



## **Ryan Chouest Cruise 4 Summary Report**

***Period covered: 1700hrs 06/18/2010-1912hrs 06/23/2010***

***858.34 – Cruise 4 Cumulative nautical miles covered***

### ***Vessel science party:***

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\*Joined crew at 1900hrs on 06/23/2010

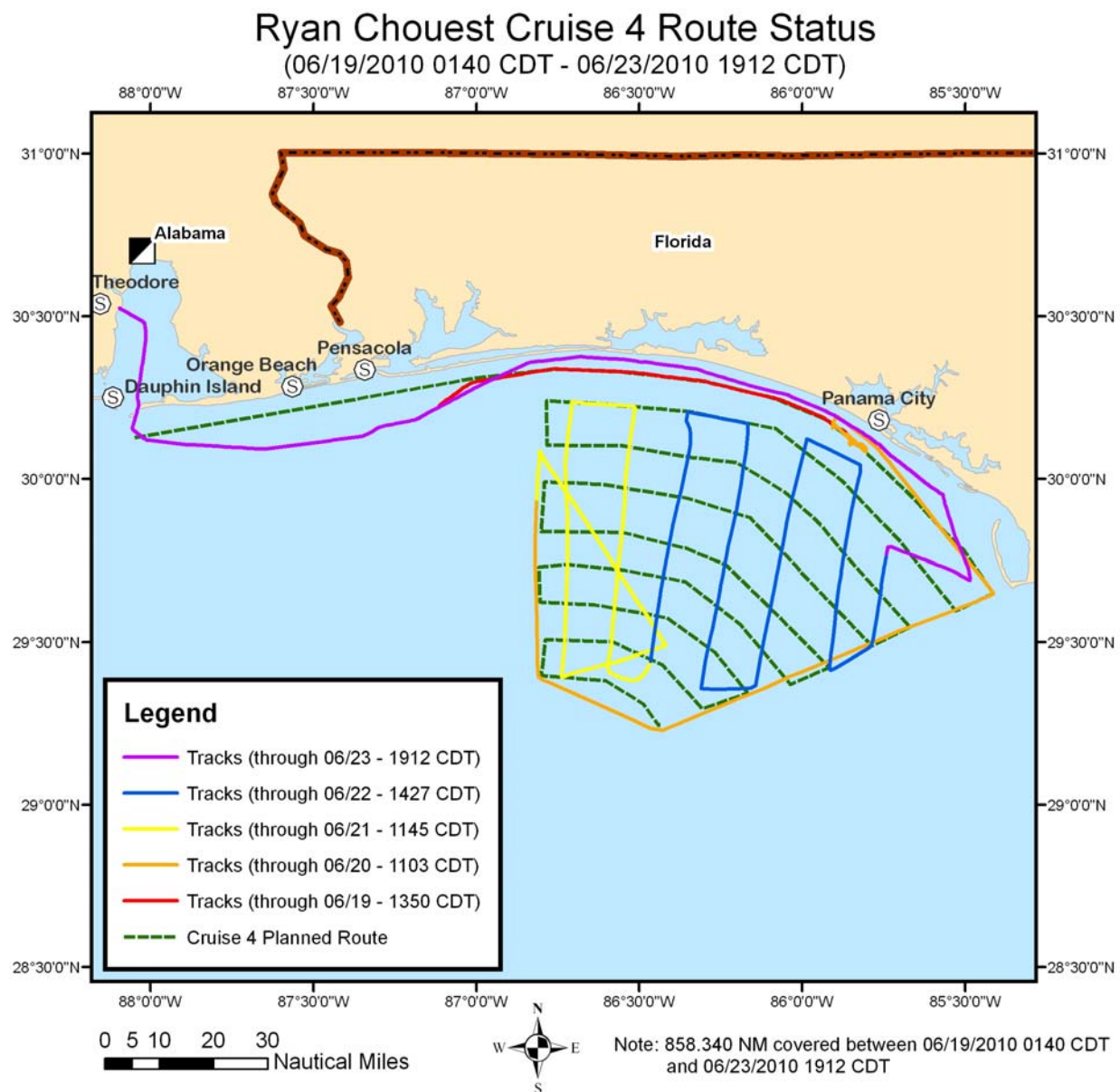
### ***Contact details:***

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+ 1 337-761-9826 - Broadband phone ship bridge

### ***Cruise notes:***

During this cruise, we have successfully monitored the inferred hydrocarbon concentrations for over 850 nautical miles off the coast of Florida and Alabama. We sailed the ship track for cruise 4 shown in Figure 1 from 1700hrs 06/18/2010 to 1912 hrs 06/23/2010. Vertical fluorometry casts were also taken to test the equipment perform chemical analyses on the water and ultimately to improve the deployment system for deeper water sampling (130m) for Cruise 5.

## Planned versus actual route taken for cruise 4:



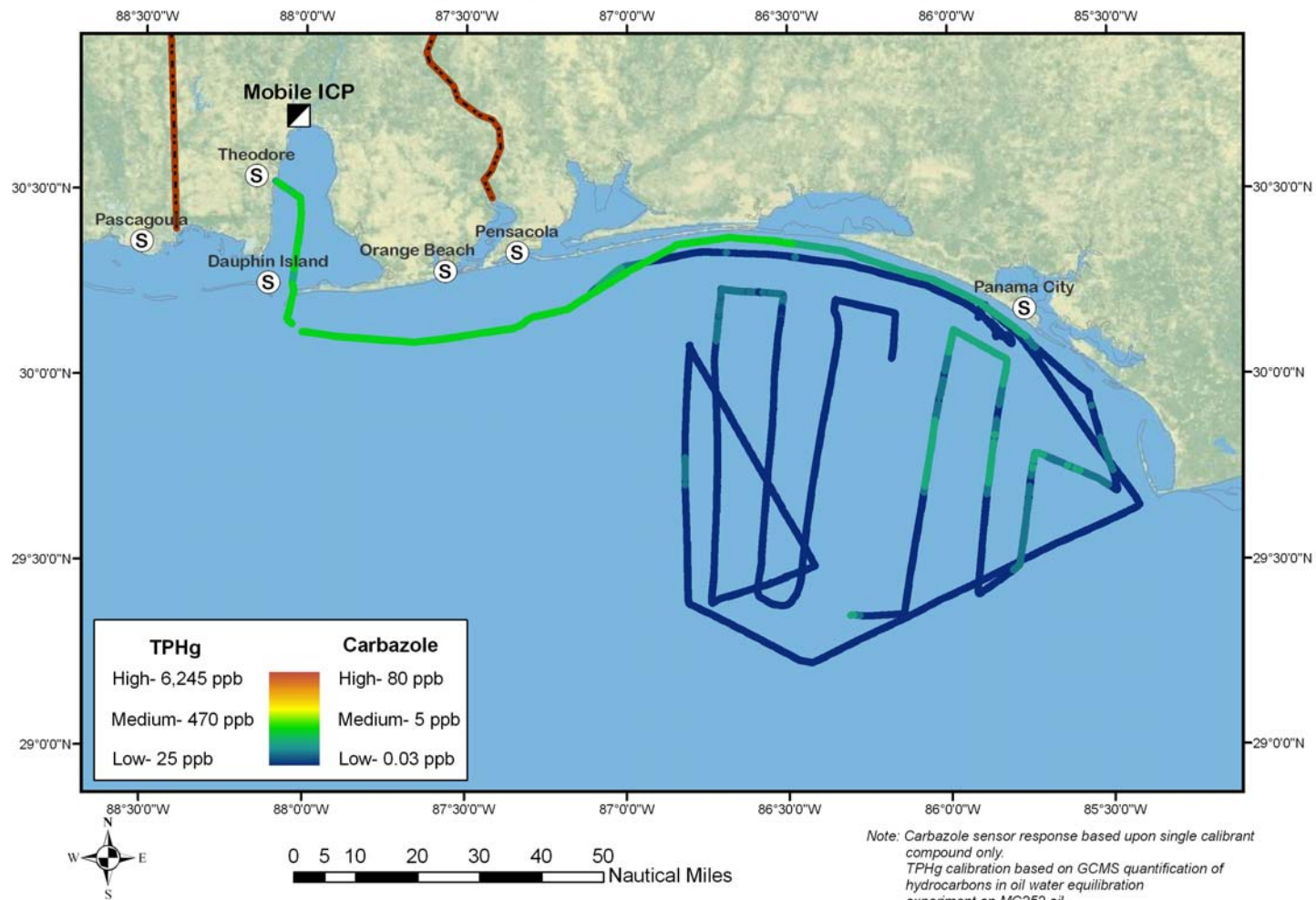
**Figure 1:** Planned versus actual route course plotted between 06/19/2010 –06/23/2010.

## ***Science results and preliminary interpretation:***

### **Fluorometry results**

*Cruise 4 General Observations:* Fluorometry measurements for all three sensors show low to medium inferred hydrocarbon concentrations and generally increase to medium levels towards Panama City and along the coast towards Theodore, Alabama (Figures 2-4). Inferred hydrocarbon concentrations ranged from 0.03 ppb to 5 ppb relative to Carbazole and 25 ppb to 0.470 ppm relative to TPHg.

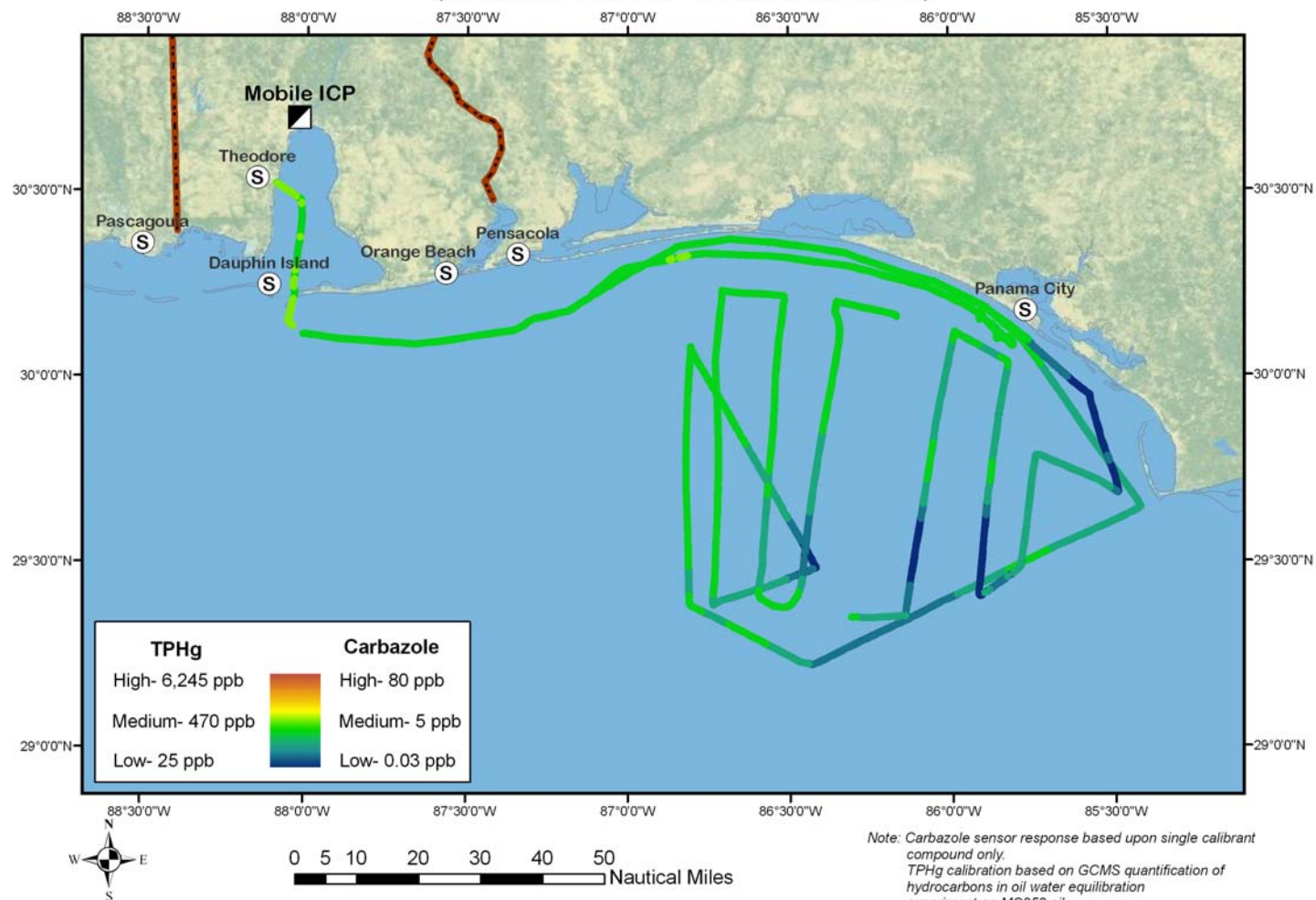
Ryan Chouest Cruise 4 Data  
 Chelsea - Fluorometer  
 (06/18/2010 1700 CDT - 06/23/2010 1912 CDT)



**Figure 2.** Chelsea fluorometer results plotted with location on cruise 4 track. Breaks in data occur when either data quality is poor or the systems were turned off due to pump problems.

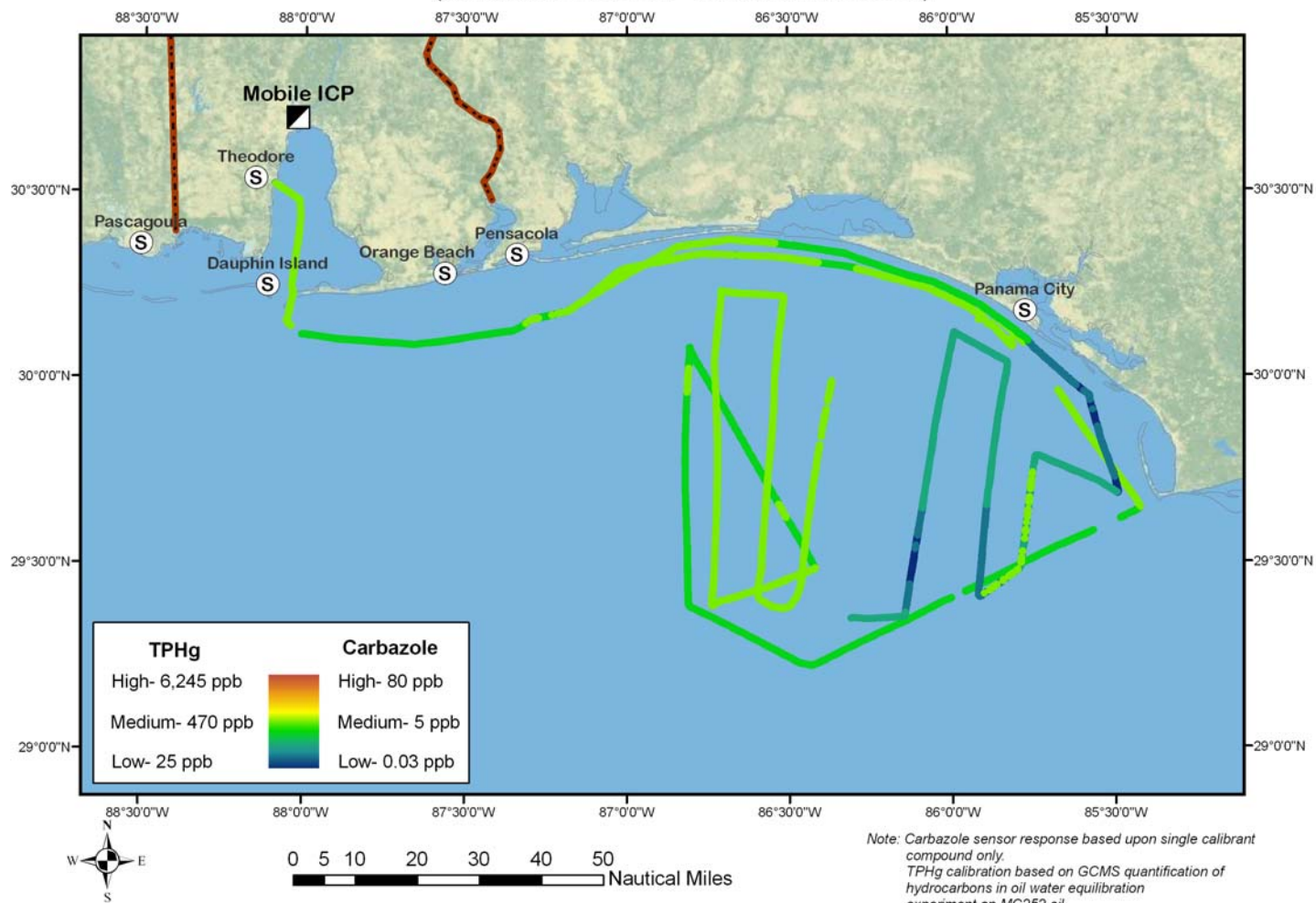
## Ryan Chouest Cruise 4 Data Trios - Fluorometer

(06/18/2010 1700 CDT - 06/23/2010 1912 CDT)



**Figure 3.** Trios fluorometer results plotted with location on cruise 4 track. Breaks in data occur when either data quality is poor or the systems were turned off due to pump problems.

Ryan Chouest Cruise 4 Data  
 Contros - Fluorometer  
 (06/18/2010 1700 CDT - 06/23/2010 1912 CDT)



**Figure 4.** Contros fluorometer results plotted with location on cruise 4 track. Breaks in data occur when either data quality is poor or the systems were turned off due to pump problems.

*Instrumental Calibrations:* The sensors have now been calibrated with a dissolved hydrocarbon equilibrated water. The hydrocarbon equilibrated water was prepared by a slow stirring method previously described. A layer of oil is placed on top of a partially water filled bottle containing vertically placed glass tube which has its end a few millimeters from the bottom of the bottle and magnetic stirrer bar. The water is stirred with the magnetic stirrer bar on low rotation for 48 hours in order to allow full equilibration between the water and oil above. Once complete the water is drawn out from the bottle via the glass tube with a pipette and in this case was extracted using the SPE methodology and then subsequently analyzed and quantified by GCMS to obtain the Total Petroleum (see the chemistry section and figures 16 and 17) Hydrocarbons dissolved fraction (TPHg). The oil used for this calibration was the MC252 oil. The sensors are calibrated by a serial addition of the hydrocarbon equilibrated water into a known volume of water in a calibration cell to build a calibration curve of each sensors response. Both the original single compound carbazole and TPHg calibrations are shown on the same scale for reference in the figures showing sensor response.

*Potential Oiling Footprints:* We continue to observe that the use of the previous day's potential oiling footprint from ERMA does not necessarily compare well to the actual oil extent during the period over which the sensor results and visual observations are made. The relationship between the potential oiling footprint and the shallow subsurface fluorometry readings is still unclear; however, there has been little opportunity to fully explore the data. In addition, the use of remotely sensed data alone may prove to be misleading as the potential oiling extents are collected during a 24 hour period, do not give any information on the character of the slick (sheen, mousse, or its thickness) nor the degree of weathering that the potential slick has undergone. In addition, the sensor readings are taken below the sea surface where there may be a decoupling of the surface expression of the oil and the oil components dissolved into the water column. This would be especially true for weathered oil accumulations where the components that are monitored by the fluorometers have been effectively removed by water washing, photo oxidation, and/or evaporative losses.

## **Surface Observations**

We observed a wide variety of oil slicks on Cruise 4 as shown in Figures 5A -5C. By far, the most common slicks observed were light surface sheens and in some places with small, dispersed pieces of orange mousse (Photographs 1-3). Seaweed aggregates are common throughout the surveyed transects (Photographs 4-5), but they are particularly concentrated in areas of current convergence (Photograph 7). A person could mistake seaweed for brown mousse depending on the height/angle of observer from sea surface and angle that the sun hits the sea surface. Variations in surface sheen are also quite common (Photograph 2) and may result from slight differences in the thickness and/or concentrations of hydrocarbons in the surface neuston layer. Wind fields do not seem to cause all of the slick variations because these are observed on days with very calm winds. Less frequent observations were rainbow sheens (Figure 5B; Photograph 6), red-orange emulsions (Figure 5A&B; Photograph 8), and orange pancake mousses (Figure 5A, Photographs 9-10).

# Ryan Chouest Cruise 4 Route Status

(06/19/2010 0140 CDT - 06/23/2010 1912 CDT)

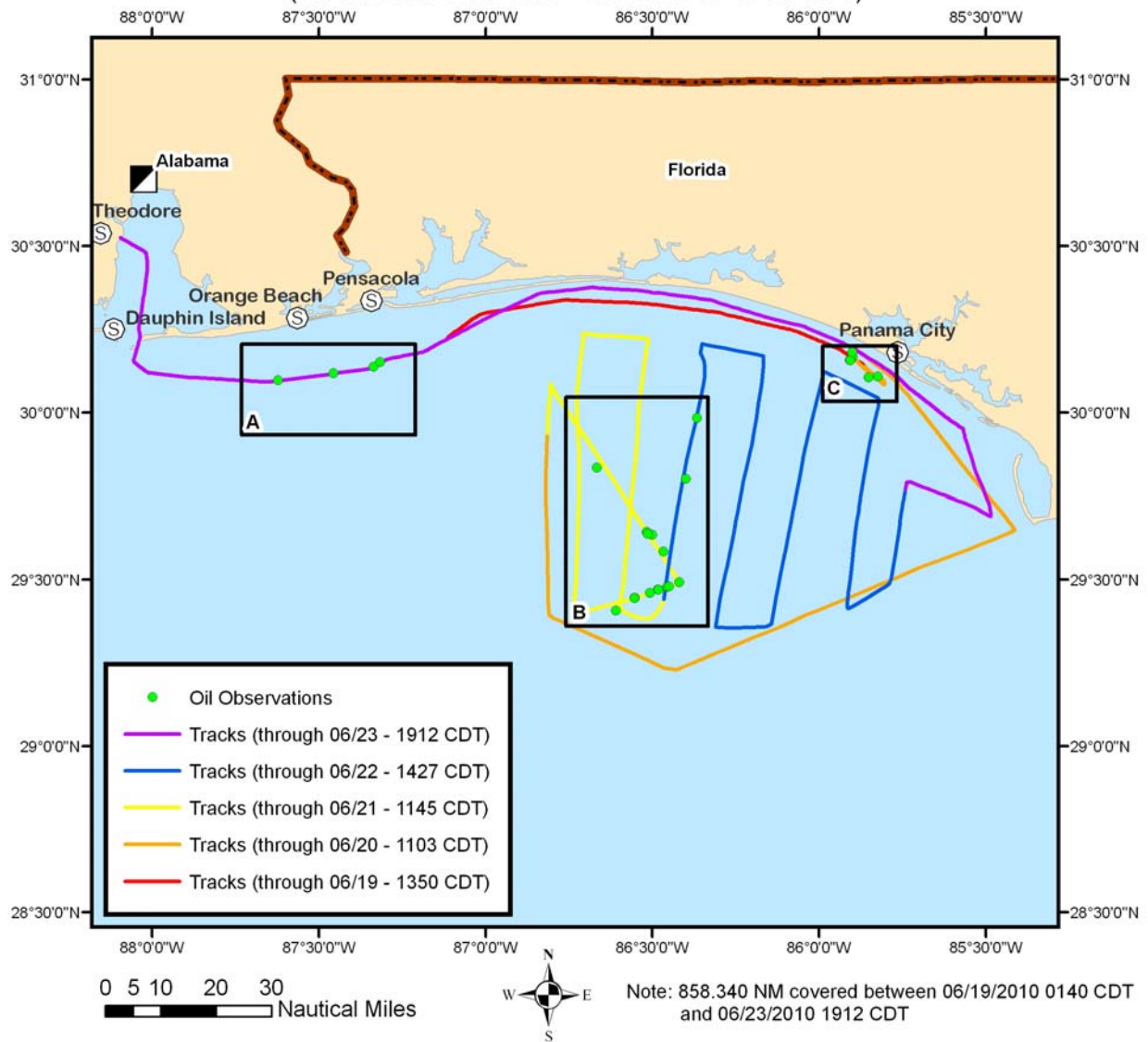


Figure 5. Total oil slick observations plotted between 06/19/2010 –06/23/2010.

Ryan Chouest Cruise 4 Data  
 Oil Observations - A  
 (06/19/2010 0140 CDT - 06/23/2010 1912 CDT)

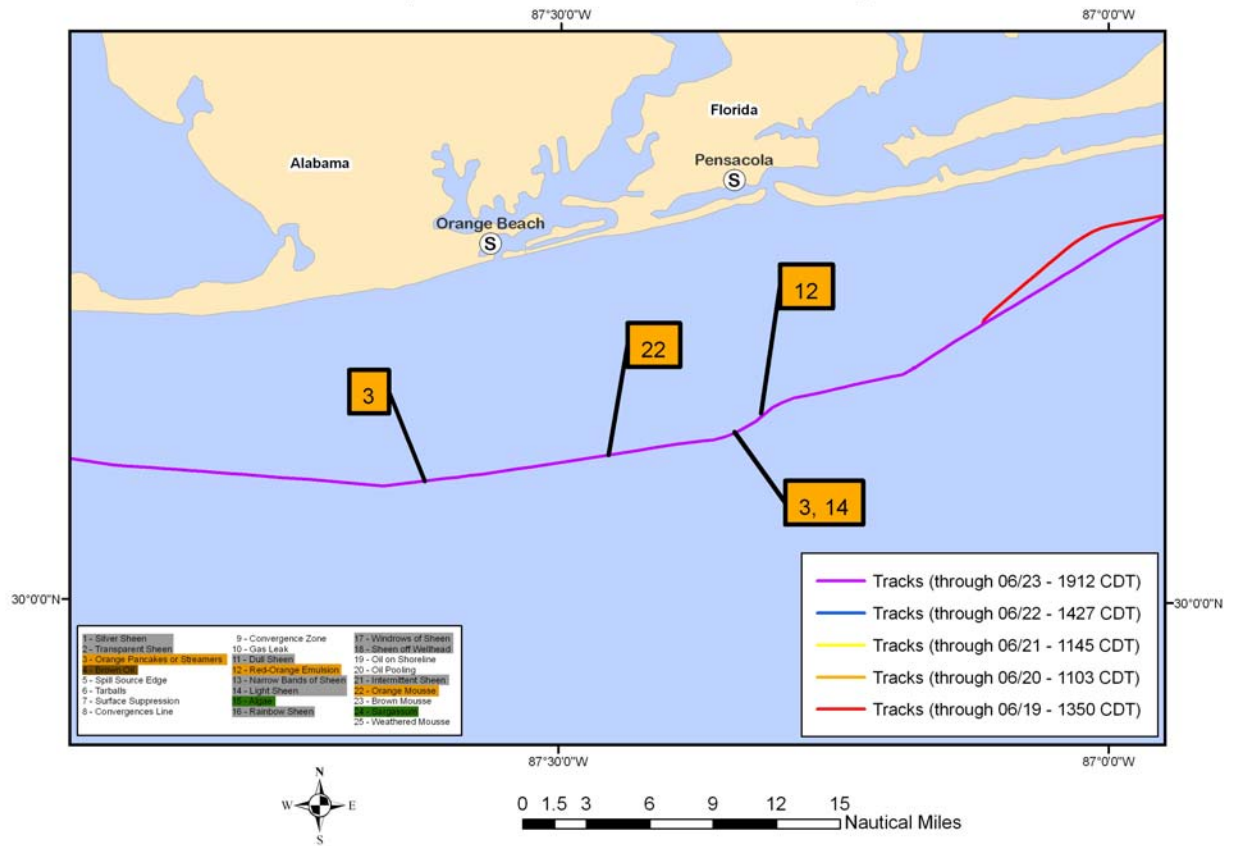


Figure 5A. Large scale map of region A in Figure 5 showing oil slick observations. See also Photographs 9-10.



Ryan Chouest Cruise 4 Data  
 Oil Observations - B  
 (06/19/2010 0140 CDT - 06/23/2010 1912 CDT)

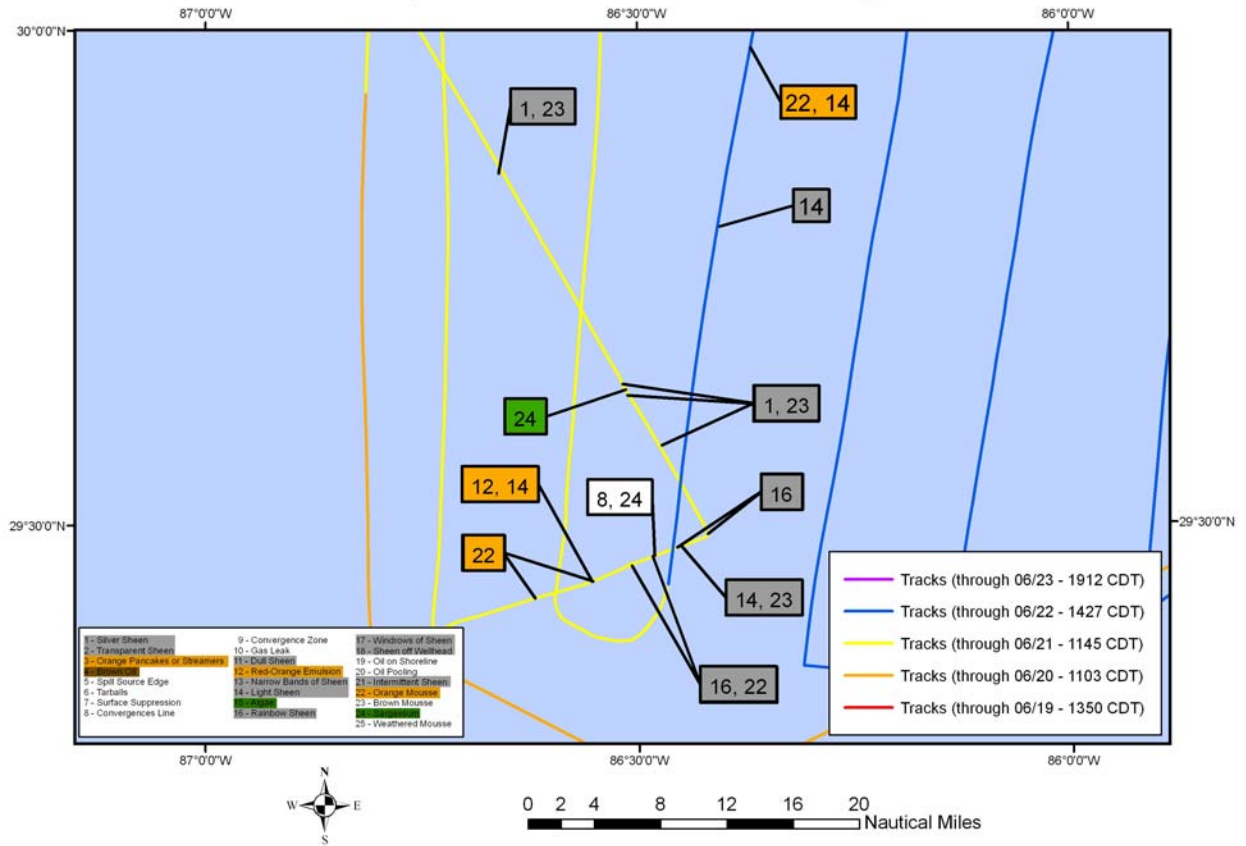


Figure 5B. Large scale map of region B in Figure 5 showing oil slick observations. See also Photographs 4-8.

Ryan Chouest Cruise 4 Data  
Oil Observations - C  
(06/19/2010 0140 CDT - 06/23/2010 1912 CDT)

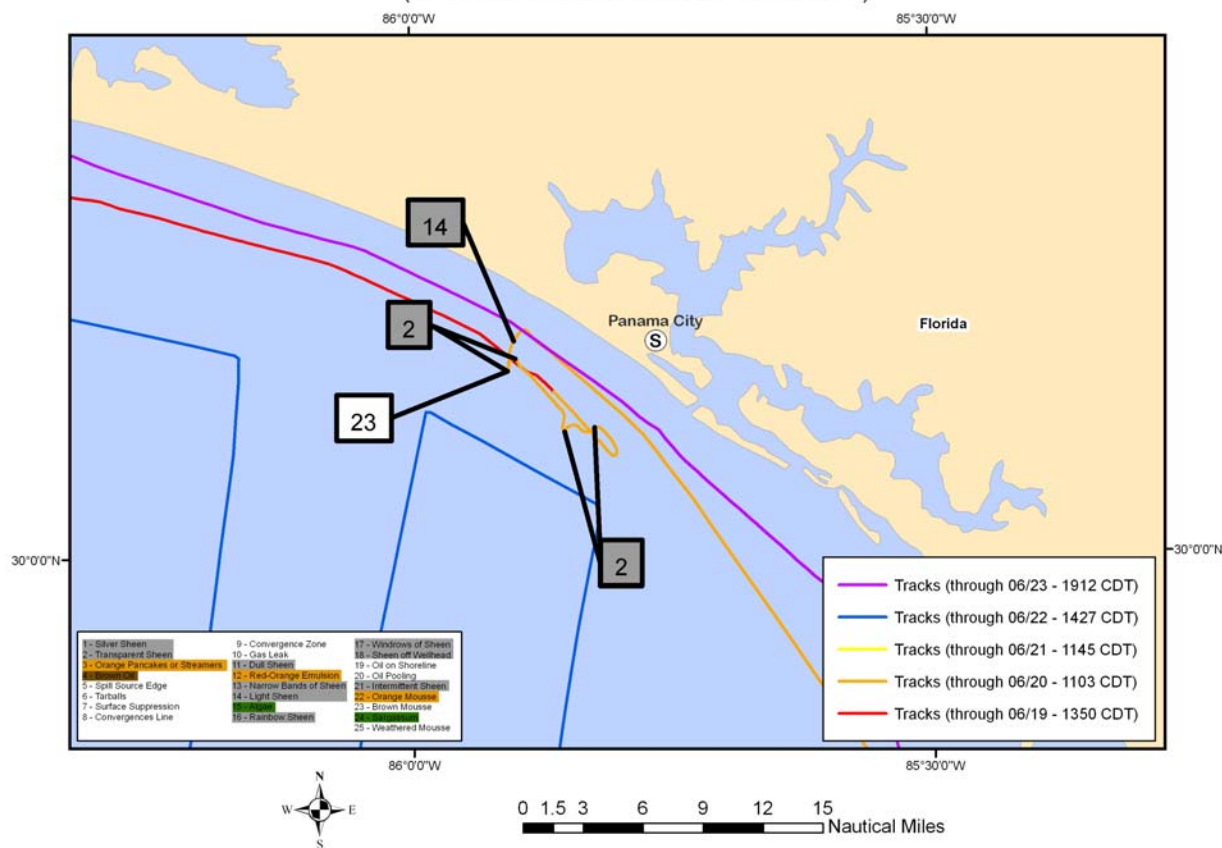


Figure 5C. Large-scale map of region C in Figure 5 showing oil slick observations. See also Photographs 1-3.

## Chemistry

Part of the science capability onboard the Ryan Chouest includes a Gas Chromatograph Mass Spectrometer (GCMS) over the last few weeks limited surface water samples have been taken for method development and testing for organic compounds in the surface waters. This activity will now become routine and the science team onboard will sample both the shallow surface waters (1-2 m deep) but also water close to the sea floor in coastal waters. In addition samples of sheens and mousses will also be taken and subsequently analysed in order to build a deeper understanding between the surface slick expression and the waters below and tie this into the sensor readings.

Analyses to date have focused on the use of Solid Phase Extraction (SPE) where water is passed through a cartridge containing an adsorbent phase which traps hydrocarbons. These hydrocarbons are subsequently released by passing a solvent through the cartridge. The method offers potential advantages over liquid-liquid extraction another extraction method commonly used. The advantages of using solid phase extraction are: they can potentially reduce the volumes of solvents used on board; allow greater concentration of hydrocarbons by passing large volumes of water through them; have been designed specifically for oil and grease analysis pertaining to EPA method 1664. The two stage SPE water extraction method briefly comprises:

1. Collecting a 1 L sample of water in a cleaned glass jar, where an SPE cartridge can be fitted.
2. Conditioning of the SPE cartridge with isopropyl alcohol
3. Attach the SPE cartridge to the glass sample jar and pass the sample through the SPE cartridge.
4. Dry the SPE cartridge for 10 min.
5. Rinse the 2<sup>nd</sup> cartridge SPE cartridge with Dichloromethane (DCM).
6. Place the 1<sup>st</sup> cartridge on top of the 2<sup>nd</sup> cartridge and elute with 15 mL of DCM.
7. Collect the sample containing the aliphatic and aromatic hydrocarbons and put in a vial for analysis on a GC-MS

The analysis of the SPE hydrocarbon extract takes place through the use of a Gas Chromatograph-Mass Spectrometer (GC-MS). A liquid aliquot of the sample obtained by the SPE method is injected into GC (Agilent 7890A) via a splitless injector connected to a DB-5MS (J&W, 60 m, 0.25 mm ID, 0.25 µm film thickness). The temperature program of the GC oven starts at 40 °C (2 min hold) with a ramp of 8 °C/min to 310 °C (20 min hold). The MS (Agilent 5975C MSD) is run on scan mode from 10-300 AMU to increase the sensitivity of low to medium molecular weight hydrocarbons which are generally more volatile and are subject to evaporative losses.

Typical results for the SPE separation followed by GCMS analysis are shown in figure 6. The figure shows a Total Ion Chromatogram (TIC) of a 5 litre water sample over the virtually the whole GCMS run time. Figures 7-12 and 13-14 all show sections of these full TIC's as it aids presentation if certain sections of the TIC can be enlarged as the compound peaks are more easily identified, especially in samples where there are low concentrations of hydrocarbons. Each of the figures (a) and (b) TICs are equally scaled, however each separate figure is scaled appropriate to the height of the peaks within the TIC. Figures 7 and 8 show the results of two tests, a blank SPE run using milliQ water and a second test using 5 L of seawater collected when sensor readings were very low. It is immediately apparent from the figures that the SPE blank sample contains numerous hydrocarbon compound peaks, albeit at low concentrations.

It is not uncommon in geochemistry to find a few contaminant peaks within blanks, however the objective of any blank is that it is just that. Similar blanks using liquid-liquid extraction procedures as well as GCMS analyses of all the solvents used have eliminated all other sources of possible contamination. As such we are very disappointed with the manufacturer of the SPE cartridges (whose name we have left out of this report). We are investigating with the manufacturer if anything can be done to solve the problem however, in the near term we will use well-established liquid-liquid extraction methods even though they do not enable us to concentrate hydrocarbons from large volumes of water.

A significant problem with the blank is that contamination peaks co-elute in regions of interest for hydrocarbon compounds which more readily dissolve into the aqueous phase such as toluene, xylenes, naphthalenes, methylnaphthalenes (figure 7). This inhibits their accurate detection and quantification in water using this method. Within the higher molecular weight range this is less of a problem (figure 8). The results between the blank and seawater collected within a zone of low sensor response show fewer compounds present in the seawater sample than the blank in the low molecular weight range (figure 7). However in the higher molecular weight range normal and branched alkanes are detectable (identification based on fragment ion pattern). It is not clear the source of these compounds due to their low concentration in the sample.

A series of tests of the waters below silver sheen and mousse fragments were carried out at 29° 27.5368 N 86° 30.4297 W on the 06\20\2010 at 20:00. Figure 9 and 10 show the results of analyses carried out on 5 L water samples from 3 m beneath the water's surface compared to those of the SPE blank. The sample shows and that there are no hydrocarbon compounds observable in addition to those already found in the blank analyses. Once again a 1 L sample of surface sheen failed to detect hydrocarbons in

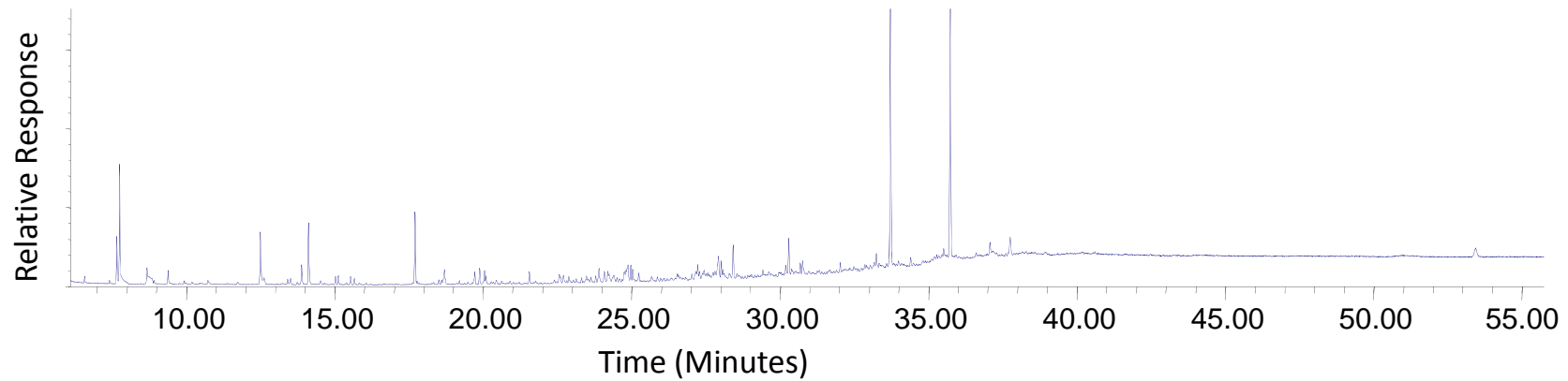
addition to those found in the SPE blank (figures 11 and 12). This may have been due to the very low concentration of hydrocarbons associated with the surface sheen or due to an inefficient sampling of the sheen into the sample bottle from over the side of the vessel.

The analysis of the associated mousse showed a distinct hydrocarbon compound profile (figure 13). The TIC shows a distinct hump overprinted by a homologous series of waxy *n*-alkanes from *n*-C<sub>17</sub> to *n*-C<sub>35</sub>. The existence of *n*-alkanes shows that significant biodegradation of the mousse has not occurred and the absence of low molecular weight compounds shows that the mousse has undergone significant evaporative and water washing losses. The hydrocarbon signature in the water under these accumulations may be expected to have a relative absence of hydrocarbons as most if not all of the hydrocarbons which readily partition into water have been lost.

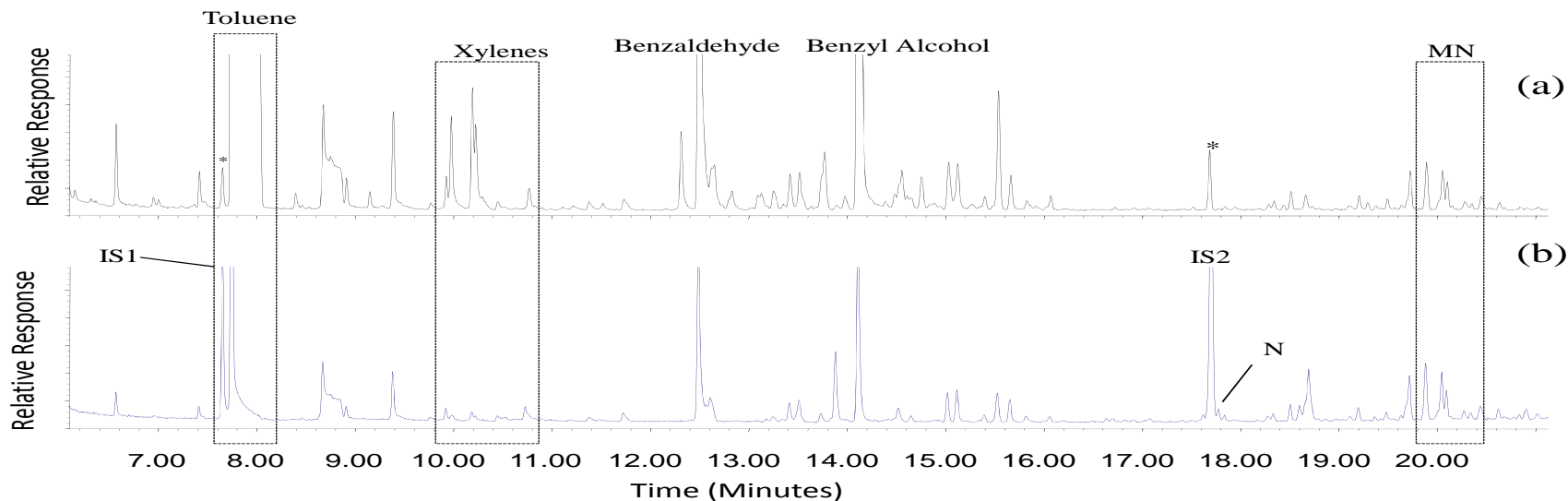
During cruise 4 the vertical cast system was operated for a number of shallow coastal water tests. One such test took place at 30° 05.8732 N, 85° 45.3941 W outside the Mobile shipping channel. The pump assembly was slowly lowered 20m to close to the seafloor during which time sensor responses were recorded. At the near surface (1 m depth) and bottom of the cast (20 m) water samples were taken for liquid-liquid extraction followed by GCMS analysis. In addition procedural blanks were also performed at the same time. These results (figures 14 and 15) show that procedural blank produced a much cleaner baseline than the SPE analysis and thus illustrates the level of contamination being imparted into the sample by the cartridges by the SPE method. Another observation that can be made from the data is that within the surface sample there are low but measurable concentrations of naphthalenes, quinolones, styrene and toluene (from library ion chromatogram matches). In the bottom sample only the toluene present from these compounds in much reduced abundance. Further casts recording both fluorometry readings and taking water samples are required to show if these samples are representative of the surface waters of the Gulf of Mexico.

To calibrate the sensors and understand which hydrocarbon compounds readily partition into water from the parent MC252, we performed a slow stirring experiment. Which has been previously described above in the sensor calibration section. The results shown in figures 16 and 17 show a much enhanced response when compared to those of the SPE blank. Within the low molecular weight section of the TIC there are many compounds visible which have partitioned from the parent oil into the water. In areas where the oil from the slick has not undergone significant weathering, it may be expected that these compounds may be detectable in trace quantities.

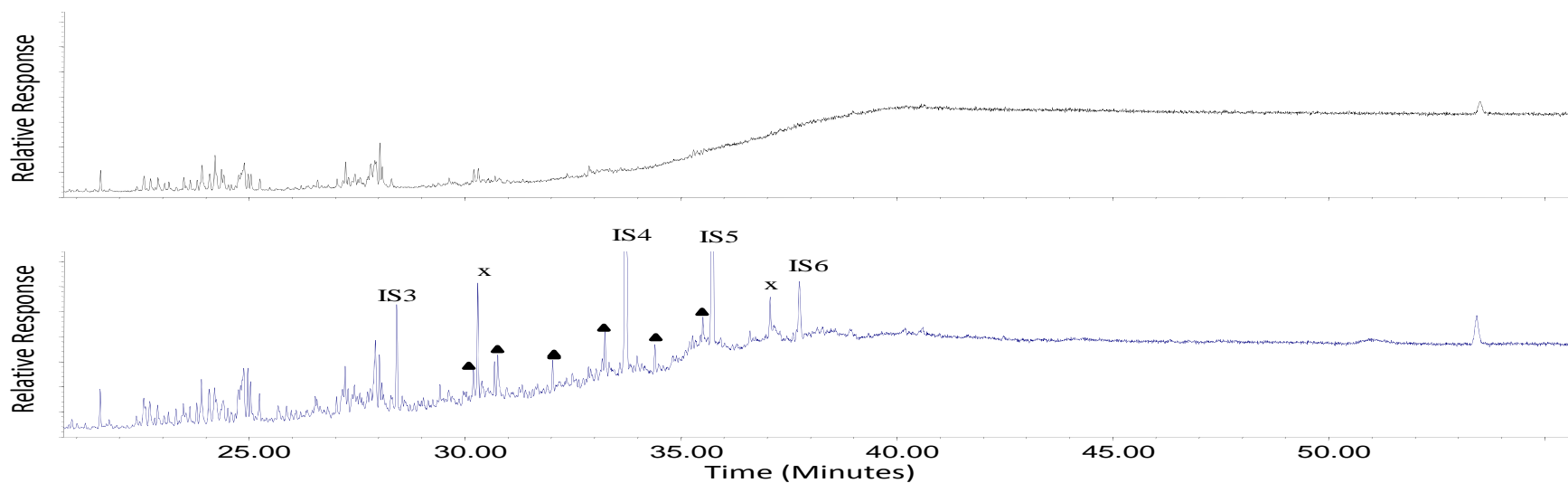
The whole oil TIC for MC252 parent oil (figure 18) shows an unbiodegraded (presence of *n*-alkanes and low molecular weight hydrocarbons) aliphatic *n* alkane dominated crude oil with abundant of toluene and Xylene. Work on the geochemical methodologies will continue and routine water sampling is now part of the workflow on board and further results will be presented as they become available.



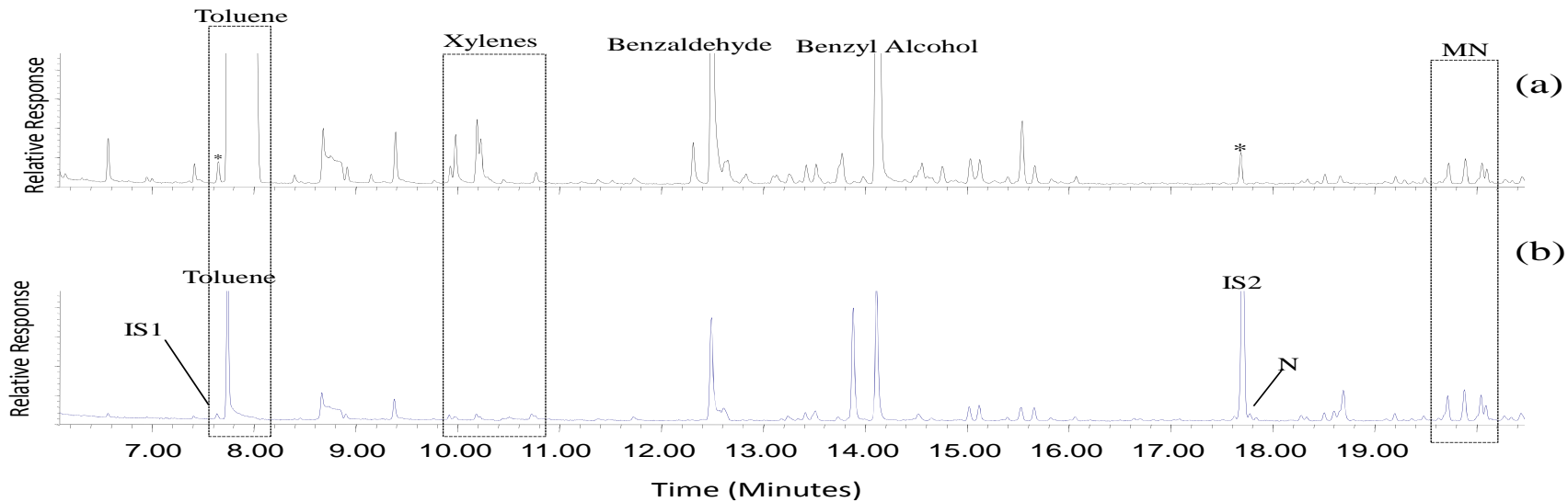
**Figure 6.** Example Total Ion Chromatogram (TIC) for a 5 litre sample of clean seawater extracted using Solid Phase Extraction (SPE).



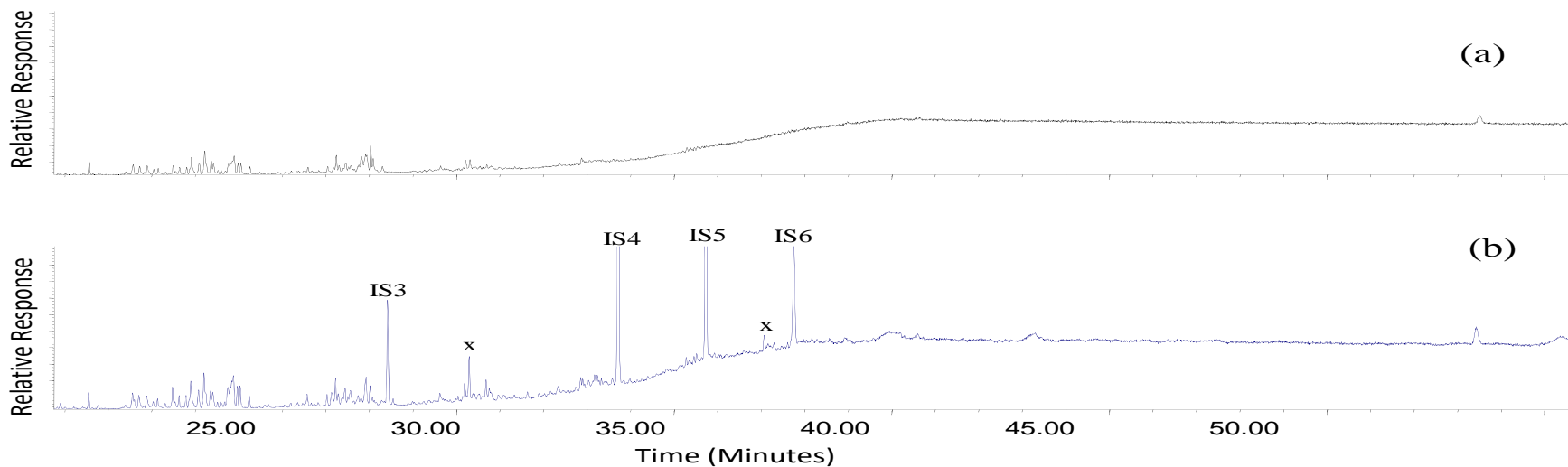
**Figure 7.** SPE Blank (a) versus (b) SPE of seawater collected when sensor readings were very low showing the TIC region with low molecular weight range of compounds from 6 minutes to 21 minutes. IS1= d-toluene, IS2= d-Naphthalene. \*indicated that the peak is not the same as found in the corresponding chromatogram.



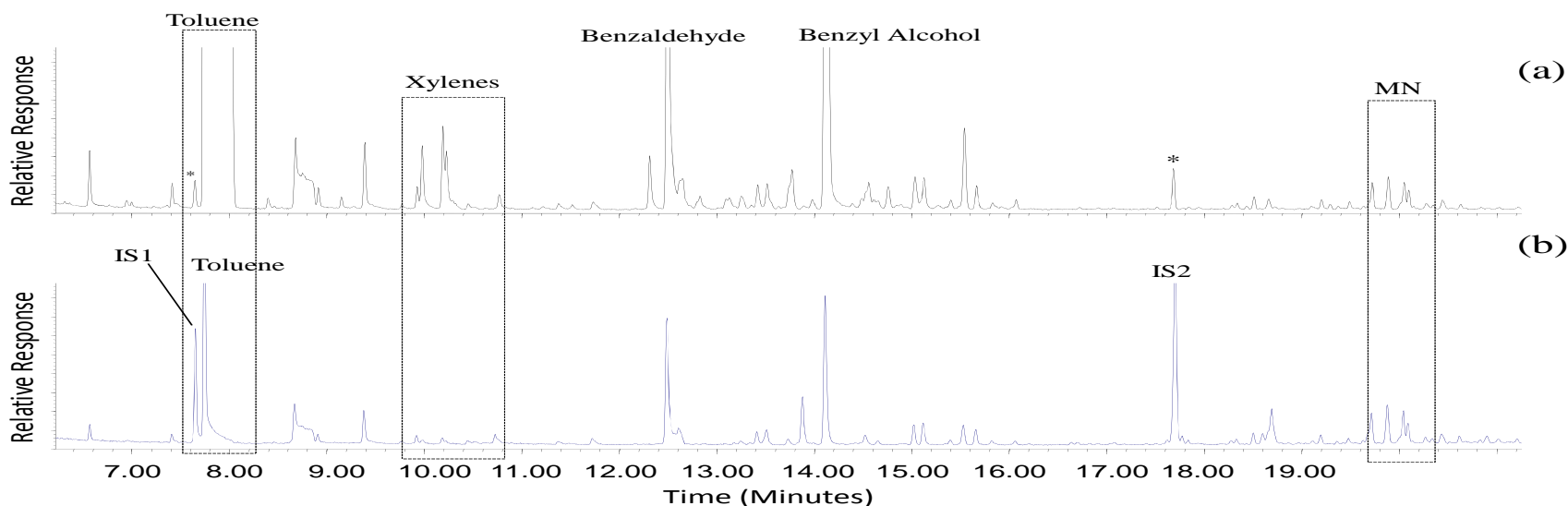
**Figure 8.** SPE Blank (a) versus SPE of 5 L seawater collected when sensor readings were very low (b) showing the TIC region of high molecular weight range of compounds from 20 to 55 minutes. IS3= d-anthracene, IS4=p-terphenyl, IS5= 1,1-Binaphthyl, IS6= squalane. X indicate contamination peaks associated with phthalates.. The small triangles indicate normal alkane or branched aliphatic alkane peaks.



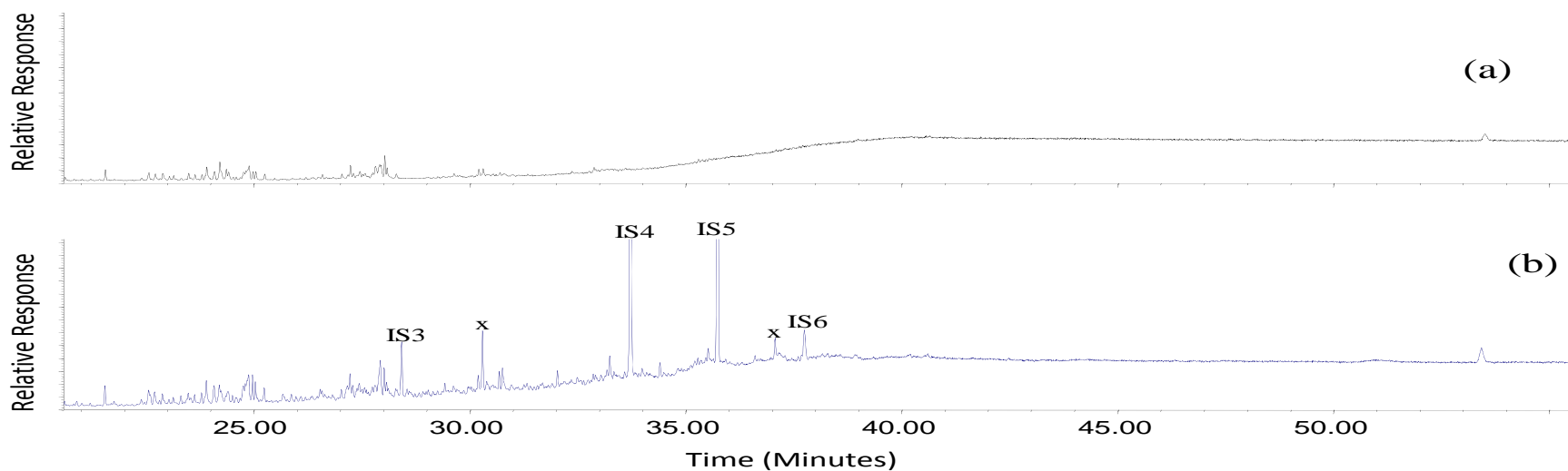
**Figure 9.** SPE Blank (a) versus (b) SPE of 5L of seawater collected under the slick showing the TIC region with low molecular weight range of compounds from 6 minutes to 21 minutes. IS1= d-toluene, IS2= d-Naphthalene. \*indicated that the peak is not the same as found in the corresponding chromatogram.



**Figure 10.** SPE Blank (a) versus (b) SPE 5 L of seawater collected under a surface sheen showing the TIC region of high molecular weight range of compounds from 20 to 55 minutes. IS3= d-anthracene, IS4=p-terpthenyl, IS5= 1,1-Binaphthyl, IS6= squalane. X indicate contamination peaks associated with phthalates.

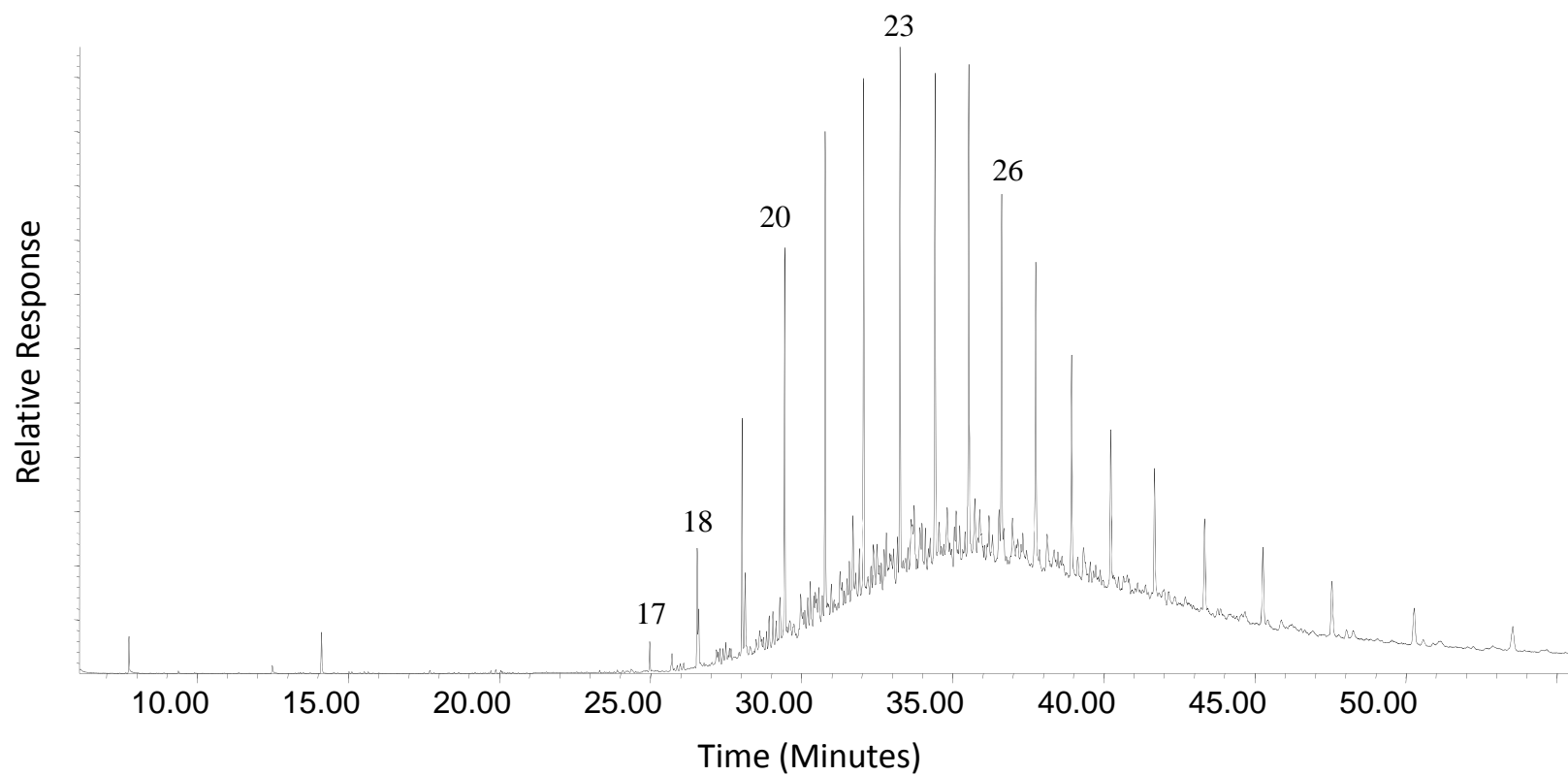


**Figure 11.** SPE Blank (a) versus (b) SPE of 1 L of seawater surface sheen showing the TIC region with low molecular weight range of compounds from 6 minutes to 21 minutes. IS1= d-toluene, IS2= d-Naphthalene. \*indicated that the peak is not the same as found in the corresponding chromatogram.

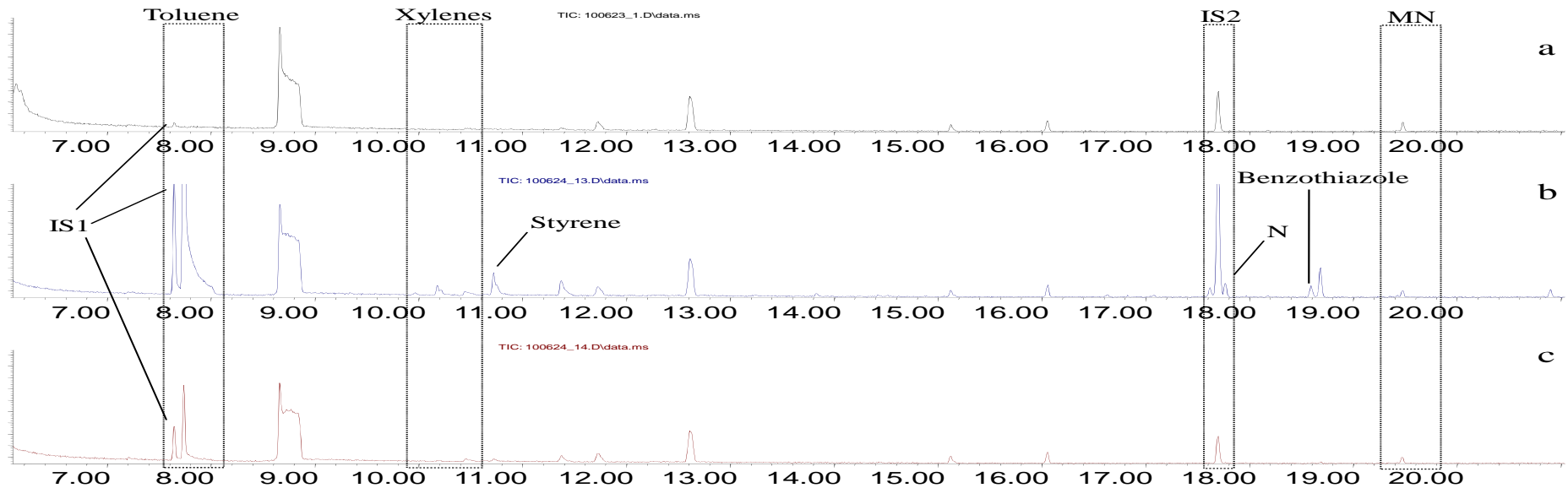


**Figure 12.** SPE Blank (a) versus (b) SPE 1 L of seawater surface sheen showing the TIC region of high molecular weight range of compounds from 20 to 55 minutes. IS3= d-anthracene, IS4=p-terpthenyl, IS5= 1,1-Binaphthyl, IS6= squalane. X indicate contamination peaks associated with phthalates.

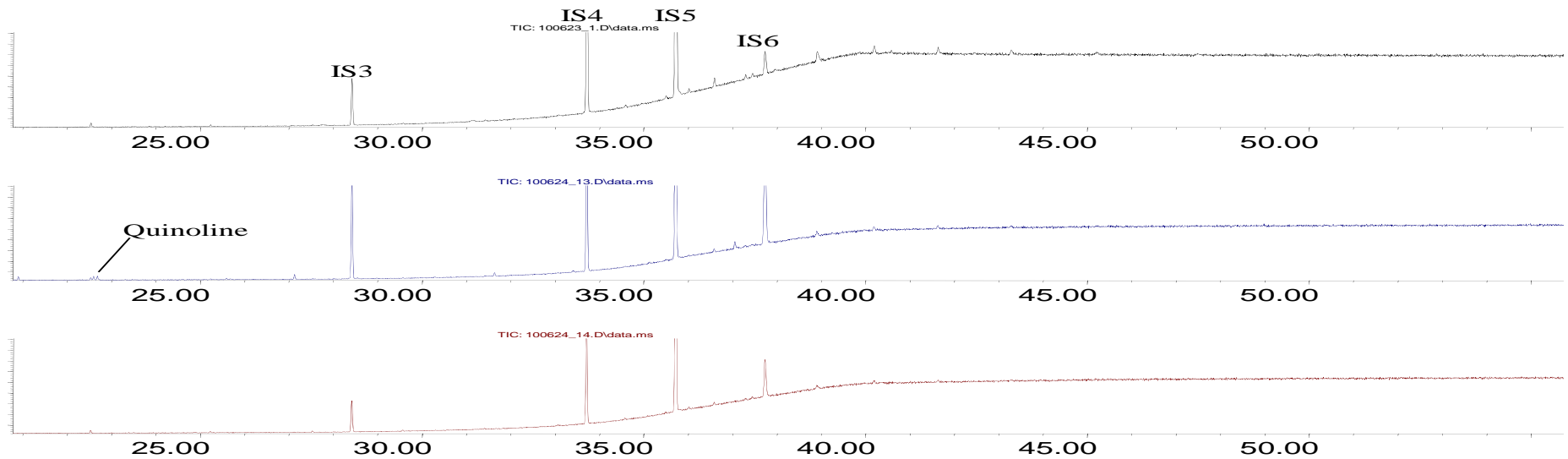




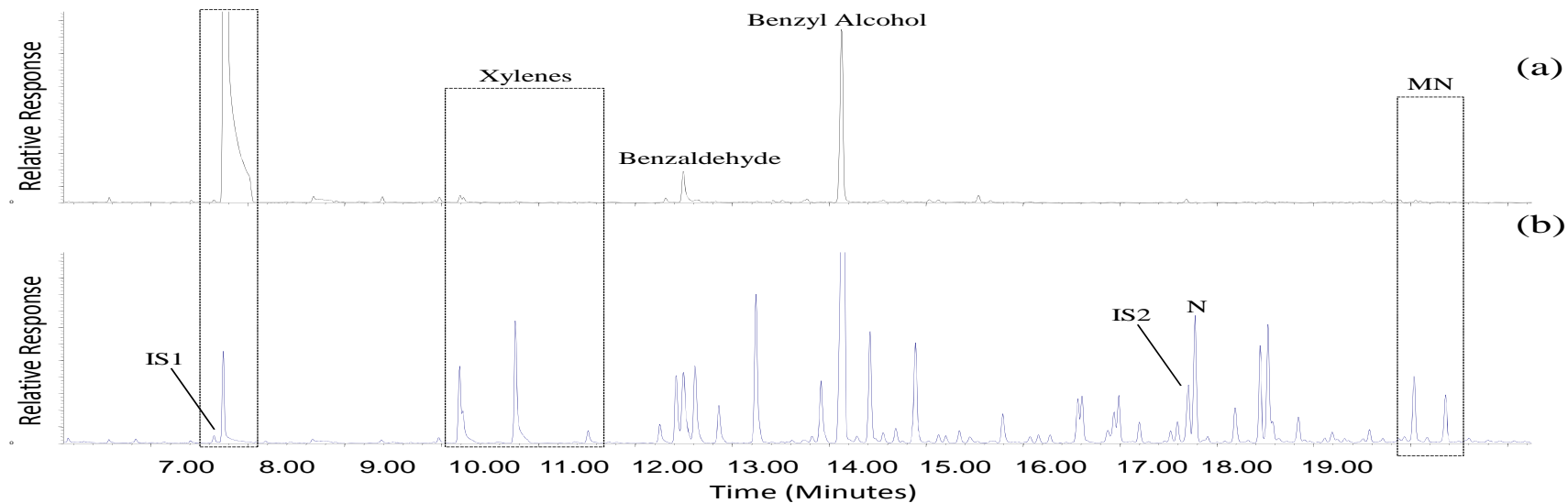
**Figure 13.** TIC of extracted mouse sample prepared by dissolved in DCM and then passed through SPE. Numbered peaks equate to the aliphatic *n*-alkane chain length. Note the absence of low molecular weight compounds.



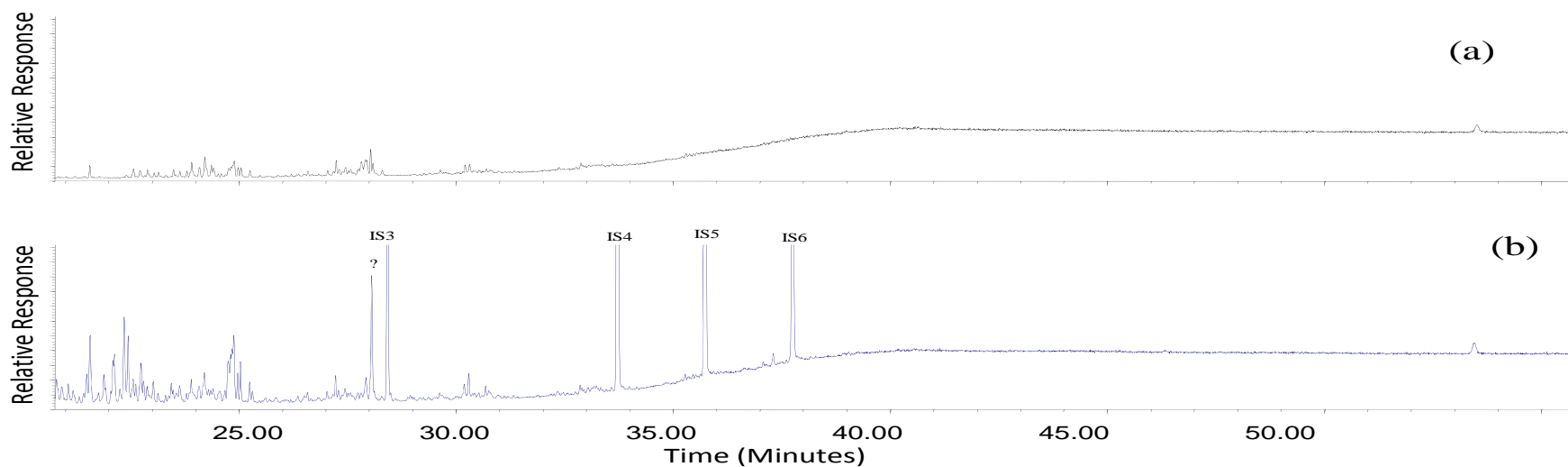
**Figure 14.** TIC region with low molecular weight range compounds from 6 minutes to 21 minutes showing (a) liquid-liquid extraction procedural blank, (b) 1L surface seawater sample near Mobile shipping channel liquid-liquid extraction and (c) 1L sample taken at the same location at 20 m depth liquid-liquid extraction. IS1= d-toluene, IS2= d-Naphthalene.



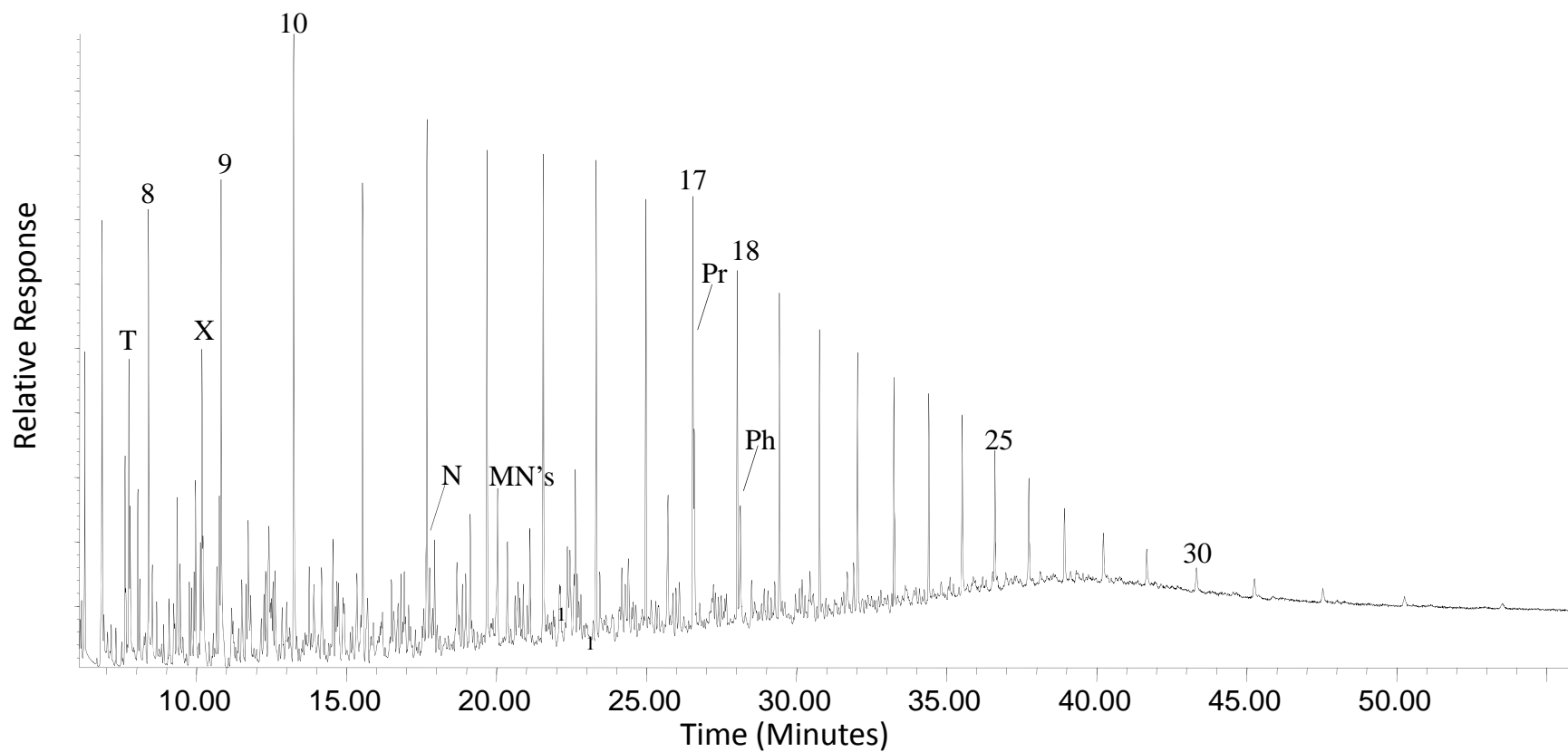
**Figure 15.** TIC region of high molecular weight range of compounds from 20 to 55 minutes from liquid/liquid extractions of (a) procedural blank, (b) 1L surface seawater sample near Mobile shipping channel and (c) 1L sample taken at the same location at 20 m depth IS3= d-anthracene, IS4=p-terphenyl, IS5= 1,1-Binaphthyl, IS6= squalane.



**Figure 16.** SPE Blank (a) versus (b) SPE of 275mL of oil saturated water fraction showing the TIC region with low molecular weight range of compounds from 6 minutes to 21 minutes. IS1= d-toluene, IS2= d-Naphthalene.



**Figure 17.** SPE Blank (a) versus (b) SPE of 275mL of oil saturated water fraction showing the TIC region of high molecular weight range of compounds from 20 to 55 minutes. IS3= d-anthracene, IS4=p-terpthenyl, IS5= 1,1-Binaphthyl, IS6= squalane. X shows contamination by phthalates



**Figure 18.** Whole oil TIC of the MC252 oil. The oil aliquot was dissolved in DCM and injected into the GC-MS. Numbers refer to the aliphatic carbon chain length, T= Toluene, X= Xylenes, N= Naphthalene, MN= Methyl Naphthalenes, Pr = Pristane, Ph= Phytane.

### ***Vessel science operations:***

Cruise 4 focused on logging of fluorometer measurements and photo-documenting observations of sea-surface conditions. The Chelsea fluorometers experienced lower than usual baselines during report time for 6/21 to 6/22 and in the one or two preceding days. Testing was carried out to establish whether or not baseline drift occurred in all three sensors. The instruments were tested in blank solutions and they gave accurate results as expected. As a precaution, the Chelsea fluorometer was replaced with an identical loan instrument. The reasons for the lower than expected observed values are yet to be determined. However, it was noted during daily cleaning that hydrophobic films accumulate on the optical sensor windows. These were removed with isopropyl alcohol and samples of these films will be analysed by GCMS to determine their composition.

### ***Problems/operational issues:***

Since the beginning of Cruise 4, we have added a jib crane, 150 m of nitrile coated hose, and a reel system to deploy and retrieve deep pumped water fluorometry casts. We have made additions during the cruise to augment the system such as replacing the electrical wire with a continuous 600' metal sheathed electrical cable (Photograph 11). This new cable will take the weight of the pump, resist stretch during deployment, and not come unplugged during operation. In addition, the swivel block was mounted into a fixed position for added rigidity and the blocks were replaced with rotating wheel rims to further reduce stress on the hose/cable assembly (Photograph 12). Currently, the system will accommodate a 50 m cast, but it will soon be able to take the full 150 m drops.

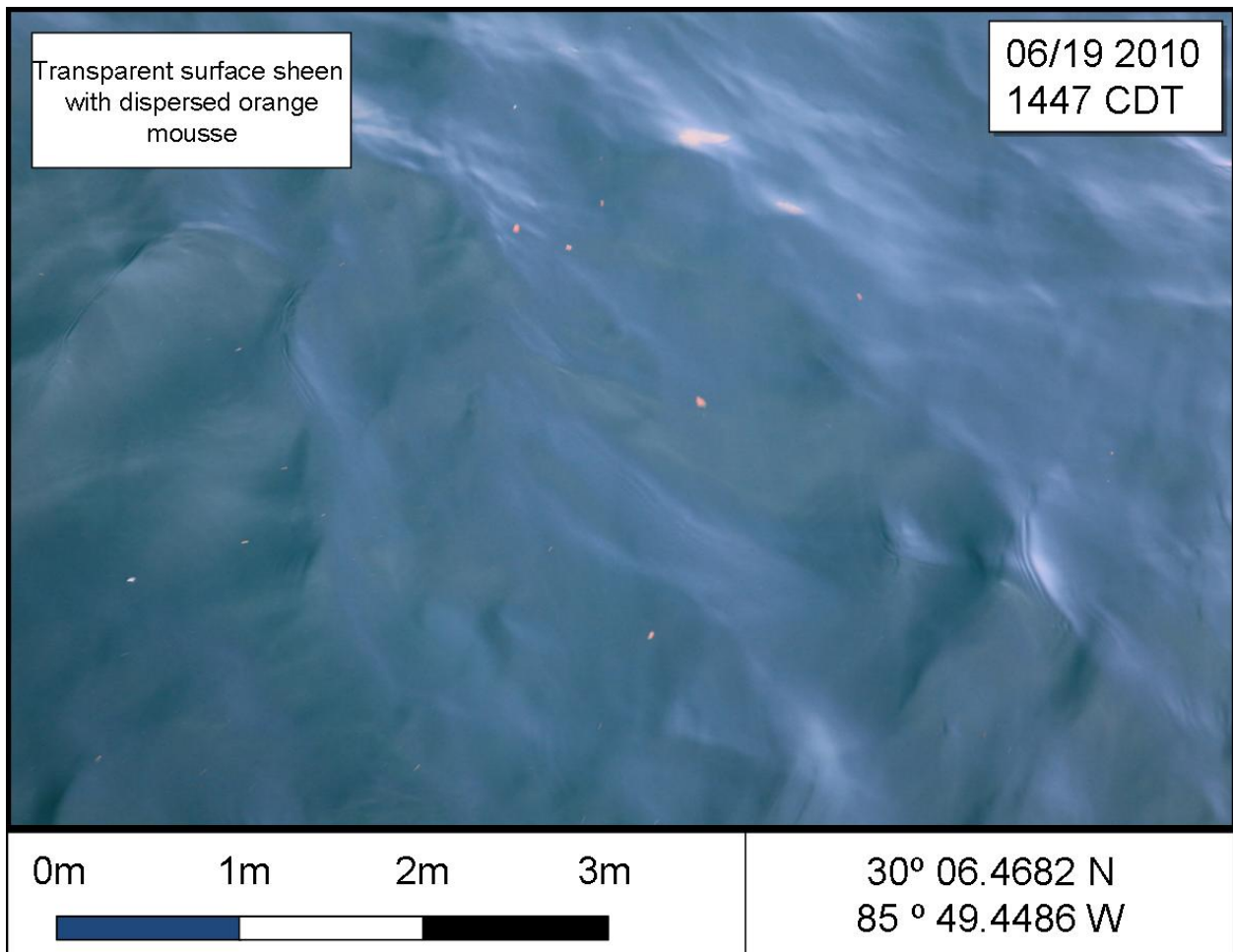
### ***Planned activities for next 24 hours:***

We are currently continuing on the planned route for Cruise 5.

### ***Acknowledgements:***

We thank the Captain and crew of the R/V Ryan Chouest for their assistance during Cruise 4. In particular, we thank Master and Captain Bill Smith for his ingenuity and resourcefulness to help make the vertical fluorometry system operational. The full list of personnel is shown on the last page of this report.

**Selected Photographs :**



Photograph 1. Transparent surface sheen with several noticeable pieces of dispersed mousse approximately 1 to 7 cm in diameter.

Transparent surface sheen  
with heterogeneity shown  
near horizon

06/19 2010  
1511 CDT

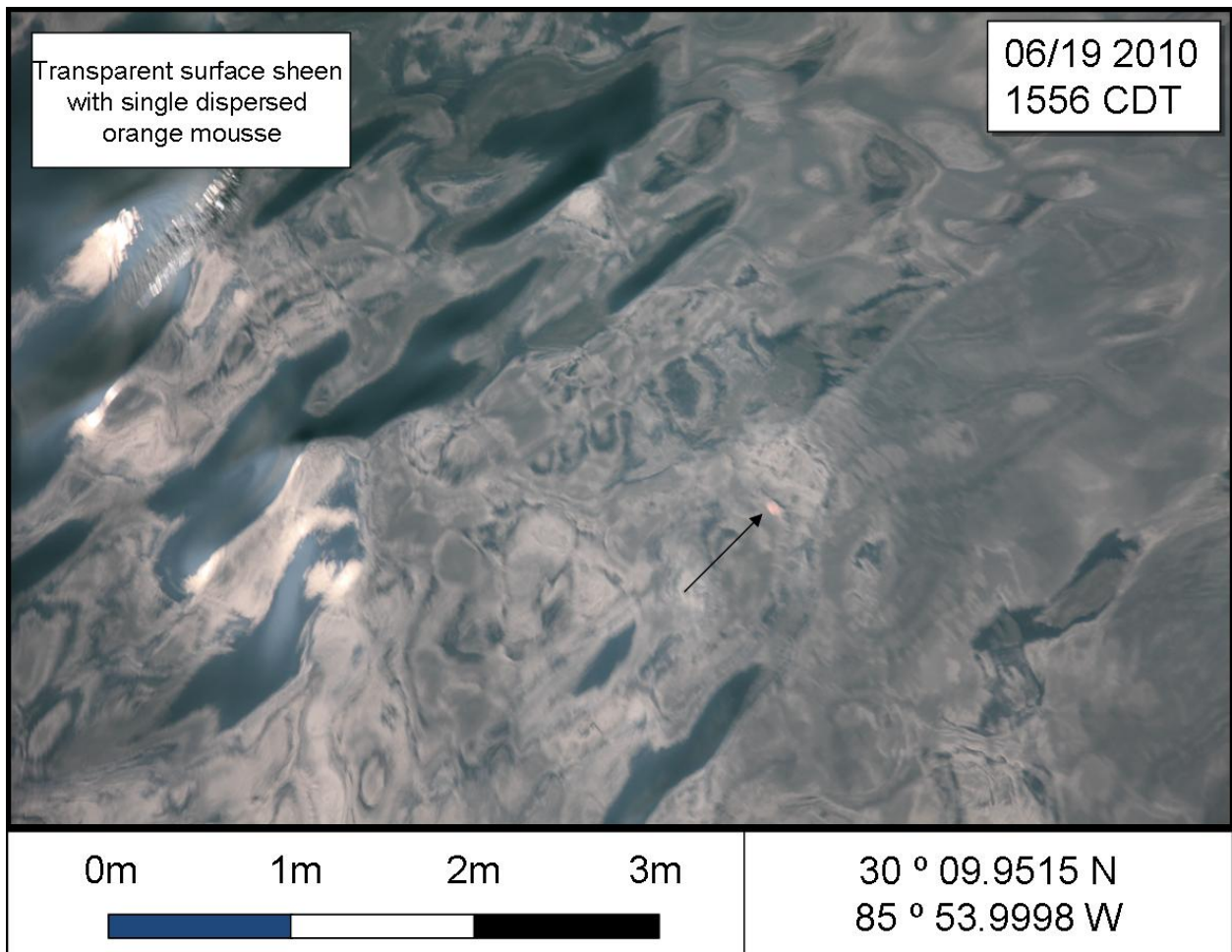


0m 1m 2m 3m 4m 5m



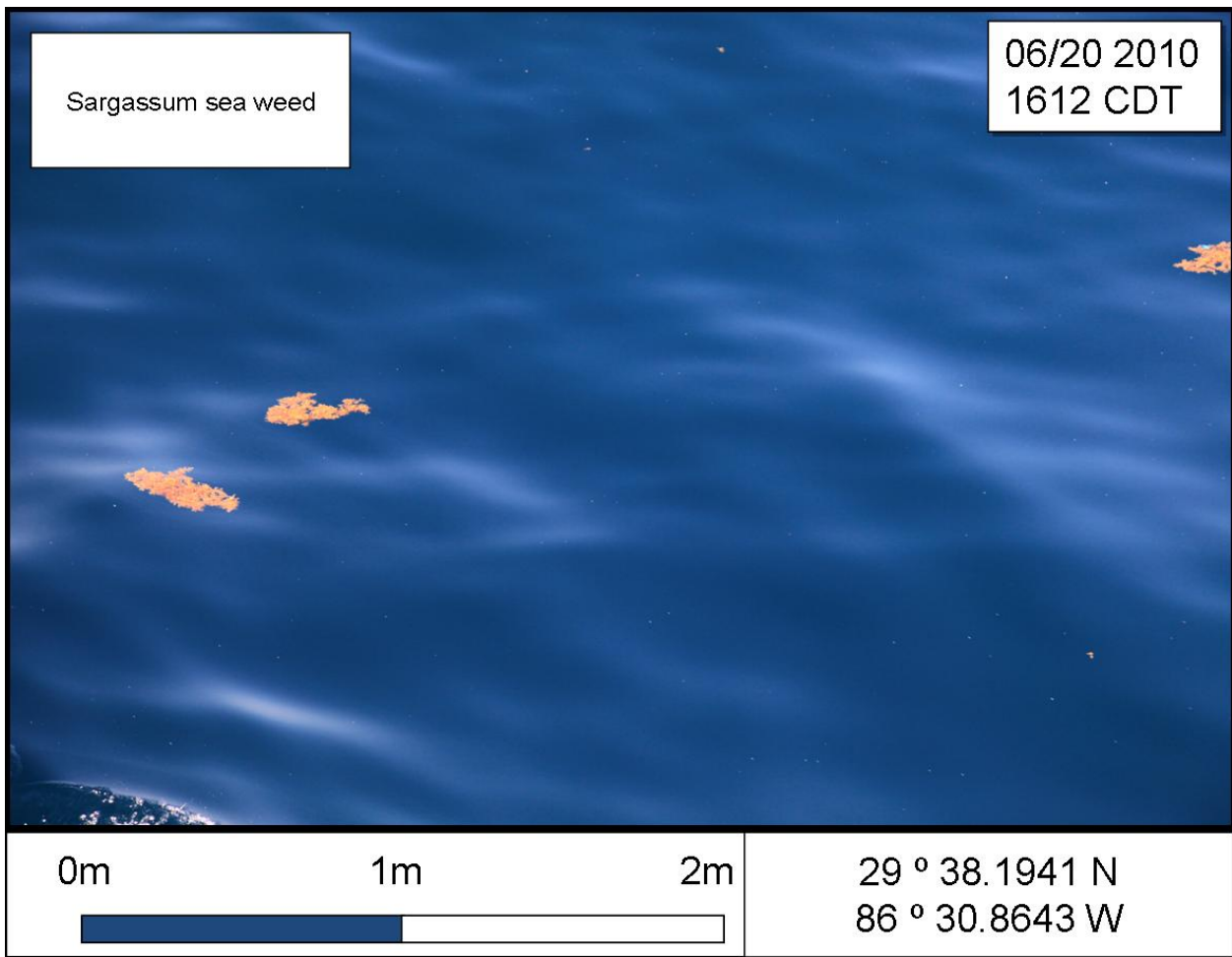
30 ° 06.2552 N  
85 ° 51.1668 W

Photograph 2. Transparent surface sheen with no observable mousse. Note the linear pattern near the horizon that shows differences in the ocean's surface reflectance from the observation point, which can be likely attributed to sheen variability.



Photograph 3. Transparent surface sheen with a single piece of orange mousse, approximately 4 to 5 cm in diameter. This image better illustrates the optical characteristics of transparent type sheens.





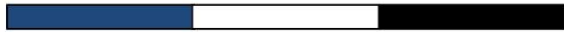
Photograph 4. Sargassum seaweed floating on surface sheen. Although seaweed is brownish green up close, it may resemble orange mousse depending on observation distance and angle of solar illumination.

Close up of Sargassum

06/20 2010  
1615 CDT



0m      1m      2m      3m

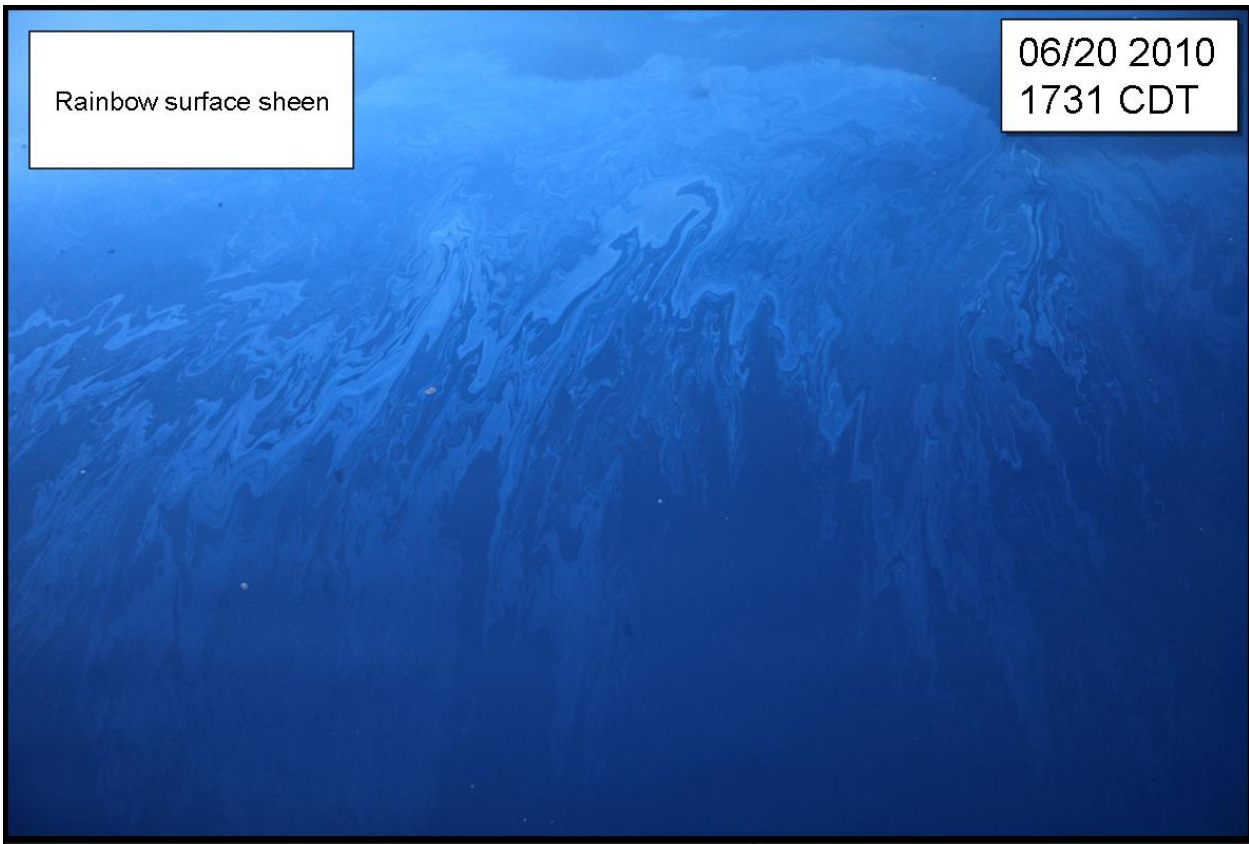


29 ° 37.8459 N  
86 ° 30.6255 W

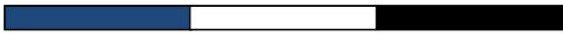
Photograph 5. Zoomed image of seaweed showing grape-sized float bladders a little more clearly.

Rainbow surface sheen

06/20 2010  
1731 CDT



0m      1m      2m      3m



29° 29.4576 N  
86 ° 25.1878 W

Photograph 6. Rainbow surface sheen amongst transparent surface sheen.

Convergence line of  
Sargassum sea weed  
with some orange mousse

06/20 2010  
1941 CDT



0m 1m 2m 3m 4m 5m

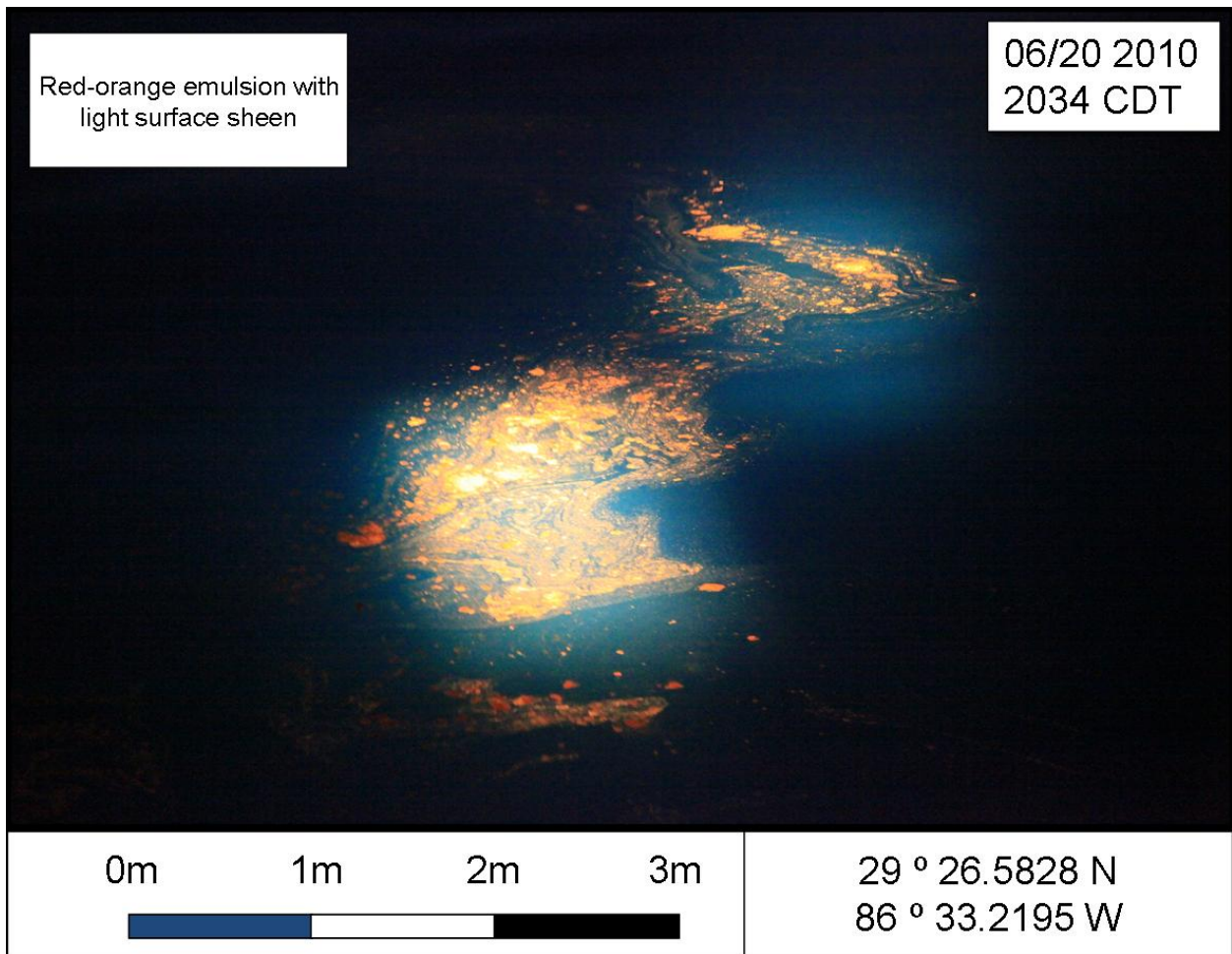


27 ° 28.1297 N  
86 ° 28.8999 W

Photograph 7. Convergence line of predominantly seaweed, some smaller pieces of orange mousse also present.

Red-orange emulsion with  
light surface sheen

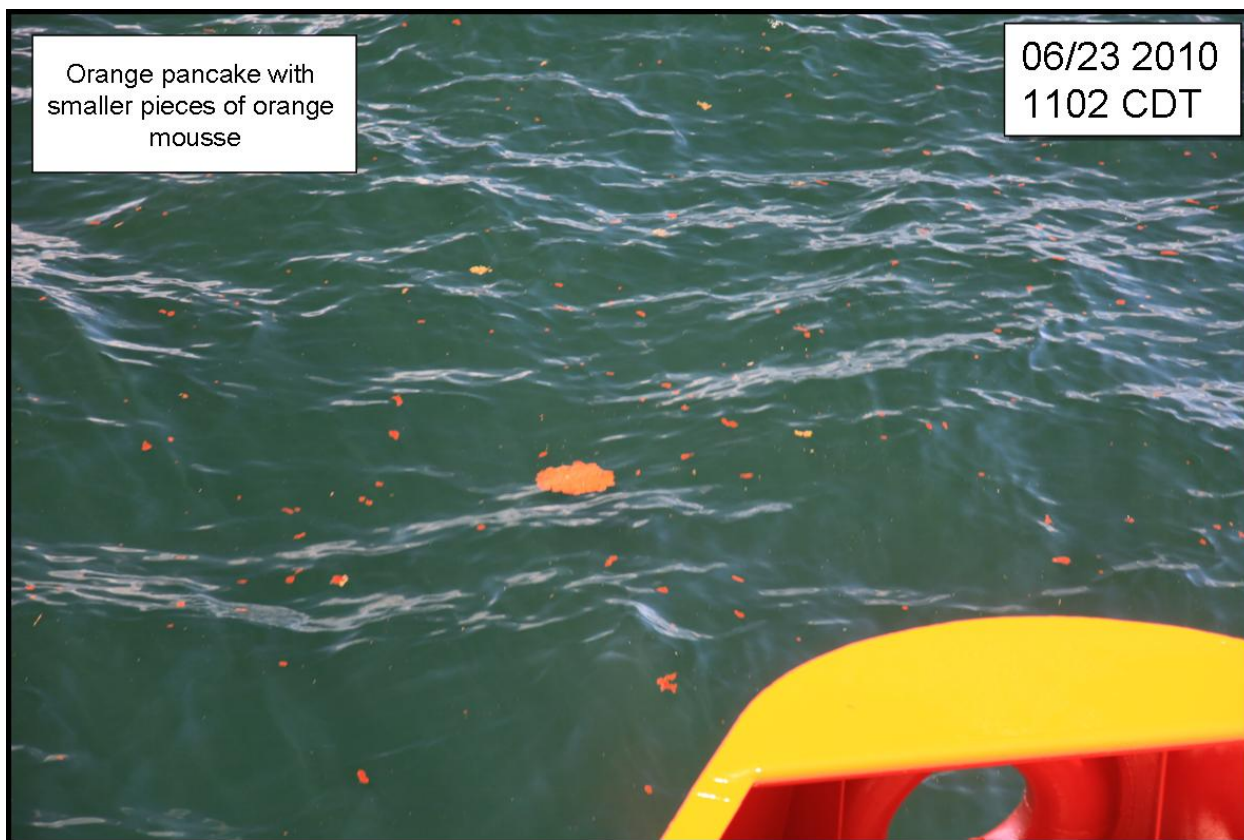
06/20 2010  
2034 CDT



Photograph 8. Red-orange emulsion surrounded by light surface sheen. A surface water sample and mousse sample was collected at this station.

Orange pancake with  
smaller pieces of orange  
mousse

06/23 2010  
1102 CDT

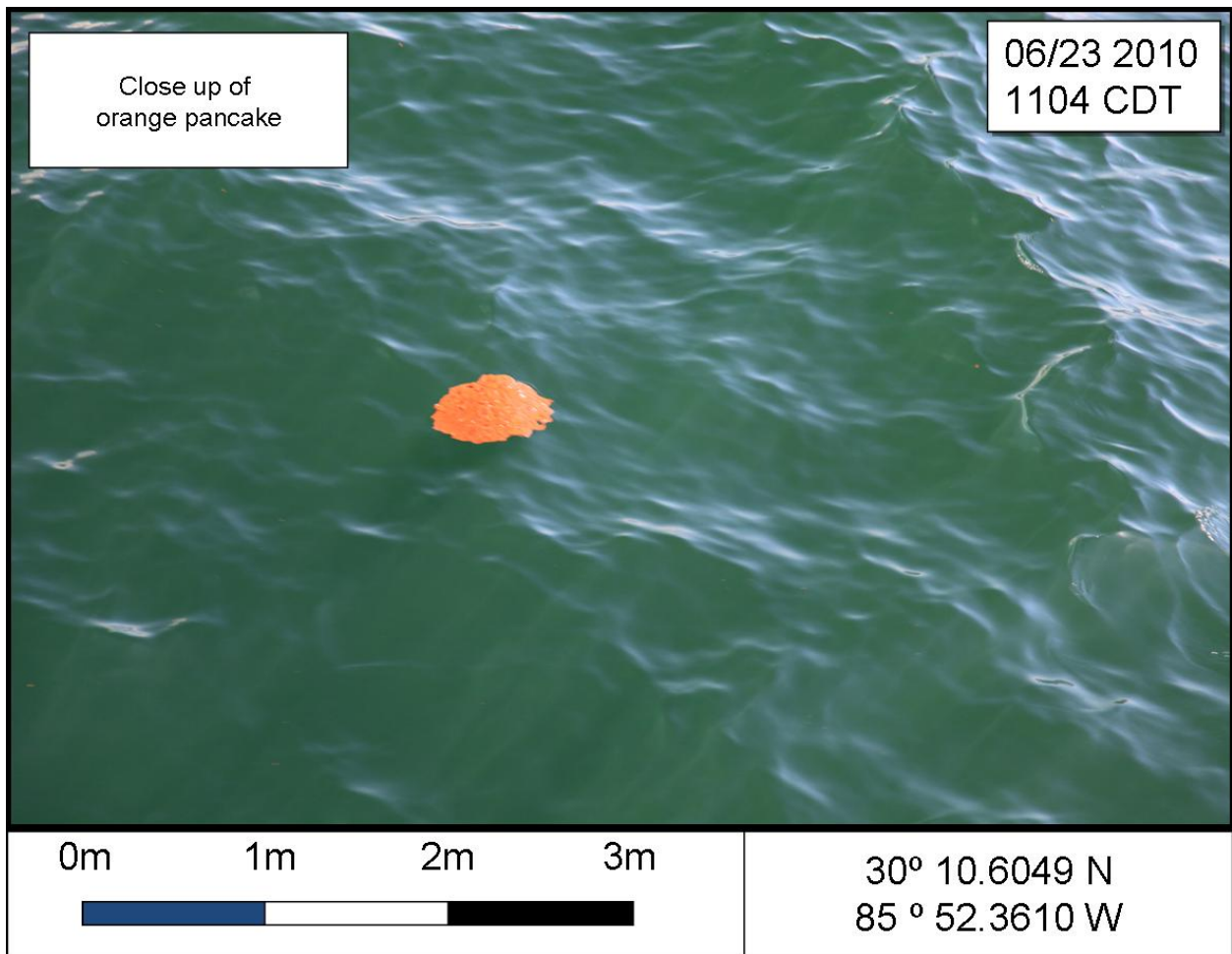


0m 1m 2m 3m 4m 5m



30° 10.4366 N  
85 ° 52.1009 W

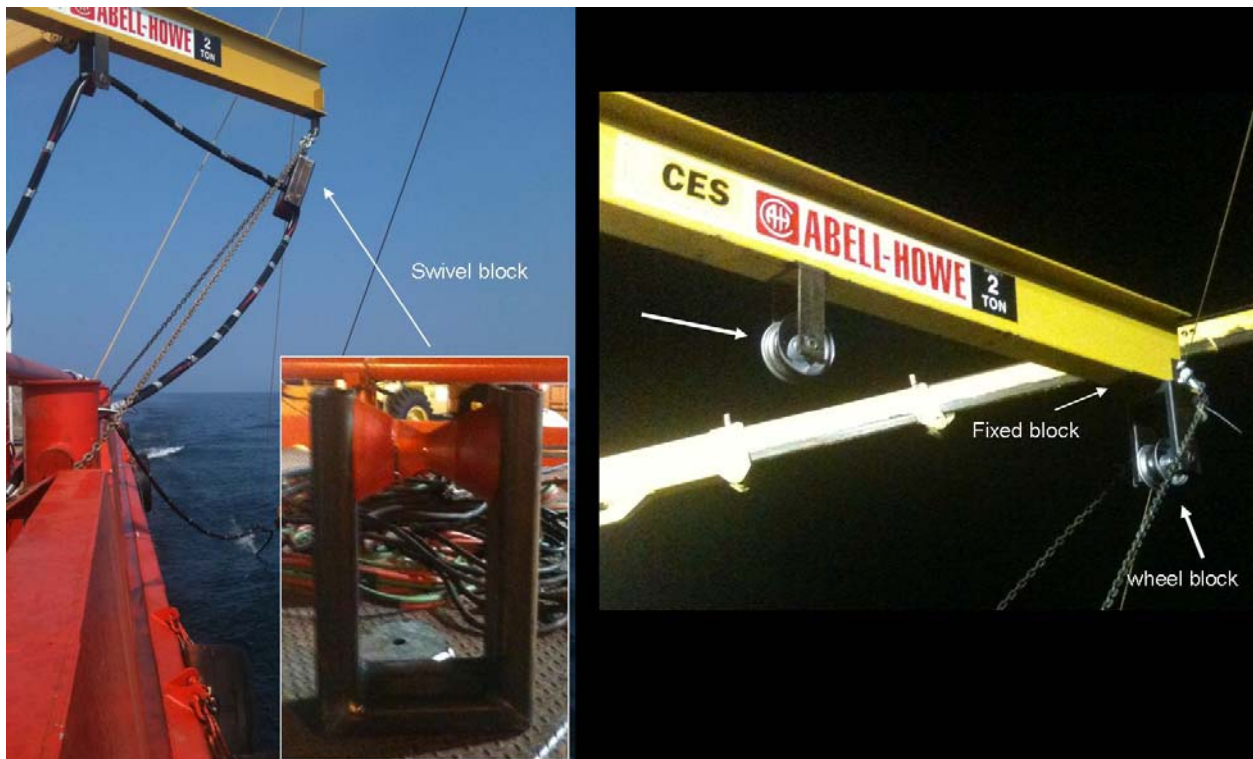
Photograph 9. Orange pancake surrounded by smaller pieces of disseminated orange mousse. Pancakes were as large as 0.5 meters in diameter. This was the typical surface observation for the region labeled with slick type 3 in Figure 1.



Photograph 10. Close up of typical orange pancakes observed in parts of map transect labeled with slick type 3.



Photograph 11. New electrical cable sheathed in stainless steel wire for 150m pump hose. The steel weaved mesh will support over 800lbs of weight.



Photograph 12. Modifications to the blocks on the Jib Crane. The swivel block was welded into a fixed position and the rollers were replaced with wheel rims.



## Full Crew List:

William A. Smith	MASTER
Demarco Jones	A/B
Elijah Benjamin	O/S RIG
Jon Cheney	Capt.
Brian Corley	Mate
Eduardo Zepeda	A/B
Mark Harmon	A/B
Samuel Nwosu	QMED
Craig Lyons	CHIEF ENG.
Emma Crooke	CSIRO
Xiubin Qi	CSIRO
Stephane Armand	CSIRO
David Fuentes	CSIRO
Andrew Ross	CSIRO
Lawrence Febo	BP
Guilherme De Almeida	Entrix
Brian Harmon	C&C
Greg Richard	C&C
Roderick Baker	OS/COOK
Brandon Wilson	C-PORT
Ben Autin	C-PORT