.005 to 0.04 mg/L. There were no values reported as less than detection/quantitation limits that were determined to be false negatives. Methods EPA 365.1 and USGS I-2601-90 were the only methods to report values. No other analyses were conducted for OP for Alligator Harbor. See Figures 13 & 14 and Tables 39 – 45 for scatter-plots of values obtained by individual laboratories, F-pseudosigma values, summary statistics, inter-laboratory comparisons, and method comparisons.

OP				
	FSU CML			
	F-pseudosigma	**% F-pseudosigma**	**Median**	**Range**
	0.007	8.24%	0.090	0.032
Method	**N**	**Mean**	**Median**	**Range**
EPA 365.1	12	0.087	0.086	0.015
Lachat 10-115-01-1-I	3	0.102	0.098	0.014
SM 4500 P E	3	0.083	0.083	0.002
SM 4500 P F	6	0.088	0.088	0.004
USGS I-2601-90	3	0.094	0.094	0.001
	Alligator Harbor			
	F-pseudosigma	**% F-pseudosigma**	**Median**	**Range**
	0.002	28.54%	0.006	0.003
Method	**N**	**Mean**	**Median**	**Range**
EPA 365.1	12 (nine non-values)	0.005	0.005	0.001
Lachat 10-115-01-1-I	3	All Non-detect	N/A	N/A
SM 4500 P E	3	All Non-detect	N/A	N/A
SM 4500 P F	6	All Non-detect	N/A	N/A
USGS I-2601-90	3	0.007	0.007	0.001

Table 39. F-pseudosigma values for OP.

OP

Lab ID	FSU CML N	FSU CML Lab Median	FSU CML Range	FSU CML Mean Z-value	Alligator Harbor N	Alligator Harbor Lab Median	Alligator Harbor Range	Alligator Harbor Mean Z-value
A	3	0.098	0.014	1.71	3*	NR	NR	NR
B	3	0.090	0.000	0.00	3*	NR	NR	NR
C	3	0.094	0.001	0.62	3	0.007	0.001	N/A
E	3	0.085	0.001	0.67	3	0.005	0.001	N/A
F	3	0.086	0.000	0.57	3*	NR	NR	NR
G	3	0.090	0.010	0.48	3*	NR	NR	NR
H	3	0.082	0.003	1.29	3*	NR	NR	NR
I	3	0.083	0.002	1.00	3*	NR	NR	NR
J	3	0.094	0.001	0.52	3*	NR	NR	NR

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

Table 40. Summary statistics and Z-values by Laboratory for OP.

OP		
Method	**MDL Range**	**PQL Range**
All	0.0019 - 0.009	0.005 - 0.04
EPA 365.1	0.0019 - 0.008	0.01 - 0.04
Lachat 10-115-01-1-I	0.0025	0.005
SM 4500 P E	0.008	0.032
SM 4500 P F	0.004 - 0.009	0.016 - 0.036
USGS I-2601-90	0.004	Not Reported

Table 41. Methods and detection/quantitation limits 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	.10200	.007810	.004509	.08260	.12140	.097	.111
B	3	.09000	.000000	.000000	.09000	.09000	.090	.090
C	3	.09433	.000577	.000333	.09290	.09577	.094	.095
E	3	.08533	.000577	.000333	.08390	.08677	.085	.086
F	3	.08600	.000000	.000000	.08600	.08600	.086	.086
G	3	.08667	.005774	.003333	.07232	.10101	.080	.090
H	3	.08100	.001732	.001000	.07670	.08530	.079	.082
I	3	.08300	.001000	.000577	.08052	.08548	.082	.084
J	3	.09367	.000577	.000333	.09223	.09510	.093	.094
Total	27	.08911	.006913	.001330	.08638	.09185	.079	.111

Table 42. Descriptive statistics by laboratory for OP for FSU CML.

Descriptives

Orthophosphate mg/L

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
C	3	.00680	.000286	.000165	.00609	.00751	.006	.007
E	3	.00467	.000577	.000333	.00323	.00610	.004	.005
Total	6	.00573	.001238	.000505	.00443	.00703	.004	.007

Table 43. Descriptive statistics by laboratory for OP for Alligator Harbor.

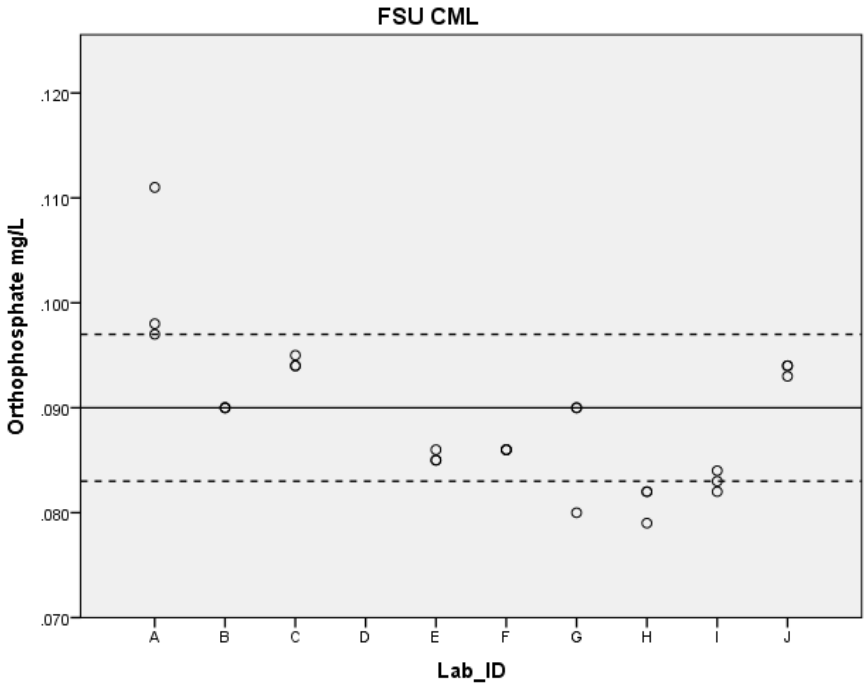


Figure 13. Scatter-plot of OP values obtained by nine laboratories for FSU CML. The solid line indicates the overall median, and the dashed lines indicate +/- 1 F-pseudosigma.

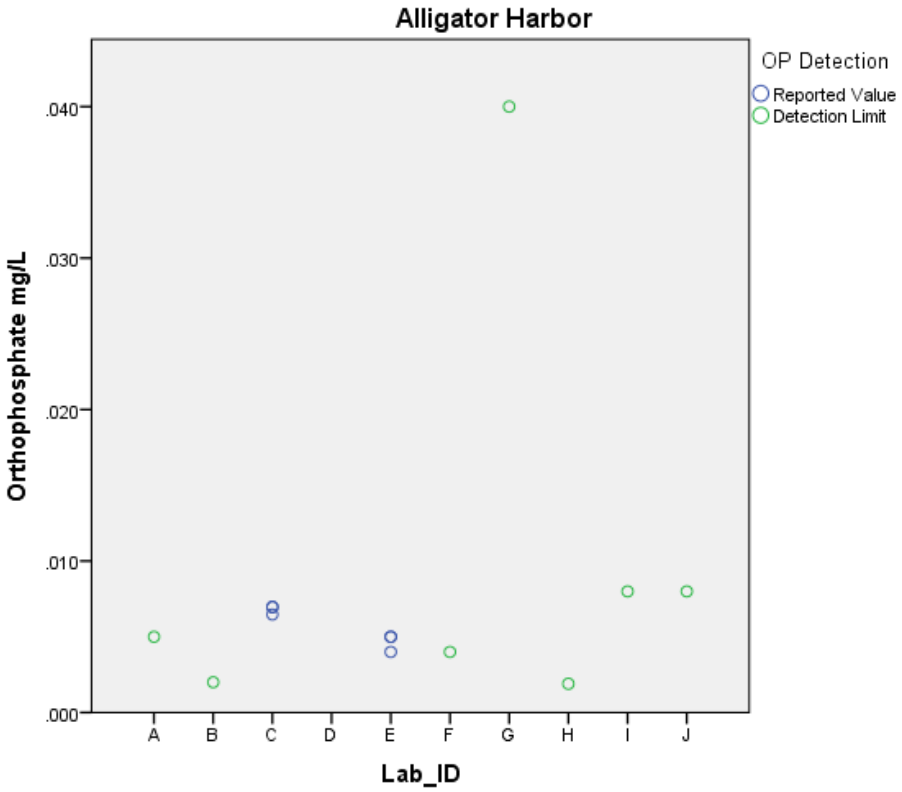


Figure 14. Scatter-plot of OP values and detection/quantitation limits obtained by nine laboratories for Alligator Harbor.

Hypothesis Test Summary				
	Null Hypothesis	Test	Sig.	Decision
1	The distribution of Orthophosphate 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 Orthophosphate mg/L					
		Subset			
		1	2	3	4
Sample[1]	H	3.000			
	I	5.667	5.667		
	E	9.500	9.500		
	G	11.333	11.333		
	F	11.500	11.500		
	B		16.000		
	J			20.667	
	C			22.333	
	A				26.000
Test Statistic		7.781	8.495	1.667	.[2]
Sig. (2-sided test)		.100	.075	.197	.
Adjusted Sig. (2-sided test)		.190	.144	.666	.

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 44. Kruskal-Wallis test and results of nonparametric pair-wise comparisons of OP for FSU CML.

Hypothesis Test Summary				
	Null Hypothesis	Test	Sig.	Decision
1	The medians of Orthophosphate mg/L are the same across categories of OP_ID.	Independent-Samples Median Test	.002	Reject the null hypothesis.
2	The distribution of Orthophosphate mg/L is the same across categories of OP_ID.	Independent-Samples Kruskal-Wallis Test	.004	Reject the null hypothesis.

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

Homogeneous Subsets based on Orthophosphate mg/L				
		Subset		
		1	2	3
Sample[1]	SM 4500 P E	5.667		
	EPA 365.1	11.125		
	SM 4500 P F	13.750		
	USGS I-2601-90		22.333	
	Lachat 10-115-01-1-I			26.000
Test Statistic		3.477	.[2]	.[2]
Sig. (2-sided test)		.176	.	.
Adjusted Sig. (2-sided test)		.275	.	.

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 45. Kruskal-Wallis test and results of nonparametric pair-wise comparisons of OP by method for FSU CML.

G. Total Organic Carbon. Although there were only eighteen reported values for TOC at both locations (vs. the 21 needed) analyses were run; however, caution should be exercised in interpreting the results due to the lack of statistical power. Fifteen of the eighteen reported values for FSU CML were within acceptable ranges. Lab A reported all three values outside acceptable ranges. No results were reported as below detection limits. The %F-pseudosigma value was moderate (>20% and <30%), indicating a lack of precision among laboratories. Of the eighteen reported values, 78% were within 1 F-pseudosigma and 83% were within 2 F-pseudosigma. There was no statistical difference between the three methods used.

At Alligator Harbor, fourteen of the eighteen values were within acceptable ranges. Lab A reported all values outside acceptable ranges, Lab G reported one. The %F-pseudosigma value was very low (less than 10%), indicating a high degree of precision among the laboratories. Of the eighteen reported values, 50% were within 1 F-pseudosigma and 78% were within 2 F-pseudosigma. There was no statistical difference between the three methods used. At both sites, Lab A reported values that were 1.6 – 2.7 times greater than all the other laboratories' results, and may be due to a faulty SO_3 scrubber. See Figures 14 & 17 and Tables 46 – 51 for scatter-plots of values obtained by individual laboratories, F-pseudosigma values, summary statistics, inter-laboratory comparisons, and method comparisons.

TOC				
	FSU CML			
	F-pseudosigma	**% F-pseudosigma**	**Median**	**Range**
	0.014	25.36%	3.58	5.30
Method	**N**	**Mean**	**Median**	**Range**
EPA 415.1	3	3.43	3.49	0.32
SM 5310 B	9	3.87	3.70	1.39
SM 5310 C	6	5.50	5.30	5.30
	Alligator Harbor			
	F-pseudosigma	**% F-pseudosigma**	**Median**	**Range**
	0.019	9.62%	5.14	8.70
Method	**N**	**Mean**	**Median**	**Range**
EPA 415.1	3	5.01	4.95	0.18
SM 5310 B	9	5.71	5.93	1.50
SM 5310 C	6	7.60	7.95	8.70

Table 46. F-pseudosigma values for TOC.

TOC

	FSU CML				Alligator Harbor			
Lab ID	N	Lab Median	Range	Mean Z-value	N	Lab Median	Range	Mean Z-value
A	3	8.10	0.70	6.31	3	11.00	0.80	6.12
B	3	4.20	0.77	1.16	3	6.20	0.10	1.08
F	3	3.51	0.03	0.11	3	5.14	0.86	0.24
G	3	3.00	0.00	0.83	3	4.00	2.00	1.15
H	3	3.49	0.32	0.21	3	4.95	0.18	0.13
J	3	3.70	0.30	0.22	3	5.10	1.50	0.40

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

Table 47. 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	8.0000	.36056	.20817	7.1043	8.8957	7.60	8.30
B	3	4.3900	.41869	.24173	3.3499	5.4301	4.10	4.87
F	3	3.5000	.01732	.01000	3.4570	3.5430	3.48	3.51
G	3	3.0000	.00000	.00000	3.0000	3.0000	3.00	3.00
H	3	3.4300	.16823	.09713	3.0121	3.8479	3.24	3.56
J	3	3.7333	.15275	.08819	3.3539	4.1128	3.60	3.90
Total	18	4.3422	1.74896	.41223	3.4725	5.2120	3.00	8.30

Table 48. Descriptive statistics by laboratory for TOC from FSU CML.

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	11.2000	.43589	.25166	10.1172	12.2828	10.90	11.70
B	3	6.2133	.05132	.02963	6.0859	6.3408	6.17	6.27
F	3	5.3800	.47760	.27574	4.1936	6.5664	5.07	5.93
G	3	4.0000	1.00000	.57735	1.5159	6.4841	3.00	5.00
H	3	5.0100	.10392	.06000	4.7518	5.2682	4.95	5.13
J	3	5.5333	.83865	.48419	3.4500	7.6167	5.00	6.50
Total	18	6.2228	2.44203	.57559	5.0084	7.4372	3.00	11.70

Table 49. Descriptive statistics by laboratory for TOC from Alligator Harbor.

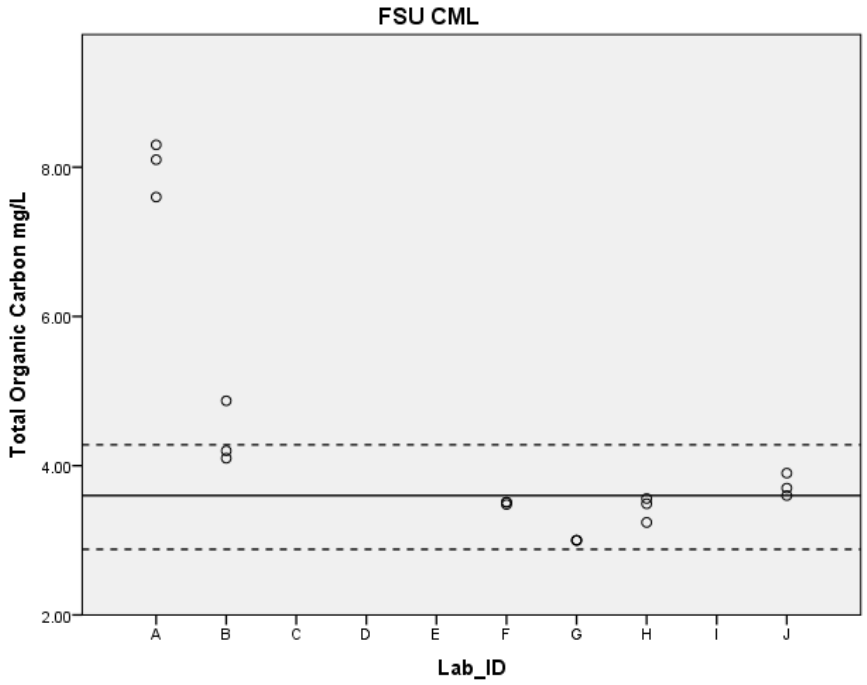


Figure 14. Scatter-plot of TOC values obtained by six laboratories for FSU CML. The solid line indicates the overall median, and the dashed lines indicate +/- 1 F-pseudosigma.

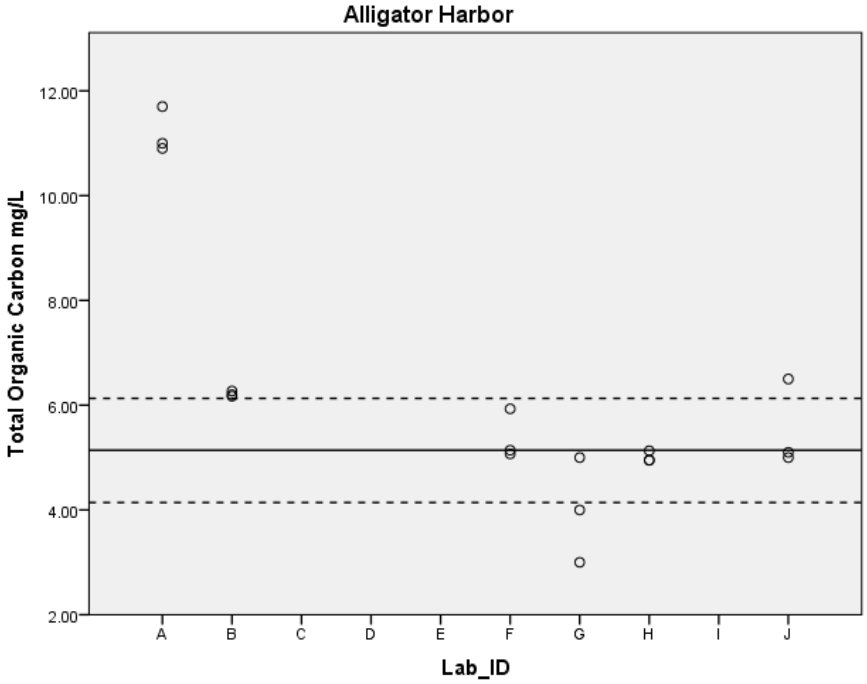


Figure 15. Scatter-plot of TOC values obtained by six laboratories for Alligator Harbor. The solid line indicates the overall median, and the dashed lines indicate +/- 1 F-pseudosigma.

Hypothesis Test Summary				
	Null Hypothesis	Test	Sig.	Decision
1	The distribution of Total Organic Carbon mg/L is the same across categories of Lab_ID.	Independent-Samples Kruskal-Wallis Test	.006	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	2.000			
	H	6.333	6.333		
	F	6.667	6.667		
	J		11.000		
	B			14.000	
	A				17.000
Test Statistic		5.658	5.468	.[2]	.[2]
Sig. (2-sided test)		.059	.065	.	.
Adjusted Sig. (2-sided test)		.184	.201	.	.

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 50. Kruskal-Wallis test and results of nonparametric pair-wise comparisons of TOC by laboratory for all reported values for FSU CML.

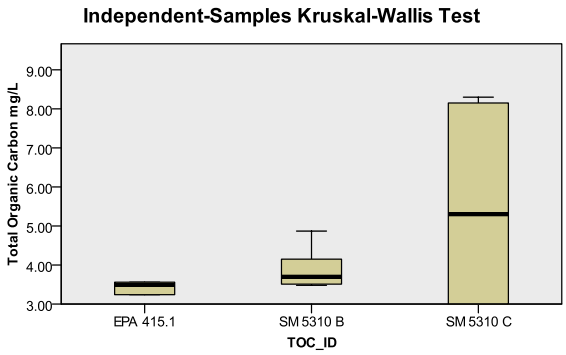
Total Organic Carbon mg/L

	Lab_ID	N	Subset for alpha = 0.05		
			1	2	3
Gabriel[a]	G	3	4.0000		
	H	3	5.0100	5.0100	
	F	3	5.3800	5.3800	
	J	3	5.5333	5.5333	
	B	3		6.2133	
	A	3			11.2000
	Sig.		.098	.291	1.000

Means for groups in homogeneous subsets are displayed.

a. Uses Harmonic Mean Sample Size = 3.000.

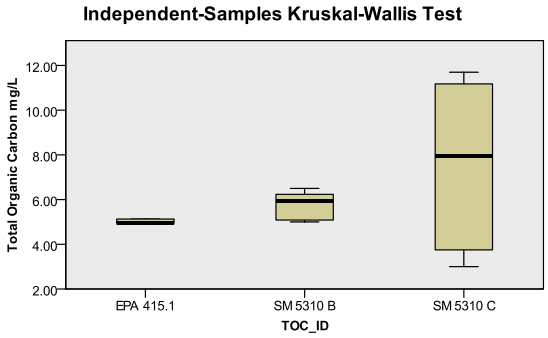
Table 51. Post hoc inter-laboratory comparisons for TOC from Alligator Harbor.



Total N	18
Test Statistic	1.415
Degrees of Freedom	2
Asymptotic Sig. (2-sided test)	.493

1. The test statistic is adjusted for ties.
2. Multiple comparisons are not performed because the overall test does not show significant differences across samples.

Figure 16. Results of Kruskal-Wallis test of TOC by method for FSU CML.



Total N	18
Test Statistic	2.259
Degrees of Freedom	2
Asymptotic Sig. (2-sided test)	.323

1. The test statistic is adjusted for ties.
2. Multiple comparisons are not performed because the overall test does not show significant differences across samples.

Figure 17. Results of Kruskal-Wallis test of TOC by method for Alligator Harbor.

H. Chlorophyll a. Twenty-five of the 27 reported values for FSU CML were within acceptable ranges. Labs E and I each reported one value outside acceptable ranges. Lab I reported one statistical outlier (12 µg/L). Lab I's results were also highly variable. The %F-pseudosigma value was large (greater than 30%), indicating a lack of precision among laboratories. Of the 27 reported values, 81% were within 1 F-pseudosigma and 93% were within 2 F-pseudosigma. There was no statistical difference in ChlA methods at this site.

At Alligator Harbor, all 27 values were within acceptable ranges. There were no outliers or non-values reported. The %F-pseudosigma value was moderate (between 20 and 30%), indicating a lack of precision among the laboratories. Of the 27 reported values, 78% were within 1 F-pseudosigma and 100% were within 2 F-pseudosigma. Results reported for method SM 10200 H were significantly greater than those reported for EPA 445.0. See Figures 18 - 20 and Tables 52 – 58 for scatter-plots of values obtained by individual laboratories, F-pseudosigma values, summary statistics, inter-laboratory comparisons, and method comparisons.

Chlorophyll a				
	FSU CML			
	F-pseudosigma	**% F-pseudosigma**	**Median**	**Range**
	1.96	36.79%	3.58	5.30
Method	**N**	**Mean**	**Median**	**Range**
EPA 445.0	9	6.28	6.60	2.75
SM 10200 H	18	5.56	4.89	10.93
	Alligator Harbor			
	F-pseudosigma	**% F-pseudosigma**	**Median**	**Range**
	3.11	28.30%	11.00	8.75
Method	**N**	**Mean**	**Median**	**Range**
EPA 445.0	9	8.17	8.00	2.14
SM 10200 H	18	11.44	11.85	8.75

Table 52. F-pseudosigma values for ChlA.

ChlA

	FSU CML				Alligator Harbor			
Lab ID	N	Lab Median	Range	Mean Z-value	N	Lab Median	Range	Mean Z-value
A	3	6.60	0.60	0.61	3	8.00	0.60	1.03
B	3	6.90	1.70	0.81	3	12.70	1.50	0.60
D	3	5.12	1.06	0.11	3	8.34	1.44	0.77
E	3	4.27	4.27	0.91	3	12.82	4.27	0.81
F	3	4.32	0.65	0.42	3	11.93	0.16	0.28
G	3	7.25	0.37	0.94	3	7.78	1.82	0.94
H	3	4.84	0.43	0.26	3	8.07	0.90	1.01
I	3	9.00	5.00	2.04	3	11.00	0.00	0.00
J	3	4.20	0.20	0.58	3	13.00	6.40	0.17

Table 53. Summary statistics 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	6.5333	.30551	.17638	5.7744	7.2922	6.20	6.80
B	3	6.9333	.85049	.49103	4.8206	9.0461	6.10	7.80
D	3	5.1200	.53000	.30600	3.8034	6.4366	4.59	5.65
E	3	3.5600	2.22178	1.28274	-1.9592	9.0792	1.07	5.34
F	3	4.5167	.36692	.21184	3.6052	5.4282	4.29	4.94
G	3	7.1867	.19296	.11141	6.7073	7.6660	6.97	7.34
H	3	4.8367	.21502	.12414	4.3025	5.3708	4.62	5.05
I	3	9.3333	2.51661	1.45297	3.0817	15.5849	7.00	12.00
J	3	4.2000	.10000	.05774	3.9516	4.4484	4.10	4.30
Total	27	5.8022	2.01651	.38808	5.0045	6.5999	1.07	12.00

Table 54. Descriptive statistics by laboratory for ChlA for FSU CML.

Descriptives

Chlorophyll a µg/L

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
A	3	7.8000	.34641	.20000	6.9395	8.6605	7.40	8.00
B	3	12.8667	.76376	.44096	10.9694	14.7640	12.20	13.70
D	3	8.6133	.75791	.43758	6.7306	10.4961	8.03	9.47
E	3	13.5300	2.22178	1.28274	8.0108	19.0492	11.75	16.02
F	3	11.8833	.08963	.05175	11.6607	12.1060	11.78	11.94
G	3	8.0867	.94796	.54731	5.7318	10.4415	7.33	9.15
H	3	7.8367	.49329	.28480	6.6113	9.0621	7.27	8.17
I	3	11.0000	.00000	.00000	11.0000	11.0000	11.00	11.00
J	3	11.5333	3.44287	1.98774	2.9808	20.0859	7.60	14.00
Total	27	10.3500	2.50514	.48211	9.3590	11.3410	7.27	16.02

Table 55. Descriptive statistics by laboratory for ChlA for Alligator Harbor.

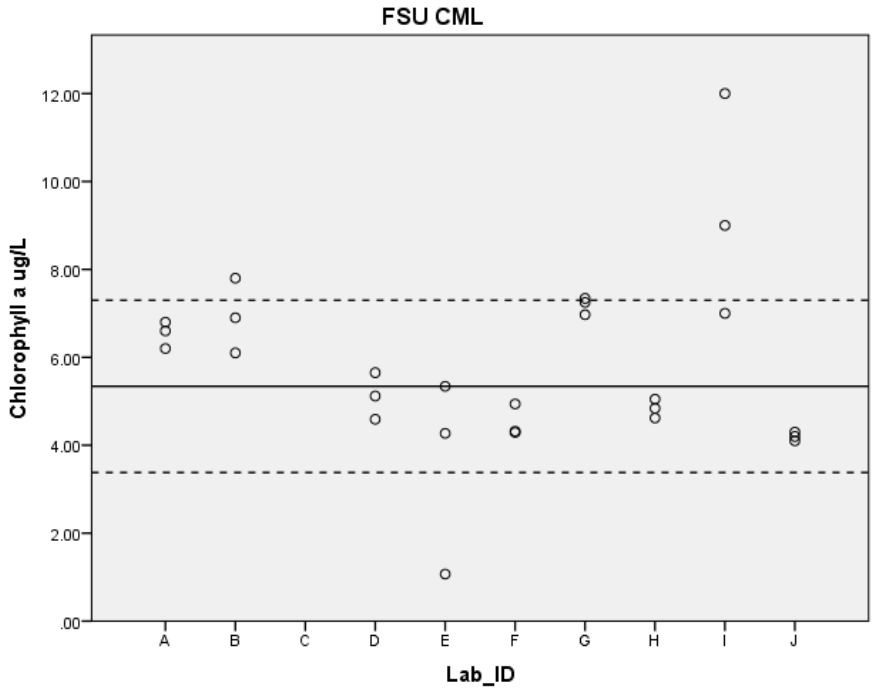


Figure 18. Scatter-plot of ChlA values obtained by nine laboratories for FSU CML. The solid line indicates the overall median, and the dashed lines indicate +/- 1 F-pseudosigma.

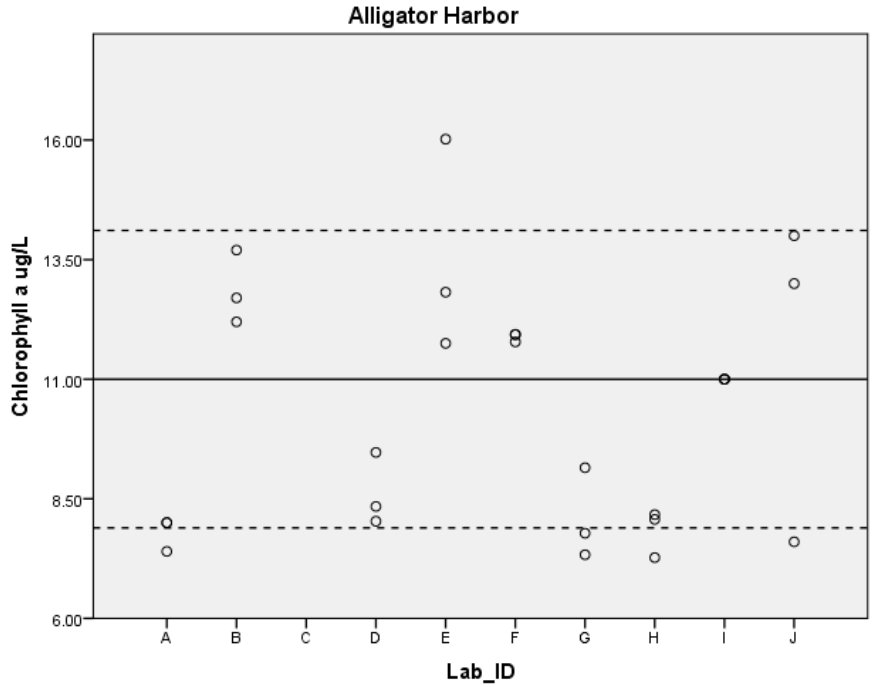


Figure 19. Scatter-plot of ChlA values obtained by nine laboratories for Alligator Harbor. The solid line indicates the overall median, and the dashed lines indicate +/- 1 F-pseudosigma.

Hypothesis Test Summary				
	Null Hypothesis	Test	Sig.	Decision
1	The distribution of Chlorophyll a µg/L is the same across categories of Lab_ID.	Independent-Samples Kruskal-Wallis Test	.004	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
Sample[1]	J	3.667			
	E	6.333	6.333		
	F	7.667	7.667		
	H	10.333	10.333		
	D	12.000	12.000	12.000	
	A		18.000	18.000	18.000
	B			20.333	20.333
	G				22.667
	I				25.000
Test Statistic		6.467	8.633	5.600	6.282
Sig. (2-sided test)		.167	.071	.061	.099
Adjusted Sig. (2-sided test)		.306	.137	.189	.229

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

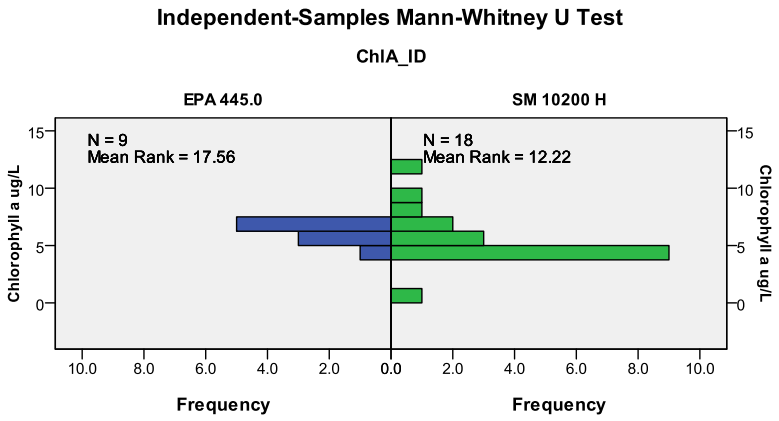
[1]Each cell shows the sample average rank of Chlorophyll a µg/L.

Table 56. Kruskal-Wallis test and results of nonparametric inter-laboratory comparisons of ChlA from FSU CML.

Hypothesis Test Summary				
	Null Hypothesis	Test	Sig.	Decision
1	The distribution of Chlorophyll a µg/L is the same across categories of Lab_ID.	Independent-Samples Kruskal-Wallis Test	.019	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
Sample[1]	A	5.333		
	G	6.333		
	H	6.667	6.667	
	D	10.667	10.667	10.667
	I	15.000	15.000	15.000
	J	18.000	18.000	18.000
	F	19.000	19.000	19.000
	E		22.333	22.333
	B			22.667
Test Statistic		12.022	10.494	9.413
Sig. (2-sided test)		.061	.062	.094
Adjusted Sig. (2-sided test)		.087	.102	.151
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.				

Table 57. Kruskal-Wallis test and results of nonparametric inter-laboratory comparisons of ChlA for Alligator Harbor.



Total N	27
Mann-Whitney U	113.000
Wilcoxon W	158.000
Test Statistic	113.000
Standard Error	19.442
Standardized Test Statistic	1.646
Asymptotic Sig. (2-sided test)	.100
Exact Sig. (2-sided test)	.106

Figure 20. Results of Mann-Whitney test of ChlA by method for FSU CML.

Group Statistics

Method ID		N	Mean	Std. Deviation	Std. Error Mean
Chlorophyll a µg/L	SM 10200 H	18	11.4417	2.35906	.55604
	EPA 445.0	9	8.1667	.72519	.24173

Independent Samples Test

		Levene's Test for Equality of Variances		t-test for Equality of Means						
									95% Confidence Interval of the Difference	
		F	Sig.	t	df	Sig. (2-tailed)	Mean Difference	Std. Error Difference	Lower	Upper
Chlorophyll a µg/L	Equal variances assumed	5.756	**.024**	4.035	25	.000	3.27500	.81164	1.60339	4.94661
	Equal variances not assumed			**5.402**	**22.338**	**.000**	**3.27500**	**.60631**	**2.01870**	**4.53130**

Table 58. Results of t-test comparisons of ChlA by method for Alligator Harbor.

I. Biochemical Oxygen Demand. Ten of the eighteen results for FSU CML were reported as values; the other 44% were reported as qualifiers. The MDLs for all participating laboratories ranged from 0.1 to 2 mg/L; the PQLs for Labs A, E and G ranged from 2 to 3 mg/L. No other analyses were conducted for BOD for FSU CML.

At Alligator Harbor, Fifteen of the eighteen results were reported values; the other 17% were reported as qualifiers. The MDLs for all participating laboratories ranged from 0.1 to 2 mg/L; the PQLs for Labs A, E and G ranged from 2 to 3 mg/L. There were no values reported as less than detection/quantitation limits that were determined to be false negatives for either site. No other analyses were conducted for BOD for Alligator Harbor. See Figures 21 - 23 and Tables 59 – 63 for scatter-plots of values obtained by individual laboratories, F-pseudosigma values, summary statistics, inter-laboratory comparisons, and method comparisons.

Biochemical Oxygen Demand					
	F-pseudosigma	**% F-pseudosigma**	**Mean**	**Median**	**Range**
FSU CML	0.11	5.56%	2.05	2.00	1.80
Alligator Harbor	0.96	24.71%	3.17	3.40	1.80

Table 59. F-pseudosigma values for BOD.

BOD

	FSU CML				Alligator Harbor			
Lab ID	N	Lab Median	Range	Mean Z-value	N	Lab Median	Range	Mean Z-value
A	3	NR	NR	NR	3	2.30	0.40	N/A
B	3	1.90	0.80	N/A	3	2.50	0.10	N/A
E	3*	2.10	N/A	N/A	3	3.60	0.30	N/A
G	3	NR	NR	NR	3	NR	NR	NR
I	3	2.00	1.00	N/A	3	4.00	0.00	N/A
J	3	2.10	0.20	N/A	3	3.40	0.50	N/A

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

Table 60. Summary statistics and Z-values by Laboratory for BOD.

BOD		
Method	**MDL Range**	**PQL Range**
SM 5210 B	0.1 - 2	0.4 - 3

Table 61. Method and detection/quantitation limits 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		
B	3	1.7000	.43589	.25166	.6172	2.7828	1.20	2.00
E	1	2.1000	N/A	N/A	N/A	N/A	2.10	2.10
I	3	2.3333	.57735	.33333	.8991	3.7676	2.00	3.00
J	3	2.1000	.10000	.05774	1.8516	2.3484	2.00	2.20
Total	10	2.0500	.43269	.13683	1.7405	2.3595	1.20	3.00

Table 62. Descriptive statistics by laboratory for BOD for FSU CML.

Descriptives

Biochemical Oxygen Demand mg/L

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
A	3	2.3667	.20817	.12019	1.8496	2.8838	2.20	2.60
B	3	2.4667	.05774	.03333	2.3232	2.6101	2.40	2.50
E	3	3.6333	.15275	.08819	3.2539	4.0128	3.50	3.80
I	3	4.0000	.00000	.00000	4.0000	4.0000	4.00	4.00
J	3	3.3667	.25166	.14530	2.7415	3.9918	3.10	3.60
Total	15	3.1667	.68208	.17611	2.7889	3.5444	2.20	4.00

Table 63. Descriptive statistics by laboratory for BOD for Alligator Harbor.

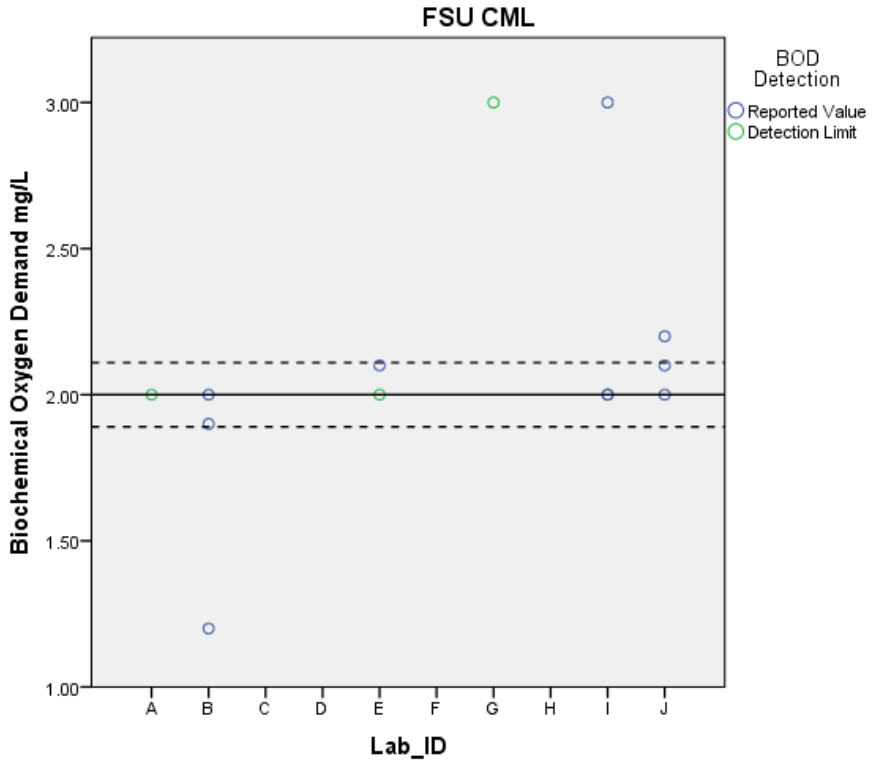


Figure 21. Scatter-plot of BOD values and detection/quantitation limits obtained by six laboratories for FSU CML. The solid line indicates the overall median, and the dashed lines indicate +/- 1 F-pseudosigma.

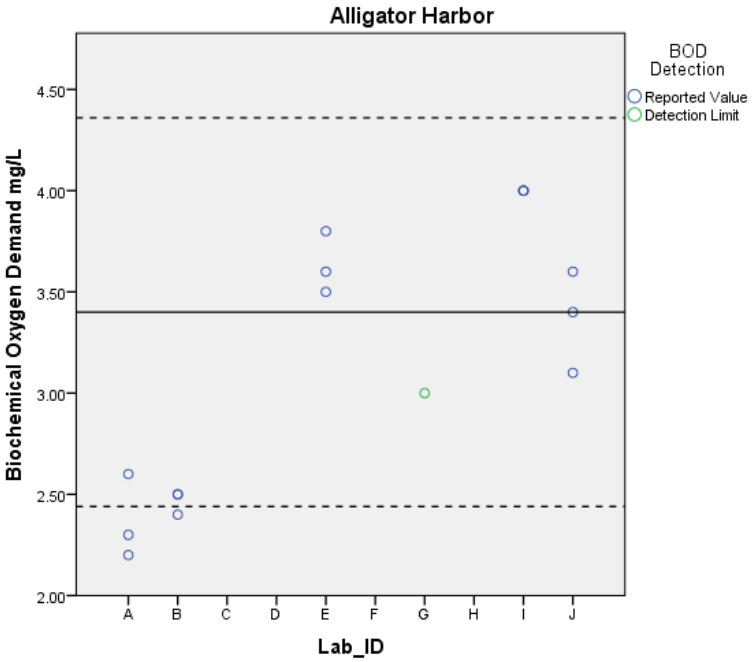
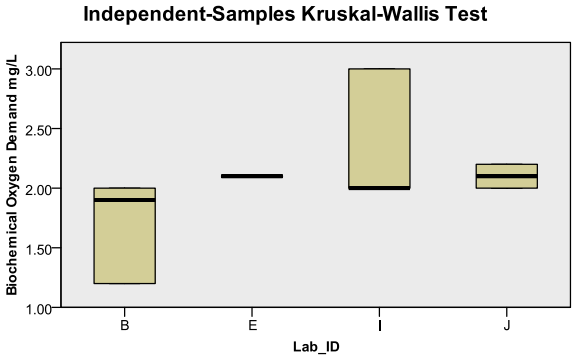


Figure 22. Scatter-plot of BOD values and detection/quantitation limits obtained by six laboratories for Alligator Harbor. The solid line indicates the overall median, and the dashed lines indicate +/- 1 F-pseudosigma.



Total N	10
Test Statistic	4.656
Degrees of Freedom	3
Asymptotic Sig. (2-sided test)	.199

1. The test statistic is adjusted for ties.
2. Multiple comparisons are not performed because the overall test does not show significant differences across samples.

Figure 23. Results of Kruskal-Wallis test of BOD by laboratory for FSU CML.

J. Carbonaceous Biochemical Oxygen Demand. Seven of the eighteen results for FSU CML were reported as values; the other 61% were reported as qualifiers. The MDLs for all participating laboratories ranged from 0.2 to 2 mg/L; the PQLs for Labs A, E and G ranged from 2 to 3 mg/L. No other analyses were conducted for CBOD for FSU CML.

At Alligator Harbor, eleven of the eighteen results were reported values; the other 39% were reported as qualifiers. The MDLs for all participating laboratories ranged from 0.2 to 2 mg/L; the PQLs for Labs A, E and G ranged from 2 to 3 mg/L. There were no values reported as less than detection/quantitation limits that were determined to be false negatives from either location. No other analyses were conducted for CBOD for Alligator Harbor. See Figures 24 - 25 and Tables 64 – 68 for scatter-plots of values obtained by individual laboratories, F-pseudosigma values, summary statistics, inter-laboratory comparisons, and method comparisons.

Carbonaceous Biochemical Oxygen Demand				
	FSU CML			
	F-pseudosigma	**% F-pseudosigma**	**Median**	**Range**
	0.67	33.36%	2.00	1.10
Method	**N**	**Mean**	**Median**	**Range**
SM 5210 B	15	1.84	2.00	1.10
SM 5210 C	3	All Non-detect	N/A	N/A
	Alligator Harbor			
	F-pseudosigma	**% F-pseudosigma**	**Median**	**Range**
	0.67	24.71%	2.70	1.20
Method	**N**	**Mean**	**Median**	**Range**
SM 5210 B	15	2.55	2.70	1.20
SM 5210 C	3	All Non-detect	N/A	N/A

Table 64. F-pseudosigma values for CBOD.

CBOD

	FSU CML				Alligator Harbor			
Lab ID	N	Lab Median	Range	Mean Z-value	N	Lab Median	Range	Mean Z-value
A	3	NR	NR	NR	3	NR	NR	NR
B	3	2.20	0.90	N/A	3	2.70	0.30	N/A
E	3*	2.20	N/A	N/A	3	2.20	0.10	N/A
G	3	NR	NR	NR	3	NR	NR	NR
I	3	NR	NR	NR	3	2.00	0.00	N/A
J	3	1.90	0.90	N/A	3	3.10	0.40	N/A

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

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

CBOD		
Method	**MDL Range**	**PQL Range**
SM 5210 B	0.2 - 2	0.8 - 3
SM 5210 C	2	2

Table 66. Methods and detection/quantitation limits 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		
B	3	1.9000	.51962	.30000	.6092	3.1908	1.30	2.20
E	1	2.2000	N/A	N/A	N/A	N/A	2.20	2.20
J	3	1.6667	.49329	.28480	.4413	2.8921	1.10	2.00
Total	7	1.8429	.45774	.17301	1.4195	2.2662	1.10	2.20

Table 67. Descriptive statistics by laboratory for CBOD from FSU CML.

Descriptives

Carbonaceous Biochemical Oxygen Demand mg/L

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
B	3	2.8000	.17321	.10000	2.3697	3.2303	2.70	3.00
E	3	2.1667	.05774	.03333	2.0232	2.3101	2.10	2.20
I	2	2.0000	.00000	.00000	2.0000	2.0000	2.00	2.00
J	3	3.0333	.20817	.12019	2.5162	3.5504	2.80	3.20
Total	11	2.5455	.45687	.13775	2.2385	2.8524	2.00	3.20

Table 68. Descriptive statistics by laboratory for CBOD from Alligator Harbor.

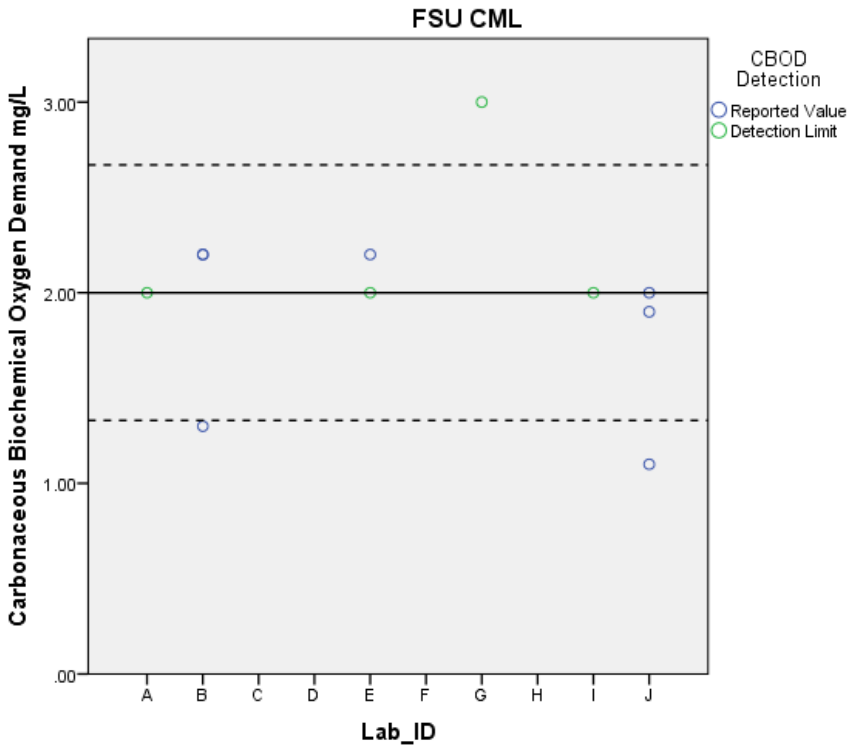


Figure 24. Scatter-plot of CBOD values and detection/quantitation limits obtained by six laboratories for FSU CML. The solid line indicates the overall median, and the dashed lines indicate +/- 1 F-pseudosigma.

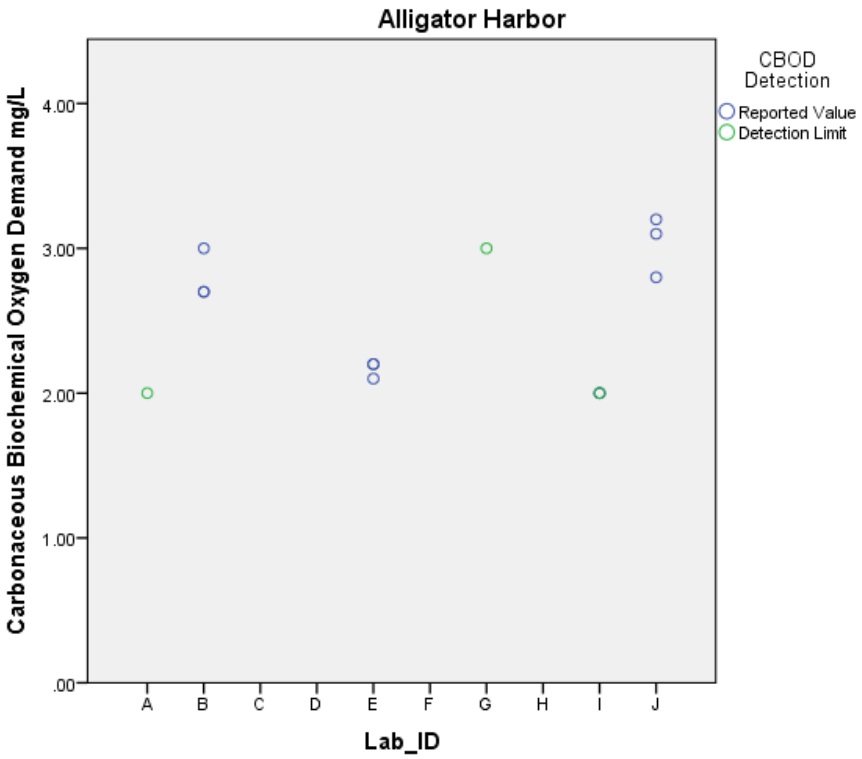


Figure 25. Scatter-plot of CBOD values and detection/quantitation limits obtained by six laboratories for Alligator Harbor.

4. Conclusions and Recommendations

Total Kjeldahl Nitrogen: There was little variability among laboratories for total Kjeldahl nitrogen from the unspiked aliquot, but was quite variable in the spiked aliquot. However, values from Lab E were highly variable from both sites, and values from Lab I were typically higher than all other laboratories' values. Detection and quantitation limits were not an issue for this analyte. The three methods used were statistically the same for the Alligator Harbor site; however, results for Lachat 10-107-06-2-D were significantly lower at the FSU CML site.

Ammonia: Ammonia was extremely variable at lower concentrations. At higher concentrations, the variability among results was reduced but remained quite variable. Results reported from Lab I were very high for both locations and may be due to the method of digestion. Detection and quantitation limits need to be addressed, as more than one-half of the results from Alligator Harbor (the unspiked site) were non-values. Results from the FSU CML aliquot showed method Lachat 10-107-06-1-J to be significantly lower than methods EPA 350.1 and SM 4500 NH3 G (the two of which were statistically the same). Analyses of methods were not run for Alligator Harbor due to the large number of non-values reported; however, EPA 350.1 was the only method to report values.

Total Nitrite + Nitrate: There was little variability among most results for NO_x for FSU CML. Lab G reported two statistical outliers for FSU CML; results for Lab G at this site were highly variable. Results reported by Lab A from Alligator Harbor were approximately an order of magnitude higher than the other laboratories' values, and may represent typographical errors. Detection and quantitation limits were issues for this analyte in the unspiked sample from Alligator Harbor, as more than half of the results were non-values.

Dissolved Nitrite: There was very little variability in results for DNO_2 from the spiked aliquot. Labs G and I reported values outside acceptable ranges at this site. Method SM 4500 NO2 B was statistically lower than all other methods at FSU CML; EPA 353.2 was equivalent to both Lachat 10-107-04-1-C and USGS I-2540-90. At the low concentration site, the variability was very high, due mostly to the large number of non-values reported. Method EPA 353.2 was the only method to report values. Detection and quantitation limits need to be addressed, as nearly 80% of the results from Alligator Harbor were non-values.

Total Phosphorus: Results from the FSU CML site were all within acceptable ranges for TP. In addition, there were no outliers or non-values reported. Results obtained using Method EPA 365.4 were significantly higher than those obtained using the other methods at this site. Results from the Alligator Harbor site were more variable than those of the FSU CML site. Labs B and I reported values outside acceptable ranges, and Lab G reported a non-detect. At Alligator Harbor, results from method EPA 365.1 were statistically lower than those obtained from the other two methods. Other than the one non-detect, detection and quantitation limits were not an issue for this analyte during this round robin.

Orthophosphate: With the exception of one outlier reported by Lab A, results from the FSU CML site varied little. Results from three of the five methods employed at this site were statistically equivalent (EPA 365.1, SM 4500 P E and SM 4500 P F), whereas those from USGS I-2601-90 were significantly greater than the prior three methods; results obtained using Lachat 10-115-01-1-I were significantly higher than all other methods. At Alligator Harbor, nearly 80% of the results were reported as non-values. Methods EPA 365.1 and USGS I-2601-90 were the only methods to report values from this site. Detection and quantitation limits need to be addressed for OP.

Total Organic Carbon: There was little variability among laboratories, or within laboratories, for TOC; however, Lab A reported all values outside of acceptable ranges and 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. This is most likely due to the fact that results were reported as "chlorophyll a" and not either "chlorophyll a, corrected for phaeophytin" or "chlorophyll a, uncorrected for phaeophytin." This is evidenced by the fact that scatter-plots from both sites appear to be centered around two values (one high and one low) at each site. Lab E was highly variable at both sites. Lab I reported the only outlier from both sites. At FSU CML, there was no statistical difference in ChlA methods; however, at Alligator Harbor, results from method SM 10200 H were significantly greater than those reported for EPA 445.0.

Biochemical Oxygen Demand and Carbonaceous Biochemical Oxygen Demand: Very few values were reported for BOD and CBOD. In addition, few laboratories participated in analyzing the particular analyte. Therefore, detection and quantitation limits need to be addressed, as well as laboratory participation.

Overall: Although the data were quite similar among most laboratories, 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 within 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).

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

Helsel, D.R. 2012. Statistics for Censored Environmental Data Using Minitab® and R. 2nd Edition. John Wiley, Inc. New York, NY.

Hoaglin, D.C, F. Mosteller, and J.W. Tukey Eds. 1983. Understanding Robust and Exploratory Data Analysis. John Wiley, Inc. New York, NY.

Quality Assurance of Information in Marine Environmental Monitoring (QUASIMEME). 2012. QUASIMEME Laboratory Performance Studies. WEPAL. Netherlands.

Woodworth, M.T and B.F. Connor. 2003. Results of the U.S. Geological Survey's Analytical Evaluation Program for Standard Reference Samples Distributed in March 2003. U.S. Geological Survey, U.S. Department of Interior. OFR 03-261. Lakewood, CO.

GOMA Analytical Round Robin #5 Results - October 20, 2010

Samples collected from the Florida State University Coastal and Marine Laboratory, Florida

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	E	F	G	H	I	J
	0.540	0.853	0.900		0.955		0.850		1.260	0.890
	0.550	0.808	0.910		1.546		0.830		1.100	0.770
	0.500	0.827	0.866		1.319		0.890		1.160	0.750
Average:	**0.530**	**0.829**	**0.892**		**1.273**		**0.857**		**1.173**	**0.803**
Std. Dev.	**0.026**	**0.023**	**0.023**		**0.298**		**0.031**		**0.081**	**0.076**

Ammonia mg/L

	A	B	C	D	E	F	G	H	I	J
	0.040	0.079	0.131		0.026	0.071	0.070	0.080	0.220	0.086
	0.040	0.076	0.129		0.027	0.066	0.080	0.082	0.210	0.084
	0.040	0.081	0.125		0.027	0.069	0.070	0.089	0.220	0.085
Average:	**0.040**	**0.079**	**0.128**		**0.027**	**0.069**	**0.073**	**0.084**	**0.217**	**0.085**
Std. Dev.	**0.000**	**0.003**	**0.003**		**0.001**	**0.003**	**0.006**	**0.005**	**0.006**	**0.001**

Total Nitrite + Nitrate mg/L

	A	B	C	D	E	F	G	H	I	J
	0.240	0.179	0.161		0.160	0.139	0.460		0.155	0.140
	0.240	0.181	0.163		0.159	0.139	0.460		0.156	0.140
	0.240	0.181	0.163		0.160	0.142	0.300		0.147	0.140
Average:	**0.240**	**0.180**	**0.162**		**0.160**	**0.140**	**0.407**		**0.153**	**0.140**
Std. Dev.	**0.000**	**0.001**	**0.001**		**0.001**	**0.002**	**0.092**		**0.005**	**0.000**

Dissolved Nitrite mg/L

	A	B	C	D	E	F	G	H	I	J
	0.113	0.107	0.119		0.112	0.111	0.130	0.110	0.122	0.110
	0.113	0.109	0.119		0.111	0.110	0.120	0.110	0.126	0.110
	0.111	0.107	0.119		0.111	0.111	0.130	0.112	0.122	0.110
Average:	**0.112**	**0.108**	**0.119**		**0.111**	**0.111**	**0.127**	**0.111**	**0.123**	**0.110**
Std. Dev.	**0.001**	**0.001**	**0.000**		**0.001**	**0.001**	**0.006**	**0.001**	**0.002**	**0.000**

Total Phosphorus mg/L

	A	B	C	D	E	F	G	H	I	J
	0.150	0.208	0.151		0.148	0.141	0.190	0.128	0.180	0.130
	0.170	0.202	0.155		0.148	0.140	0.180	0.126	0.187	0.130
	0.140	0.204	0.155		0.149	0.141	0.190	0.144	0.159	0.130
Average:	**0.153**	**0.205**	**0.154**		**0.148**	**0.141**	**0.187**	**0.133**	**0.175**	**0.130**
Std. Dev.	**0.015**	**0.003**	**0.002**		**0.001**	**0.001**	**0.006**	**0.010**	**0.015**	**0.000**

Orthophosphate mg/L

	A	B	C*	D	E	F	G	H	I	J
	0.097	0.090	0.094		0.085	0.086	0.090	0.082	0.083	0.093
	0.098	0.090	0.094		0.086	0.086	0.090	0.079	0.084	0.094
	0.111	0.090	0.095		0.085	0.086	0.080	0.082	0.082	0.094
Average:	**0.102**	**0.090**	**0.094**		**0.085**	**0.086**	**0.087**	**0.081**	**0.083**	**0.094**
Std. Dev.	**0.008**	**0.000**	**0.001**		**0.001**	**0.000**	**0.006**	**0.002**	**0.001**	**0.001**

Total Organic Carbon mg/L

	A	B	C	D	E	F	G	H	I	J*
	7.600	4.870				3.510	3.000	3.490		3.700
	8.300	4.200				3.510	3.000	3.240		3.900
	8.100	4.100				3.480	3.000	3.560		3.600
Average:	**8.000**	**4.390**				**3.500**	**3.000**	**3.430**		**3.733**
Std. Dev.	**0.361**	**0.419**				**0.017**	**0.000**	**0.168**		**0.153**

Notes **Lab A'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*
	6.800	6.900		4.590	5.340	4.940	7.340	5.050	12.000	4.200
	6.200	6.100		5.120	4.270	4.290	7.250	4.840	9.000	4.100
	6.600	7.800		5.650	1.070	4.320	6.970	4.620	7.000	4.300
Average:	**6.533**	**6.933**		**5.120**	**3.560**	**4.517**	**7.187**	**4.837**	**9.333**	**4.200**
Std. Dev.	**0.306**	**0.850**		**0.530**	**2.222**	**0.367**	**0.193**	**0.215**	**2.517**	**0.100**

Biochemical Oxygen Demand mg/L

	A	B	C	D	E	F	G	H	I	J
	I	1.200			U		U		2.000	2.000
	I	2.000			U		U		3.000	2.200
	I	1.900			2.100		U		2.000	2.100
Average:		**1.700**			**2.100**				**2.333**	**2.100**
Std. Dev.		**0.436**	**0.000**						**0.577**	**0.100**

Carbonaceous Biochemical Oxygen Demand mg/L

	A	B	C	D	E	F	G	H	I	J*
	I	1.300			U		U		U	2.000
	I	2.200			U		U		U	1.900
	I	2.200			2.200		U		U	1.100
Average:		**1.900**			**2.200**					**1.667**
Std. Dev.		**0.520**								**0.493**

GOMA Analytical Round Robin #5 Results - October 20, 2010

Samples collected from Alligator Harbor, Florida

Total Kjeldahl Nitrogen mg/L

	A	B	C	D	E	F	G	H	I	J
	0.660	0.730	0.829		1.030		0.770		1.100	0.650
	0.660	0.744	0.812		0.277		0.790		0.980	0.830
	0.680	0.744	0.754		0.791		0.510		1.090	0.800
Average:	**0.667**	**0.739**	**0.798**		**0.699**		**0.690**		**1.057**	**0.760**
Std. Dev.	**0.012**	**0.008**	**0.039**		**0.385**		**0.156**		**0.067**	**0.096**

Ammonia mg/L

	A	B	C	D	E	F	G	H	I	J
	I	0.019	0.058		I	U	I	0.016	0.160	U
	I	0.021	0.061		I	U	I	0.016	0.150	U
	I	0.020	0.062		I	U	I	0.015	0.150	U
Average:		**0.020**	**0.060**					**0.016**	**0.153**	
Std. Dev.		**0.001**	**0.002**					**0.001**	**0.006**	

Total Nitrite + Nitrate mg/L

	A	B	C	D	E*	F	G	H	I*	J
	0.080	U	U		0.020	U	I		0.026	U
	0.090	U	U		0.020	U	I		U	U
	0.100	U	U		0.020	U	I		U	U
Average:	**0.090**				**0.020**				**0.026**	
Std. Dev.	**0.010**				**0.000**					

Dissolved Nitrite mg/L

	A	B	C	D	E*	F	G	H*	I	J
	I	U	U		0.002	U	I	0.0007	U	U
	I	U	U		0.002	U	I	0.0004	U	U
	I	U	U		0.002	U	I	0.0004	U	U
Average:					**0.002**			**0.0005**		
Std. Dev.					**0.000**			**0.000**		

Total Phosphorus mg/L

	A	B	C	D	E	F	G	H	I	J
	0.060	0.092	0.037		0.036	0.038	0.070	0.040	0.103	0.043
	0.070	0.094	0.040		0.036	0.036	0.070	0.046	0.098	0.041
	0.070	0.094	0.038		0.036	0.033	I	0.044	0.068	0.044
Average:	**0.067**	**0.093**	**0.038**		**0.036**	**0.036**	**0.070**	**0.043**	**0.090**	**0.043**
Std. Dev.	**0.006**	**0.001**	**0.002**		**0.000**	**0.003**	**0.000**	**0.003**	**0.019**	**0.002**

Orthophosphate mg/L										
	A	B	C	D	E*	F	G	H	I	J
	I	U	0.007		0.005	U	I	U	U	U
	I	U	0.007		0.004	U	I	U	U	U
	I	U	0.006		0.005	U	I	U	U	U
Average:			**0.007**		**0.005**					
Std. Dev.			**0.001**		**0.001**					

Total Organic Carbon mg/L										
	A	B	C	D	E	F	G	H	I	J
	11.700	6.170				5.930	5.000	4.950		6.500
	10.900	6.200				5.070	3.000	4.950		5.100
	11.000	6.270				5.140	4.000	5.130		5.000
Average:	**11.200**	**6.213**				**5.380**	**4.000**	**5.010**		**5.533**
Std. Dev.	**0.436**	**0.051**				**0.478**	**1.000**	**0.104**		**0.839**

Notes **Lab A'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
	7.400	12.700		8.340	11.750	11.940	7.780	8.170	11.000	13.000
	8.000	13.700		9.470	12.820	11.780	7.330	8.070	11.000	14.000
	8.000	12.200		8.030	16.020	11.930	9.150	7.270	11.000	7.600
Average:	**7.800**	**12.867**		**8.613**	**13.530**	**11.883**	**8.087**	**7.837**	**11.000**	**11.533**
Std. Dev.	**0.346**	**0.764**		**0.758**	**2.222**	**0.090**	**0.948**	**0.493**	**0.000**	**3.443**

Biochemical Oxygen Demand mg/L										
	A	B	C	D	E	F	G	H	I	J
	2.200	2.500			3.600		U		4.000	3.600
	2.600	2.400			3.800		U		4.000	3.400
	2.300	2.500			3.500		U		4.000	3.100
Average:	**2.367**	**2.467**			**3.633**				**4.000**	**3.367**
Std. Dev.	**0.208**	**0.058**			**0.153**				**0.000**	**0.252**

Carbonaceous Biochemical Oxygen Demand mg/L										
	A	B	C	D	E	F	G	H	I	J
	I	2.700			2.200		U		2.000	2.800
	I	3.000			2.100		U		U	3.100
	I	2.700			2.200		U		2.000	3.200
Average:		**2.800**			**2.167**				**2.000**	**3.033**
Std. Dev.		**0.173**			**0.058**				**0.000**	**0.208**

FSU CML

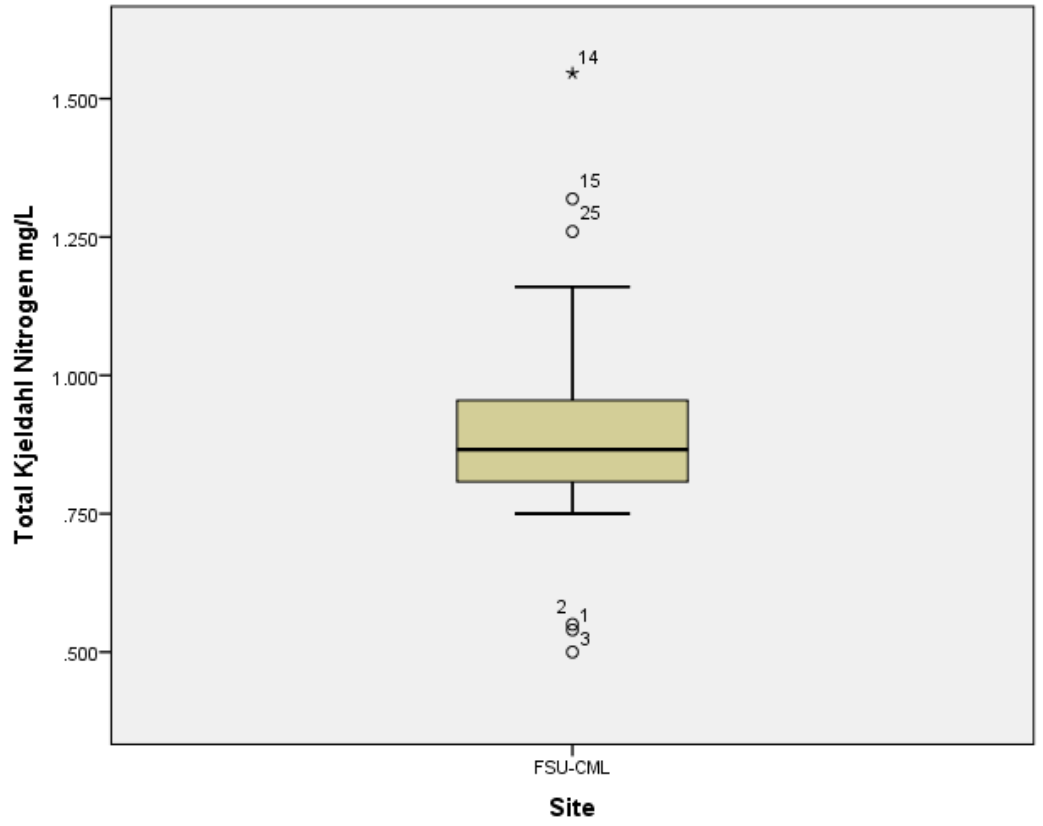
	TKN		NH3		NOx		D_NO2		TP		OP		TOC		ChlA		BOD		CBOD	
	Stat.	Std. Err.	Stat.	Std. Err.	Stat.	Std. Err.	Stat.	Std. Err.	Stat.	Std. Err.	Stat.	Std. Err.	Stat.	Std. Err.	Stat.	Std. Err.	Stat.	Std. Err.	Stat.	Std. Err.
Descriptives																				
N (Total)	21		27		24		27		27		27		18		27		18		18	
N (Greater than PQL)	21		27		24		27		27		27		15		23		10		5	
N Analyzed	21		27		24		27		27		27		18		27		10		7	
Mean	0.908	0.056	0.089	0.010	0.198	0.018	0.115	0.001	0.158	0.005	0.089	0.001	4.342	0.412	5.802	0.388	2.050	0.137	1.843	0.173
95% CI (LB)	0.792		0.068		0.159		0.112		0.148		0.086		3.473		5.005		1.741		1.420	
95% CI (UB)	1.025		0.110		0.236		0.117		0.168		0.092		5.212		6.600		2.360		2.266	
5% Trimmed	0.896		0.085		0.186		0.114		0.157		0.089		4.197		5.720		2.044		1.864	
Median	0.866		0.080		0.161		0.111		0.150		0.090		3.580		5.340		2.000		2.000	
Variance	0.065		0.003		0.008		0.000		0.001		0.000		3.059		4.066		0.187		0.210	
Std. Dev.	0.256		0.054		0.091		0.007		0.025		0.007		1.749		2.017		0.433		0.458	
Min	0.500		0.026		0.139		0.107		0.126		0.079		3.000		1.070		1.200		1.100	
Max	1.546		0.220		0.460		0.130		0.208		0.111		8.300		12.000		3.000		2.200	
Range	1.046		0.194		0.321		0.023		0.082		0.032		5.300		10.930		1.800		1.100	
IQR	0.239		0.023		0.082		0.009		0.040		0.010		0.950		2.650		0.150		0.900	
Skew	0.734	0.501	1.427	0.448	2.277	0.472	1.116	0.448	0.636	0.448	1.122	0.448	1.701	0.536	0.796	0.448	0.417	0.687	-1.044	0.794
Kurtosis	0.887	0.972	1.704	0.872	4.695	0.918	0.215	0.872	-0.838	0.872	2.378	0.872	1.508	1.038	2.939	0.872	3.989	1.334	-0.714	1.587
Huber's ψ	0.872		0.078		0.165		0.112		0.155		0.089		3.713		5.618		2.033		1.994	
Kaplan-Meier (KM) Method																				
Minimum Non-Detect	N/A		N/A		N/A		N/A		N/A		N/A		N/A		N/A		2.000		2.000	
Maximum Non-Detect	N/A		N/A		N/A		N/A		N/A		N/A		N/A		N/A		3.000		3.000	
Mean	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	1.870	0.157	1.624	0.179
SD	N/A		N/A		N/A		N/A		N/A		N/A		N/A		N/A		0.443		0.433	
95% KM UCL	1.005		0.134		0.229		0.117		0.167		0.091		5.059		6.464		2.143		1.936	
Normality																				
Test of Skew	0.136		**0.004**		**0.000**		**0.018**		0.148		**0.017**		**0.004**		0.076		0.531		N/A	
Test of Kurtosis	0.295		0.091		**0.004**		0.627		0.244		**0.040**		0.159		**0.021**		**0.027**		0.726	
Jarque & Bera	0.412		**0.008**		**0.000**		0.083		0.280		**0.015**		**0.021**		**0.018**		0.490		N/A	
Outliers																				
F Crit. (Mahalanobis D2)	7.470		8.170		7.850		8.170		8.170		8.170		7.030		8.170		5.240		4.080	
Mahalanobis D2 Max	6.220		5.950		8.390		5.290		3.840		10.020		5.120		9.450		4.820		2.630	
+ 2 Std. Dev.	1.420		0.196		0.379		0.128		0.209		0.103		7.840		9.835		2.915		2.758	
- 2 Std. Dev.	0.397		-0.018		0.017		0.101		0.108		0.075		0.844		1.769		1.185		0.927	
# Outside 2 Std. Dev.	1		3		2		2		0		1		2		2		1		0	
+ 2 F-Pseudosigma	1.220		0.114		0.282		0.124		0.086		0.105		4.980		9.270		2.220		3.330	
- 2 F-Pseudosigma	0.512		0.046		0.039		0.098		0.028		0.075		2.180		1.410		1.780		0.670	
# Outside 2 F-Pseudosigma	4		12		3		3		0		1		3		2		2		0	
# from Boxplots	6		9		2		0		0		1		3		1		2		0	
Homoscedasticity (between laboratories)																				
Levene's	**0.011**		**0.003**		**0.000**		**0.000**		**0.002**		**0.000**		**0.007**		**0.005**		**0.047**		0.882	
Detection Limits																				
< MDL	0		0		0		0		0		0		0		0		5		8	
% < MDL	0%		0%		0%		0%		0%		0%		0%		0%		28%		44%	
< PQL	0		0		0		0		0		0		3		4		3		5	
% < PQL	0%		0%		0%		0%		0%		0%		17%		15%		44%		72%	
Precision																				
%F-Pseudosigma	20.42%		21.31%		37.87%		6.01%		19.77%		8.24%		27.85%		36.79%		5.56%		33.36%	
%RSD	28.16%		60.37%		45.80%		5.82%		15.98%		7.76%		41.33%		34.75%		21.12%		24.85%	

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

Alligator Harbor

	TKN		NH3		NOx		D_NO2		TP		OP		TOC		ChlA		BOD		CBOD	
	Stat.	Std. Err.	Stat.	Std. Err.	Stat.	Std. Err.	Stat.	Std. Err.	Stat.	Std. Err.	Stat.	Std. Err.	Stat.	Std. Err.	Stat.	Std. Err.	Stat.	Std. Err.	Stat.	Std. Err.
Descriptives																				
N (Total)	21		27		24		24		27		27		18		27		18		18	
N (Greater than PQL)	21		12		3		0		26		3		18		27		12		8	
N Analyzed	21		12		7		6		26		6		18		27		15		11	
Mean	0.773	0.041	0.062	0.017	0.043	0.017	0.001	0.000	0.057	0.005	0.006	0.001	6.223	0.576	10.350	0.482	3.167	0.176	2.546	0.138
95% CI (LB)	0.688		0.026		0.002		0.000		0.047		0.004		5.008		9.359		2.789		2.239	
95% CI (UB)	0.858		0.099		0.085		0.002		0.066		0.007		7.437		11.341		3.544		2.852	
5% Trimmed	0.782		0.060		0.042		0.001		0.056		0.006		6.098		10.234		3.174		2.539	
Median	0.770		0.040		0.026		0.001		0.044		0.006		5.135		11.000		3.400		2.700	
Variance	0.035		0.003		0.002		0.000		0.001		0.000		5.964		6.276		0.465		0.209	
Std. Dev.	0.186		0.058		0.045		0.001		0.023		0.001		2.442		2.505		0.682		0.457	
Min	0.277		0.015		0.002		0.000		0.033		0.004		3.000		7.270		2.200		2.000	
Max	1.100		0.160		0.100		0.002		0.103		0.007		11.700		16.020		4.000		3.200	
Range	0.823		0.145		0.098		0.002		0.070		0.003		8.700		8.750		1.800		1.200	
IQR	0.159		0.111		0.088		0.002		0.032		0.002		1.340		4.200		1.300		0.900	
Skew	-0.450	0.501	0.983	0.637	0.314	0.794	-0.068	0.845	0.805	0.456	-0.294	0.845	1.445	0.536	0.382	0.448	-0.150	0.580	0.094	0.661
Kurtosis	1.747	0.972	-0.760	1.232	-2.468	1.587	-3.158	1.741	-0.833	0.887	-1.920	1.741	1.214	1.038	-0.925	0.872	-1.751	1.121	-1.764	1.279
Huber's ψ	0.768		0.042		0.032		0.001		0.047		0.006		5.586		10.264		3.184		2.546	
Kaplan-Meier (KM) Method																				
Minimum Non-Detect	N/A		0.007		0.003		0.001		0.020		0.0019		N/A		N/A		3.000		2.000	
Maximum Non-Detect	N/A		0.05		0.050		0.02		0.020		0.04		N/A		N/A		3.000		3.000	
Mean	N/A	N/A	0.037	0.009	0.014	0.007	0.001	0.000	0.056	0.004	0.005	0.000	N/A	N/A	N/A	N/A	3.042	0.016	2.371	0.111
SD	N/A		0.044		0.029		0.001		0.023		0.001		N/A		N/A		0.666		0.429	
95% KM UCL	0.843		0.052		0.026		0.001		0.075		0.005		7.224		11.170		3.322		2.565	
Normality																				
Test of Skew	0.349		0.119		N/A		N/A		0.078		N/A		**0.011**		0.372		0.785		0.882	
Test of Kurtosis	0.108		0.576		**0.046**		**0.025**		0.261		0.239		0.220		0.171		**0.008**		**0.049**	
Jarque & Bera	0.441		0.386		N/A		N/A		0.185		N/A		0.064		0.437		0.442		0.570	
Outliers																				
F Crit. (Mahalanobis D2)	7.470		5.820		4.080		3.560		8.070		3.560		7.030		8.170		6.490		5.540	
Mahalanobis D2 Max	7.090		2.850		1.600		1.050		3.950		1.960		5.030		5.120		2.010		2.050	
+ 2 Std. Dev.	1.145		0.178		0.133		0.003		0.103		0.008		11.107		15.360		4.531		3.459	
- 2 Std. Dev.	0.400		-0.053		-0.047		0.000		0.010		0.003		1.339		5.340		1.803		1.632	
# Outside 2 Std. Dev.	1		0		0		0		0		0		1		1		0		0	
+ 2 F-Pseudosigma	1.006		0.204		0.156		0.004		0.092		0.009		7.120		17.230		5.330		4.030	
- 2 F-Pseudosigma	0.534		-0.125		-0.104		-0.001		-0.004		0.002		3.150		4.770		1.470		1.370	
# Outside 2 F-Pseudosigma	5		0		0		0		4		0		4		0		0		0	
# from Boxplots	3		0		0		0		0		0		4		0		0		0	
Homoscedasticity (between laboratories)																				
Levene's	**0.003**		**0.007**		0.116		**0.016**		**0.000**		0.145		0.069		**0.000**		0.074		**0.048**	
Detection Limits																				
< MDL	0		6		14		15		0		15		0		0		3		4	
% < MDL	0%		22%		58%		63%		0%		56%		0%		0%		17%		22%	
< PQL	0		9		7		9		1		9		3		0		0		3	
% < PQL	0%		56%		88%		100%		4%		89%		17%		0%		17%		39%	
Precision																				
%F-Pseudosigma	15.36%		208.78%		250.90%		87.86%		54.33%		28.54%		19.34%		28.30%		28.34%		24.71%	
%RSD	24.10%		93.55%		104.65%		100.00%		40.93%		16.67%		39.24%		24.20%		21.53%		17.95%	

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


Total Kjeldahl Nitrogen mg/L
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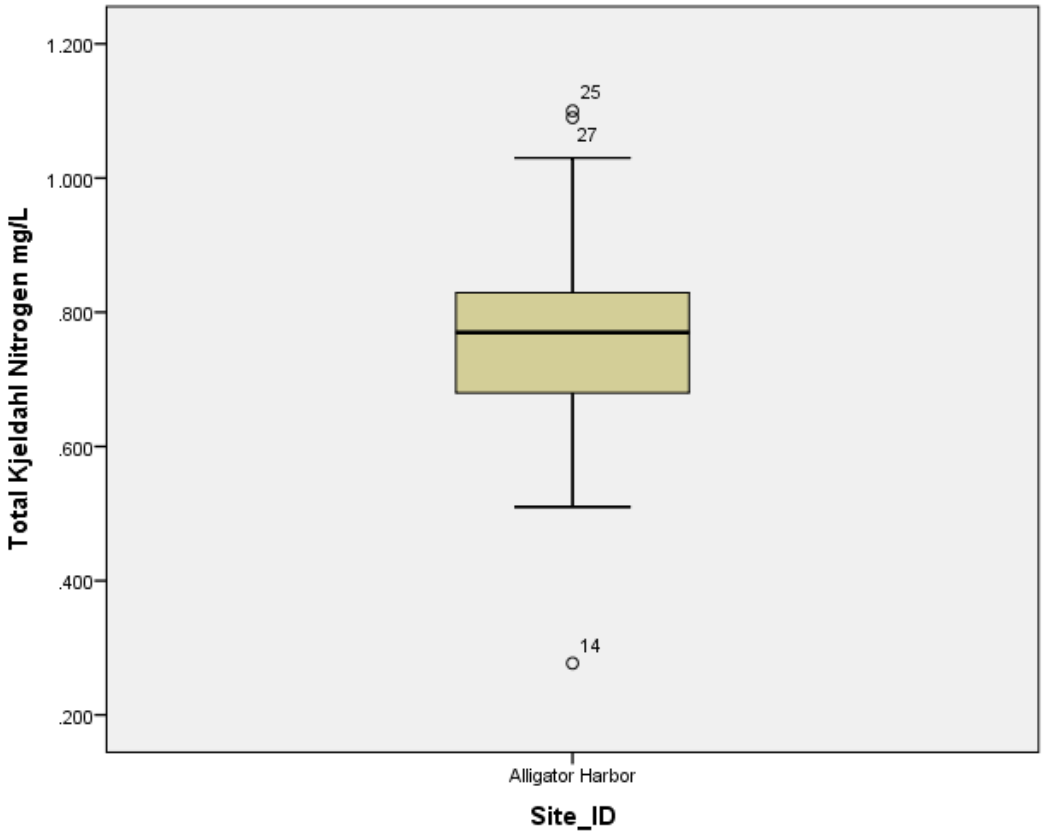
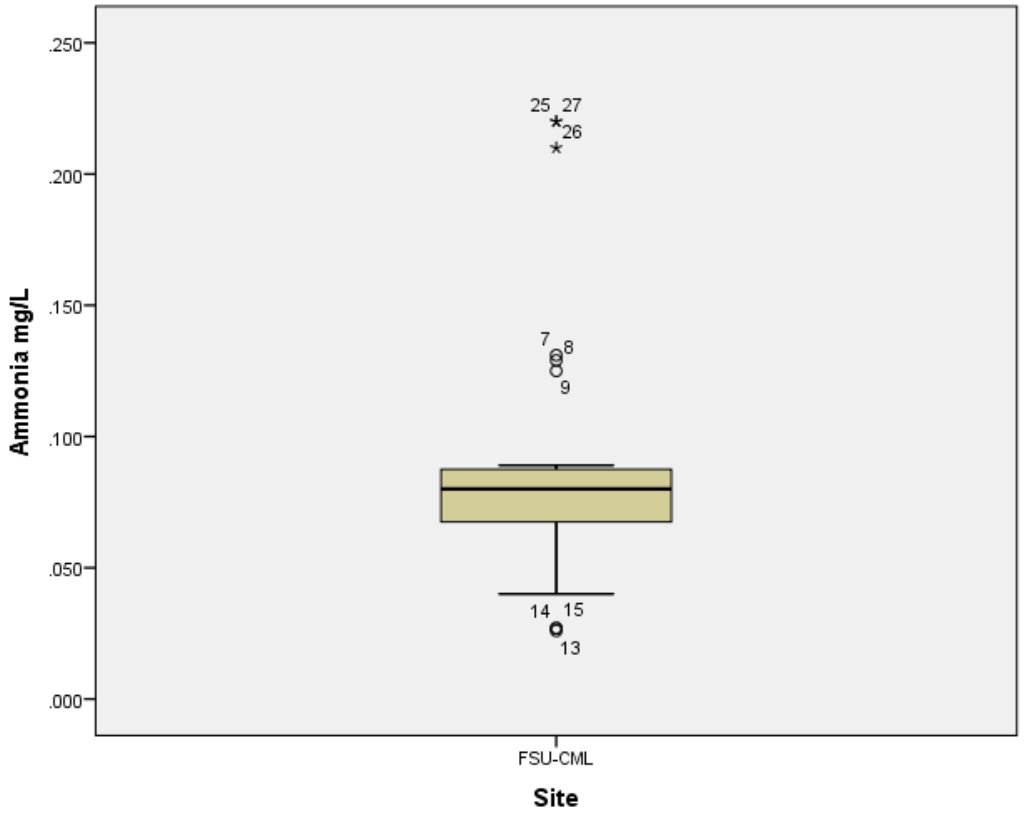
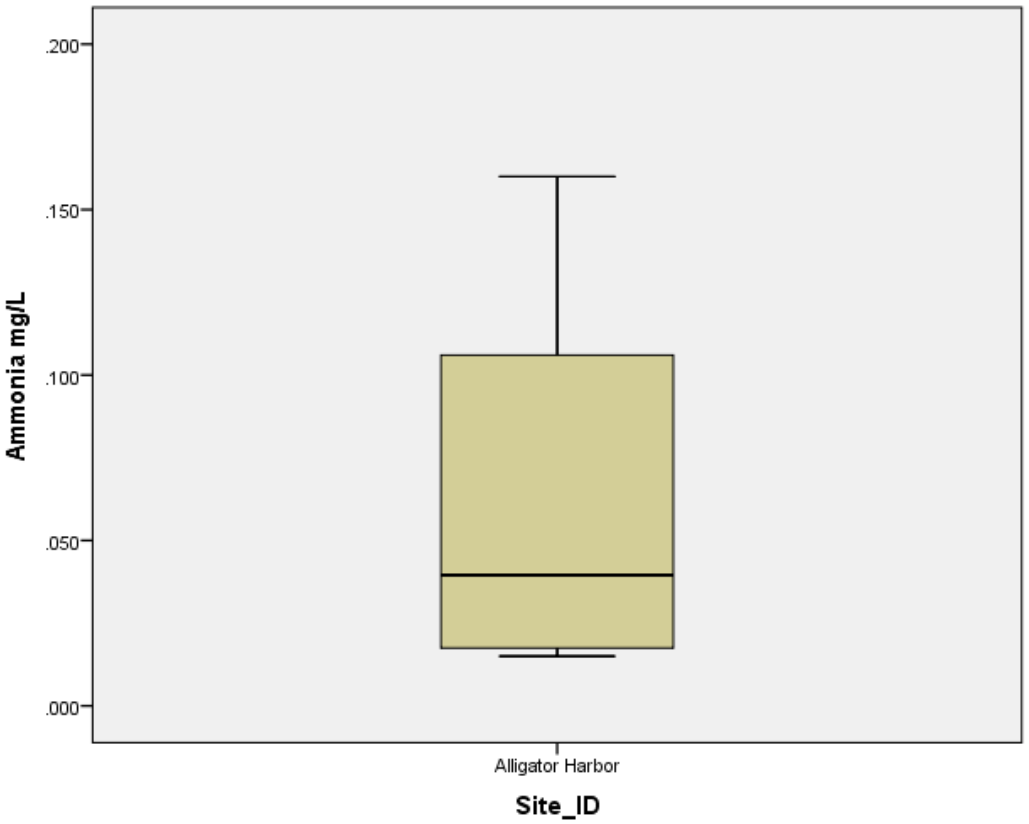
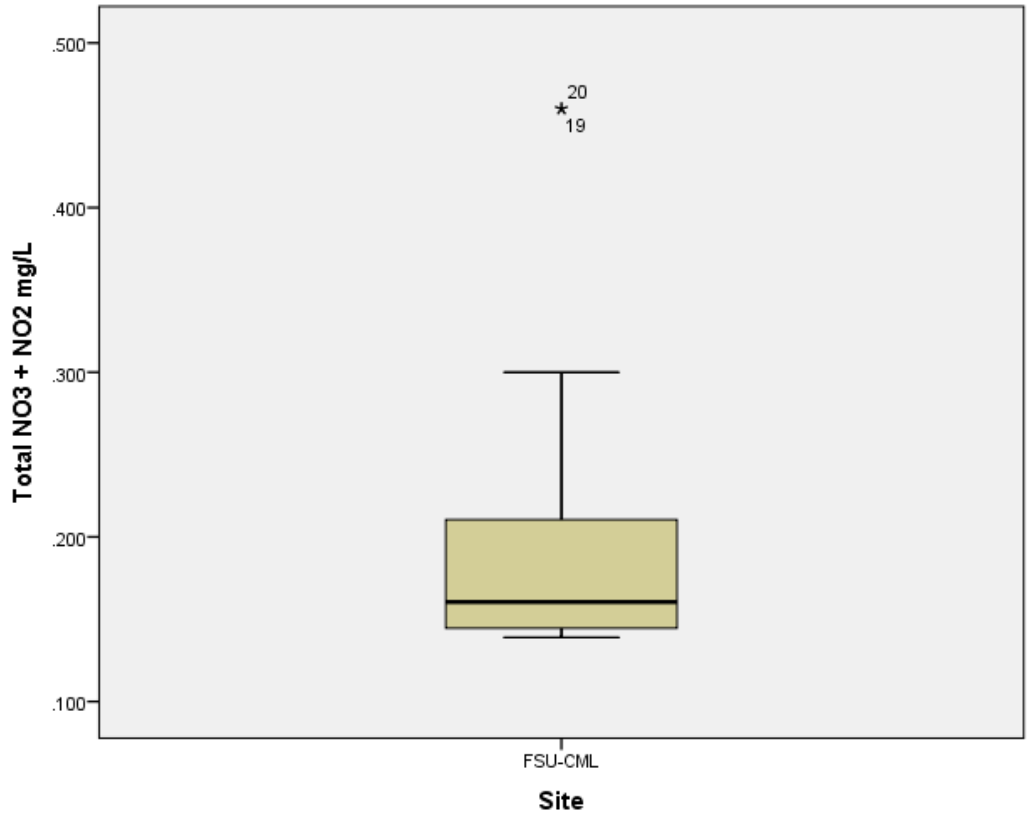
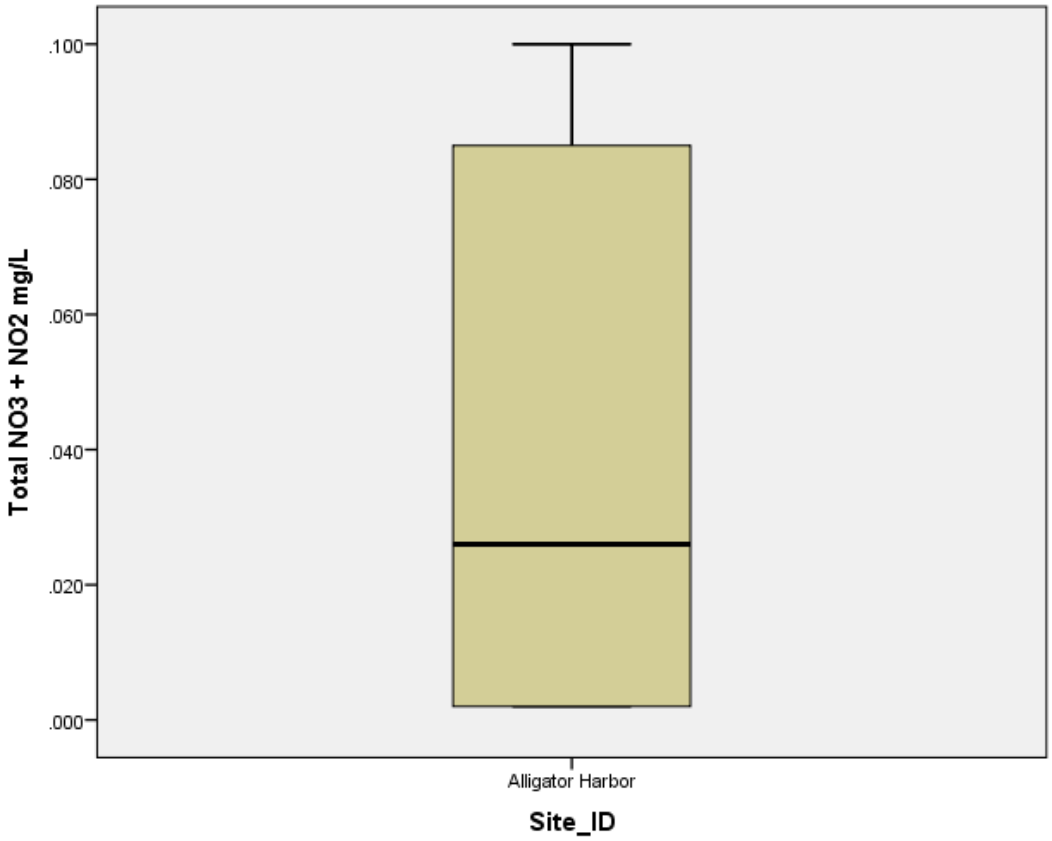
1.250
1.000
.750
.500
14
15
25
2
1
3
FSU-CML
Site

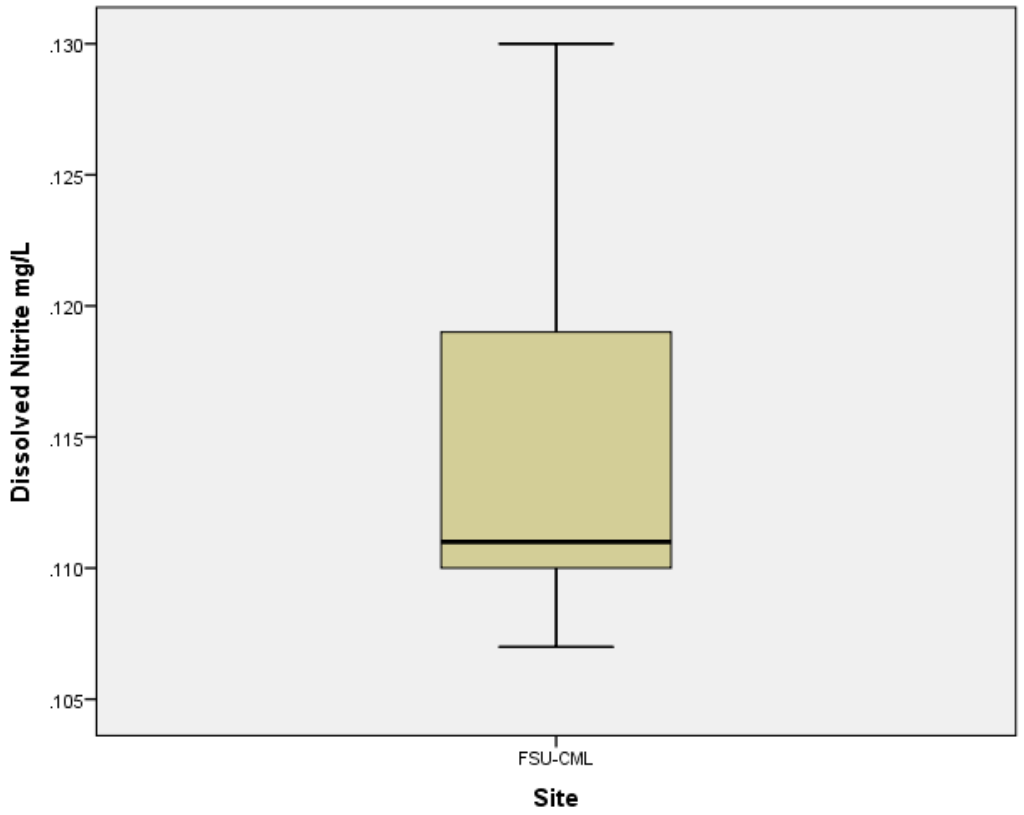

Total Kjeldahl Nitrogen mg/L
1.200
1.000
.800
.600
.400
.200
25
27
14
Alligator Harbor
Site_ID

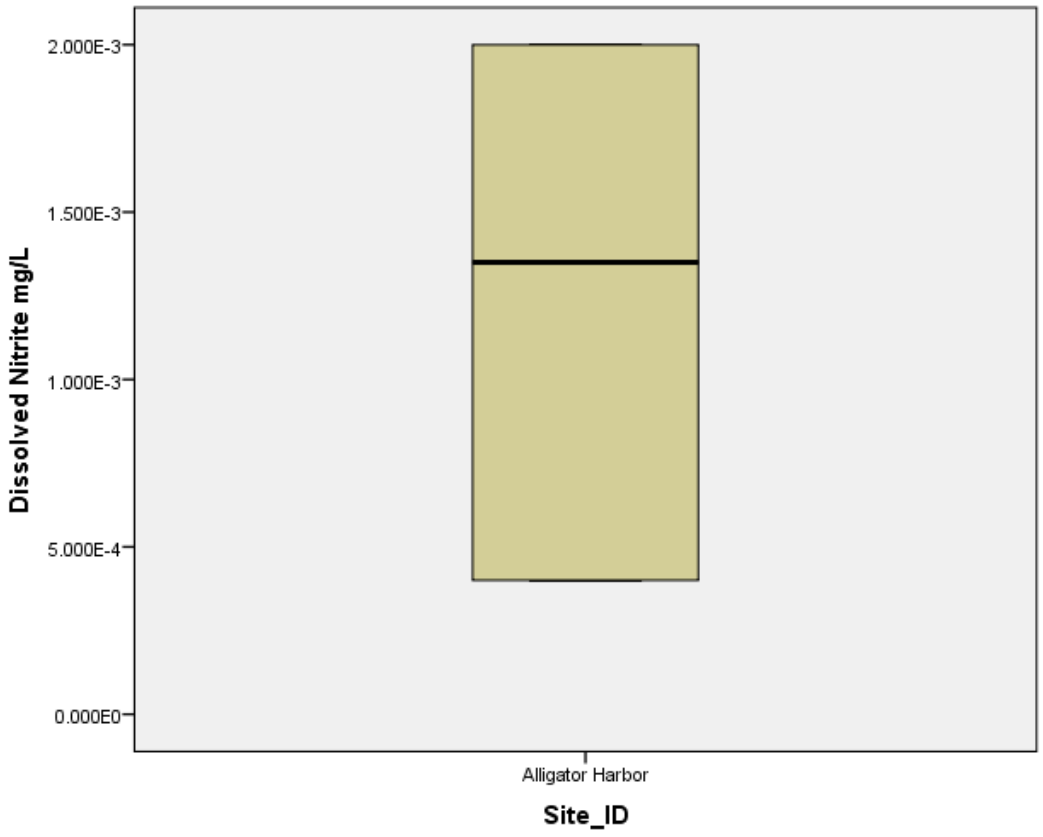

.250
.200
.150
.100
.050
.000
Ammonia mg/L
25
27
26
7
8
9
14
15
13
FSU-CML
Site


.200
.150
.100
.050
.000
Ammonia mg/L
Alligator Harbor
Site_ID


.500
.400
.300
.200
.100
Total NO3 + NO2 mg/L
20
19
FSU-CML
Site

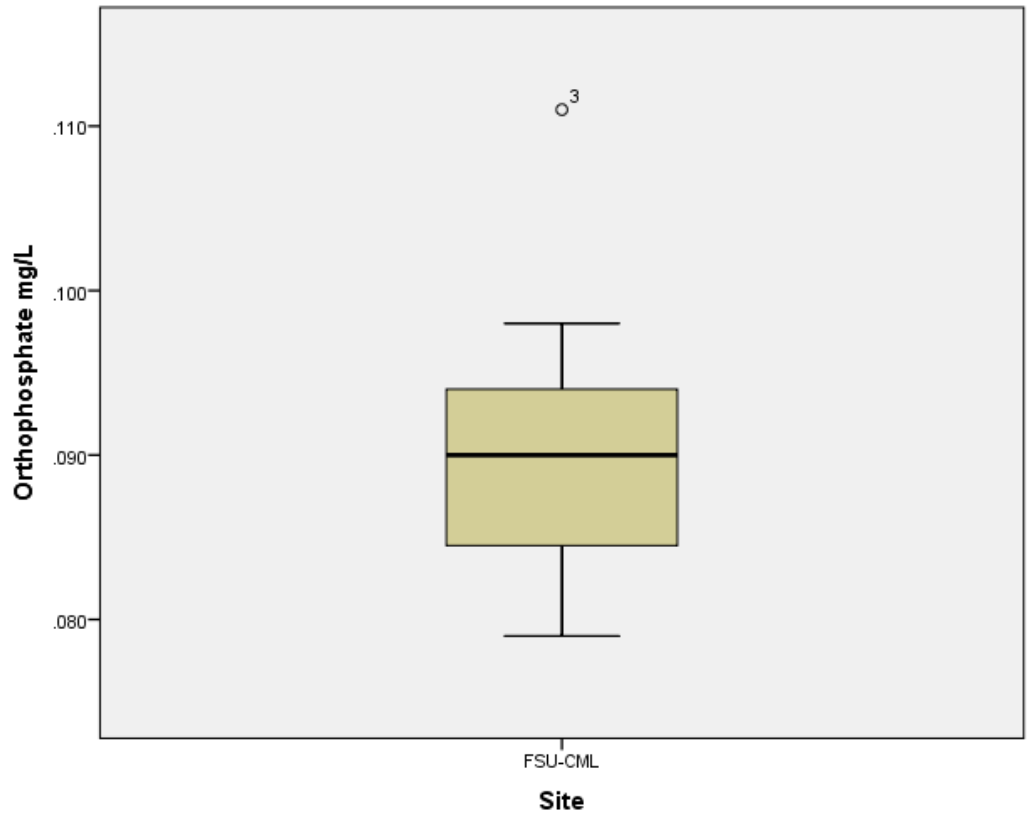

.100
.080
.060
.040
.020
.000
Total NO3 + NO2 mg/L
Alligator Harbor
Site_ID

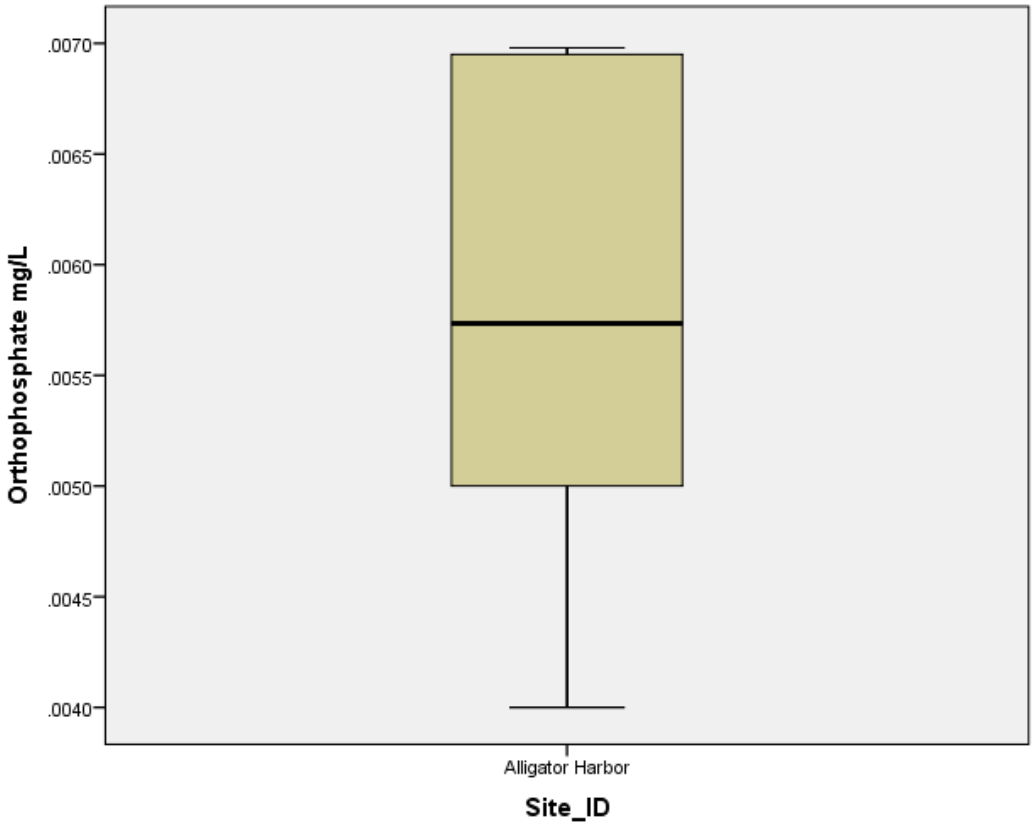

.130
.125
.120
.115
.110
.105
Dissolved Nitrite mg/L
FSU-CML
Site

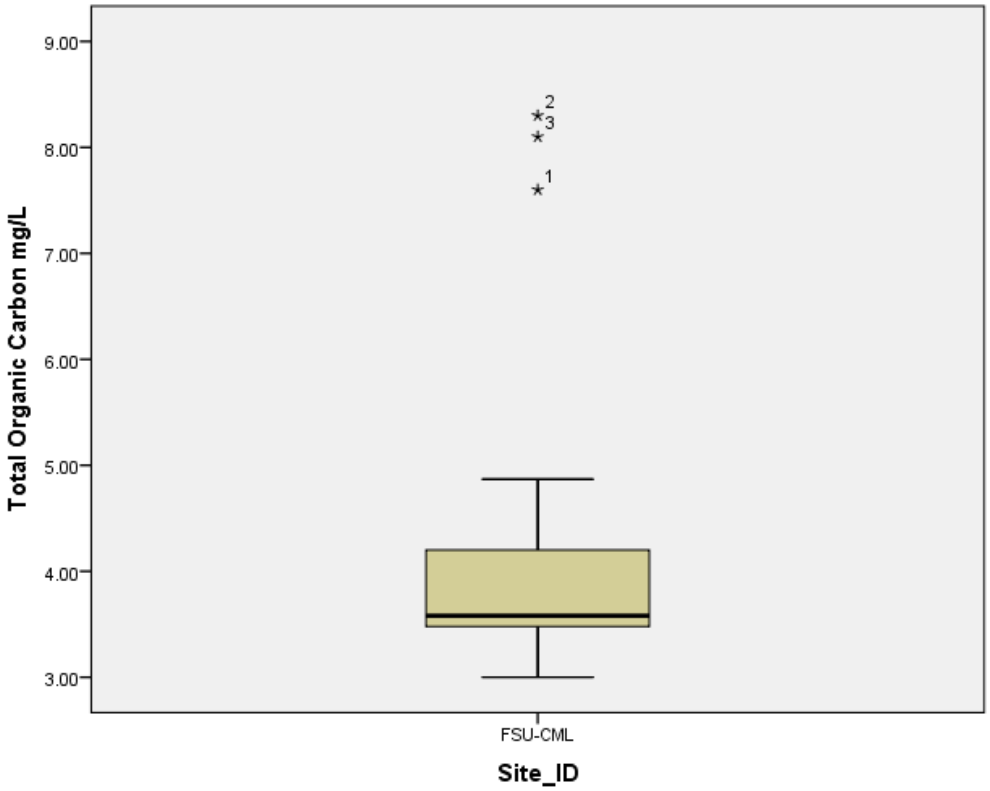

2.000E-3
1.500E-3
1.000E-3
5.000E-4
0.000E0
Dissolved Nitrite mg/L
Alligator Harbor
Site_ID

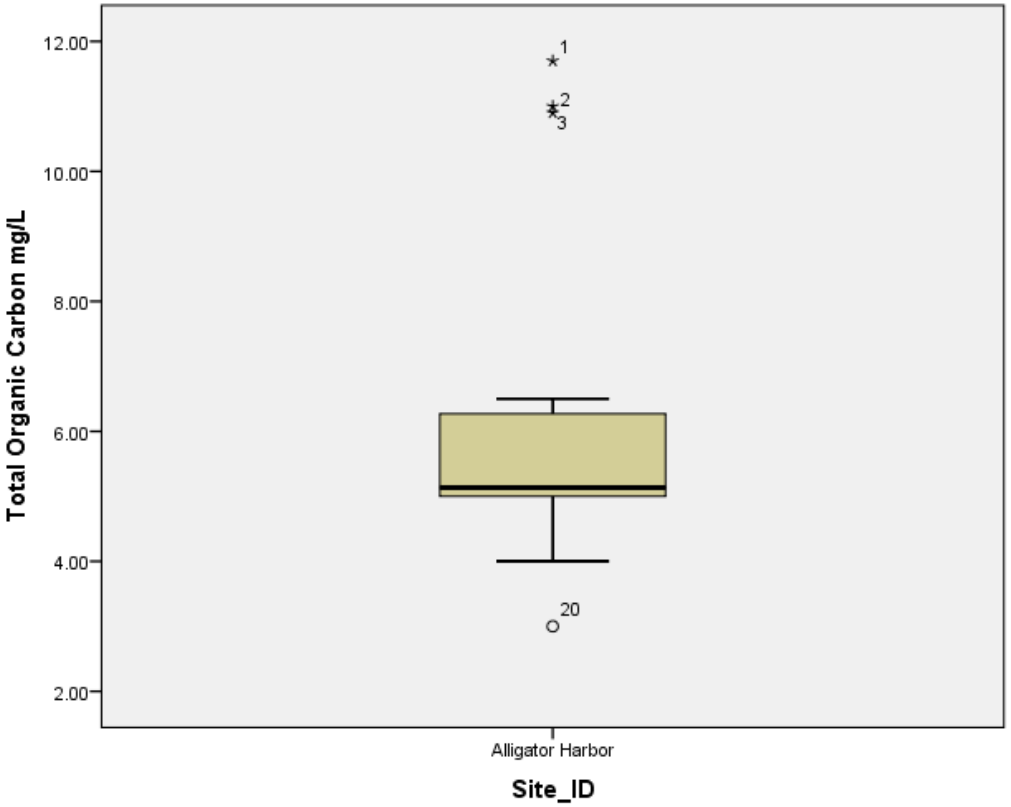

.220
.200
.180
.160
.140
.120
Total Phosphorus mg/L
FSU-CML
Site

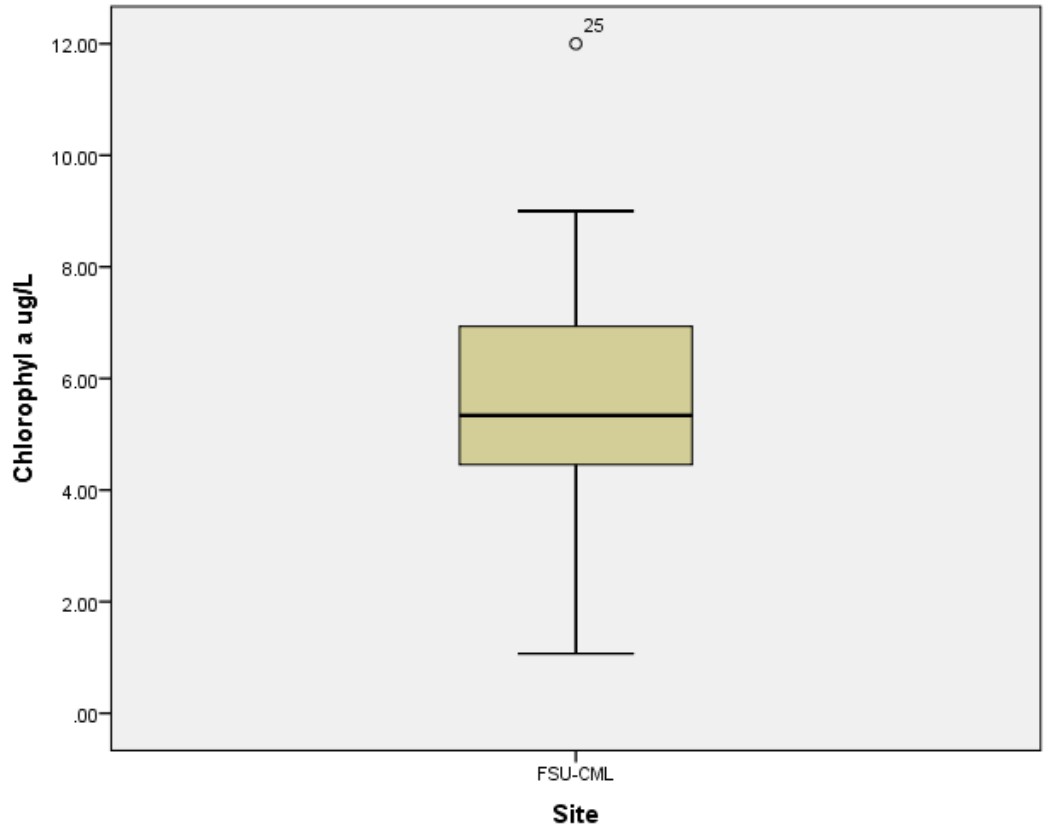

.100
.080
.060
.040
Total Phosphorus mg/L
Alligator Harbor
Site_ID

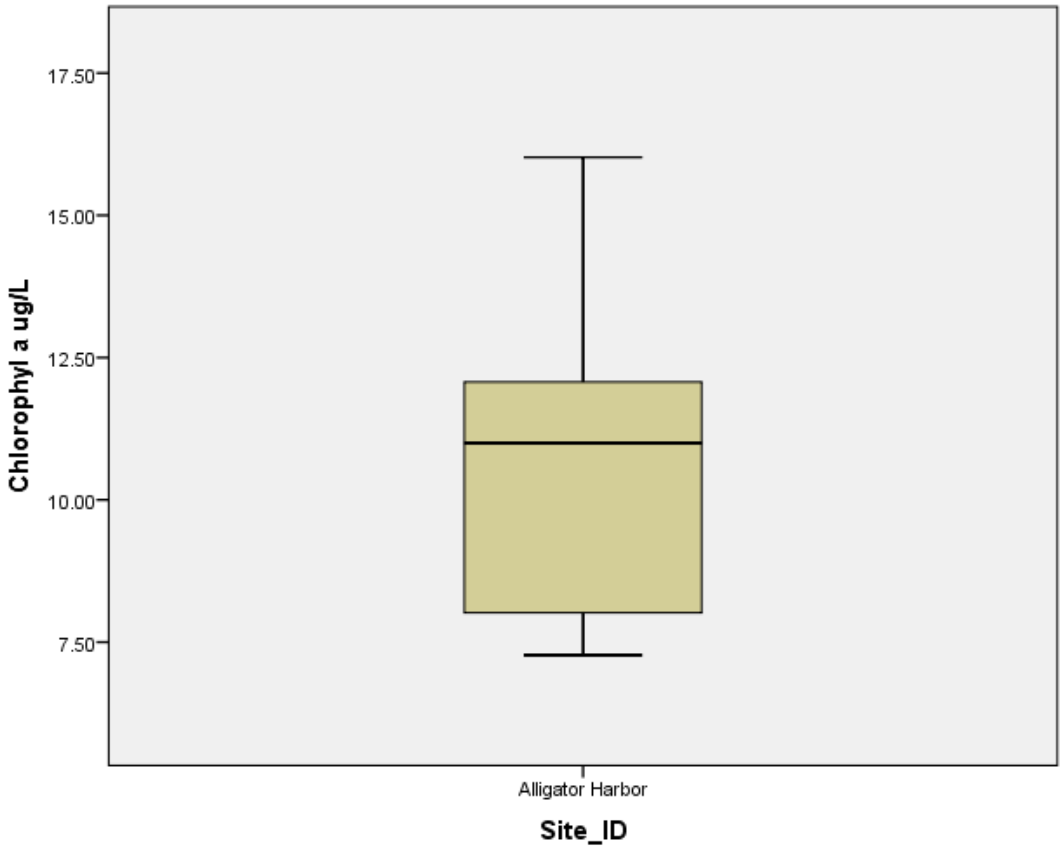

Orthophosphate mg/L
.110
.100
.090
.080
3
FSU-CML
Site

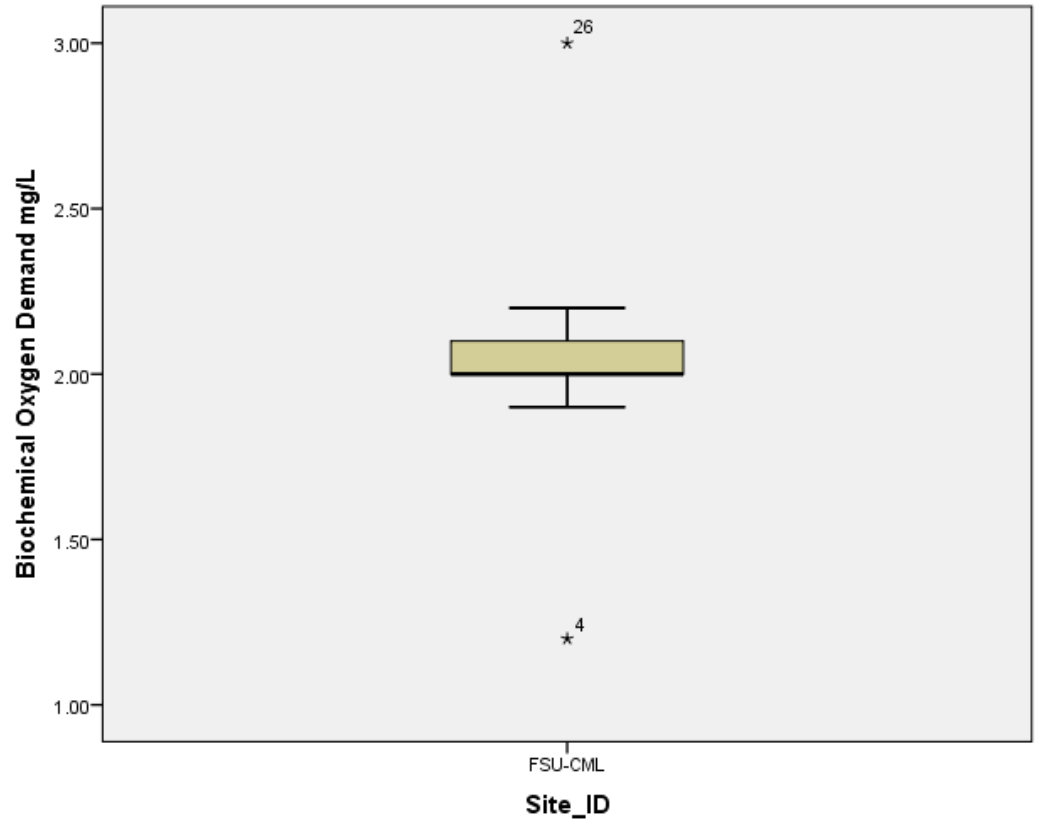

Orthophosphate mg/L
.0070
.0065
.0060
.0055
.0050
.0045
.0040
Alligator Harbor
Site_ID

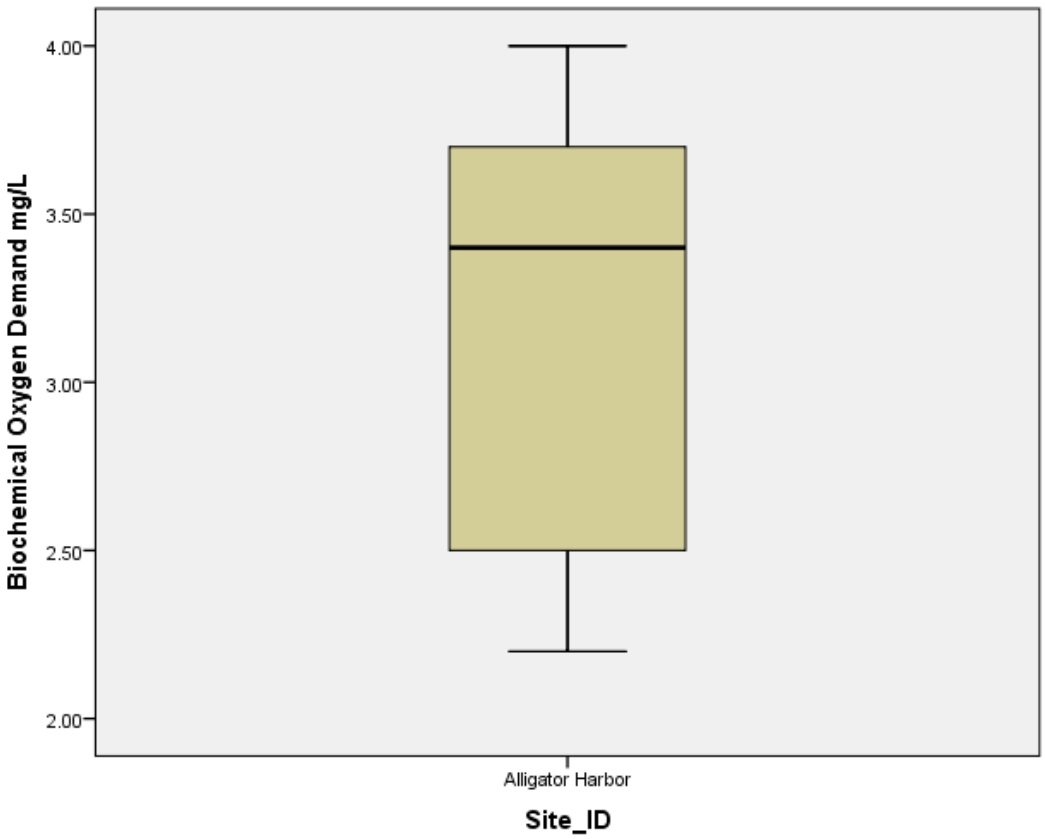

9.00
8.00
7.00
6.00
5.00
4.00
3.00
Total Organic Carbon mg/L
2
3
1
FSU-CML
Site_ID

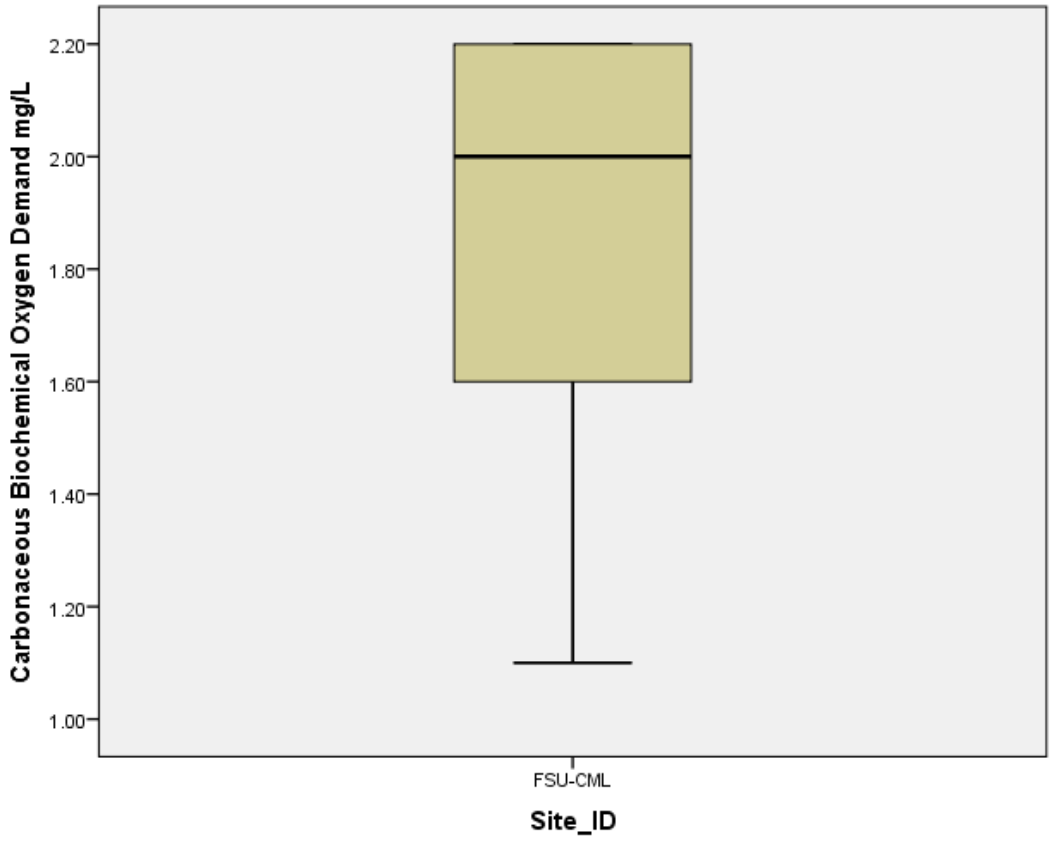

12.00
10.00
8.00
6.00
4.00
2.00
Total Organic Carbon mg/L
1
2
3
20
Alligator Harbor
Site_ID

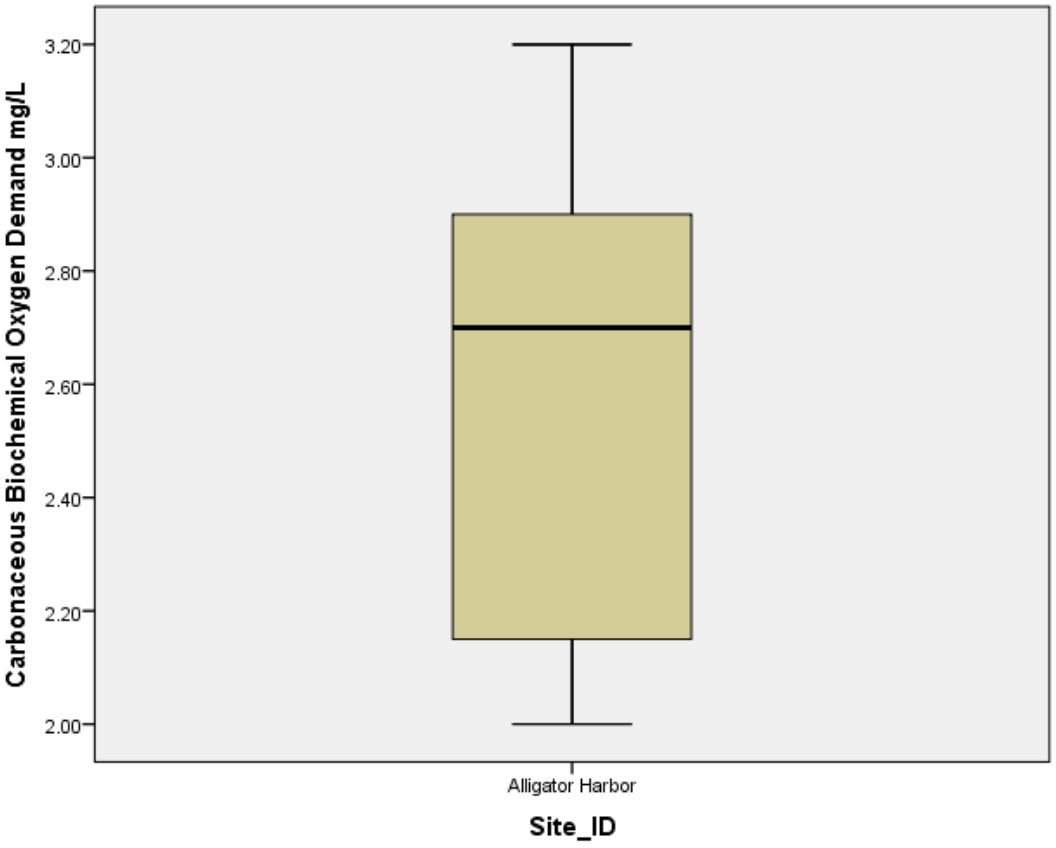

25
12.00
10.00
8.00
6.00
4.00
2.00
.00
Chlorophyl a ug/L
FSU-CML
Site


17.50
15.00
12.50
10.00
7.50
Chlorophyl a ug/L
Alligator Harbor
Site_ID


Biochemical Oxygen Demand mg/L
3.00
2.50
2.00
1.50
1.00
26
4
FSU-CML
Site_ID


Biochemical Oxygen Demand mg/L
4.00
3.50
3.00
2.50
2.00
Alligator Harbor
Site_ID


Carbonaceous Biochemical Oxygen Demand mg/L
2.20
2.00
1.80
1.60
1.40
1.20
1.00
FSU-CML
Site_ID


Carbonaceous Biochemical Oxygen Demand mg/L
3.20
3.00
2.80
2.60
2.40
2.20
2.00
Alligator Harbor
Site_ID