

**Analysis of Hydrocarbons in Samples Provided from the
Cruise of the R/V WEATHERBIRD II, May 23-26, 2010**

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Summary

The National Oceanic and Atmospheric Administration (NOAA) undertook, through a certified testing laboratory, an independent analysis of 25 water samples provided from the cruise of the R/V WEATHERBIRD II during its mission to sample for hydrocarbons associated with the Mississippi Canyon 252 (MC-252) incident. One liter samples were provided in amber bottles from six to 12 depths at three discrete sampling locations: Station 01 was 142 nautical miles southeast of the MC-252 incident; Station 07 was 45 n. miles northeast of the incident, and the Station labeled "slick1" was 40 n. miles northeast.

Concentrations of total petroleum hydrocarbons (TPH) were less than 0.5 mg/L (parts per million) at all stations and depths. TPH concentrations in these 25 samples ranged from 0.085 to 0.480 mg/L (parts per million), with a median value of 0.203 mg/L (mean 0.223 mg/L). Concentrations of the individual 16 EPA priority pollutants¹ ranged from below reporting limits (< 10-13 ng/L or parts per trillion) to 79.2 ng/L (naphthalene, DSH Slick1-09). Five samples had reportable concentrations of these 16 polycyclic aromatic hydrocarbons (PAHs), with Total concentrations for the 16 priority pollutant PAHs (Total PAH₁₆ or TPAH₁₆) ranging from 17.7 to 79.2 ng/L. PAH concentrations were estimated below the reporting limits (but above the minimum detection limits – MDLs).² For TPAH₁₆, PAHs were detected above the MDLs in all samples, ranging from 9 to 112 ng/L with a median value for all 25 samples of 26 ng/L.

¹ EPA Priority Pollutants: naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenz[a,h]anthracene, benzo[g,h,i]perylene, and indeno[1,2,3-cd]pyrene.

² Note that reporting limit is defined as the lowest level to which the analytical instrumentation is calibrated. Although instrumentation has a defined "lower limit", it is still possible to detect compounds below this lowest

A comparison of TPH and TPAH₁₆ concentrations among the three stations (see Table 1, Figures 2 and 3) suggests that all three locations have similar depth distributions of TPH and TPAH₁₆ concentrations. Further, comparisons of the individual PAH₁₆ concentrations to eco-toxicological benchmarks pulled together from the literature (e.g., NOAA SQuiRTs Tables), illustrate that the PAH concentrations measured in these 25 water samples are well below these eco-toxicological benchmarks.

Despite low overall concentrations several samples had sufficient concentrations of petroleum biomarkers that allowed for a preliminary assessment with the MC 252 source oil:

- a. At the station labeled “slick1”, surface samples had hydrocarbons present³ and based on the distribution of diagnostic petroleum compounds these hydrocarbons are CONSISTENT with an MC 252 source.
- b. At Station DHS-01 at 100 meters depth, and at 300 meters depth, hydrocarbons were detected, but based on the distribution of diagnostic petroleum compounds these hydrocarbons are INCONSISTENT with an MC 252 source
- c. At station DSH-07, samples from the surface, 50, and 400 meters depth appear to have trace oil present, but concentrations are too low to allow for source determination.
- d. The petroleum concentrations in the remaining samples are too low for correlation.

Report

A recent joint USF/NOAA cruise was recently conducted by the R/V Weatherbird II. One of the objectives of the cruise was to evaluate if reflecting layers identified by acoustics were related to subsea petroleum. Of immediate concern was the ability to identify and potentially track deep subsurface

calibration level, but still meet the criteria for determining if a compound is actually present. If these criteria are met as determined by seasoned analysts, these compound(s) are confirmed to be present and the concentration is reported but qualified with a “J” to denote an estimated value.

The method detection limit (MDL) is defined in *40CFR part 136*. Laboratories determine a MDL for each compound analyzed by processing a series of laboratory-spiked replicates through the entire sample extraction and analytical process. Statistics – as defined in *40CFR part 136* - are then applied to the results in order to mathematically determine the MDL for each compound.

³ See Table 1 for sample hydrocarbons concentrations.

plumes that may be derived from the dispersed MC 252 oil. To accomplish this, the crew conducted fluorometry, salinity, temperature, dissolved oxygen, and conducted acoustic analyses, in addition to collecting water samples for chemical identification of the signals derived from their onboard instrumentation. Seawater samples were collected by scientist from the University of South Florida (USF) at each sampling station, and 130 one liter splits were provided to NOAA for independent analysis. USF scientists identified the 25 highest priority samples from three stations (Figure 1). Station DSH-01 was located 142 nautical miles southeast of the MC-252 incident; Station DHS-07 was 45 n. miles northeast of the Deepwater Horizon MC 252 incident, and the Station labeled “slick1” was 40 n. miles northeast of the location of the Deepwater Horizon MC 252 site. NOAA sent these samples to Alpha Analytical for quantification of TPH and PAHs using EPA SW846 for TPH and a modified method 8270c for PAHs.

In light of the Deepwater Horizon MC252 (DWH-MC252) release, including the unprecedented use of surface and subsurface applied dispersants, it’s important for NOAA to understand the distribution and magnitude of any sub surface dispersed oil derived from this release. The measurement of TPH and PAH concentrations provide a quantitative evaluation of the amount of any hydrocarbons in these samples. Additionally, NOAA is interested in understanding if hydrocarbons found at depth are from the DWH-MC252 release or from natural or other anthropogenic sources of oil. To accomplish the source identification, results from the Gas Chromatography/Mass Spectrometry (GCMS) analysis were evaluated by experienced petroleum geochemists who developed their conclusions based on review of the m/z 85, 191, and 217 ion traces⁴. An important consideration with these analyses is to understand that they require a minimum amount of hydrocarbons in the samples to ensure that the diagnostic hydrocarbon signal is strong enough to measure.

Results and Discussion

TPH

Results for TPH are presented in Table 1 and Figure 2. TPH concentrations for all water samples are fairly low; ranging from 0.085 to 0.48 mg/L (parts per million) with a median value of 0.203 mg/L. As illustrated in Figure 1, there is a general decrease in TPH concentrations with increasing depth at all three stations. For DHS-01, the TPH concentration decreases from 0.35 mg/L at the surface to 0.14 mg/L at 500 m. For DSH-07, the TPH concentrations generally decrease with depth, with an elevated concentration of 0.40 mg/L at a depth of 300 m. At station Slick1, TPH concentrations are highest at a depth of 50 m (0.48 mg/L), and generally constant with depth from 100 m to 400 m.

PAHs

Total PAH concentrations for all 16 EPA priority pollutants are presented in Table 2. Concentrations of individual PAHs were measured above the reporting limits in only 5 of the 25 samples. In these samples, TPAH₁₆ range from 17.7 to 18.7 ng/L. For 4 of the 5 samples, the TPAH₁₆ concentrations are supported

⁴ The mass to charge ratios for 85 is for n-alkanes and isoprenoids, 191 is the ion used for terpanes, and 217 is for steranes and diasteranes. Which are diagnostic of petroleum.

by one or two, two or three-ring PAH compounds. Only one of the samples analyzed has reportable concentrations of the EPA priority pollutant PAHs in the high molecular weight range (i.e., 4 to 6 ring PAHs).

Considering the potential for subsurface dispersed oil and the presence of surface oil and mousse at stations Slick1 and DHS 07, the TPH and PAH concentrations measured in these samples are relatively low. As noted above, the TPH and TPAH₁₆ concentration profiles from all three stations are similar, even though station DHS-01 is far to the south (see figure 1) and surface oil was found at stations Slick1 and DSH07. Comparison of the maximum individual PAH concentrations (or estimated concentrations where it fell below the reporting limit) to benchmark exposure concentrations from the literature (e.g., NOAA SQuiRTs) supports the contention that these hydrocarbon concentrations are low.

Source

Evaluation of the mass spectra from these analyses indicates that for most of the samples, the hydrocarbons present are at concentrations too low to discern a pattern. However, despite low overall concentrations several samples had sufficient concentrations of diagnostic petroleum hydrocarbons that allowed for a preliminary assessment with the MC 252 source oil:

- a. At the station labeled “slick1”, surface samples had trace hydrocarbons present⁵ and based on the distribution of diagnostic petroleum compounds these hydrocarbons are CONSISTENT with an MC 252 source (Fig. 4).
- b. At Station DHS-01 at 100 meters depth, and at 300 meters depth, trace hydrocarbons were detected, but based on diagnostic petroleum compounds these hydrocarbons are INCONSISTENT with an MC 252 source.
- c. At station DSH-07, samples from the surface, 50, and 400 meters depth appear to have trace oil present, but concentrations were too low to allow for source determination.
- d. Concentrations of diagnostic petroleum compounds in the remaining samples were too low for correlation.

⁵ See Table 1 for sample hydrocarbons concentrations.

Interim conclusions

Hydrocarbons are present in a number of the water samples collected from all three stations. TPH concentrations measured in these samples are low, with none being above 0.5 mg/L. Individual PAH concentrations are also low, being in the ng/L or parts per trillion range. Only 5 of the 25 samples had reportable levels of any of the 16 EPA priority pollutant PAHs, and of these, the highest TPAH₁₆ value was 79 ng/L (Station DHS-07, 200 m depth). The next highest TPAH₁₆ value was 49 ng/L (Slick1, 350 m depth).

These data do not show a substantial difference between the hydrocarbon concentrations or distributions measured in samples from station DHS-01, 142 nautical miles southeast of the Deepwater Horizon MC 252 well head and stations DHS-07 and Slick1 located 45 and 40 nautical miles (respectively) to the northeast of the well site. The Slick1 station does have an elevated TPH concentration at 50 m, while station DHS-07 has an elevated TPH concentration at 300 m depth. Neither of these depths corresponds with an elevated TPAH₁₆ concentration.

Mass spectral analysis of the m/z 85, 191, and 217 mass spectra suggest the surface sample from the Slick1 station contains hydrocarbons consistent with a Deepwater Horizon MC252 source. Hydrocarbons are also present in samples from station DHS-01 at 100 m and 300 m depths that are inconsistent with a Deepwater Horizon MC 252 source. Finally, results from station DHS-07 indicate that trace hydrocarbons are present in water samples from the surface, 50 m, and 400 meters depth; but that the concentrations are too low to allow for source determination.

While this data set does not conclusively demonstrate that hydrocarbons found in waters collected from northeast and southwest of the Deepwater Horizon MC 252 well site are derived from a specific source, it does demonstrate that the concentrations of hydrocarbons in these waters are generally low. These data further indicate that concentrations of TPH and PAH₁₆ from waters collected from stations 142 n. miles southeast of the wellhead and from stations 40 and 42 n. miles northeast of the wellhead are not substantially different.

Additional work is needed to better understand the fate and transport of hydrocarbons within the deeper waters of the Northern Gulf of Mexico. As well, a more complete and robust understanding of the fate and transport of hydrocarbons at depths will be critical to evaluating and correlating hydrocarbons found throughout the water column with the varying sources of hydrocarbons, both natural and anthropogenic, that are present in the waters of the northern Gulf of Mexico.

Table 1. Analysis of WEATHERBIRD II Data from three stations

| Station | Lat. | Long. | Date | Sample Name | Depth (m) | Total Petroleum Hydrocarbons (C9-C44) mg/L | RL ¹ mg/L | TPAH-16 ² ng/L | RL ng/L | LMW ³ TPAH-16 ng/L | HMW ⁴ TPAH-16 ng/L |
|---------|----------|----------|---------|-------------|-----------|-----------------------------------------------|-------------------------|------------------------------|------------|----------------------------------|----------------------------------|
| Slick 1 | 29 13.82 | 87 49.85 | 5/26/10 | -0 | 0 | 0.306 | 0.00109 | 20.5 | 10.9 | ND | 20.5 |
| Slick 1 | 29 13.82 | 87 49.85 | 5/26/10 | -1 | 50 | 0.480 | 0.00123 | | 12.3 | ND | ND |
| Slick 1 | 29 13.82 | 87 49.85 | 5/26/10 | -2 | 100 | 0.114 | 0.00114 | | 11.4 | ND | ND |
| Slick 1 | 29 13.82 | 87 49.85 | 5/26/10 | -3 | 150 | 0.184 | 0.00122 | | 12.2 | ND | ND |
| Slick 1 | 29 13.82 | 87 49.85 | 5/26/10 | -4 | 200 | 0.206 | 0.00118 | | 11.8 | ND | ND |
| Slick 1 | 29 13.82 | 87 49.85 | 5/26/10 | -5 | 250 | 0.232 | 0.00118 | | 11.8 | ND | ND |
| Slick 1 | 29 13.82 | 87 49.85 | 5/26/10 | -7 | 350 | 0.203 | 0.00118 | 48.68 | 11.8 | 48.68 | ND |
| Slick 1 | 29 13.82 | 87 49.85 | 5/26/10 | -8 | 400 | 0.180 | 0.00120 | | 12.0 | ND | ND |
| Slick 1 | 29 13.82 | 87 49.85 | 5/26/10 | -9 | 425 | 0.235 | 0.00112 | 17.7 | 11.2 | 17.7 | ND |
| 01 | 27 28.67 | 86 06.50 | 5/23/10 | -0 | 0 | 0.349 | 0.00118 | | 11.8 | ND | ND |
| 01 | 27 28.67 | 86 06.50 | 5/23/10 | -10 | 100 | 0.259 | 0.00116 | | 11.6 | ND | ND |
| 01 | 27 28.67 | 86 06.50 | 5/23/10 | -9 | 200 | 0.257 | 0.00108 | 79.17 | 10.8 | 79.17 | ND |
| 01 | 27 28.67 | 86 06.50 | 5/23/10 | -8 | 300 | 0.163 | 0.00119 | | 11.9 | ND | ND |
| 01 | 27 28.67 | 86 06.50 | 5/23/10 | -7 | 400 | 0.112 | 0.00119 | | 11.9 | ND | ND |
| 01 | 27 28.67 | 86 06.50 | 5/23/10 | -6 | 500 | 0.140 | 0.00118 | | 11.8 | ND | ND |
| 07 | 29 15.20 | 87 44.07 | 5/25/10 | -0 | 0 | 0.425 | 0.00114 | 36.31 | 11.4 | 36.31 | ND |
| 07 | 29 15.20 | 87 44.07 | 5/25/10 | -1 | 50 | 0.174 | 0.00127 | | 12.7 | ND | ND |
| 07 | 29 15.20 | 87 44.07 | 5/25/10 | -2 | 100 | 0.237 | 0.00128 | | 12.8 | ND | ND |
| 07 | 29 15.20 | 87 44.07 | 5/25/10 | -3 | 150 | 0.189 | 0.00114 | | 11.4 | ND | ND |
| 07 | 29 15.20 | 87 44.07 | 5/25/10 | -4 | 200 | 0.153 | 0.00122 | | 12.2 | ND | ND |
| 07 | 29 15.20 | 87 44.07 | 5/25/10 | -5 | 250 | 0.210 | 0.00122 | 28.2 | 12.2 | 28.2 | ND |
| 07 | 29 15.20 | 87 44.07 | 5/25/10 | -6 | 300 | 0.404 | 0.00119 | | 11.9 | ND | ND |
| 07 | 29 15.20 | 87 44.07 | 5/25/10 | -7 | 350 | 0.085 | 0.00119 | | 11.9 | ND | ND |
| 07 | 29 15.20 | 87 44.07 | 5/25/10 | -8 | 400 | 0.141 | 0.00111 | | 11.1 | ND | ND |
| 07 | 29 15.20 | 87 44.07 | 5/25/10 | -9 | 423 | 0.146 | 0.00120 | | 12.0 | ND | ND |

Notes: 1 – Reporting Limit, 2 – Summation of 16 EPA Priority Pollutants, 3 – LMW – 2+3 Ring PAHs, 4 – HMW – 4+5+6 ring PAHs

Table 2. Statistics of Total Petroleum Hydrocarbons (TPHs) in 25 samples obtained from three locations where WEATHERBIRD II collected water.

| Station | Count | Median | Standard Deviation | Minimum | Maximum |
|-----------------------|-------|--------|--------------------|---------|---------|
| All Stations Combined | 25 | 0.203 | 0.10 | 0.085 | 0.480 |
| Station DHS-01 | 6 | 0.210 | 0.09 | 0.112 | 0.349 |
| Station DHS-07 | 10 | 0.182 | 0.11 | 0.085 | 0.425 |
| "Slick1" | 9 | 0.206 | 0.10 | 0.114 | 0.480 |

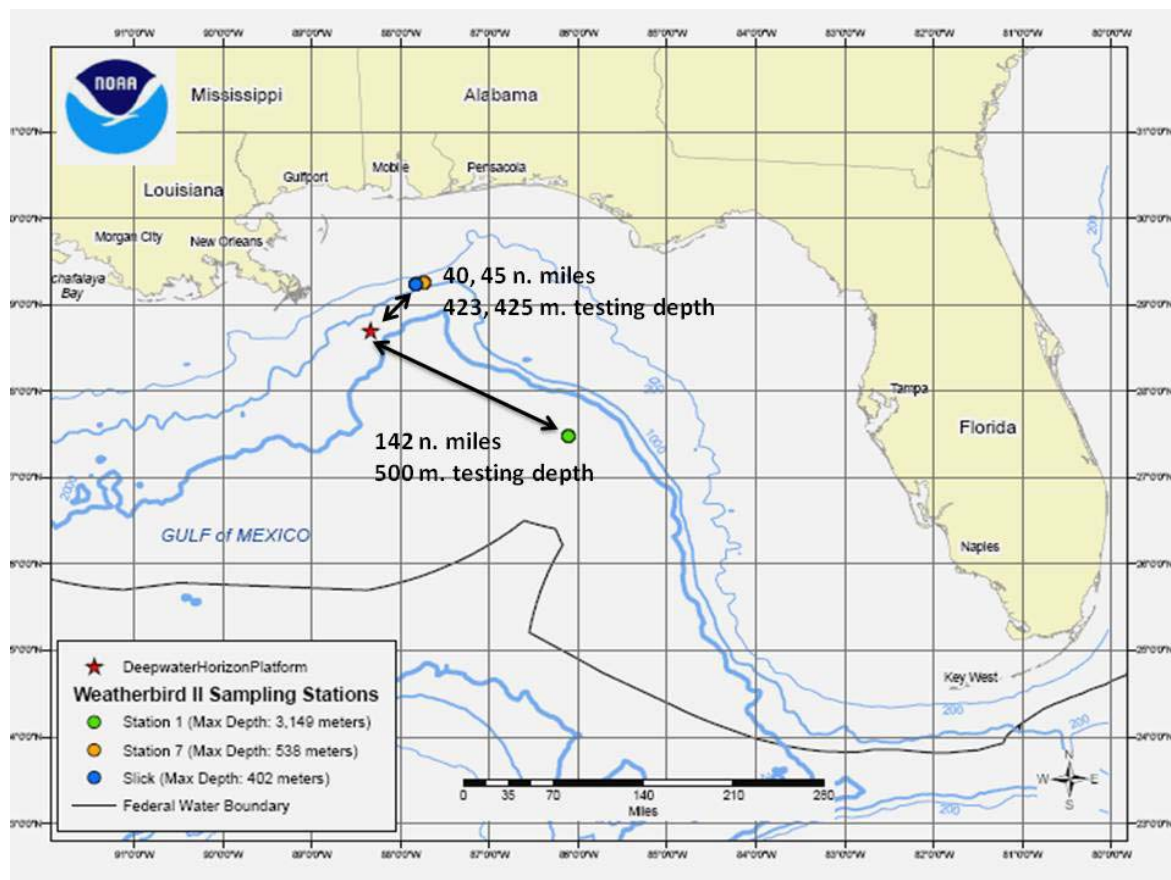


Figure 1 Sampling locations tested by NOAA from the R/V WEATHERBIRD II cruise.

Weatherbird II, Cruise II, NOAA Results

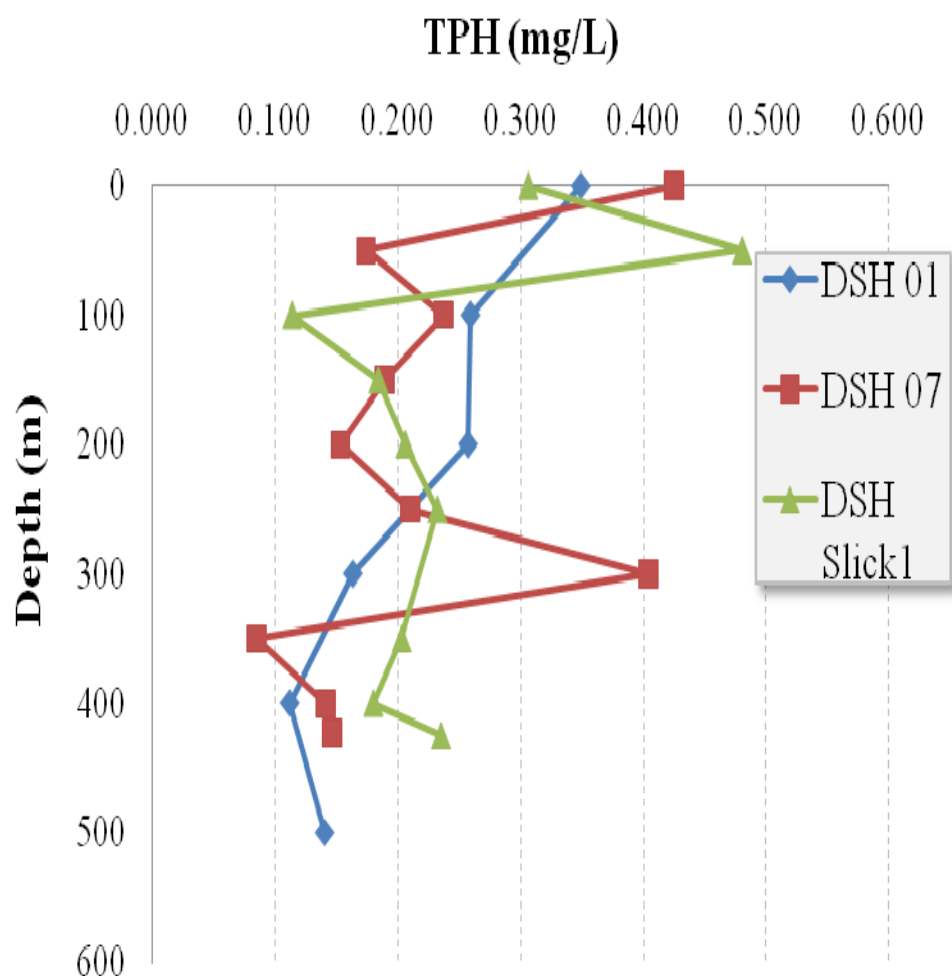


Figure 2. TPH concentrations at depth for three WEATHERBIRD II stations

Weatherbird II, Cruise II, NOAA Results

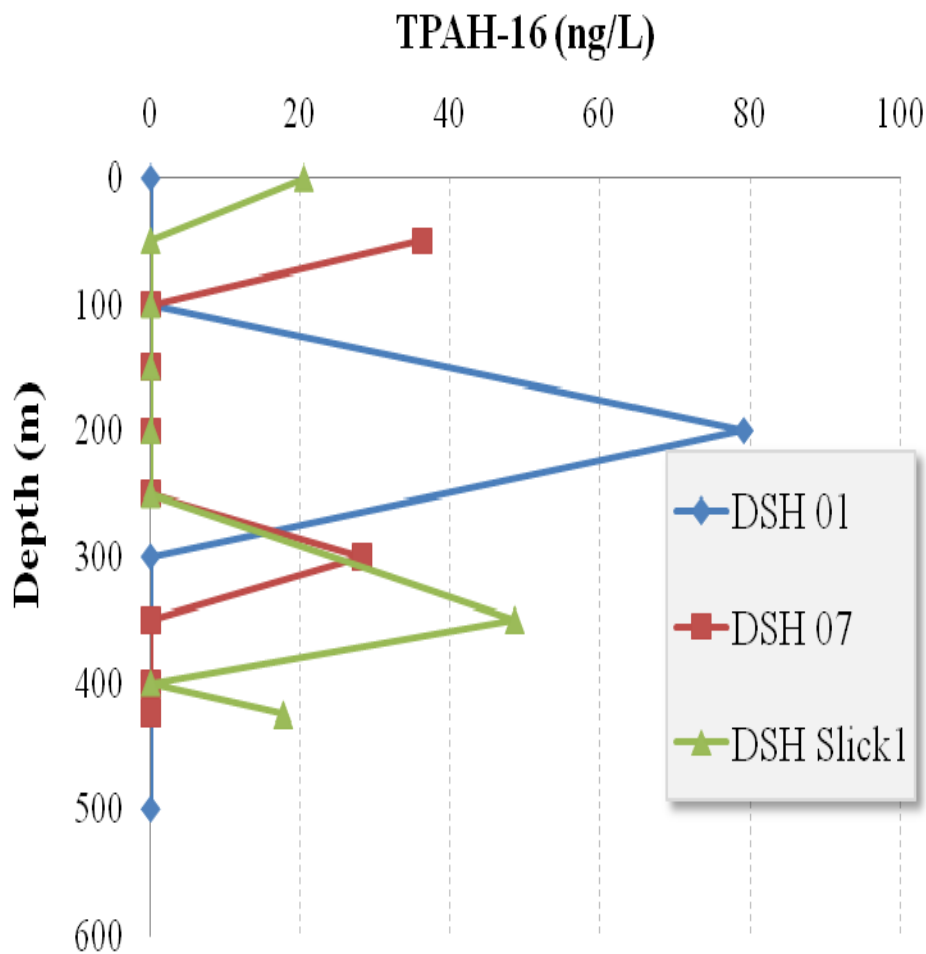


Figure 3. Total PAH compounds measured at depth in three WEATHERBIRD II stations

Figure 4. Chromatographic Comparisons of Source Oil, Slick 1-0 (Surface), and DSH 01-10 (100 m)

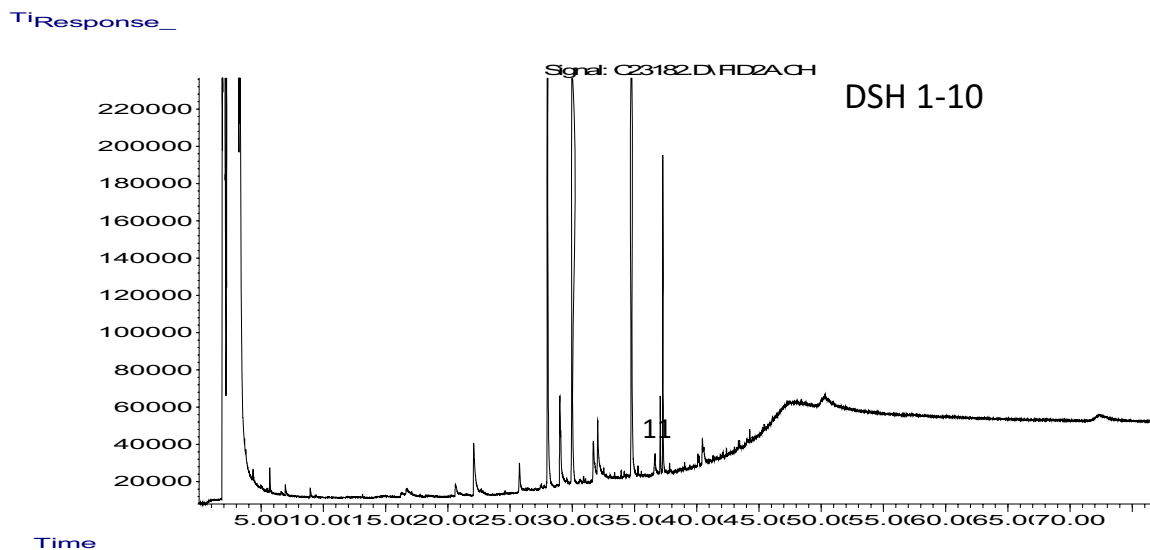
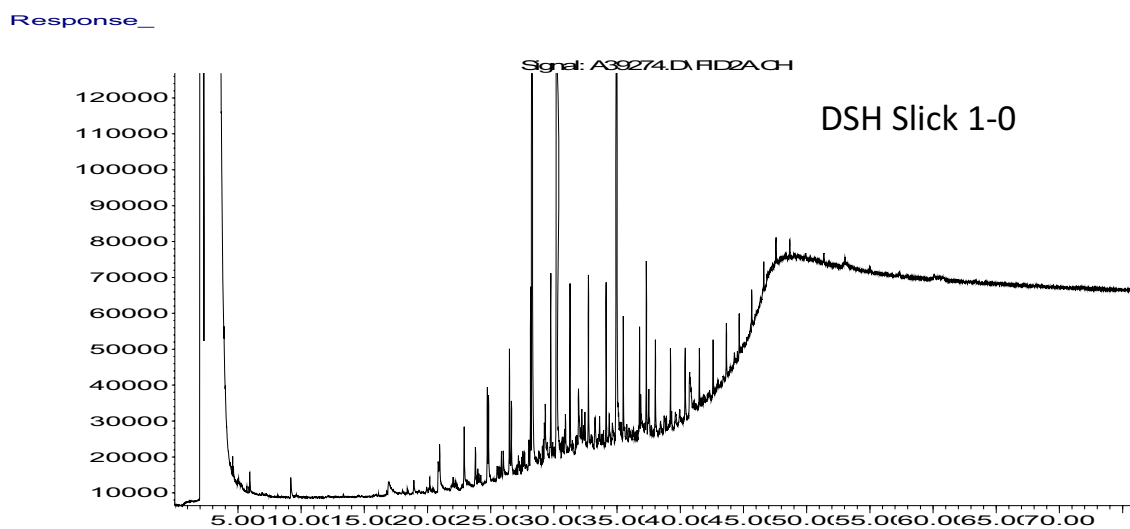
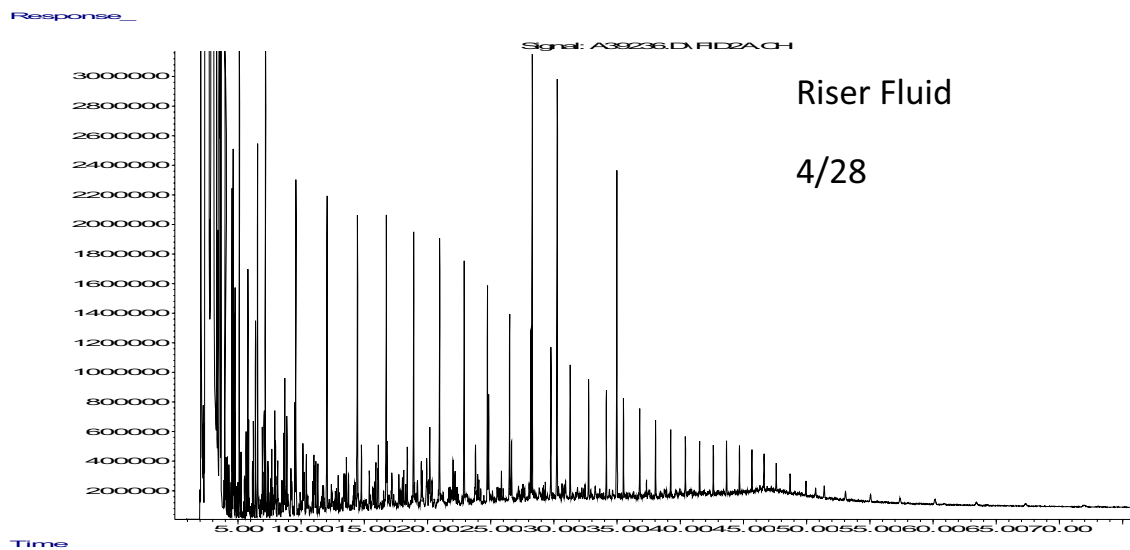


Fig 4 (cont.) m/z 85

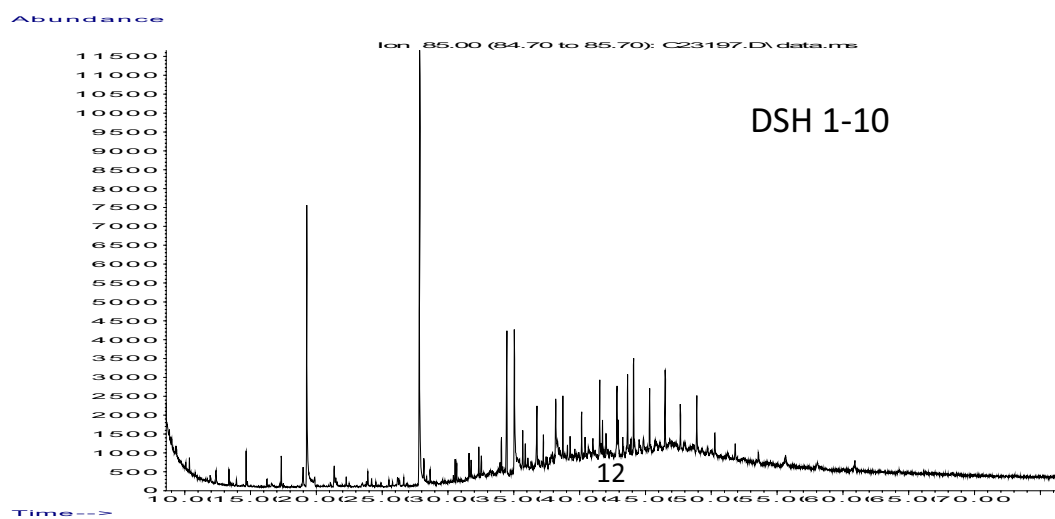
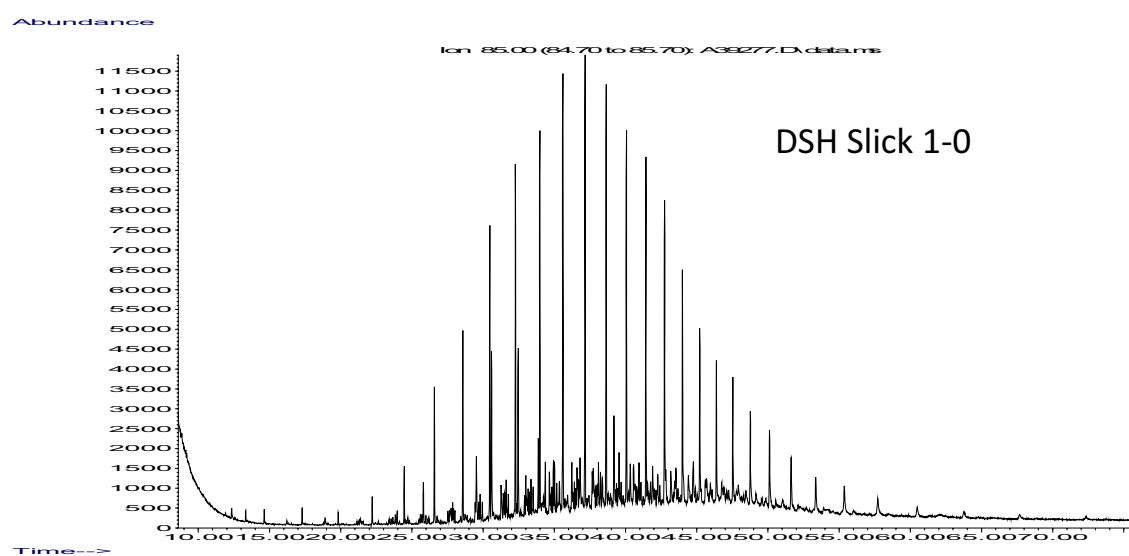
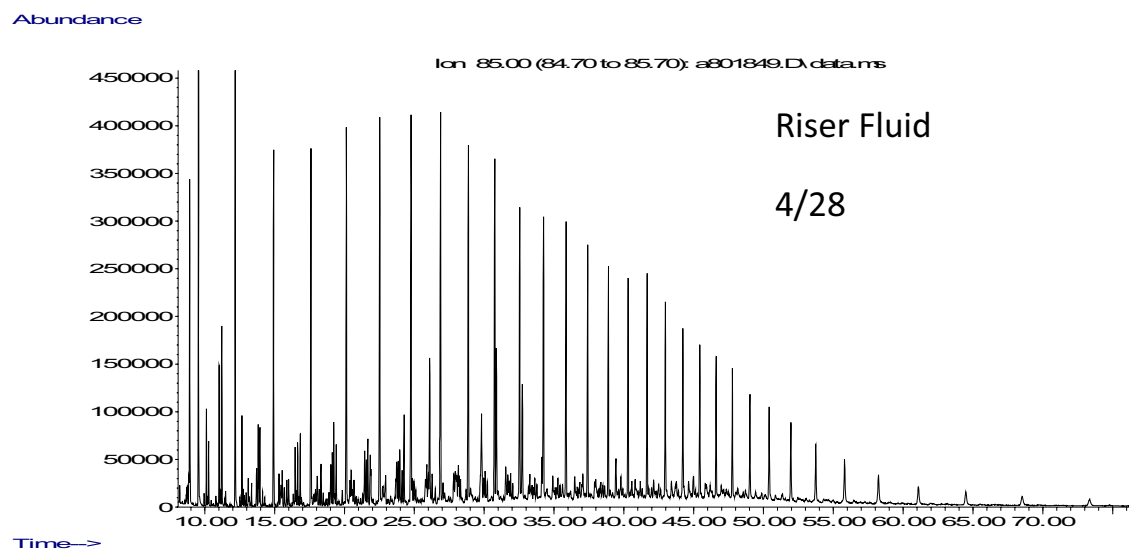


Fig.4 (cont.) m/z 191

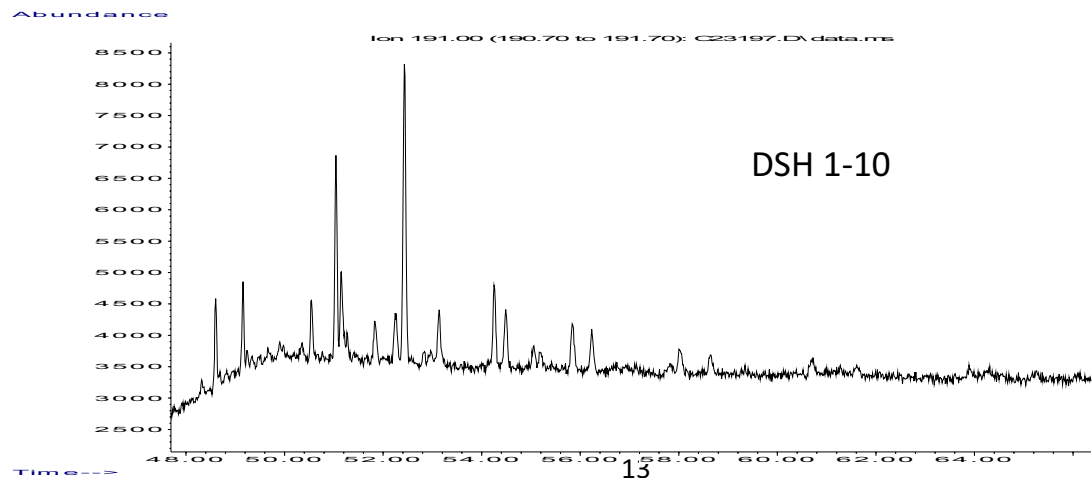
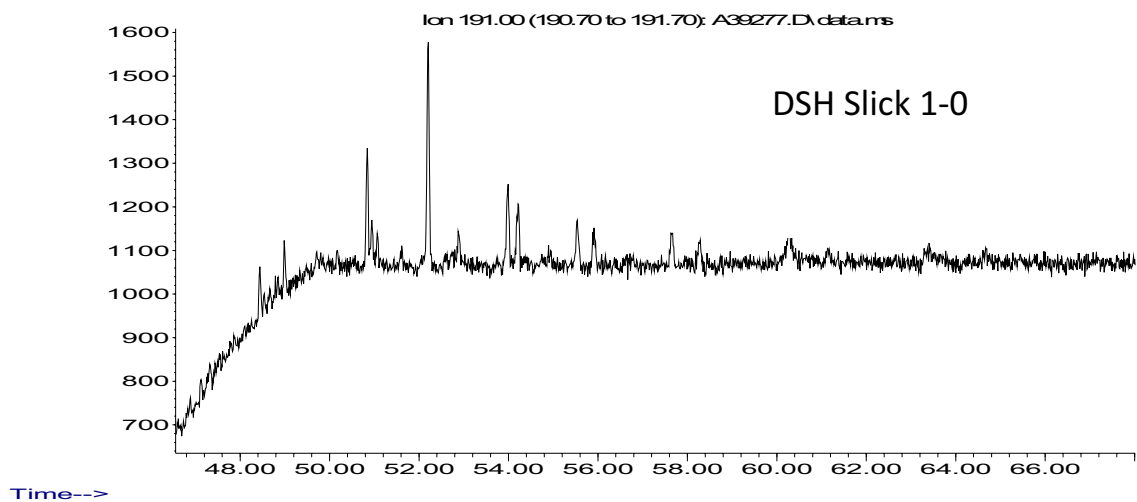
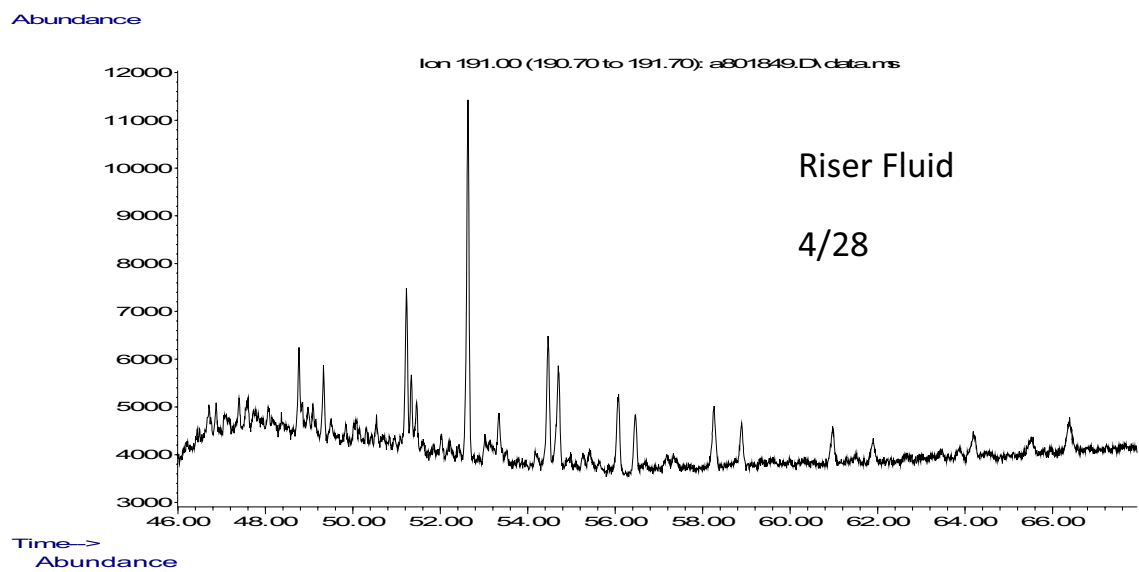


Fig. 4 (cont.) m/z 217

