Ryan Chouest daily data transmission and report

Period covered: 1147hrs 06/21/2010-1427hrs 06/22/2010

232.972 - Nautical miles covered

Vessel science party:

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Cruise notes:

Since 1147 hrs 06/21/2010 we have sailed on the course as planned (Figure 1).

Science results and preliminary interpretation:

Fluorometry results

Fluorometry values are low to medium as observed in previous reports. The Chelsea sensor shows low to lower medium values (Figure 2) and a great deal more character than the past two days. The Trios and Contros sensors exhibit low to medium inferred hydrocarbon concentrations (Figures 3 and 4). In some places, the mapped values correlate reasonably well with potential oiling extent for the previous day but in other places along the transect they do not. Generally, the sensor data show slightly more variability than yesterday's measurements.

Trios sensor data was once again tested against yesterdays potential oiling extent over the same time (Figure 5). The relationship between the potential oiling footprint and the shallow subsurface fluorometry readings is unclear, however there has been little opportunity to fully explore the data. In addition the use of remotely acquired data alone to 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 and there may be a decoupling of the surface expression of the oil and the components of oil dissolved into the water column. This would be especially true for weathered accumulations where the components of oil monitored by the fluorometers have been effectively removed by water washing, photo oxidation and evaporative losses. Some of these ideas will be further explored in the geochemistry section at the end of this report.

Surface Observations

Surface observations noted were light surface sheens and small pieces of orange mousse (Figure 1) no photographs were taken.

Planned versus actual route taken for cruise 4:

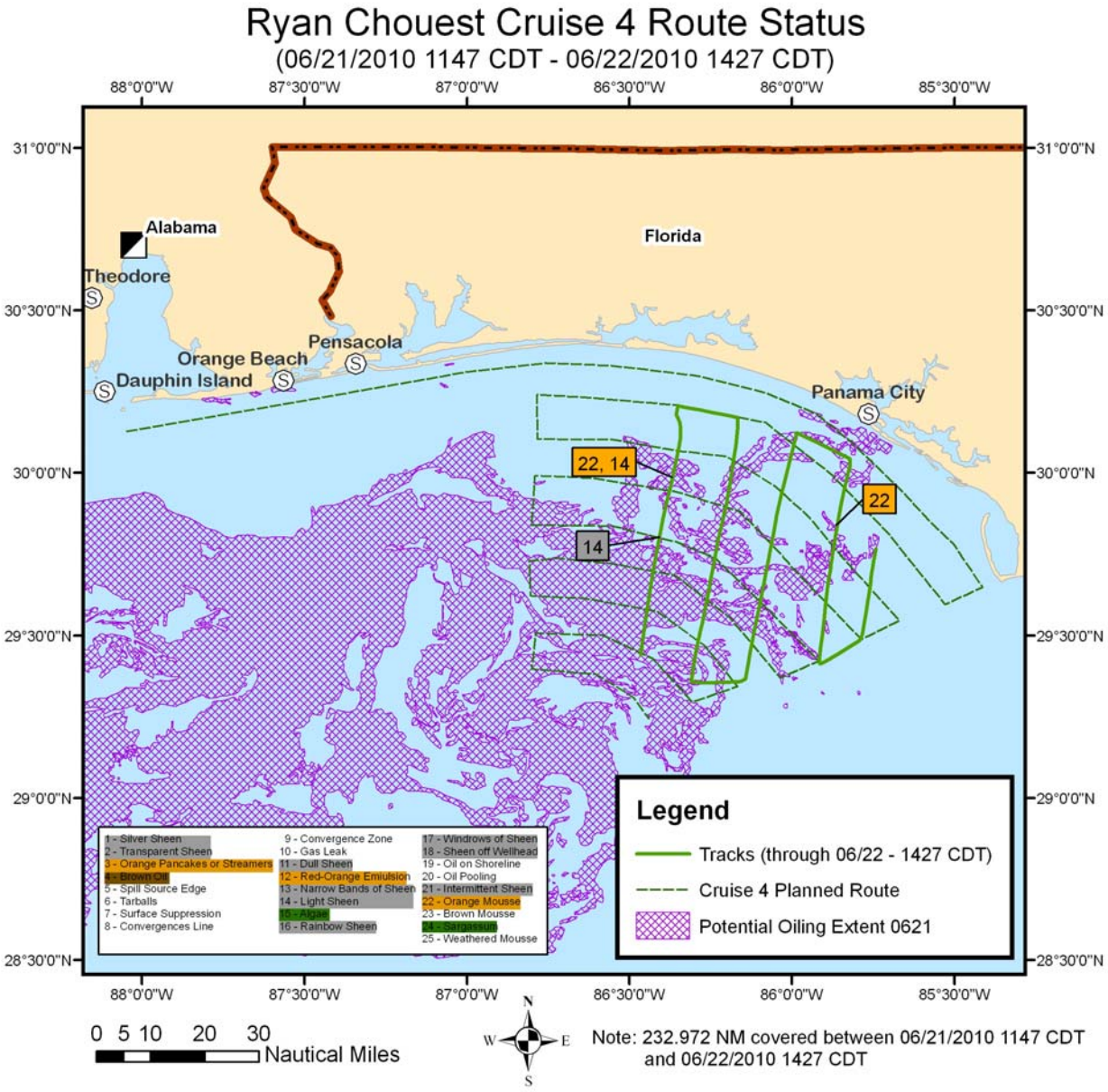

Figure 1: Planned versus actual route course plotted between 06/21/2010 –06/22/2010. Purple shaded area represents outline extent of the slick from 06/21 ERMA composite.

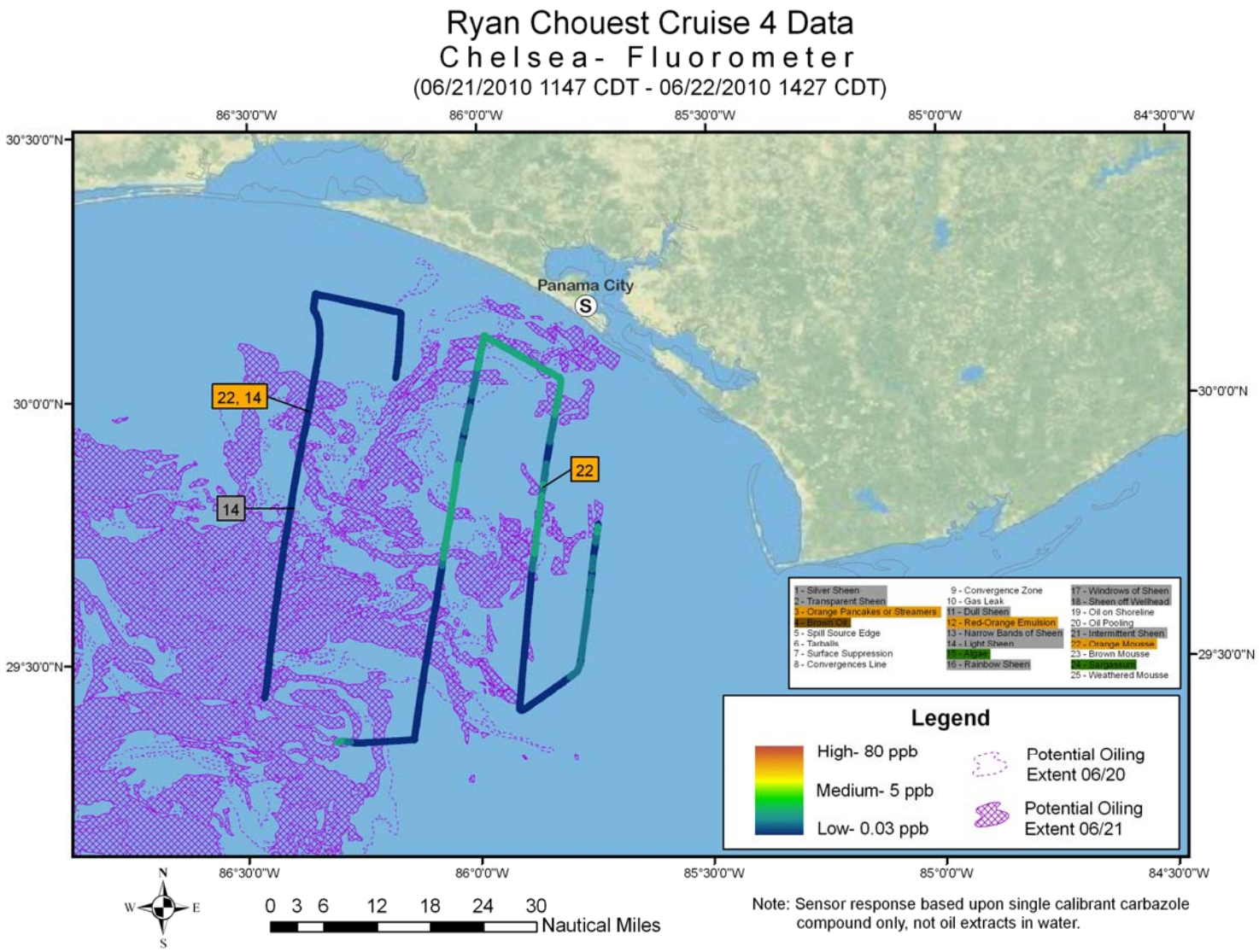

Figure 2. Chelsea fluorometer results plotted with location on cruise 4 track. Breaks in data occur when either data quality is poor or the systems were turned off due to pump problems.

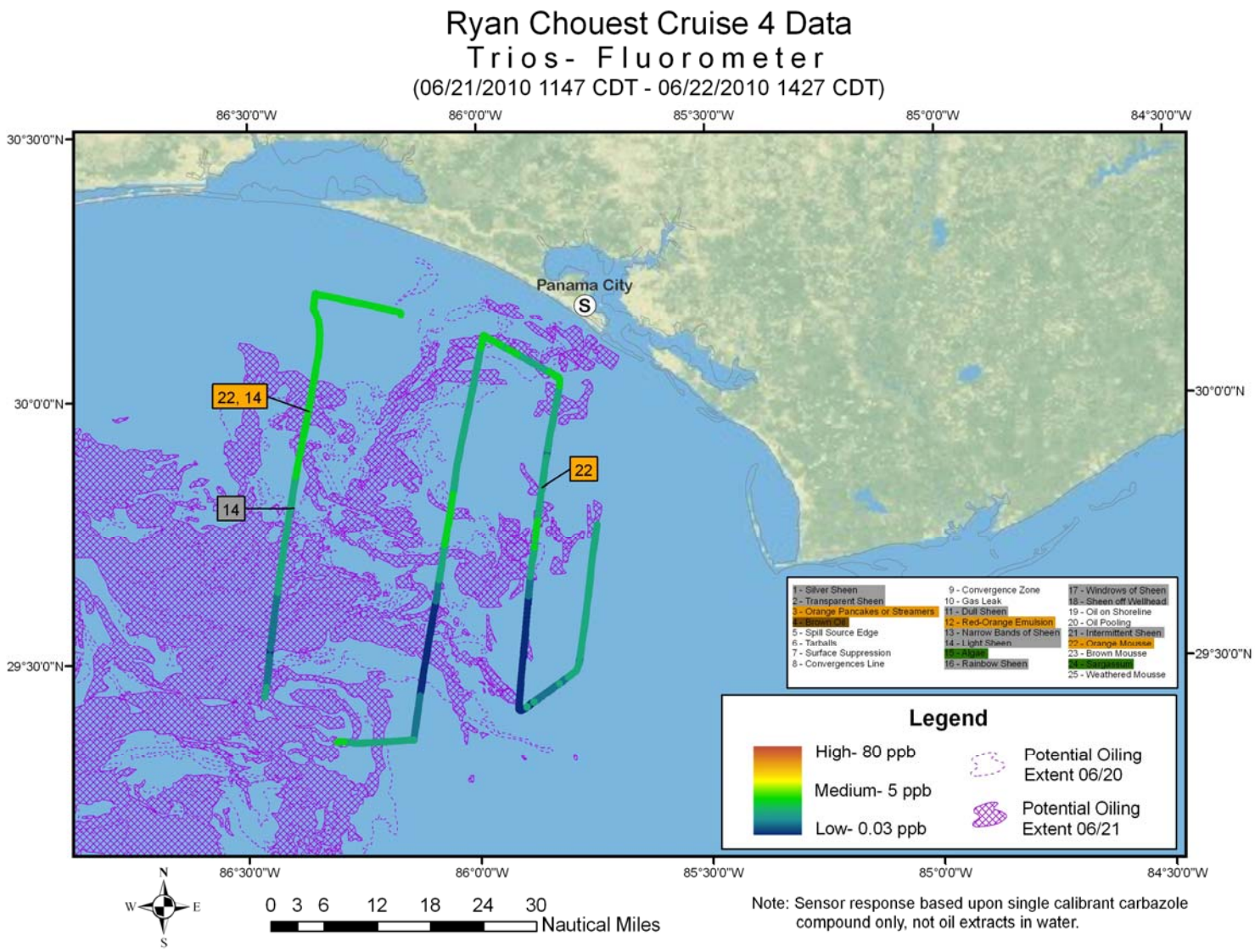

Figure 3. Trios fluorometer results plotted with location on cruise 4 track. Breaks in data occur when either data quality is poor or the systems were turned off due to pump problems.

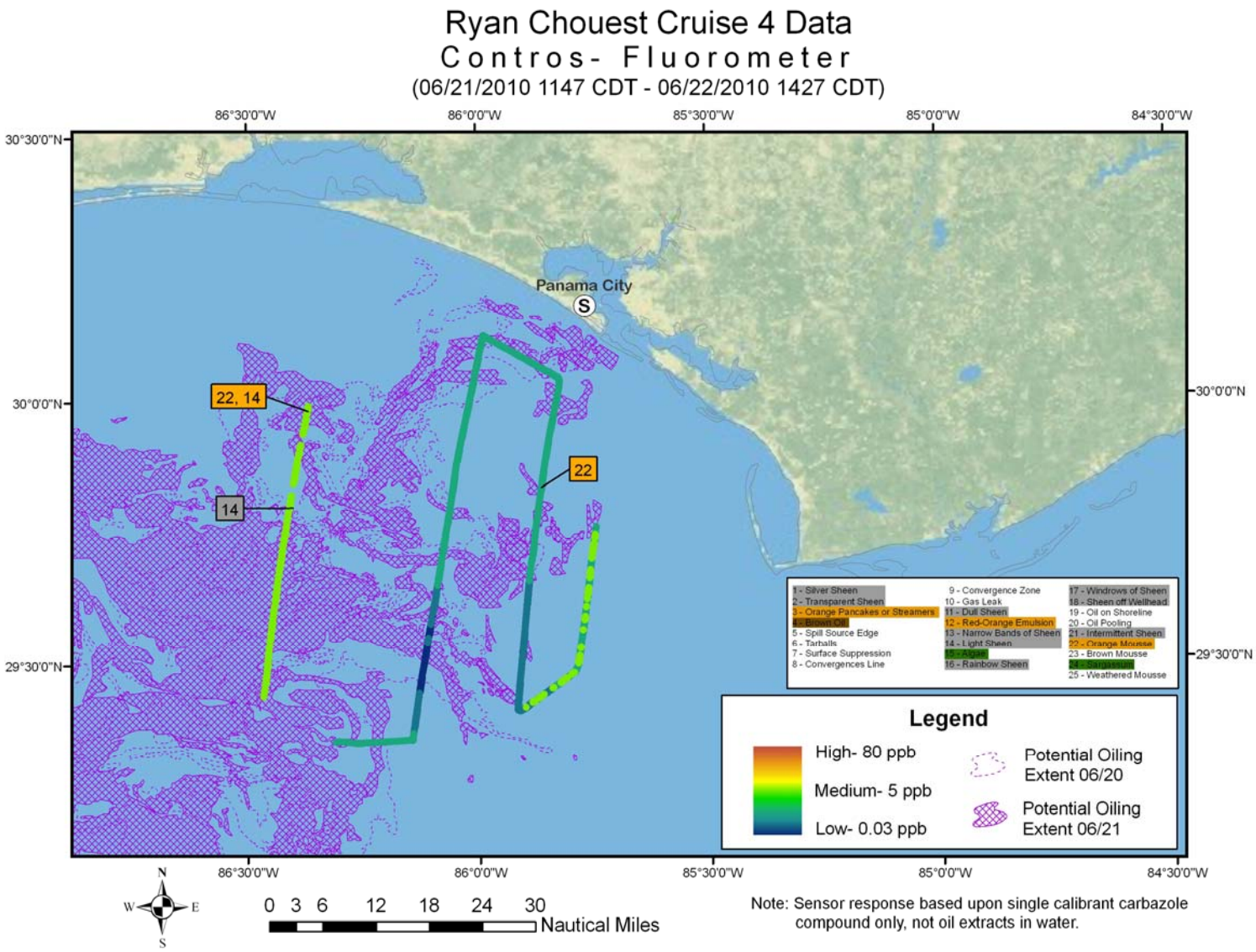

Figure 4. Contros fluorometer results plotted with location on cruise 4 track. Breaks in data occur when either data quality is poor or the systems were turned off due to pump problems.

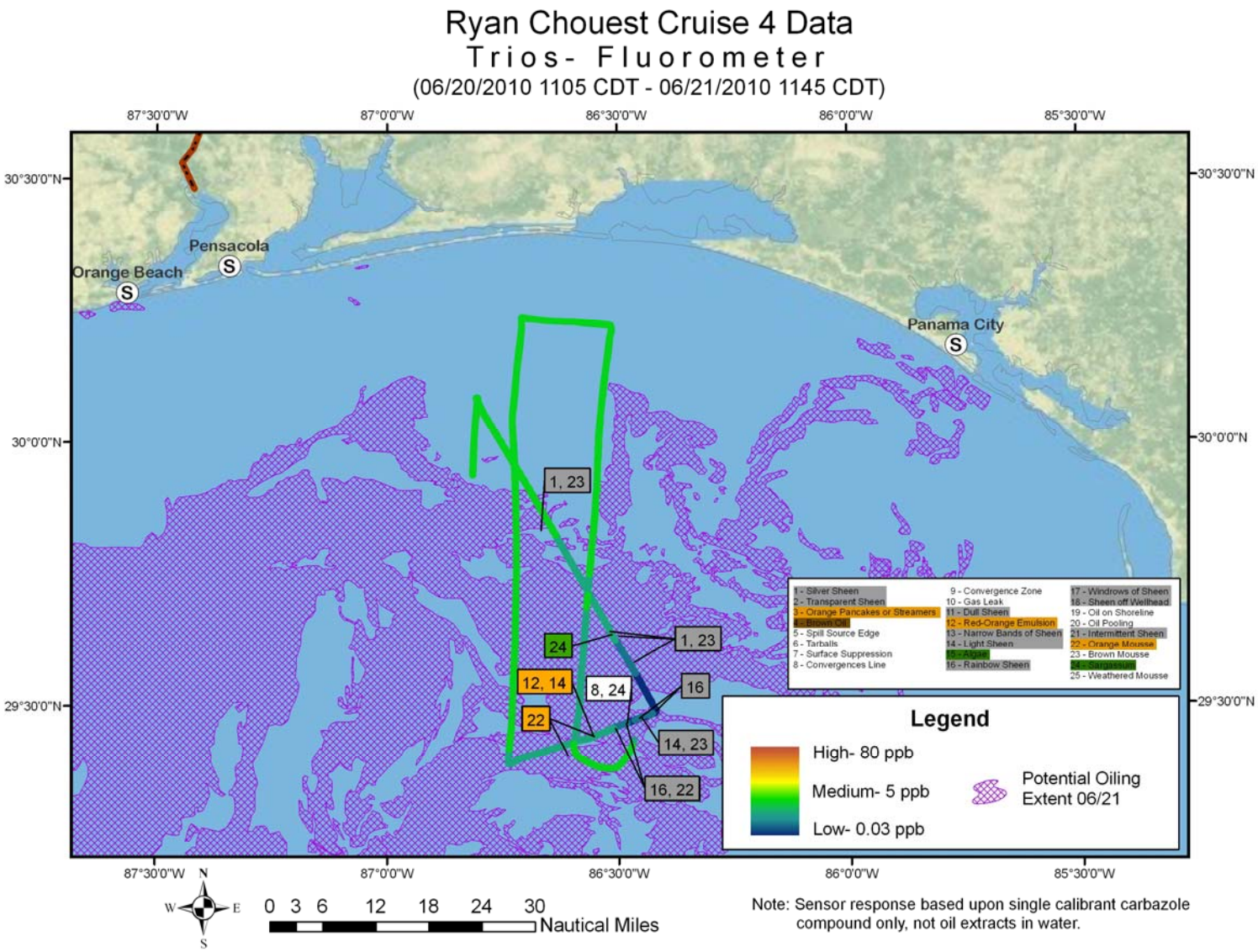

Figure 5. Trios fluorometer results plotted as of 06/21/2010 with potential oiling extent for the same time frame. Breaks in data occur when either data quality is poor or the systems were turned off due to pump problems.

Vessel science operations:

Continued logging of fluorometer measurements and observations and photography documenting sea-surface conditions. Low than usual baselines have been observed in the sensor over the last few days, therefore testing was carried out to establish if there was baseline drift in all three sensors. The instruments were tested in blank solutions and they gave results as expected. For caution the Chelsea fluorometer was swapped with an identical loan instrument. The reasons for the lower than expected values seen while underway are yet to be determined. During daily cleaning, hydrophobic films were observed on the optical sensor windows. These were removed with isopropyl alcohol. Samples of these films will be analysed by GCMS to determine their character.

.Problems/operational issues:

(Includes items up to report submission time)

There are no problems at this time. The shallow (50m) vertical fluorometry casts are being successfully deployed today.

Planned activities for next 24 hours:

We will complete our cruise track and sail back to Port in Theodore to pick up the two CSIRO scientists and some additional equipment and consumables.

Additional section on the preliminary GCMS results

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. 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 a greater concentration 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 2nd cartridge SPE cartridge with Dichloromethane (DCM).
6. Place the 1st cartridge on top of the 2nd 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 stars 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, napthalenes, 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 086 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 duce 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_{17} to *n*-C_{35}. 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.

To calibrate the sensors and understand which hydrocarbon compounds readily partition in to water from the parent MC252 oil a slow striring experiment was performed where a layer of oil is placed on top of a partially water filled bottle containing vertically placed glass tube which has it's 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 by GCMS. The results shown in figures 14 and 15, 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. Finally figure 16 shows the whole TIC for the MC 252 parent oil for comparative purposes.

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.

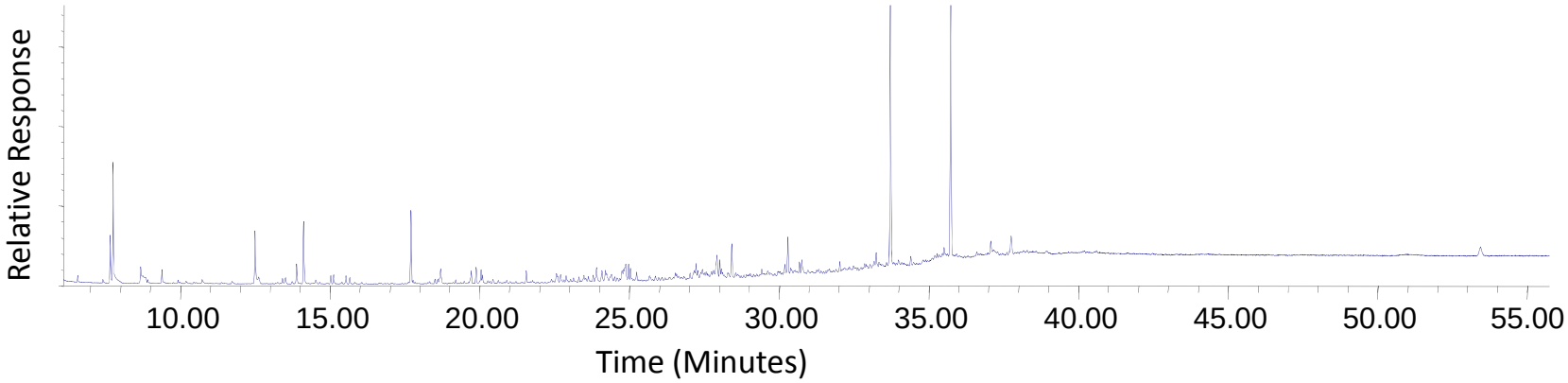

Figure 6. Example Total Ion Chromatogram (TIC) for a 5 litre sample of clean seawater extracted using Solid Phase Extraction (SPE).

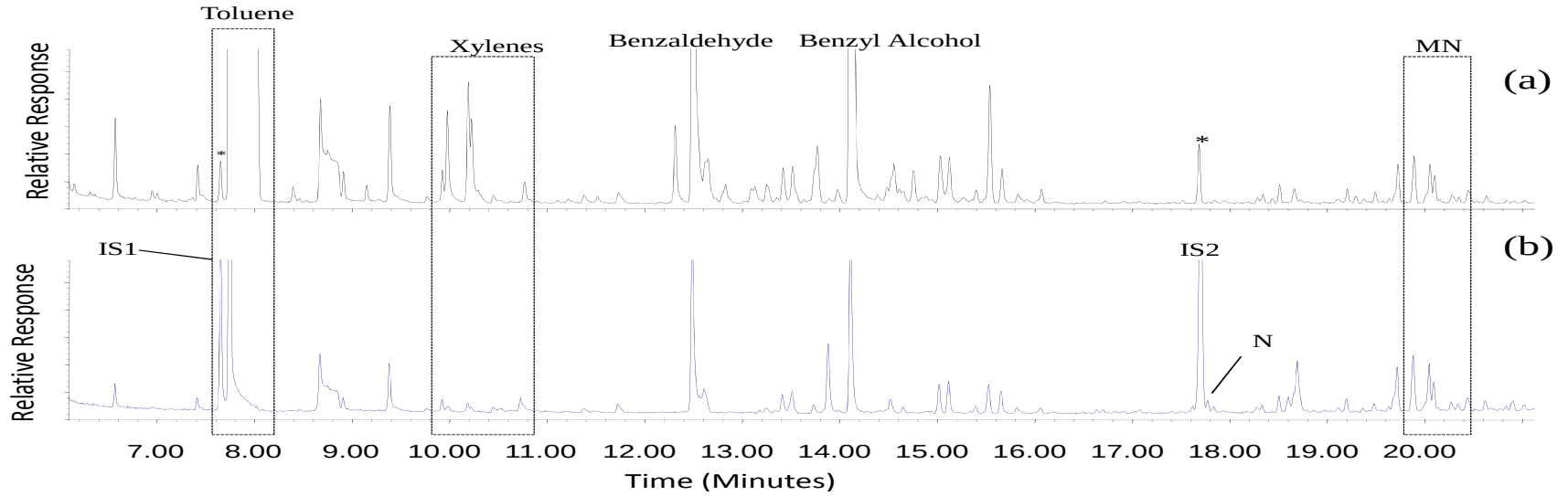

Figure 7. SPE Blank (a) versus (b) SPE of seawater collected when sensor readings were very low showing the TIC region with low molecular weight range of compounds from 6 minutes to 21 minutes. IS1= d-toluene, IS2= d-Naphthalene. *indicated that the peak is not the same as found in the corresponding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

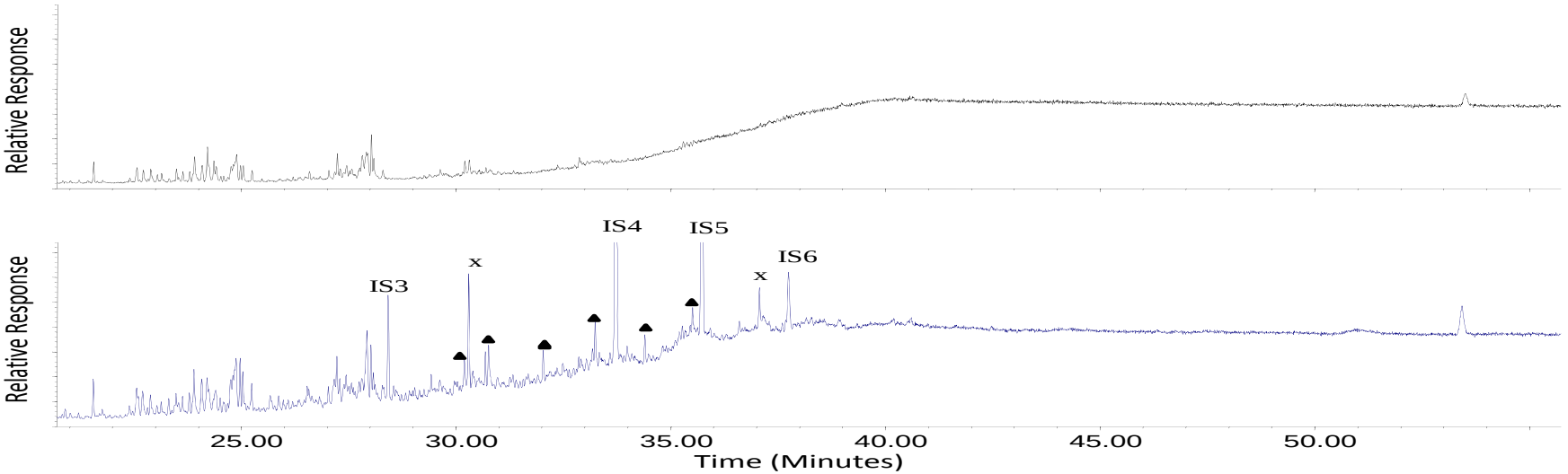

Figure 8. SPE Blank (a) versus SPE of 5 L seawater collected when sensor readings were very low (b) showing the TIC region of high molecular weight range of compounds from 20 to 55 minutes. IS3= d-anthracene, IS4=p-terpthenyl, IS5= 1,1-Binaphthyl, IS6= squalane. X indicate contamination peaks associated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

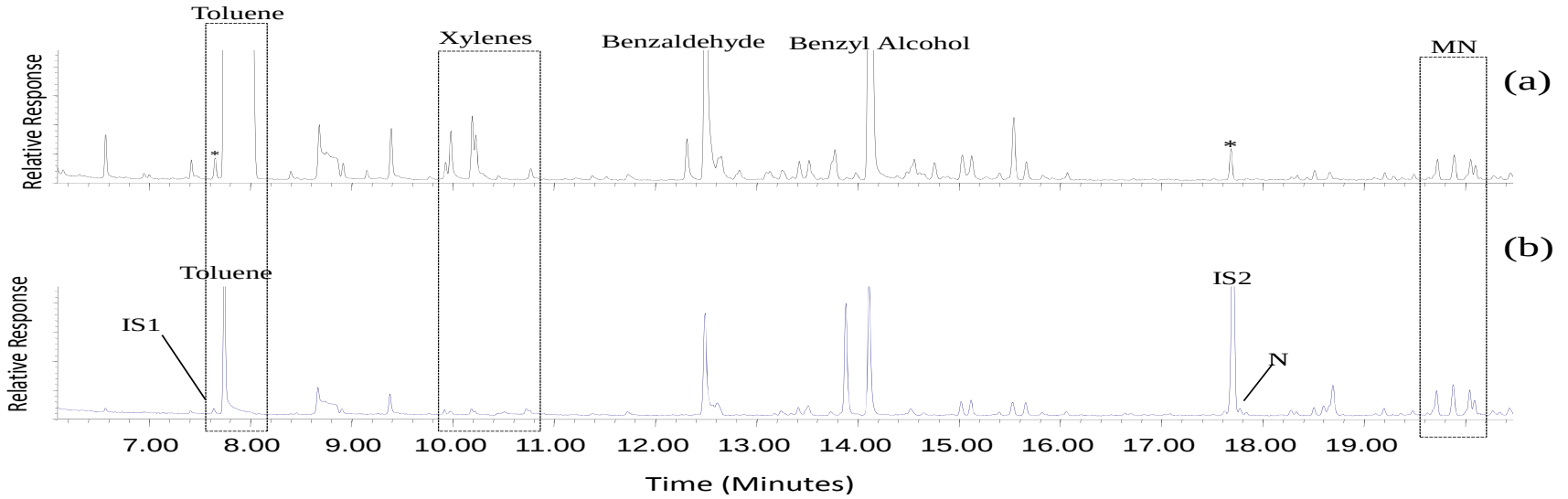

Figure 9. SPE Blank (a) versus (b) SPE of 5L of seawater collected under the slick showing the TIC region with low molecular weight range of compounds from 6 minutes to 21 minutes. IS1= d-toluene, IS2= d-Naphthalene. *indicated that the peak is not the same as found in the corresponding chromatogram.

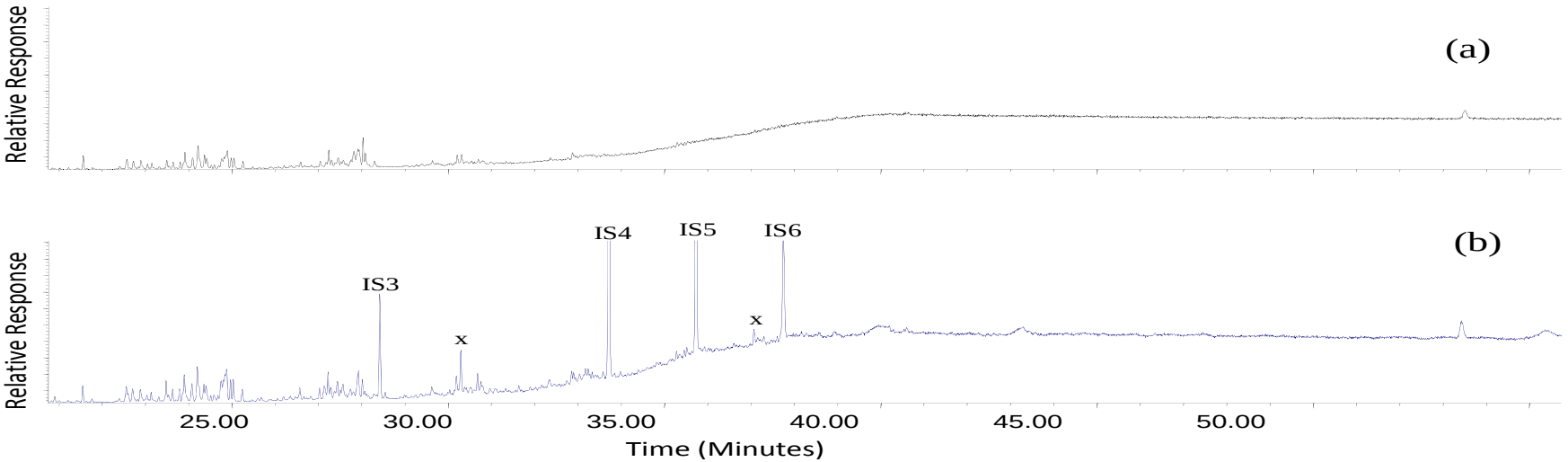

Figure 10. SPE Blank (a) versus (b) SPE 5 L of seawater collected under a surface sheen showing the TIC region of high molecular weight range of compounds from 20 to 55 minutes. IS3= d-anthracene, IS4=p-terpthenyl, IS5= 1,1-Binaphthyl, IS6= squalane. X indicate contamination peaks associated with phthalates.

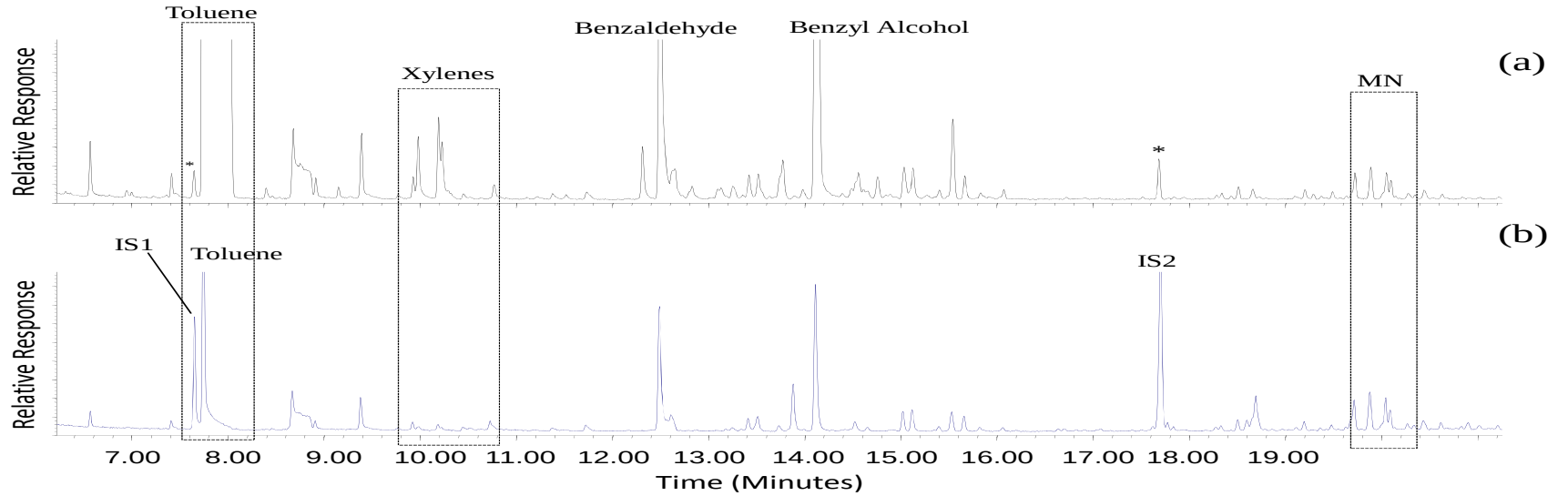

Figure 11. SPE Blank (a) versus (b) SPE of 1 L of seawater surface sheen showing the TIC region with low molecular weight range of compounds from 6 minutes to 21 minutes. IS1= d-toluene, IS2= d-Naphthalene. *indicated that the peak is not the same as found in the corresponding chromatogram.

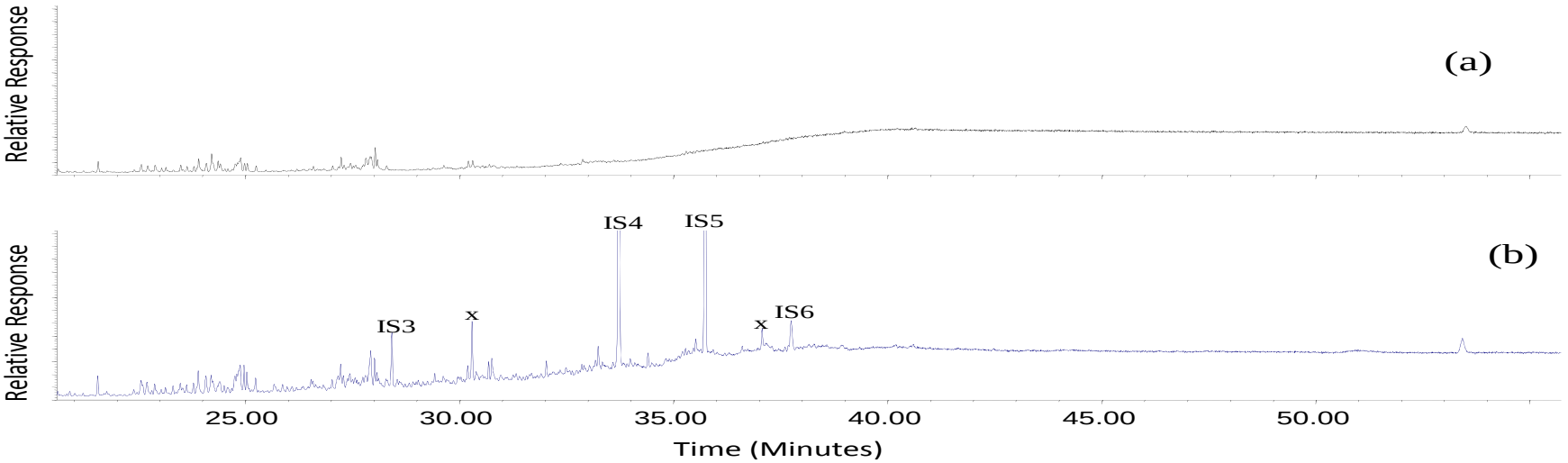

Figure 12. SPE Blank (a) versus (b) SPE 1 L of seawater surface sheen showing the TIC region of high molecular weight range of compounds from 20 to 55 minutes. IS3= d-anthracene, IS4=p-terpthenyl, IS5= 1,1-Binaphthyl, IS6= squalane. X indicate contamination peaks associated with phthalates.

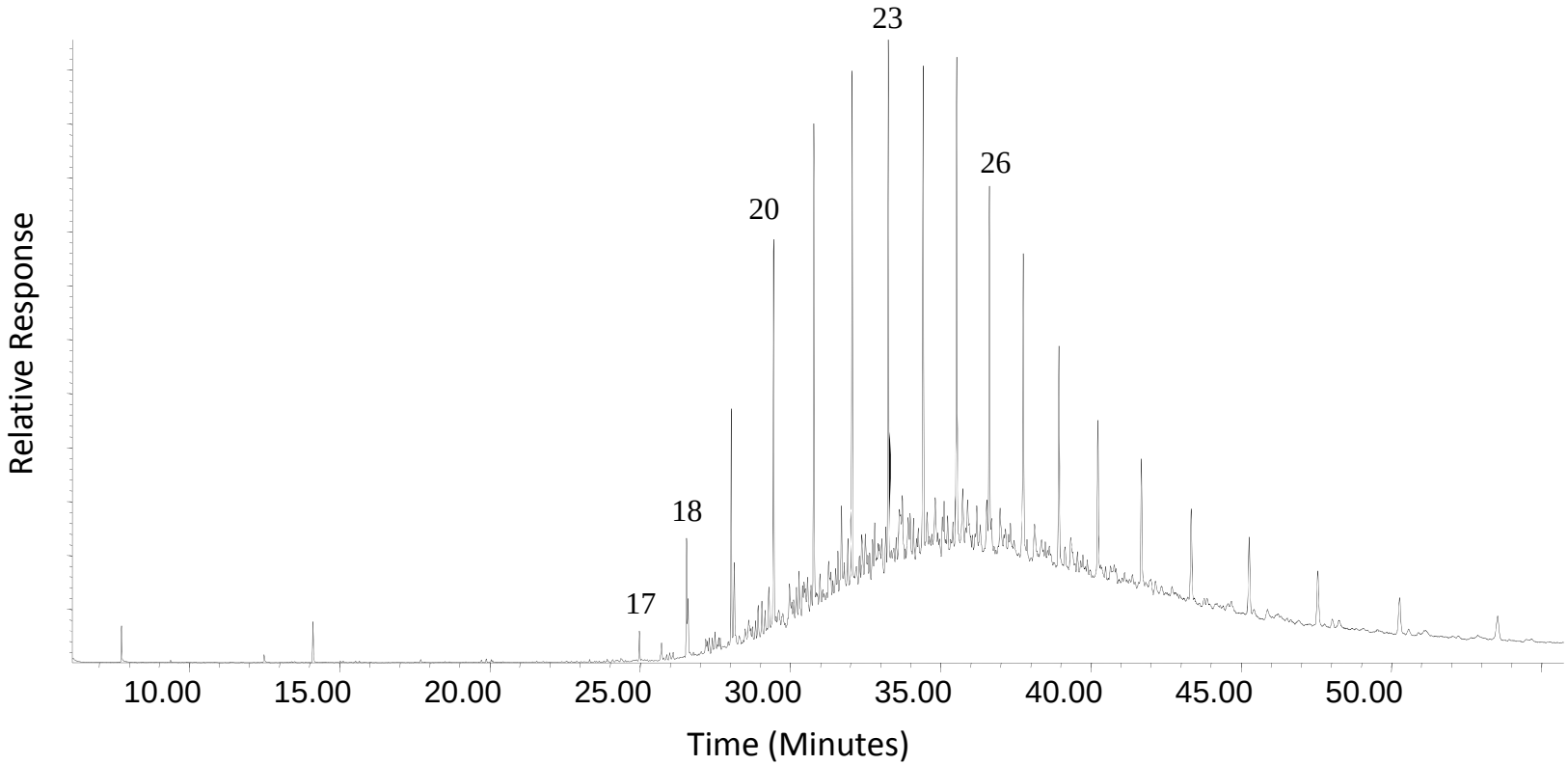

Figure 13. TIC of extracted mousse sample prepared by dissolved in DCM and then passed through SPE. Numbered peaks equate to the aliphatic *n*-alkane chain length. Note the absence of low molecular weight compounds.

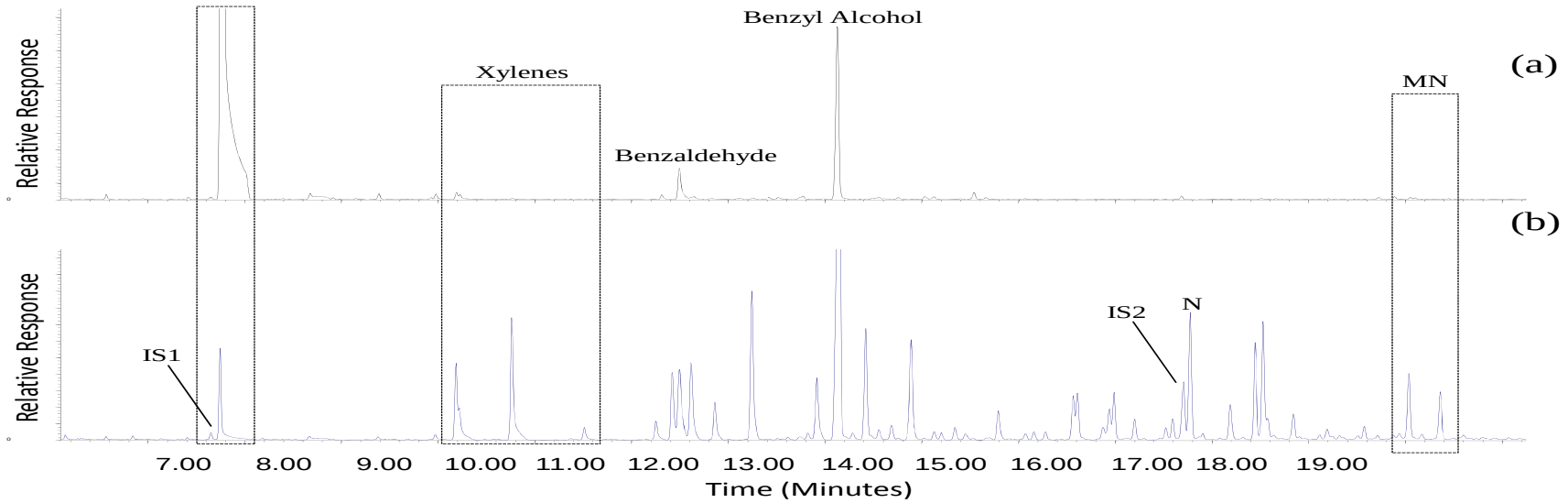

Figure 14. SPE Blank (a) versus (b) SPE of 275mL of oil saturated water fraction showing the TIC region with low molecular weight range of compounds from 6 minutes to 21 minutes.. IS1= d-toluene, IS2= d-Naphthalene.

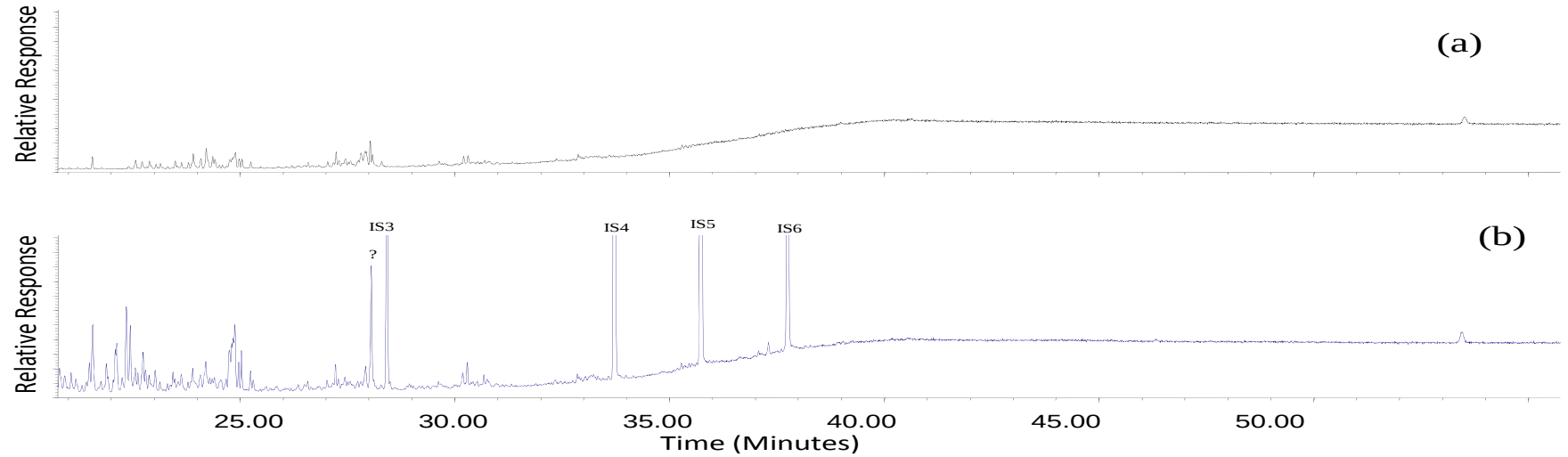

Figure 15. SPE Blank (a) versus (b) SPE of 275mL of oil saturated water fraction showing the TIC region of high molecular weight range of compounds from 20 to 55 minutes. IS3= d-anthracene, IS4=p-terpthenyl, IS5= 1,1-Binaphthyl, IS6= squalane. X shows contamiantion by phthalates

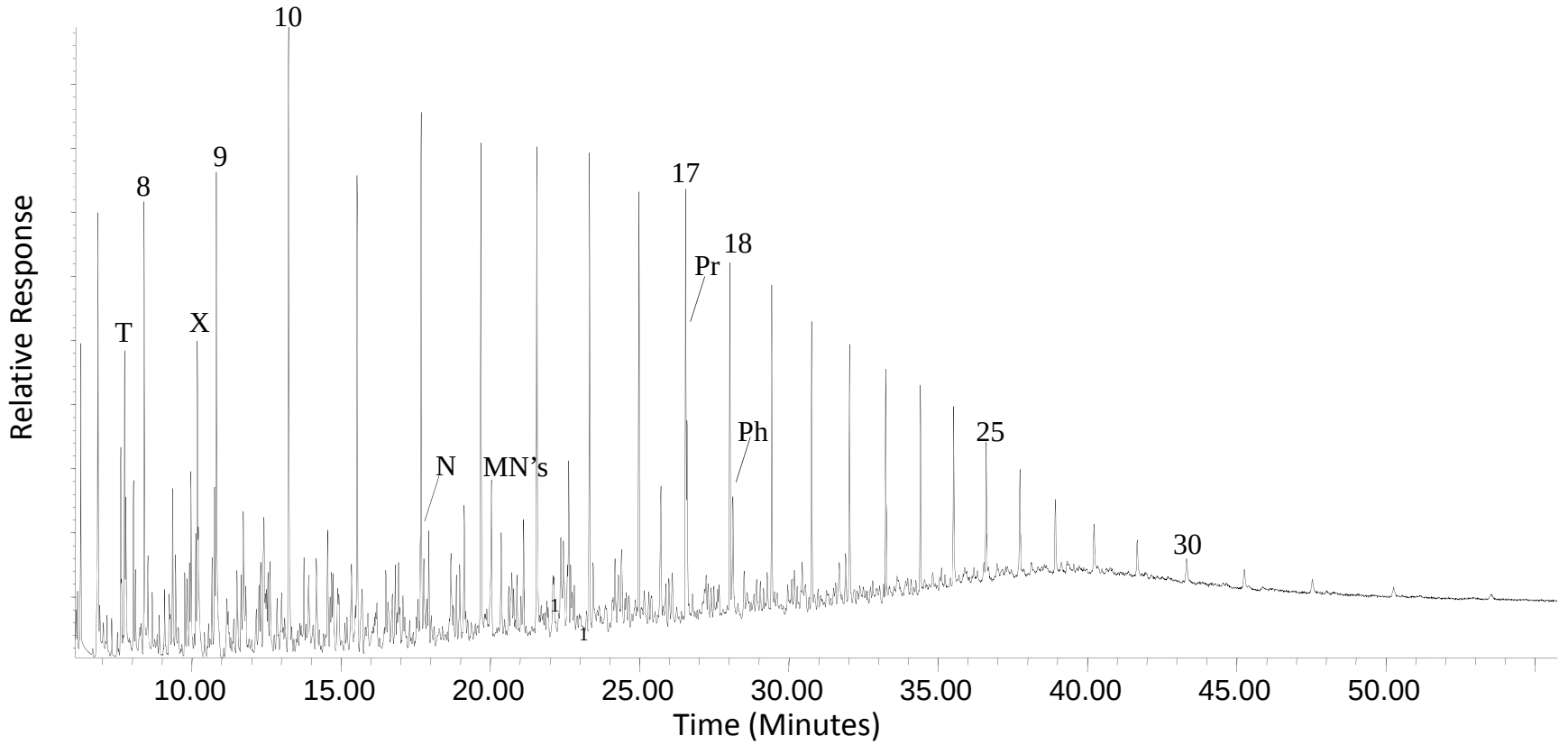

Figure 16. Whole oil TIC of the MC252 oil. The oil aliquot was dissolved in DCM and injected into the GC-MS Numbers refer to the aliphatic carbon chain length, T= Toluene, X= Xylenes, N= Naphthalene, MN= Methyl Naphthalenes, Pr = Pristane, Ph= Phytane.