LONG-TERM ENVIRONMENTAL MONITORING PROGRAM:
2020 SAMPLING RESULTS AND INTERPRETATIONS

JAMES R. PAYNE, PH.D.
PAYNE ENVIRONMENTAL CONSULTANTS, INC.
ENCINITAS, CA

WILLIAM B. DRISKELL
INDEPENDENT CONSULTANT
SEATTLE, WA

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Cover image – "Staging at Berth 5" Photo by William Driskell.

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ABBREVIATIONS

Stations:

AMT-B	Alyeska Pipeline Service Company's Valdez Marine Terminal, Saw Island, Port Valdez
AMT-S	Alyeska Pipeline Service Company's Valdez Marine Terminal, Berth 4, Port Valdez
AIB	Aialik Bay, west of Seward
COH	Constantine Harbor, Hinchinbrook Entrance, PWS (no longer sampled)
DII	Disk Island, Knight Island Group, western PWS
GOC	Gold Creek, Port Valdez
JAP	Jackson Point, Port Valdez
KNH	Knowles Head, eastern PWS
SHB	Sheep Bay, eastern PWS
SHH	Shuyak Harbor, Kodiak
SLB	Sleepy Bay, Latouche Island, western PWS
WIB	Windy Bay, outer Kenai Peninsula
ZAB	Zaikof Bay, Montague Island, central PWS
*-B	suffix code for biological (tissue) sample, e.g., AMT-B
*-S	suffix code for sediment sample, e.g., AMT-S
ABL	Auke Bay Laboratory, NOAA/NMFS, Juneau, Alaska
AHC	Aliphatic hydrocarbons (same as saturated hydrocarbons – SHC)
ANS	Alaska North Slope
APDES	Alaska Pollutant Discharge Elimination System, successor to NPDES
BTT	Biological Treatment Tank
BWTF	Ballast Water Treatment Facility
cm	Centimeter
DMR	Discharge monitoring report
DW	Dry weight
EMAP	Environmental Mapping Project, EPA/Cook Inlet Regional Citizens Advisory Council
EMP	Environmental Monitoring Program, Alyeska Terminal
EPA	Environmental Protection Agency
EVOS	*Exxon Valdez* oil spill
g	Gram
GC/FID	Gas chromatography/flame ionization detector
GC/MS	Gas chromatography/mass spectrometry
GERG	Geochemical and Environmental Research Group, Texas A&M University
GOA	Gulf of Alaska
GPS	Global Positioning System
KLI	Kinnetic Laboratories, Inc., Anchorage, Alaska
km	Kilometers
L	Liter
LTEMP	Long-Term Environmental Monitoring Program
m	Meter
MDL	Analytic method detection limit
MGD	Million gallons per day
mL	Milliliter
ng/g	nanogram per gram
NIST	National Institute of Standards and Technology
NMFS	National Marine Fisheries Service
NOAA	National Oceanic and Atmospheric Administration
NPDES	National Pollutant Discharge Elimination System
NRDA	Natural Resource Damage Assessment
OSU	Oregon State University
PAH	Polycyclic (or polynuclear) aromatic hydrocarbons (listed in App. I)

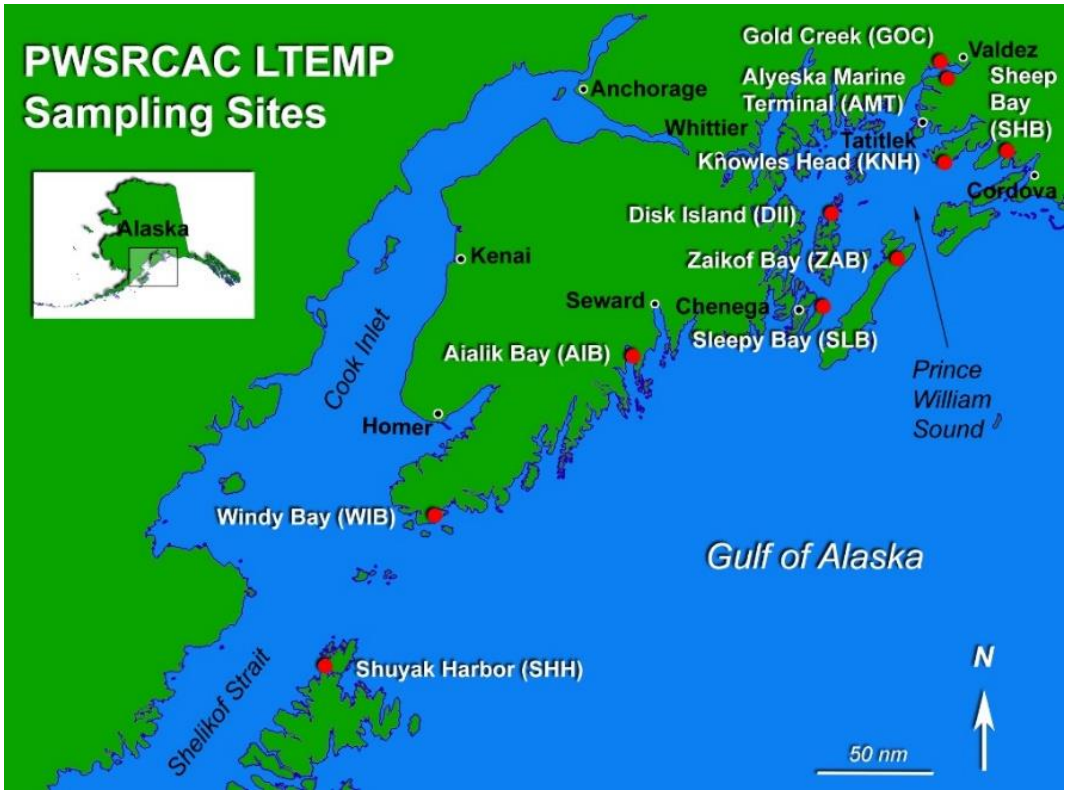
PECI	Payne Environmental Consultants, Inc., Encinitas, California
PGS	Particle grain size
PSD	Passive sampling device
PW	Produce waters
PWS	Prince William Sound
PWSRCAC	Prince William Sound Regional Citizens' Advisory Council
QC	Quality control
RL	Reporting level
SHC	Saturated hydrocarbons (same as AHC: n-alkanes + pristane and phytane) (listed in App. I)
SIM	Selected ion monitoring
SOP	Standard operating procedure
SQV	Sediment quality values
SRM	Standard reference material, National Institute of Standards and Technology
S/T	Sterane/triterpane oil biomarkers (listed in App. I)
TAS	Triaromatic steroids
TOC	Total organic carbon
TPAH	Total PAH
TSHC	Total saturated hydrocarbons (same as total alkanes)
UAF	University of Alaska Fairbanks
VMT	Valdez Marine Terminal, Alyeska Pipeline Service Company

NOTE: The abbreviation lists for PAH, SHC, and biomarker analytes can be found in Appendix 1.

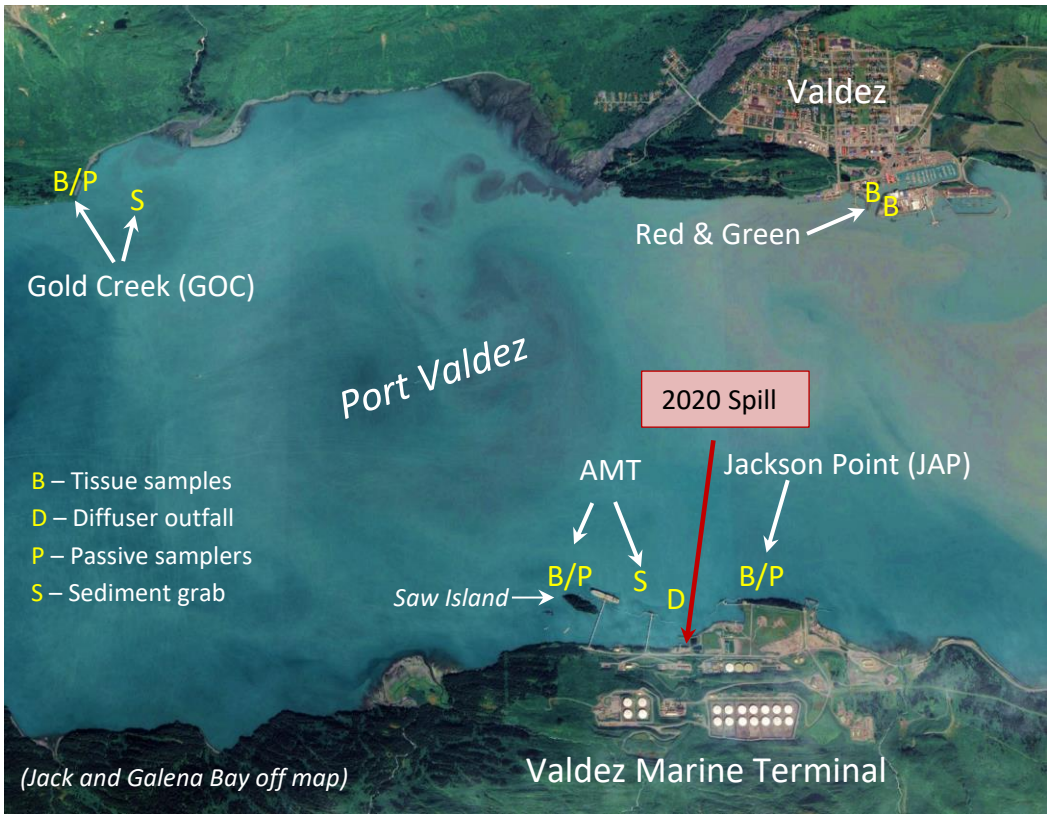
RESULTS AND INTERPRETATIONS FROM LTEMP SAMPLING, 2020

EXECUTIVE SUMMARY

The Prince William Sound Regional Citizens' Advisory Council (PWSRCAC) Long-Term Environmental Monitoring Program (LTEMP) was begun in 1993, following the 1989 *Exxon Valdez* oil spill (EVOS), with the goal of monitoring environmental impacts from oil transportation activities. To accomplish this task, the program has historically sampled for oil-related contaminants in both mussel tissues and sediments in Port Valdez next to and across from Alyeska's Valdez Marine Terminal (VMT) in addition to sampling mussels at locations along the track of the EVOS through Prince William Sound (PWS) and across the Gulf of Alaska (GOA) (last sampled in 2018 on a five-year cycle).



Over the last 27 years, the program has documented EVOS oil's disappearance at the spill-impacted sites (albeit buried oil still exists at a few unique sheltered locations in PWS). Occasionally within the Port, a few tanker- and diesel-spill incidents have been documented, notably with the recent VMT sump spill in April 2020. Data on mussel contamination in the VMT spill zone and nearby LTEMP sites, as well as oil-purging rates and gene transcription responses are being prepared as a separate report and manuscript. Four additional sampling sites were added this year, two on the Valdez Small Harbor breakwater to assess harbor contamination as possible input to the Port, and two remote sites in Jack and Galena Bays to validate and/or evaluate alternatives to the Gold Creek (GOC) control site.



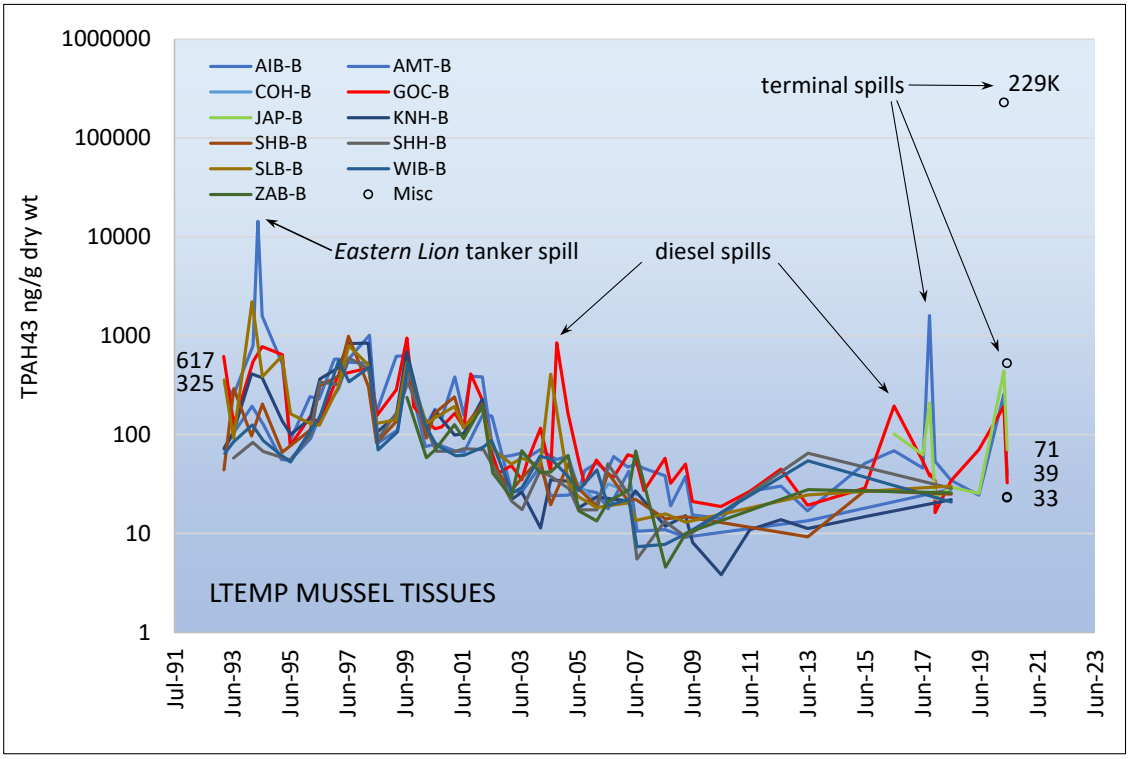
In brief, mussels from the traditional and these added control sites came back exceptionally clean of oil hydrocarbons except within the immediate vicinity of the VMT spill. For a fifth year, passive sampling devices (PSD) were again deployed for a month nearby the traditional sites. These devices were intended to compliment the mussel samples in accumulating only the most bioavailable, dissolved hydrocarbons. And indeed, they returned exceptionally clean with only a low-level dissolved-phase signal. Subtidal sediment samples again showed that Alaska North Slope (ANS) oil continues to accumulate at low concentrations near the terminal's tanker Ballast Water Treatment Facility (BWTF) discharge outfall.

The program's field samples (sediments, mussels, and PSD) are processed and analyzed by certified laboratories, wherein three groups of petroleum hydrocarbons are examined in the data set: polycyclic aromatic hydrocarbons (PAH), saturated hydrocarbons (SHC), and oil biomarker steranes and terpanes (S/T). The data are then reviewed from two perspectives: 1) assessing concentrations of oil contaminants, and 2) characterizing the chemical profiles as to the likely source and degradation state of the hydrocarbons.

Traditionally looking at just total PAH concentrations (conventionally summing 43 analytes into TPAH), it is obvious that Port Valdez contaminant-oil from Alyeska's VMT and tanker operations has been trending downward over the last two decades in both the mussels and sediments. This trend reflects a combination of 1) reduced BWTF discharge volumes from historically decreasing ANS crude oil production, 2) the transition to double-hulled tankers with segregated ballast tanks, and 3) improved BWTF efficiency in removing particulate/oil-phase PAH.

From the second perspective, subtly viewing the data as profile patterns, the presence/absence of individual analytes and their relative concentrations, enables a forensic assessment to determine the source of the oil components and perhaps their fate as they diminish and weather away in the environment. For example, rather than just viewing oil contamination by its proxy sum (TPAH), LTEMP mussel profiles from Saw Island (AMT-B),

adjacent to the VMT, have been seen generally shifting over the last several years, away from the terminal's earlier oil-dominated patterns and into trace-level background or combustion-derived PAH patterns. This assessment task can be complex or confounded as there are non-oil sources for some analytes in the profiles (i.e., combustion products and natural hydrocarbons from marine plankton and terrestrial plant waxes). But using all three analyte groups, PAH, SHC, and biomarkers can create a high confidence in the task. Interpreting the profiles permits insight into the fate and transport of the oil, information obscured by the common industry practice of just reporting TPAH, or worse, a subset of PAH.



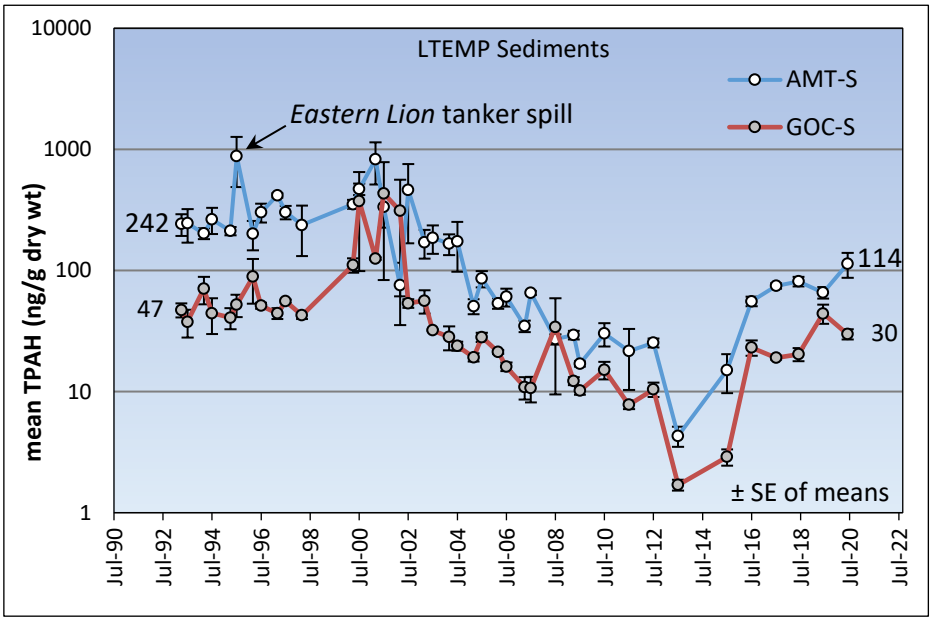
In 2018, tissue hydrocarbon concentrations at all 11 LTEMP stations (both inside and outside Port Valdez) were barely detectible as most individual analytes were below the instruments' Method Detection Limit (MDL) and TPAH totals reached lows in the 6-40 ng/g dry weight range. Results were similar in 2019, when the three Port Valdez stations showed the same trace-level components that were essentially indistinguishable from the laboratory quality-control blanks. At the Gold Creek reference site (GOC), where there had been a minor diesel spill in summer 2016, only trace-level background and combustion profiles were reported in 2018-19. Against these low background levels, elevated TPAH values and ANS crude oil fingerprints from the April 2020 spill incident at the terminal were easily detected at the two terminal stations (AMT and JAP).

Comparing nationwide environments, the most recent (albeit dated) National Oceanic and Atmospheric Administration (NOAA) West Coast Mussel Watch data (2004-05) and the more recent 2008-10 Alaska Mussel Watch sites, strongly contrast with 2018-2020 LTEMP mussel-tissue results that show 10 to 1,000 times lower TPAH concentrations. The 2020 LTEMP sites are exceptionally clean of the PAH oil indicators. But during the April 2020 VMT spill incident, mussels within the spill's "Hot Zone" exhibited TPAH concentrations approaching 230,000 ng/g.

PSDs are specifically designed to sample only the more bioavailable, dissolved hydrocarbons (versus oil microdroplets that mussels may ingest) and from their month-long submerged deployment, can theoretically increase the detection sensitivity. All PSD results from the May-June 2020 deployment, however, continued to show

only a low-level, but heavily weathered, dissolved naphthalene profiles. There was a three-to-five-fold increase in the reported concentrations at the Saw Island (traditionally, AMT) and Jackson Point (JAP) sites, respectively. But the PAH patterns were essentially identical to those observed at the Gold Creek (GOC) reference site, which showed concentrations in line with those observed earlier in 2018 and 2019. In previous year's deployments both inside and outside the Port, the commonality of concentrations and patterns suggested that these signals were unrelated to the BWTF effluent. This year's elevated PSD concentrations at JAP and AMT probably reflected dissolved-phase PAH released in the April 2020 spill incident. But it is almost impossible to identify dissolved-PAH sources without other lines of evidence. We speculate, without water samples, the possibility that the increased concentrations at JAP and AMT after the April 2020 spill may have broached toxicity thresholds for sensitive marine organisms and life stages. PSD-measured dissolved PAH concentrations in water at JAP following the April 2020 VMT spill were at a level that has been shown to cause cardiotoxicity in oil-exposed early life stages of Pacific herring.

These mussel and PSD results differ greatly from the sediments near the terminal that are still a repository for the BWTF's chronic hydrocarbon inputs. Sampling bottom sediments near the outfall, the oil compounds are still measurable at low levels and, in part, still directly traceable to the BWTF discharge. But the patterns are changing.



AMT-S sediment patterns, although historically dominated by an ANS oil signature from the outfall, began changing to mostly combustion sources in 2011-2015. More recent 2016-2020 patterns again changed and now reflect a mix of low-level background, combustion, and weathered BWTF oil components. The biomarker profiles (the analytic hydrocarbon group that are highly resistant to degradation) still solidly confirm that the major oil contaminant source is the ANS-patterned, BWTF effluent. The 2020 SHC profiles show higher levels of marine and terrestrial biological components compared to the higher-molecular-weight oil waxes, which have remained relatively constant between 2008 and 2020. Together, these patterns suggest variable low-level inputs of PAH from weathered ANS oil (BWTF discharge), plus combustion products from local vessel traffic, runoff, or aerial deposition, and the ubiquitous trace background. We speculate that being variable and low level, these patterns were likely underlying the earlier years' dominant oil signature and are now just more apparent as the total oil concentrations diminish.

At the GOC-S reference site, the situation is different: total concentrations are lower, the patterns are mostly from background and combustion products and there is no evidence of BWTF-derived PAH accumulation in sediments at the site.

In companion projects, gene transcription data were assessed for the LTEMP mussels and mussels from two alternate control sites away from the terminal and harbor and nearer to the mouth of Port Valdez (Jack and Galena Bays). Additional samples were collected near the April 2020 terminal spill location for both oil chemistry and gene transcription to document acute oiling levels, their relation to gene transcription, and their eventual return to normal levels. From the panel of selected genes, several showed positive correlation with degree of oiling (i.e., the genes were turned on to physiologically mitigate exposure to oiling). The LTEMP transcription results are as a separate report. A manuscript will combine both chemistry and transcription results from the spill samples.

INTRODUCTION

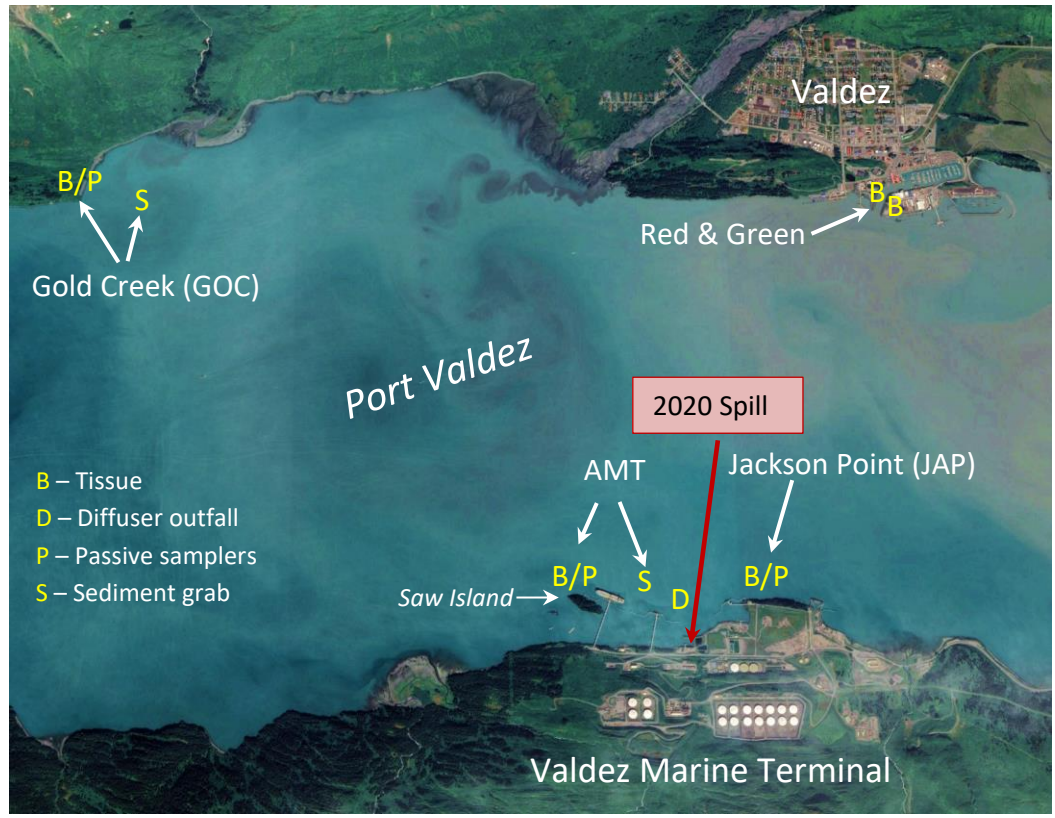
The primary goal of the Prince William Sound Regional Citizens' Advisory Council (PWSRCAC) Long-Term Environmental Monitoring Program (LTEMP) is to monitor impacts from Alyeska's Valdez Marine Terminal (VMT) operations and oil transportation activities on the environment at selected sites within Port Valdez, Prince William Sound (PWS), and Gulf of Alaska (GOA) for "as long as the oil flows through the pipeline." The project was begun in 1993 as a mandate to the PWSRCAC's charter. To streamline this report, additional static sections on the project's history have been moved into Appendix 3.

The program consists of field samples from sediments, mussels, and passive sampling devices (PSDs), processed and analyzed by two laboratories: one for tissues, sediments, and occasional water and oil matrices (Alpha Analytical/NewFields Environmental Forensics), and another for the PSDs (Oregon State University). The labs report three groups of petroleum hydrocarbons: polycyclic aromatic hydrocarbons (PAH), saturated hydrocarbons (SHC), and sterane/terpane oil biomarkers (S/T). For LTEMP, the data are then compiled and assessed from two perspectives: 1) the concentrations of oil contaminants, and 2) characterizing the whole suite of analytes, the chemical profiles for weathering and source determinations.

From just the profiles, presence/absence patterns of individual analytes and their relative concentrations can forensically establish the source, transport, and fate of the oil components as they diminish and weather away in the environment. The task can be complex as there are non-oil sources for some compounds that may be mixed into the profiles (e.g., combustion products, and natural plankton and plant waxes). The components are generally described as being from petrogenic (oil sourced), pyrogenic (combustion sourced) or biogenic (natural biological sourced) origins, or in some mixed combination. In Port Valdez, the levels of oil hydrocarbons have been decreasing over the past two decades and they are currently at low levels that reflect the reduced inputs from the BWTF effluent. Spiking above these low levels, spill events are easily detected.

LTEMP sampling locations have been mostly fixed since the program's 1993 inception. At Alyeska's VMT, the Ballast Water Treatment Facility (BWTF) treats and discharges oil-contaminated ballast water offloaded from tankers prior to onloading the Alaska North Slope (ANS) oil. Here, two stations serve to assess direct exposures from BWTF effluent: one adjacent to the offshore discharge diffusers near Berth 4 for sediments (AMT-S) and a second at Saw Island near Berth 5 for mussels (AMT-B). Jackson Point (JAP) was added in 2016 on the opposite (eastern) side of the diffuser, near Berth 3. Gold Creek (GOC) is sampled as a reference station for both sediments and mussels, 6 kilometers (km) across the Port (Figure 1). Also in 2016, the program was expanded to deploy PSDs at all three Port stations to measure just the bioavailable, dissolved-phase hydrocarbons. Beyond Port Valdez, eight additional permanent stations, comprising the geographic reach of the *Exxon Valdez* oil spill (EVOS) out to Kodiak, were sampled for mussels but now only every five years (last sampled in 2018) (Figure 2, Table 1). Multi-seasonal sampling was more frequent during the program's early years but now has been reduced to just summer or incident sampling.

Sediment samples were also consistently collected throughout the program at two stations, one near the BWTF's underwater discharge diffuser and the other, at the GOC reference site across the Port (Figure 1). These are analyzed for the same hydrocarbon chemistry components as the tissues, plus particle grain size and total organic carbon content. Sampling and analytical methods are modelled after the protocols developed by the National Oceanic and Atmospheric Administration (NOAA) Status and Trends Mussel Watch Program as fully detailed in previous annual monitoring reports.



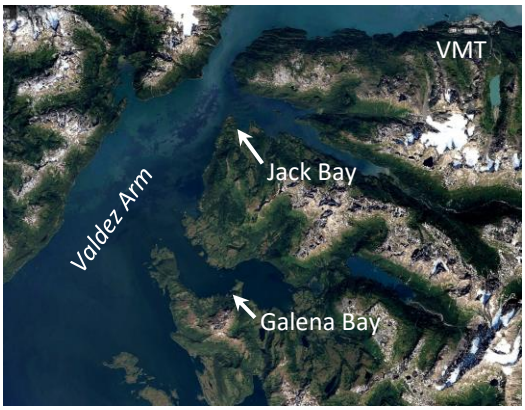


Figure 1. LTEMP sampling stations in Port Valdez adjacent to the terminal (AMT-B, AMT-S, and JAP) and 6 km NW of the VMT (GOC). New stations in 2020 include Red and Green sites in the Valdez Harbor entrance plus Jack and Galena Bay in Valdez Arm. This Google Earth image (June 2019) shows a tanker docked at Berth 5.

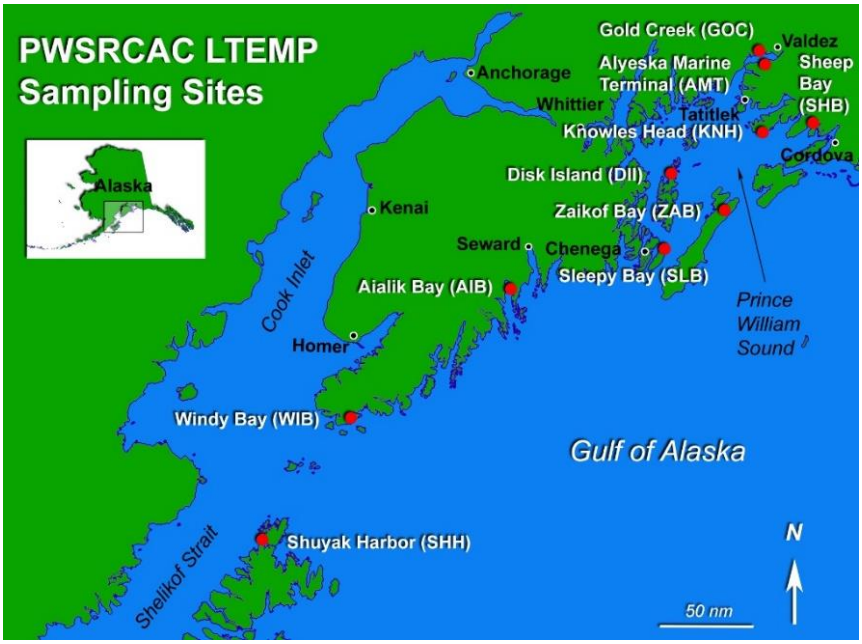


Figure 2. Map of the LTEMP sites with station abbreviations. PWS and GOA sites are sampled every five years, whereas Port Valdez sites are sampled annually.

The ensuing report sections introduce and assess the sampled matrices, sediments, tissues, and PSDs. The written style is intended for the technical reader to fully assess our processes and interpretations; however, many of the methods and ancillary results sections have been moved to appendices to streamline the main report results.

In this report, the annual results begin with the BWTF effluent characterization. Re-reported here from previous years (2016-17), this section shows our only examples of what the degraded ANS oil currently looks like as it is discharged into the Port (versus the fresh ANS oil from the pipeline). We caution that only two seasonal samples, highly different, were collected to compare to the current field samples. Using these as references against which to evaluate field samples requires a discerning eye and some flex in judgment but it is possible to confirm or parse out the presence of ANS oil from biogenic and pyrogenic inputs in a mixed-source sample. Subtle details regarding the state of weathering (degradation from the original patterns) usually suggests an interpretive scenario of the sources, transport, and fate for the contaminated sample.

Reported next are results from the sediments near the BWTF outfall that are still accumulating oil, in contrast to the sediments across the Port at GOC that are generally free of oil. To discriminate just current conditions, the grab-sampler sediments are collected from just the intact top layer of recently deposited, unconsolidated, fine sediment (~0.5-1 cm deep). PAH patterns near the outfall are typically extensively weathered (microbially) but the samples still contain a fairly intact suite of the more recalcitrant S/T biomarkers. Sediments from the GOC reference site generally do not contain PAH from the BWTF oil, but occasionally, traces of the S/T biomarkers can be observed.

Next sections in this report are the mussel tissues and PSD results, both of which show that, in most samples, there are essentially only near-method-detection-limit (MDL) traces of oil. Exceptions to these typically low traces were from the April 2020 VMT spill, as shown in the spill's "Hot Zone" and nearby Jackson Point (JAP) mussels. Additional details on depuration kinetics and genetic transcriptomic responses in these samples are contained in a separate

Table 1. LTEMP tissue sampling history showing change in annual events coded for seasons. Spring, summer (SS); spring, summer, autumn (SSA); or summer only (S). Sediments (not shown) have only been sampled in spring and summer at AMT-S and GOC-S from 1993-2008, and afterwards only in summer.

LTEMP Station Mussel Samplings												
	Port Valdez			Prince William Sound						Gulf of Alaska		
	AMT-B	JAP	GOC-B	KNH	DII	SLB	ZAI	SHB	COH	AIB	WIB	SHH
1993	SS		SS	SS	SS	SS	SS	SS		SS	SS	SS
1994	SS		SS	SA	SA	SA	SA	SA		SA	SA	SA
1995	SS		SS	SS	SS	SS	SS	SS		SS	SS	SS
1996	SS		SS	SS	SS	SS	SS	SS		SS	SS	SS
1997	SS		SS	SS	SS	SS	SS	SS		SS	SS	SS
1998	SS		SS	SS	SS	SS	SS	SS		SS	SS	SS
1999	SSA		SSA	SS	SS	SS	SS	SS		SS	SS	SS
2000	SSA		SSA	SS	SS	SS	SS	SS		SS	SS	SS
2001	SSA		SSA	SS	SS	SS	SS	SS		SS	SS	SS
2002	SSA		SSA	SS	SS	SS	SS	SS		SS	SS	SS
2003	SSA		SSA	SS	SS	SS	SS	SS		SS	SS	SS
2004	SSA		SSA	SS	SS	SS	SS	SS		SS	SS	SS
2005	SSA		SSA	SS	SS	SS	SS	SS	S	SS	SS	SS
2006	SSA		SSA	SS	SS	SS	SS	SS	SS	SS	SS	SS
2007	SSA		SSA	SS	SS	SS	SS	SS	S	SS	SS	SS
2008	SA		SSA	S	S	S	S	S		S	S	S
2009	SS		SS	S	S	S	S	S		S	S	S
2010	S		S	S								
2011	S		S	S								
2012	S		S	S								
2013	S		S	S	S	S	S	S		S	S	S
2014												
2015	S		S	S				S				
2016	S	S	S									
2017	S	S	S									
2018	S	S	S	S	S	S	S	S		S	S	S
2019	S	S	S									
2020	S	S	S									

report (in preparation). Traditionally, the mussels would ingest both dissolved-phase and particulate-phase (micro-droplets) of oil while the PSDs are designed to sample only dissolved-phase hydrocarbons and, after a month-long deployment, with more sensitive detection limits. Both sample types agree, showing only background dissolved-phase contaminants and combustion products in the water column. Furthermore, the low-level PAH concentrations are too low to be toxic.

The mostly static and more ancillary sections from prior reports (e.g., Collection and Analytic Methods, Lab Performance, Grain Size and TOC, Oxygenated Compounds, and "Beyond LTEMP" that compares LTEMP TPAH with historic studies) have been moved to appendices. Relevant conclusions still appear in summary points.

Valdez Marine Terminal BWTF Effluent

The primary source of oil contamination in Port Valdez has historically been the partially degraded, ANS crude oil discharged from the VMT's BWTF. Last analyzed in 2004-2005 prior to current low production levels and the BWTF redesign (Payne et al., 2005b, 2005c), re-sampling the effluent was added as an element to the 2016/2017 program. Sampled during July 2016, the effluent turned out to be nearly 80% freshwater, an unexpectedly low salinity value that reflects the collected runoff from the terminal and smaller treated tanker-ballast volumes during the summer months. Anticipating less runoff and more ballast water in the system during winter operations, effluent samples were again collected in March 2017. For both sampling events, raw effluent as well as filtered samples were obtained to examine particulate, oil-phase, and dissolved-phase constituents (Payne et al., 1999).

As expected, compared to the summer samples, winter effluent had higher TPAH values (7,605 ng/L vs. 2,885ng/L), and were less weathered and biodegraded relative to initially fresh ANS crude oil (red line overlay in Figure 3). During winter, more frequent and stronger winter storms necessitate additional ballast in the tanker cargo holds and thus, higher volumes and throughput for the BWTF. Also, there is reduced freshwater runoff at the terminal during the colder winter months. In both seasons, however, particulate/oil-phase droplets were present in the effluent (Figure 4) at similar concentrations and with essentially identical degrees of weathering. At the same time, the winter Biological Treatment Tank (BTT) effluent sample had a much higher proportion of bioavailable,

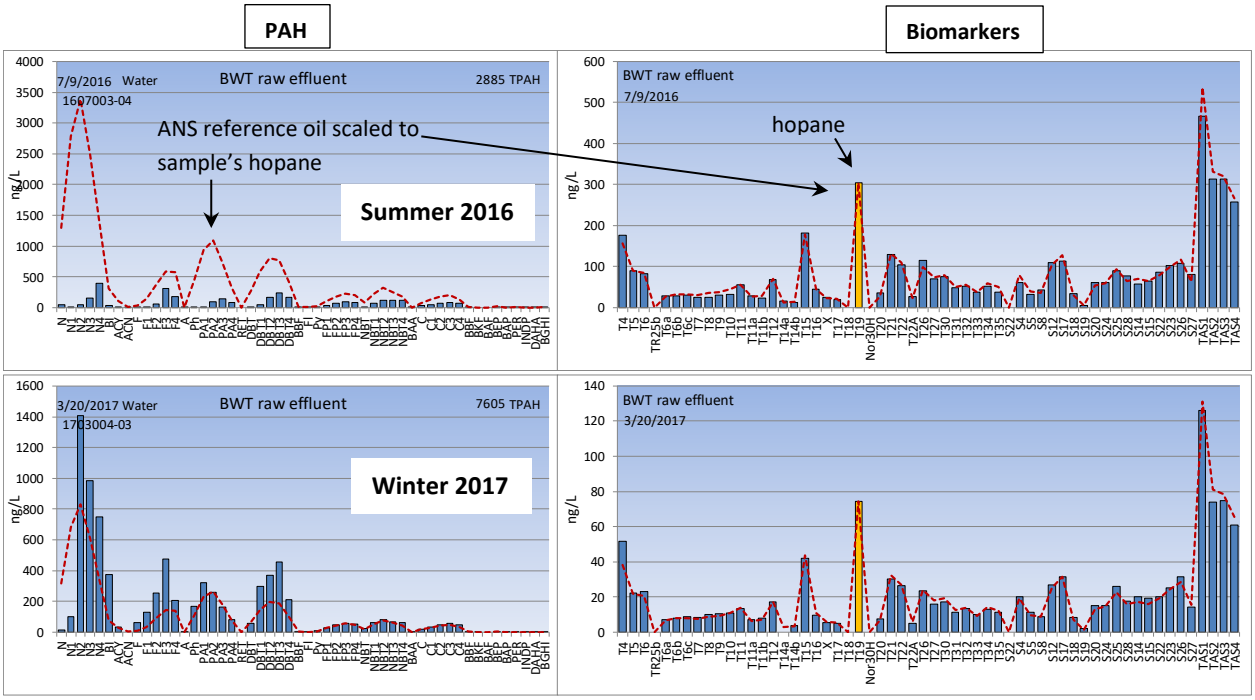


Figure 3. PAH and biomarker profiles (ng/L) of raw (unfiltered) BWTF-BTT effluent samples from July 2016 (upper plots) and March 2017 (lower plots). The dotted red line represents an overlay of fresh ANS crude oil normalized (scaled) to hopane (T19, colored gold in the biomarker profiles). Excess dissolved PAH constituents are observed in 2017 as N-, F- and DBT-group analytes above the source reference line (lower left).

dissolved-phase components (Figure 5). It must be cautioned that this profile "snapshot" of the BWTF winter operation occurred as the BTT was recovering from a shutdown from an overnight power outage; the profile may be unknowingly biased as normal conditions were reestablished.

Lower-molecular-weight SHC are subject to both dissolution/evaporation losses and microbial degradation (NAS 1975, 1985, and 2003). In a sample's profile, microbial degradation processes initially appear as decreases in the more easily assimilated n-alkanes, n-C_{17} and n-C_{18}, relative to the branched-chain isoprenoids, pristane and phytane. In the BWTF's BTT, particulate/oil-phase SHC are well degraded by the combined abiotic and microbial processes in both seasons, but also partially due to the longer summer residence-time within the tank (Figure 4).

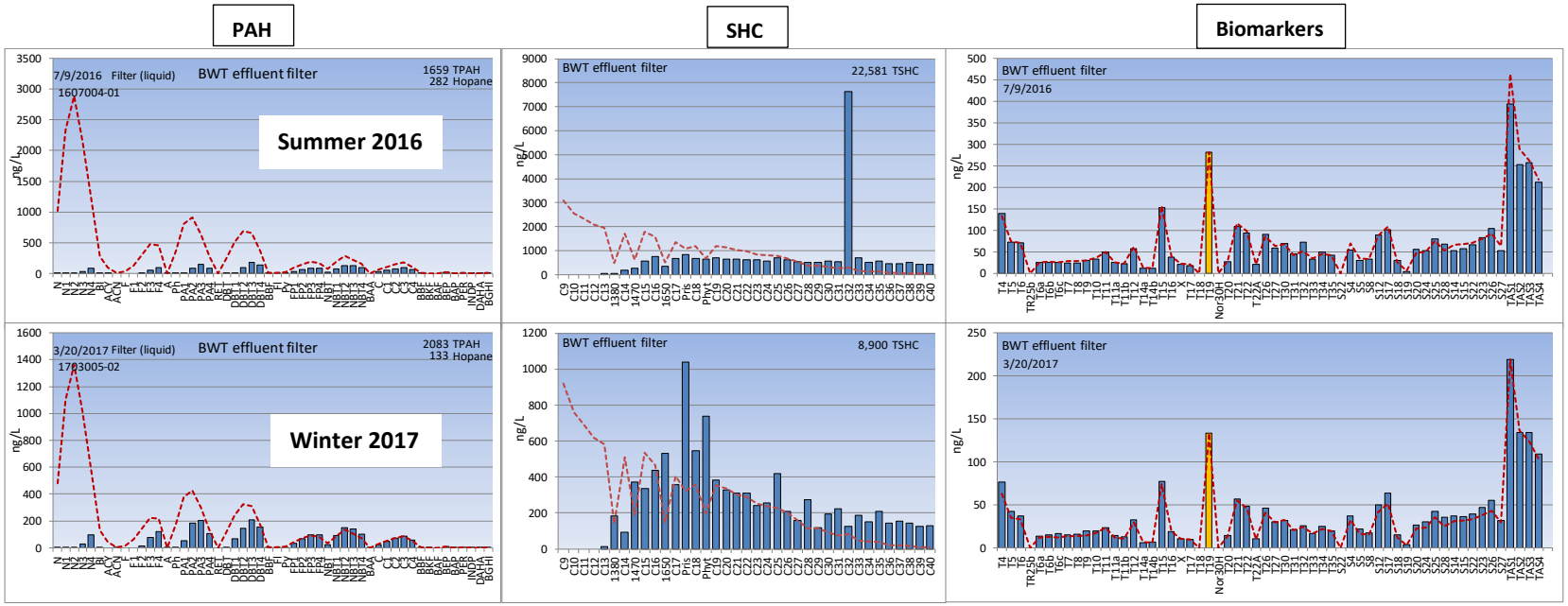


Figure 4. PAH, SHC, and biomarker profiles (ng/L) of the filtered, particulate/oil-phase droplets in the BWTF-BTT effluent. The red line overlay represents fresh ANS scaled to the sample's hopane (T19, colored gold in the biomarker plots). The gaps between the measured PAH and the overlay portray the extent of weathering. The TPAH concentrations are similar (1,639 and 2,083 ng/L) but there is additional loss of the higher-molecular-weight (FPs, NBTs, and Cs) in the summer due to enhanced biodegradation and longer residence time in the BTT. Biomarkers show essentially no degradation in both seasons. SHC (middle plots) show losses of lower-molecular-weight C_9 through C_{15} components in fresh ANS crude oil largely due to evaporation. In summer SHC, C_{32} was a matrix interferent; SHC are scaled to C_{27}.

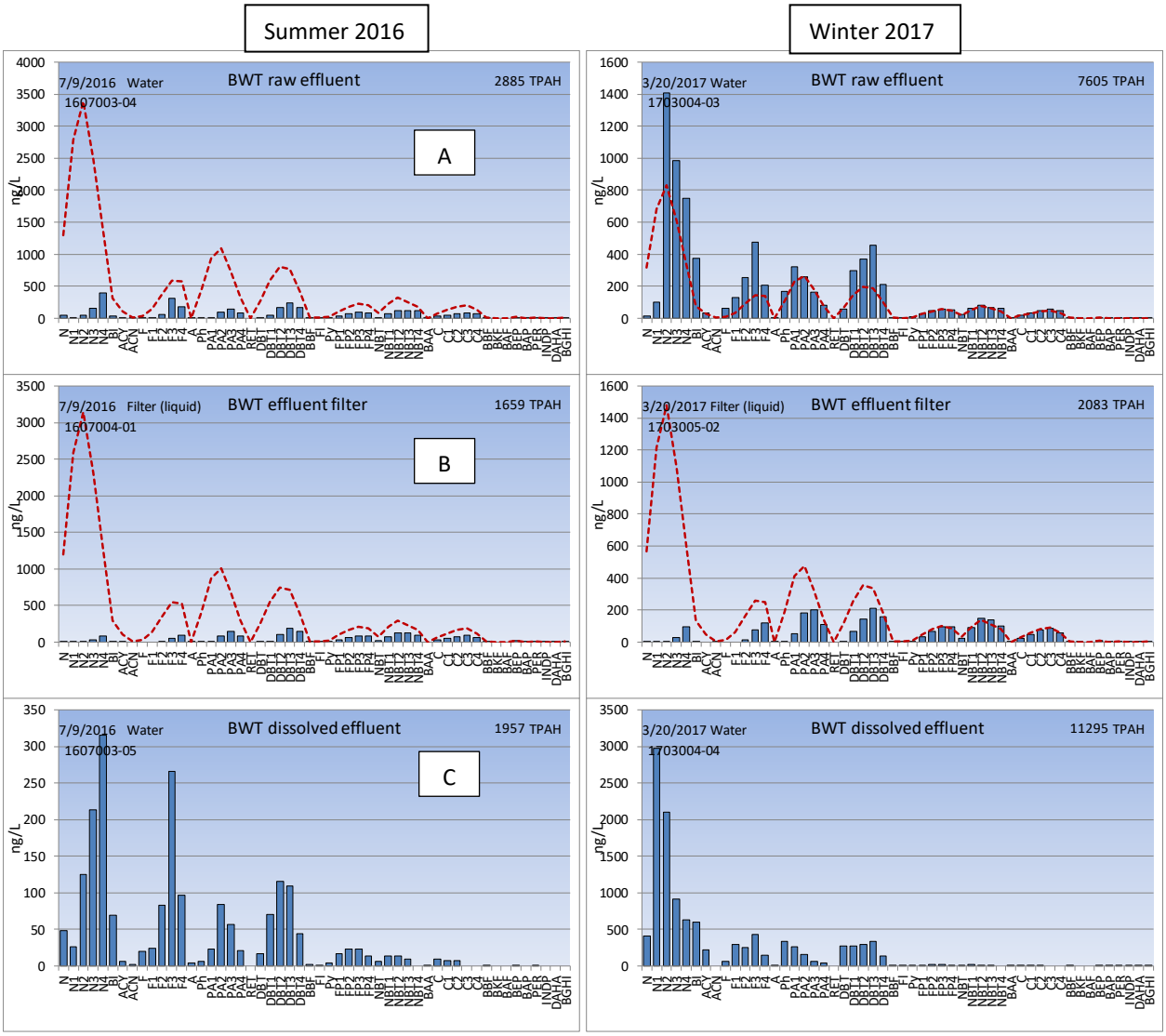


Figure 5. PAH profiles of BTT effluent samples collected under summer (July 2016) and late winter (March 2017) conditions: A) whole unfiltered sample; B) particulate/oil phase trapped on the glass-fiber-filter; and C) dissolved phase. The dotted red lines represent fresh ANS crude oil PAH profile normalized to hopane to show evaporation and dissolution effects on lower-molecular-weight PAH (C profiles lack the indissolvable hopane for scaling). Note, however, that while the dissolved-phase patterns are similar, the winter TPAH concentrations are an order of magnitude higher.

The lower summer BTT throughput requires facility operators to retain and recycle a portion of the BTT contents just to keep the biological system active. This prolonged recycling practice produces a highly weathered oil profile as reflected in the two SHC isoprenoids, pristane and phytane, that microbially degrade slower than the straight-chain alkanes, C_{17} and C_{18}. Thus, the reduced n-C_{17}/pristane and n-C_{18}/phytane ratios for the oil-phase droplets in the BTT effluent (Table 2) indicate they have undergone extensive microbial degradation compared to fresh ANS oil.

Table 2. Ratios of n-C_{17}/pristane and n-C_{18}/phytane for July 2016 and March 2017 BTT effluent samples (concentrations in ng/L). Lower ratios indicate extent of microbes preferentially degrading the alkanes over the pristane and phytane isoprenoids.

	n-C_{17}	pristane	Ratio		n-C_{18}	phytane	Ratio
ANS Crude Oil	3060	2190	1.40		2710	1410	1.93
July 2016 BTT							
Raw effluent	813	944	0.86		602	662	0.91
Particulate phase	658	836	0.79		682	642	1.06
Dissolved phase	243	0	n.a.		0	0	n.a.
March 2017 BTT							
Raw effluent	1200	1370	0.88		1140	716	1.59
Particulate phase	359	1040	0.35		548	739	0.74
Dissolved phase	0	290	n.a.		500	189	2.65

PORT VALDEZ SEDIMENTS

In the subsequent discussions, note that we consider TPAH concentrations to be a very rough proxy of oil contamination (like discussing weather but only talking about the temperature); a truer picture and relevant insights are in the weathering-profile interpretations. But for historical interests and trend perspectives, TPAH concentrations are presented and discussed.

SEDIMENT TPAH TRENDS 1993-2020

Between 1993 and 2004, with TPAH levels dropping from historic highs in the hundreds-thousands of ng/g dry weight (DW) (including a spike in 1995 from the *Eastern Lion* tanker spill at the terminal), average sediment TPAH concentrations at the 68-72 meter (m) deep terminal Berth 4 site (AMT-S) continued to decrease from values in the low hundreds of ng/g in the 2002-2004 period until they dropped to around 50-60 ng/g DW in March 2005. This decline continued in a range between 20-50 ng/g until April 2012 (Figure 6 and Table 3). Then in 2013, concentrations unexpectedly dropped further to all-time lows, around 4 ng/g. Sediment samples were not collected in 2014 due to a temporary hiatus in the program but in July 2015, the TPAH concentrations rebounded slightly to around 15 ng/g and further up to a range of 55 – 80 ng/g between 2016 and 2019 (Table 3 and Table 4).

The most recent, June 2020 TPAH concentration increase from 66 to 114 ng/g in the AMT-S sediments was at first believed to possibly suggest a minor contribution from oiled intertidal substrate erosion or oil/suspended particulate loads and sedimentation after the April 2020 intertidal spill between Berths 4 and 5. The biomarker profiles observed in the June 2020 AMT-S samples match the April 2020 spilled oil as well as the July 2016 particulate-phase BWTF effluent reference; however, closer examination of the most recent sediment PAH profiles (discussed further below) suggests that the increase in the mean TPAH value is actually derived from higher levels of combustion products in two of the three 2020 AMT sediment replicates.

Sediment TPAH trends at GOC-S have generally tracked with those observed at the terminal (Figure 6), but the concentrations are usually 2-4 times lower, now around 20-40 ng/g since 2016 (Table 3 and Table 4). The TPAH concentrations and PAH profiles at GOC-S remained essentially the same in 2019 and 2020.

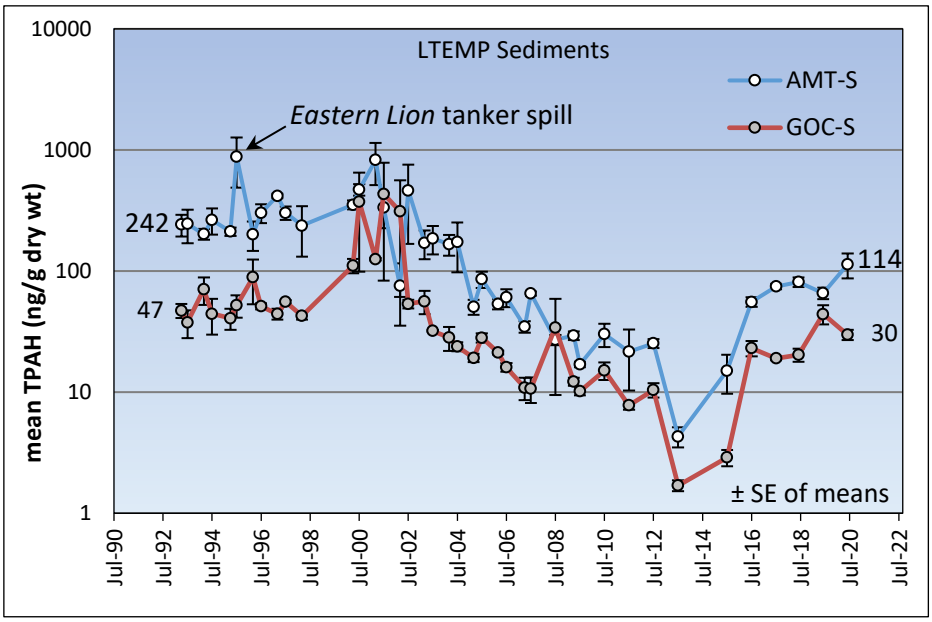


Figure 6. Time series of log (TPAH43) in sediments at AMT-S and GOC-S, 1993-2020.

Table 3. Summary statistics for 2020 TPAH50 and TPAH43 concentrations (ng/g DW).

2020	TPAH50					TPAH43				
	avg	max	min	count	± SE	avg	max	min	count	± SE
AMT-S	130.6	182.1	88.1	3	27.5	113.6	163.0	73.9	3	26.2
GOC-S	30.9	34.4	24.2	3	3.4	29.9	33.0	24.0	3	1.3

Table 4. Historic average sediment TPAH43 values (ng/g DW), 2000-2020.

	AMT-S	GOC-S		AMT-S	GOC-S
Apr-00	353	111	Jul-07	65	11
Jul-00	472	374	Jul-08	27	34
Mar-01	828	126	Apr-09	29	12
Jul-01	335	433	Jul-09	17	10
Mar-02	76	312	Jul-10	30	15
Jul-02	464	54	Jul-11	22	8
Mar-03	172	56	Jul-12	25	10
Jul-03	187	32	Jul-13	4	2
Mar-04	167	28	Jul-15	15	3
Jul-04	175	24	Jul-16	56	23
Mar-05	51	19	Jul-17	75	19
Jul-05	86	28	Jun-18	81	20
Mar-06	54	21	Jun-19	66	44
Jul-06	61	16	Jun-20	114	30
Mar-07	35	11			

Sediment Biomarkers

Biomarkers' persistence in the BWTF effluent (and spilled oil) enables tracking the ANS signal in the surrounding sediments even as the PAH and SHC components are severely degraded. Conceptually, as small oil droplets are discharged with the effluent, they readily adsorb onto waterborne suspended particulates (e.g., glacial flour) and eventually settle to the seafloor where microbial degradation and dissolution preferentially weather the SHC and PAH. In an example profile where PAH are plotted with a fresh ANS profile overlay re-scaled to the sample's hopane (Figure 7, top), the individual components almost completely disappear relative to the reference, thus suggesting nearly complete loss of PAH due to *in situ* weathering during or after sedimentation (upper-left plot in Figure 7). Note that there is some degradation/loss of the biomarkers (the small gaps between the hopane-normalized ANS profile and the individual components in the upper-right panel). Although the biomarkers are recalcitrant (here microbially non-preferred), they are not invincible. Yet, a sufficiently diagnostic profile exists to confidently assign the signal to the BWTF effluent. For illustration, when the PAH and biomarker data are re-scaled to the sample's NBT2 rather than hopane (Figure 7, bottom plots), another forensic phenomena emerges; an excess of biomarkers above the fresh-ANS overlay demonstrates the accumulation of slowly degrading biomarkers and slightly less recalcitrant, higher-alkylated NBT and chrysene homologues over time.

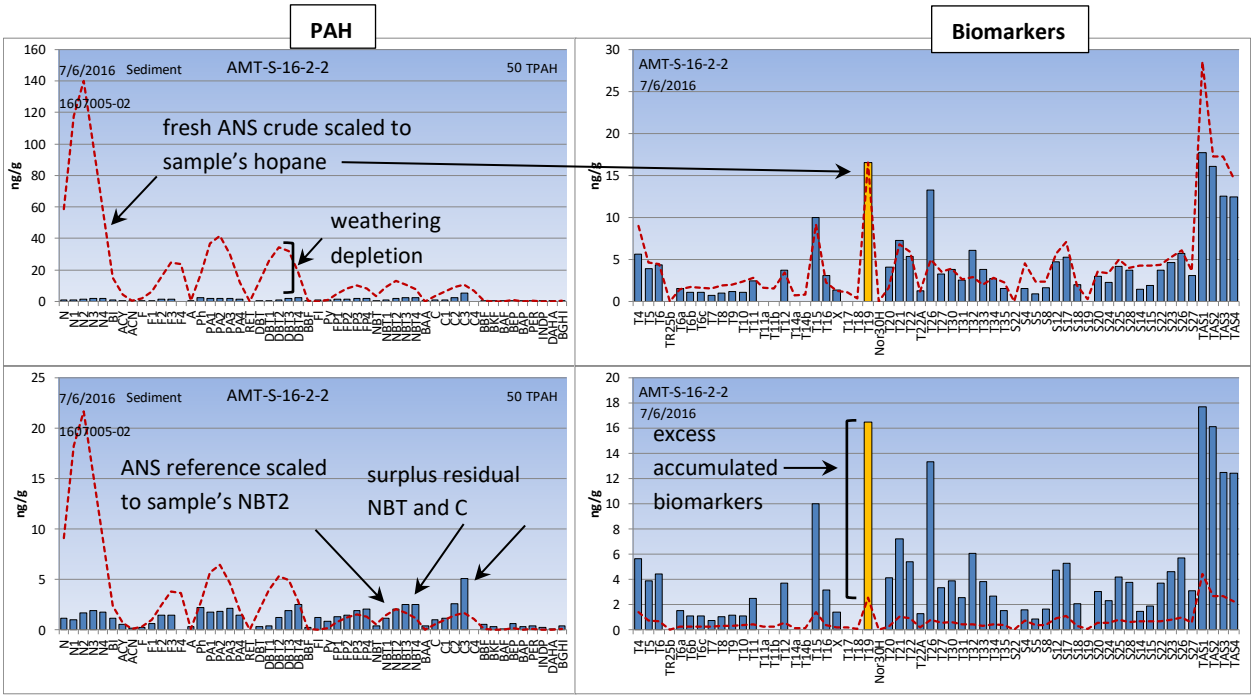


Figure 7. PAH and biomarker profiles of a representative 2016 AMT-S sediment sample overlaid with fresh ANS crude oil reference (dotted red lines) when alternatively scaled by the highly conservative biomarker, hopane (upper plots), versus the less recalcitrant PAH, NBT2 (lower plots). The lower plot biomarkers exceeding the reference profile (here pointing out hopane, colored gold) demonstrate an accumulated excess relative to the more easily degraded, residual PAH in this sample, plus an accumulation of the more recalcitrant NBT and chrysene PAH homologues.

Valdez Marine Terminal Sediments

The PAH, SHC and biomarker profiles from all three 2020 AMT-S sediment samples superficially appear very similar (Figure 8) but closer examination of PAH patterns from the first two replicates in the upper and middle plots show significantly elevated levels of combustion products outside of the BWTF particulate-phase template. Parent PAH-

dominated phenanthrenes, fluoranthene/pyrenes, chrysenes, and HMW combustion products (BBF through BGHIP) contribute to the overall measured TPAH value, but these constituents are completely missing in the third replicate (lower left panel in the figure). The excess parent and alkylated naphthalenes (N, N1, N2, and N3) in all three samples are most likely derived from the Port's glacial and riverine sediment inputs (Payne et al., 2010a, 2010b, 2015, Payne and Driskell, 2017b, Saupe et al., 2005). However, the fluorene, dibenzothiophene, naphthobenzothiophene, and chrysene groups (Fs, DBTs, NBTs and Cs) in the third replicate (bottom left panel) show an ascending water-washed pattern consistent with a petrogenic source. The SHC profiles show the almost complete loss of the n-alkane components that would be expected from the particulate BWTF effluent (or recently spilled ANS oil) due to evaporation/dissolution processes and microbial degradation. The SHC patterns reflect the typical dominant contribution from terrestrial plant waxes (n-C_{25}, n-C_{27}, n-C_{29}, and n-C_{33}) with only a minor contribution from higher-molecular-weight C_{34} – C_{40} petroleum waxes. Although the biomarkers are a missing a few components, possibly reflecting background sediment dilution from riverine and glacial flour, the remaining constituents are a close match to the expected S/T profile template and demonstrate that they are sourced as ANS oil from the BWTF effluent. The norhopane (T15)/hopane (T19) ratios and the triaromatic steranes (TAS1 through TAS5) are particularly noteworthy in this regard. Thus, the overall patterns suggest a mixture of petroleum-sourced and combustion-derived PAH plus background naphthalenes.

Between 2011 and 2020, the changes in the PAH and SHC patterns reflect different sources and concentration-dependent, weathering behavior (Figure 9). Specifically, in 2011, the higher-molecular-weight PAH were almost exclusively pyrogenic as recognized by their patterns of a dominant parent PAH with the alkylated homologues decreasing in a descending stair-step pattern (note red downward sloping arrows in Figure 9, top panel). This pattern persisted with the phenanthrenes in 2017 through 2019; however, the other PAH over the last three sampling periods have been characterized by more of a petrogenic pattern where the parent PAH (FL, DBT, PY, C) within each group is generally less than the C-2 or C-3 homologues yielding the hump patterns denoted by the red "tents" in 2017 and 2019. In 2020, a mixed source pattern was again noted but with differences among the replicates. Two replicates (top two panels in Figure 8) had mixed sources, as shown in the bottom profile from the time-series (Figure 9) but the third replicate (bottom profile in Figure 8) is almost exclusively a petrogenic water-washed profile (parent PAH < C1 < C2 < C3, etc.). This is one of the first instances where source signatures are so dramatically different among sediment replicates.

The SHC profile trends since 2011 reflect more background, terrestrial-plant-wax, biogenic inputs as reflected in the alternating spiking of the odd- vs. even-numbered-carbon n-alkanes between n-C_{23} and n-C_{29} (Figure 9). In the 2011 SHC plots, the alkanes exhibited a mix of biogenic n-alkanes and higher-molecular-weight C_{32}-C_{36} petroleum waxes (Figure 9 top right panel). The 2017 and 2018, AMT-S SHC patterns were very similar in reflecting lower relative contributions of high-molecular-weight petrogenic waxes compared to 2011. In 2019 and 2020, the petrogenic waxes were much, much lower compared to the terrestrial plant waxes. Because the absolute concentrations of the petrogenic waxes in 2017 and 2028 are relatively constant (generally between 40 to 100 ng/g), the increasing terrestrial-plant-wax contributions since then suggest greater background sediment contributions (riverine and glacial flour) over this period.

Considering the very low but higher-trending TPAH levels since 2013 (Figure 6), the transitions from pyrogenic patterns between 2011 and 2015 to petrogenic or mixed petrogenic/combustion sources in 2017 through 2020 presumably reflect a dynamic balance between variable PAH loads from BWTF effluent and accumulation of pyrogenics (soot). Because background combustion product or soot accumulation at GOC-S is over two-times lower

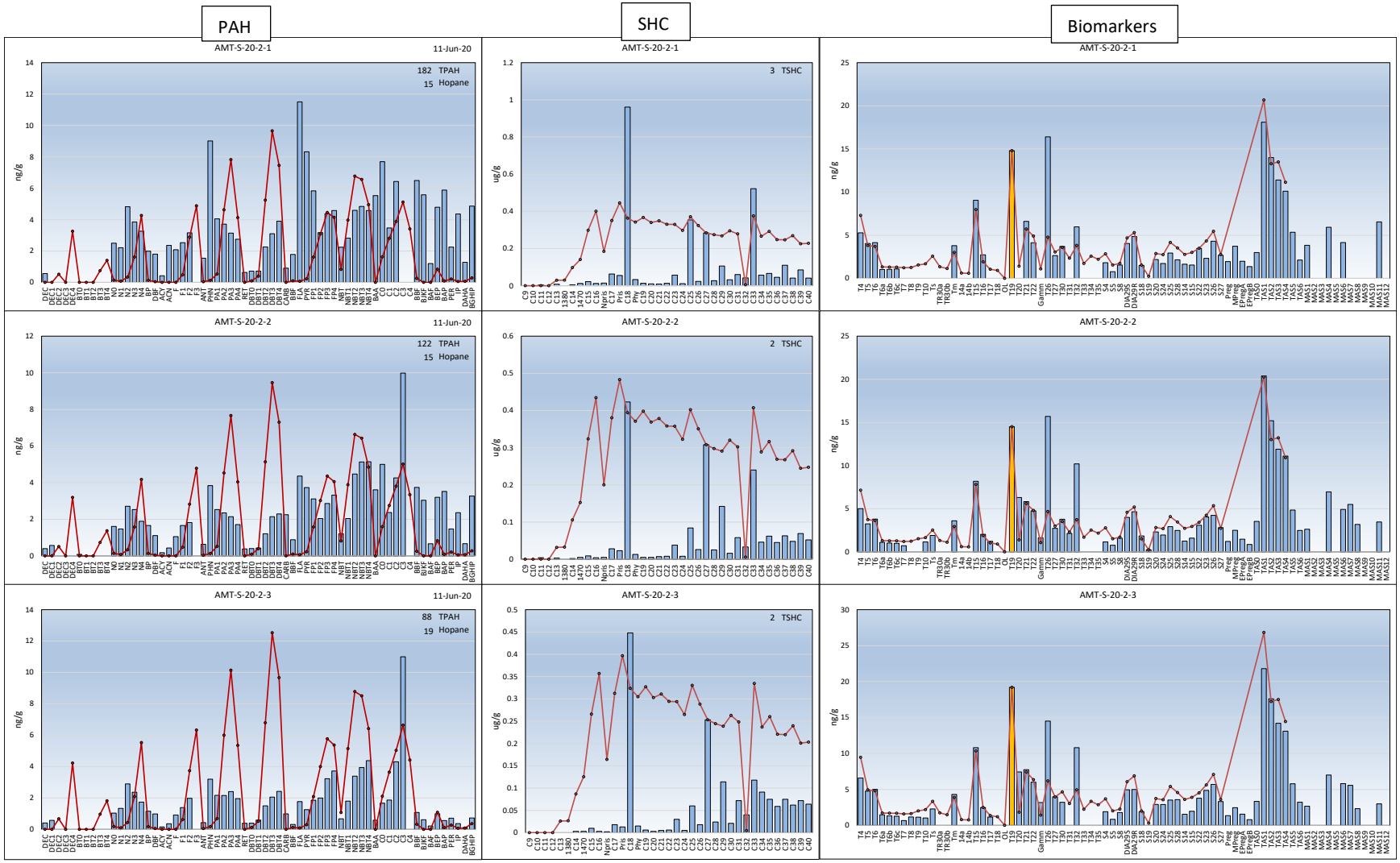


Figure 8. PAH, SHC, and biomarker concentrations and profiles of 2020 AMT-S sediment replicates with mixed background, petrogenic, and combustion sources. The dotted red line in the PAH and biomarker profiles is the July 2016 particulate-phase BWTF reference (Figure 4 and Figure 5) normalized against the sample's hopane; SHC ref normalized to C27. Biomarkers confirm the presence of a weathered ANS profile in the PAH.

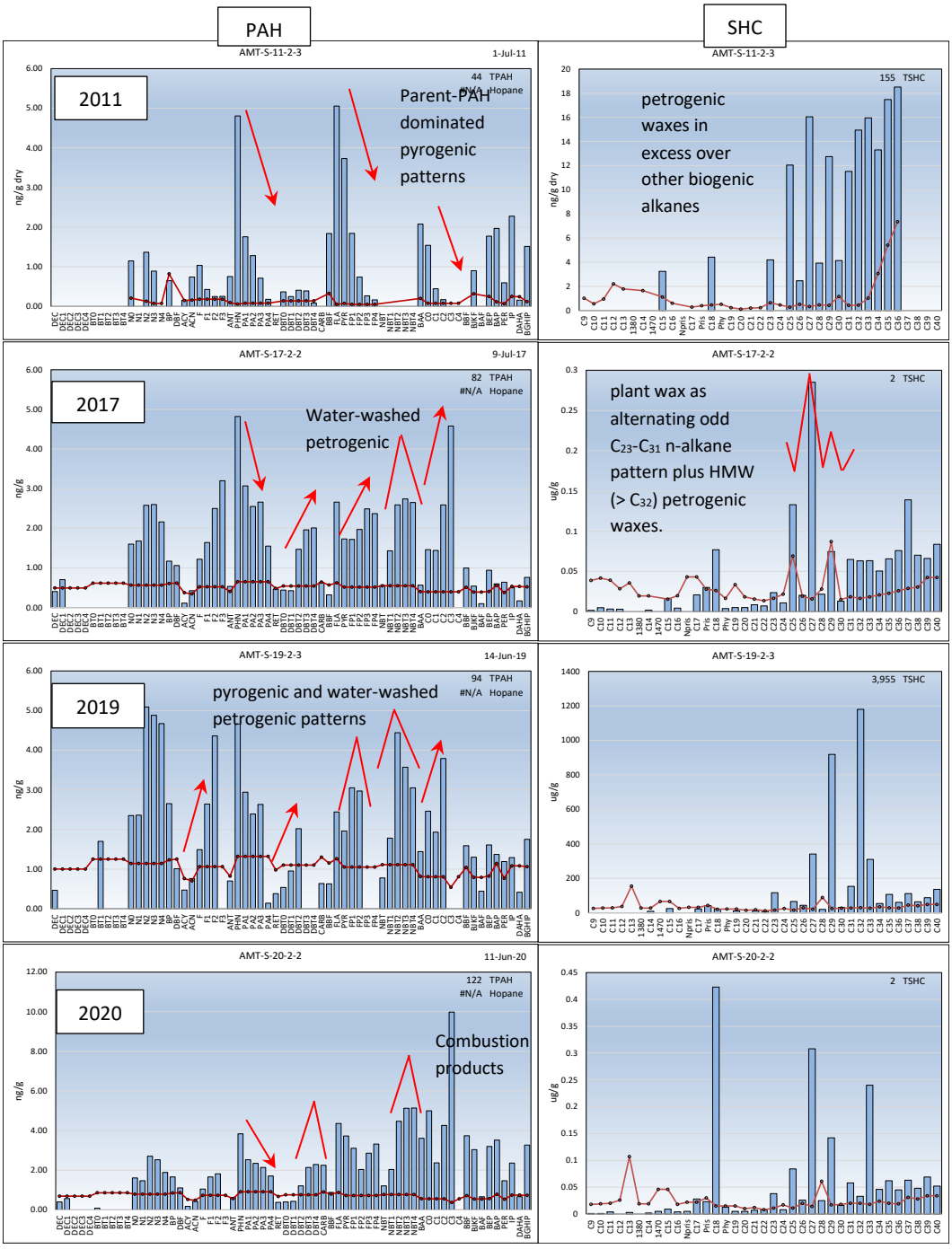


Figure 9. Representative PAH and SHC signatures of AMT sediments between 2011 and 2020 showing the progression from a primarily pyrogenic PAH signature to a mix of pyrogenic and water-washed petrogenic components with increasing terrestrial biogenic SHC and decreasing higher-molecular-weight residual petrogenic waxes through 2020. Note dominance of 2019 background naphthalenes (N-N4).

(see next section), the likely source at AMT-S is tanker and workboat exhaust while working at or near the berths. Despite the variable PAH patterns, the biomarker patterns over this timeframe (Figure 10) suggest a consistent, continued accumulation of BWTF-derived ANS components even as the PAH patterns reflect extensively weathered oil and the variable addition from combustion sources.

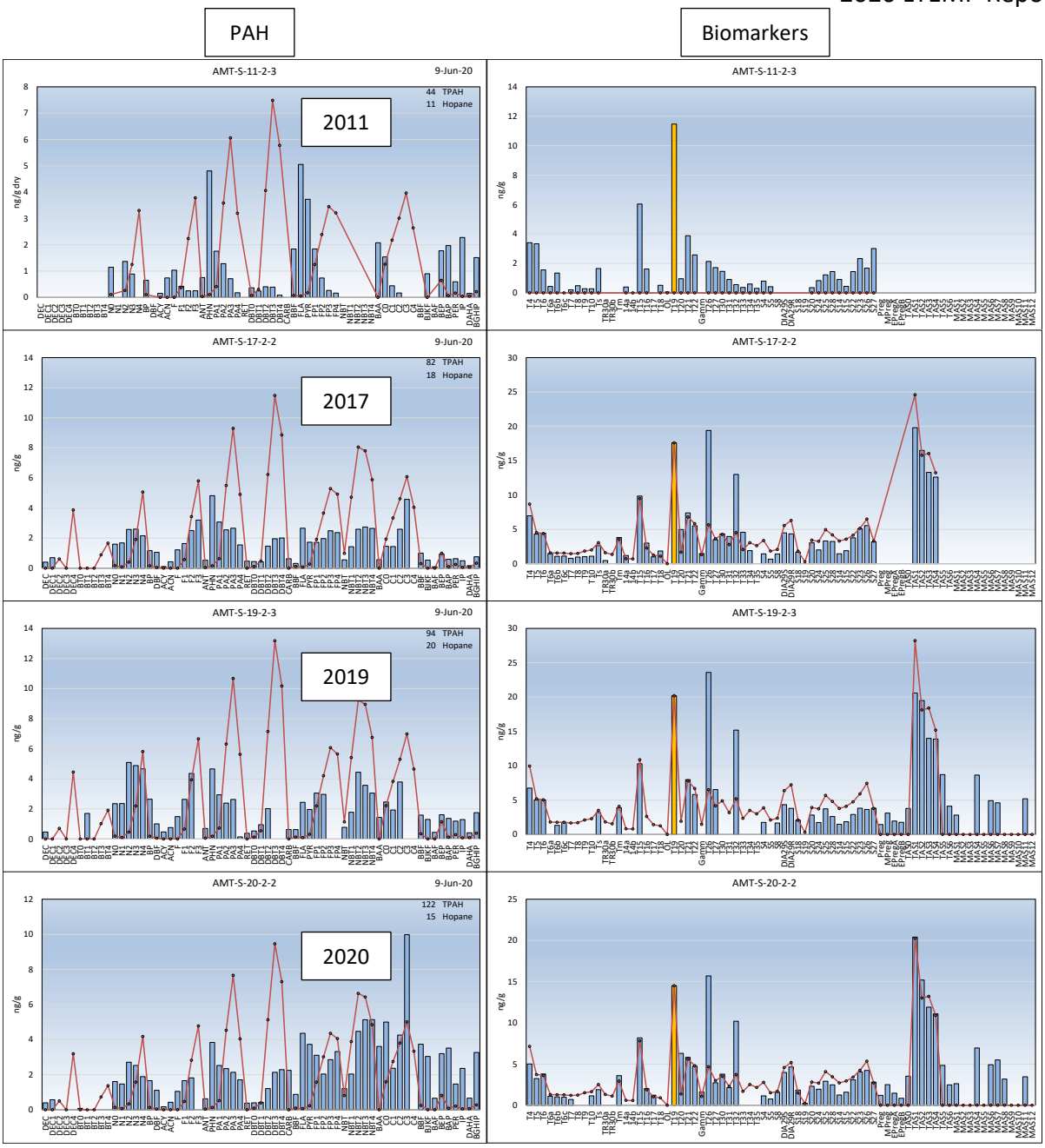


Figure 10. Time-series AMT-S sediment PAH profiles from 2011 and 2017 through 2020 along with the biomarker profiles obtained after introducing those analyses to LTEMP in 2011. The dotted red line denotes the PAH and biomarker profiles from the July 2016 BWTF particulate-phase normalized to hopane (see Figure 4 top). Biomarkers confirm ANS oil in all samples. Reporting of TAS biomarkers began in 2017, MAS biomarkers in 2018.

Gold Creek Sediments

Sediments at the shallower (28-30m deep), GOC-S reference site have consistently exhibited lower TPAH concentrations than AMT-S throughout the duration of the program (Figure 6). In 2013, the GOC-S samples, like AMT-S, showed record-low PAH concentrations but unlike the sediments at the terminal that rebounded slightly in 2015, the GOC-S levels remained in single digits (no sampling occurred in 2014). TPAH concentrations then increased modestly from ~6 ng/g in 2015 to around 20 ng/g DW in 2016 and remained at this level through 2018. In 2019, the TPAH concentrations increased again to around 20 ng/g, which was tentatively attributed to a surge in background

naphthalenes and increased levels of combustion products in one replicate. In 2020, the TPAH levels at GOC-S ranged from 24-33 with a mean of 30 ng/g DW (Figure 6, Table 3). Although the TPAH rise from 6 to 30 ng/g represents a 5-fold increase since 2015, the values are still quite low.

In 2020, remarkable fidelity in both profiles and concentrations was observed in the three GOC sediment grabs (Figure 11). As in previous years, the PAH profiles suggest little or no petrogenic inputs from the terminal. They are instead dominated by ubiquitous low-level background naphthalenes and combustion products. This is nicely demonstrated by the cluster of naphthalenes (N), fluorenes (F), phenanthrenes/anthracenes (PA), and chrysenes (C) analytes appearing in excess of the red reference overlay of the particulate-phase BWTF effluent (Figure 11). The SHC patterns show a mix of trace-level marine planktonic alkanes (n-C_{18} plus odd-carbon-numbered, terrestrial-plant-wax components (C_{23}, C_{25}, C_{27}, C_{29}, C_{31}) but none of the residual higher-molecular-weight (C_{33}-C_{40}) petrogenic waxes associated with the terminal (Payne et al., 2015, 2017b).

From 2011 through 2017, the GOC sediment PAH patterns have been essentially identical, dominated by background naphthalenes and pyrogenics, with TPAH levels modestly increasing (particularly in 2019 due to a spike in higher-molecular-weight combustion products; Figure 12, bottom panel). The SHC profiles during this period have always been biogenic, reflecting primarily only background inputs of terrestrial plant waxes. From biomarker data (Figure 13), in addition to natural background biomarkers, low-level traces of some ANS-derived biomarkers are accumulating in the GOC sediments. While these data are sparse (with many missing components), the observed biomarkers and diagnostic ratios, norhopane (T15) to hopane (T19), confirm ANS-derived hydrocarbons, presumably from the BWTF. But despite the biomarkers, there is no evidence of BWTF-derived PAH or SHC accumulation at GOC. The few biomarkers appear to be the sparse remains of a highly weathered signal transported across the fjord.

The similarity of the PAH and SHC profiles in time-series plots (Figure 12) further supports the notion of a relatively consistent source over time. In addition to the pyrogenic components, GOC sediments also contain a moderate and relatively invariant suite of above-MDL parent (N) to N4 naphthalenes (Figure 12), which are also present in the sediments at AMT-S (Figure 10). These background PAH are believed to derive from glacial and riverine sediment input to the Port (Payne et al., 2010a, 2010b; Saupe et al., 2005). Similar naphthalene contents were seen to varying degrees in all 10 major Cook Inlet rivers surveyed during the 2008 EMAP program (ICIEMAP, Susan Saupe, personal communication, 2009). In these Cook Inlet sediment samples, there was a tentative link to peat inputs (Lees et al., 2000; Saupe et al., 2005).

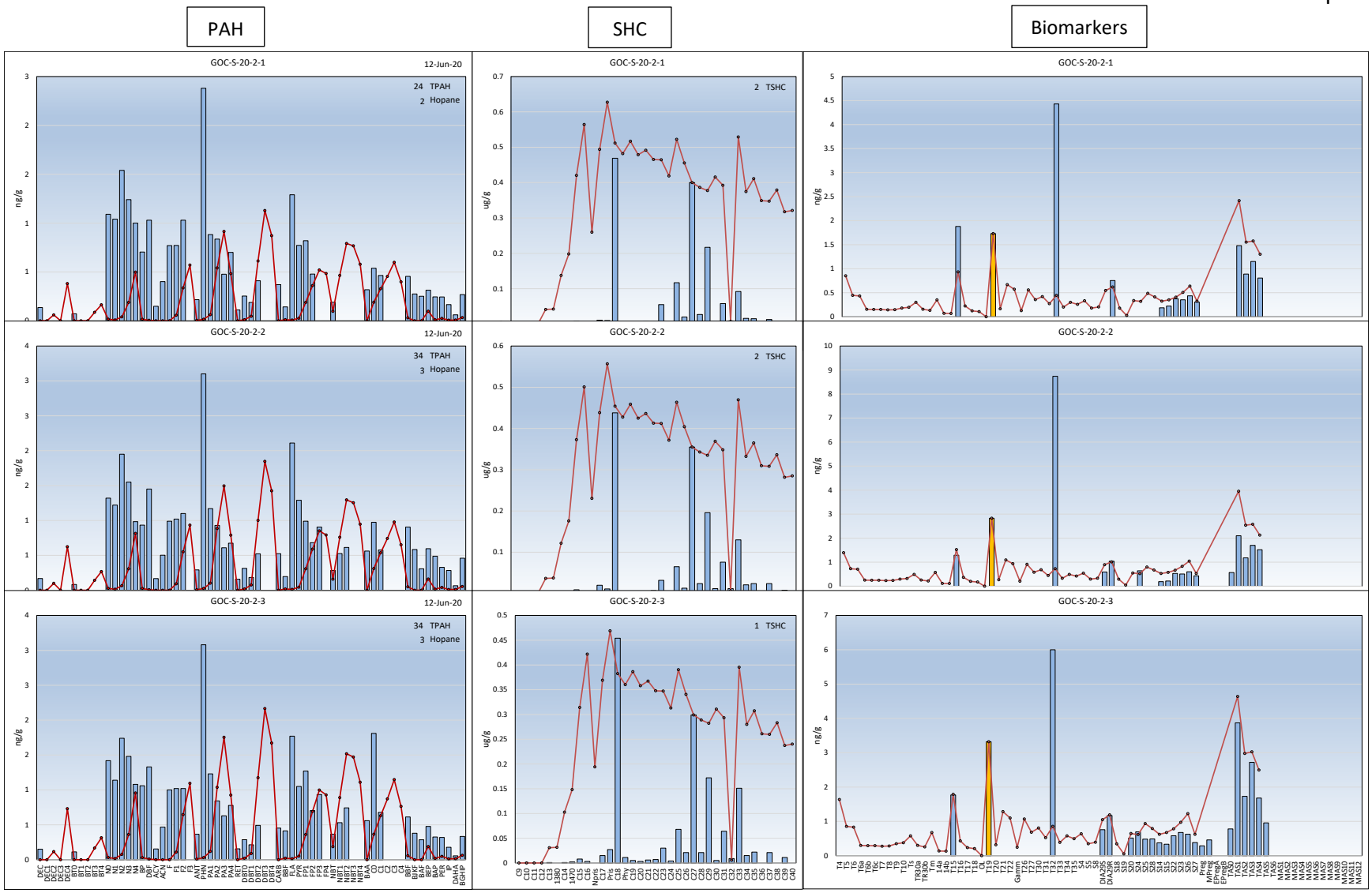


Figure 11. PAH, SHC, and biomarker profiles of 2020 GOC-S sediment replicates. The dotted red line is July 2016 BWTF particulate phase reference (Figure 4) normalized against the sample's hopane; for SHC normalized to C_{27} (Figure 4). The T32 biomarker spikes are laboratory artifacts.

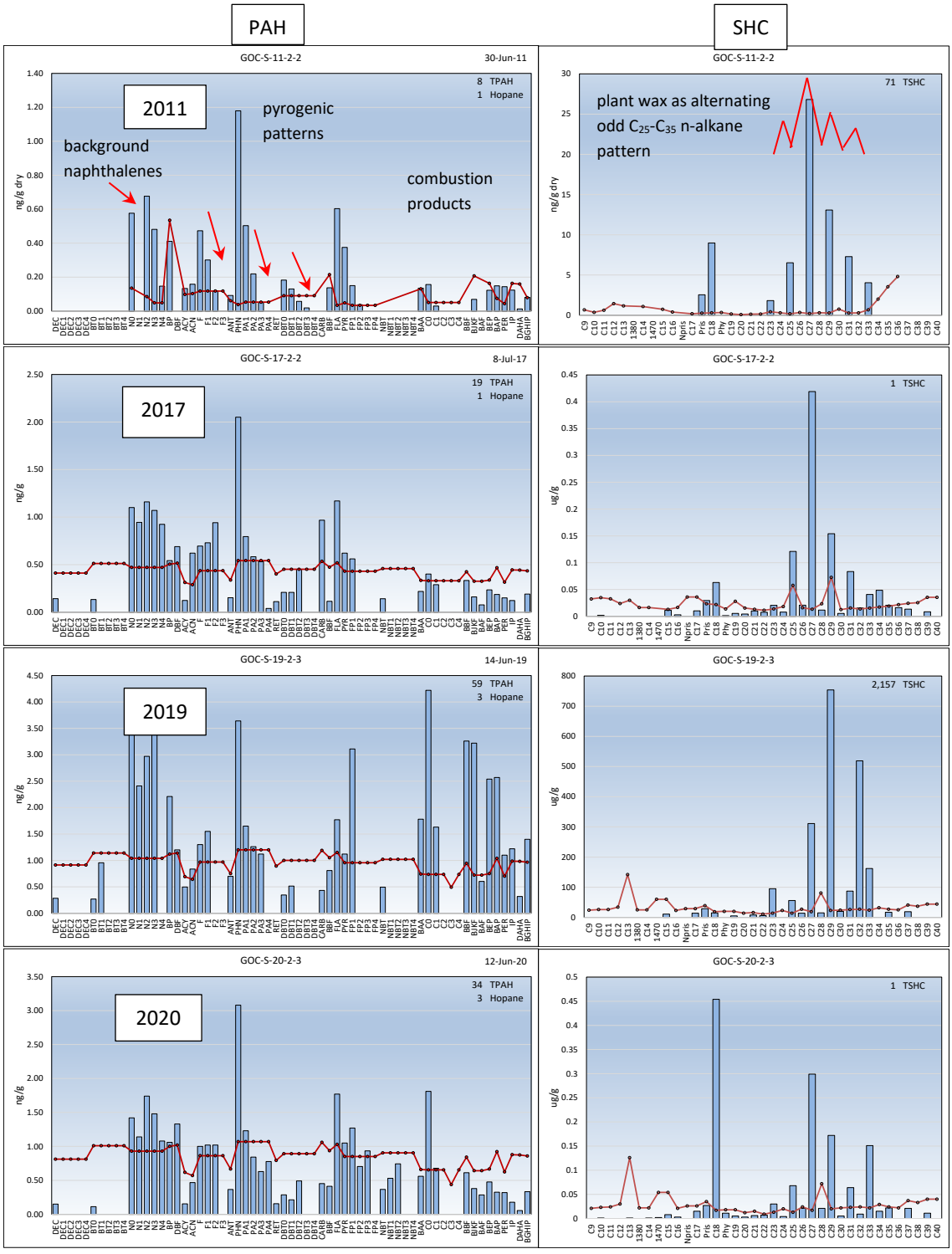


Figure 12. Representative PAH and SHC from GOC-S sediments between 2011 and 2020 showing very similar, background naphthalene components and pyrogenic, parent-dominated, PAH and higher-molecular-weight combustion products. SHC patterns and concentrations reflect terrestrial (plant wax) biogenic inputs since 2011. Red dashed line is sample-specific MDL.

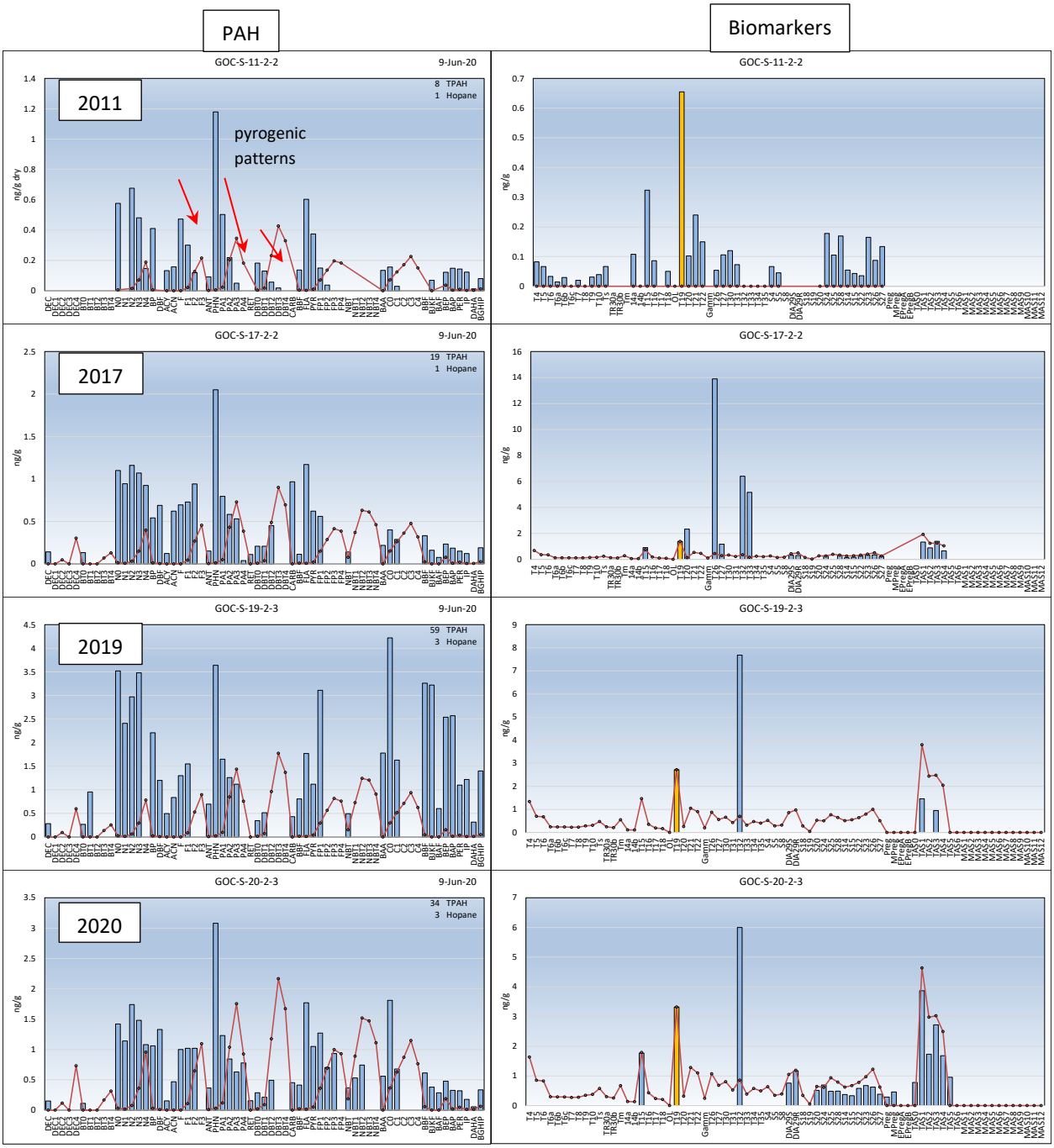


Figure 13. GOC-S sediment PAH and biomarker profiles between 2011 and 2020. The dotted red line is July 2016 BWTF particulate-phase reference. Analyses in 2011 by ABL did not include the triaromatic steroid biomarkers (TAS); later included in the analyses by Alpha/NewFields.

PORT VALDEZ MUSSEL TISSUES

HISTORICAL TRENDS IN PORT VALDEZ MUSSEL TISSUES

Reflecting the changing operations at the terminal, oil discharge into Port Valdez from terminal operations has been declining over the last two decades. This trend reflects a combination of reduced BWTF discharge volumes from historically decreased ANS oil production, the transition from single-hulled to double-hulled tankers with segregated ballast tanks, and improved BWTF efficiency in removing particulate/oil-phase PAH. As a result, over the last several years, contamination in mussels at the AMT-B sampling site has also been generally shifting away from the terminal's earlier petrogenic profiles to background dissolved-phase or pyrogenic (combustion-derived) PAH patterns. As noted in the sediments section (above), decreasing petrogenic inputs have made the background and pyrogenic inputs more visible.

Although historically TPAH concentrations in mussels sampled from both the AMT-B and the background-reference site at GOC-B were commonly reported in hundreds of ng/g, the concentrations dropped to ~80 ng/g levels in 2002 (Figure 14), and with several spill-related exceptions discussed below, they have generally ranged from ~10 to less than 100 ng/g DW through 2020. The first major exception occurred with a mystery diesel spill at GOC-B in the summer 2004 when TPAH concentrations approached 1,000 ng/g. By the 2005 collections, the diesel PAH at GOC-B were long purged and concentrations were back in the pre-spill range around 80 ng/g. They continued to gradually decline at both locations until 2010, after which the concentrations at GOC-B equaled or slightly exceed those at AMT-B in 2011 and 2012. In the summer of 2013, collections were very low and only near-MDL, traces of petrogenic components were present. No samples were collected in 2014 due to a program hiatus, but in 2015, AMT mussels' PAH increased slightly and transitioned into a primarily dissolved-phase, naphthalene pattern while the GOC-B tissues were more equivocal (see below). In 2016, another mussel collection site at Jackson Point (JAP), east of the terminal, was added with the intent of capturing any east-to-west gradients associated with the BWTF discharge. At that time, the TPAH concentrations near the Terminal ranged from ~70-100 ng/g, while they jumped to 195 ng/g at GOC-B due to yet another localized diesel spill across the Port. In 2017, the TPAH concentrations at all three Port Valdez stations ranged from 46 to 63, clustering together around 30-35 ng/g in 2018 and 2019 (Figure 14 and Table 5). At these exceptionally low levels, the individual PAH components at all three Port Valdez sites in 2018-19 were all below-MDL. Against these low values it was easy to observe the diesel spill at GOC in 2016 and two terminal spills of ANS crude oil in September 2017 and April 2020 (discussed further below).

Because of the below-MDL concentrations and the presence of the same PAH profiles in all the field samples and associated laboratory method blanks, source identifications for the routinely collected LTEMP tissue samples from 2018 and 2019 were not possible (Payne and Driskell, 2019, 2020). These findings again reflected the clean environment from which the samples were collected. However, an isolated and localized September 2017 spill incident with the Berth 5 Tanker Loading Arm again demonstrated the utility of mussels for monitoring and detecting oil contamination (Payne and Driskell, 2018b, 2019). Mussels from the event exhibited elevated TPAH levels (Figure 14) from the spill and then, within three months, purged themselves to background levels (Figure 15).

Similarly, in April 2020, an estimated 635 gallons (16 barrels) of ANS crude oil from an overflow sump at the terminal reached the intertidal zone (ADEC 2020). This resulted in elevated TPAH at all three Port Valdez sites, JAP, AMT and GOC (438, 256, and 194 ng/g respectively) (Figure 14). The PAH profiles at the traditional LTEMP station at the eastern Jackson Point site showed a distinct petrogenic signal but by June 2020, the levels had dropped back to the 51-165 ng/g range (discussed further below). Mussels within the "Hot Zone" immediately adjacent to the spill were heavily oiled (approaching 230,000 ng/g) with obvious ANS-crude-oil profiles. Another report and journal manuscript are in preparation addressing mussel depuration rates and transcriptomic responses.

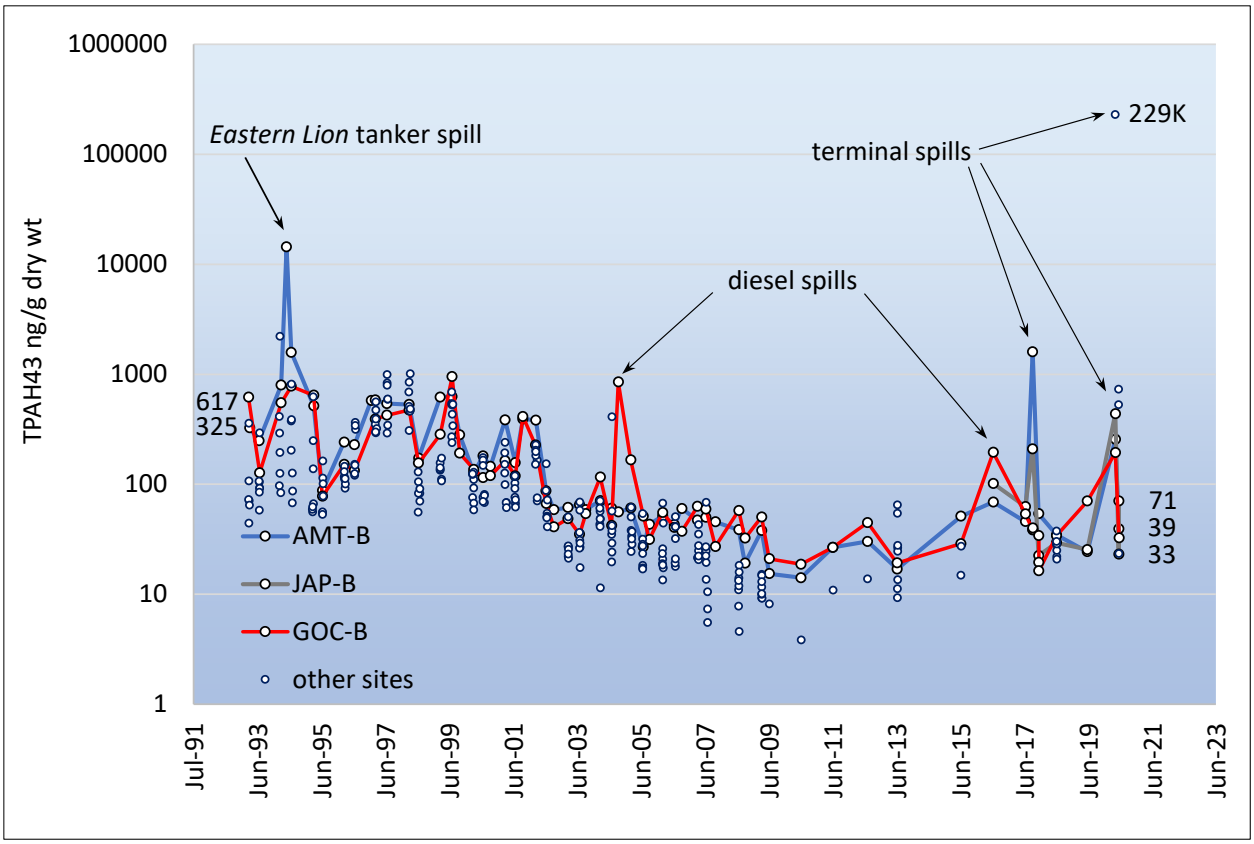


Figure 14. Time series of mean mussel TPAH43 concentrations comparing 2020 AMT-B, JAP-B and GOC-B with prior LTEMP collections at other regional sites (open circles). Note the log scale for TPAH concentrations.

Table 5. Time series of mean TPAH43 (ng/g DW, n=3) from AMT-B, GOC-B, and JAP-B mussels, 2008-2020.

	Jul-08	Sep-08	Apr-09	Jul-09	Jul-10	Jul-11	Jul-12	Jul-13	Jul-15	Jul-16	Jul-17	Jun-18	Jun-19	Jun-20
mean TPAH43														
AMT-B	39	19	38	15	14	30	27	17	51	69	46	35	24	39
GOC-B	58	32	50	21	19	27	45	19	29	195	54	34	70	33
JAP-B										102	63	29	25	71
± SE of means														
AMT-B	5.3	1.8	6.9	0.8	0.9	2.1	2.8	3.0	9.1	13.9	0.8	4.5	12.9	19.9
GOC-B	6.0	3.8	2.8	1.1	1.2	3.0	6.6	2.2	3.1	91.0	3.0	2.2	37.1	16.3
JAP-B										12.0	17.6	0.8	12.7	41.3

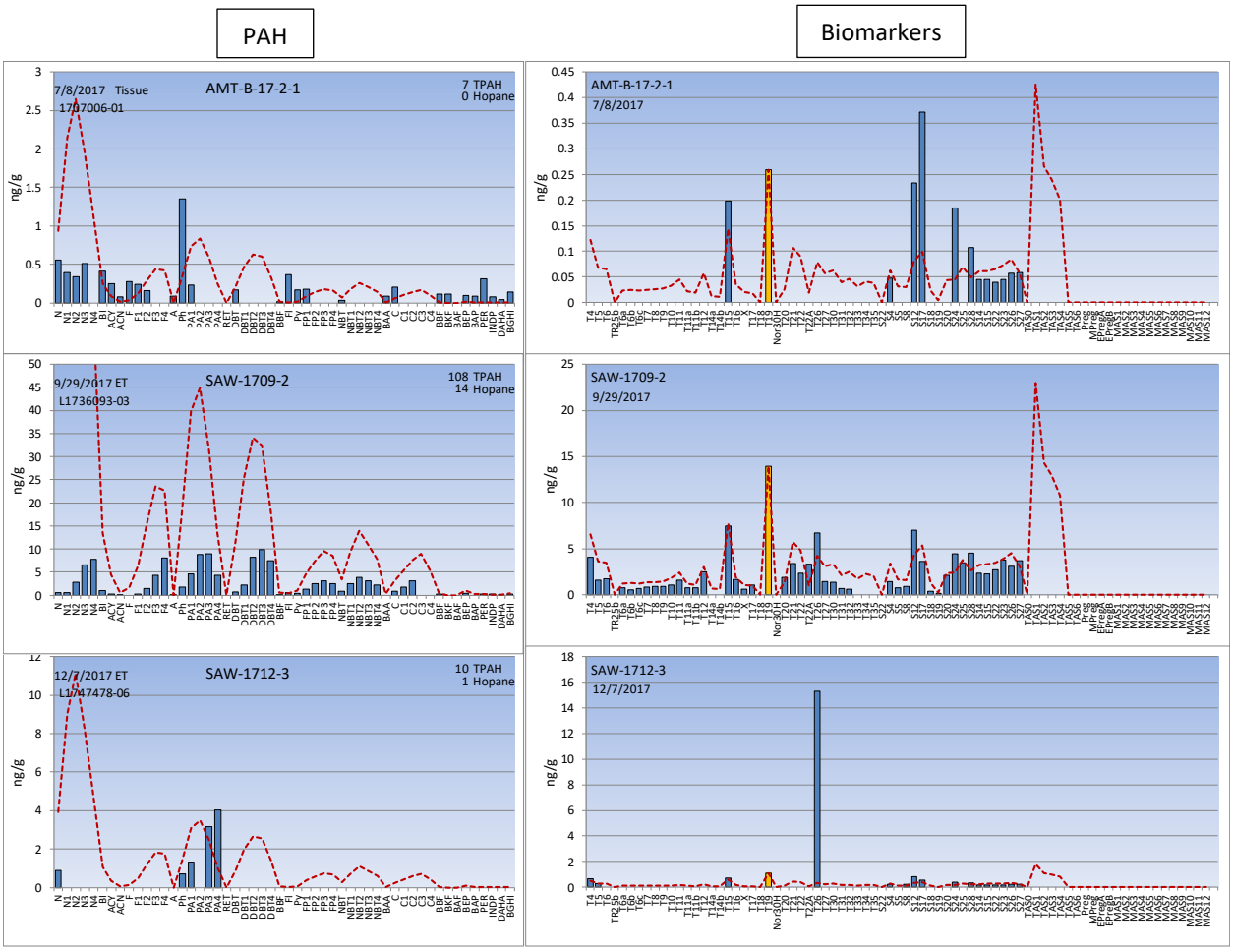


Figure 15. PAH and biomarker patterns at AMT-B relating to the tanker loading arm spill at the terminal in September 2017. The samples show the background profile from the normal LTEMP collections pre-spill (top, July 2017, TPAH 7 ng/g), the weathered oil in the mussels ~one-week post spill (middle, 108 ng/g), and three months post-spill (bottom, 10 ng/g). Dotted red lines represent fresh ANS crude oil profiles normalized to the sample's hopane. The below-red-line gaps (middle left panel) show loss (evaporation and dissolution weathering) of lower-molecular-weight PAH. Biomarker T26 is a laboratory artifact.

Non-Spill-Related Patterns in Port Valdez Mussels

From 2020 LTEMP samplings, representative PAH, SHC, and biomarker plots sampled two months post spill (Figure 16) show near- or below-MDL, mixed pyrogenic-dominated PAH patterns and biogenic SHC. All replicate mussel samples from the three Port Valdez sites are shown in Appendix 2. There are slightly elevated (and more complex but still below MDL) traces of residual components from the April 2020 VMT spill at AMT and JAP (seen in water-washed dibenzothiophene, naphthobenzothiophene, and chrysenes (red tent) PAH patterns) but the GOC profile is derived solely from local combustion products. The associated quality-control (QC) method blank run with these samples confirms that the observed PAH in the field samples most likely truly represent trace-level products and not laboratory artifacts. Identical SHC patterns from these sites reflect only marine biogenic (n-C15, n-C17, and pristane) plus odd-carbon-number n-alkane traces (n-C23, n-C25, n-C27, n-C29, and n-C31) derived from terrestrial plant waxes. Biomarker traces were only observed at Jackson Point but with no definitive pattern, no source inference can be asserted.

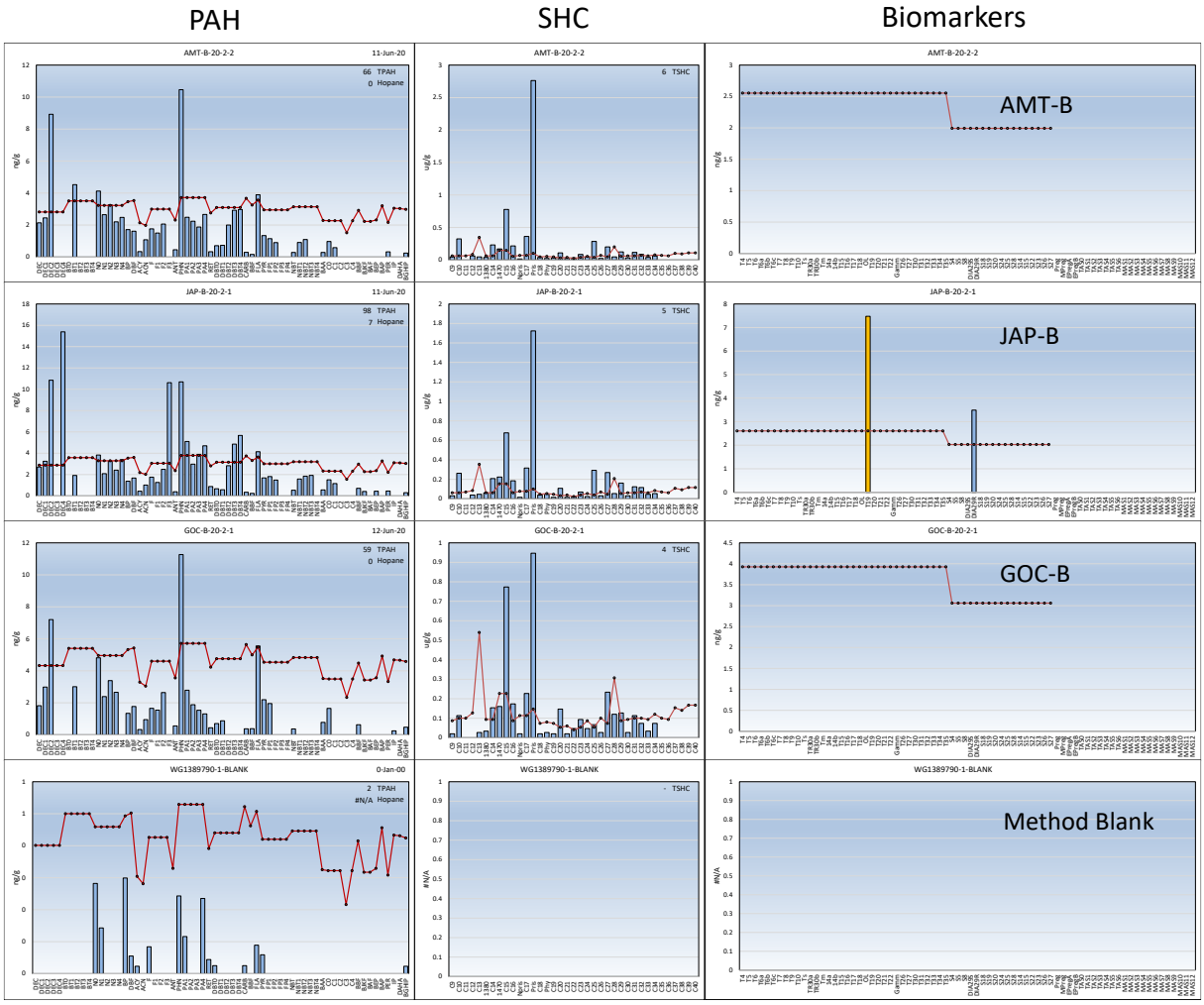


Figure 16. Representative LTEMP Tissue results from June 2020 showing near- or below-MDL, mixed pyrogenic-dominated PAH patterns and biogenic SHC at AMT, JAP, and GOC along with an associated laboratory method blank. The dotted red line is the sample's method detection limit. There is a slightly elevated (but still below MDL) and more complex PAH pattern at AMT and JAP which may indicate traces of residual PAH from the VMT spill in April 2020 but this is not reflected in either the SHC or biomarker patterns.

Valdez Marine Terminal Historical Mussel Patterns, Pre-2020 Spill

To illustrate relevant points in the VMT times series, selected years' results are presented and discussed in comparison to the current year. For the AMT site (Figure 17), recent PAH data showed the presence of water-washed naphthalenes (possibly petrogenic) in 2008 and, in 2015, an increase in dissolved-phase naphthalenes (plus above-MDL traces of combustion products) (Figure 14). Dissolved-phase naphthalenes were also observed to a lesser extent in 2015 at GOC (discussed in later section). Recall that the forensically sourcing dissolved-phase PAH is problematic; as the most abundant and dissolvable PAH, naphthalenes (and other low-molecular-weight PAH) can

derive from any source and cannot be identified from just their profiles. For the 2015 AMT pattern, however, the naphthalene pattern did not match with BWTF effluent's naphthalenes (where the parent PAH is depleted in the processing), so presumably they were derived from another unknown source.

In addition to the dissolved-phase components, parent-PAH-dominated combustion products (e.g., phenanthrene (Ph), fluoranthenes/pyrenes (FL/PY), and perylene (PER)) are occasionally observed (Figure 17).[1] In both 2018 and 2019 (not shown) collections, most of the below-MDL components with the exception of the higher-molecular-weight (BBF through BGHI) combustion products in 2018 were also associated with the laboratory blanks and were thus ignored. In June 2020 (two months after the VMT spill), the PAH were mostly at below-MDL levels and showed a distinct pyrogenic (combustion-derived) source.

The SHC data for 2008 and 2015 AMT samples (Figure 17) show contributions from marine biogenic sources (Payne et al., 2015) and in the majority of AMT tissues examined since 2008, the SHC have been dominated by biogenic constituents (e.g., n-C_{15}, n-C_{17}, and pristane) with only very rare observations of petrogenic components. The 2018 and 2020 SHC profiles are nearly identical and show only biogenic-marine-plankton and terrestrial-plant-wax input with concentrations more that 10-times higher than, and profiles different from, those observed in the method blanks. Also, there was no indication of the sediment-bound, higher-molecular-weight n-C_{31} to n-C_{40} petroleum waxes (Figure 9) observed in the AMT mussels adjacent to the terminal.

[1] Perylene, a 5-ringed PAH, occurs in crude oil but also is naturally generated from biologic processes or early stages of diagenesis in marine sediments (Bence et al., 2007) and thus, potentially being of non-petroleum origins, is not considered for forensics nor included in TPAH summations when evaluating non-oil matrices.

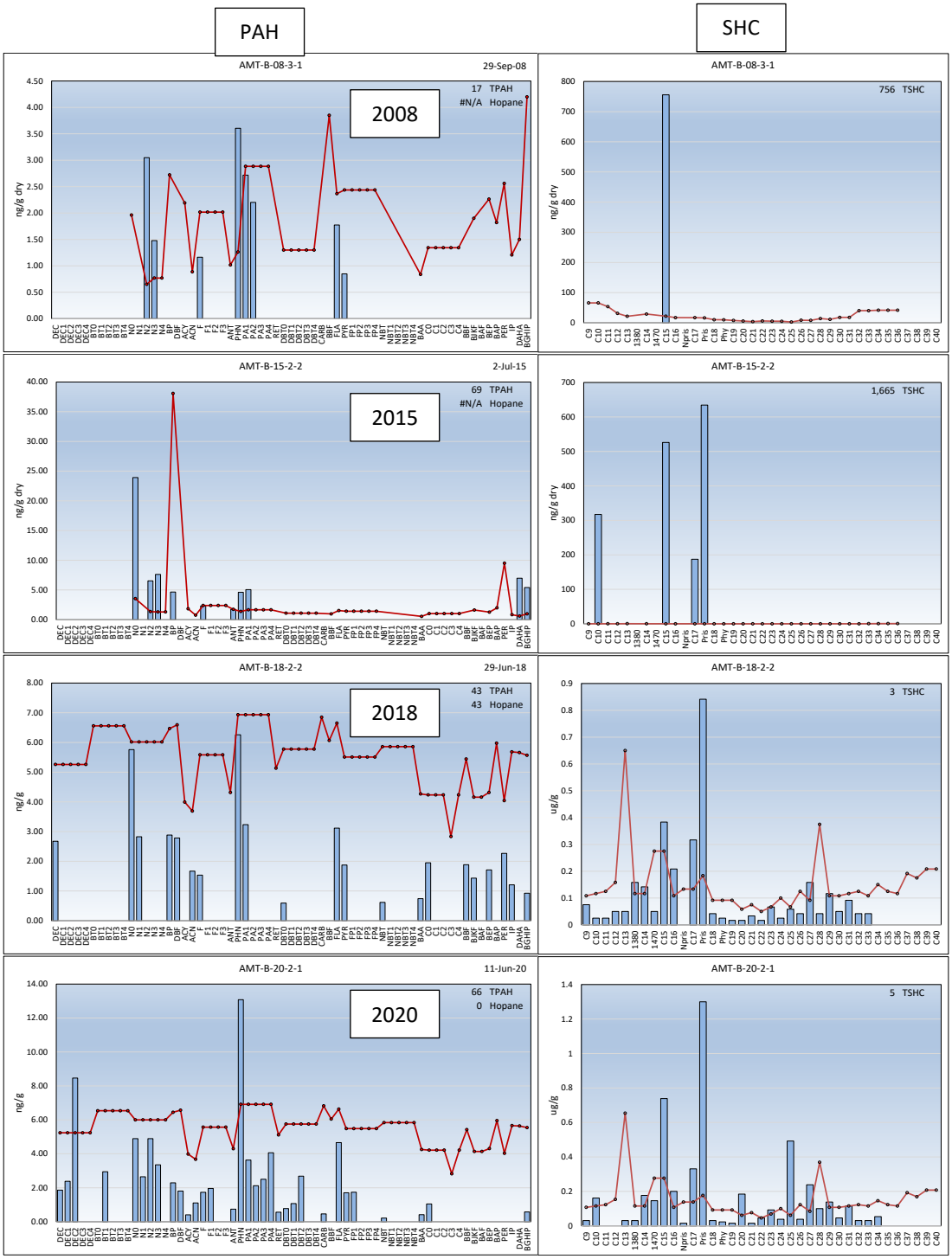


Figure 17. Time-series mussel PAH and SHC profiles from AMT-B. In 2008, the patterns show primarily below-MDL water-washed (possibly petrogenic) naphthalenes and combustion products (P/A and FL plus PY). In 2015, there are above-MDL dissolved-phase naphthalenes and trace-level combustion-product PAHs. In both 2018 and 2019, most of the below-MDL components are also associated with the lab blank. In June 2020, all of the below MDL PAH are derived from combustion products. Planktonic biogenic SHC (n-C_{15}, n-C_{17}, and pristane) are also present in most of the samples. The dotted red line denotes the sample-specific MDL.

JACKSON POINT MUSSELS

Because mussel samples were only collected from JAP starting in 2016, prolonged time-series data before that are not available. But comparisons of representative samples from 2016 through June 2020 (Figure 18) show the possible background contribution of glacial flour/riverine-sourced naphthalenes in 2017 along with trace-level, combustion-derived PAH in patterns not corresponding with the BWTF effluent. Unfortunately, 2018 and 2019 PAH sources cannot be assigned because the same components were detected in laboratory method blanks at similar below-MDL concentrations. The SHC reflect only background marine biogenic components (n-C_{15}, n-C_{17}, and pristane) plus terrestrial (n-C_{25}, n-C_{27}, and n-C_{29}) plant waxes.

Extra Jackson Point mussels were collected in connection with the April 12, 2020 VMT sump overflow spill. In these samples, there is unequivocal evidence of the uptake and depuration of PAH and biomarker components from the spilled oil (Figure 19 and Figure 20). Interestingly, the SHC did not show much accumulation at Jackson Point itself. Additional mussel collections in the "Hot Zone" closer to the release location did show significant uptake of all three analyte groups (Figure 19). These findings will be covered in another PWSRCAC report and manuscript (in preparation).

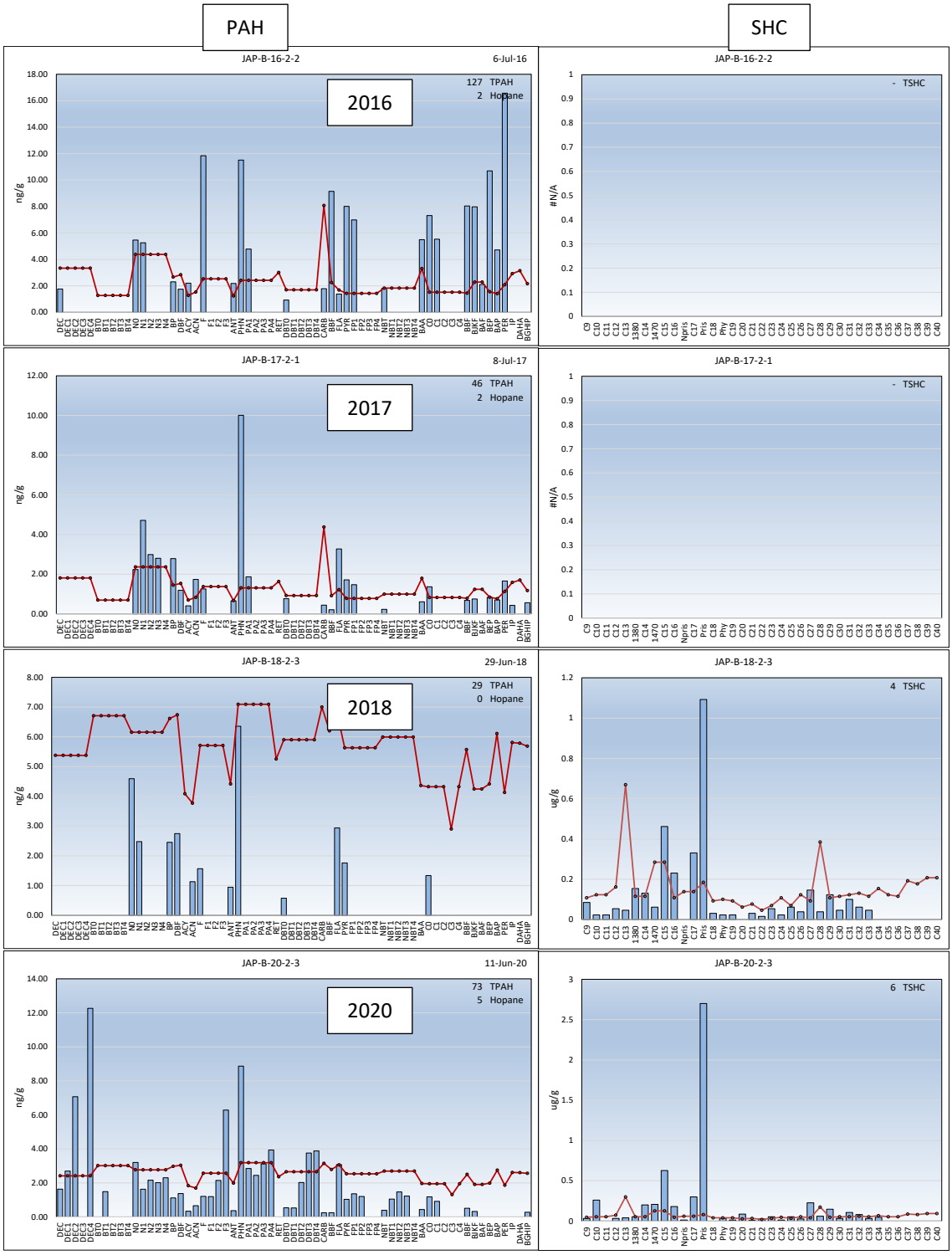


Figure 18. Time-series PAH and SHC profiles of mussels collected at JAP in 2016 through 2020 showing primarily trace-level dissolved- and (possibly) particulate-phase background naphthalenes plus combustion product PAHs (Ph, FL, PY, C, BBF, BKE, BEP), and perylene (PER) in 2016 and 2017. The below-MDL PAH in 2018 are suspected of being procedural artifacts associated with the laboratory method blanks). The dotted red line denotes the sample-specific MDL.

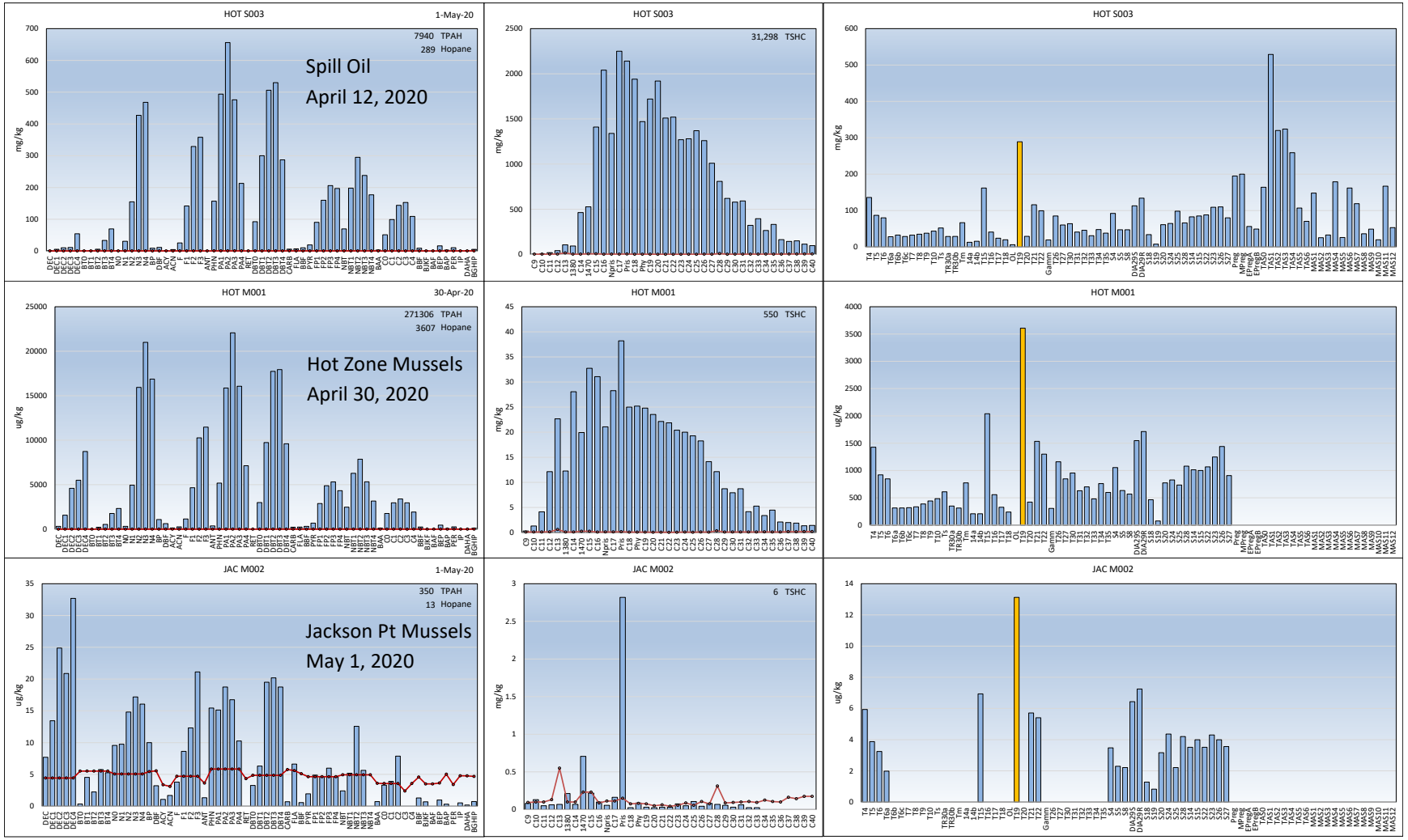


Figure 19. April 2020 VMT spilled oil, Hot Zone mussels (TPAH 271,000 ng/g DW), and Jackson Point mussels (TPAH 350 ng/g DW) collected approximately three weeks after the spill. TAS and higher-molecular-weight biomarkers are measured in oil but are not available for mussel extracts (gap on right). The dotted red line denotes the sample-specific MDL.

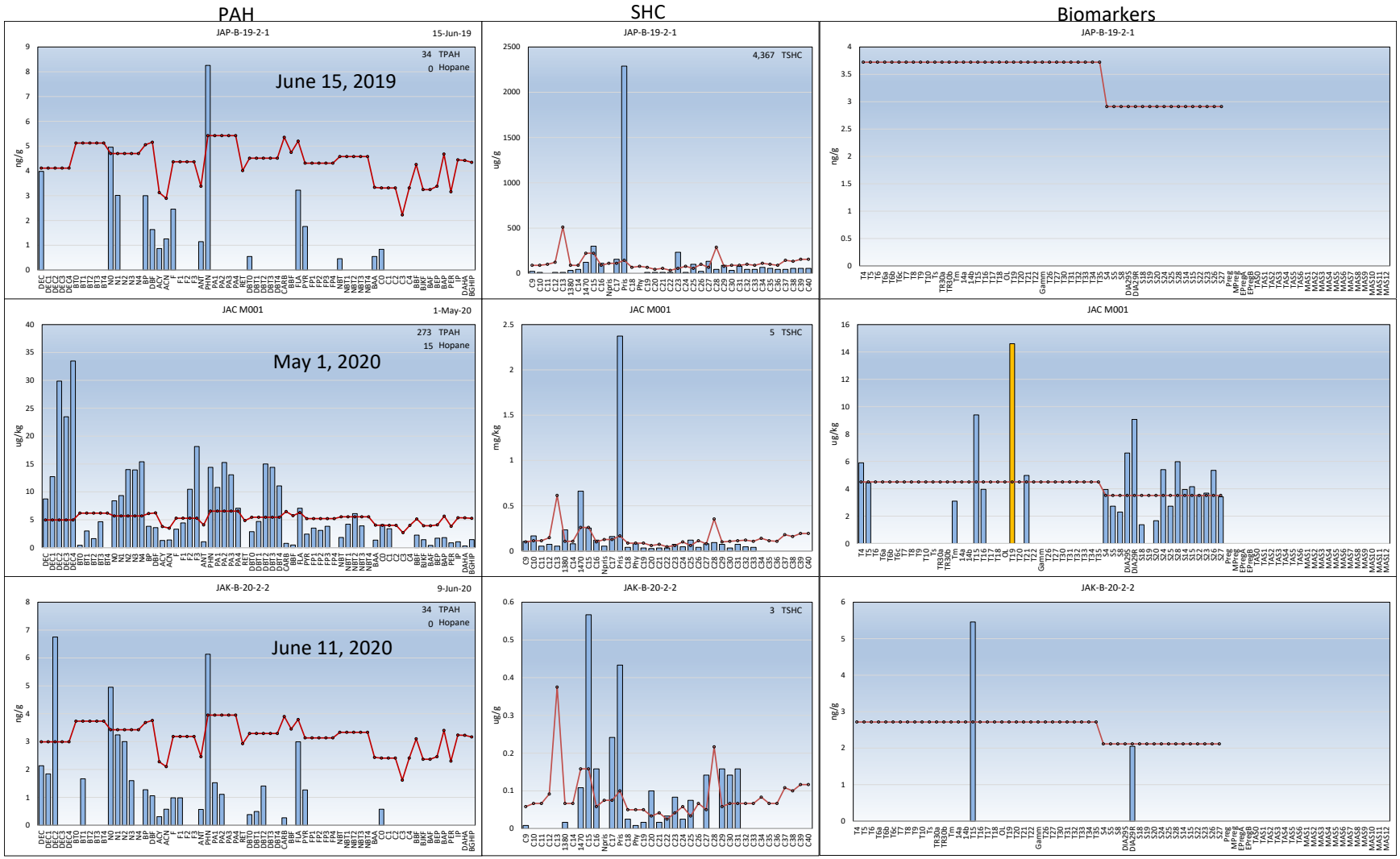


Figure 20. Jackson Point Mussels histograms showing the June 2019 unoiled background pattern, the May 2020 petrogenic profile collected three weeks post spill, and the June 2020 LTEMP profile demonstrating the recovery to a mixed petrogenic and biogenic pattern. The dotted red line denotes the sample-specific MDL.

GOLD CREEK MUSSELS

At GOC, average mussel TPAH levels during the early years of the program (1993-2003) were consistently lower than or very close to those at AMT-B (Figure 14 and Table 5). In those GOC profiles, mixed dissolved-phase petrogenic and pyrogenic signals were common and roughly trending with similar-phase patterns or discharge events at AMT-B (Payne et al., 2008a; 2008b; 2010a; 2015); BWTF oil was commonly present at both sites. After 2002, as TPAH levels at both stations trended lower, the TPAH levels at GOC have been close to or just slightly above those at AMT-B, largely due to pyrogenic and occasional petrogenic components--except in 2004 when the PAH and SHC profiles at GOC documented a fresh diesel spill (Payne et al., 2006). By summer 2005, the diesel signal had largely cleared, and TPAH levels again generally tracked with AMT through 2015. In 2016, TPAH concentrations at GOC-B increased dramatically again from 29 to 195 ng/g due to another localized diesel spill (Payne and Driskell, 2019) while the corresponding levels at AMT-B only increased modestly from 51 to 69 ng/g (Figure 14). By 2017, there was no evidence of residual diesel at GOC and the TPAH levels at both GOC and AMT-B were 46 and 54 ng/g, respectively. They have remained in the 40-79 ng/g range through 2020, notwithstanding the ANS crude oil spill at the terminal in April 2020, and they are generally dominated by combustion products (Figure 16). There was clearly a spike in TPAH concentrations in the mussel tissues at all three Port Valdez stations in April/May 2020 (Figure 14), but by the scheduled and routine/traditional LTEMP collections in June, the levels and PAH patterns had almost returned to background.

The time-series PAH and SHC GOC profiles during non-spill years (2008, 2015, and 2018 through 2020) show variable sources of dissolved, pyrogenic, and occasionally petrogenic hydrocarbons (Figure 21). In 2008, the at- or just-above-MDL PAH suggest possible water-washed petrogenic naphthalenes (N-N4), fluorenes (F-F2), and dibenzothiophenes (DBT-DBT2) plus combustion-derived phenanthrenes (Ph>P/A1>P/A2>P/A3). In 2015, dissolved-phase naphthalene (N) was the only PAH detected at elevated concentrations (13 ng/g, significantly above MDL) and an even more complete and descending dissolved-phase (N–N3) naphthalene pattern was also observed at the same time in the mussels at AMT-B (Figure 17) suggesting a possible common background source. In 2018 and 2019, the GOC PAH concentrations were all below MDLs (Figure 21) and like the two stations adjacent to the terminal during this period, the PAH profiles were remarkably similar with only traces of dissolved-phase naphthalenes plus combustion products at- or just-below MDL. But as noted in previous sections, these patterns were almost identical to those observed in laboratory method blanks run in parallel with the samples. In 2020, the PAH patterns in the mussels at GOC were exclusively derived from mostly below MDL combustion products with only the parent PAH from phenanthrene and fluoranthene above the MDL (Figure 21).

SHC in 2008 and 2015 are mostly trace-level biogenic components (e.g., n-C_{15}, n-C_{17}, and pristane) derived from marine phytoplankton, algae, and copepods. These same components plus odd-carbon n-alkanes (n-C_{25}, n-C_{27}, n-C_{29}, n-C_{31}) from terrestrial plant waxes were observed in 2018, 2019, and 2020.

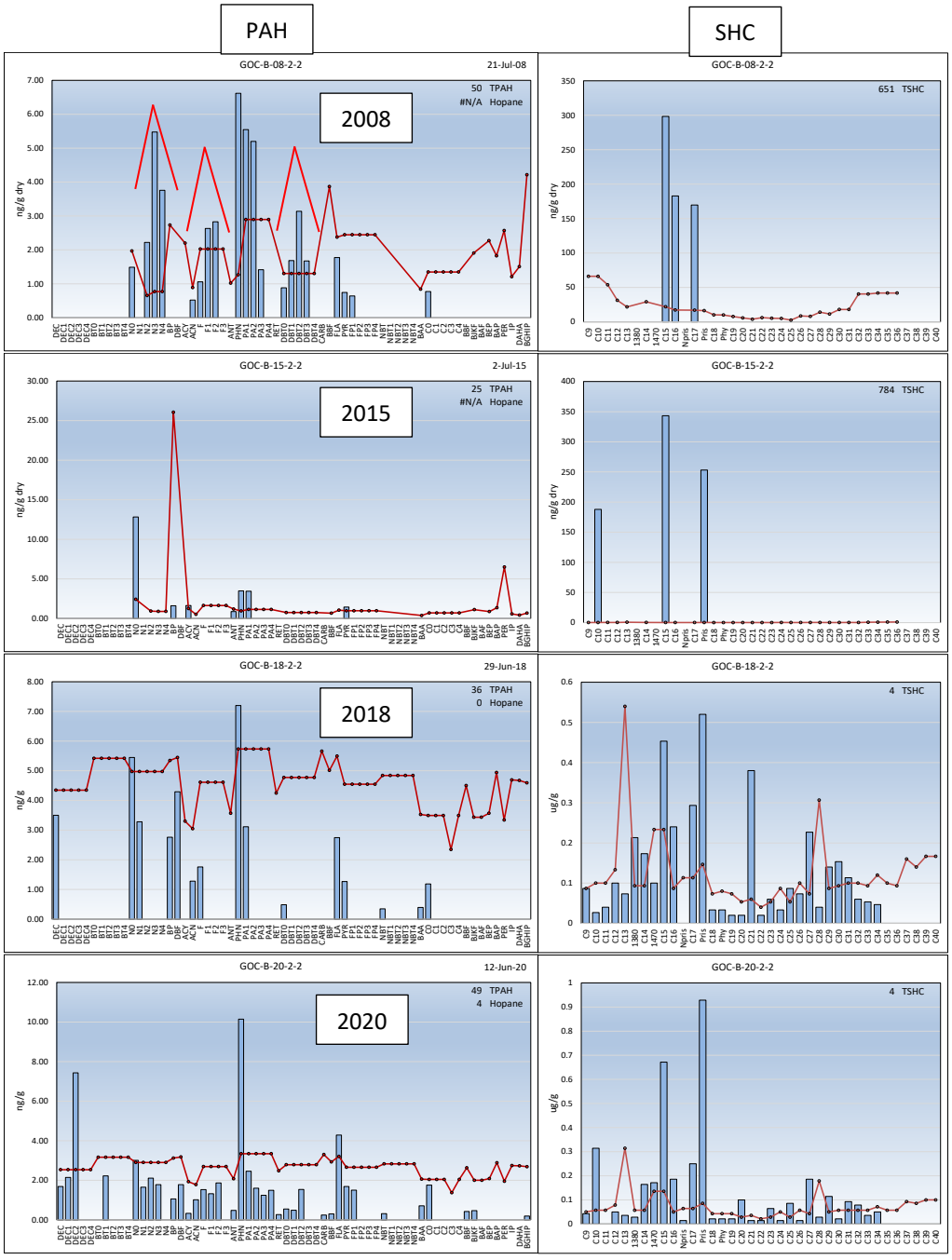


Figure 21. Time-series PAH and SHC profiles of GOC mussels collected between 2008 and 2020. The 2008 PAH suggest possibly particulate-phase, water-washed petrogenic naphthalenes, fluorenes, and DBTs (red tents) plus below-MDL combustion products. 2015 shows only above-MDL dissolved-phase naphthalenes (also observed at AMT-B at that time). In 2018 (and 2019, not shown), only at- or below-MDL traces of dissolved naphthalenes and combustion products are suggested but these same patterns were observed in the laboratory method blanks. The 2020 PAH profiles are derived exclusively from combustion products. SHC in all years are derived from marine phytoplankton and copepods. Dotted red line denotes the sample-specific MDLs.

SUPPLEMENTAL MUSSEL STATIONS IN 2020

Four new mussel-sampling stations were added to the 2020-2021 LTEMP collection effort for two purposes: 1) to resample the Valdez Small Boat Harbor from a matrix more benign than a previous creosote-piling sample (collected in 2019 as part of the transcriptomics program) and 2) to evaluate other control sites within Port Valdez both for chemistry and transcriptomics.

Using LTEMP protocols, mussels were collected in the intertidal zone: 1) beneath the red and green harbor lights on the breakwater riprap entrance to the Valdez Small Boat Harbor and 2) at two more distal locations within the Port, Jack Bay and Galena Bay (Figure 22). The Jack Bay and Galena Bay stations, further to the west, were added to scope out potential reference/control sites further from anthropogenic sources associated with the VMT and harbor activities. They were also intended to support PWSRCAC's Transcriptomics Project being undertaken by Dr. Lizabeth Bowen of U.S. Geological Survey (Davis, CA).

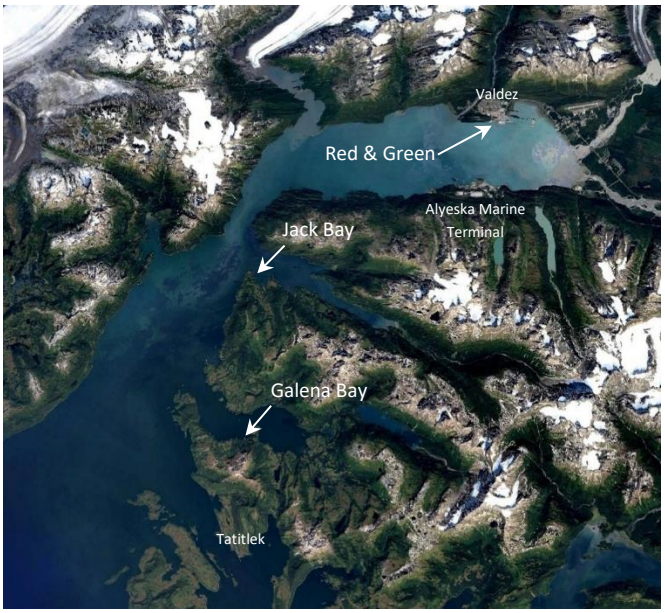


Figure 22. Supplemental stations at Galena Bay, Jack Bay, and Valdez Small Boat Harbor entrance (Red and Green navigation lights). Image from Google Earth dated 12/2016.

The PAH profiles from the Red and Green harbor stations, occupied in June following the April 2020 terminal spill, show elevated TPAH concentrations (977 and 916 ng/g, respectively; upper plots in Figure 23) with combustion products dominating the higher-molecular-weight components (parent phenanthrene, fluoranthene, pyrene, and chrysene with trailing alkylated homologues). The SHC show primarily biogenic n-alkanes and isoprenoids (n-C_{15}, n-C_{17}, pristane), and higher-molecular-weight, odd-carbon-number, terrestrial plant waxes (n-C_{23}, n-C_{25}, n-C_{27} and n-C_{29}). The more complex, underlying pattern of odd and even-carbon numbered n-alkanes in the n-C_{12} to n-C_{20} range plus phytane suggest traces of lighter distillate products (e.g., IFO 180, diesel fuel oil #4; Wang et al., 2007). The PAH profiles lack the expected patterns for distillates, which either offers little support for the conjecture or they are overwhelmed by the dominant combustion products. In the biomarker plots, the descending T4-T6 terpanes also hint at diesel but relative to T4-T6, the other biomarker levels exceed any expectation for diesel and are instead a close match to the crude ANS oil from the VMT spill. So, it is possible that traces of the spilled oil may have reached the entrance to the small boat harbor, but the signal is confounded by harbor pyrogenics and diesel contaminants.

PAH profiles from the much cleaner Jack Bay and Galena Bay sites (lower plots in Figure 23) show mostly below-MDL combustion products at TPAH concentrations more than 30-times lower than the Red and Green harbor sites. Likewise, from the SHC and biomarker plots, it is apparent that neither Jack Bay nor Galena Bay were contaminated from the spill oil (there are no tell-tale biomarkers present). The SHC profiles show primarily marine biogenic components (n-C_{15}, n-C_{17}, pristane) and higher-molecular-weight, odd-carbon-number, terrestrial plant waxes (n-C_{23}, n-C_{25}, n-C_{27} and n-C_{29}). At these remote sites, there is no evidence of the evenly repeating series of n-C_{12} through n-C_{20} alkanes plus phytane associated with lighter distillates (Wang et al., 2007).

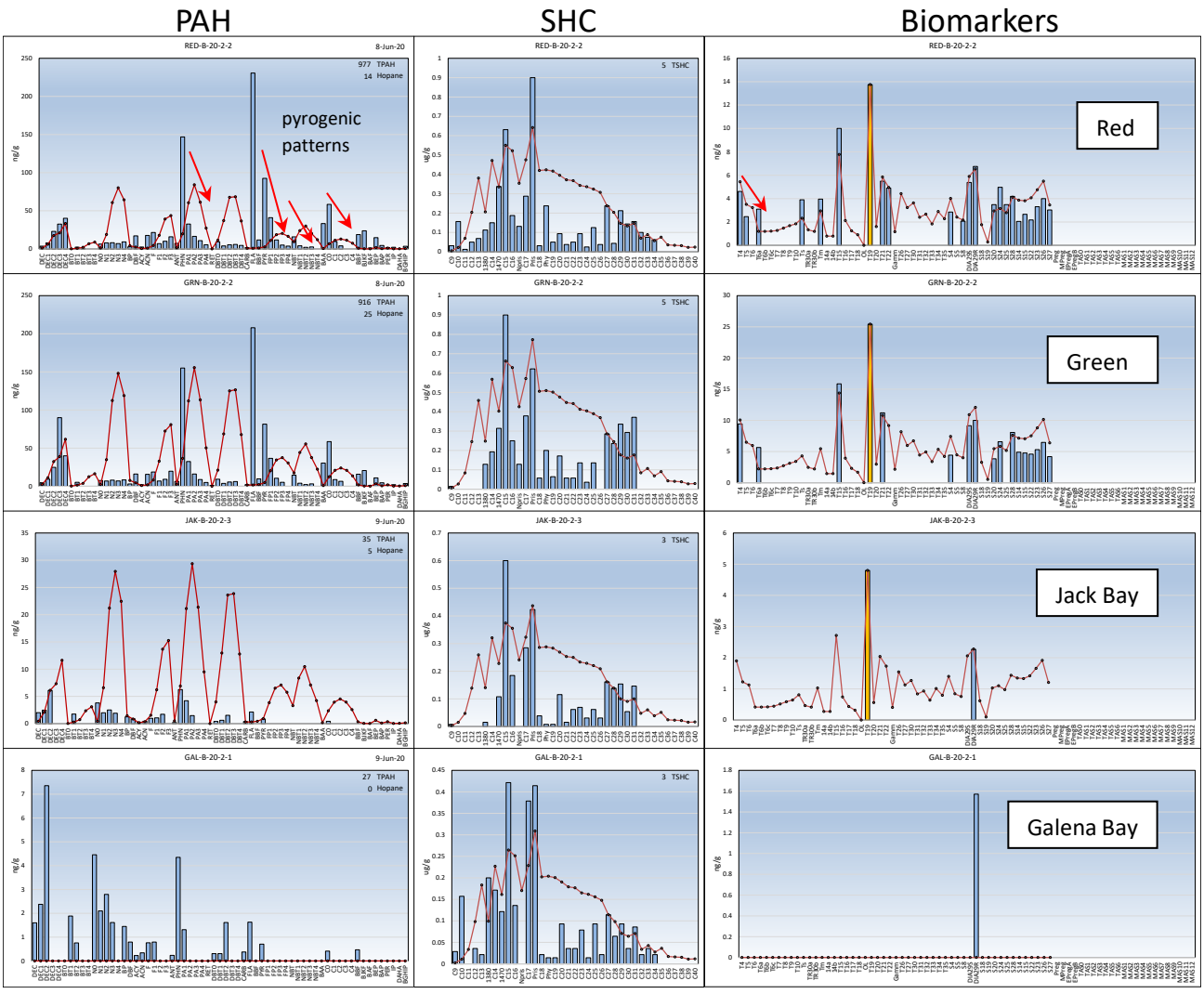


Figure 23. Representative PAH, SHC, and S/T patterns from the four new stations Red and Green (below the red and green channel navigation lights on the Valdez Small Boat Harbor entrance breakwater) and Jack Bay and Galena Bay. The dotted red line represents ANS oil from the VMT spill incident.

Greater PWS and GOA Stations

Beginning with the 2009 LTEMP program, sampling frequencies in the greater PWS and GOA region were reduced from twice annually to once every five years. These outer stations were last sampled in 2018 (reported in Payne and Driskell, 2019). The next sampling will occur in 2023. Like the Port Valdez stations, 2018 TPAH trends continued to

decline to all below-MDL lows ranging from 21-38 ng/g (Figure 14) and comprised primarily of components that were also associated with the laboratory method blanks and occasional variations of the dissolved-phase, background patterns.

Passive Sampling Devices

Starting in 2016, the LTEMP program incorporated passive sampling devices (PSDs) deployed in subsurface near-shore waters adjacent to established LTEMP sites (Figure 24) to monitor PAHs and other petroleum hydrocarbons in the water column. This sampling effort was motivated by a multi-year trend of observing trace concentrations of PAHs in mussel tissues, many of which were below the MDLs, and an interest in having data that are toxicologically relevant to sensitive marine resources, such as early life stages of fish. The goal was to compliment the LTEMP mussel tissue and sediment data with an integrative, highly sensitive sampling approach that could be used to evaluate the potential for oil exposure and toxic effects in water-column organisms.

Figure 24. Passive sampling devices (PSD) consisting of a low-density polyethylene membrane enclosed in a stainless-steel container and deployed subsurface in near-shore subtidal waters adjacent to LTEMP mussel collection sites for up to 30 days prior to mussel sampling. Sampling photo courtesy of David Janka.

The PSD, a low-density polyethylene membrane in this case, is intended to only sample a fraction of the total hydrocarbon analytes present, namely, freely dissolved compounds and labile complexes that diffuse into the membrane that, for biota, are the most bioavailable hydrocarbons. The LTEMP devices were expected to sample dissolved PAHs and other non-polar or semi-polar hydrocarbons discharged from the BWTF or other sources. The analytic laboratory at Oregon State University reports 61 PAH isomers as their normal PSD analyte list but in 2018, the list was expanded to include 40 parent and alkylated PAH homologs used routinely for forensic interpretations. As a critical part of the method, various deuterated surrogate compounds are pre-infused into the membrane prior to deployment. Their estimated rate of diffusion out of the membrane while the environmental dissolved-phase hydrocarbons are infusing calibrates the results for the desired calculation of average dissolved-phase water concentrations. High detection sensitivity is attained from longer-term deployments in which minute ambient concentrations are integrated into detectible amounts, similar to how chemicals bioconcentrate in tissues and organisms.

Beginning in 2016 and 2017, LTEMP PSDs were anchored and constantly submerged for approximately 30 days in shallow nearshore locations adjacent to the LTEMP mussel sites (Minick and Allan, 2016; Allan, 2018). In 2018, the program was expanded to encompass Knowles Head (KNH), a clean site outside of Port Valdez located near a

transient tanker anchorage, and Disk Island (DII), a site known to contain residual EVOS oil. In 2019 and 2020, only the three Port Valdez sites were sampled.

In 2020, the PSDs were deployed between May 12 and June 11 at JAP and SAW and June 12 at GOC. PAHs were detected in the PSDs at all three sites with summed dissolved-PAH concentrations in water (similar to TPAH43) of 213, 68, and 29 ng/L at JAP, SAW, and GOC, respectively. Given their proximity to the April 12, 2020 VMT spill, this concentration gradient could be expected. A similar trend was also noted in the mussel TPAH values evaluated for the June spill impacts at these sites (Table 5 and Figure 16). In contrast, the 2019 non-spill-impacted, dissolved-PAH concentrations were 27.7, 23.7, and 34.9 ng/L at the same three sites.

The dissolved-PAH water concentrations in Port Valdez are low compared to other marine ports in the United States and comparable to background levels in other parts of Prince William Sound (Lindeberg, Maselko et al. 2017). More importantly, except for post-spill concentrations at Jackson Point in April 2020, the water concentrations in the Port are all at least two or three orders of magnitude below published water quality standards and an order of magnitude below published toxic effects thresholds for aquatic organisms. Again, except for the post-spill concentrations at JAP, the PSD-derived concentrations of both total PAHs and the sum of 3-ring PAHs in the Port are also less than demonstrated embryonic exposure concentration thresholds for cardiotoxicity in herring and salmon (Incardona, Vines et al. 2012, Incardona, Carls et al. 2015). The concentration of dissolved PAHs at JAP following the spill (213 ng/L) is equivalent to summed dissolved-PAH (TPAH43) concentrations shown to cause cardiotoxicity and associated metabolic impacts in Pacific herring (230 ± 10 ng/L) (Incardona, Carls, et al. 2015). However, the PSD samples from JAP contained a lower proportion of the three-ring PAHs thought to be primarily associated with cardiotoxicity than the herring embryos that were exposed to dissolved PAHs from weathered oil in Incardona, Carls, et al 2015.

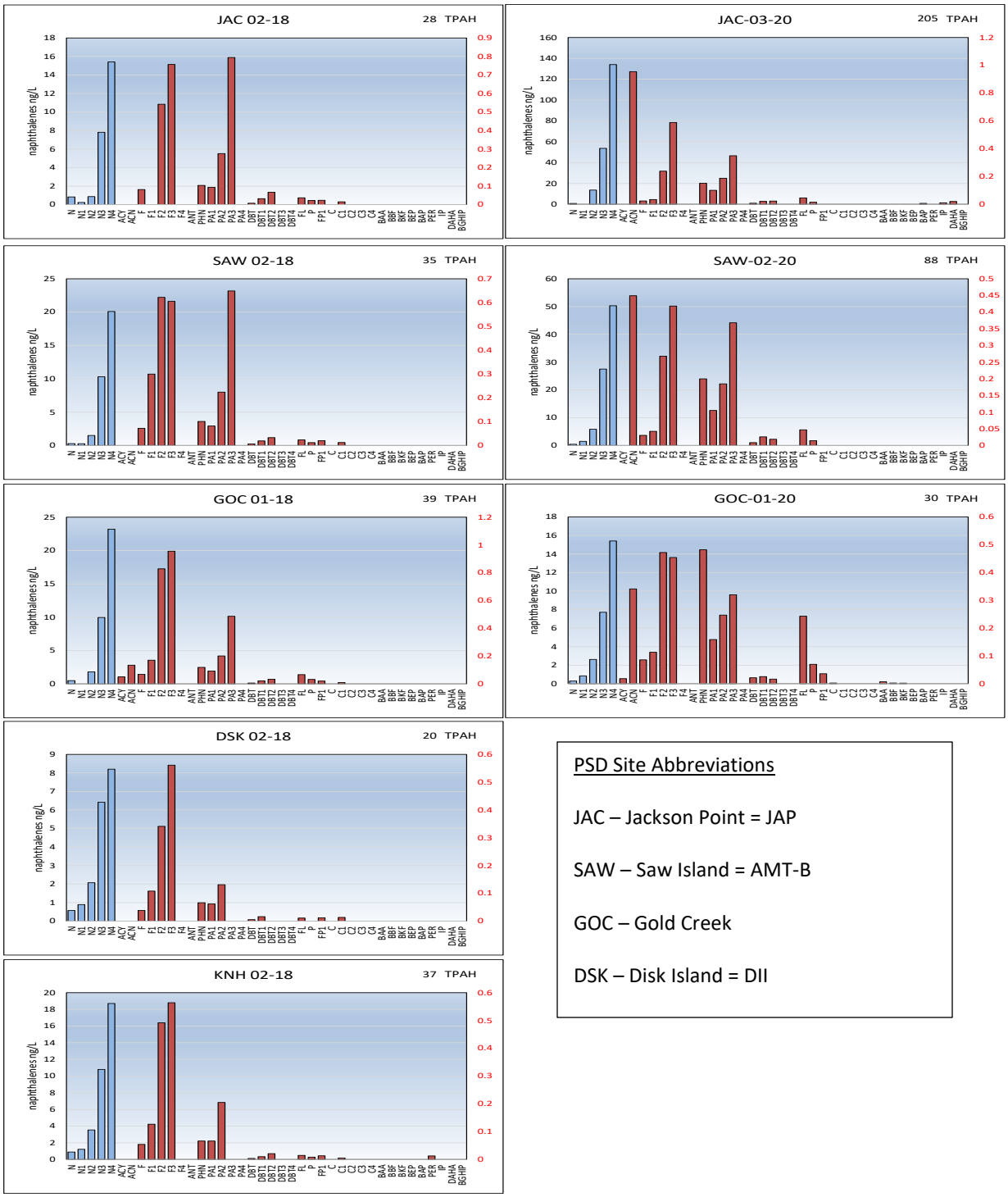
From a forensic perspective, there is still uncertainty regarding the origin of the PSD signals. The dissolved-phase PAH patterns were essentially identical at the terminal and the control station (Figure 25) and indeed, for all samples within and outside the Port throughout the five years' sampling. All PSD samples have a supra-dominant and largely invariant evaporatively-weathered naphthalene pattern and two-order-of-magnitude-lower traces of water-washed alkylated PAH (Figure 25). These observations would strongly suggest some ubiquitous background hydrocarbons but with the increased and graduated levels correlating with the 2020 spill, the Port Valdez results seem to be truly recording some form of environmental loadings related to VMT inputs.

The enigma is that the observed dominance of the ascending N<N1<N2<N3<N4 pattern observed at all PSD stations is the reverse pattern expected from a dissolution process. Specifically, the commonly encountered, dissolved-phase pattern as based on oil/water partition coefficients (Payne and McNabb, 1984) such that seawater partitioning against fresh oil or observed in near-shore intertidal waters adjacent to oiled shorelines (Figure 26) shows a more parent-PAH dominated profile. This pattern was observed from nearshore waters immediately adjacent to remarkably fresh oil still sequestered in Knight Island intertidal 15 years after EVOS (Payne et al, 2005d). It was also observed in the dissolved-phase BWTF effluent sampled in March 2017 when the oil was less weathered under colder, late-winter conditions (Figure 5c, lower right). The reverse pattern with ascending naphthalenes in the PSDs suggests that to create the pattern either 1) there have been evaporative losses to transform the sequence (slim possibility to create similar patterns across PWS), 2) some unknown earlier dissolution or aerial process has pre-determined the pattern that is eventually transported into Port Valdez and PWS waters, or 3) the PSDs are normally seeing a ubiquitous background but the spill contributed a stronger petrogenic signal on top of the background to create the gradient.

Still more to consider is that the PSD profiles are similar to a number of the 2013 regional mussel profiles (Payne et al., 2015). Those low-level, dissolved patterns appearing from Valdez to Kodiak invoked a hypothesis that natural

background inputs of PAH were likely derived from large-scale phenomena such as wildfires, glacial melts, riverine inputs, or terrestrial runoff (e.g., peat and coal are naphthalene rich). As an example of these large-scale processes, recall that following the EVOS event, there was debate over the unique PAH profile found in the depths of PWS. Eventually, it was resolved to have originated from source rock formations in the Yakutat region and transported by coastal currents into PWS (Deepthike et al., 2009). Later Environmental Mapping Project (EMAP) survey work, a joint project of the Environmental Protection Agency (EPA) and Cook Inlet Regional Citizens Advisory Council, traced those same offshore, PAH-laden particulates completely across the northern GOA and down the Alaska Peninsula (Saupe et al., 2005). We suspect that the ubiquitous naphthalene levels in many Port Valdez sediment profiles are tentatively linked with sediment loads from terrestrial runoff and increased glacial melt. While most of the PAH associated with these inputs are believed to be very tightly bound to the sediment particles, they may still be a source of low-level dissolved-phase naphthalenes in the region (Payne et al., 2010b).

With the exceptions of the naphthalene group, concentrations for all other PAH analytes were below 1 ng/L (ppt). PAH detected at lower levels include fluorenes (F), fluoranthenes (FL), dibenzothiophenes (DBT), phenanthrenes (Ph), and anthracenes (A) but as dissolved patterns, they defy source characterization. Finally, no matter the source, from 2016-2020, all the mussels and PSD analyzed throughout all regions (Port Valdez, PWS, and the GOA) were exceptionally clean with hydrocarbon concentrations below toxicity levels.



PSD Site Abbreviations

JAC – Jackson Point = JAP

SAW – Saw Island = AMT-B

GOC – Gold Creek

DSK – Disk Island = DII

Figure 25. PAH profiles from 2018 and 2020 PSD deployments. The dominant naphthalenes (blue) are scaled to the left axis and the two order-of-magnitude lower concentrations of other PAH (Fs. P/As, DBTs, and Cs) (red) are scaled to the right axis of each plot.

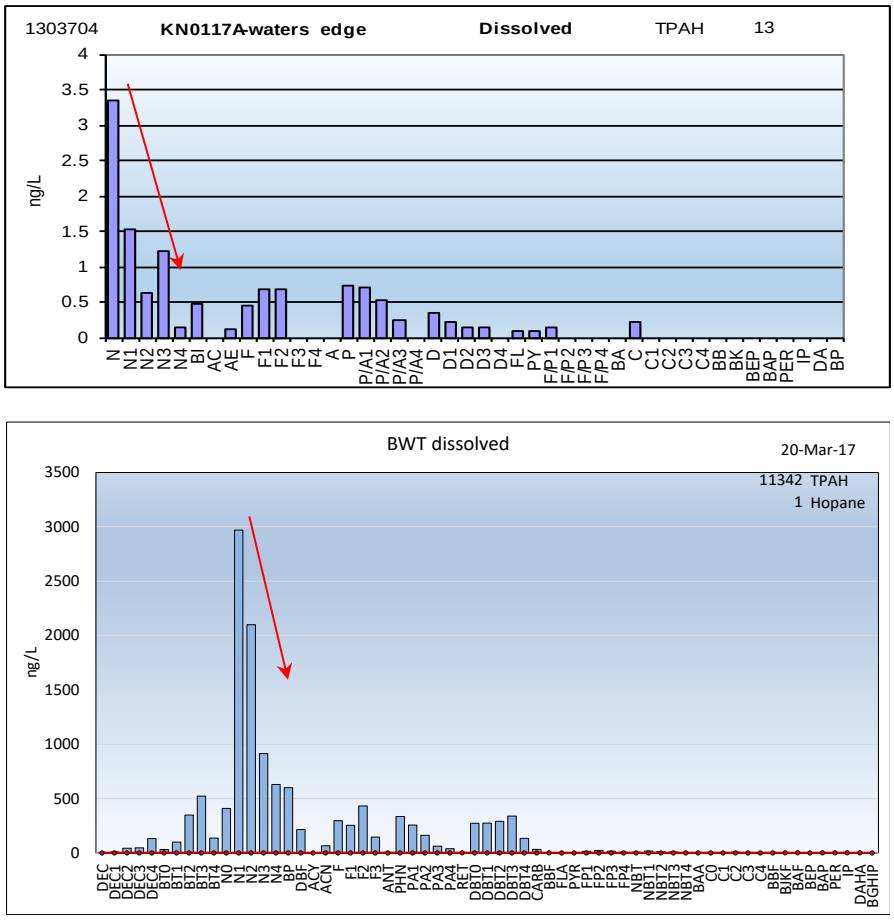


Figure 26. Example PAH profiles of dissolved-phase PAH, A) leaching from remarkably fresh residual *Exxon Valdez* oil on Knight Island, 15 years post-spill (from Payne et al., 2005d); B) dissolved-phase BWTF effluent from March 2017. Descending naphthalene patterns are the compliment to ascending patterns in water-washed particulate oil.

Related Topics

In last year's report, we presented discussion on topics indirectly related to LTEMP Monitoring. These included: 1) hydrocarbon bioavailability may not be just limited to dissolved-phase exposures, 2) low level toxicity effects on fish, 3) potential climate change effects on stream flows in relation to enhanced sorption and settling of particulate oil, and 4) seasonal variability of TPAH due to lipid loss in spawning events. These topics are still relevant but static and so have been moved to Appendix 9.

A fundamental problem with the LTEMP program is the frequency of sampling. Essentially, the annual data collections within the Port are equivalent to just a single snapshot of the constantly varying conditions both within the treatment system, the discharge, stratification of and transport in the receiving waters, subsequent oil weathering, and the seasonal condition of the mussel populations (feeding, purging, spawning, thermal and freshwater stresses, etc.). From Alyeska's Discharge Monitoring Reports (DMR) to EPA (now under ADEC), documenting the performance and any violations in the BWTF system, various parameters' time series demonstrate how little of the variability is captured with LTEMP's annual, snapshot collections (Figure 27).

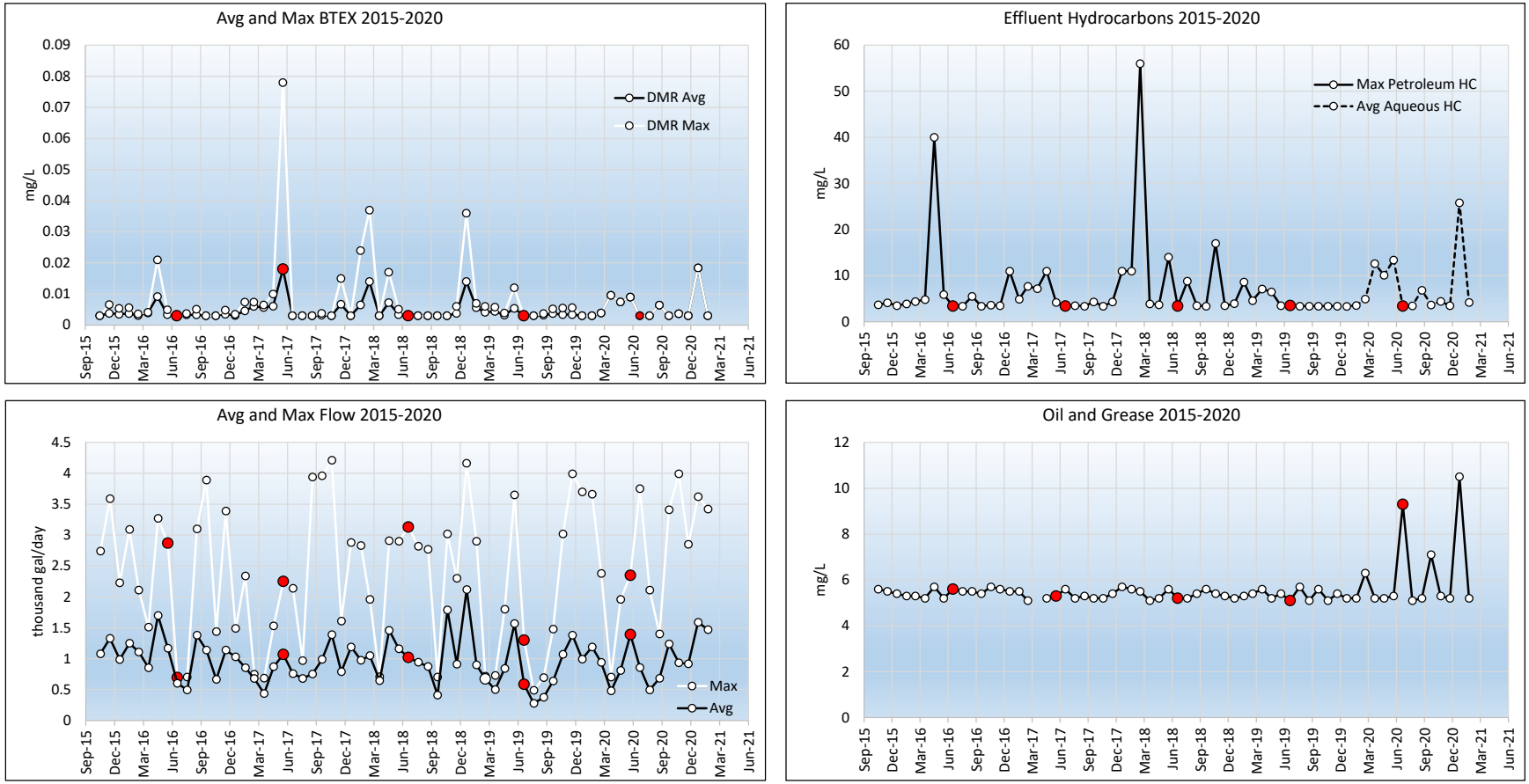


Figure 27. Time series of various DMR parameters as reported in Alyeska's monthly DMRs from October 2015 through January 2021. Red dots represent LTEMP's June or July sampling events to demonstrate the variance not captured by the "snapshot" mussel and sediment collection frequencies.

It was fortunate that in 2016 and 2017, our forensics understanding was greatly improved by full analyses of phase-separated, seasonal effluent samples from the BTT at Alyeska's BWTF (Figure 3, Figure 4, and Figure 5). These data provided a detailed fingerprint of the dominant hydrocarbon source to the Port, which when compared to the LTEMP data, enables us to discriminate the petrogenic (oil-based) vs. pyrogenic (combustion-derived) sources. However, unlike the ANS-source oil, the weathered BWTF effluent has no standard effluent profile for forensic interpretations. These two seasonally dissimilar profiles emphasize the effluent's dynamically changing character. Considering the cycling Oil and Grease DMR chart and its trend-busting 2020 fluctuations, or similar behavior of the effluent hydrocarbons (Figure 27), a time-series effluent sampling program might be revealing. If the currently proposed Oxygenated Hydrocarbon project is accepted by PWSRCAC, this time-series goal may be achieved. But note that additional analyses may be necessary for full-suite forensic data.

SUMMARY POINTS

As oft stated, due to a combination of reduced BWTF discharge volumes from historically decreased North Slope oil production, the transition to double-hulled tankers with segregated ballast tanks, and improved BWTF efficiency in recent years, TPAH levels in both sediments and tissues have been trending down since LTEMP's inception (see Appendix 3).

In sediments, Port Valdez TPAH levels have been decreasing and reached all-time lows in 2013 but unlike the trend observed with the mussel tissues (excluding site-specific spill events), sediment TPAH concentrations at both stations have slightly increased (~50%) over the last four years.

- At the terminal (AMT-S), there has been a transition in the sediment PAH profiles from a dominant pyrogenic pattern in 2011-2015, to the current mix of background naphthalenes (possibly from variable riverine and glacial flour input), combustion products, and highly weathered petrogenic components derived from the BWTF effluent. Biomarker profiles strongly confirm the linkage to the BWTF effluent throughout the entire period. Recent SHC patterns show a mixture of marine and terrestrial biogenic components at increasing relative levels compared to the higher-molecular-weight petrogenic waxes from BWTF discharges that have been observed at this site for years. These signatures suggest variable or increased background inputs of glacial or riverine flour, weathered ANS oil from the BWTF, and combustion products from local vessel traffic, runoff, or aerial deposition.
- At the GOC-S reference site, sediment PAH profiles since 2000 have shown a dominant pyrogenic pattern with little or no input from the terminal. Instead, they are characterized by variable naphthalenes and dominant combustion products. SHC profiles continue to be biogenic, reflecting only phytoplankton sources and terrestrial plant waxes. Trace-level accumulations of biomarkers associated with the BWTF effluent are accumulating in GOC sediments. They can be attributed to the terminal even though their associated petrogenic PAH and SHC are largely absent.
- It is speculated that climate-change-accelerated glacial melt and increased stream flows might cause increased suspended sediment loads and thus, oil adhering to the particles and settling from the water column (Appendix 9).

TPAH concentrations in mussels at AMT-B, JAP-B, and GOC-B were impacted by the April 2020 VMT spill, but they largely purged back to normal levels with only slightly elevated levels by the June LTEMP sampling.

- At AMT-B, mussel PAH contamination over the last 10-plus years has been shifting away from the earlier petrogenic profiles towards trace-level background, dissolved-phase or mixed pyrogenic and

petrogenic patterns. In 2018-19 the concentrations were so low, that the PAH patterns could not be differentiated from trace level components in the laboratory blanks. The immediate impacts of spills at the terminal were easily detected in mussels collected in September 2017 after the tanker loading-arm spill but to a lesser extent in May 2020 following the sump overflow incident on April 12, 2020.

- JAP-B mussels have generally tracked those at AMT-B and sampling since 2016 has not demonstrated any obvious east-west gradients during BWTF operating conditions. Like the 2018-2019 AMT-B mussels, the concentrations were so low that the PAH patterns could not be differentiated from laboratory blanks' trace-level components. By way of comparison, the Jackson Point mussels did show the greatest impacts from the 2020 sump overflow incident (covered in a separate PWSRCAC report and manuscript in preparation).
- GOC-B mussels have generally shown only low-level pyrogenic PAH profiles since 2006. Like the other two Port Valdez stations, the 2018 and 2019 PAH concentrations were extremely low with profiles that could not be differentiated from the laboratory blanks. In the June 2020 collections, the parent PAH associated with combustion products were again above the MDL, but all other alkylated homologues were below it. SHC profiles showed only biogenic marine and terrestrial input.
- The mussels from the recently added RED and GRN stations from the riprap entrance to the Valdez Small Boat Harbor showed significantly elevated (> 900 ng/g) concentrations of combustion products and possible traces of intermediate fuel oil or diesel from local boat traffic. Additional mussel sampling along the northern shoreline of the Port between the Harbor and Gold Creek will be needed to assess the possible influence of combustion products from the Valdez Small Boat Harbor on the tissues and sediments at Gold Creek.
- The more remote mussel from Jack Bay and Galena Bay showed only trace-level combustion products and no evidence of any oil from the spill at the VMT.
- Except during the most recent spill incident, current mussel tissue results from the traditional LTEMP stations are all below TPAH concentrations reported from anywhere else in the United States and are mostly below even what the National Mussel Watch program categorizes as “low levels” (~63-1,187 ppb dry weight of PAHs) (Appendix 10).
- These results suggesting an exceptionally clean environment are based on a once-a-year assessment of tissue (and PSD) contaminant levels. Variable biological and physical conditions plus variable effluent composition during the rest of the year may greatly influence contaminant levels.

Like their corresponding mussel samples, PSDs showed only a low-level background pattern at all stations; however, there does appear to be a spatial relationship between measured TPAH concentrations and proximity to the recent spill at the terminal. With the possible exception of the PSDs from Jackson Point, the concentrations appear to be below levels of toxic concern.

Pilot analyses of BWTF effluent showed high levels of oxygenated hydrocarbons from weathered ANS oil after biological degradation in the BTT (Appendix 8). Concentrations of these compounds exceed those of the analyzed PAH suite. Academic and agency research is ongoing in determining what compounds are present and which are relevant to toxicity.

In 2016 and 2017, our interpretations were greatly improved by analyses of effluent samples from the BTT at Alyeska’s BWTF. But these seasonal samples are merely two snapshots of a variable discharge product. We recommend effluent sampling as a reoccurring component of the program. Also, sampling suspended glacial flour and river silt from the Valdez Glacier and Lowe Rivers may be warranted to characterize their hydrocarbon inputs to the Port and further understand the effects of glacial flour scavenging oil in water and sediment profiles (Appendix 9).

CONCLUSIONS

For the list of reasons (atop the previous section and in Appendix 3), petrogenic hydrocarbon (oil) inputs into Port Valdez from the VMT and tanker operations, as reflected in TPAH concentrations in both sediments and mussels, have been declining.

SEDIMENTS

Interpreting the patterns, between 2016 and 2020, the sediments from near the outfall (AMT-S) showed mixed PAH profiles that included low-level oil components from the BWTF discharge. The profiles were significantly weathered but were confirmed by the biomarkers to contain ANS-derived oil. The mixture also suggested variable inputs of background and combustion products (from local vessel traffic, runoff, or aerial deposition).

At the reference site (GOC-S), the sediments' PAH patterns are dominated by low-level background naphthalenes plus combustion products; no oil. The naphthalenes may derive from riverine silt and glacial flour from nearby Mineral Creek and the Lowe and Valdez Glacier Rivers. Combustion products are likely introduced by local fishing or pleasure boat traffic, atmospheric input, or as recently hypothesized, possible contributions from the Valdez Small Boat Harbor. The biomarker data suggests that in addition to natural background biomarkers, minor residual traces of some ANS-derived biomarkers are accumulating in the GOC sediments.

TISSUES

From 2018-20 mussels, both terminal locations (AMT-B and JAP-B) showed very low-level background PAH (<70 ng/g) but with no suggestion of BWTF-derived oil.

However, just prior to LTEMP sampling, the April 2020 sump overflow spill at the terminal occurred, which led to exceptionally high TPAH loads, spiking to ~230,000 ng/g within the spill zone (see Figure 14 and forthcoming report). Much lower concentrations (438 and 256 ng/g) were observed in May at the nearby LTEMP stations JAP-B and AMT-B, respectively. When the LTEMP stations were reoccupied in June 2020, the PAH patterns and concentrations had almost returned to baseline.

GOC-B mussels in both May (spill samples) and June 2020 (LTEMP samples) showed similar low-level background patterns, including some combustion products; no oil.

PASSIVE SAMPLERS

Data from the PSDs corroborate mussel-tissue measurements that only extremely low concentrations of dissolved-phase PAH are generally present in the region. The 2020 PAH patterns were identical with those observed in the 2016-2019 series; however, there was a concentration gradient that corresponded with proximity to the April sump-overflow spill at the terminal. But even at the station closest to the spill (JAP-B), the observed PSD concentrations from the May to June deployment were below any known toxicity thresholds for sensitive marine organisms and life stages. The source of the background PAH observed both within and outside Port Valdez remains enigmatic.

Finally, compared to the recent West Coast Mussel Watch data (2004-05) and the more recent 2008-10 Alaska Mussel Watch sites, the 2018-20 LTEMP results continue to demonstrate that the sampled region is exceptionally clean.

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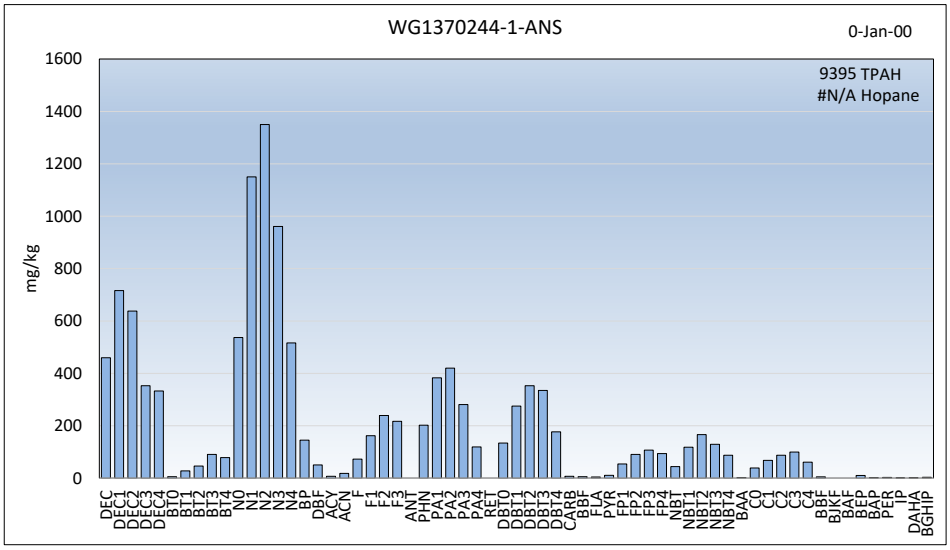
APPENDIX 1. POLYCYCLIC AROMATIC HYDROCARBON (PAH), SATURATED HYDROCARBON (SHC), AND BIOMARKER ANALYTES

Analytes	Abbreviation
Naphthalene	N
C1-Naphthalene	N1
C2-Naphthalene	N2
C3-Naphthalene	N3
C4-Naphthalene	N4
Biphenyl	BI
Acenaphthylene	ACY
Acenaphthene	ACN
Fluorene	F
C1-Fluorene	F1
C2-Fluorene	F2
C3-Fluorene	F3
C4-Fluorene	F4
Anthracene	A
Phenanthrene	Ph
C1-Phenanthrene/Anthracene	PA1
C2-Phenanthrene/Anthracene	PA2
C3-Phenanthrene/Anthracene	PA3
C4-Phenanthrene/Anthracene	PA4
Retene	RET
Dibenzothiophene	DBT
C1-Dibenzothiophene	DBT1
C2-Dibenzothiophene	DBT2
C3-Dibenzothiophene	DBT3
C4-Dibenzothiophene	DBT4
Benzo(b)fluorene	BF

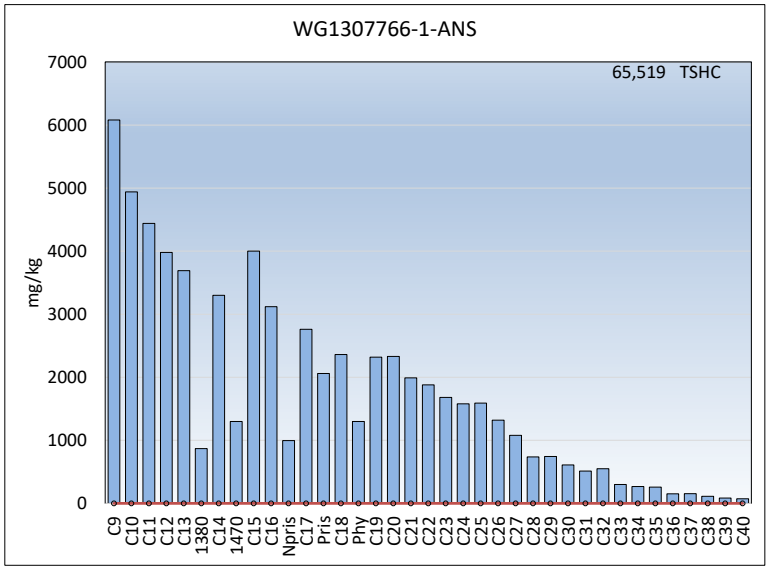
Analytes	Abbreviation
Fluoranthene	FL
Pyrene	PY
C1-Fluoranthene/Pyrene	FP1
C2-Fluoranthene/Pyrene	FP2
C3-Fluoranthene/Pyrene	FP3
C4-Fluoranthene/Pyrene	FP4
Napthobenzothiophene	NBT
C1-Napthobenzothiophene	NBT1
C2-Napthobenzothiophene	NBT2
C3-Napthobenzothiophene	NBT3
C4-Napthobenzothiophene	NBT4
Benzo(a)Anthracene	BAA
Chrysene	C
C1-Chrysene	C1
C2-Chrysene	C2
C3-Chrysene	C3
C4-Chrysene	C4
Benzo(b)fluoranthene	BBF
Benzo(k)fluoranthene	BKF
Benzo(e)pyrene	BEP
Benzo(a)pyrene	BAP
Perylene	PER
Indeno(1,2,3-cd)pyrene	IND
Dibenzo(a,h)anthracene	DAHA
Benzo(g,h,i)perylene	BGH
Total PAH	TPAH



ANS Crude oil example

Saturated hydrocarbons (SHC or n-alkanes)

Analyte	Abbrev
Nonane (C9)	C9
Decane (C10)	C10
Undecane (C11)	C11
Dodecane (C12)	C12
Tridecane (C13)	C13
2,6,10 Trimethyldodecane (1380)	1380
Tetradecane (C14)	C14
2,6,10-Trimethyltridecane (1470)	1470
Pentadecane (C15)	C15
Hexadecane (C16)	C16
Norpristane (1650)	Pristane
Heptadecane (C17)	C17
Pristane	Phytane
Octadecane (C18)	C18
Phytane	Phy
Nonadecane (C19)	C19
Eicosane (C20)	C20
Heneicosane (C21)	C21
Docosane (C22)	C22
Tricosane (C23)	C23
Tetracosane (C24)	C24
Pentacosane (C25)	C25
Hexacosane (C26)	C26
Heptacosane (C27)	C27
Octacosane (C28)	C28
Nonacosane (C29)	C29
Triacontane (C30)	C30
Hentriacontane (C31)	C31
Dotriacontane (C32)	C32
Tritriacontane (C33)	C33
Tetratriacontane (C34)	C34
Pentatriacontane (C35)	C35
Hexatriacontane (C36)	C36
Heptatriacontane (C37)	C37
Octatriacontane (C38)	C38
Nonatriacontane (C39)	C39
Tetracontane (C40)	C40
Total SHC	**TSHC**



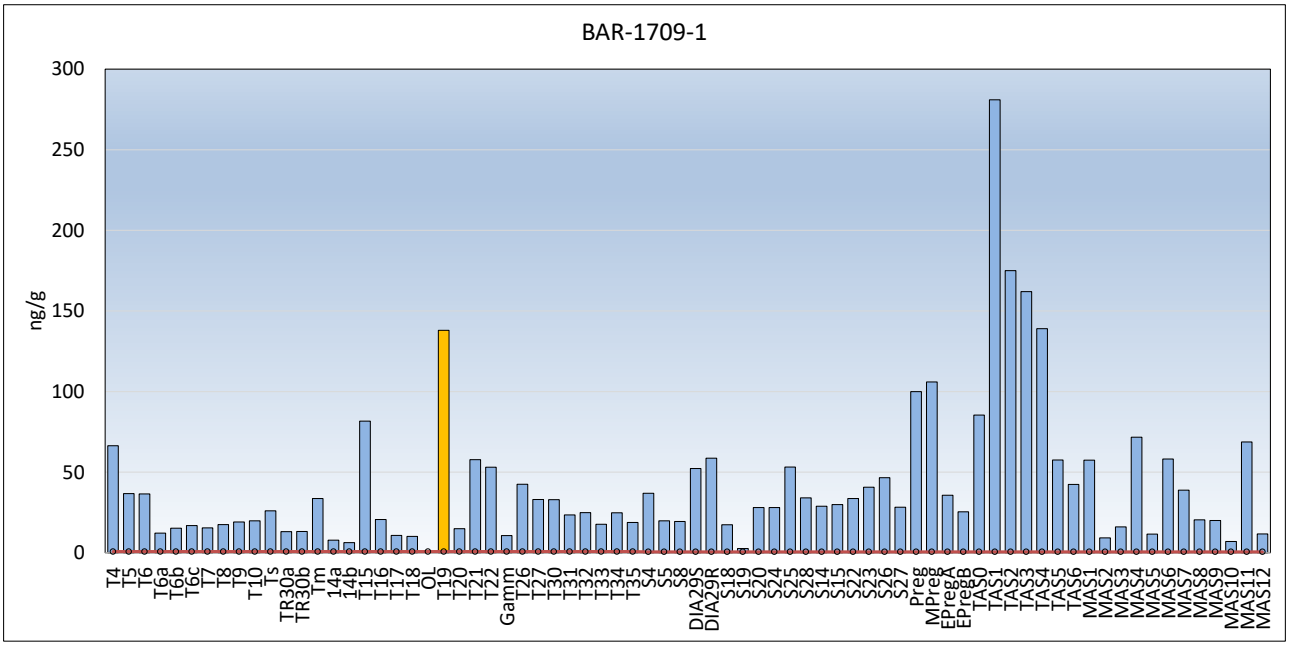
Petroleum Biomarkers

Class	Biomarker	Abbrev
Terpanes	C23 Tricyclic Terpane (T4)	T4
	C24 Tricyclic Terpane (T5)	T5
	C25 Tricyclic Terpane (T6)	T6
	C24 Tetracyclic Terpane (T6a)	T6a
	C26 Tricyclic Terpane-22S (T6b)	T6b
	C26 Tricyclic Terpane-22R (T6c)	T6c
	C28 Tricyclic Terpane-22S (T7)	T7
	C28 Tricyclic Terpane-22R (T8)	T8
	C29 Tricyclic Terpane-22S (T9)	T9
	C29 Tricyclic Terpane-22R (T10)	T10
	18a-22,29,30-Trisnorneohopane-	Ts
	C30 Tricyclic Terpane-22S	C30Ts
	C30 Tricyclic Terpane-22R	C30Tr
Hopanes	17a(H)-22,29,30-Trisnorhopane-	Tm
	17a/b,21b/a 28,30-Bisnorhopane	14a
	17a(H),21b(H)-25-Norhopane	14b
	30-Norhopane (T15)	T15
	18a(H)-30-Norneohopane-C29Ts	T16
	17a(H)-Diahopane (X)	X
	30-Normoretane (T17)	T17
	18a(H)&18b(H)-Oleananes (T18)	T18
	Hopane (T19)	T19
	Moretane (T20)	T20
	30-Homohopane-22S (T21)	T21
	30-Homohopane-22R (T22)	T22
	Gammacerane/C32-Diahopane	T22a
	30,31-Bishomohopane-22S (T26)	T26
	30,31-Bishomohopane-22R (T27)	T27
	30,31-Trishomohopane-22S (T30)	T30
	30,31-Trishomohopane-22R (T31)	T31
	Tetrakishomohopane-22S (T32)	T32
	Tetrakishomohopane-22R (T33)	T33
	Pentakishomohopane-22S (T34)	T34
	Pentakishomohopane-22R (T35)	T35
Steranes	13b(H),17a(H)-20S-Diacholestane (S4)	S4
	13b(H),17a(H)-20R-Diacholestane (S5)	S5

Class	Biomarker	Abbrev
	13b,17a-20S-Methyldiacholestane (S8)	S8
	17a(H)20SC27/C29dia	DIA29S
	17a(H)20rc27/C29dia	DIA29R
	Unknown Sterane (S18)	S18
	13a,17b-20S-Ethyldiacholestane (S19)	S19
	14a,17a-20S-Methylcholestane (S20)	S20
	14a,17a-20R-Methylcholestane (S24)	S24
	14a(H),17a(H)-20S-Ethylcholestane (S25)	S25
	14a(H),17a(H)-20R-Ethylcholestane (S28)	S28
	14b(H),17b(H)-20R-Cholestane (S14)	S14
	14b(H),17b(H)-20S-Cholestane (S15)	S15
	14b,17b-20R-Methylcholestane (S22)	S22
	14b,17b-20S-Methylcholestane (S23)	S23
	14b(H),17b(H)-20R-Ethylcholestane (S26)	S26
	14b(H),17b(H)-20S-Ethylcholestane (S27)	S27
	C20 Pregnane	Preg
	C21 20-Methylpregnane	MPreg
	C22 20-Ethylpregnane (a)	EPregA
	C22 20-Ethylpregnane (b)	EPregB
Triaromatic Steroids	C26,20S TAS	TAS0
	C26,20R+C27,20S TAS	TAS1
	C28,20S TAS	TAS2
	C27,20R TAS	TAS3
	C28,20R TAS	TAS4
	C29,20S TAS	TAS5
	C29,20R TAS	TAS6
Mono-aromatic Steroids	5b(H)-C27 (20S) MAS+	MAS1
	5b(H)-C27 (20R) MAS+	MAS2

Class	Biomarker	Abbrev
	5a(H)-C27 (20S) MAS	MAS3
	5b(H)-C28 (20S) MAS+	MAS4
	5a(H)-C27 (20R) MAS	MAS5
	5a(H)-C28 (20S) MAS	MAS6
	5b(H)-C28 (20R) MAS+	MAS7

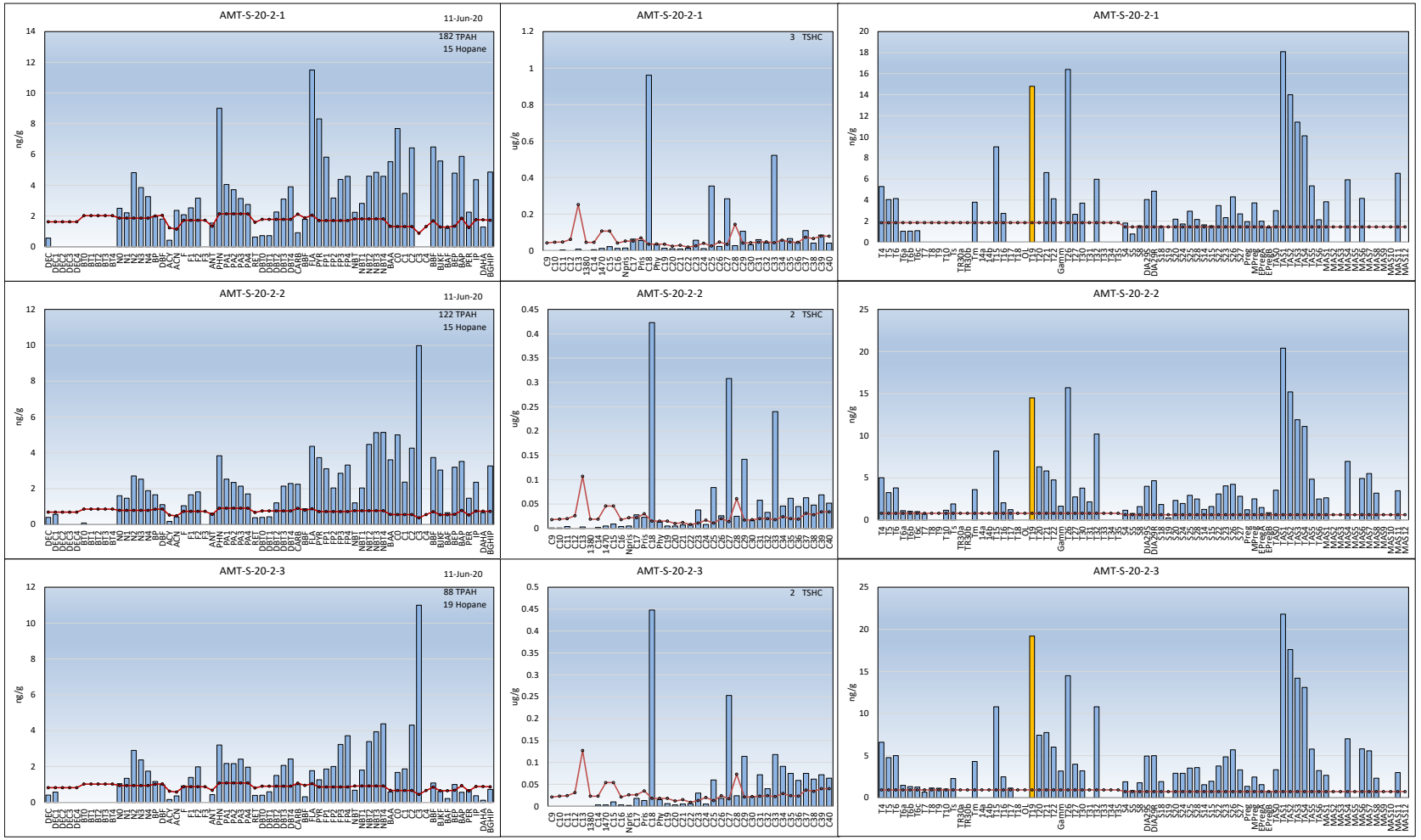
Class	Biomarker	Abbrev
	5b(H)-C29 (20S) MAS+	MAS8
	5a(H)-C29 (20S) MAS	MAS9
	5a(H)-C28 (20R) MAS	MAS10
	5b(H)-C29 (20R) MAS+	MAS11
	5a(H)-C29 (20R) MAS	MAS12



Spill oil from 2017

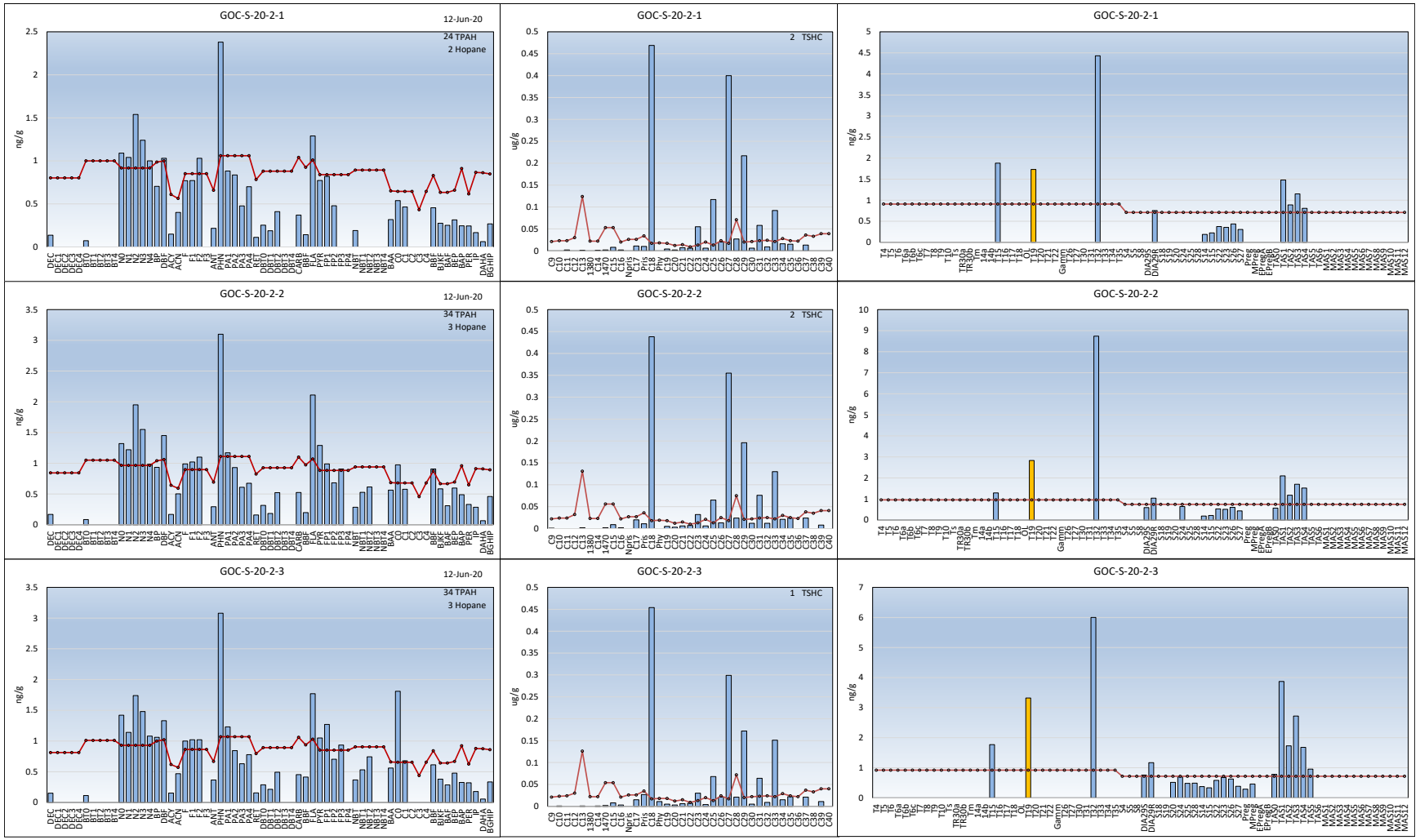
APPENDIX 2. Analytic Results for 2020 Field Samples and Blanks

2020 AMT Sediments (PAH, SHC, and Biomarkers)



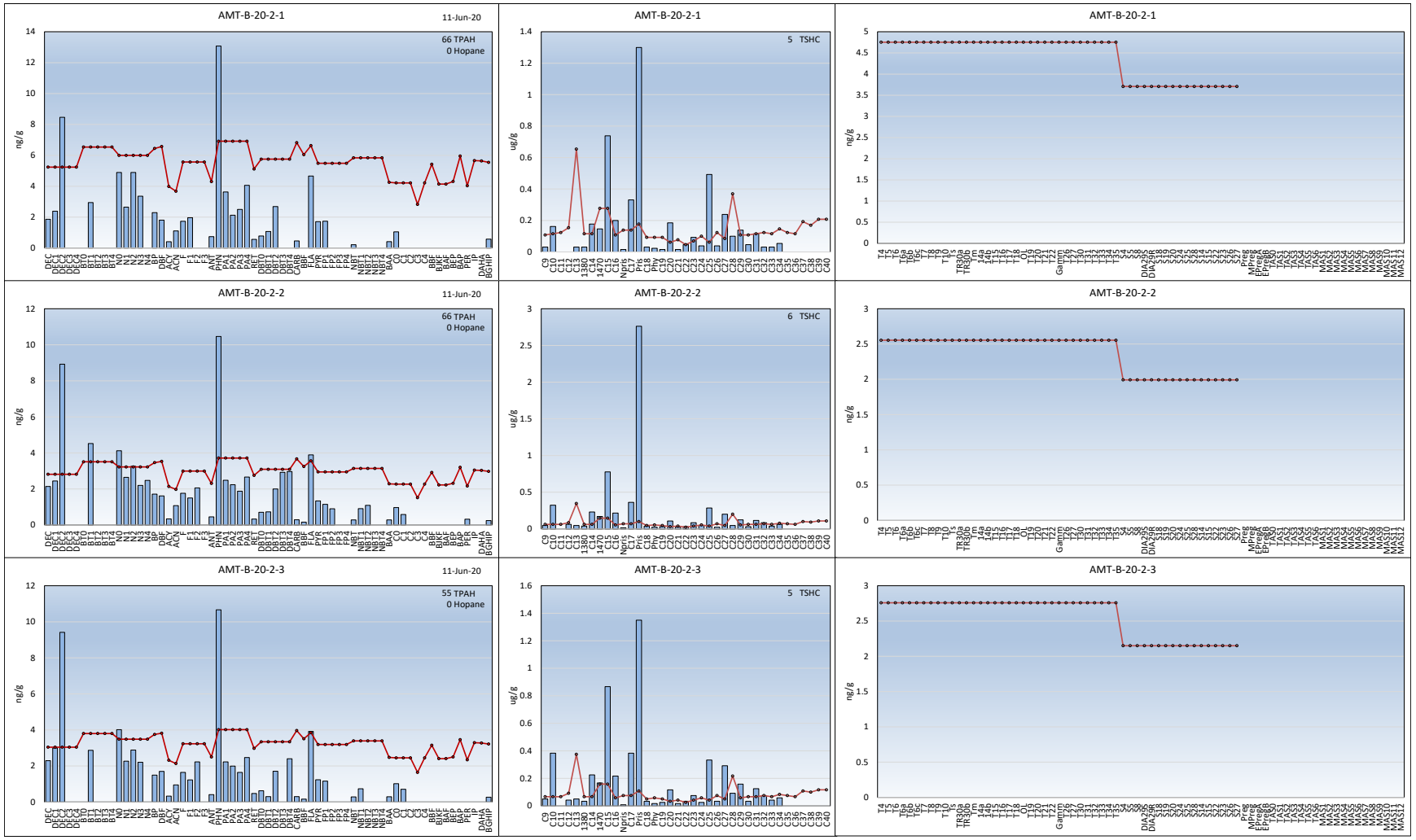
The dotted red line represents the sample-specific method detection limits (MDL) for PAH, SHC, and biomarkers. The biomarker, hopane (T19; highlighted in gold), is used for scaling reference overlay patterns.

2020 GOC Sediments (PAH, SHC, and Biomarkers)



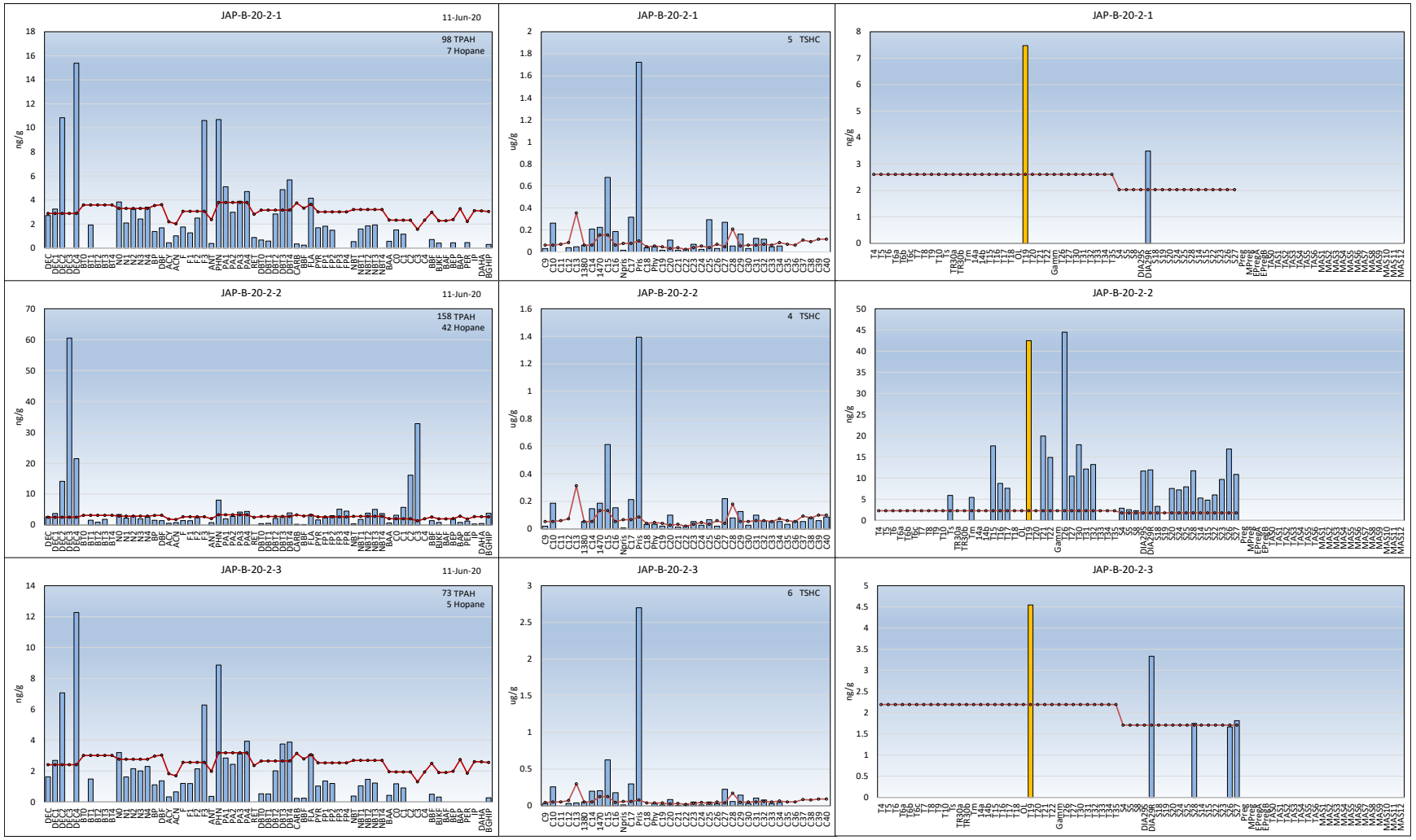
The dotted red line represents the sample-specific method detection limits (MDL) for PAH, SHC, and biomarkers.

2020 AMT Tissues (PAH, SHC, and Biomarkers)



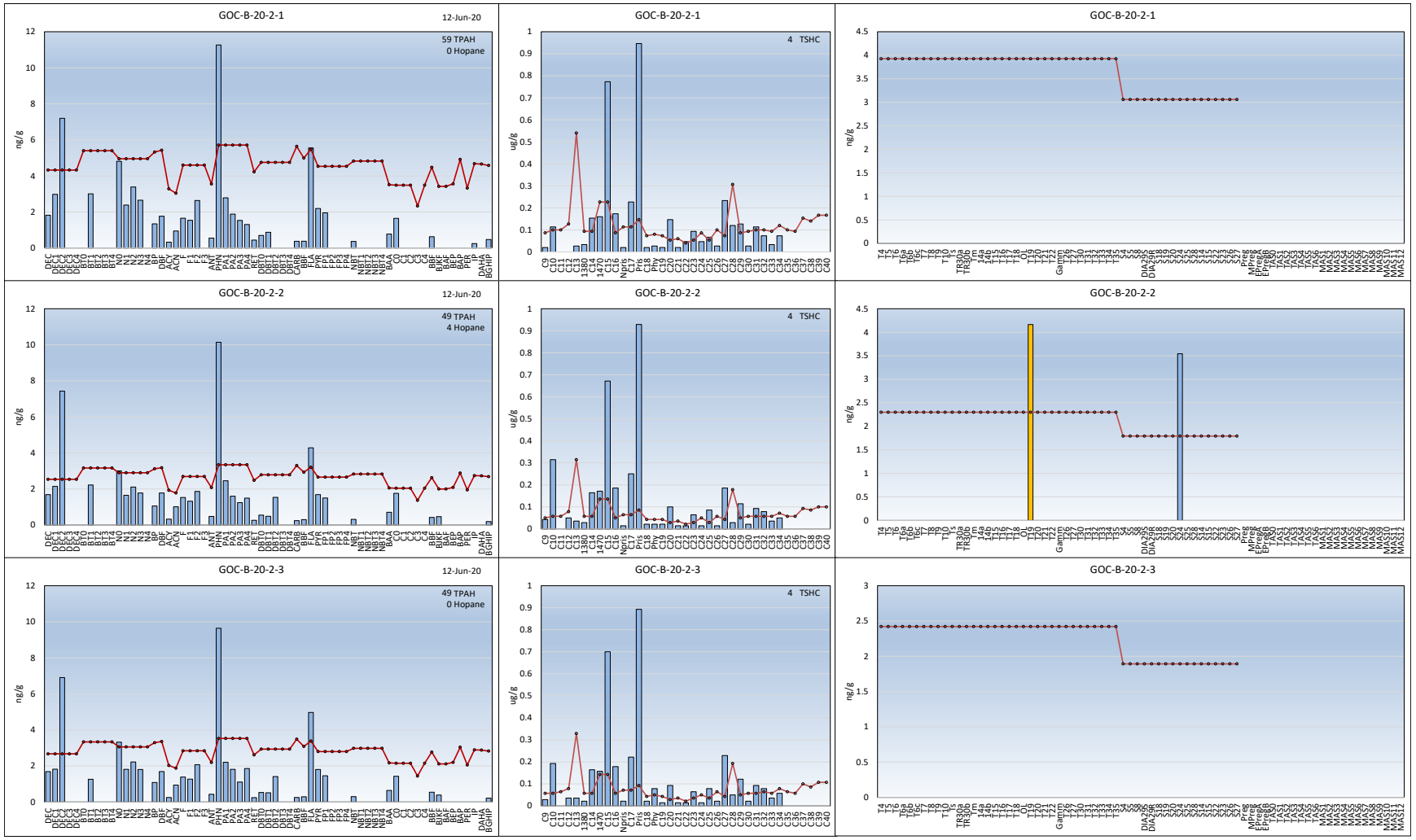
The dotted red line represents the sample-specific method detection limits (MDL) for PAH, SHC, and biomarkers.

2020 JAP Tissues (PAH, SHC, and Biomarkers)



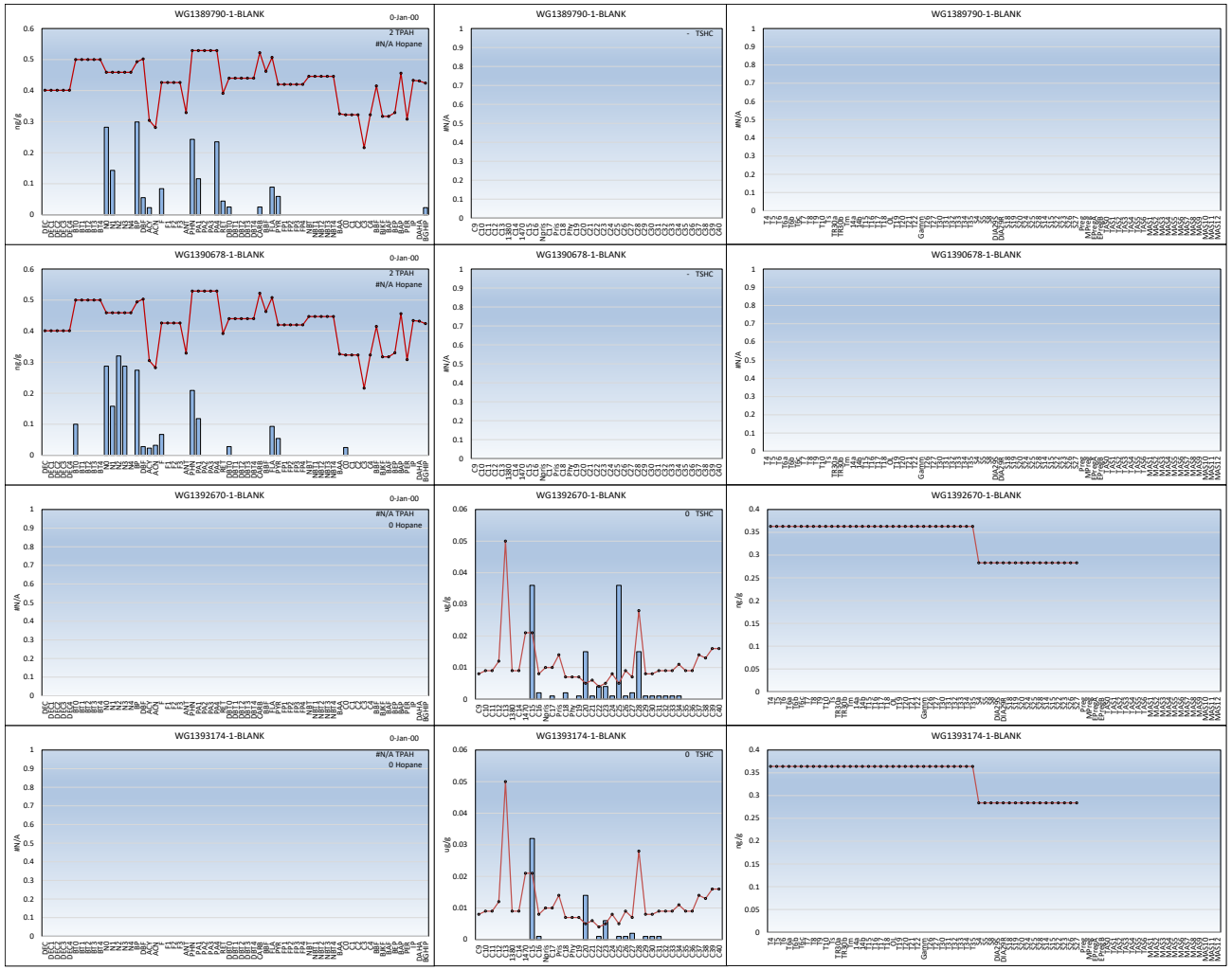
The dotted red line represents the sample-specific method detection limits (MDL) for PAH, SHC, and biomarkers.

2020 GOC Tissues (PAH, SHC, and Biomarkers)



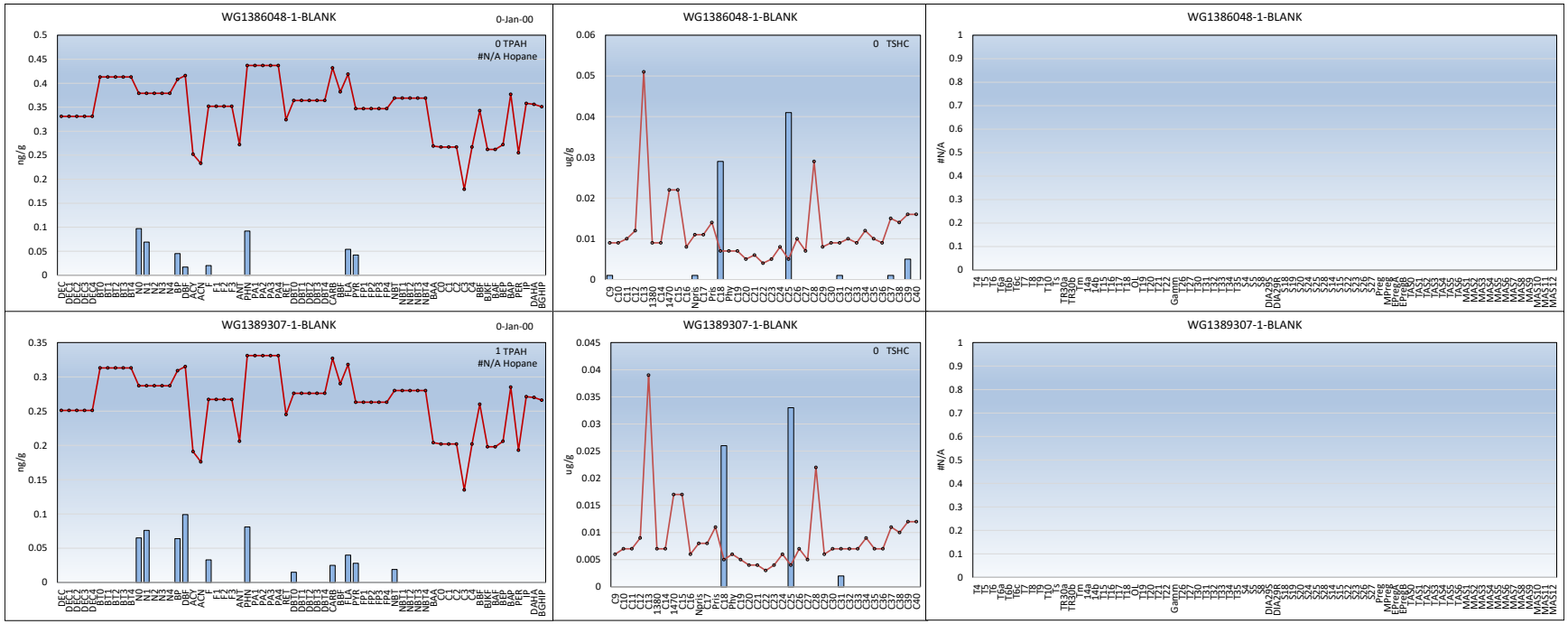
The dotted red line represents the sample-specific method detection limits (MDL) for PAH, SHC, and biomarkers.

2020 Tissue Lab Method Blanks



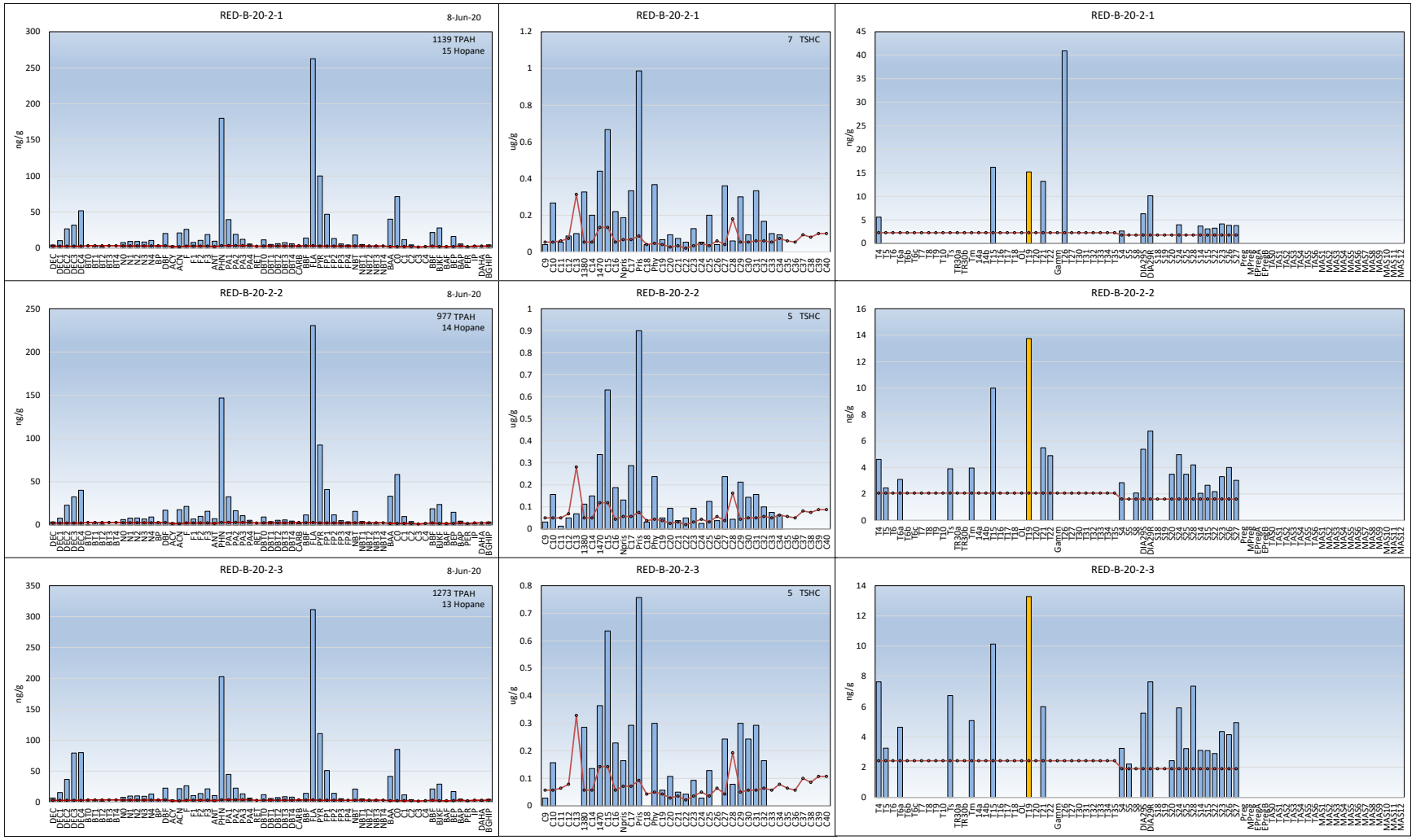
The dotted red line represents the sample-specific method detection limits (MDL) for PAH, SHC, and biomarkers.

2020 Sediment Lab Method Blanks



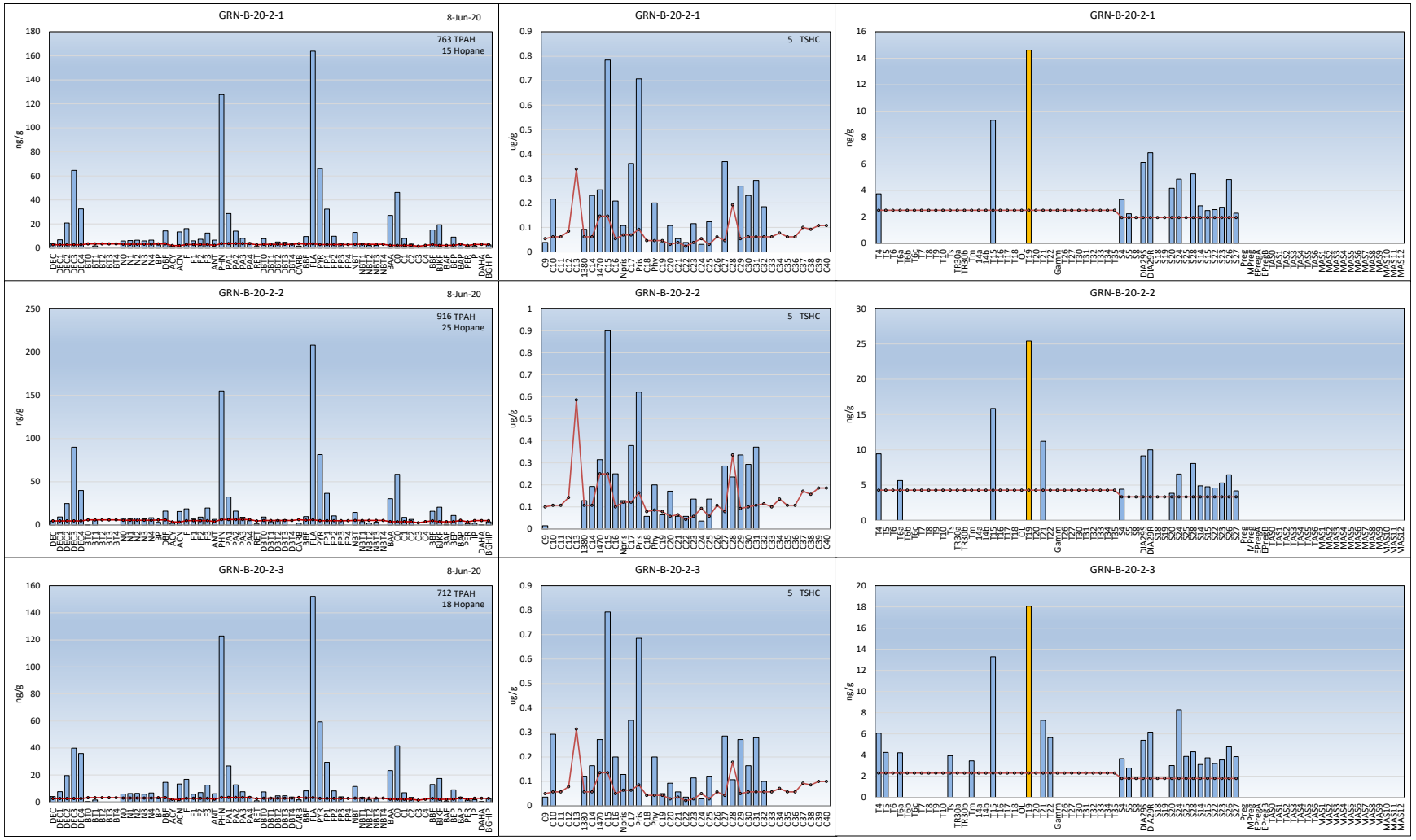
The dotted red line represents the sample-specific method detection limits (MDL) for PAH, SHC, and biomarkers.

2020 Red Tissues (Valdez Small Boat Harbor Entrance)



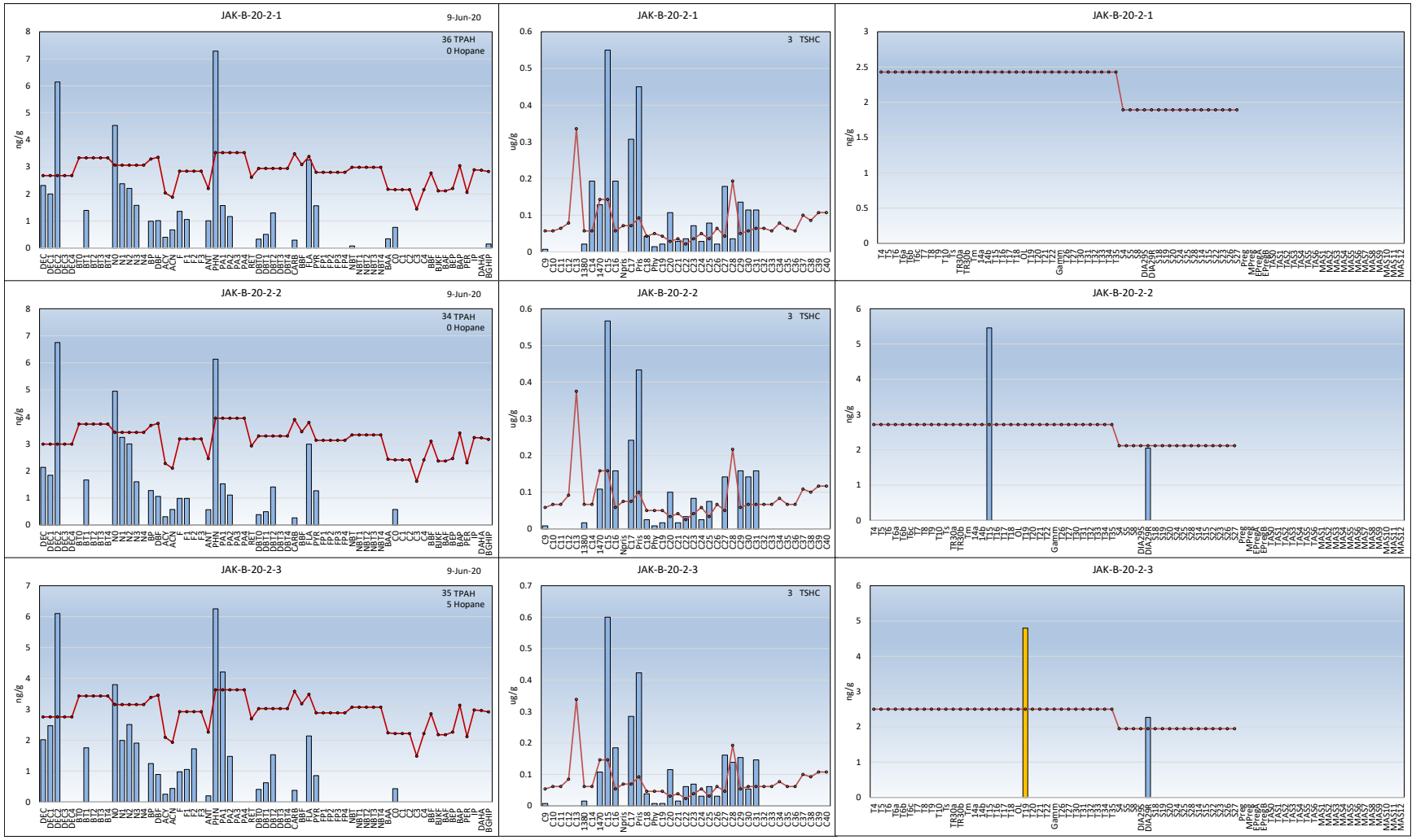
The dotted red line represents the sample-specific method detection limits (MDL) for PAH, SHC, and biomarkers.

2020 Green Tissues (Valdez Small Boat Harbor Entrance)



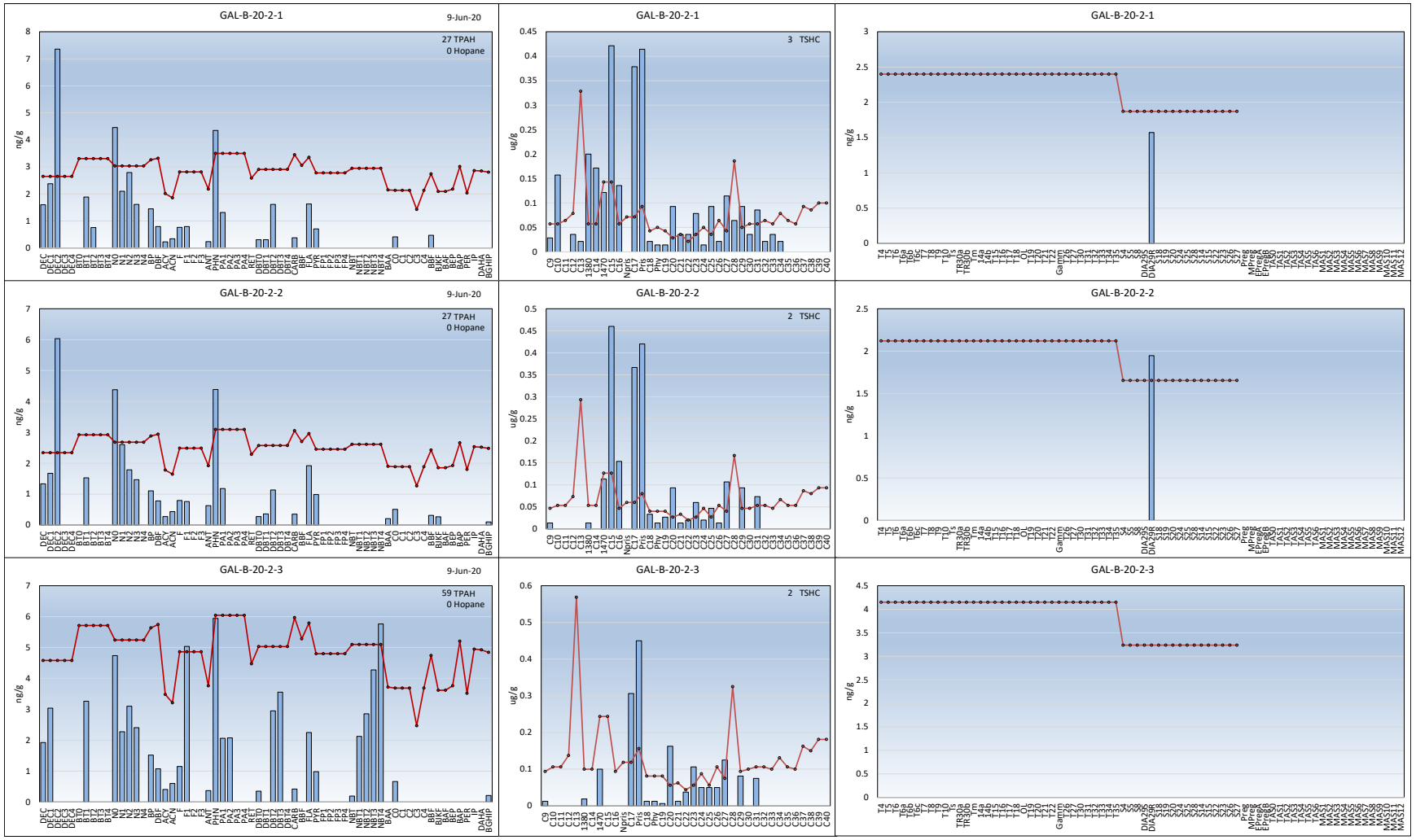
The dotted red line represents the sample-specific method detection limits (MDL) for PAH, SHC, and biomarkers.

2020 Jack Bay Tissues (PAH, SHC and Biomarkers)



The dotted red line represents the sample-specific method detection limits (MDL) for PAH, SHC, and biomarkers.

2020 Galena Bay Tissues (PAH, SHC and Biomarkers)



The dotted red line represents the sample-specific method detection limits (MDL) for PAH, SHC, and biomarkers.

APPENDIX 3. PROJECT HISTORY

The Long-Term Environmental Monitoring Program (LTEMP) data serve to monitor and provide independent quality-control for Alyeska Pipeline Service Company's Valdez Marine Terminal (VMT) and tanker operations throughout the Prince William Sound (PWS) and Gulf of Alaska (GOA) region. The primary goal of this on-going Prince William Sound Regional Citizens' Advisory Council (PWSRCAC) program is to monitor impacts from oil transportation activities on the environment at selected sites from PWS and GOA for "as long as the oil flows through the pipeline."

At the VMT, the Ballast Water Treatment Facility (BWTF) treats and discharges oil-contaminated ballast water offloaded from tankers utilizing the terminal. Since the Program's inception in 1993, two stations have been traditionally sampled to assess impacts from the effluent: at Alyeska's terminal adjacent to the offshore BWTF discharge diffusers near Berth 4 for sediments (AMT-S) and at Saw Island near Berth 5 for mussels (AMT-B); and at Gold Creek (GOC), a reference station 6 km across the Port (Figure 28) for both sediments and mussels. Another station, Jackson Point (JAP), was added in 2016 near Berth 3, towards the opposite (eastern) end of the terminal. Currently measured variables include levels of polycyclic aromatic hydrocarbons (PAH) and saturated hydrocarbons (SHC), as well as oil biomarkers in mussel (*Mytilus trossulus*) tissues from the three stations within the Port. Eight additional stations, comprising the geographic reach of the *Exxon Valdez* oil spill (EVOS), are now sampled every five years (last sampled in 2018) between Valdez and Kodiak (Figure 29, Table 6).

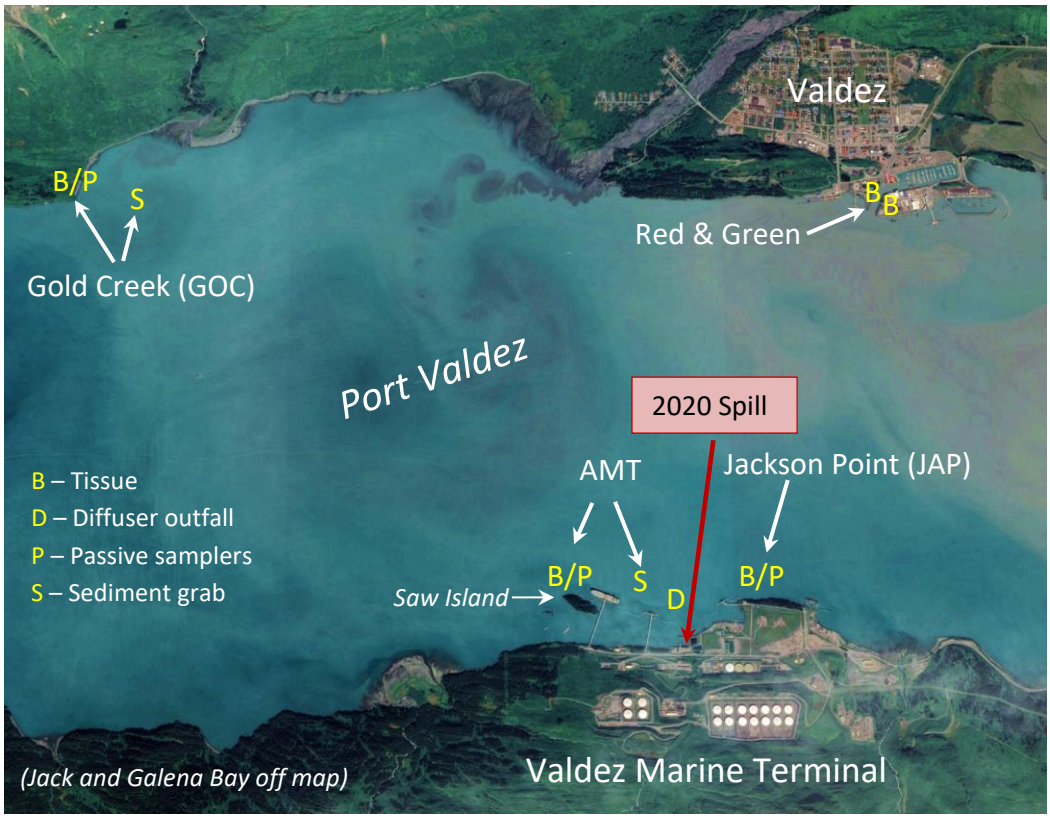


Figure 28. LTEMP sampling stations in Port Valdez adjacent to (AMT-B, AMT-S, and JAP) and 6 km northwest (GOC) of the VMT. This Google Earth image shows a tanker docked at Berth 5.

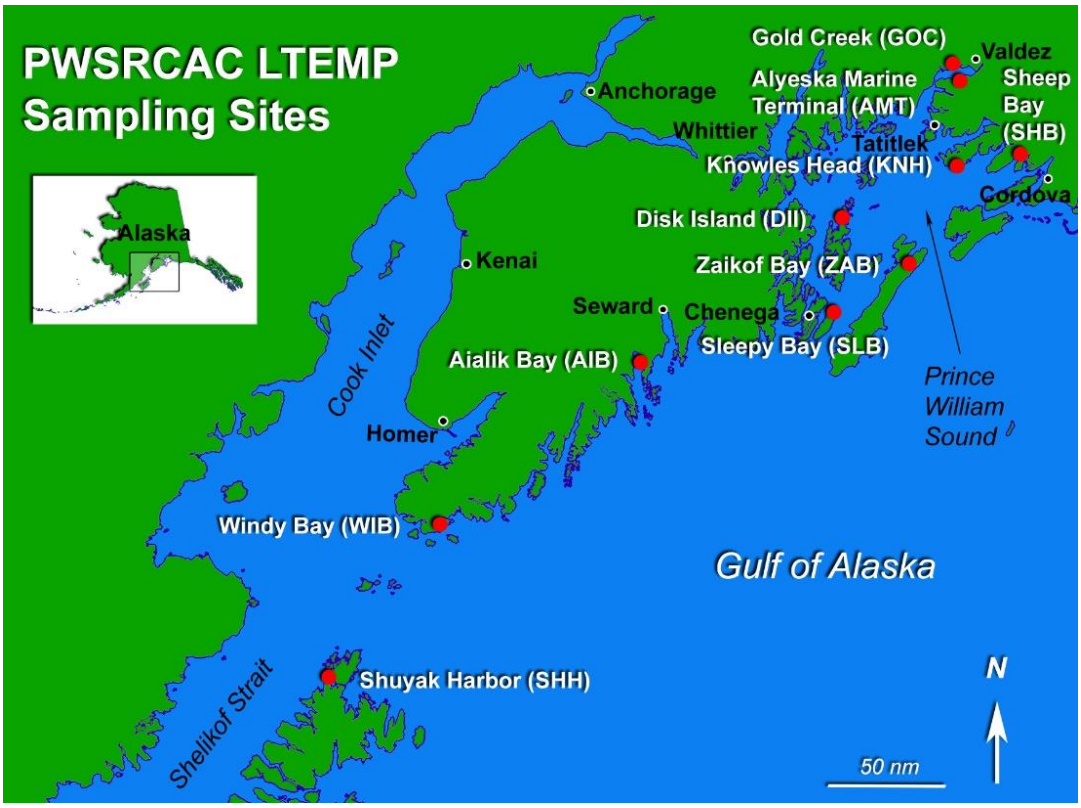


Figure 29. Map of the LTEMP sites with station abbreviations.

Sediment samples collected from the two Port stations are analyzed for PAH, SHC, particle grain size, and total organic carbon content, with oil biomarkers added in recent years to confirm petrogenic sources. Sampling and analytical methods are modelled after the protocols developed by the National Oceanic and Atmospheric Administration (NOAA) Status and Trends Mussel Watch Program as fully detailed in previous annual monitoring reports prepared by Kinnetic Laboratories, Inc. (KLI), the Geochemical and Environmental Research Group (GERG), and Payne Environmental Consultants, Inc. (PECI).

Following the first five years of the program, the collective results from the KLI/GERG team were reviewed in a synthesis paper (Payne et al., 1998). At that time, sampling was more extensive, and identification of weathered sources was important (Table 5-1 in Payne et al., 1998). The results effectively documented higher background oil levels while identifying hot spots and both large and small spill events. Subsequently, the PWSRCAC reduced the scope of the program from triannual to just spring and summer sampling of regional mussel tissues and Port Valdez sediments. Fall mussel sampling (without sediments) was then re-added just in Port Valdez (AMT-B and GOC-B) to better track the terminal's discharge. Mussel-tissue SHC analyses that were dropped from the original program in 1995 (due to results being confounded by lipid interference) were reinstated in 1998 using improved laboratory methods.

Table 6. LTEMP tissue sampling history showing change in annual events coded for seasons. Spring, summer (SS); spring, summer, autumn (SSA); or summer only (S). Sediments (not shown) were sampled in spring and summer at AMT-S and GOC-S from 1993-2008, and afterwards only in summer.

LTEMP Station Mussel Samplings												
	Port Valdez			Prince William Sound						Gulf of Alaska		
	AMT-B	JAP	GOC-B	KNH	DII	SLB	ZAI	SHB	COH	AIB	WIB	SHH
1993	SS		SS	SS	SS	SS	SS	SS		SS	SS	SS
1994	SS		SS	SA	SA	SA	SA	SA		SA	SA	SA
1995	SS		SS	SS	SS	SS	SS	SS		SS	SS	SS
1996	SS		SS	SS	SS	SS	SS	SS		SS	SS	SS
1997	SS		SS	SS	SS	SS	SS	SS		SS	SS	SS
1998	SS		SS	SS	SS	SS	SS	SS		SS	SS	SS
1999	SSA		SSA	SS	SS	SS	SS	SS		SS	SS	SS
2000	SSA		SSA	SS	SS	SS	SS	SS		SS	SS	SS
2001	SSA		SSA	SS	SS	SS	SS	SS		SS	SS	SS
2002	SSA		SSA	SS	SS	SS	SS	SS		SS	SS	SS
2003	SSA		SSA	SS	SS	SS	SS	SS		SS	SS	SS
2004	SSA		SSA	SS	SS	SS	SS	SS		SS	SS	SS
2005	SSA		SSA	SS	SS	SS	SS	SS	S	SS	SS	SS
2006	SSA		SSA	SS	SS	SS	SS	SS	SS	SS	SS	SS
2007	SSA		SSA	SS	SS	SS	SS	SS	S	SS	SS	SS
2008	SA		SSA	S	S	S	S	S		S	S	S
2009	SS		SS	S	S	S	S	S		S	S	S
2010	S		S	S								
2011	S		S	S								
2012	S		S	S								
2013	S		S	S	S	S	S	S		S	S	S
2014												
2015	S		S	S				S				
2016	S	S	S									
2017	S	S	S									
2018	S	S	S	S	S	S	S	S		S	S	S
2019	S	S	S									
2020	S	S	S									

In 2001, another comprehensive data evaluation and synthesis was completed on just the Port Valdez sites' LTEMP results (Payne et al., 2001). From AMT-B and the GOC-B reference site, Alaska North Slope (ANS) crude oil residues from the terminal's BWTF were shown to accumulate in the intertidal mussels. However, the sediment and tissue (and the estimated water-column) PAH and SHC levels were very low.

More importantly, the pattern and trend of signatures suggested a novel transport/exposure mechanism; discrimination of particulate (oil droplet) and dissolved-phase signals in the water column correlated with seasonal

uptake in Port Valdez mussels (Payne et al., 2001). Stratified waters formed during the milder seasonal winds of late-spring/summer kept the discharge plume's particulate oil-phase droplets from the surface but dissolved-phase components could be observed in the intertidal mussels. The wind-mixed, non-stratified waters of fall/winter allowed some portion of the plume's particulate/oil phase to surface, which was then visible in the mussel tissues. The results suggested a surface microlayer mechanism may be responsible for seasonal transport of ANS weathered oil residues from the BWTF diffuser to intertidal zones across the fjord. Combined with other study results showing toxic absorption in herring eggs at trace levels, the authors warned that the potential for photo-enhanced toxicity of concentrated contaminants in a surface microlayer should be considered in future impact investigations (Payne et al., 2001, 2003a, 2003b, 2005c). This effect has likely disappeared with the current diminished discharge flows.

In July 2002, PECI and the NOAA/National Marine Fisheries Service (NMFS) Auke Bay Laboratory (ABL) began collecting and analyzing the LTEMP samples. Changing laboratories can be problematic; detailed discussions of the transitional 2002/2003 LTEMP samples and inter-laboratory comparisons of split samples and Standard Reference Materials (SRMs) analyzed by both GERG and ABL are presented in Payne et al., (2003b). The results from the 2003/2004 LTEMP and a comprehensive review and synthesis of all analyses completed since the beginning of the program are available in Payne et al., (2005a, 2006, 2008a). Results and discussion of the program through 2006 were also published in the journal, "Marine Pollution Bulletin" (Payne et al., 2008b).

The program again changed analytical services in 2016 when ABL closed its hydrocarbon facilities in Juneau, Alaska. This decision necessitated a switch to Alpha/NewFields in Mansfield, Massachusetts as the PWSRCAC contract laboratory for LTEMP. Alpha/NewFields was the primary laboratory used by NOAA and other State and Federal Trustees for the 2010-2016 Natural Resource Damage Assessment (NRDA) effort following the BP *Deepwater Horizon* oil spill (Driskell and Payne, 2018a, 2018b; Payne and Driskell, 2017a, 2018a; Stout and Payne, 2016a, 2016b, 2017; Stout et al., 2016a, 2016b). For that event, Alpha/NewFields analyzed ~30 thousand sediment, water, and tissue samples, all with independent, third-party quality control (QC) validation as part of that litigation-sensitive effort. The LTEMP lab transition also involved performance-based round-robin intercalibration programs in which both ABL and Alpha/NewFields participated to demonstrate they were generating comparable data with known precision, accuracy, method detection limits, and representativeness.

Prior to this report, all 10 LTEMP sites were most recently visited in July 2008, April 2009, and then, beginning the reduced effort, 5-year interval scheme, in July 2013 and 2018 (Table 6). Visits included three sites in or near the Port to monitor terminal and tanker operations, six others to monitor the more remote sites for lingering EVOS impacts, plus Sheep Bay (SHB) which serves as a non-EVOS-impacted control. Initially, to more thoroughly monitor Port operations, LTEMP collections had been taken tri-annually at the two Port sites and nearby Knowles Head (KNH) but efforts were later reduced to annual sampling. Under this modified plan, in 2015, sampling occurred at four of the 10 LTEMP stations: AMT, GOC, KNH, and SHB (Payne et al., 2016). In 2016, another mussel sampling site was added at JAP at the terminal but on the opposite side (east) of the active berths and the traditional station at Saw Island (AMT-B). This site was meant to evaluate a potential PAH gradient to either side of the BWTF outfall and to correlate tissue data with passive-sampling devices (PSDs) that were concurrently deployed subsurface at the same terminal locations (Minick and Allan, 2016; Allan, 2018).

Sampling in 2018 fell on the five-year cycle and covered all 11 sites (Payne and Driskell, 2019). In 2019-20, just the 3 Port Valdez sites were visited (Payne and Driskell, 2020).

Recent years have brought change to both the system and the environment as pipeline throughput has dropped from 85.3 million gallons per day (MGD) at its peak in 1988 to current levels of 20.2 MGD (Figure 30). Likewise, tanker regulations have instituted double-hulled tankers with segregated ballast. Aboard segregated-ballast vessels, empty

cargo tanks are typically used for supplemental ballast only when operationally necessary (e.g., during winter storms), (i.e., the normal segregated ballast waters are uncontaminated seawater that do not require treatment for hydrocarbons). Treated-ballast water discharges to the Port have also swung from a maximum of around 15 MGD in 1990 to currently only 0.96 MGD (Table 7). Facility operators estimate, and Alyeska's Discharge Monitoring Report (DMR) data confirm, that more than half of the current BWTF effluent discharge in summer is from the terminal's stormwater runoff (Rich Loftin, personal communication, 2016). In summary, less tanker traffic, cleaner ballast, and an improved ballast-water-treatment configuration at the VMT have resulted in substantial reductions in detected hydrocarbon concentrations and composition in the field samples. All discharges are made under an Alaska Pollutant Discharge Elimination System (APDES) Permit for which the PWSRCAC submitted detailed reviews during the last three permit renewal cycles (Payne et al., 2003c and 2012, PWSRCAC, 2019).

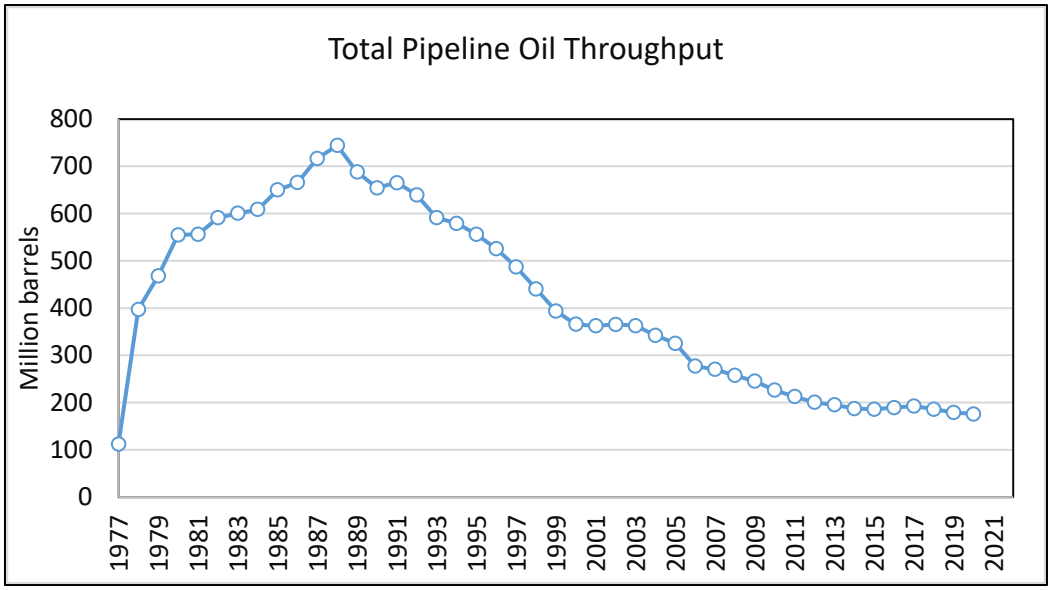


Figure 30. Annual pipeline oil throughput (M barrels) from Alyeska statistics.

Table 7. Recent average daily throughput of Alyeska Pipeline and ballast water treatment (MGD).

	2015	2016	2017	2018	2019	2020
Pipeline throughput	20.6	21.8	22.3	21.4	20.6	20.2
BWTF throughput	1.10	1.00	0.88	1.11	0.81	0.96

APPENDIX 4. METHODS

Collection and analytical methods have been described in previous LTEMP reports (Payne et al., 2003b, 2005a, 2006, 2008a, 2010a, 2013, 2015, 2016; Payne and Driskell 2017b, 2018c, 2019). Briefly, three replicates of 30 mussels are collected by hand at each site while triplicate sediment samples are collected from the two Port locations (AMT-S and GOC-S) using a modified Van Veen grab (Figure 31). Sampling protocols have remained the same but as noted in Appendix 3, Alpha Analytical Laboratory (Mansfield, MA) under the guidance of NewFields Environmental Forensics Practice (Rockland, MA) now provides the analytical services.

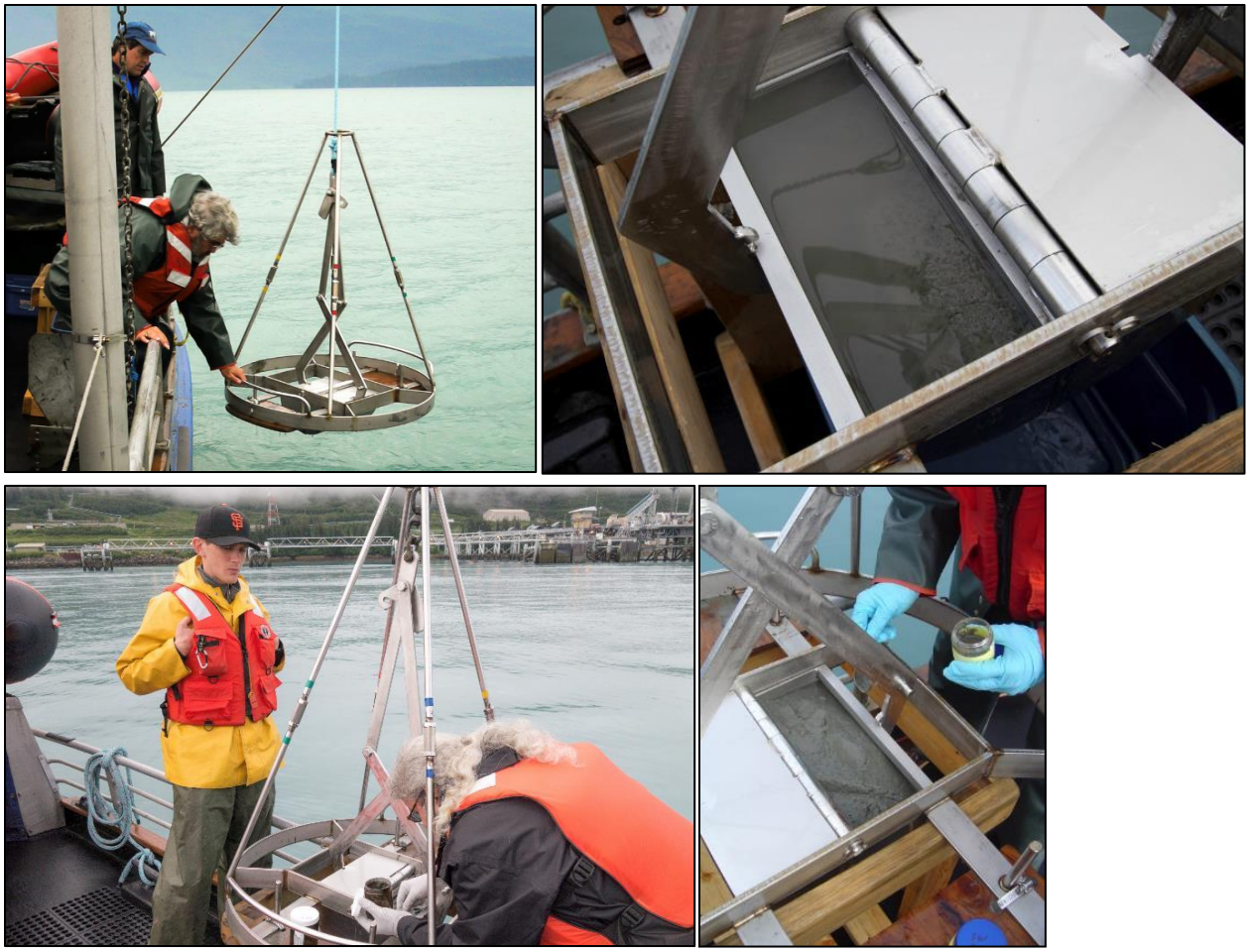


Figure 31. Deploying the Van Veen grab (upper left). View of benthic sediments collected with intact surface layer (and residual water) in jaws (upper right) before sampling (bottom). Work photos courtesy of David Janka.

The usual hydrocarbon data are reported: polycyclic aromatic hydrocarbons (PAH), sterane/triterpane biomarkers (S/T), and saturated hydrocarbons (SHC). Semi-volatile compounds, the PAH, alkylated PAH, and petroleum biomarkers, are analyzed using selected ion monitoring gas chromatography/mass spectrometry (SIM GC/MS) via a modified Environmental Protection Agency (EPA) Method 8270 (aka 8270M). This analysis provides the concentration of 1) approximately 80 PAH, alkylated PAH homologues, individual PAH isomers, and sulfur-containing aromatics and 2) approximately 50 tricyclic and pentacyclic triterpanes, regular and rearranged steranes, and triaromatic and monoaromatic steroids. Complete lists of PAH, SHC, and biomarker (S/T) analytes are presented in Appendix 1 along with the analyte abbreviations used in figures throughout this report.

Using a modified EPA Method 8015B, SHC in sediments and tissues are quantified as total extractable materials (TEM; C_9-C_{44}) and as concentrations of n-alkanes (C_9-C_{40}) and selected (C_{15}-C_{20}) acyclic isoprenoids (e.g., pristane and phytane). A high-resolution gas chromatography-flame ionization detector (GC/FID) fingerprint of the sediment and tissue samples is also provided.

Added to the project in 2017, low-density polyethylene, PSD were deployed for ~30 days following Oregon State University (OSU) protocols (Figure 32) (Sowers et al., 2008, Huckins et al., 2006, O'Connell et al., 2013). Laboratory handling, sample extraction and analyses of the PSDs followed respective OSU, Food Safety and Environmental Stewardship (FSES) Program Standard Operating Procedures (SOPs).

Figure 32. Example of passive sampling device (PSD) consisting of a low-density polyethylene membrane strip enclosed in a stainless-steel container and deployed subsurface in near-shore subtidal waters adjacent to LTEMP mussel collection sites. Work photos courtesy of David Janka.

DATA ANALYSIS

Port Valdez LTEMP data are interesting in a couple of respects; the data are quite rich in number of analytes and long in time span but only represent three locations in the Port. From these data, there are two main questions: 1) do the detected hydrocarbons come from the ballast-water operations and 2) do the hydrocarbons reach a level for concern?

There have been three approaches to addressing these questions. Initially, the PWSRCAC contractors, Kinnetic Laboratories, Inc. (KLI), used hypothesis-testing statistical methods (e.g., ANOVAs and t-tests) to see whether various values, ratios, and indices were significantly different in order to highlight trends. University of Alaska Fairbanks (UAF) contractors for Alyeska tend towards exploratory multivariate approaches (e.g., PCA, MDS, kriging) on various values to understand sources, correlations, and trends. The results are impressive with a much larger set of stations sampled but considering the subset of PAH analytes they report, which constrains any fuller understanding, the project leaves many questions unanswered. In contrast, since the LTEMP data set represents only three Port stations, we emphasize expert pattern recognition to tease out/confirm the source and phase state of the sample and then apply those results for the Port's environmental trends scenario.

Per common practice, analytical chemistry results are presented in this report as bar plot profiles for each analyte. Note that for the alkylated PAH (whereby C1-, C2-, C3- and C4- are the alkyl members, meaning carbons attached to the parent molecule), the plotted bars are actually histograms representing the sum of alkylated homologue components. For example, C1-naphthalene, a two-ringed compound with an attached methyl group (one carbon) has two isomer forms with each appearing as a unique peak on the instrument. They are individually quantified but

reported and plotted as a combined sum (abbreviated as "N1"); C2-naphthalenes (with two attached methyl groups or one ethyl group) have 12 isomers (abbreviated as "N2"), and C4-chrysenes have 1,016 possible isomers (abbreviated as "C4" when plotted). Again, these alkylated isomer homologues are summed into one value for the bar plots. Also, as described in each sample's figure caption in this report, some appropriate reference is depicted as a red-colored reference line scaled and overlaid on the selected individual tissue or sediment's profile (e.g., the summer BWTF-effluent profile or ANS source oil). Method detection limit (MDL) overlays are commonly shown for selected time-series data profiles and are shown for all 2020 samples in Appendix 2. Details of our BWTF-effluent sampling and analytical procedures and the importance of differentiating between dissolved and particulate/oil phases are published in Appendix 2 of Payne and Driskell (2017b).

BIOMARKERS

Petroleum biomarkers are conservative, weathering-resistant, hydrocarbon compounds, unique to each oil formation, which present a less degraded hydrocarbon signature than those of the SHC and PAH. In the environment, the SHC are quickly consumed by microbes, which gives forensic reviewers a perspective of "freshness" of crude oil patterns while also distinguishing petroleum distillates (diesel vs. fuel oil vs. crude oil, etc.), and tagging contributions from other (primarily biogenic) sources. PAH compounds are more persistent, weathering slower in predictable patterns and rates, which serve to track a longer-term fate, behavior, and mixing with other sources. In contrast, the biomarkers are the hydrocarbon "tattoos," enduring telltales of oil's presence even as the PAH and SHC patterns are weathering and disappearing. For LTEMP, biomarkers can facilitate and confirm detection of VMT-derived, ANS crude-oil constituents in Port sediments – even when the PAH are heavily degraded. [2]

Beginning in 2011, biomarkers were analyzed for sediments and in 2016, also for tissues. For routine monitoring, however, mussel tissue biomarkers are generally less effective than in sediments as the mussels regularly purge and, currently at most LTEMP stations, only carry trace-level, dissolved-phase, and combustion-derived PAH components (i.e., no biomarkers). Note that the biomarkers are water-insoluble and thus, would only be detected in tissues when particulate oil was present, for example, free oil droplets from a chronic or recent release such as the 2020 VMT sump spill (report in prep).

Multiple approaches have been suggested for interpreting biomarker data, but some degree of expert-guided pattern matching must be employed. Most schemes involve various diagnostic ratios (Stout and Wang, 2016) with several ratios normalized to the highly conservative 17α(H),21β(H)-hopane (also labeled T19 or C30 hopane and herein tagged in the bar plots with a golden fill color for visual reference). But despite the purported persistence of biomarkers, depending on the local environs and microbial adeptness, all ratios are not equally effective and must be individually evaluated for a given spill/habitat. For interpreting LTEMP data, we initially screen PAH and biomarker results graphically with an ANS-oil-reference overlay normalized to the sample's hopane. For biomarkers, the frequently reliable, Ts/Tm and norhopane (T15)/hopane ratios were used to confirm the visual similarities. For this report, we utilize all appropriate and available ratio data and present the overall patterns to facilitate their interpretations.

[2] For readers who are not familiar with oil spill fingerprinting or forensics, see Appendix 6 in our 2015 LTEMP Report (Payne et al., 2015) for a background primer specific to ANS crude oil, combustion products, and other potential oil sources in Port Valdez and the PWS/GOA region. Additional details are available in Stout and Wang (2007 and 2016).

APPENDIX 5. LABORATORY PERFORMANCE

LABORATORY QUALITY CONTROL

All Alpha/NewFields-analyzed constituents (Appendix 1) are reported on a ng/g dry weight (DW) basis uncorrected for blanks or surrogate recoveries. Surrogates are novel or deuterated compounds added in known amounts to each raw sample to assess, by their final percent recovery, the efficiency of extraction and analysis. Surrogate recoveries are considered acceptable if they are between 40% and 120%. A single recovery deviance flags the sample with cautionary remarks; multiple recovery deviations would require batch reanalysis. Surrogate recovery standards were met for all PAH, biomarker and alkane surrogate hydrocarbons analyzed during the 2020 reporting period (Table 8). Laboratory method blanks for each analytic sample batch demonstrated (sub-ng/g) laboratory or analytic background PAH interference.

Table 8. Surrogate recovery statistics by matrix from 2020 Alpha Laboratory analyses.

	Tissue					Sediment				
Surrogate	Average (%)	Max	Min	Count	StdDev	Average (%)	Max	Min	Count	StdDev
5B(H)Cholane	97	109	87	25	6	94	100	89	15	3
Benzo[a]pyrene-d12	83	94	73	29	5	95	102	87	15	5
d50-Tetracosane	91	101	81	24	5	93	102	85	15	4
Naphthalene-d8	64	76	55	29	6	82	95	68	15	7
o-terphenyl						93	96	85	15	3
Phenanthrene-d10	80	91	74	29	3	99	108	90	15	4

Mussel-tissue hydrocarbon levels are often so low throughout the study region that individual PAH were reported at below-MDL concentrations and patterns in both tissues and their associated laboratory/method blanks. At these exceptionally low PAH levels, it is not possible to assure that the measured analytes in the field samples accurately quantify the analytes (discussed in next section).

In addition, some matrix interferents were flagged for two sediment biomarkers, T26 and T32, and one SHC, C_{32}, in their lab qualifiers. As obvious anomalies, they were ignored for sediment data-pattern interpretations. Per our standard forensic reporting practices, the data discussed herein are neither blank-corrected nor surrogate-recovery-corrected but are simply reported as raw data (with below-MDL values flagged as estimated). All PAH, biomarker, and SHC profiles presented in Appendix 2 are shown with their analytical-batch-associated method blanks along with sample-specific MDLs overlaid on the histogram profiles.

METHOD DETECTION LIMITS

One lab-performance quality control (QC) measure is the EPA-formulated, statistically-derived, analyte-specific, Method Detection Limit (MDL) that EPA defines as "the minimum measured concentration of a substance that can be reported with 99% confidence that the measured concentration is distinguishable from method blank results." Alpha Analytical Laboratory's MDLs for hydrocarbons exceed the performance of most commercial labs, falling within the accepted stricter levels for forensic purposes (Table 9).

Table 9. Alpha Analytical MDL target ranges.

Analytes	Sediment (30 g, sample size)	Tissue (15 g sample size)	Water (1 L sample size)	Oil Reporting Level (RL)
PAH and biomarkers	0.1-0.5 ng/g DW	0.2-1.0 ng/g DW	1-5 ng/L	2.0 µg/g
SHC	0.05 µg/g DW	0.01-0.08 µg/g DW	0.8 µg/L	200 µg/g

For data interpretation, there are generally two approaches on the use of MDLs: 1) censor all below-MDL data to some pre-decided level (which leads to further issues on how to interpret partially censored, multi-analyte data sets such as LTEMP) or 2) treat below-MDL data as estimated real values. For reasons described below, it is felt that the second option best serves the purpose of the LTEMP program. For both the readers and our benefit in reviewing data, individual analyte MDLs (adjusted to sample weight) appear as red dotted lines on PAH and SHC plots where appropriate in report figures and in all sample plots presented in Appendix 2.[3]

By definition, EPA's MDL protocol is designed to control against false positives at the 99% confidence level in an ideal matrix. In other words, MDLs are meant to represent a trustworthy value of low detection, below which, due to expected uncontrolled factors, lower results are not as reliable—the values are estimates of lesser confidence. This reporting bulwark is certainly required when reviewing a crucial single-analyte result (e.g., water arsenic concentrations, where the statistically determined MDL value ensures against toxic consequences). But there are two differences between this example and the LTEMP dataset.

First, there are no "critical values" involved in the current LTEMP data review; false positives will not affect the overall findings of "PAH are dropping to lower historic lows." While the MDL procedure is designed to avoid false positives at the 99% confidence level; if a lower confidence level is acceptable, then EPA-defined MDL levels are unnecessarily stringent for the application.

Secondly, because LTEMP data interpretations are based on multi-analyte patterns rather than single values, additional confidence accrues from "pattern expectations." Conceptually, the more information known about a system or data set, the higher the confidence when seeing recognizable patterns. Such is the case with LTEMP data. Oil weathers predictably (see Appendix 6 in Payne et al., 2015) and if a sample's PAH profile appears to represent a recognizable pattern, then applying the statistically established, single-analyte MDLs to censure the data would be unnecessarily conservative. For example, if a sample's phenanthrenes/anthracenes (P/As) were reported above MDL levels while dibenzothiophenes and chrysenes (DBTs and Cs) were reported below MDLs but in the same pattern and ratio as the source oil, there would be sufficient confidence in the expected patterns that those detected analytes, albeit below-MDL, were not false positives and that the values had been reasonably estimated. In past LTEMP efforts where near-trace-level tissue data were reported, this added-confidence was further bolstered by seeing higher-level coincidence patterns of within-site fidelity and regional-wide commonalities that collectively changed between years—which could only occur if the patterns were real, reflecting conditions in the field, and not false positives from lab or procedural artifacts (e.g., see Appendix 3 in Payne et al., 2015). In LTEMP data, MDLs mainly serve to tag when reported values have become, to some degree, estimated. Conversely, when an unrecognizable pattern or anomalous spike appears, it is easily spotted, flagged as an outlier, and closely examined along with any corroborating evidence (e.g., lab QC and field notes) to see if it makes any sense or is indeed a lab, sampling, or field anomaly.

[3] For forensics evaluations, PAH, SHC, and S/T plots in the main body of this report are typically shown with dotted-red-line overlays corresponding to a relevant reference source oil or BWTF effluent.

In the 2018 and 2019 mussel-tissue samples, however, similar trace-level, below-MDL PAH patterns were observed in all the field samples and their batch-associated laboratory method blanks. With these PAH data, source-identifications based on pattern recognition are not possible; it can only be reported that the individual and total PAH (TPAH) concentrations are below a background level. In 2020, concentrations rose above MDLs.

APPENDIX 6. SEDIMENT GRAIN SIZE

The LTEMP sediment-sampling locations comprise a heterogeneous slope at AMT-S and sediment shelf at GOC-S inside a fjord dynamically swept by tidal currents (and prop wash at AMT-S). Plus, with LTEMP sampling guided by GPS, the sites have been accruing grab-sampler pock marks and drag scars at the same locations for 20 years. Reassuringly, when the sampling vessel gets off-site at GOC-S, we begin to see gravel tell-tales in the grab. The grain-size component trends are presented here with only modest confidence considering the non-rigorous collection methods (i.e., spooning up 250 mL of sediment remnants after collecting the less consolidated, top cm of surface floc for hydrocarbon analyses). There was also a change in analytical labs in 2016.

Sediment particle-grain-size (PGS) samples are presented for all 2006-2020 collections in two formats: the standard cumulative (%) grain-size curves and a 3D trend plot. For this project, the grain-size data only serve to demonstrate the long-term constancy and comparability of the sampling site environs.

Both sites are dominated by glacial flour inputs, showing approximately equal portions of clay and silt with minor sand components (Figure 33 and Table 10) and with both sites showing minor trends and outliers. In the 3D plots (Figure 34), note there are annual shifts at GOC-S (~30m depth) to higher sand content and back (albeit still a minor component, mostly ~10%) and with a return to earlier conditions in 2013. But in 2015, a shift to coarser particles occurred when silt increased and clay decreased dramatically. In 2016, 2017, and 2018, there was further return towards a clay- and slit-dominated substrate. The 2019 GOC-S samples have remained close to the average portions. At AMT-S (~70 m depth), there has been a cycle of increasing clay content through 2009 and then a decrease, returning to 2006 levels by 2015-16. In 2016, there was also a halving of sand, albeit still a minor component (~3%). In 2017, the sand portion decreased further as clay became dominant, but in 2018 all of the percentages more closely matched the 12-year averages with clay still being slightly dominant (Table 10). In 2019, an anomaly occurs in AMT-S data; an unexpectedly high portion of sand appears in the second and third of the three samples collected as the first replicate shows the normal fine sand portion with a dramatic increase in silt (Figure 34). We suspect the second and third PGS replicates, taken by a new sampling technician on the project, reflect digging deeper into the grab sample than normal, i.e., rather than just the surface layer. Note that the PGS sample is always taken after the chemistry sample and would not affect the chemistry assessment.

In 2020, all PGS sample parameters returned to their respective station's centroids (Table 10).

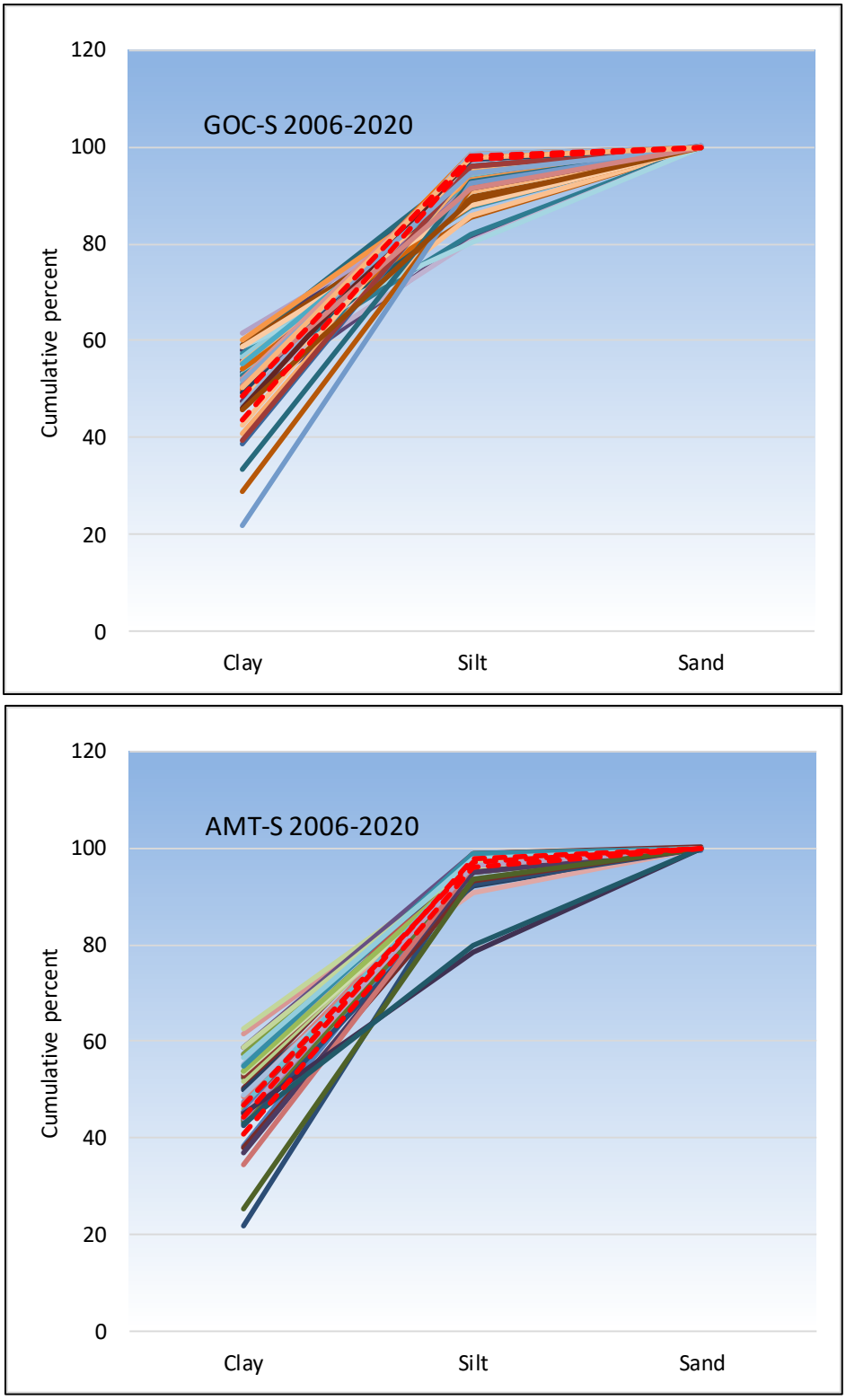


Figure 33. Individual replicate cumulative grain-size curves (%) for GOC-S and AMT-S, 2006-2020. 2020's reps are indicated by dotted red lines.

Table 10. Average grain size components for GOC-S and AMT-S, 2006-2020.

AMT-S				GOC-S			
Year	% Sand	% Silt	% Clay	Year	% Sand	% Silt	% Clay
2006	1	55	43	2006	6	44	51
2007[1]	2	54	44	2007[1]	7	37	56
2008	2	54	44	2008	9	36	55
2009[1]	4	40	56	2009[1]	10	35	55
2010	3	49	48	2010	9	38	53
2011	3	45	51	2011	16	32	52
2012	7	40	53	2012	17	27	56
2013	5	42	53	2013	7	37	56
2015	6	54	40	2015	8	64	28
2016	3	55	42	2016	4	56	40
2017	1	42	57	2017	2	49	50
2018	3	44	53	2018	2	52	46
2019	16[2]	46	38	2019	8	42	49
2020	3	53	44	2020	2	50	48
avg	4	48	48	avg	8	43	50

[1]Combines two seasons of sampling

[2]Likely biased high

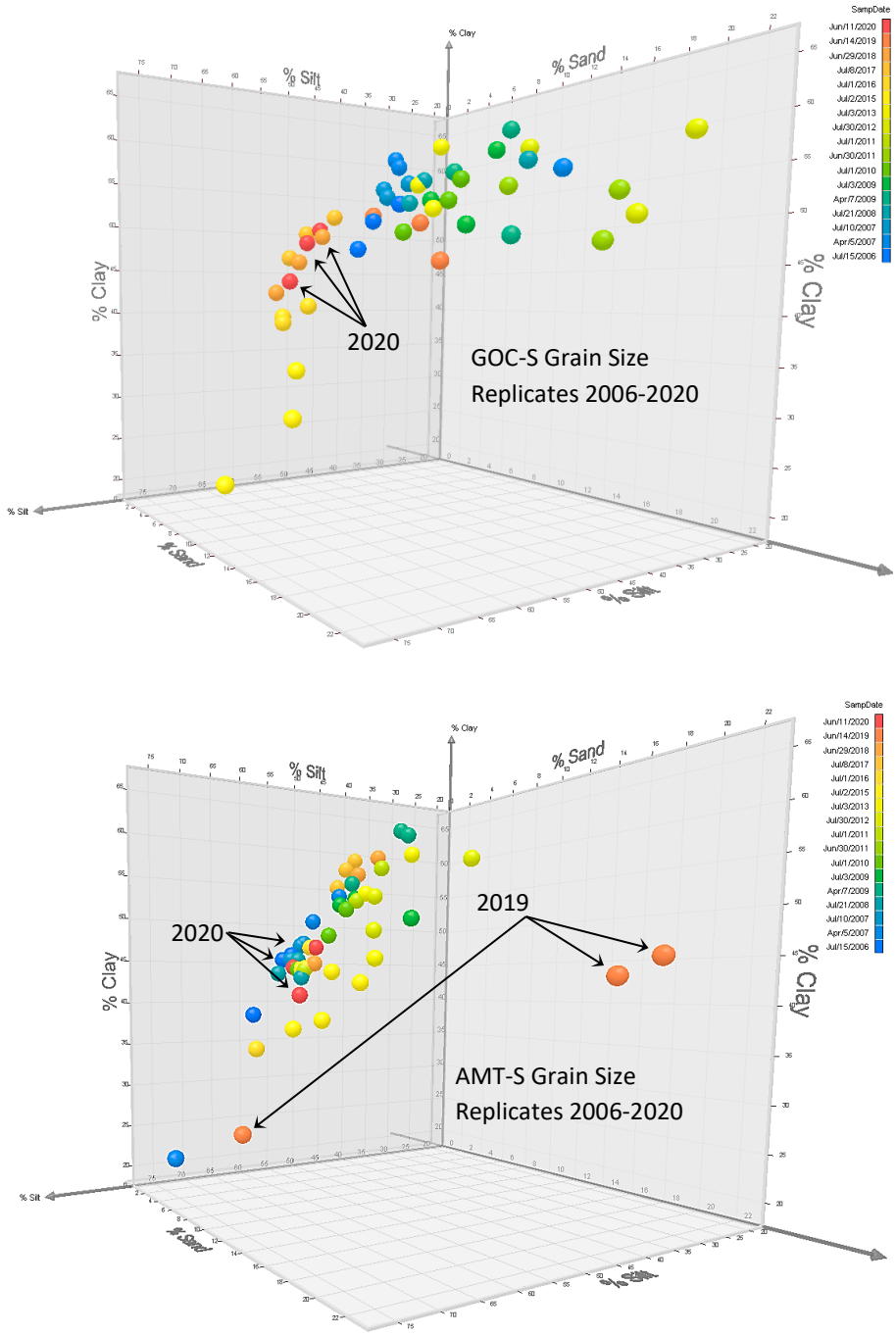


Figure 34. 3D plots of grain size components from GOC-S and AMT-S 2006-2020. Sampling years are color coded: blue to orange, 2006-2019; Red, 2020. Note the clipped axes emphasize a decreasing shift in clay vs silt at GOC-S in 2015. The two 2019 AMT-S outlier samples with anomalously high sand content (~20%) appear to be sampling method errors.

APPENDIX 7. SEDIMENT TOC

Total organic carbon (TOC as the percentage of sediment dry weight) serves as a non-specific measurement of all organics in a sample. Typically ranging from 0.1 to 30% in marine sediments, it is used to express the nutritional quality of food available to benthic organisms. For pollution work, metals and anthropogenic organic compounds tend to sorb and concentrate in or on finer grained sediments and TOC, respectively, and thus TOC can be used to normalize contaminant concentrations to do site-to-site contaminant comparisons.

During the more frequent samplings early in the LTEMP program, TOC values showed seasonal cycles (reflecting spring plankton blooms) and with a slow increase in concentration plateauing around 2003 (Figure 35 and Table 11). There was an uptick at GOC-S in 2012 and 2013 and mildly so at AMT-S in 2013. Since then, GOC-S TOC levels have dropped in 2015-2019 and risen again in 2020, while AMT-S has ranged between 0.53 and 0.63% since 2012. Perhaps the only conclusion is to note that TOC tends to fall within the low 0.5 – 0.8% DW range and suggests similar organic-sparse sources at both locations within the fjord. This is not surprising considering the dominance of primarily inorganic glacial flour in the sediments. For comparison, Port Valdez sediments collected for Alyeska's Environmental Monitoring Program (EMP, Shaw & Blanchard 2018, 2019) ranged between 0.3-0.6% (Figure 36). Intertidal sediments collected in Cook Inlet ranged from 0.03 to 0.98% (Lees et al., 2001).

Also, note that the data are not continuous, that sampling prior to 2002 was performed by KLI, and that 2016 reflects the third laboratory change for the project.

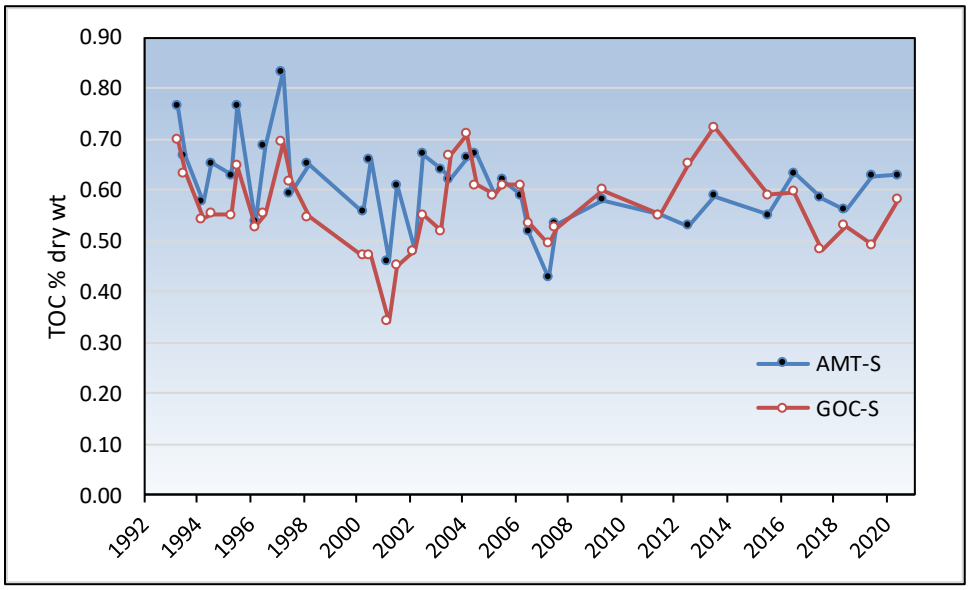


Figure 35. LTEMP Total Organic Carbon trends in AMT-S and GOC-S sediments (% DW), 1993-2020.

Table 11. LTEMP Total Organic Carbon in AMT-S and GOC-S sediments (% DW), 1993-2020.

Sample Date	AMT	GOC	Sample Date	AMT	GOC	Sample Date	AMT	GOC
Apr-93	0.77	0.70	Mar-01	0.46	0.34	Jul-07	0.53	0.53
Jul-93	0.67	0.63	Jul-01	0.61	0.45	Apr-09	0.58	0.60
Mar-94	0.58	0.54	Mar-02	0.48	0.48	Jun-11	0.55	0.55
Jul-94	0.65	0.55	Jul-02	0.67	0.55	Jul-12	0.53	0.65
Apr-95	0.63	0.55	Mar-03	0.64	0.52	Jul-13	0.59	0.72
Jul-95	0.77	0.65	Jul-03	0.62	0.67	Jul-15	0.55	0.59
Mar-96	0.54	0.53	Mar-04	0.66	0.71	Jul-16	0.63	0.60
Jul-96	0.69	0.55	Jul-04	0.67	0.61	Jul-17	0.58	0.48
Mar-97	0.83	0.69	Mar-05	0.59	0.59	Jun-18	0.56	0.53
Jul-97	0.59	0.62	Jul-05	0.62	0.61	Jun-19	0.63	0.49
Mar-98	0.65	0.55	Mar-06	0.59	0.61	Jun-20	0.63	0.58
Apr-00	0.56	0.47	Jul-06	0.52	0.54			
Jul-00	0.66	0.47	Apr-07	0.43	0.49			

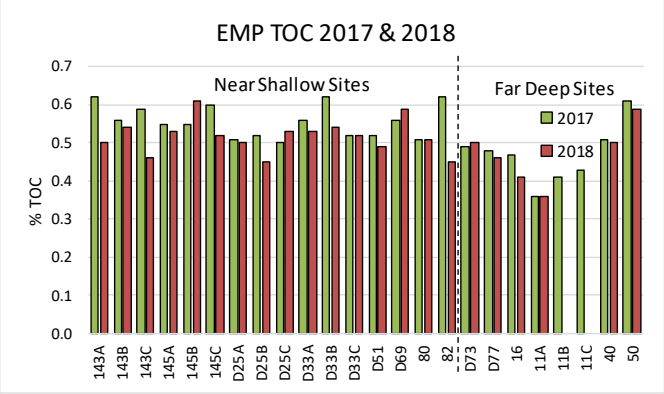


Figure 36. Total organic carbon for sediments in Alyeska's 2017 and 2018 monitoring program (from Shaw & Blanchard, 2018, 2019) in vicinity of the terminal (near shallow sites) and deeper within the fjord (far deep sites).

APPENDIX 8. OXYGENATED PRODUCTS IN TREATED BALLAST WATER DISCHARGES

During the 2010 *Deepwater Horizon* event, a whole oil sample was analyzed on a high-resolution instrument, Fourier transform-ion cyclotron resonance (FT-ICR; McKenna et al., 2013). While traditional oil spill forensics has relied upon GC/MS and GC-FID instruments capably reporting ~300 hydrocarbons, the newer instrument saw an unexpected universe of ~10,000 compounds. While it is unknown whether these are likely to be bioavailable or perhaps even toxic, environmental monitoring based upon traditional chemical detection, to date, has "just been looking where the light is good."

As described in the 2017 report (Payne and Driskell 2018c), three effluent samples, raw, filtered (particulate oil droplets), and dissolved phase, were collected from the BWTF discharge pipe in July 2016 and March 2017. In addition to the standard PAH, SHC, and biomarkers analyzed as part of LTEMP, we independently (without PWSRCAC support) had the July 2016 sample extracts screened for oxygenated products by a colleague, Dr. Christoph Aeppli of Bigelow Laboratory (Maine). Oxygenated hydrocarbons, whether created microbially, by solar radiation, or by chemical processes, are currently considered by hydrocarbon fate-and-weathering scientists to be the "Holy Grail" in understanding oil-degradation products (Aeppli et al., 2012). Conceptually, the effluent from a ballast water treatment facility designed to promote oil biodegradation would be an ideal substrate to use for oxidized-product method development and validation.

To date, Dr. Aeppli has used an Iatroscan (TLC-FID) method to separate components in the July 2016 extracts into saturated, aromatic, mono-oxygenates, and di-oxygenates. Extracts from fresh ANS crude oil and the three effluent samples from July 2016 (Figure 37) showed the expected depletion of the saturate (SHC) and aromatic (PAH) in the fresh ANS oil with their subsequent conversion into oxygenated products with one- and two-oxygen additions. Because of the increased water solubility of oxygenated products, the highest relative concentrations of mono- and di-oxygenated constituents were observed in the filtered, dissolved-phase fraction sample. Over 93% of the measured components in that fraction were oxygenates compared to only 36% in the starting oil. These results confirmed our expectations and help to document the biological treatment tank's efficacy in converting hydrocarbons into water-soluble, biodegradation-products. Subsequently, after discharge into the Port, oxygenated products are more easily diluted and further weathered.

Continuing with method development, additional analyses are being undertaken using HPLC/MS, GC x GC/MS, and by selected ion monitoring GC/MS after chemical derivatization into tri-methyl-silane (TMS) ethers and esters. To date, a series of alcohols, carboxylic acids, diols, and dioic acids have been detected although explicit compound identifications have not been completed. Nevertheless, these unfunded studies are expected to help expand this line of investigation and may eventually help to track oxygenated products as they further degrade following discharge from the BWTF or in future oil-spill releases.

In an approach that may be instructive to LTEMP projects, Sørensen et al., (2019) used very innovative chemical analyses to characterize previously unquantified constituents of produced waters (PW) from five North Sea oil platforms. Processing by fractionation and elution into polar and apolar fractions and derivatization allowed analysis using gas chromatography (GC), GC-mass spectrometry (GC/MS), two dimensional GC/MS (GC × GC/MS) and liquid chromatography with high-resolution spectrometry (LC-HRMS) techniques. A rich suite of polar and apolar constituents were characterized and quantified within each fraction. Acute toxicity tests were then run using a marine copepod subject. Toxicity varied significantly for different produced waters' extractions and subfractions with some different polar and apolar fractions being toxic within different produced water samples. Sørensen et al.

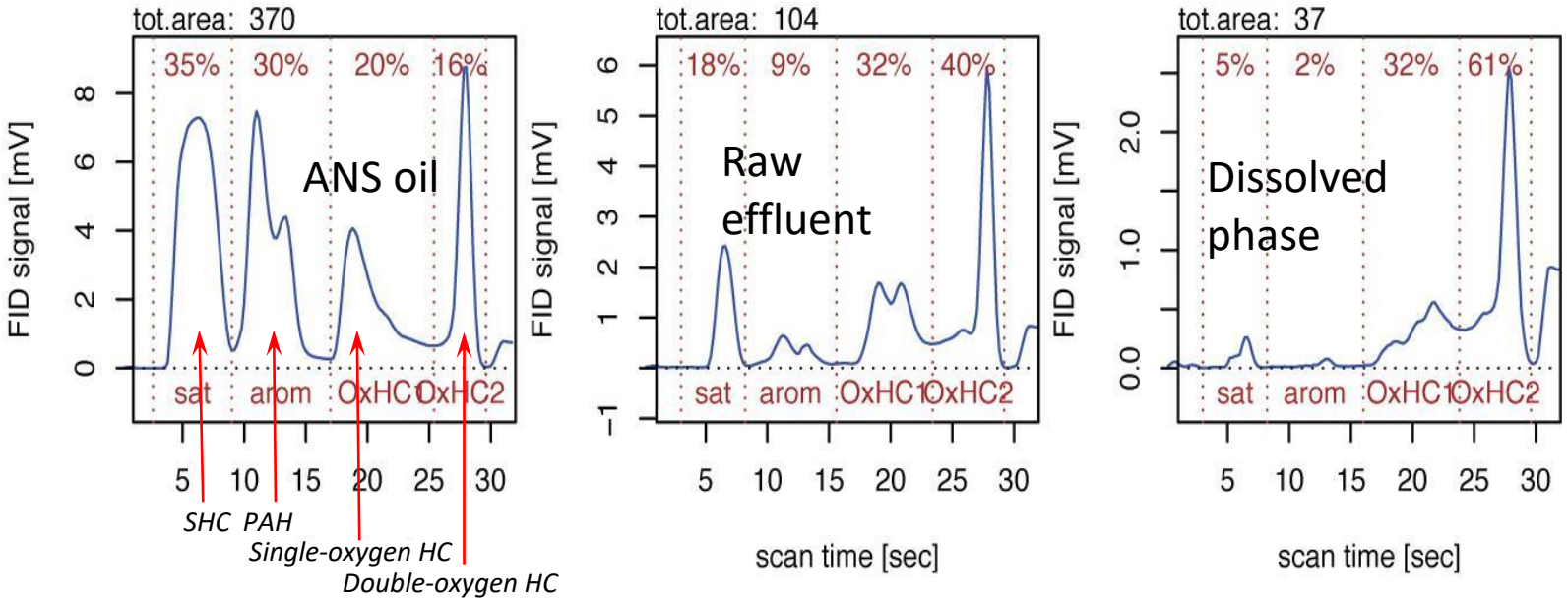


Figure 37. Iatroscan (TLC-FID) of ANS oil, BWTF raw effluent, and BWTF dissolved components from July 2016 showing relative abundance of single- and double-oxygenated (weathered) hydrocarbons relative to SHC and PAH components. Courtesy of Christoph Aeppli.

conclude, “Although, due to the vast chemical complexity even of the sub-fractions of the PW extracts, specific compounds driving the observed toxicity could not be elucidated in this study, the proposed approach may suggest a way forward for future revisions of monitoring regimes for PW discharges.” The BWTF extracts from previous (or possibly future) LTEMP efforts may be ideal candidates for such analyses of biodegradation products as the extracts may not contain the high levels of production chemicals (PCs) that were major constituents identified in the North Sea produced waters.

APPENDIX 9. RELATED TOPICS

These topics were presented in last year’s LTEMP report but have no additional updates this year. Being still relevant to LTEMP monitoring, they are presented here for completeness.

Bioavailability of Particulate Phase Oil Hydrocarbons

Three studies should be mentioned regarding the assumption that only dissolved-phase hydrocarbons would be bioavailable. In 2015, Auke Bay Lab (ABL) did a study for the PWSRCAC looking for oil in Port Valdez shrimp eggs (Carls et al., 2016). They posited, as did others, that a clutch of eggs attached to the pleopods of gravid shrimp would be exposed to and absorb a dissolved-PAH signal from residual hydrocarbons in the soft sediments. Although ABL did not analyze for particulate-phase-confirming biomarkers, in at least one sample (Figure 38), the profile appears to be a water-washed particulate profile. Either particulate oil is capable of infusing through a shrimp’s chitin eggshell and inner lipid membranes or there was a problem with the lab’s sample cleanup methods, and a minor contribution from particulate oil was present in the sample. Another study was more conclusive in showing a particulate signal in eggs, this time on red crabs sampled on the abyssal plain in the Gulf of Mexico during the *Deepwater Horizon* incident, which included a full suite of biomarkers (Douglas and Liu, 2015; G.S. Douglas, personal communication, 2015). Thus, crustacean eggs appear to absorb more than just dissolved-phase contaminants. If this is the case, then the general supposition of dissolved-phase hydrocarbons’ exclusive bioavailability versus particulate-phase non-bioavailability is perhaps over-simplified. This would certainly be the case when copepods that have ingested oil micro-droplets in Port Valdez (Carls et al., 2006) are later consumed by predators (e.g., salmon smolt) or when mussels filter micro-droplets from the water column.

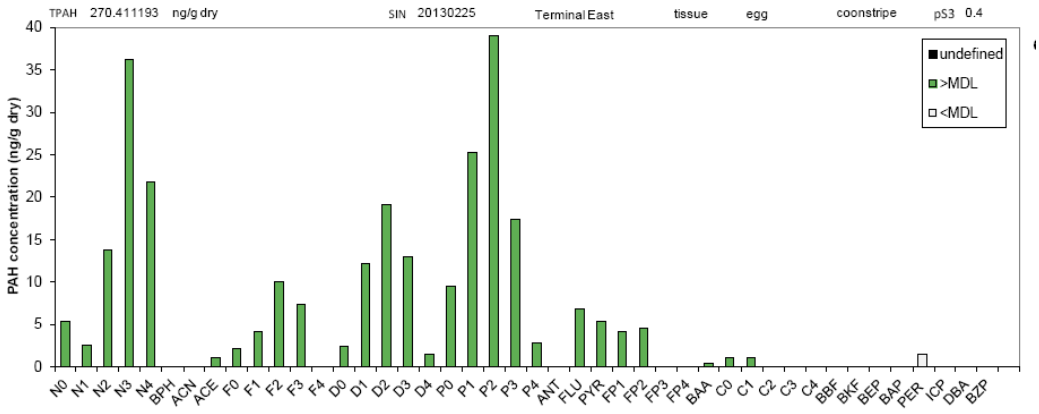


Figure 38. PAH plot of shrimp eggs taken east of the VMT, which in our assessment, shows a water-washed, weathered particulate-oil pattern absorbed through the chitin, lipid membrane and into the fat of the eggs. From Carls et al., 2016.

Low Level Toxicity Effects on Fish

Also notable is recent work documenting oil droplets unexpectedly adhering directly to certain fish species' eggs (but not others) (Laurel et al., 2019, Hansen et al., 2018, Sørenson et al., 2017, Sørhus et al., 2015) and demonstrating increased toxicity relative to eggs with just dissolved component exposures. This work, so far, has just been looking at three commercial fish species – cod, arctic cod, and haddock – with the latter one not susceptible to egg membrane (chorion) oiling. Obviously, this research topic is in initial phases and far from garnering a deeper understanding of the biomechanical differences in adsorbent versus non-adsorbent chorions. Therefore, it is currently prudent to assume that all eggs in the water column, both vertebrate and invertebrate may be susceptible to adhering oil droplets. Furthermore, this research is nascent; adhered or absorbed, insights into oils' physiologic and teratologic impacts on embryos are just developing. As concisely summarized by Laurel et al., (2019):

> "Crude oil contains polycyclic aromatic hydrocarbons (PAHs) that are cardiotoxic. Three-ringed PAH families (e.g., phenanthrenes) enriched in crude oil block K^+ and Ca^{2+} ion conductances in cardiomyocytes, disrupting the normal rhythmic pumping of the heart (Brette et al., 2014, 2017). When this occurs in oil exposed fish embryos, disruption of cardiac function leads to abnormal heart development (Incardona, 2017; Incardona and Scholz, 2016). Although cardiocirculatory defects alone would be sufficient to impact growth, more recent findings indicate that reduced cardiac function during embryonic and early larval development has other indirect effects that may be equally if not more consequential for individual fitness. Specifically, recent advances in RNA sequencing of oil-exposed Atlantic haddock (Melanogrammus aeglefinus) embryos identified alterations in the expression of genes involved in lipid metabolism (Sørhus et al., 2017). This suggests that disruption of bioenergetics during early development may be a prominent mechanism underlying latent impacts on fish growth and survival at later life stages. Oil spill science in marine systems has thus far focused on fish species with distinct ecophysiological characteristics (Incardona and Scholz, 2016). This includes nearshore and pelagic species spawning in cold northern waters (Carls et al., 1999; Incardona et al., 2015) and rapidly developing sub-tropical species (Incardona and Scholz, 2018). In general, cold water species or those with strong cold tolerance are more sensitive to oil-induced toxicity (Edmunds et al., 2015; Incardona et al., 2014, 2015; Morris et al., 2018; Sørensen et al., 2017; Sørhus et al., 2016). Although common morphological and functional abnormalities are usually evident shortly after embryonic exposure, delayed reductions in growth and juvenile survival have been documented in pink salmon exposed to low concentrations of oil that did not cause externally visible malformation (Heintz, 2007; Heintz et al., 2000). These effects on growth could reflect a latent and lasting dysregulation of lipid metabolism. If so, this would have important consequences for global marine fisheries because management paradigms are premised on a positive relationship between juvenile bioenergetics and successful recruitment to adult populations (Bouchard et al., 2017; Copeman et al., 2017; Heintz et al., 2013)."

Effects of Climate Change Enhanced Stream Flows on Sorptive Floc in the Water Column

In a more speculative vein, while the decline in environmental contaminants is obviously related to declining inputs into the Port, another factor also seems relevant. Because discharged oil droplets sorb onto particulates in the water column (Payne et al., 2003d and references therein), an increase in glacial flour brought into the Port from the nearby Lowe and Valdez Glacier Rivers would affect dilution and settling rates of the oil. Streamflow records from the U.S. Geographical Survey (USGS) from 2015-2019 do show high stream flows in the Valdez Glacier River but mostly normal flows from Lowe River (Figure 39). We might speculate that with climate change accelerating the melt of glaciers, it seems intuitive to expect higher flows and thus, greater flocculant loads delivered to the Port environs and potentially increased dilution of oil signatures in the sediment. The degree of relevance to sediment hydrocarbon loads measured by LTEMP and Alyeska is unknown.

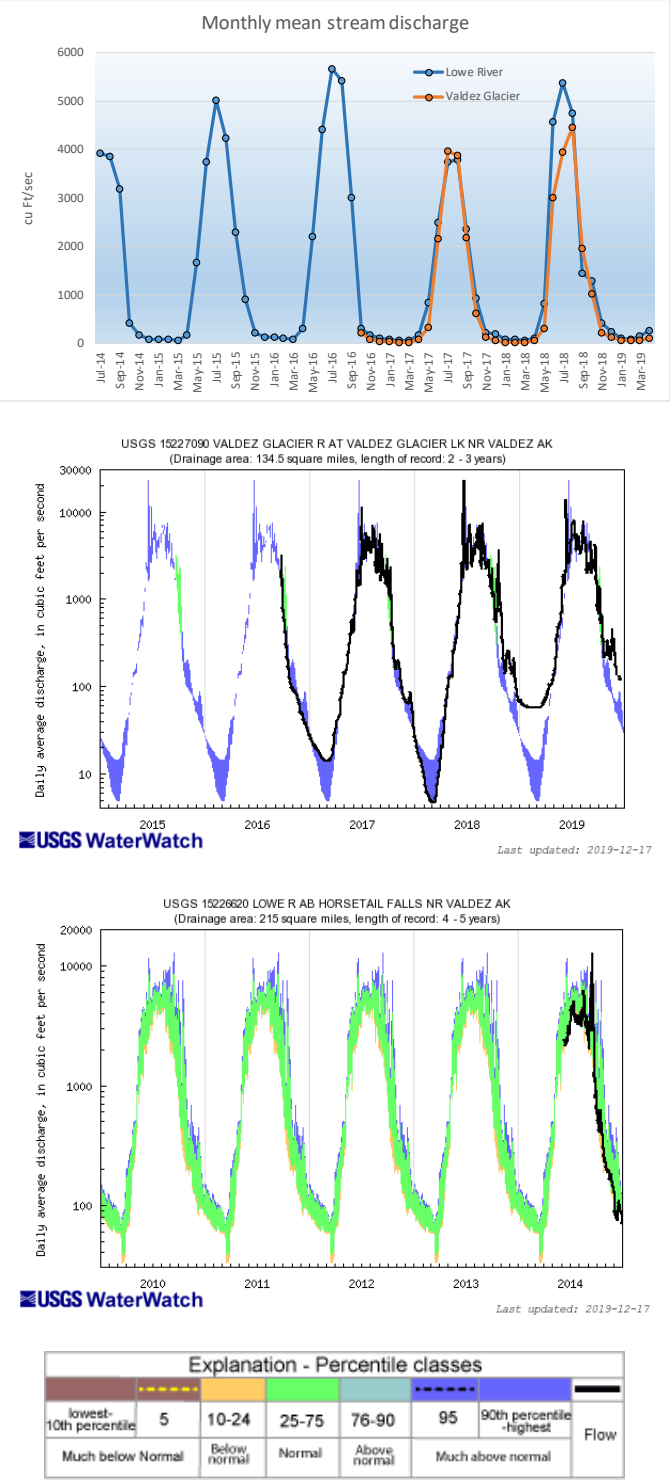


Figure 39. Historic monthly stream discharge rates (cubic ft/sec) for Lowe River and Valdez Glacier Stream, 2015-2019 (from USGS 2019).

Seasonal Variability of TPAH Related to Lipid-reducing Spawning Events

Finally, recall three observations from previous sections, 1) there are substantial seasonal differences in the BWTF effluent profiles and concentrations, 2) the mussels sampled at the Berth 5 spill in 2017 purged the oil in less than three months, and 3) spiking volumes of freshwater inputs loaded with glacial flour occur during the summer sampling period. A fourth point is that hydrocarbons tend to infuse into and accumulate in an organism's lipids (e.g., eggs). Therefore, a spawning event may greatly reduce accumulated oil-contaminant loads in mussels if they've spawned just prior to sampling. LTEMP sampling generally occurs in late June-early July, presumably post-spawning. Together, these observations suggest that hydrocarbon contaminate loads likely vary substantially throughout the year. While the limited LTEMP results suggest an exceptionally clean environment, it is a presumptuous conclusion when little is known about off-schedule conditions. As such, we suggest a pilot project doing more frequent mussel sampling be considered to gather more insights into current mussel contaminant variations.

APPENDIX 10. BEYOND LTEMP

How do the measured tissue-hydrocarbon levels compare with other Alaska sites? Unfortunately, comparable studies are scarce, no longer current, and variable concerning which analytes are actually summed. Nevertheless, earlier reported values still seem reasonable (Table 12). Follow-up mussel sampling in 2004 for oil residues from the 1997 M/V Kuroshima grounding in Summer Bay, Unalaska, found TPAH levels between 25 and 85 ng/g DW, with an average of 57 ng/g DW (Helton et al., 2004). This is actually higher than LTEMP's July 2013 range of 9-28 ng/g DW from the six stations inside the Sound but similar to the 13-65 ng/g DW range at three GOA sites (overall average 50 ng/g DW) collected at the same time. Compared to the 2018 data for all three LTEMP regions, the 2004 *Kuroshima* sites were significantly higher, but there are no more recent data against which to compare. The current LTEMP data suggest a natural dissolved-phase background TPAH somewhere between 33-71 ng/g DW.

Reaching farther, data from the 2004-2005 National Status and Trends, Mussel Watch Program (Figure 40) and 2008-2010 Alaska sites (Figure 41 and Table 12) (now summing only 38 parent and alkylated PAH homologues versus 43 LTEMP PAH analytes) show that average TPAH concentrations in mussels for other West Coast sites have been nearly 12-25 times higher (825 ng/g DW) than LTEMP's current levels. The highest level reported on the West Coast was 6,962 ng/g DW in Seattle, Washington. The lowest, 63 ng/g DW, was from mussels collected on Santa Catalina Island, 26 miles offshore of Orange County in Southern California. In 2004, the average TPAH mussel concentration in mussels from the five Alaska Mussel Watch sites (Ketchikan, Nahku Bay, Port Valdez, Unakwik Inlet, and Cook Inlet) was 267 ng/g DW with levels ranging from 105-441 ng/g DW (Kimbrough et al., 2008). In 2010, the average from four Alaska sites (Nanwalek, Port Graham (two stations), and Seldovia Bay) was 413 ng/g DW while Nash Road in Resurrection Bay exceeded all the other stations at 1,570 ng/g DW. Considering these and even more recent 2008-2010 values from the Mussel Watch data portal, the LTEMP results demonstrate that these remote locations are still exceptionally clean.

Finally, a 2005 EVOS Trustee Council Program, Long-Term Monitoring of Anthropogenic Hydrocarbons in the *Exxon Valdez* Oil Spill Region, examined 10 intertidal sites within the Naked-Knight-Southwest Island complex to measure the extent of buried oil still present 16 years after the spill. At previously heavily oiled EVOS sites, 10 to 50 random pits (depending on the beach width) were excavated to a depth of ~0.5 m to look for residual oil. If oil was detected, available nearby mussels were also collected. The results have been published elsewhere (Short et al., 2007) but, as co-authors, PAH and SHC sample profiles were included in Appendix E of our 2005/2006 Report (Payne et al., 2008a). Briefly, TPAH levels in the oiled pits ranged from a low of 42 ng/g (on Knight Island) to a high of 567,000 ng/g (on

Table 12. Most recent TPAH concentrations in LTEMP mussel tissues (ppb, ng/g DW) relative to 2004-2010 NOAA Mussel Watch monitoring data and a recovered Alaska oil spill event.

LTEMP	2020	Port Valdez tissues	AMT-B, JAP & GOC	33-71
	2019	Port Valdez tissues	AMT-B, JAP & GOC	24-34
	2018	Port Valdez tissues	AMT-B, JAP & GOC	29-40
	2017	Port Valdez tissues	AMT-B, JAP & GOC	46-63
	2016	Port Valdez tissues	AMT-B, JAP & GOC	69-195
	2015	Port Valdez tissues	AMT-B & GOC	39-87
	2013	Port Valdez tissues	AMT-B & GOC	17-20
	2018	PWS	Five stations	22-38
		GOA	Three stations	21-29
	2015	PWS (KNH & SHB)	KNH & SHB	15-27
	2013	PWS	Six stations	9-28
		GOA	Three stations	13-65
West Coast Mussel Watch		average (Kimbrough et al., 2008)		825
		So. Calif.	Santa Catalina Island	63
		Seattle	Elliot Bay, WA	6,962
Alaska Mussel Watch 2010		Resurrection Bay	Nash Road	1,570
		Nanwalek	Nanwalek	194
		Port Graham	Port Graham	376
		Port Graham	Murphy's Slough	428
		Seldovia Bay	Powder Island	652
	2009	Kachemak Bay	Chrome Bay	173
		Kachemak Bay	Tutka Bay	485
		Ketchikan	Mountain Point	231
		Nahku Bay	East Side	229
		Port Valdez	Mineral Creek Flats	332
		Resurrection Bay	Nash Road	602
		Resurrection Bay	Nash Road	765
		Resurrection Bay	Nash Road	929
		Resurrection Bay	Nash Road	713
		Unakwit Inlet	Siwash Bay	257
	2008	Cook Inlet	Bear Cove	119
		Cook Inlet	Homer Spit	208
		Port Valdez	Alyeska Marine Terminal	52
		Port Valdez	Gold Creek	31
M/V Kuroshima (1997)	2004	Unalaska		25-85

Latouche Island) with the oil showing states of weathering varying from extensively degraded to very fresh. On the other hand, nearby mussel samples only showed low *dissolved-phase* TPAH concentrations (11-42 ng/g DW, derived primarily from naphthalenes and phenanthrenes/anthracenes) that were in the same concentration range but compositionally different from the signals observed at LTEMP PWS and GOA sites sampled in April 2009. From these studies, it was concluded that although in 2005, there were still persistent buried EVOS residues at a number of beaches, they were highly sequestered and did not appear to be bioavailable unless disturbed.

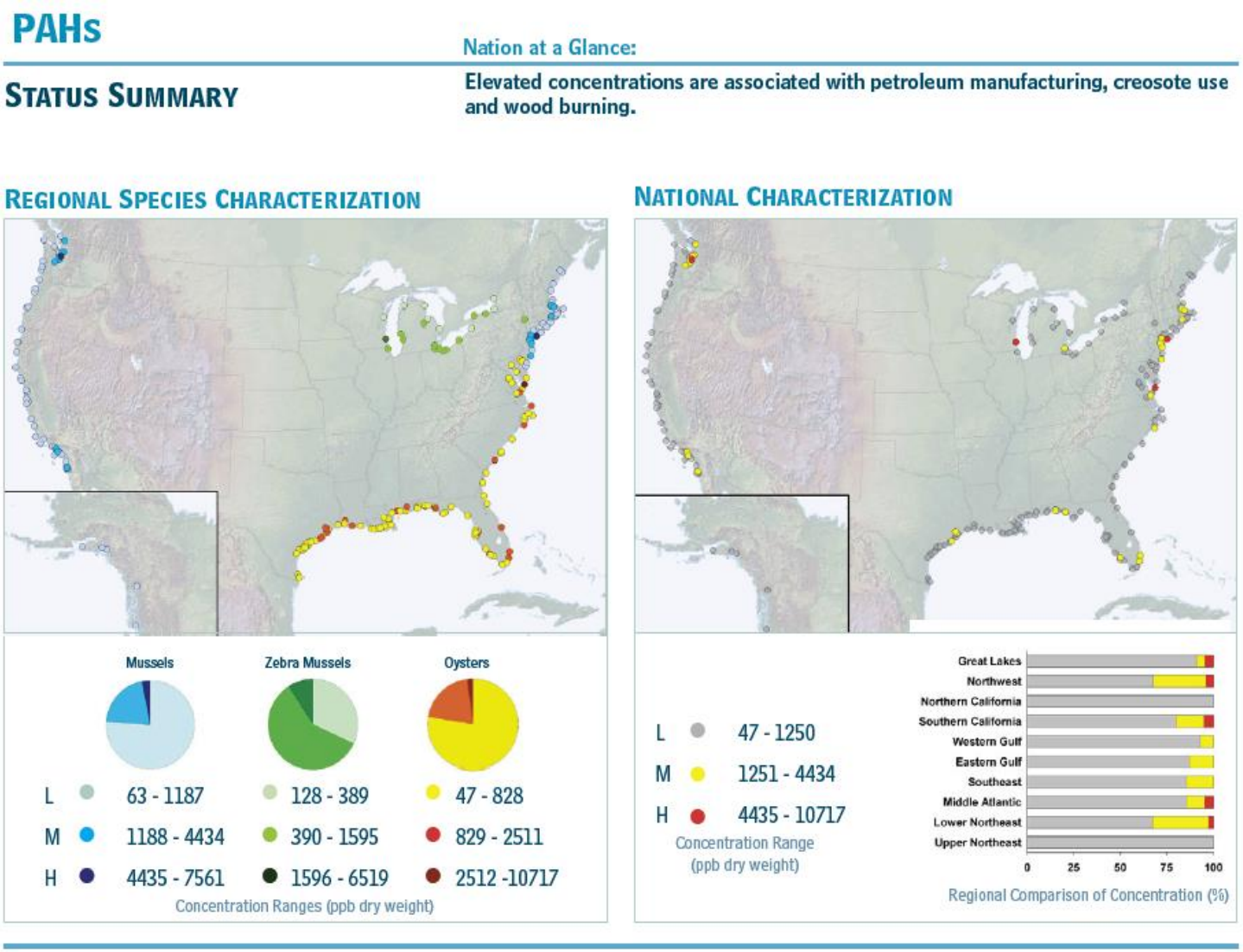


Figure 40. Status and trends result from National Mussel Watch data (Kimbrough et al., 2008). All Alaska sites characterized as low concentrations.

APPENDIX 2: RESULTS BY STATE

ALASKA (AK)

Regional (r)
Mussels (M)
- Medium
- High

Zebra Mussels (ZM)
- Medium
- High

Oysters (O)
- Medium
- High

Status (s)
National Status
- Medium
- High

Trend (t)
National Trend
- Decreasing
- Increasing

Concentrations derived from 2004-2005 data.

Markers represent the Regional Species Characterization (r), National Characterization (s) and National Trends maps (t).

Site	Latitude	Longitude	General Location	Location
KTMP	55.2938	-131.5480	Ketchikan	Mountain Point
NBES	59.4533	-135.3365	Nahku Bay	East Side
PVMC	61.1328	-146.4610	Port Valdez	Mineral Creek Flats
UISB	60.9608	-147.6460	Unakwit Inlet	Siwash Bay
CIHS	59.6145	-151.4442	Cook Inlet	Homer Spit

METALS (ppm)

Site	Spec	AS	r	s	t	CD	r	s	t	CU	r	s	t	HG	r	s	t	NI	r	s	t	PB	r	s	t	SN	r	s	t	ZN	r	s	t
KTMP	M	11		●		7.1	●	●		7				0.06				1.2				0.59				0				97			
NBES	M	9.2				5.4	●	●	▲	6				0.1				2				2.1		●		0				72			
PVMC	M	12	●	●		3.5		●		27	●			0.09				8.9	●	●		3	●	●		0.18				89			▼
UISB	M	12	●	●		2.6				33	●			0.11				7.4	●			2				1.4	●	●		108			
CIHS	M	12	●	●		1.7				10				0.12				3.4				1.3				0				105			

ORGANICS (ppb)

Sites	Spec	Butyltins	r	s	t	Chlordanes	r	s	t	DDTs	r	s	t	Dieldrins	r	s	t	PAHs	r	s	t	PCBs	r	s	t
KTMP	M	2.1				0.47				1.4				0.58				152				3.5			
NBES	M	3.7				2.7				2.2				0.98				316				7.7			
PVMC	M	7.3				2.6				1.7				0.31				441				6.4			
UISB	M	1.7				0.87				0.38				0.56				176				3.7			
CIHS	M	4.4				1.1				0.3				0.42				250				11			

Figure 41. Summary page of Alaska regional Mussel Watch results and trends based on 2004-05 report from Kimbrough et al., 2008.

The low 2018 TPAH and 2019 values in mussels collected from these sites and the PSD data from the formerly oiled DII site vs. the clean-control site at KNH (Figure 25) seem to confirm these findings, although recent studies with oil-sniffing dogs suggest that bioavailability at concentrations below our analytical detection limits may still be a concern for sub-lethal effects with some species. In 2005, rates of EVOS oil disappearance had diminished to an estimated 4% per year. If left undisturbed, Short et al., (2007) predicted that sequestered hydrocarbons would be there for decades. Revisiting the sites in 2015, Auke Bay researchers found mostly unchanged conditions since 2001 (Lindeberg et al., 2018). Lindeberg again concluded that an estimated 0.6% EVOS oil would remain sequestered unless disturbed and will likely persist in the environment on a decadal scale. They also comment that viewing this survey in the context of previous surveys makes it clear that Exxon researcher claims made after the spill that beaches would clean themselves were overly optimistic. To address these residual deposits, the EVOS Trustee Council has sponsored various beach remediation studies and pilot projects (ADEC 2016).