

US EPA ARCHIVE DOCUMENT

Dissolved oxygen measurement methods aboard the RV Brooks McCall May 2010.

The R/V Brooks McCall was outfitted with a full ocean depth CTD package, including a SBE dissolved oxygen sensor to capture the dissolved oxygen profile during CTD cast. Discrete measurements were also made using colorimetric method and potentiometric methods. The colorimetric method employed a LaMotte 5860 Field Kit with premade reagents. The potentiometric method used an Extech DO700 hand-held probe to measure dissolved oxygen, which was applied to each water sample as it was retrieved from the Niskin bottle. The corresponding SBE output data and discrete measurements are contained in the electronically attached excel file "File 8 RV Brooks McCall DO Comparisons Cruise Leg 2 05-14-110 to 05-17-10.xls". The workbook contains a data comparison for Stations B19 – B28, with graphical presentation of available data for stations B20 – B28. At Station B25, 5 colorimetric and 11 potentiometric data points were acquired, as well as SBE DO data. It is evident from this data that the Extech probe show significantly better agreement to the CTD data at all depths. It also appears that the LaMotte kit cannot satisfactorily determine the dissolved oxygen concentration. As a result, the suggested method for dissolved oxygen measurements will be to use the Extech hand-held probe. The colorimetric method for dissolved oxygen analysis employing a LaMotte 5860 Field Kit continued to give spurious results that were incompatible with results from the CTD data and the Extech DO700 hand-held probe, which was applied to each sample as it was retrieved. A correlation among these dissolved oxygen analytical techniques is shown in graphical format as attachment 6. While there is good correlation between CTD and hand-held probe data, the colorimetric method apparently gives low dissolved oxygen results, which become more evident at higher dissolved oxygen levels. As a result, the colorimetric method was discontinued and dissolved oxygen measurements continued using the CTD and the Extech hand-held probe. Preliminary data from the first leg of the R/V Brooks McCall oil spill response cruise (5-10 May) included measurements of DO concentrations in the water column via a Winkler chemistry using a LaMotte DO kit. The data suggested severely depleted dissolved oxygen (as low as 0.5 mg L⁻¹) at depths throughout the water column. This was a troubling finding because it implied that the oil and/or dispersants may be causing DO depletion in the area, which could be a threat to marine life. This possibility had also been brought up in sensationalized media reports from a recent cruise on the R/V Pelican. Beginning on the 2nd leg (~5/15-5/19), 2 additional independent means of measuring DO were employed for comparison

the LaMotte kit. These included: 1) a brand new and freshly calibrated Seabird SBE43 DO sensor which collects continuous profiles of DO in the water column and 2) an Ex-Tech handheld DO probe which is calibrated before each use against water-saturated air. The Ex-Tech probe was used on discrete water samples collected from the Niskin bottles. After analysis of all 3 data types, it became very clear that the 2 DO probes agreed almost perfectly with each other (Fig 1), both of which were much higher than comparable measurements using the LaMotte kit. It therefore appears that the initial LaMotte results were biased low for unknown reasons. Further comparisons with historical DO data (Fig 2) clearly showed that both DO probes reproduced the expected vertical distribution, both qualitatively and quantitatively, that is a permanent feature of deep Gulf of Mexico waters. Based on this analysis, we conclude that we currently have no credible evidence to support the theory that DO concentrations are abnormal in the immediate vicinity of the oil spill.

The RV Brooks McCall was onsite at the MS Canyon 252 on three separation occasion during May, 2010. The dissolved oxygen data were collected using several methods throughout these three segments.

Segment 1: May 8, 2010 – May 12, 2010

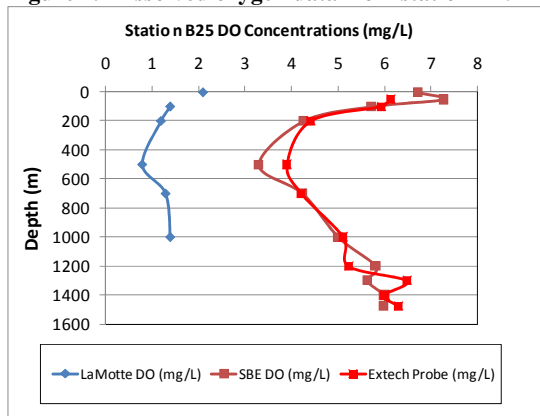
On this cruise there was no profiling DO sensor deployed. All data from this cruise segment were acquired with the LaMotte 5860 DO Field Kit. Three Niskin bottles were available, and samples were collected at 1 meter, 275 meter, and 550 meter depths. DO results with the LaMotte kit could not be compared to other available instrumentation.

Segment 2: May 13 – May 17, 2010

A new CTD unit with full ocean depth rating was acquired while in port, including a SBE DO Sensor. DO profiles were acquired with each cast. It was also discovered that an Extech DO700 handheld probe was available, and this was used to perform some measurements in an attempt to validate the SBE data and the LaMotte data. The Extech probe generally showed good agreement with the SBE data for the corresponding depth, however the LaMotte Field kit data was significantly lower and did not appear to represent the structure of the dissolved oxygen profile as seen with the SBE instrument and replicated with the Extech probe. Figure 1 presents the results from Station B25 data. The agreement between the Extech probe and the SBE sensor appeared quite good while the LaMotte kit results were quite different. As a result of the lack of

agreement observed by the LaMotte kit, it was believed that the Extech probe was providing more reliable results.

Figure 1. Dissolved oxygen data from station B25



Segment 3: May 19 – 20

Dissolved oxygen measurement methods aboard the RV Brooks McCall May 21, 2010

The RV Brooks McCall occupied 4 stations today. Dissolved oxygen (DO) measurements were made using three separate methods:

1. SBE DO profiles collected during CTD deployment
2. Extech DO700 hand held probe
3. LaMotte 5860 Dissolved Oxygen Field Test Kit

SBE profiles were collected at each of the stations. Extech probe measurements were made on all 11 discrete samples collected during each of the four CTD casts. LaMotte kit measurements were made on 7 of the 11 water samples for each cast. A comparison of the DO results from analyses on May 21, 2010 is presented in Figure 1 through Figure 3. Figure 1 is a comparison of the two discrete measurement methods. Figure 2 is a comparison of the discrete colorimetric measurements and corresponding SBE profile data. Figure 3 is a comparison of the Extech hand-held probe data with the corresponding SBE profile data. A 1:1 trendline is plotted across the diagonal for comparison purposes.

Figure 2.

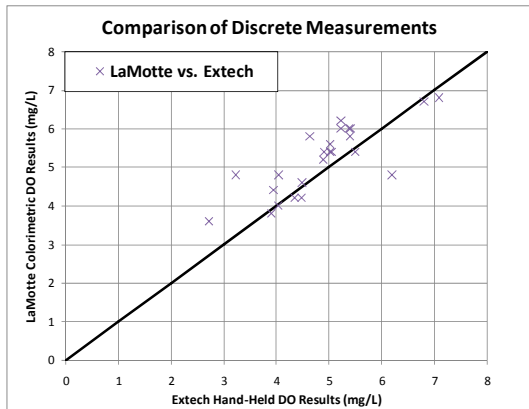


Figure 2.

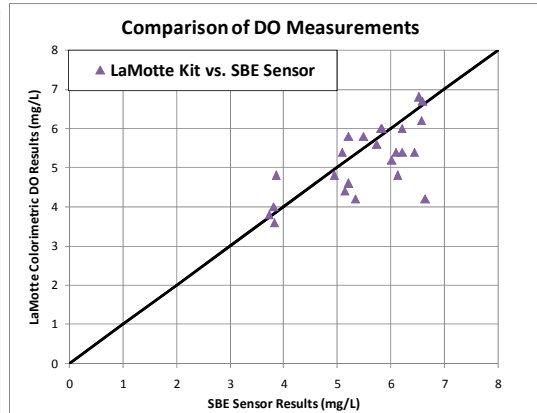
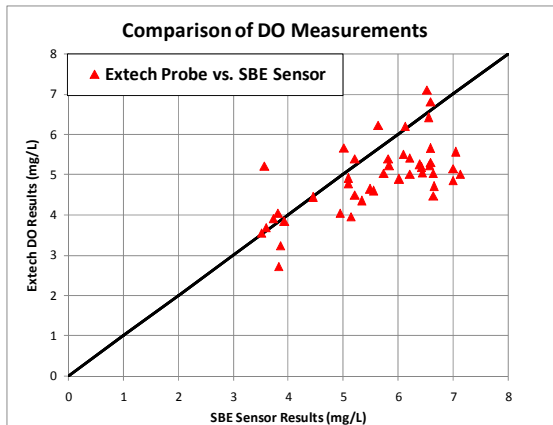


Figure 3.



The results indicate that the colorimetric measurements generally produced a higher result for the same water sample than the Extech hand-held probe, It also indicates that both the LaMotte measurements (Figure 2) and the Extech measurements (Figure 3) were slightly lower than the profile results. It appears that the Extech probe might need some cleaning to perform as well as it has been shown to previously.

Dissolved oxygen measurements during Segment 3 were initially performed with the Extech probe and verification with the SBE data. A request was made to perform a series of colorimetric tests using fresh LaMotte kits and replicate samples. Three samples were collected from the same Niskin bottle at two depths. Each of the samples was analyzed using a separate LaMotte kit. Extech probe measurements were also made. This was performed for three separate stations. The data are presented in the following figures. Station B35 showed

reasonable agreement between all three dissolved oxygen methodologies, but stations B34 and B37 showed poorer agreement. The results from the LaMotte kits showed a larger range of variability overall.

Figure 3. Station B34 Dissolved Oxygen Data

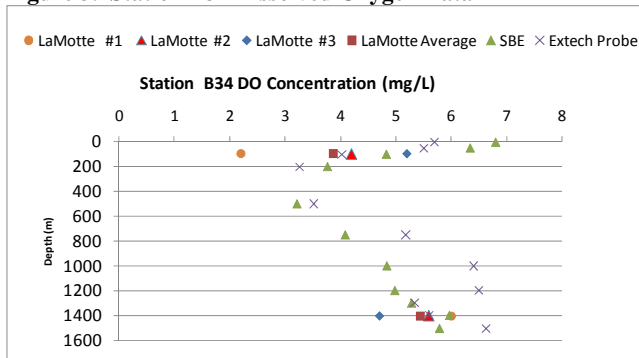


Figure 4 Station B35 Dissolved Oxygen Data

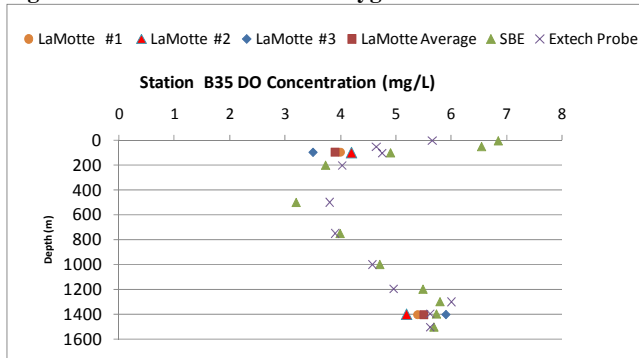
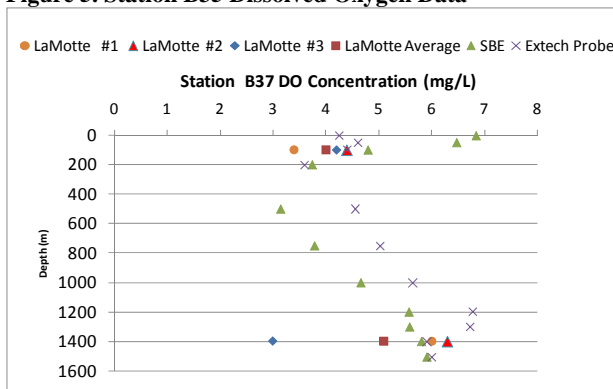


Figure 5. Station B35 Dissolved Oxygen Data



A more suitable method for validating both the SBE sensor and Extech probe data would be to employ a true Winkler titration system for these shipboard measurements, or preserve samples onboard for outside analysis. The results from these analyses are indicate normal, typical levels of dissolved oxygen for the Gulf of Mexico. The low dissolved oxygen values from previous LaMotte kit measurements may be the result of reagent degradation or operator error.

Dissolved oxygen measurement methods aboard the RV Brooks McCall May 23, 2010

The RV Brooks McCall occupied 3 stations today. Dissolved oxygen (DO) measurements were made using three separate methods:

4. SBE DO profiles collected during CTD deployment
5. Extech DO700 hand held probe
6. LaMotte 5860 Dissolved Oxygen Field Test Kit

SBE profiles were collected at each of the stations. Extech probe measurements were made on all 11 discrete samples collected during each of the three CTD casts. LaMotte kit measurements were made on 7 of the 11 water samples for each cast. A comparison of the DO results from analyses on May 23, 2010 is presented in Figure 1 through Figure 3. Figure 1 is a comparison of the two discrete measurement methods. Figure 2 is a comparison of the discrete colorimetric measurements and corresponding SBE profile data. Figure 3 is a comparison of the Extech hand-held probe data with the corresponding SBE profile data. A 1:1 trendline is plotted across the diagonal for comparison purposes.

Figure 6.

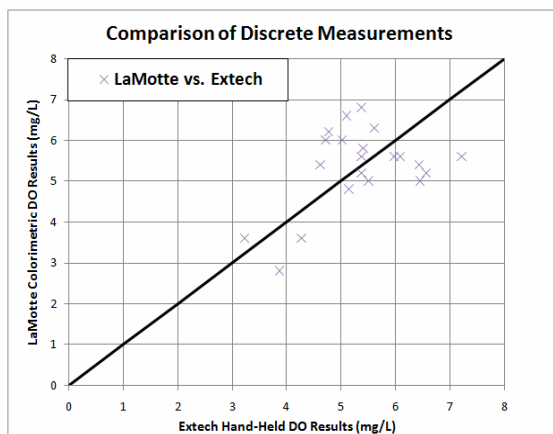


Figure 2.

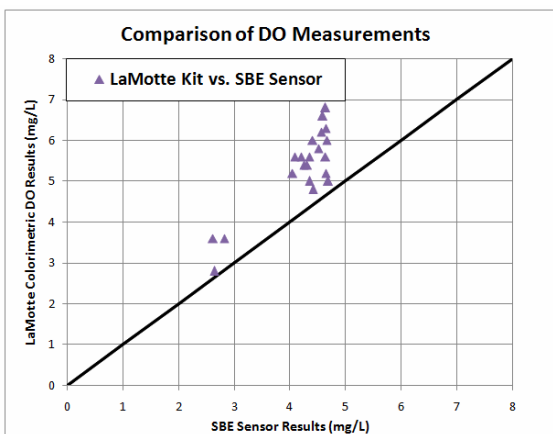
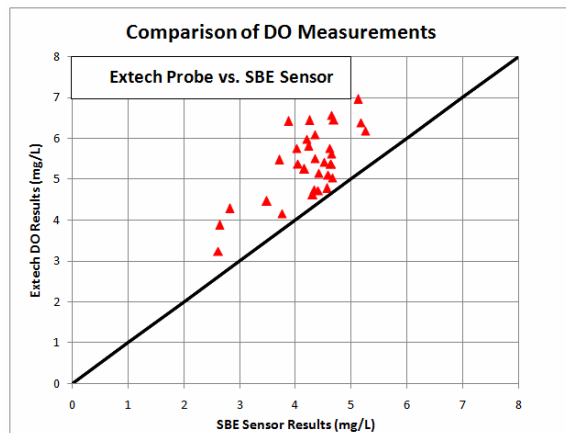


Figure 3.



The results indicate that the colorimetric measurements were generally in agreement with the Extech hand-held probe for the same water sample than, It also indicates that both the LaMotte measurements (Figure 2) and the Extech measurements (Figure 3) were slightly higher than the profile results.

Dissolved oxygen measurement methods aboard the RV Brooks McCall May 24, 2010

The RV Brooks McCall occupied 4 stations today. Dissolved oxygen (DO) measurements were made using three separate methods:

1. SBE DO profiles collected during CTD deployment
2. Extech DO700 hand held probe
3. LaMotte 5860 Dissolved Oxygen Field Test Kit

SBE profiles were collected at each of the stations. Extech probe measurements were made on all 11 discrete samples collected during each of the four CTD casts. LaMotte kit measurements were made on 7 of the 11 water samples for each cast. A comparison of the DO results from analyses on May 24, 2010 is presented in Figure 1 through Figure 3. Figure 1 is a comparison of the two discrete measurement methods. Figure 2 is a comparison of the discrete colorimetric measurements and corresponding SBE profile data. Figure 3 is a comparison of the Extech hand-held probe data with the corresponding SBE profile data. A 1:1 trendline is plotted across the diagonal for comparison purposes.

Figure 7.

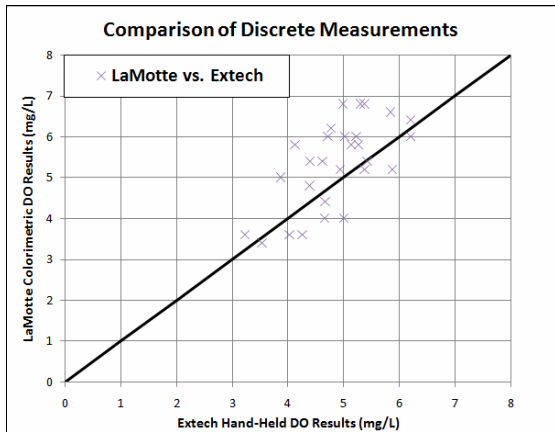


Figure 2.

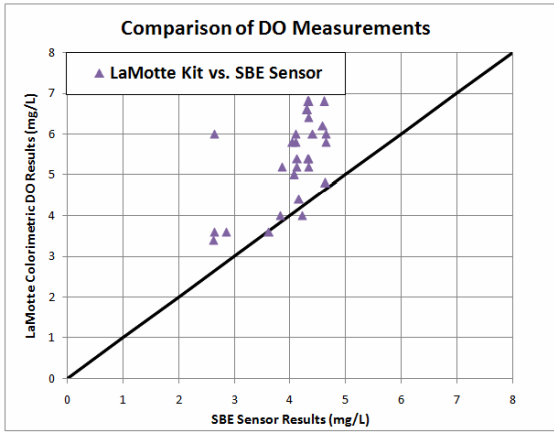
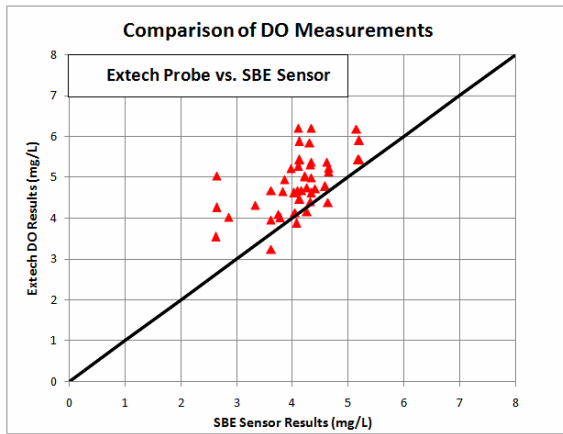


Figure 3.



The results indicate that the colorimetric measurements were generally in agreement with the Extech hand-held probe for the same water sample, It also indicates that the LaMotte measurements (Figure 2) were slightly higher than the profile results, much like the previous day. The Extech hand-held probe was still reading higher, but not as high as the previous day.

Dissolved oxygen measurement methods aboard the RV Brooks McCall May 25, 2010

The RV Brooks McCall occupied 4 stations today. Dissolved oxygen (DO) measurements were made using three separate methods:

1. SBE DO profiles collected during CTD deployment
2. Extech DO700 hand held probe
3. LaMotte 5860 Dissolved Oxygen Field Test Kit

SBE profiles were collected at each of the stations. Extech probe measurements were made on all 11 discrete samples collected during each of the four CTD casts. LaMotte kit measurements were made on 7 of the 11 water samples for each cast except for cast 49 where only 6 of the 11 water samples were tested with the LaMotte kit. A comparison of the DO results from analyses on May 25, 2010 is presented in Figure 1 through Figure 3. Figure 1 is a comparison of the two discrete measurement methods. Figure 2 is a comparison of the discrete colorimetric measurements and corresponding SBE profile data. Figure 3 is a comparison of the Extech hand-held probe data with the corresponding SBE profile data. A 1:1 trendline is plotted across the diagonal for comparison purposes.

Figure 8.

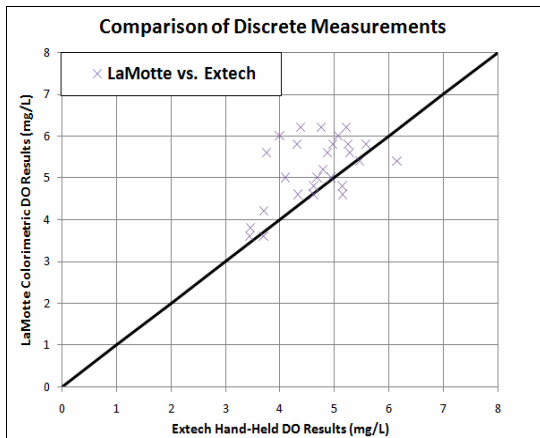


Figure 2.

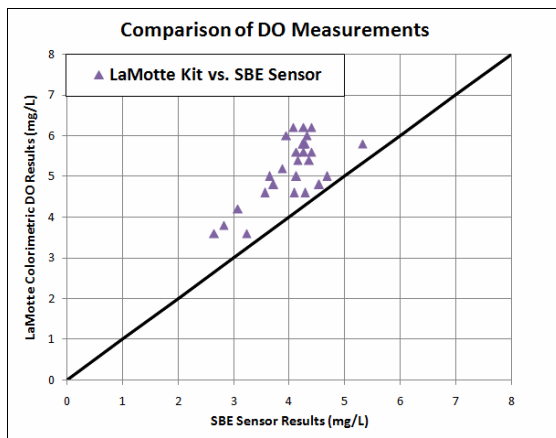
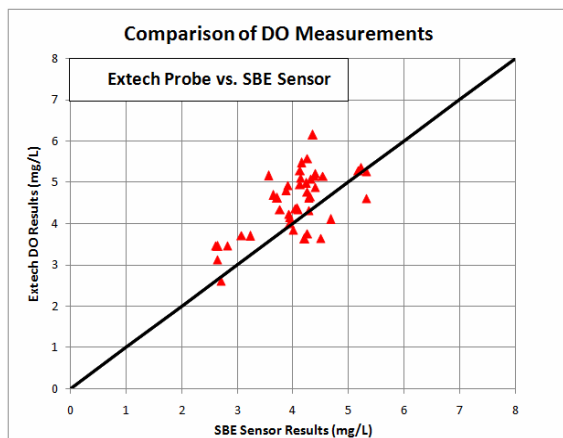


Figure 3.



The results indicate that the colorimetric measurements generally produced a higher result for the same water sample than the Extech hand-held probe, It also indicates that both the LaMotte measurements (Figure 2) and the Extech measurements (Figure 3) were slightly higher than the profile results.