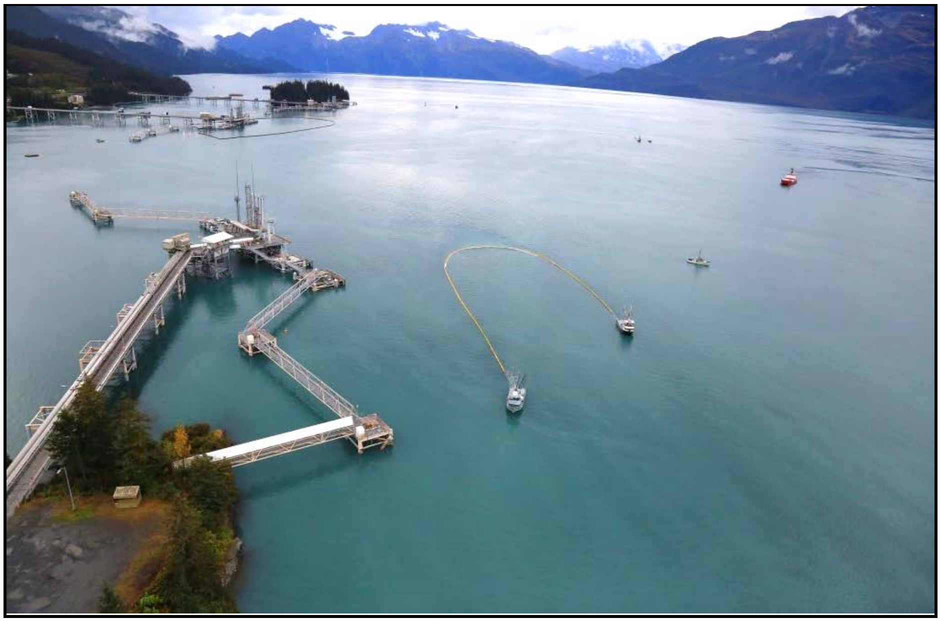
SEPTEMBER 2017 BERTH 5 OIL SPILL - Sampling Results and Interpretations



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The opinions expressed in this commissioned report are not necessarily those of PWSRCAC

Cover photo – Oil spill cleanup operations proceed near Berth 3 in the foreground with Berths 4 & 5 further west on 24 September 2017. Saw Island sampling site lies just beyond Berth 5; Jackson Point sampling site is below photo in foreground. Photograph courtesy of Alyeska Pipeline Service Company.

9-22-2017 Sheen under Berth 5. PWSRCAC Photo.

9-22-2017 Boom under Berth 5. PWSRCAC Photo.

9-29-2017 Jackson Pt. Mussel Sampling. PWSRCAC Photo.

12-7-2017 Jackson Pt. Mussel Sampling. PWSRCAC Photo.

2017 Berth 5 Oil Spill - Sampling Results and Interpretations

James R. Payne, Ph.D. and William B. Driskell

Introduction

On 21 September 2017, an estimated 150 gallons of Alaska North Slope (ANS) crude oil were accidentally released during crude oil loading arm leak testing at Berth 5 of the Alyeska Marine Terminal. As part of the post-spill monitoring efforts, mussels were collected from the same 3 Port Valdez stations annually sampled as part of the PWSRCAC Long Term Environmental Monitoring Program (LTEMP). Collections at Saw Island (SAW) adjacent to Berth 5, Jackson Point (JAC) east of Berth 3, and Gold Creek (GOC) across the port occurred on Sept 29-30 and again, as a follow up, 70 days later on Dec 7-9, 2017 (Figure 1). Two of the sampling sites, SAW and JAC, bracket the shoreline of the release location with the Saw Island site immediately adjacent (west) of Berth 5 (Figure 2). The GOC reference site is 6 km across the Port.

This report describes and illustrates the pre- and immediate post-spill hydrocarbon signatures plus the state of recovery in Port Valdez mussels 70 days after the spill.

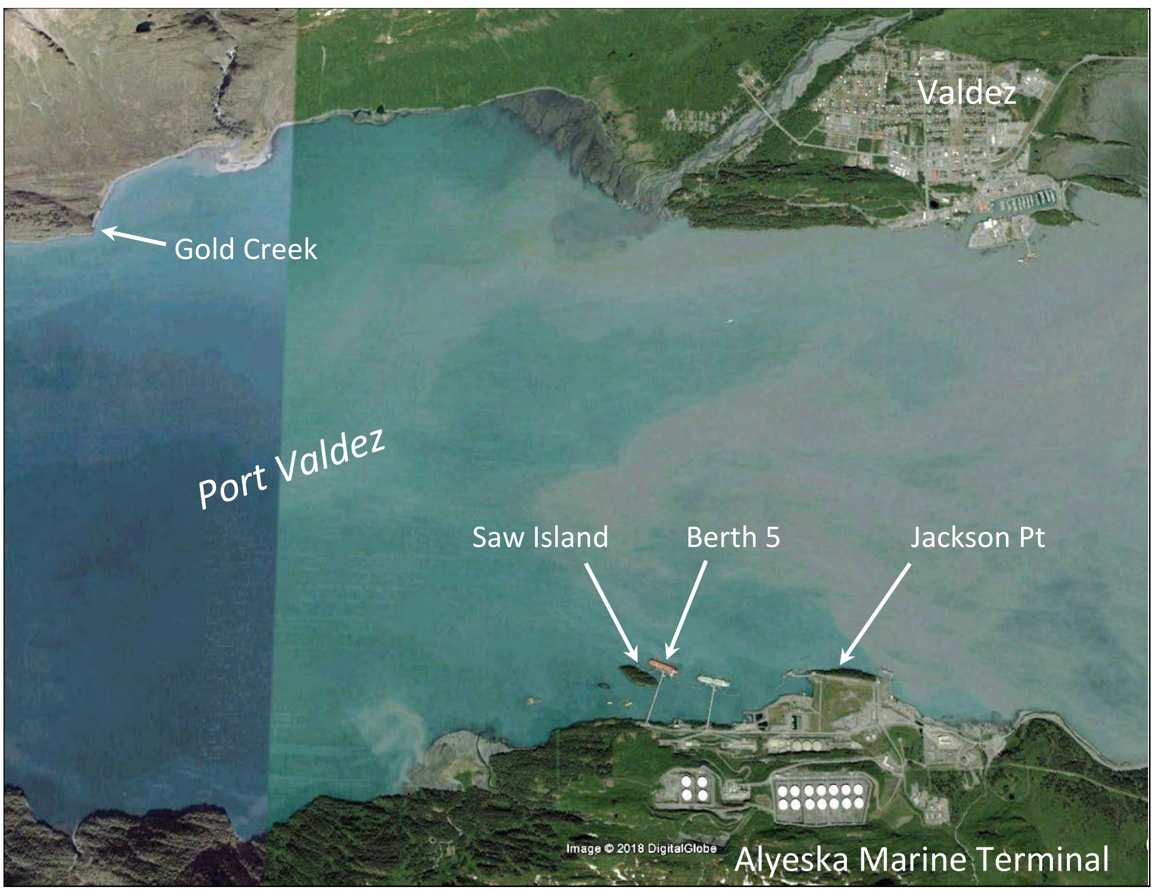


Figure 1. Spill and sampling locations within Port Valdez (satellite image from Google Earth). Tankers are seen docked at both Berths 4 and 5.

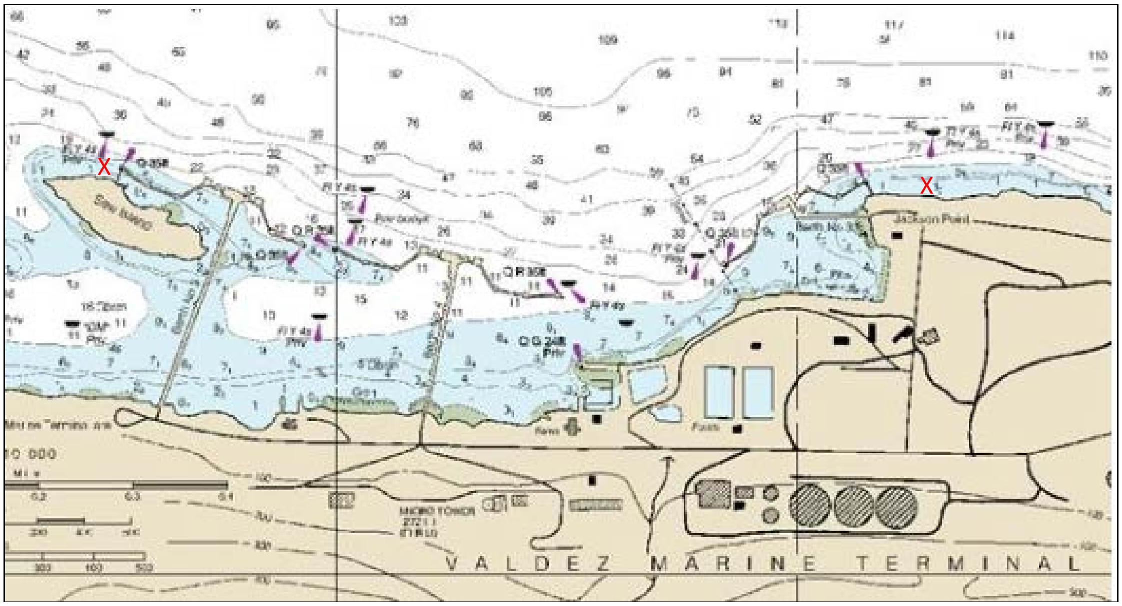


Figure 2. Nautical chart of the offshore area immediately adjacent to the Valdez Marine Terminal detailing the Berth 5 incident site. Saw Island (the traditional LTEMP AMT sampling site) and Jackson Point (added to LTEMP in 2016) are denoted by a red X.

During the spill and subsequent cleanup efforts between 21 and 27 September 2017, oil and sheen were observed between Berths 4 and 5 and trending westward including some shoreline impacts between the berths and west and south of Saw Island. Berths 4 and 5 were entirely boomed to contain sheen and oil (Figure 3). Protective booms were also installed around the Solomon Gulch Fish Hatchery (to the east) and Duck Flats (to the northeast), although no oil or sheen was observed in those areas.

Figure 3. Sheen observed between Berths 4 and 5 during cleanup activities in September 2017. Photograph courtesy of Alyeska Pipeline Service Company.

Methods

Following established LTEMP protocols, triplicate samples comprising approximately 30 adult mussels (*Mytilus trossulus*) were collected by Austin Love (PWSRCAC) along the shorelines at each location. Handling, processing and chemical analyses followed standard methods previously described in earlier LTEMP reports (Payne et al., 2010; and Payne and Driskell 2017b). Chemical analyses were conducted by PWSRCAC's LTEMP contractor, Alpha Analytical Laboratory, in Mansfield, MA. Analyses comprised standard methods for polycyclic aromatic hydrocarbons (PAH) and sterane and triterpane biomarkers, using a modified 8270 EPA method on gas chromatography/mass spectrometry (GC/MS SIM) instruments, plus saturated hydrocarbons (SHC), using gas chromatography with flame-ionization detection (GC/FID). From these analyses, 63 PAH, 74 biomarkers and 37 SHC target compounds are reported. Note that the suite of 55 biomarkers normally reported for LTEMP was expanded to include additional mono- and tri-aromatic steranes. These components were recently added to Alpha Laboratory's target analyte list, and it is believed that they will aid with oil fingerprinting in the future. PAH and biomarker analytes in tissues are reported on a µg/kg dry wt. (ppb) basis, while SHC in tissues are mg/kg (ppm), and all oil components are mg/kg (ppm). For forensic interpretations, an Excel application was assembled to review individual samples graphically overlaid by a source signature scaled to the sample. Comparative excesses or depletions in the patterns of individual analytes reveal the effects of weathering, mixing, or absence of spill oil. These methods are more fully described in Payne and Driskell, 2018; Driskell and Payne, 2018; Payne and Driskell 2017a,b; and Payne et al., 2008, 2010.

Source Oil Characterization

During the response activities, a reference source sample was obtained by PWSRCAC from the spilled-oil collection barge on 29 September 2017. The source oil signature (Figure 4) show a slightly weathered ANS profile containing a full suite of PAH, partially evaporated but non-biodegraded SHC, and characteristic biomarkers that permit direct comparisons to the oiled and residual trace profiles observed in the mussel samples (discussed below).

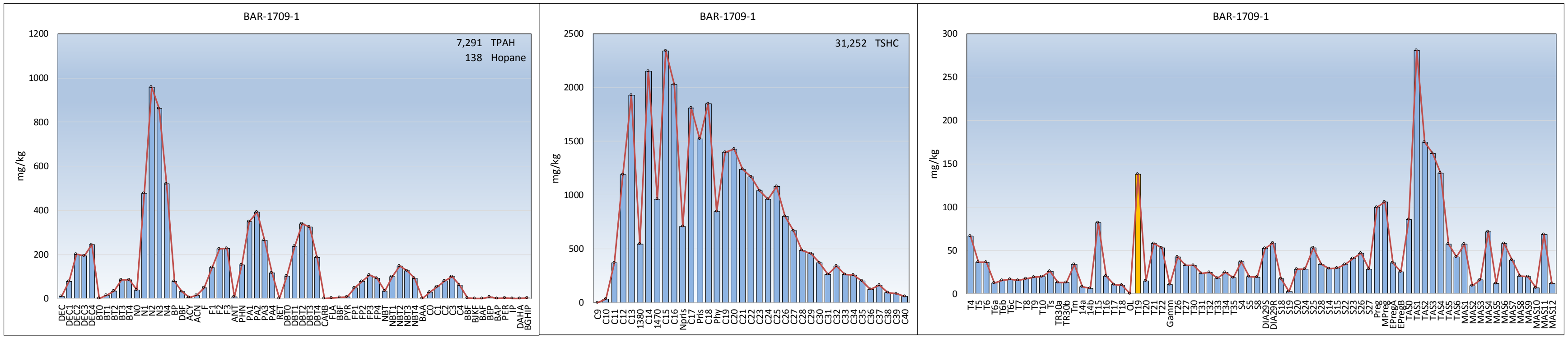


Figure 4. Analytic results of the source-oil sample comprise PAH (left plot), SHC (middle plot) and biomarkers (right plot; hopane highlighted). The red overlay line is the spilled source oil and thus exactly matches bar plot of the same source sample. This reference overlay method is used to compare the mussel samples to the source when reviewing each sample plot. Typically, the overlay is scaled to hopane for PAH and biomarkers and n-C_{27} for SHC.

Pre-spill Conditions

Routine LTEMP monitoring samples collected in early July 2017 showed expected trace background signatures both near the terminal and across the Port at the GOC reference site (Figure 5). These patterns do not appear to be from the degraded oil discharges of the Ballast Water Treatment Facility (BWTF) (Payne and Driskell, 2017; and 2018 in preparation). Instead, these are low-concentration background patterns, all similar, in which the PAH reflect primarily dissolved-phase (parent-dominated) naphthalenes (N), phenanthrene/anthracenes (P/A), fluoranthene/pyrenes (FP) and traces of particulate-phase combustion products.

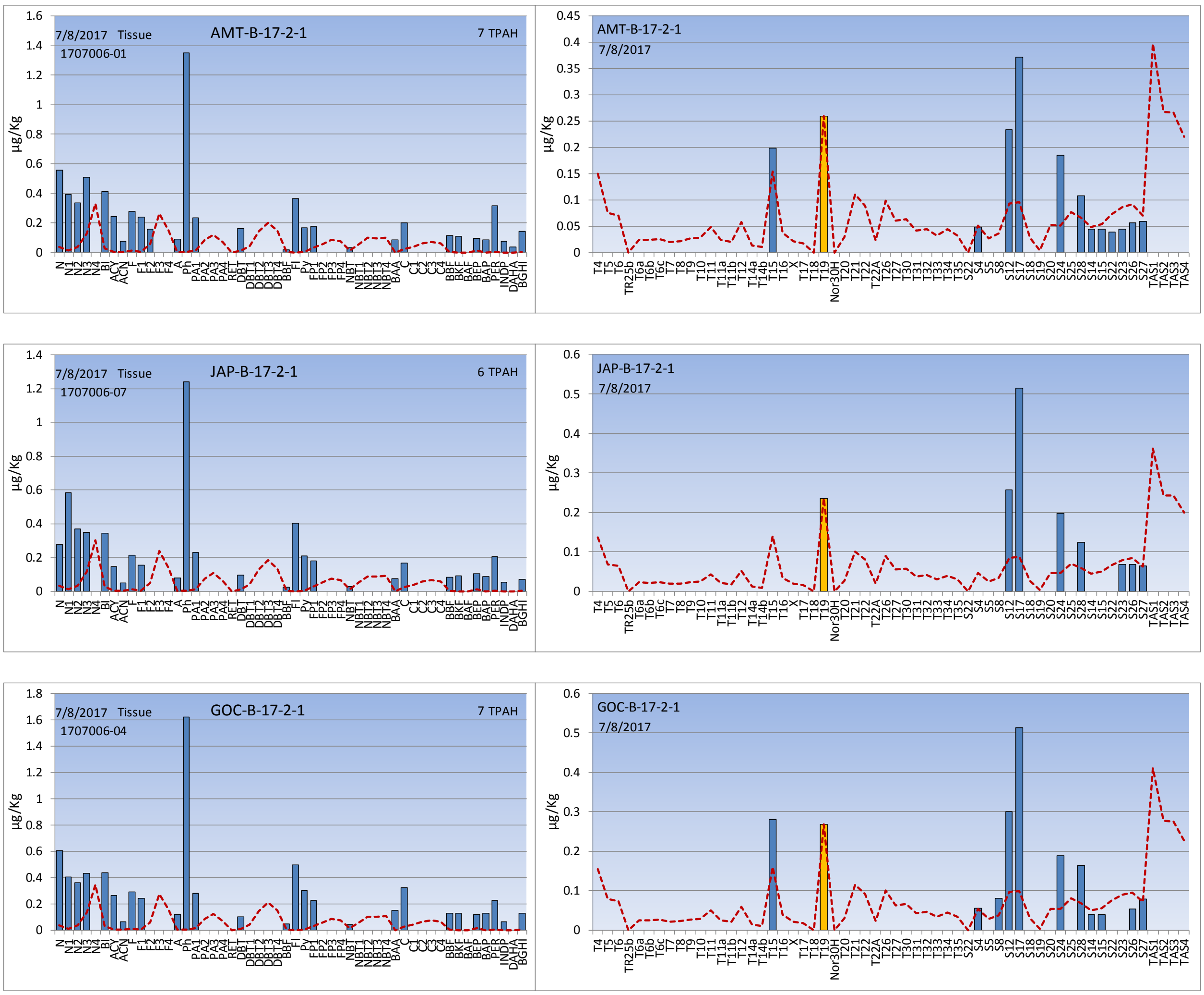


Figure 5. Representative PAH and biomarker profiles from July 2017 mussel collections at Saw Island, Jackson Point, and Gold Creek (LTEMP stations: AMT, JAP and GOC, respectively). The dotted red line shows the expected scaled profiles from the fresh spill oil (Figure 4) normalized to hopane. Note that the triaromatic steranes and newly added biomarkers do not appear in tissue samples because they are removed during L/C chromatography to separate lipids.

As confirmed by the dissimilarity to fresh spill-oil patterns (indicated by the red dotted line), neither the PAH or biomarker patterns show any solid evidence of ANS crude oil. Instead, the background, dissolved-phase patterns and concentrations at AMT and JAP are essentially the same as those measured in July 2016 (Payne and Driskell 2017). During the July 2016 sampling at GOC there was evidence of a localized diesel spill (Payne and Driskell, 2017), but that, too, had disappeared by July 2017 when the background pattern at GOC more closely matched those at the other two Port Valdez locations (Figure 5).

Post-Berth 5 Oil Spill Signatures

Mussel samples collected at SAW and JAC just over a week after the Berth 5 spill show weathered PAH and biomarker patterns associated with the released ANS oil (Figure 6). At GOC, however, there was no evidence that the oil or sheen had migrated across the Port. Only traces of background PAH and biomarkers were observed (not matching any known source). Note that the newly added triaromatic steranes and extended biomarkers do not appear in tissue samples because they are removed during HPLC clean-up of the extracts to eliminate lipid interference. The additional components added by the lab are of primary interest for oil sample characterizations.

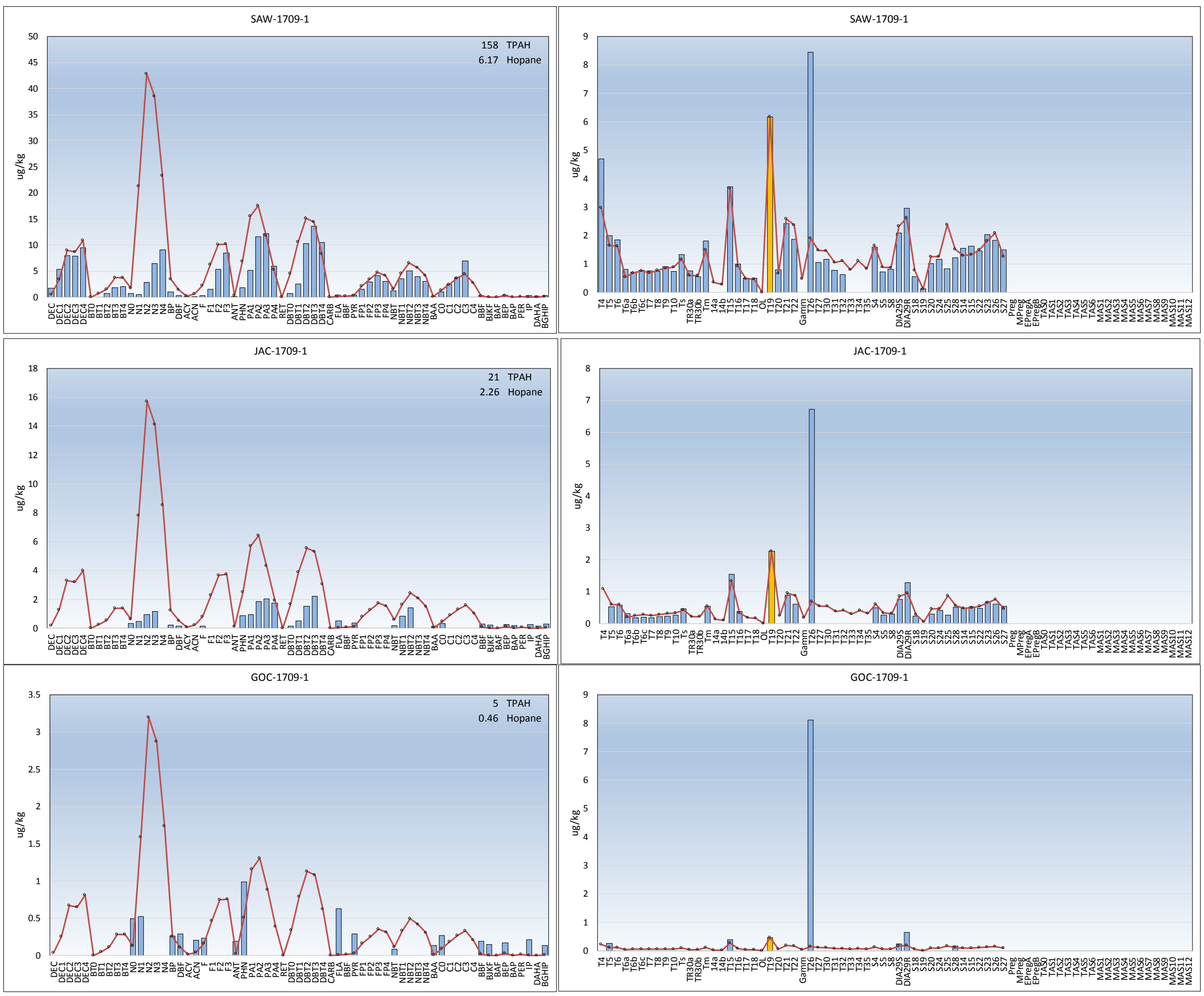


Figure 6. PAH and Biomarker patterns at SAW, JAC, and GOC collected on 29 September 2017, just over a week after the spill. The dotted red lines represent the anticipated profiles from the collected spill oil (Figure 4) normalized to hopane. Profiles from all three replicates at each site are shown in Appendix 1.

In agreement with observations and photographic evidence obtained during the spill response, the PAH and biomarker concentrations also confirm that most of the released oil migrated to the west, impacting the adjacent

Saw Island site, as the TPAH concentrations were significantly higher at SAW compared to JAC (see further discussion below).

Spill Recovery Signatures

By December (70 days post), hydrocarbon levels in the mussel samples at all three locations were reduced to near-background concentrations with patterns nearly identical to pre-spill conditions (Figure 7). Total PAH (TPAH) concentrations (Figure 8) also reflect the spilled-oil uptake and rapid depuration after the spill. Other studies have suggested that mussels can purge themselves fairly rapidly following short episodic oil exposures with the decreases in the hydrocarbon concentrations following an exponential curve. Early work reported a depuration half-life of less than a week (Lee, 1977 and Mason, 1988). Later work following the *Prestige* oil spill suggested more complex processes with two phases of depuration (Neito et al., 2006). A number of factors may affect depuration rates; oil composition, exposure period, water temperature, mussel size, maturity, body lipid content, stress, etc. The Berth 5 spill data are too limited to establish depuration rates but suffice to say, 70 days after the episodic event, the mussels were effectively clean.

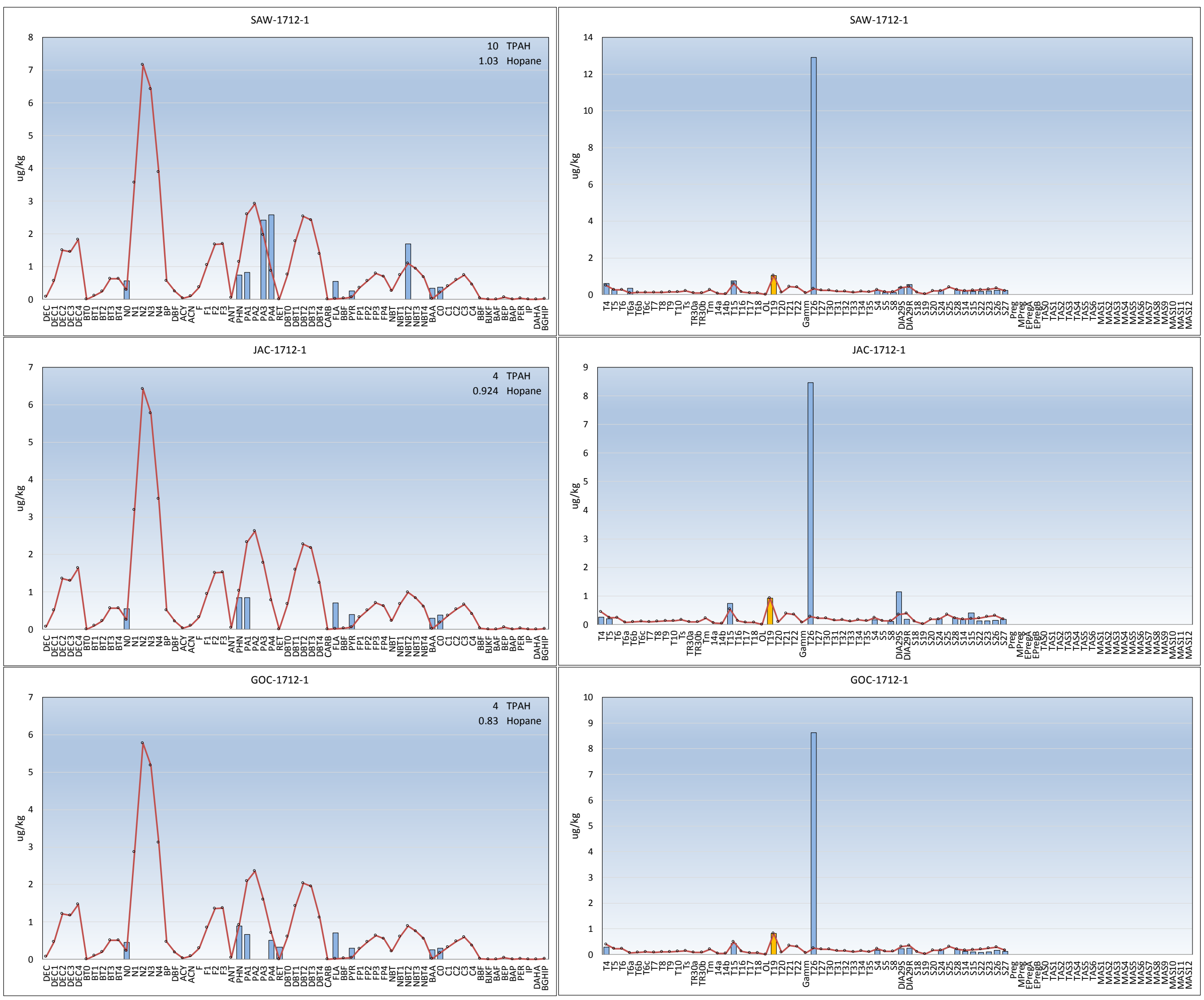


Figure 7. PAH and Biomarker patterns at SAW, JAC, and GOC collected on 12 December 2017, just over 10 weeks (71 days) after the spill. The dotted red lines represent the anticipated profiles from the collected spill oil (Figure 4) normalized to hopane. Profiles from all three replicates at each site are shown in Appendix 1.

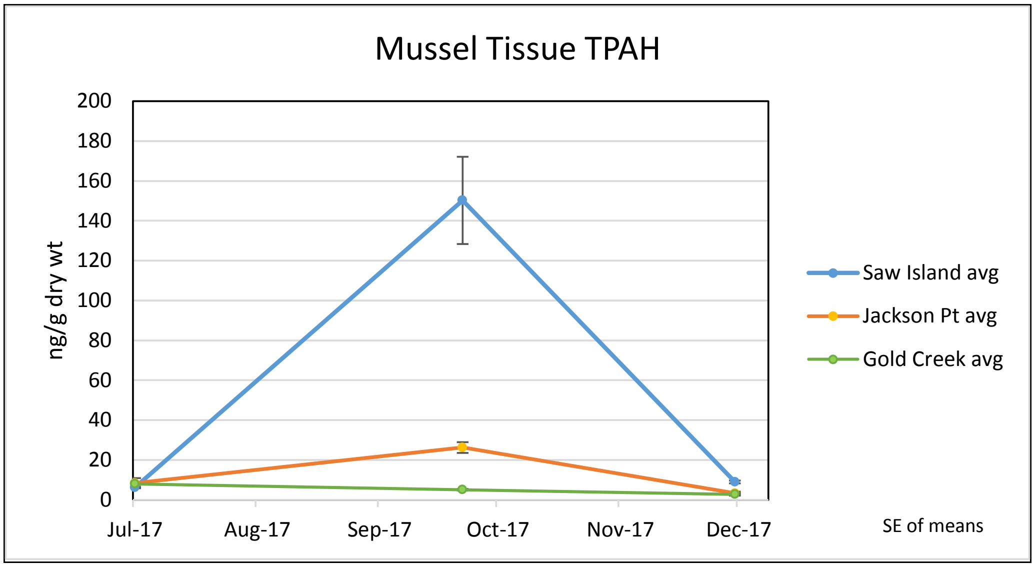


Figure 8. Average total PAH (TPAH) concentrations measured at the three collection sites between July 2017 and December 2017.

Table 1. TPAH values, means and std error of means for all samples.

				Means			SE of Means		
Date	Saw Island	Jackson Pt	Gold Creek	Saw Island	Jackson Pt	Gold Creek	Saw Island	Jackson Pt	Gold Creek
7/8/2017	6.7	5.7	7.5	6.3	8.4	8.0	0.23	2.58	0.44
7/8/2017	6.0	5.9	7.7						
7/8/2017	6.1	13.6	8.9						
9/29/2017	157.7	21	5.5	150.2	26.2	5.1	21.86	2.64	0.38
9/29/2017	109.2	28.2	4.3						
9/29/2017	183.8	29.5	5.4						
12/7/2017	10.4	4.1	4.1	9.0	3.3	2.7	0.70	0.8	0.68
12/7/2017	8.2	4.1	2.1						
12/7/2017	8.4	1.7	2						*ng/g dry wt*

These data also show the relative impacts based on the TPAH loadings in the western (Saw Island) versus eastern (Jackson Point) collection sites adjacent to the terminal. As noted above, these data support the prevailing surface oil/sheen transport to the west observed during the spill event.

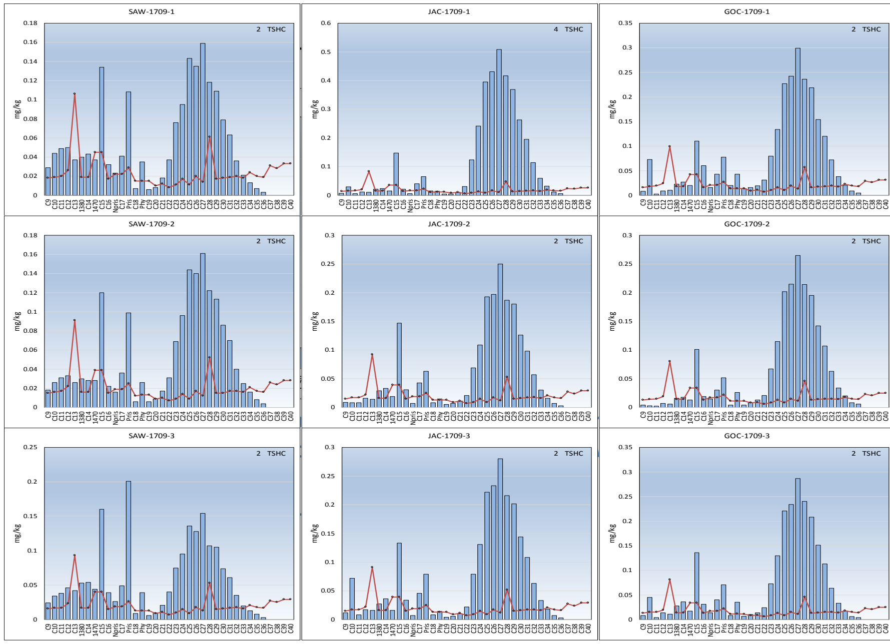
Quality Control

All sample results were validated by Alpha Laboratory QC personnel as meeting lab performance standards. Noted artifacts include the T26 biomarker interferant and below-MDL trace-level n-C_{23}-n-C_{34} "haystack" patterns in the method blanks. That haystack pattern also appeared in all of the mussel samples collected in September and December 2017 (Figure 9) where the concentrations were all well above the sample-specific MDLs.

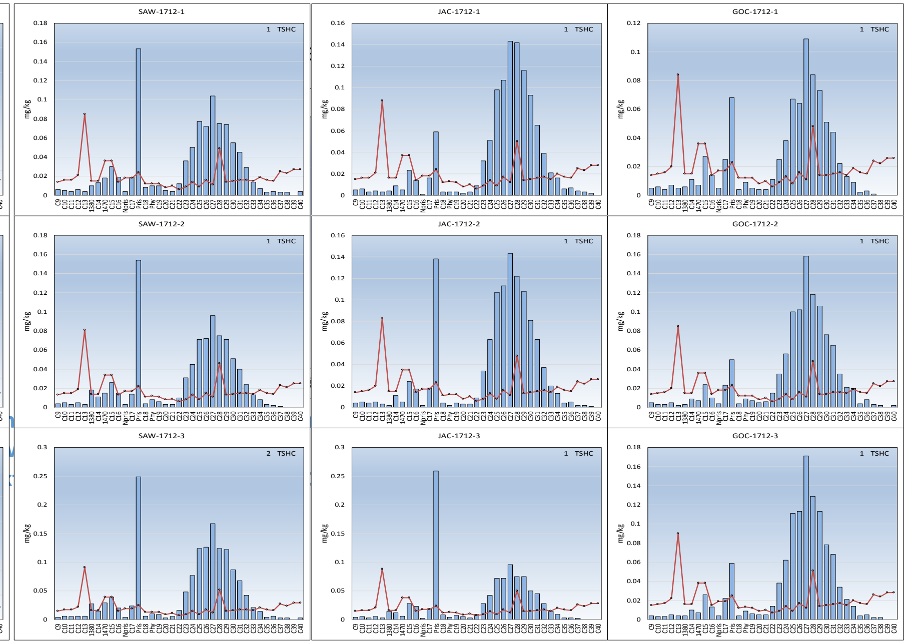
Table 2. Summary of surrogate analyte recoveries for field and QC samples (acceptable range 40-120%).

QC Recovery (%)	Average	Max	Min	Count
Naphthalene-d8	61.0	111	44	25
Phenanthrene-d10	76.0	105	60	25
Benzo[a]pyrene-d12	75.4	116	54	25
o-terphenyl	96.7	97	96	3
d50-Tetracosane	95.3	111	78	25
5B(H)Cholane	106.8	123	96	25

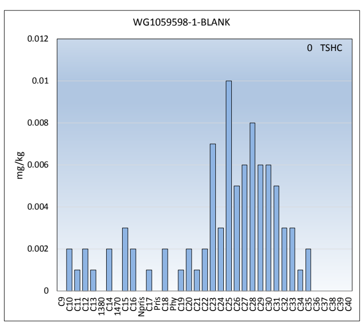
Mussel Tissue SHC – September 2017



Mussel Tissue SHC – December 2017



QC Method Blanks – September 2017 Samples



QC Method Blanks – December 2017 Samples

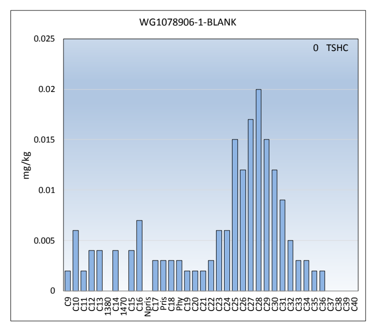


Figure 9. SHC patterns in September and December 2017 mussel-tissue samples at all three sites with the red line denoting the sample-specific MDL (upper plots) and the laboratory method blanks (note at order-of-magnitude lower concentrations) analyzed with the September and December sample batches (lower plots). The n-C_{15}, n-C_{17}, and pristane observed in the tissues represent input from phytoplankton and zooplankton (Short, 2005) while the C_{23}-C_{34} "haystack" likely derives from marine bacteria (Davis, 1968; Han and Calvin 1969; and NAS 1975).

SHC Artifacts

One intriguing aspect of the data analysis regarded the ubiquitous n-C_{23} to n-C_{34} "haystack" pattern observed in the SHC distributions for all the mussel samples reviewed (Figure 9 and Appendix 1). It was thought at first that they might be associated with the spill event because the pattern neatly fit beneath the spilled-oil, SHC fingerprint normalized to n-$C_{27.}$ But that couldn't be because the pattern (based on m/z 85 ion data) also appeared in one of three AMT samples, two of three GOC samples, and at varying concentrations in two of three JAC samples from the July 2017 LTEMP collections before the Berth 5 spill (Payne and Driskell, 2018 in preparation). Note that SHC were not quantified in the mussel samples for 2016 LTEMP. The next potential source could possibly be laboratory or field contamination, but the lab blanks (while showing a similar pattern, but at an order-of-magnitude lower concentration – see Figure 9) seemed to rule that out. Field contamination was also unlikely because the July 2017 samples were collected by Payne and Janka as part of the LTEMP effort on the *Auklet*, while the September and December 2017 samples were collected by Austin Love using a water taxi out of Valdez. It seems highly unlikely that three separate field efforts completed by different personnel from different vessels over a six-month time frame would encounter the same contamination.

Review of pre-2017 LTEMP data generated by the NOAA Auke Bay Laboratory also showed the occasional presence of this n-C_{23} to n-C_{35} haystack (Payne et al., 2010). After further literature review, we believe that the haystack pattern can be traced to bacterial sources. NAS (1975, p 29) reports that an odd-to-even n-alkanes ratio of one in the C_{25}-C_{33} range may not always be due to oil as some bacteria can generate alkanes with this distribution (Davis, 1968; Han and Calvin, 1969). For additional details on biogenic and petrogenic sources, see the LTEMP Oil Primer in Appendix A of our Final 2006-2008 LTEMP report (Payne, Driskell, Short, and Larsen, 2010).

Summary

Pre-spill samples showed traces of hydrocarbons whose signatures could not be attributed to the degraded oil discharges of the Ballast Water Treatment Facility. In the week after the Berth 5 spill event, crude oil was present in the tissues from the adjacent Saw Island site and from Jackson Point. The reference site across the Port was unaffected. By December, all three locations had returned to near-background concentrations and to patterns, nearly identical to pre-spill patterns.

References

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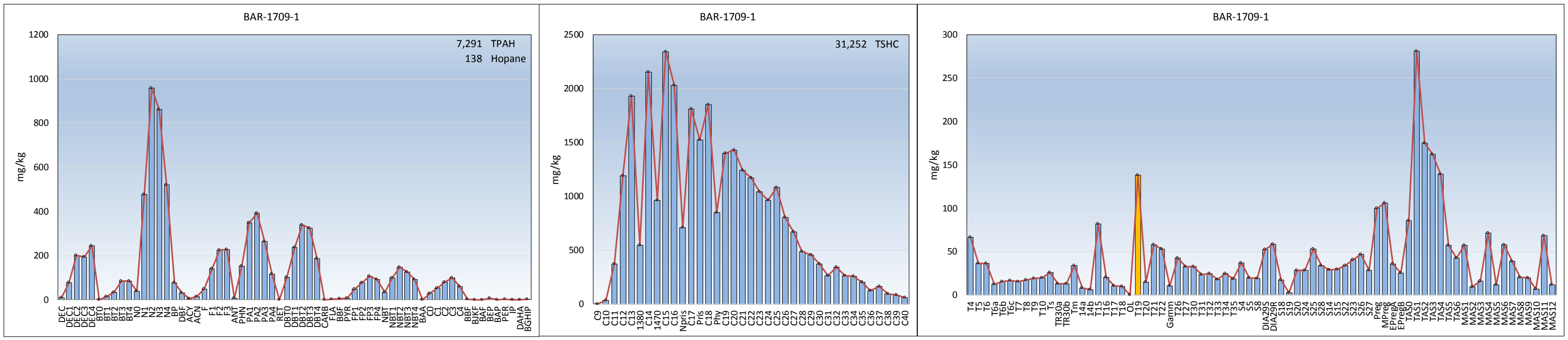
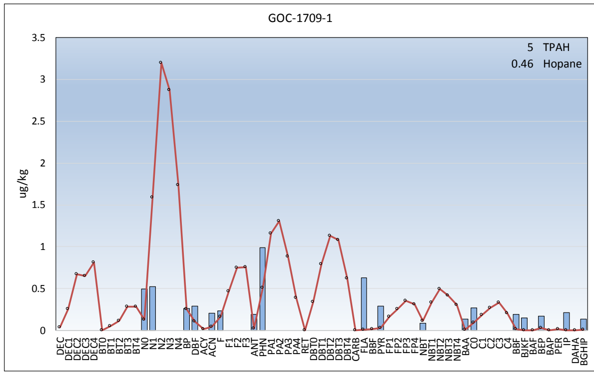
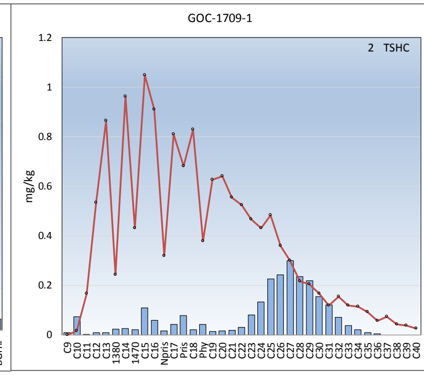
Appendix 1 – All analytic results

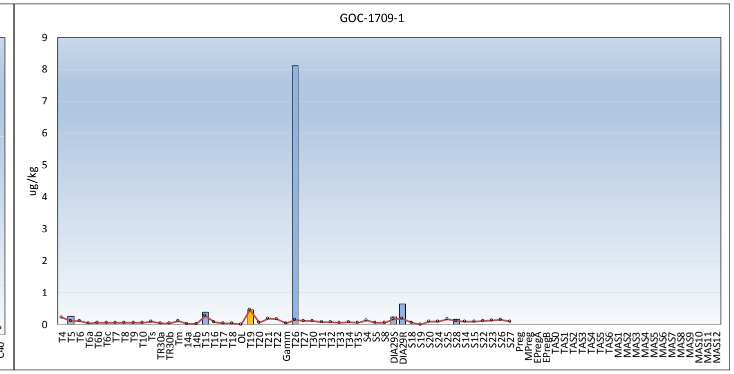
Source oil from spill collection barge. Here, the red overlay is also the source oil; highlighted biomarker is hopane.

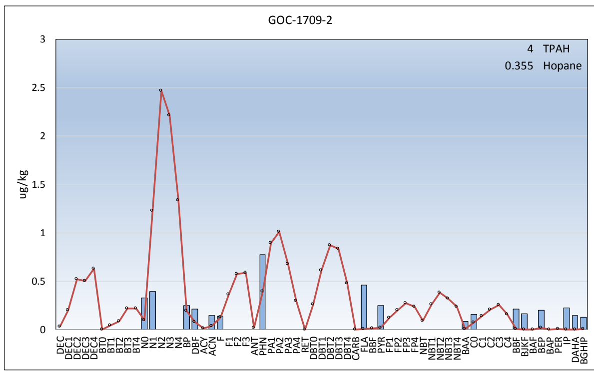


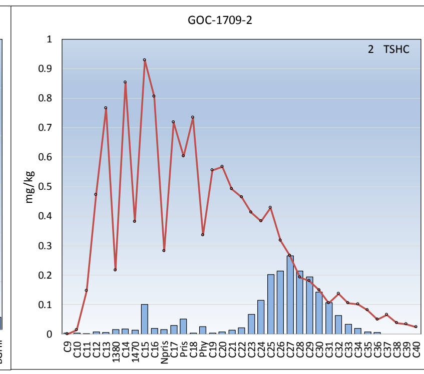
Gold Creek Reference site, Sept 2017, with hopane- or C-27-scaled source oil overlay.

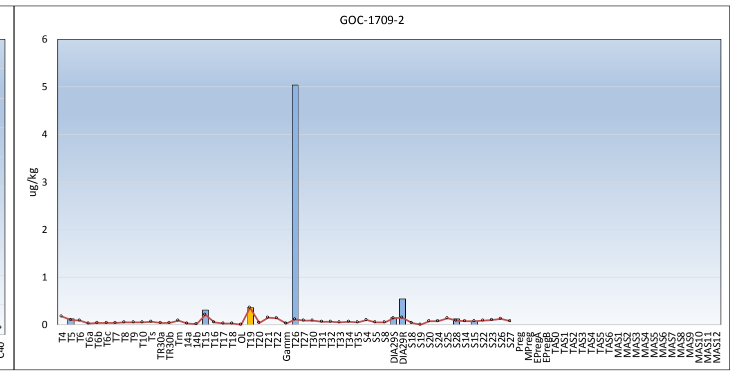


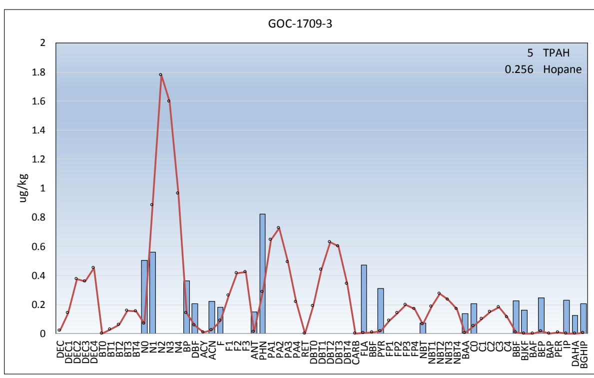


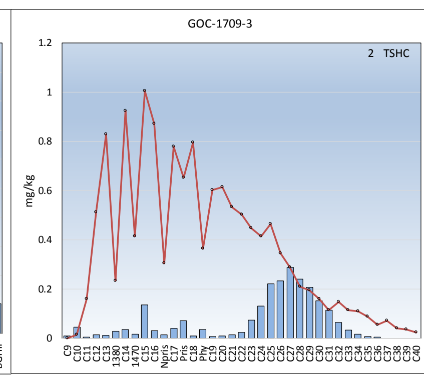


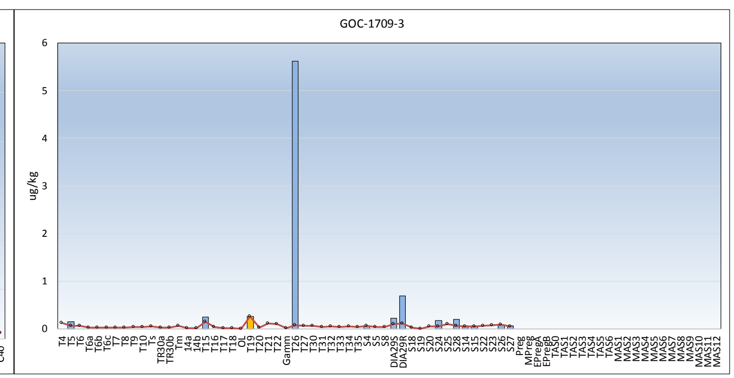




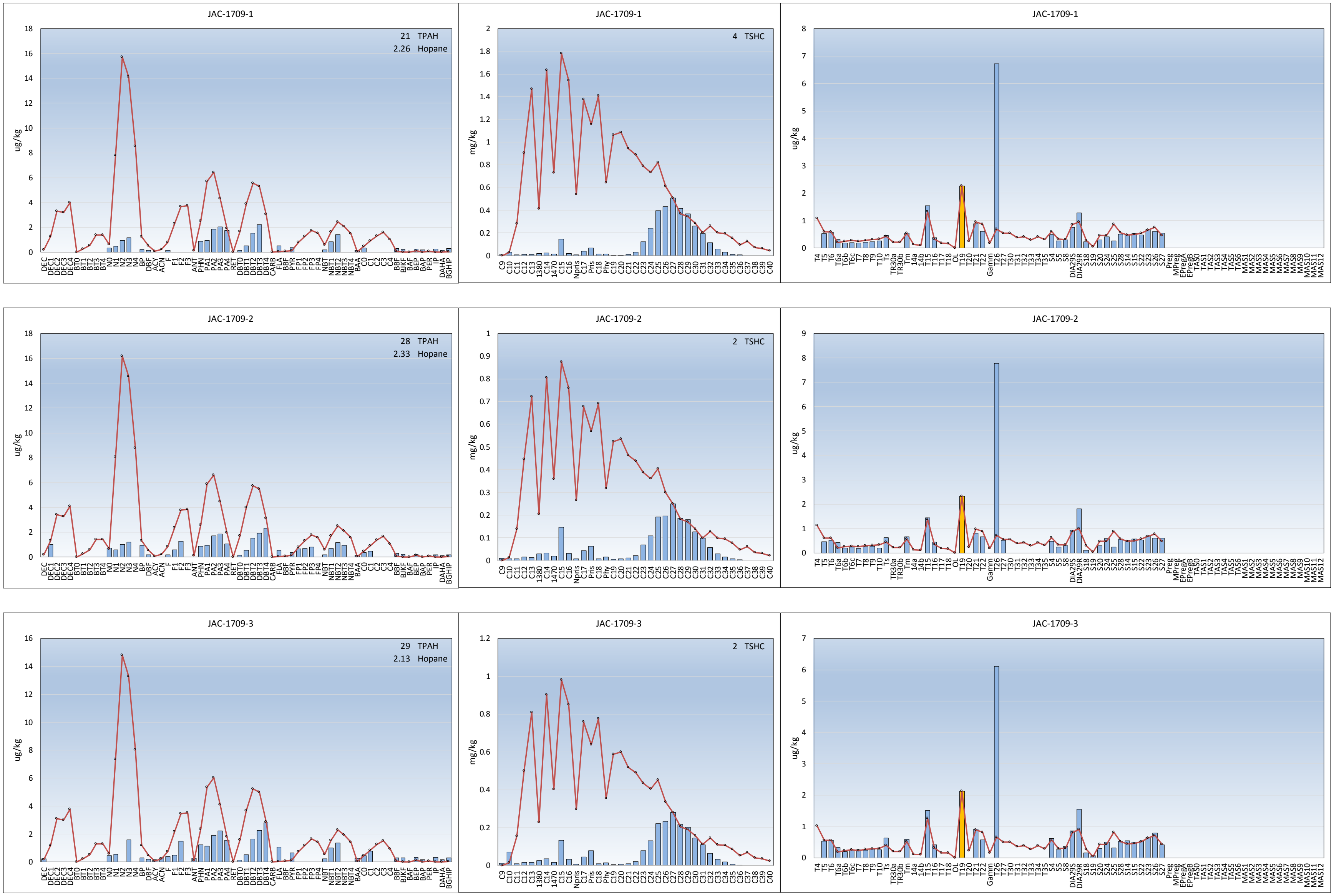




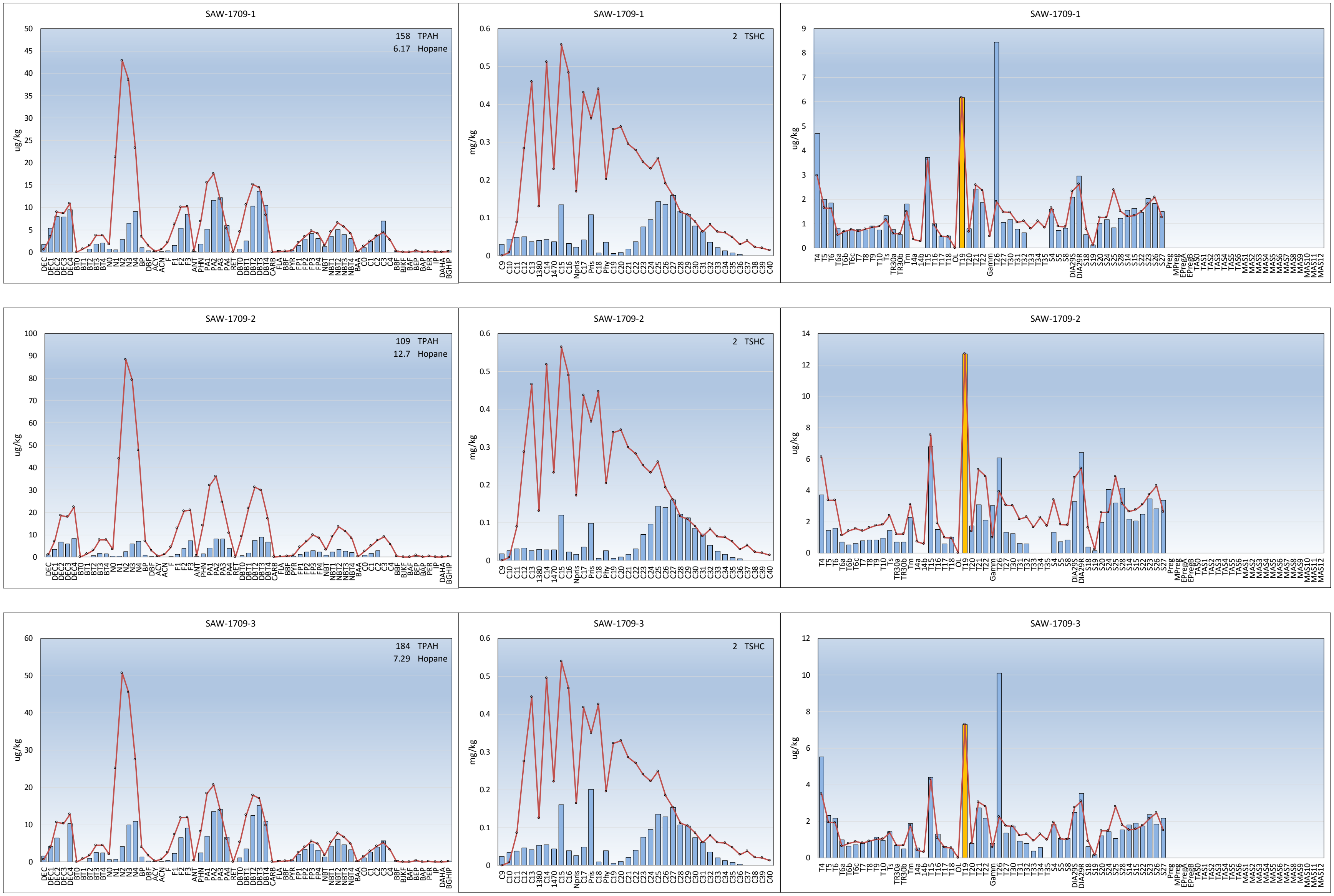




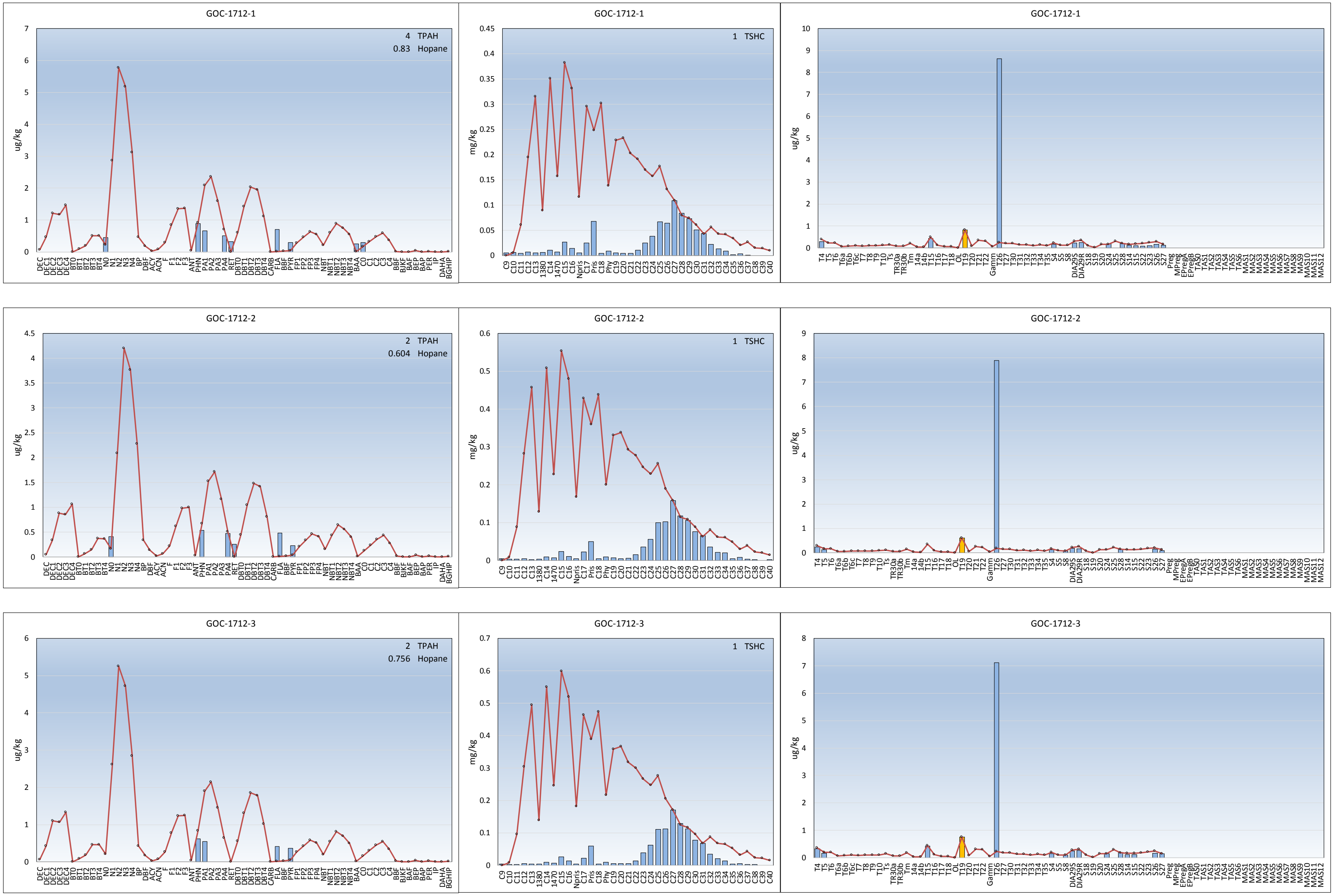
Jackson Point impact site, Sept 2017, with hopane- or C-27-scaled source oil overlay.



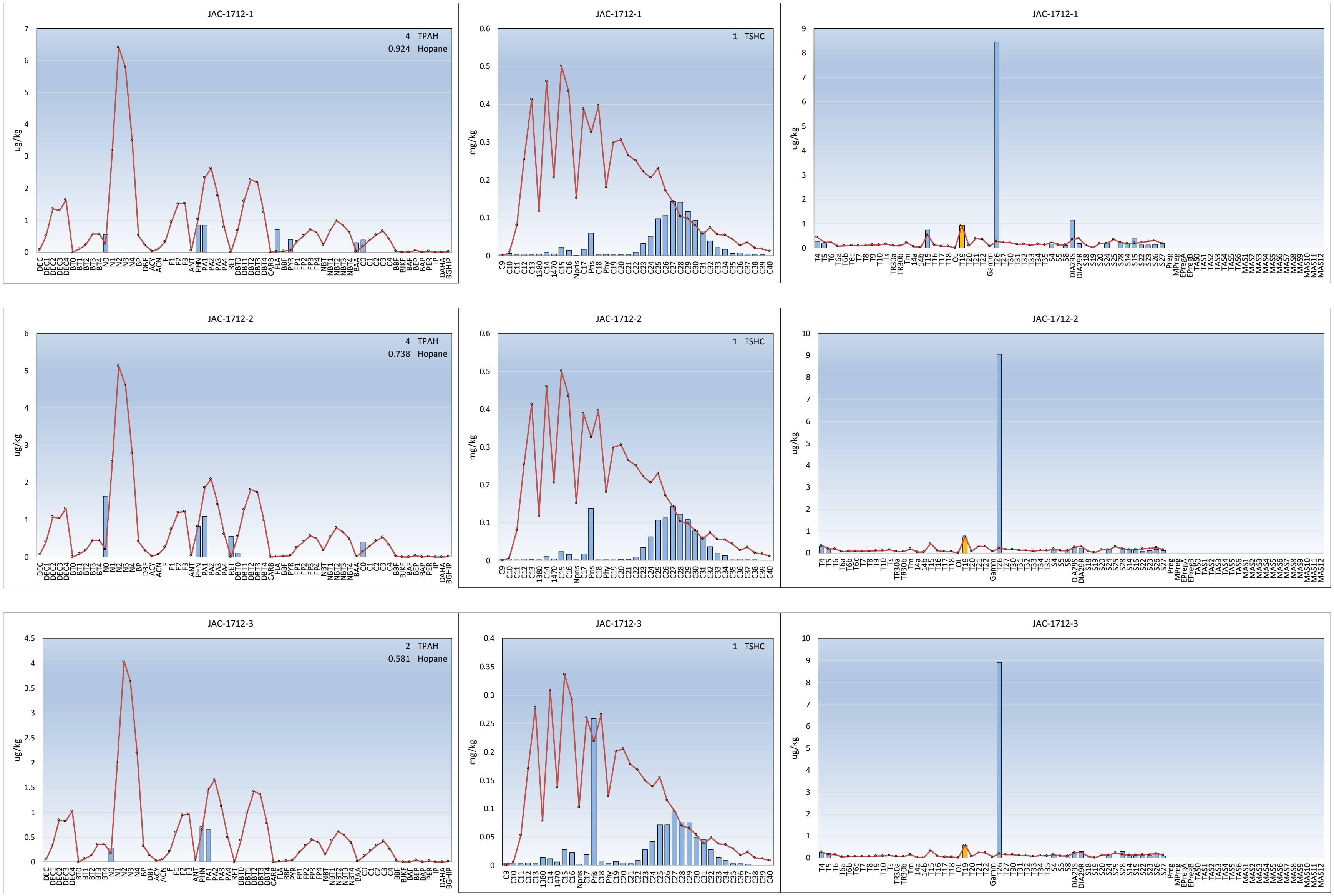
Saw Island impact site, Sept 2017, with hopane- or C-27-scaled source oil overlay.



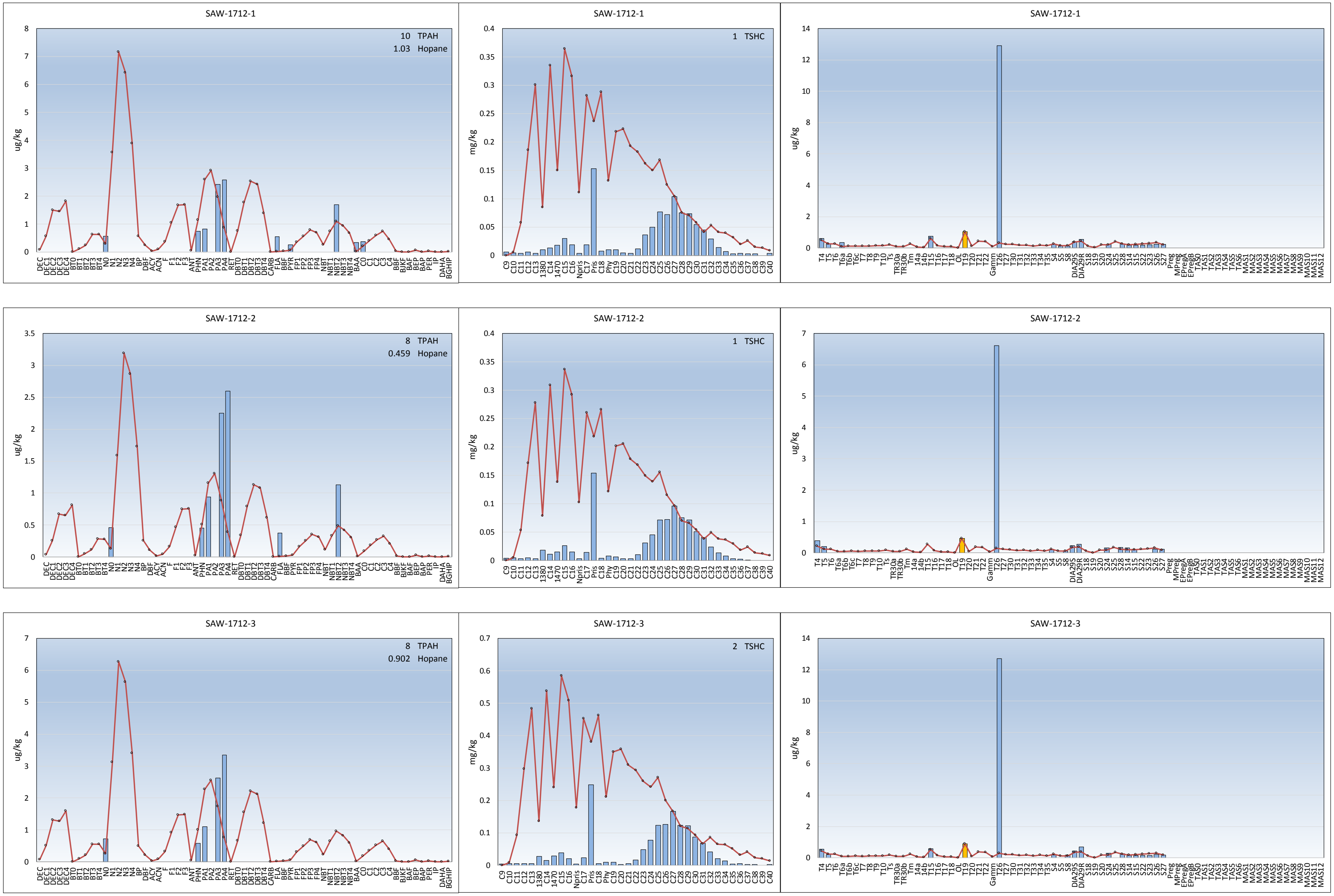
Gold Creek Reference Site, Dec 2017, with hopane- or C-27-scaled source oil overlay.



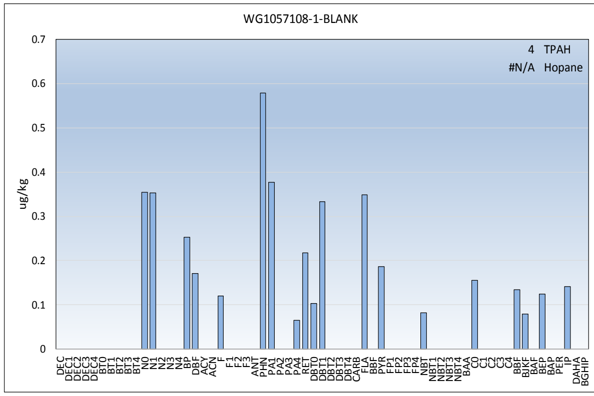
Jackson Point Impact Site, Dec 2017, with hopane- or C-27-scaled source oil overlay.

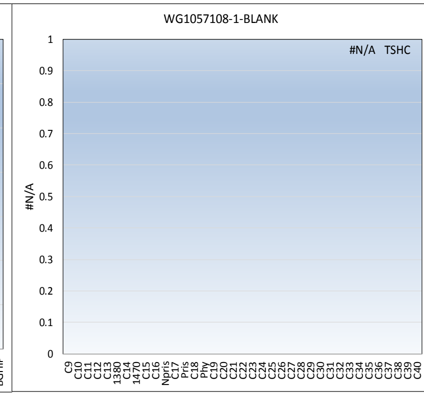


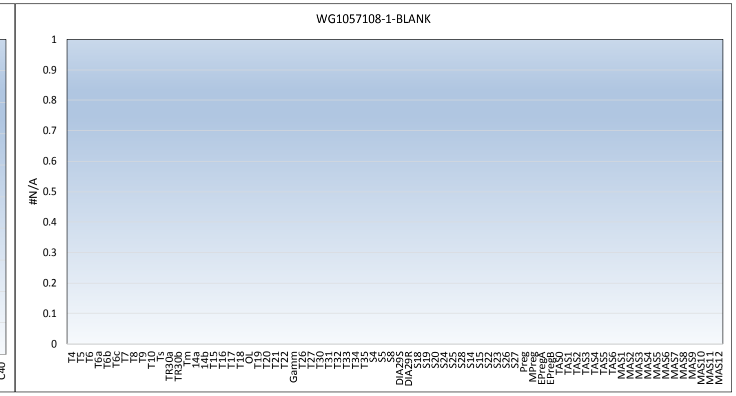
Saw Island Impact Site, Dec 2017, with hopane- or C-27-scaled source oil overlay.

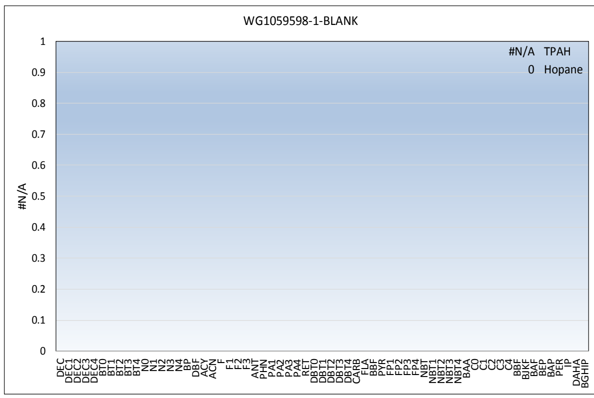


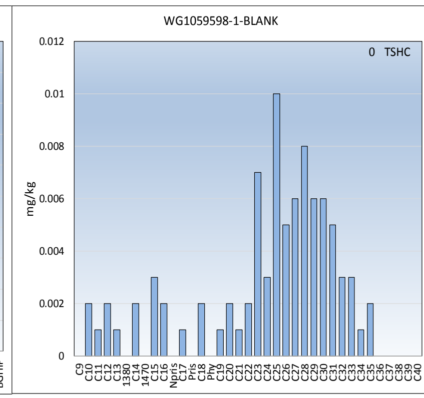
PAH and SHC Method Blanks, Sept 2017

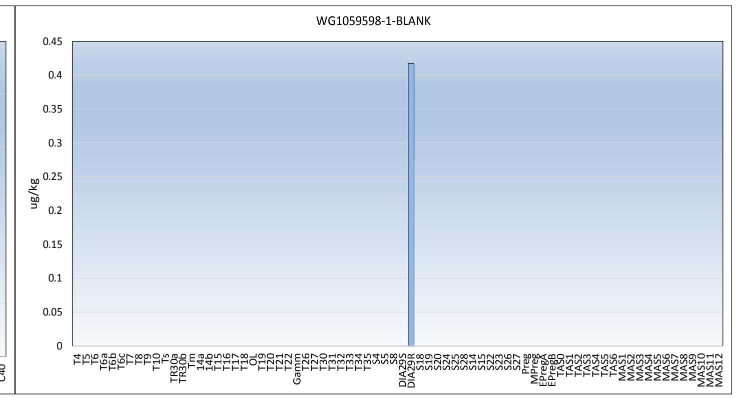






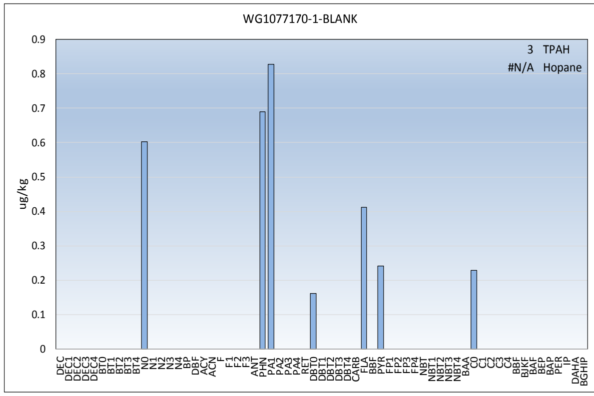


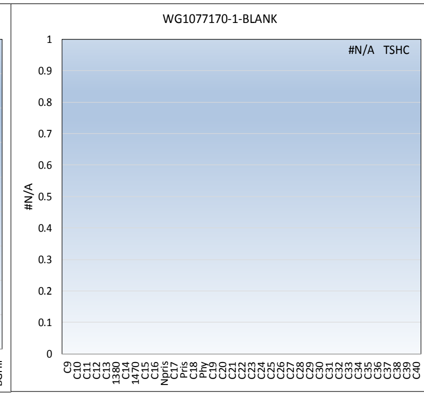


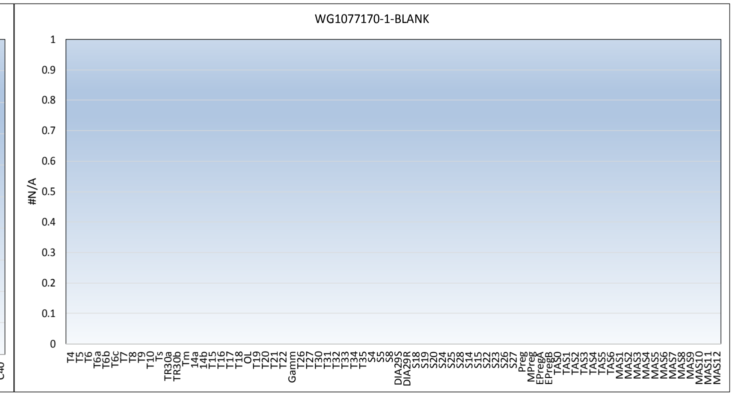


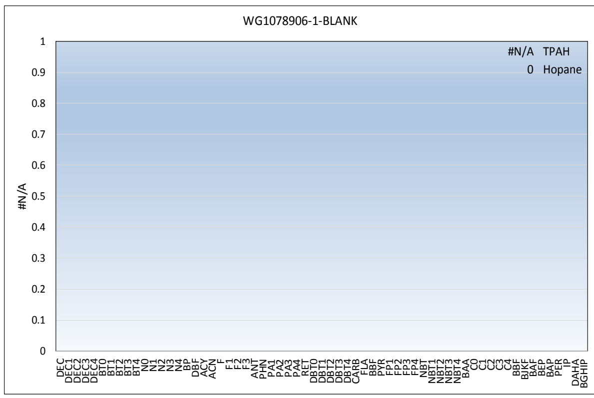
Note dramatically lower (more sensitive) SHC concentration scale (0.00 – 0.012 mg/kg) for WG1059598 1-BLANK vs. September field samples (0.00 – 2 mg/kg).

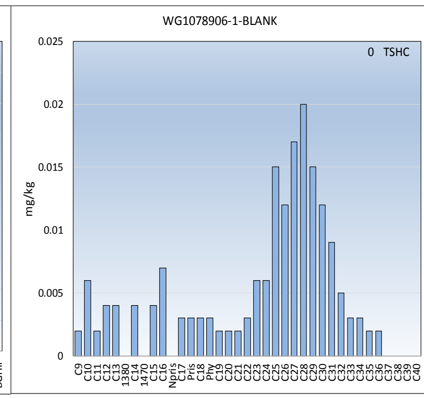
PAH and SHC Method Blanks, Dec 2017

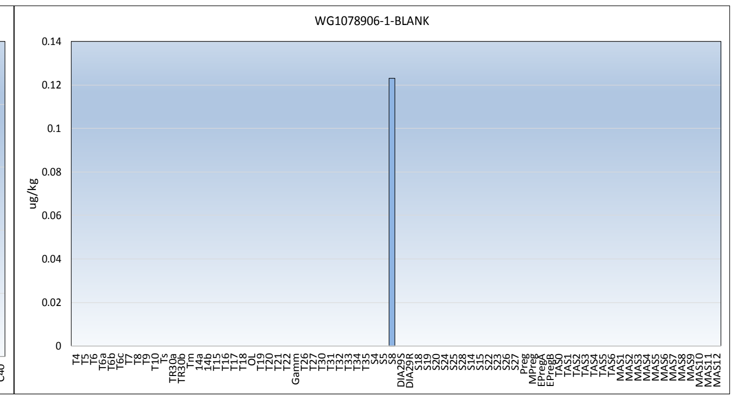












Note lower SHC (more sensitive) concentration scale (0.00 – 0.025 mg/kg) for WG1078906-1-BLANK vs. December field samples (0.00 – 0.7 mg/kg).