



## **Statistical analysis and summary of Field Round Robin #6 – a data comparability study**

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

Samples collected June 18, 2012  
From the Gulf of Mexico  
Near Corpus Christi, TX

# GOMA Field Round Robin #6, June 18, 2012 Corpus Christi, TX

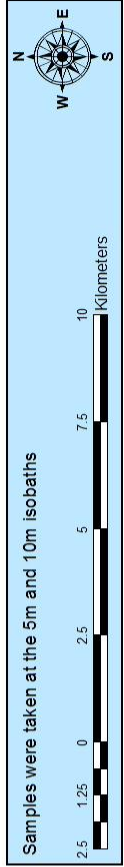
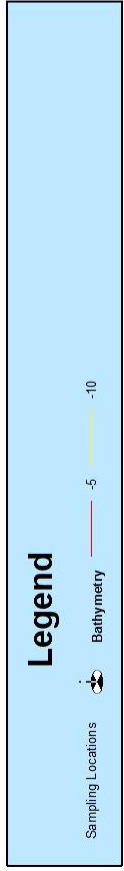
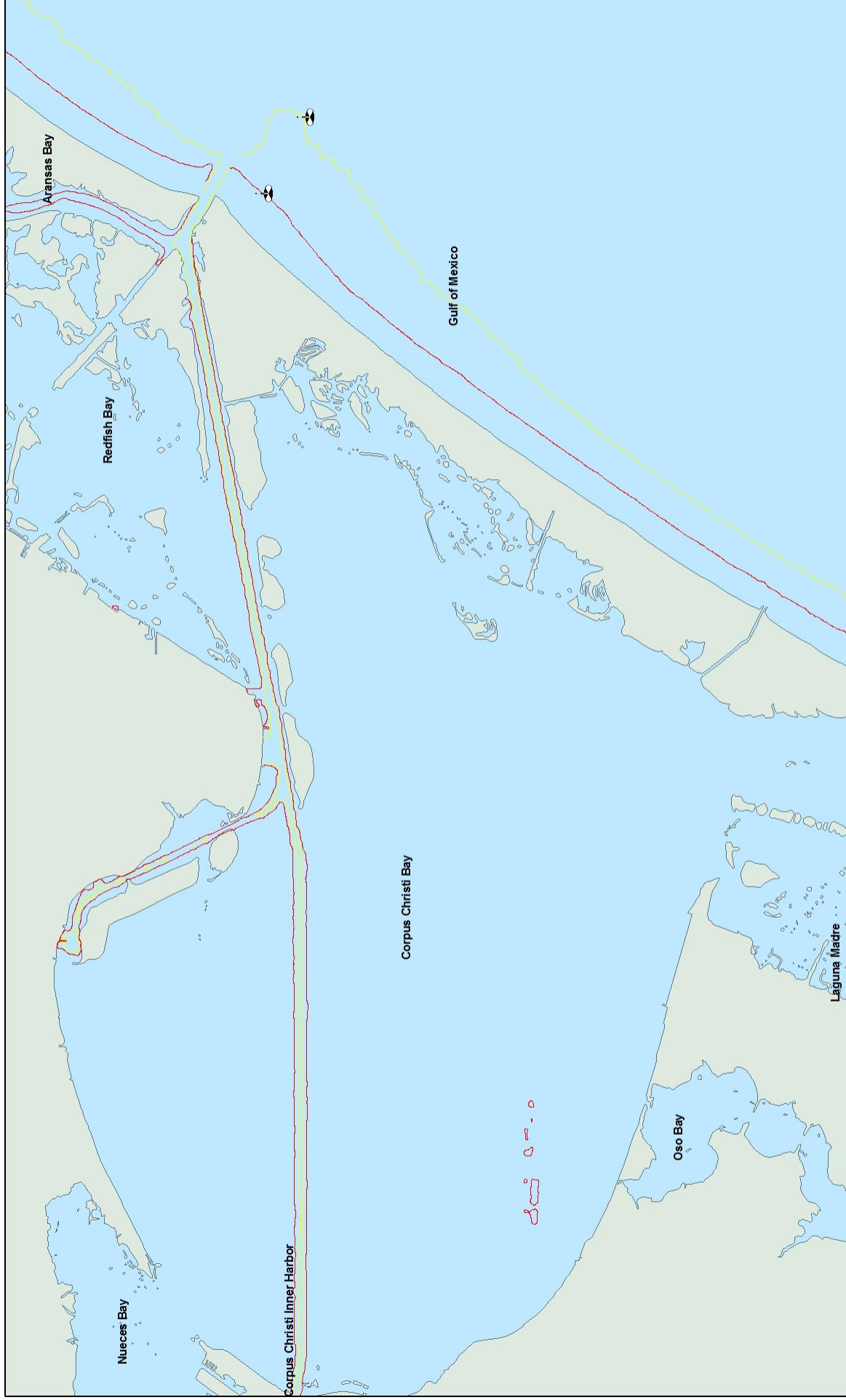


Figure 1. Field Round Robin #6 Sampling Sites.



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## **Field Round Robin #6 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 18 June 2012 near Corpus Christi Bay, Texas in the Gulf of Mexico. Samplers from all five Gulf of Mexico States were represented. A total of eleven samplers (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 samplers are listed in alphabetical order in Table 1. Samples were collected from the Gulf of Mexico near Corpus Christi, Texas. All samplers were asked to carry out their routine field measurements. First, each sampler collected three discrete field measurements at the 5m isobath (approximately 1 mile off shore). The measurements were taken at two set depths (0.3m from the surface and 0.1m above the bottom). Each sampler took a measurement at each depth, removed the meter from the water, and then reinserted the meter. The samplers 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 samplers then participated in the sample collection portion. Samples were taken from surface waters only. For water samples, samplers collected and



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split water samples from a set depth of 0.3m and prepared them for three different analytes (ammonium, total nitrate + nitrite, and orthophosphate). Both ammonium and total nitrate + nitrite, the water was acid-preserved but not filtered at 0.45 microns. For orthophosphate, the water was not acid preserved, but it was filtered. Depending on the sampling gear (bucket, Van-Dorn, or bailer) 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 the 10m isobath (approximately 2 miles offshore). The coolers were delivered the same day to the Harte Research Institute laboratory for analyses. The sampling portion of this round robin will not be discussed, due to the majority of the results being reported as non-detects.

Agency	Sampling	Measurement
Alabama Department of Environmental Management	✓✓	✓
Florida Department of Environmental Protection	✓	✓
Florida Fish and Wildlife Conservation Commission	✓	✓
Louisiana Department of Environmental Quality	✓✓	✓✓
Mississippi Department of Environmental Quality	✓✓	✓✓
Texas Commission on Environmental Quality	✓✓	✓✓
Texas Parks and Wildlife Department	✓	✓

Table 1. Samplers who participated in field round robin #6. Each check mark represents an individual from that agency who participated in a given portion of the field round robin.

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 samplers was measured by calculating F-pseudostandard deviation, which approximates the standard deviation but without the assumption of normal distribution. In addition, %F-pseudostandard deviation 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. Although this system of rating will be used, it is important to note that, as the groups’ precision increases, the Z-values can become inflated, making comparable values appear to be non-comparable.

Samplers were anonymized by assigning letter designations. The identities of the samplers are not revealed to others, so that samplers do not feel



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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:**

**Field-measurement portion:** The following measurements were taken: dissolved oxygen, temperature, conductivity, and pH. Samplers were allowed time to get prepared. Once all samplers were ready, they were told to take their readings all at one time. All samplers reported that they passed their post calibration verification after the round robin. For all analyses at the 5m isobath, N = 33; and at the 10 m isobath, N = 30 (due to sampler A not participating at this site).

*Dissolved Oxygen.* All values at the 5m isobath were within acceptable ranges for both surface and bottom waters, with the exception of Sampler C. The %F-pseudostigma values for both surface and bottom waters were small, indicating a high degree of precision among samplers. At the 10m isobath, all values were within acceptable ranges, with the exception of Samplers C and I. Again, the %F-pseudostigma value was small, indicating a high degree of precision among samplers. It should be noted that the values reported for Boat 2 were typically higher than those from Boat 1 at both locations and at all depths. Samplers C and I reported, on average, the lowest and highest values, respectively, at all depths and locations. The accuracy ranges for the instruments were: HydroLab = +/- 0.1 and YSI = +/- 0.2 mg/L. See Figures 2 - 4 for scatter-plots of values obtained by individual samplers. See Tables 2 - 4 for F-pseudostigma values and summary statistics.

Location	Gulf of Mexico 5m Isobath			
	F-pseudostigma	%F-pseudostigma	Median	Range
Surface	0.44	6.72%	6.51	3.74
Bottom	0.45	7.13%	6.29	4.00
<b>Boat 1</b>				
Surface	0.56	9.03%	6.22	3.74
Bottom	0.45	7.36%	6.07	2.40
<b>Boat 2</b>				
Surface	0.14	1.25%	6.50	0.55
Bottom	0.08	1.35%	6.61	1.65
Location	Gulf of Mexico 10m Isobath			
	F-pseudostigma	%F-pseudostigma	Median	Range
Surface	0.40	6.26%	6.45	3.59
<b>Boat 1</b>				
Surface	0.47	7.69%	6.07	2.47
<b>Boat 2</b>				
Surface	0.09	1.35%	6.61	1.16

Table 2. F-pseudostigma values for dissolved oxygen.



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**5m Isobath Dissolved Oxygen**

Sampler ID	Instrument	Surface			Bottom		
		Sampler Median	Range	Mean Z-value	Sampler Median	Range	Mean Z-value
A	YSI	5.82	0.32	1.78	5.69	0.10	1.38
B	YSI	6.61	0.01	0.22	6.27	0.04	0.03
C	YSI	4.17	0.22	5.23	3.94	0.17	5.13
D	YSI	6.02	0.06	1.14	5.88	0.06	0.93
E	HydroLab	6.45	0.02	0.12	6.29	0.05	0.01
F	HydroLab	6.42	1.45	0.88	6.24	0.05	0.09
G	HydroLab	6.52	0.03	0.03	6.50	0.06	0.44
H	HydroLab	6.70	0.01	0.44	6.50	0.06	0.45
I	YSI	6.88	0.21	0.94	6.77	1.23	1.86
J	YSI	6.50	0.03	0.00	6.31	0.13	0.44
K	HydroLab	6.59	0.05	0.19	6.49	0.11	0.44

Table 3. Summary statistics and Z-values by sampler for dissolved oxygen at the 5 m isobath.

**10m Isobath Dissolved Oxygen**

Sampler ID	Instrument	Surface		
		Sampler Median	Range	Mean Z-value
B	YSI	6.07	0.07	0.93
C	YSI	4.08	0.10	5.96
D	YSI	5.82	0.04	1.58
E	HydroLab	6.44	0.04	0.01
F	HydroLab	6.43	0.06	0.05
G	HydroLab	6.61	0.02	0.38
H	HydroLab	6.61	0.00	0.40
I	YSI	7.39	0.27	2.46
J	YSI	6.44	0.06	0.01
K	HydroLab	6.50	0.03	0.10

Table 4. Summary statistics and Z-values by sampler for dissolved oxygen at the 10m isobath.



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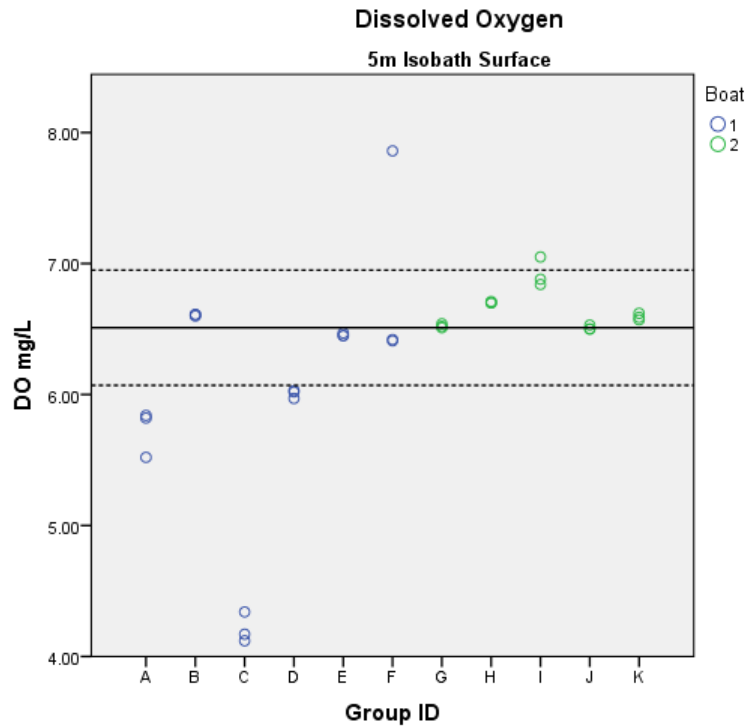


Figure 2. Scatter-plot of dissolved oxygen values obtained by the eleven samplers at 0.3m from the surface. The solid line indicates the overall median, and the dashed lines indicate +/- 1 F-pseudosigma.

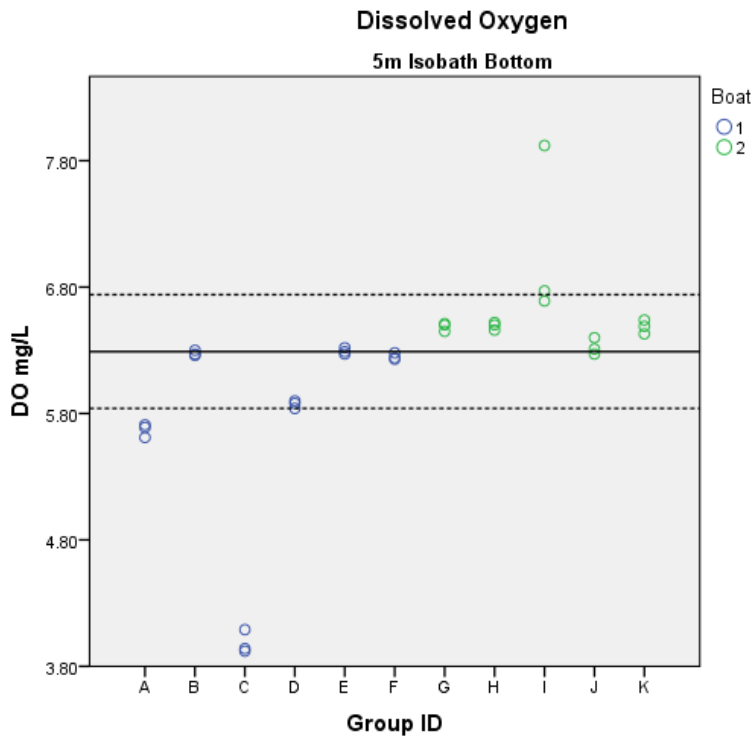


Figure 3. Scatter-plot of dissolved oxygen values obtained the eleven samplers at 0.1m from the bottom. The solid line indicates the overall median, and the dashed lines indicate +/- 1 F-pseudosigma.



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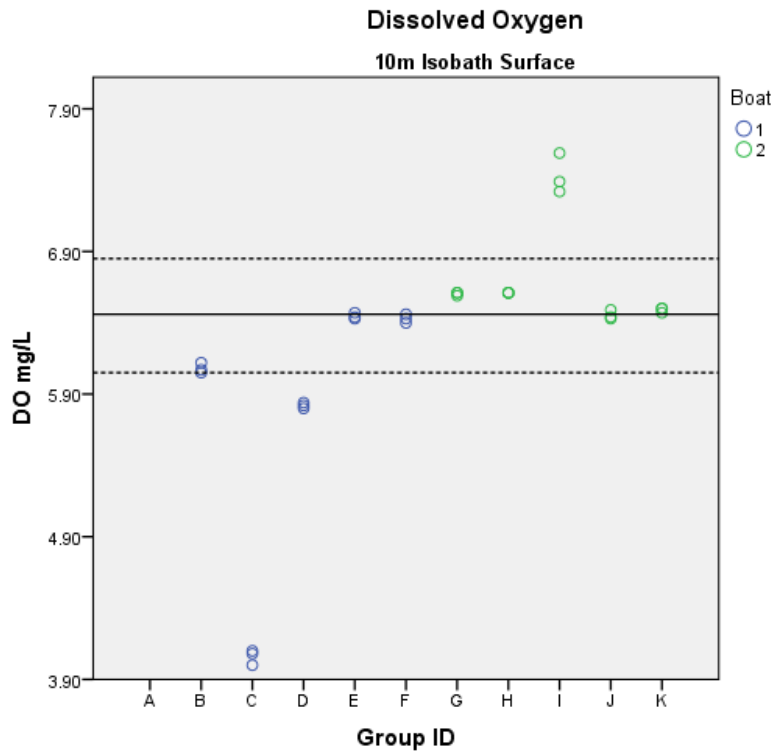


Figure 4. Scatter-plot of dissolved oxygen values obtained the ten samplers at 0.3m from the surface. The solid line indicates the overall median, and the dashed lines indicate  $\pm 1$  F-pseudostandard deviation.





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*Temperature.* Most values were within acceptable ranges at all sites and depths. However, for surface water at the 5m isobath, Sampler A was a statistical outlier; for bottom water at the 5m isobath, Sampler K was a statistical outlier. The %F-pseudostigma values for all sites and depths were small, indicating a high degree of precision among samplers. There was little difference in values between the two boats. The accuracy ranges for the instruments were: HydroLab = +/- 0.1 and YSI = +/- 0.15°C. Most results were within the accuracy ranges for the instruments. See Figures 5 - 7 for scatter-plots of values obtained by individual samplers. See Tables 5 - 7 for F-pseudostigma values and summary statistics.

Location	Gulf of Mexico 5m Isobath			
	F-pseudostigma	%F-pseudostigma	Median	Range
Surface	0.09	0.29%	29.53	0.36
Bottom	0.13	0.45%	29.42	0.57
<b>Boat 1</b>				
Surface	0.11	0.36%	29.48	0.27
Bottom	0.09	0.32%	29.51	0.24
<b>Boat 2</b>				
Surface	0.05	0.18%	29.57	0.19
Bottom	0.23	0.78%	29.35	0.47
Location	Gulf of Mexico 10m Isobath			
	F-pseudostigma	%F-pseudostigma	Median	Range
Surface	0.09	0.31%	29.57	0.38
<b>Boat 1</b>				
Surface	0.11	0.38%	29.56	0.38
<b>Boat 2</b>				
Surface	0.04	0.15%	29.57	0.22

Table 5. F-pseudostigma values for temperature.

**5m Isobath Temperature**

Group ID	Instrument	Surface			Bottom		
		Group Median	Range	Mean Z-value	Group Median	Range	Mean Z-value
A	YSI	29.35	0.06	2.07	29.32	0.02	0.72
B	YSI	29.53	0.02	0.07	29.50	0.05	0.69
C	YSI	29.39	0.04	1.48	29.42	0.02	0.05
D	YSI	29.52	0.08	0.11	29.52	0.04	0.82
E	HydroLab	29.53	0.05	0.19	29.55	0.03	0.97
F	HydroLab	29.45	0.02	0.81	29.51	0.04	0.79
G	HydroLab	29.58	0.07	0.37	29.44	0.02	0.21
H	HydroLab	29.62	0.06	1.15	29.14	0.27	1.82
I	YSI	29.50	0.03	0.37	29.35	0.26	1.00
J	YSI	29.57	0.01	0.48	29.42	0.24	0.41
K	HydroLab	29.56	0.03	0.44	29.07	0.38	2.13

Table 6. Summary statistics and Z-values by sampler for temperature at the 5 m isobath.



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**10m Isobath Temperature**

Group ID	Instrument	Surface		
		Group Median	Range	Mean Z-value
B	YSI	29.54	0.07	0.44
C	YSI	29.40	0.06	1.96
D	YSI	29.62	0.12	1.00
E	HydroLab	29.58	0.11	0.22
F	HydroLab	29.64	0.19	0.37
G	HydroLab	29.61	0.04	0.52
H	HydroLab	29.60	0.01	0.37
I	YSI	29.43	0.06	1.41
J	YSI	29.54	0.04	0.19
K	HydroLab	29.55	0.38	0.19

Table 7. Summary statistics and Z-values by sampler for temperature at the 10m isobath.

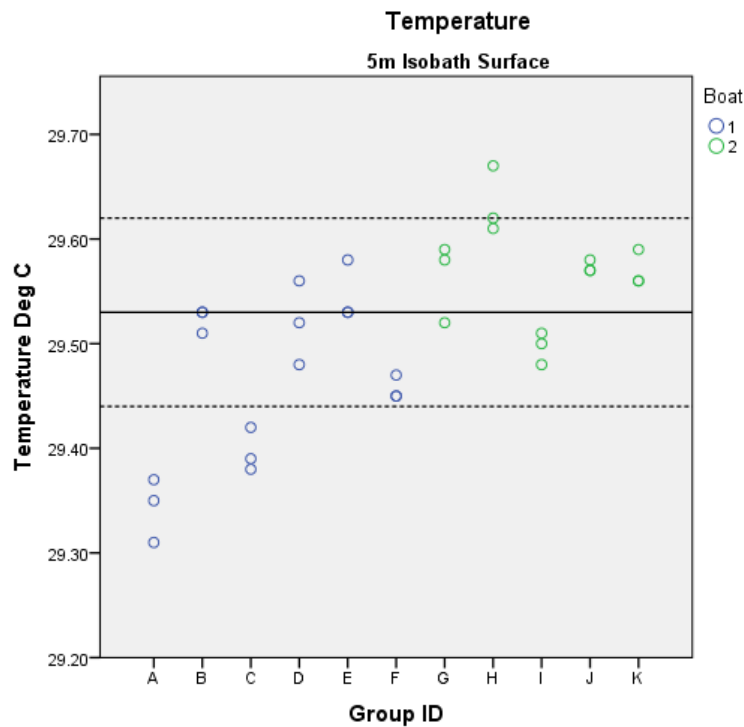


Figure 5. Scatter-plot of temperature values obtained by the eleven samplers at 0.3m from the surface. The solid line indicates the overall median, and the dashed lines indicate +/- 1 F-pseudosigma.



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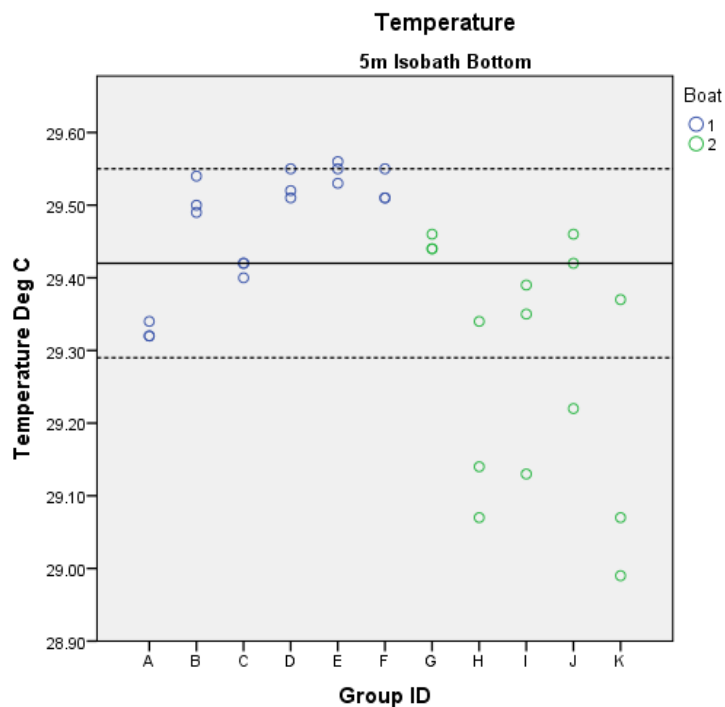


Figure 6. Scatter-plot of temperature values obtained the eleven samplers at 0.1m from the bottom. The solid line indicates the overall median, and the dashed lines indicate +/- 1 F-pseudostigma.

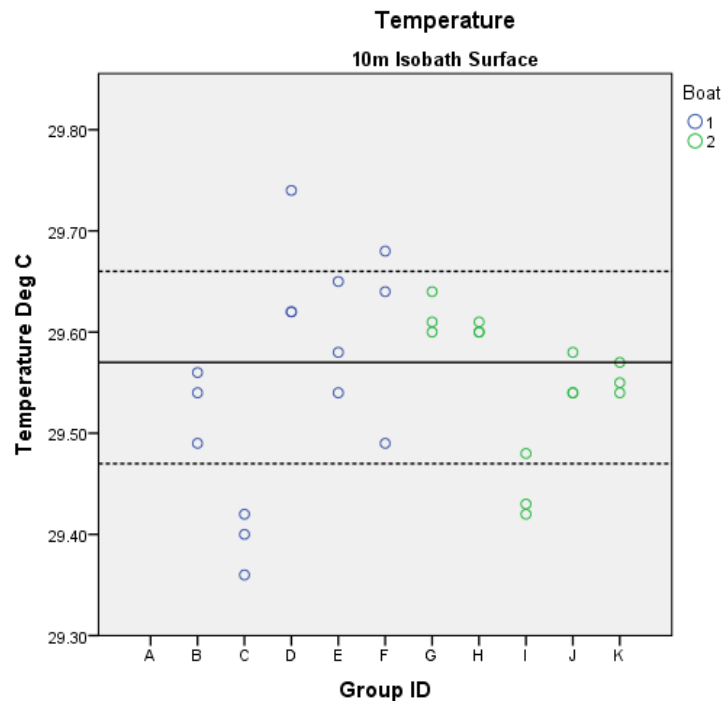


Figure 7. Scatter-plot of temperature values obtained the ten samplers at 0.3m from the surface. The solid line indicates the overall median, and the dashed lines indicate +/- 1 F-pseudostigma.



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*Specific Conductance.* Most values were within acceptable ranges for all sites and depths. However, at all locations and depths, Sampler I's results were statistical outliers; and Sampler K was a statistical outlier at both surface water locations. The %F-pseudostigma values for all sites and depths were small, indicating a high degree of precision among samplers. It should be noted that the values reported for Boat 2 were typically lower than those reported on Boat 1. Sampler I reported the lowest values at all depths and locations. Most values were reported within the instruments' accuracy ranges. The accuracy ranges for the instruments were: HydroLab and YSI = +/- 0.5%. See Figures 8 - 10 for scatter-plots of values obtained by individual samplers. See Tables 8 - 10 for F-pseudostigma values and summary statistics.

Location	Gulf of Mexico 5m Isobath			
	F-pseudostigma	%F-pseudostigma	Median	Range
Surface	0.60	1.09%	55.02	5.01
Bottom	0.78	1.41%	55.16	4.46
<b>Boat 1</b>				
Surface	0.41	0.74%	55.29	0.73
Bottom	0.40	0.72%	55.39	1.29
<b>Boat 2</b>				
Surface	0.96	1.76%	54.49	4.55
Bottom	1.12	2.06%	54.37	3.91
Location	Gulf of Mexico 10m Isobath			
	F-pseudostigma	%F-pseudostigma	Median	Range
Surface	0.64	1.17%	54.84	4.13
<b>Boat 1</b>				
Surface	0.36	0.65%	55.08	0.80
<b>Boat 2</b>				
Surface	1.05	1.94%	54.22	3.52

Table 8. F-pseudostigma values for specific conductance.

**5m Isobath Specific Conductance**

Group ID	Instrument	Surface			Bottom		
		Group Median	Range	Mean Z-value	Group Median	Range	Mean Z-value
A	YSI	54.89	0.05	0.19	54.56	0.57	0.61
B	YSI	54.96	0.01	0.11	55.13	0.04	0.03
C	YSI	55.49	0.02	0.79	55.74	0.05	0.73
D	YSI	55.51	0.11	0.88	55.66	0.05	0.65
E	HydroLab	55.29	0.04	0.46	55.48	0.07	0.42
F	HydroLab	55.04	0.58	0.34	55.31	0.04	0.19
G	HydroLab	55.02	0.03	0.01	55.19	0.01	0.04
H	HydroLab	55.14	0.03	0.20	55.01	0.15	0.13
I	YSI	51.08	0.69	6.70	51.37	0.27	4.82
J	YSI	54.49	0.26	1.01	54.37	0.87	1.26
K	HydroLab	53.74	0.02	2.13	53.67	0.04	1.91

Table 9. Summary statistics and Z-values by sampler for specific conductance at the 5 m isobath.



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**10m Isobath Specific Conductance**

Group ID	Instrument	Surface		
		Group Median	Range	Mean Z-value
B	YSI	54.74	0.03	0.15
C	YSI	55.34	0.20	0.88
D	YSI	55.25	0.03	0.64
E	HydroLab	55.08	0.01	0.37
F	HydroLab	54.78	0.01	0.09
G	HydroLab	54.91	0.00	0.11
H	HydroLab	54.91	0.02	0.11
I	YSI	51.43	0.06	5.32
J	YSI	54.22	0.03	0.98
K	HydroLab	53.50	0.01	2.10

Table 10. Summary statistics and Z-values by sampler for specific conductance at the 10m isobath.

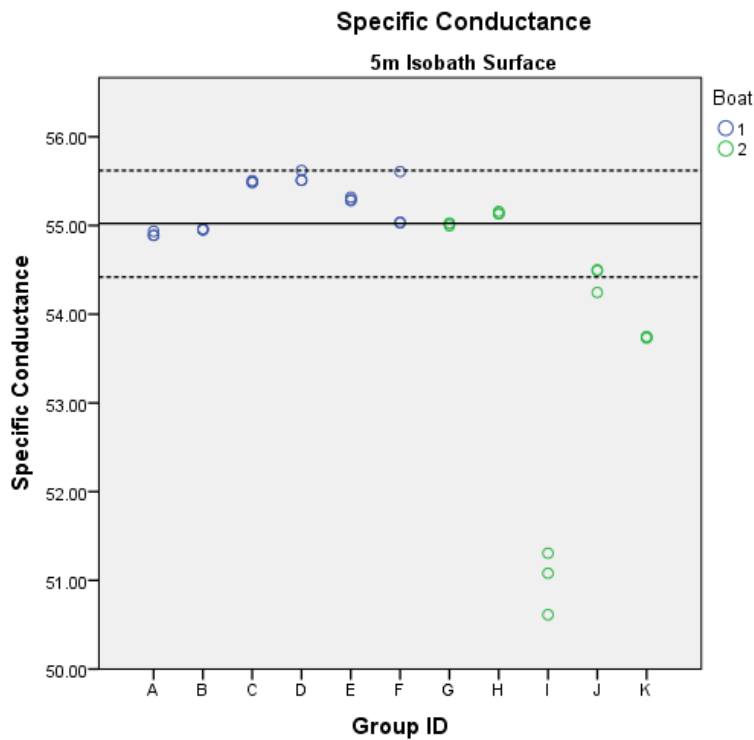


Figure 8. Scatter-plot of specific conductance values obtained by the eleven samplers at 0.3m from the surface. The solid line indicates the overall median, and the dashed lines indicate +/- 1 F-pseudostigma.



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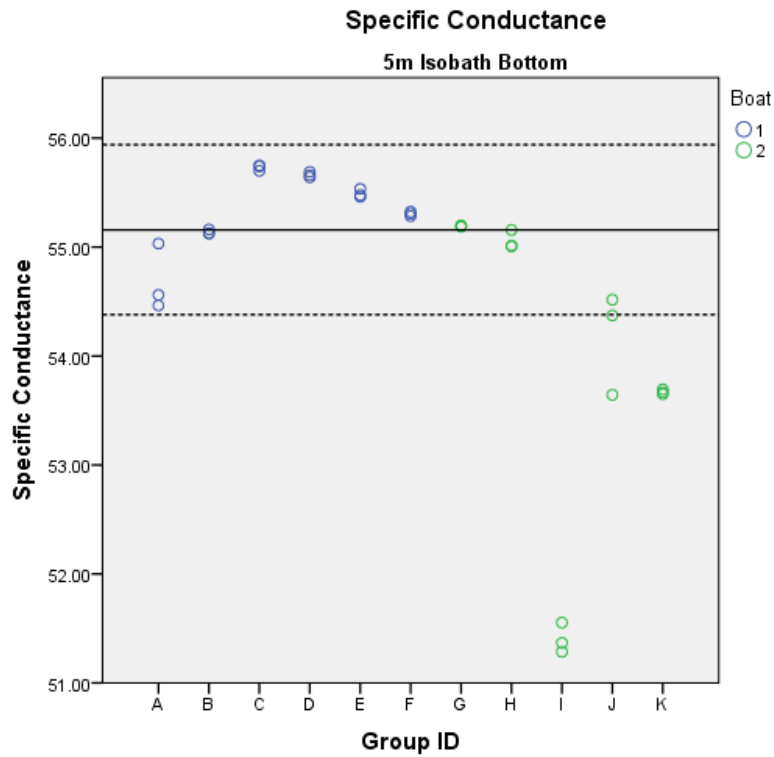


Figure 9. Scatter-plot of specific conductance values obtained the eleven samplers at 0.1m from the bottom. The solid line indicates the overall median, and the dashed lines indicate +/- 1 F-pseudostigma.

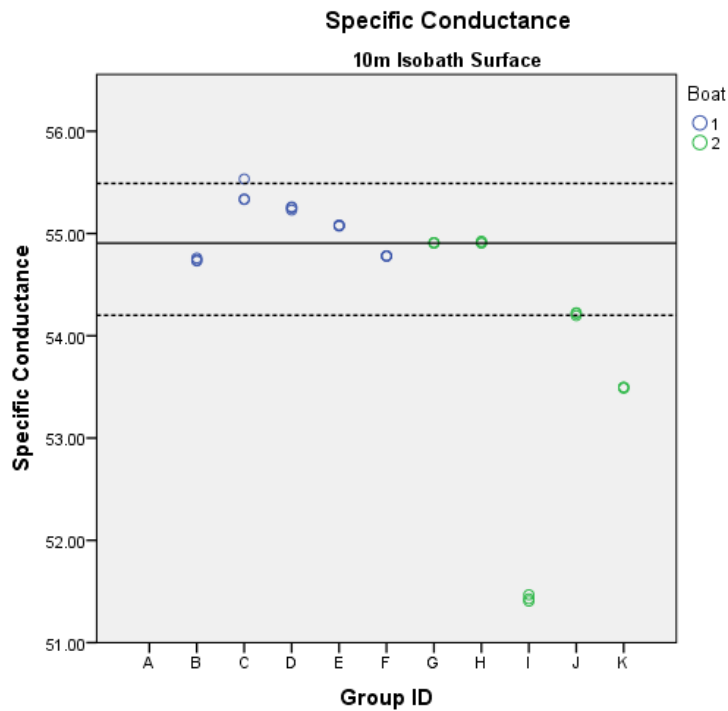


Figure 10. Scatter-plot of specific conductance values obtained the ten samplers at 0.3m from the surface. The solid line indicates the overall median, and the dashed lines indicate +/- 1 F-pseudostigma.



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pH. Most values were within acceptable ranges for all sites and depths; with the exception of Sampler I, whose results were statistical outliers at all depths and locations. The %F-pseudostigma values at all sites and depths were small, indicating a high degree of precision among samplers. Boat 2's values were typically lower than Boat 1's values. Sampler I reported the lowest values at all depths and locations. Most results at the 10m isobath were within the instruments' accuracy ranges. The accuracy ranges for the instruments were: HydroLab and YSI = +/- 0.2 SU. See Figures 11 - 13 for scatter-plots of values obtained by individual samplers. See Tables 11 - 13 for F-pseudostigma values and summary statistics.

Location	Gulf of Mexico 5m Isobath			
	F-pseudostigma	%F-pseudostigma	Median	Range
Surface	0.08	0.96%	8.12	0.80
Bottom	0.06	0.78%	8.09	1.50
<b>Boat 1</b>				
Surface	0.04	0.48%	8.13	0.18
Bottom	0.05	0.66%	8.13	0.18
<b>Boat 2</b>				
Surface	0.02	0.28%	8.06	0.74
Bottom	0.05	0.64%	8.06	1.46
Location	Gulf of Mexico 10m Isobath			
	F-pseudostigma	%F-pseudostigma	Median	Range
Surface	0.07	0.83%	8.09	0.29
<b>Boat 1</b>				
Surface	0.03	0.36%	8.13	0.22
<b>Boat 2</b>				
Surface	0.01	0.18%	8.06	0.25

Table 11. F-pseudostigma values for pH.

5m Isobath pH

Group ID	Instrument	Surface			Bottom		
		Group Median	Range	Mean Z-value	Group Median	Range	Mean Z-value
A	YSI	8.13	0.00	0.13	8.09	0.01	0.06
B	YSI	8.15	0.00	0.38	8.12	0.01	0.56
C	YSI	8.12	0.00	0.00	8.13	0.00	0.67
D	YSI	8.02	0.01	1.21	8.02	0.02	1.17
E	HydroLab	8.19	0.08	0.63	8.19	0.00	1.67
F	HydroLab	8.18	0.02	0.75	8.16	0.02	1.06
G	HydroLab	8.04	0.00	1.00	8.06	0.01	0.56
H	HydroLab	8.06	0.00	0.75	8.06	0.00	0.50
I	YSI	7.79	0.45	5.50	7.92	1.23	9.67
J	YSI	8.06	0.02	0.75	8.07	0.07	0.72
K	HydroLab	8.13	0.01	0.17	8.15	0.01	0.94

Table 12. Summary statistics and Z-values by sampler for pH at the 5 m isobath.



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10m Isobath pH

Group ID	Instrument	Surface		
		Group Median	Range	Mean Z-value
B	YSI	8.10	0.00	0.14
C	YSI	8.13	0.00	0.57
D	YSI	7.97	0.00	1.71
E	HydroLab	8.19	0.01	1.38
F	HydroLab	8.14	0.01	0.67
G	HydroLab	8.07	0.00	0.29
H	HydroLab	8.06	0.00	0.43
I	YSI	7.91	0.02	2.57
J	YSI	8.05	0.00	0.57
K	HydroLab	8.14	0.01	0.76

Table 13. Summary statistics and Z-values by sampler for pH at the 10m isobath.

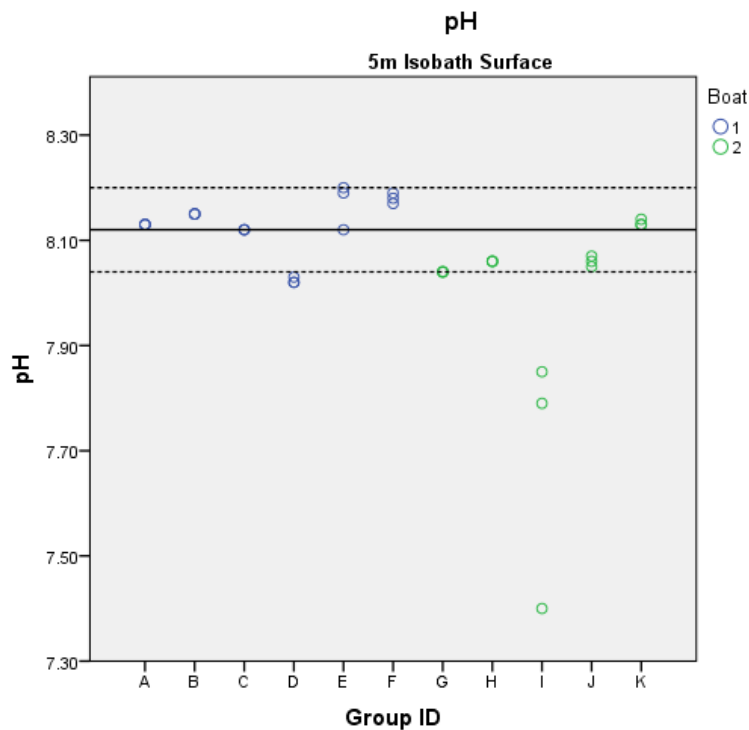


Figure 11. Scatter-plot of pH values obtained by the eleven samplers at 0.3m from the surface. The solid line indicates the overall median, and the dashed lines indicate +/- 1 F-pseudosigma.





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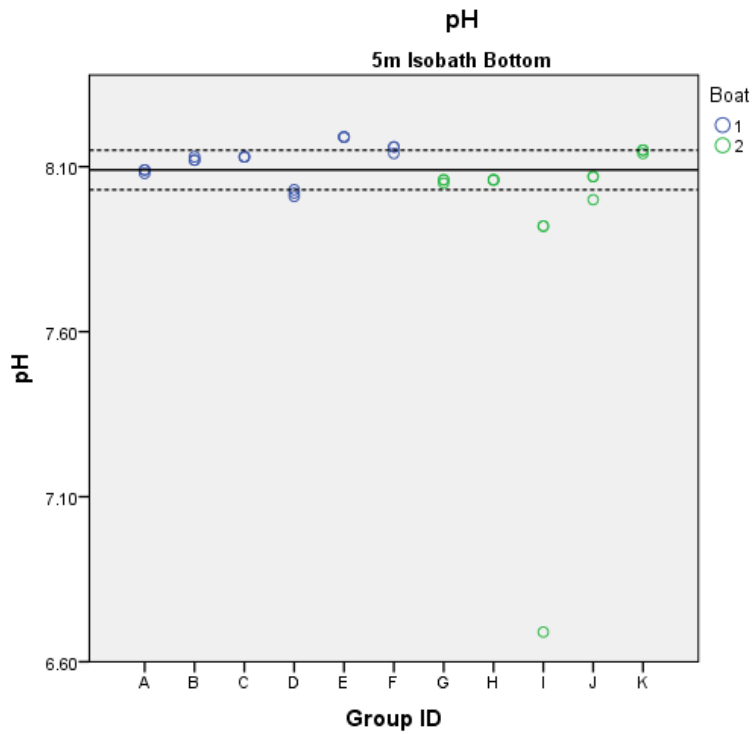


Figure 12. Scatter-plot of pH values obtained the eleven samplers at 0.1m from the bottom. The solid line indicates the overall median, and the dashed lines indicate +/- 1 F-pseudostigma.

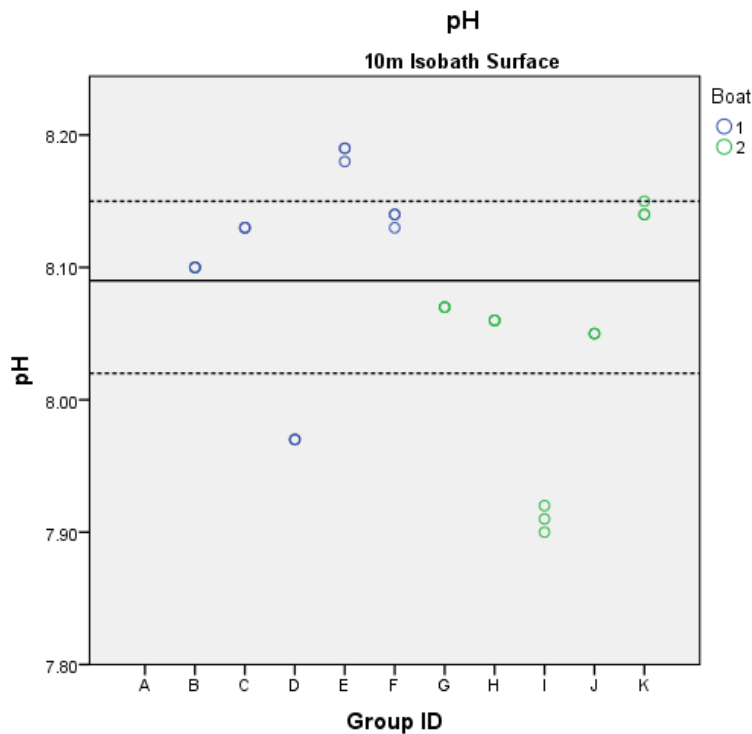


Figure 13. Scatter-plot of pH values obtained the ten samplers at 0.3m from the surface. The solid line indicates the overall median, and the dashed lines indicate +/- 1 F-pseudostigma.



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### Conclusions

The sampling portion of this round robin was not discussed, due to the majority of the results being reported as non-detects. However, in the future, care must be taken to find laboratories with suitable detection limits for estuarine and coastal waters.

**Field-measurement portion:** Eleven samplers from seven agencies, representing all five Gulf of Mexico states, participated in this Field Round Robin. The samplers measured dissolved oxygen, temperature, specific conductance, and pH. One sampler was sea-sick the entire trip and may have rushed readings by not allowing the sonde to stabilize; another was sea-sick and did not participate at the second site. There was good agreement among the samplers regarding temperature values, whereas dissolved oxygen, pH and specific conductance values were somewhat variable. Much of the variability for these parameters is reduced when Samplers C and I are removed from consideration. However, the range for specific conductance was typically reported within the equipments' (both HydroLab and YSI) accuracy range. As in previous Field Round Robins, samplers who allowed their equipment to stabilize showed decreased variability in their values.

**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. It is recommended that in the future, samplers use TRIS buffers for calibrating pH.

The identification of 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, efforts need to be made to ensure samplers are reporting the same parameters (e.g., reporting specific conductance, which is temperature corrected, rather than conductivity, which is not temperature corrected). Also, care must be taken to identify laboratories with suitable detection limits for estuarine and coastal waters. The host state could provide a mock training session, as well. 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.