



Environmental Applications

Fingerprinting Crude Oils and Tarballs Using Biomarkers and Comprehensive Two-Dimensional Gas Chromatography

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Abstract

Petroleum biomarkers are “molecular fossils” that can be analyzed with gas chromatography to fingerprint crude oil. Fingerprints can then be used to determine the source oil for an oil spill or highly weathered tarballs. This unique fingerprint is developed by evaluating several ratios of key biomarkers, such as steranes and hopanes. Comprehensive two-dimensional gas chromatography time-of-flight mass spectrometry (GCxGC-TOFMS) was used to evaluate biomarker ratios in several crude oils from various regions and also in tarballs that washed ashore on the gulf coast of Florida up to a year after the Deepwater Horizon oil spill of 2010. While one-dimensional GC-MS is often used for this analysis, the power of GCxGC provides enhanced specificity and peak capacity with increased resolving power that can separate diagnostic biomarkers from potential isobaric interferences. Also, GCxGC provides a structured chromatogram, which allows compound identification that would be impossible with GC-MS due to the complexity of crude oil. In this study, using 43 different biomarker ratios from GCxGC-TOFMS analysis, we identified one tarball from a Florida beach that was a possible match to oil from a broken riser pipe collected via an underwater robot during the Deepwater Horizon oil spill. Others were considered non-matches.

Introduction

The formation of crude oil occurred many millions of years ago from decaying plants and animals. Sediment and rock covered the organic material creating an anaerobic environment that eventually, under temperature and pressure conditions, formed crude oil [1]. This fossil fuel is refined for numerous applications from heating fuel to cosmetics. Crude oils from various regions differ in the plant and animal source materials, as well as the time, temperature, and pressure conditions that occurred during formation. Therefore, each crude oil has a unique fingerprint that can potentially be determined using biomarkers. Petroleum biomarkers are “molecular fossils”; they are complex hydrocarbon molecules that retain a remarkable structural similarity to the original natural product formed from dead organisms in the source rock. These biomarkers, which are resistant to weathering and degradation, are utilized by geologists to determine the relative age and environment in which the oil was created. Environmental forensic chemists use biomarkers to fingerprint crude oils, providing valuable information when evaluating source oils, weathered oils, and tarballs.

The NORDTEST oil spill identification system recommends methodology to determine oil spill source and uses a multi-tiered analytical approach [2]. Level one provides basic hydrocarbon information and degree of weathering by GC-FID. Level two utilizes GC-MS in selected ion monitoring (SIM) mode to determine diagnostic ratios for polycyclic aromatic hydrocarbons (PAHs) and several hopane (m/z 191) and sterane (m/z 217) biomarkers. Level three looks at a statistical approach to results from levels one and two. Any diagnostic ratios that are found to have a high degree of analytical variance are eliminated from consideration. The most robust diagnostic ratios are used for a correlation plot that can help identify potential source oil matches. While GC-MS (SIM) can provide semiquantitative results for target analytes, the complexity of crude oil makes it difficult to rule out isobaric interferences that alter important source oil identification information.

Comprehensive two-dimensional gas chromatography time-of-flight mass spectrometry (GCxGC-TOFMS) uses two columns of different selectivities with thermal modulation to create two dimensions of separation. Compounds that typically must be analyzed separately in one-dimensional GC, sometimes with tedious off-line cleanups (e.g., PAHs and hydrocarbons), can be resolved in one analysis using GCxGC. Here, we used a highly efficient GCxGC-TOFMS setup to fingerprint light crude oil samples from various regions by evaluating ratios of diagnostic biomarkers. An oil sample from the Deepwater Horizon oil spill of 2010 collected at a broken riser pipe via an underwater robot was then evaluated as potential source oil for tarballs that were collected on the beaches of Florida. The NORDTEST methodology provides a good background for the type of information needed to identify source oil; however, the use of GCxGC-TOFMS instead of GC-MS (SIM) was beneficial in the characterization of crude oils and tarballs. These benefits include easier identification of diagnostic biomarkers because of the structured GCxGC chromatogram, full mass spectral information with the sensitivity of selected ion monitoring, and increased resolution of biomarkers, which reduces the potential for isobaric interferences.

Experimental

Sample Preparation

Calibration standards were prepared in isooctane by mixing a 12-component hopane/sterane calibration mix (Chiron cat. # S-4436-10-IO); a fuel oil degradation mix (Restek cat.# 31240); and single solutions of adamantane (Sigma Aldrich cat.# 100277); 2,2,4,4,6,8,8-heptamethylnonane (Sigma Aldrich cat.# 128511); 2,6,10-trimethyldodecane (Sigma Aldrich cat.# 5603228); 1-phenyltetradecane (Sigma Aldrich cat.# 87204); 5 α -cholest-3-ene (Sigma Aldrich cat.# R205990); and tricyclo(14.2.2.2(7,10)docosane (Sigma Aldrich cat.# S310727).

Crude oil samples from various regions around the world were purchased from ONTA. The riser pipe oil collected via an underwater robot during the Deepwater Horizon oil spill was provided by Ed Overton, Professor Emeritus at Louisiana State University. The light crude samples were weighed and diluted to 10 mg/mL in methylene chloride. A simulated weathered sample of the riser oil was produced by placing the sample on a hot plate at 70 °C under a gentle stream of nitrogen until the final weight was approximately 50% of the initial weight of the oil. Tarball samples were provided by Susan Forsyth, a citizen in Walton County, Florida, who helps with nearby beach cleanups. Approximately 100 mg of a tarball was diluted with 1 mL methylene chloride and allowed to soak overnight in the refrigerator. The samples were shaken, filtered using 0.45 μ m PTFE Millex® Smplicity® filters (Millipore cat. # SAMPLCR01) on the Smplicity® filtration system (Millipore cat. # SAMPYSYSGR), and diluted to a final volume of 1 mL in methylene chloride. An internal standard of deuterated PAHs (SV internal standard mix, Restek cat.# 31206) was added to every sample extract and calibration standard prior to analysis at 5 ng/ μ L.

GCxGC-TOFMS Analysis

A LECO Pegasus® 4D GCxGC-TOFMS equipped with an Agilent 6890 GC and 7683 injector was used for all analyses. A 60 m, 0.25 mm ID, 0.10 μ m Rxi®-17Sil MS column installed in the primary GC oven was press-fitted (BGB Analytik AG cat.# 2525LD) to a 1 m, 0.25 mm ID, 0.10 μ m Rxi®-1HT column (piece cut from Restek cat.# 13950) in the secondary oven. Helium was used as the carrier gas with a corrected constant flow of 1 mL/min. Fast injections of 1 μ L (10:1 split) were performed using an autoamplifier with a 0.5 sec viscosity delay at a temperature of 275 °C into a Restek Premium 4.0 mm ID Precision® inlet liner with wool (Restek cat.# 23305.5). The primary oven conditions were: 40 °C (hold 1 min) ramped at 2.5 °C/min to 320 °C (hold 7 min) for a total analysis time of 120 minutes. The secondary oven temperature programming tracked the primary program with a + 5 °C offset. The modulation period was 2.8 sec with a + 20 °C modulation temperature offset. Data were acquired from 45 to 550 u with an acquisition rate of 100 spectra/sec. The transfer line temperature was 300 °C and the MS source temperature was set to 250 °C.

Data Processing

Data were acquired and processed using LECO ChromaTOF® software. Raw data file size was reduced by using a resampling feature in the software. Three subgroups were set up. The first group was steranes and hopanes, which were resampled from retention times 4,599.2 to 7,194.78 sec with a mass range of 45 to 450 u. Within this group data processing methods were also set up for chrysenes (Chry), triaromatic steranes (TAS), benzonaphthylthiophenes (BNT), and methyl-substituted fluoranthenes (C1-Fl) and phenathrenes (C1-Ph). The second resampling group was dibenzothiophenes (DBT) and phenanthrenes, which were resampled from 45 to 350 u for retention times between 3,498.8 and 4,797.98 seconds. The final group was alkyl benzenes (AB), resampled from 1,900 to 6,298.79 sec across the m/z range of 70 to 340 u.

Diagnostic biomarker ratios were calculated using this equation: ratio = 100*A/(A+B), where A and B were concentrations generated from a multi-point calibration curve for biomarker compound with standards. For biomarkers with no corresponding standard, the values for A and B were (area of analyte)/(area of internal standard).

Results and Discussion

Highly Efficient Analysis with GCxGC

Efficiency as peak capacity in gas chromatography can be described by how many resolved peaks can fit into a certain time period. In order to achieve an efficient analysis several chromatographic parameters must be optimized. First, a column that has a high number of theoretical plates must be used. We chose an Rxi®-17 Sil MS that is relatively long (60 m) and narrow bore (0.25 mm) with a thin film (0.10 µm) in order to maximize column efficiency. Second, selecting a flow rate that is near the minimum height equivalent to a theoretical plate (HETP) in the van Deemter curve for the carrier gas is critical. In this case, since helium carrier gas and a 60 m x 0.25 mm ID column were used, we chose a flow rate of 1 mL/min, which produces an average linear velocity of 25.5 cm/sec. The optimal linear velocity based on the van Deemter curve for helium is between 20 and 40 cm/sec. Finally, the optimal heating rate (OHR) in °C/min for the GC oven is calculated as 10/holdup time [3]. Using the Agilent column pressure/flow calculator we find that the holdup time is 3.92 minutes, which yields an OHR of approximately 2.5 °C/min. While this may produce long analysis times, it is advantageous when analyzing extremely complex petroleum samples because it provides the most efficient first dimension separation.

We can optimize the column and conditions in the first dimension to get a highly efficient analysis; however, we also need to further optimize the setup to include the secondary column. Often the first dimension separation is compromised in GCxGC because of the desire to slice the first dimension peak at least three times at the modulator. In order to get a modulation time that is not so fast that a second dimension separation cannot be performed (i.e., when the second dimension holdup time is longer than the modulation time or when an impractically short second dimension column is called for) one must have a relatively wide first dimension peak. One way to accomplish this is by operating the first dimension column under less than optimal conditions to achieve a wider peak, sacrificing the first dimension separation. However, in order to achieve a true peak capacity increase, we use a long first dimension column that naturally has broader peaks even when operated efficiently. We set the modulation period to 2.8 sec so 3 slices could be made across the peak without compromising the first dimension separation (Figure 1). Increasing the peak capacity by operating the first and second dimensions efficiently benefits petroleum sample analysis by providing a detailed fingerprint that can be used to elucidate source oil for an oil spill sample.

Reducing GCxGC-TOFMS Data File Size for Easier Processing and Review

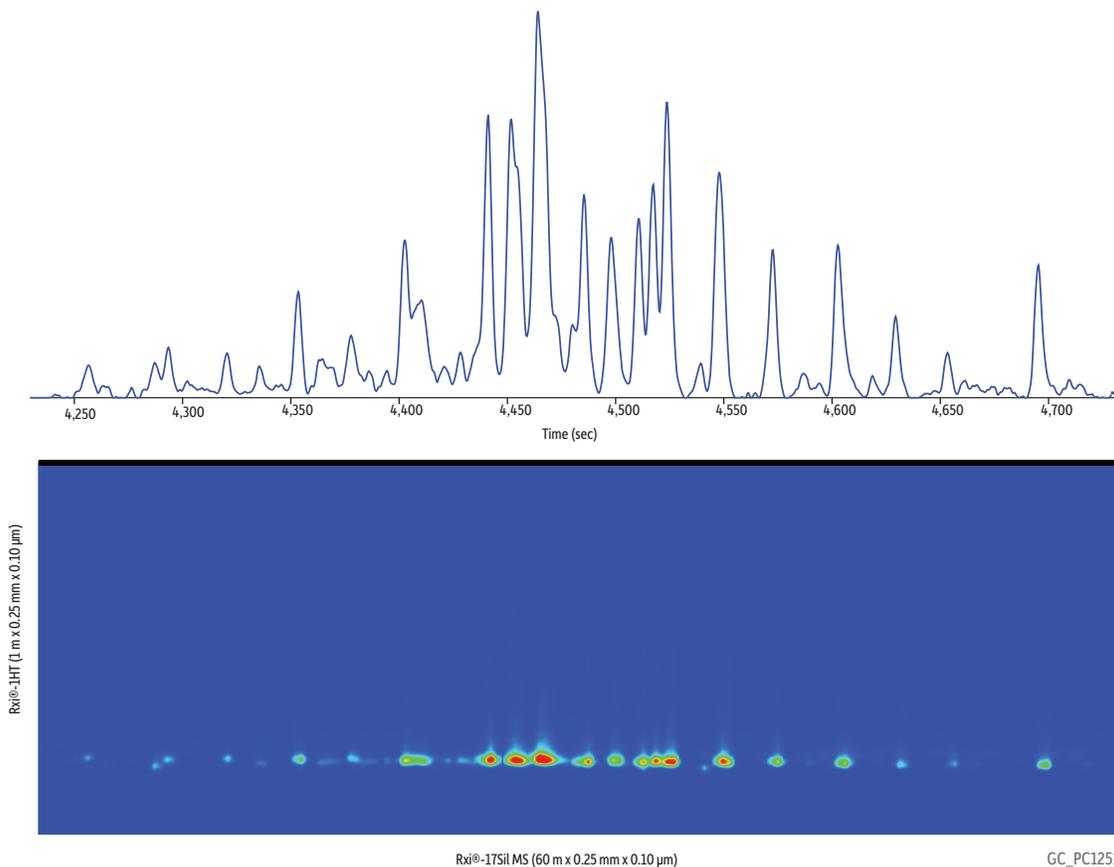
One of the major hesitations when deciding to adopt GCxGC-TOFMS is the amount of data that can be acquired in a single analysis. In the riser pipe oil over 18,000 peaks were found at or above a signal-to-noise ratio (S/N) of 20 and the original unprocessed data file exceeded 660 megabytes (MB). There are strategies one can employ to help manage the seemingly overwhelming amount of data that has been collected, including splitting the data into smaller, more manageable file sizes for processing and review. We split the data processing into multiple groups, three represented in the body of this work: steranes and hopanes, dibenzothiophenes and phenanthrenes, and alkyl benzenes. The raw data were resampled in the ChromaTOF® software for each group, focusing only on the retention time window and m/z range of the target compounds. By resampling and focusing only on the steranes and hopanes, for example, the data file was decreased to just over 200 MB and the number of found peaks was approximately 400. While 400 peaks may not be considered a small number, for source oil fingerprinting a large selection of potential diagnostic biomarkers can be desirable.

Resolving a Complex Mixture with GCxGC

Column choice plays an important role when analyzing crude oil samples using GCxGC. Using two orthogonal columns will separate the sample matrix across both the first and second dimension creating better overall resolution of the analytes. The typical setup for a GCxGC analysis of crude oil is a nonpolar column in the first dimension and a relatively polar column in the second dimension. This puts the aliphatic hydrocarbons, which are not well retained in the second dimension on a more polar column, in the bottom region of the chromatogram and the aromatic hydrocarbons towards the top. By switching the typical setup so the more polar Rxi®-17Sil MS column is in the first dimension and the nonpolar Rxi®-1HT column is in the second, the elution profile of the chromatogram is switched. Now the aliphatic hydrocarbons are retained on the nonpolar column and elute toward the top of the chromatogram, and we see a better separation of PAHs near the bottom of the chromatogram due to the selectivity of the Rxi®-17Sil MS in the first dimension (Figure 2).

In one-dimensional GC analysis, finding multiple compound classes in complex mixtures like crude oil can be difficult due to overlapping peaks and interferences from matrix components. In comprehensive two-dimensional GC the compound classes elute together in bands across the chromatogram. This makes peak identification much easier. For example, we can plot the extracted ion chromatogram for steranes (m/z 217) and hopanes (m/z 191) and see the structured area where these compound classes elute (Figure 3). Homologous series of compounds will elute in these bands, which greatly speeds up analyte identification. Using the structure of the chromatogram, mass spectra, and available standards as a starting point, we were able to tentatively utilize numerous biomarkers that we did not have standards for and that are not found in the NIST library.

Figure 1: C3-phenanthrenes (m/z 220) analyzed by efficient 1D and 2D GC. The first dimension separation is maintained in the 2D GC plot for structural isomers by highly efficient GCxGC conditions.



Column	Rxi®-17Sil MS 60 m, 0.25 mm ID, 0.10 µm (cat.# custom) Rxi®-1HT 1 m, 0.25 mm ID, 0.10 µm (cat.# 13950)	Detector	MS
Sample	Riser pipe oil from Deepwater Horizon oil spill	Mode:	
Diluent:	Methylene chloride	Transfer Line	
Conc.:	10 mg/mL	Temp.:	300 °C
Injection		Analyzer Type:	TOF
Inj. Vol.:	1.0 µL split (split ratio 10:1)	Source Temp.:	250 °C
Liner:	Restek Premium 4 mm Precision® liner w/wool (cat.# 23305.5)	Electron Energy:	-70 eV
Inj. Temp.:	275 °C	Mass Defect:	100 mu/100 u
Oven		Ionization Mode:	EI
Oven Temp.:	Rxi®-17Sil MS: 40 °C (hold 1 min) to 320 °C at 2.5 °C/min (hold 7 min) Rxi®-1HT: 45 °C (hold 1 min) to 325 °C at 2.5 °C/min (hold 7 min) He, corrected constant flow (1 mL/min)	Acquisition Range:	45 to 550 amu
Carrier Gas		Spectral Acquisition	
Modulation		Rate:	100 spectra/sec
Modulator Temp.		Instrument	LECO Pegasus 4D GCxGC-TOFMS
Offset:	20 °C	Notes	1D chromatogram collected using same instrument conditions except: Second Dimension Separation Time: 0 sec Spectral Acquisition Rate: 3 spectra/sec
Second Dimension			
Separation Time:	2.8 sec		
Hot Pulse Time:	1.0 sec		
Cool Time			
between Stages:	0.4 sec		

The enhanced resolving power of GCxGC can provide critical information on potential diagnostic biomarkers for source oil identification or geological characterization of the crude oil. In a side-by-side comparison of one-dimensional GC and comprehensive two-dimensional GC, Eiserbeck et al. found that GCxGC revealed a coelution with hopane that was previously not detected in 1D GC [4]. We also found that by using GCxGC-TOFMS it was possible to resolve a diamondoid that would have had an isobaric interference in a 1D separation (Figure 4). Diamondoids include adamantane, diamantine, and their alkyl homologs. Interest in these low boiling biomarker compounds have been increasing for petroleum exploration because the distribution pattern of methyl substitution can help elucidate the thermal maturity of oil [5]. The usefulness of diamondoids for source oil identification is minimal for heavy crude or highly weathered samples because little to no diamondoids exist in these oils.

Figure 2: Aromatic compounds elute near the bottom of the contour plot and aliphatic hydrocarbons elute toward the top when a more polar Rxi®-17Sil MS column is used in the first dimension and a nonpolar Rxi®-1HT column is used in the second dimension. The highly efficient Rxi®-17Sil MS column can separate important aromatic petroleum biomarkers in the first dimension.

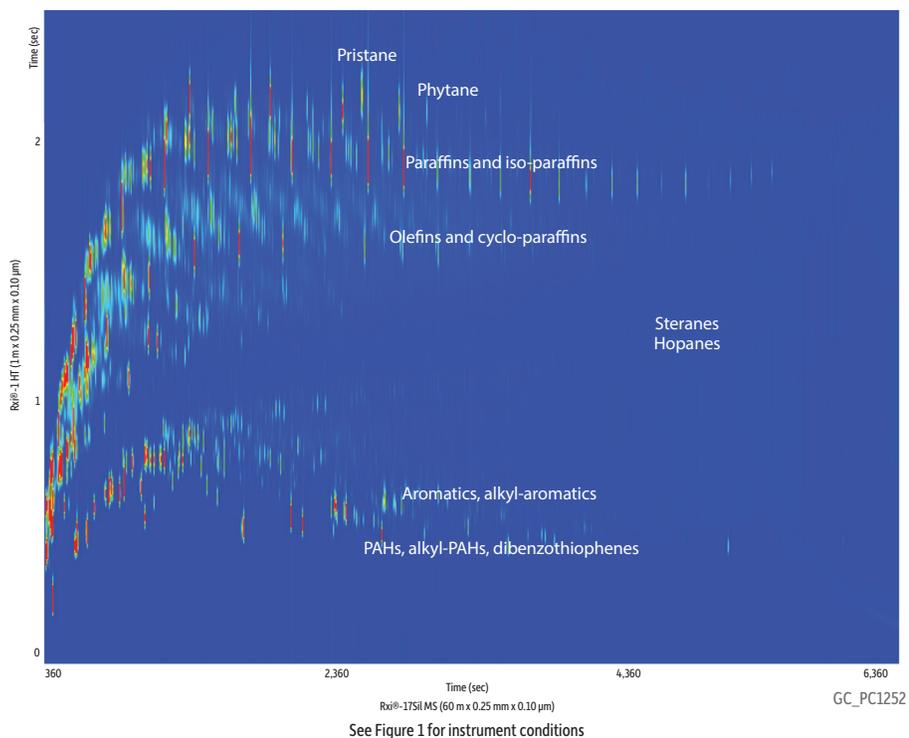


Figure 3: The GCxGC contour plot shows that similar compound classes elute in structured bands across the chromatogram, which aids in compound identification and allows their unbiased use for fingerprinting.

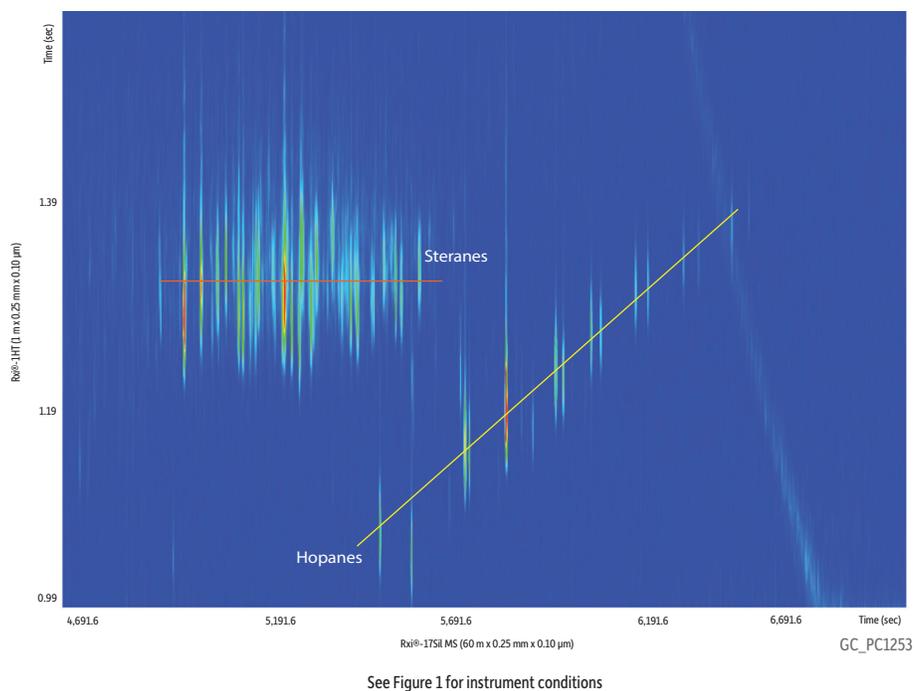


Figure 4: Using 2D GC, adamantane is separated from an isobaric interference (both have 136 m/z ions) that would have coeluted with it on an Rxi®-17Sil MS column in 1D GC.

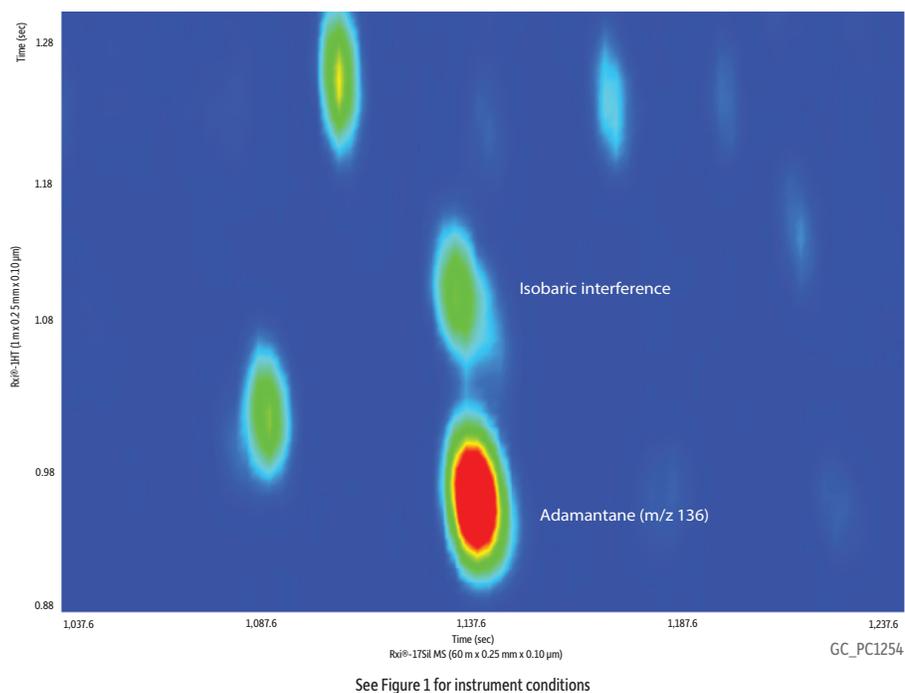
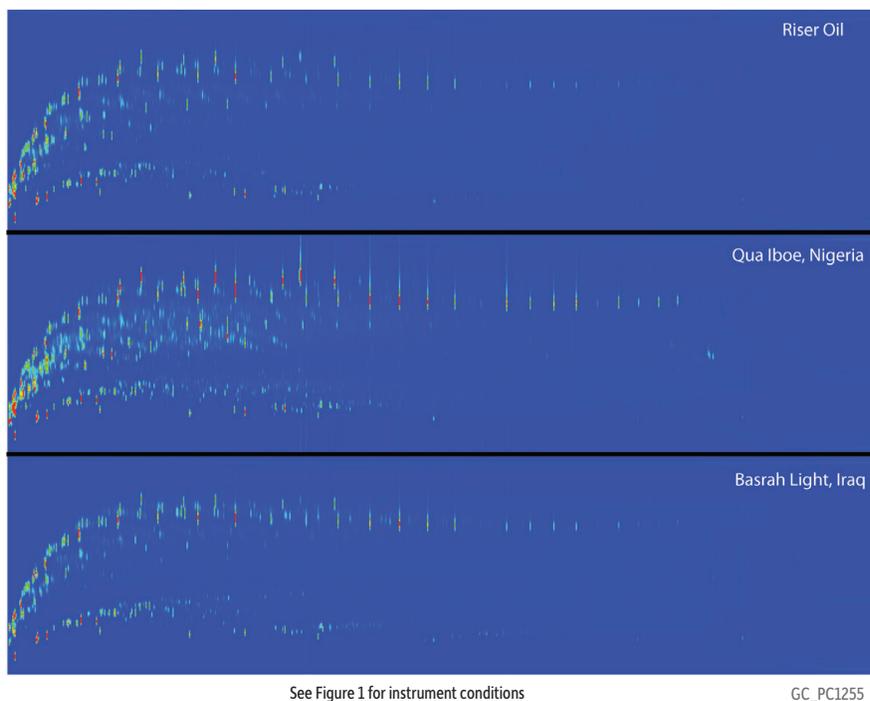


Figure 5: Total ion chromatograms of light crude oil samples from around the world show similarities among the crude oils.

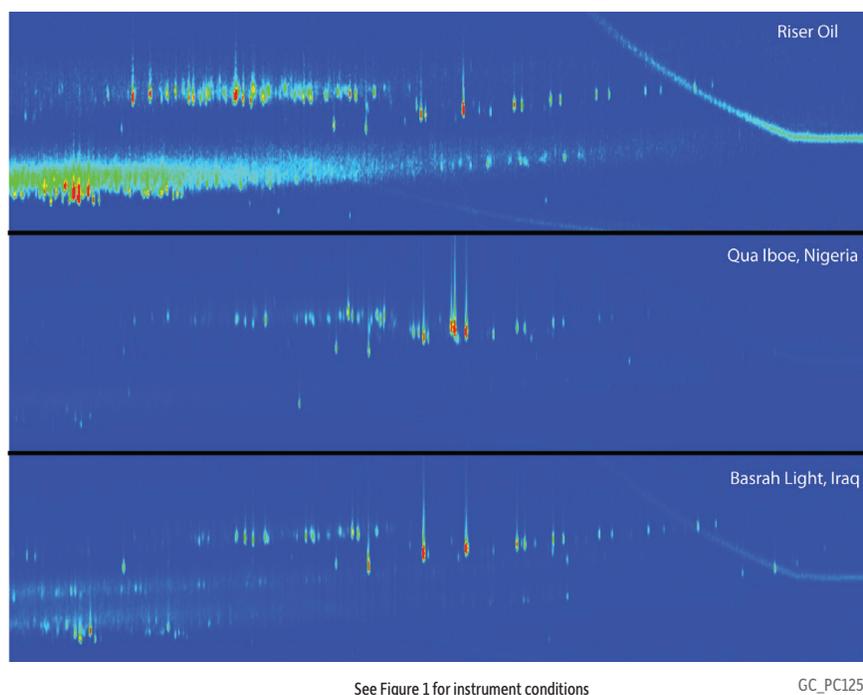


Fingerprinting Crude Oil With GCxGC

When assessing which biomarkers are diagnostic of particular source oils, the NORDTEST method recommends acquiring data for a large set of potentially useful compounds [2]. Using GC-MS (SIM) this would require multiple injections of the same sample to collect all of the specific ion chromatograms and perhaps off-line cleanup to eliminate interferences that would skew results and lead to inaccurate data. Even then, due to the lower peak capacity of a one-dimensional GC analysis, the number of potentially useful biomarkers would be limited. Using GCxGC-TOFMS, all of this information was collected in a single analysis and potential diagnostic biomarkers can be evaluated without reanalysis.

Light crude oil samples from the U.S., Canada, Saudi Arabia, Iraq, and Nigeria were evaluated to determine characteristic biomarker ratios that could be used to fingerprint the individual oils. Visual inspection of GCxGC contour plots provided a striking picture that helped show similarities and differences in the samples. While total ion chromatogram (TIC) contour plots of the light crude oils showed little to no major differences between the oils (Figure 5), the extracted ion chromatograms (EIC) proved to be helpful when evaluating samples. Comparing EICs of biomarkers, such as the steranes (m/z 217, 218) and hopanes (m/z 191), showed clear differences in the presence or absence and intensity of compound in oils from around the world (Figure 6).

Figure 6: Extracted ion chromatograms of steranes (m/z 217, 218) and hopanes (m/z 191) show a clear difference among oils from around the world and can help fingerprint individual oils.



Crude oil samples that were closer in geographical location proved to be more difficult to uniquely fingerprint. Focusing only on a few sterane and hopane ratios provided some small differences, although without any statistical data from multiple injections analytical variance could not be ruled out as a possibility for these differences. We found that adding alkylated dibenzothiophenes and phenanthrenes to the diagnostic ratios provided a better distinction between crude oils even when their sources were in relatively close proximity to each other geographically (Figure 7). The ratio of C3 alkylated dibenzothiophenes and C3 alkylated phenanthrenes proved to vary the most for oil samples from North America.

Figure 7: Diagnostic biomarker ratios can be used to uniquely fingerprint light crude oil samples of various origins.

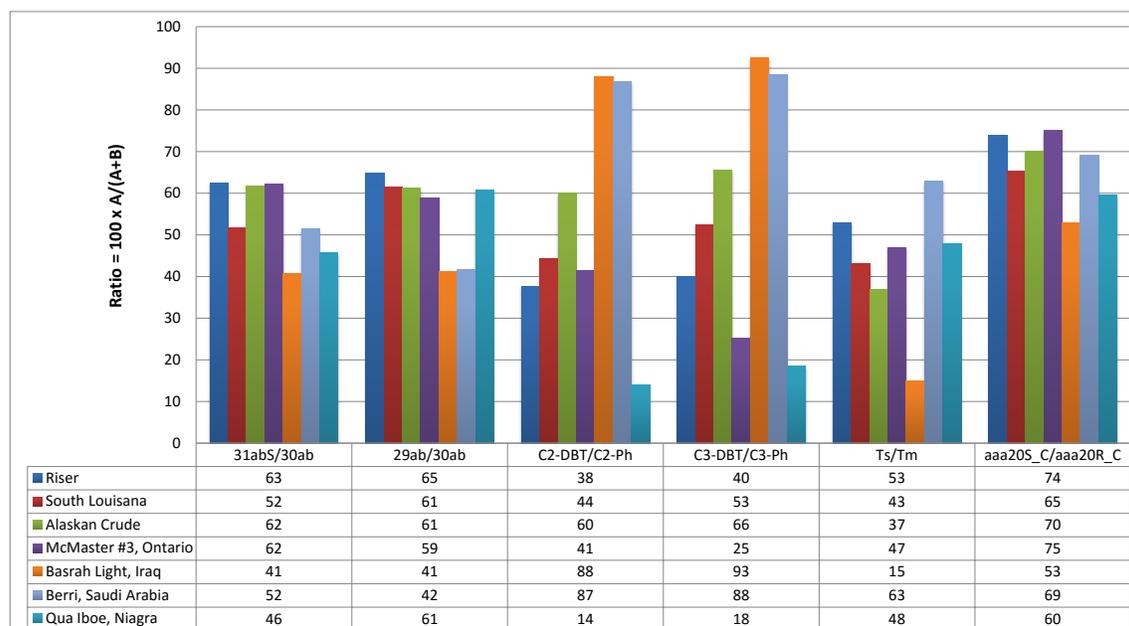


Table I: Biomarkers used for fingerprinting oil samples.

Biomarkers	Abbreviation
aaa 20S-Cholestane	aaa20S_C
abb 20R-Cholestane	abb20R_C
aaa 20R-Cholestane	aaa20R_C
abb 20R 24S-Methylcholestane	abbMEC
abb 20R 24R-Ethylcholestane	abbEC
aaa 20R 24R-Ethylcholestane	aaaEC
17a(H), 21b(H)-Hopane	30ab
17a(H), 21b(H)-22S-Homohopane	31abS
17a(H) 21b(H)-22R-Homohopane	31abR
17a(H), 21b(H)-30-Norhopane	29ab
17a(H)-22,29,30-Trisnorhopane	27Tm
18 -22,29,30-Trisnorneohopane	27Ts
24-ethyl-5a(H), 14a(H), 17a, 20S-cholestane	29aaS
24-ethyl-5a(H), 14a(H), 17a, 20R-cholestane	29aaR
Dibenzothiophene	DBT
Phenanthrene	Ph
Chrysene	Chry
Triaromatic sterane	TAS
Fluoranthene	Fl
Pyrene	Py
Methyl substitution	C1
Dimethyl or ethyl substitution	C2
C3 substitution	C3
Benzenaphthylthiophene	BNT

Source Oil Identification

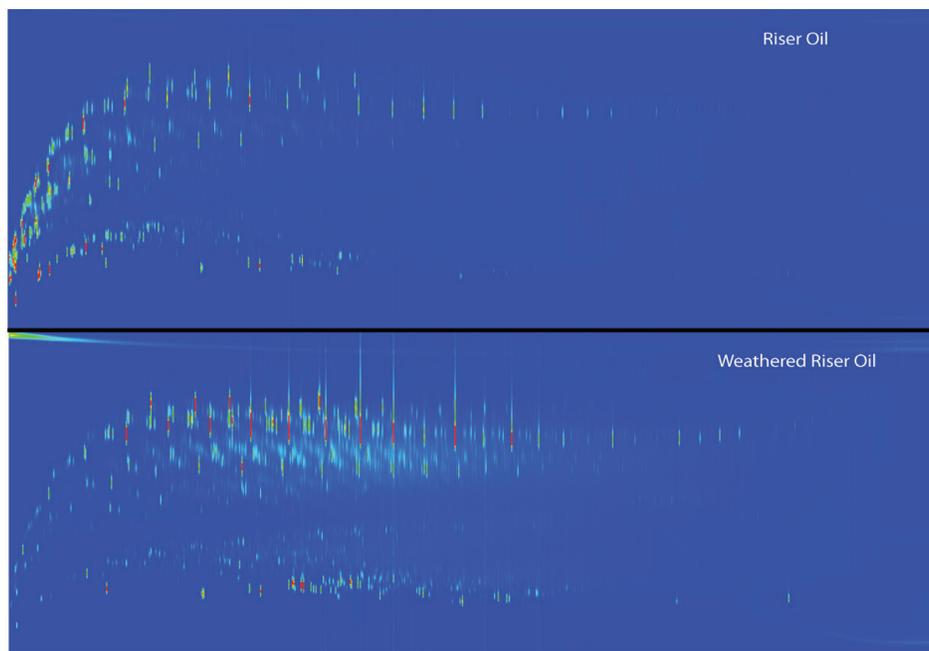
In order to check if the selected biomarker ratios used to fingerprint the light crude oil samples were still applicable after weathering, we simulated weathering of the riser oil sample. The oil sample was heated on a hotplate and evaporated to approximately 50% of the initial weight. We then analyzed the weathered oil using GCxGC-TOFMS and compared the diagnostic biomarker ratios to the ratios obtained for the unweathered riser oil. Early eluting analytes were evaporated during the weathering process, eliminating lighter biomarker compounds like adamantane from being considered as diagnostic for oil spill source identification (Figure 8).

In the petroleum industry, ratios of the isoprenoids pristane and phytane are used to determine the biodegradation of oil and these compounds can also potentially be used to help identify the source of relatively fresh oils from spills. However, we found that the pristane and phytane ratios changed after the weathering study and therefore we did not use them in subsequent comparisons (Figure 9).

One way that the NORDTEST method recommends evaluating a potential match of source oil is to use correlation plots. In order to test the validity of our chosen biomarkers, we used a correlation plot that compared ratios for 43 different diagnostic biomarkers, including steranes, hopanes, triaromatic steranes, PAHs and dibenzothiophenes, and their alkylated homologues (Table II). Coeluting analytes were not included in the correlation plots. When two samples are a positive match, like the weathered and unweathered riser oil, the correlation plot shows a linear relationship between the biomarkers of the source oil and the oil in question (Figure 10).

After the Deepwater Horizon oil spill in the Gulf of Mexico in 2010, oil residue and tarballs washed up on beaches. While cleanup efforts have mostly subsided, we received several tarball samples from a beach in northern Florida that were collected over many months and up to a year after the spill. The samples ranged from an oily residue, to a tarball with a hard outer shell and a soft, sticky interior, to tarball that was very sandy and stiff. When possible, the interior of the tarball, which should have less weathering and biodegradation, was used for GCxGC-TOFMS analysis. Correlation plots were used to compare the tarball samples to the riser pipe oil that was collected during the spill.

Figure 8: Contour plot (TIC) of weathered and unweathered Deepwater Horizon riser oil illustrates the loss of volatiles in the weathered riser oil.



See Figure 1 for instrument conditions

GC_PC1257

Table II: Diagnostic biomarker ratios used for correlation plots of petroleum samples analyzed by GCxGC-TOFMS.

Diagnostic Ratios	
%A v B = 100 x A/(A+B)	
% aaa2OS_C v aaa2OR_C	% Sum C-DBTs v Sum C-Phs
% aaa2OS_C v abb2OR_C	%DBT v Chry
% abb2OR_C v aaa2OR_C	%C1-DBT 1 v C1-Chry 3
% abbMEC v abbEC	%C1-DBT 2 v C1-Chry 6
%aaaEC v abbEC	%C1-DBT 3 v C1-Chry 9
%31abS v 30ab	%C2-DBT 1 v C2-Chry 3
% 30ab v Tm	%C2-DBT 3 v C2-Chry 9
%29ab v 30ab	%C2-DBT 4 v C2-Chry 13
%31abS v 31abR	% Sum DBTs v Sum Chrys
%Ts/Tm	% Sum C-DBTs v Sum C-Chrys
%29ab v 30ab	% C1-Ph 1 v TAS 231 1
29aaS/29aaR	% C1-Ph 5 v TAS 231 3
%DBT v Ph	% C1-Ph 6 v TAS 231 7
%C1-DBT 1 v C1-Ph 1	% C1-FIPy 1 v C1-BNT 1
%C1-DBT 2 v C1-Ph 2	% C1-FIPy 2 v C1-BNT 1
%C1-DBT 3 v C1-Ph 5	% C1-FIPy 3 v C1-BNT 1
%C1-DBT 4 v C1-Ph 6	% C1-FIPy 4 v C1-BNT 1
%C2-DBT 1 v C2-Ph 1	% C1-FIPy 5 v C1-BNT 1
%C2-DBT 3 v C2-Ph 3	% C1-FIPy 6 v C1-BNT 1
%C2-DBT 4 v C2-Ph 4	% C1-FIPy 3 v C1-BNT 3
%C3-DBT 3 v %C3-Ph 3	% C1-FIPy 5 v C1-BNT 4

Figure 9: Isoprenoid ratios of pristane and phytane change when the oil sample is weathered, making it less useful for source oil identification of a spill or weathered crude oil.

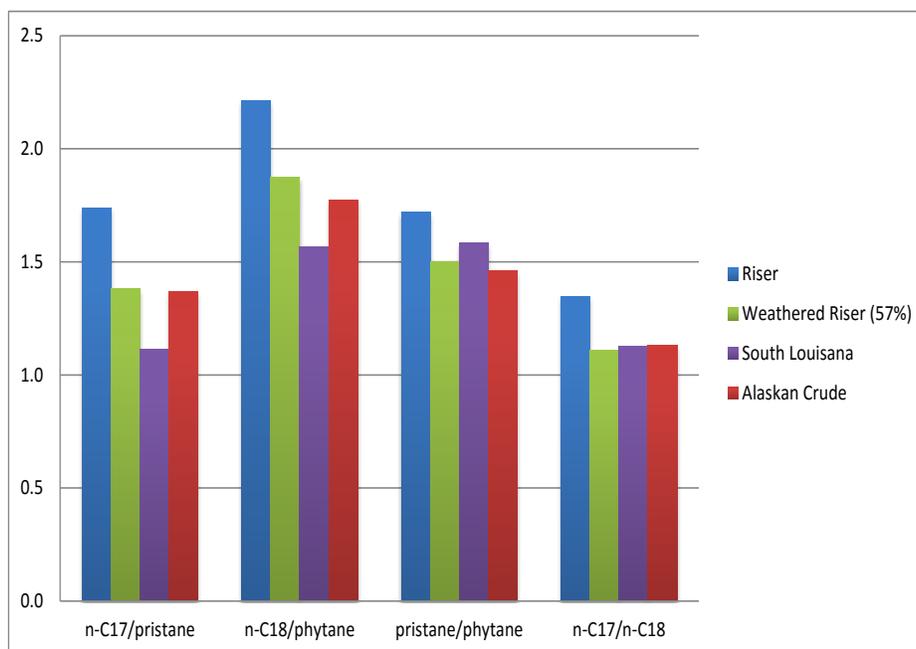


Figure 10: Good correlation of diagnostic biomarkers prove that a weathered oil sample can still be matched to unweathered source oil.

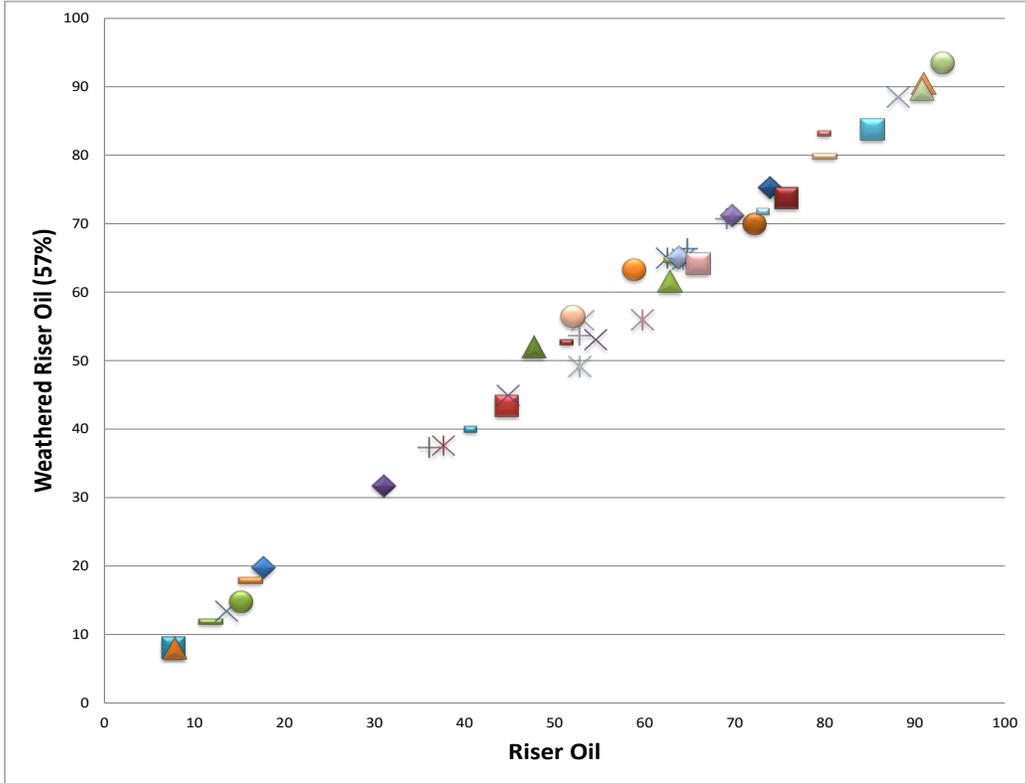
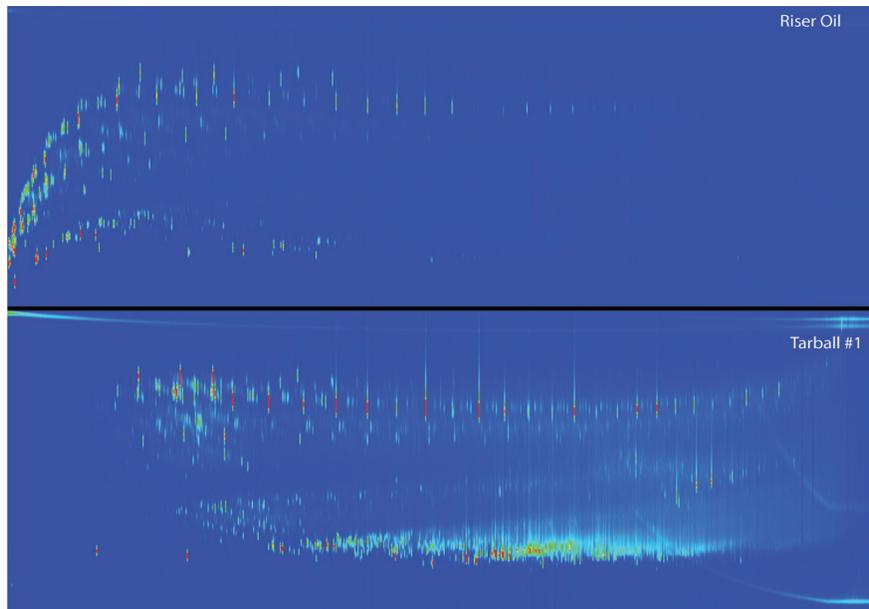


Figure 11: GCxGC-TOFMS total ion chromatograms for riser pipe oil and tarball #1 collected on April 5, 2011 at Ed Walline Park, Florida.



See Figure 1 for instrument conditions

GC_PC1258

Tarball #1 was an oily mix that was sampled on April 5, 2011 at Ed Walline Park, Florida. The TIC shows that the sample was more weathered compared to the potential source oil (Figure 11). Visual inspection of the EIC of hopanes (m/z 191) showed a very similar pattern. However, when looking at the C2 and C3 dibenzothiophenes (m/z 212, 226) clear visual differences were noted (Figure 12). In order to clearly rule out the riser oil as a potential source, a correlation plot was evaluated and clearly showed a non-match (Figure 13).

Of the six tarball samples that we evaluated, only one was found to be a possible match to the Deepwater Horizon riser pipe source oil. Tarball #11, collected at Ed Walline Park, Florida on July 16, 2011, one year after the oil spill had been stopped, was a five-pound tarball that had a hard outer shell and a soft interior. We analyzed the soft core of the tarball and found that it still retained diagnostic PAHs and had a very similar TIC to the riser pipe oil. The visual inspection of the steranes, hopanes, and alkylated dibenzothiophenes showed little to no major differences (Figure 14), further suggestion of a possible match. Without the statistical representation that is needed in the NORDTEST method for legally defensible data, we cannot assign a positive match. However, the correlation plot does suggest a possible match between Deepwater Horizon source oil and tarball #11 (Figure 15).

Figure 12: Extracted ion chromatograms of diagnostic biomarkers show visual differences between tarball #1 and the riser oil from the Deepwater Horizon spill.

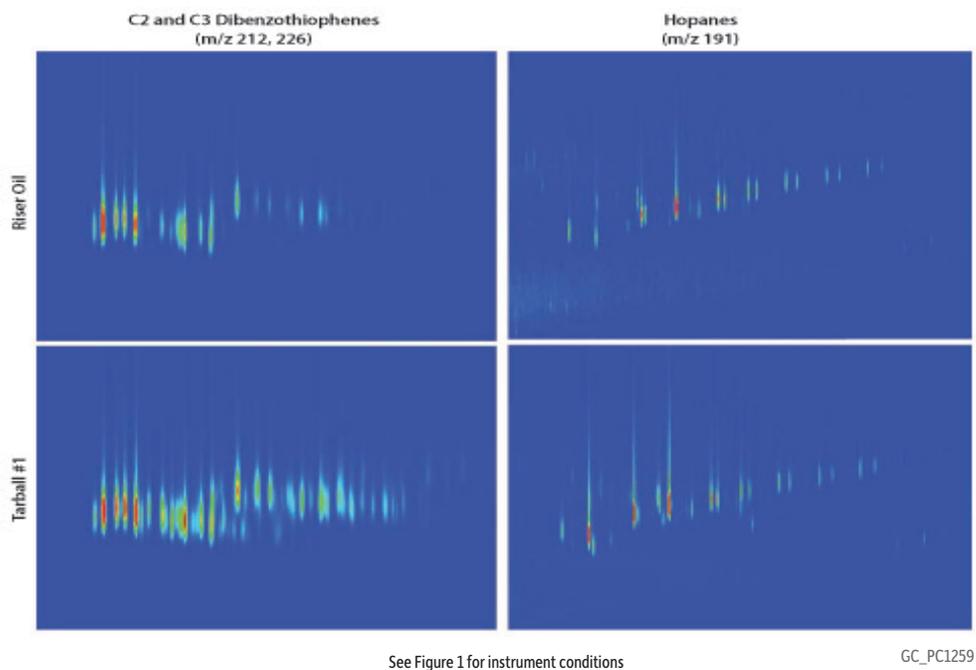


Figure 13: Biomarker correlation plot indicates a non-match for Deepwater Horizon riser oil and tarball #1.

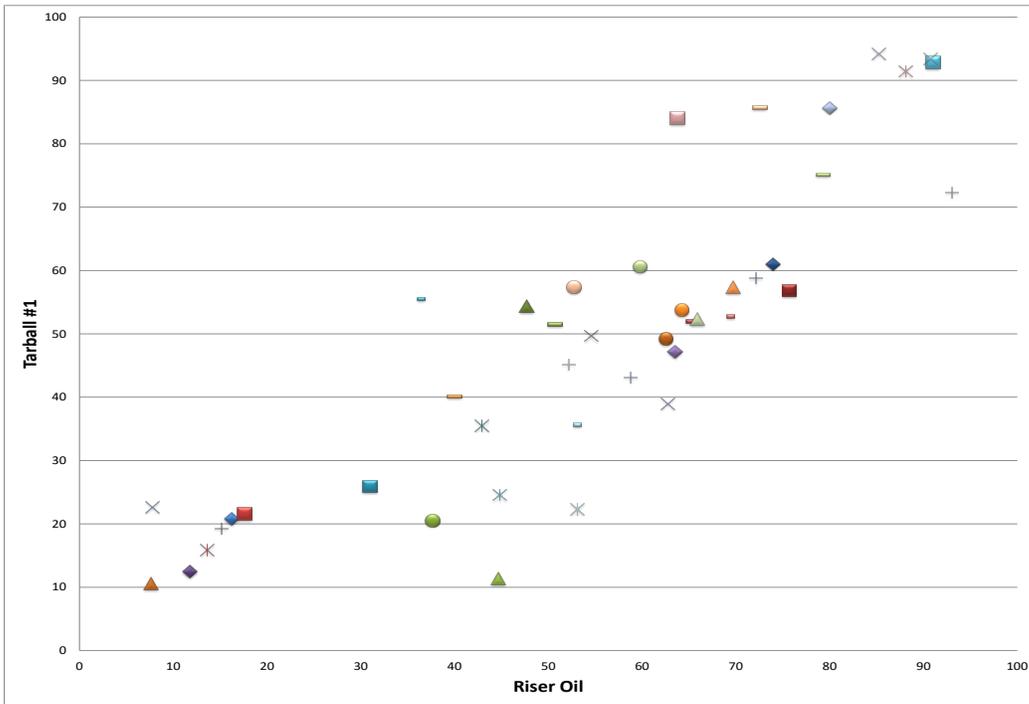
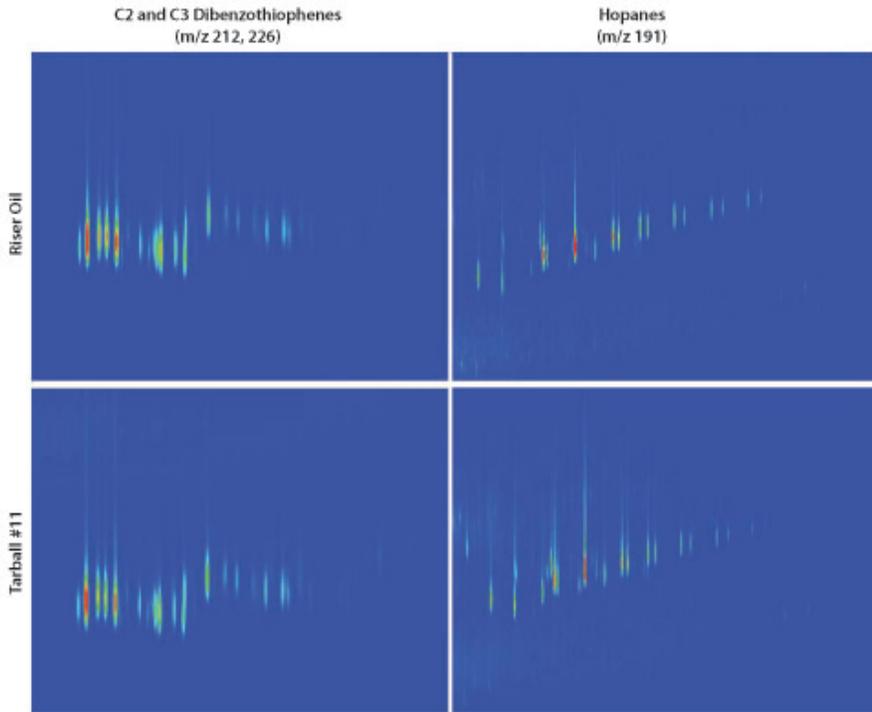


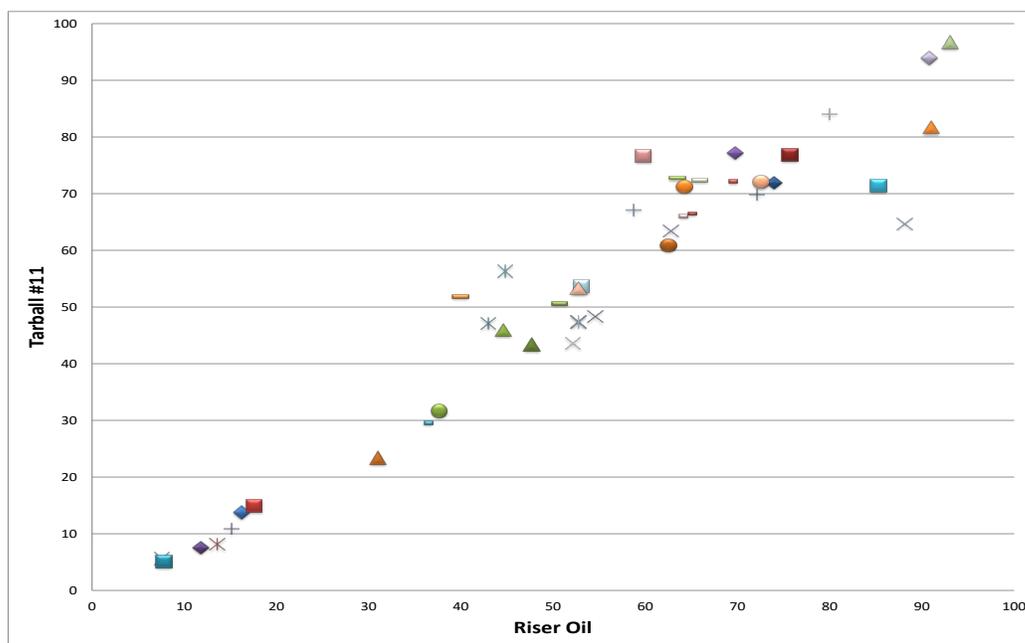
Figure 14: GCxGC-TOFMS extracted ion chromatograms of diagnostic biomarkers show very close visual resemblance of the Deepwater Horizon riser source oil and tarball #11.



See Figure 1 for instrument conditions

GC_PC1260

Figure 15: Biomarker correlation plot of Deepwater Horizon riser oil and tarball #11 shows a possible match.



Conclusion

Fingerprinting petroleum samples can be done with greater certainty by using highly efficient, comprehensive two-dimensional gas chromatography time-of-flight mass spectrometry instead of one-dimensional gas chromatography. Advantages include increased chromatographic resolution of potential diagnostic biomarkers, a structured chromatogram that simplifies and strengthens compound identification, and full mass spectra. GCxGC-TOFMS with highly efficient GC columns that differ in selectivity is an important tool for environmental forensic chemists who perform source oil identification.

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References

- [1] C. Hickman, K. Bowman, Crude oil and natural gas formation, BP energy education program, BP Australia Pty Ltd, 2008.
- [2] L. Faksness, H. Weiss, P. Daling, Revision of the Nordtest Methodology for Oil Spill Identification, SINTEF Report STF66 A02028, 2002.
- [3] L. Blumberg, M. Klee, Characteristic thermal constant and dimensionless heating rate. The links to optimum heating rate in GC. Anal. Chem. 72 (2000) 4080.
- [4] C. Eiserbeck, R. Nelson, K. Grice, J. Curiale, C. Reddy, Comparison of GC-MS, GC-MRM-MS, and GCxGC to characterize higher plant biomarkers in tertiary oils and rock extracts, Geochimica et Cosmochimica Acta, 87 (2012) 299.
- [5] Z. Wang, S. Stout, Oil spill environmental forensics, fingerprinting and source identification, Elsevier (2007) 214.