Statistical Analyses and Summary of Analytical Round Robin #6 – a Data Comparability Study

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Samples collected March 7, 2011 from St. Louis Bay, MS by the Mississippi Department of Environmental Quality
Preserved and split March 8, and shipped March 9, 2011 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 sixth 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 eleven laboratories, representing local, state, federal, academic, and private laboratories participated in this round robin. Samples were collected on 7 March 2011 from St. Louis Bay, MS by the Mississippi Department of Environmental Quality. Although only one site was sampled, it was treated as if it were two discrete samples and was prepared and analyzed as such.

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. Each laboratory received three replicates of each of the above sample types for "site." 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.

Laboratories participating in Analytical Round Robin #6:

ADEM_Mob – Alabama Department of Environmental Management, Mobile Laboratory (AL)
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 will guide 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 it

differs. These include Gabriel's test, Dunnett's T[3], 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.

Many of the methods utilized by participating laboratories involved are considered "equivalent." Table 2 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 2. Methods used by laboratories participating in the sixth analytical round robin.

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

	Sample A		Sample B	
Analyte	N laboratories	N values >MDL	N laboratories	N values >MDL
TKN	8	23*	8	23*
NH_3	10	9*	10	9*
NO_x	10	17*	10	20*
DNO_2	10	7*	10	10*
TP	10	30	10	30
OP	10	23*	10	24*
TOC	6	18	6	18
ChlA	10	26	10	25
BOD	7	6*	7	6*
CBOD	7	6*	7	6*

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

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

3. Results and Discussion

A. Total Kjeldahl Nitrogen. Twenty of the 23 reported values for Sample A were within acceptable ranges. Lab C reported all three values outside acceptable ranges. There were no statistical outliers. Lab E was the only laboratory to report a non-value. This was not determined to be false negative. The %F-pseudosigma value was large (greater than 30%), indicating a lack of precision among laboratories. Of the 20 reported values, 74% were within 1 F-pseudosigma and 87% were within 2 F-pseudosigma. There was no statistical difference among the methods employed for TKN.

For Sample B, nineteen of the 23 values were within acceptable ranges. Lab C reported all three values outside acceptable ranges, and Lab K reported one value outside acceptable ranges. The result for Lab K was a statistical outlier (1.14 mg/L). As with Sample A, Lab E was the only laboratory to report a non-value. This was not determined to be false negative. The %F-pseudosigma value was large (greater than 30%), indicating a lack of precision among laboratories. Of the 23 reported values, 83% were within 1 F-pseudosigma; there were no other values within 2 F-pseudosigma. There was no statistical difference among the methods employed for TKN.

When looking at all of the results combined (since they all originated from a single sample), 39 of the 46 reported values were within acceptable ranges. All of Lab C's values were outside acceptable ranges, and Lab K reported one outside acceptable ranges. This value was a statistical outlier. The % F-pseudosigma remained large even after combining Samples A and B. Of the 46 reported values, 80% were within 1 F-pseudosigma and 85% were within 2 F-pseudosigma. There was no statistical difference between the two samples or the methods that were employed. See Figures 1 – 4 and Table 4 - 14 for scatter-plots of values obtained by individual laboratories, F-pseudosigma values, summary statistics, inter-laboratory comparisons, and method comparisons.

Total Kjeldahl Nitrogen				
	Sample A			
	F-pseudosigma	**% F-pseudosigma**	**Median**	**Range**
	0.148	43.61%	0.340	0.685
Method	**N**	**Mean**	**Median**	**Range**
EPA 351.2	18	0.396	0.335	0.685
Lachat 10-107-06-2-D	3 (one non-value)	0.235	0.235	0.030
USGS I-4515-91	3	0.377	0.380	0.030
	Sample B			
	F-pseudosigma	**% F-pseudosigma**	**Median**	**Range**
	0.156	47.17%	0.330	0.951
Method	**N**	**Mean**	**Median**	**Range**
EPA 351.2	18	0.414	0.325	0.951
Lachat 10-107-06-2-D	3 (one non-value)	0.265	0.265	0.050
USGS I-4515-91	3	0.380	0.370	0.070
	All			
	F-pseudosigma	**% F-pseudosigma**	**Median**	**Range**
	0.146	43.70%	0.335	0.965
Method	**N**	**Mean**	**Median**	**Range**
EPA 351.2	36	0.405	0.330	0.965
Lachat 10-107-06-2-D	6 (two non-values)	0.250	0.245	0.070
USGS I-4515-91	6	0.378	0.375	0.070

Table 4. F-pseudosigma values for TKN.

TKN

Lab ID	Sample A N	Sample A Lab Median	Sample A Range	Sample A Mean Z-value	Sample B N	Sample B Lab Median	Sample B Range	Sample B Mean Z-value	All N	All Lab Median	All Range	All Mean Z-value
A	3	0.330	0.050	0.14	3	0.330	0.210	0.45	6	0.330	0.210	0.31
C	3	0.840	0.170	3.09	3	0.700	0.060	2.29	6	0.705	0.210	2.79
D	3	0.191	0.044	0.98	3	0.199	0.029	0.82	6	0.195	0.044	0.93
E	3*	0.235	0.030	0.71	3*	0.265	0.050	0.42	6*	0.245	0.070	0.58
H	3	0.420	0.000	0.54	3	0.440	0.060	0.75	6	0.420	0.060	0.67
I	3	0.380	0.030	0.25	3	0.370	0.070	0.32	6	0.375	0.070	0.30
J	3	0.220	0.040	0.77	3	0.220	0.030	0.68	6	0.220	0.040	0.75
K	3	0.420	0.280	0.81	3	0.320	0.830	1.79	6	0.370	0.860	1.38

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

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

TKN		
Method	**MDL Range**	**PQL Range**
ALL	0.031 - 0.08	0.1 - 0.2
EPA 351.2	0.031 - 0.08	0.1 – 0.2
Lachat 10-107-06-2-D	Not Reported	0.1
USGS I-4515-91	0.05	Not Reported

Table 6. Methods and detection/quantitation limits 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	.32000	.026458	.015275	.25428	.38572	.290	.340
C	3	.79667	.092916	.053645	.56585	1.02748	.690	.860
D	3	.19500	.022271	.012858	.13968	.25032	.175	.219
E	2	.23500	.021213	.015000	.04441	.42559	.220	.250
H	3	.42000	.000000	.000000	.42000	.42000	.420	.420
I	3	.37667	.015275	.008819	.33872	.41461	.360	.390
J	3	.22667	.020817	.012019	.17496	.27838	.210	.250
K	3	.42000	.140000	.080829	.07222	.76778	.280	.560
Total	23	.37978	.192728	.040186	.29644	.46312	.175	.860

Table 7. Descriptive statistics by laboratory for TKN for Sample A.

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	.33333	.105040	.060645	.07240	.59427	.230	.440
C	3	.68667	.032146	.018559	.60681	.76652	.650	.710
D	3	.20200	.014731	.008505	.16541	.23859	.189	.218
E	2	.26500	.035355	.025000	-.05266	.58266	.240	.290
H	3	.44667	.030551	.017638	.37078	.52256	.420	.480
I	3	.38000	.036056	.020817	.29043	.46957	.350	.420
J	3	.22333	.015275	.008819	.18539	.26128	.210	.240
K	3	.59000	.476340	.275015	-.59329	1.77329	.310	1.140
Total	23	.39635	.224402	.046791	.29931	.49339	.189	1.140

Table 8. Descriptive statistics by laboratory for TKN for Sample B.

Descriptives

Total Kjeldahl Nitrogen mg/L

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
A	6	.32667	.068896	.028127	.25436	.39897	.230	.440
C	6	.74167	.086583	.035347	.65080	.83253	.650	.860
D	6	.19850	.017318	.007070	.18033	.21667	.175	.219
E	4	.25000	.029439	.014720	.20316	.29684	.220	.290
H	6	.43333	.024221	.009888	.40791	.45875	.420	.480
I	6	.37833	.024833	.010138	.35227	.40439	.350	.420
J	6	.22500	.016432	.006708	.20776	.24224	.210	.250
K	6	.50500	.327521	.133710	.16129	.84871	.280	1.140
Total	46	.38807	.206998	.030520	.32659	.44954	.175	1.140

Table 9. Descriptive statistics by laboratory for TKN for all samples.

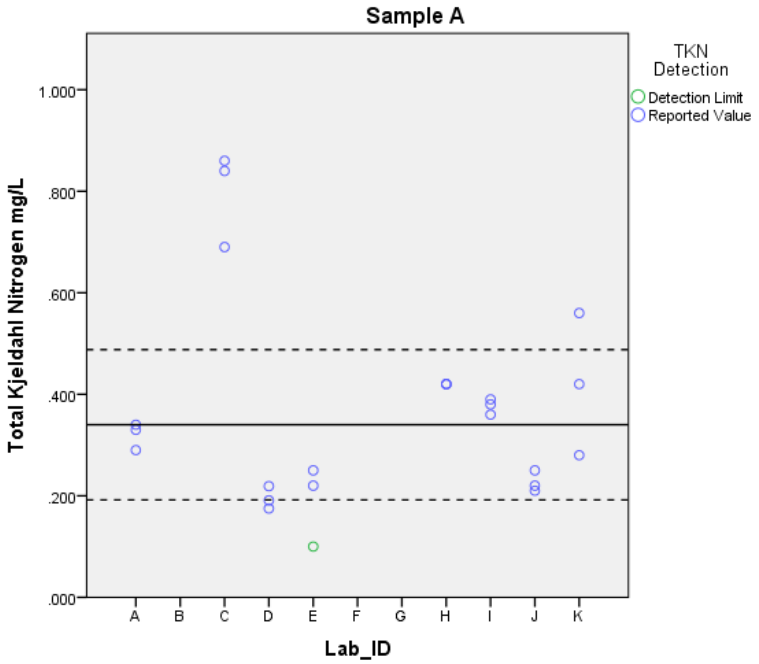


Figure 1. Scatter-plot of TKN values and detection/quantitation limits obtained by eight laboratories for Sample A. The solid line indicates the overall median, and the dashed lines indicate +/- 1 F-pseudosigma.

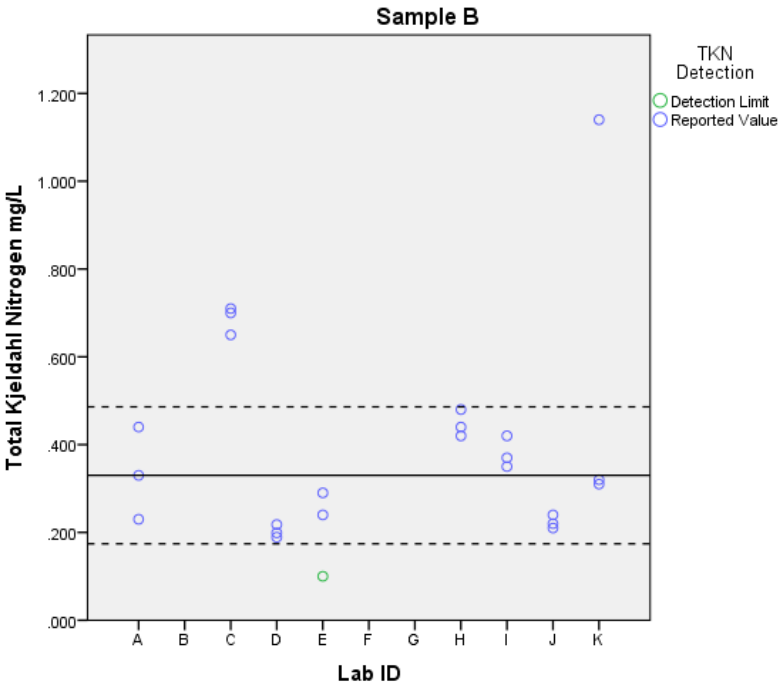


Figure 2. Scatter-plot of TKN values and detection/quantitation limits obtained by eight laboratories for Sample B. The solid line indicates the overall median, and the dashed lines indicate +/- 1 F-pseudosigma.

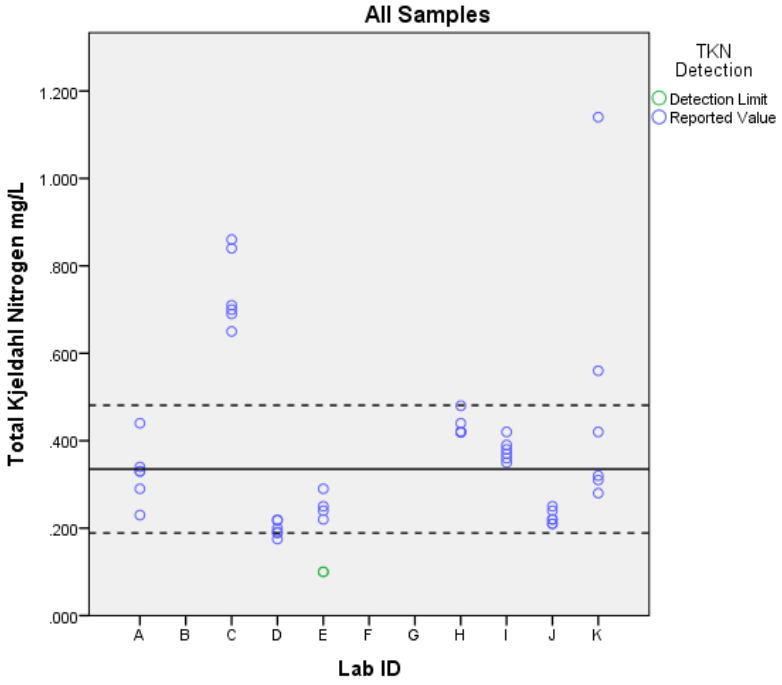


Figure 3. Scatter-plot of TKN values and detection/quantitation limits obtained by eight laboratories for all samples. The solid line indicates the overall median, and the dashed lines indicate +/- 1 F-pseudosigma.

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	.005	Reject the null hypothesis.

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

Homogeneous Subsets based on Total Kjeldahl Nitrogen mg/L

		Subset			
		1	2	3	4
Sample[1]	D	2.333			
	J	5.333	5.333		
	E	6.500	6.500	6.500	
	A		11.000	11.000	
	I			14.000	
	K			15.500	15.500
	H			17.500	17.500
	C				22.000
Test Statistic		4.126	5.264	8.852	5.891
Sig. (2-sided test)		.127	.072	.065	.053
Adjusted Sig. (2-sided test)		.392	.239	.137	.180

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 10. Kruskal-Wallis and post hoc inter-laboratory comparisons for TKN for Sample A.

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	.013	Reject the null hypothesis.

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

Homogeneous Subsets based on Total Kjeldahl Nitrogen mg/L				
		Subset		
		1	2	3
Sample[1]	D	2.333		
	J	5.167	5.167	
	E	8.250	8.250	8.250
	A	11.833	11.833	11.833
	I		14.167	14.167
	K		14.667	14.667
	H		17.333	17.333
	C			21.000
Test Statistic		7.264	10.340	9.251
Sig. (2-sided test)		.064	.066	.099
Adjusted Sig. (2-sided test)		.166	.118	.175

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 11. Kruskal-Wallis and post hoc inter-laboratory comparisons for TKN for Sample B.

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	.000	Reject the null hypothesis.

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

Homogeneous Subsets based on Total Kjeldahl Nitrogen mg/L

		Subset				
		1	2	3	4	5
Sample[1]	D	4.167				
	J		10.000			
	E		14.375	14.375		
	A			22.667	22.667	
	I				27.917	
	K				29.250	
	H				34.083	
	C					42.500
Test Statistic		.[2]	2.326	3.324	6.793	.[2]
Sig. (2-sided test)		.	.127	.068	.079	.
Adjusted Sig. (2-sided test)		.	.527	.322	.202	.

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

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

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

Table 12. Kruskal-Wallis and post hoc inter-laboratory comparisons for TKN for all samples.

Test of Homogeneity of Variances

Total Kjeldahl Nitrogen mg/L

Levene's Statistic	df1	df2	Sig.
2.948	2	20	.076

ANOVA

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	.047	2	.023	.609	.554
Within Groups	.770	20	.039		
Total	.817	22			

	Method ID	N	Subset for alpha = 0.05
			1
Gabriel[a,b]	Lachat 10-107-06-2-D	2	.23500
	USGS I-4515-91	3	.37667
	EPA 351.2	18	.39639
	Sig.		.642

Means for groups in homogeneous subsets are displayed.

a. Uses Harmonic Mean Sample Size = 3.375.

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

Table 13. ANOVA and post hoc comparisons for TKN values by method for all reported values for Sample A.

Test of Homogeneity of Variances

Total Kjeldahl Nitrogen mg/L

Levene's Statistic	df1	df2	Sig.
2.248	2	20	.132

ANOVA

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	.041	2	.020	.381	.688
Within Groups	1.067	20	.053		
Total	1.108	22			

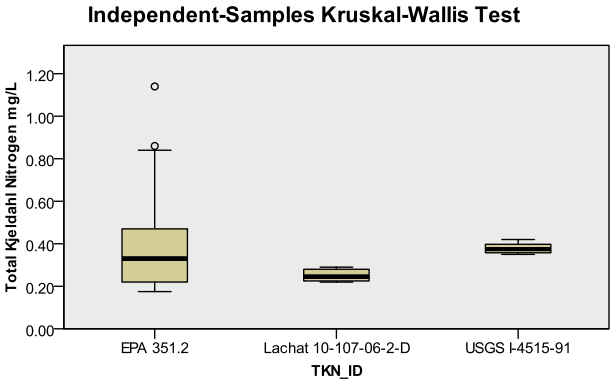
	Method ID	N	Subset for alpha = 0.05
			1
Gabriel[a,b]	Lachat 10-107-06-2-D	2	.26500
	USGS I-4515-91	3	.38000
	EPA 351.2	18	.41367
	Sig.		.788

Means for groups in homogeneous subsets are displayed.

a. Uses Harmonic Mean Sample Size = 3.375.

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

Table 14. ANOVA and post hoc comparisons for TKN values by method for all reported values for Sample B.



Total N	46
Test Statistic	2.521
Degrees of Freedom	2
Asymptotic Sig. (2-sided test)	.284

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 4. Results of Kruskal-Wallis method comparisons for TKN for all samples.

B. Ammonia. Nine of the 30 results were reported values for Sample A; the other 70% were reported as qualifiers. The MDLs for all laboratories ranged from 0.003 to 0.02 mg/L; and the PQLs for Labs C, E, and J ranged from 0.02 to 0.05 mg/L. No reported values were determined to be statistical outliers. There were no values reported as less than detection/quantitation limits that were determined to be false negatives. The %F-pseudosigma value was high (greater than 30%), indicating a lack of precision among laboratories. The same patterns in the data were noted for Sample B, as well.

When looking at all of the results combined, eighteen of the 60 results were reported as values. No reported values were outside acceptable ranges, nor were any values determined to be statistical outliers. There were no values reported as less than detection/quantitation limits that were determined to be false negatives. The % F-pseudosigma was very large (>300%). Results reported for EPA 350.1 were significantly greater than those reported for SM 4500 NH3 G; no values were reported for Lachat 10-107-06-1-C. No other analyses were conducted for ammonia. There was no statistical difference between Sample A and Sample B. See Figures 5 - 7 and Tables 15 - 22 for scatter-plots of values obtained by individual laboratories, F-pseudosigma values, summary statistics, inter-laboratory comparisons, and method comparisons.

Ammonia				
	Sample A			
	F-pseudosigma	**% F-pseudosigma**	**Median**	**Range**
	0.104	347.17%	0.030	0.163
Method	**N**	**Mean**	**Median**	**Range**
EPA 350.1	24 (eighteen non-values)	0.101	0.106	0.144
Lachat 10-107-06-1-C	3	All Non-detect	N/A	N/A
SM 4500 NH3 G	3	0.012	0.012	0.010
	Sample B			
	F-pseudosigma	**% F-pseudosigma**	**Median**	**Range**
	0.113	375.59%	0.030	0.160
Method	**N**	**Mean**	**Median**	**Range**
EPA 350.1	24 (eighteen non-values)	0.096	0.096	0.146
Lachat 10-107-06-1-C	3	All Non-detect	N/A	N/A
SM 4500 NH3 G	3	0.012	0.011	0.005
	All			
	F-pseudosigma	**% F-pseudosigma**	**Median**	**Range**
	0.110	366.32%	0.030	0.163
Method	**N**	**Mean**	**Median**	**Range**
EPA 350.1	48 (36 non-values)	0.099	0.106	0.146
Lachat 10-107-06-1-C	6	All Non-detect	N/A	N/A
SM 4500 NH3 G	6	0.012	0.012	0.010

Table 15. F-pseudosigma values for ammonia.

NH_3

Lab ID	Sample A N	Sample A Lab Median	Sample A Range	Sample A Mean Z-value	Sample B N	Sample B Lab Median	Sample B Range	Sample B Mean Z-value	All N	All Lab Median	All Range	All Mean Z-value
A	3*	NR	NR	NR	3*	NR	NR	NR	6*	NR	NR	NR
C	3*	NR	NR	NR	3*	NR	NR	NR	6*	NR	NR	NR
D	3*	NR	NR	NR	3*	NR	NR	NR	6*	NR	NR	NR
E	3*	NR	NR	NR	3*	NR	NR	NR	6*	NR	NR	NR
F	3	0.030	0.045	N/A	3	0.030	0.007	N/A	6	0.030	0.047	N/A
G	3	0.012	0.010	N/A	3	0.011	0.005	N/A	6	0.012	0.010	N/A
H	3*	NR	NR	NR	3*	NR	NR	NR	6*	NR	NR	NR
I	3*	NR	NR	NR	3*	NR	NR	NR	6*	NR	NR	NR
J	3*	NR	NR	NR	3*	NR	NR	NR	6*	NR	NR	NR
K	3	0.170	0.030	N/A	3	0.170	0.010	N/A	6	0.170	0.030	N/A

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

Table 16. Summary statistics and Z-values by laboratory for ammonia.

Ammonia		
Method	**MDL Range**	**PQL Range**
ALL	0.003 - 0.02	0.012 - 0.05
EPA 350.1	0.003 - 0.02	0.012 - 0.05
Lachat 10-107-06-1-C	Not Reported	0.04
SM 4500 NH3 G	0.007	0.028

Table 17. Methods and detection/quantitation limits for NH_3.

Descriptives

Ammonia mg/L

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean Lower Bound	95% Confidence Interval for Mean Upper Bound	Minimum	Maximum
F	3	.04233	.024906	.014380	-.01954	.10420	.026	.071
G	3	.01200	.005000	.002887	-.00042	.02442	.007	.017
K	3	.16000	.017321	.010000	.11697	.20303	.140	.170
Total	9	.07144	.069426	.023142	.01808	.12481	.007	.170

Table 18. Descriptive statistics by laboratory for ammonia for Sample A.

Descriptives

Ammonia mg/L

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean Lower Bound	95% Confidence Interval for Mean Upper Bound	Minimum	Maximum
F	3	.02833	.003786	.002186	.01893	.03774	.024	.031
G	3	.01200	.002646	.001528	.00543	.01857	.010	.015
K	3	.16667	.005774	.003333	.15232	.18101	.160	.170
Total	9	.06900	.073683	.024561	.01236	.12564	.010	.170

Table 19. Descriptive statistics by laboratory for ammonia for Sample B.

Descriptives

Ammonia mg/L

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean Lower Bound	95% Confidence Interval for Mean Upper Bound	Minimum	Maximum
F	6	.03533	.017682	.007219	.01678	.05389	.024	.071
G	6	.01200	.003578	.001461	.00825	.01575	.007	.017
K	6	.16333	.012111	.004944	.15062	.17604	.140	.170
Total	18	.07022	.069461	.016372	.03568	.10476	.007	.170

Table 20. Descriptive statistics by laboratory for ammonia for all samples.

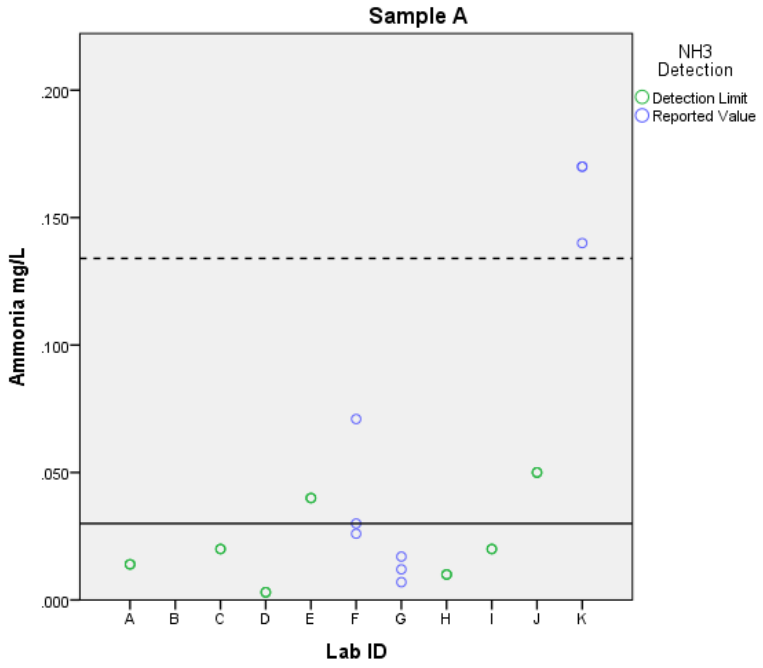


Figure 5. Scatter-plot of ammonia values and detection/quantitation limits obtained by ten laboratories for Sample A. The solid line indicates the overall median, and the dashed lines indicate +/- 1 F-pseudosigma.

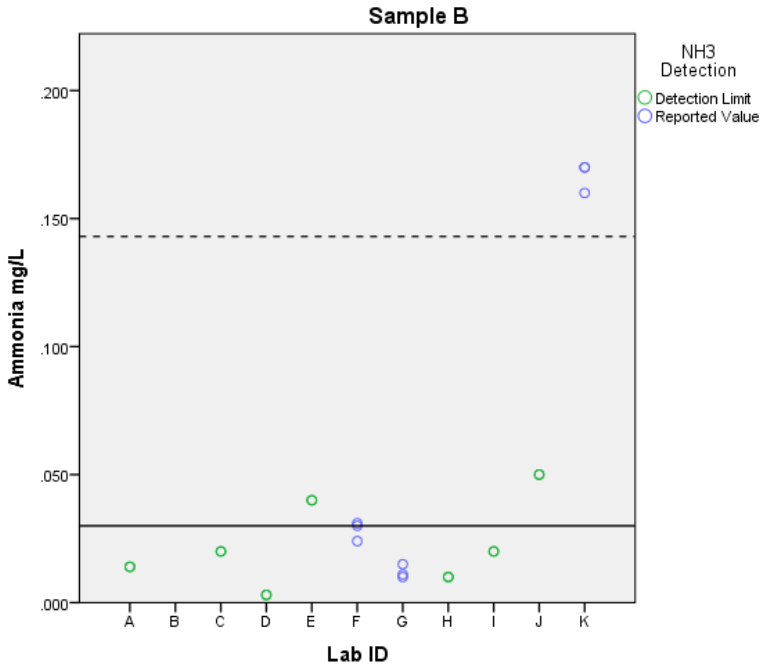


Figure 6. Scatter-plot of ammonia values and detection/quantitation limits obtained by ten laboratories for Sample B. The solid line indicates the overall median, and the dashed lines indicate +/- 1 F-pseudosigma.

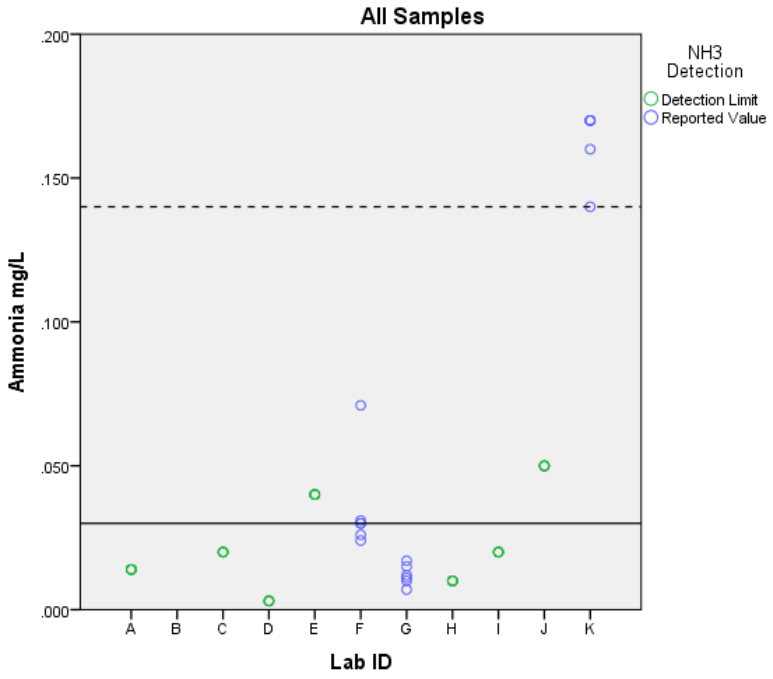


Figure 7. Scatter-plot of ammonia values and detection/quantitation limits obtained by ten laboratories for all samples. The solid line indicates the overall median, and the dashed lines indicate +/- 1 F-pseudosigma.

Test of Homogeneity of Variances

Ammonia mg/L

Levene's Statistic	df1	df2	Sig.
2.000	2	15	.170

ANOVA

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	.080	2	.040	253.087	.000
Within Groups	.002	15	.000		
Total	.082	17			

Ammonia mg/L

	Lab ID	N	Subset for alpha = 0.05		
			1	2	3
Tukey HSD[a]	G	6	.01200		
	F	6		.03533	
	K	6			.16333
	Sig.		1.000	1.000	1.000

Means for groups in homogeneous subsets are displayed.

Table 21. ANOVA and post hoc inter-laboratory comparisons for ammonia for all samples.

Group Statistics

	Method ID	N	Mean	Std. Deviation	Std. Error Mean
Ammonia mg/L	EPA 350.1	12	.09933	.068390	.019742
	SM 4500 NH3 G	6	.01200	.003578	.001461

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
Ammonia mg/L	Equal variances assumed	103.863	**.000**	3.078	16	.007	.087333	.028371	.027191	.147476
	Equal variances not assumed			**4.412**	**11.120**	**.001**	**.087333**	**.019796**	**.043819**	**.130848**

Table 22. Results of t-test comparisons of ammonia by method for all samples.

C. Total Nitrite + Nitrate. Although there were only seventeen and 20 reported values for NO_x for each sample (vs. the 21 needed, respectively), analyses were run; however, caution should be exercised in interpreting the results due to the lack of statistical power. Sixteen of the seventeen reported values for Sample A were within acceptable ranges. Lab A reported the only value outside acceptable ranges. There were no statistical outliers, and no results reported as less than the MDL (or PQL) were determined to be false negatives. The %F-pseudosigma value was large (greater than 30%), indicating a lack of precision among laboratories. Results reported By Lab A were highly variable. Of the seventeen reported values, 75% were within 1 F-pseudosigma and 94% were within 2 F-pseudosigma. The only method to report values for this sample was EPA 353.2.

Sample B had nineteen of the 20 reported values within acceptable ranges. Lab A reported the only value outside acceptable ranges. There were no statistical outliers, and no results reported as less than the MDL (or PQL) were determined to be false negatives. The %F-pseudosigma value was large (greater than 30%), indicating a lack of precision among laboratories. Results reported By Lab A were highly variable. Of the 20 reported values, 75% were within 1 F-pseudosigma and 95% were within 2 F-pseudosigma. Results reported for EPA 353.2 were significantly greater than those reported for SM 4500 NO3 F; no values were reported for Lachat 10-107-04-1-C or USGS I-2545-90.

When looking at all of the results combined, 35 of the 37 reported values were within acceptable ranges. Lab A reported two values outside acceptable ranges. Results for Lab A were highly variable. There were no statistical outliers, and no results reported as less than the MDL (or PQL) were determined to be false negatives. The % F-pseudosigma was large (greater than 30%), indicating a lack of precision among laboratories. Of the 37 reported values, 76% were within 1 F-pseudosigma and 95% were within 2 F-pseudosigma. Results reported for EPA 353.2 were significantly greater than those reported for SM 4500 NO3 F; no values were reported for Lachat 10-107-04-1-C or USGS I-2545-90. The MDLs for all laboratories ranged from 0.002 to 0.02 mg/L; and the PQLs for Labs E and J ranged from 0.02 to 0.04 mg/L. There was no statistical difference between Sample A and Sample B. See Figures 8 - 12 and Tables 23 - 31 for scatter-plots of values obtained by individual laboratories, F-pseudosigma values, summary statistics, inter-laboratory comparisons, and method comparisons.

NO_x				
	Sample A			
	F-pseudosigma	**% F-pseudosigma**	**Median**	**Range**
	0.008	101.93%	0.008	0.022
Method	**N**	**Mean**	**Median**	**Range**
EPA 353.2	21 (four non-values)	0.013	0.008	0.022
Lachat 10-107-04-1-C	3	All Non-detect	N/A	N/A
SM 4500 N03 F	3	All Non-detect	N/A	N/A
USGS I-2545-90	3	All Non-detect	N/A	N/A
	Sample B			
	F-pseudosigma	**% F-pseudosigma**	**Median**	**Range**
	0.008	81.54%	0.010	0.027
Method	**N**	**Mean**	**Median**	**Range**
EPA 353.2	21 (three non-values)	0.014	0.011	0.022
Lachat 10-107-04-1-C	3	All Non-detect	N/A	N/A
SM 4500 N03 F	3 (one non-value)	0.003	0.003	0.000
USGS I-2545-90	3	All Non-detect	N/A	N/A
	All Samples			
	F-pseudosigma	**% F-pseudosigma**	**Median**	**Range**
	0.008	77.84%	0.010	0.027
Method	**N**	**Mean**	**Median**	**Range**
EPA 353.2	42 (seven non-values)	0.013	0.010	0.023
Lachat 10-107-04-1-C	6	All Non-detect	N/A	N/A
SM 4500 N03 F	6 (four non-values)	0.003	0.003	0.000
USGS I-2545-90	6	All Non-detect	N/A	N/A

Table 23. F-pseudosigma values for NO_x.

NO_x

	Sample A				Sample B				All			
Lab ID	N	Lab Median	Range	Mean Z-value	N	Lab Median	Range	Mean Z-value	N	Lab Median	Range	Mean Z-value
A	3*	0.023	0.012	1.88	3	0.022	0.014	1.58	6	0.022	0.014	1.60
C	3	0.008	0.001	0.04	3	0.008	0.001	0.21	6	0.008	0.002	0.25
D	3*	NR	NR	NR	3*	0.003	0.000	0.88	6*	0.003	0.000	0.88
E	3*	NR	NR	NR	3*	NR	NR	NR	6*	NR	NR	NR
F	3	0.022	0.002	1.75	3	0.021	0.001	1.33	6	0.021	0.003	1.42
G	3	0.008	0.000	0.00	3	0.010	0.001	0.04	6	0.009	0.002	0.15
H	3	0.008	0.000	0.00	3	0.008	0.001	0.21	6	0.008	0.001	0.23
I	3*	NR	NR	NR	3*	NR	NR	NR	6*	NR	NR	NR
J	3*	NR	NR	NR	3*	NR	NR	NR	6*	NR	NR	NR
K	3	0.011	0.001	0.42	3	0.011	0.001	0.17	6	0.011	0.001	0.17

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

Table 24. Summary statistics and Z-values by Laboratory for NO_x.

NO_x		
Method	**MDL Range**	**PQL Range**
All	0.002 - 0.02	0.01 - 0.04
EPA 353.2	0.002 - 0.02	0.01 - 0.04
Lachat 10-107-04-1-C	Not Reported	0.02
SM 4500 N03 F	0.003	0.012
USGS I-2545-90	0.02	Not Reported

Table 25. 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	2	.02300	.008485	.006000	-.05324	.09924	.017	.029
C	3	.00767	.000577	.000333	.00623	.00910	.007	.008
F	3	.02200	.001000	.000577	.01952	.02448	.021	.023
G	3	.00800	.000000	.000000	.00800	.00800	.008	.008
H	3	.00800	.000000	.000000	.00800	.00800	.008	.008
K	3	.01133	.000577	.000333	.00990	.01277	.011	.012
Total	17	.01276	.006897	.001673	.00922	.01631	.007	.029

Table 26. Descriptive statistics by laboratory for NO_x for Sample A.

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	.02267	.007024	.004055	.00522	.04011	.016	.030
C	3	.00833	.000577	.000333	.00690	.00977	.008	.009
D	2	.00300	.000000	.000000	.00300	.00300	.003	.003
F	3	.02067	.000577	.000333	.01923	.02210	.020	.021
G	3	.00967	.000577	.000333	.00823	.01110	.009	.010
H	3	.00833	.000577	.000333	.00690	.00977	.008	.009
K	3	.01133	.000577	.000333	.00990	.01277	.011	.012
Total	20	.01245	.006977	.001560	.00918	.01572	.003	.030

Table 27. Descriptive statistics by laboratory for NO_x for Sample B.

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	5	.02280	.006535	.002922	.01469	.03091	.016	.030
C	6	.00800	.000632	.000258	.00734	.00866	.007	.009
D	2	.00300	.000000	.000000	.00300	.00300	.003	.003
F	6	.02133	.001033	.000422	.02025	.02242	.020	.023
G	6	.00883	.000983	.000401	.00780	.00987	.008	.010
H	6	.00817	.000408	.000167	.00774	.00860	.008	.009
K	6	.01133	.000516	.000211	.01079	.01188	.011	.012
Total	37	.01259	.006845	.001125	.01031	.01488	.003	.030

Table 28. Descriptive statistics by laboratory for NO_x for all samples.

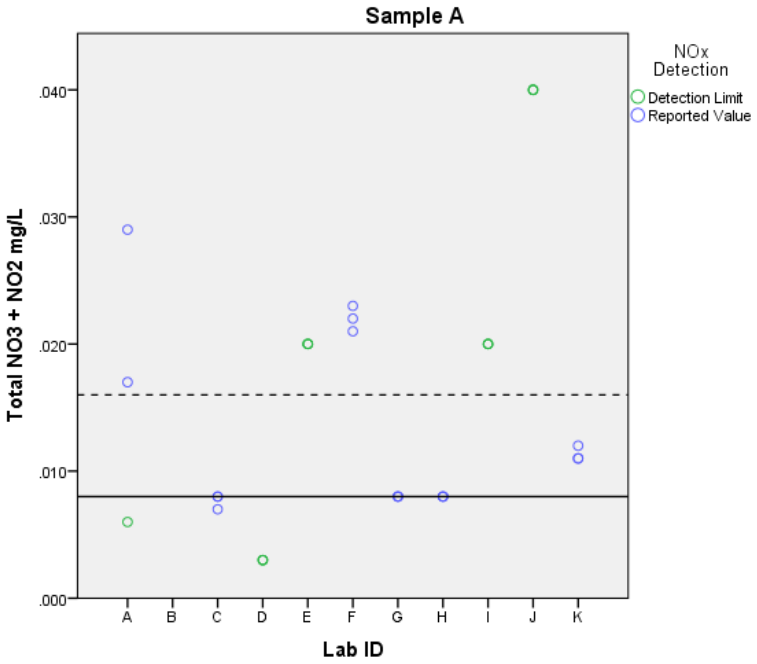


Figure 8. Scatter-plot of NO_x values and detection/quantitation limits obtained by ten laboratories for Sample A. The solid line indicates the overall median, and the dashed lines indicate +/- 1 F-pseudosigma.

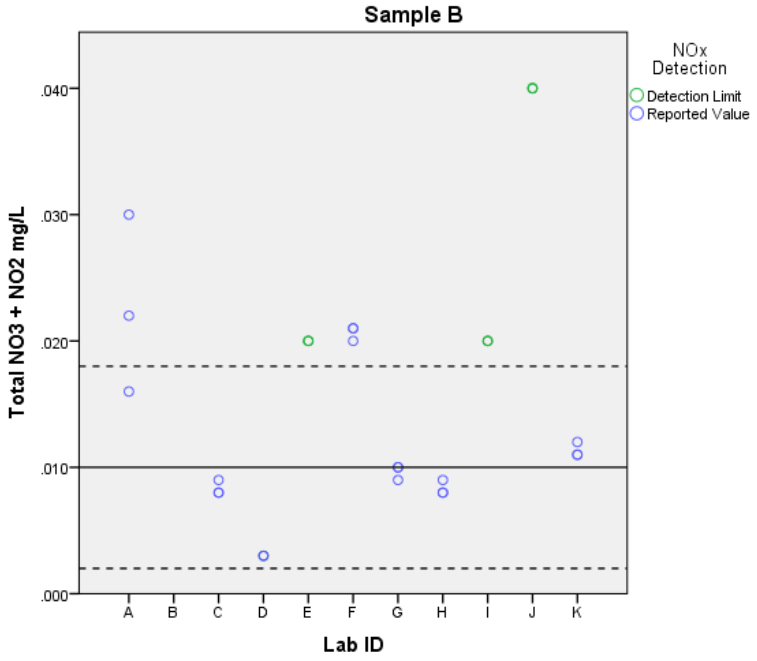


Figure 9. Scatter-plot of NO_x values and detection/quantitation limits obtained by ten laboratories for Sample B. The solid line indicates the overall median, and the dashed lines indicate +/- 1 F-pseudosigma.

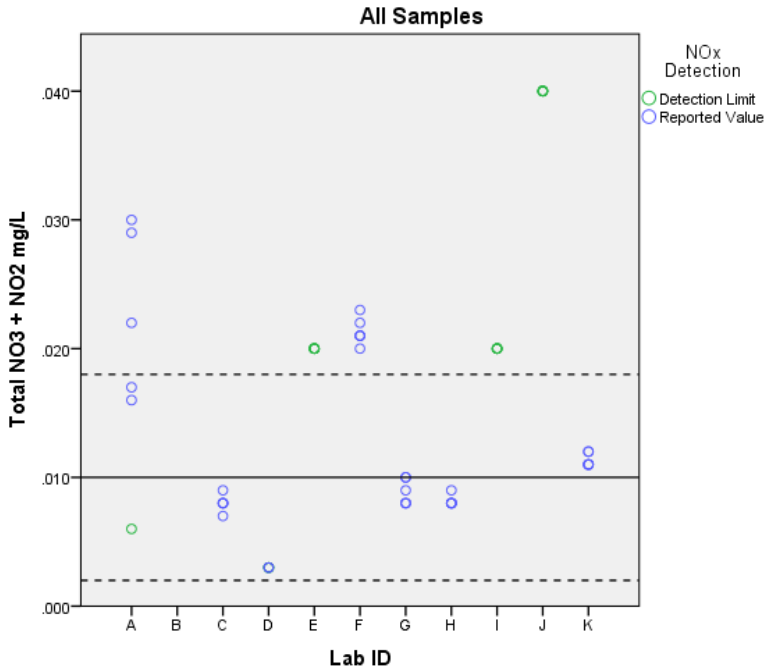


Figure 10. Scatter-plot of NO_x values and detection/quantitation limits obtained by ten laboratories for all samples. The solid line indicates the overall median, and the dashed lines indicate +/- 1 F-pseudosigma.

Hypothesis Test Summary				
	Null Hypothesis	Test	Sig.	Decision
1	The distribution of Total NO_3 + NO_2 mg/L is the same across categories of Lab ID.	Independent-Samples Kruskal-Wallis Test	.011	Reject the null hypothesis.
Asymptotic significances are displayed. The significance level is .05.				

Homogeneous Subsets based on Total NO_3 + NO_2 mg/L			
		Subset	
		1	2
Sample[1]	C	4.000	
	G	5.500	
	H	5.500	
	K		11.000
	F		15.000
	A		15.000
Test Statistic		2.000	5.060
Sig. (2-sided test)		.368	.080
Adjusted Sig. (2-sided test)		.814	.262
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.			

Table 29. Kruskal-Wallis and post hoc inter-laboratory comparisons for NO_x for Sample A.

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	.006	Reject the null hypothesis.
Asymptotic significances are displayed. The significance level is .05.				

Homogeneous Subsets based on Total NO_3 + NO_2 mg/L				
		Subset		
		1	2	3
Sample[1]	D	1.500		
	C	5.667	5.667	
	H	5.667	5.667	
	G		9.667	
	K			13.000
	F			17.000
	A			18.000
Test Statistic		4.667	4.876	5.695
Sig. (2-sided test)		.097	.087	.058
Adjusted Sig. (2-sided test)		.312	.285	.197
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.				

Table 30. Kruskal-Wallis and post hoc inter-laboratory comparisons for NO_x for Sample B.

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	.000	Reject the null hypothesis.

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

Homogeneous Subsets based on Total NO_3 + NO_2 mg/L

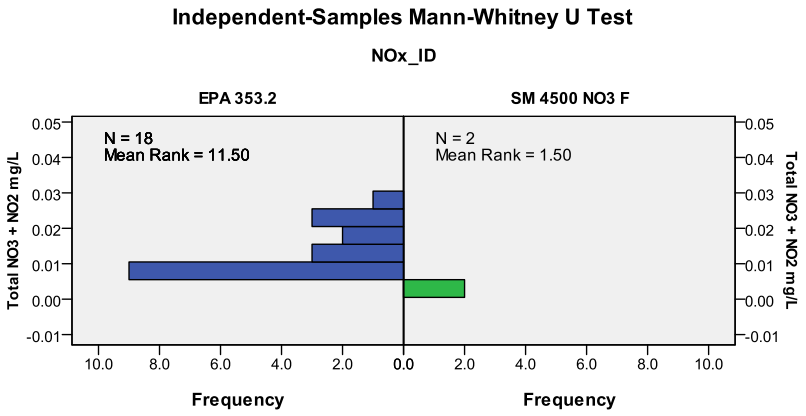
		Subset			
		1	2	3	4
Sample[1]	D	1.500			
	C		9.667		
	H		10.750		
	G		14.083		
	K			23.500	
	F				31.750
	A				32.300
Test Statistic		.[2]	3.189	.[2]	.077
Sig. (2-sided test)		.	.203	.	.782
Adjusted Sig. (2-sided test)		.	.565	.	1.000

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.

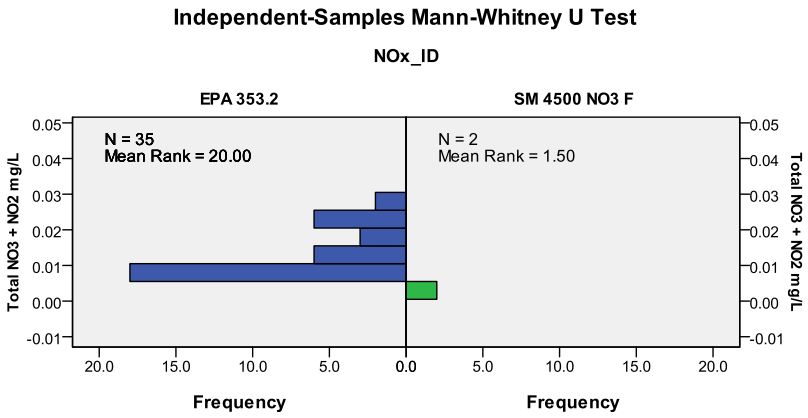
[2]Unable to compute because the subset contains only one sample.

Table 31. Kruskal-Wallis and post hoc inter-laboratory comparisons for NO_x for all samples.



Total N	20
Mann-Whitney U	.000
Wilcoxon W	3.000
Test Statistic	.000
Standard Error	7.883
Standardized Test Statistic	-2.283
Asymptotic Sig. (2-sided test)	.022
Exact Sig. (2-sided test)	.011

Figure 11. Results of Mann-Whitney method comparisons for NO_x for Sample B.



Total N	37
Mann-Whitney U	.000
Wilcoxon W	3.000
Test Statistic	.000
Standard Error	14.614
Standardized Test Statistic	-2.395
Asymptotic Sig. (2-sided test)	.017
Exact Sig. (2-sided test)	.003

Figure 12. Results of Mann-Whitney method comparisons for NO_x for all samples.

D. Dissolved Nitrite. Seven of the 30 results were reported values for Sample A; the other 77% were reported as qualifiers. The MDLs for all laboratories ranged from 0.0003 to 0.004 mg/L; and the PQLs for Labs E and J ranged from 0.005 to 0.02 mg/L. No reported values were determined to be statistical outliers. There were no values reported as less than detection/quantitation limits that were determined to be false negatives. The %F-pseudosigma value was high (greater than 30%), indicating a lack of precision among laboratories. The same general patterns in the data were noted for Sample B, as well; however, three more values were reported as results for Sample B and Lab K reported one value (0.015 mg/L) that was outside acceptable ranges and was a statistical outlier. In addition, method comparisons for Sample A showed no difference in results reported for EPA 353.2 and USGS I-2540-90; whereas, for Sample B, results reported for EPA 353.2 were significantly greater than results reported for USGS I-2540-90. No values were reported for Lachat 10-107-04-1-C or SM 4500 NO2 B for either sample.

When looking at all of the results combined, seventeen of the 60 results were reported as values. Lab K reported one value outside acceptable ranges; this value was determined to be a statistical outlier, as well. There were no values reported as less than detection/quantitation limits that were determined to be false negatives. The %F-pseudosigma value was high (greater than 30%), indicating a lack of precision among laboratories. Results reported for EPA 353.2 were significantly greater than results reported for USGS I-2540-90. No values were reported for Lachat 10-107-04-1-C or SM 4500 NO2 B. There was no statistical difference between Sample A and Sample B. No other analyses were conducted for dissolved nitrite. See Figures 13 - 18 and Tables 32 - 37 for scatter-plots of values obtained by individual laboratories, F-pseudosigma values, summary statistics, inter-laboratory comparisons, and method comparisons.

DNO_2				
	Sample A			
	F-pseudosigma	**% F-pseudosigma**	**Median**	**Range**
	0.001	37.06	0.002	0.001
Method	**N**	**Mean**	**Median**	**Range**
EPA 353.2	21 (seventeen non-values)	0.002	0.002	0.000
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	0.001	0.001	0.000
	Sample B			
	F-pseudosigma	**% F-pseudosigma**	**Median**	**Range**
	0.001	37.06	0.002	0.014
Method	**N**	**Mean**	**Median**	**Range**
EPA 353.2	21 (fourteen non-values)	0.004	0.002	0.013
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	0.001	0.001	0.000
	All Samples			
	F-pseudosigma	**% F-pseudosigma**	**Median**	**Range**
	0.001	37.06	0.002	0.014
Method	**N**	**Mean**	**Median**	**Range**
EPA 353.2	42 (31 non-values)	0.003	0.002	0.013
Lachat 10-107-04-1-C	6	All Non-detect	N/A	N/A
SM 4500 N02 B	6	All Non-detect	N/A	N/A
USGS I-2540-90	6	0.001	0.001	0.000

Table 32. F-pseudosigma values for DNO_2.

DNO_2

Lab ID	Sample A N	Sample A Lab Median	Sample A Range	Sample A Mean Z-value	Sample B N	Sample B Lab Median	Sample B Range	Sample B Mean Z-value
A	3*	NR	NR	NR	3*	NR	NR	NR
C	3*	0.002	N/A	N/A	3*	0.002	0.000	N/A
D	3*	NR	NR	NR	3*	NR	NR	NR
E	3*	NR	NR	NR	3*	NR	NR	NR
F	3	0.002	0.000	N/A	3	0.002	0.000	N/A
G	3*	NR	NR	NR	3*	NR	NR	NR
H	3*	NR	NR	NR	3*	0.002	N/A	N/A
I	3	0.001	0.000	N/A	3	0.001	0.000	N/A
J	3*	NR	NR	NR	3*	NR	NR	NR
K	3*	NR	NR	NR	3*	0.015	N/A	N/A

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

Table 33. 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	Not Reported	0.005
SM 4500 N02 B	0.002	0.008
USGS I-2540-90	0.001	Not Reported

Table 34. Methods and detection/quantitation limits for DNO_2.

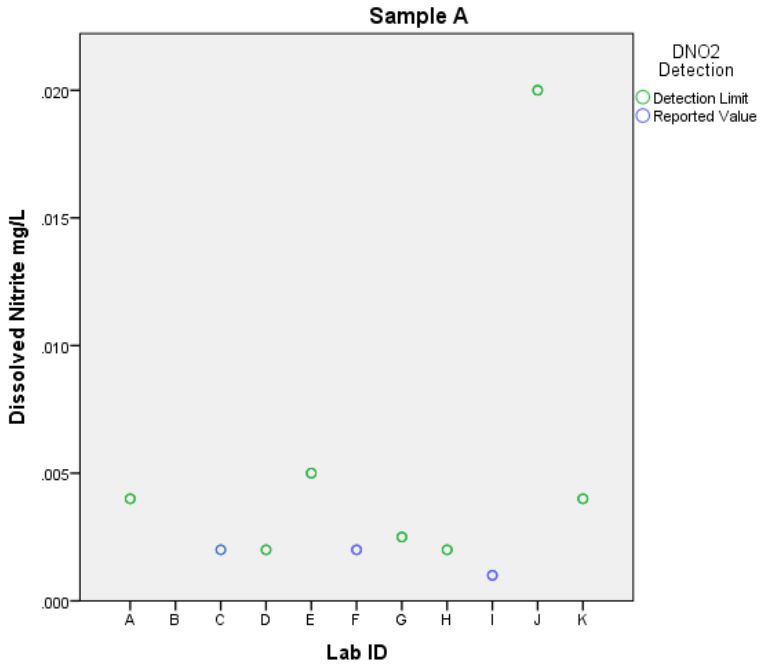


Figure 13. Scatter-plot of DNO_2 values and detection/quantitation limits obtained by ten laboratories for Sample A.

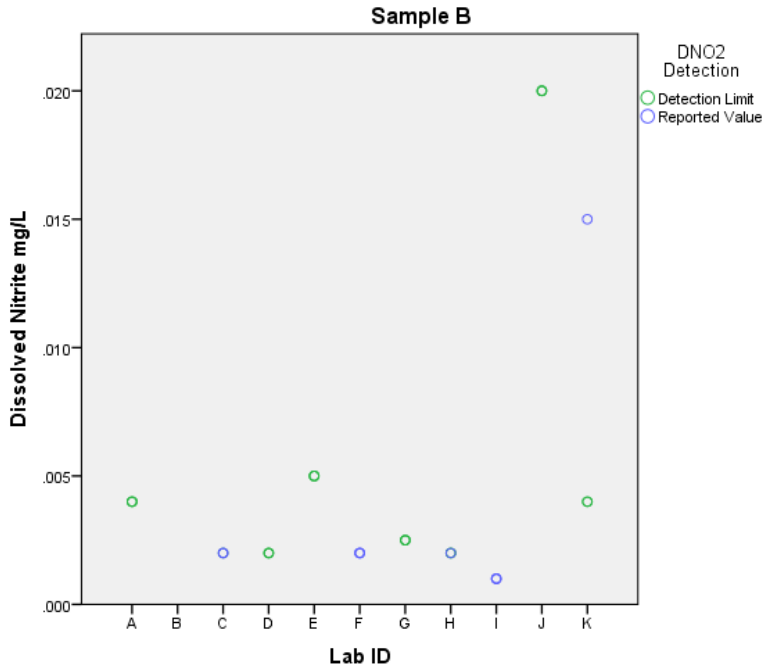


Figure 14. Scatter-plot of DNO_2 values and detection/quantitation limits obtained by ten laboratories for Sample B.

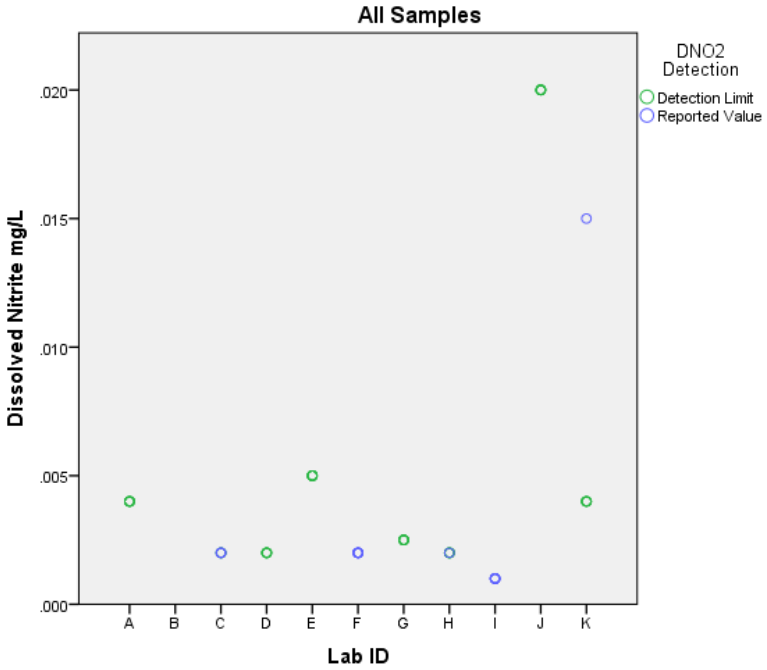
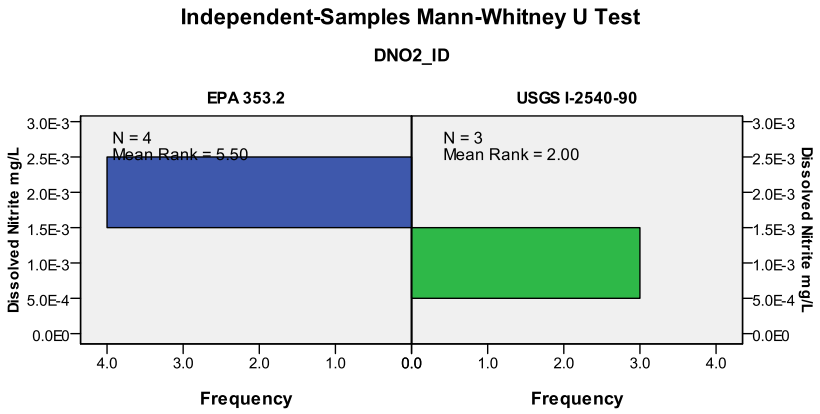
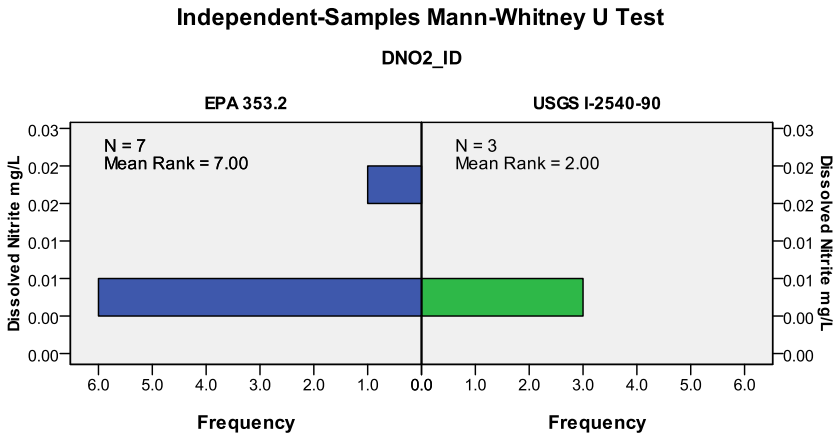


Figure 15. Scatter-plot of DNO_2 values and detection/quantitation limits obtained by ten laboratories for all samples.



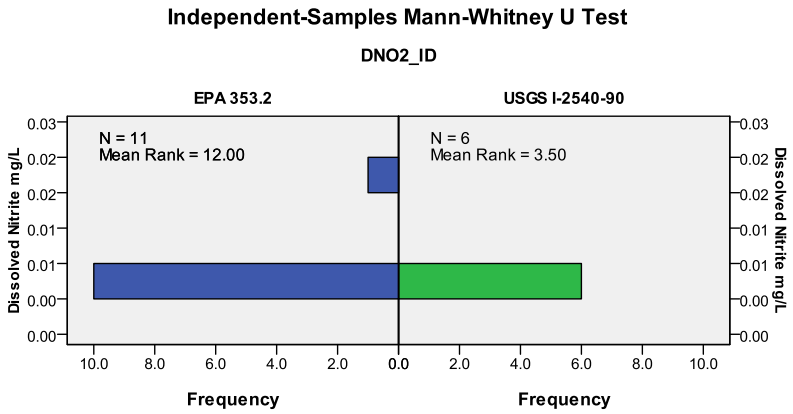
Total N	7
Mann-Whitney U	.000
Wilcoxon W	6.000
Test Statistic	.000
Standard Error	2.449
Standardized Test Statistic	-2.449
Asymptotic Sig. (2-sided test)	.014
Exact Sig. (2-sided test)	.057

Figure 16. Results of Mann-Whitney method comparisons for DNO_2 for Sample A.



Total N	10
Mann-Whitney U	.000
Wilcoxon W	6.000
Test Statistic	.000
Standard Error	3.834
Standardized Test Statistic	-2.739
Asymptotic Sig. (2-sided test)	.006
Exact Sig. (2-sided test)	.017

Figure 17. Results of Mann-Whitney method comparisons for DNO_2 for Sample B.



Total N	17
Mann-Whitney U	.000
Wilcoxon W	21.000
Test Statistic	.000
Standard Error	8.645
Standardized Test Statistic	-3.817
Asymptotic Sig. (2-sided test)	.000
Exact Sig. (2-sided test)	.000

Figure 18. Results of Mann-Whitney method comparisons for DNO_2 for all samples.

E. Total Phosphorus. Twenty-four of the 30 reported values for Sample A were within acceptable ranges. Lab D reported all three values outside acceptable ranges; Lab E reported two and Lab K reported one. Lab K reported one statistical outlier (0.085 mg/L). The %F-pseudosigma value was large (greater than 30%), indicating a lack of precision among laboratories. Of the 30 reported values, 77% were within 1 F-pseudosigma and 80% were within 2 F-pseudosigma. Results reported for method EPA 365.1 were significantly less than results for both EPA 365.4 and Lachat 10-115-01-1-C; there was no statistical difference between results for EPA 365.4 and Lachat 10-115-01-1-C.

For Sample B, 26 of the 30 values were within acceptable ranges. Lab D reported all three values outside acceptable ranges, and Lab K reported one value outside acceptable ranges. There were no statistical outliers reported. The %F-pseudosigma value was large (greater than 30%), indicating a lack of precision among laboratories. Of the 30 reported values, 77% were within 1 F-pseudosigma and 87% were within 2 F-pseudosigma. Results reported for method EPA 365.1 were significantly less than results for both EPA 365.4 and Lachat 10-115-01-1-C; there was no statistical difference between results for EPA 365.4 and Lachat 10-115-01-1-C.

When looking at all of the results combined, 50 of the 60 reported values were within acceptable ranges. All of Lab D's values were outside acceptable ranges, and Labs E and K each reported two values outside acceptable ranges. Lab K reported one statistical outlier (0.085 mg/L). The % F-pseudosigma remained large even after combining Samples A and B. Of the 60 reported values, 77% were within 1 F-pseudosigma and 83% were within 2 F-pseudosigma. Lab K's results were highly variable. Results reported for method EPA 365.1 were significantly less than results for both EPA 365.4 and Lachat 10-115-01-1-C; there was no statistical difference between results for EPA 365.4 and Lachat 10-115-01-1-C. There was no statistical difference between Sample A and Sample B. See Figures 19 - 21 and Tables 35 - 45 for scatter-plots of values obtained by individual laboratories, F-pseudosigma values, summary statistics, inter-laboratory comparisons, and method comparisons.

TP				
	Sample A			
	F-pseudosigma	% F-pseudosigma	Median	Range
	0.013	45.72%	0.028	0.067
Method	N	Mean	Median	Range
EPA 365.1	18	0.024	0.024	0.012
EPA 365.4	9	0.050	0.042	0.049
Lachat 10-115-01-1-C	3	0.053	0.060	0.020
	Sample B			
	F-pseudosigma	% F-pseudosigma	Median	Range
	0.012	43.71%	0.028	0.042
Method	N	Mean	Median	Range
EPA 365.1	18	0.026	0.027	0.012
EPA 365.4	9	0.044	0.046	0.042
Lachat 10-115-01-1-C	3	0.043	0.050	0.020
	Sample B			
	F-pseudosigma	% F-pseudosigma	Median	Range
	0.012	42.13%	0.028	0.069
Method	N	Mean	Median	Range
EPA 365.1	36	0.025	0.025	0.013
EPA 365.4	18	0.047	0.044	0.069
Lachat 10-115-01-1-C	6	0.048	0.050	0.030

Table 35. F-pseudosigma values for TP.

TP

Lab ID	Sample A N	Sample A Lab Median	Sample A Range	Sample A Mean Z-value	Sample B N	Sample B Lab Median	Sample B Range	Sample B Mean Z-value	All N	All Lab Median	All Range	All Mean Z-value
A	3	0.018	0.003	0.69	3	0.020	0.001	0.69	6	0.020	0.003	0.72
C	3	0.023	0.002	0.38	3	0.023	0.001	0.39	6	0.023	0.002	0.40
D	3	0.057	0.001	2.21	3	0.058	0.001	2.47	6	0.057	0.002	2.43
E	3	0.060	0.020	1.95	3	0.050	0.020	1.28	6	0.050	0.030	1.69
F	3	0.025	0.002	0.23	3	0.028	0.002	0.06	6	0.026	0.004	0.15
G	3	0.026	0.001	0.18	3	0.027	0.000	0.08	6	0.027	0.002	0.14
H	3	0.030	0.000	0.15	3	0.031	0.000	0.25	6	0.031	0.001	0.21
I	3	0.023	0.001	0.40	3	0.026	0.003	0.13	6	0.024	0.006	0.28
J	3	0.040	0.000	0.92	3	0.040	0.010	0.72	6	0.040	0.010	0.86
K	3	0.042	0.049	2.03	3	0.046	0.039	1.58	6	0.044	0.069	1.89

Table 36. 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	.01900	.001732	.001000	.01470	.02330	.018	.021
C	3	.02300	.001000	.000577	.02052	.02548	.022	.024
D	3	.05667	.000577	.000333	.05523	.05810	.056	.057
E	3	.05333	.011547	.006667	.02465	.08202	.040	.060
F	3	.02500	.001000	.000577	.02252	.02748	.024	.026
G	3	.02567	.000577	.000333	.02423	.02710	.025	.026
H	3	.03000	.000000	.000000	.03000	.03000	.030	.030
I	3	.02283	.000569	.000328	.02142	.02425	.022	.023
J	3	.04000	.000000	.000000	.04000	.04000	.040	.040
K	3	.05433	.026727	.015431	-.01206	.12073	.036	.085
Total	30	.03498	.016189	.002956	.02894	.04103	.018	.085

Table 37. Descriptive statistics by laboratory for TP for Sample A.

Descriptives

Total Phosphorus mg/L

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
A	3	.01967	.000577	.000333	.01823	.02110	.019	.020
C	3	.02333	.000577	.000333	.02190	.02477	.023	.024
D	3	.05767	.000577	.000333	.05623	.05910	.057	.058
E	3	.04333	.011547	.006667	.01465	.07202	.030	.050
F	3	.02733	.001155	.000667	.02446	.03020	.026	.028
G	3	.02700	.000000	.000000	.02700	.02700	.027	.027
H	3	.03100	.000000	.000000	.03100	.03100	.031	.031
I	3	.02660	.001572	.000907	.02270	.03050	.025	.028
J	3	.03667	.005774	.003333	.02232	.05101	.030	.040
K	3	.03900	.020421	.011790	-.01173	.08973	.016	.055
Total	30	.03316	.012626	.002305	.02845	.03787	.016	.058

Table 38. Descriptive statistics by laboratory for TP for Sample B.

Descriptives

Total Phosphorus mg/L

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
A	6	.01933	.001211	.000494	.01806	.02060	.018	.021
C	6	.02317	.000753	.000307	.02238	.02396	.022	.024
D	6	.05717	.000753	.000307	.05638	.05796	.056	.058
E	6	.04833	.011690	.004773	.03606	.06060	.030	.060
F	6	.02617	.001602	.000654	.02449	.02785	.024	.028
G	6	.02633	.000816	.000333	.02548	.02719	.025	.027
H	6	.03050	.000548	.000224	.02993	.03107	.030	.031
I	6	.02472	.002318	.000946	.02228	.02715	.022	.028
J	6	.03833	.004082	.001667	.03405	.04262	.030	.040
K	6	.04667	.022871	.009337	.02267	.07067	.016	.085
Total	60	.03407	.014423	.001862	.03035	.03780	.016	.085

Table 39. Descriptive statistics by laboratory for TP for all samples.

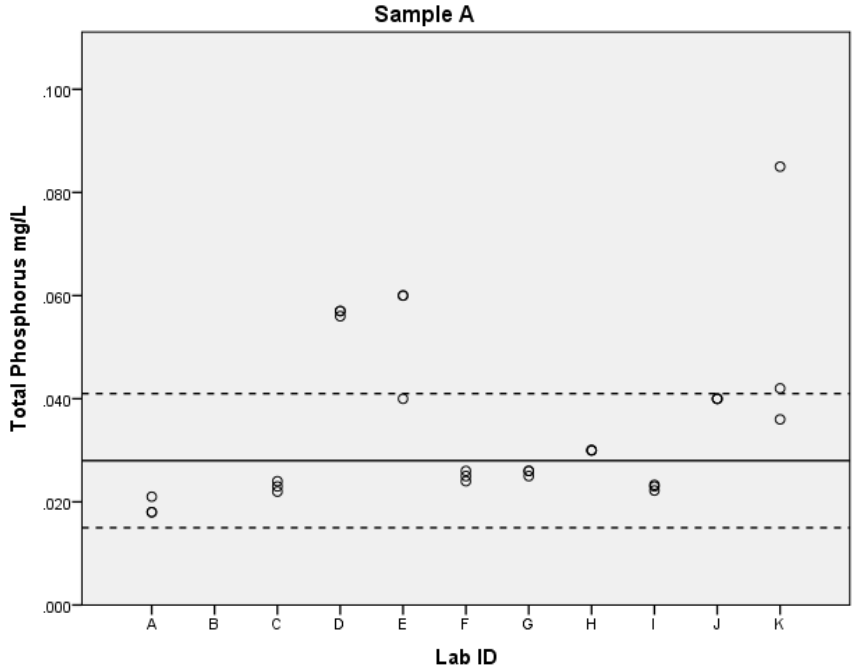


Figure 19. Scatter-plot of TP values obtained by ten laboratories for Sample A. The solid line indicates the overall median, and the dashed lines indicate +/- 1 F-pseudosigma.

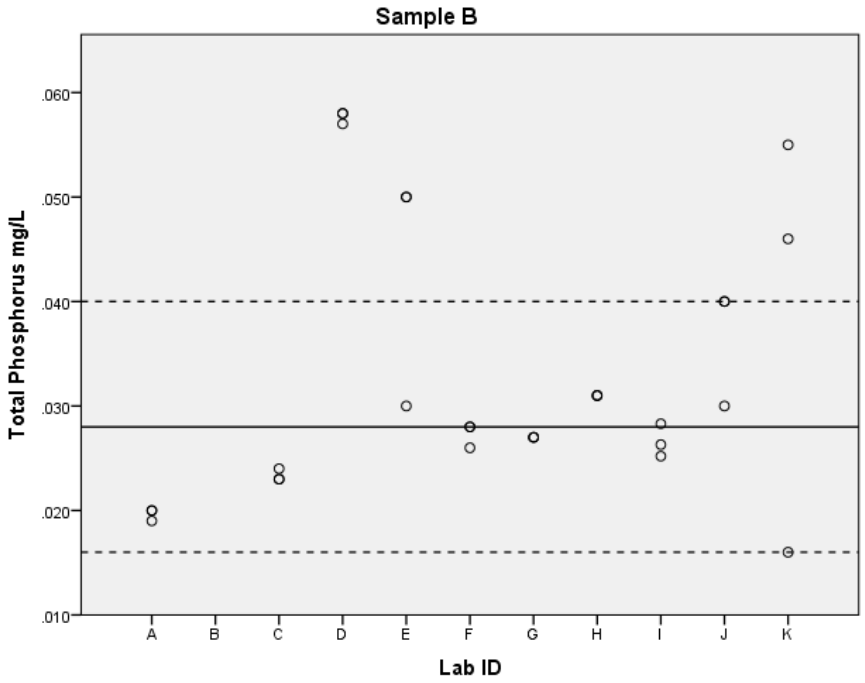


Figure 20. Scatter-plot of TP values obtained by ten laboratories for Sample B. The solid line indicates the overall median, and the dashed lines indicate +/- 1 F-pseudosigma.

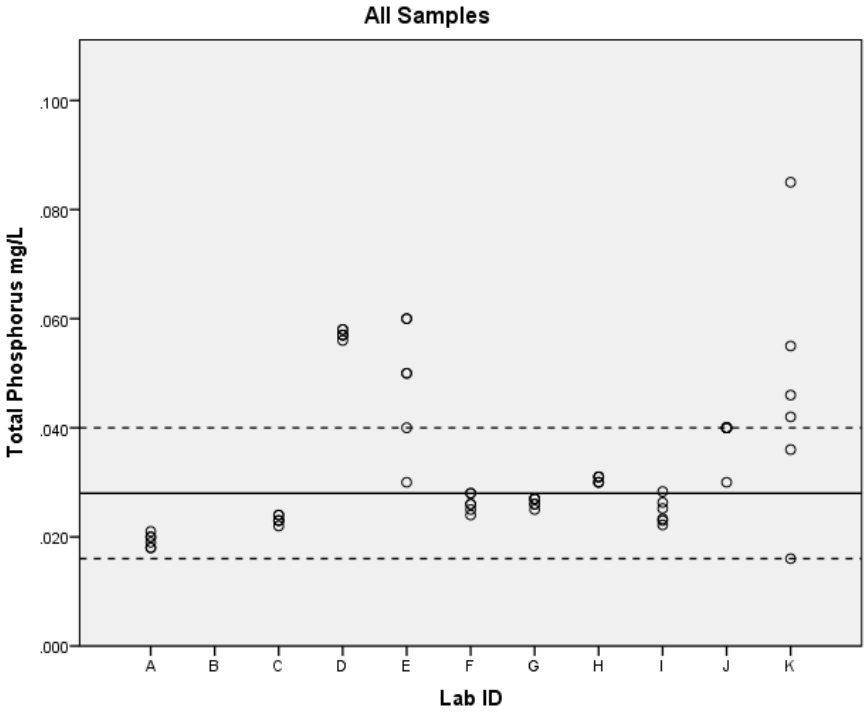


Figure 21. Scatter-plot of TP values obtained by ten laboratories for all samples. The solid line indicates the overall median, and the dashed lines indicate +/- 1 F-pseudosigma.

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	.001	Reject the null hypothesis.

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

Homogeneous Subsets based on Total Phosphorus mg/L

		Subset			
		1	2	3	4
Sample[1]	A	2.000			
	I	6.500	6.500		
	C	6.667	6.667	6.667	
	F		11.667	11.667	
	G			13.167	
	H				17.000
	J				21.500
	K				24.333
	D				26.000
	E				26.167
Test Statistic		5.492	4.904	5.544	9.119
Sig. (2-sided test)		.064	.086	.063	.058
Adjusted Sig. (2-sided test)		.216	.281	.211	.124

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 40. Kruskal-Wallis and nonparametric post hoc inter-laboratory comparisons for TP for Sample A.

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	.008	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]	A	3.000			
	C	6.000	6.000		
	I	11.333	11.333	11.333	
	G	12.000	12.000	12.000	
	F	12.667	12.667	12.667	12.667
	K	17.333	17.333	17.333	17.333
	H	20.000	20.000	20.000	20.000
	J		20.833	20.833	20.833
	E			22.833	22.833
	D				29.000
Test Statistic		11.842	11.528	10.921	10.944
Sig. (2-sided test)		.066	.073	.091	.053
Adjusted Sig. (2-sided test)		.101	.113	.139	.094

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 41. Kruskal-Wallis test and results of nonparametric inter-laboratory comparisons of TP for Sample B.

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	.000	Reject the null hypothesis.
Asymptotic significances are displayed. The significance level is .05.				

Homogeneous Subsets based on Total Phosphorus mg/L							
		Subset					
		1	2	3	4	5	6
Sample[1]	A	4.500					
	C		12.417				
	I		18.417	18.417			
	F			23.083			
	G			24.083			
	H				36.000		
	K				41.167	41.167	
	J					41.917	
	E					48.917	48.917
	D						54.500
Test Statistic		.[2]	1.500	1.822	3.799	2.885	.946
Sig. (2-sided test)		.	.221	.402	.051	.236	.331
Adjusted Sig. (2-sided test)		.	.746	.848	.251	.628	.890
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 42. Kruskal-Wallis test and results of nonparametric inter-laboratory comparisons of TP for all samples.

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

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

Homogeneous Subsets based on Total Phosphorus mg/L			
		Subset	
		1	2
Sample[1]	EPA 365.1	9.500	
	EPA 365.4		23.944
	Lachat 10-115-01-1-C		26.167
Test Statistic		.[2]	.892
Sig. (2-sided test)		.	.345
Adjusted Sig. (2-sided test)		.	.345

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 43. Kruskal-Wallis test and results of nonparametric comparisons for TP values by method for Sample A.

Hypothesis Test Summary				
	Null Hypothesis	Test	Sig.	Decision
1	The distribution of Total Phosphorus mg/L is the same across categories of TP_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 Phosphorus mg/L			
		Subset	
		1	2
Sample[1]	EPA 365.1	10.833	
	EPA 365.4		22.389
	Lachat 10-115-01-1-C		22.833
Test Statistic		.[2]	.139
Sig. (2-sided test)		.	.710
Adjusted Sig. (2-sided test)		.	.710

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

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

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

Table 44. Kruskal-Wallis test and results of nonparametric comparisons for TP values by method for Sample B.

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

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

Homogeneous Subsets based on Total Phosphorus mg/L			
		Subset	
		1	2
Sample[1]	EPA 365.1	19.750	
	EPA 365.4		45.861
	Lachat 10-115-01-1-C		48.917
Test Statistic		.[2]	.222
Sig. (2-sided test)		.	.638
Adjusted Sig. (2-sided test)		.	.638

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

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

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

Table 45. Kruskal-Wallis test and results of nonparametric comparisons for TP values by method for all samples.

F. Orthophosphate. Twenty-three percent of the results for OP from Sample A were reported as non-values. Twenty-two of the 23 reported values for Sample A were within acceptable ranges. Lab D reported the only value outside acceptable ranges; this value was a statistical outlier (0.042 mg/L). The MDLs for all laboratories ranged from 0.0019 to 0.009 mg/L; and the PQLs for Labs E and J ranged from 0.002 to 0.04 mg/L. There were no values reported as less than detection/quantitation limits that were determined to be false negatives. The %F-pseudosigma value was large (greater than 30%), indicating a lack of precision among laboratories. Of the 23 reported values, 52% were within 1 F-pseudosigma and 96% were within 2 F-pseudosigma. There was no statistical difference among results reported for the five methods employed; however, SM 4500 P F was typically greater than the other methods.

For Sample B, 20% of the results were reported as non-values; of the 24 values reported, all were within acceptable ranges. There were no statistical outliers reported. The %F-pseudosigma value was large (greater than 30%), indicating a lack of precision among laboratories. Of the 24 reported values, 63% were within 1 F-pseudosigma and 100% were within 2 F-pseudosigma. There was no statistical difference among results reported for the five methods employed, although the mean for SM 4500 P F was typically higher than the other methods.

When looking at all of the results combined (since they all originated from a single sample), 46 of the 47 reported values were within acceptable ranges. Lab D reported the only value outside acceptable ranges; this was determined to be a statistical outlier (0.042 mg/L). The % F-pseudosigma remained large even after combining Samples A and B. Of the 60 reported values, 68% were within 1 F-pseudosigma and 98% were within 2 F-pseudosigma. Results reported for method SM 4500 P F were significantly greater than results from all other methods; there was no statistical difference between results for EPA 365.1, Lachat 10-115-01-1-I, SM 4500 P E, or USGS I-2601-90. There was no statistical difference between Sample A and Sample B. See Figures 20 - 23 and Tables 46 - 56 for scatter-plots of values obtained by individual laboratories, F-pseudosigma values, summary statistics, inter-laboratory comparisons, and method comparisons.

OP				
	Sample A			
	F-pseudosigma	**% F-pseudosigma**	**Median**	**Range**
	0.004	40.43%	0.011	0.038
Method	**N**	**Mean**	**Median**	**Range**
EPA 365.1	15 (three non-values)	0.011	0.012	0.014
Lachat 10-115-01-1-I	3	0.011	0.011	0.000
SM 4500 P E	3	0.010	0.009	0.002
SM 4500 P F	6 (two non-values)	0.023	0.018	0.026
USGS I-2601-90	3 (two non-values)	0.010	0.010	0.000
	Sample B			
	F-pseudosigma	**% F-pseudosigma**	**Median**	**Range**
	0.004	31.36%	0.013	0.014
Method	**N**	**Mean**	**Median**	**Range**
EPA 365.1	15 (three non-values)	0.013	0.013	0.014
Lachat 10-115-01-1-I	3	0.013	0.013	0.001
SM 4500 P E	3	0.012	0.011	0.007
SM 4500 P F	6 (three non-values)	0.018	0.018	0.000
USGS I-2601-90	3	0.012	0.012	0.001
	All Samples			
	F-pseudosigma	**% F-pseudosigma**	**Median**	**Range**
	0.004	37.06%	0.012	0.038
Method	**N**	**Mean**	**Median**	**Range**
EPA 365.1	30 (six non-values)	0.012	0.012	0.016
Lachat 10-115-01-1-I	6	0.012	0.012	0.003
SM 4500 P E	6	0.011	0.010	0.007
SM 4500 P F	12 (five non-values)	0.021	0.018	0.026
USGS I-2601-90	6 (two non-values)	0.012	0.012	0.003

Table 46. F-pseudosigma values for OP.

OP

	Sample A				Sample B				All			
Lab ID	N	Lab Median	Range	Mean Z-value	N	Lab Median	Range	Mean Z-value	N	Lab Median	Range	Mean Z-value
A	3	0.017	0.001	1.58	3	0.019	0.002	1.50	6	0.018	0.003	1.54
C	3	0.010	0.001	0.17	3	0.012	0.000	0.25	6	0.012	0.002	0.21
D	3*	0.042	N/A	7.75	3*	NR	NR	NR	6*	0.042	N/A	7.50
E	3	0.011	0.000	0.00	3	0.013	0.001	0.08	6	0.012	0.003	0.29
F	3	0.004	0.001	1.67	3	0.008	0.002	1.42	6	0.006	0.004	1.54
G	3	0.016	0.003	1.50	3	0.018	0.000	1.25	6	0.018	0.003	1.38
H	3	0.012	0.000	0.25	3	0.013	0.001	0.08	6	0.013	0.002	0.17
I	3*	0.010	N/A	0.25	3	0.012	0.001	0.17	6	0.012	0.003	0.19
J	3*	NR	NR	NR	3*	NR	NR	NR	6*	NR	NR	NR
K	3	0.009	0.002	0.33	3	0.011	0.007	0.75	6	0.010	0.007	0.63

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

Table 47. Summary statistics and Z-values by Laboratory for OP.

OP		
Method	**MDL Range**	**PQL Range**
All	0.0019 - 0.009	0.002 - 0.04
EPA 365.1	0.0019 - 0.008	0.01 - 0.04
Lachat 10-115-01-1-I	Not Reported	0.002
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 48. 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	.01733	.000577	.000333	.01590	.01877	.017	.018
C	3	.01033	.000577	.000333	.00890	.01177	.010	.011
D	1	.04200	N/A	N/A	N/A	N/A	.042	.042
E	3	.01100	.000000	.000000	.01100	.01100	.011	.011
F	3	.00433	.000577	.000333	.00290	.00577	.004	.005
G	3	.01700	.001732	.001000	.01270	.02130	.016	.019
H	3	.01200	.000000	.000000	.01200	.01200	.012	.012
I	1	.01000	N/A	N/A	N/A	N/A	.010	.010
K	3	.00967	.001155	.000667	.00680	.01254	.009	.011
Total	23	.01291	.007567	.001578	.00964	.01619	.004	.042

Table 49. Descriptive statistics by laboratory for OP for Sample A.

Descriptives

Orthophosphate mg/L

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
A	3	.01900	.001000	.000577	.01652	.02148	.018	.020
C	3	.01200	.000000	.000000	.01200	.01200	.012	.012
E	3	.01333	.000577	.000333	.01190	.01477	.013	.014
F	3	.00733	.001155	.000667	.00446	.01020	.006	.008
G	3	.01800	.000000	.000000	.01800	.01800	.018	.018
H	3	.01333	.000577	.000333	.01190	.01477	.013	.014
I	3	.01233	.000577	.000333	.01090	.01377	.012	.013
K	3	.01200	.003606	.002082	.00304	.02096	.009	.016
Total	24	.01342	.003706	.000756	.01185	.01498	.006	.020

Table 50. Descriptive statistics by laboratory for OP for Sample B.

Descriptives

Orthophosphate mg/L

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
A	6	.01817	.001169	.000477	.01694	.01939	.017	.020
C	6	.01117	.000983	.000401	.01013	.01220	.010	.012
D	1	.04200	N/A	N/A	N/A	N/A	.042	.042
E	6	.01217	.001329	.000543	.01077	.01356	.011	.014
F	6	.00583	.001835	.000749	.00391	.00776	.004	.008
G	6	.01750	.001225	.000500	.01621	.01879	.016	.019
H	6	.01267	.000816	.000333	.01181	.01352	.012	.014
I	4	.01175	.001258	.000629	.00975	.01375	.010	.013
K	6	.01083	.002714	.001108	.00798	.01368	.009	.016
Total	47	.01317	.005858	.000855	.01145	.01489	.004	.042

Table 51. Descriptive statistics by laboratory for OP for all samples.

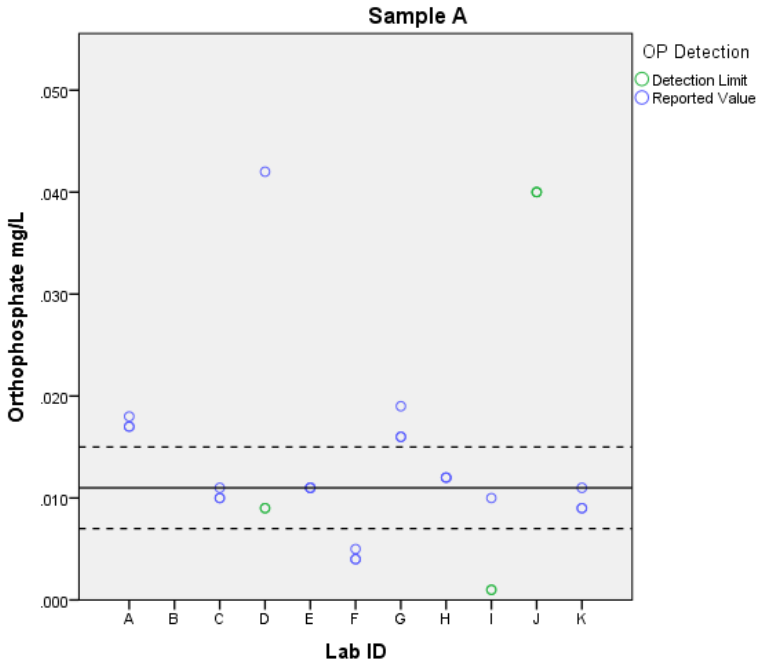


Figure 20. Scatter-plot of OP values and detection/quantitation limits obtained by ten laboratories for Sample A. The solid line indicates the overall median, and the dashed lines indicate +/- 1 F-pseudosigma.

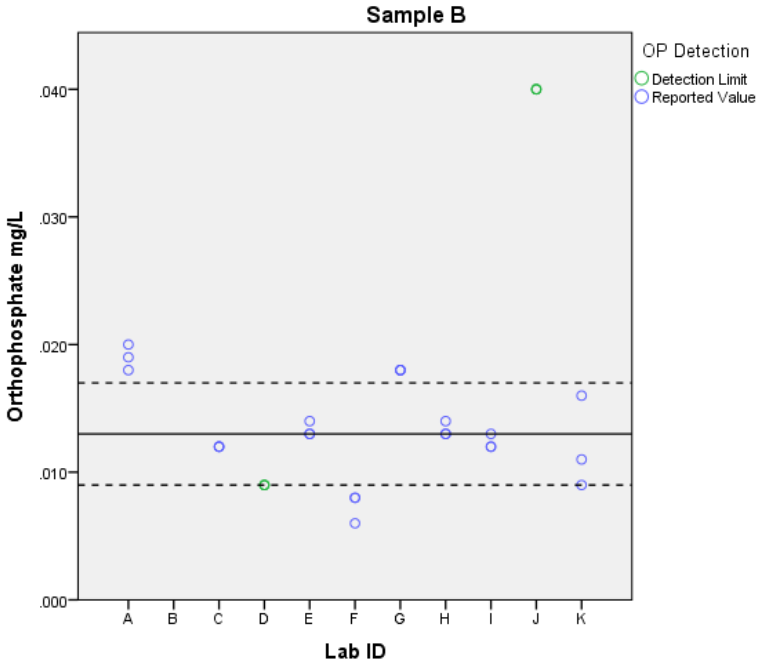


Figure 21. Scatter-plot of OP values and detection/quantitation limits obtained by ten laboratories for Sample B. The solid line indicates the overall median, and the dashed lines indicate +/- 1 F-pseudosigma.

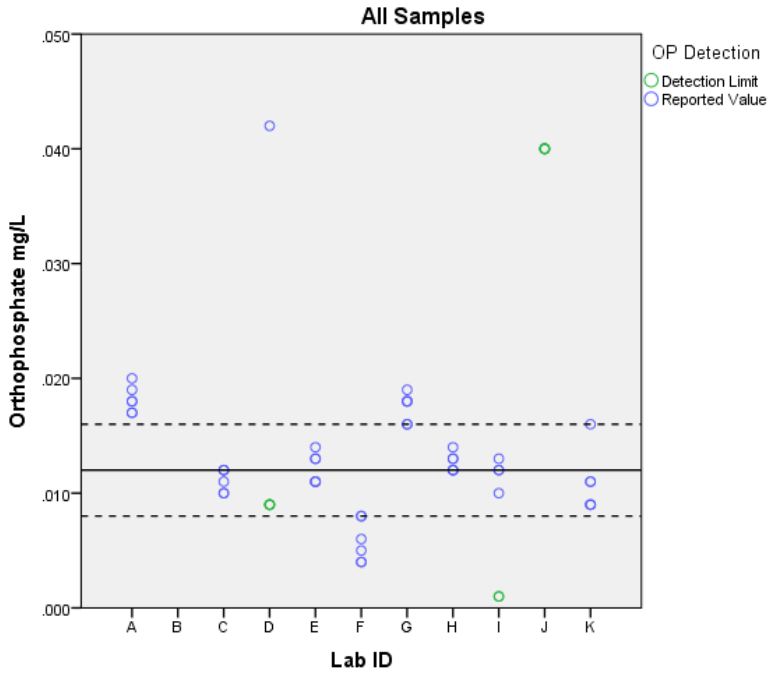


Figure 22. Scatter-plot of OP values and detection/quantitation limits obtained by ten laboratories for all samples. The solid line indicates the overall median, and the dashed lines indicate +/- 1 F-pseudosigma.

Hypothesis Test Summary				
	Null Hypothesis	Test	Sig.	Decision
1	The distribution of Orthophosphate mg/L is the same across categories of Lab ID.	Independent-Samples Kruskal-Wallis Test	.008	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]	F	2.000		
	K	6.667	6.667	
	I	7.000	7.000	
	C	8.333	8.333	
	E	11.000	11.000	
	H		15.000	15.000
	G			19.000
	A			20.000
	D			23.000
Test Statistic		9.136	9.218	7.302
Sig. (2-sided test)		.058	.056	.063
Adjusted Sig. (2-sided test)		.123	.119	.164

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

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

Table 52. Kruskal-Wallis test and results of nonparametric pair-wise comparisons of OP for Sample A.

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	.006	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]	F	2.000			
	C	8.000	8.000		
	K	9.000	9.000	9.000	
	I	9.667	9.667	9.667	
	E	14.167	14.167	14.167	
	H		14.167	14.167	
	G			20.500	20.500
	A				22.500
Test Statistic		9.351	5.638	8.835	2.400
Sig. (2-sided test)		.053	.228	.065	.121
Adjusted Sig. (2-sided test)		.113	.434	.138	.509

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

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

Table 53. Kruskal-Wallis test and results of nonparametric pair-wise comparisons of OP for Sample B.

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	.000	Reject the null hypothesis.

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

Homogeneous Subsets based on Orthophosphate mg/L

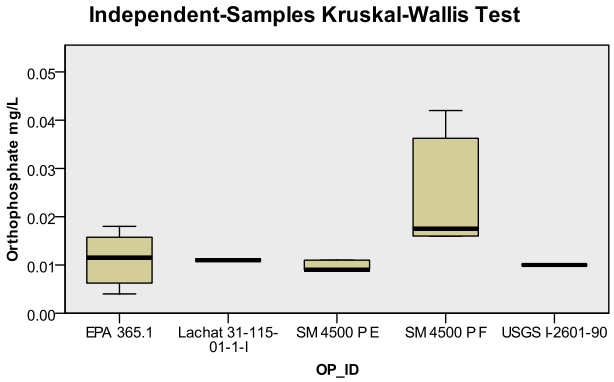
		Subset		
		1	2	3
Sample[1]	F	3.500		
	K		15.000	
	C		17.500	
	I		21.250	
	E		22.833	
	H		26.333	
	G			39.583
	A			41.250
	D			47.000
Test Statistic		.[2]	7.482	3.220
Sig. (2-sided test)		.	.113	.200
Adjusted Sig. (2-sided test)		.	.231	.559

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 54. Kruskal-Wallis test and results of nonparametric pair-wise comparisons of OP for all samples.



Total N	23
Test Statistic	8.276
Degrees of Freedom	4
Asymptotic Sig. (2-sided test)	.082

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 method comparisons for OP for Sample A.

Test of Homogeneity of Variances

Orthophosphate mg/L

Levene's Statistic	df1	df2	Sig.
2.427	4	19	.084

ANOVA

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	.000	4	.000	1.494	.243
Within Groups	.000	19	.000		
Total	.000	23			

	Method ID	N	Subset for alpha = 0.05
			1
Gabriel[a,b]	SM 4500 P E	3	.01200
	USGS I-2601-90	3	.01233
	EPA 365.1	12	.01292
	Lachat 31-115-01-1-I	3	.01333
	SM 4500 P F	3	.01800
	Sig.		.284

Means for groups in homogeneous subsets are displayed.
a. Uses Harmonic Mean Sample Size = 3.529.
b. The group sizes are unequal. The harmonic mean of the group sizes is used. Type I error levels are not guaranteed.

Table 55. ANOVA and post hoc comparisons for OP values by method for all reported values for Sample B.

Hypothesis Test Summary				
	Null Hypothesis	Test	Sig.	Decision
1	The distribution of Orthophosphate mg/L is the same across categories of OP_ID.	Independent-Samples Kruskal-Wallis Test	.008	Reject the null hypothesis.

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

Homogeneous Subsets based on Orthophosphate mg/L			
		Subset	
		1	2
Sample[1]	SM 4500 P E	15.000	
	USGS I-2601-90	21.250	
	EPA 365.1	22.146	
	Lachat 31-115-01-1-I	22.833	
	SM 4500 P F		40.643
Test Statistic		1.779	.[2]
Sig. (2-sided test)		.620	.
Adjusted Sig. (2-sided test)		.620	.

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 56. Kruskal-Wallis test and results of nonparametric pair-wise comparisons of OP by method for all samples.

G. Total Organic Carbon. Twelve of the eighteen reported values for Sample A were within acceptable ranges. Labs E and J both reported all three values outside acceptable ranges. There were no statistical outliers reported, nor were any results reported as non-values. The %F-pseudosigma value was small (less than 20%), indicating a high degree of precision among laboratories. Of the 18 reported values, 61% were within 1 F-pseudosigma and 67% were within 2 F-pseudosigma. There was no statistical difference among reported results for the three methods employed; however, those reported from SM 5310 C were highly variable. Results for Sample B follow the same pattern as Sample A (i.e., they mirror each other).

When looking at all of the results combined, 24 of the 36 reported values were within acceptable ranges. Labs E and J both reported all six values outside acceptable ranges, one of which was determined to be a statistical outlier (8 mg/L). The % F-pseudosigma was small (less than 20%). Of the 36 reported values, 61% were within 1 F-pseudosigma and 67% were within 2 F-pseudosigma. There was no statistical difference among reported results for the three methods employed; however, SM 5310 C was highly variable. There was no statistical difference between Sample A and Sample B. See Figures 23 - 28 and Tables 57 - 64 for scatter-plots of values obtained by individual laboratories, F-pseudosigma values, summary statistics, inter-laboratory comparisons, and method comparisons.

TOC				
	Sample A			
	F-pseudosigma	% F-pseudosigma	Median	Range
	0.50	12.13%	4.11	3.00
Method	N	Mean	Median	Range
EPA 415.1	3	3.63	3.63	0.05
SM 5310 B	9	4.17	4.18	0.39
SM 5310 C	6	4.50	4.50	3.00
	Sample B			
	F-pseudosigma	% F-pseudosigma	Median	Range
	0.43	10.76%	4.00	6.00
Method	N	Mean	Median	Range
EPA 415.1	3	3.57	3.69	0.38
SM 5310 B	9	4.03	4.02	0.36
SM 5310 C	6	4.67	4.50	6.00
	All Samples			
	F-pseudosigma	% F-pseudosigma	Median	Range
	0.42	10.37%	4.04	6.00
Method	N	Mean	Median	Range
EPA 415.1	6	3.60	3.64	0.38
SM 5310 B	18	4.10	4.09	0.56
SM 5310 C	12	4.58	4.50	6.00

Table 57. F-pseudosigma values for TOC.

TOC

Lab ID	Sample A N	Sample A Lab Median	Sample A Range	Sample A Mean Z-value	Sample B N	Sample B Lab Median	Sample B Range	Sample B Mean Z-value	All N	All Lab Median	All Range	All Mean Z-value
D	3	4.18	0.11	0.17	3	4.08	0.15	0.21	6	4.16	0.24	0.26
E	3	6.00	0.00	3.78	3	7.00	2.00	6.98	6	6.00	2.00	5.87
F	3	3.63	0.05	0.97	3	3.69	0.38	1.00	6	3.64	0.38	1.05
G	3	4.06	0.06	0.13	3	3.88	0.15	0.22	6	4.00	0.23	0.19
H	3	4.20	0.20	0.31	3	4.10	0.20	0.23	6	4.20	0.40	0.37
J	3	3.00	0.00	2.22	3	2.00	1.00	3.88	6	3.00	1.00	3.28

Table 58. 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		
D	3	4.1967	.05686	.03283	4.0554	4.3379	4.15	4.26
E	3	6.0000	.00000	.00000	6.0000	6.0000	6.00	6.00
F	3	3.6267	.02517	.01453	3.5642	3.6892	3.60	3.65
G	3	4.0467	.03215	.01856	3.9668	4.1265	4.01	4.07
H	3	4.2667	.11547	.06667	3.9798	4.5535	4.20	4.40
J	3	3.0000	.00000	.00000	3.0000	3.0000	3.00	3.00
Total	18	4.1894	.94385	.22247	3.7201	4.6588	3.00	6.00

Table 59. Descriptive statistics by laboratory for TOC for Sample A.

Descriptives

Total Organic Carbon mg/L

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
D	3	4.0900	.07550	.04359	3.9025	4.2775	4.02	4.17
E	3	7.0000	1.00000	.57735	4.5159	9.4841	6.00	8.00
F	3	3.5700	.21656	.12503	3.0320	4.1080	3.32	3.70
G	3	3.9033	.07767	.04485	3.7104	4.0963	3.84	3.99
H	3	4.1000	.10000	.05774	3.8516	4.3484	4.00	4.20
J	3	2.3333	.57735	.33333	.8991	3.7676	2.00	3.00
Total	18	4.1661	1.50054	.35368	3.4199	4.9123	2.00	8.00

Table 60. Descriptive statistics by laboratory for TOC for Sample B.

Descriptives

Total Organic Carbon mg/L

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
D	6	4.1433	.08359	.03412	4.0556	4.2311	4.02	4.26
E	6	6.5000	.83666	.34157	5.6220	7.3780	6.00	8.00
F	6	3.5983	.14134	.05770	3.4500	3.7467	3.32	3.70
G	6	3.9750	.09482	.03871	3.8755	4.0745	3.84	4.07
H	6	4.1833	.13292	.05426	4.0438	4.3228	4.00	4.40
J	6	2.6667	.51640	.21082	2.1247	3.2086	2.00	3.00
Total	36	4.1778	1.23551	.20592	3.7597	4.5958	2.00	8.00

Table 61. Descriptive statistics by laboratory for TOC for all samples.

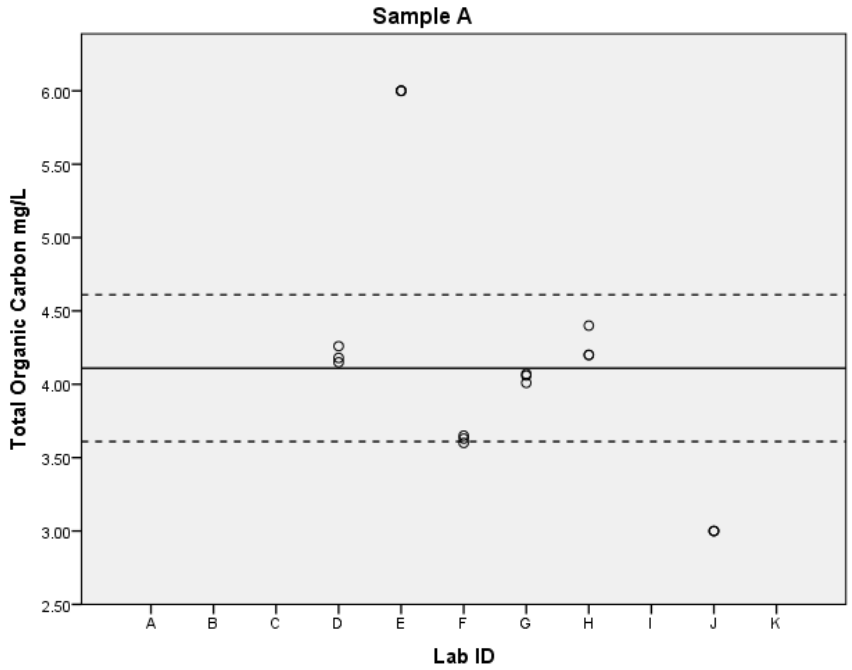


Figure 23. Scatter-plot of TOC values obtained by six laboratories for Sample A. The solid line indicates the overall median, and the dashed lines indicate +/- 1 F-pseudosigma.

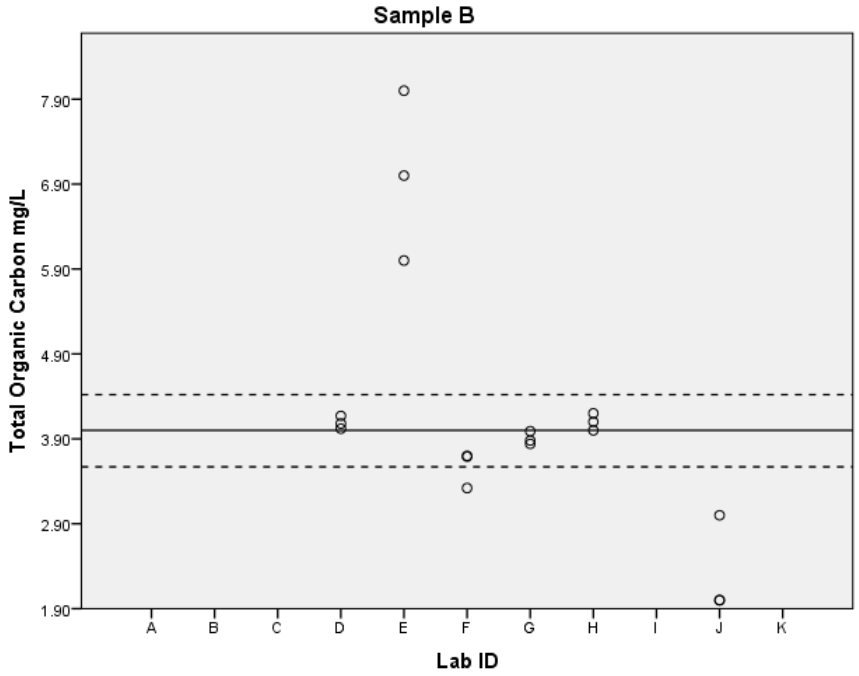


Figure 24. Scatter-plot of TOC values obtained by six laboratories for Sample B. The solid line indicates the overall median, and the dashed lines indicate +/- 1 F-pseudosigma.

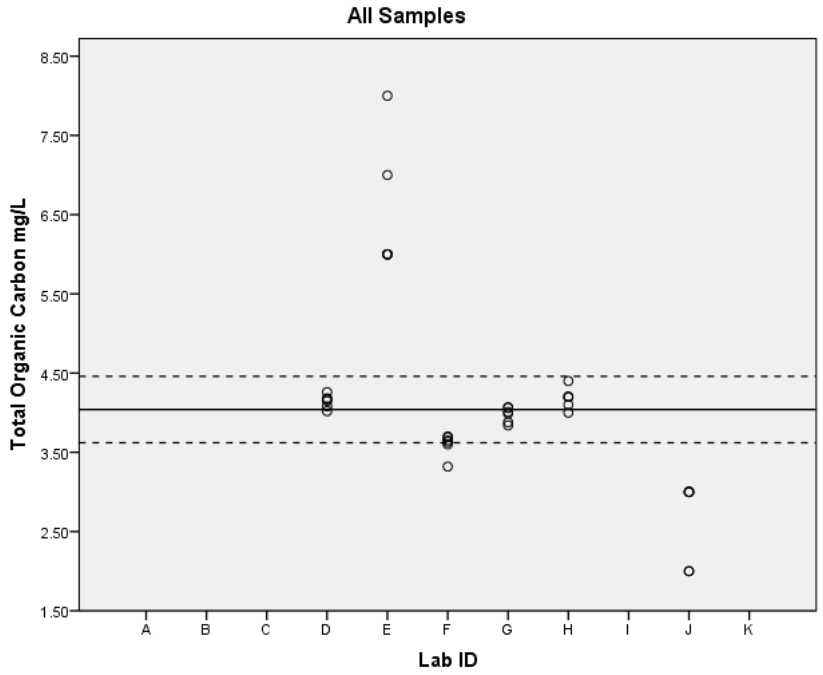


Figure 25. Scatter-plot of TOC values obtained by six laboratories for all samples. The solid line indicates the overall median, and the dashed lines indicate +/- 1 F-pseudosigma.

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	5
Sample[1]	J	2.000				
	F		5.000			
	G			8.000		
	D				11.667	
	H				13.333	
	E					17.000
Test Statistic		.[2]	.[2]	.[2]	1.225	.[2]
Sig. (2-sided test)		.	.	.	.268	.
Adjusted Sig. (2-sided test)		.	.	.	.821	.

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 62. Kruskal-Wallis test and results of nonparametric pair-wise comparisons of TOC by laboratory for Sample A.

Total Organic Carbon mg/L

	Lab ID	N	Subset for alpha = 0.05		
			1	2	3
Tukey-Kramer	J	3	2.3333		
	F	3	3.5700	3.5700	
	G	3		3.9033	
	D	3		4.0900	
	H	3		4.1000	
	E	3			7.0000
	Sig.		.100	.917	1.000

Means for groups in homogeneous subsets are displayed.

Table 63. Post hoc inter-laboratory comparisons for TOC for Sample B.

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	.000	Reject the null hypothesis.

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

Homogeneous Subsets based on Total Organic Carbon mg/L

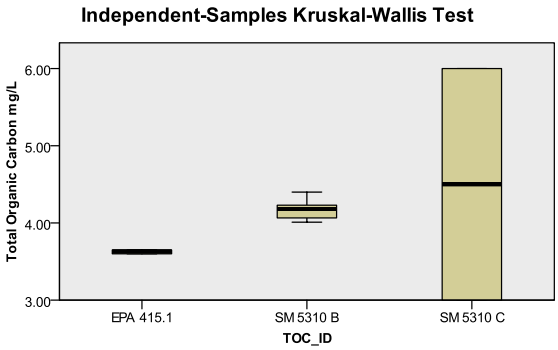
		Subset				
		1	2	3	4	5
Sample[1]	J	3.500				
	F		9.500			
	G			16.333		
	D				23.333	
	H				24.833	
	E					33.500
Test Statistic		.[2]	.[2]	.[2]	.650	.[2]
Sig. (2-sided test)		.	.	.	.420	.
Adjusted Sig. (2-sided test)		.	.	.	.950	.

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.

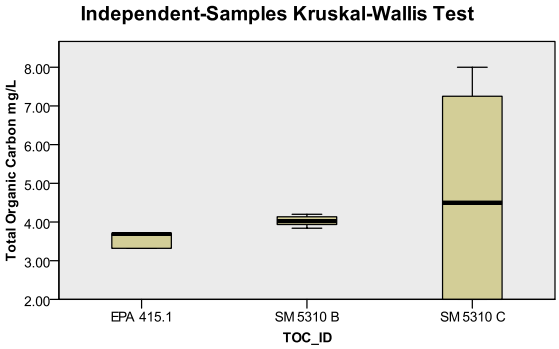
Table 64. Kruskal-Wallis test and results of nonparametric pair-wise comparisons of TOC by laboratory for all samples.



Total N	18
Test Statistic	2.869
Degrees of Freedom	2
Asymptotic Sig. (2-sided test)	.238

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.

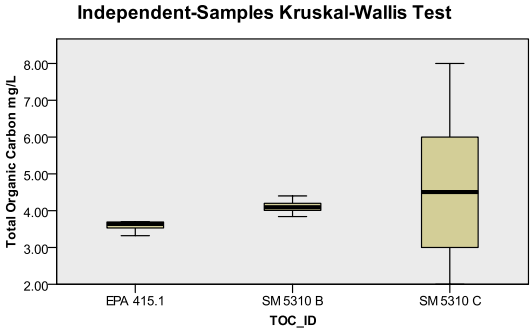
Figure 26. Results of Kruskal-Wallis test of TOC by method for Sample A.



Total N	18
Test Statistic	2.845
Degrees of Freedom	2
Asymptotic Sig. (2-sided test)	.241

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 27. Results of Kruskal-Wallis test of TOC by method for Sample B.



Total N	36
Test Statistic	5.857
Degrees of Freedom	2
Asymptotic Sig. (2-sided test)	.053

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 28. Results of Kruskal-Wallis test of TOC by method for all samples.

H. Chlorophyll a. Thirteen percent of the results for ChlA from Sample A were reported as non-values. Twenty-two of the 26 reported values for Sample A were within acceptable ranges. Labs A and C each reported two values outside acceptable ranges. There were no statistical outliers reported. The MDLs for all laboratories ranged from 0.033 to 3 µg/L; and the PQLs for Labs E and J ranged from 0.02 to 1 µg/L. Lab A reported one result as less than detection/quantitation limits; that result was determined to be a false negative. The %F-pseudosigma value was moderate (between 20 and 30%), indicating a lack of precision among laboratories. Of the 26 reported values, 81% were within 1 F-pseudosigma and 85% were within 2 F-pseudosigma. There was no statistical difference between results reported for EPA 445.0 and SM 10200 H.

For Sample B, 17% of the results were reported as non-values; of the 25 values reported, eighteen were within acceptable ranges. Lab C reported all three results outside acceptable ranges, Lab K reported two, and Labs A, C, F, and G all reported one value outside acceptable ranges. There were no statistical outliers reported. Lab A reported two results as less than detection/quantitation limits; these were determined to be false negatives. The %F-pseudosigma value was small (less than 20%), indicating a high degree of precision among laboratories. Of the 25 reported values, 28% were within 1 F-pseudosigma and 72% were within 2 F-pseudosigma. There was no statistical difference between results reported for EPA 445.0 and SM 10200 H.

When looking at all of the results combined, 46 of the 51 reported values were within acceptable ranges. Lab C reported three values outside acceptable ranges, and Lab A reported two. There were no statistical outliers reported. Lab A reported three results as less than detection/quantitation limits; these were determined to be false negatives. The % F-pseudosigma was moderate. Of the 51 reported values, 78% were within 1 F-pseudosigma and 90% were within 2 F-pseudosigma. There was no statistical difference between results reported for EPA 445.0 and those for SM 10200 H. There was no statistical difference between Sample A and Sample B. See Figures 28 - 30 and Tables 65 - 76 for scatter-plots of values obtained by individual laboratories, F-pseudosigma values, summary statistics, inter-laboratory comparisons, and method comparisons.

Chlorophyll a				
	Sample A			
	F-pseudosigma	**% F-pseudosigma**	**Median**	**Range**
	1.01	24.05%	4.20	3.77
Method	**N**	**Mean**	**Median**	**Range**
EPA 445.0	9	3.69	3.53	0.99
SM 10200 H	21 (four non-values)	3.86	4.60	3.77
	Sample B			
	F-pseudosigma	**% F-pseudosigma**	**Median**	**Range**
	0.43	11.81%	3.64	3.88
Method	**N**	**Mean**	**Median**	**Range**
EPA 445.0	9	3.61	3.55	1.37
SM 10200 H	21 (five non-values)	3.69	4.40	3.88
	All Samples			
	F-pseudosigma	**% F-pseudosigma**	**Median**	**Range**
	1.03	25.76%	4.00	4.05
Method	**N**	**Mean**	**Median**	**Range**
EPA 445.0	18	3.65	3.54	1.37
SM 10200 H	42 (nine non-values)	3.78	4.41	4.05

Table 65. F-pseudosigma values for ChlA.

ChlA

Lab ID	Sample A N	Sample A Lab Median	Sample A Range	Sample A Mean Z-value	Sample B N	Sample B Lab Median	Sample B Range	Sample B Mean Z-value	All N	All Lab Median	All Range	All Mean Z-value
A	3*	1.40	0.00	2.77	3*	2.40	N/A	2.88	6*	1.40	1.00	2.20
B	3	3.35	0.32	0.83	3	3.12	0.46	1.15	6	3.28	0.60	0.72
C	3	2.14	1.12	1.97	3	1.69	1.13	4.54	6	1.92	1.69	1.99
D	3*	NR	NR	NR	3*	NR	NR	NR	6*	NR	NR	NR
E	3	4.20	0.00	0.00	3	4.10	0.40	1.07	6	4.20	0.40	0.18
F	3	4.87	0.71	0.63	3	3.51	1.39	1.18	6	4.55	1.92	0.71
G	3	4.60	0.31	0.34	3	4.50	0.53	2.27	6	4.55	0.58	0.56
H	3	4.70	0.10	0.46	3	4.40	0.10	1.85	6	4.55	0.30	0.53
J	3	3.45	0.15	0.70	3	3.55	0.11	0.16	6	3.54	0.20	0.45
K	3	5.00	1.00	0.59	3	5.00	2.00	2.60	6	5.00	2.00	0.81

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

Table 66. Summary statistics by Laboratory for ChlA.

ChlA		
Method	**MDL Range**	**PQL Range**
All	0.033 - 3	0.02 - 12
EPA 445.0	0.033	0.02 - 0.1
SM 10200 H	0.1 - 3	1 - 12

Table 67. Methods and detection/quantitation limits 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	2	1.4000	.00000	.00000	1.4000	1.4000	1.40	1.40
B	3	3.3633	.16042	.09262	2.9648	3.7618	3.21	3.53
C	3	2.2133	.56359	.32539	.8133	3.6134	1.69	2.81
E	3	4.2000	.00000	.00000	4.2000	4.2000	4.20	4.20
F	3	4.8333	.35642	.20578	3.9479	5.7187	4.46	5.17
G	3	4.5433	.16258	.09387	4.1395	4.9472	4.36	4.67
H	3	4.6667	.05774	.03333	4.5232	4.8101	4.60	4.70
J	3	3.4933	.08386	.04842	3.2850	3.7017	3.44	3.59
K	3	4.6667	.57735	.33333	3.2324	6.1009	4.00	5.00
Total	26	3.7977	1.12170	.21998	3.3446	4.2508	1.40	5.17

Table 68. Descriptive statistics by laboratory for ChlA for Sample A.

Descriptives

Chlorophyll a µg/L

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
A	1	2.4000	N/A	N/A	N/A	N/A	2.40	2.40
B	3	3.1467	.23116	.13346	2.5724	3.7209	2.93	3.39
C	3	1.6867	.56501	.32621	.2831	3.0902	1.12	2.25
E	3	4.1000	.20000	.11547	3.6032	4.5968	3.90	4.30
F	3	3.8000	.73899	.42665	1.9643	5.6357	3.25	4.64
G	3	4.6167	.28361	.16374	3.9121	5.3212	4.41	4.94
H	3	4.4333	.05774	.03333	4.2899	4.5768	4.40	4.50
J	3	3.5733	.05859	.03383	3.4278	3.7189	3.53	3.64
K	3	4.3333	1.15470	.66667	1.4649	7.2018	3.00	5.00
Total	25	3.6588	1.02837	.20567	3.2343	4.0833	1.12	5.00

Table 69. Descriptive statistics by laboratory for ChlA for Sample B.

Descriptives

Chlorophyll a µg/L

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
A	3	1.7333	.57735	.33333	.2991	3.1676	1.40	2.40
B	6	3.2550	.21389	.08732	3.0305	3.4795	2.93	3.53
C	6	1.9500	.58134	.23733	1.3399	2.5601	1.12	2.81
E	6	4.1500	.13784	.05627	4.0053	4.2947	3.90	4.30
F	6	4.3167	.76785	.31347	3.5109	5.1225	3.25	5.17
G	6	4.5800	.21062	.08598	4.3590	4.8010	4.36	4.94
H	6	4.5500	.13784	.05627	4.4053	4.6947	4.40	4.70
J	6	3.5333	.07815	.03190	3.4513	3.6153	3.44	3.64
K	6	4.5000	.83666	.34157	3.6220	5.3780	3.00	5.00
Total	51	3.7296	1.06848	.14962	3.4291	4.0301	1.12	5.17

Table 70. Descriptive statistics by laboratory for ChlA for all samples.

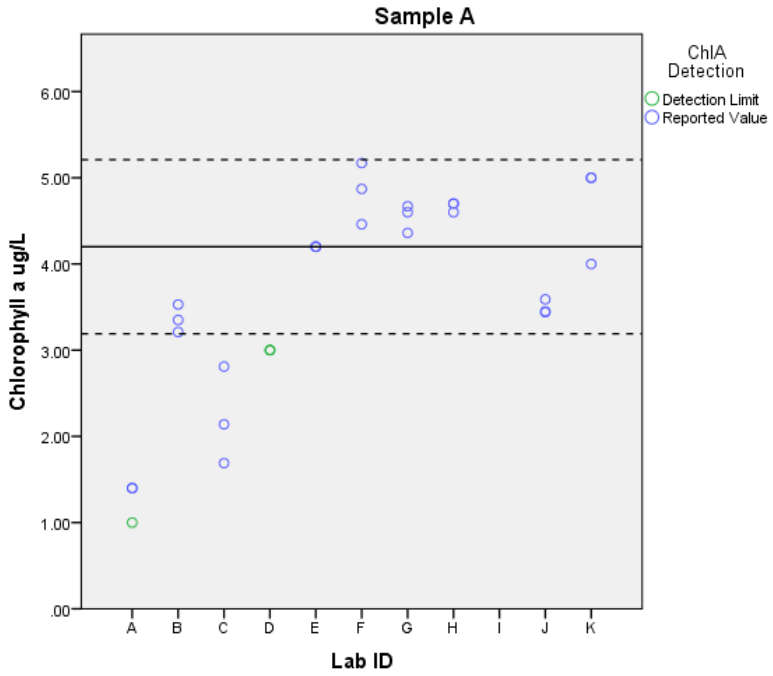


Figure 28. Scatter-plot of ChlA values and detection/quantitation limits obtained by ten laboratories for Sample A. The solid line indicates the overall median, and the dashed lines indicate +/- 1 F-pseudosigma.

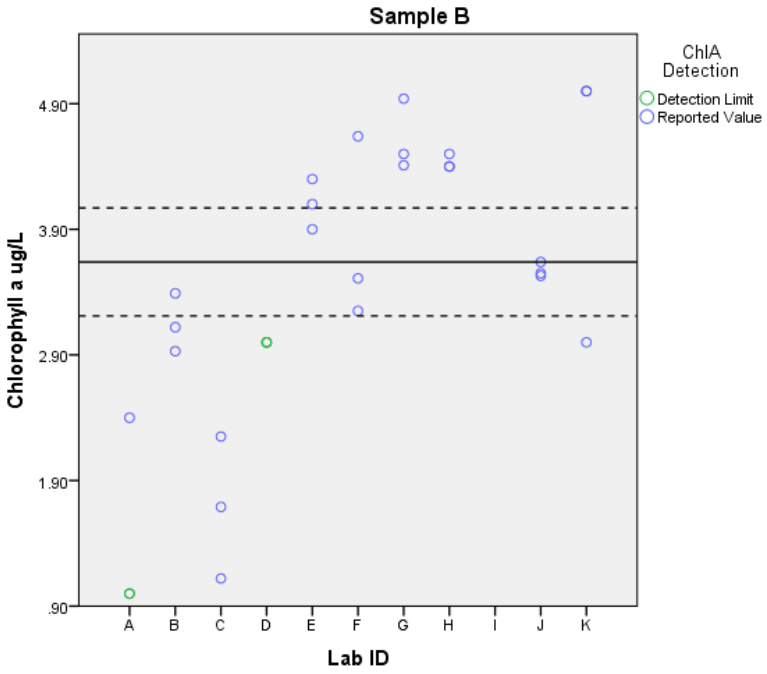


Figure 29. Scatter-plot of ChlA values and detection/quantitation limits obtained by ten laboratories for Sample B. The solid line indicates the overall median, and the dashed lines indicate +/- 1 F-pseudosigma.

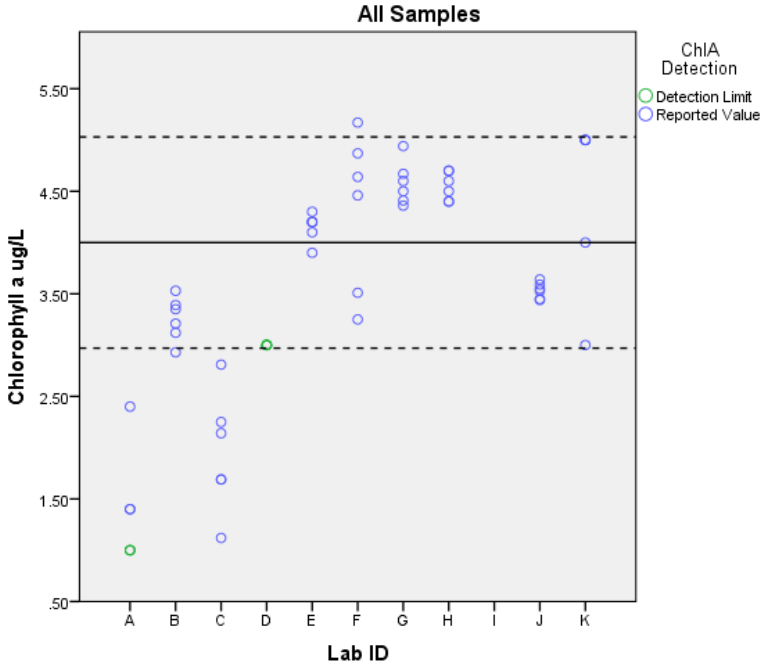


Figure 30. Scatter-plot of ChlA values and detection/quantitation limits obtained by ten laboratories for all samples. The solid line indicates the overall median, and the dashed lines indicate +/- 1 F-pseudosigma.

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	.005	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]	A	1.500			
	C	4.000	4.000		
	B		7.667		
	J		9.333	9.333	
	E			14.000	14.000
	G			18.167	18.167
	K			20.333	20.333
	H				20.500
	F				22.000
Test Statistic		3.158	5.956	7.751	5.882
Sig. (2-sided test)		.076	.051	.051	.208
Adjusted Sig. (2-sided test)		.351	.174	.135	.402

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 71. Kruskal-Wallis test and results of nonparametric inter-laboratory comparisons of ChlA from Sample A.

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	.029	Reject the null hypothesis.
Asymptotic significances are displayed. The significance level is .05.				

Homogeneous Subsets based on Chlorophyll a µg/L			
		Subset	
		1	2
Sample[1]	C	2.000	
	A	4.000	4.000
	B	7.000	7.000
	J		12.000
	F		13.333
	E		15.000
	K		18.333
	H		18.500
	G		20.833
Test Statistic		5.143	12.234
Sig. (2-sided test)		.076	.093
Adjusted Sig. (2-sided test)		.253	.126
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 72. Kruskal-Wallis test and results of nonparametric inter-laboratory comparisons of ChlA for Sample B.

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	.000	Reject the null hypothesis.

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

Homogeneous Subsets based on Chlorophyll a µg/L

		Subset			
		1	2	3	4
Sample[1]	A	4.333			
	C	5.333			
	B		14.417		
	J			20.750	
	E			28.333	28.333
	F			34.333	34.333
	H				38.500
	K				38.500
	G				38.667
Test Statistic		.271	.[2]	5.966	7.004
Sig. (2-sided test)		.603	.	.051	.136
Adjusted Sig. (2-sided test)		.994	.	.173	.274

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

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

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

Table 73. Kruskal-Wallis test and results of nonparametric inter-laboratory comparisons of ChlA for all samples.

Group Statistics

Method ID		N	Mean	Std. Deviation	Std. Error Mean
Chlorophyll a µg/L	EPA 445.0	9	3.6856	.40028	.13343
	SM 10200 H	17	3.8571	1.36931	.33211

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	**.002**	-.364	24	.719	-.17150	.47063	-1.14285	.79984
	Equal variances not assumed			**-.479**	**20.513**	**.637**	**-.17150**	**.35791**	**-.91689**	**.57389**

Table 74. Results of t-test comparisons of ChlA by method for Sample A.

Group Statistics

Method ID		N	Mean	Std. Deviation	Std. Error Mean
Chlorophyll a µg/L	EPA 445.0	9	3.6067	.44187	.14729
	SM 10200 H	16	3.6881	1.25912	.31478

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	12.348	**.002**	-.186	23	.854	-.08146	.43737	-.98623	.82331
	Equal variances not assumed			**-.234**	**20.449**	**.817**	**-.08146**	**.34753**	**-.80538**	**.64247**

Table 75. Results of t-test comparisons of ChlA by method for Sample B.

Group Statistics

Method ID		N	Mean	Std. Deviation	Std. Error Mean
Chlorophyll a µg/L	EPA 445.0	18	3.6461	.41101	.09688
	SM 10200 H	33	3.7752	1.29923	.22617

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	28.247	**.000**	-.409	49	.685	-.12904	.31572	-.76351	.50543
	Equal variances not assumed			**-.524**	**42.149**	**.603**	**-.12904**	**.24604**	**-.62552**	**.36744**

Table 76. Results of t-test comparisons of ChlA by method for all samples.

I. Biochemical Oxygen Demand. Six of the 21 results for Sample A were reported as values; the other 71% were reported as qualifiers. The MDLs for all participating laboratories ranged from 0.1 to 2 mg/L; the PQLs for Labs C, E, J and K ranged from 2 to 3 mg/L. No other analyses were conducted for BOD for Sample A.

At Sample B, six of the 21 results were reported values; the other 71% were reported as qualifiers. Values reported as less than detection/quantitation limits were not determined to be false negatives for either sample. No other analyses were conducted for BOD for Sample B. There was no statistical difference between Sample A and Sample B. See Figures 31 - 33 and Tables 77 - 79 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**
Sample A	0.28	21.38%	1.25	1.30	0.60
Sample B	0.28	19.86%	1.38	1.40	0.60
All Samples	0.26	18.53%	1.32	1.40	0.80

Table 77. F-pseudosigma values for BOD.

BOD

Lab ID	Sample A N	Sample A Lab Median	Sample A Range	Sample A Mean Z-value	Sample B N	Sample B Lab Median	Sample B Range	Sample B Mean Z-value	All N	All Lab Median	All Range	All Mean Z-value
A	3*	NR	NR	NR	3*	NR	NR	NR	6*	NR	NR	NR
C	3*	NR	NR	NR	3*	NR	NR	NR	6*	NR	NR	NR
D	3	1.40	0.60	N/A	3	1.40	0.30	N/A	6	1.40	0.80	N/A
E	3*	NR	NR	NR	3*	NR	NR	NR	6*	NR	NR	NR
H	3	1.20	0.30	N/A	3	1.20	0.40	N/A	6	1.20	0.40	N/A
J	3*	NR	NR	NR	3*	NR	NR	NR	6*	NR	NR	NR
K	3*	NR	NR	NR	3*	NR	NR	NR	6*	NR	NR	NR

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

Table 78. 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 79. Method and detection/quantitation limits for BOD.

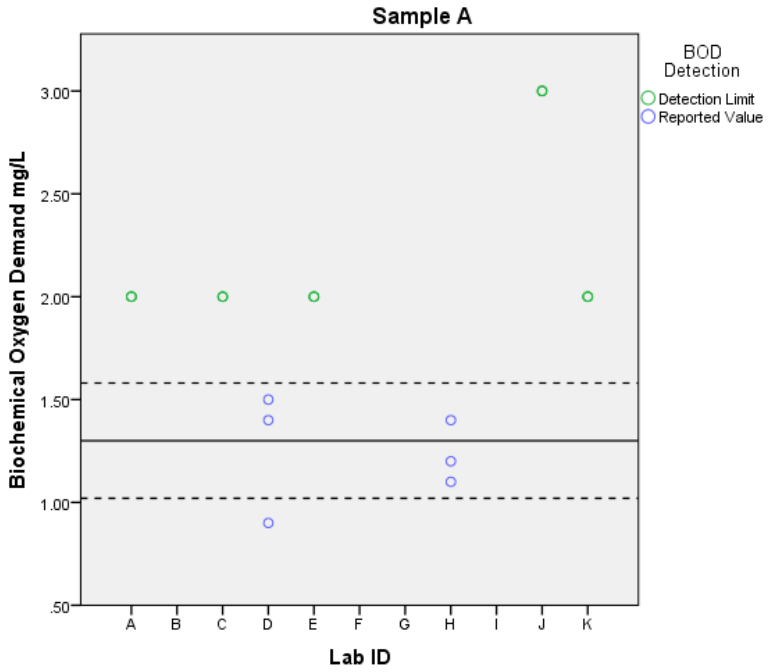


Figure 31. Scatter-plot of BOD values and detection/quantitation limits obtained by seven laboratories for Sample A. The solid line indicates the overall median, and the dashed lines indicate +/- 1 F-pseudosigma.

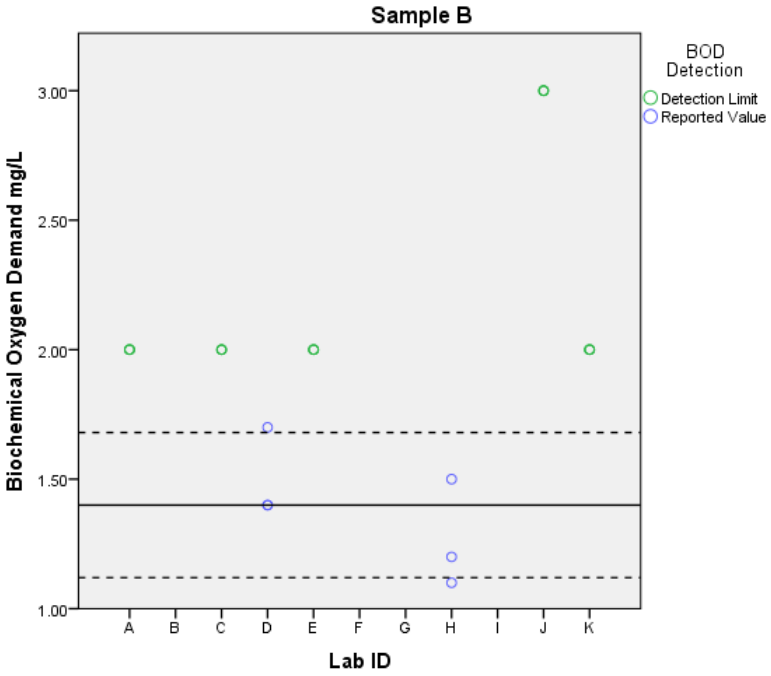


Figure 32. Scatter-plot of BOD values and detection/quantitation limits obtained by seven laboratories for Sample B. The solid line indicates the overall median, and the dashed lines indicate +/- 1 F-pseudosigma.

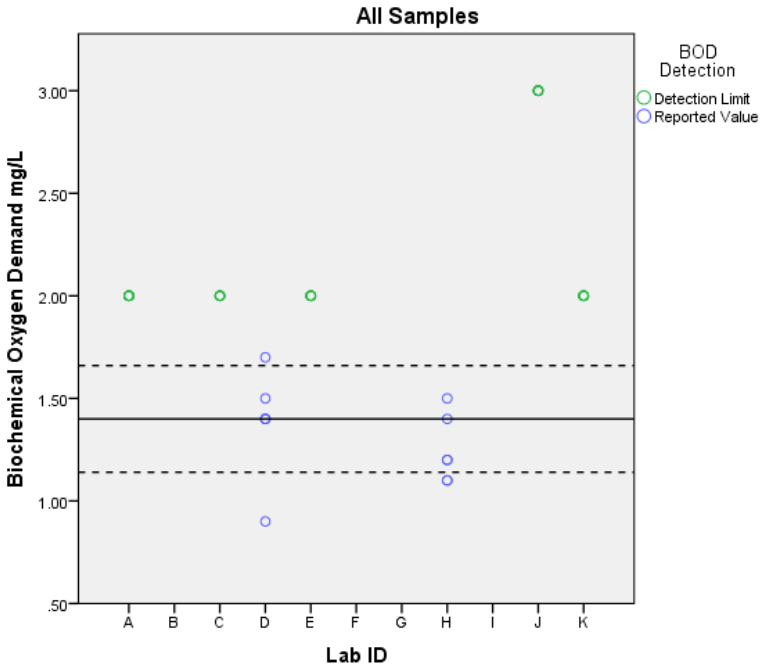


Figure 33. Scatter-plot of BOD values and detection/quantitation limits obtained by seven laboratories for all samples. The solid line indicates the overall median, and the dashed lines indicate +/- 1 F-pseudosigma.

J. Carbonaceous Biochemical Oxygen Demand. Six of the 21 results for Sample A were reported as values; the other 71% were reported as qualifiers. The MDLs for all participating laboratories ranged from 0.1 to 2 mg/L; the PQLs for Labs C, E, J and K ranged from 2 to 3 mg/L. No other analyses were conducted for CBOD for Sample A.

At Sample B, six of the 21 results were reported values; the other 71% were reported as qualifiers. Values reported as less than detection/quantitation limits were not determined to be false negatives for either sample. No other analyses were conducted for CBOD for Sample B. There was no statistical difference between Sample A and Sample B. See Figures 34 - 36 and Tables 80 - 82 for scatter-plots of values obtained by individual laboratories, F-pseudosigma values, summary statistics, inter-laboratory comparisons, and method comparisons.

Carbonaceous Biochemical Oxygen Demand				
	Sample A			
	F-pseudosigma	**% F-pseudosigma**	**Median**	**Range**
	0.32	26.25%	1.20	0.50
Method	**N**	**Mean**	**Median**	**Range**
SM 5210 B	15 (nine non-values)	1.25	1.20	0.50
SM 5210 C	6	All Non-detect	N/A	N/A
	Sample B			
	F-pseudosigma	**% F-pseudosigma**	**Median**	**Range**
	0.17	13.90%	1.20	0.30
Method	**N**	**Mean**	**Median**	**Range**
SM 5210 B	15 (nine non-values)	1.25	1.20	0.30
SM 5210 C	6	All Non-detect	N/A	N/A
	All Samples			
	F-pseudosigma	**% F-pseudosigma**	**Median**	**Range**
	0.22	18.53%	1.20	0.50
Method	**N**	**Mean**	**Median**	**Range**
SM 5210 B	30 (eighteen non-values)	1.25	1.20	0.50
SM 5210 C	12	All Non-detect	N/A	N/A

Table 80. F-pseudosigma values for CBOD.

CBOD

	Sample A				Sample B				All			
Lab ID	N	Lab Median	Range	Mean Z-value	N	Lab Median	Range	Mean Z-value	N	Lab Median	Range	Mean Z-value
A	3*	NR	NR	NR	3*	NR	NR	NR	6*	NR	NR	NR
C	3*	NR	NR	NR	3*	NR	NR	NR	6*	NR	NR	NR
D	3	1.50	0.20	N/A	3	1.20	0.20	N/A	6	1.35	0.30	N/A
E	3*	NR	NR	NR	3*	NR	NR	NR	6*	NR	NR	NR
H	3	1.10	0.10	N/A	3	1.20	0.30	N/A	6	1.10	0.40	N/A
J	3*	NR	NR	NR	3*	NR	NR	NR	6*	NR	NR	NR
K	3*	NR	NR	NR	3*	NR	NR	NR	6*	NR	NR	NR

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

Table 81. Summary statistics and Z-values by Laboratory for CBOD.

CBOD		
Method	**MDL Range**	**PQL Range**
SM 5210 B	0.2 - 1	0.8 - 3
SM 5210 C	1 - 2	2

Table 82. Methods and detection/quantitation limits for CBOD.

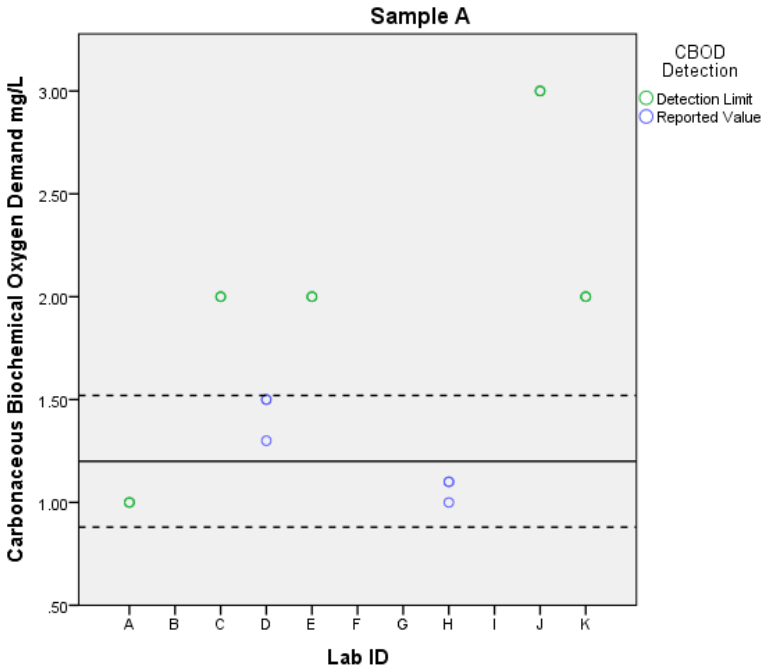


Figure 34. Scatter-plot of CBOD values and detection/quantitation limits obtained by seven laboratories for Sample A. The solid line indicates the overall median, and the dashed lines indicate +/- 1 F-pseudosigma.

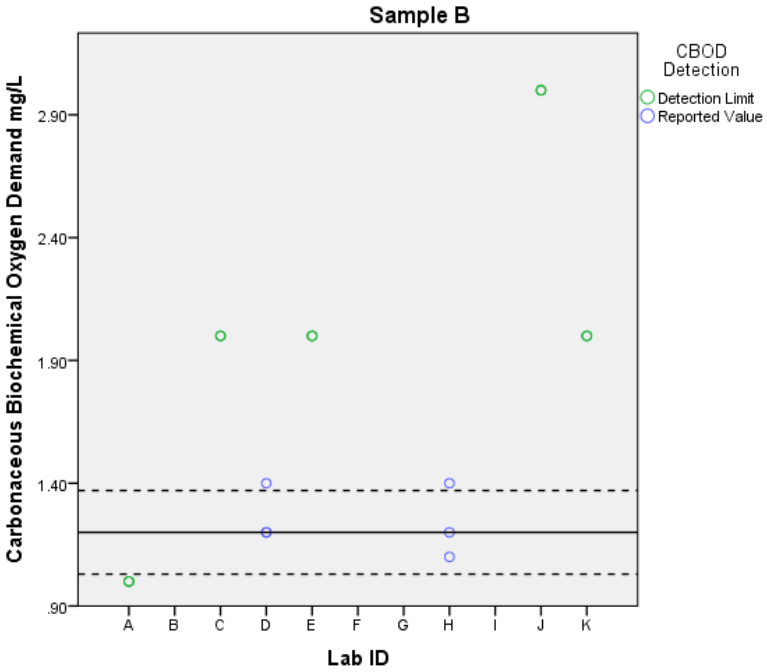


Figure 35. Scatter-plot of CBOD values and detection/quantitation limits obtained by seven laboratories for Sample B. The solid line indicates the overall median, and the dashed lines indicate +/- 1 F-pseudosigma.

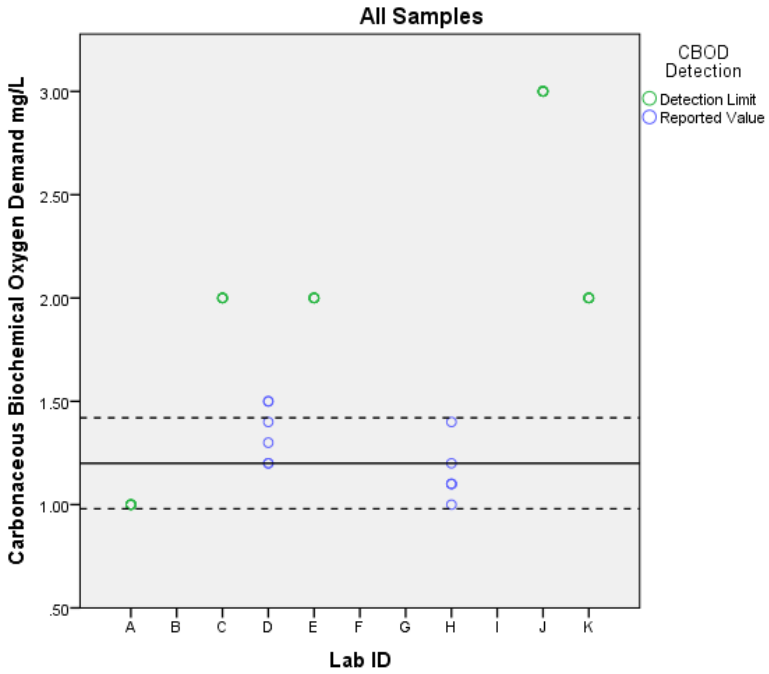


Figure 36. Scatter-plot of CBOD values and detection/quantitation limits obtained by seven laboratories for all samples. The solid line indicates the overall median, and the dashed lines indicate +/- 1 F-pseudosigma.

4. Conclusions and Recommendations

Total Kjeldahl Nitrogen: Results for total Kjeldahl nitrogen for both samples were highly variable. Lab C's reported values were all outside acceptable ranges for both samples and for all data combined (this was done because both aliquots came from a single sample and were not altered in any way), and Lab K reported one value outside acceptable ranges for Sample B and for all samples combined. This value was a statistical outlier. Lab E was the only laboratory to report non-values; it did so once for Sample A and once for Sample B. However, these were not determined to be false negatives. With the exception of Lab E, detection and quantitation limits were not an issue for this analyte. There was no statistical difference between the two sample aliquots, nor was there a difference among results reported for the three methods that were employed.

Ammonia: Ammonia values, when reported, were extremely variable for both individual samples, and for all samples combined. Results reported from Lab K were very high for both locations and may be due to the method of digestion. Detection and quantitation limits need to be addressed, as nearly three-quarters of the results were non-values. Analyses of methods were not run for Samples A or B due to the large number of non-values reported; however, when combining the results, values reported for EPA 350.1 were significantly greater than those for SM 4500 NH3 G. No values were reported for Lachat 10-107-06-1-C. There was no statistical difference in results reported for the two sample aliquots.

Total Nitrite + Nitrate: There was great variability among most results for NO_x from Samples A, B, and A & B combined. Lab A's results were highly variable; in addition, Lab A was the only laboratory to report values outside acceptable ranges for NO_x. Detection and quantitation limits continue to be issues for this analyte, as approximately one-third of the results were non-values. Results reported for EPA 353.2 were significantly greater than those reported for SM 4500 NO3 F; no values were reported for Lachat 10-107-04-1-C or USGS I-2545-90. Results from the two sample aliquots were statistically the same.

Dissolved Nitrite: There was little intra-laboratory variability in results for DNO_2, whereas inter-laboratory results were quite variable. Lab K reported one statistical outlier for Sample B; this result remained an outlier when combining results from A & B. Results reported for EPA 353.2 were significantly greater than results reported for USGS I-2540-90; no values were reported for Lachat 10-107-04-1-C or SM 4500 NO2 B. There was no statistical difference between Sample A and Sample B. Detection and quantitation limits continue to plague results for this analyte, as nearly 70% of the results were non-values.

Total Phosphorus: The majority of results reported for TP from Sample A and Sample B were within acceptable ranges. Lab K reported one statistical outlier for Sample A; this result was determined to be a statistical outlier for all results combined as well. Results reported from Sample A, B and A & B for method EPA 365.1 were significantly less than results for both EPA 365.4 and Lachat 10-115-01-1-C; there was no statistical difference between results for EPA 365.4 and those of Lachat 10-115-01-1-C. Detection and quantitation limits were not an issue for this analyte during this round robin. Samples A and B were statistically the same.

Orthophosphate: With the exception of one outlier reported by Lab D, all results for OP varied little. Results for SM 4500 P F were typically greater than the other methods employed for OP; however, these were not statistically significant for individual samples, whereas for all results combined results for SM 4500 P F were significantly greater than the other four methods' results. There was no statistical difference between results for EPA 365.1, Lachat 10-115-01-1-I,

SM 4500 P E, or USGS I-2601-90. Detection and quantitation limits need to be addressed for OP. There was no statistical difference between results reported for Sample A and those reported for Sample B.

Total Organic Carbon: There was little variability among laboratories, or within laboratories, for TOC; however, Labs E and J reported all values outside of acceptable ranges; Lab J's results were on the low end, whereas Lab E's results were high. This was true for both samples individually, as well as for all results combined. Lab E's results may be due to an improperly functioning SO_3 scrubber. No values were reported as below detection or quantitation limits for either sample. There was no statistical difference among reported results for the three methods employed; however, SM 5310 C was highly variable. There was no statistical difference between Sample A and Sample B.

Chlorophyll a: Variability among laboratories was small to moderate for chlorophyll a from both samples. Lab A reported one result for Sample A and two for Sample B as less than detection/quantitation limits; these were determined to be false negatives. Labs A and C's results were highly variable, lower than all the other results, and were typically outside acceptable ranges. There was no statistical difference between results reported for EPA 445.0 and SM 10200 H. There was no statistical difference between Sample A and Sample B.

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: The splitting of samples had little effect upon the reported results from this round robin: however, the results reported for this round robin tended to be more variable than those in the past. Participating laboratories need to continue efforts to improve data comparability, including modifying or standardizing practices. 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 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 # 6 Results - March 9, 2011, Sample A

Samples collected from St. Louis Bay, Mississippi

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	K
	0.340		0.690	0.219	0.220			0.420	0.390	0.250	0.280
	0.330		0.860	0.175	0.250			0.420	0.380	0.210	0.560
	0.290		0.840	0.191	I			0.420	0.360	0.220	0.420
Average:	**0.320**		**0.797**	**0.195**	**0.235**			**0.420**	**0.377**	**0.227**	**0.420**
Std. Dev.	**0.026**		**0.093**	**0.022**	**0.021**			**0.000**	**0.015**	**0.021**	**0.140**

Ammonia mg/L

	A	B	C	D	E	F	G*	H	I	J	K
	U		U	U	I	0.071	0.017	U	U	I	0.170
	U		U	U	I	0.030	0.012	U	U	I	0.170
	U		U	U	I	0.026	0.007	U	U	I	0.140
Average:						**0.042**	**0.012**				**0.160**
Std. Dev.						**0.025**	**0.005**				**0.017**

Total Nitrite + Nitrate mg/L

	A	B	C*	D	E	F	G*	H*	I	J	K*
	U		0.007	U	I	0.023	0.008	0.008	U	I	0.011
	0.029		0.008	U	I	0.022	0.008	0.008	U	I	0.012
	0.017		0.008	U	I	0.021	0.008	0.008	U	I	0.011
Average:	**0.023**		**0.008**			**0.022**	**0.008**	**0.008**			**0.011**
Std. Dev.	**0.008**		**0.001**			**0.001**	**0.000**	**0.000**			**0.001**

Dissolved Nitrite mg/L

	A	B	C*	D	E	F*	G	H	I	J	K
	U		U	U	I	0.002	U	U	0.001	I	U
	U		0.002	U	I	0.002	U	U	0.001	I	U
	U		U	U	I	0.002	U	U	0.001	I	U
Average:			**0.002**			**0.002**			**0.001**		
Std. Dev.						**0.000**			**0.000**		

Total Phosphorus mg/L

	A	B	C	D*	E	F	G	H	I	J	K*
	0.021		0.023	0.057	0.040	0.025	0.026	0.030	0.022	0.040	0.042
	0.018		0.022	0.056	0.060	0.026	0.025	0.030	0.023	0.040	0.085
	0.018		0.024	0.057	0.060	0.024	0.026	0.030	0.023	0.040	0.036
Average:	**0.019**		**0.023**	**0.057**	**0.053**	**0.025**	**0.026**	**0.030**	**0.023**	**0.040**	**0.054**
Std. Dev.	**0.002**		**0.001**	**0.001**	**0.012**	**0.001**	**0.001**	**0.000**	**0.001**	**0.000**	**0.027**

Orthophosphate mg/L

	A	B	C	D	E	F*	G	H	I	J	K*
	0.018		0.011	U	0.011	0.004	0.016	0.012	U	I	0.011
	0.017		0.010	U	0.011	0.004	0.016	0.012	0.010	I	0.009
	0.017		0.010	0.042	0.011	0.005	0.019	0.012	U	I	0.009
Average:	**0.017**		**0.010**	**0.042**	**0.011**	**0.004**	**0.017**	**0.012**	**0.010**		**0.010**
Std. Dev.	**0.001**		**0.001**		**0.000**	**0.001**	**0.002**	**0.000**			**0.001**

Total Organic Carbon mg/L

	A	B	C	D	E	F	G	H*	I	J	K
				4.180	6.000	3.630	4.060	4.200		3.000	
				4.260	6.000	3.600	4.010	4.200		3.000	
				4.150	6.000	3.650	4.070	4.200		3.000	
Average:				**4.197**	**6.000**	**3.627**	**4.047**	**4.200**		**3.000**	
Std. Dev.				**0.057**	**0.000**	**0.025**	**0.032**	**0.000**		**0.000**	

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

Chlorophyll a µg/L

	A	B*	C	D	E	F	G	H	I	J*	K
	U	3.210	2.140	U	4.200	4.870	4.600	4.700		3.590	5.000
	1.400	3.530	1.690	U	4.200	5.170	4.670	4.700		3.440	5.000
	1.400	3.350	2.810	U	4.200	4.460	4.360	4.600		3.450	4.000
Average:	**1.400**	**3.363**	**2.213**		**4.200**	**4.833**	**4.543**	**4.667**		**3.493**	**4.667**
Std. Dev.	**0.000**	**0.160**	**0.564**		**0.000**	**0.356**	**0.163**	**0.058**		**0.084**	**0.577**

Biochemical Oxygen Demand mg/L

	A	B	C	D	E	F	G	H	I	J	K
	U		U	0.900	U			1.100		I	U
	U		U	1.400	U			1.400		I	U
	U		U	1.500	U			1.200		I	U
Average:				**1.267**				**1.233**			
Std. Dev.			**0.000**	**0.321**				**0.153**			

Carbonaceous Biochemical Oxygen Demand mg/L

	A	B	C	D	E	F	G	H	I	J*	K
	U		U	1.500	U			1.000		I	U
	U		U	1.500	U			1.100		I	U
	U		U	1.300	U			1.100		I	U
Average:				**1.433**				**1.067**			
Std. Dev.				**0.115**				**0.058**			

GOMA Analytical Round Robin # 6 Results - March 9, 2011, Sample B

Samples collected from St. Louis Bay, Mississippi

Total Kjeldahl Nitrogen mg/L

	A	B	C	D	E	F	G	H	I	J	K
	0.440		0.710	0.199	0.290			0.480	0.420	0.220	0.310
	0.330		0.650	0.189	0.240			0.420	0.370	0.210	1.140
	0.230		0.700	0.218	I			0.440	0.350	0.240	0.320
Average:	**0.333**		**0.687**	**0.202**	**0.265**			**0.447**	**0.380**	**0.223**	**0.590**
Std. Dev.	**0.105**		**0.032**	**0.015**	**0.035**			**0.031**	**0.036**	**0.015**	**0.476**

Ammonia mg/L

	A	B	C	D	E	F	G*	H	I	J	K
	U		U	U	I	0.031	0.015	U	U	I	0.170
	U		U	U	I	0.024	0.011	U	U	I	0.170
	U		U	U	I	0.030	0.010	U	U	I	0.160
Average:						**0.028**	**0.012**				**0.167**
Std. Dev.						**0.004**	**0.003**				**0.006**

Total Nitrite + Nitrate mg/L

	A	B	C*	D*	E	F	G*	H*	I	J	K*
	0.016		0.008	0.003	I	0.021	0.010	0.008	U	I	0.012
	0.022		0.009	0.003	I	0.020	0.009	0.008	U	I	0.011
	0.030		0.008	U	I	0.021	0.010	0.009	U	I	0.011
Average:	**0.023**		**0.008**	**0.003**		**0.021**	**0.010**	**0.008**			**0.011**
Std. Dev.	**0.007**		**0.001**	**0.000**		**0.001**	**0.001**	**0.001**			**0.001**

Dissolved Nitrite mg/L

	A	B	C*	D	E	F*	G	H*	I	J	K*
	U		U	U	I	0.002	U	0.002	0.001	I	0.015
	U		0.002	U	I	0.002	U	U	0.001	I	U
	U		0.002	U	I	0.002	U	U	0.001	I	U
Average:			**0.002**			**0.002**		**0.002**	**0.001**		**0.015**
Std. Dev.			**0.000**			**0.000**			**0.000**		

Total Phosphorus mg/L

	A	B	C	D*	E	F	G	H	I	J	K*
	0.020		0.023	0.057	0.030	0.028	0.027	0.031	0.025	0.030	0.046
	0.020		0.023	0.058	0.050	0.028	0.027	0.031	0.026	0.040	0.055
	0.019		0.024	0.058	0.050	0.026	0.027	0.031	0.028	0.040	0.016
Average:	**0.020**		**0.023**	**0.058**	**0.043**	**0.027**	**0.027**	**0.031**	**0.026**	**0.037**	**0.039**
Std. Dev.	**0.001**		**0.001**	**0.001**	**0.012**	**0.001**	**0.000**	**0.000**	**0.002**	**0.006**	**0.020**

Orthophosphate mg/L											
	A	B	C	D	E	F*	G	H	I	J	K*
	0.018		0.012	U	0.013	0.008	0.018	0.014	0.013	I	0.009
	0.020		0.012	U	0.013	0.006	0.018	0.013	0.012	I	0.016
	0.019		0.012	U	0.014	0.008	0.018	0.013	0.012	I	0.011
Average:	**0.019**		**0.012**		**0.013**	**0.007**	**0.018**	**0.013**	**0.012**		**0.012**
Std. Dev.	**0.001**		**0.000**		**0.001**	**0.001**	**0.000**	**0.001**	**0.001**		**0.004**

Total Organic Carbon mg/L											
	A	B	C	D	E	F	G	H*	I	J	K
				4.080	6.000	3.690	3.990	4.200		3.000	
				4.170	7.000	3.700	3.880	4.100		2.000	
				4.020	8.000	3.320	3.840	4.000		2.000	
Average:				**4.090**	**7.000**	**3.570**	**3.903**	**4.100**		**2.333**	
Std. Dev.				**0.075**	**1.000**	**0.217**	**0.078**	**0.100**		**0.577**	

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

Chlorophyll a µg/L											
	A	B	C	D	E	F	G	H	I	J	K
	U	3.120	1.120	U	3.900	3.250	4.410	4.400		3.550	3.000
	2.400	2.930	1.690	U	4.100	3.510	4.500	4.500		3.530	5.000
	U	3.390	2.250	U	4.300	4.640	4.940	4.400		3.640	5.000
Average:	**2.400**	**3.147**	**1.687**		**4.100**	**3.800**	**4.617**	**4.433**		**3.573**	**4.333**
Std. Dev.		**0.231**	**0.565**		**0.200**	**0.739**	**0.284**	**0.058**		**0.059**	**1.155**

Biochemical Oxygen Demand mg/L											
	A	B	C	D	E	F	G	H	I	J	K
	U		U	1.400	U			1.100		I	U
	U		U	1.400	U			1.500		I	U
	U		U	1.700	U			1.200		I	U
Average:				**1.500**				**1.267**			
Std. Dev.			**0.000**	**0.173**				**0.208**			

Carbonaceous Biochemical Oxygen Demand mg/L											
	A	B	C	D	E	F	G	H	I	J	K
	U		U	1.400	U			1.200		I	U
	U		U	1.200	U			1.400		I	U
	U		U	1.200	U			1.100		I	U
Average:				**1.267**				**1.233**			
Std. Dev.				**0.115**				**0.153**			

Sample A

	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)	24		30		30		30		30		30		18		30		21		21	
N (Greater than PQL)	23		6		5		3		26		17		15		26		3		3	
N Analyzed	23		9		17		7		30		23		18		26		6		6	
Mean	0.380	0.040	0.071	0.023	0.013	0.002	0.002	0.000	0.035	0.003	0.013	0.002	4.189	0.222	3.798	0.220	1.250	0.092	1.250	0.089
95% CI (LB)	0.296		0.018		0.009		0.001		0.029		0.010		3.720		3.345		1.013		1.023	
95% CI (UB)	0.463		0.125		0.016		0.002		0.041		0.016		4.659		4.251		1.487		1.478	
5% Trimmed	0.365		0.070		0.012		0.002		0.034		0.012		4.155		3.857		1.256		1.250	
Median	0.340		0.030		0.008		0.002		0.028		0.011		4.110		4.200		1.300		1.200	
Variance	0.037		0.005		0.000		0.000		0.000		0.000		0.891		1.258		0.051		0.047	
Std. Dev.	0.193		0.069		0.007		0.001		0.016		0.008		0.944		1.122		0.226		0.217	
Min	0.175		0.007		0.007		0.001		0.018		0.004		3.000		1.400		0.900		1.000	
Max	0.860		0.170		0.029		0.002		0.085		0.042		6.000		5.170		1.500		1.500	
Range	0.685		0.163		0.022		0.001		0.067		0.038		3.000		3.770		0.600		0.500	
IQR	0.200		0.141		0.011		0.001		0.017		0.006		0.670		1.360		0.370		0.420	
Skew	1.428	0.481	0.688	0.717	1.232	0.550	-0.374	0.794	1.383	0.427	2.644	0.481	0.962	0.536	-0.974	0.456	-0.625	0.845	0.265	0.845
Kurtosis	1.520	0.935	-1.614	1.400	0.283	1.063	-2.800	1.587	1.666	0.833	9.949	0.935	0.459	1.038	0.032	0.887	-0.750	1.741	-2.214	1.741
Huber's ψ	0.333		0.044		0.009		N/A		0.030		0.012		4.036		4.020		1.277		1.231	
Kaplan-Meier (KM) Method																				
Minimum Non-Detect	0.1		0.003		0.003		0.002		N/A		0.001		N/A		1		2		1	
Maximum Non-Detect	0.1		0.05		0.04		0.02		N/A		0.04		N/A		3		3		3	
Mean	0.371	0.039	0.027	0.009	0.011	0.001	0.001	0.000	N/A	N/A	0.012	0.001	N/A	N/A	3.519	0.237	1.250	0.092	1.167	0.073
SD	0.189		0.046		0.006		0.000		N/A		0.007		N/A		1.259		0.206		0.200	
95% KM UCL	0.435		0.043		0.013		0.001		0.040		0.014		4.576		4.554		1.409		1.293	
Normality																				
Test of Skew	**0.006**		0.328		**0.030**		N/A		**0.003**		**0.000**		0.074		**0.037**		N/A		N/A	
Test of Kurtosis	0.131		0.159		0.616		**0.016**		0.086		**0.000**		0.506		0.786		0.727		0.158	
Jarque & Bera	**0.021**		0.530		0.168		N/A		**0.005**		**0.000**		0.313		0.158		N/A		N/A	
Outliers																				
F Crit. (Mahalanobis D2)	7.730		4.91		6.86		4.08		8.460		7.730		7.030		8.070		3.56		3.56	
Mahalanobis D2 Max	6.210		2.02		5.54		1.14		**9.540**		**14.770**		3.680		4.570		2.40		1.33	
+ 2 Std. Dev.	0.765		0.210		0.027		0.003		0.067		0.028		6.077		6.041		1.702		1.684	
- 2 Std. Dev.	-0.006		-0.067		-0.001		0.001		0.003		-0.002		2.302		1.554		0.798		0.816	
# Outside 2 Std. Dev.	2		0		1		0		1		1		0		2		0		0	
+ 2 F-Pseudosigma	0.637		0.238		0.024		0.003		0.054		0.020		5.110		6.220		1.860		1.830	
- 2 F-Pseudosigma	0.043		-0.178		-0.008		0.001		0.002		0.002		3.110		2.180		0.740		0.570	
# Outside 2 F-Pseudosigma	3		0		1		0		6		1		6		4		0		0	
# from Boxplots	2		0		0		0		1		1		3		0		0		0	
Homoscedasticity (between laboratories)																				
Levene's	**0.032**		0.052		**0.000**		N/A		**0.000**		**0.001**		**0.001**		**0.006**		0.165		0.148	
Detection Limits																				
< MDL	0		15		7		17		0		4		0		4		12		12	
% < MDL	0%		50%		23%		57%		0%		13%		0%		13%		57%		57%	
< PQL	1		9		18		10		4		9		3		0		6		6	
% < PQL	4%		80%		83%		90%		13%		43%		17%		13%		86%		86%	
Precision																				
%F-Pseudosigma	43.61%		347.17%		101.93%		37.06%		45.72%		40.43%		12.13%		24.05%		21.38%		26.25%	
%RSD	50.75%		97.18%		54.03%		34.08%		46.34%		58.60%		22.53%		29.54%		18.07%		17.34%	

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

Sample B

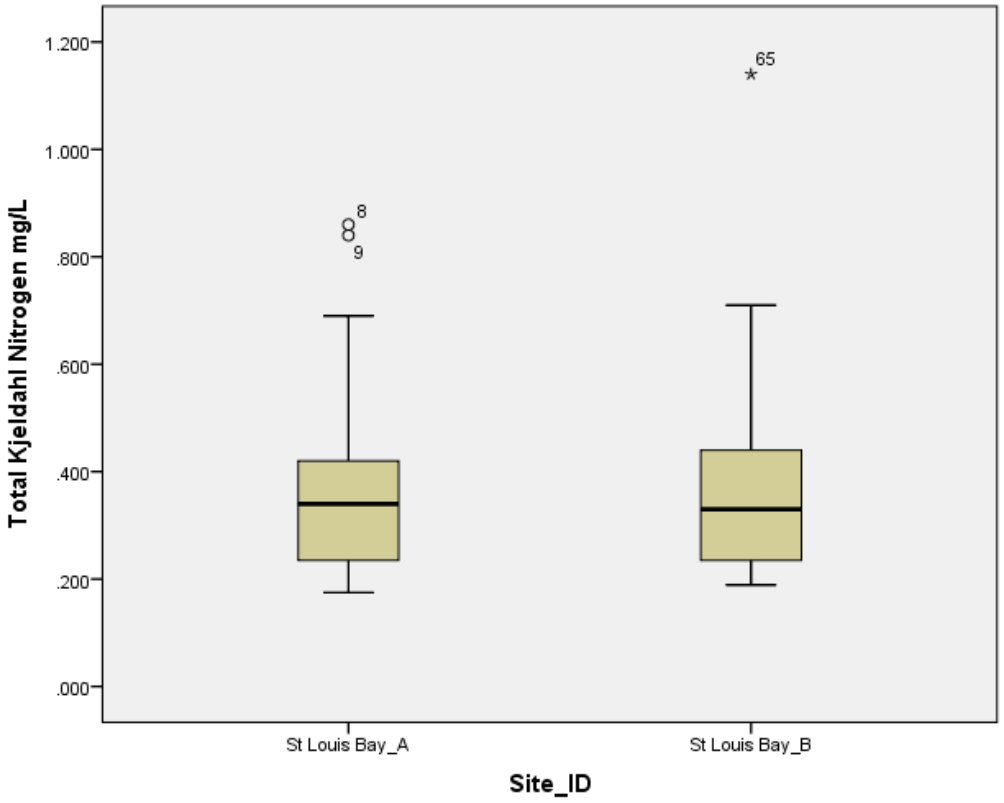
	TKN		NH3		NOx		D_NO2		TP		OP		TOC		ChlA		BOD		CBOD	
	Stat.	Std. Err.	Stat.	Std. Err.	Stat.	Std. Err.	Stat.	Std. Err.	Stat.	Std. Err.	Stat.	Std. Err.	Stat.	Std. Err.	Stat.	Std. Err.	Stat.	Std. Err.	Stat.	Std. Err.
Descriptives																				
N (Total)	24		30		30		30		30		30		18		30		21		21	
N (Greater than PQL)	23		6		6		3		26		18		15		25		3		3	
N Analyzed	23		9		20		10		30		24		18		25		6		6	
Mean	0.396	0.047	0.069	0.025	0.012	0.002	0.003	0.001	0.033	0.002	0.013	0.001	4.166	0.354	3.659	0.206	1.383	0.087	1.250	0.050
95% CI (LB)	0.299		0.012		0.009		0.000		0.028		0.012		3.420		3.234		1.159		1.122	
95% CI (UB)	0.493		0.126		0.016		0.006		0.038		0.015		4.912		4.083		1.608		1.379	
5% Trimmed	0.370		0.067		0.012		0.002		0.033		0.013		4.074		3.719		1.382		1.250	
Median	0.330		0.030		0.010		0.002		0.028		0.013		3.995		3.640		1.400		1.200	
Variance	0.050		0.005		0.000		0.000		0.000		0.000		2.252		1.058		0.046		0.015	
Std. Dev.	0.224		0.074		0.007		0.004		0.013		0.004		1.501		1.028		0.214		0.122	
Min	0.189		0.010		0.003		0.001		0.016		0.006		2.000		1.120		1.100		1.100	
Max	1.140		0.170		0.030		0.015		0.058		0.020		8.000		5.000		1.700		1.400	
Range	0.951		0.160		0.027		0.014		0.042		0.014		6.000		3.880		0.600		0.300	
IQR	0.210		0.152		0.011		0.001		0.017		0.005		0.580		1.400		0.380		0.220	
Skew	1.930	0.481	0.824	0.717	0.999	0.512	3.088	0.687	0.904	0.427	0.020	0.472	1.224	0.536	-0.793	0.464	0.137	0.845	0.490	0.845
Kurtosis	4.481	0.935	-1.690	1.400	0.585	0.992	9.665	1.334	-0.441	0.833	-0.488	0.918	1.982	1.038	0.214	0.902	-0.270	1.741	-1.467	1.741
Huber's ψ	0.343		0.033		0.010		N/A		0.029		0.013		3.940		3.779		1.377		1.220	
Kaplan-Meier (KM) Method																				
Minimum Non-Detect	0.1		0.003		0.003		0.002		N/A		0.009		N/A		1		2		1	
Maximum Non-Detect	0.1		0.05		0.04		0.02		N/A		0.04		N/A		3		3		3	
Mean	0.388	0.046	0.028	0.009	0.011	0.001	0.002	0.001	N/A	N/A	0.013	0.001	N/A	N/A	3.304	0.236	1.383	0.087	1.200	0.042
SD	0.219		0.047		0.006		0.003		N/A		0.004		N/A		1.241		0.195		0.115	
95% KM UCL	0.468		0.051		0.014		0.003		0.037		0.014		4.781		3.705		1.534		1.273	
Normality																				
Test of Skew	**0.001**		0.243		0.054		**0.000**		**0.039**		0.964		**0.027**		0.086		N/A		N/A	
Test of Kurtosis	**0.006**		0.131		0.427		**0.000**		0.665		0.663		0.095		0.632		0.961		0.401	
Jarque & Bera	**0.000**		0.467		0.240		**0.000**		0.130		0.818		0.092		0.314		N/A		N/A	
Outliers																				
F Crit. (Mahalanobis D2)	7.730		4.910		7.330		5.240		8.460		7.850		7.030		7.960		3.560		3.560	
Mahalanobis D2 Max	**10.980**		1.880		6.330		**8.000**		3.870		4.010		6.530		6.090		2.200		1.500	
+ 2 Std. Dev.	0.845		0.216		0.026		0.011		0.058		0.021		7.167		5.716		1.811		1.495	
- 2 Std. Dev.	-0.052		-0.078		-0.002		-0.005		0.008		0.006		1.165		1.602		0.956		1.005	
# Outside 2 Std. Dev.	1		0		0		1		0		0		1		1		0		0	
+ 2 F-Pseudosigma	0.641		0.255		0.026		0.003		0.053		0.021		4.850		4.500		1.960		1.530	
- 2 F-Pseudosigma	0.019		-0.195		-0.006		0.001		0.004		0.005		3.140		2.780		0.840		0.870	
# Outside 2 F-Pseudosigma	4		0		0		1		4		0		6		8		0		0	
# from Boxplots	1		0		0		1		0		0		5		1		0		0	
Homoscedasticity (between laboratories)																				
Levene's	**0.000**		0.202		**0.016**		N/A		**0.000**		**0.002**		0.051		**0.002**		0.725		0.653	
Detection Limits																				
< MDL	0		15		4		14		0		3		0		5		12		12	
% < MDL	0%		50%		13%		47%		0%		10%		0%		17%		57%		57%	
< PQL	2		9		20		13		4		9		3		0		6		6	
% < PQL	8%		80%		80%		90%		13%		40%		17%		17%		86%		86%	
Precision																				
%F-Pseudosigma	47.17%		375.59%		81.54%		37.06%		43.71%		31.36%		10.76%		11.81%		19.86%		13.90%	
%RSD	56.62%		106.79%		56.04%		141.43%		38.15%		27.62%		36.02%		28.14%		15.45%		9.80%	

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

Samples A + B

	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)	48		60		60		60		60		60		36		60		42		42	
N (Greater than PQL)	46		12		11		6		52		35		30		51		6		6	
N Analyzed	46		18		37		17		60		47		36		51		12		12	
Mean	0.388	0.031	0.069	0.025	0.013	0.001	0.002	0.001	0.034	0.002	0.013	0.001	4.178	0.206	3.730	0.150	1.317	0.064	1.250	0.048
95% CI (LB)	0.327		0.012		0.010		0.001		0.030		0.011		3.760		3.429		1.176		1.143	
95% CI (UB)	0.450		0.126		0.015		0.004		0.038		0.015		4.596		4.030		1.457		1.357	
5% Trimmed	0.367		0.067		0.012		0.002		0.033		0.013		4.111		3.791		1.319		1.250	
Median	0.335		0.030		0.010		0.002		0.028		0.012		4.040		4.000		1.400		1.200	
Variance	0.043		0.005		0.000		0.000		0.000		0.000		1.526		1.142		0.049		0.028	
Std. Dev.	0.207		0.074		0.007		0.003		0.014		0.006		1.236		1.068		0.221		0.168	
Min	0.175		0.010		0.003		0.001		0.016		0.004		2.000		1.120		0.900		1.000	
Max	1.140		0.170		0.030		0.015		0.085		0.042		8.000		5.170		1.700		1.500	
Range	0.965		0.160		0.027		0.014		0.069		0.038		6.000		4.050		0.800		0.500	
IQR	0.197		0.152		0.011		0.001		0.016		0.006		0.570		1.390		0.350		0.300	
Skew	1.704	0.350	0.824	0.717	1.052	0.388	3.969	0.550	1.264	0.309	2.519	0.347	1.185	0.393	-0.849	0.333	-0.252	0.637	0.277	0.637
Kurtosis	3.157	0.688	-1.690	1.400	0.230	0.759	16.124	1.063	1.306	0.608	11.993	0.681	2.178	0.768	-0.058	0.656	-0.130	1.232	-1.201	1.232
Huber's ψ	0.337		0.033		0.010		N/A		0.030		0.012		3.985		3.915		1.326		1.226	
Kaplan-Meier (KM) Method																				
Minimum Non-Detect	0.1		0.003		0.003		0.002		N/A		0.001		N/A		1		2		1	
Maximum Non-Detect	0.1		0.05		0.04		0.02		N/A		0.04		N/A		3		3		3	
Mean	0.379	0.030	0.027	0.006	0.011	0.001	0.002	0.000	N/A	N/A	0.012	0.001	N/A	N/A	3.405	0.168	1.317	0.064	1.167	0.043
SD	0.205		0.047		0.007		0.002		N/A		0.006		N/A		1.267		0.211		0.176	
95% KM UCL	0.510		0.040		0.013		0.002		0.037		0.014		4.526		4.137		1.424		1.240	
Normality																				
Test of Skew	**0.000**		0.190		**0.011**		**0.000**		**0.000**		**0.000**		**0.005**		**0.015**		0.679		0.650	
Test of Kurtosis	**0.006**		**0.013**		0.593		**0.000**		0.072		**0.000**		**0.035**		0.905		0.922		0.252	
Jarque & Bera	**0.000**		0.247		0.043		**0.000**		**0.000**		**0.000**		**0.002**		0.054		0.885		0.651	
Outliers																				
F Crit. (Mahalanobis D2)	9.580		7.030		9.020		6.860		10.240		9.630		8.940		9.840		5.820		5.820	
Mahalanobis D2 Max	**13.200**		2.060		6.470		**14.730**		**12.470**		**24.220**		**9.570**		5.970		3.560		2.220	
+ 2 Std. Dev.	0.802		0.216		0.026		0.009		0.063		0.025		6.649		5.867		1.758		1.586	
- 2 Std. Dev.	-0.026		-0.078		-0.001		-0.004		0.005		0.001		1.707		1.593		0.875		0.914	
# Outside 2 Std. Dev.	3		0		2		1		1		1		2		3		0		0	
+ 2 F-Pseudosigma	0.628		0.250		0.026		0.003		0.052		0.021		4.878		6.061		1.920		1.640	
- 2 F-Pseudosigma	0.042		-0.190		-0.006		0.001		0.004		0.003		3.202		1.939		0.880		0.760	
# Outside 2 F-Pseudosigma	7		0		2		1		10		1		12		5		0		0	
# from Boxplots	4		0		0		1		1		1		8		1		0		0	
Homoscedasticity (between laboratories)																				
Levene's	**0.000**		0.170		**0.000**		N/A		**0.000**		0.299		**0.000**		**0.000**		0.753		0.687	
Detection Limits																				
< MDL	0		30		11		31		0		7		0		9		24		24	
% < MDL	0%		50%		18%		52%		0%		12%		0%		15%		57%		57%	
< PQL	1		18		38		23		8		18		6		0		12		12	
% < PQL	2%		80%		82%		90%		13%		42%		17%		15%		86%		86%	
Precision																				
%F-Pseudosigma	43.70%		366.32%		77.84%		37.06%		42.13%		37.06%		10.37%		25.76%		18.53%		18.53%	
%RSD	53.35%		107.25%		53.85%		136.10%		41.18%		46.15%		29.58%		28.63%		16.78%		13.44%	

Bold values are significant p-values at the 0.05 level.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1.200
1.000
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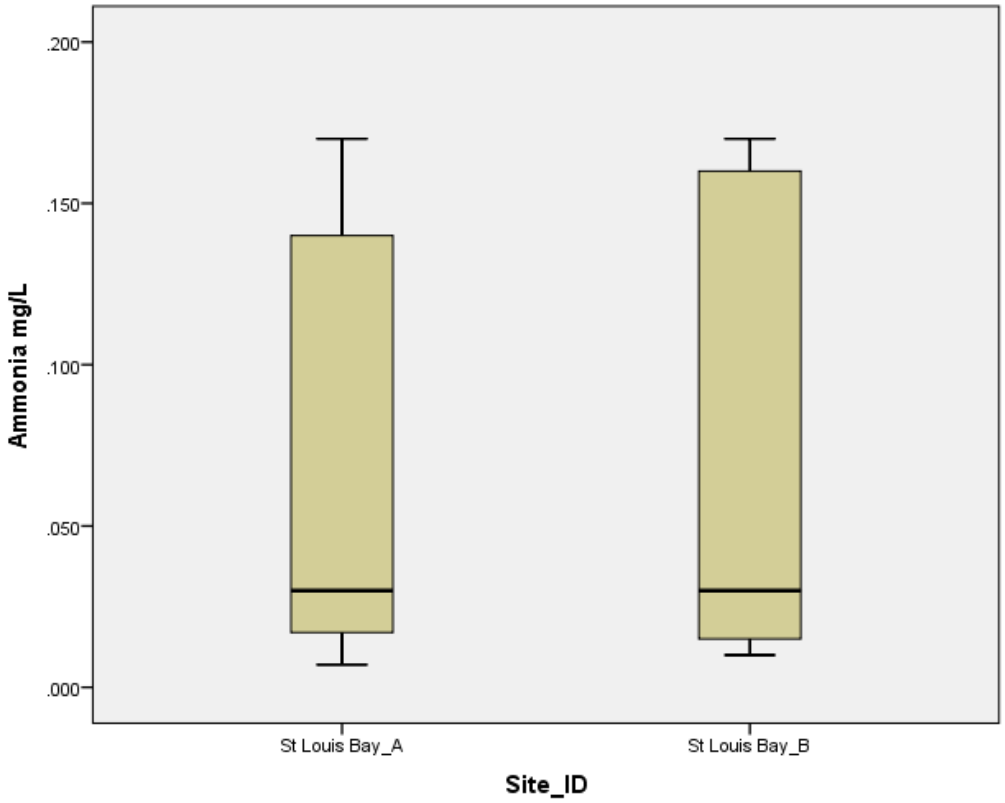
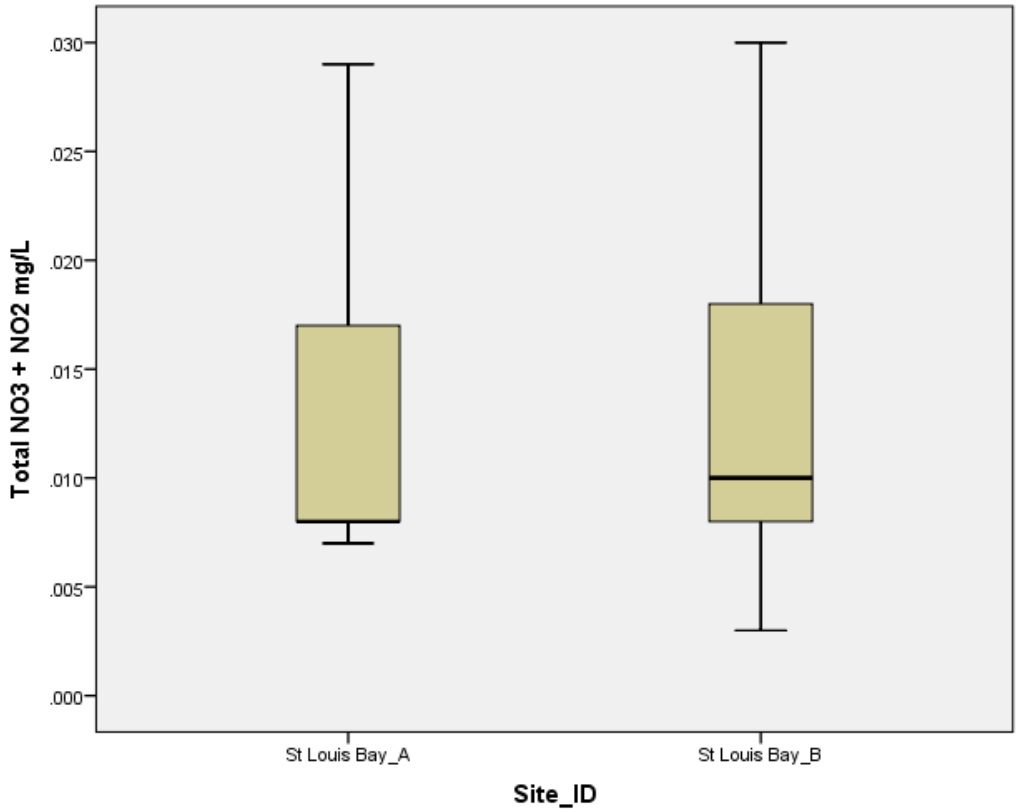
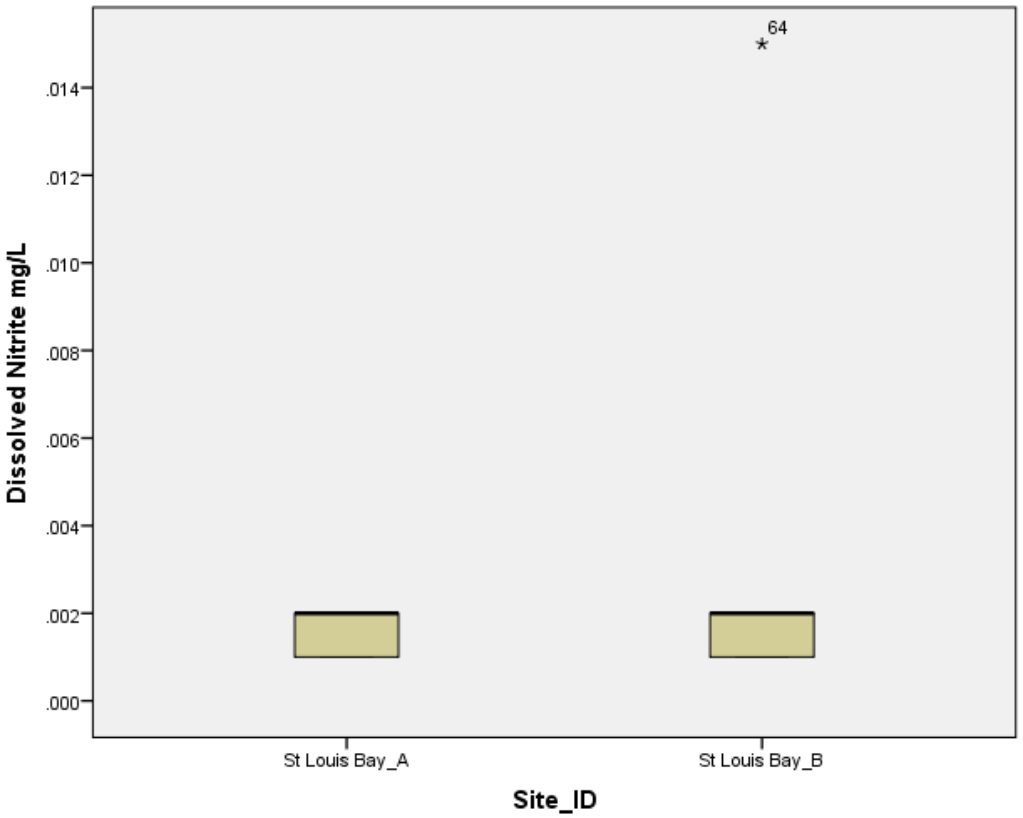
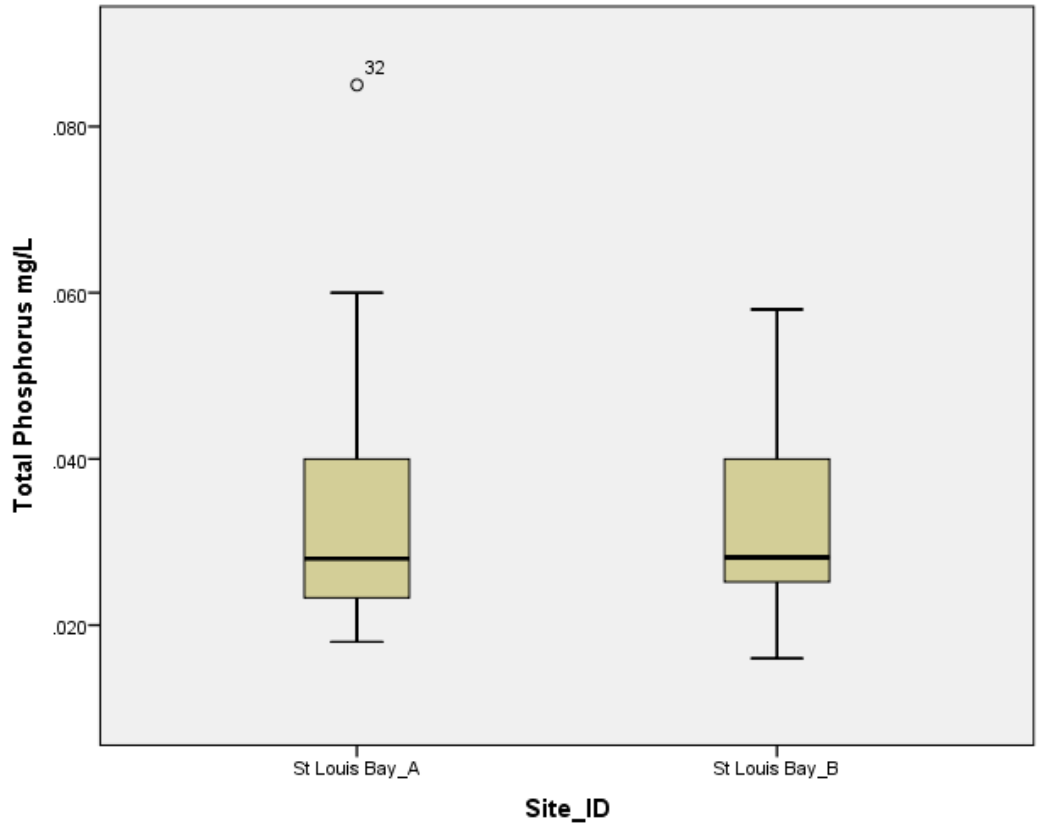
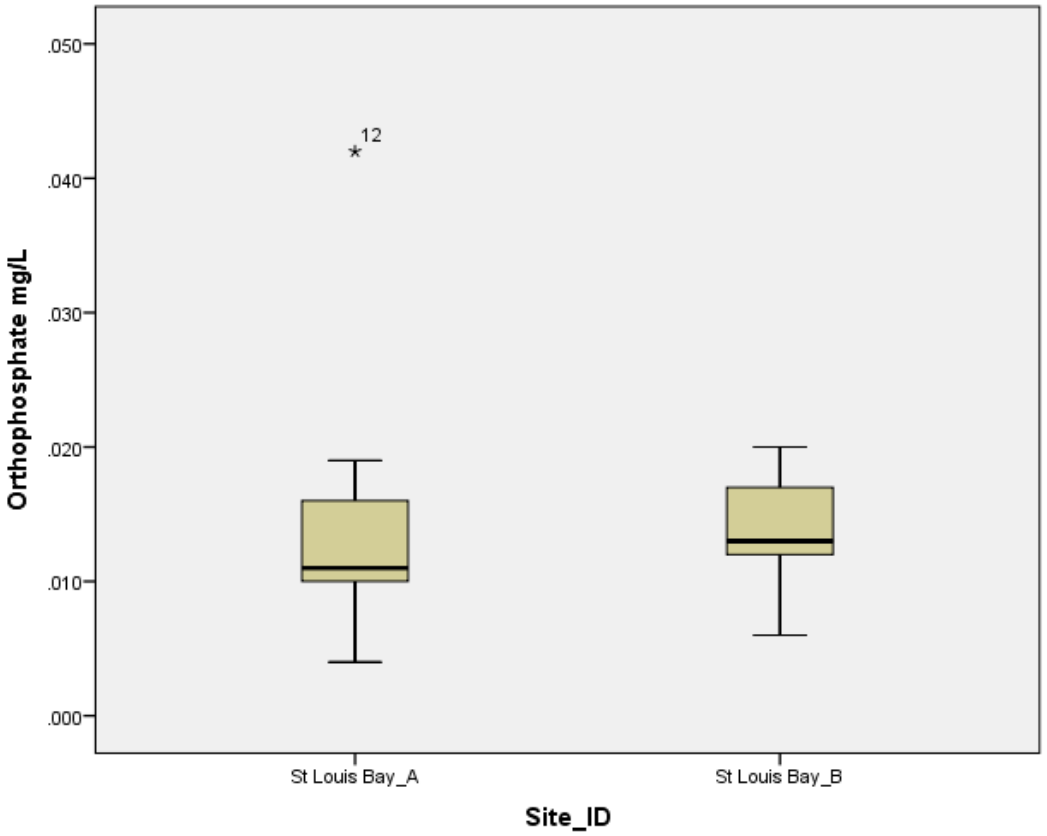
.600
.400
.200
.000
65
8
8
9
St Louis Bay_A
St Louis Bay_B
Site_ID

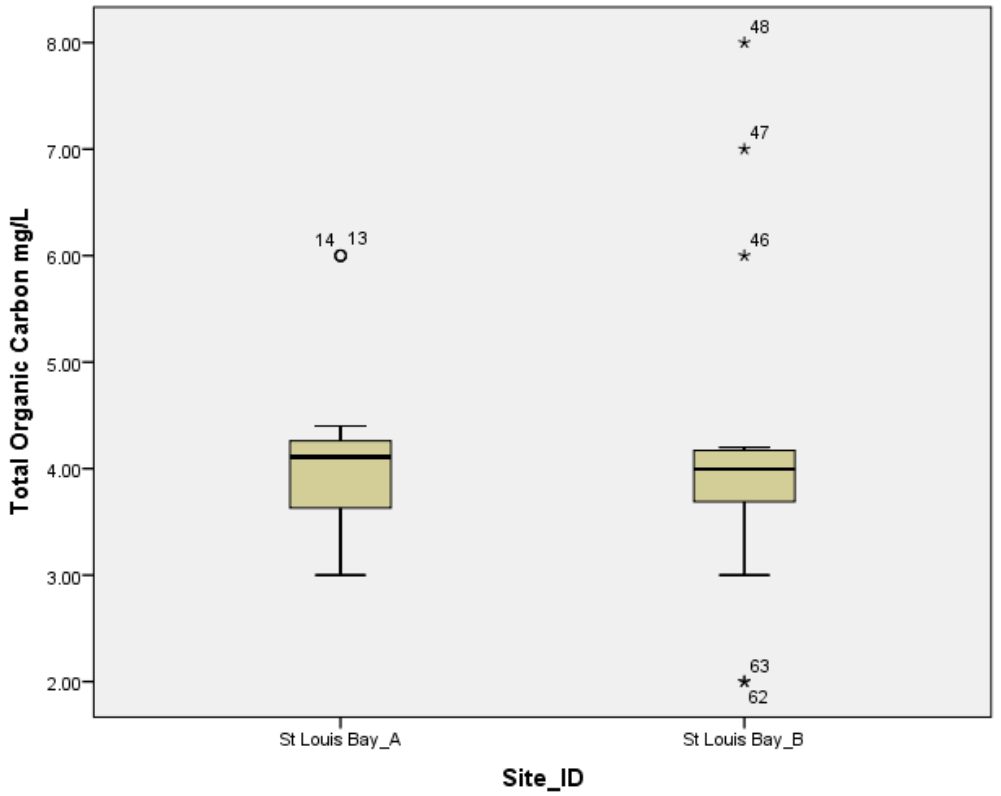

Ammonia mg/L
.200
.150
.100
.050
.000
St Louis Bay_A
St Louis Bay_B
Site_ID


Total NO3 + NO2 mg/L
.030
.025
.020
.015
.010
.005
.000
St Louis Bay_A
St Louis Bay_B
Site_ID


Dissolved Nitrite mg/L
64
.014
.012
.010
.008
.006
.004
.002
.000
St Louis Bay_A
St Louis Bay_B
Site_ID


32
.080
.060
.040
.020
Total Phosphorus mg/L
St Louis Bay_A
St Louis Bay_B
Site_ID


12
.050
.040
.030
.020
.010
.000
Orthophosphate mg/L
St Louis Bay_A
St Louis Bay_B
Site_ID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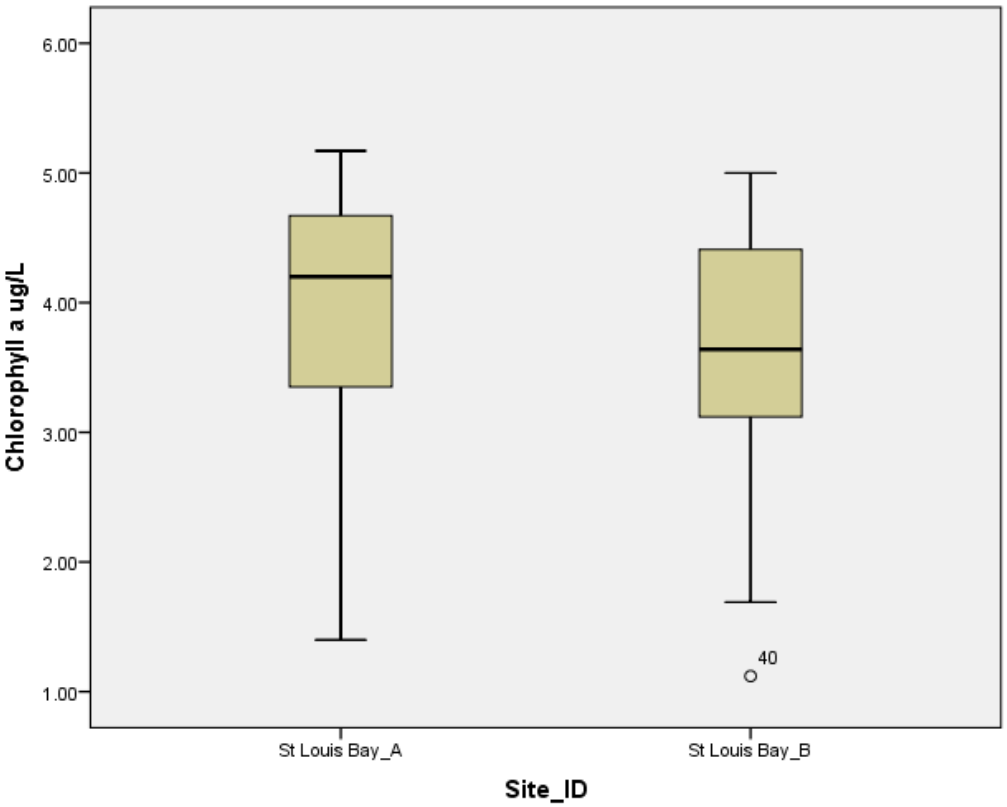
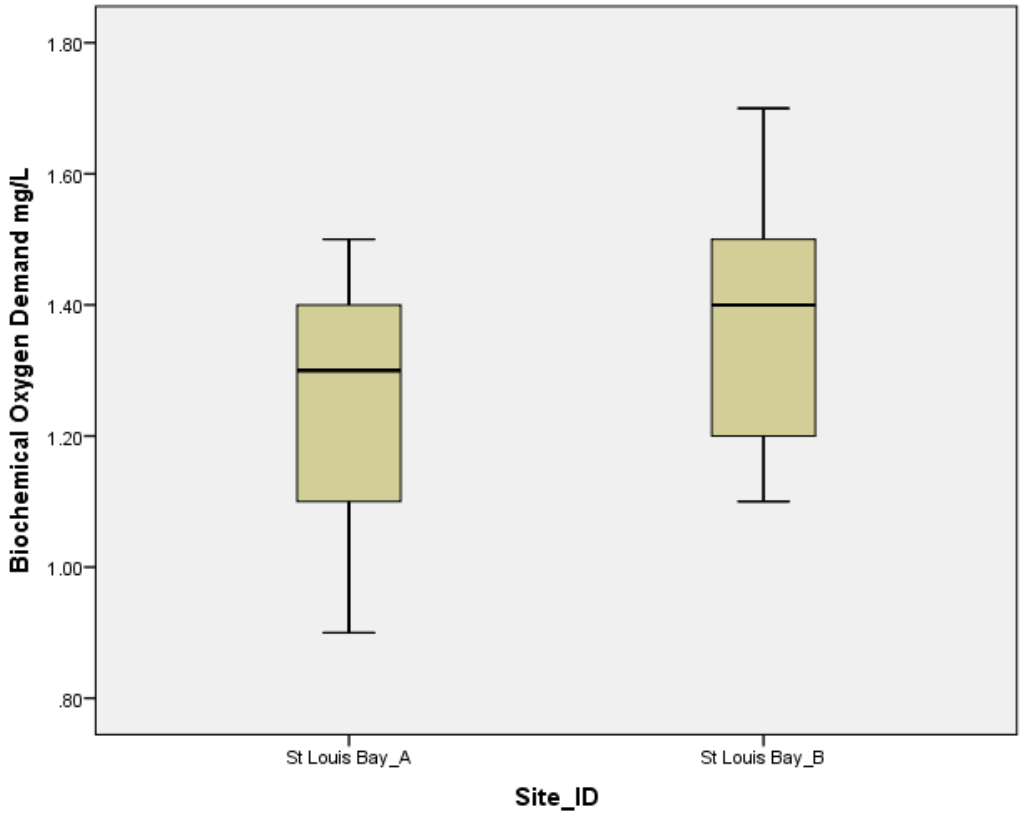
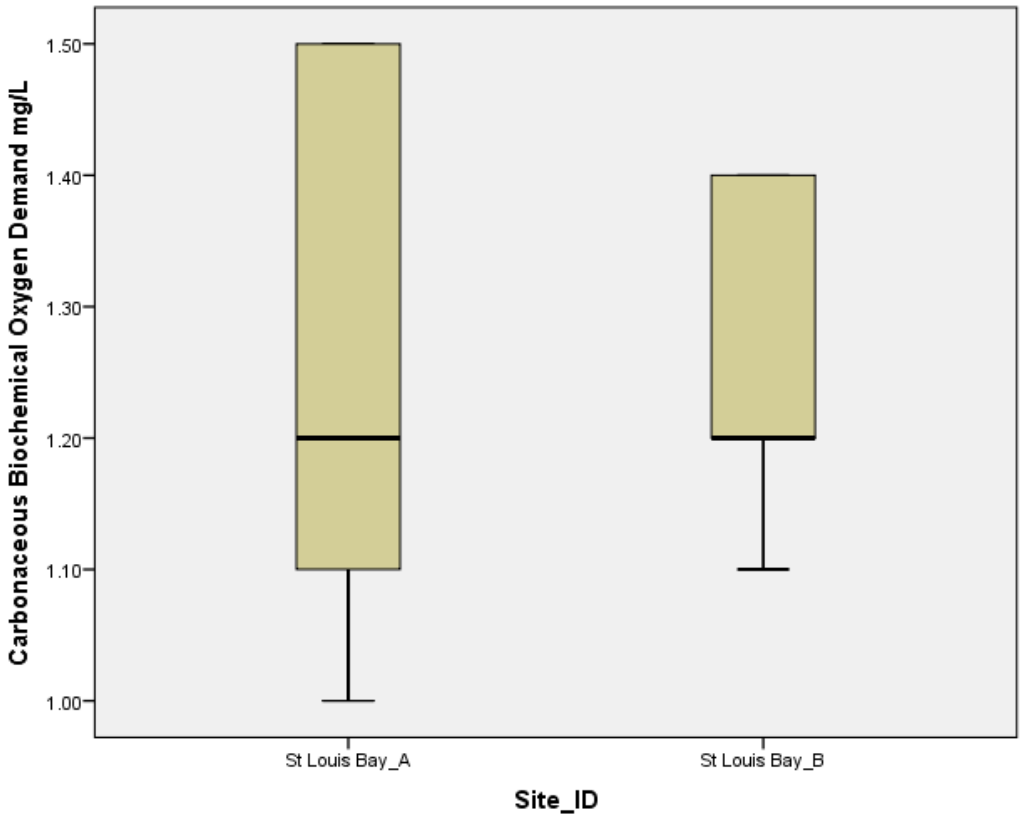
8.00
7.00
6.00
5.00
4.00
3.00
2.00
48
47
46
14
13
63
62
St Louis Bay_A
St Louis Bay_B
Site_ID


Chlorophyll a ug/L
6.00
5.00
4.00
3.00
2.00
1.00
40
St Louis Bay_A
St Louis Bay_B
Site_ID


Biochemical Oxygen Demand mg/L
1.80
1.60
1.40
1.20
1.00
.80
St Louis Bay_A
St Louis Bay_B
Site_ID


Carbonaceous Biochemical Oxygen Demand mg/L
1.50
1.40
1.30
1.20
1.10
1.00
St Louis Bay_A
St Louis Bay_B
Site_ID