Joint Analysis Group (JAG)

Review of R/V Brooks McCall Data to Examine Subsurface Oil

Background

This report considers data collected by the R/V *Brooks McCall* near the site of the Deepwater Horizon MC252 between May 8 and May 25, 2010. The Deepwater Horizon MC252 was releasing methane gas and oil in a turbulent mixture from the broken riser pipe attached to the well during this time. A plume of oil and gas rose from the release point; most of the oil reached the surface in about three hours. During the trip to the surface, some of the oil dissolved in the water column and some formed droplets. The pressure that propelled the oil out of the wellhead was strong enough to cause at least some of the oil to form water-in-oil emulsion, or mousse.

Dispersing oil at depth, either naturally or chemically, has the effect of breaking up the oil into small droplets within the water column. Dispersed droplets vary in both size and buoyancy, so droplets of different sizes take different lengths of time to rise to the water's surface. Very small droplets, less than about 100µ in diameter, rise to the surface so slowly that ocean turbulence is likely strong enough to keep them mixed within the water column for at least several months.

As a requirement of the response effort of injecting chemical dispersants into oil being released from the well, ship-based water column sampling was undertaken from the R/V *Brooks McCall*. These data continue to be collected from the R/V *Brooks McCall* and its relief vessel the R/V *Ocean Veritas*. The period of data analyzed in this report extends from May 8 and through four cruises until May 25, 2010 (Fig. 1). During the time of these cruises, approximately 230,000 gallons of subsea dispersants were used. If the subsurface oil was successfully dispersed into small droplets, processes can result in oil remaining in subsurface waters, with horizontal transport potentially more than 10 km beyond the well.

Methods and Procedures

The R/V *Brooks McCall* was deployed to meet an EPA requirement to monitor subsurface dispersant. The sample stations were not established in a regular pattern around the wellhead, but were placed to anticipate the likely flow field at depth (primarily a southwest axis from the wellhead). This leaves large spatial gaps and nonhomogeneous observational data that limit conclusions that can be drawn about the

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full spatial extent of subsurface oil. It is therefore important and necessary in future analysis to integrate the full collection of observations from ships and other observation platforms from government, academic institutions, and privately funded operations.

The R/V Brooks McCall deployed a Sea-Bird Electronics, Inc., SBE 25 SEALOGGER CTD (Conductivity, Temperature and Depth) to measure temperature, salinity, and dissolved oxygen (O_2) , with Niskin water samples taken at 1-m, 275-m, and 550-m depth on Cruise 1 (May 8-12). A Sea-Bird 911 plus CTD with a Wet Labs ECO Colored Dissolved Organic Matter (CDOM) FLCDRTD-1800 fluorometer and a Sea-Bird SBE 43 dissolved O_2 sensor to measure continuous profiles of temperature, salinity, O_2 , and fluorescence with bottle samples at 11 planned depths from the water surface to near seabed was used on Cruise 2 (May 15–17), Cruise 3 (May 19–21) and Cruise 4 (May 23– 25). Water samples were taken with a rosette of Niskin bottles. Two onboard measurements were made from these water samples: particle size using a LISST-100X particle counter and dissolved O₂. In addition, samples were preserved for laboratory chemistry analyses for Total Petroleum Hydrocarbons (TPH) and Volatile Organic Analysis (VOA). Volatile organic chemical compounds, which have significant vapor pressures, can affect the environment and human health. No sampling was conducted closer than 1 km from the well during cruises 2–4 due to restrictions related to wellhead operations.

The data from measurements below the sea-surface mixed layer of approximately 150 m were examined by the Joint Assessment Group (JAG) to determine if there was evidence of subsurface oil and, if so, the concentration, location, and extent of that oil. Experimental data and simulation models of subsurface releases indicated that oil from the MC252 release would be expected at depth.

Data Analysis and Conclusions

The preponderance of evidence from the data examined leads us to conclude that MC252 oil exists in subsurface waters near the well site in addition to the oil observed at the sea surface. While no chemical "fingerprinting" of samples was conducted to conclusively determine origin, the proximity to the well site and the following analyses support this conclusion. These analyses should be revised and refined with data from subsequent cruises.

• Fluorometry measurements show a reoccurring anomaly that first appears at approximately 1000 m and is attenuated between 1300 m and 1400 m deep. The

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- fluorometry anomaly begins near the release area and trends primarily southwest, which is consistent with water movement along an isobath. (Figs. 2–8).
- Vertical profiles of fluorescence show fine-scale structure, distinguishable from background; the separation between the bottom of the fluorometry anomaly and the seafloor is clear (Fig. 9). This suggests that the fluorescence source is not CDOM from the seafloor.
- Taken as a whole, fluorometry, TPH, VOA, and LISST measurements indicate that the anomaly (1) is oil associated with the spill site; (2) is decreasing with distance from the source; and (3) falls off significantly to the southwest beyond 10 km within the area sampled.
- Fluorometer oil response data indicate a maximum concentration of about 34 ppm oil above background, based on preliminary laboratory instrument response curves. See, for example, Figure (10) for stations B20 and B25 (background).
- Water sample analysis results for TPH show a correspondence with peaks in the in situ fluorescence measurements at some stations. See in particular stations B30, B42-46, and B48-50 (Figs. 12, 24-28, 30-32).
- TPH concentration data show levels at or below 2 ppm beyond the sea-surface mixed layer with a detection limit of about 0.8 ppm.
- Water-sample analysis results for VOA show a correspondence with peaks in the in situ fluorescence measurements at some stations. In particular, see stations B34, B38, and B41 (Figs. 16, 20, 23).
- VOA concentration data show levels at or below 800 ppb beyond the sea-surface mixed layer.
- Water sample analysis for oil and dispersant particles in the range of 2.5–60μm using the LISST shows a correspondence with peaks in the in situ fluorescence.
 See in particular stations B45-46, and B48-50 (Figs. 27-28, 30-32).
- There are no known biological or physical processes in the area that can account
 for the fluorescence pattern other than the presence of oil from the MC-252.
 Natural seeps in the immediate area could contribute in part to the fluorescence
 anomalies seen in the data.

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- Based on the CTD data, there is no evidence of large-scale changes in O₂ levels (>0.2 ml/L) in the water column at the time of sampling, which otherwise might indicate a response to increased biological activity. O₂ levels in the water column are largely what are expected when compared with historical data (Figs. 35-42).
- CTD dissolved O₂ measurements show deviations and noise that begins at 1000 m and extends to the bottom. Preliminary analysis of the response suggests that the deviations and noise below 1000 m are instrumental issues rather than real O₂ deviations.
- No indication of large-scale impacts on O₂ levels corresponding with the fluorescence anomalies is found between 1000 m and 1400 m during the first 35 days of the spill. While large-scale hypoxia in the Northern Gulf of Mexico due to oil breakdown by microbes is not likely at present, the recently increased release estimates suggest scenarios where the oxidation could impact natural background levels of O₂.
- O₂ levels should continue to be monitored to understand the potential effects of increases in subsurface oil releases since the sampling referenced in these data.
- Preliminary analysis of the R/V *Brooks McCall* CTD cruise data shows that below the layer of most direct seasonal influence, the subsurface temperature and salinity data compare well with historical data as a function of depth.
- There is no evidence to suggest significant oil accumulation at density boundaries or discontinuities in the water column below the seasurface mixed layer.
- The spatial coverage of the samples is not uniform around the wellhead, and most
 of the samples after Cruise 1 were taken west–southwest of the well site and
 within 15 km of the site. The full horizontal extent of the oil cannot be determined
 because of limited sample stations.
- A statistical correlation between TPH and VOA data with CDOM fluorescence cannot be determined at this time. Additional samples and analytical results will be necessary to determine if any correlation exists.
- This analysis does not consider or imply anything about the ecological consequences of the oil.

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Oceanographic Setting

The location of the leaking Deepwater Horizon MC252 well is approximately 80 km southeast of the mouth of the Mississippi River, 40 km seaward of the shelf break, 120 km east of the Mississippi Canyon center, and at 1500 m depth. The vertical structure of temperature and salinity in the water column from recent R/V *Brooks McCall* observations is consistent with the range of historical vertical profiles in the vicinity of the well as available through the National Oceanographic Data Center (NODC).

From historical data: During May–June, the near-surface portion of the water column is being modified by increasing solar radiation. The mixed layer of approximately 150 m (nominally 18° C water) established during the previous spring and winter is being capped by the surface warming. Below 150 m, the temperature decreases to 4.5° C at the bottom. Surface salinity is variable at the site due to proximity to the Mississippi River plume, but a representative winter–spring surface mixed-layer salinity is approximately 36.2. Below the mixed layer, salinity decreases, and the water is nearly isohaline at approximately 34.9 below 700 m to the bottom. Variations in the annual density structure are confined to the upper 150 m. Dissolved O₂ maxima in the water column are above 80 m and contained within the nominal mixed layer of 150 m (>3 ml/L above 150 m). O₂ decreases below 150 m to a broad minimum in the water column of approximately 2.75 ml/L located at approximately 400–500 m. Dissolved O₂ concentrations increase below 450 m above 4.0 ml/L at 1000 m to bottom levels of about 4.9 ml/L.

The R/V *Brooks McCall* data were compared to measured in situ observations (World Ocean Database—WOD) and climatological objectively analyzed (including mean and monthly-to-seasonal anomalies) values (World Ocean Atlas—WOA). Preliminary analysis of the R/V *Brooks McCall* CTD cruise data shows that below the layer of most direct seasonal influence, the subsurface temperature and salinity data from cruise to cruise compare well with WOD and WOA data as a function of depth.

The O₂ data derived from the R/V *Brooks McCall* cruises were relatively lower than WOA and WOD data, particularly below 1000 m depth. However, we believe that the lower values at depth are due to sensor issues (elaborated on below). On casts where no sensor problems were apparent, the R/V *Brooks McCall* casts are within the range of data represented in the WOA and WOD data sets.

Here we provide a brief synopsis of the O_2 measurements from the R/V Brooks McCall Cruises 2–4. The focus is on the processed results from the O_2 sensor connected to the

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CTD (SBE 43). This dataset is comprised of binned data (0.5 m resolution) from 33 stations that were obtained within about 15 km of the wellhead, with the majority of station within 4 km (Fig. 1).

It is important to measure O_2 levels in the water surrounding the wellhead of the Deep Horizon spill because it can provide two important pieces of information:

- 1. Decreasing O₂ concentrations would be indicative of oxidation of the oil and these decreases could impact ecosystem health.
- 2. O₂, along with temperature and salinity, serves as an important water mass tracer in the interior of the ocean.

Overall the results from the SBE 43 probe correspond well with the historical data in the vicinity as provided in the WOA database (Fig. 43). However, we did not have at hand concurrent, discrete, high quality, dissolved O_2 measurements that could be used to validate the spatial and temporal CTD O_2 data.

Interpretation

Large-scale features

Based on the profiles there is no evidence of large-scale changes in O_2 levels (>0.2 ml/L) in the water column. The profiles are largely what are expected compared to the historical comparison.

Small-scale features

In several instances, the increase in fluorescence corresponds to an approximately 0.2 ml/L decrease in O_2 (Fig. 44). This decrease could be an effect of oxidation of oil or a spurious sensor response to adsorption of oil on the membrane. In either case it provides a rough and very qualitative impact of the oil on the sensor, or O_2 , in the water column.

General Assessment

Based on the 33 stations taken near the leaking wellhead, there was no indication of large-scale impacts of the oil on O₂ levels during the first 35 days of the spill. The largest changes observed by the sensor were about 0.3 ml/L, which at this time, we do not believe are true O₂ signals. If such a decrease occurred in the O₂ minimum layer at 400 m with concentrations of about 2.7 ml/L, then the values would still be above what is generally considered hypoxic (1.4 ml/L or 2.0 mg/L). We therefore do not believe that

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the threat of large-scale hypoxia as a consequence of [microbial] oxidation near the wellhead at this time is a likely occurrence. However, simple calculations using the higher estimates (6/10/2010) for the amount of oil released of 1.3 million gallons/day suggest O_2 levels could decrease approximately 10 % in the deep water if a significant fraction of oil remains subsurface and the rate of dispersion of the oil is low.

Notes on Fluorometry

The SBE 911*plus* is equipped with a Wet Labs ECO CDOM FLCDRTD-1800 fluorometer that can operate to a maximum of 6000 m. The instrument is used to detect fluorescence from a broad spectrum of chemical compounds (excitation 370 nm, emission 460 nm, sensitivity 0.09 ppb of a laboratory standard, range 0–500 ppb), and is not specific to fluorescence from petroleum hydrocarbons. The instruments are calibrated at the factory with quinine sulfate dihydrate (QSde), and the concentrations quoted above are for QSde, not crude oil. The manufacturer recently completed a response curve using three concentrations of South Louisiana Light Sweet Crude Oil. The curves suggested a minimum detection limit (MDL) of about 1 ppm for South Louisiana Crude Oil (Fig. 45).

The CDOM crude oil response curve from the manufacturer demonstrated that the sensor could detect parts per million concentrations of oil. Maximum values within the Brooks-McCall CTD data set of 40-41 ppb QSde at 1285-1294m at Station B20 corresponds to about 34-ppm oil using the manufacturer's response curve (-0.0048X² + 1.09X + 3.83) after subtraction of background fluorescence values of 6-7 ppb QSde from a station outside the plume (B25) at depths between 1000m and 1400m. The 34-ppm value should only be interpreted as an approximate indicator until more complete instrument calibration and response data are available.

Notes on Chemical Analysis

The TPH method is a modified method for detection of semivolatile petroleum hydrocarbons. It is a CH₂Cl₂ extraction with a UV/VIS detection (MDL) of about 0.8 ppm TPH. Detectable amounts were determined by concentrating extracts and reanalyzing them with a Gas Chromatograph/Mass Spectrometer to verify that, in fact, the source oil is detected. Polycyclic Aromatic Hydrocarbons (PAHs) are quantifiable in these samples. TPH analysis could under represent MC252 oil due to low levels of PAHs in the source oil.

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Total VOAs include all the priority pollutant analytes along with the "Tentatively Identified Compounds" (TICs). The concentrations of each group were added together. The priority pollutant petroleum hydrocarbons included benzene, toluene, xylenes, etc., and the TICs included alkanes (such as propane, butane, pentane and branched alkanes, i.e., isobutane, along with cyclic alkanes, etc.). These compounds were quantitated as an estimated concentration based on surrogates added to the mixture, given their responses are reasonably equivalent.

At the time of this report VOA data were available for only a subset of the stations occupied during Cruises 2, 3, and 4. This analysis considered only VOA analysis from Cruises 3 and 4. Unfortunately, the depths at which bottle samples were taken on Cruise 2 were not recorded, so the VOA results cannot be directly compared with fluorometry and LISST data.

Notes on Sampling

The nature of sampling with Niskin bottles presents some potential for sampling errors. Niskin bottles are open as they pass through the sea surface. The bottles are open on the transit to the bottom and then triggered to close en route to the surface. There is a potential for oil to remain inside of Niskin bottles as they traverse the water column both at the surface and at depth. This oil could cause measured VOA and TPH measurement to be too high at shallower depths. It might also account for TPH values at 500 m and 200 m seen at some stations (i.e., B42 and B47).

Oil droplets rise; their ascent rate depends upon their size. The protocol does call for an inspection of the water surface for sheening within the Niskin bottle, but the appearance of a sheen might not be sufficient to account for oil droplets rising within the bottle or sticking to the inside of the bottle during the time between sampling the water and transferring the samples to glass bottles for TPH measurements. Droplet rise and oil sticking to the surface of the Niskin bottle could cause TPH measurements to be artificially low. LISST data did not find variations in particle size distributions between the middle and top of Niskin bottle samples.

Water samples were collected at fixed depths determined without guidance from real-time levels of CDOM fluorescence. Fluorometer measurements showed high variability through the 1000 m to 1400 m zone when fluorescence was detected. Therefore, the exact vertical location of water samples does not always correspond to areas of high CDOM fluorescence. It is possible that when TPH values were below MDL for stations with

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significant fluorescence peaks, the water sample could have missed the fluorescing material.

Notes on Oxygen Measurement

A composite of the last 10 stations is provided in Figure 46. An interesting aspect is the decreased sensor response of about 0.2 ml/L below 1000 m for several of the casts. The rapid decrease suggests a sensor artifact rather than a real O₂ decrease, particularly because there are no associated changes in T, S or fluorescence at these depths. The depth at which the decrease occurs differs for different casts. The data shown in Figure 46 are processed data for downcasts. Figure 47 shows a trace for upcast and downcast for Station 31. During the downcast, the signal decreases by 0.2–0.3 ml/L at 1000 m and turns noisy. This offset and noise remains on the upcast up to about 550 m, at which point it merges with the downcast trace. The manufacturer, Sea-Bird Electronics, is investigating possible causes for these variations and agrees with our assessment that it is likely caused by sensor malfunction.

The accuracy of the SBE 43 sensor on the CTD was checked during the cruise by taking samples from 11 bottles tripped for each profile and then analyzing the samples using a "Lamotte kit" or with a handheld probe. The low resolution and accuracy of these validation methods render them useless for accurate calibration (at the level of 0.02 ml/L). Based on the reproducibility of the SBE 43 probe on the CTD for the subsequent stations and correspondence with historical data (Fig. 43) we believe that the SBE 43 sensor faithfully represents the O₂ content and water-column features at the sampling stations.

Development of this Report

The JAG was recognized formally by the National Incident Command (NIC) on June 8, 2010, subsuming work that had been proceeding on an ad hoc basis motivated by the need to synthesize available information on subsurface sampling. The JAG operated at two levels for the production of its findings. For purposes of information exchange and metadata development, the group includes industry representatives responsible for providing data from contracted ships. For the purposes of final report development and approval of findings, just the federal agency representatives are involved. This report is the first in an anticipated series of data products from the JAG concerning data from the spill related to subsurface sampling.

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- Dr. Robert Pavia, Contractor, NOAA Office of Response and Restoration, Seattle, WA (Deputy Lead)
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Figure 1. Location of sampling stations for R/V Brooks McCall Cruises 1-4.

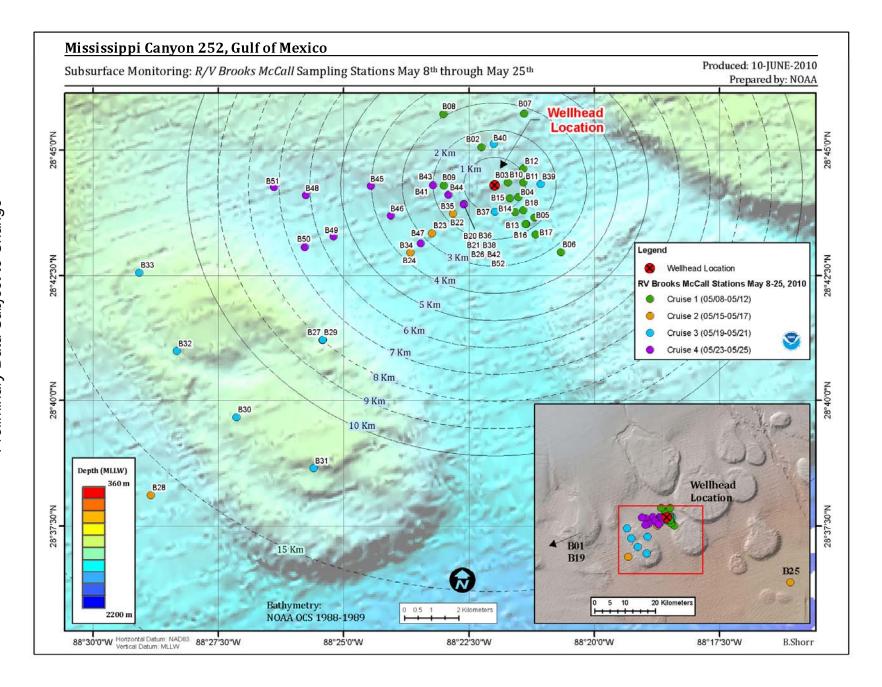


Figure 2. Fluorescence data from cruises 2-4 contoured at 5 meter depth. This figure shows measurements taken over an 11 day period.

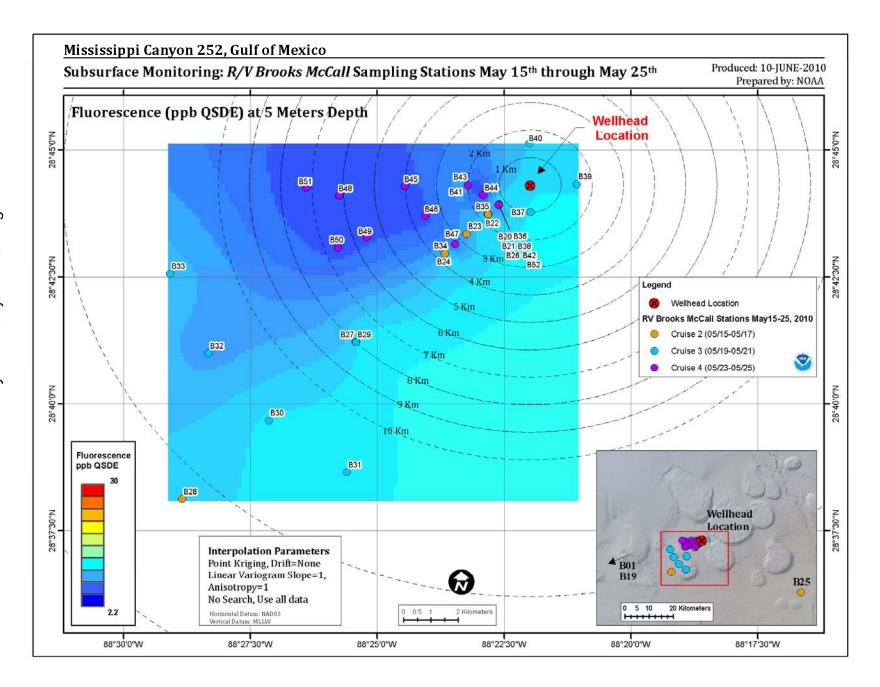


Figure 3. Fluorescence data from cruises 2-4 contoured at 500 meter depth. This figure shows measurements taken over an 11 day period.

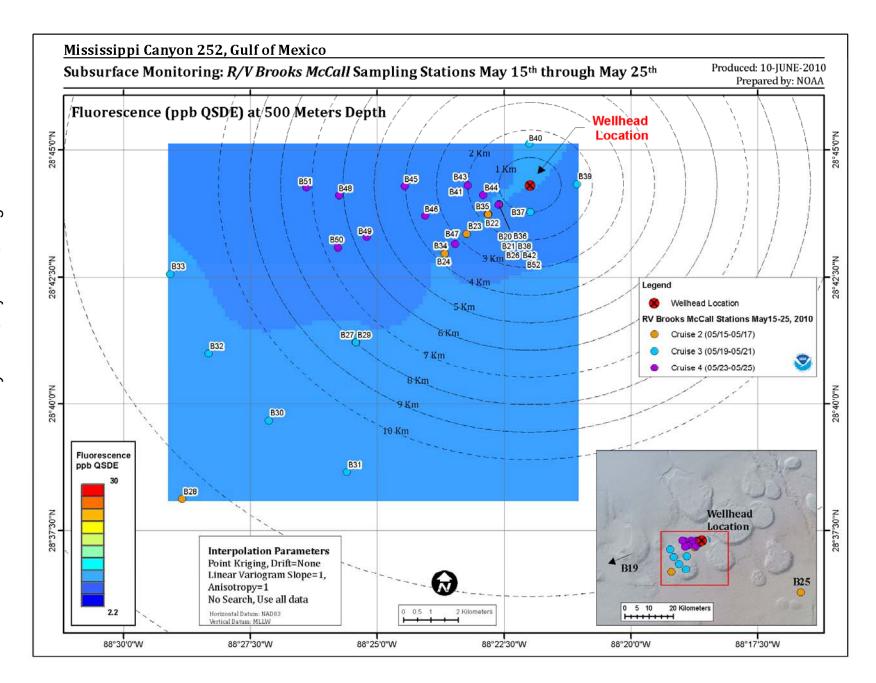


Figure 4. Fluorescence data from cruises 2-4 contoured at 1000 meter depth. This figure shows measurements taken over an 11 day period.

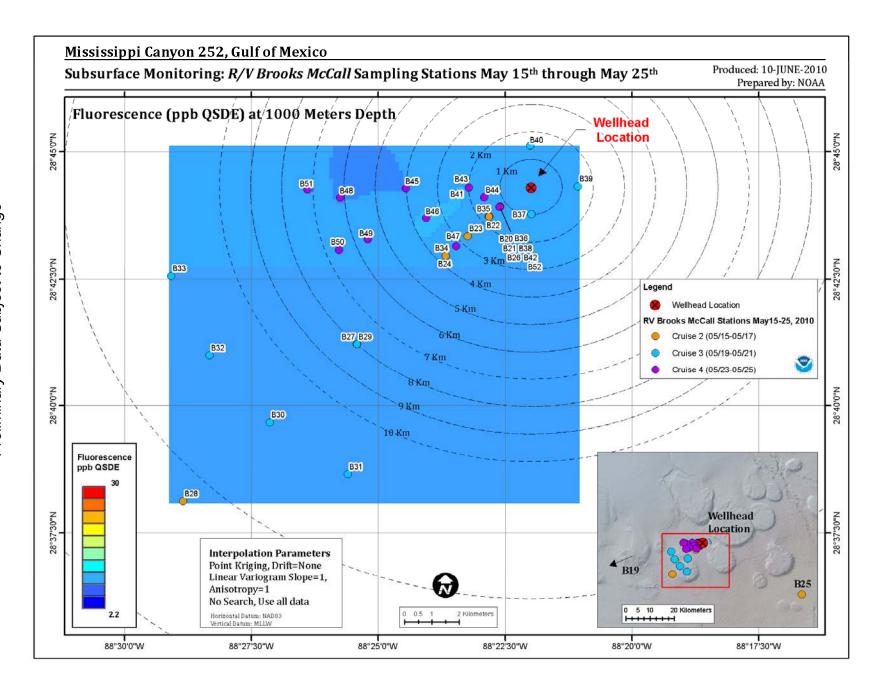


Figure 5. Fluorescence data from cruises 2-4 contoured at 1100 meter depth. This figure shows measurements taken over an 11 day period.

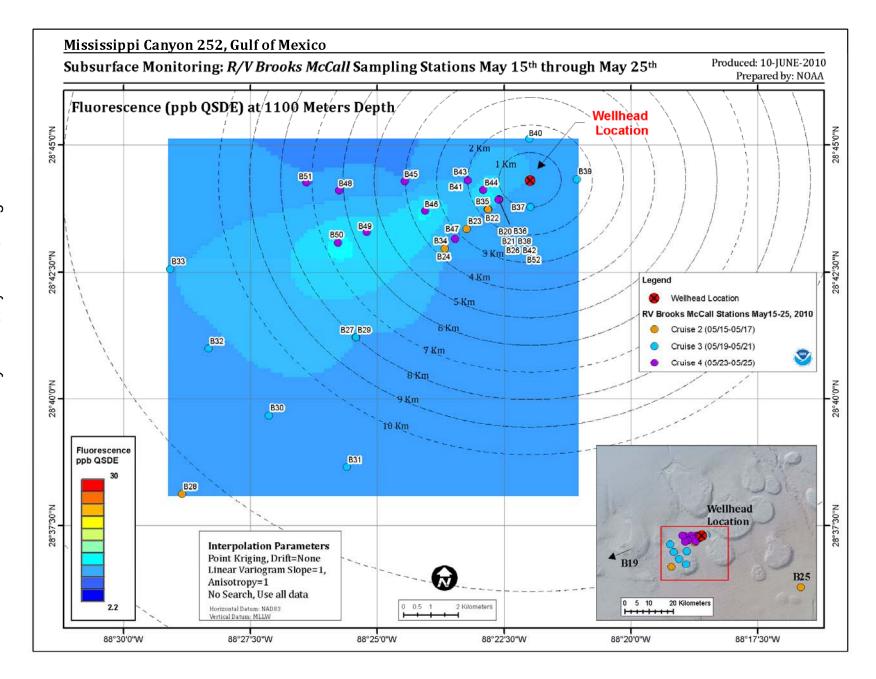


Figure 6. Fluorescence data from cruises 2-4 contoured at 1200 meter depth. This figure shows measurements taken over an 11 day period.

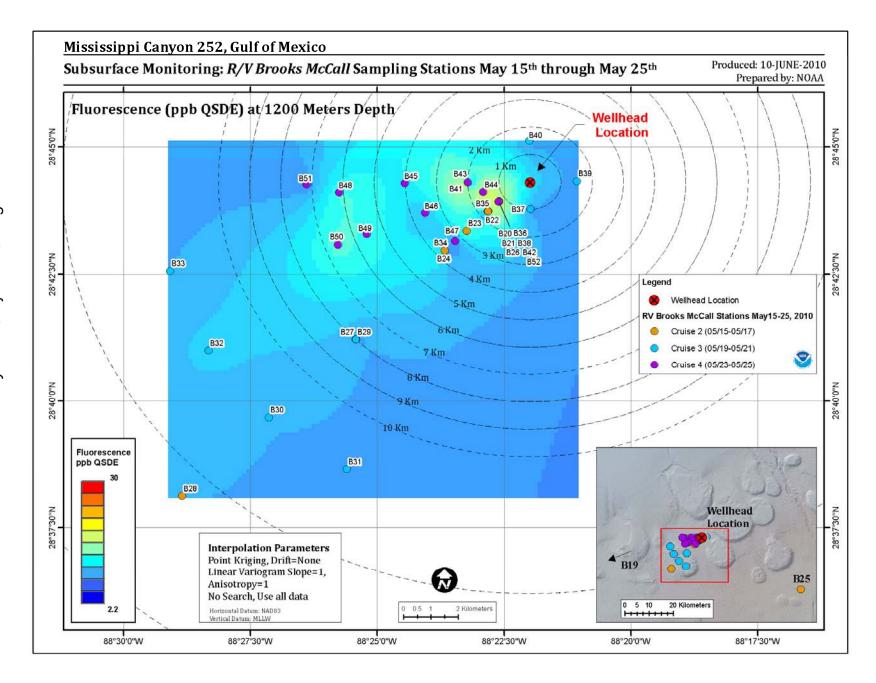


Figure 7. Fluorescence data from cruises 2-4 contoured at 1300 meter depth. This figure shows measurements taken over an 11 day period.

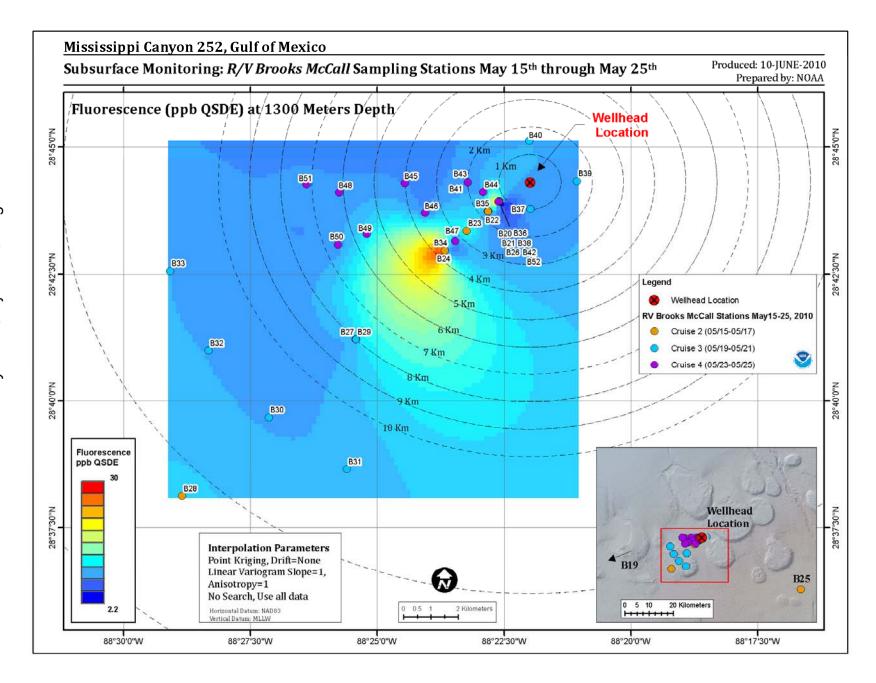


Figure 8. Fluorescence data from cruises 2-4 contoured at 1400 meter depth. This figure shows measurements taken over an 11 day period.

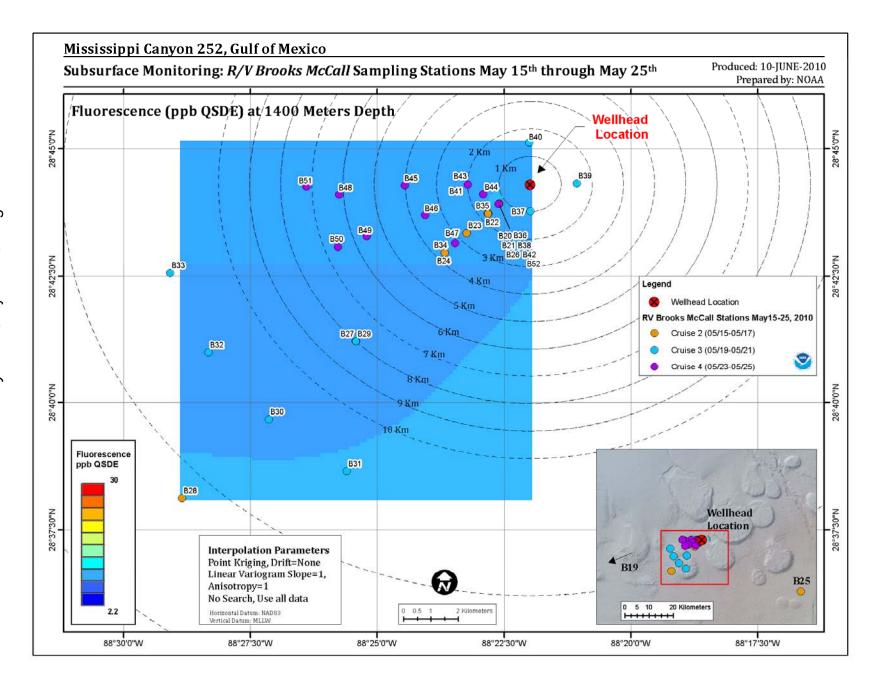


Figure 9. Fluorescence data from cruises 2-4 contoured at bottom depth. This figure shows measurements taken over an 11 day period.

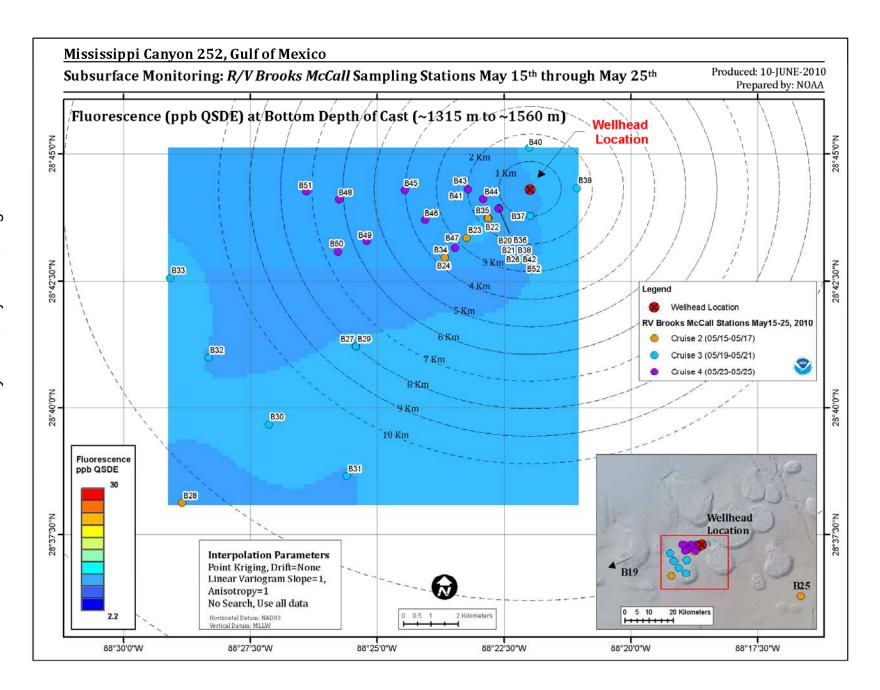
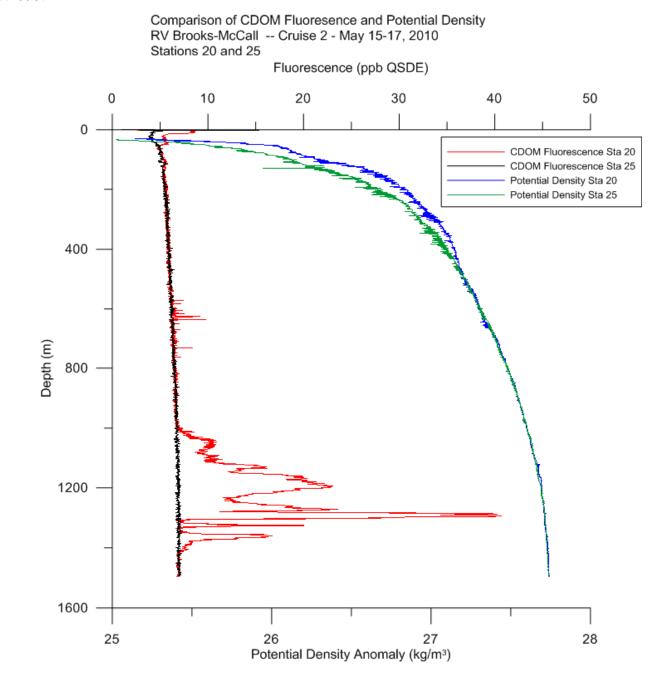
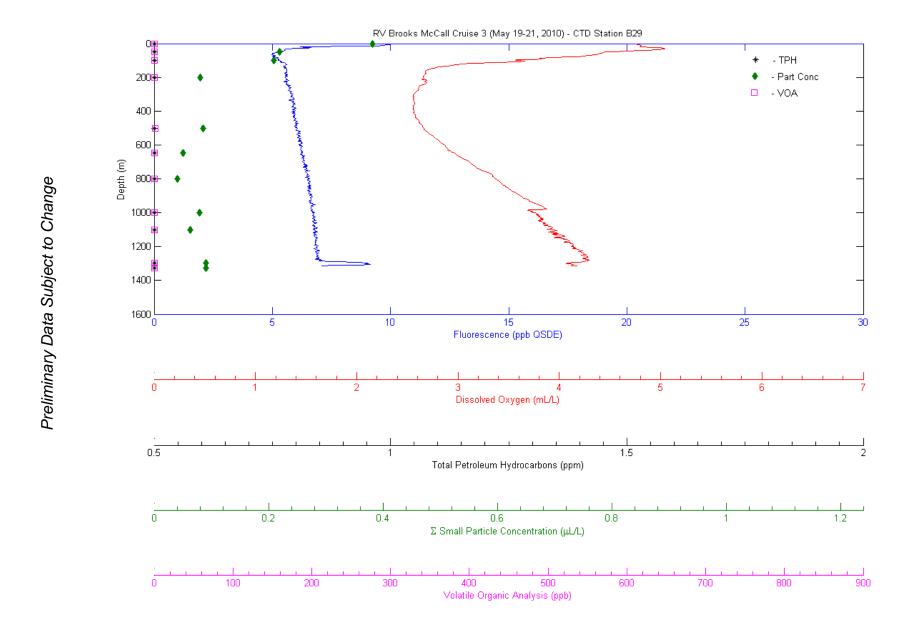
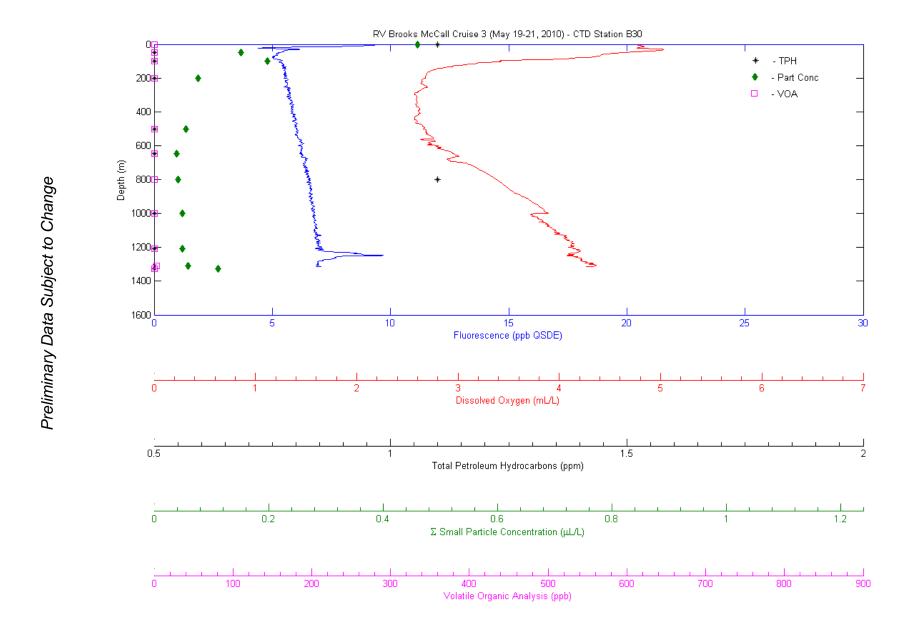
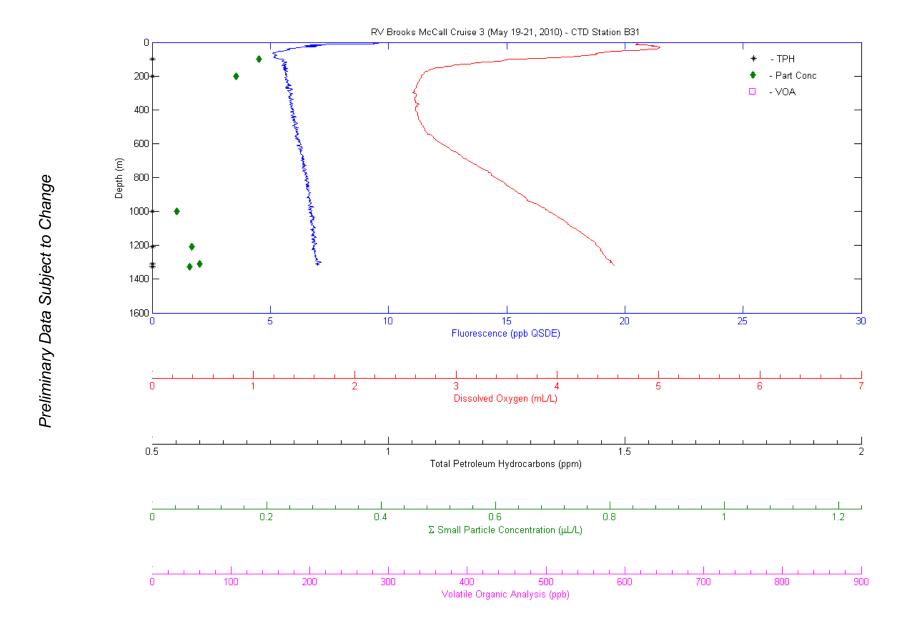


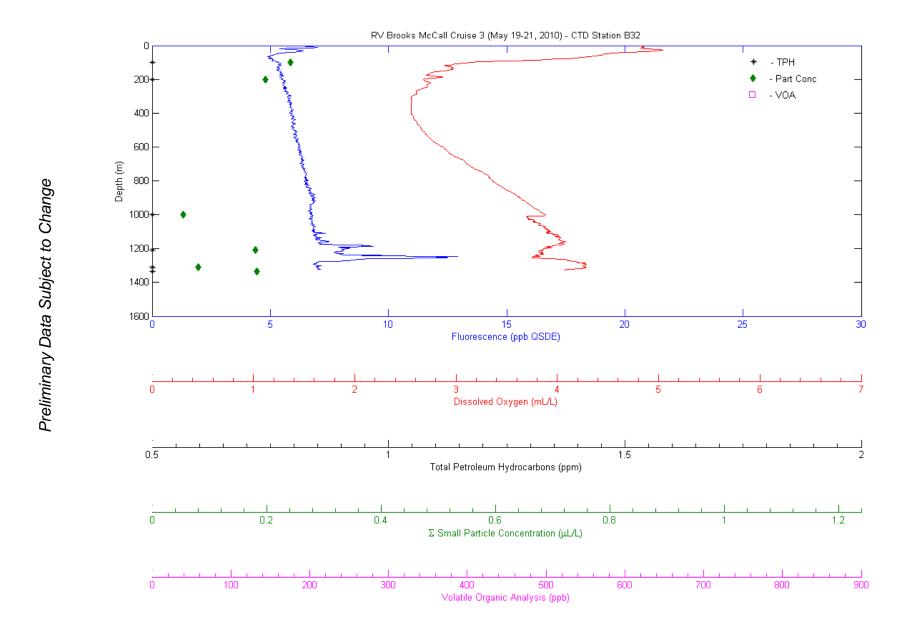
Figure 10. Fluorescence from station B20, the highest value at any location compared to station B25 a reference site more than 30 km to the southeast.

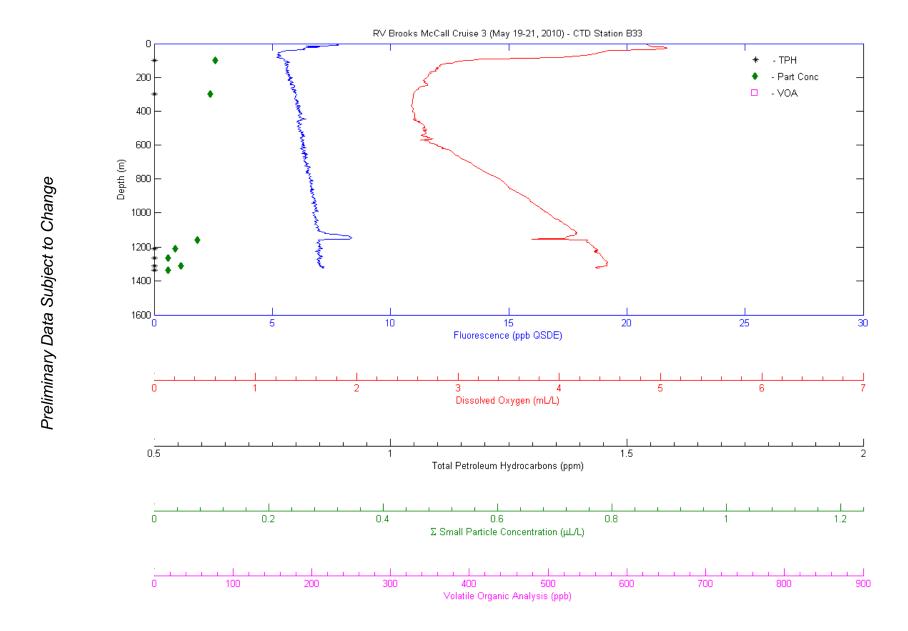


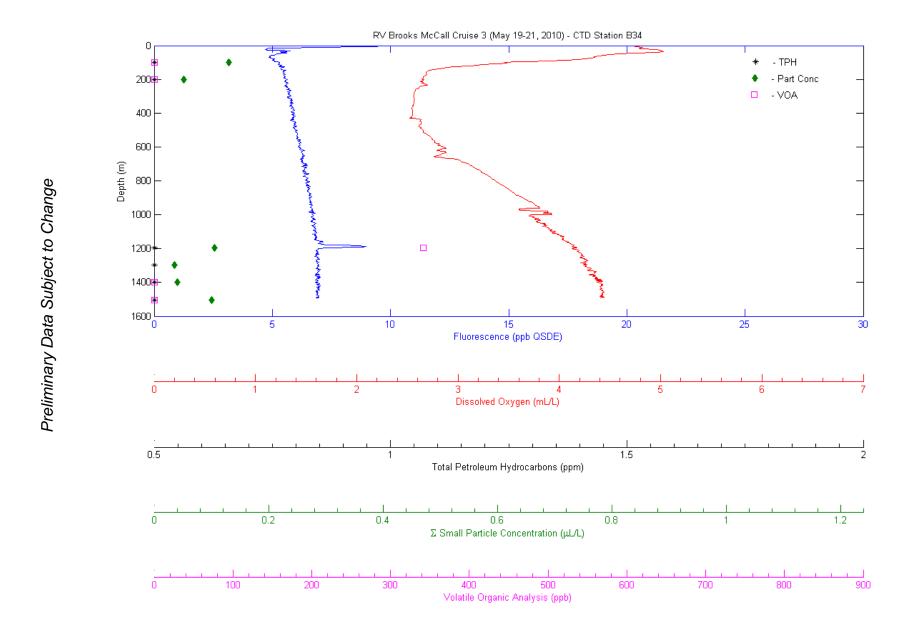


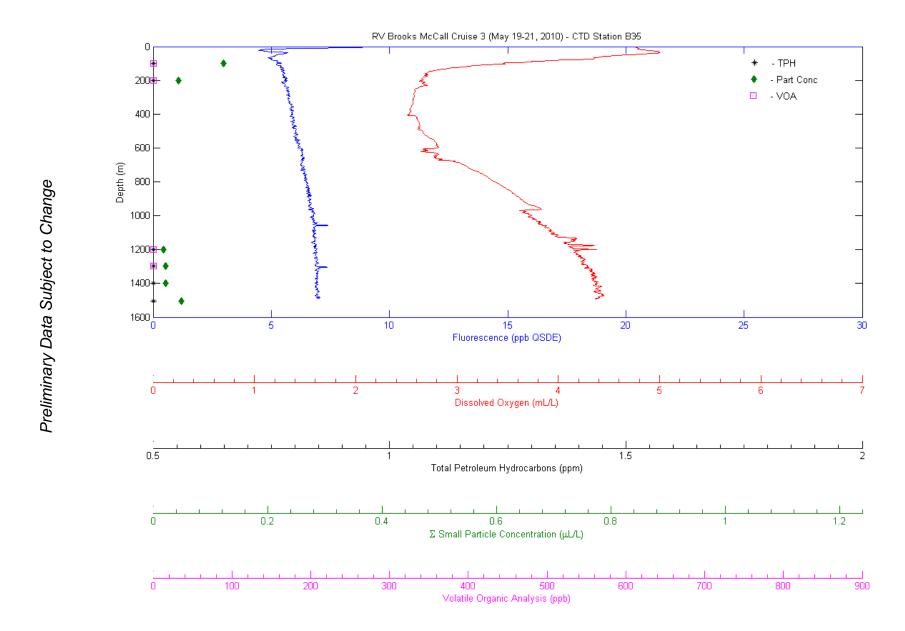


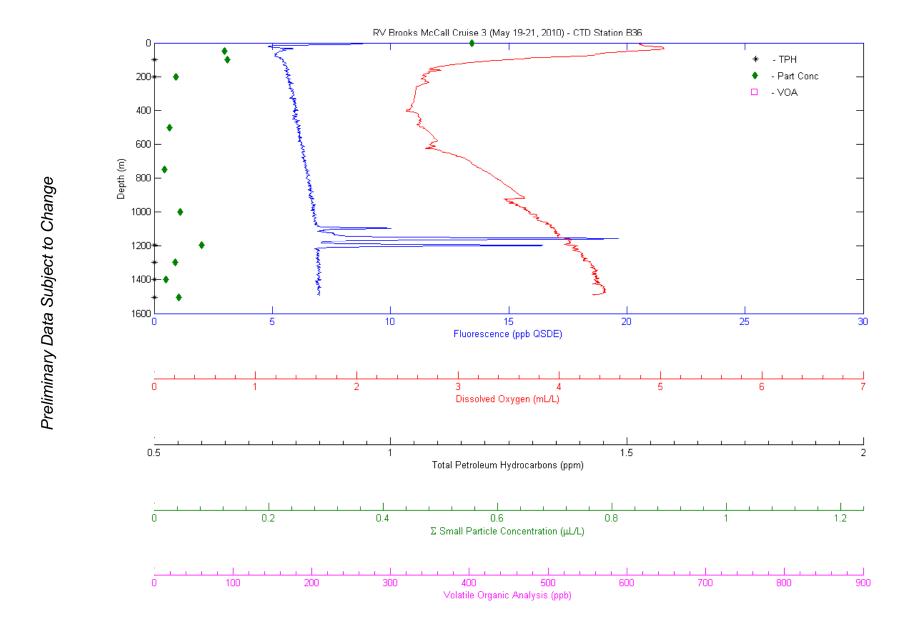


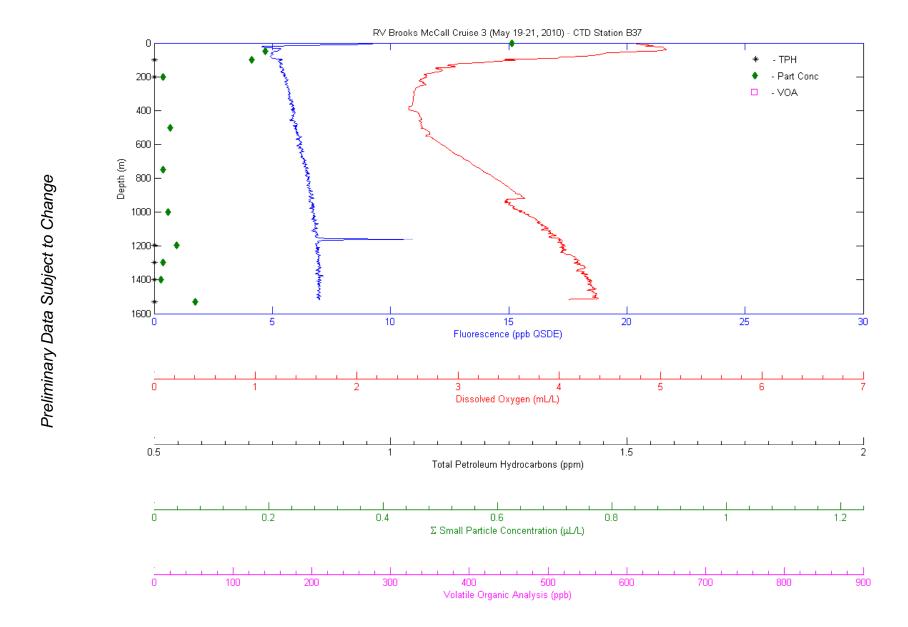


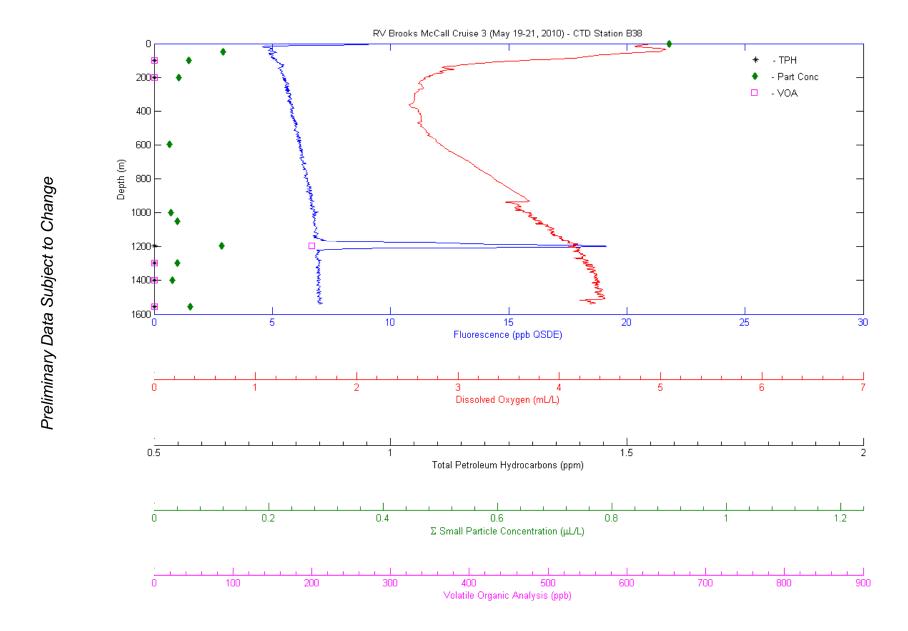


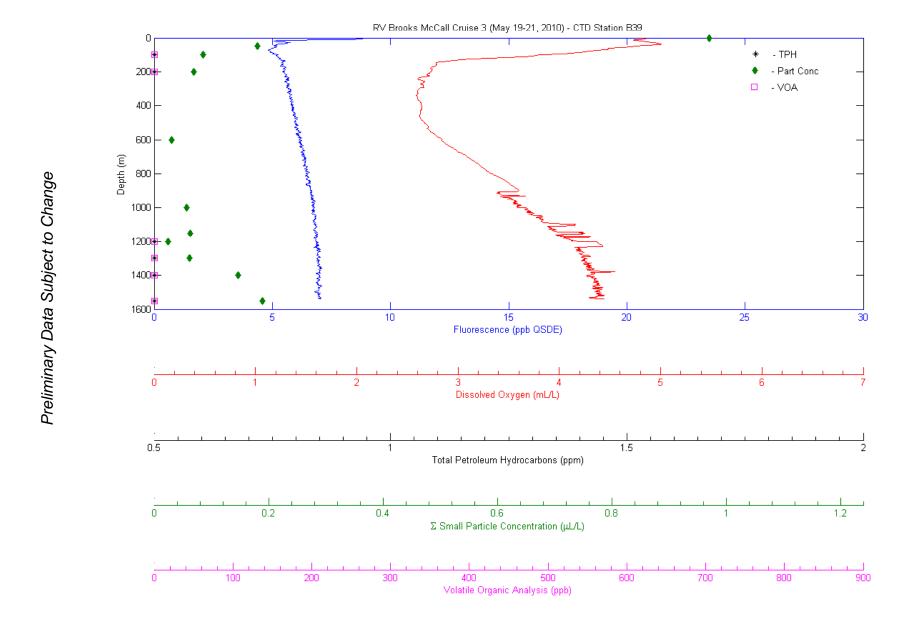


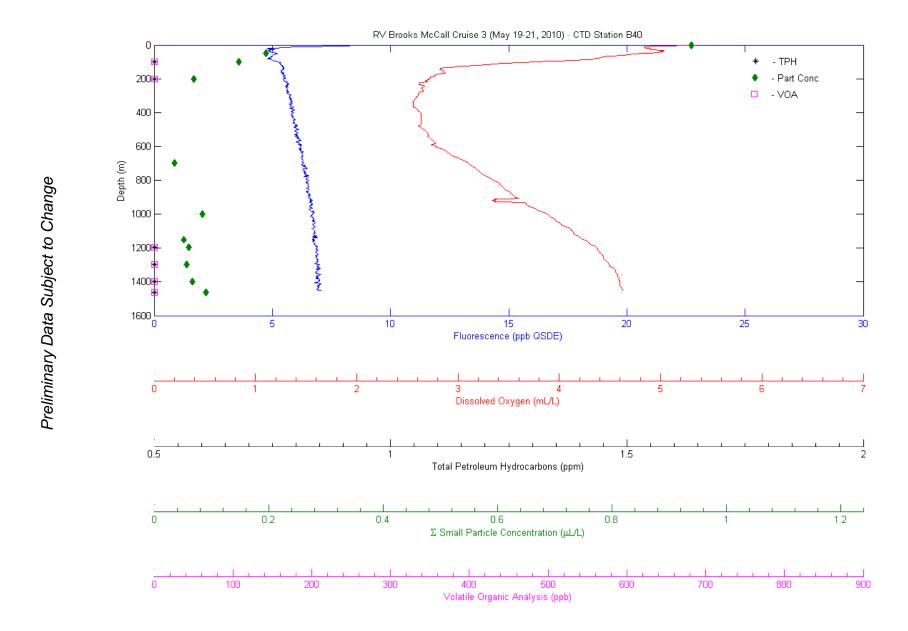


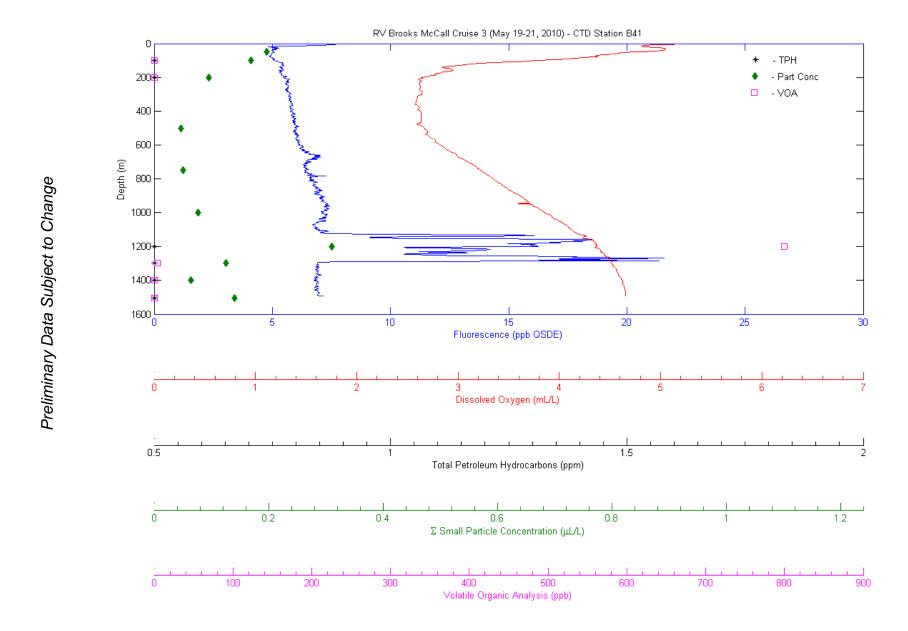


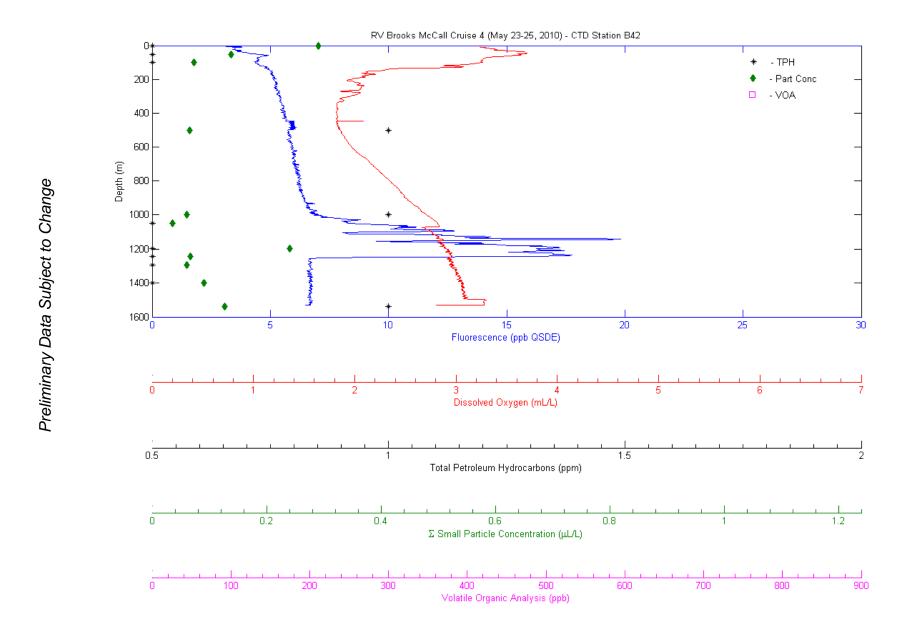


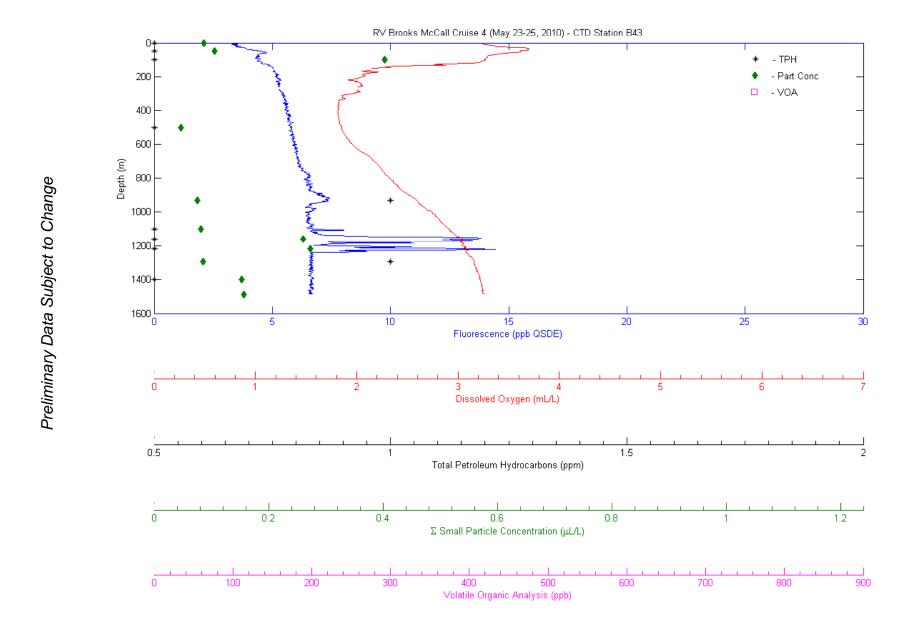


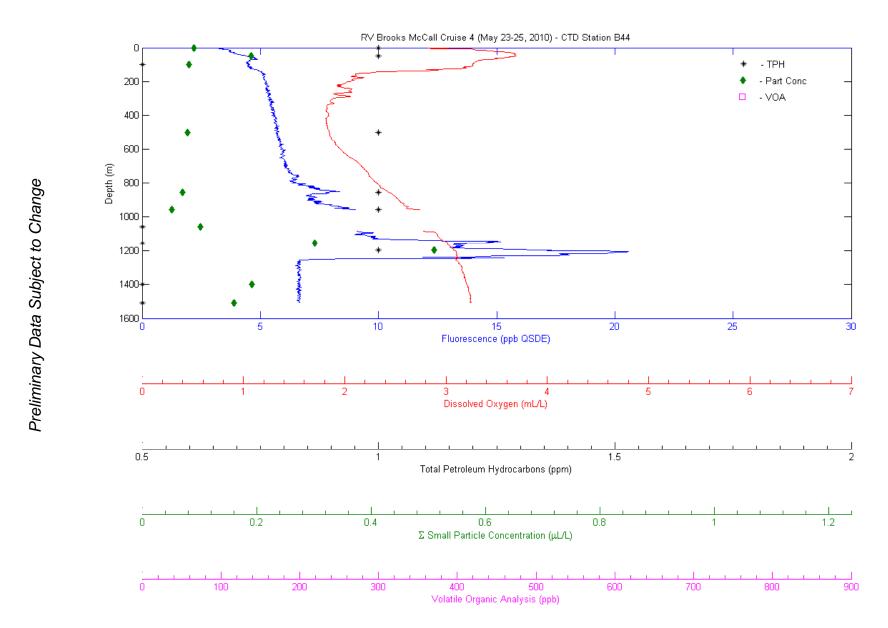


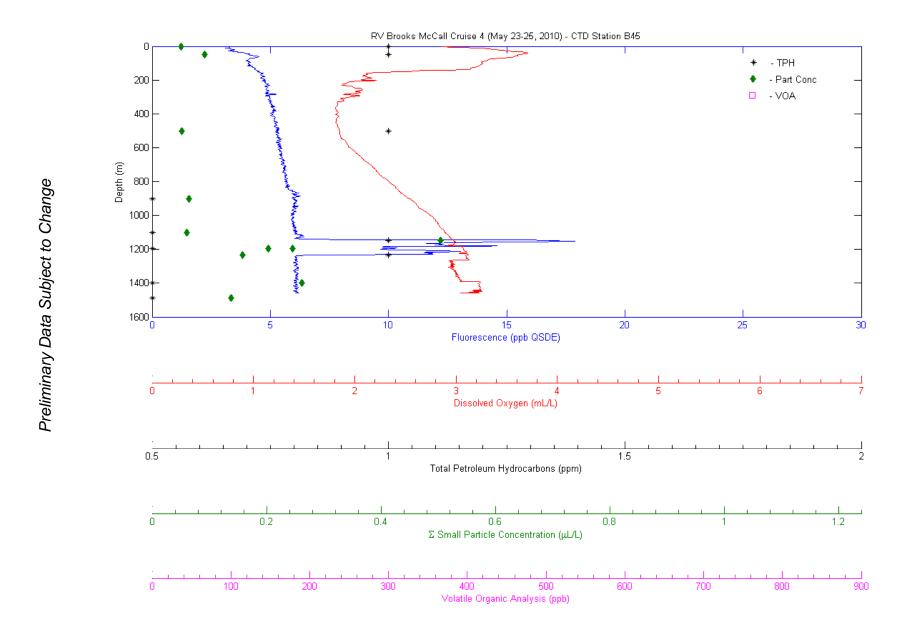


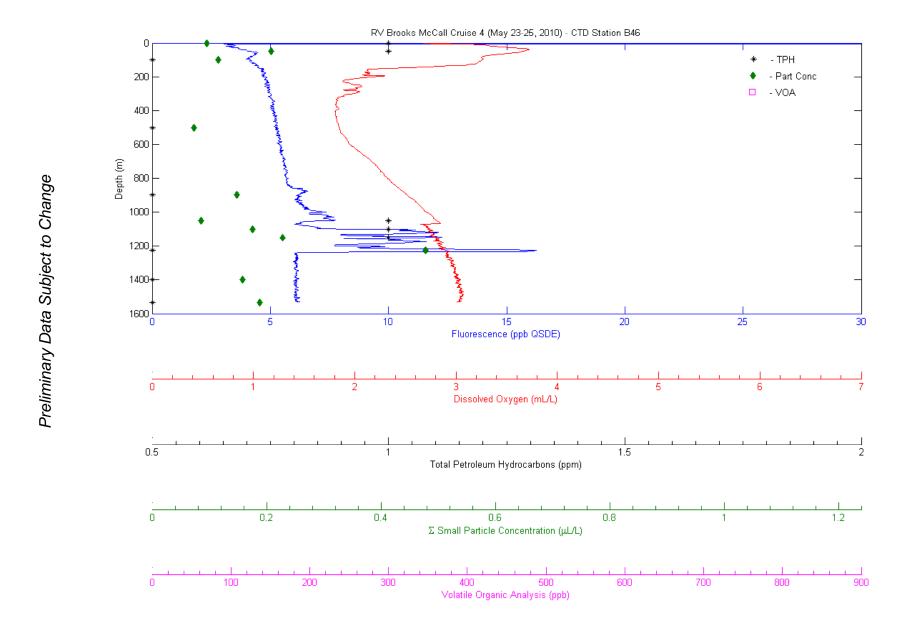


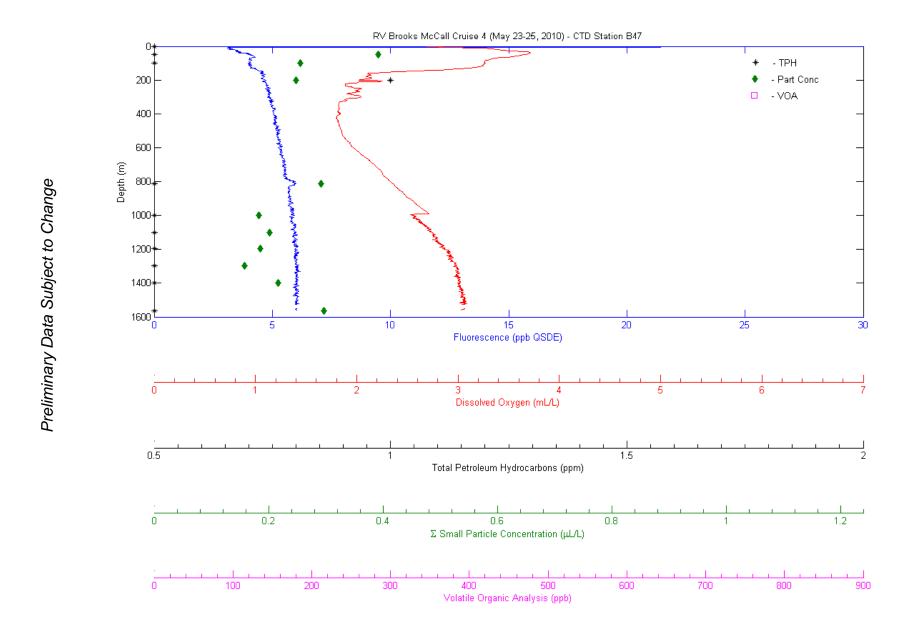


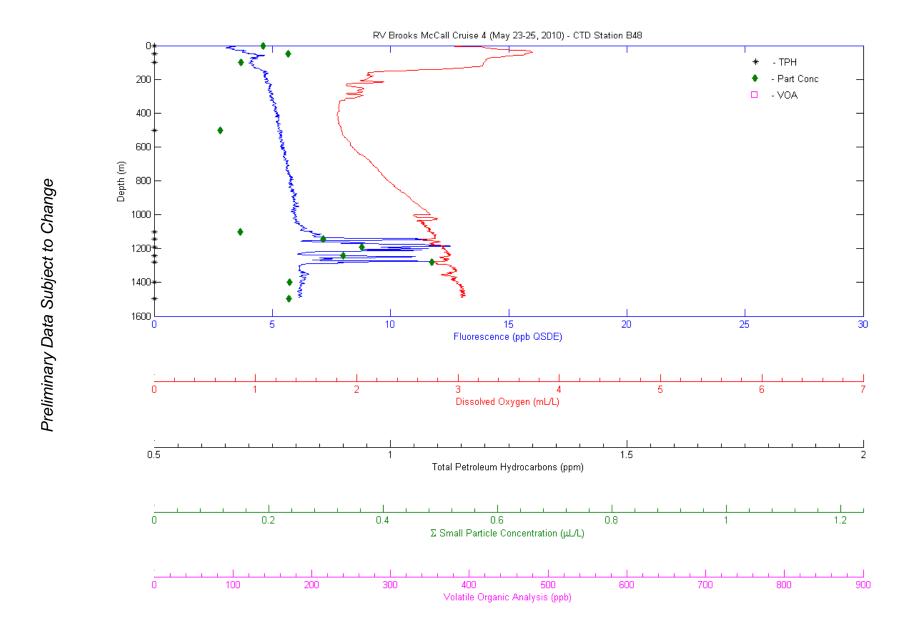


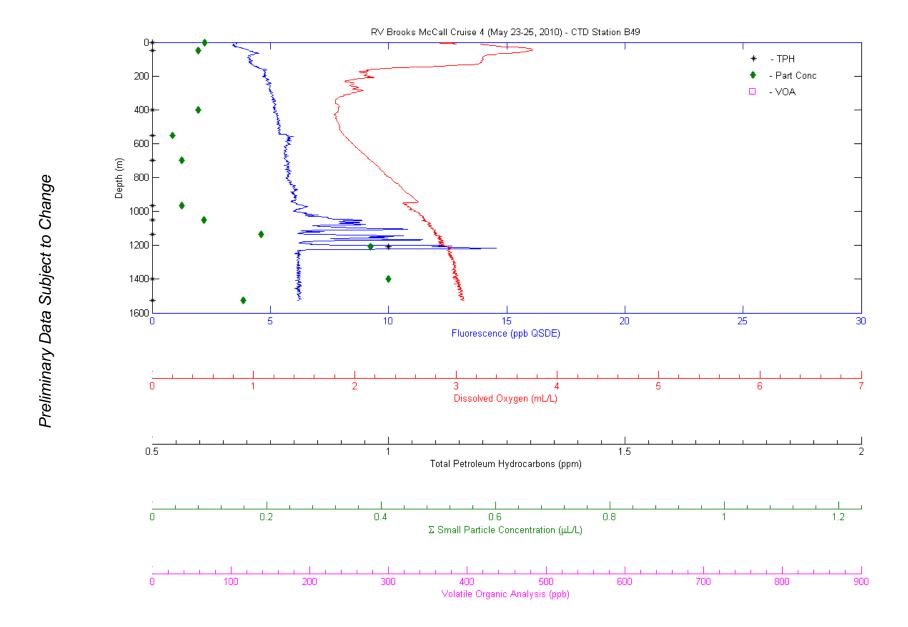


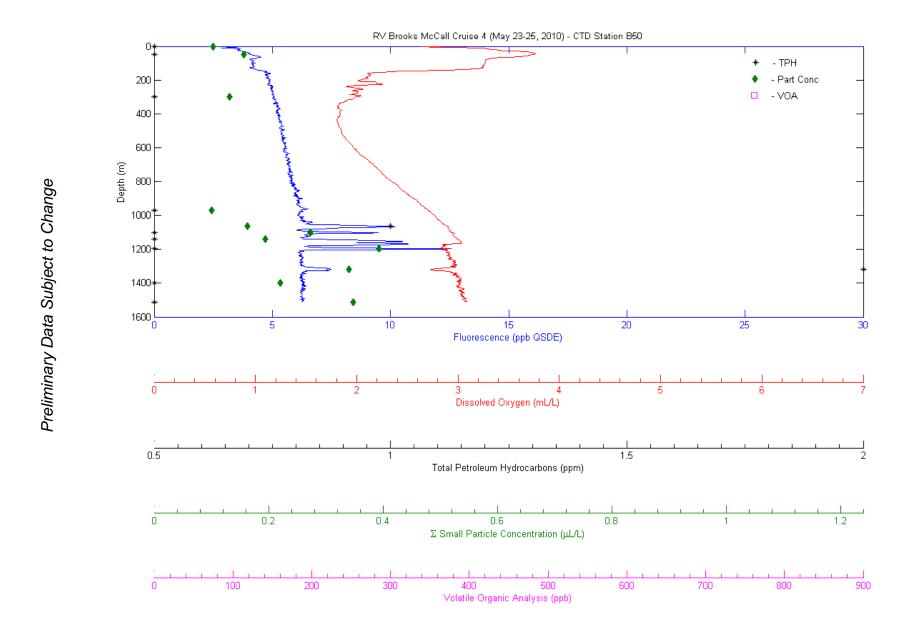


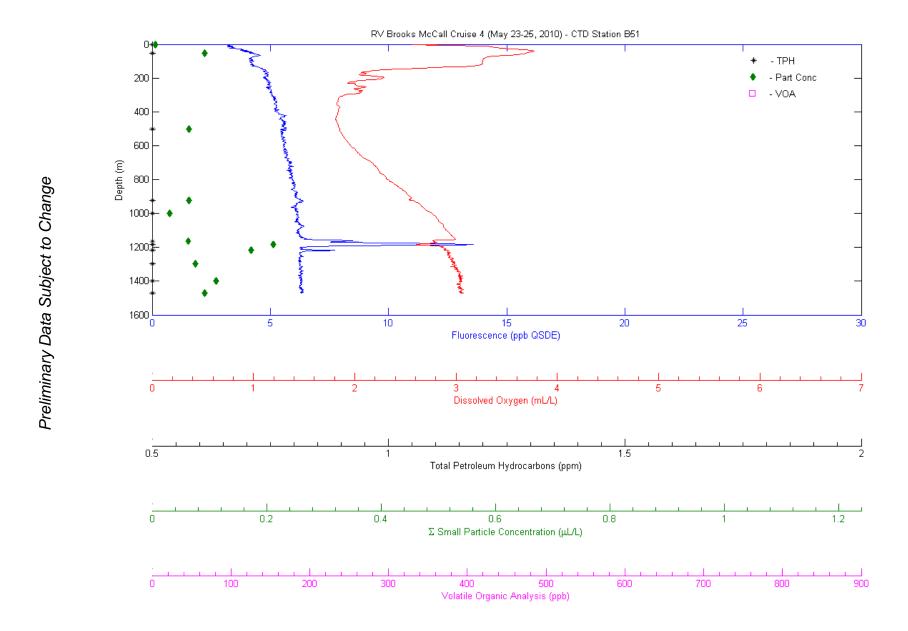












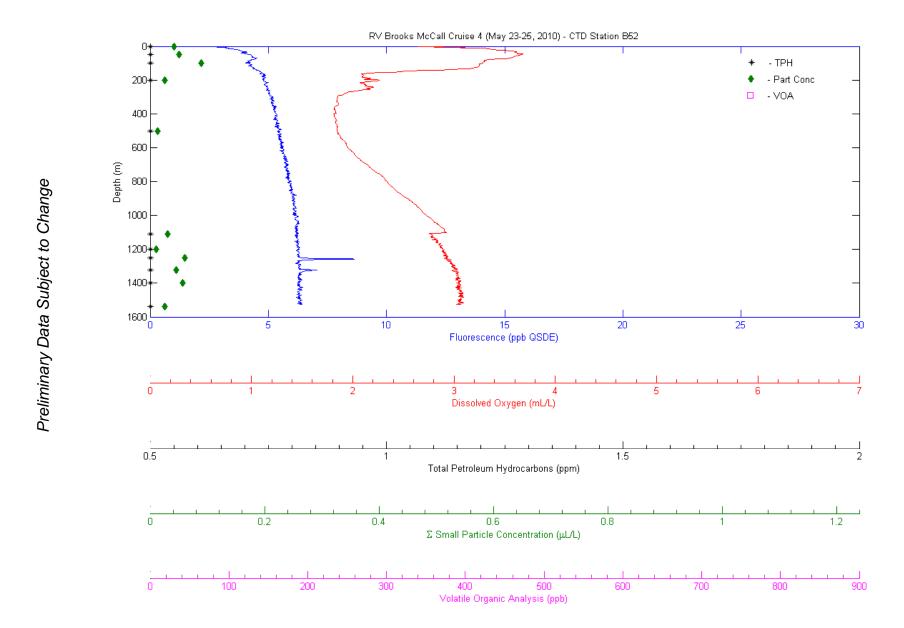


Figure 35. Dissolved oxygen data from cruises 2-4 contoured at 5 meter depth. This figure shows measurements taken over an 11 day period.

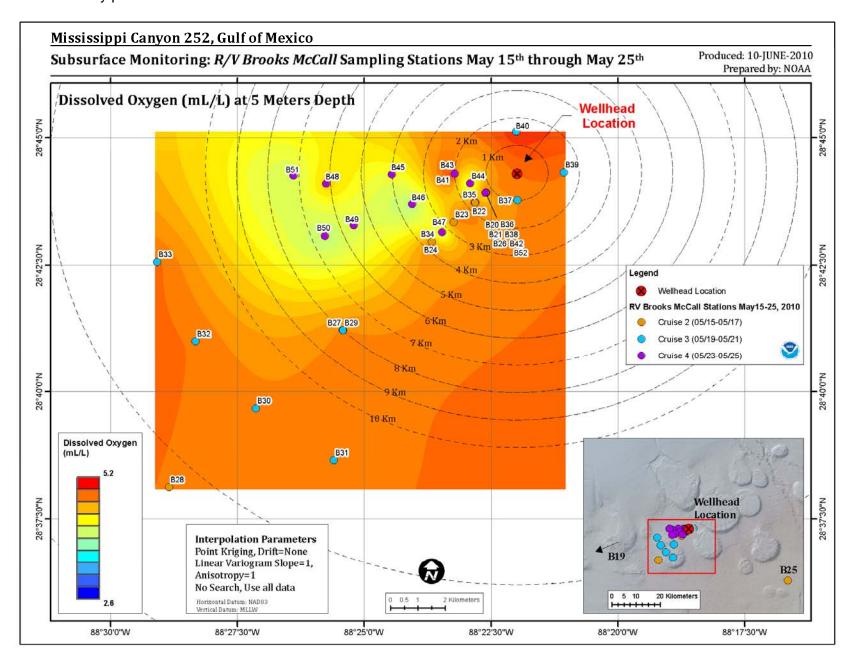


Figure 36. Dissolved oxygen data from cruises 2-4 contoured at 500 meter depth. This figure shows measurements taken over an 11 day period.

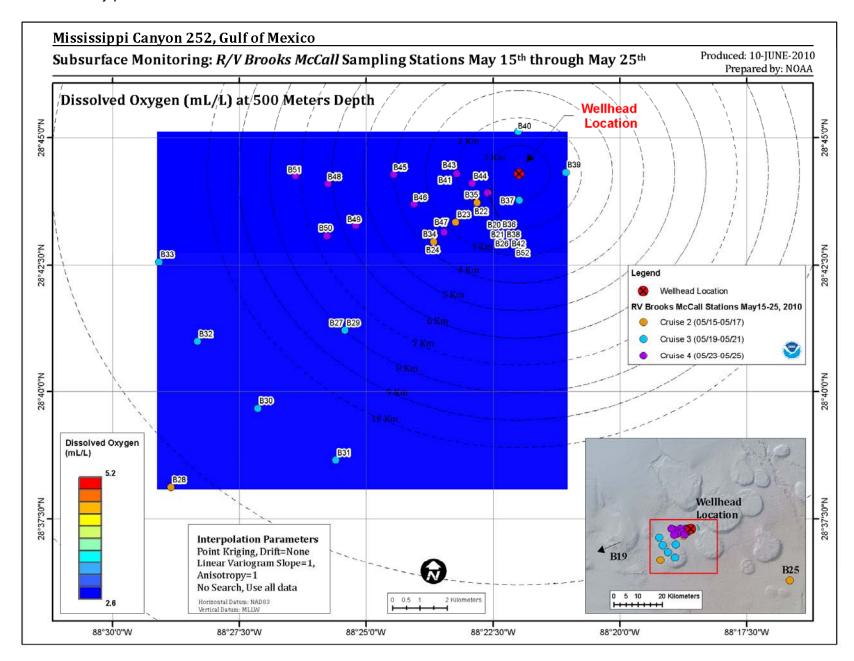


Figure 37. Dissolved oxygen data from cruises 2-4 contoured at 1000 meter depth. This figure shows measurements taken over an 11 day period.

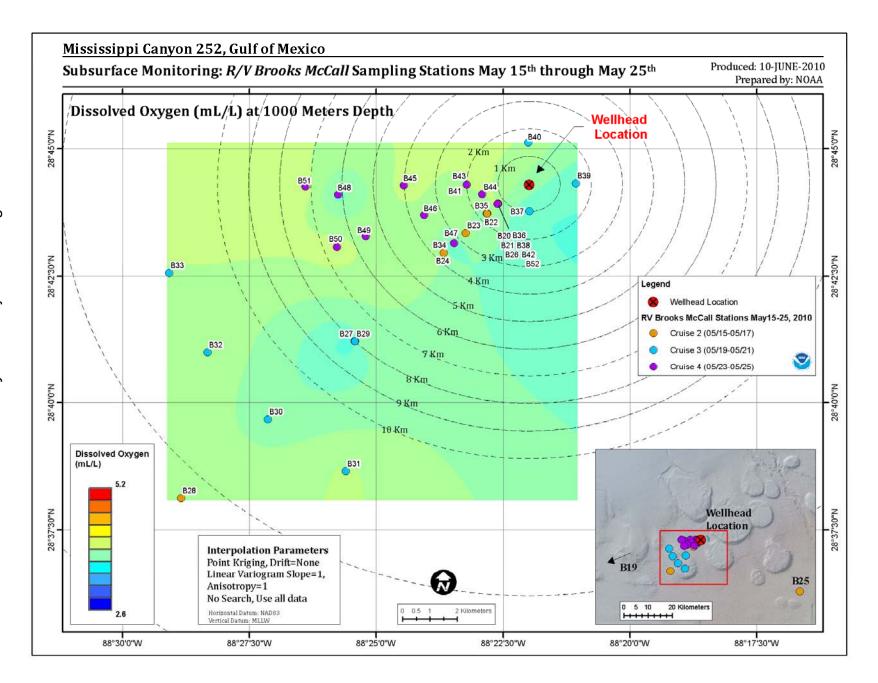


Figure 38. Dissolved oxygen data from cruises 2-4 contoured at 1100 meter depth. This figure shows measurements taken over an 11 day period.

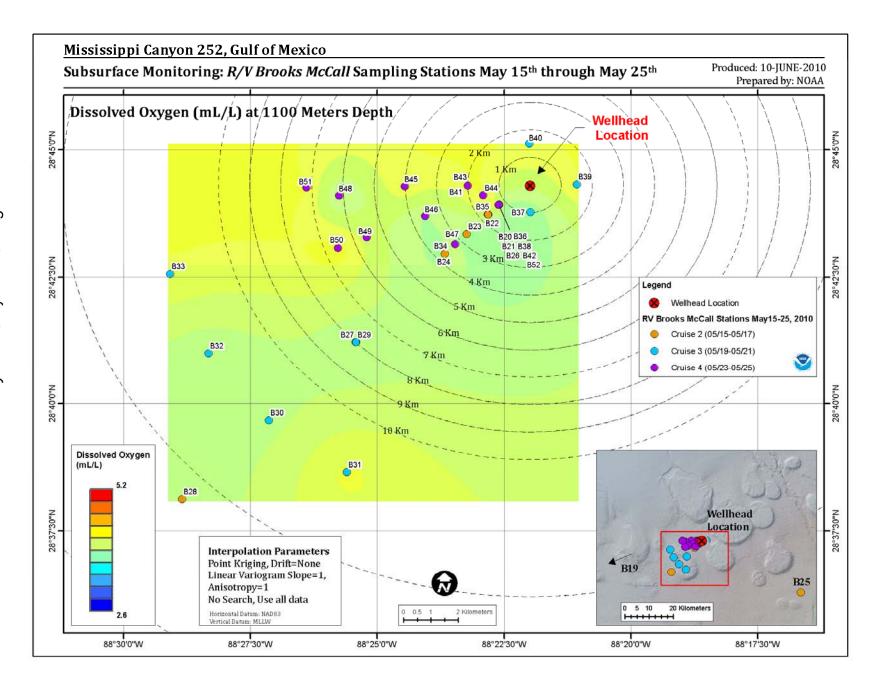


Figure 39. Dissolved oxygen data from cruises 2-4 contoured at 1200 meter depth. This figure shows measurements taken over an 11 day period.

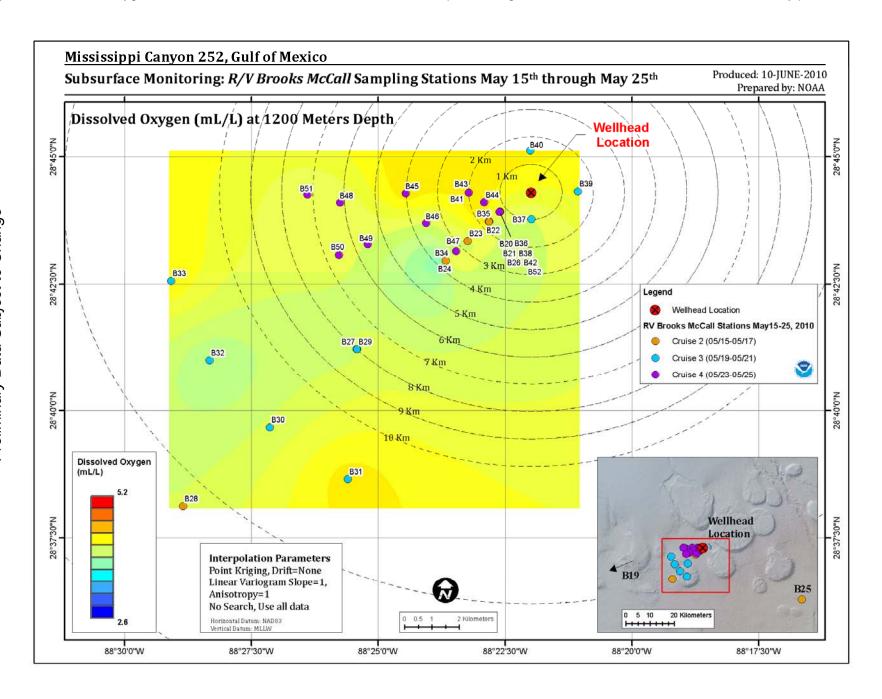


Figure 40. Dissolved oxygen data from cruises 2-4 contoured at 1300 meter depth. This figure shows measurements taken over an 11 day period.

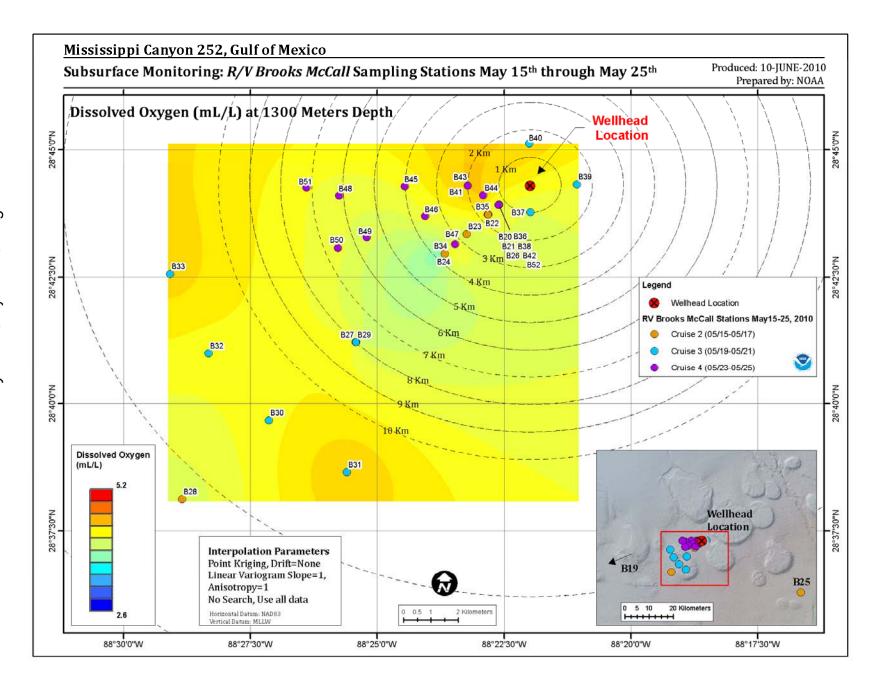


Figure 41. Dissolved oxygen data from cruises 2-4 contoured at 1400 meter depth. This figure shows measurements taken over an 11 day period.

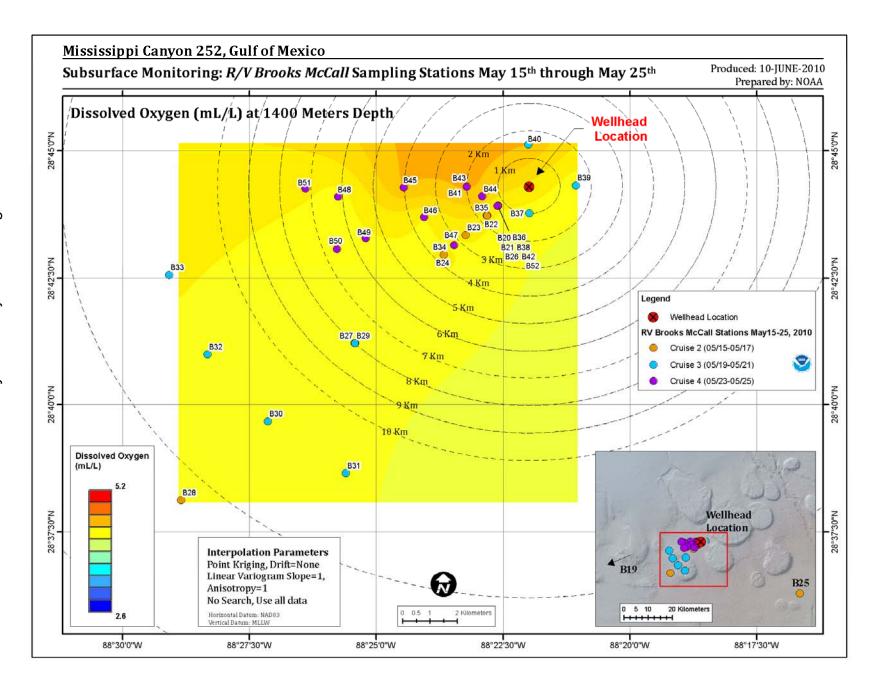


Figure 42. Dissolved oxygen data from cruises 2-4 contoured at bottom depth. This figure shows measurements taken over an 11 day period.

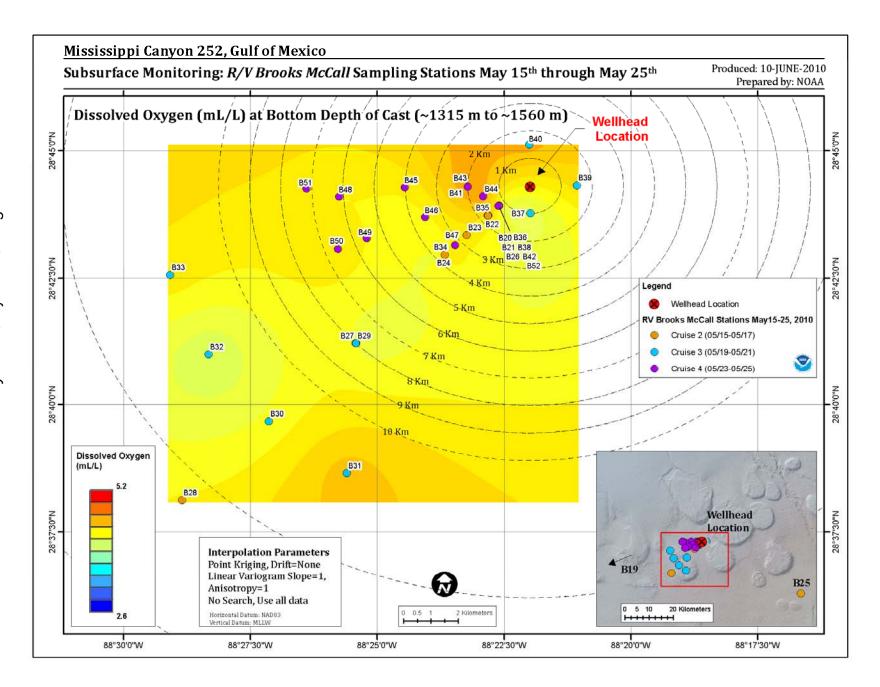


Figure 43. Comparison of RV Brook McCall O₂ data (black plus symbols) with historical May data (red circles) and complete dataset (green circles). The lower trend in waters below 1000 meters is attributed to the anomalous sensor response shown in Figure 44.

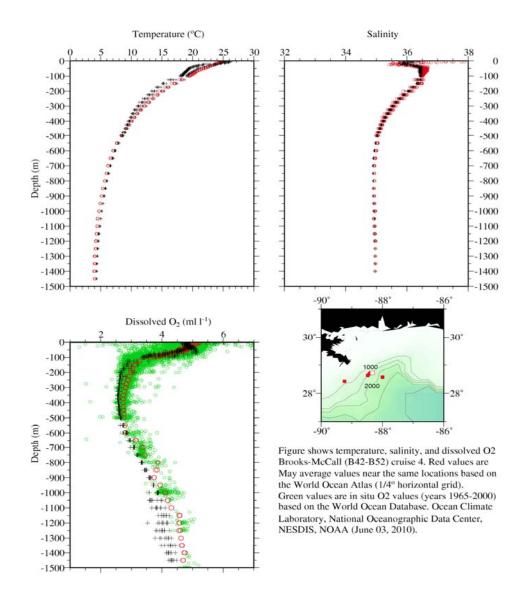


Figure 44. O₂ and fluorometer trace for station 48 between 1000 and 1500 meters. The sharp peaks in fluorescence at 1150, 1180, 1210 and 1380 m) often correspond to decreases in O₂. The small offset in depth between O₂ and fluorometry is attributed to known O₂ sensor response lag.

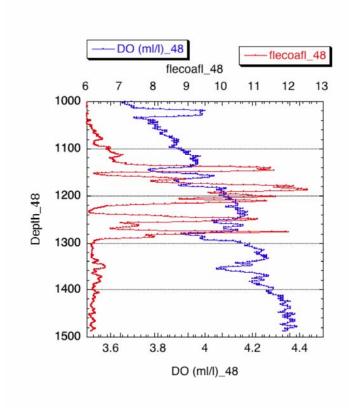
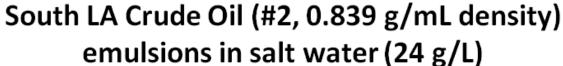


Figure 45. CDOM response curves produced by WET Labs for Louisiana Light Sweet crude oil. Instrument models: ECO FLCDs (CDS); ECO FLCDrt 2000 m rated (CD2000); ECO FLNTU (CHL and NTU). Source: http://www.wetlabs.com/Crude%20Oil%20Lab%20Test%20Client%20UpdateRZ_CK.doc.pdf



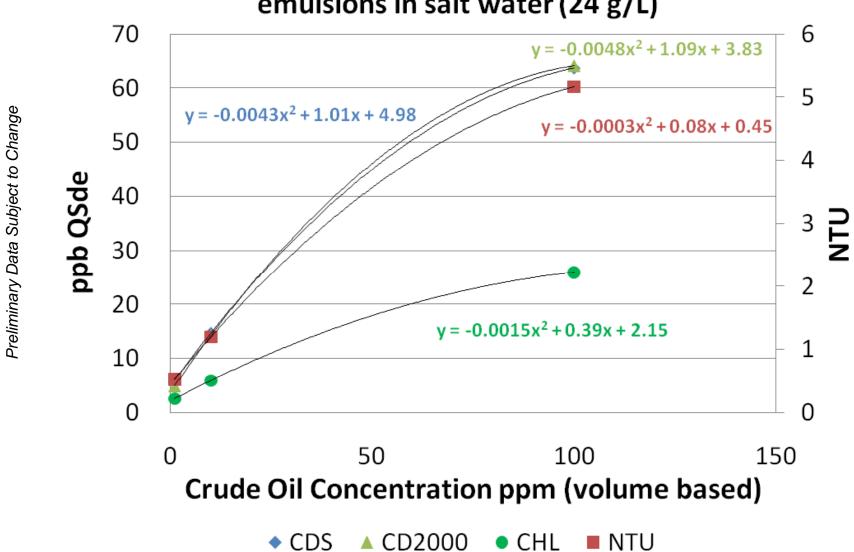


Figure 46. Composite graph of all processed data for leg 4 (= stations 42-52) of the RV Brooks McCall. The sudden drop in response below 1000 meters is attributed by the authors to sensor malfunction.

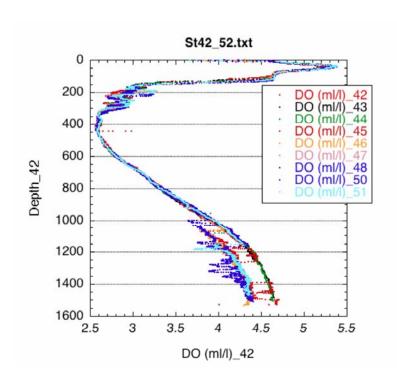


Figure 47. Downcast (blue) and upcast (red) for cast 22 showing the abrupt decrease in sensor response and increase in noise at 1000 m and recovery at 550 meters. The behavior is attributed by the authors to sensor malfunction.

