



## **Statistical Analyses and Summary of Analytical Round Robin #8 – a Data Comparability Study**

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Samples collected September 17, 2012  
from Oyster Bay, FL, and preserved, split, and prepared for shipment  
September 18, 2012 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 eighth 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- $\mu$ m filtered
Chlorophyll a (both corrected and uncorrected for phaeophytin)	No	No
Turbidity	No	No
Total Nitrite*	No	No
Total Nitrate*	No	No
Total Kjeldahl Nitrogen	Yes	No
Ammonia	Yes	No
Total Nitrate + Nitrite*	Yes	No
Total Phosphorous	Yes	No
Total Organic Carbon	Yes	No
Orthophosphate	No	Yes

\* Depending upon the method employed, the laboratories may have used either acid preserved or unacidified samples bottles for NO<sub>x</sub>, NO<sub>2</sub>, and NO<sub>3</sub>.

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

A total of 20 laboratories, representing local, state, federal, academic, and private laboratories participated in this round robin. Samples were collected on 17 September 2012 from Oyster Bay, FL by Ray Leary. The water was colored and turbid during collection. Sample depth was approximately 0.5 meter. Field measurements are listed in Table 2.

	Oyster Bay, FL
Temperature (°C)	28.97
pH	8.51
Dissolved Oxygen (mg/L)	7.58
Salinity (PSU; calculated from conductivity)	~22
Conductivity (mS)	36.52

Table 2. Field measurements.

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

For each participating laboratory, samples were split to provide:

- 1 L of unfiltered, unpreserved sample for chlorophyll a (ChlA)
- 250 mL of unfiltered, unpreserved sample for turbidity (and for NO<sub>x</sub>, NO<sub>2</sub>, and NO<sub>3</sub> for labs that utilize methods requiring unacidified samples)

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- 250 mL of unfiltered, acid-preserved sample for total nitrate + nitrite (NO<sub>x</sub>) , ammonia (NH<sub>3</sub>) , Total Kjeldahl Nitrogen (TKN), total phosphorous (TP), and total organic carbon (TOC)
- 125 mL of 0.45-µm filtered, unpreserved sample for orthophosphate (OP)

Samples for each bottle type were kept homogenized by constant stirring. Each laboratory received four replicates of each of the above sample types (with the exception of ChlA, for which the labs received three replicates). Samples were kept in a walk-in cooler at 4 °C until shipment, and were shipped in coolers on ice.

Laboratories were given approximately four weeks to complete their analyses and provide results. Many of the methods utilized by participating laboratories involved are considered “equivalent.” One of the goals of this, and future round robins, is to test the true equivalency of these methods. In order to conduct statistical analyses of the variability in data reported between laboratories, each laboratory was required to report only values above its detection limit. Table 3 lists the methods used.

TKN	NH <sub>3</sub>	Total NO <sub>x</sub>	Total NO <sub>2</sub>	Total NO <sub>3</sub>	TP	OP	TOC	ChlA Corrected	ChlA Uncorrected	Turbidity
EPA 351.2	EPA 350.1	EPA 353.2	EPA 353.2	EPA 353.2	EPA 365.1	EPA 300.0	EPA 415.1	EPA 445.0	EPA 445.0	EPA 180.1
Lachat 10-107-06-2-E	Lachat 10-107-06-1-J	Lachat 10-107-04-1-C	Lachat 10-107-04-1-C	Lachat 10-107-04-1-C	EPA 365.3	EPA 365.1	SM 5310 B	SM 10200 H	Holm-Hansen	SM 2130 B
SM 4500 NH <sub>3</sub> D	Lachat 31-107-06-1-B	Lachat 31-107-04-1-D	Lachat 31-107-05-1-A	SM 4500 NO <sub>3</sub> F	EPA 365.4	EPA 365.3	SM 5310 D		SM 10200 H	
USGS I-4515-91	SM 4500 NH <sub>3</sub> D	SM 4500 NO <sub>3</sub> E	SM 4500 NO <sub>2</sub> B		Lachat 10-115-01-1-C	Lachat 10-115-01-1-M				
	SM 4500 NH <sub>3</sub> F	SM 4500 NO <sub>3</sub> F	SM 4500 NO <sub>3</sub> F		SM 4500 P E	Lachat 31-115-01-1-I				
	SM 4500 NH <sub>3</sub> G	SM 4500 NO <sub>3</sub> H	USGS I-2540-90			SM 4500 P E				
	USGS I-2522-90	Systea Easy (1-Reagent)				SM 4500 P F				
		USGS I-2545-90				USGS I-2601-90				

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

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### **Laboratories participating in Analytical Round Robin #8:**

Accutest – Accutest Gulf Coast, contracted by the Louisiana Department of Environmental Quality (LA)  
ADEM\_Mob – Alabama Department of Environmental Management, Mobile Laboratory (AL)  
ADEM\_Mon – Alabama Department of Environmental Management, Montgomery, Field Operations Central Laboratory (AL)  
Benchmark – Benchmark EnviroAnalytical, Inc. (FL)  
CCPC – Collier County Pollution Control & Prevention (FL)  
ELS – Lower Colorado River Authority, Environmental Laboratory Services (TX)  
EPA – U.S. Environmental Protection Agency, Region 4 Laboratory (GA)  
EPCHC – Environmental Protection Commission of Hillsborough County (FL)  
FDEP – Florida Department of Environmental Protection (FL)  
FWRI – Florida Fish & Wildlife Conservation Commission, Fish & Wildlife Research Institute, Harmful Algal Blooms (FL)  
GB NERR – Mississippi Department of Marine Resources/NOAA, Grand Bay National Estuarine Research Reserve (MS)  
MDEQ – Mississippi Department of Environmental Quality (MS)  
Pace – Pace Analytical Services, Inc., Contracted by the Louisiana Department of Environmental Quality (LA)  
RB NERR – Florida Department of Environmental Protection/NOAA, Rookery Bay National Estuarine Research Reserve (FL)  
SERC – Florida International University, Southeast Environmental Research Center (FL)  
Southern Analytical – Southern Analytical Laboratories, Inc. (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)  
UWF – University of West Florida, Center for Environmental Diagnostics and Bioremediation, Wetlands Research Laboratory (FL)

## 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.,  $\mu\text{g/L}$  to  $\text{mg/L}$ ). 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.,  $N \geq 21$ ; 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 qualifiers such as:  $<$ ,  $<\text{PQL}$ ,  $\text{BDL}$ , 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 whose data contained that value and was closest to the mean and median of the laboratory reporting multiple results.

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

Within subjects tests are comparisons of three or more groups. They only tell you if there is a difference among groups, not which ones or how they are different. Examples are ANOVA and Kruskal-Wallis. Between subjects tests are a follow-up to the within subjects test (i.e., post hoc). They tell you which group(s) is different and how they differ. These include Gabriel's test, t-tests, Mann-Whitney, and many other pair-wise comparisons. In the situation where there are

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only two groups to compare, the within subjects tests and the between subjects tests are the same.

Table 4 lists the analytes and the number of laboratories that carried out each. In all cases, scatter-plots show all data values reported by all laboratories.

Analyte	N laboratories	N values >MDL
TKN	14	51
NH <sub>3</sub>	17	33*
NO <sub>x</sub>	16	19*
NO <sub>2</sub>	10	11*
NO <sub>3</sub>	5	2*
TP	16	47*
OP	18	20*
TOC	12	44
ChlA Corrected	12	34
ChlA Uncorrected	9	25
Turbidity	12	44

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

Table 4. Analytes of interest for this round robin; the number of laboratories that ran each; and the number of values above a given laboratory's detection limit.

Laboratory identities were concealed by assigning letter designations so that laboratories do not feel judged by their results. Furthermore, laboratories are not listed with the methods they use or the number of results they reported, in order to maintain anonymity. 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.** Forty-one of the 51 values were within acceptable ranges. Labs E, G and R reported three values each that were outside of acceptable ranges, and Lab S reported one value that was outside of acceptable ranges. Lab E reported detecting the analyte in the method blank for all four of its results, and may be the cause of internal variability. Lab E had one statistical outlier (1.46 mg/L). Lab G reported two values below its detection limit, which appear to be typographical errors, as it reported all other results below detection limits as non-detects. Lab G was the only lab to report a result below the detection limit; this was determined to be a false negative. The %F-pseudosigma value was relatively small (less than 20%), indicating a high degree of precision among laboratories. Of the 51 reported values, 69% were within 1 F-pseudosigma and 80% were within 2 F-pseudosigma. There were no statistical differences between the methods. See Figures 1 & 2 for scatter-plots of values obtained by individual laboratories and method comparisons. See Tables 5 - 8 for F-pseudosigma values, summary statistics and inter-laboratory comparisons.

Total Kjeldahl Nitrogen				
	F-pseudosigma	% F-pseudosigma	Median	Range
All Results	0.116	17.23%	0.671	1.431
Method	N	Mean	Median	Range
EPA 351.2	40 (one non-detect)	0.679	0.677	1.001
Lachat 10-107-06-2-E	4	0.615	0.610	0.080
SM 4500 NH <sub>3</sub> D	4	0.600	0.413	1.346
USGS I-4515-91	4	0.708	0.724	0.078

Table 5. F-pseudosigma values for TKN.

Lab ID	TKN			
	N	Lab Median	Range	Mean Z-value
B	4	0.72	0.08	0.40
D	4	0.68	0.09	0.31
E	4	0.41	1.35	4.13
F	4	0.61	0.08	0.48
G	4*	0.03	0.30	4.67
I	4	0.59	0.11	0.78
K	4	0.67	0.04	0.09
L	4	0.61	0.18	0.66
N	1	0.63	N/A	0.36
O	4	0.73	0.22	0.71
Q	4	0.83	0.08	1.31
R	3	0.94	0.04	2.32
S	4	0.68	0.37	0.86
T	4	0.76	0.06	0.81

\* One non-detect reported.

Table 6. Summary statistics and Z-values by laboratory for TKN.



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### Descriptives

Total Kjeldahl Nitrogen mg/L

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
B	4	.70800	.036815	.018407	.64942	.76658	.653	.731
D	4	.68300	.043397	.021699	.61395	.75205	.639	.732
E	4	.59975	.634857	.317428	-.41045	1.60995	.114	1.460
F	4	.61500	.033166	.016583	.56223	.66777	.580	.660
G	3	.12900	.169753	.098007	-.29269	.55069	.029	.325
I	4	.58075	.049969	.024985	.50124	.66026	.517	.628
K	4	.66350	.017991	.008995	.63487	.69213	.637	.677
L	4	.64325	.083711	.041856	.51005	.77645	.589	.768
N	1	.62900	N/A	N/A	N/A	N/A	.629	.629
O	4	.74250	.092150	.046075	.59587	.88913	.650	.870
Q	4	.82250	.035000	.017500	.76681	.87819	.780	.860
R	3	.94000	.020000	.011547	.89032	.98968	.920	.960
S	4	.76075	.180103	.090051	.47417	1.04733	.656	1.030
T	4	.76500	.026458	.013229	.72290	.80710	.740	.800
Total	51	.67004	.236361	.033097	.60356	.73652	.029	1.460

Table 7. Descriptive statistics by laboratory for TKN.

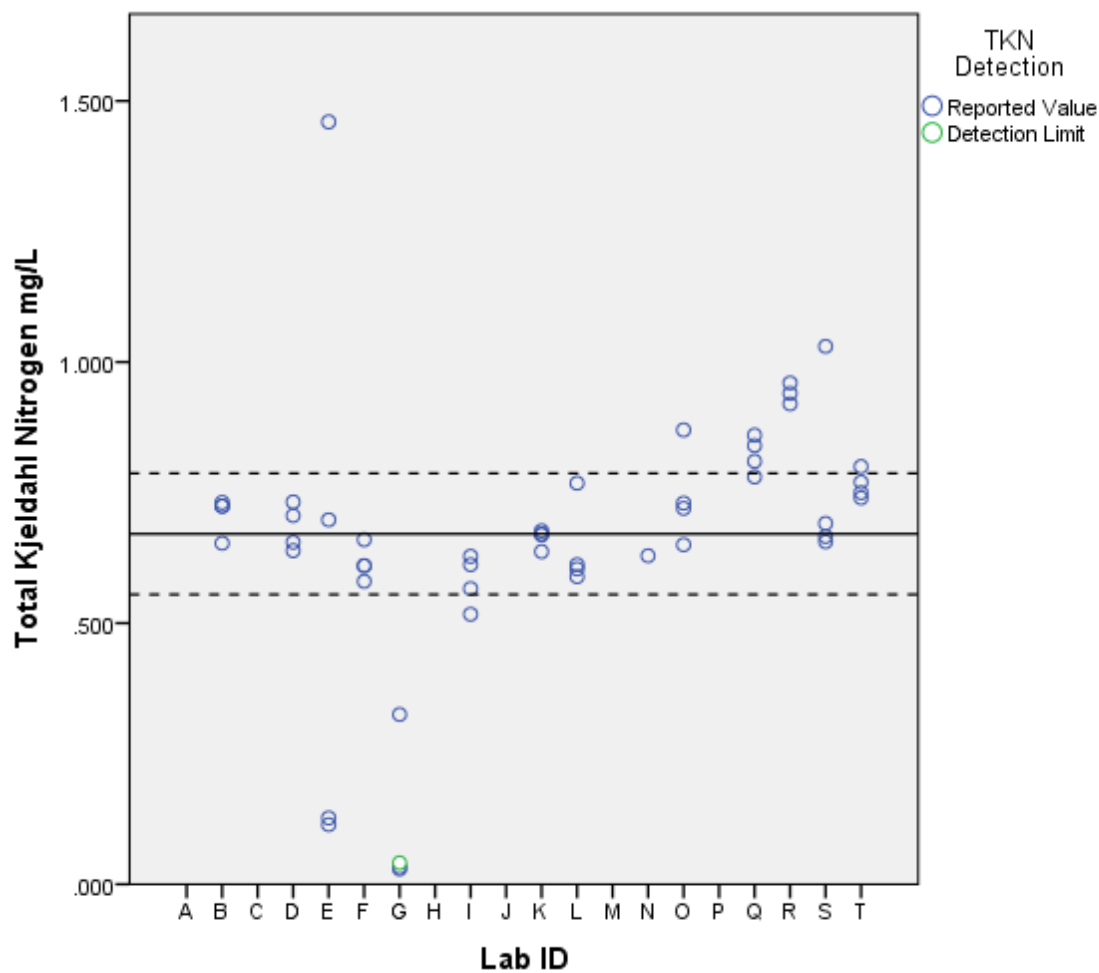
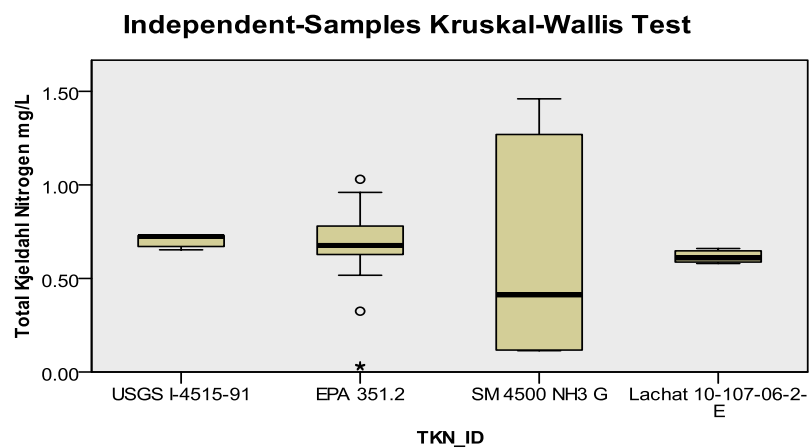


Figure 1. Scatter-plot of TKN values and one detection limit obtained by fourteen laboratories. The solid line indicates the overall median, and the dashed lines indicate  $\pm 1$  F-pseudosigma.

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<b>Total N</b>	51
<b>Test Statistic</b>	3.747
<b>Degrees of Freedom</b>	3
<b>Asymptotic Sig. (2-sided test)</b>	.290

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 2. Kruskal-Wallis test of TKN values by method for all reported values.

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Total Kjeldahl Nitrogen mg/L				
Lab ID	N	Subset for alpha = 0.05		
		1	2	
Gabriel <sup>a,b</sup>	G	3	.12900	
	I	4	.58075	.58075
	E	4	.59975	.59975
	F+N	5	.61780	.61780
	L	4	.64325	.64325
	K	4		.66350
	D	4		.68300
	B	4		.70800
	O	4		.74250
	S	4		.76075
	T	4		.76500
	Q	4		.82250
	R	3		.94000
	Sig.		.051	.572

Means for groups in homogeneous subsets are displayed.

a. Uses Harmonic Mean Sample Size = 3.861.

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

Table 8. Post hoc inter-laboratory (between subjects) comparison for TKN.

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**B. Ammonia.** Twenty-six of the 33 reported values were within acceptable ranges. Lab L reported three values outside acceptable ranges, and Lab O reported all four values outside of acceptable ranges. Both labs were more than an order of magnitude greater than the other labs and may represent transcription errors. Labs D, G, J, K, and Q reported all four results below the detection limits, and Lab S reported one result below detection limits. Labs F and T reported all four results as below the PQL, and Labs L and N reported one result as less than the PQL (i.e., no value was reported; these four labs did not report any results for any analytes that fell between the MDL and PQL; the results are treated as non-detects). Lab L had one statistical outlier (0.45 mg/L). The MDLs ranged from 0.0007 to 0.025 mg/L; and the PQLs for Labs F, L, N and T ranged from 0.01 to 0.1 mg/L. Of the 68 total results, 35 were non-values (51%). The %F-pseudosigma value was large (>30%), indicating a lack of precision among laboratories (due mainly to the results of Labs L and O). Of the 33 reported values, 79% were within 1 F-pseudosigma; no additional values were within 2 F-pseudosigma. Of the four methods used for sample analysis, SM 4500 NH<sub>3</sub> F was significantly lower than EPA 350.1 and SM 4500 NH<sub>3</sub> G. See Figures 3 & 4 for scatter-plots of values obtained by individual laboratories and method comparisons. See Tables 9 - 12 for F-pseudosigma values, summary statistics and inter-laboratory comparisons.

<b>Ammonia</b>				
	<b>F-pseudosigma</b>	<b>% F-pseudosigma</b>	<b>Median</b>	<b>Range</b>
All Results	0.018	72.65%	0.025	0.443
<b>Method</b>	<b>N</b>	<b>Mean</b>	<b>Median</b>	<b>Range</b>
EPA 350.1	40 (22 non-values)	0.083	0.034	0.264
Lachat 10-107-06-1-J	4	All Non-detect	N/A	N/A
Lachat QuickChem 31-107-06-1-B	4	All Non-detect	N/A	N/A
SM 4500 NH <sub>3</sub> D	4	0.016	0.016	0.003
SM 4500 NH <sub>3</sub> F	4	0.010	0.010	0.005
SM 4500 NH <sub>3</sub> G	8 (one non-value)	0.112	0.020	0.434
USGS I-2522-90	4	All Non-detect	N/A	N/A

Table 9. F-pseudosigma values for ammonia.

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Lab ID	NH <sub>3</sub>			
	N	Lab Median	Range	Mean Z-value
A	4	0.010	0.005	0.86
D	4	NR	NR	NR
E	4	0.016	0.003	0.50
F	4	NR	NR	NR
G	4	NR	NR	NR
H	4	0.020	0.004	0.35
I	4	0.040	0.006	0.76
J	4	NR	NR	NR
K	4	NR	NR	NR
L	4*	0.130	0.320	11.76
N	1	NR	NR	NR
O	4	0.270	0.010	13.75
P	4	0.018	0.003	0.42
Q	4	NR	NR	NR
R	3	0.028	0.011	0.26
S	4*	0.028	0.005	0.22
T	4	NR	NR	NR

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

Table 10. Summary statistics and Z-values by Laboratory for ammonia.

### Descriptives

Ammonia mg/L

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
A	4	.00950	.002082	.001041	.00619	.01281	.007	.012
E	4	.01600	.001414	.000707	.01375	.01825	.015	.018
H	4	.01875	.001893	.000946	.01574	.02176	.016	.020
I	4	.03875	.002630	.001315	.03457	.04293	.035	.041
L	3	.23667	.184752	.106667	-.22228	.69562	.130	.450
O	4	.27250	.005000	.002500	.26454	.28046	.270	.280
P	4	.01750	.001291	.000645	.01545	.01955	.016	.019
R	3	.02967	.005686	.003283	.01554	.04379	.025	.036
S	3	.02900	.002646	.001528	.02243	.03557	.027	.032
Total	33	.07206	.108593	.018904	.03356	.11057	.007	.450

Table 11. Descriptive statistics by laboratory for ammonia.

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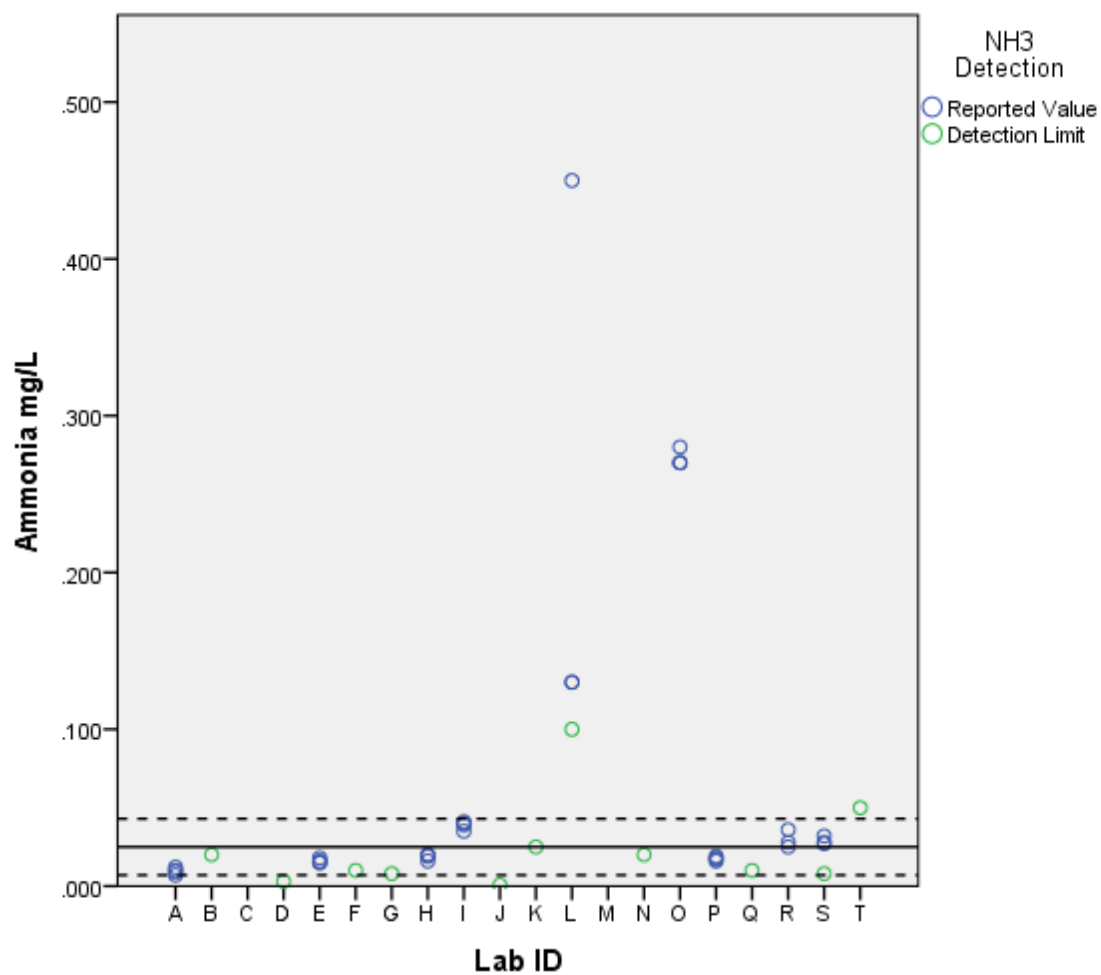


Figure 3. Scatter-plot of ammonia values and detection/quantitation limits obtained by seventeen laboratories. The solid line indicates the overall median, and the dashed lines indicate  $\pm 1$  F-pseudosigma.

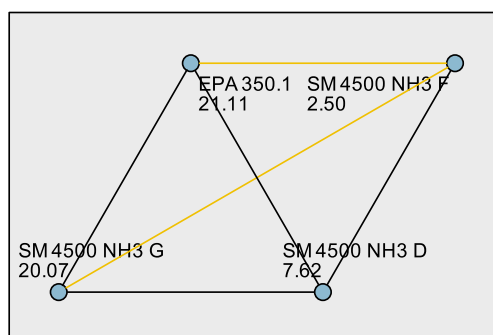
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### Hypothesis Test Summary

	Null Hypothesis	Test	Sig.	Decision
1	The medians of Ammonia mg/L are the same across categories of NH3_ID.	Independent-Samples Median Test	.009	Reject the null hypothesis.
2	The distribution of Ammonia mg/L is the same across categories of NH3_ID.	Independent-Samples Kruskal-Wallis Test	.001	Reject the null hypothesis.

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

### Pairwise Comparisons of NH3\_ID



Each node shows the sample average rank of NH3\_ID.

Sample1-Sample2	Test Statistic	Std. Error	Std. Test Statistic	Sig.	Adj.Sig.
SM 4500 NH3 F-SM 4500 NH3 D	-5.125	6.829	-.750	.453	1.000
SM 4500 NH3 F-SM 4500 NH3 G	-17.571	6.054	-2.903	.004	.022
SM 4500 NH3 F-EPA 350.1	-18.611	5.339	-3.486	.000	.003
SM 4500 NH3 D-SM 4500 NH3 G	-12.446	6.054	-2.056	.040	.239
SM 4500 NH3 D-EPA 350.1	13.486	5.339	2.526	.012	.069
SM 4500 NH3 G-EPA 350.1	1.040	4.302	.242	.809	1.000

Each row tests the null hypothesis that the Sample 1 and Sample 2 distributions are the same.

Asymptotic significances (2-sided tests) are displayed. The significance level is .05.

Figure 4. Kruskal-Wallis test for ammonia values by method for all reported values.

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Ammonia mg/L				
Lab ID	N	Subset for alpha = 0.05		
		1	2	
Gabriel <sup>a,b</sup>	A	4	.00950	
	E	4	.01600	
	P	4	.01750	
	H	4	.01875	
	S	3	.02900	
	R	3	.02967	
	I	4	.03875	
	L	3		.23667
	O	4		.27250
	Sig.		1.000	1.000

Means for groups in homogeneous subsets are displayed.

a. Uses Harmonic Mean Sample Size = 3.600.

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

Table 12. Post hoc inter-laboratory (between subjects) comparison for ammonia.



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**C. Total Nitrite + Nitrate.** Nineteen of the 63 results were reported values; the other 70% were reported as qualifiers. Lab R reported one value that was a statistical outlier (0.02 mg/L). No detection limits were determined to be false negatives. Lab J reported dissolved NO<sub>x</sub>, and its results were not included in analyses. However, there was no statistical difference from its results and those of the other laboratories'. No other analyses were conducted for NO<sub>x</sub>. See Figure 5 for a scatter-plot of values and detection/quantitation limits obtained by individual laboratories. See Tables 13 & 14 for Methods and summary statistics.

Total NO <sub>x</sub>		
Method	MDL Range	PQL Range
ALL	0.0002 - 0.02	0.01 - 0.05
EPA 353.2	0.002 - 0.015	0.01 - 0.04
Lachat 10-107-04-1-C	0.002	0.02
Lachat QuickChem 31-107-04-1-D*	0.0002	Not Reported
SM 4500 NO <sub>3</sub> E	0.01	Not Reported
SM 4500 NO <sub>3</sub> F	0.003 - 0.012	0.012 - 0.05
SM 4500 NO <sub>3</sub> H	0.004	0.04
Systea Easy (1-Reagent)	0.00675	0.01
USGS I-2545-90	0.02	Not Reported

\* Dissolved NO<sub>x</sub>.

Table 13. Methods and detection/quantitation limits for NO<sub>x</sub>.

Lab ID	NO <sub>x</sub>			
	N	Lab Median	Range	Mean Z-value
A	3	0.004	0.002	N/A
C	4	NR	NR	NR
D	4	NR	NR	NR
E	4	NR	NR	NR
F	4	NR	NR	NR
G	4	NR	NR	NR
H	4	0.006	0.000	N/A
I	4	0.004	0.002	N/A
J	4	0.004	0.001	N/A
K	4	NR	NR	NR
L	4	NR	NR	NR
O	4	NR	NR	NR
P	4	0.010	0.002	N/A
Q	1*	0.004	N/A	N/A
R	1*	0.020	N/A	N/A
S	2*	0.011	0.005	N/A
T	4	NR	NR	NR

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

Table 14. Summary statistics and Z-values by Laboratory for NO<sub>x</sub> (Lab J is dissolved NO<sub>x</sub>).

## GOMA Analytical Round Robin #8

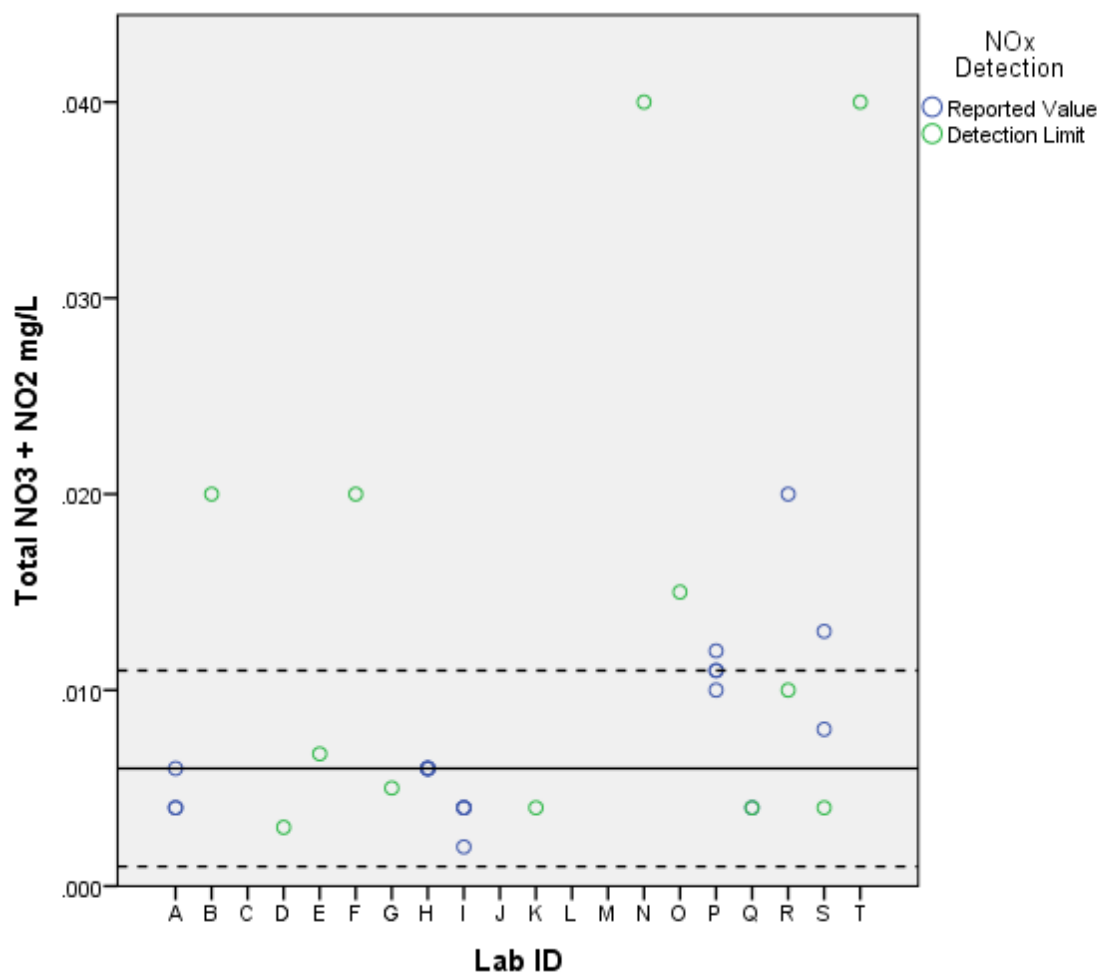


Figure 5. Scatter-plot of NO<sub>x</sub> values and detection limits obtained by sixteen laboratories (Lab J is not displayed). The solid line indicates the overall median, and the dashed lines indicate  $\pm 1$  F-pseudosigma.

## GOMA Analytical Round Robin #8

**D. Total Nitrite.** Thirteen of the 29 results were reported values; the remaining 67% were reported as qualifiers. Lab J reported dissolved NO<sub>2</sub>, and its results were not included in analyses. However, there was no statistical difference from its results and those of the other labs. No other analyses were conducted for NO<sub>2</sub>. See Figure 6 for a scatter-plot of values and detection/quantitation limits obtained by individual laboratories. See Tables 15 & 16 for methods and summary statistics.

Total NO <sub>2</sub>		
Method	MDL Range	PQL Range
ALL	0.00014 - 0.006	0.0022 - 0.05
EPA 353.2	0.0006 - 0.006	0.0022 - 0.01
Lachat 10-107-04-1-C	0.001	0.005
Lachat QuickChem 31-107-05-1-A*	0.00014	Not Reported
SM 4500 NO <sub>2</sub> B	0.002 - 0.01	0.008 - 0.04
SM 4500 NO <sub>3</sub> F	0.012	0.05
USGS I-2540-90	0.001	Not Reported

\* Dissolved NO<sub>2</sub>.

Table 15. Methods and detection/quantitation limits for NO<sub>2</sub>.

Lab ID	NO <sub>2</sub>			
	N	Lab Median	Range	Mean Z-value
C	4	NR	NR	NR
D	4	NR	NR	NR
F	4	0.008	0.001	N/A
G	4	NR	NR	NR
H	2*	0.006	0.001	N/A
J	4	0.002	0.000	N/A
L	4	NR	NR	NR
P	4	0.001	0.000	N/A
Q	1*	0.002	0.000	N/A
R	3	NR	NR	NR
S	4	NR	NR	NR

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

Table 16. Summary statistics and Z-values by Laboratory for NO<sub>2</sub> (Lab J is dissolved NO<sub>2</sub>).

## GOMA Analytical Round Robin #8

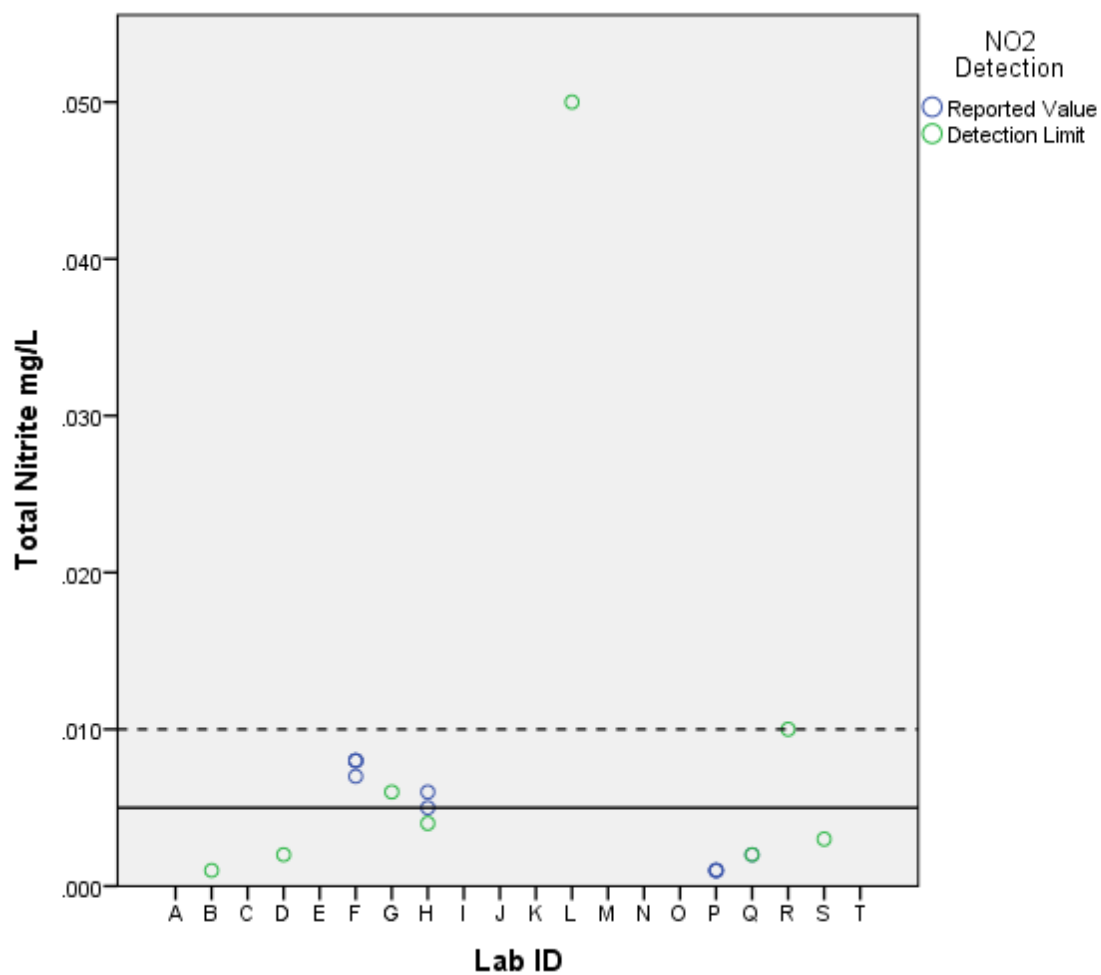


Figure 6. Scatter-plot of NO<sub>2</sub> values and detection limits obtained by ten laboratories (Lab J is not displayed). The solid line indicates the overall median, and the dashed lines indicate  $\pm 1$  F-pseudosigma.

## GOMA Analytical Round Robin #8

**E. Total Nitrate.** Two of the nineteen results were reported values; the other 89% were reported as qualifiers. Lab R was the only laboratory to report values (two: 0.01 and 0.02 mg/L). There were too few reported values to conduct further analyses. See Figure 7 for a scatter-plot of values and detection/quantitation limits obtained by individual laboratories. See Table 17 for methods summary.

Total NO <sub>3</sub>		
Method	MDL Range	PQL Range
ALL	0.003 - 0.012	0.005 - 0.05
EPA 353.2	0.005 - 0.01	0.02 - 0.04
Lachat 10-107-04-1-C	0.004	0.005
SM 4500 NO <sub>3</sub> F	0.003 - 0.012	0.012 - 0.05

Table 17. Methods and detection/quantitation limits for NO<sub>3</sub>.

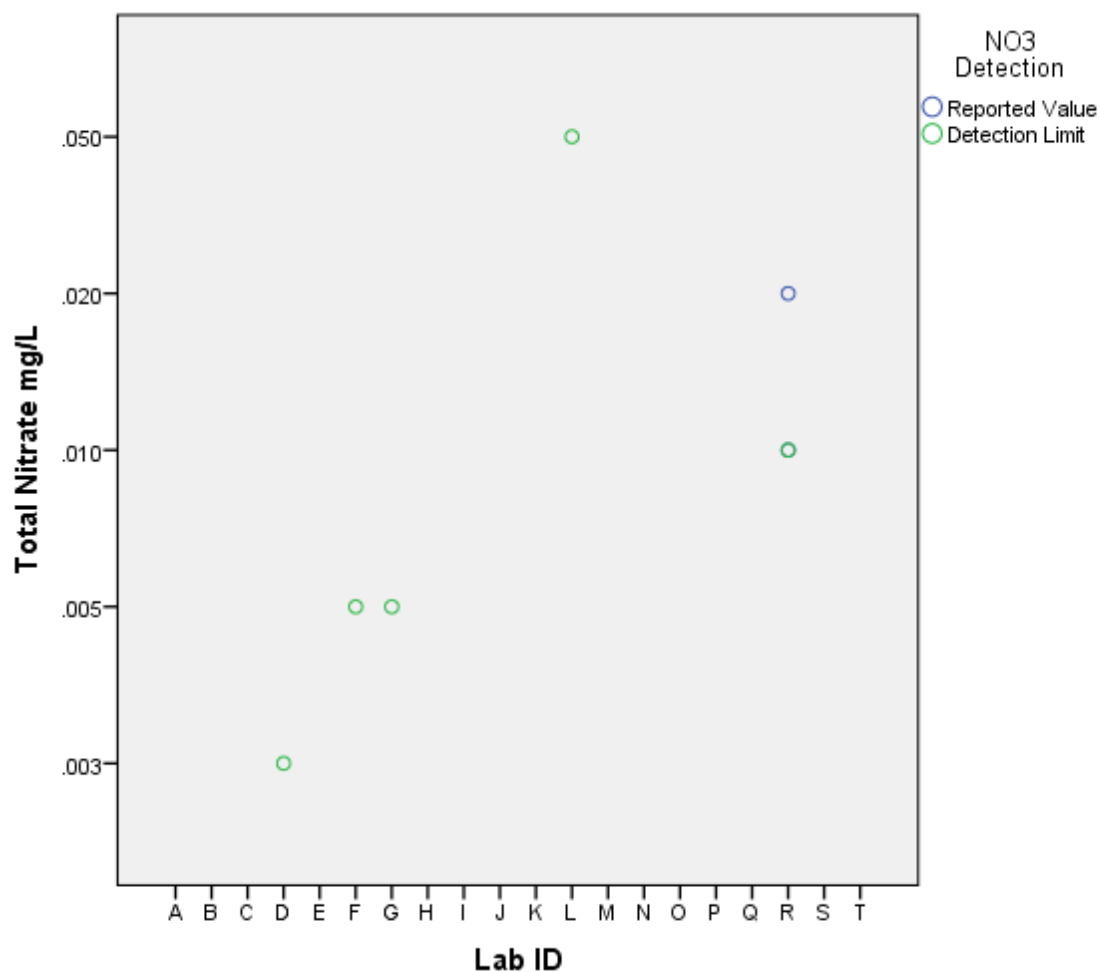


Figure 7. Scatter-plot of NO<sub>3</sub> values and detection/quantitation limits obtained by five laboratories.

## GOMA Analytical Round Robin #8

**F. Total Phosphorus.** Forty of the 47 values were within acceptable ranges. Lab T reported three values outside acceptable ranges, and Labs D, E, I, and N reported one value outside of acceptable ranges. Lab E reported one statistical outlier (0.115 mg/L). Labs E and S had results reported as below their detection limits; these were determined to be false negatives. Lab L reported all results as below its quantitation limit; these were not false negatives. The MDLs ranged from 0.0012 to 0.1 mg/L; and the PQLs for Labs F, L, N and T ranged from 0.02 to 0.05 mg/L. The %F-pseudosigma value was moderate (between 20 and 30%), indicating a lack of precision among laboratories. Of the 47 reported values, 66% were within 1 F-pseudosigma and 85% were within 2 F-pseudosigma. Of the four methods which reported values, EPA 365.4 was significantly higher than EPA 365.1 and SM 4500 P E. See Figures 8 & 9 for scatter-plots of values obtained by individual laboratories and method comparisons. See Tables 18 - 21 for F-pseudosigma values, summary statistics and inter-laboratory comparisons.

Total Phosphorus				
	F-pseudosigma	% F-pseudosigma	Median	Range
All Results	0.012	29.65%	0.040	0.100
Method	N	Mean	Median	Range
EPA 365.1	24	0.038	0.038	0.019
EPA 365.3	4	All Non-detects	N/A	N/A
EPA 365.4	17 (eight non-values)	0.066	0.065	0.010
Lachat 10-115-01-1-C	4	0.040	0.040	0.000
SM 4500 P E	11 (one non-value)	0.043	0.046	0.100

Table 18. F-pseudosigma values for TP.

Lab ID	TP			
	N	Lab Median	Range	Mean Z-value
B	4	0.032	0.007	0.63
D	4	0.064	0.002	2.00
E	4*	0.051	0.074	2.42
F	4	0.040	0.000	0.00
G	4	0.047	0.008	0.48
H	4	0.033	0.006	0.54
I	4	0.018	0.003	1.92
K	4	NR	NR	NR
L	4	NR	NR	NR
N	1	0.068	N/A	2.33
O	4	0.041	0.004	0.13
P	4	0.039	0.006	0.19
Q	4	0.038	0.001	0.21
R	3	0.053	0.003	1.06
S	4	NR	NR	NR
T	4	0.070	0.010	2.29

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

Table 19. Summary statistics and Z-values by Laboratory for TP.

## GOMA Analytical Round Robin #8

### Descriptives

Total Phosphorus mg/L

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
B	4	.03250	.003109	.001555	.02755	.03745	.030	.037
D	4	.06400	.000816	.000408	.06270	.06530	.063	.065
E	3	.06900	.040150	.023180	-.03074	.16874	.041	.115
F	4	.04000	.000000	.000000	.04000	.04000	.040	.040
G	4	.04575	.003403	.001702	.04033	.05117	.041	.049
H	4	.03350	.002646	.001323	.02929	.03771	.031	.037
I	4	.01700	.001414	.000707	.01475	.01925	.015	.018
N	1	.06800	N/A	N/A	N/A	N/A	.068	.068
O	4	.04050	.001732	.000866	.03774	.04326	.038	.042
P	4	.03775	.002630	.001315	.03357	.04193	.034	.040
Q	4	.03750	.000577	.000289	.03658	.03842	.037	.038
R	3	.05267	.001528	.000882	.04887	.05646	.051	.054
T	4	.06750	.005000	.002500	.05954	.07546	.060	.070
Total	47	.04462	.017589	.002566	.03945	.04978	.015	.115

Table 20. Descriptive statistics by laboratory for TP.

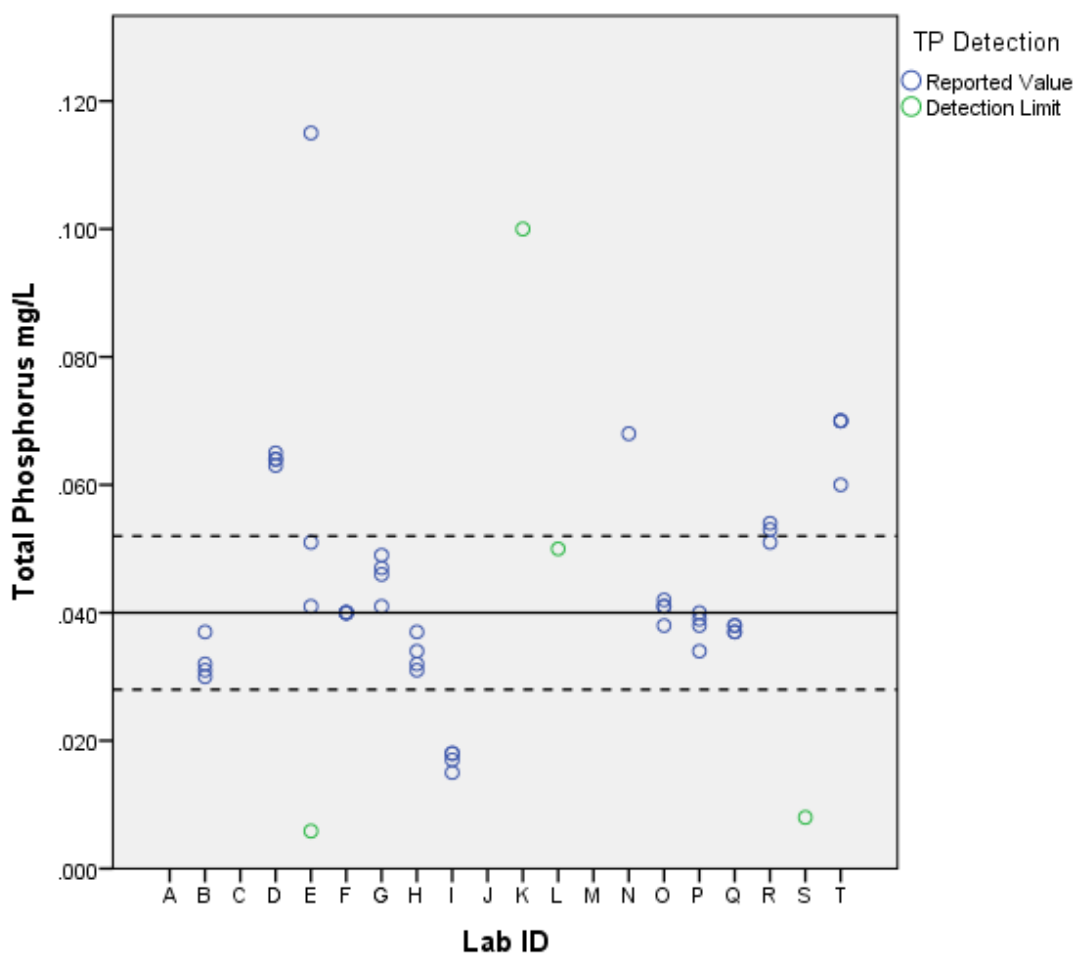


Figure 8. Scatter-plot of TP values and detection limits obtained by sixteen laboratories. The solid line indicates the overall median, and the dashed lines indicate  $\pm 1$  F-pseudosigma.

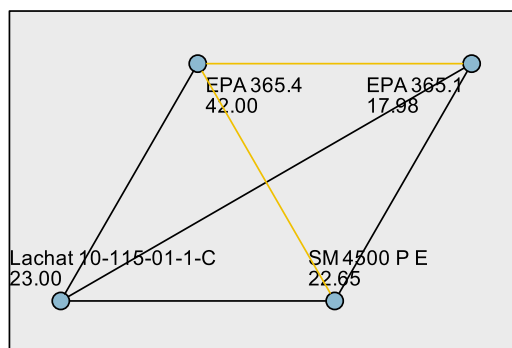
## GOMA Analytical Round Robin #8

### Hypothesis Test Summary

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

### Pairwise Comparisons of TP\_ID



Each node shows the sample average rank of TP\_ID.

Sample1-Sample2	Test Statistic	Std. Error	Std. Test Statistic	Sig.	Adj.Sig.
EPA 365.1-SM 4500 P E	-4.671	5.152	-.907	.365	1.000
EPA 365.1-Lachat 10-115-01-1-C	-5.021	7.392	-.679	.497	1.000
EPA 365.1-EPA 365.4	-24.021	5.350	-4.490	.000	.000
SM 4500 P E-Lachat 10-115-01-1-C	-.350	8.098	-.043	.966	1.000
SM 4500 P E-EPA 365.4	19.350	6.289	3.077	.002	.013
Lachat 10-115-01-1-C-EPA 365.4	19.000	8.225	2.310	.021	.125

Each row tests the null hypothesis that the Sample 1 and Sample 2 distributions are the same.

Asymptotic significances (2-sided tests) are displayed. The significance level is .05.

Figure 9. Kruskal Wallis test of TP values by method for all reported values.



## GOMA Analytical Round Robin #8

Total Phosphorus mg/L				
Lab ID	N	Subset for alpha = 0.05		
		1	2	3
I	4	.01700		
B	4	.03250	.03250	
H	4	.03350	.03350	.03350
Q	4	.03750	.03750	.03750
P	4	.03775	.03775	.03775
F	4	.04000	.04000	.04000
Gabriel <sup>a,b</sup> O	4	.04050	.04050	.04050
G	4	.04575	.04575	.04575
R	3		.05267	.05267
E	4		.05322	.05322
D	4		.06400	.06400
T+N	5			.06760
Sig.		.222	.114	.057

Means for groups in homogeneous subsets are displayed.

a. Uses Harmonic Mean Sample Size = 3.956.

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

Table 21. Post hoc inter-laboratory (between subjects) comparison for TP.

## GOMA Analytical Round Robin #8

**G. Orthophosphate.** Twenty of the 68 results were reported values; the other 71% were reported as qualifiers. No values were statistical outliers. Due to the few values reported, no further analyses were conducted. See Figure 10 for a scatter-plot of values and detection/quantitation limits obtained by individual laboratories. See Tables 22 & 23 for methods and summary statistics.

OP		
Method	MDL Range	PQL Range
ALL	0.00017 - 0.012	0.002 - 0.05
EPA 300.0	0.002	0.04
EPA 365.1	0.0019 - 0.005	0.01 - 0.04
EPA 365.3	0.002	0.008
Lachat 10-115-01-1-M	0.0007	0.002
Lachat QuickChem 31-115-01-1-I	0.00017	Not Reported
SM 4500 P E	0.003 - 0.012	0.02 - 0.05
SM 4500 P F	0.004 - 0.009	0.016 - 0.036
USGS I-2601-90	0.004	Not Reported

Table 22. Methods and detection/quantitation limits for OP.

Lab ID	OP			
	N	Lab Median	Range	Mean Z-value
A	1*	0.002	0.000	N/A
C	4	NR	NR	NR
D	4	NR	NR	NR
E	4	NR	NR	NR
F	4	0.008	0.000	N/A
G	4	NR	NR	NR
H	4	0.005	0.001	N/A
I	4	NR	NR	NR
J	3*	0.001	0.003	N/A
K	4	0.011	0.001	N/A
L	4	NR	NR	NR
N	1	NR	NR	NR
O	4	NR	NR	NR
P	2*	0.002	0.000	N/A
Q	2*	0.005	0.002	N/A
R	3	NR	NR	NR
S	4	NR	NR	NR
T	4	NR	NR	NR

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

Table 23. Summary statistics by Laboratory for OP.

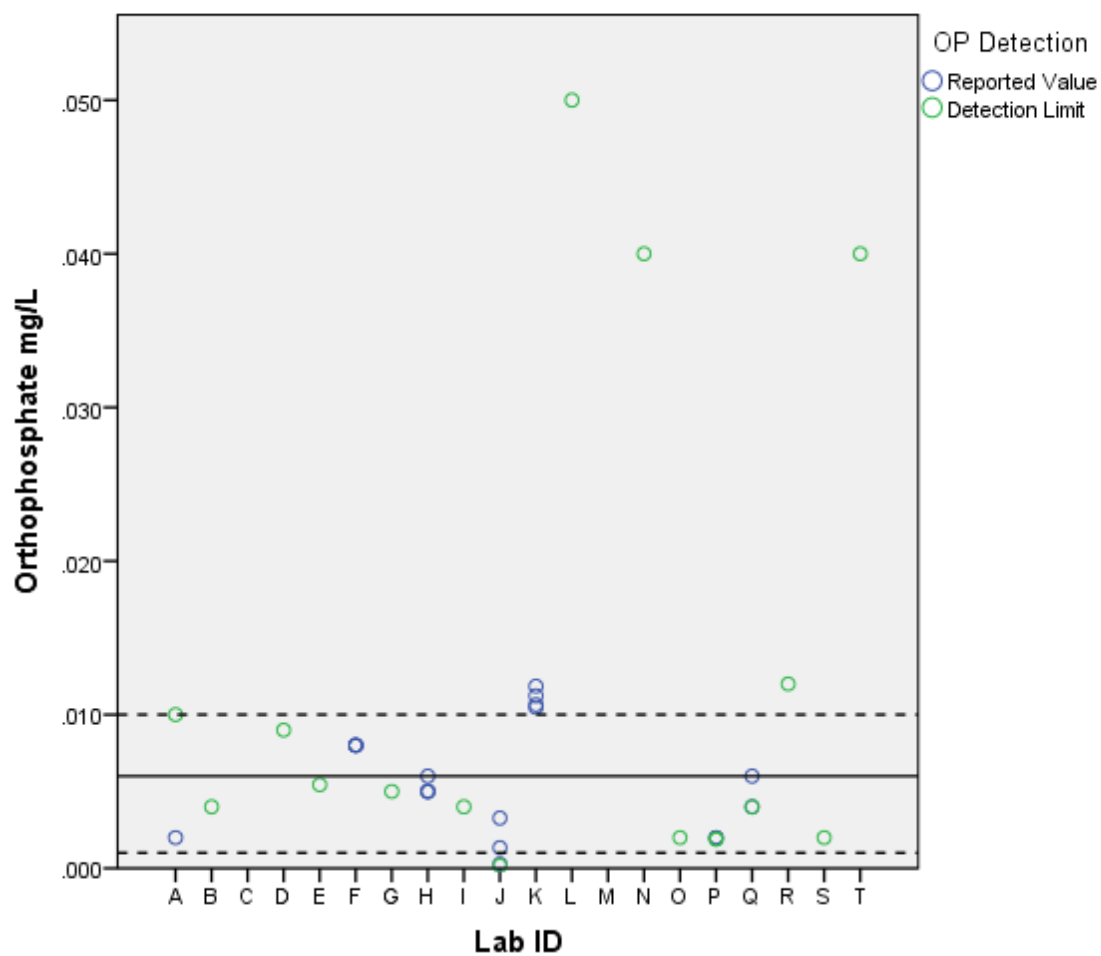


Figure 10. Scatter-plot of OP values and detection limits obtained by eighteen laboratories. The solid line indicates the overall median, and the dashed lines indicate  $\pm 1$  F-pseudosigma.

## GOMA Analytical Round Robin #8

**H. Total Organic Carbon.** Thirty-nine of the 44 values were within acceptable ranges. Labs F and N reported all values outside of acceptable ranges. No laboratories reported any values below their detection or quantitation limits. The %F-pseudosigma value was relatively small (less than 20%), indicating a high degree of precision among laboratories. Of the 44 reported values, 70% were within 1 F-pseudosigma and 89% were within 2 F-pseudosigma. Of the three methods used for sample analysis, EPA 415.1 was significantly lower than SM 5310 B; statistical comparisons could not be made with SM 5310 D due to only one value reported. However, it was considerably lower than all other reported results (the next lowest value was 4.44 mg/L greater). See Figures 11 & 12 for scatter-plots of values obtained by individual laboratories and method comparisons. See Tables 24 - 27 for F-pseudosigma values, summary statistics and inter-laboratory comparisons.

Total Organic Carbon				
	F-pseudosigma	% F-pseudosigma	Median	Range
All Results	1.329	17.02%	7.805	15.302
<b>Method</b>	<b>N</b>	<b>Mean</b>	<b>Median</b>	<b>Range</b>
EPA 415.1	4	7.19	7.20	0.11
SM 5310 B	39	9.24	8.00	10.58
SM 5310 D	1	2.68	N/A	N/A

Table 24. F-pseudosigma values for TOC.

Lab ID	TOC			
	N	Lab Median	Range	Mean Z-value
D	4	9.30	0.30	1.14
E	4	9.83	0.38	1.55
F	4	18.00	0.00	7.67
H	4	7.95	0.27	0.11
I	4	7.49	0.08	0.24
L	4	7.55	0.16	0.21
N	1	2.68	N/A	3.86
P	4	7.20	0.11	0.47
Q	4	7.95	0.30	0.11
R	3	7.70	0.00	0.08
S	4	7.46	0.12	0.25
T	4	9.00	1.00	0.71

Table 25. Summary statistics and Z-values by Laboratory for TOC.

## GOMA Analytical Round Robin #8

### Descriptives

Total Organic Carbon mg/L

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
D	4	9.3250	.12583	.06292	9.1248	9.5252	9.20	9.50
E	4	9.8700	.16693	.08347	9.6044	10.1356	9.72	10.10
F	4	18.0000	.00000	.00000	18.0000	18.0000	18.00	18.00
H	4	7.9475	.12816	.06408	7.7436	8.1514	7.81	8.08
I	4	7.4825	.03304	.01652	7.4299	7.5351	7.44	7.52
L	4	7.5300	.07118	.03559	7.4167	7.6433	7.43	7.59
N	1	2.6800	N/A	N/A	N/A	N/A	2.68	2.68
P	4	7.1850	.04796	.02398	7.1087	7.2613	7.12	7.23
Q	4	7.9500	.17321	.08660	7.6744	8.2256	7.80	8.10
R	3	7.7000	.00000	.00000	7.7000	7.7000	7.70	7.70
S	4	7.4675	.05500	.02750	7.3800	7.5550	7.42	7.54
T	4	8.7500	.50000	.25000	7.9544	9.5456	8.00	9.00
Total	44	8.9048	3.13508	.47263	7.9516	9.8579	2.68	18.00

Table 26. Descriptive statistics by laboratory for TOC.

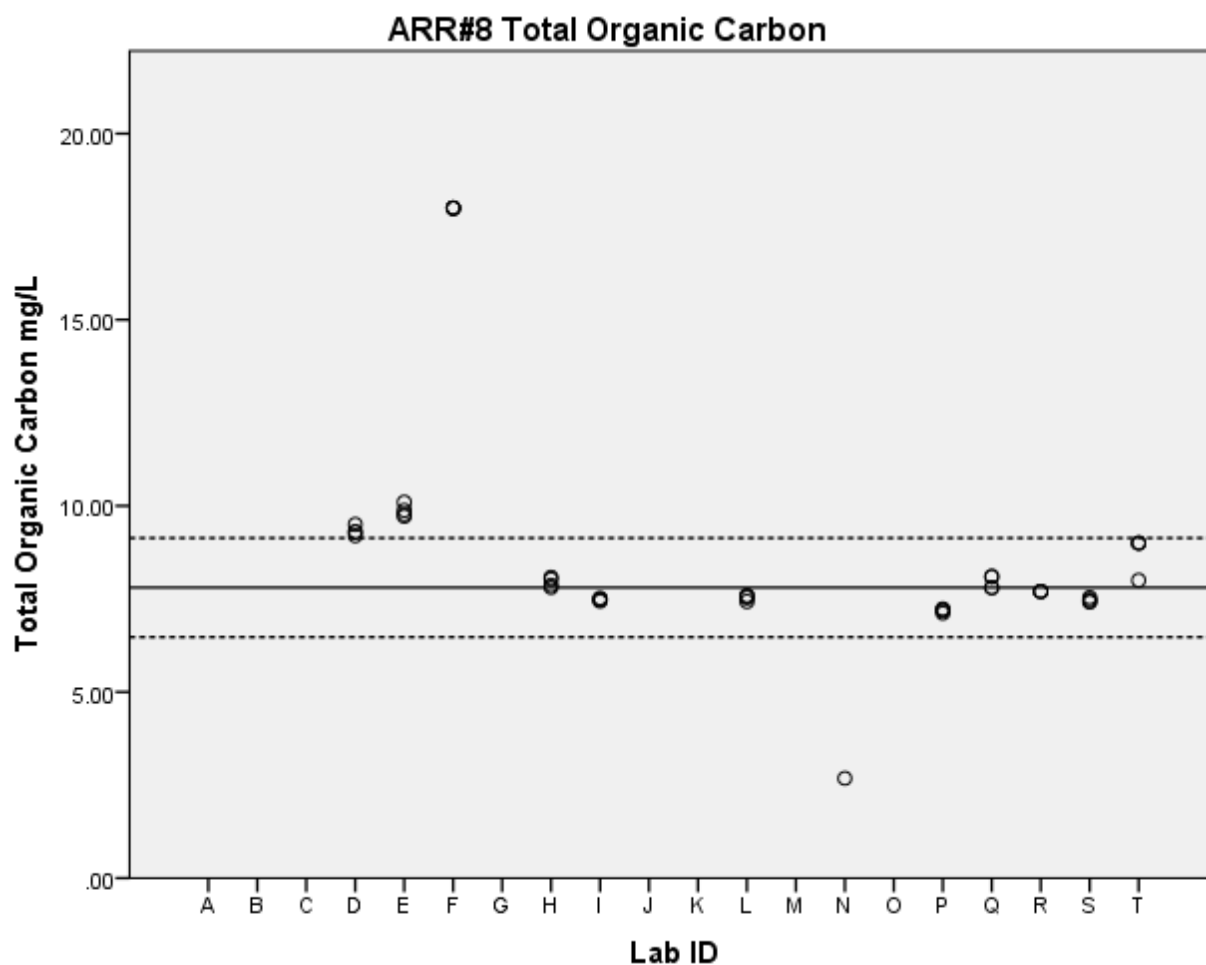


Figure 11. Scatter-plot of TOC values obtained by twelve laboratories. The solid line indicates the overall median, and the dashed lines indicate  $\pm 1$  F-pseudosigma.

## GOMA Analytical Round Robin #8

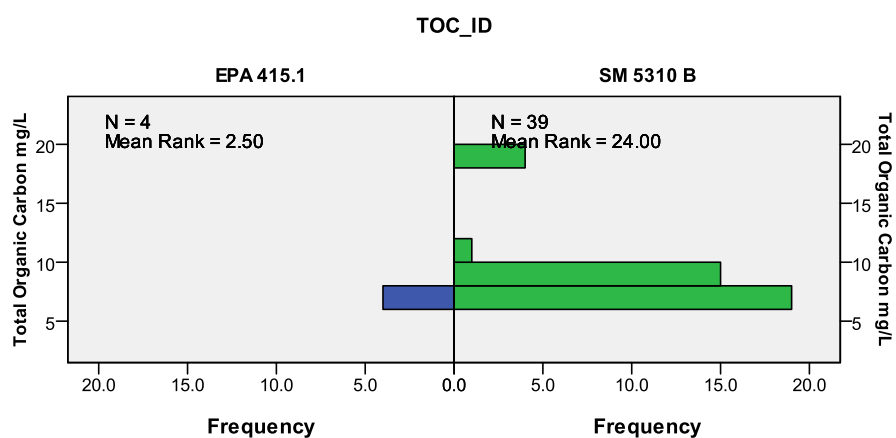
### Hypothesis Test Summary

	Null Hypothesis	Test	Sig.	Decision
1	The distribution of Total Organic Carbon mg/L is the same across categories of TOC_ID.	Independent-Samples Mann-Whitney U Test	.000 <sup>1</sup>	Reject the null hypothesis.
2	The distribution of Total Organic Carbon mg/L is the same across categories of TOC_ID.	Independent-Samples Kolmogorov-Smirnov Test	.001	Reject the null hypothesis.

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

<sup>1</sup>Exact significance is displayed for this test.

### Independent-Samples Mann-Whitney U Test



Total N	43
Mann-Whitney U	.000
Wilcoxon W	10.000
Test Statistic	.000
Standard Error	23.896
Standardized Test Statistic	-3.264
Asymptotic Sig. (2-sided test)	.001
Exact Sig. (2-sided test)	.000

Figure 12. Mann-Whitney test for TOC values by method.

## GOMA Analytical Round Robin #8

Total Organic Carbon mg/L (without Lab N)

Lab ID	N	Subset for alpha = 0.05						
		1	2	3	4	5	6	7
Gabriel <sup>a,b</sup>	P	7.1850						
	S	7.4675	7.4675					
	I	7.4825	7.4825	7.4825				
	L	7.5300	7.5300	7.5300				
	R		7.7000	7.7000				
	H			7.9475				
	Q			7.9500				
	T				8.7500			
	D					9.3250		
	E						9.8700	
	F							18.0000
	Sig.	.418	.962	.053	1.000	1.000	1.000	1.000

Means for groups in homogeneous subsets are displayed.

a. Uses Harmonic Mean Sample Size = 3.882.

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

Table 27. Post hoc inter-laboratory (between subjects) comparison for TOC. Lab N was not included due to the single data value reported being substantially less than all others.

## GOMA Analytical Round Robin #8

**I. Chlorophyll a, Corrected for Phaeophytin.** Twenty-eight of the 34 values were within acceptable ranges. Labs F and O reported all values outside of acceptable ranges. Both laboratories' results were significantly lower than those of all other labs. Lab O's values appear to be the actual phaeophytin values. No laboratories reported any values below their detection limits; however, Lab D reported its values as below its quantitation limit. The %F-pseudosigma value was relatively small (less than 20%), indicating a high degree of precision among laboratories. Of the 34 reported values, 62% were within 1 F-pseudosigma and 82% were within 2 F-pseudosigma. There was no statistical difference between lab results obtained using EPA 445.0 and SM 10200 H. See Figures 13 & 14 for scatter-plots of values obtained by individual laboratories and method comparisons. See Tables 28 - 31 for F-pseudosigma values, summary statistics and inter-laboratory comparisons.

<b>Chlorophyll a, Corrected for Phaeophytin</b>				
	<b>F-pseudosigma</b>	<b>% F-pseudosigma</b>	<b>Median</b>	<b>Range</b>
All Results	1.59	15.75%	10.08	9.40
<b>Method</b>	<b>N</b>	<b>Mean</b>	<b>Median</b>	<b>Range</b>
EPA 445.0	13	9.14	7.20	0.11
SM 10200 H	21	9.32	8.00	10.58

Table 28. F-pseudosigma values for ChlA.

Lab ID	ChlA Corrected			
	N	Lab Median	Range	Mean Z-value
A	3	8.86	0.43	0.85
C	3	10.20	0.30	0.09
D	3	9.50	0.90	0.51
F	3	6.50	0.60	2.29
H	3	10.30	0.20	0.14
I	3	11.00	2.20	0.65
M	3	10.20	0.60	0.15
N	1	8.40	N/A	1.06
O	3	2.70	0.20	4.64
Q	3	11.00	1.00	0.79
R	3	12.00	0.00	1.21
S	3	10.30	0.92	0.24

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



## GOMA Analytical Round Robin #8

### Descriptives

Chlorophyll a corrected  $\mu\text{g/L}$

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
A	3	8.7233	.24542	.14170	8.1137	9.3330	8.44	8.87
C	3	10.1333	.16073	.09280	9.7341	10.5326	9.95	10.25
D	3	9.2667	.49329	.28480	8.0413	10.4921	8.70	9.60
F	3	6.4333	.30551	.17638	5.6744	7.1922	6.10	6.70
H	3	10.3000	.10000	.05774	10.0516	10.5484	10.20	10.40
I	3	10.9333	1.10151	.63596	8.1970	13.6696	9.80	12.00
M	3	10.0000	.34641	.20000	9.1395	10.8605	9.60	10.20
N	1	8.4000	N/A	N/A	N/A	N/A	8.40	8.40
O	3	2.7000	.10000	.05774	2.4516	2.9484	2.60	2.80
Q	3	11.3333	.57735	.33333	9.8991	12.7676	11.00	12.00
R	3	12.0000	.00000	.00000	12.0000	12.0000	12.00	12.00
S	3	10.2600	.46130	.26633	9.1141	11.4059	9.78	10.70
Total	34	9.2544	2.54244	.43603	8.3673	10.1415	2.60	12.00

Table 30. Descriptive statistics by laboratory for ChlA.

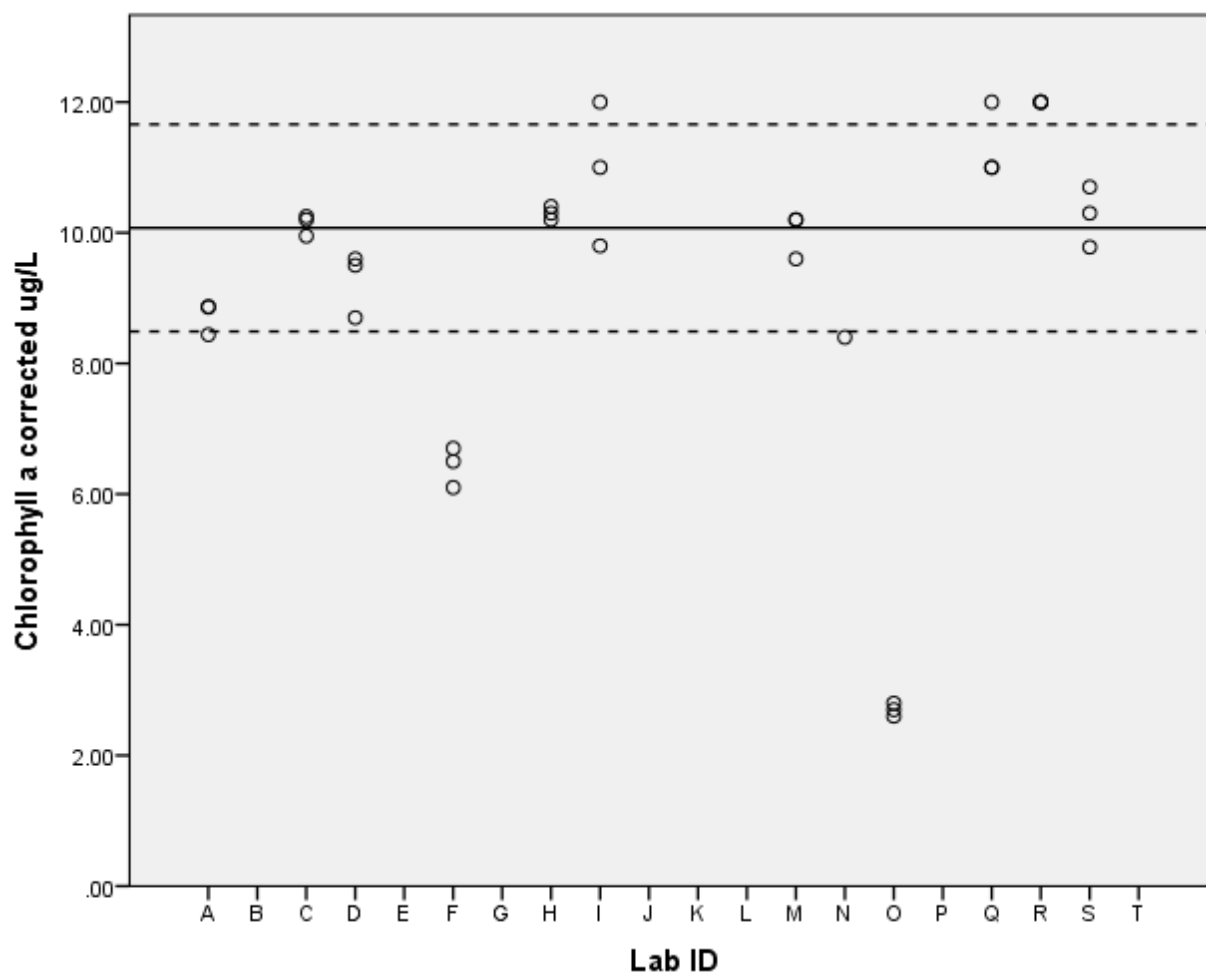


Figure 13. Scatter-plot of ChlA values obtained by twelve laboratories. The solid line indicates the overall median, and the dashed lines indicate  $\pm 1$  F-pseudosigma.

## GOMA Analytical Round Robin #8

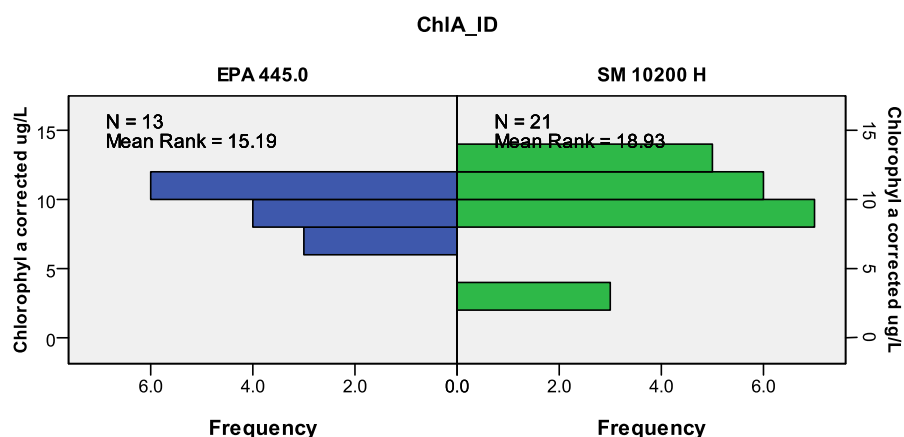
### Hypothesis Test Summary

	Null Hypothesis	Test	Sig.	Decision
1	The distribution of Chlorophyll a corrected ug/L is the same across categories of ChlA_ID.	Independent-Samples Mann-Whitney U Test	.292 <sup>1</sup>	Retain the null hypothesis.
2	The distribution of Chlorophyll a corrected ug/L is the same across categories of ChlA_ID.	Independent-Samples Kolmogorov-Smirnov Test	.194	Retain the null hypothesis.

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

<sup>1</sup>Exact significance is displayed for this test.

### Independent-Samples Mann-Whitney U Test



Total N	34
Mann-Whitney U	106.500
Wilcoxon W	197.500
Test Statistic	106.500
Standard Error	28.140
Standardized Test Statistic	-1.066
Asymptotic Sig. (2-sided test)	.286
Exact Sig. (2-sided test)	.292

Figure 14. Mann-Whitney test for ChlA values by method.

## GOMA Analytical Round Robin #8

Chlorophyll a corrected $\mu\text{g/L}$							
Lab ID	N	Subset for alpha = 0.05					
		1	2	3	4	5	6
Gabriel <sup>a,b</sup>	O	3	2.7000				
	F	3		6.4333			
	A+N	4			8.6425		
	D	3			9.2667	9.2667	
	M	3			10.0000	10.0000	10.0000
	C	3				10.1333	10.1333
	S	3				10.2600	10.2600
	H	3				10.3000	10.3000
	I	3					10.9333
	Q	3					11.3333
	R	3					12.0000
	Sig.		1.000	1.000	.053	.324	.061
						.276	

Means for groups in homogeneous subsets are displayed.

a. Uses Harmonic Mean Sample Size = 3.070.

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

Table 31. Post hoc inter-laboratory (between subjects) comparison for ChlA.

## GOMA Analytical Round Robin #8

**J. Chlorophyll a, Uncorrected for Phaeophytin.** Twenty-three of the 25 values were within acceptable ranges. Lab G reported two values outside of acceptable ranges. Labs G and J reported values that were significantly lower than those of the other labs. Lab G's values were quite variable. No laboratories reported any values below their detection limits; however, Lab D qualified its values as below its quantitation limit. The %F-pseudosigma value was large (>30%), indicating a lack of precision among laboratories. Of the 25 reported values, 68% were within 1 F-pseudosigma and 92% were within 2 F-pseudosigma. There was no statistical difference between the three methods. However, results from the Holm-Hansen method typically had lower results than the other two methods. See Figures 15 & 16 for scatter-plots of values obtained by individual laboratories and method comparisons. See Tables 32 - 35 for F-pseudosigma values, summary statistics and inter-laboratory comparisons.

<b>Chlorophyll a, Uncorrected for Phaeophytin</b>				
	<b>F-pseudosigma</b>	<b>% F-pseudosigma</b>	<b>Median</b>	<b>Range</b>
All Results	3.77	32.25%	11.70	14.40
<b>Method</b>	<b>N</b>	<b>Mean</b>	<b>Median</b>	<b>Range</b>
EPA 445.0	4	11.43	11.50	0.90
Holm-Hansen	3	5.27	5.35	0.93
SM 10200 H	18	11.21	12.60	14.40

Table 32. F-pseudosigma values for ChlA Uncorrected.

Lab ID	ChlA Uncorrected			
	N	Lab Median	Range	Mean Z-value
D	3	12.10	0.80	0.11
G	3	3.74	2.67	2.25
H	3	13.40	0.50	0.46
J	3	5.35	0.93	1.71
N	1	11.30	N/A	0.11
P	3	10.38	0.21	0.34
Q	3	13.00	1.00	0.43
R	3	16.00	3.00	0.88
T	3	11.70	0.90	0.08

Table 33. Summary statistics and Z-values by Laboratory for ChlA Uncorrected.

## GOMA Analytical Round Robin #8

### Descriptives

Chlorophyll a uncorrected  $\mu\text{g/L}$

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
D	3	11.9000	.43589	.25166	10.8172	12.9828	11.40	12.20
G	3	3.2033	1.41359	.81614	-.3082	6.7149	1.60	4.27
H	3	13.4333	.25166	.14530	12.8082	14.0585	13.20	13.70
J	3	5.2667	.47057	.27168	4.0977	6.4356	4.76	5.69
N	1	11.3000	N/A	N/A	N/A	N/A	11.30	11.30
P	3	10.4167	.10970	.06333	10.1442	10.6892	10.33	10.54
Q	3	13.3333	.57735	.33333	11.8991	14.7676	13.00	14.00
R	3	15.0000	1.73205	1.00000	10.6973	19.3027	13.00	16.00
T	3	11.4667	.49329	.28480	10.2413	12.6921	10.90	11.80
Total	25	10.5344	3.94743	.78949	8.9050	12.1638	1.60	16.00

Table 34. Descriptive statistics by laboratory for ChlA Uncorrected.

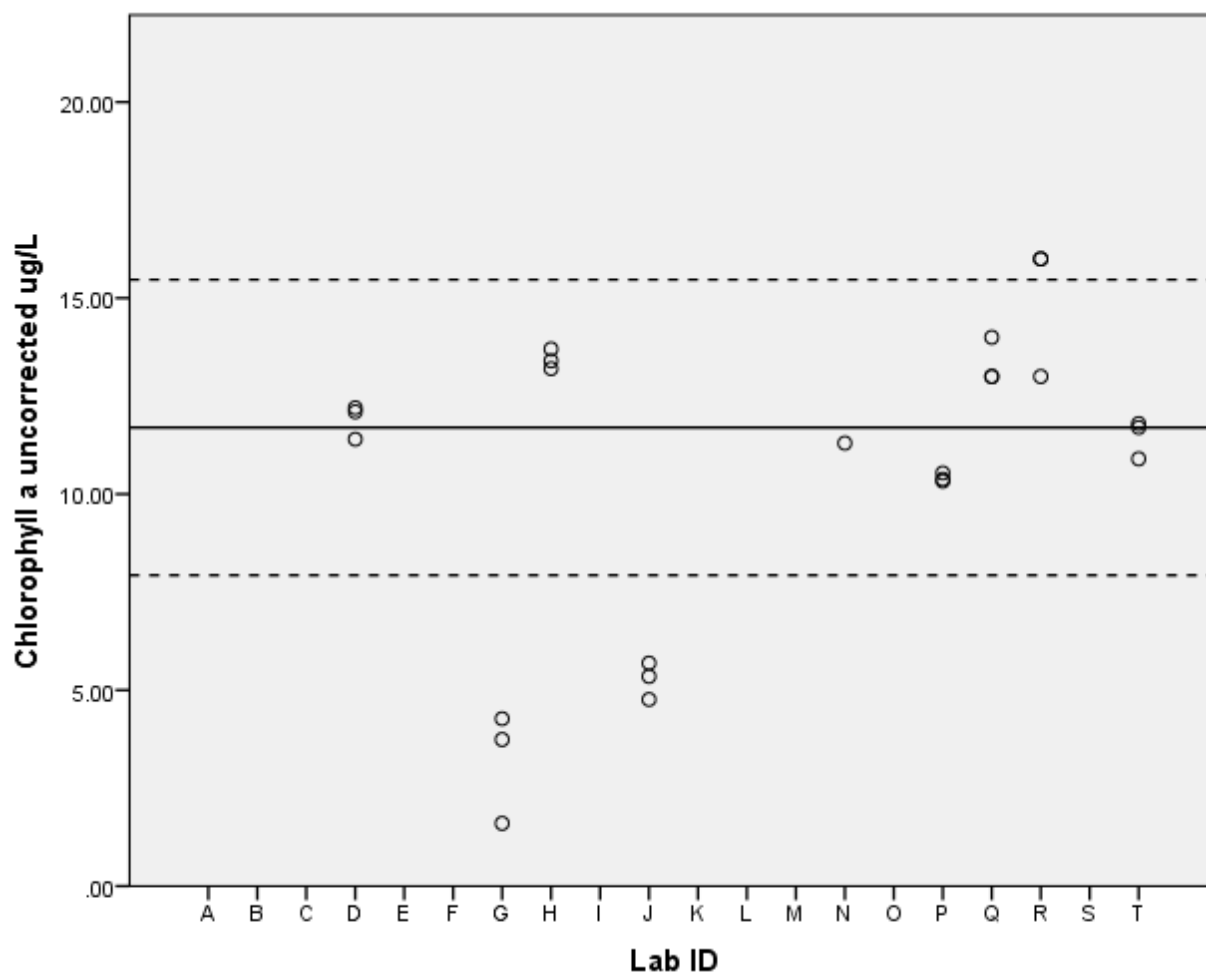


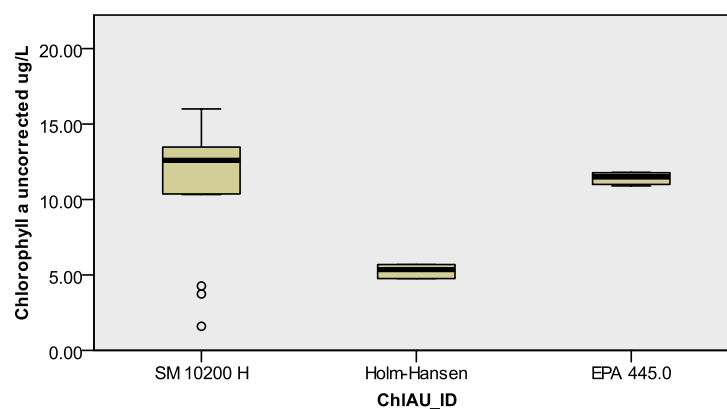
Figure 15. Scatter-plot of ChlA Uncorrected values obtained by nine laboratories. The solid line indicates the overall median, and the dashed lines indicate  $\pm 1$  F-pseudosigma.

## Hypothesis Test Summary

	Null Hypothesis	Test	Sig.	Decision
1	The medians of Chlorophyll a uncorrected ug/L are the same across categories of ChIAU_ID.	Independent-Samples Median Test	.088	Retain the null hypothesis.
2	The distribution of Chlorophyll a uncorrected ug/L is the same across categories of ChIAU_ID.	Independent-Samples Kruskal-Wallis Test	.109	Retain the null hypothesis.

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

## Independent-Samples Kruskal-Wallis Test



Total N	25
Test Statistic	4.431
Degrees of Freedom	2
Asymptotic Sig. (2-sided test)	.109

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

Figure 16. Kruskal-Wallis test for ChlA Uncorrected values by method.

## GOMA Analytical Round Robin #8

Chlorophyll a uncorrected µg/L					
Lab ID	N	Subset for alpha = 0.05			
		1	2	3	4
G	3	3.2033			
J	3	5.2667			
P	3		10.4167		
T+N	4		11.4250	11.4250	
D	3		11.9000	11.9000	
Q	3			13.3333	13.3333
H	3			13.4333	13.4333
R	3				15.0000
Sig.		.153	.585	.178	.409

Means for groups in homogeneous subsets are displayed.

a. Uses Harmonic Mean Sample Size = 3.097.

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

Table 35. Post hoc inter-laboratory (between subjects) comparison for ChlA Uncorrected.

## GOMA Analytical Round Robin #8

**K. Turbidity.** Thirty-five of the 44 values were within acceptable ranges. Labs D, E, and N reported all values outside of acceptable ranges. These laboratories' results were significantly lower than those of other labs. No laboratories reported any values below their detection or quantitation limits. The %F-pseudosigma value was relatively small (less than 20%), indicating a high degree of precision among laboratories. Of the 44 reported values, 68% were within 1 F-pseudosigma and 80% were within 2 F-pseudosigma. There was no statistical difference between the two methods. See Figure 17 for a scatter-plot of values obtained by individual laboratories and method comparisons. See Tables 36 - 40 for F-pseudosigma values, summary statistics, method comparisons, and inter-laboratory comparisons.

Turbidity				
	F-pseudosigma	% F-pseudosigma	Median	Range
All Results	2.354	18.10%	13.00	14.80
<b>Method</b>	<b>N</b>	<b>Mean</b>	<b>Median</b>	<b>Range</b>
EPA 180.1	24	10.66	13.00	14.80
SM 2130 B	20	12.46	12.55	13.34

Table 36. F-pseudosigma values for turbidity.

Lab ID	Turbidity			
	N	Lab Median	Range	Mean Z-value
B	4	12.85	2.20	0.33
D	4	2.85	0.90	4.35
E	4	3.13	1.38	4.16
F	4	15.50	1.00	1.06
H	4	15.00	1.50	0.88
I	4	12.80	2.00	0.25
L	4	11.90	5.67	0.84
N	1	2.56	N/A	4.44
O	4	14.50	2.00	0.53
Q	4	13.00	1.00	0.11
R	3	12.00	0.00	0.42
S	4	15.00	4.00	0.85

Table 37. Summary statistics and Z-values by Laboratory for turbidity.



## GOMA Analytical Round Robin #8

### Descriptives

Turbidity NTU

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
B	4	12.9750	.98107	.49054	11.4139	14.5361	12.00	14.20
D	4	2.7500	.38730	.19365	2.1337	3.3663	2.20	3.10
E	4	3.2000	.64057	.32029	2.1807	4.2193	2.58	3.96
F	4	15.5000	.57735	.28868	14.5813	16.4187	15.00	16.00
H	4	15.0750	.63966	.31983	14.0572	16.0928	14.40	15.90
I	4	13.0000	.85245	.42622	11.6436	14.3564	12.20	14.20
L	4	11.6325	2.34099	1.17049	7.9075	15.3575	8.53	14.20
N	1	2.5600	N/A	N/A	N/A	N/A	2.56	2.56
O	4	14.2500	.95743	.47871	12.7265	15.7735	13.00	15.00
Q	4	13.2500	.50000	.25000	12.4544	14.0456	13.00	14.00
R	3	12.0000	.00000	.00000	12.0000	12.0000	12.00	12.00
S	4	15.0000	1.63299	.81650	12.4015	17.5985	13.00	17.00
Total	44	11.4793	4.63499	.69875	10.0702	12.8885	2.20	17.00

Table 38. Descriptive statistics by laboratory for turbidity.

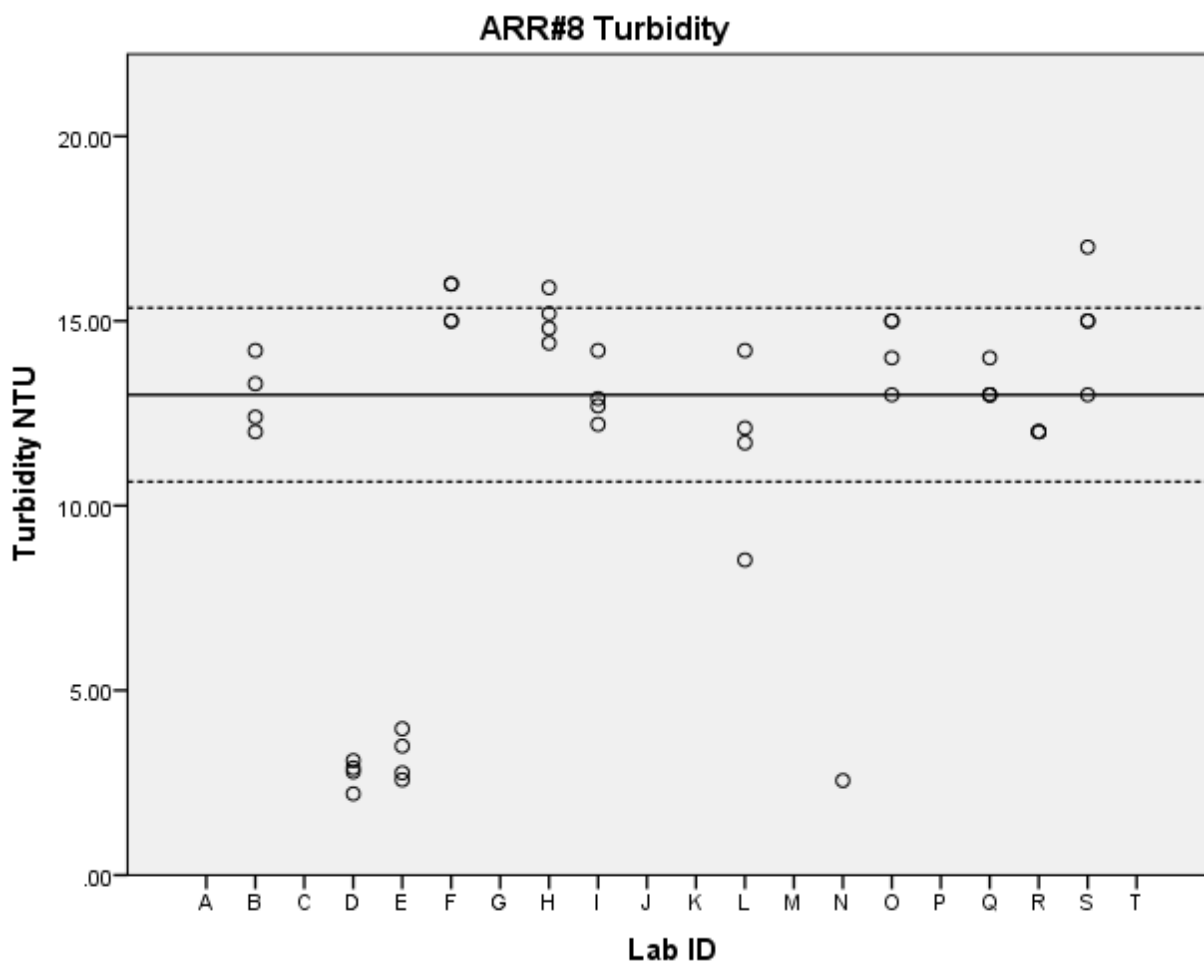


Figure 17. Scatter-plot of turbidity values obtained by twelve laboratories. The solid line indicates the overall median, and the dashed lines indicate  $\pm 1$  F-pseudosigma.

## GOMA Analytical Round Robin #8

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### Robust Tests of Equality of Means

Turbidity NTU Method

	Statistic <sup>a</sup>	df1	df2	Sig.
Welch	1.880	1	35.174	.179
Brown-Forsythe	1.880	1	35.174	.179

a. Asymptotically F distributed.

Table 39. Robust F-tests for turbidity values by method.

### Turbidity NTU

Lab ID	N	Subset for alpha = 0.05		
		1	2	3
D+N	5	2.7120		
E	4	3.2000		
L	4		11.6325	
R	3		12.0000	
B	4		12.9750	12.9750
I	4		13.0000	13.0000
Q	4		13.2500	13.2500
O	4		14.2500	14.2500
S	4			15.0000
H	4			15.0750
F	4			15.5000
Sig.		1.000	.069	.093

Means for groups in homogeneous subsets are displayed.

a. Uses Harmonic Mean Sample Size = 3.952.

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

Table 40. Post hoc inter-laboratory (between subjects) comparison for turbidity.

## 4. Conclusions and Recommendations

**Total Kjeldahl Nitrogen:** There was little variability among laboratories for total Kjeldahl nitrogen. However, Lab E was highly variable, and Lab G's results were extremely low. As noted earlier, two of Lab G's results may be typographical errors. There was one false negative reported by Lab G; otherwise, detection and quantitation limits were not an issue for this analyte. The four methods used were statistically the same; however, results for SM 4500 NH3 D were highly variable and needs to be explored further.

**Ammonia:** Ammonia was highly variable, due mainly to Labs L and O reporting values that were an order of magnitude greater than all other reported values. It is likely that these are transcription errors, as the methods employed by these laboratories were the same as with other labs. Detection and quantitation limits need to be addressed, as roughly half of the results were values and the other half were non-values. Of the four methods which reported values, values obtained using SM 4500 NH3 F were significantly lower than EPA 350.1 and SM 4500 NH3 G; whereas, results obtained using SM 4500 NH3 D were equivalent to all other methods. The following methods reported all non-detects: Lachat 10-107-06-1-J, Lachat QuickChem 31-107-06-1-B, and USGS I-2522-90.

**Total Nitrite, Nitrate, and Nitrite + Nitrate:** Very few values were reported for NO<sub>2</sub>, NO<sub>3</sub>, and NO<sub>x</sub>. Therefore, detection and quantitation limits need to be addressed.

**Total Phosphorus:** Results for total phosphorus were somewhat variable; however, 85% of the results were within acceptable ranges. Lab E's results were highly variable, and reported the only statistical outlier. In addition, Labs E and S reported false negatives. Of the four methods which reported values, value obtained using method EPA 365.4 were significantly higher than those obtained using EPA 365.1 and SM 4500 P E; whereas results obtained using Lachat 10-115-01-1-C were equivalent to all other methods. The only method to report all values as non-detects was EPA 365.3.

**Orthophosphate:** Very few values were reported for OP. However, the twenty that were reported were very similar. Detection and quantitation limits need to be addressed.

**Total Organic Carbon:** There was little variability among laboratories, or within laboratories, for total organic carbon. Lab F reported all values outside of acceptable ranges on the high end; this may be due to an improperly functioning SO<sub>3</sub> scrubber that can create positive interference in the method employed. Lab N reported a low result that fell outside acceptable ranges; is unclear as to why this result was so different. Method SM 5310 D could not be evaluated against other methods due to only one value being reported; whereas values obtained using method EPA 415.1 were statistically lower than those obtained using SM 5310 B. No values were reported as below detection or quantitation limits.

**Chlorophyll a, Corrected for Phaeophytin:** Variability among laboratories was low for chlorophyll a, corrected. Labs F and O reported values below acceptable ranges; Lab O may have recorded the phaeophytin values rather than the ChlA values. There was no statistical difference between values obtained using methods EPA 445.0 and SM 10200 H. Lab D reported its results below its quantitation limit and should re-calculate this limit.

**Chlorophyll a, Uncorrected for Phaeophytin:** Variability among laboratories was high for chlorophyll a, uncorrected. Lab G reported two values outside of acceptable ranges. Labs G

and J reported values significantly lower than the others. Labs G and R's values were quite variable. There was no statistical difference between values obtained using EPA 445.0, SM 10200 H, or Holm-Hansen; however, the Holm-Hansen method typically resulted in lower values. Lab D reported its results below its quantitation limit and should re-calculate this limit.

**Turbidity:** There was little variability among laboratories for turbidity; however, Labs D, E, and N reported all values low and outside of acceptable ranges. These three labs had similar results, which suggests that their low values are due to techniques that are not quantified in the method (e.g., EPA 180.1 "Mix the sample thoroughly" and SM 2130 B "Gently agitate sample" are both vague and may affect results). In addition, both methods are susceptible to the presence of coarse sediments which can settle out (these were observed in the preparation of bottles for shipment) and to the presence of true color (the sample water was highly colored when collected). These can both cause the reported values to be lower, and require additional care in the preparation of the samples for analyses. There was no statistical difference between values obtained using methods SM 2130 B and EPA 180.1. No laboratories reported values below their detection or quantification limits.

**Overall:** Overall, the data were quite similar among laboratories and between the methods employed. The greatest challenge is addressing the high number of nutrient results reported as below detection and quantitation limits. In order to adequately monitor water quality in and around the Gulf of Mexico, the nutrient detection problem must be resolved. There is sufficient evidence that nutrients exist in coastal and estuarine waters around the Gulf of Mexico in sufficient quantity to promote the growth of micro-phytoplankton, seagrasses, zooxanthellae in corals, and macro algae. 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 to help them to achieve detectable and quantifiable results. The overall results indicate that laboratories should accurately calculate their detection and quantitation limits. As technology advances and equipment becomes more accurate and precise, the detection limits should come down; additionally calculations for quantitation limits need to be more than just "2 - 5 times" the detection limit, or other overly simplistic ways of quantifying noise. Gross errors due to unit conversions, calculation errors, dilution errors, transcription errors (and other typographical errors), etc. need to be limited as much as possible. This may be through automation, improved quality control and quality assurance plans, as well as by other means. Agencies should revise methods to better quantify their techniques to reduce the amount of variability in the methods employed. Finally, we recommend that GOMA and its partners obtain funding to facilitate laboratory education and information exchange to address the challenges listed above.

### 5. References

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## GOMA Analytical Round Robin #8

### GOMA Analytical Round Robin #8 Results - September 18, 2012

Samples collected from Oyster Bay, Wakulla County, Florida

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

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

All results listed below the detection limit are listed with a U qualifier.

Calculations include reported values listed below the PQL.

\* = Less than PQL

Total Kjeldahl Nitrogen mg/L																		
	B	D	E	F	G	I	K	L	N	O	Q	R	S	T				
	0.724	0.732	0.127	0.580	0.325	0.612	0.669	0.768	0.629	0.870	0.840	0.920	0.666	0.750				
	0.653	0.639	0.114	0.610	0.033	0.628	0.671	0.604		0.730	0.810	0.940	0.656	0.770				
	0.731	0.655	1.460	0.610	0.029	0.566	0.677	0.612		0.650	0.780	0.960	0.691	0.740				
	0.724	0.706	0.698	0.660	U	0.517	0.637	0.589		0.720	0.860		1.030	0.800				
Average:	0.703	0.675	0.567	0.600	0.129	0.602	0.672	0.661	0.629	0.750	0.810	0.940	0.671	0.753				
Std. Dev.	0.043	0.050	0.773	0.017	0.170	0.032	0.004	0.092	#DIV/0!	0.111	0.030	0.020	0.018	0.015				
Notes	Lab G bottles 2 & 3 appear to be typos, otherwise they are below the MDL.																	
Ammonia mg/L																		
	A*	B	D	E*	F	G	H*	I	J	K	L	N	O	P	Q	R*	S*	T*
	0.012	U	U	0.016	I	U	0.020	0.040	U	U	0.130	I	0.270	0.019	U	0.025	0.032	I
	0.007	U	U	0.015	I	U	0.020	0.039	U	U	0.130		0.270	0.016	U	0.036	0.027	I
	0.009	U	U	0.018	I	U	0.016	0.041	U	U	I		0.270	0.018	U	0.028	0.028	I
	0.010	U	U	0.015	I	U	0.019	0.035	U	U	0.450		0.280	0.017	U		U	I
Average:	0.010	#DIV/0!	#DIV/0!	0.016	#DIV/0!	#DIV/0!	0.019	0.039	#DIV/0!	#DIV/0!	0.237	#DIV/0!	0.273	0.018	#DIV/0!	0.030	0.029	#DIV/0!
Std. Dev.	0.002	#DIV/0!	#DIV/0!	0.001	#DIV/0!	#DIV/0!	0.002	0.003	#DIV/0!	#DIV/0!	0.185	#DIV/0!	0.005	0.001	#DIV/0!	0.006	0.003	#DIV/0!
Notes	Labs L and O may be typos since they are an order of magnitude greater than the other labs' values.																	
Total Nitrite + Nitrate mg/L																		
	A*	B	D	E	F	G	H*	I	J^	K	L	O	P*	Q*	R*	S*	T	
	0.004	U	U	U	I	U	0.006	0.002	0.004	U	I	U	0.012	U	0.020	0.008	I	
	0.004	U	U	U	I	U	0.006	0.004	0.004	U	I	U	0.011	0.004	U	0.013	I	
	0.006	U	U	U	I	U	0.006	0.004	0.004	U	I	U	0.011	U	U	U	I	
		U	U	U	I	U	0.006	0.004	0.005	U	I	U	0.010	U		U	I	
Average:	0.005	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	0.006	0.004	0.004	#DIV/0!	#DIV/0!	#DIV/0!	0.011	0.004	0.020	0.011	#DIV/0!	
Std. Dev.	0.001	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	0.000	0.001	0.000	#DIV/0!	#DIV/0!	#DIV/0!	0.001	#DIV/0!	#DIV/0!	0.004	#DIV/0!	
Notes	^Lab J is dissolved NO <sub>x</sub>																	

## GOMA Analytical Round Robin #8

Total Nitrite mg/L																		
	B	D	F	G	H*	J^	L	P*	Q*	R	S							
	U	U	0.008	U	U	0.002	I	0.001	U	U	U							
	U	U	0.008	U	0.005	0.002	I	0.001	0.002	U	U							
	U	U	0.008	U	U	0.002	I	0.001	U	U	U							
	U	U	0.007	U	0.006	0.002	I	0.001	U		U							
Average:	#DIV/0!	#DIV/0!	0.008	#DIV/0!	0.006	0.002	#DIV/0!	0.001	0.002	#DIV/0!	#DIV/0!							
Std. Dev.	#DIV/0!	#DIV/0!	0.001	#DIV/0!	0.001	0.000	#DIV/0!	0.000	#DIV/0!	#DIV/0!	#DIV/0!							
Notes	^Lab J is dissolved NO <sub>2</sub>																	
Total Nitrate																		
	D	F	G	L	R*													
	U	I	U	I	0.020													
	U	I	U	I	0.010													
	U	I	U	I	U													
	U	I	U	I														
Average:	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	0.015													
Std. Dev.	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	0.007													
Total Phosphorus mg/L																		
	B	D	E*	F	G	H	I*	K	L	N	O	P	Q	R	S	T		
	0.030	0.064	0.041	0.040	0.041	0.031	0.017	U	I	0.068	0.041	0.039	0.038	0.053	U	0.070		
	0.037	0.065	0.115	0.040	0.046	0.037	0.018	U	I		0.041	0.038	0.037	0.054	U	0.070		
	0.031	0.063	0.051	0.040	0.047	0.034	0.018	U	I		0.042	0.040	0.038	0.051	U	0.060		
	0.032	0.064	U	0.040	0.049	0.032	0.015	U	I		0.038	0.034	0.037		U	0.070		
Average:	0.033	0.064	0.069	0.040	0.046	0.034	0.017	#DIV/0!	#DIV/0!	0.068	0.041	0.038	0.038	0.053	#DIV/0!	0.068		
Std. Dev.	0.003	0.001	0.040	0.000	0.003	0.003	0.001	#DIV/0!	#DIV/0!	#DIV/0!	0.002	0.003	0.001	0.002	#DIV/0!	0.005		
Orthophosphate mg/L																		
	A*	B	D	E	F	G	H*	I	J	K	L	N	O	P*	Q*	R	S	T
	U	U	U	U	0.008	U	0.005	U	0.001	0.010	I	I	U	U	0.006	U	U	I
	0.002	U	U	U	0.008	U	0.006	U	0.003	0.011	I		U	0.002	I	U	U	I
	U	U	U	U	0.008	U	0.005	U	U	0.011	I		U	0.002	0.004	U	U	I
	U	U	U	U	0.008	U	0.005	U	0.00027	0.012	I		U	U	I		U	I
Average:	0.002	#DIV/0!	#DIV/0!	#DIV/0!	0.008	#DIV/0!	0.005	#DIV/0!	0.001	0.011	#DIV/0!	#DIV/0!	#DIV/0!	0.002	0.005	#DIV/0!	#DIV/0!	#DIV/0!
Std. Dev.	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	0.000	#DIV/0!	0.001	#DIV/0!	0.001	0.001	#DIV/0!	#DIV/0!	#DIV/0!	0.000	0.001	#DIV/0!	#DIV/0!	#DIV/0!

## GOMA Analytical Round Robin #8

Total Organic Carbon mg/L													
	D	E	F	H	I	L	N	O	P	Q	R	S	T
	9.50	9.88	18.00	8.08	7.44	7.57	2.68		7.12	8.10	7.70	7.54	8.00
	9.30	10.10	18.00	8.03	7.48	7.53			7.23	8.10	7.70	7.42	9.00
	9.20	9.72	18.00	7.87	7.52	7.59			7.18	7.80	7.70	7.48	9.00
	9.30	9.78	18.00	7.81	7.49	7.43			7.21	7.80		7.43	9.00
Average:	9.33	9.87	18.00	7.95	7.48	7.53	2.68	#DIV/0!	7.19	7.95	7.70	7.47	8.75
Std. Dev.	0.126	0.167	0.000	0.128	0.033	0.071	#DIV/0!	#DIV/0!	0.048	0.173	0.000	0.055	0.500
Notes	Lab F's high values may be due to positive interference due to SO <sub>3</sub> detection caused by H <sub>2</sub> SO <sub>4</sub> preservation. May require an SO <sub>3</sub> scrubber.												
Chlorophyll a, Corrected for Phaeophytin µg/L													
	A	C	D*	F	H	I	M	N	O	Q	R	S	
	8.44	9.95	9.60	6.10	10.20	11.00	10.20	8.40	2.60	12.00	12.00	10.30	
	8.86	10.20	8.70	6.50	10.40	9.80	10.20		2.70	11.00	12.00	9.78	
	8.87	10.25	9.50	6.70	10.30	12.00	9.60		2.80	11.00	12.00	10.70	
Average:	8.72	10.13	9.27	6.43	10.30	10.93	10.00	8.40	2.70	11.33	12.00	10.26	
Std. Dev.	0.245	0.161	0.161	0.493	0.306	0.100	1.102	0.346	#DIV/0!	0.100	0.577	0.000	
Chlorophyll a, Uncorrected for Phaeophytin µg/L													
	D*	G	H	J	N	P	Q	R	T				
	12.20	1.60	13.70	4.76	11.30	10.54	14.00	13.00	11.80				
	11.40	4.27	13.20	5.69		10.38	13.00	16.00	10.90				
	12.10	3.74	13.40	5.35		10.33	13.00	16.00	11.70				
Average:	11.90	3.20	13.43	5.27	11.30	10.42	13.33	15.00	11.47				
Std. Dev.	0.436	1.414	0.252	0.471	#DIV/0!	0.110	0.577	1.732	0.493				
Turbidity NTU													
	B^	D	E	F	H	I	L	N	O	Q	R	S	
	12.00	3.10	3.49	16.00	14.80	14.20	12.10	2.56	13.00	13.00	12.00	15.00	
	13.30	2.20	2.77	16.00	14.40	12.20	14.20		14.00	13.00	12.00	13.00	
	12.40	2.80	2.58	15.00	15.90	12.90	11.70		15.00	13.00	12.00	17.00	
	14.20	2.90	3.96	15.00	15.20	12.70	8.53		15.00	14.00		15.00	
Average:	12.98	2.75	3.20	15.50	15.08	13.00	11.63	2.56	14.25	13.25	12.00	15.00	
Std. Dev.	0.981	0.387	0.641	0.577	0.640	0.852	2.341	#DIV/0!	0.957	0.500	0.000	1.633	
Notes	^ = Estimated, less than lowest calibration standard The lowest QC sample recorded was 8.7 NTU, and the highest was 9.9 NTU. Readings taken at the beginning, twice in the middle of the split, and at the end of the split were: 13.5, 13.6, 15.9 and 12.3 NTU, respectively. There were larger particles that may have settled out causing the low values.												



## GOMA Analytical Round Robin #8

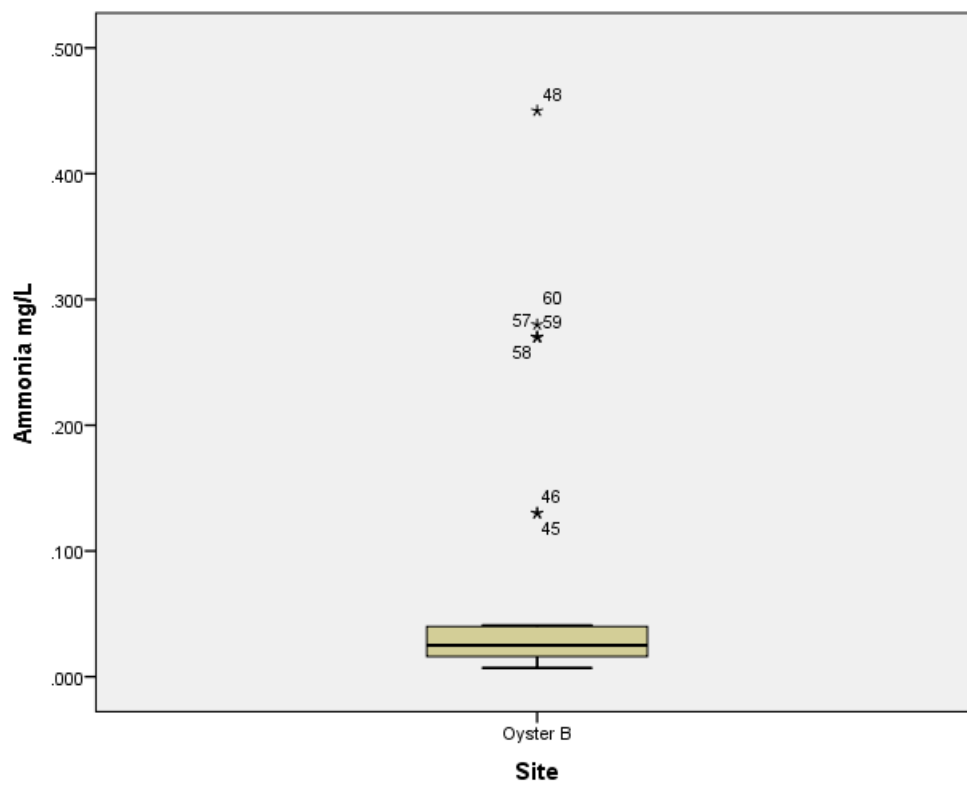
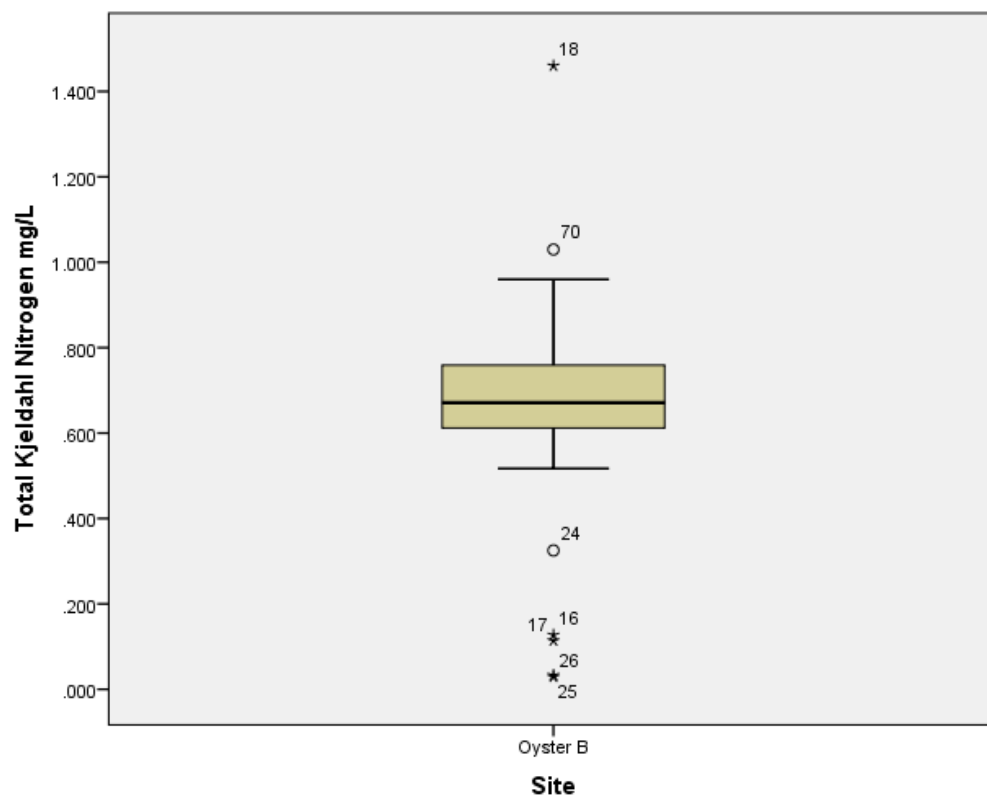
	TKN		NH3		NOx		NO2		NO3		TP		OP		TOC		ChIA_Cor		ChIA_U		Turbidity	
	Stat.	S.Er.	Stat.	S.Er.	Stat.	S.Er.	Stat.	S.Er.	Stat.	S.Er.	Stat.	S.Er.	Stat.	S.Er.	Stat.	S.Er.	Stat.	S.Er.	Stat.	S.Er.	Stat.	S.Er.
<b>Descriptives</b>																						
<b>N (Total)</b>	52		68		67		39		19		60		68		44		34		25		44	
<b>N (&gt; PQL)</b>	49		17		4		4		0		42		13		44		32		23		44	
<b>N Analyzed</b>	51		33		19		11		2		47		20		44		34		25		44	
<b>Mean</b>	0.670	0.033	0.072	0.019	0.007	0.001	0.004	0.001	0.015	0.005	0.045	0.003	0.006	0.001	8.90	0.47	9.25	0.44	10.53	0.79	11.48	0.70
<b>95% CI (LB)</b>	0.604		0.034		0.005		0.002		-0.049		0.039		0.004		7.95		8.37		8.91		10.07	
<b>95% CI (UB)</b>	0.737		0.111		0.010		0.006		0.079		0.050		0.008		9.86		10.14		12.16		12.89	
<b>5% Trimmed</b>	0.676		0.058		0.007		0.004		N/A		0.044		0.006		8.61		9.47		10.70		11.71	
<b>Median</b>	0.671		0.025		0.006		0.005		0.015		0.040		0.006		7.81		10.08		11.70		13.00	
<b>Variance</b>	0.056		0.012		0.000		0.000		0.000		0.000		0.000		9.83		6.46		15.58		21.48	
<b>Std. Dev.</b>	0.236		0.109		0.004		0.003		0.007		0.018		0.004		3.14		2.54		3.95		4.63	
<b>Min</b>	0.029		0.007		0.002		0.001		0.010		0.015		0.0003		2.68		2.60		1.60		2.20	
<b>Max</b>	1.460		0.450		0.020		0.008		0.020		0.115		0.012		18.00		12.00		16.00		17.00	
<b>Range</b>	1.431		0.443		0.018		0.007		0.010		0.100		0.012		15.32		9.40		14.40		14.80	
<b>IQR</b>	0.156		0.025		0.007		0.007		N/A		0.016		0.006		1.79		2.14		5.09		3.18	
<b>Skew</b>	-0.431	0.333	2.158	0.409	1.400	0.524	0.007	0.661	N/A	N/A	1.428	0.347	0.161	0.512	2.14	0.36	-1.54	0.40	-0.90	0.46	-1.17	0.36
<b>Kurtosis</b>	3.737	0.656	4.043	0.798	2.195	1.014	-2.129	1.279	N/A	N/A	4.376	0.681	-1.069	0.992	4.80	0.70	1.99	0.79	-0.17	0.90	-0.16	0.70
<b>Huber's <math>\psi</math></b>	0.682		0.026		0.006		0.004		0.015		0.042		0.006		7.90		9.86		11.65		13.08	
<b>Kaplan-Meier (KM) Method</b>																						
<b>Minimum ND</b>	0.041		0.0007		0.003		0.001		0.003		0.006		0.00017		N/A		N/A		N/A		N/A	
<b>Maximum ND</b>	0.041		0.1		0.05		0.05		0.05		0.1		0.05		N/A		N/A		N/A		N/A	
<b>Mean</b>	0.658	0.035	0.039	0.010	0.005	0.001	0.002	0.000	0.011	0.001	0.041	0.002	0.003	0.000	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
<b>SD</b>	0.248		0.081		0.004		0.002		0.002		0.018		0.003		N/A		N/A		N/A		N/A	
<b>95% KM UCL</b>	0.809		0.060		0.006		0.003		0.012		0.045		0.004		9.70		9.96		13.57		14.53	
<b>Normality</b>																						
<b>Test of Skew</b>	0.187		0.000		0.012		0.991		N/A		0.000		0.739		0.000		0.001		0.056		0.003	
<b>Test of Kurtosis</b>	0.002		0.004		0.072		0.006		N/A		0.001		0.161		0.001		0.049		0.989		0.974	
<b>Jarque &amp; Bera</b>	0.000		0.000		0.035		0.485		N/A		0.000		0.579		0.000		0.004		0.213		0.009	

## GOMA Analytical Round Robin #8

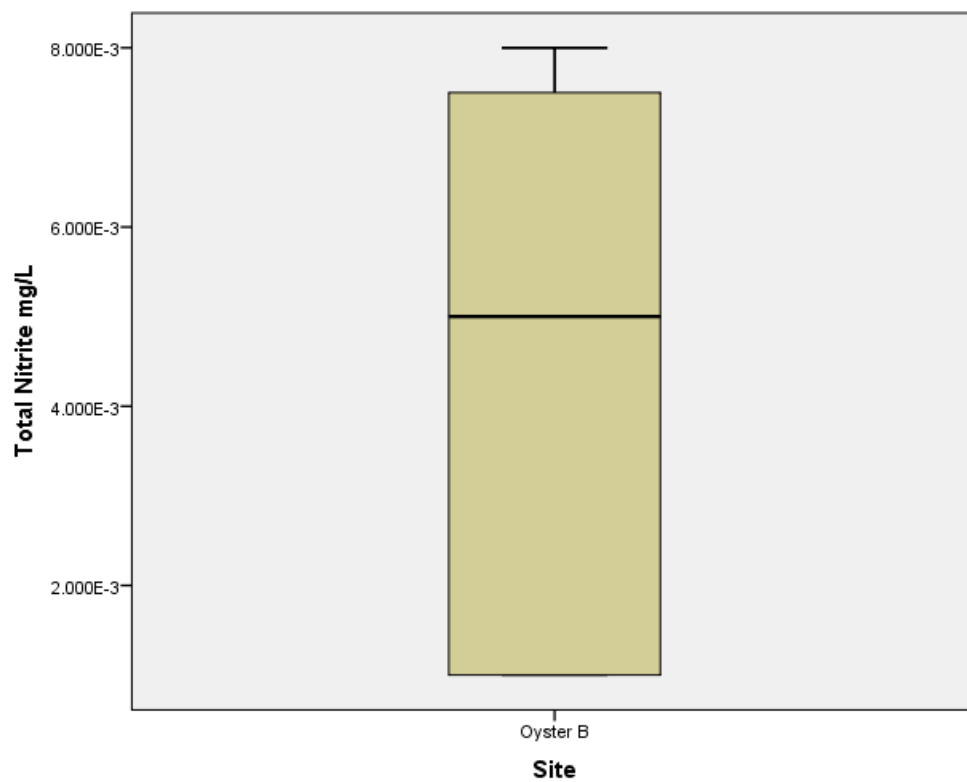
	TKN		NH3		NOx		NO2		NO3		TP		OP		TOC		ChIA_Cor		ChIA_U		Turbidity	
	Stat.	S.Er.	Stat.	S.Er.	Stat.	S.Er.	Stat.	S.Er.	Stat.	S.Er.	Stat.	S.Er.	Stat.	S.Er.	Stat.	S.Er.	Stat.	S.Er.	Stat.	S.Er.	Stat.	S.Er.
<b>Outliers</b>																						
F Crit. (Mahalanobis D2)	9.84		8.71		7.19		5.54		N/A		9.63		7.33		9.46		8.79		7.96		9.46	
Mahalanobis D2 Max	11.17		12.11		8.08		1.32		N/A		16.01		2.85		8.42		6.85		5.12		4.01	
+ 2 Std. Dev.	1.143		0.289		0.016		0.011		0.029		0.080		0.013		15.17		14.34		18.43		20.75	
- 2 Std. Dev.	0.197		-0.145		-0.001		-0.002		0.001		0.009		-0.001		2.63		4.17		2.64		2.21	
# Outside 2 Std. Dev.	5		1		1		0		0		1		0		4		3		1		1	
+ 2 F-Pseudosigma	0.902		0.061		0.016		0.015		N/A		0.064		0.014		10.46		13.25		19.25		17.71	
- 2 F-Pseudosigma	0.440		-0.011		-0.004		-0.005		N/A		0.016		-0.003		5.15		6.90		4.15		8.29	
# Outside 2 F-Pseudosigma	10		7		1		0		N/A		9		0		5		6		2		9	
# from Boxplots	7		7		0		0		N/A		1		0		5		3		6		9	
<b>Homoscedasticity (between laboratories)</b>																						
Levene's	0.000		0.000		0.000		0.015		N/A		0.000		0.005		0.000		0.018		0.001		0.185	
<b>Detection Limits</b>																						
< MDL	1		27		38		28		9		9		42		0		0		0		0	
% < MDL	2%		40%		57%		65%		47%		15%		58%		0%		0%		0%		0%	
< PQL	0		24		25		11		10		9		17		0		2		2		0	
% < PQL	2%		75%		94%		91%		100%		30%		82%		0%		6%		9%		0%	
<b>Precision</b>																						
%F-Pseudosigma	17.2%		72.7%		86.5%		103.8%		N/A		29.7%		76.6%		17.0%		15.8%		32.3%		18.1%	
%RSD	31.0%		150.7%		59.6%		69.0%		N/A		39.4%		60.6%		35.2%		24.5%		37.5%		40.4%	

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

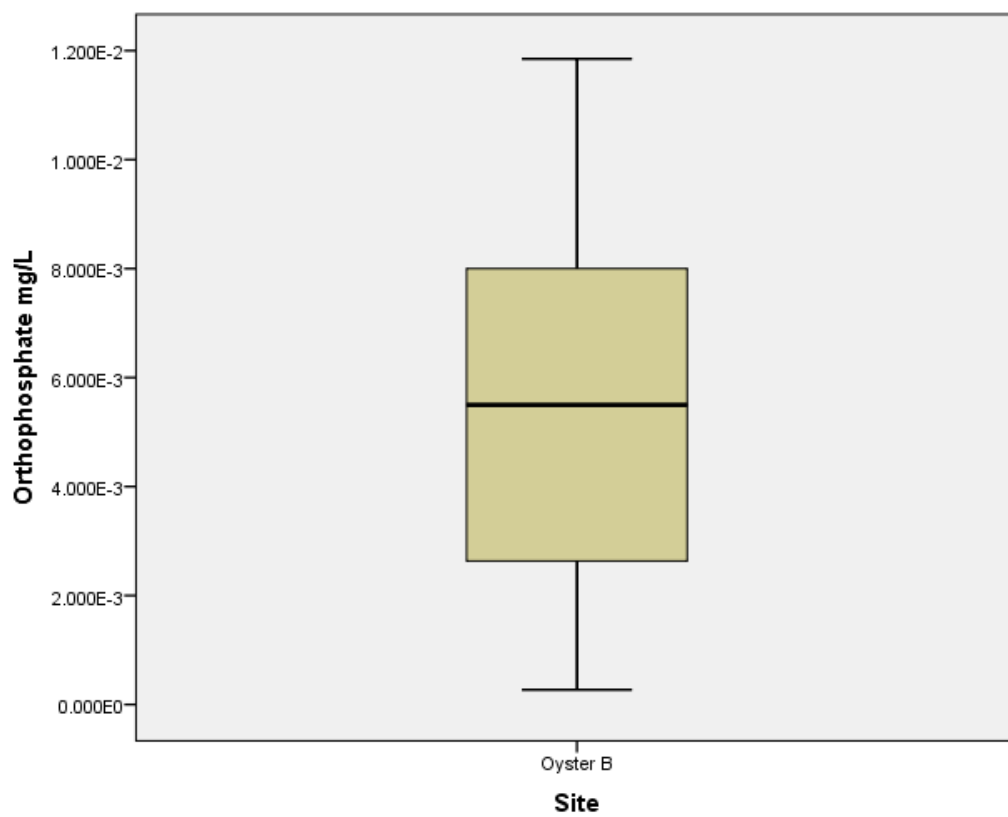
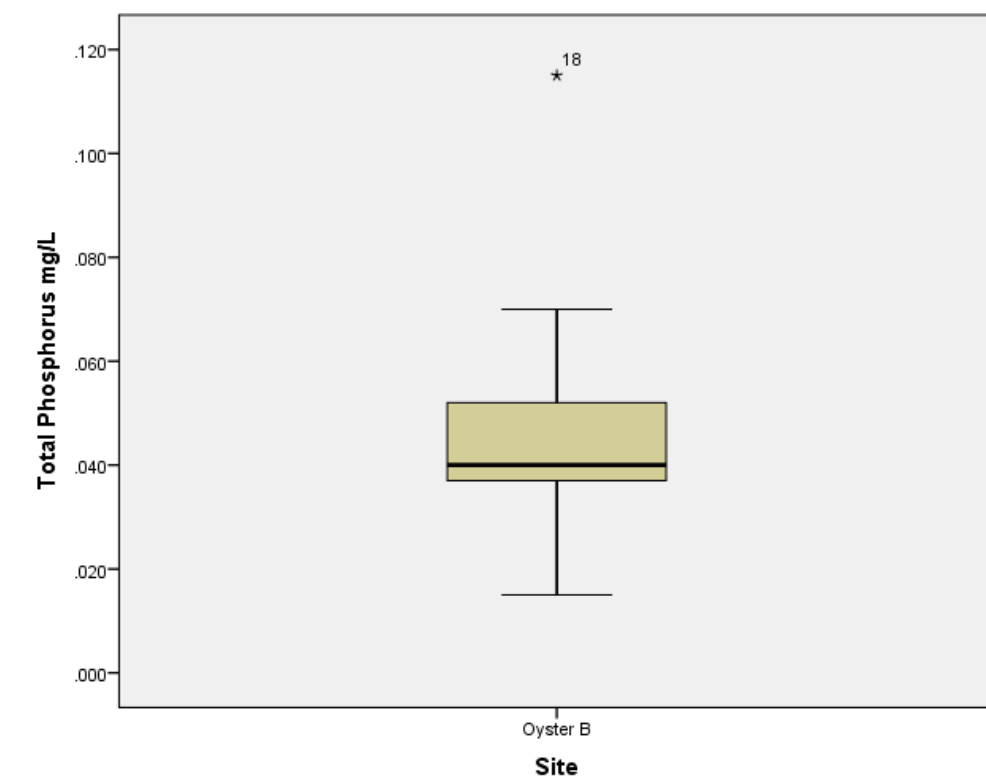
## GOMA Analytical Round Robin #8



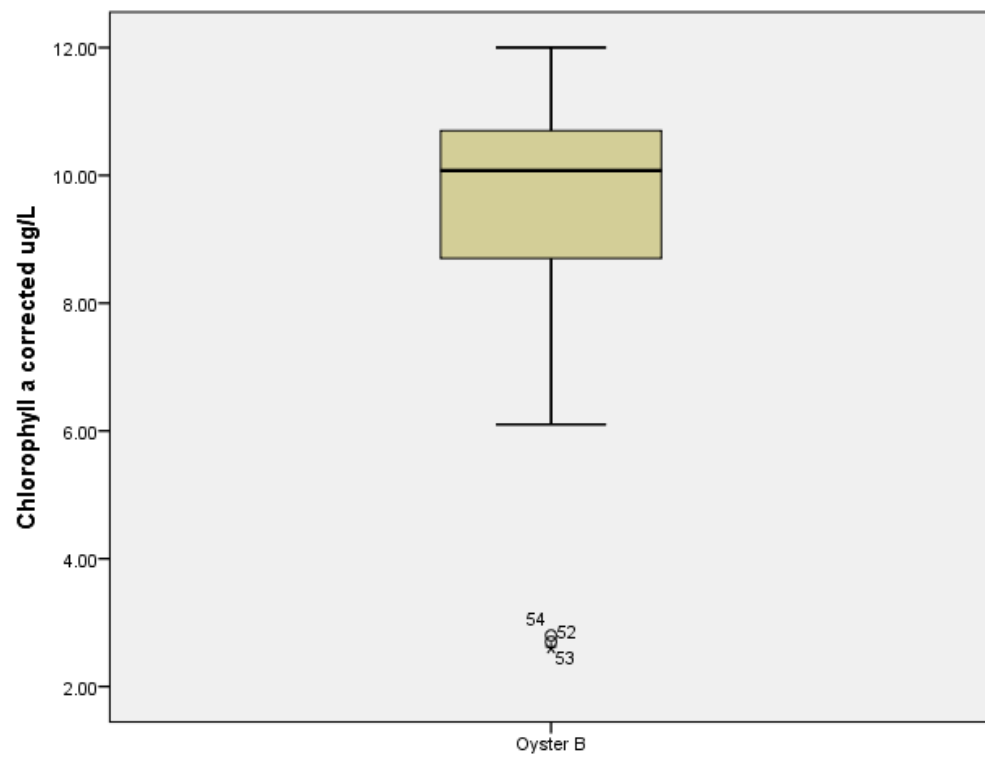
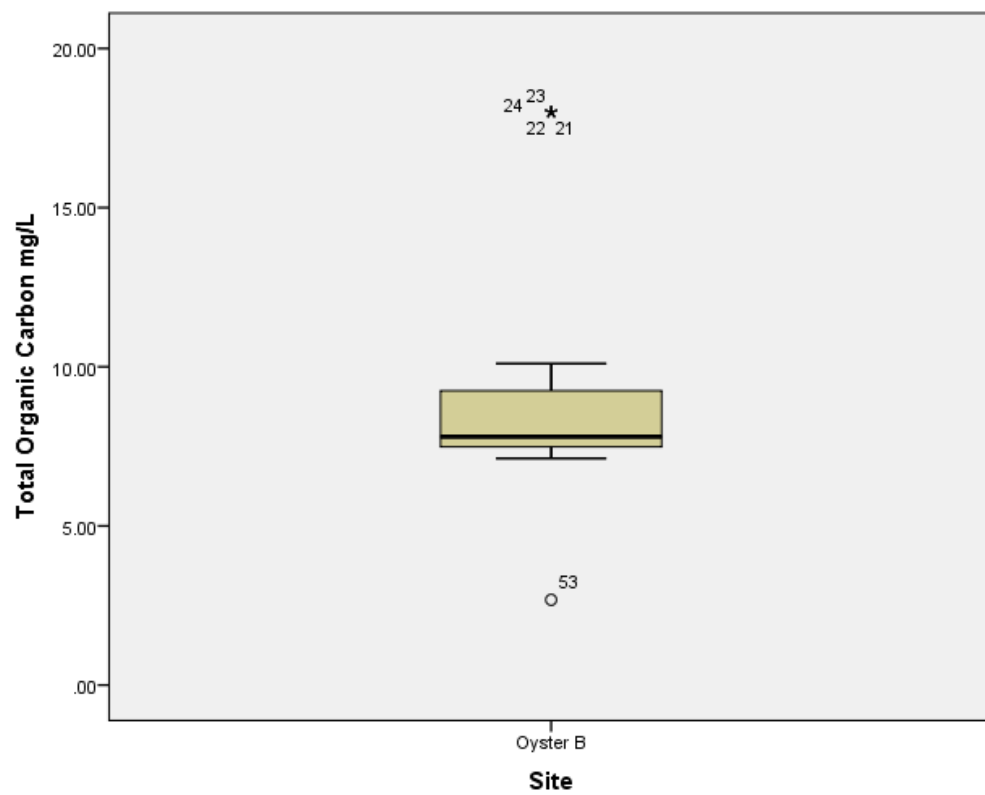
## GOMA Analytical Round Robin #8



## GOMA Analytical Round Robin #8



## GOMA Analytical Round Robin #8



## GOMA Analytical Round Robin #8

