

May 23, 2019

John Roberson
U.S. Dept. of Justice
1100 L Street, NW, Room 10118
Washington, DC 20530

Jacqueline Michel, Ph.D.
President
Research Planning, Inc.
1121 Park Street
Columbia, SC 29201

***Summary of Chemical Analyses of Off-Load Oils –
MC-20 Taylor Energy Corporation Response***

Dear Mr. Roberson and Dr. Michel,

As per your request, NewFields is pleased to provide you with a summary of the results of recent chemical (fingerprinting) analyses performed on six crude oil samples recently collected from the containment system from the MC-20 Taylor Energy Corporation (TEC) Response activities. The six oils studied were collected during off-loading of the system's oil storage containers on April 30, 2019 and represents crude oil collected between April 23 and April 30, 2019 (Table 1). I understand this was the second off-load event since the containment system was installed.

The objectives of the study were (1) to determine the specific chemical character of the six off-loaded crude oils collected with emphasis on assessing their homo/heterogeneity and (2) to compare the off-loaded oils to the large population of previously-analyzed oils collected from the environment or sub-surface at the TEC site (Table 2). The previously-analyzed oils included surface sheens (n=84) and water column ROV-collected (n=15) that were collected and analyzed in 2017 and 2018, as well as reservoired crude oils (n=3) collected from two MC-20 wells in the early 1980s.¹

These comparisons are relevant to the issue of the current sources of oil exiting the seafloor in the vicinity of the erosional pit/containment system and provide a baseline against which future sub-surface Response activities' impact(s) may be measured.

Analysis

The six off-load oils (Table 1) were analyzed Alpha Analytical Labs (Mansfield, MA) using robust "chemical fingerprinting" methods described in detail elsewhere.² These same methods were

¹ These samples recently were obtained from an archive at Texas A&M, Geochemical & Environmental Research Group (GERG) and analyzed as part of the DOJ's TEC investigation. Available information from GERG: API well #: 608174017300 (11,185') and 608174023300 (8668' and 10,016'). These two API well #s correspond to Well 001 and Well A002, respectively, per the BSEE on-line database.

² Douglas, G.D. et al. (2015) Chemical fingerprinting of hydrocarbons and polychlorinated biphenyls. In: *Introduction to Environmental Forensics, 3rd Ed.*, B. Murphy and R. Morrison, Eds., Academic Press, New York, pp. 201-309.



used on the previously-studied oils (Table 2) and included:

- (1) modified US EPA Method 8015B utilizing gas chromatography-flame ionization detection (GC/FID) in which the concentrations of total petroleum hydrocarbons (TPH; C₉-C₄₄) and individual saturated hydrocarbons (SHC), including *n*-alkanes (C₉-C₄₀) and (C₁₅-C₂₀) acyclic isoprenoids were determined. Additionally, this analysis provided a detailed GC/FID chromatogram, or “fingerprint”, of each sample.
- (2) modified US EPA Method 8270D utilizing gas chromatography-mass spectrometry (GC/MS) operated in the selected ion monitoring mode (SIM) in which the concentrations of 75 parent and alkylated decalins, polycyclic aromatic hydrocarbons (PAH), and sulfur-containing aromatics and 75 petroleum biomarkers (triterpanes, steranes, diasteranes, monoaromatic steroids, and triaromatic steroids) were determined.

The Alpha data for the off-load oils (Alpha Batch ID: L1918800) were separately provided to Research Planning, Inc. and therefore are not attached to this letter.

Results and Discussion

General Character

The GC/FID chromatograms (“fingerprints”) of the off-load oils are shown in Figure 1. Inspection of Figure 1 shows:

- there is an overall consistency among the six recovered oils; and
- all six oils are comprised of a moderately biodegraded crude oil, as evidenced by the relative absence of *n*-alkanes and prominence of acyclic isoprenoids (including pristane and phytane) and large unresolved complex mixture (“hump”).

Comparison of Level of Biodegradation

The previously-studied water column (ROV) oils and surface sheens from 2017 and 2018 also showed that the oil exiting the seafloor at the TEC site consisted of biodegraded oils. However, the range in the degree of biodegradation among the water column oils and surface sheens was greater than exhibited by the off-loaded oils. This can be seen in a cross-plot of common biodegradation ratios (nC₁₇/Pr and nC₁₈/Ph; Fig. 2). Inspection of Figure 2 shows:

- all six off-load oils are comparably biodegraded (and plot in a tight cluster)³;
- the previously-studied water column oils and surface sheens, which consisted of discrete (grab) samples collected at specific locations over specific (short) time periods, exhibit greater variation in their levels of biodegradation than the off-load oils (and plot much more scattered);

³ There is a weak relationship between the samples’ off-load time (potentially proportional to on-load/collection time) and the level of biodegradation as measured by nC₁₇/Pr ($r^2 = 0.78$). The relationship is driven by very slightly higher nC₁₇/Pr ratios for the A1 and A4 oils versus the B and C oils, which are uniform and very slightly lower. No other metrics demonstrate any sort of temporal trend among the off-load oils (see below), therefore, I would not over-interpret this very slight variation at this time.



- scatter among the different “groups” of previously-studied oils and sheens collected at different times in 2017 and 2018 indicates there has been no obvious temporal trend(s) in the level of biodegradation of oil exiting the seafloor in 2017 and 2018; and
- the range of biodegradation among the three MC-20 reservoir oils far exceeds that of the off-load oils and nearly spans the range of all of the previously-studied water column oils and surface sheens.

This last point is important because it shows (1) at least one MC-20 reservoir contains crude oil that is (already) moderately biodegraded, (2) not all biodegradation exhibited by the water column oils and sheens necessarily only occurred after a leaked oil(s) entered the environment, and (3) mixing of variably biodegraded oils from multiple leaking wells could explain or (at least) contribute to the range of biodegradation evident among discrete (grab) oil samples from the water column and sea surface (Fig. 2).⁴

Comparison of Source-Specific Character

Oil spill fingerprinting relies on comparison of various diagnostic features of crude oils that are independent of (i.e., stable despite) weathering. The diagnostic features, which are typically measured as ratios among source-specific chemicals in the oil (e.g., PAHs, sulfur-containing aromatics, and petroleum biomarkers), speak to the conditions under which the crude oil formed and can vary on small geologic scales (e.g., individual reservoirs). My previous work on water column oils and surface sheens utilized 22 to 26 diagnostic ratios (DRs),⁵ which were also determined for the six off-load oils (Table 3). Quantitative (statistical) comparisons among the six off-loaded oils’ DRs⁶⁻⁷ showed:

- all six of the off-load oils are statistical matches to one another, i.e., they are all comprised of the same (single) oil or, more likely (see *Synthesis and Conclusions*), the same oil blend. In other words,
- there was no chemical difference (a) between the two oils collected from any one oil storage container or (b) among the oils from all three oil storage containers (in this case, A, B, and C).

⁴ This comparison to the three MC-20 reservoir oils is not made in order to identify the wells that are the sources of oil exiting the seafloor. It is being made only to demonstrate that the oil from different MC-20 wells is chemically varying and therefore, leakage of oils from multiple wells could explain the variation among oils exiting the seafloor at a specific point in time, as represented by the discrete (grab) samples.

⁵ Stout, S.A. (2018) Expert Report of Scott A. Stout, Ph.D., P.G., dated Sept. 11, 2018; Taylor Energy Company LLC v The United States of America, US Court of Federal Claims, Case No. 16-12C. Produced on behalf of U.S. Dept. of Justice. Only 22 DRs were available for the 57 sheens collected by SSLWG, which had not quantified the concentrations of pregnane, methyl-pregnane, C26(20S)TAS, or DAT-16 and used in four DRs (Table 3).

⁶ CEN (2012) Oil spill identification – Waterborne petroleum and petroleum products – Part 2: Analytical methodology and interpretation of results based upon GC-FID and GC-MS low resolution analysis. Center for European Norms, Technical Report 15522-2, Oct. 3, 2012.

⁷ The quantitative (statistical) comparisons relied upon the 95% repeatability limit ($r_{95\%}$) for each DR wherein:

$$r_{95\%} = 14\% \text{ or } 2.8 * RSD_R \text{ where } RSD_R = 5\%$$

If the relative difference between the measured DRs between two samples <14% the DRs were considered to be statistically matched, and *vice versa*.



However, akin to what was observed with respect to the levels of biodegradation (Fig. 1), cross-plots of most source-specific DRs shows the same relationship between the off-load oils and the previously-studied water column oils and surface sheens. Two examples of these are shown in Figures 3 and 4, which show:

- the six off-load oils exhibit highly comparable DRs reflective of their relative sulfur contents (Fig. 3) and biomarkers (Fig. 4; and plot in tight clusters in each figure);
- the previously-studied water column oils and surface sheens, which consisted of discrete (grab) samples collected at specific locations over specific (short) time periods, exhibit greater variations in their relative sulfur contents (Fig. 3) and diagnostic biomarkers (Fig. 4) than the off-load oils (and plot much more scattered);
- scatter among the different “groups” of previously-studied oils and sheens collected at different times in 2017 and 2018 indicates there has been no obvious temporal trend(s) in the source-specific features of oil exiting the seafloor; and
- the ranges of both relative sulfur abundance (Fig. 3) and some biomarkers (notably DAT16/Hop; Fig. 4) among the three MC-20 reservoir oils far exceed those of the off-load oils and nearly spans the range among all of the water column oils and surface sheens.⁸

Synthesis and Conclusion

Comparisons of the detailed chemical compositions of six crude oil samples collected during off-loading of the containment system’s oil storage containers (A, B, and C) on April 30, 2019 (Table 1) to each other and to 99 previously-studied discrete (grab) water column oils and surface sheens from 2017-2018 (Table 2) has shown:

- the six off-load oils are chemically homogeneous;
- the discrete (grab) water column and surface sheens oils are chemically heterogeneous; and
- the six off-load oils typically exhibit chemical features that are largely intermediate to the discrete oils’ features (Figs. 2-4).

Collectively, these results indicate that the oil droplets exiting the sea floor are heterogeneous over short intervals of time, perhaps minutes or tens of minutes.⁹ This heterogeneity has been previously recognized and is consistent with active leakage of slightly different oils from multiple MC-20 wells.¹⁰ These heterogeneous oil droplets are being collected by the containment system wherein they became blended and homogenized.

⁸ See footnote 4. Additionally, but not surprisingly, because none of the three MC-20 reservoir oils studied exhibit a higher C27dia/Hop ratio (i.e., higher C27 (20S/20R) diasteranes to hopane), these three oils cannot alone explain the mixture of oils exiting the seafloor.

⁹ This estimate is based on the chemical heterogeneity observed among some water column (ROV) oils or surface sheens collected only minutes or tens of minutes apart.

¹⁰ Stout, S.A. (2018) Expert Report of Scott A. Stout, Ph.D., P.G., dated Sept. 11, 2018; Taylor Energy Company LLC v The United States of America, US Court of Federal Claims, Case No. 16-12C. Produced on behalf of U.S. Dept. of Justice.



Recommendation for Future Monitoring

As such, based upon the available results it can be hypothesized that until the sub-surface conditions change at the TEC site we might anticipate no-to-limited variation in the detailed chemical composition of the crude oil being collected in the containment system. This hypothesis can be tested by repeating this study of recovered (off-loaded) oils at some time(s) in the future (but before any subsurface intervention).

As intended, the off-loaded oil data from the present study provide a baseline by which any future Response activities in the TEC site's sub-surface have on the oil exiting the seafloor in may be measured. Specifically, if/when intervention occurs (e.g., plugging an actively leaking well) a change or shift in the composition of oil being collected by the containment system may occur (depending, of course, on the proportion which the plugged well was contributing to the total oil leakage).

Please do not hesitate to contact me if you have any questions.

Sincerely,

Scott A. Stout, Ph.D.
Sr. Geochemist



Table 1: Inventory of Off-load Oil Samples Analyzed.

Tank	Sample ID	Alpha Lab ID	Date Collected	Time Collected
A	043019 A1	L1918800-01	4/30/2019	1811 CDT
A	043019 A1 (dup)*	WG1235194-4	4/30/2019	1811 CDT
A	043019 A4	L1918800-04	4/30/2019	1826 CDT
B	043019 B1	L1918800-05	4/30/2019	1854 CDT
B	043019 B3	L1918800-08	4/30/2019	1930 CDT
C	043019 C1	L1918800-09	4/30/2019	2011 CDT
C	043019 C4	L1918800-12	4/30/2019	2058 CDT



Table 2: Inventory of Previously-Analyzed Oils from MC-20 Investigations to which Off-load Oils (Table 1) were compared.

Collection Time	Samples	Origin of Samples	Alpha Batch ID
<i>Surface Sheens</i>			
Mar. 3-April 8, 2017	57	SSLWG ¹	Various
Aug. 15-17, 2017	12	DOJ ²	L1729263
April 28, 2017	6	DOJ ²	L1815564
August 15-17, 2018	6	DOJ ³	L1832969
Dec. 18, 2018	3	DOJ ³	L1853006
<i>Water-Column Oils</i>			
Oct. 2, 2017	7	BSEE ²	L1800856
Sept. 2-3, 2018	8	NOAA ³	L1914310
<i>MC-20 Reservoir Oils</i>			
Early-1980s	3	DOJ ³	L1916830

¹Reddy and Overton (Nov. 13, 2017) – Report to SSLWG

²Stout (Sept. 11, 2018) – Expert report in TEC v USA case

³data not previously reported, but provided to NOAA/DIVER



Table 3: Selected Diagnostic Ratios for the Six Off-load Oils studied.

Diagnostic Ratios	A1	A1 (dup)	A4	B1	B3	C1	C4
Ts/Hop	0.20	0.22	0.19	0.20	0.19	0.18	0.20
Tm/Hop	0.17	0.16	0.16	0.18	0.17	0.17	0.19
H29/Hop	0.51	0.53	0.50	0.52	0.50	0.49	0.51
H31S/Hop	0.40	0.38	0.35	0.38	0.37	0.37	0.39
27dia R/S	0.61	0.65	0.59	0.61	0.61	0.64	0.63
27bb/29bb	0.87	0.86	0.84	0.85	0.85	0.88	0.85
NR-SC26/ RC26+SC27	0.29	0.32	0.31	0.29	0.31	0.33	0.31
28S/26R+27S	0.73	0.81	0.83	0.80	0.76	0.80	0.77
27R/26R+27S	0.59	0.64	0.64	0.63	0.60	0.63	0.62
28R/26R+27S	0.62	0.64	0.62	0.65	0.64	0.61	0.64
DBT2/PA2	0.35	0.35	0.35	0.35	0.35	0.35	0.36
DBT3/PA3	0.48	0.48	0.49	0.49	0.48	0.48	0.47
C28-C29Tri/Hop	0.21	0.23	0.21	0.24	0.20	0.23	0.21
29aaS/29aaR	1.69	1.60	1.73	1.71	1.68	1.55	1.64
C20TA/C21TA	1.03	0.98	1.02	0.97	1.02	1.03	0.99
C21TA/RC26+SC27	0.40	0.42	0.42	0.43	0.40	0.41	0.41
C24Tet/C26Tri	0.41	0.36	0.31	0.45	0.30	0.29	0.43
Tri/Hop	0.21	0.23	0.21	0.24	0.20	0.23	0.21
H29/29Ts	2.60	2.88	2.95	2.70	2.89	2.69	2.79
H35/Hop	0.22	0.21	0.21	0.31	0.21	0.26	0.29
C27dia/Hop	0.99	0.98	0.96	0.96	0.97	0.98	1.00
C29dia/Hop	1.66	1.67	1.61	1.69	1.61	1.59	1.70
27dia/27aa	0.59	0.59	0.60	0.57	0.60	0.62	0.59
TAS/Hop	6.17	6.19	5.94	6.16	6.02	5.89	6.18
Steranes/Hopanes	1.40	1.41	1.43	1.43	1.43	1.39	1.40
DAT16/Hop	0.08	0.08	0.07	0.08	0.08	0.08	0.08

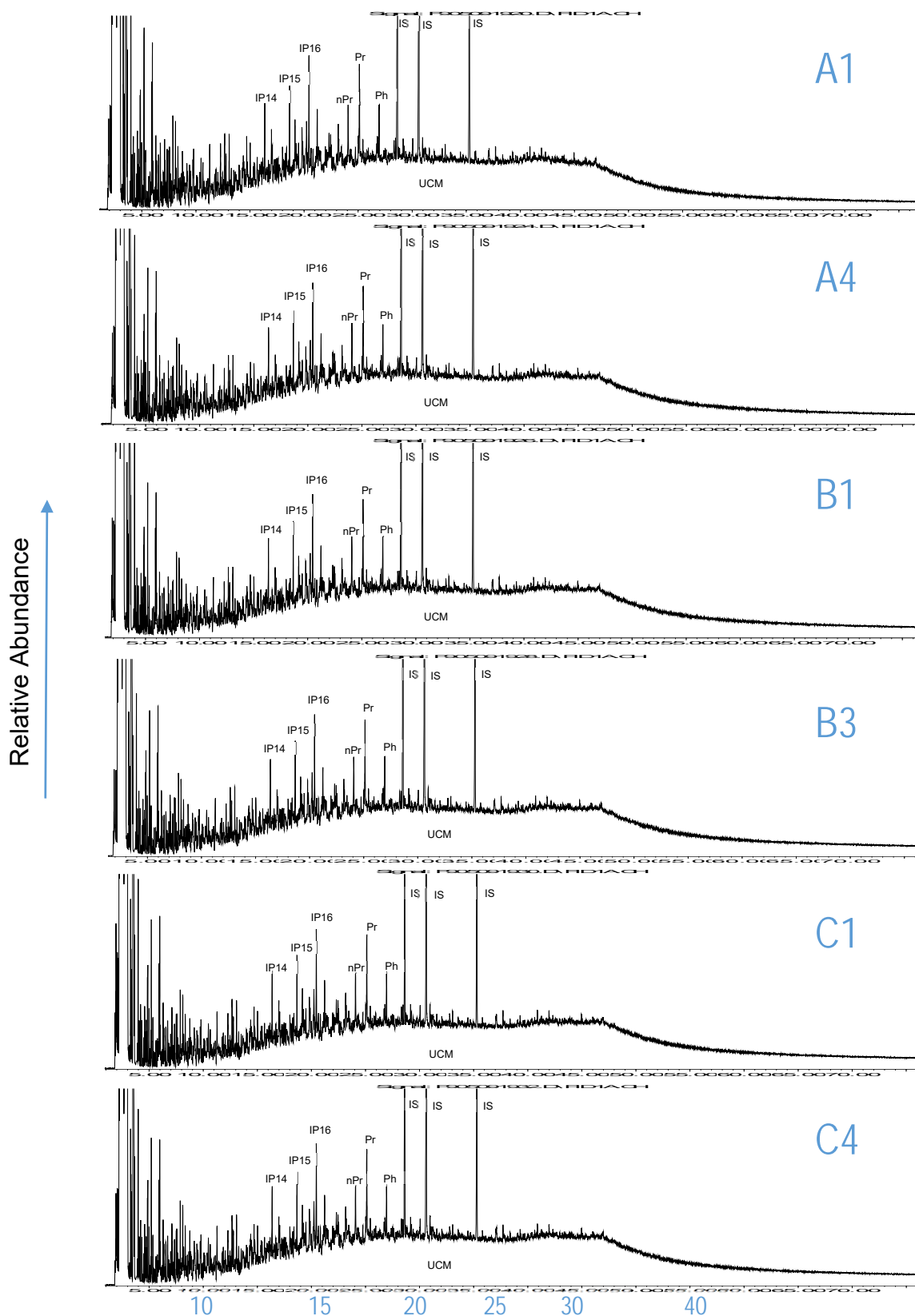


Figure 1: GC/FID chromatogram for the April 30, 2019 off-load oils (Table 1). IP# - acyclic isoprenoids carbon number; nPr – norpristane; Pr – pristane; Ph – phytane; UCM – unresolved complex mixture. IS – laboratory internal standards. Carbon range (approximate) indicated across bottom.

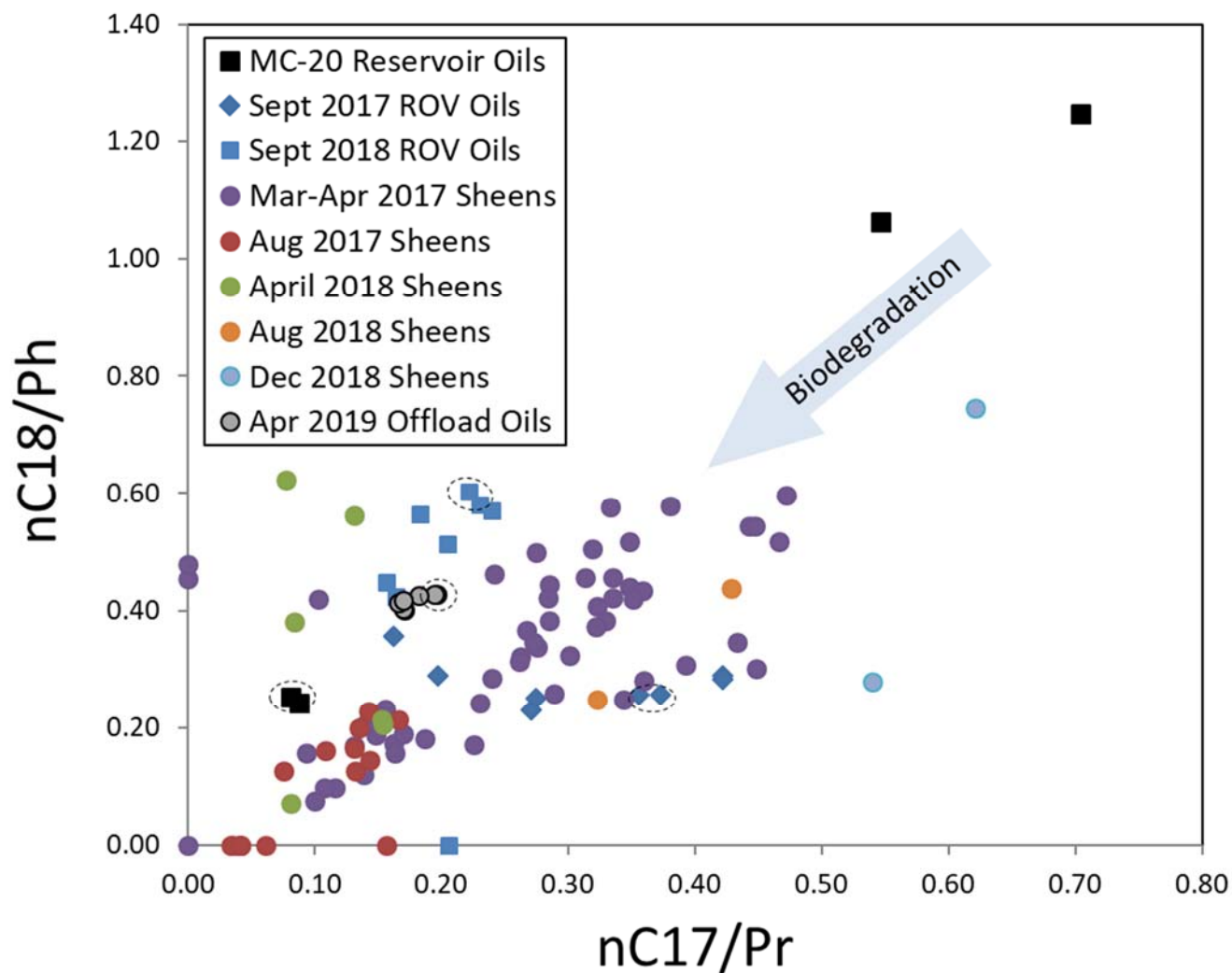


Figure 2: Cross-plot of $n\text{-C}_{17}/\text{Pr}$ and $n\text{-C}_{18}/\text{Ph}$ ratios demonstrating the level of biodegradation among oils studied. Note the tight cluster of the six April 2019 off-load oils compared to the scatter among previously-studied discrete (grab) water column (ROV) oils and surfaces sheens. Note also the diversity between the three recently obtained MC-20 reservoir oils. Dashed ovals show laboratory duplicate results. See text for description.

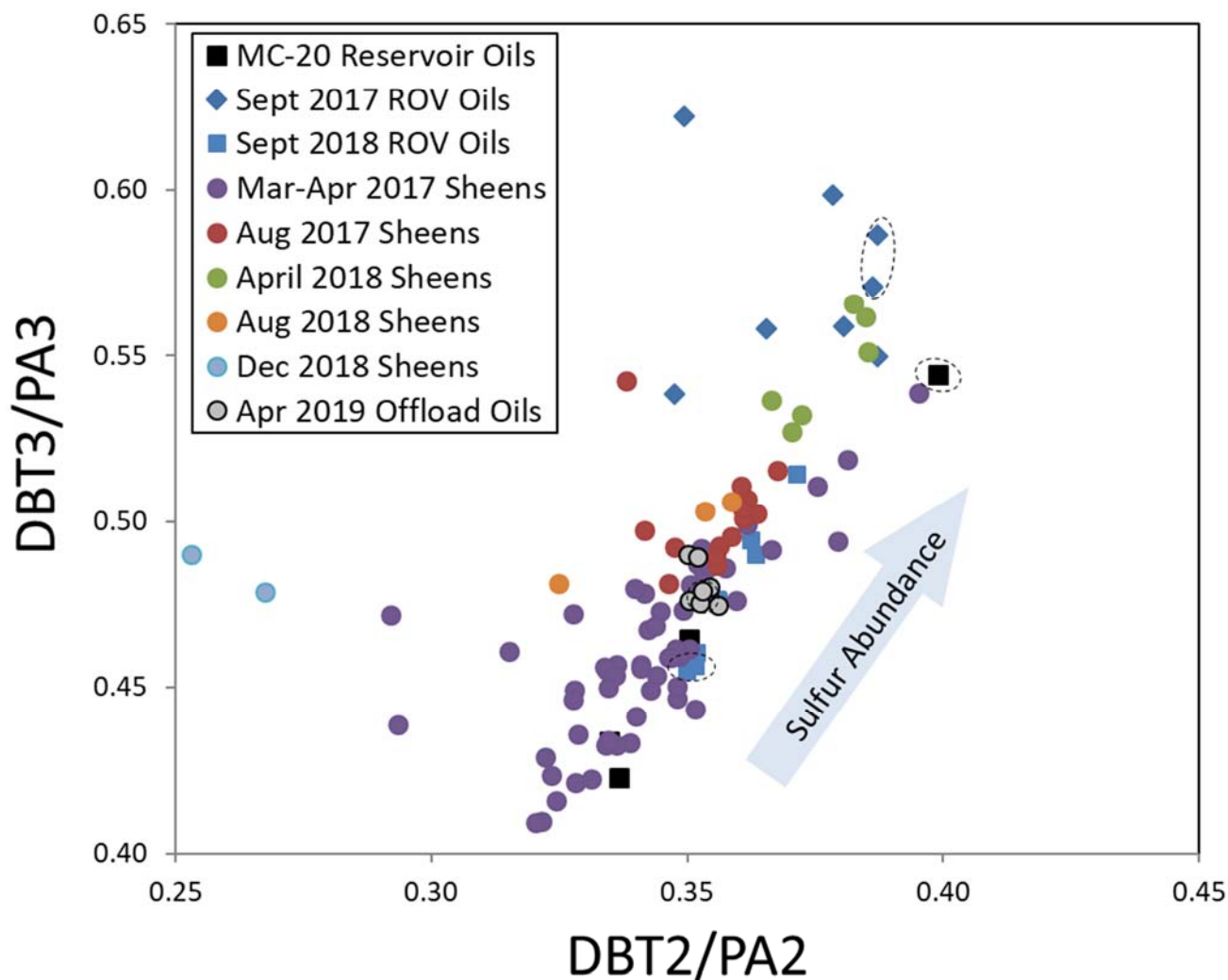


Figure 3: Cross-plot of diagnostic ratios demonstrating the relative sulfur abundance among oils studied. DBT#: dibenzothiophene alkyl carbon number, PA#: phenanthrene/anthracene carbon number. Note the tight cluster of the six April 2019 off-load oils compared to the scatter among previously-studied discrete (grab) water column (ROV) oils and surfaces sheens. Note also the diversity between the three recently obtained MC-20 reservoir oils. Dashed ovals show laboratory duplicate results. See text for description.

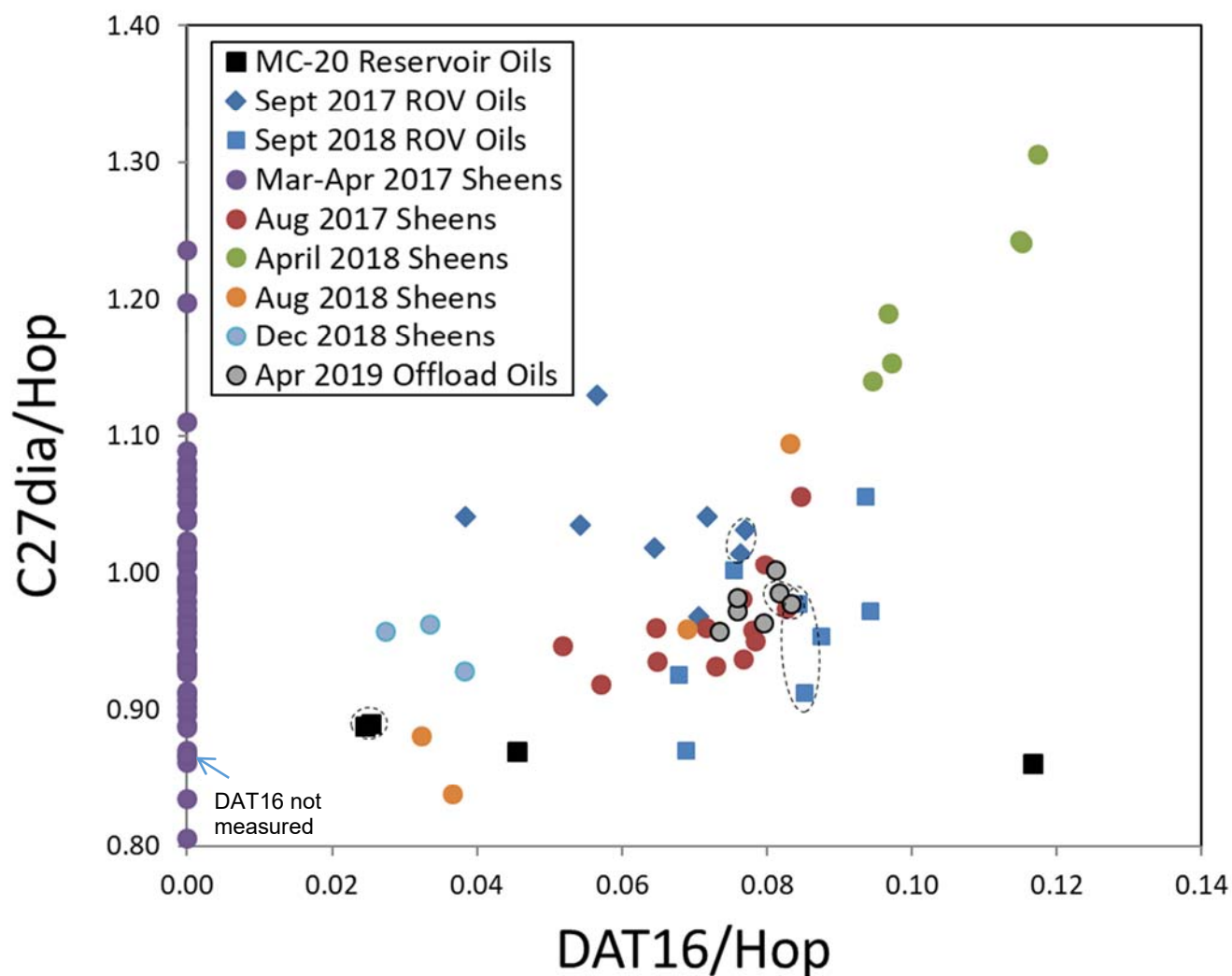


Figure 4: Cross-plot of diagnostic ratios demonstrating the biomarker-based features of the oils studied. DAT16: D-ring aromatized triterpenoid (tentative), C27dia: 13b(H),17a(H)-20(S+R)-diacholestanes, Hop: 17a(H),21b(H)-hopane. Note the tight cluster of the six April 2019 off-load oils compared to the scatter among previously-studied discrete (grab) water column (ROV) oils and surfaces sheens. Note also the diversity between the three recently obtained MC-20 reservoir oils. Dashed ovals show laboratory duplicate results. See text for description.