



Statistical analysis and summary of Field Round Robin #5 – a data comparability study

**Report prepared by Raymond E. Leary
September 2012**

Samples collected April 24, 2012
near Lake Pontchartrain at Bayous Cane and Castine
in St. Tammany Parish, LA



Figure 1. Bayous Cane and Castine



25 September 2012

Field Round Robin #5
Slidell, LA – April 24, 2012
Field Round Robin #5
Report on findings

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 chose to carry out round robins to assess the variability and then use subsequent discussions to help improve data comparability. For the Field Round Robins, two areas were identified that may lead to a lack of data comparability: (1) measurements taken while in the field (= field measurements) and (2) samples collected (= water samples). The second part focuses on the variability in data reported by laboratories that might result from differences in how the samples were collected. In the case of these field round robins, the samplers are the focus.

This field round robin was hosted by the Louisiana Department of Environmental Quality on 24 April 2012 near Lake Pontchartrain at Bayous Cane and Castine in St. Tammany, Louisiana. Samplers from all five Gulf of Mexico States were represented. A total of five sampling groups (see Table 1 below) participated in the exercise. The data collected were graphed and statistically analyzed for significant differences in variability.

Differences in defined sample depths, as well as those in calibration standards were not examined in this round robin, due to little variability noted from these items of interest in previous round robins.

Methods:

Participating sampling groups are listed in alphabetical order in Table 1. Samples were collected from Bayous Cane and Castine in St. Tammany, Louisiana. First, each sampling group collected three discrete field measurements at Bayou Cane. All sampling groups were asked to carry out their routine field measurements. The measurements were taken at two set depths (0.3m from the surface and 0.1m above the bottom). Each sampling group took a measurement at each depth, removed the meter from the water, and then reinserted the meter. The sampling groups took the following field measurements: dissolved oxygen, temperature, specific conductance, and pH. This was repeated two more times to give three measurements at each depth.

The sampling groups then participated in the sample collection portion. Samples were taken from surface waters only. For water samples, sampling



Field Round Robin #5
Slidell, LA – April 24, 2012

groups collected and split water samples from a set depth of 0.3m and prepared them for three different analytes (turbidity, total Kjeldahl nitrogen, and orthophosphate). For turbidity, the water was neither acid-preserved nor filtered. For total Kjeldahl nitrogen, the water was acid-preserved but not filtered. For orthophosphate, the water was not acid preserved, but it was filtered. In this round robin, all groups acidified their total Kjeldahl nitrogen, however not all sampling groups field-filtered their orthophosphate samples. Depending on the sampling gear (bucket, Van-Dorn, bailer, or grab sample) used to take the samples, one to three separate water samples were taken yielding three samples for each analyte. Each water sample was used to prepare a single bottle for each of the three analytes. The water samples were then placed in a cooler and iced. These procedures for field measurements, sample collection, preservation, and shipment were then repeated at Bayou Castine. The coolers were delivered the next day to the Florida Department of Environmental Protection's Central Laboratory for analyses.

Agency	Sampling portion	Field measurement portion
Alabama Department of Environmental Management	✓✓	✓✓
Florida Department of Environmental Protection	✓	✓
Louisiana Department of Environmental Quality	✓✓	✓✓
Mississippi Department of Environmental Quality	✓✓	✓
Texas Commission on Environmental Quality	✓	✓

Table 1. Sampling groups who participated in field round robin #5. Each check mark represents an individual from that agency that participated in a given portion of the field round robin. Note: MDEQ had two sampling groups for Bayou Castine only.

The data values from the sampling and field-measurement portions were graphed. Data were analyzed using statistical method 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 sampling groups was measured by calculating F-pseudosigma, which approximates the standard deviation but without the assumption of normal distribution. In addition, %F-pseudosigma was calculated, which is equivalent to % relative standard deviation under normal distributions. In order to evaluate inter-group variability, Z-values were calculated, the average of which was used to rate the sample-groups' 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. It is important to note that although this system of rating will be used, as the groups' precision increases; the Z-values can become inflated, making comparable values appear to be non-comparable.



Field Round Robin #5
Slidell, LA – April 24, 2012

Sampling groups were anonymized by assigning letter designations. The identities of the samplers are not revealed to others, so that samplers do not feel judged by their results. 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 sampling programs on their results.

Results and discussion:

Bayou Cane - Field-measurement portion: The following measurements were taken: dissolved oxygen, temperature, conductivity, and pH. Sampling groups were allowed time to get prepared. Once all sampling groups were ready, they were told to wade out to roughly waist-deep and take their readings as they would normally do in the field. All sampling groups reported that they passed their post calibration verification after the round robin. For all analyses, N = 21.

Dissolved Oxygen. All values were within acceptable ranges for both surface and bottom waters. However, the %F-pseudostigma for bottom waters was quite large, indicating a lack of precision in such hypoxic waters. The accuracy ranges for the instruments were: HydroLab = +/- 0.1 and YSI = +/- 0.2 mg/L. See Figures 2 & 3 for scatter-plots of values obtained by individual sampling groups. See Tables 2 & 3 for F-pseudostigma values and summary statistics.

	F-pseudostigma	%F-pseudostigma	Median	Range
Location				
Surface	0.52	12.12%	4.25	1.14
Bottom	0.71	51.14%	1.38	1.90

Table 2. F-pseudostigma values for dissolved oxygen.

Bayou Cane Dissolved Oxygen

Group ID	Instrument	Surface			Bottom		
		Group Median	Range	Mean Z-value	Group Median	Range	Mean Z-value
A	HydroLab	4.25	0.34	0.17	0.84	0.61	0.54
B	HydroLab	4.59	0.49	0.48	1.33	0.10	0.05
C	HydroLab	4.66	0.40	0.70	1.21	0.74	0.27
D	HydroLab	3.83	0.17	0.84	2.22	0.33	1.05
E	YSI	4.75	0.47	0.80	1.62	0.51	0.18
F	YSI	4.09	0.30	0.42	1.86	0.70	0.91
G	YSI	4.16	0.84	0.12	0.73	0.23	0.97

Table 3. Summary statistics and Z-values by group for dissolved oxygen.

Field Round Robin #5
Slidell, LA – April 24, 2012

Bayou Cane, Surface Dissolved Oxygen

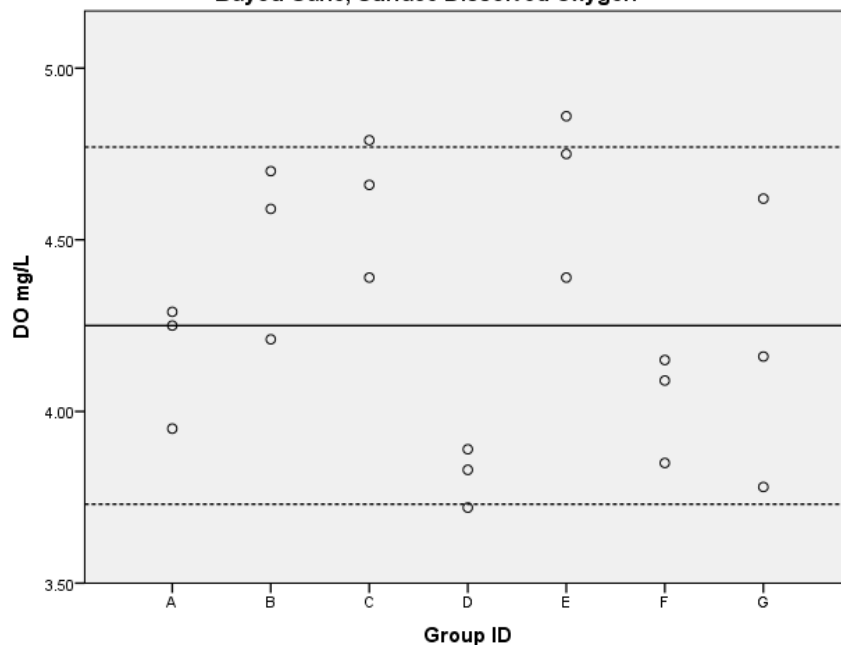


Figure 2. Scatter-plot of dissolved oxygen values obtained by seven sampling groups at 0.3m from the surface. The solid line indicates the overall median, and the dashed lines indicate +/- 1 F-pseudostandard deviation.

Bayou Cane, Bottom Dissolved Oxygen

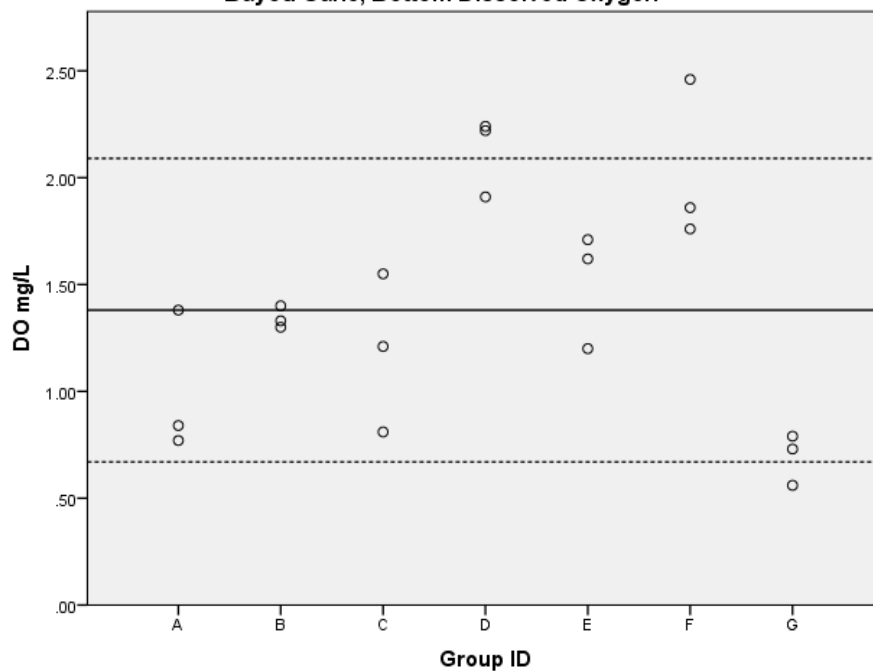


Figure 3. Scatter-plot of dissolved oxygen values obtained by seven sampling groups at 0.1m from the bottom. The solid line indicates the overall median, and the dashed lines indicate +/- 1 F-pseudostandard deviation.



Field Round Robin #5
Slidell, LA – April 24, 2012

Temperature. All values were within acceptable ranges for surface water. However, for bottom water, Group D's results were statistical outliers, all other were within acceptable ranges. The %F-pseudosigma values for both surface and bottom waters were small, indicating a high degree of precision among sampling groups. The accuracy ranges for the instruments were: HydroLab = +/- 0.1 and YSI = +/- 0.15°C. See Figures 4 & 5 for scatter-plots of values obtained by individual sampling groups. See Tables 4 & 5 for F-pseudosigma values and summary statistics.

	F-pseudosigma	%F-pseudosigma	Median	Range
Location				
Surface	0.30	1.37%	22.01	0.73
Bottom	0.50	2.52%	19.97	2.02

Table 4. F-pseudosigma values for temperature.

Bayou Cane Temperature

Group ID	Instrument	Surface			Bottom		
		Group Median	Range	Mean Z-value	Group Median	Range	Mean Z-value
A	HydroLab	22.05	0.26	0.11	19.71	0.13	0.45
B	HydroLab	22.24	0.06	0.79	20.38	0.05	0.83
C	HydroLab	22.24	0.02	0.77	20.14	0.46	0.27
D	HydroLab	21.90	0.08	0.41	21.17	0.30	2.44
E	YSI	22.04	0.06	0.10	19.94	0.42	0.30
F	YSI	21.73	0.16	0.87	19.98	0.66	0.37
G	YSI	21.73	0.20	1.11	19.35	0.03	1.25

Table 5. Summary statistics and Z-values by group for dissolved oxygen.

Field Round Robin #5
Slidell, LA – April 24, 2012

Bayou Cane, Surface Temperature

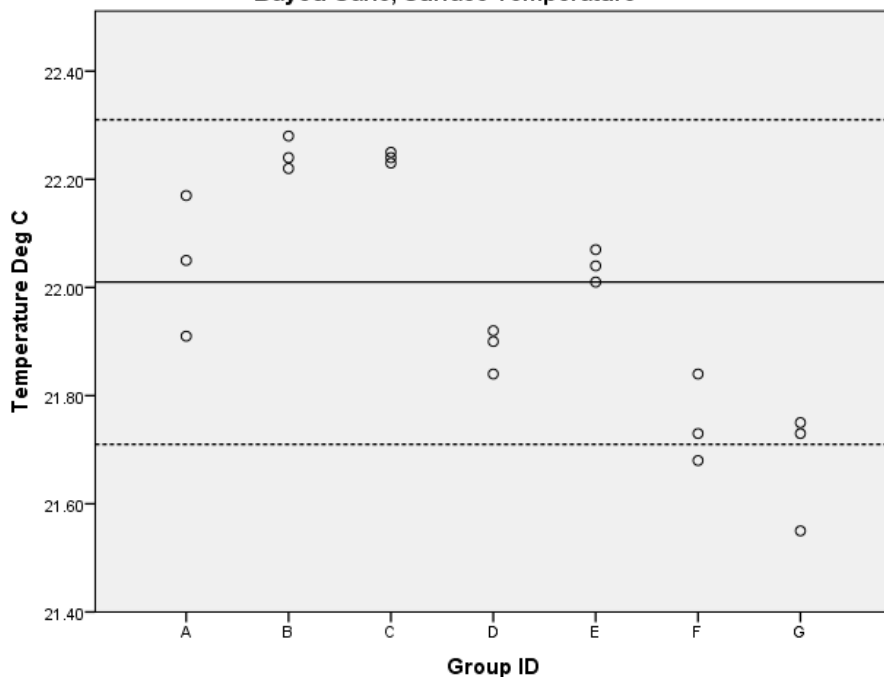


Figure 4. Scatter-plot of temperature values obtained by seven sampling groups at 0.3m from the surface. The solid line indicates the overall median, and the dashed lines indicate +/- 1 F-pseudosigma.

Bayou Cane, Bottom Temperature

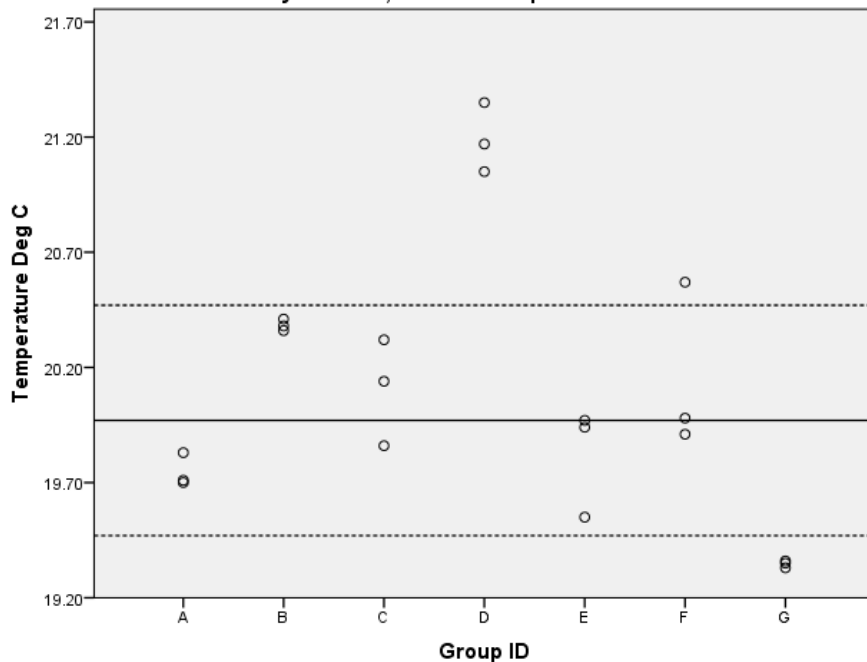


Figure 5. Scatter-plot of temperature values obtained by seven sampling groups at 0.1m from the bottom. The solid line indicates the overall median, and the dashed lines indicate +/- 1 F-pseudosigma.



Field Round Robin #5
Slidell, LA – April 24, 2012

Specific Conductance. All values were within acceptable ranges for surface water. However, for bottom water, Group D's results were statistical outliers, all others were within acceptable ranges. The %F-pseudostigma values for both surface and bottom waters were small, indicating a high degree of precision among sampling groups. The accuracy ranges for the instruments were: HydroLab and YSI = +/- 0.5%. See Figures 6 & 7 for scatter-plots of values obtained by individual sampling groups. See Tables 6 & 7 for F-pseudostigma values and summary statistics.

	F-pseudostigma	%F-pseudostigma	Median	Range
Location				
Surface	7.6	3.39%	225.0	29.0
Bottom	9.0	7.14%	126.1	45.1

Table 6. F-pseudostigma values for specific conductance.

Bayou Cane Specific Conductance

Group ID	Instrument	Surface			Bottom		
		Group Median	Range	Mean Z-value	Group Median	Range	Mean Z-value
A	HydroLab	218.00	7.00	1.23	121.00	1.00	0.60
B	HydroLab	226.20	3.90	0.21	126.10	2.20	0.01
C	HydroLab	226.90	2.00	0.27	121.60	3.30	0.61
D	HydroLab	216.50	11.00	1.43	147.70	27.20	2.56
E	YSI	232.00	4.00	0.83	133.00	9.00	0.80
F	YSI	225.00	10.00	0.00	130.00	30.00	1.54
G	YSI	224.00	21.00	0.96	124.00	1.00	0.27

Table 7. Summary statistics and Z-values by group for specific conductance.

Field Round Robin #5
Slidell, LA – April 24, 2012

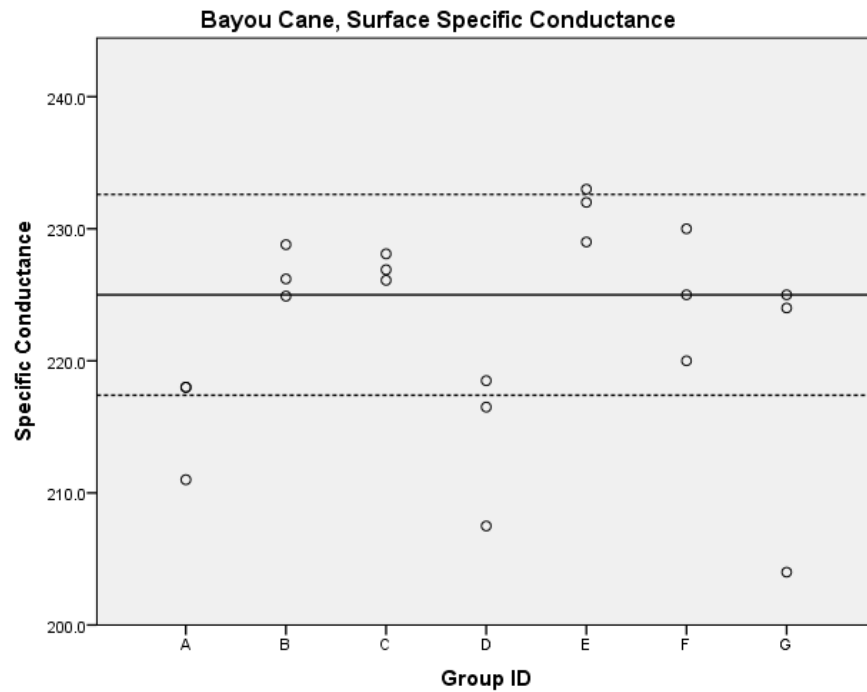


Figure 6. Scatter-plot of specific conductance values obtained by seven sampling groups at 0.3m from the surface. The solid line indicates the overall median, and the dashed lines indicate ± 1 F-pseudostandard deviation.

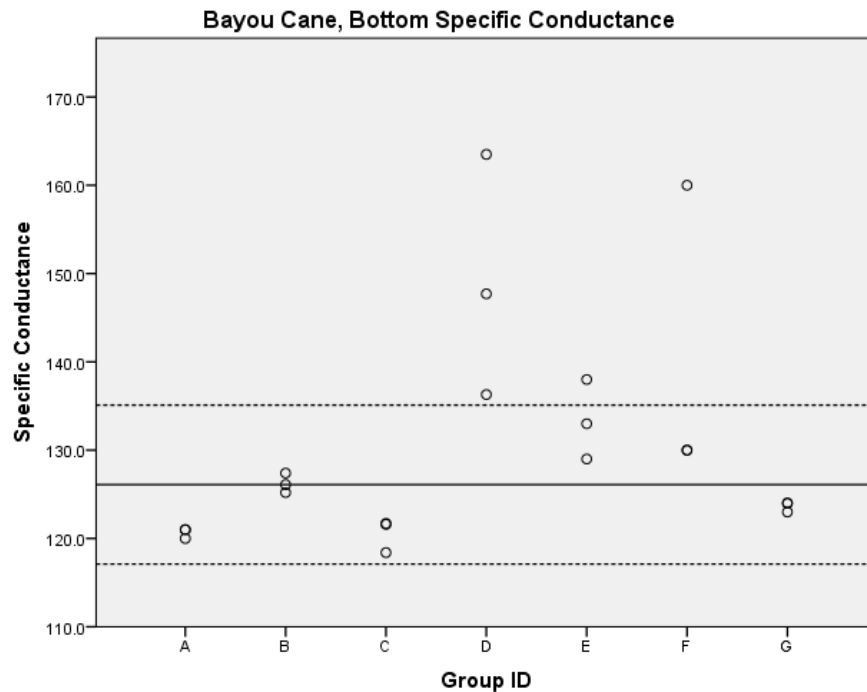


Figure 7. Scatter-plot of specific conductance values obtained by seven sampling groups at 0.1m from the bottom. The solid line indicates the overall median, and the dashed lines indicate ± 1 F-pseudostandard deviation.



Field Round Robin #5
Slidell, LA – April 24, 2012

pH. All values were within acceptable ranges for both surface and bottom waters. The %F-pseudosigma values for both surface and bottom waters were small, indicating a high degree of precision among sampling groups. The accuracy ranges for the instruments were: HydroLab and YSI = +/- 0.2 SU. See Figures 8 & 9 for scatter-plots of values obtained by individual sampling groups. See Tables 8 & 9 for F-pseudosigma values and summary statistics.

	F-pseudosigma	%F-pseudosigma	Median	Range
Location				
Surface	0.36	5.42%	6.66	1.22
Bottom	0.42	6.68%	6.28	1.13

Table 8. F-pseudosigma values for pH.

Bayou Cane pH

Group ID	Instrument	Surface			Bottom		
		Group Median	Range	Mean Z-value	Group Median	Range	Mean Z-value
A	HydroLab	6.39	0.03	0.76	5.98	0.02	0.71
B	HydroLab	6.88	0.04	0.61	6.77	0.19	1.24
C	HydroLab	6.67	0.35	0.30	6.59	0.15	0.78
D	HydroLab	6.11	0.08	1.55	5.81	0.11	1.08
E	YSI	7.05	0.38	1.16	6.46	0.12	0.44
F	YSI	6.68	0.05	0.05	6.28	0.12	0.08
G	YSI	6.66	0.07	0.06	6.28	0.01	0.01

Table 9. Summary statistics and Z-values by group for pH.



Field Round Robin #5
Slidell, LA – April 24, 2012

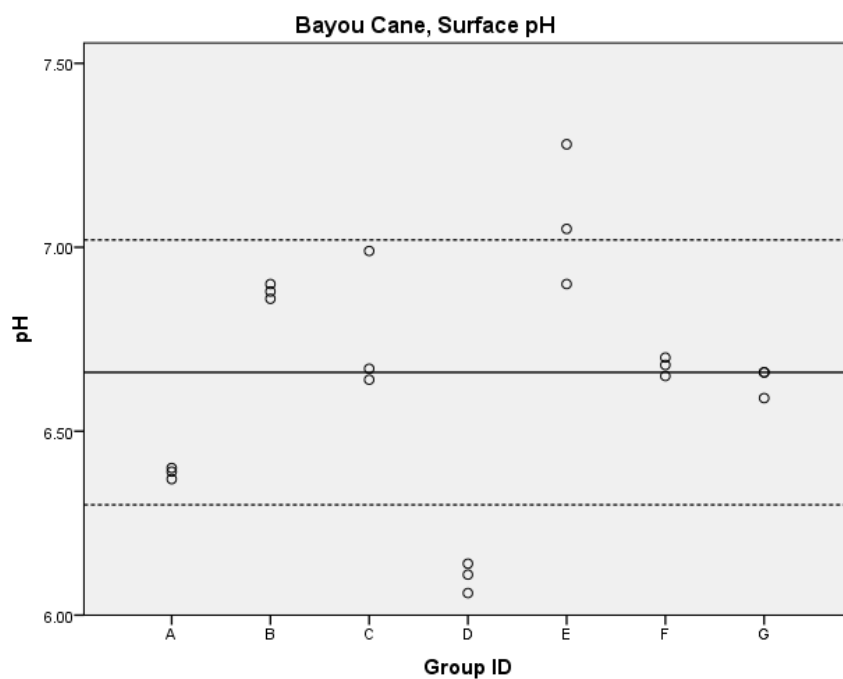


Figure 8. Scatter-plot of pH values obtained by seven sampling groups at 0.3m from the surface. The solid line indicates the overall median, and the dashed lines indicate ± 1 F-pseudosigma.

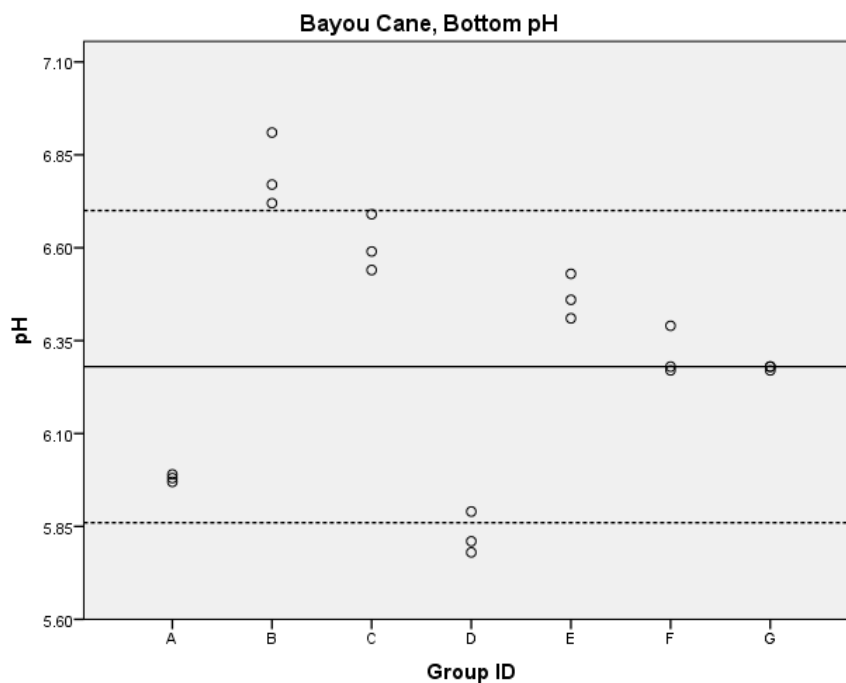


Figure 9. Scatter-plot of pH values obtained by seven sampling groups at 0.1m from the bottom. The solid line indicates the overall median, and the dashed lines indicate ± 1 F-pseudosigma.



Field Round Robin #5
Slidell, LA – April 24, 2012

Bayou Castine - Field-measurement portion: The following measurements were taken: dissolved oxygen, temperature, conductivity, and pH. Sampling groups were lined-up along a pier, put their sondes in the water to allow their equipment to stabilize, and told to take their readings all at one time. All sampling groups reported that they passed their post calibration verification after the round robin. For all analyses, N = 21.

Dissolved Oxygen. All Z-values were within acceptable ranges for both surface and bottom waters, with the exception of Group B for surface water. However, the %F-pseudosigma for both depths was quite small, indicating a high degree of precision among sampling groups. As mentioned earlier, due to the high precision, even small changes in the results will hyper-inflate the Z-values. The accuracy ranges for the instruments were: HydroLab = +/- 0.1 and YSI = +/- 0.2 mg/L. The range of values for surface water was within the equipments' accuracy range. See Figures 10 & 11 for scatter-plots of values obtained by individual sampling groups. See Tables 10 & 11 for F-pseudosigma values and summary statistics.

	F-pseudosigma	%F-pseudosigma	Median	Range
Location				
Surface	0.05	0.64%	8.06	0.19
Bottom	0.16	2.13%	7.73	0.50

Table 10. F-pseudosigma values for dissolved oxygen.

Bayou Cane Dissolved Oxygen

Group ID	Instrument	Surface			Bottom		
		Group Median	Range	Mean Z-value	Group Median	Range	Mean Z-value
A	HydroLab	8.06	0.09	0.47	7.79	0.10	0.21
B	HydroLab	8.16	0.01	2.07	7.77	0.08	0.25
C	HydroLab	8.05	0.03	0.27	7.53	0.10	1.17
D	HydroLab	8.11	0.04	1.27	7.82	0.09	0.75
E	YSI	8.05	0.07	0.13	7.86	0.04	0.85
F	YSI	8.08	0.08	0.00	7.70	0.12	0.40
G	YSI	8.04	0.02	0.40	7.58	0.25	1.13

Table 11. Summary statistics and Z-values by group for dissolved oxygen.

Field Round Robin #5
Slidell, LA – April 24, 2012

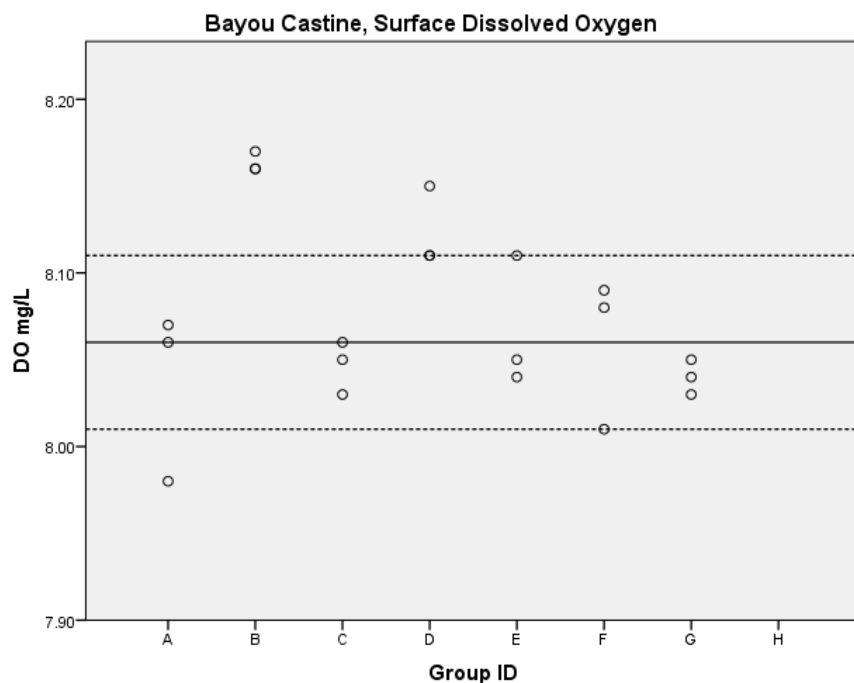


Figure 10. Scatter-plot of dissolved oxygen values obtained by seven sampling groups at 0.3m from the surface. The solid line indicates the overall median, and the dashed lines indicate ± 1 F-pseudosigma.

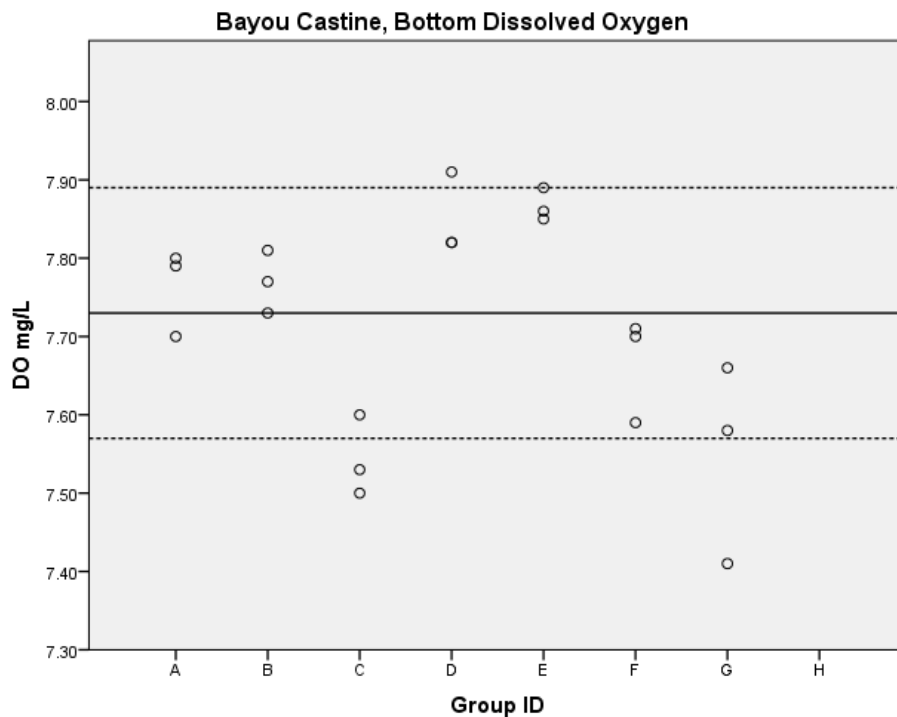


Figure 11. Scatter-plot of dissolved oxygen values obtained by seven sampling groups at 0.1m from the bottom. The solid line indicates the overall median, and the dashed lines indicate ± 1 F-pseudosigma.



Field Round Robin #5
Slidell, LA – April 24, 2012

Temperature. All values were within acceptable ranges for both surface and bottom waters. The %F-pseudosigma values for both surface and bottom waters were very small, indicating a high degree of precision among sampling groups. The accuracy ranges for the instruments were: HydroLab = +/- 0.1 and YSI = +/- 0.15°C. The range of results for the bottom waters was approaching the equipments' accuracy range. See Figures 12 & 13 for scatter-plots of values obtained by individual sampling groups. See Tables 12 & 13 for F-pseudosigma values and summary statistics.

	F-pseudosigma	%F-pseudosigma	Median	Range
Location				
Surface	0.40	1.67%	24.11	0.94
Bottom	0.21	0.92%	23.39	0.42

Table 12. F-pseudosigma values for temperature.

Bayou Castine Temperature

Group ID	Instrument	Surface			Bottom		
		Group Median	Range	Mean Z-value	Group Median	Range	Mean Z-value
A	HydroLab	24.19	0.15	0.19	23.40	0.04	0.02
B	HydroLab	24.51	0.05	1.03	23.49	0.08	0.38
C	HydroLab	24.31	0.08	0.45	23.43	0.04	0.19
D	HydroLab	24.16	0.13	0.03	23.41	0.04	0.10
E	YSI	23.96	0.30	0.46	23.32	0.04	0.37
F	YSI	23.63	0.03	1.21	23.09	0.03	1.41
G	YSI	23.73	0.05	0.99	23.10	0.06	1.35

Table 13. Summary statistics and Z-values by group for dissolved oxygen.



Field Round Robin #5
Slidell, LA – April 24, 2012

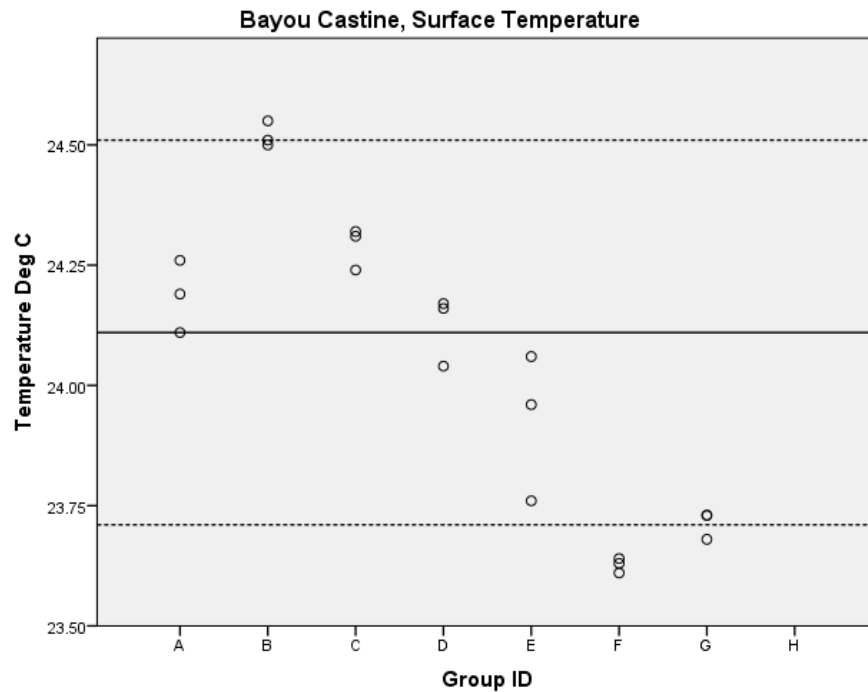


Figure 12. Scatter-plot of temperature values obtained by seven sampling groups at 0.3m from the surface. The solid line indicates the overall median, and the dashed lines indicate ± 1 F-pseudosigma.

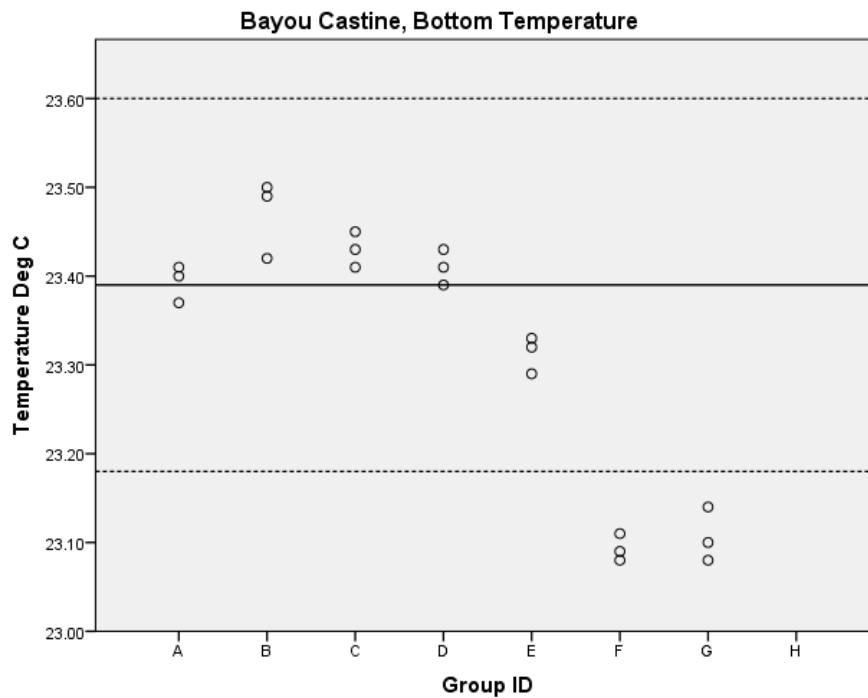


Figure 13. Scatter-plot of temperature values obtained by seven sampling groups at 0.1m from the bottom. The solid line indicates the overall median, and the dashed lines indicate ± 1 F-pseudosigma.



Field Round Robin #5
Slidell, LA – April 24, 2012

Specific Conductance. Most values were within acceptable ranges for surface water. However, both Groups A and D's results were statistical outliers for both depths. The %F-pseudosigma values for both surface and bottom waters were quite small, indicating a high degree of precision among sampling groups. The accuracy ranges for the instruments were: HydroLab and YSI = +/- 0.5%. The precision of the sampling groups was within the accuracy range for the equipment. See Figures 14 & 15 for scatter-plots of values obtained by individual sampling groups. See Tables 14 & 15 for F-pseudosigma values and summary statistics.

	F-pseudosigma	%F-pseudosigma	Median	Range
Location				
Surface	15.6	0.38%	4077.0	209.0
Bottom	7.2	0.18%	4073.0	191.0

Table 14. F-pseudosigma values for specific conductance.

Bayou Castine Specific Conductance

Group ID Instrument		Surface			Bottom		
		Group Median	Range	Mean Z- value	Group Median	Range	Mean Z- value
A	HydroLab	3944.0	20.0	8.65	3934.0	2.0	19.31
B	HydroLab	4106.0	16.0	1.56	4081.0	5.0	1.16
C	HydroLab	4078.0	22.0	0.06	4069.0	9.0	0.79
D	HydroLab	4129.0	18.0	3.42	4123.0	3.0	6.90
E	YSI	4083.0	6.0	0.26	4074.0	3.0	0.00
F	YSI	4074.0	2.0	0.15	4070.0	1.0	0.37
G	YSI	4074.0	2.0	0.19	4074.0	2.0	0.14

Table 15. Summary statistics and Z-values by group for specific conductance.

Field Round Robin #5
Slidell, LA – April 24, 2012

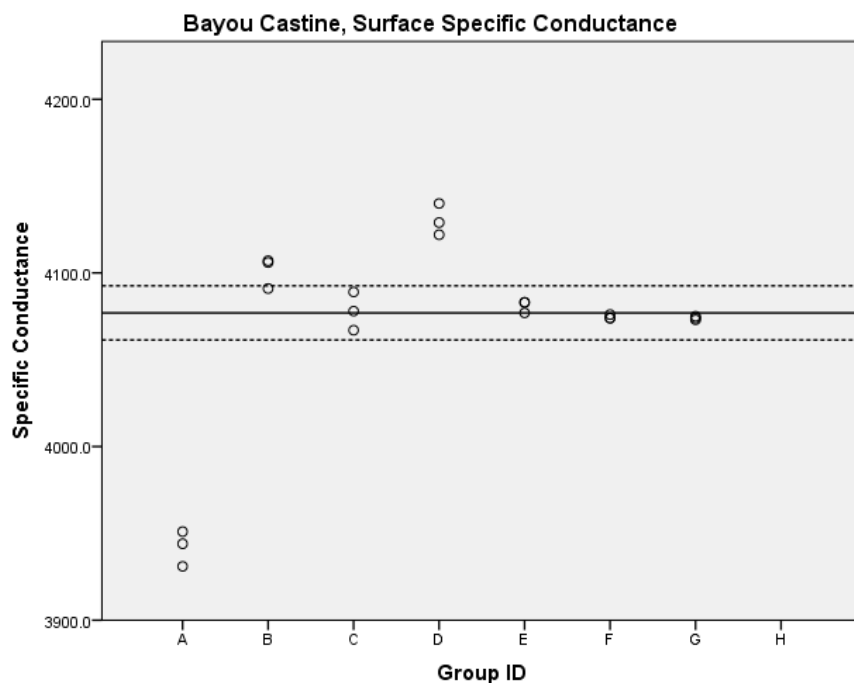


Figure 14. Scatter-plot of specific conductance values obtained by seven sampling groups at 0.3m from the surface. The solid line indicates the overall median, and the dashed lines indicate ± 1 F-pseudosigma.

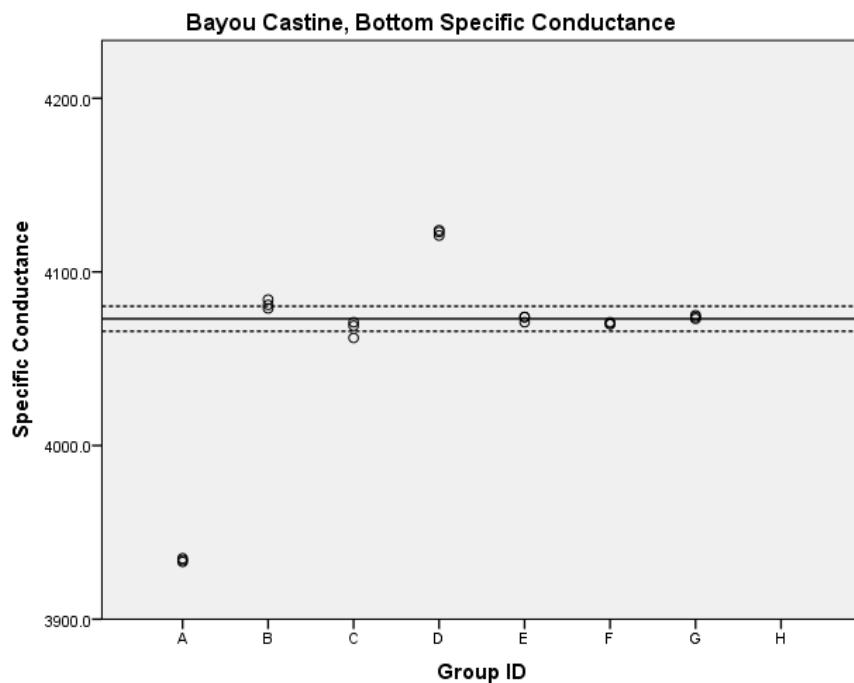


Figure 15. Scatter-plot of specific conductance values obtained by seven sampling groups at 0.1m from the bottom. The solid line indicates the overall median, and the dashed lines indicate ± 1 F-pseudosigma.



Field Round Robin #5
Slidell, LA – April 24, 2012

pH. All values were within acceptable ranges for both surface and bottom waters, with the exception of Group B's results which were statistical outliers. The %F-pseudosigma values for both surface and bottom waters were small, indicating a high degree of precision among sampling groups. The accuracy ranges for the instruments were: HydroLab and YSI = +/- 0.2 SU. For bottom waters, the range of results was within the equipments' accuracy range. See Figures 16 & 17 for scatter-plots of values obtained by individual sampling groups. See Tables 16 & 17 for F-pseudosigma values and summary statistics.

	F-pseudosigma	%F-pseudosigma	Median	Range
Location				
Surface	0.19	2.54%	7.29	0.85
Bottom	0.13	1.85%	7.20	0.35

Table 16. F-pseudosigma values for pH.

Bayou Castine pH							
Group ID	Instrument	Surface			Bottom		
		Group Median	Range	Mean Z-value	Group Median	Range	Mean Z-value
A	HydroLab	7.29	0.01	0.02	7.15	0.02	0.38
B	HydroLab	6.79	0.21	2.79	6.93	0.03	2.05
C	HydroLab	7.39	0.14	0.63	7.23	0.05	0.31
D	HydroLab	7.05	0.09	1.32	7.04	0.01	1.26
E	YSI	7.23	0.06	0.35	7.22	0.03	0.08
F	YSI	7.31	0.04	0.07	7.20	0.00	0.00
G	YSI	7.33	0.02	0.18	7.21	0.01	0.10

Table 17. Summary statistics and Z-values by group for pH.

Field Round Robin #5
Slidell, LA – April 24, 2012

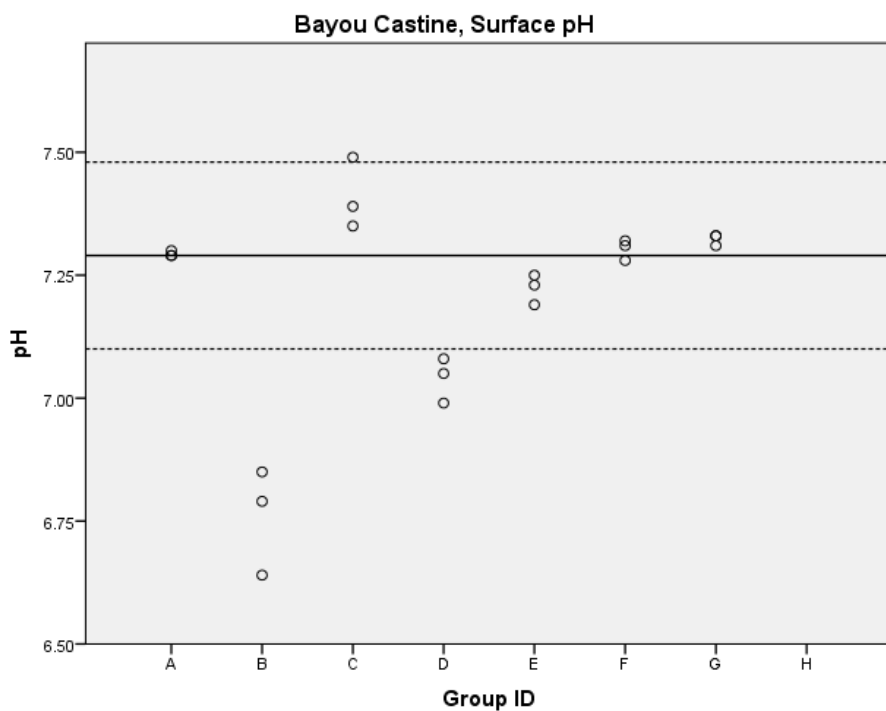


Figure 16. Scatter-plot of pH values obtained by seven sampling groups at 0.3m from the surface. The solid line indicates the overall median, and the dashed lines indicate ± 1 F-pseudosigma.

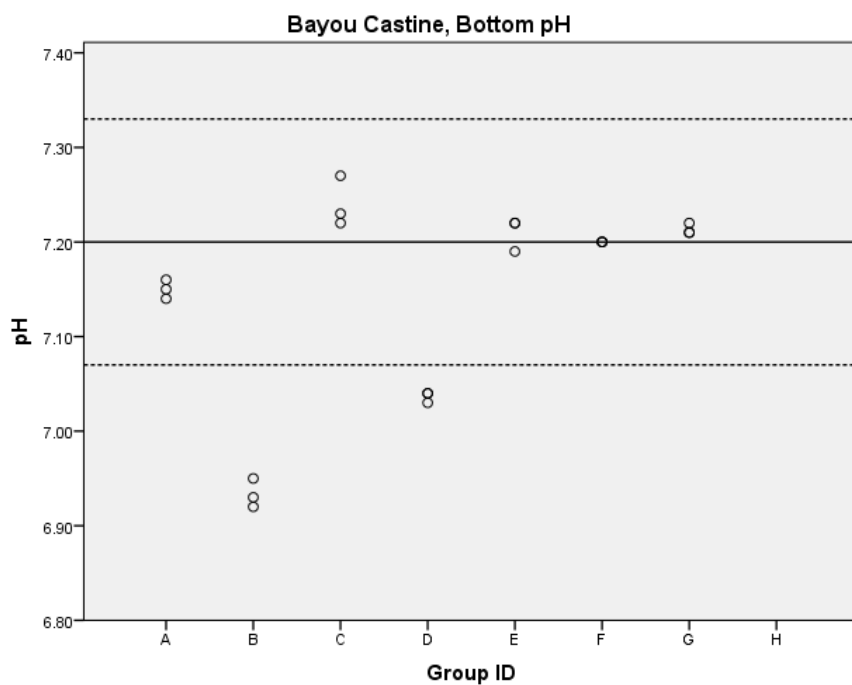


Figure 17. Scatter-plot of pH values obtained by seven sampling groups at 0.1m from the bottom. The solid line indicates the overall median, and the dashed lines indicate ± 1 F-pseudosigma.



Field Round Robin #5
Slidell, LA – April 24, 2012

Sampling portion: The following laboratory analyses were conducted on samples collected by the sampling groups: turbidity, total Kjeldahl nitrogen, and orthophosphate. For analyses at Bayou Cane, N = 21; at Bayou Castine, N = 24.

Turbidity: All values were within acceptable ranges for both Bayou Cane and Bayou Castine, with the exception of Group C, which was a statistical outlier at Bayou Cane. However, the %F-pseudosigma for Bayou Cane was large, indicating a lack of precision when sampling in situ (i.e., wading into the water when a structure or boat is not available to sample from). In addition, Group C was the last to sample at Bayou Cane, and consequently was sampling in waters that had been stirred up by the other sampling groups. The laboratory method precision range was +/- 10%. See Figures 18 & 19 for scatter-plots of values obtained by individual sampling groups. See Tables 18 & 19 for F-pseudosigma values and summary statistics.

	F-pseudosigma	%F-pseudosigma	Median	Range
Location				
Cane	2.6	19.96%	13.0	10.0
Castine	0.7	5.49%	13.5	4.4

Table 18. F-pseudosigma values for turbidity.

Turbidity							
Group ID	Sampling Gear*	Bayou Cane			Bayou Castine		
		Group Median	Range	Mean Z-value	Group Median	Range	Mean Z-value
A	Bucket	12.0	1.0	0.51	14.0	0.0	0.71
B	Bucket	15.0	2.0	0.77	13.0	0.0	0.71
C	Bucket	19.0	1.0	2.44	12.0	1.0	1.67
D	Van-Dorn	13.0	1.0	0.13	14.0	1.0	0.24
E	Van-Dorn	11.0	1.0	0.90	13.0	0.0	0.71
F	Grab	12.0	2.0	0.38	14.0	0.0	0.71
G	Grab	12.0	4.0	0.13	13.0	4.4	1.86
H	Van-Dorn				14.0	0.0	0.71

Table 19. Summary statistics and Z-values by group for turbidity.

* For Van-Dorns, one sample was collected then split; for grabs and buckets, three separate samples were collected. Sampling Groups F & G used a Van-Dorn at Bayou Castine.

Field Round Robin #5
Slidell, LA – April 24, 2012

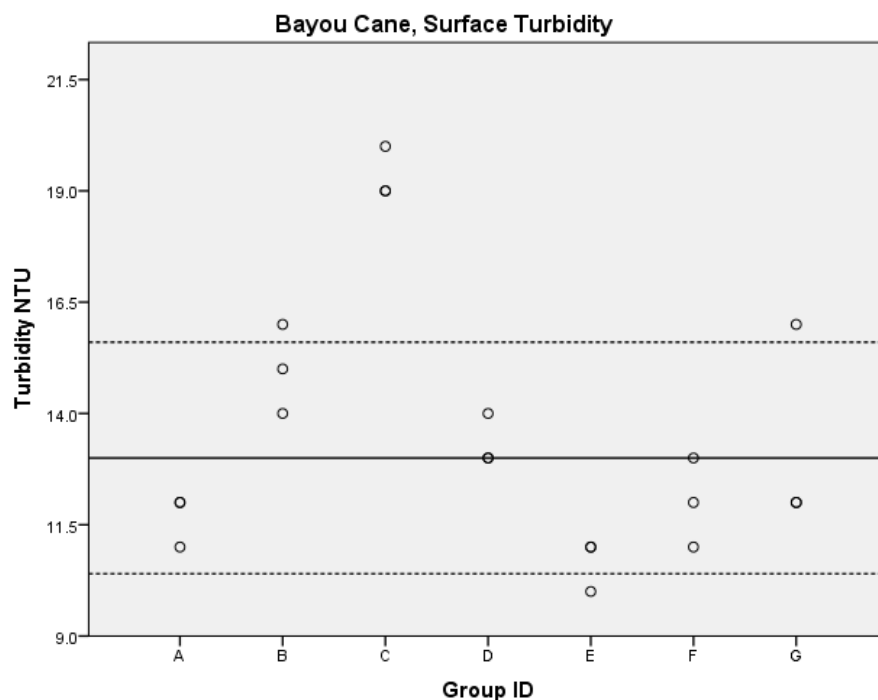


Figure 18. Scatter-plot of turbidity values obtained by seven sampling groups at 0.3m from the surface at Bayou Cane. The solid line indicates the overall median, and the dashed lines indicate ± 1 F-pseudosigma.

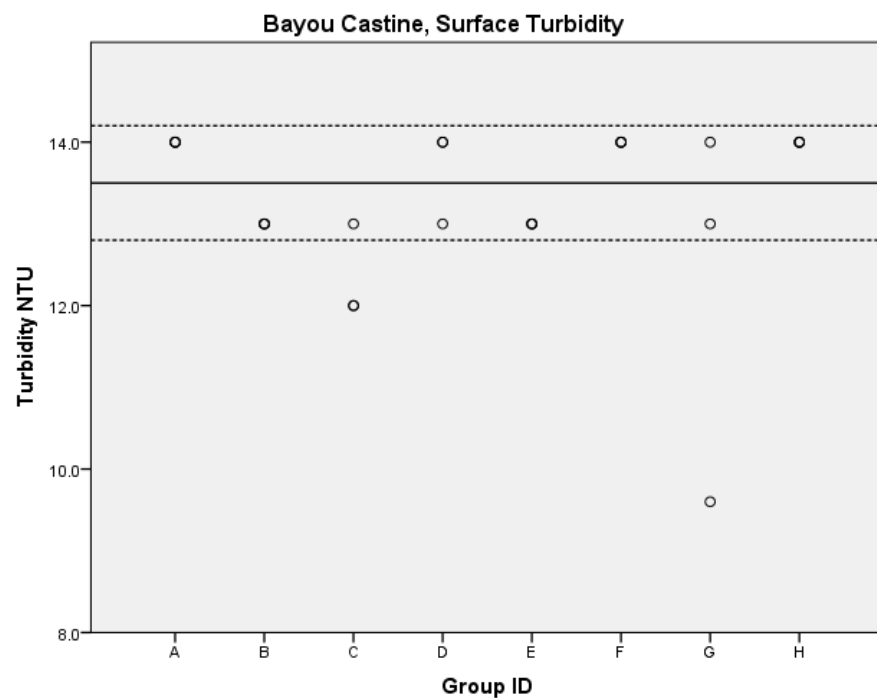


Figure 19. Scatter-plot of turbidity values obtained by eight sampling groups at 0.3m from the surface at Bayou Castine. The solid line indicates the overall median, and the dashed lines indicate ± 1 F-pseudosigma.



Field Round Robin #5
Slidell, LA – April 24, 2012

Total Kjeldahl Nitrogen. All values were within acceptable ranges for both Bayous Cane and Castine. The %F-pseudosigma values for both sites were small, indicating a high degree of precision among sampling groups. The laboratory method precision range was +/- 10%. See Figures 20 & 21 for scatter-plots of values obtained by individual sampling groups. See Tables 20 & 21 for F-pseudosigma values and summary statistics.

	F-pseudosigma	%F-pseudosigma	Median	Range
Location				
Cane	0.09	5.29%	1.30	0.40
Castine	0.06	9.85%	0.64	0.26

Table 20. F-pseudosigma values for total Kjeldahl nitrogen.

Total Kjeldahl Nitrogen

Group ID	Sampling Gear*	Bayou Cane			Bayou Castine		
		Group Median	Range	Mean Z-value	Group Median	Range	Mean Z-value
A	Bucket	1.30	0.10	0.37	0.72	0.11	0.72
B	Bucket	1.20	0.20	1.11	0.65	0.16	0.61
C	Bucket	1.20	0.20	1.11	0.68	0.06	0.56
D	Van-Dorn	1.40	0.10	1.48	0.59	0.04	0.83
E	Van-Dorn	1.20	0.10	0.74	0.56	0.12	1.22
F	Grab	1.30	0.10	0.37	0.69	0.07	0.89
G	Grab	1.30	0.20	0.74	0.64	0.01	0.06
H	Van-Dorn				0.61	0.11	0.11

Table 21. Summary statistics and Z-values by group for total Kjeldahl nitrogen.

* For Van-Dorns, one sample was collected then split; for grabs and buckets, three separate samples were collected. Sampling Groups F & G used a Van-Dorn at Bayou Castine.

Field Round Robin #5
Slidell, LA – April 24, 2012

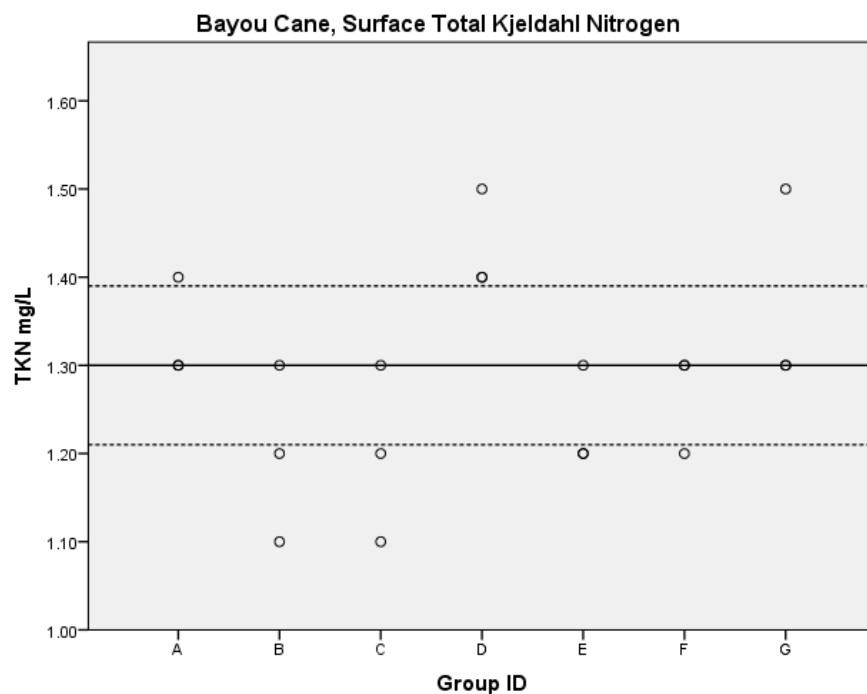


Figure 20. Scatter-plot of total Kjeldahl nitrogen values obtained by seven sampling groups at 0.3m from the surface at Bayou Cane. The solid line indicates the overall median, and the dashed lines indicate ± 1 F-pseudosigma.

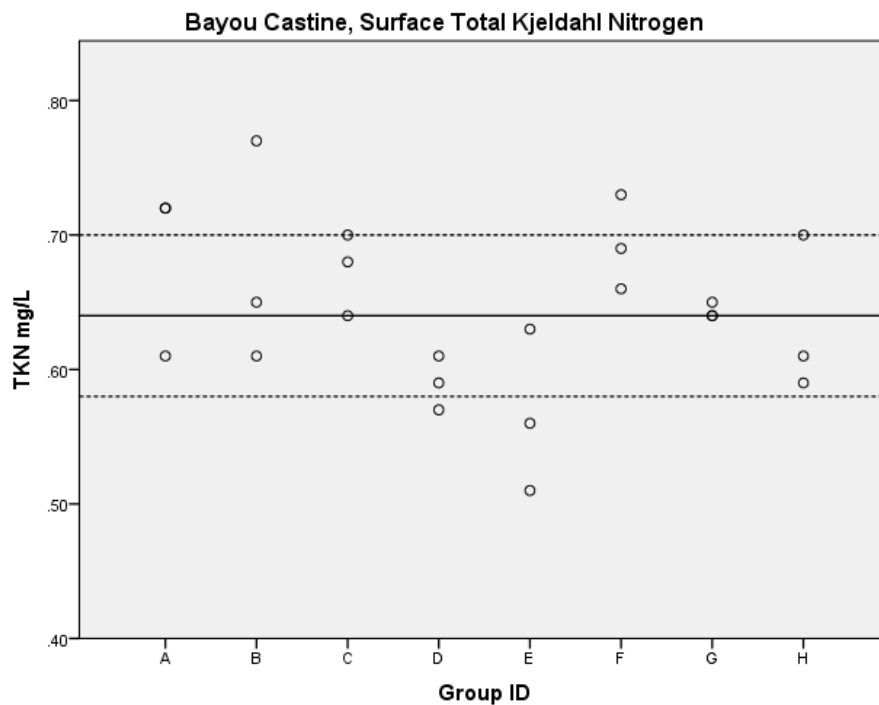


Figure 21. Scatter-plot of total Kjeldahl nitrogen values obtained by eight sampling groups at 0.3m from the surface at Bayou Castine. The solid line indicates the overall median, and the dashed lines indicate ± 1 F-pseudosigma.



Field Round Robin #5
Slidell, LA – April 24, 2012

Orthophosphate. All values were satisfactory or better for both Bayous Cane and Castine, with the exception of Groups B & C at Bayou Castine, which were marginal. The %F-pseudosigma values for both sites were small, indicating a high degree of precision among sampling groups. The laboratory method precision range was +/- 10%. Sample Groups D and H did not field-filter, and the laboratory filtered the samples prior to analyses. See Figures 22 & 23 for scatter-plots of values obtained by individual sampling groups. See Tables 22 & 23 for F-pseudosigma values and summary statistics.

	F-pseudosigma	%F-pseudosigma	Median	Range
Location				
Cane	0.007	5.29%	0.140	0.020
Castine	0.001	3.62%	0.041	0.006

Table 22. F-pseudosigma values for orthophosphate.

Orthophosphate							
Group ID	Sampling Gear*	Bayou Cane			Bayou Castine		
		Group Median	Range	Mean Z-value	Group Median	Range	Mean Z-value
A	Bucket	0.140	0.010	0.48	0.041	0.001	0.33
B	Bailer	0.130	0.010	0.95	0.040	0.002	1.67
C	Bailer	0.140	0.010	0.48	0.043	0.001	1.67
D	Van-Dorn	0.140	0.000	0.00	0.040	0.000	1.00
E	Van-Dorn	0.140	0.010	0.48	0.041	0.001	0.33
F	Grab	0.130	0.000	1.43	0.043	0.004	1.33
G	Grab	0.140	0.010	0.48	0.042	0.002	0.33
H	Van-Dorn				0.042	0.001	0.67

Table 23. Summary statistics and Z-values by group for orthophosphate.

* For Van-Dorns, one sample was collected then split; for grabs and buckets, three separate samples were collected. Sampling Groups F & G used a Van-Dorn at Bayou Castine.



Field Round Robin #5
Slidell, LA – April 24, 2012

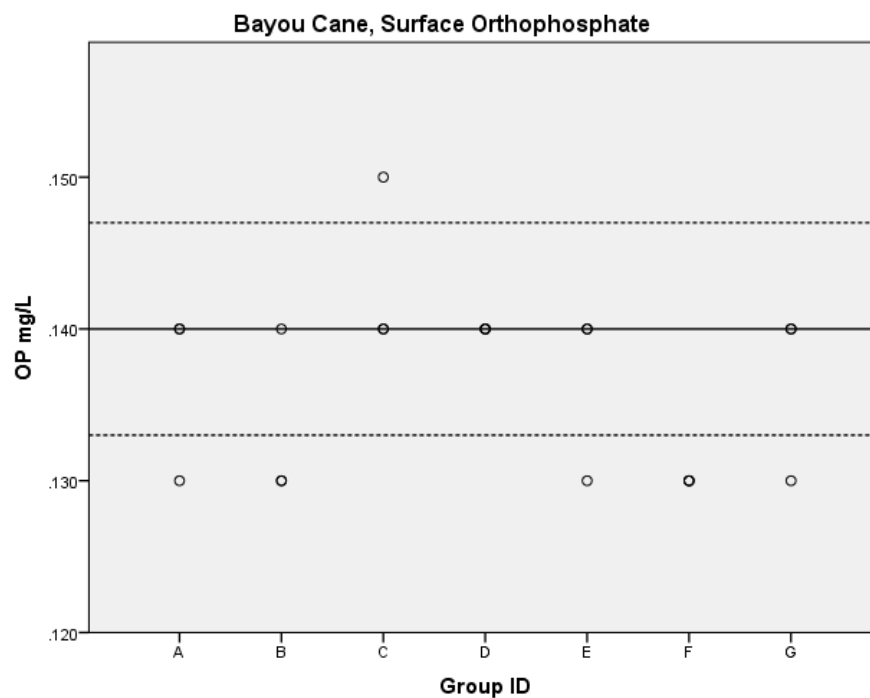


Figure 22. Scatter-plot of orthophosphate values obtained by seven sampling groups at 0.3m from the surface at Bayou Cane. The solid line indicates the overall median, and the dashed lines indicate ± 1 F-pseudosigma.

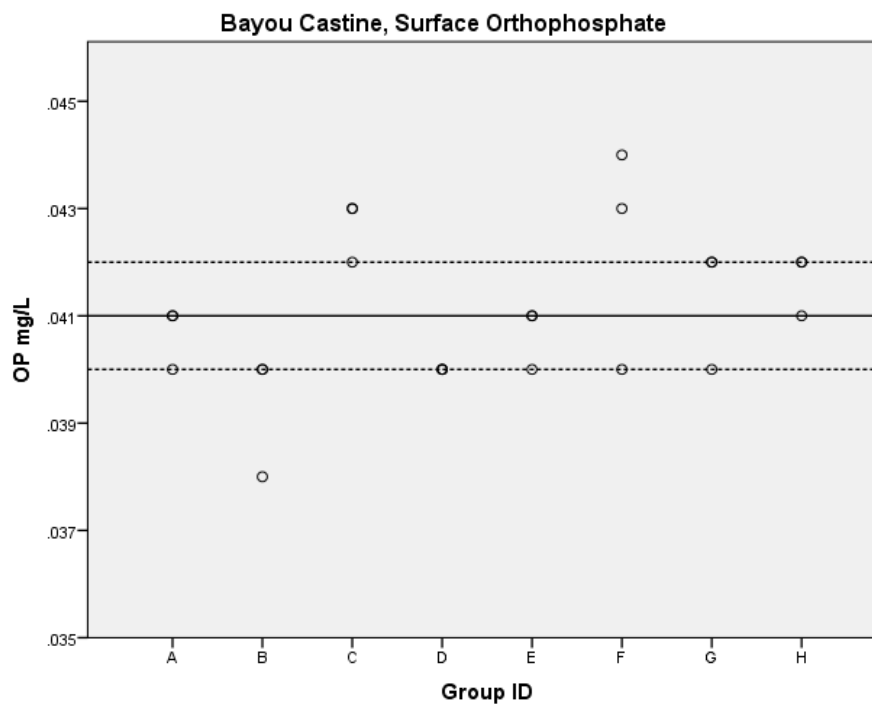


Figure 23. Scatter-plot of orthophosphate values obtained by eight sampling groups at 0.3m from the surface at Bayou Castine. The solid line indicates the overall median, and the dashed lines indicate ± 1 F-pseudosigma.



Field Round Robin #5
Slidell, LA – April 24, 2012

Conclusions

Sampling portion: There was little variability among sampling groups for total Kjeldahl nitrogen (unfiltered, preserved). Therefore, variations in preservation techniques had little influence on results. Orthophosphate (filtered, unpreserved), values were similar, as well. In addition, the lack of field filtering did not have a great influence on the two sampling groups that did not field-filter. Any variation in filtering techniques did not appear to have much influence on the results. Turbidity (unfiltered, unpreserved), data showed the most variability; however this was typically small, with the exception of one sampling group at Bayou Cane who sampled after all others had finished, which caused their values to be large in comparison. Overall, as noted in previous GOMA round robin reports, the filtering and preservation procedures used by the Gulf of Mexico states in general did not appear to cause much variability.

Field-measurement portion: Seven sampling groups from five agencies, representing all five Gulf of Mexico states, participated in this Field Round Robin. The sampling groups measured dissolved oxygen, temperature, conductivity, and pH. There was good agreement among the sampling groups regarding dissolved oxygen and temperature values, whereas pH values were somewhat variable. Specific conductance values were quite variable between sampling groups. However, the range for specific conductance was typically reported within the equipments' (both HydroLab and YSI) accuracy range. Sampling groups who allowed their equipment to stabilize showed decreased variability in their values. At Bayou Cane, the single group of samplers that completed sampling and measuring before all other groups showed higher variability in data values compared to the other groups.

It is recommended that a synthesis paper of the Field Round Robin program be created in order to demonstrate how the Field Round Robin program has improved data comparability among Gulf States.

Recommendations for future round robins: For this round robin, and in the future, efforts will continue to keep all calibration solutions and sondes at room temperature, as this can affect their values. An effort will also be made to keep the time between calibration and measurement equal for all parts of the round robin.

Variations in procedures between states needs to be identified. For example, whether or not samplers rinse sample bottles prior to sampling, the number of times sample bottles are rinsed, and time lapse between the meter entering the water and recording the sample values. In addition, the host state could provide a mock training session. This training session would allow each state to identify differences in their procedures, and discuss the SOPs' pros and cons. After the training session, each sampler could take measurements using the host state's equipment and standard operating procedures.