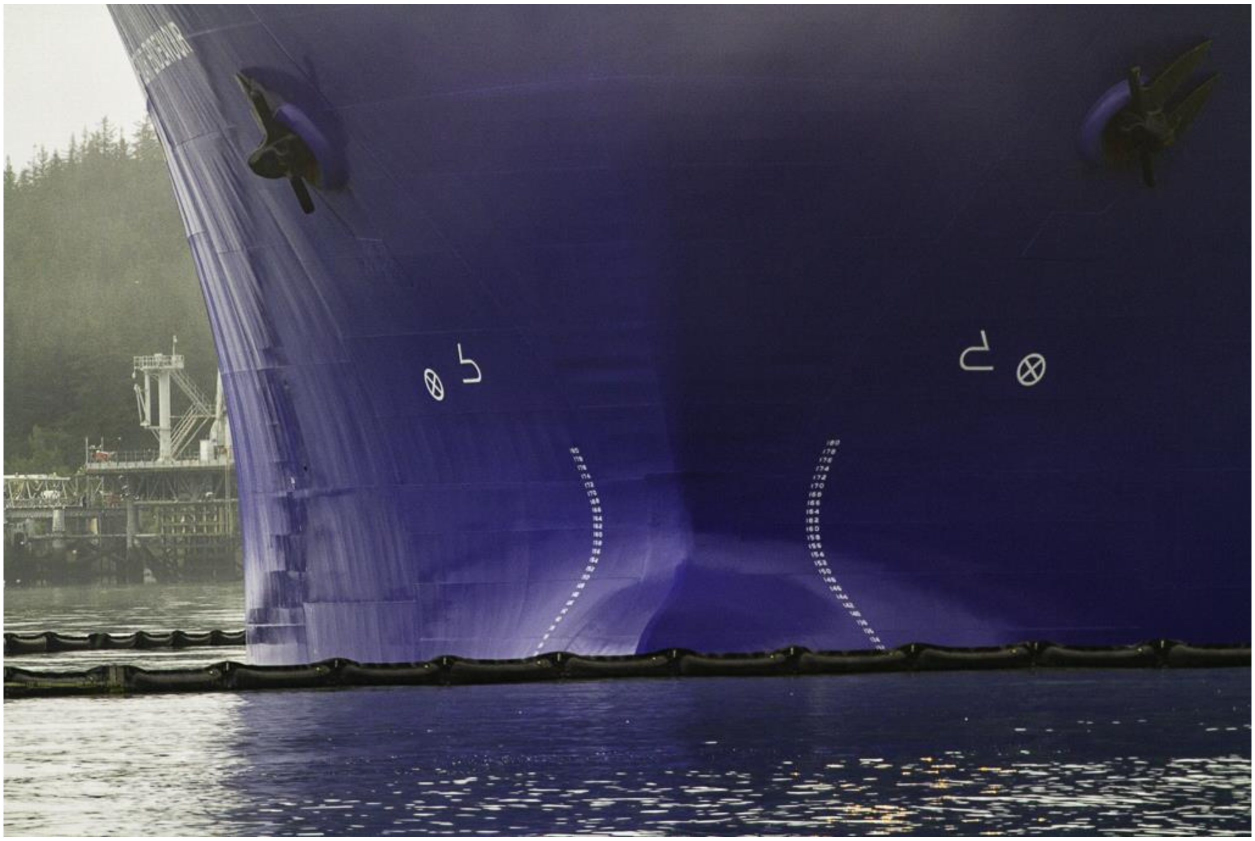
LONG-TERM ENVIRONMENTAL MONITORING PROGRAM:

2019 SAMPLING RESULTS AND INTERPRETATIONS



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

CONTENTS

Note: List of Tables and Figures appear prior to the Appendices at the end of the document.

Cover image – “Snug at berth 4.” Photo by William Driskell.

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

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, 2019

EXECUTIVE SUMMARY

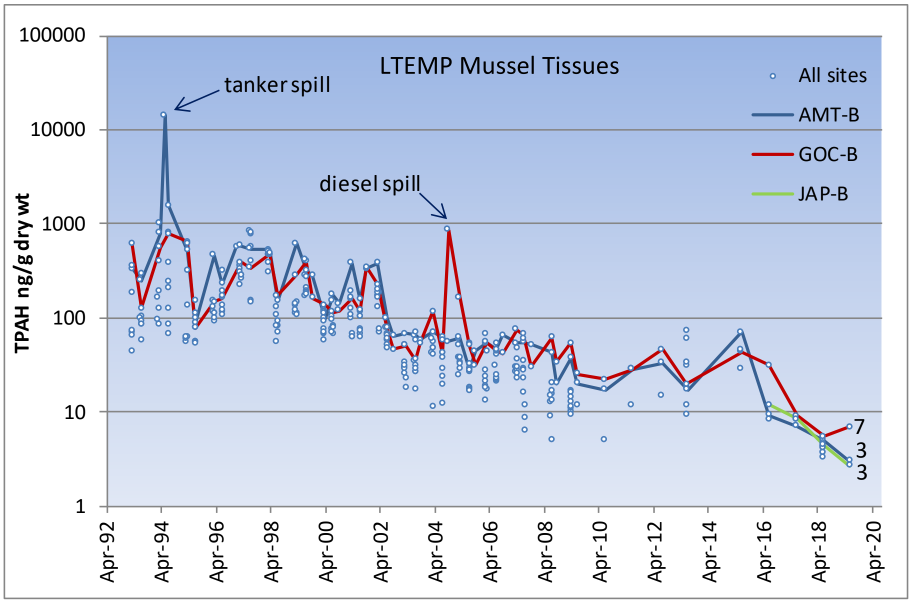
The Prince William Sound Regional Citizen's Advisory Council (PWSRCAC) Long-Term Environmental Monitoring Program (LTEMP) was begun in 1993, following the 1989 *Exxon Valdez* oil spill (EVOS), with the goal of monitoring for environmental impacts from oil transportation activities. To accomplish this 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). With the bulk of EVOS residues mostly gone from the region, LTEMP monitoring is now focused on tanker and terminal operations within the Port. In addition to mussel and sediment sampling, passive sampling devices (PSD) were again deployed at the three Port Valdez mussel sites to compliment the mussel samples in assessing the most bioavailable, dissolved hydrocarbons and their potential toxicity. Synoptically, the 2019 mussels and PSD came back extraordinarily clean while Alaska North Slope (ANS) oil is still accumulating in the bottom sediments near the terminal's discharge outfall.

The program collects field samples (sediments, mussels, PSD) that are processed and analyzed by a certified laboratory. The data are then reviewed from two perspectives: 1) characterizing the chemical profiles as to the likely source and degradation state of the hydrocarbons, and 2) the concentration of the oil contaminants. Three groups of petroleum hydrocarbons are examined in this data set: polycyclic aromatic hydrocarbons (PAH), saturated hydrocarbons (SHC), and oil biomarkers.

Traditionally looking at just total PAH concentrations (summing the 80 analytes into TPAH), Port Valdez contaminant-oil from Alyeska's Valdez Marine Terminal (VMT) and tanker operations have been trending downward over the last two decades in both the mussels and sediments. This trend reflects a combination of reduced Ballast Water Treatment Facility (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 removing particulate/oil-phase PAH.

But there is a subtler way of viewing the data: looking at the profiles, the presence/absence patterns of individual analytes and their relative concentrations, enables a forensic assessment to determine the source of the oil components and their fate as they diminish and weather away in the environment. The task can be tricky as there are non-oil sources for some of the analytes in the profiles (e.g., combustion products and natural plankton and plant waxes).

LTEMP mussel profiles from Saw Island (AMT-B), adjacent to the VMT, over the last several years, have been seen generally shifting away from the terminal's earlier oil-dominated patterns and into trace-level background or combustion-derived PAH patterns.

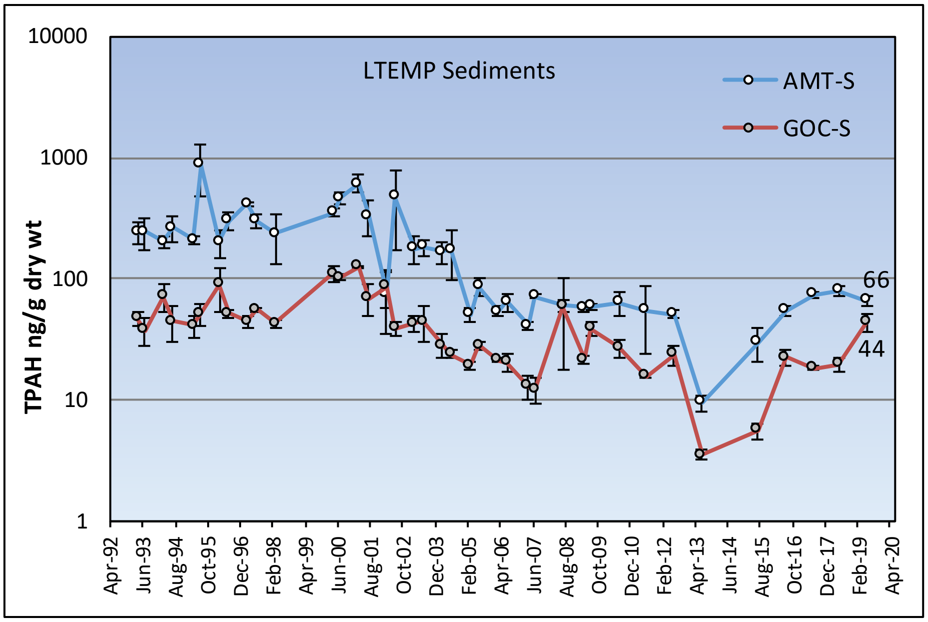


By 2018, tissue hydrocarbon concentrations from all 11 LTEMP stations (from within Port Valdez as well as outside in PWS and the GOA) were barely detectible as TPAH totals reached all-time lows (below instrument method-detection limits). Results were a repeat in 2019, when the three Port Valdez stations showed the same trace-level components. Indeed, the PAH profiles were so clean they were essentially indistinguishable from the quality control, laboratory blanks. At the Gold Creek reference site (GOC), where there had been evidence of a minor diesel spill in summer 2016, only trace-level background and combustion profiles were observed. Again, mostly clean.

In strong contrast to the most recent (albeit dated) National Oceanographic and Atmospheric Administration (NOAA) West Coast Mussel Watch data (2004-05) and the more recent 2008-10 Alaska Mussel Watch sites, the 2018 and 2019 LTEMP mussel-tissue results show 10 to 1,000 times lower TPAH concentrations. LTEMP tissues continue to suggest that the sampled sites are exceptionally clean of the PAH oil indicators.

As do the PSDs. PSDs are specifically designed to sample only the more bioavailable, dissolved hydrocarbons (versus oil microdroplets that mussels may ingest) and from their month-long deployment, increase the detection sensitivity. All PSD results showed a low-level, dissolved PAH profile plus traces of higher-molecular-weight PAH unrelated to the BWTF effluent. This year’s results confirm that whether inside or outside of Port Valdez (previous year’s deployment), the PSD only acquired similar background patterns of dissolved PAH. Most importantly, the concentrations were well below any known toxicity thresholds for sensitive marine organisms and life stages. In summary, both mussel and PSD results suggest no concerning issues in the water column.

These remarkably clean mussel and PSD results differ greatly from the sediment results; sediments near the terminal 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 a mostly combustion source in 2011-2015. More recent 2016-2019 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 BWTF effluent. The 2019 SHC profiles show higher levels of marine and terrestrial biological components compared to the oil waxes, which have remained relatively constant between 2008 and 2019. 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 dominant oil signature and are now just more apparent as the total oil concentrations diminish.

As expected 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 2018, an unfunded pilot project by a colleague at Bigelow Lab (Maine) used a different analytic method to document previously unreported, oxygenated hydrocarbons in the BWTF effluent. These compounds, created either by photo-chemical or microbial processes, represent the next steps in natural degradation of oil. Because the BWTF's Biological Treatment Tank (BTT) is operated to optimize oil's biological degradation, microbial conversion likely dominates. These new compounds are relevant to LTEMP as the raw effluent appears to have more of these single- and double-oxygenated hydrocarbons than the combined, currently reported, non-oxygenated SHC and PAH analytes. In other words, only a subset of the BWTF oil contaminants has been measured or tracked using traditional LTEMP methods. Toxicity of these compounds is mostly unknown but has become a high-interest research topic in the wake of the 2010 *Deepwater Horizon* spill event. To more fully understand the nature of the BWTF effluent, we suggest analysis of these oxygenated compounds in any future LTEMP discharge monitoring.

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 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 (sediments, mussels, passive sampling devices (PSDs)) processed and analyzed by two competent laboratories; one for tissues, sediments, and occasional water and oil matrices, another for the PSDs. Three groups of petroleum hydrocarbons are reported: polycyclic aromatic hydrocarbons (PAH), saturated hydrocarbons (SHC), and oil biomarkers. For LTEMP, the data are then compiled and reviewed from two perspectives: 1) characterizing the whole suite of analytes, the chemical profiles, and 2) the concentration of the oil contaminants.

From the profiles, the presence/absence patterns of individual analytes and their relative concentrations, serves as a forensic assessment in determining 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 can be mixed into the profiles (e.g., combustion products and natural plankton and plant waxes).

LTEMP sampling locations have been mostly fixed since the program's 1993 inception. At Alyeska's terminal, the Ballast Water Treatment Facility (BWTF) treats and discharges oil-contaminated ballast water offloaded from tankers utilizing the terminal, so two stations have been traditionally sampled to assess impacts from the effluent: at Alyeska's Valdez Marine Terminal (VMT) 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 for both sediments and mussels (Figure 1). Another station, Jackson Point (JAP), was added in 2016 on the opposite side of the diffuser, near Berth 3, towards the eastern end of the terminal. At that time, the program was expanded to include PSDs at the three Port stations to measure just the bioavailable, dissolved-phase hydrocarbons. Eight additional stations, comprising the geographic reach of the *Exxon Valdez* oil spill (EVOS) between Valdez and Kodiak, are also sampled, now every five years (last sampled in 2018) (Figure 2, Table 1). Seasonal sampling frequency has been variable over the years as the program evolved but summer sampling has been consistent throughout the 26 years.

Sediment samples are collected from the two Port stations, one near the BWTF's underwater discharger diffuser and the other, a reference site across the Port. These are analyzed for the same hydrocarbon chemistry 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.

The ensuing sections of this report present the usual technical details of chemistry and interpretive methods, and then assessments of the individual sampled matrices. These are written in a style intended for the technical reader in order to fully assess our processes and interpretations. First is the BWTF effluent, re-reported here from previous years (2016-17), this section shows our only examples of what the degraded Alaska North Slope (ANS) oil currently looks like as it is discharged into the Port (versus the fresh ANS oil from the pipeline). We caution that there are only two seasonal samples, highly different, 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 in a mixed-source sample. Looking further at the state of weathering (degradation from the original patterns) usually suggests an interpretive scenario of the sources, transport, and fate for the contaminated sample.

Presented next are results from the sediments near the BWTF outfall that are still accumulating oil, and the sediments across the Port that are free of oil. To annually reflect current conditions, sampling is limited to just the top layer of recently deposited, unconsolidated fine sediment (~1-2 cm deep). Here, the patterns near the outfall expectedly will be more extensively weathered but still contain a fairly intact suite of the more recalcitrant biomarkers. Sediments from the reference site do not contain the BWTF oil (nor the suite of biomarkers).

Next sections in this report are the mussel tissues and PSD results, both of which show that there is essentially no detectible oil in these samples. 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 month-long deployment, with more sensitive detection limits. Results from both sample types agree, showing only background contaminants and combustion products are in the water column. Furthermore, the low-level PAH concentrations are too low to be toxic.

Later sections include exposition on measuring oxygenated hydrocarbons, which are microbially degraded components of oil that are currently unresolvable using our traditional methods. Examining the BWTF raw effluent using different instruments has detected an abundance of these unmeasured compounds. And finally, several LTEMP and monitoring topics are briefly addressed as Related Topics.

The report finishes with a summary of results, recommendations, and conclusions.

Note that a mostly static section from prior reports, “Beyond LTEMP,” that compares LTEMP total PAH (TPAH) values to those from other studies, has been moved to Appendix 4. Its conclusion still appears in summary points.

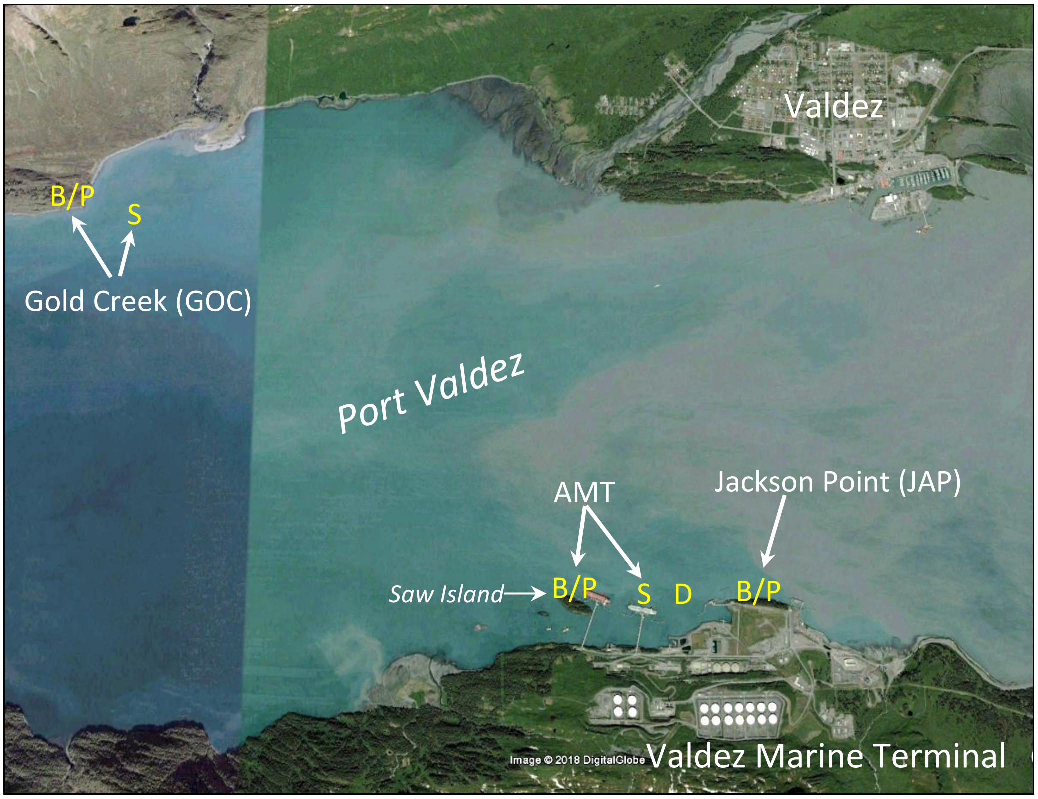


Figure 1. LTEMP sampling stations in Port Valdez adjacent to the terminal (AMT-B, AMT-S, and JAP) and 6 km northwest (GOC) of the VMT. This Google Earth image shows tankers docked at both Berth 4 and 5. The yellow "S" indicates sediment grab locations and "B/P" for biological tissue and PSD samplings; "D" denotes the location of the BWTF outfall diffuser.

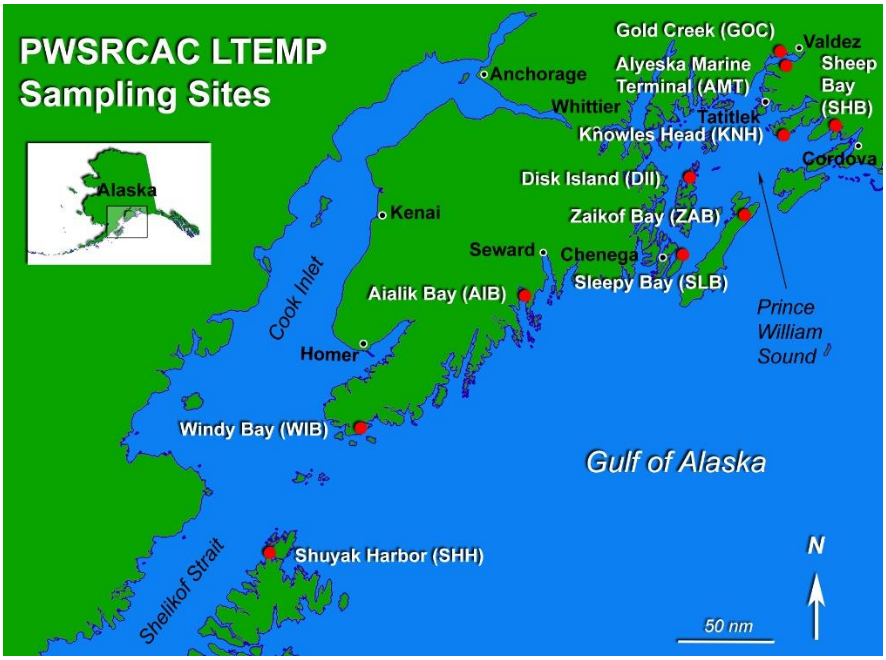


Figure 2. Map of the LTEMP sites with station abbreviations.

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									

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. 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.

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 per previous research efforts (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).

DATA ANALYSIS

Port Valdez LTEMP data are interesting in a couple of respects; the data are quite rich in analytes and time span but only represent three locations in the Port. From these data, there are two main questions: 1) are the detected hydrocarbons 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 considering the subset-PAH analytic suite that constrains any fuller understanding and, indeed, 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- meaning carbons attached to the parent molecule, the plotted bars are 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 that 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 isomers (abbreviated as C4 when plotted). These alkylated isomers are summed into one value for the bar plots. Also, as described in each figure caption for sample profiles 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 shown for selected time-series data profiles and are shown for all 2019 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. [1]

Beginning in 2011, biomarkers were analyzed on sediments and in 2016 biomarkers were added 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 (e.g., free oil droplets from a recent or chronic release such as the September 2017 Alyeska Berth 5 oil spill; Payne and Driskell, 2018b).

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.

RESULTS AND DISCUSSION

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 in order 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

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[1] 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).

were met for all PAH, biomarker and alkane surrogate hydrocarbons analyzed during the 2019 reporting period (Table 2). Laboratory method blanks for each analytic sample batch demonstrated (sub-ng/g) laboratory or analytic background PAH interference.

Table 2. Surrogate recovery statistics by matrix from 2019 Alpha Laboratory analyses.

	Tissue					Sediment				
Surrogate	Average (%)	Max	Min	Count	StdDev	Average (%)	Max	Min	Count	StdDev
5B(H)Cholane	115	129	104	11	9	109	116	101	12	4
Benzo[a]pyrene-d12	103	109	93	13	4	126	142	111	12	9
d50-Tetracosane	88	96	78	11	6	99	103	94	12	3
Naphthalene-d8	88	102	77	13	7	96	105	88	12	5
o-terphenyl						97	101	92	12	3
Phenanthrene-d10	102	107	96	13	4	111	120	105	12	4

Mussel-tissue hydrocarbon levels are now 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 actually represent environmental constituents. In addition, some matrix interferents were flagged for two sediment biomarkers, T26 and T32, 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 and are 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, 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 3).

Table 3. 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 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.[2]

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.

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.

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

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[2] 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.

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, 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.

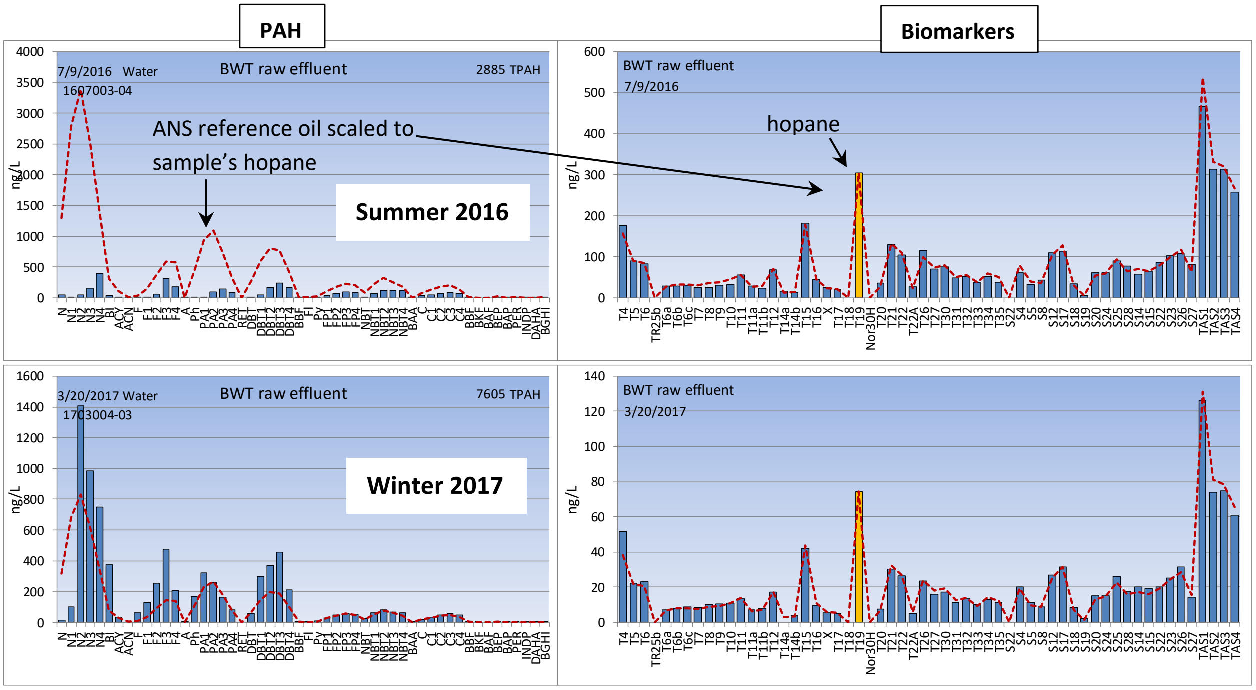


Figure 3. PAH and biomarker profiles (ng/L) of raw (unfiltered) BWTF-BTT effluent samples from July 2016 (upper plots) and March 2017 (lower plots). The dotted red line represents an overlay of fresh ANS crude oil normalized (scaled) to hopane (T19, colored gold in the biomarker profiles). Excess dissolved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

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).

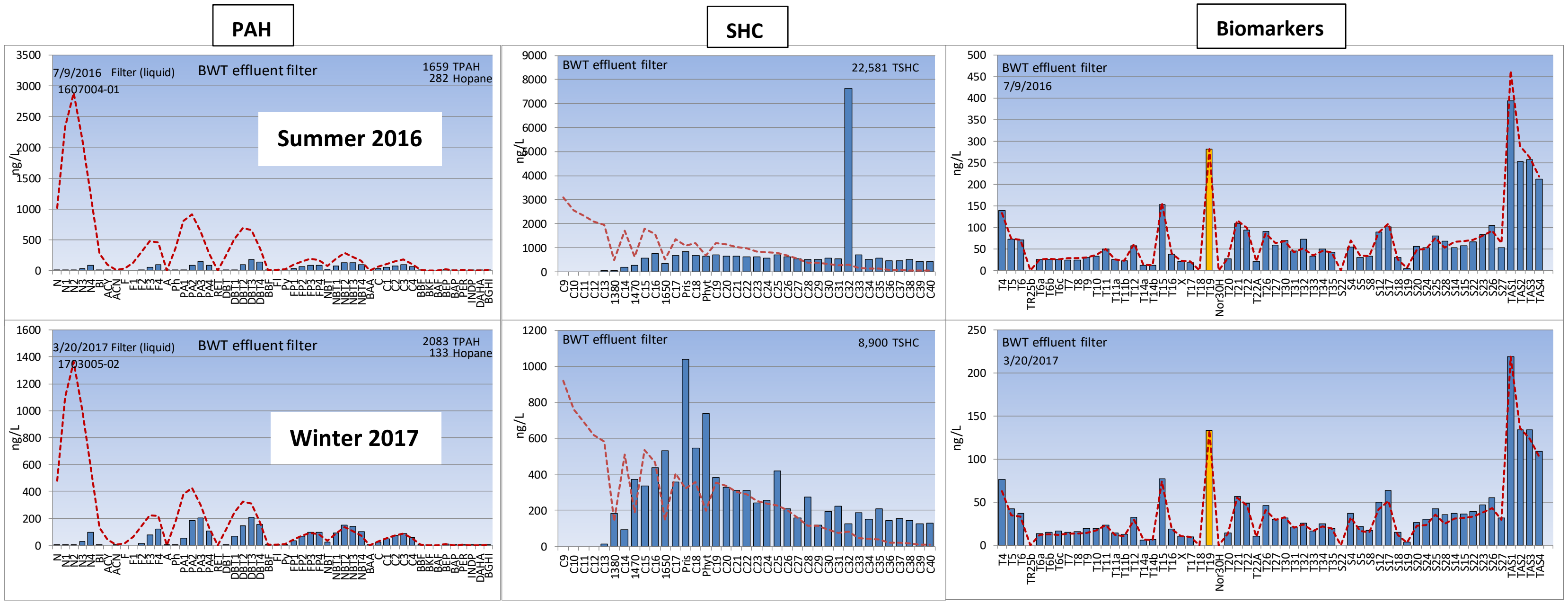


Figure 4. PAH, SHC, and biomarker profiles (ng/L) of the filtered, particulate/oil-phase droplets in the BWTF-BTT effluent. The red line overlay represents fresh ANS scaled to the sample's hopane (T19, colored gold in the biomarker plots). The gaps between the measured PAH and the overlay portray the extent of weathering. The TPAH concentrations are similar 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 summer SHC, C_{32} was a matrix interferent; SHC are scaled to C_{27}.

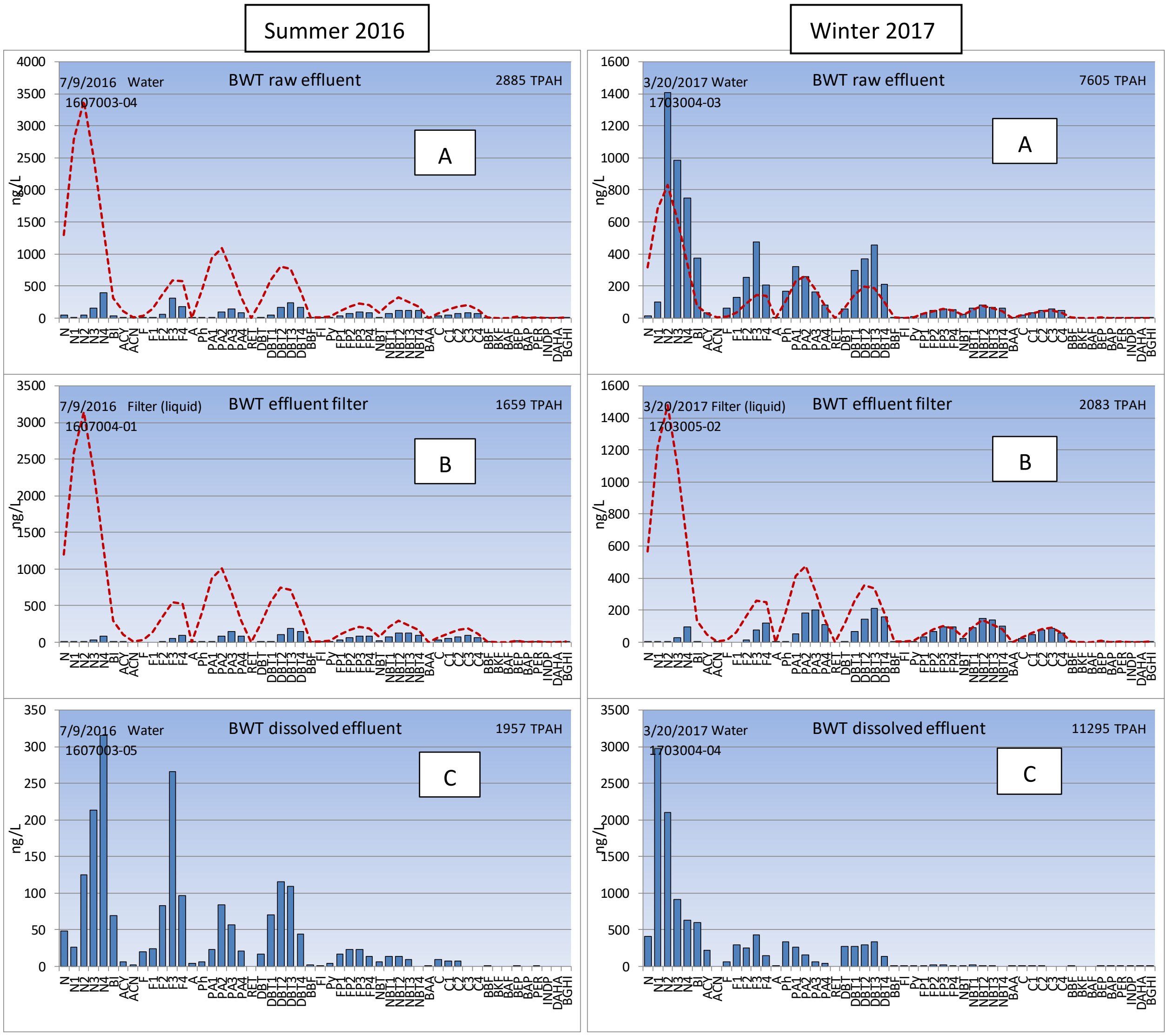


Figure 5. PAH profiles of BTT effluent samples collected under summer (July 2016) and late winter (March 2017) conditions: A) whole unfiltered sample; B) particulate/oil phase trapped on the glass-fiber-filter; and C) dissolved phase. The dotted red line in A and B represents fresh ANS crude oil PAH profile normalized to hopane to show evaporation and dissolution effects on lower-molecular-weight PAH (C profiles are all dissolved and don't have a reference pattern overlay on them (i.e., no hopane for scaling)).

The lower summer BTT throughput actually requires facility operators to retain and recycle a portion of the BTT contents just to keep the biological system active. The two SHC isoprenoids, pristane and phytane, are degraded slower than their 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 4) indicate they have undergone extensive microbial degradation compared to fresh ANS oil.

Table 4. 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

Sediment TPAH Trends 1993-2018

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 is in the profile interpretations (discussed below). But for historical and trend perspectives, TPAH concentrations are presented. With TPAH levels dropping from historic highs in the hundreds, if not thousands, of ng/g DW between 1993 and 2004 (including a spike in 1995 from the *Eastern Lion* tanker spill at the terminal), average sediment TPAH concentrations at the 68-72m deep terminal Berth 4 site (AMT-S) plateaued at around 50-60 ng/g (DW) from March 2005 through April 2012 (Figure 6). Then in 2013, concentrations dropped further to all-time lows around 10 ng/g. Sediment samples were not collected in 2014 due to a temporary hiatus in the program but after collections resumed in July 2015, the TPAH concentrations at the terminal rebounded slightly to around 30 ng/g and further up to a range of 55 – 80 ng/g between 2016 and 2019 (Table 5 and Table 6). 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 5 and Table 6).

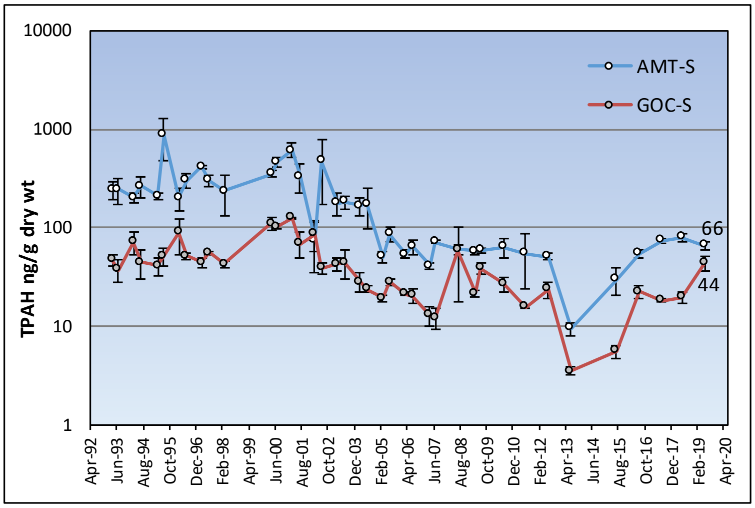


Figure 6. Time series of log (TPAH43) in sediments at AMT-S and GOC. Error bars are ± SE of means.

Table 5. Summary statistics for 2019 TPAH50 and TPAH43 concentrations (ng/g DW).

2019	TPAH50					TPAH43				
	avg	max	min	count	± SE	avg	max	min	count	± SE
AMT-S	75.3	93.7	63.1	3	9.4	65.8	80.1	56.3	3	7.3
GOC-S	44.6	59.3	31.3	3	8.1	44.2	58.8	31.2	3	8.0

Table 6. Historic average sediment TPAH43 values (ng/g DW), 2000-2019.

	AMT-S	GOC-S		AMT-S	GOC-S
Apr-00	353	111	Jul-08	61	60
Jul-00	472	103	Apr-09	59	22
Mar-01	614	126	Jul-09	60	40
Jul-01	335	69	Jul-10	64	28
Mar-02	76	86	Jul-11	55	16
Jul-02	480	39	Jul-12	51	24
Mar-03	179	43	Jul-13	9	3
Jul-03	184	45	Jul-15	30	6
Mar-04	167	28	Jul-16	55	23
Jul-04	175	24	Jul-17	74	18
Mar-05	51	19	Jun-18	80	20
Jul-05	86	28	Jun-19	66	44
Mar-06	54	21			

SEDIMENT BIOMARKERS

Biomarkers' persistence in the BWTF effluent facilitates tracking ANS signals in the surrounding sediments. 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 suggesting nearly complete loss of PAH due to *in situ* weathering during or after sedimentation. And while there is some degradation of the biomarkers (the small gaps between the hopane-normalized ANS profile and the individual components in the upper-right panel), a sufficient profile exists to confidently assign the signal to the BWTF effluent. Although the biomarkers are recalcitrant (here microbially non-preferred), they are not invincible. The losses are consistent with microbial degradation and abiotic dissolution-weathering/dilution of particulate-phase oil droplets from the diffuser. Similar losses, including microbial degradation of selected C_{28} and C_{29} tricyclic terpanes, S4 and S5 diasteranes, S14 and S15 steranes, plus abiotic dissolution losses (previously unknown) of the triaromatic steroids (TAS) compounds were observed from particulate-phase oil during transport and sedimentation following the *Deepwater Horizon* blowout in the northern Gulf of Mexico in 2010 (Stout and Payne, 2016b; Payne and Driskell 2015a, 2015b, 2018a). For illustration, when the PAH and biomarker data are re-scaled to the sample's NBT2 rather than the hopane in the sample (Figure 7, bottom plots), an excess of biomarkers appears above the fresh ANS overlay, demonstrating the residual accumulation of slowly degrading biomarkers and slightly less recalcitrant, higher-alkylated NBT and chrysene homologues over time.

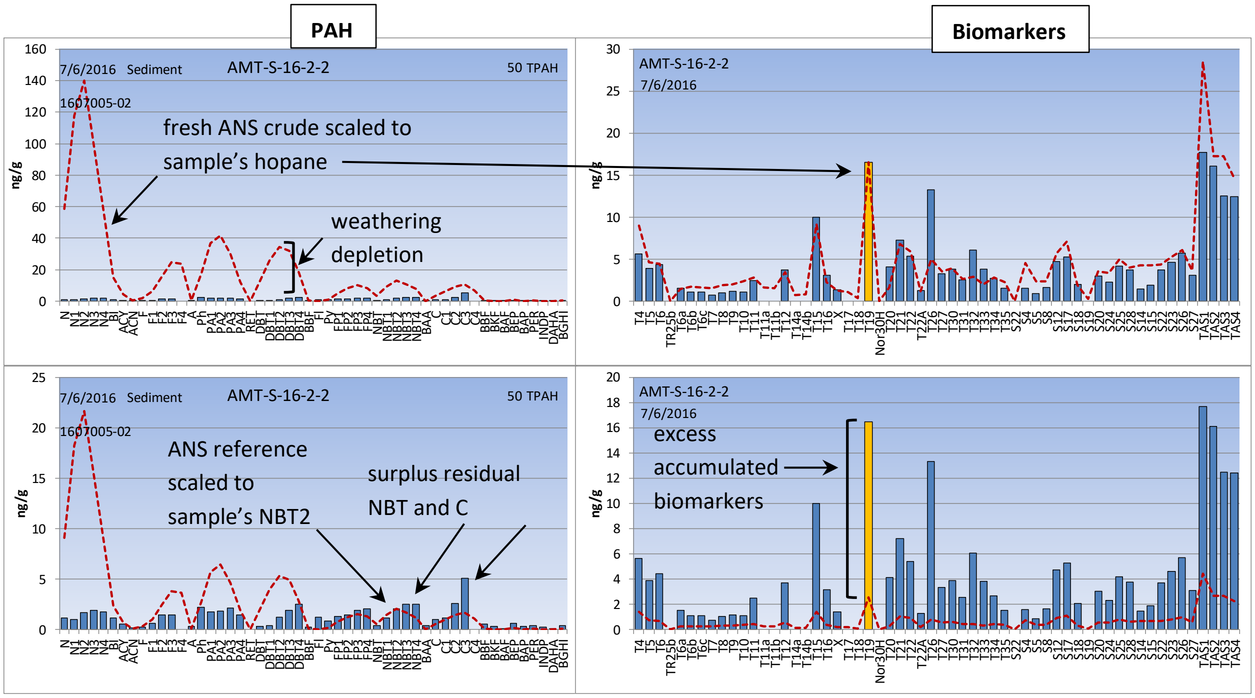


Figure 7. PAH and biomarker profiles of a representative 2016 AMT-S sediment sample overlaid with fresh ANS crude oil reference (dotted red lines) when alternatively scaled by the highly conservative biomarker, hopane (upper plots), versus the less recalcitrant PAH, NBT2 (lower plots). The lower plot 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. There is also an accumulation of the more recalcitrant PAH including higher-alkylated NBT and chrysene homologues (lower left plot).

VALDEZ MARINE TERMINAL SEDIMENTS

In the three 2019 AMT-S sediment replicates, the PAH, SHC, and biomarker profile patterns and concentrations are nearly identical to each other (Figure 8). Overlaying the most appropriate reference source for near-outfall sediments, the particulate-phase PAH pattern from the summer 2016 BWTF effluent, excess parent and alkylated naphthalenes (N, N1, N2, and N3) appear that 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) each show ascending water-washed patterns consistent with a petrogenic source. Interestingly, their higher-alkylated homologues are largely missing, contrary to what would be expected from normal microbial or abiotic weathering processes. This could be a lab noise/integration issue or the extra naphthalenes noted above and the paucity of certain biomarkers suggests sediment dilution by background riverine and glacial flour to an extent that the missing PAH may just be below detection. Conversely, the phenanthrenes (P/As) reflect a pyrogenic source (down-sloping arrows) as do the higher-molecular-weight combustion products between BBF and BGHI at the extreme right end of the PAH profile. Overall, these are mixed source PAH profiles from glacial, petrogenic, and pyrogenic sources.

The SHC patterns reflect the typical dominant contribution from terrestrial plant waxes (n-C_{25}, n-C_{27}, n-C_{29}, and n-C_{31}) with only a minor contribution from higher-molecular-weight C_{34} – C_{40} petroleum waxes. Although the biomarkers are sketchy (again reflecting background sediment dilution), the remaining constituents clearly demonstrate that they are sourced as ANS oil from the BWTF effluent. Thus, overall patterns suggest a mixture of petroleum-sourced and combustion-derived PAH plus background naphthalenes.

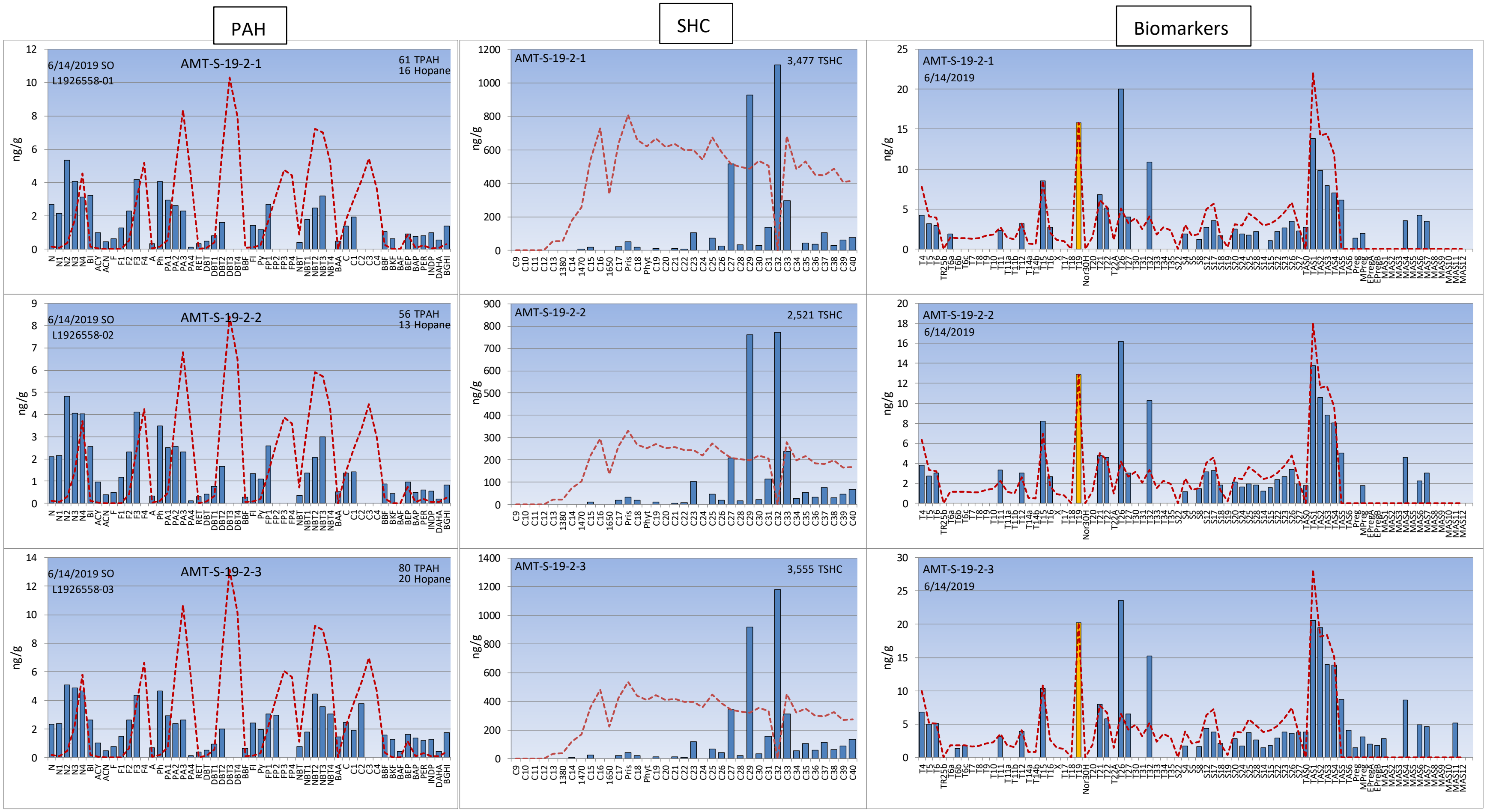


Figure 8. PAH, SHC, and biomarker concentrations and profiles of 2019 AMT-S sediment replicates with mixed background, petrogenic, and combustion sources (see text). The dotted red line in the PAH and biomarker profiles is the July 2016 BWTF filter (Figure 3 and Figure 4) normalized against the sample's hopane; SHC ref normalized to C27. Biomarkers confirm the presence of a weathered ANS profile in the PAH.

The changes in the PAH and SHC patterns between 2011 and 2019 reflect different sources and concentration-dependent weathering behavior (Figure 9). Over this period, there has been a shift in PAH profiles from a dominant pyrogenic pattern in 2011 through 2015 (not shown; see Payne and Driskell, 2017b for more details) to a mixture of background, petrogenic (ANS), and combustion sources over the last three years. Specifically, in 2011, the higher-molecular-weight PAH were almost exclusively pyrogenic as recognized by the dominant parent PAH relative to the alkylated homologues, which decreased 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 alkyl-substituted homologues yielding the hump patterns denoted by the red “tents” (Figure 9, lower three panels). In 2017, the majority of the PAH reflected a water-washed petrogenic source while, in 2018, the signal is more mixed with variable combustion-derived chrysenes. In 2019, the chrysenes reverted to a petrogenic pattern (Figure 9 bottom two panels).

The SHC profile trends since 2011 reflect more background biogenic input as the higher-molecular-weight petrogenic waxes generally decreased relative to the odd-carbon-numbered 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 and reflect lower relative contributions of high-molecular-weight petrogenic waxes compared to 2011, and in 2019 the petrogenic waxes were much, much lower compared to the terrestrial plant waxes. Because the absolute concentrations of the petrogenic waxes are relatively constant (generally between 40 to 100 ng/g), the increasing terrestrial plant wax contributions suggest greater background sediment (riverine and glacial flour) contributions 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 2019 presumably reflect a dynamic balance between variable PAH loads from BWTF effluent and accumulation of soot. Because background combustion product or soot accumulation at GOC-S is over two-times lower (see next section), the likely source is tanker and workboat exhaust while at or near the berths. The biomarker patterns over this timeframe (Figure 10) show a continued accumulation of BWTF-derived ANS components even as the PAH patterns reflect extensive weathering and the variable addition from combustion sources.

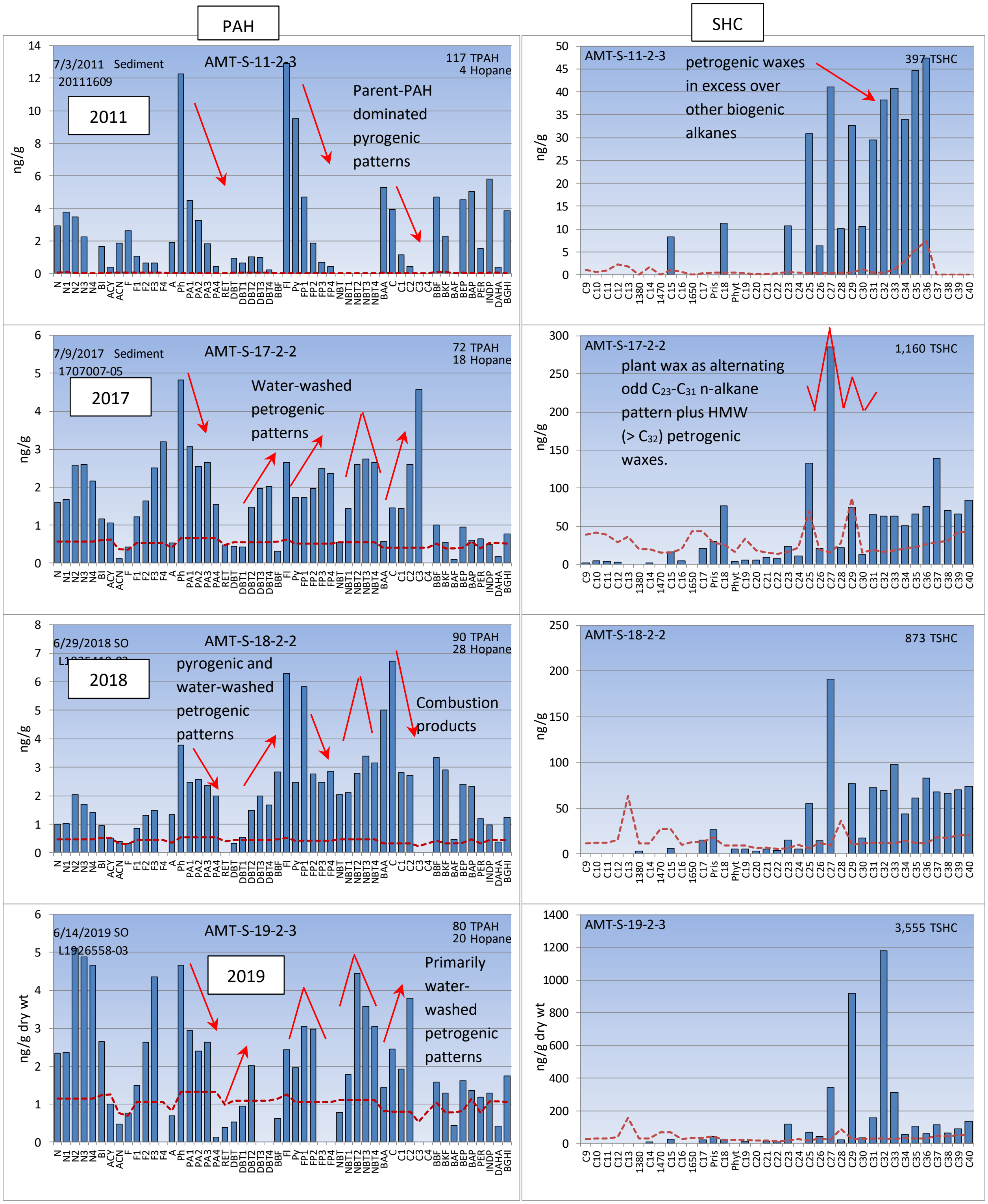


Figure 9. Representative PAH and SHC signatures of AMT sediments between 2011 and 2019 showing the progression from a primarily pyrogenic PAH signature to a mix of pyrogenic and water-washed petrogenic components with increasing terrestrial biogenic SHC and decreasing higher-molecular-weight residual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

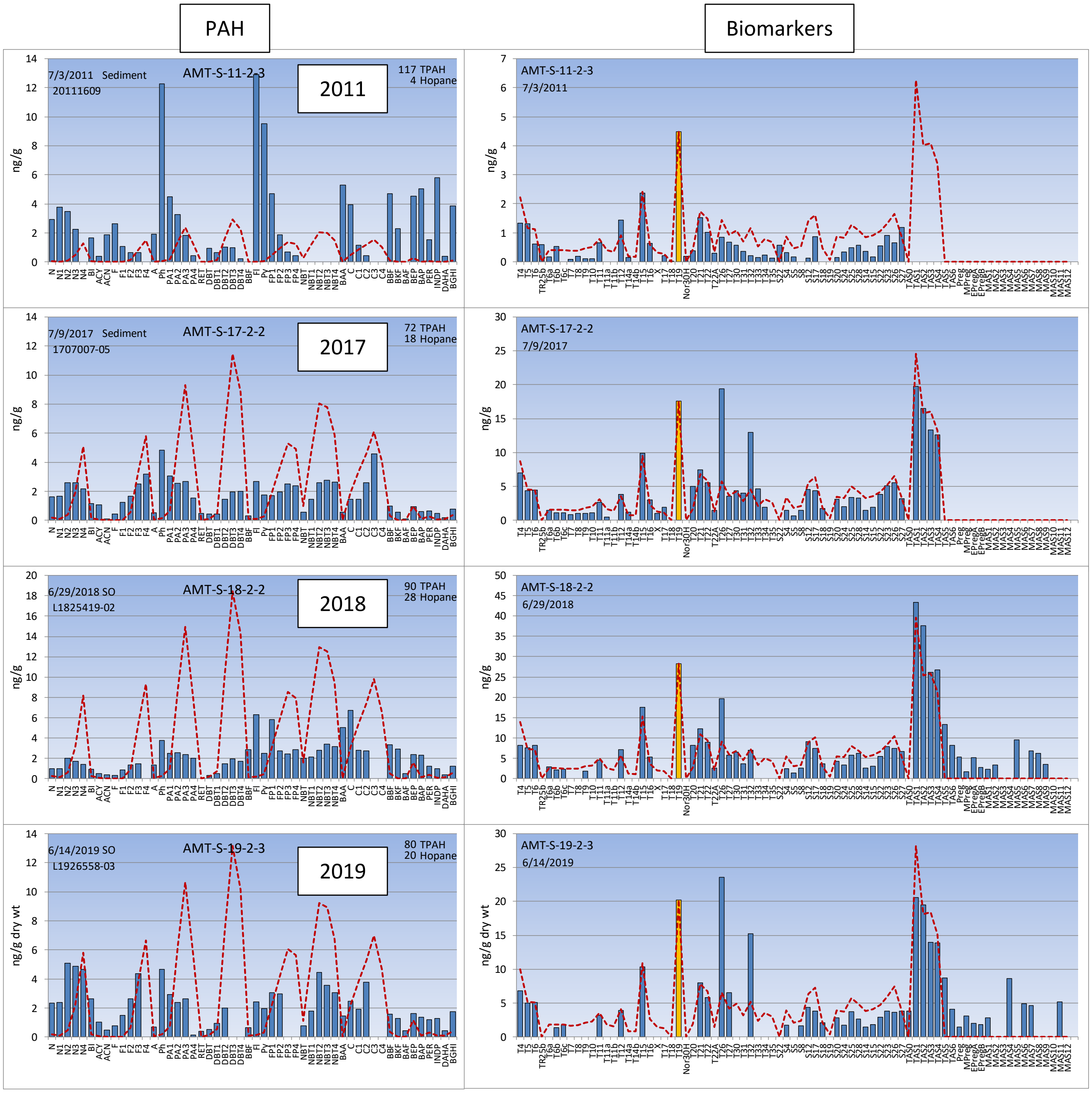


Figure 10. Time-series AMT-S sediment PAH profiles from 2011, 2017-2019 along with the biomarker profiles obtained after introducing those analyses to LTEMP in 2011. The dotted red line denotes the PAH and biomarker profiles from the July 2016 raw ballast water sample normalized to hopane (see Figure 3 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 44 ng/g, which is tentatively attributed to a surge in background naphthalenes and increased levels of combustion products in one replicate. Although the TPAH rise from 6 to 44 ng/g represents a roughly 7-fold increase since 2015, the values are still quite low.

In 2019, 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. The SHC patterns show a mix of trace-level marine planktonic alkanes (C_{15}, C_{17}, pristane) plus possibly increasing, odd-carbon-numbered, terrestrial-plant-wax components (C_{23}, C_{25}, C_{27}, C_{29}, C_{31}) but no residual higher-molecular-weight (C_{33}-C_{40}) petrogenic waxes associated with the terminal (Payne et al., 2015, 2017b).

From 2016-19, the GOC sediment PAH patterns were essentially identical, dominated by background and pyrogenics, with TPAH levels modestly increasing particularly in 2019 due to a spike in higher-molecular-weight BBF – BGHI 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), it appears that, in addition to natural background biomarkers, low-level traces of some ANS-derived biomarkers are accumulating in the GOC sediments. This is particularly so in 2016-17 but with a slightly weaker signal in 2018-19. While these data are sparse (with many missing components), the observed biomarkers and diagnostic ratios, norhopane (T15) to hopane (T19), suggest ANS-derived hydrocarbons, presumably from the BWTF. But despite these confirming biomarkers, there is no evidence of BWTF-derived PAH or SHC accumulation at this site. A few biomarkers are all that remains of the 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 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) and in Cook Inlet sediments (Lees et al., 2000; Saupe et al., 2005) where there is a tentative link to peat inputs.

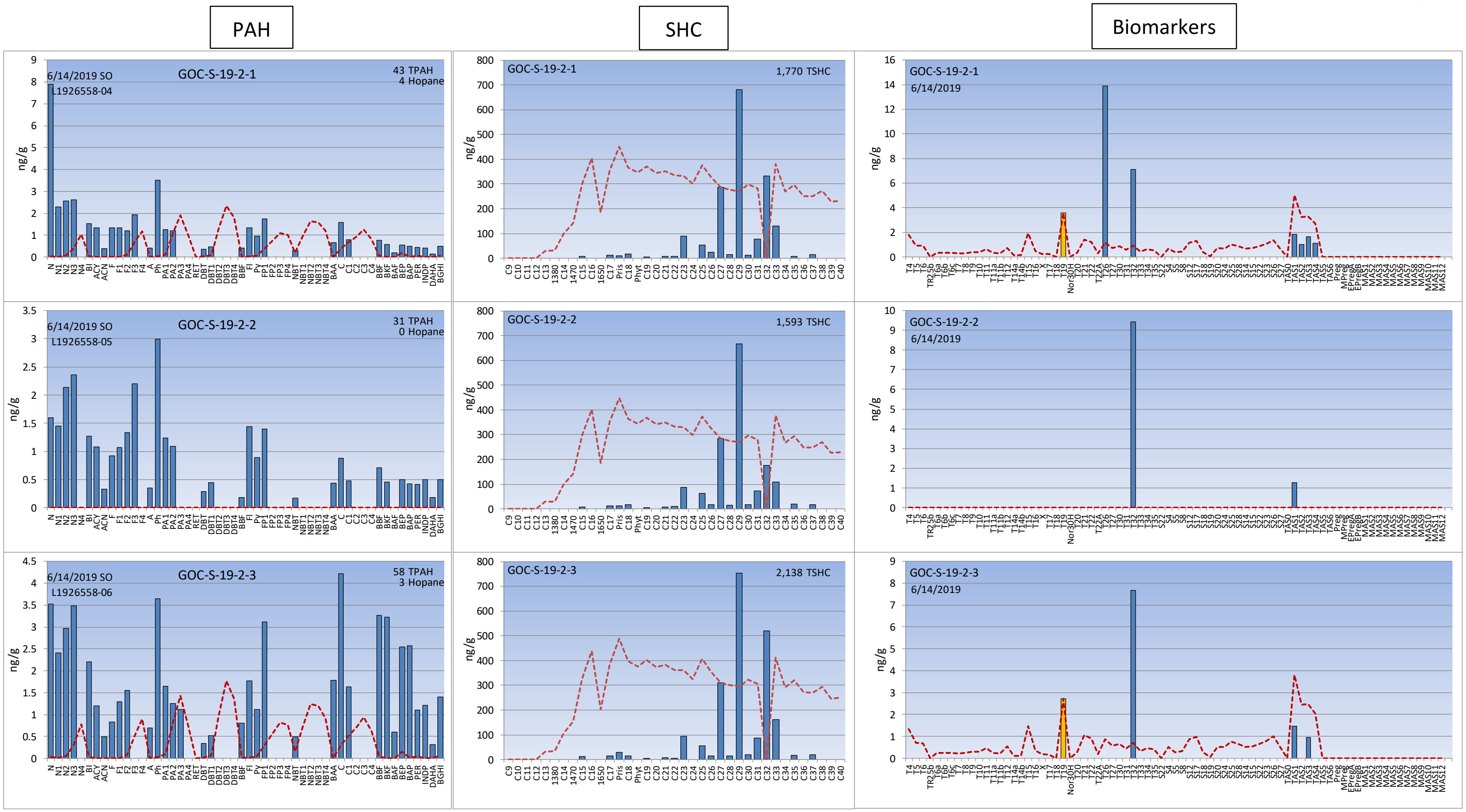


Figure 11. PAH, biomarker, and SHC concentrations and patterns of 2019 GOC-S sediment replicates. The dotted red line is July 2016 BWTF filter (Figure 3) normalized against the sample's hopane; for SHC, normalized to C27 (Figure 4). The T26 and T32 biomarker spikes are laboratory artifacts.

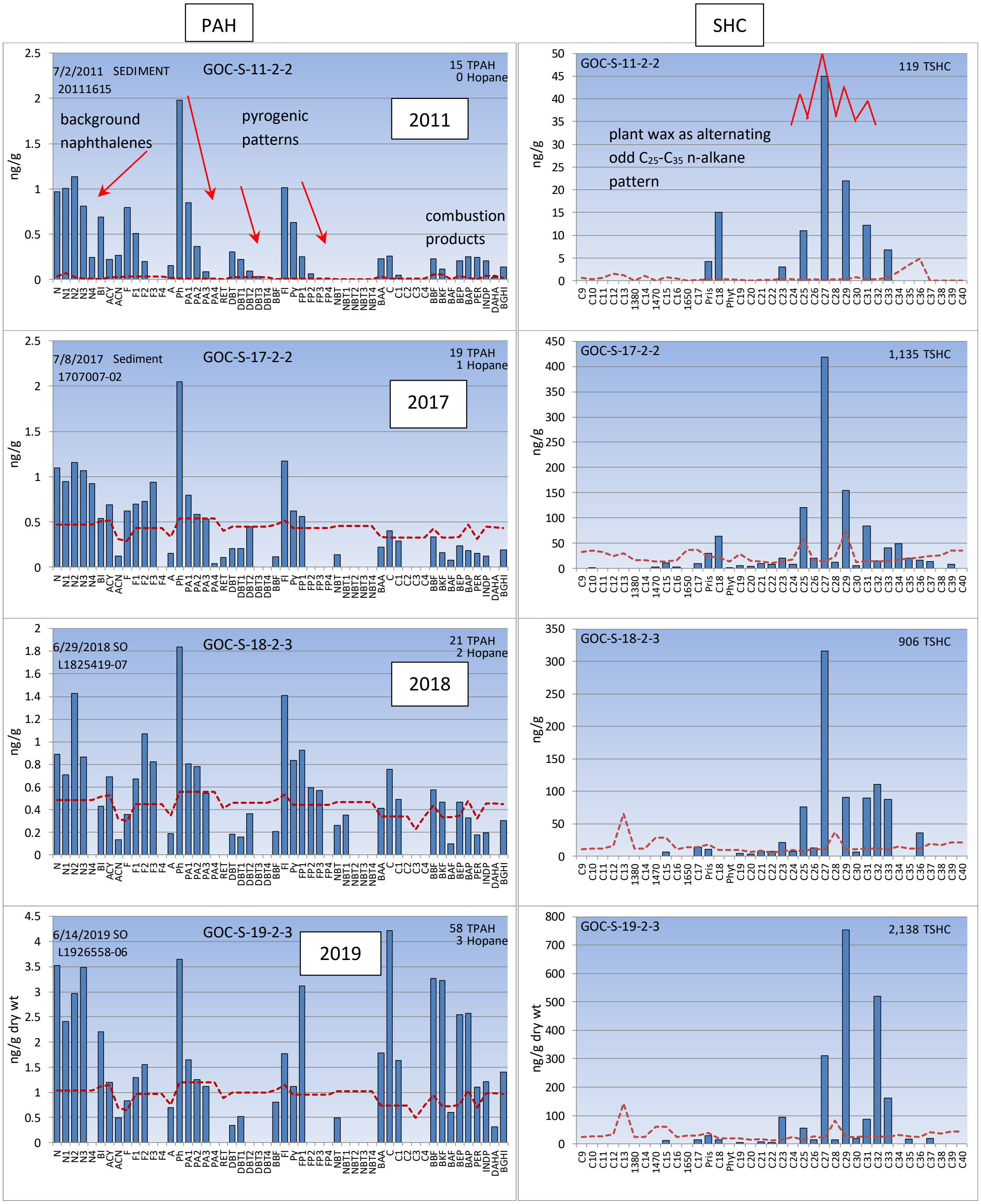


Figure 12. Representative PAH and SHC from GOC-S sediments between 2011 and 2019 showing very similar, background naphthalene components and pyrogenic, parent-dominated, PAH and higher-molecular-weight combustion products. SHC patterns and concentrations reflect possibly increasing terrestrial (plant wax) biogenic inputs since 2011. Red dashed line is sample-specific MDL.

Figure 13. GOC-S sediment PAH and biomarker profiles from 2011, 2017-19. The dotted red line denotes the sample-specific MDL. Analyses in 2011 by ABL did not include the triaromatic steroid biomarkers (TAS); later analyses by Alpha/NewFields did.

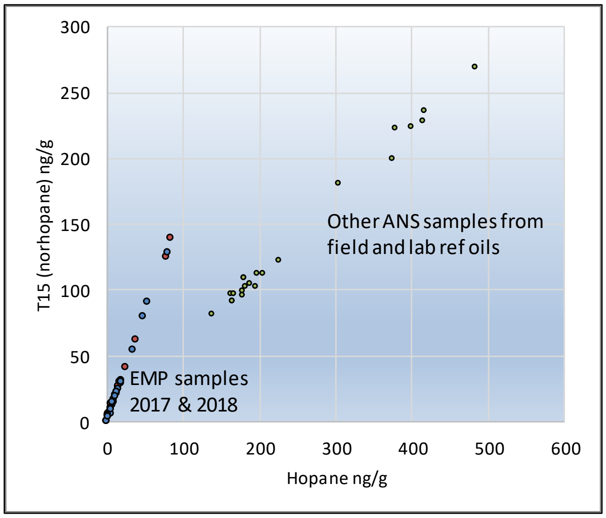
ALYESKA'S EMP SEDIMENT MONITORING

Alyeska's Alaska Pollutant Discharge Elimination System (APDES, previously National Pollutant Discharge Elimination System or NPDES) requires an Environmental Monitoring Program (EMP) to annually sample sediments within Port Valdez in a 14-station design (vs. LTEMP's two stations). Previous LTEMP reports have compared and contrasted results and evaluated conclusions from these complimentary programs. Unfortunately, 2019 EMP data were not yet available in time for this report. For continuity, the following discussion will refocus on Alyeska's 2018 results while expanding on a couple of relevant issues. In the EMP report, Shaw and Blanchard (2019) drew three main conclusions:

- "PAH concentrations in sediments in 2012 through 2018 are generally as low or lower than concentrations in 2000 to 2007 when negligible to at most minor biological effects were found to be associated with PAH. Therefore, the likelihood of adverse biological effects remains low. This conclusion is supported by concentration trends over time as shown by geostatistical and contrast analyses. Elevated PAH concentrations observed sporadically at various locations (most recently at station 11 in 2017) in Port Valdez indicate that pockets of PAH contamination have occurred.
- Hydrocarbon concentrations measured at each of the 14 stations monitored in 2018 were compared to 55 SQVs (sediment quality values; generally recognized indicators of contaminant concentration that are of concern as environmental hazards). Of 1210 comparisons made in 2018 none exceeded the SQV. The grand mean was 0.035 of the relevant SQV value and the means for near shallow and far deep stations (relative to the VMT) were essentially the same, 0.035 and 0.036. As in other years since 2012 this supports the conclusion that the likelihood of adverse biological effects associated with PAH in Port Valdez sediments is generally low.
- In 2018, as in previous years, PAH present in sediments near the BWTF effluent discharge are consistent with the effluent as their source. However, PAH in deeper sediment at greater distances from the VMT are not consistent with BWTF effluent as their primary source and appear to be derived from a mixture of refined petroleum products made from Alaska north slope (ANS) crude combined with pyrogenic PAH. This conclusion is based on statistical analysis and geochemical interpretation of the spatial distributions of individual hydrocarbons and groups of hydrocarbons in 2018 and earlier years. In recent years including 2018, PAH analyses were subject to low surrogate recoveries to a greater extent than in earlier years, a condition which introduces uncertainty to the concentrations of individual PAH present in the sediments and confounds interpretation of the results."

Of these conclusions, we concur that LTEMP results 1) suggest that PAH concentrations are low, 2) likely support SQV evaluations (not our expertise), and 3) their data thinly but positively suggest an ANS source throughout their stations. We do not agree that their data imply mixed oil sources (refined products or non-ANS oil) in their samples based on low biomarker levels or the detection of oleanane. The remainder of this section will further explore this last topic. The point of this expanded discussion is not to slight the abilities or interpretations of our respected colleagues but rather to firmly establish Alyeska terminal operations, and not some unknown source, as the primary Responsible Party for oil contamination in the Port.

Previous LTEMP reports have demonstrated how the PAH, SHC, and biomarker chemical profiles from the LTEMP sites preclude other broad-scale hydrocarbon sources arriving from within and outside the Sound (Payne et al., 2015; Payne and Driskell 2017b, 2019) albeit local diesel spills have occurred at GOC. From their 2018 efforts, Shaw and Blanchard, UAF contractors to Alyeska, concluded again from biomarker data of hopane (T19) and norhopane (T15) that all stations in the port, including deep-water EMP stations along the midline of Port Valdez, contained



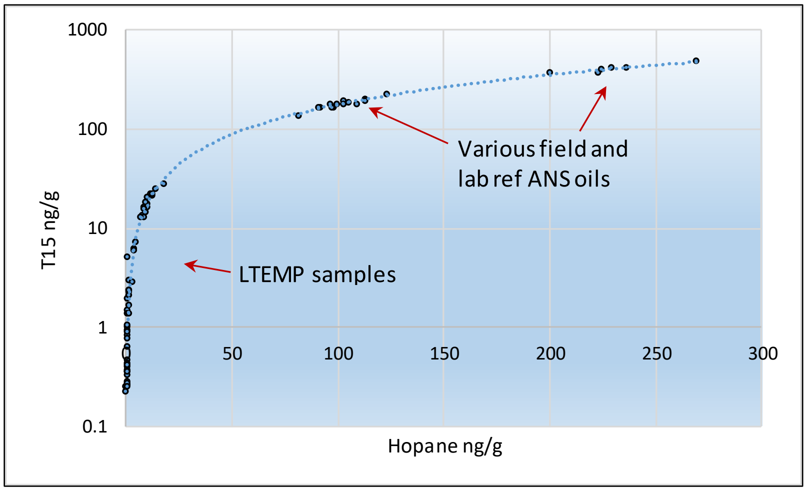


Figure 14. Plot of 2017-18 Alyeska EMP biomarkers (upper plot) showing near identical diagnostic ratios of C-30 hopane (norhopane or T15) versus hopane, which suggests an ANS oil source in all samples. LTEMP samples and ANS oils (upper and lower plots) show a similar but different linear biomarker-ratio relationship among each study's samples; likely a difference in each labs' methods. Lower plot T15 on log scale for clarity of low level field samples.

petrogenic components derived from ANS crude oil (Shaw and Blanchard, 2019). Scatterplots of hopane and norhopane (2017-18 in Figure 14 upper) showed consistent ratios for all stations for both years, which Shaw and Blanchard attribute to the presence of ANS oil throughout the Port. We agree; their stations near the outfall diffuser containing ANS oil from the BWTF (and confirmed by adjacent LTEMP samples) show the same biomarker ratios as the most distant stations and thus, imply all derive from the effluent discharge.

We include in the same plot the ratio data from LTEMP analyses of various other ANS lab reference and spill oils (including NIST standard reference materials, Environment Canada ANS samples, particulate-phase oil from the BWTF, and the 2017 tanker loading arm spill at the terminal). Note the linear relationships within each of the datasets while the slopes differ. We attribute the difference in the linear slopes to unknown analytic lab differences. Providing more specifics would require access to the lab QC data from the EMP contract lab (TDI-Brooks, College Springs, TX). The other plot (Figure 14, lower) comprises all LTEMP samples and oils from 2016-19 that contained both biomarkers. These data are included to demonstrate the similar linearity of results from EMP and LTEMP. From

LTEMP, reviewing the more extensive suite of 55 biomarkers (now expanded to 74) solidly confirms the presence of VMT-derived ANS oil. Hence from the overlap in sampling between the two programs, the ratio linearity within both data sets, and confirmation from LTEMP's full suite of analytes, we affirm that all samples reporting detectable biomarkers from both programs confirm the presence of ANS oil in those samples. By extension, the chronic oiled discharge from the BWTF is the obvious source.

So, how do Shaw and Blanchard conclude a mixed source in deeper sediment locations? Beginning in 2014, their assessment subtly suggested that while the consistent hopane ratios confirmed an ANS-derived, BWTF oil in shallow stations near the terminal, the reduced sediment hopane loads at deeper stations suggested a *refined* ANS source plus pyrogenics. The attribution to a refined ANS seems puzzling since the most abundant refined ANS source would likely be marine diesel or gasoline fuels for which the distillation points required in refining these fuels typically eliminate hopane and norhopane (Bence et al., 1996, Peters et al., 2004, Stout and Wang, 2016). An alternative explanation might be that the low-level biomarkers in the deeper sediments simply represent dilute, dispersed ANS crude inputs from terminal BWTF discharges rather than refined products. Indeed, the gradient of reduced biomarkers decreases as the stations get closer to the glacial floc discharged by Valdez Glacier and the Lowe River, suggesting simple dilution is a tenable explanation. Further evidence lies in the surrogate recoveries (%) reported in the EMP analytical data. Again, the closer the deep stations are to the head of Port Valdez and its glacial flour sediment sources, the worse are surrogate recoveries of the nearly insoluble, high-molecular-weight, chrysene d-12 and perylene-d12. Shaw and Blanchard remark about this effect, suggesting that the higher-molecular-weight chrysene and perylene surrogates are preferentially adsorbed and retained by the finer-grained substrate, but fail to relate it to proximity to the freshwater streams or the dilution of the oil profiles. We do not find low-level biomarkers to be evidence of the presence of mixed sources.

Another line of evidence for mixed sources was the presence of the biomarker oleanane in all EMP 2018 samples. Appropriately positing that oleanane, not present in ANS due to the geologic age of the formations, implies the presence of a second, oleanane-containing oil. We would agree but as discussed in the last LTEMP report (Payne and Driskell, 2019), LTEMP's lab also reported a trace of oleanane in 2018 but found it to be an analytic artifact. Furthermore, the EMP lab had detected oleanane widely in 2015 and 2016 but only rarely in prior years and then no oleanane in 2017 samples but present again in all 2018 samples. It seems highly unlikely that some new basin-wide oleanane source would suddenly disappear and reappear through the years (and not in LTEMP samples). Shaw and Blanchard are equivocal, saying that "In 2015 to 2018, all conclusions were confounded and made less certain by the frequent low surrogate recoveries at numerous stations particularly among the far-deep station group." We feel this line of evidence is too tenuous to conclude a non-ANS source is present.

As required by the current NPDES discharge permit, the EMP program only reports 33 PAH compounds and isomers and, voluntarily, the 3 biomarkers discussed above. In comparison, LTEMP now reports 74 PAH and 74 biomarkers and uses the now accepted TPAH50 suite to assess profiles, toxicity, and statistics. But within EMP's limited suite of PAH, there still are two recalcitrant, diagnostically useful hydrocarbons, chrysene and naphthobenzothiophene. These two hydrocarbons are mostly insoluble and non-preferred nutrition for microbes and thus, tend to persist similar to the biomarker, hopane. A plot of chrysene (or naphthobenzothiophene) versus hopane should show a mostly linear relationship for a given oil (Figure 15). Diagnostically, it is appropriate to suggest that samples appearing above/below the trend line are anomalous for a surplus/paucity of the given compound. In this plot,

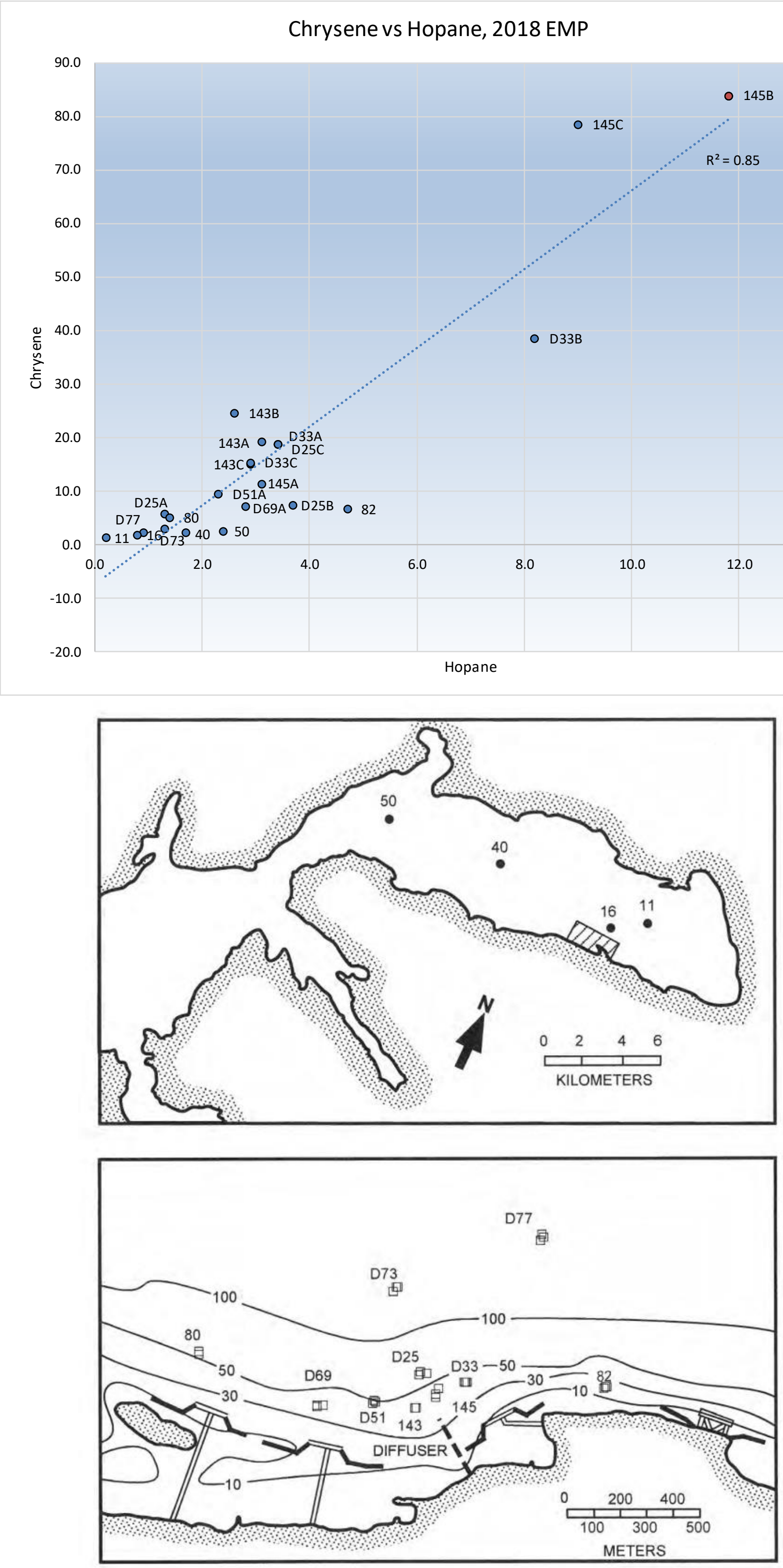


Figure 15. Relationship of chrysene versus hopane in 2018 EMP samples (upper) and map of 2018 EMP stations (lower).

samples below the line are richer than expected in hopane; samples above the line are richer in chrysene. The samples richer than expected with hopane are simply those in which the PAH have been degrading while hopane residues accumulate (discussed in Payne and Driskell, 2019). The samples above the line, richer in chrysene, are more problematic. Since hopane does not degrade, or at least much slower than chrysene, there must be another source for these chrysene values. Three scenarios seem possible: 1) as suggested by the low chrysene d-12 surrogate recoveries, the values may be arithmetically biased high (discussed in next paragraph) or 2) linear regressions are heavily influenced by outliers and these may need adjustment or 3) chrysene enrichment may be occurring from pyrogenic inputs from local Alyeska marine operations (tankers and support craft near the berths). The third hypothesis would be resolved if EMP reported the full suite of chrysene alkylated homologs.

Surrogate recoveries are a perennial issue at all labs. Surrogates are tagged analytes added in known quantities at the start of sampling processing. The final percent recovery is the amount initially added versus the amount eventually reported by the analysis. While it logically makes some sense to adjust reported values back to full recovery levels (i.e., surrogate-corrected values) as many labs do, this approach can also introduce an arithmetic bludgeoning of the data (e.g., data associated with 20% surrogate recovery gets multiplied x5 or data associated with 5% surrogate recovery gets multiplied x20, etc.). Furthermore, a single surrogate (five used in EMP PAH analyses) is applied across a suite of similar molecular-weight compounds even though each would theoretically have its own specific analytic bias depending on procedures and instrument condition. In some studies, surrogate recoveries are related to matrix or its processing (e.g., the C_{32} SHC interferent in BWT effluent, July 2016; Figure 4). This seems to be the case for EMP samples with poor recoveries of high-molecular-weight surrogates apparently related to high glacial flour loads at certain stations (mentioned above and in Shaw and Blanchard, 2019). Additionally, for 2018 EMP data, surrogate-corrected vs non-corrected chrysene seems to induce a random error as the data's linearity with hopane degrades (Figure 16). For these reasons, we prefer to use non-surrogate-corrected data for assessment purposes. EMP reports both but uses surrogate corrected data for their statistical models.

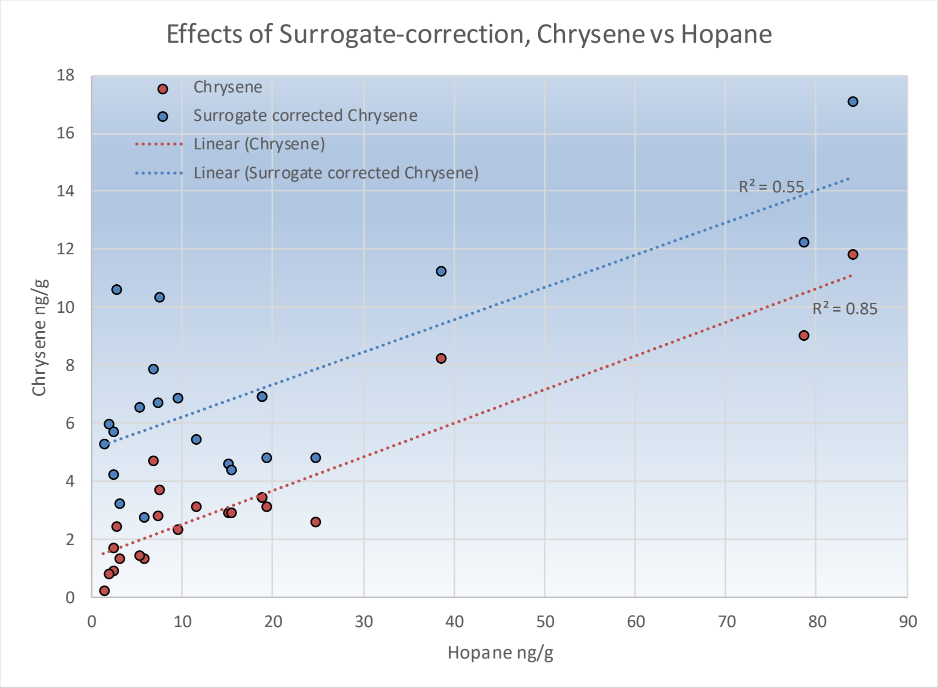


Figure 16. Effects of chrysene surrogate correction on linearity with hopane in EMP 2018 samples.

In summary, this mixed-source issue is relevant for two reasons, 1) reporting a mixed oil source appears to be a false positive and transfers some portion of oil pollution responsibility from the VMT discharge to an unknown second source and 2) it again points out the insufficiency of analyzing and reporting the ambiguous subset of PAH and biomarkers specified in the discharge permit.

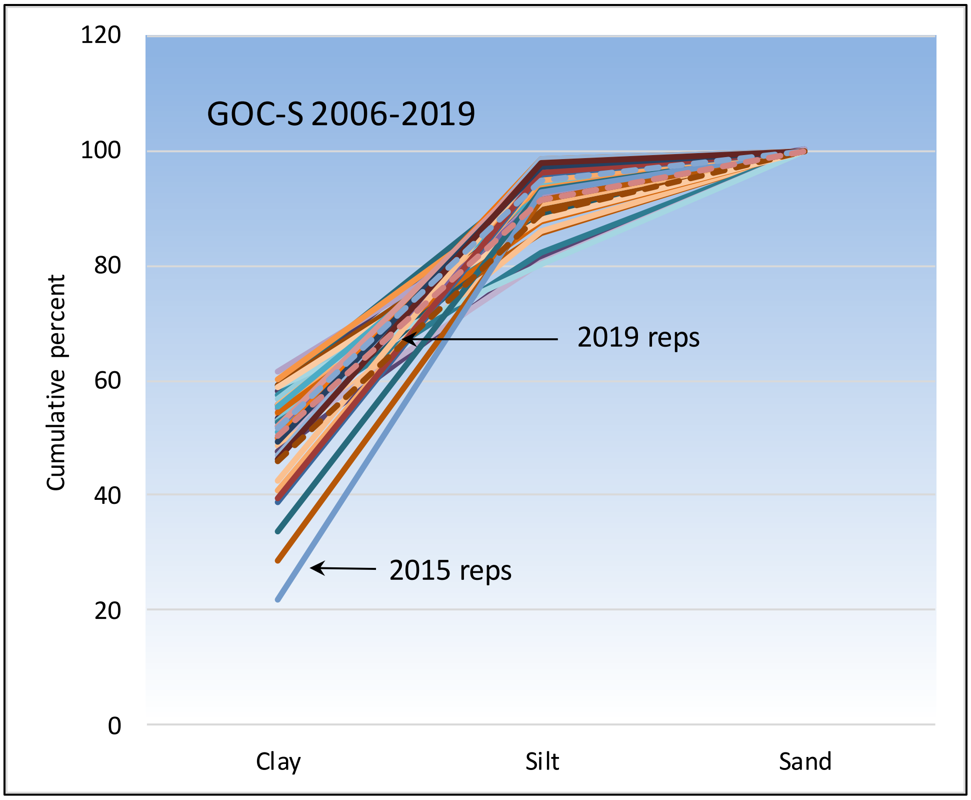
Finally, as in previous years, the 2019 EMP interpretations and conclusions cannot be fully corroborated from the abbreviated PAH33 and biomarker data available in Shaw and Blanchard's report. Nevertheless, it can be said that despite highlighting our differences in interpreting EMP data, the EMP conclusions generally agree with LTEMP's recent findings of low-level petrogenic plus pyrogenic patterns.

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 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 2006-2019 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 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 17 and Table 7) and with both sites showing minor trends and outliers. In the 3D plots (Figure 18), 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 7). 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 18). 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. Note that the PGS sample is taken after the chemistry sample and would not affect the chemistry assessment.



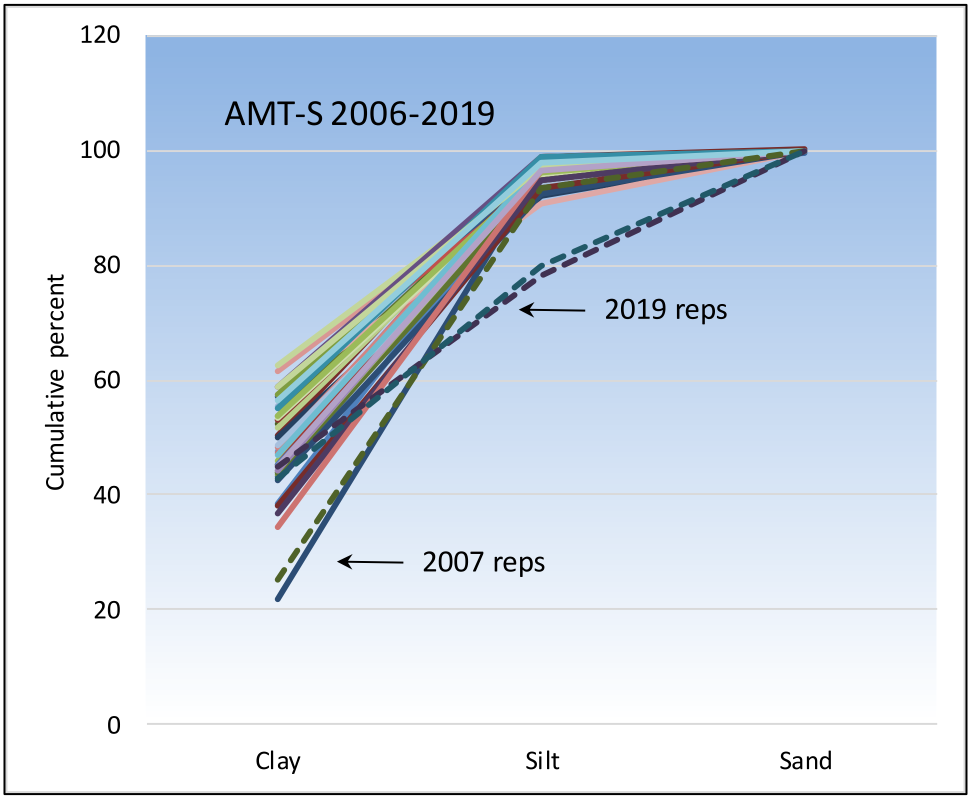


Figure 17. Individual replicate cumulative grain-size curves (%) for GOC-S and AMT-S, 2006-2019.

Table 7. Average grain size components for GOC-S and AMT-S, 2006-2019.

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
avg	3	48	48	avg	8	41	51

[1] Combines two seasons of sampling

[2] Likely biased high

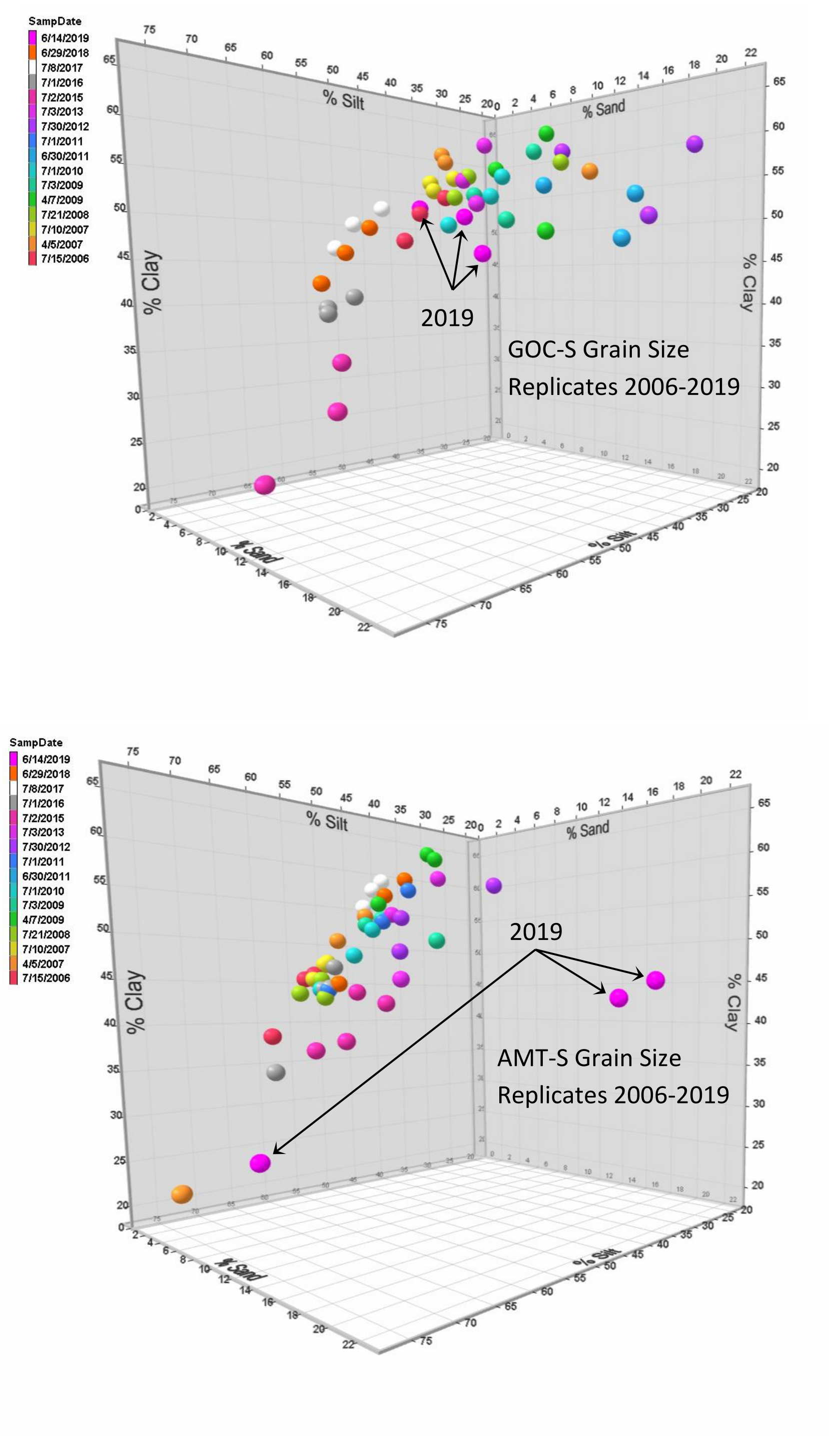


Figure 18. 3D plots of grain size components from GOC-S and AMT-S 2006-2019. Sampling years are color coded: blue to red, 2006-2018; pink, 2019. Note the clipped axes emphasize a decreasing shift in clay vs silt at GOC-S in 2015. The two 2019 AMT-S outlier samples with anomalously high sand content (~20%) appear to be sampling errors; however, the PAH, SHC, and biomarker data for all three 2019 AMT-S grabs appear essentially identical (Figure 8).

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 in order to do site-to-site contaminant comparisons.

During the more frequent samplings early in the LTEMP program, TOC values showed seasonal cycles and showed a slow increase in concentration plateauing around 2003 (Figure 19 and Table 8). 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 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 20); 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.

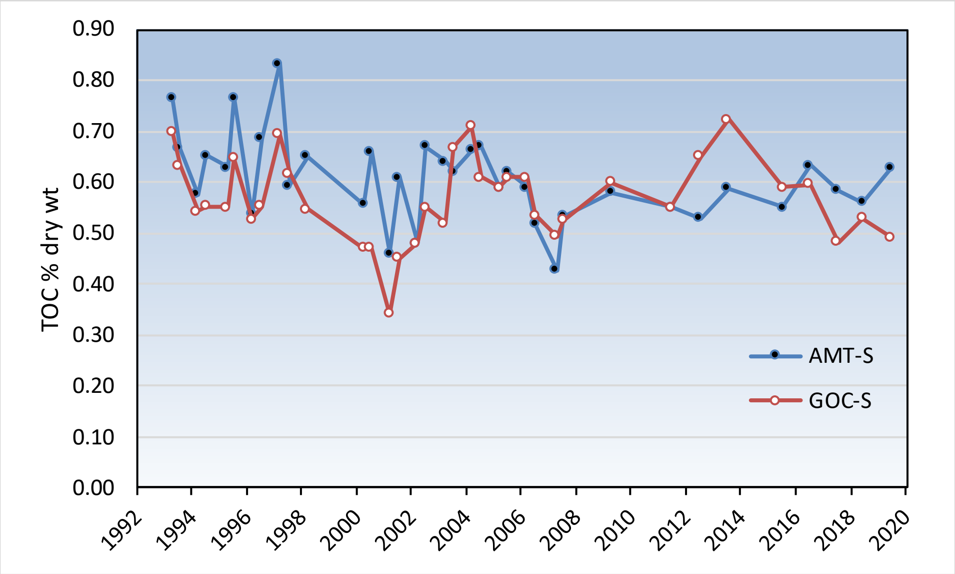


Figure 19. LTEMP Total Organic Carbon trends in AMT-S and GOC-S sediments (% DW), 1993-2019.

Table 8. LTEMP Total Organic Carbon in AMT-S and GOC-S sediments (% DW), 1993-2019.

Sample Date	AMT-S	GOC-S	Sample Date	AMT-S	GOC-S	Sample Date	AMT-S	GOC-S
Apr-93	0.77	0.70	Jul-00	0.66	0.47	Jul-06	0.52	0.54
Jul-93	0.67	0.63	Mar-01	0.46	0.34	Apr-07	0.43	0.49
Mar-94	0.58	0.54	Jul-01	0.61	0.45	Jul-07	0.53	0.53
Jul-94	0.65	0.55	Mar-02	0.48	0.48	Apr-09	0.58	0.6
Apr-95	0.63	0.55	Jul-02	0.67	0.55	Jun-11	0.55	0.55
Jul-95	0.77	0.65	Mar-03	0.64	0.52	Jul-12	0.53	0.65
Mar-96	0.54	0.53	Jul-03	0.62	0.67	Jul-13	0.59	0.72
Jul-96	0.69	0.55	Mar-04	0.66	0.71	Jul-15	0.55	0.59
Mar-97	0.83	0.69	Jul-04	0.67	0.61	Jul-16	0.63	0.60
Jul-97	0.59	0.62	Mar-05	0.59	0.59	Jul-17	0.58	0.48
Mar-98	0.65	0.55	Jul-05	0.62	0.61	Jun-18	0.56	0.53
Apr-00	0.56	0.47	Mar-06	0.59	0.61	Jun-19	0.63	0.49

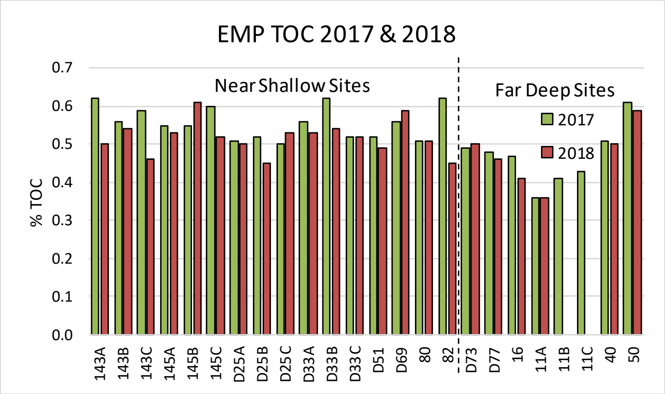


Figure 20. Total organic carbon for sediments in Alyeska's 2017 and 2018 monitoring program (from Shaw & Blanchard, 2018, 2019) in vicinity of the terminal (near shallow sites) and deeper within the fjord (far deep sites).

PORT VALDEZ MUSSEL TISSUES

HISTORICAL TRENDS IN PORT VALDEZ MUSSEL TISSUES

Reflecting the changing operations at the terminal, the trends of oil discharge into Port Valdez from terminal operations have 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 been generally shifting away from the terminal's petrogenic profiles to background dissolved-phase or pyrogenic (combustion-derived) PAH patterns. Sediments on the other hand, as discussed above, still show BWTF oil accumulation near the terminal but at much lower concentrations than in earlier years.

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, in 2002 the concentrations dropped to ~80 ng/g levels (Figure 21). One exception to this trend occurred with a diesel spill at GOC in the summer of 2004 when TPAH concentrations were approaching 1,000 ng/g. By the 2005 collections, the PAH were long purged, and concentrations were back in the pre-spill range. They continued to fall at both locations until summer 2013 when very low, near-MDL, traces of petrogenic components were present. No samples were collected in 2014 due to a program hiatus, but in 2015, the PAH tissue burden at AMT-B increased slightly and transitioned into a primarily dissolved-phase naphthalene pattern while the GOC-B tissues were more equivocal (see below). TPAH concentrations in 2016 remained essentially the same at GOC-B (~31 ng/g) but they dropped to single digits at AMT-B (Figure 21). Since 2017, the TPAH concentrations have remained in single digits at all three Port Valdez stations (Table 9). At these exceptionally low levels, the individual PAH components at all three Port Valdez sites in 2018-19 were all below MDLs.

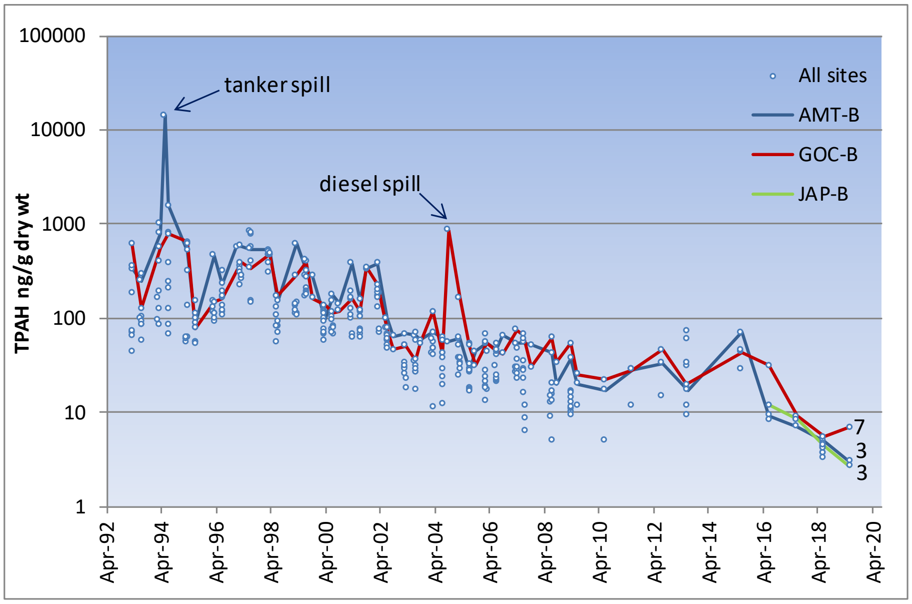


Figure 21. Time series of mean mussel TPAH43 concentrations comparing 2019 AMT-B and GOC-B with prior LTEMP collections at other regional sites (open circles). Note the log scale for TPAH concentrations. See standard errors of mean in Table 9.

Table 9. Time series of mean TPAH43 (ng/g DW, n=3) from AMT-B, GOC-B, and JAP mussels, 2008-2019.

	July 08	Sept 08	Apr 09	July 09	July 10	July 11	July 12	July 13	July 15	July 16	July 17	Jun 18	Jun 19
Mean TPAH													
AMT-B	43	20	38	20	17	29	33	17	70	9	7	5	7
GOC-B	62	34	54	25	22	29	46	20	43	31	9	6	3
JAP										14	9	4	3
± SE of means													
AMT-B	5.8	1.9	6.8	0.8	0.9	2.2	3.1	2.9	8.6	1.9	0.3	0.5	0.7
GOC-B	6.3	3.5	2.8	1.2	1.4	3.3	6.6	2.4	3.6	15.7	0.5	0.6	2.5
JAP										1.6	2.6	0.2	0.2

Because of the below-MDL concentrations and the presence of the same PAH profiles in all the field samples and associated laboratory method blanks (Figure 22), source identifications for the 2019 tissue samples are not possible. This same issue was encountered in the 2018 mussel collections (Payne and Driskell, 2019) again reflecting the clean environment from which the samples were collected. A local 2017 incident with the Berth 5 Tanker Loading Arm spill of ANS crude oil (Payne and Driskell, 2019) demonstrated the utility of mussels in monitoring and detecting oil contamination. Mussels near the event captured the initial oiling and then purged themselves back to background levels within three months (Figure 23).

The 2019 tissue replicates from all three Port Valdez stations are presented in Appendix 2, and as was the case for the 2018 collections, all of the 2019 sample profiles are essentially identical. Rather than replotting those data here, the reader is referred to the appendix (and Figure 22) to see representative examples of the overall patterns. Of greater relevance is the change in the profiles over time.

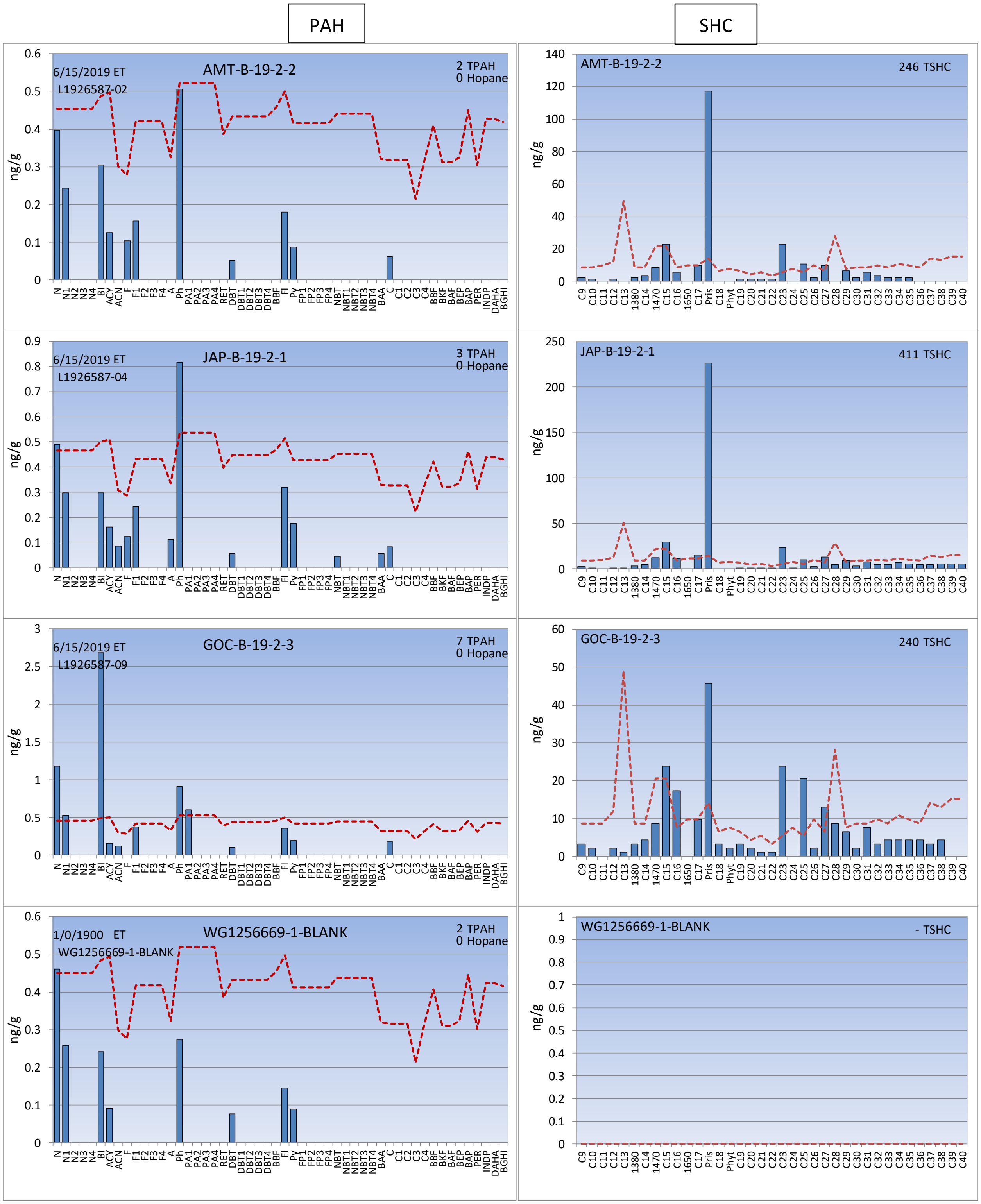


Figure 22. PAH and SHC profiles from representative 2019 mussel samples collected at AMT-B, JAP, and GOC-B along with the laboratory method blank. The dotted red line is the sample's method detection limit. Note that most PAH in the samples are also in the method blank (bottom profile) at similar, below MDL concentrations. SHC profiles reflect only background biogenic hydrocarbons from marine biota (n-C$_{15}$, n-C$_{17}$, and pristane) plus trace-level odd-carbon number n-alkanes (n-C$_{23}$, n-C$_{25}$, n-C$_{27}$, n-C$_{29}$, and n-C$_{31}$) derived from terrestrial plant waxes.

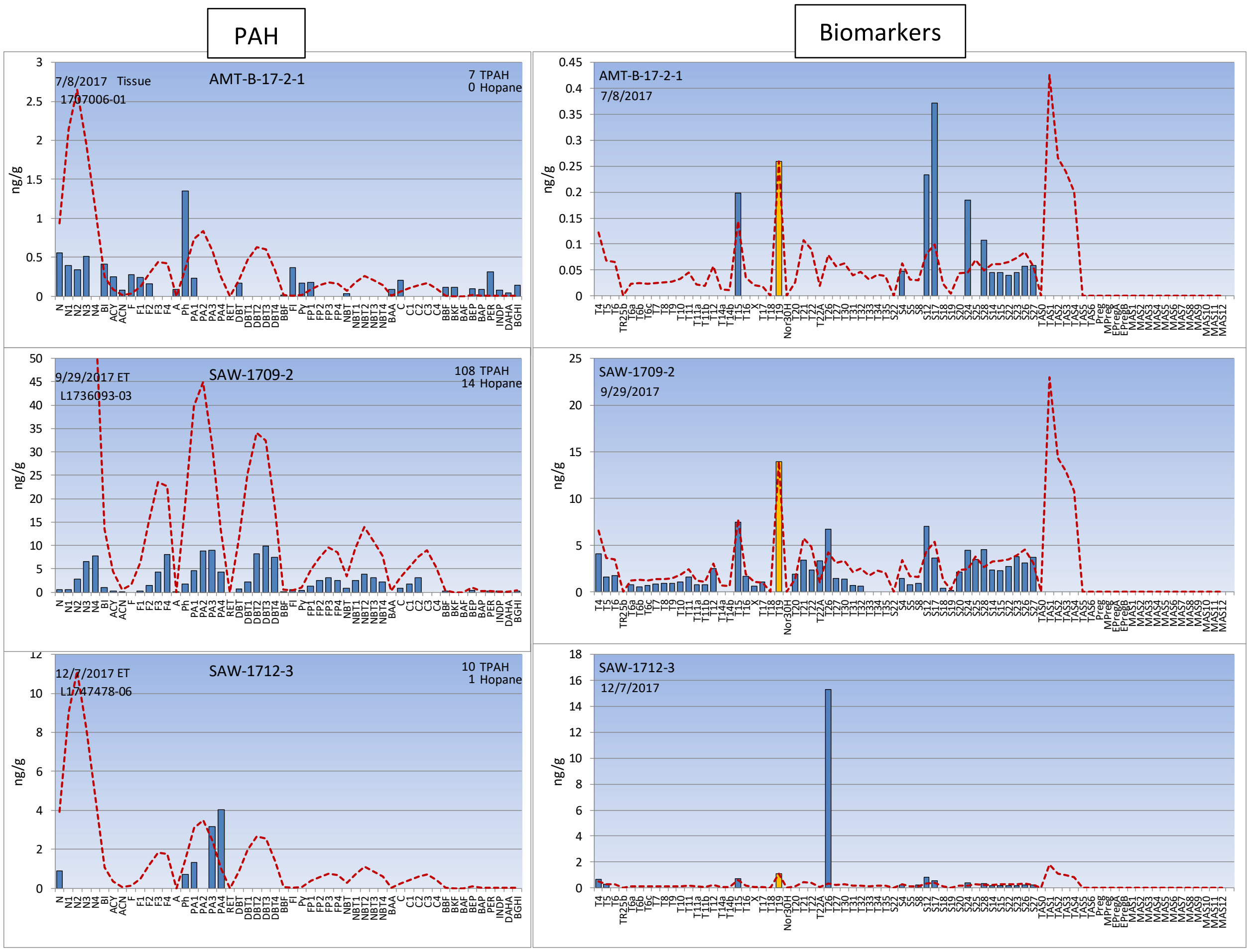


Figure 23. PAH and biomarker patterns at AMT-B relating to the tanker loading arm spill at the terminal in September 2017. The samples show the background profile from the normal LTEMP collections pre-spill (top, July 2017, TPAH 7 ng/g), the weathered oil in the mussels ~one-week post spill (middle, 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 lab artifact.

Valdez Marine Terminal Mussels

Historical PAH data for the traditional AMT-B site (Figure 24) suggest the presence of water-washed (possibly petrogenic) naphthalenes in 2008, dissolved-phase naphthalenes in 2015 (and 2017, not shown) plus at- or below-MDL traces of combustion products in most of the samples. At these trace concentrations, results must be qualified as estimates but because of their patterns, they are not considered to be false positives. Although TPAH levels increased slightly in 2015 (Figure 21), the majority of the PAH were dissolved-phase naphthalenes (Figure 24), which also were observed to a lesser extent at GOC-B (next section). Recall that the source of dissolved-phase PAH cannot be definitively determined just from their profiles. These, however, did not match the naphthalene pattern

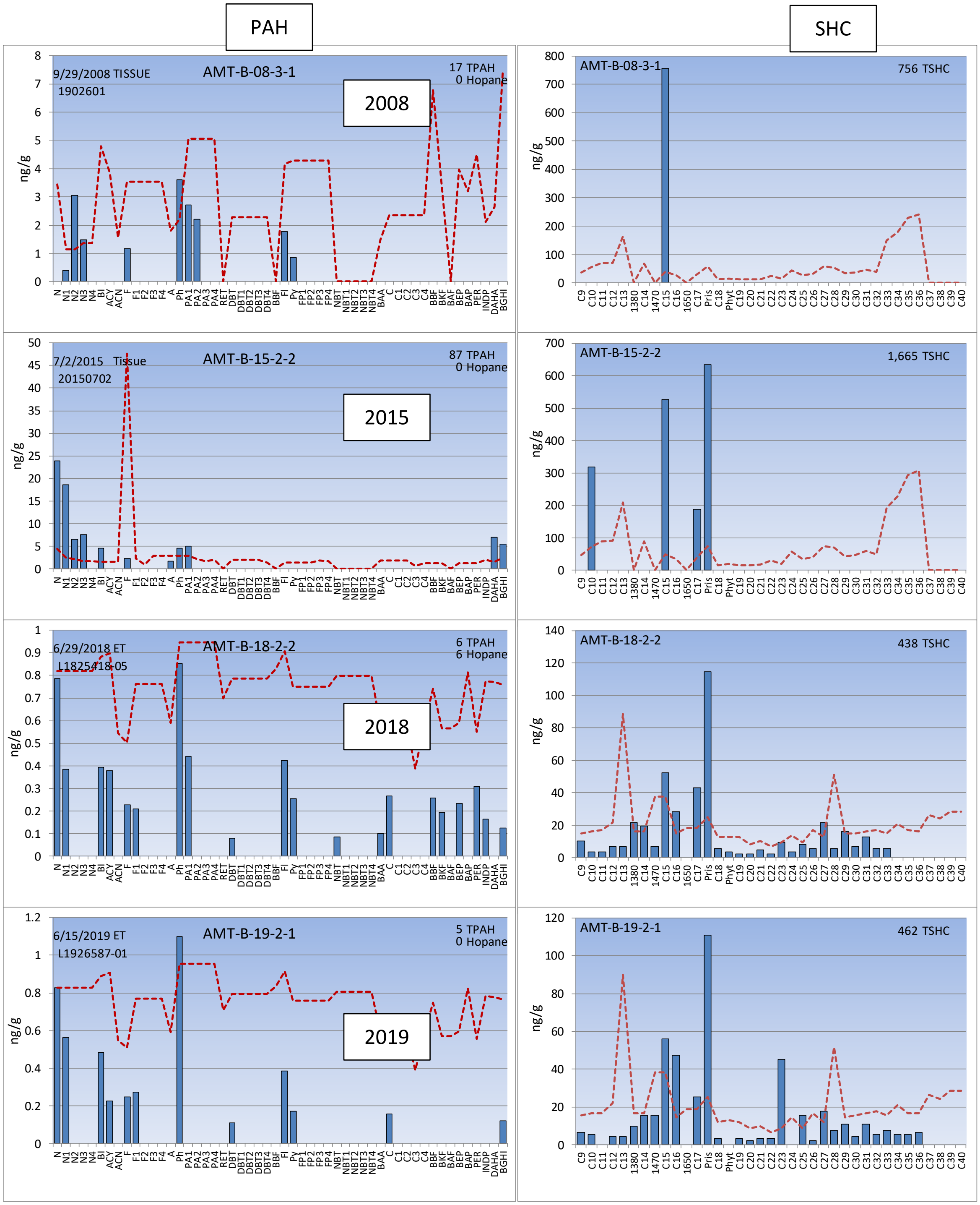


Figure 24. Time-series mussel PAH and SHC profiles from AMT-B. In 2008, showing primarily below-MDL water-washed (possibly petrogenic) naphthalenes and combustion products (P/A and FL plus PY), in 2015, dissolved-phase naphthalenes and trace-level combustion-product PAHs, and, in both 2018 and 2019, all components <MDL are also associated with the lab blank (except combustion products and perylene in 2018) (Figure 22). Planktonic biogenic SHC (n-C$_{15}$, n-C$_{17}$, and pristane) are also present in other years. The dotted red line denotes the sample-specific MDL as neither hopane nor NBT2 were present in any of the samples for scaling.

associated with BWTF effluent (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.[3]

The SHC data for 2008 and 2015 AMT-B samples (Figure 24) show contributions from marine biogenic sources (Payne et al., 2015), and in the majority (30 of 34) of AMT-B 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 (Payne et al., 2015). Quantified SHC data are not available for 2016 and 2017 mussels. The 2018 and 2019 SHC profiles in the mussels at AMT-B showed 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-B mussels adjacent to the terminal.

JACKSON POINT MUSSELS

Because mussel samples were only collected from JAP starting in 2016, prolonged time-series data are not available. But comparisons of representative samples from 2016 through 2019 (Figure 25) show the possible background contribution of glacial flour/riverine-sourced naphthalenes in 2017 along with trace-level combustion-derived PAH and presumably biogenic steranes whereby the constituent patterns do not correspond with the BWTF effluent. Unfortunately, the source of the 2018 and 2019 PAH cannot be attributed in the field sample because the same components were observed in the 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.

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 21 and Figure 26). In those GOC-B 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 at both sites. After 2002, as TPAH levels at both stations trended lower, the TPAH levels at GOC-B 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-B showed evidence of a fresh diesel spill (Figure 21). The diesel signal had largely cleared by summer 2005, and then the TPAH levels again generally tracked with AMT-B through 2015. In 2016, the GOC-B TPAH concentrations only dropped to 27 ng/g while the corresponding levels at AMT-B dropped to all-time lows at 8 ng/g. As noted in Payne and Driskell (2019), the slightly higher 2016 TPAH levels at GOC-B reflected a diesel spill at that location. The PAH data at that time exhibited above-MDL petrogenic fluorenes and phenanthrenes/anthracenes, and oiling was confirmed by a descending T4-T6 triterpane biomarker pattern and from an m/z 85 reconstructed ion chromatogram, biogenic n-C_{15} and pristane plus the characteristic C_{16}-C_{24} n-alkane pattern associated with diesel oil (see Payne and Driskell,

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[3] 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.

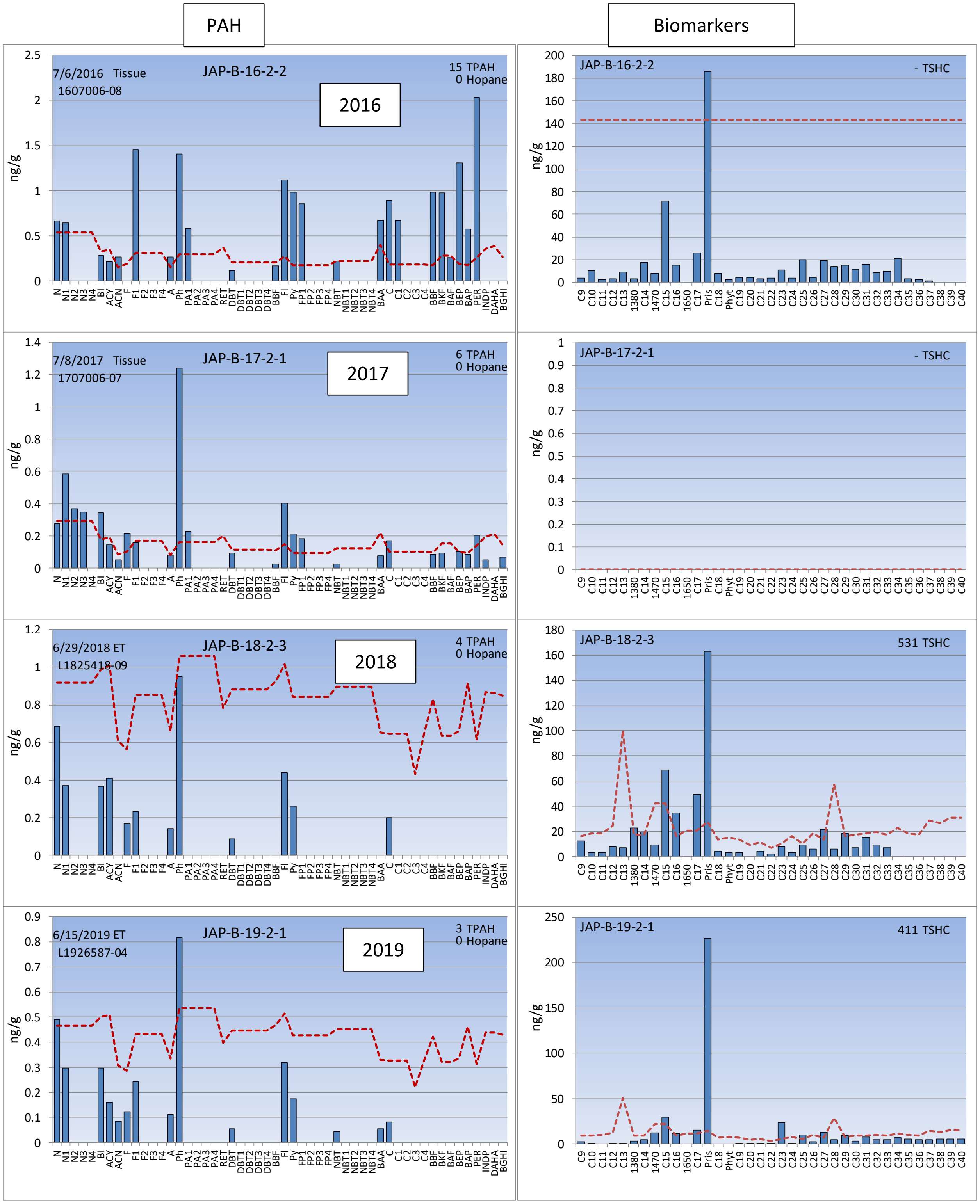


Figure 25. Time-series PAH and S/T profiles of mussels collected at JAP in 2016 through 2019 showing primarily trace-level dissolved- and (possibly) particulate-phase background naphthalenes plus combustion product PAHs (Ph, FL, PY, C, BBF, BKE, BEP), and perylene (PER) in 2016 and 2017. Quantified SHC data are not available for 2017 mussel samples. The below MDL PAH in 2018 and 2019 are suspected of being procedural artifacts associated with the laboratory method blanks (see Figure 22). The dotted red line denotes the sample-specific MDL as neither hopane nor NBT2 were present for scaling.

2019). In 2017, there was no evidence of residual diesel, and the TPAH at GOC-B and AMT-B were both in single digits at 8 and 6 ng/g, respectively, and they have remained in this range through 2019. The time-series PAH and SHC profiles of mussels collected at GOC-B in 2008, 2015, 2018, and 2019 (Figure 26) suggest possible particulate-phase, water-washed petrogenic naphthalenes and dibenzothiophenes (DBT) plus combustion products in 2008. In 2015, dissolved phase naphthalenes (N and N1) were the only PAH detected at significant concentrations. An even more complete (N–N3) descending, dissolved phase naphthalene pattern was observed at the same time in the mussels at AMT-B (Figure 24) suggesting a common background source. In 2018 and 2019, the GOC-B PAH concentrations were all below the MDLs (Figure 26), and like the two stations adjacent to the terminal during this period, the PAH profiles were very similar with only traces of dissolved-phase naphthalenes and at- or just-below MDL combustion products. As noted in previous sections, these patterns were almost identical to those observed in laboratory method blanks run in parallel with the samples (Figure 22).

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, and 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 and 2019. No mussel-tissue SHC data were obtained in 2016 or 2017, but as described in Payne and Driskell (2017b), SIM m/z 85 GC/MS profiles were used along with and T4 – T6 biomarkers to confirm the presence of low-level diesel contamination in 2016.

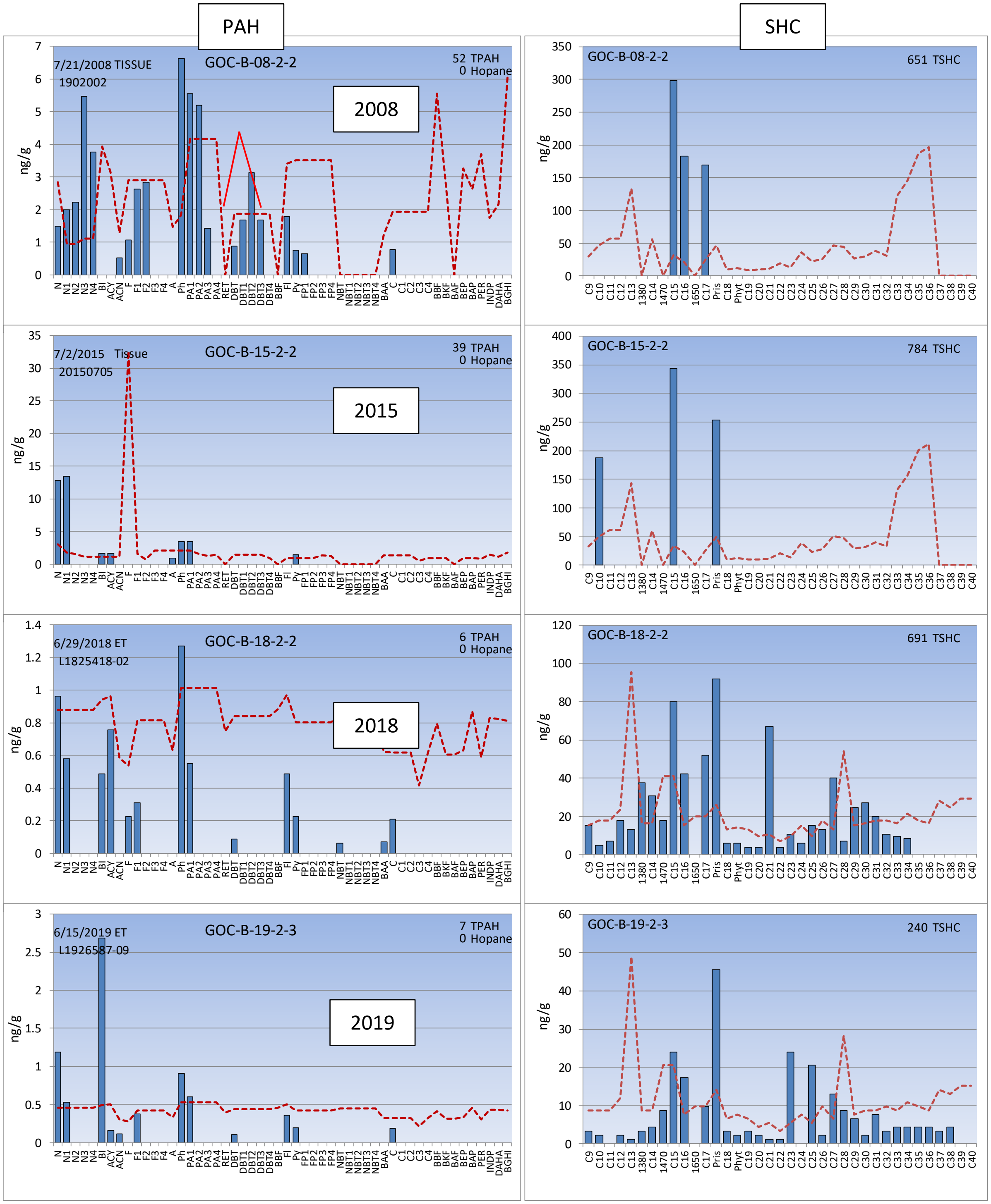


Figure 26. Time-series PAH and SHC profiles of mussels collected at GOC-B in 2008, 2015, 2018, and 2019. The 2008 PAH suggest possibly particulate-phase, water-washed petrogenic naphthalenes and DBTs (red tent) plus combustion products. 2015 shows only dissolved-phase naphthalenes (also observed at AMT-B at that time). Only at- or below MDL traces of dissolved naphthalenes and combustion products are suggested in 2018 and 2019, and these same patterns were observed in the laboratory method blanks. SHC in all years are derived from marine phytoplankton, and copepods. Dotted red line denotes the sample-specific MDLs.

PRINCE WILLIAM SOUND AND THE GULF OF ALASKA MUSSEL TISSUES

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 and 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-time lows ranging from 4-6 ng/g (Figure 21) and comprised primarily variations of the dissolved-phase, background patterns.

PASSIVE SAMPLING DEVICES

Starting in 2016, the LTEMP program incorporated passive sampling devices (PSDs) 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 integrative, highly-sensitive sampling that could be used to evaluate the potential for oil exposure and toxic effects in water column organisms.

In 2016 and 2017, PSDs were deployed at the three Port Valdez sites to sample concurrent with the LTEMP mussel collections (Minick and Allan, 2016; Allan, 2018). In 2018, the program was expanded to encompass Knowles Head (KNH), a clean site originally located near a tanker anchorage, and Disk Island (DII), a site known to contain residual EVOS oil. In 2019, only the 3 Port Valdez sites were sampled with results similar to previous years.

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. For biota, these are the most bioavailable hydrocarbons. The LTEMP devices were expected to sample lower-concentration dissolved PAHs and other non-polar or semi-polar hydrocarbons. The PSD analytic laboratory at Oregon State University reports 61 PAH isomers as their normal analyte list but in 2018, the analyte 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 were pre-infused into the membrane prior to deployment. Their measured rate of diffusion out of the membrane while the environmental dissolved-phase hydrocarbons are infusing enables the desired calculation of the time weighted average dissolved phase water concentrations. LTEMP PSDs were anchored and constantly submerged for approximately 30 days in shallow nearshore locations adjacent to the LTEMP mussel sites.

PAHs were detected in PSDs at all three sites; summed dissolved PAH concentrations (± SD) were 27.7 ± 1.4, 34.9 ± 5.7, and 23.7 ± 1.4 ng/L at JAP-B, GOC-B, and AMT-B, respectively. With the exceptions of C0-C4-naphthalenes, all of the dissolved water concentrations for individual PAH analytes were below 1 ng/L (ppt) (Figure 27). Naphthalenes contributed between 93-95% of the dissolved PAH at all sites. Other PAHs that were detected at lower levels at most of the sites were fluorenes (F), fluoranthene (FL), dibenzothiophenes (DBT), phenanthrenes (I), and anthracenes (A). PAH and profiles were also similar at all three sites. However, two PAHs were only detected at GOC, acenaphthene (ACY) and benzo(a)fluorene (BF). Selected oxygenated PAH were analyzed in previous years but none were detected.

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, LTEMP 2018). More importantly, the water concentrations in the Port were all at least three orders of magnitude below published water quality standards. The observed concentrations are also at least an order of magnitude below

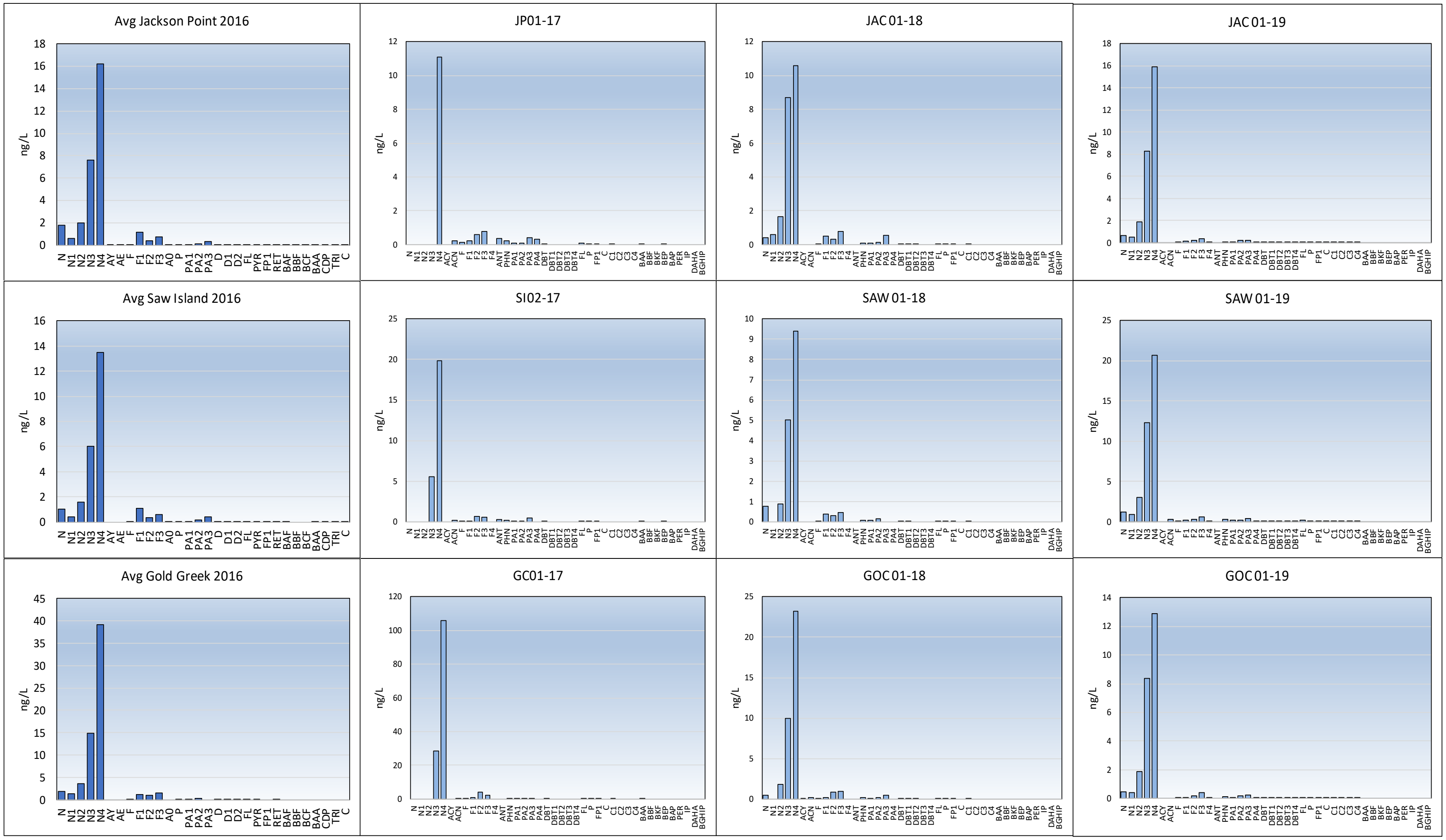


Figure 27. Example PAH profiles of PSD sampling from 2016 to 2019. Each show a dominant naphthalene group suggesting a mostly dissolved-phase but highly weathered signal.

published toxic effects thresholds for aquatic organisms. The PSD-derived concentrations of both total PAHs and the of sum 3-ring PAHs in the Port are less than demonstrated embryonic exposure concentration thresholds for cardiotoxicity in herring and salmon (Incardona, Vines et al. 2012, Incardona, Carls et al. 2015).

Though not the primary focus of the water sampling effort, PSD PAH patterns were also forensically assessed for source identification. All PSD samples from 2016-2019 were similar, with a supra-dominant, water-washed naphthalene pattern and assorted traces of parent and alkylated PAH up to chrysene (Figure 27). The predominance and pattern of dissolved naphthalenes (ascending with alkylation) suggests a highly-weathered, dissolved-phase signal.

Multiple lines of evidence indicate that the majority of the PSD-detected PAHs are not derived from ANS oil. The naphthalenes in all years are too excessive, relative to the other PAH, to have come from ANS oil (Figure 5). Secondly, two 2018 PSD collections from outside Port Valdez were quite distant from any BWTF influence and yet still showed basically the same patterns (Figure 28). One of the stations, DII, is known to have fresh-looking, residual EVOS oil buried within the cobble substrate, but the other, KNH, is an extremely clean control site, and yet both have essentially the same patterns as in Port Valdez. And, it’s important to remember that, in 2018, all the mussels throughout all regions were clean. Also, none of the PSD profiles look like the dissolved effluent samples taken directly from the BWTF discharge pipe in 2016-17 (Figure 5c).

PSD profiles were similar to a number of the regional mussel profiles presented in the 2013 LTEMP report (Payne et al., 2015). Those low-level, dissolved patterns 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 EPA and Cook Inlet Regional Citizens Advisory Council, traced those same offshore, non-bioavailable, PAH-laden particulates completely across the northern GOA and down the Alaska Peninsula (Saupe et al., 2005). In the discussion of Alyeska’s EMP results, the high naphthalene levels in Port Valdez profiles are tentatively linked with sediment loads from increased glacial melt.

In summary, both the 2019 LTEMP mussels and PSDs were extremely clean with mussels showing only confounding components from the laboratory method blanks while the PSDs showed only a background, weathered naphthalene pattern at all stations and with no recent petroleum hydrocarbon contamination. Waterborne dissolved PAH concentrations were low compared to other marine waters that have been characterized, similar to baseline levels that have been observed in PWS, and below known toxicity thresholds for aquatic organisms, including sensitive early life stages of fish. The dissolved source is irresolvable from the LTEMP and/or PSD data sets. But together, they say both Port Valdez and PWS contained only low levels of dissolved PAH contaminants in 2018 and 2019.

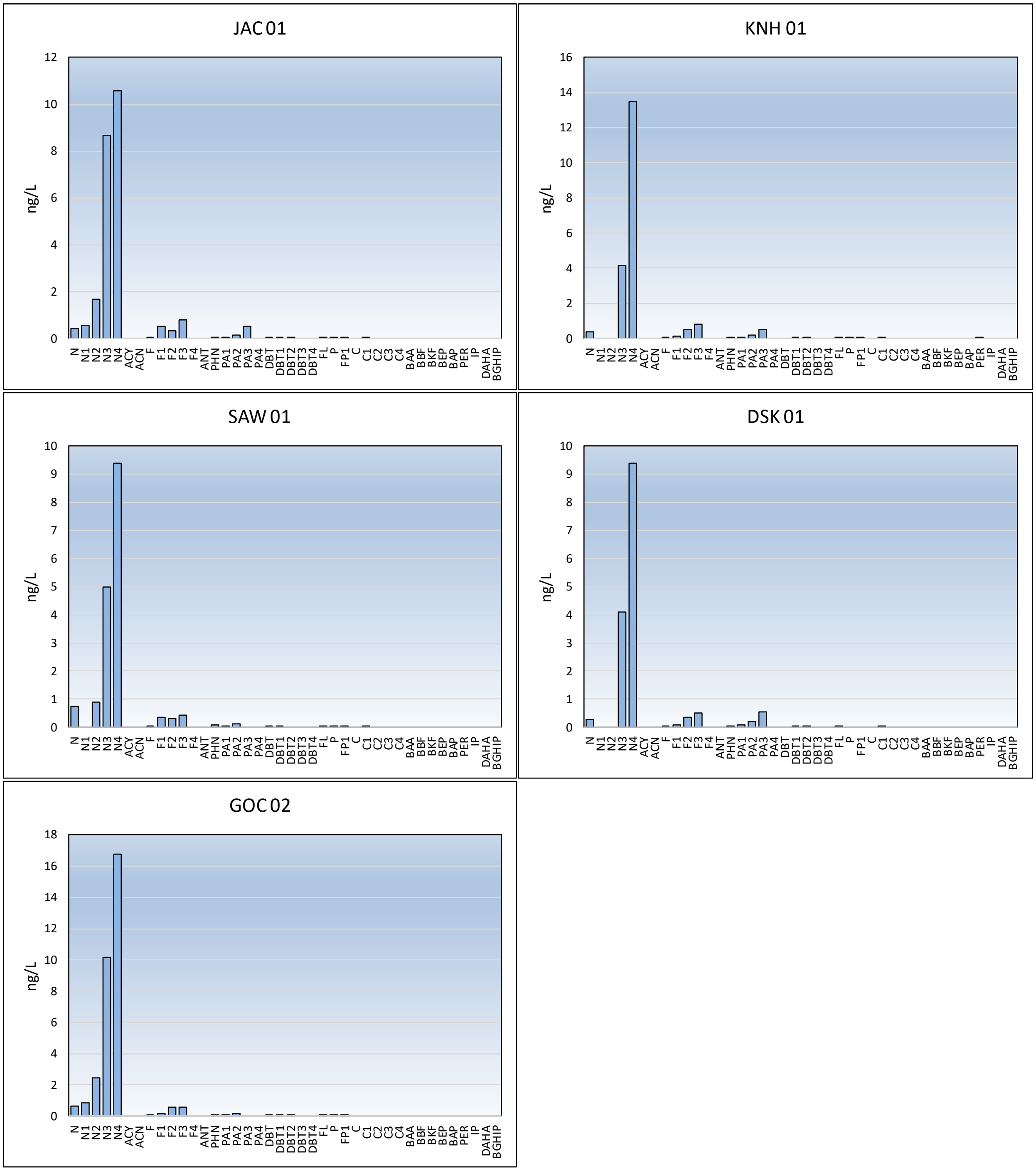


Figure 28. PAH profile examples from 2018 PSD deployment. Left panels from Port Valdez stations (see previous figure). Right panels from KNH and DII.

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 as to whether or not 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 29) 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 sample 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. conclude, “Although, due to the vast chemical complexity even of the sub-fractions of the PW extracts, specific compounds driving the observed toxicity could be 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.

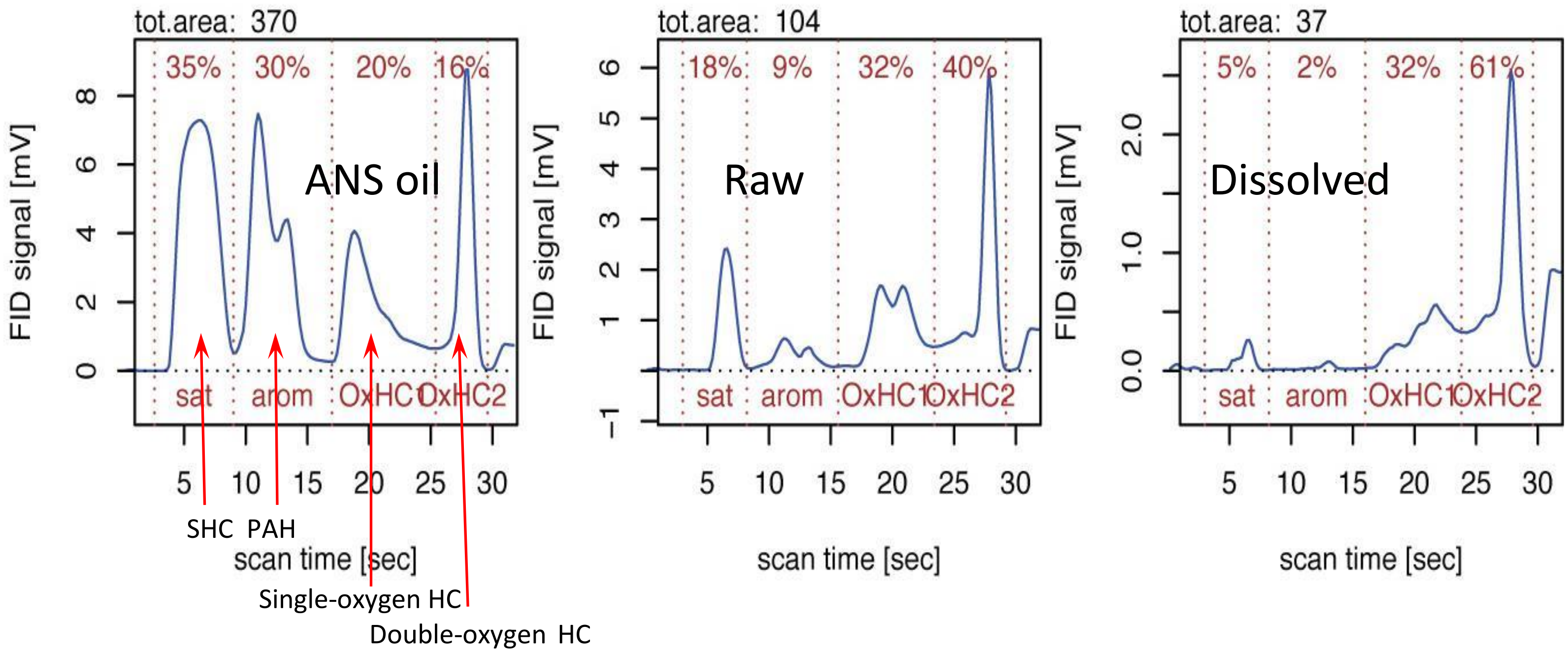


Figure 29. Iatroscan (TLC-FID) of ANS oil, BWTF raw effluent, and BWTF dissolved components from July 2016 showing relative abundance of single- and double-oxygenated (weathered) hydrocarbons relative to SHC and PAH components. Courtesy of Christoph Aeppli.

RELATED TOPICS

A fundamental problem with the LTEMP program is the frequency of sampling. Essentially, the annual data 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, documenting the performance and any violations in the BWTF system, various parameters' time series demonstrate how little of the variability is observed with LTEMP's annual, snapshot collections (Figure 30).

It was fortunate that in 2016 and 2017, our forensics understanding was greatly improved by analyses (PAH, SHC, and biomarker) 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 and also allowed direct comparison of the effluent profiles to the time-series sediment and tissue data to parse the relative petrogenic (oil-based) vs. pyrogenic (combustion-derived) portions in the samples. Unfortunately, the two seasonally dissimilar profiles further emphasize the dynamically changing character of the effluent. Unlike the ANS-source oil, after variable degradation, there is no standard effluent profile for forensic interpretations. A time-series effluent sampling program might be revealing.

On another topic, 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 31), the profile appears to be a water-washed particulate profile. Either particulate oil is capable of infusing through a shrimp's chitin egg shell and inner lipid membranes or there was a problem with the lab's sample cleanup methods. 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.

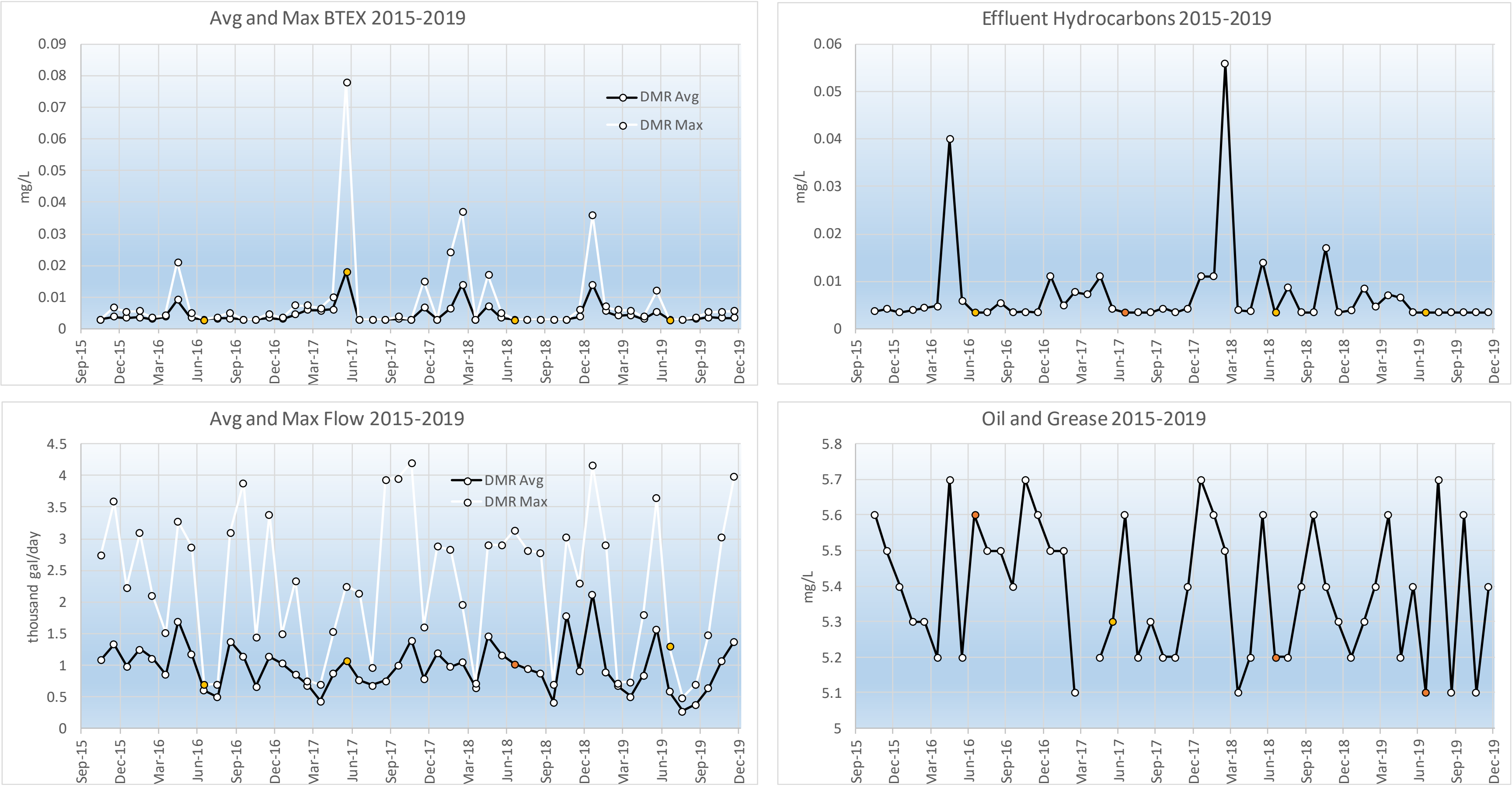


Figure 30. Time series of various DMR parameters as reported in Alyeska's monthly DMRs from October 2015 through November 2019. Orange dots represent LTEMP's June or July sampling events to demonstrate the variance not captured by the "snapshot" mussel and sediment collection frequency.

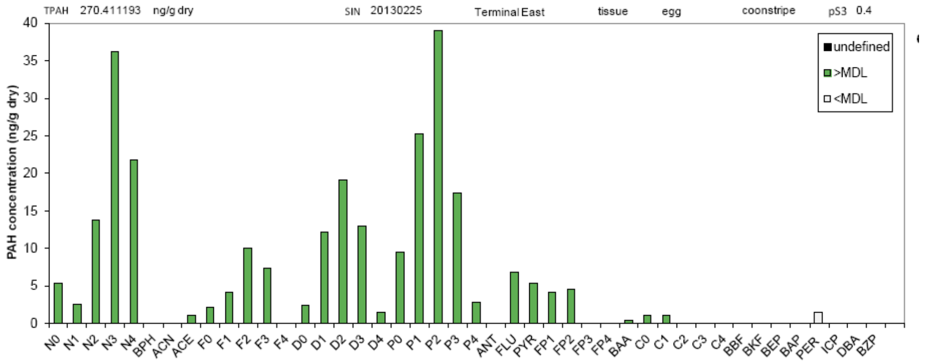


Figure 31. PAH plot of shrimp eggs taken east of the VMT, which in our assessment, shows a water-washed, weathered particulate-oil pattern absorbed through the chitin, lipid membrane and into the fat of the eggs. From Carls et al., 2016.

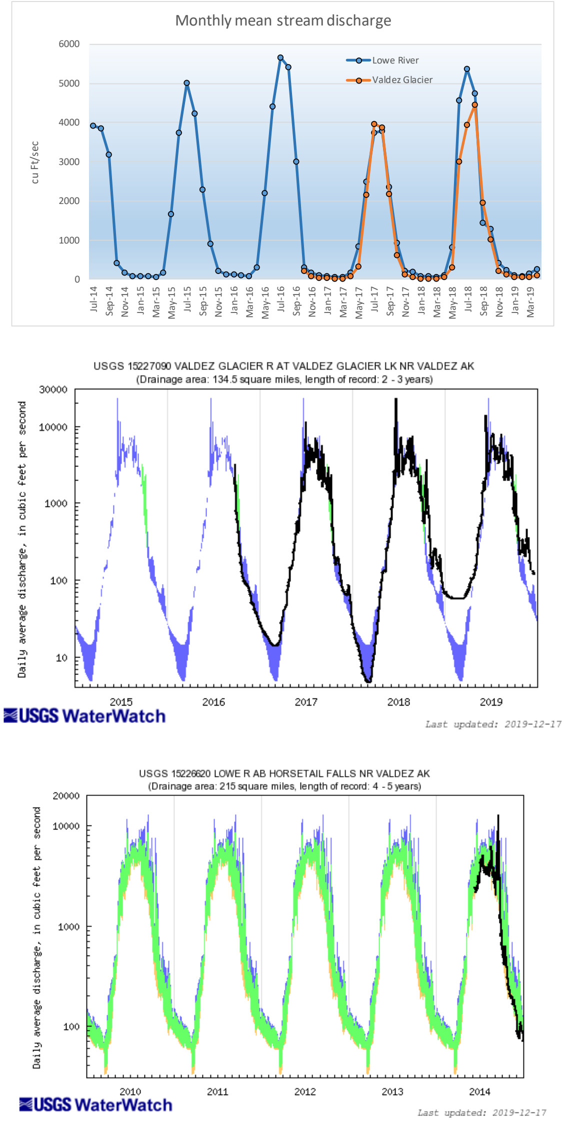
Also notable is recent work documenting oil droplets unexpectedly adhering directly to certain fish species' eggs (but not others) (Laurel et al., 2019, Hansen et al., 2018, Sørenson et al., 2017, Sørhus et al., 2015) and demonstrating increased toxicity relative to eggs with just dissolved component 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):

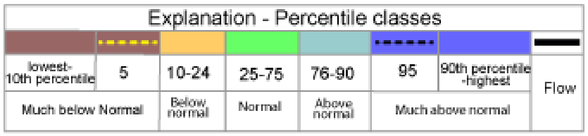
> "Crude oil contains polycyclic aromatic hydrocarbons (PAHs) that are cardiotoxic. Three-ringed PAH families (e.g., phenanthrenes) enriched in crude oil block K^+ and Ca^{2+} ion conductances in cardiomyocytes, disrupting the normal rhythmic pumping of the heart (Brette et al., 2014, 2017). When this 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)."

The overall approach to environmental monitoring also deserves examination. Conceptually, the traditional approach used by Alyeska, EPA, and the Alaska Department of Environmental Conservation has been to measure contaminant levels in sediments to assess the potential impact from chronic pollution of the BWTF discharge. The objective is to subsequently compare the measured concentrations to critical values generalized from other projects and agencies' promulgated values to determine whether they are sufficient to cause harm. This pragmatic approach assumes the critical levels are relevant and applicable to the Port Valdez environment and is not without its drawbacks. Appropriately, live toxicity tests are then performed periodically on a suite of lab organisms using the effluent to actually test for mortality effects; again, perhaps a practical approach but not without issues. For example, the results from this approach when used to declare little-to-no expected impacts are enigmatic, unable to detect any sublethal effects like those in the ongoing research discussed above. The LTEMP program goes a half-step further than just measuring contaminants in sediments and analyzes for contaminants in the target monitoring species, namely, the mussels, but doesn't assess the real question, population effects.

A new LTEMP approach goes much further by assessing whether the monitoring species, mussels, is responding to contaminant stressors by initiating mitigating genetic activity to physiologically "fix the issue" (Bowen et al., 2018, Counihan et al., 2019). While transcription assessment methods are still being adapted for LTEMP's needs, a transcriptomics pilot study was performed on mussels from Port Valdez (Bowen et al., 2019). Mussels from the three LTEMP sites and from a creosoted piling in the Valdez boat harbor were analyzed and compared to similar studies in western PWS and three southcentral Alaska National Parks. Findings suggested, not surprisingly, that all four Port Valdez sites showed higher transcription levels related to contaminants (and thus, exposure) than the background level activities at more remote sites. In particular, Valdez Harbor mussels, like those from other tested Alaska harbors, were dramatically more stressed than other field populations (albeit perhaps indicative of their piling proximity rather than the general harbor environs). While still not addressing the population effects question, we consider this work a much subtler perspective on stressor/response detection and complimentary to the current chemical analyses. We strongly support the use of gene expression analyses in mussels or any other species of interest as an additional method to monitor the presence and effect of LTEMP contaminants.

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, 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 32). 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.





Explanation - Percentile classes

🟫	▬ ▬	🟧	🟩	🟦	▬ ▬	🟦	▬
lowest-10th percentile	5	10-24	25-75	76-90	95	90th percentile -highest	Flow
Much below Normal		Below normal	Normal	Above normal	Much above normal		

Figure 32. Historic monthly stream discharge rates (cubic ft/sec) for Lowe River and Valdez Glacier Stream, 2015-2019 (from USGS 2019).

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.

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 removing particulate/oil-phase hydrocarbons, permitted oil inputs into Port Valdez from the VMT have been declining in recent years.

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, sediment TPAH concentrations at both stations have slightly increased over the last three 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 a mix of 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 slightly higher 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 dominated by low-level naphthalenes and 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.
- Proposed additional mitigation from accelerating glacial melt causing increased suspended sediment loads and sorbing oil in the water column is speculative.

TPAH concentrations in mussels at AMT-B, JAP-B, and GOC-B are now reaching all-time, single-digit lows (4-6 ng/g DW, ppb).

- 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. Mussels from the more recent JAP-B station on the east side of the berths, opposite from AMT-B, produced identical results.
- GOC-B mussels have generally shown only low-level pyrogenic PAH profiles since 2006. The 2018 and 2019 PAH concentrations were extremely low with profiles that could not be differentiated from the laboratory blanks.
- Current LTEMP mussel tissue results are all below TPAH concentrations reported from most anywhere else in the United States and are far below what the National Mussel Watch program categorizes as “low” (63-1,187 ppb dry weight of PAHs).

- These 2019 samples are exceptionally clean as were 2018 samples from all other LTEMP sites. But be cautioned that the suggestion of a clean environment is 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 with no evidence of recent petroleum hydrocarbon contamination. The concentrations were far below levels of toxic concern.

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.

Pilot analyses of BWTF effluent showed high levels of oxygenated hydrocarbons from weathered ANS oil after biological degradation in the BTT. 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.

CONCLUSIONS

For the summarized reasons (beginning of the previous section), 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.

Interpreting the patterns, between 2016 and 2019, the AMT-S sediment PAH showed mixed profiles that included low-level BWTF oil components. The mixture suggested variable inputs of background and combustion products (from local vessel traffic, runoff, or aerial deposition) plus weathered ANS oil. As expected, the oil was significantly weathered compared to the effluent but was confirmed by the biomarkers.

At the GOC-S reference site, the sediment PAHs are dominated by low-level naphthalenes plus combustion products. These may derive from river silt and glacial flour from the Lowe and Valdez Glacier Rivers. The biomarker data suggests that in addition to natural background biomarkers, minor traces of some ANS-derived biomarkers are accumulating in the GOC sediments.

From 2018-19 mussels, both terminal locations showed very similar tissue profiles of very low-level background PAH but with no suggestion of BWTF-derived uptake. GOC-B mussels showed similar but different low-level background patterns, including some combustion products. Most of the PAH reported in the tissue samples were below the laboratory MDL, and they were also observed at similar concentrations in the procedural blanks.

Data from the PSDs corroborate mussel-tissue measurements that only extremely low concentrations of dissolved-phase PAH are present in the region. These concentrations are well below any known toxicity thresholds for sensitive marine organisms and life stages. The source of the background PAH remains enigmatic.

Compared to the recent West Coast Mussel Watch data (2004-05) and the more recent 2008-10 Alaska Mussel Watch sites, the 2018-19 LTEMP results continue to demonstrate that the sampled region is exceptionally clean.

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Stout, S.A. and Z. Wang, 2016. Chemical Fingerprinting Methods and Factors Affecting Petroleum Fingerprints in the Environment. Chapter 3, Standard Handbook Oil Spill Environmental Forensics: Fingerprinting and Source Identification. 2nd Edition. Stout, S.A. and Z. Wang (eds), Academic Press, Burlington, MA. 1107 pp. DOI: 10.1016/B978-0-12-809659-8.00003-6

LIST OF FIGURES

LIST OF TABLES

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

Analytes	Abbreviation
PAH	
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
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

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**

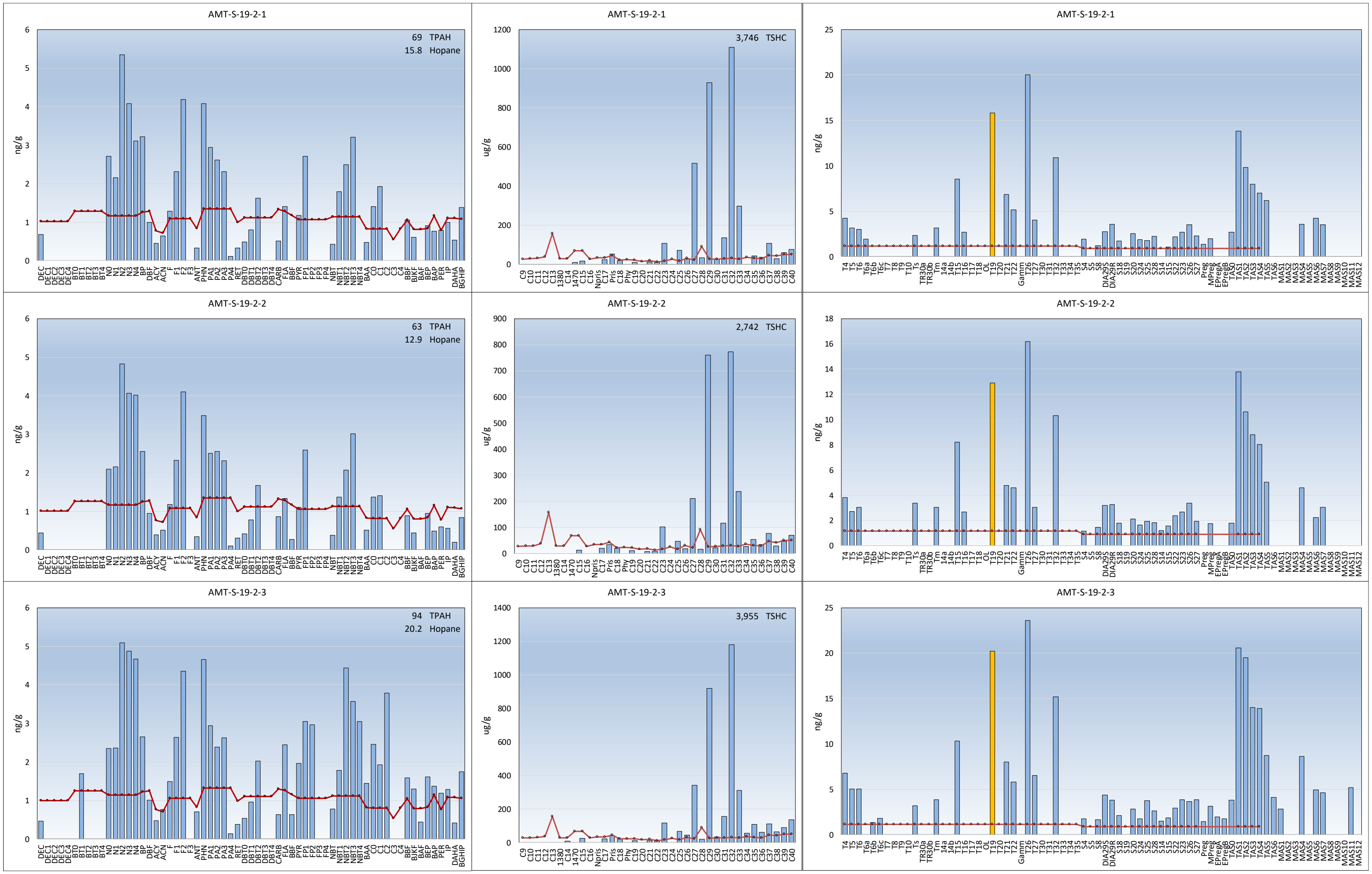
Petroleum Biomarkers

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 (T11)	Ts
	C30 Tricyclic Terpane-22S	C30Ts
	C30 Tricyclic Terpane-22R	C30Tr
Hopanes	17a(H)-22,29,30-Trisnorhopane-TM	Tm
	17a/b,21b/a 28,30-Bisnorhopane (T14a)	14a
	17a(H),21b(H)-25-Norhopane (T14b)	14b
	30-Norhopane (T15)	T15
	18a(H)-30-Norneohopane-C29Ts (T16)	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
	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
Monoaromatic Steroids	5b(H)-C27 (20S) MAS+	MAS1
	5b(H)-C27 (20R) MAS+	MAS2
	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
	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

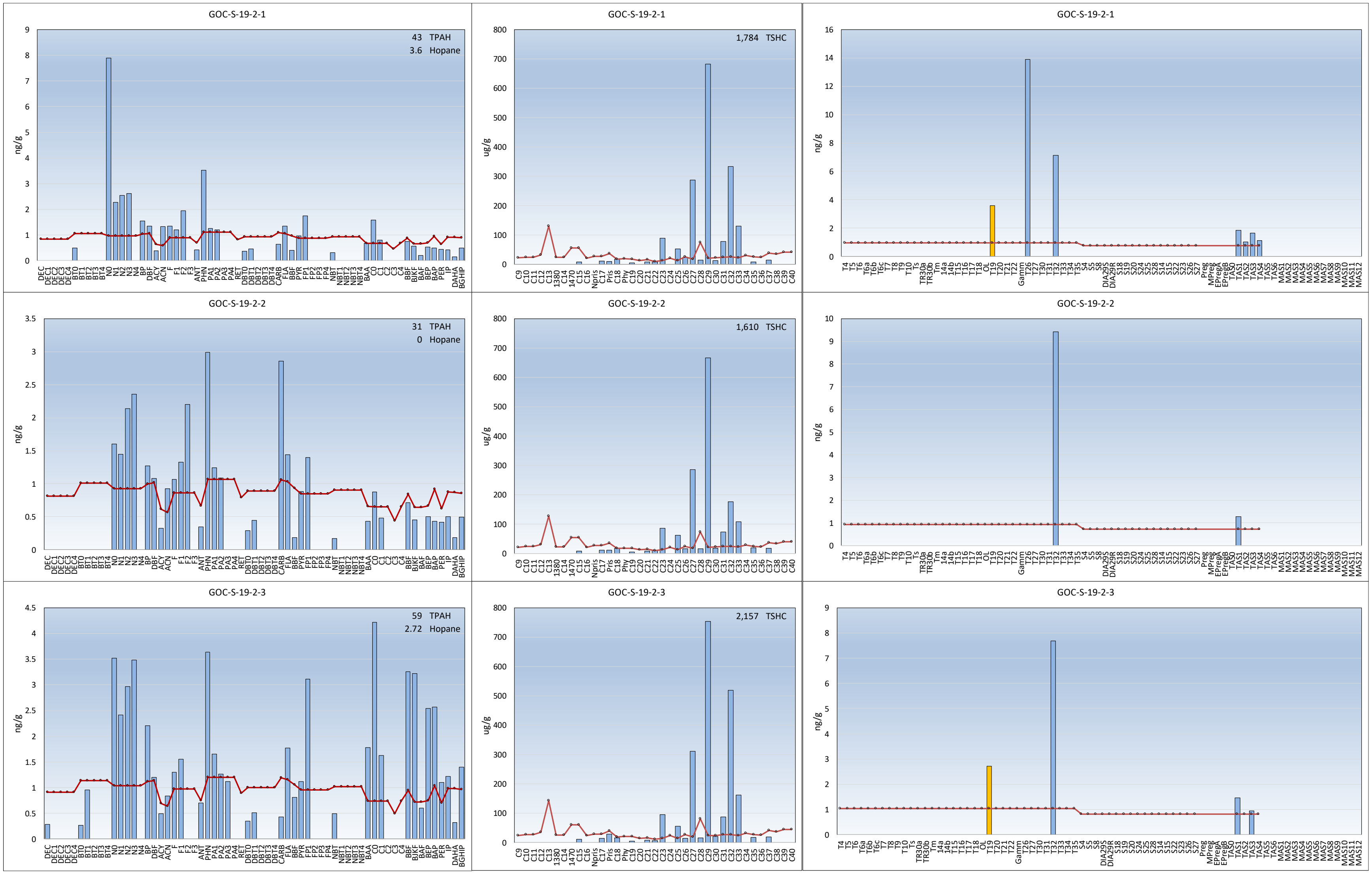
APPENDIX 2. Analytic Results for 2019 Field Samples and Blanks

2019 AMT Sediments (PAH, SHC, and Biomarkers)



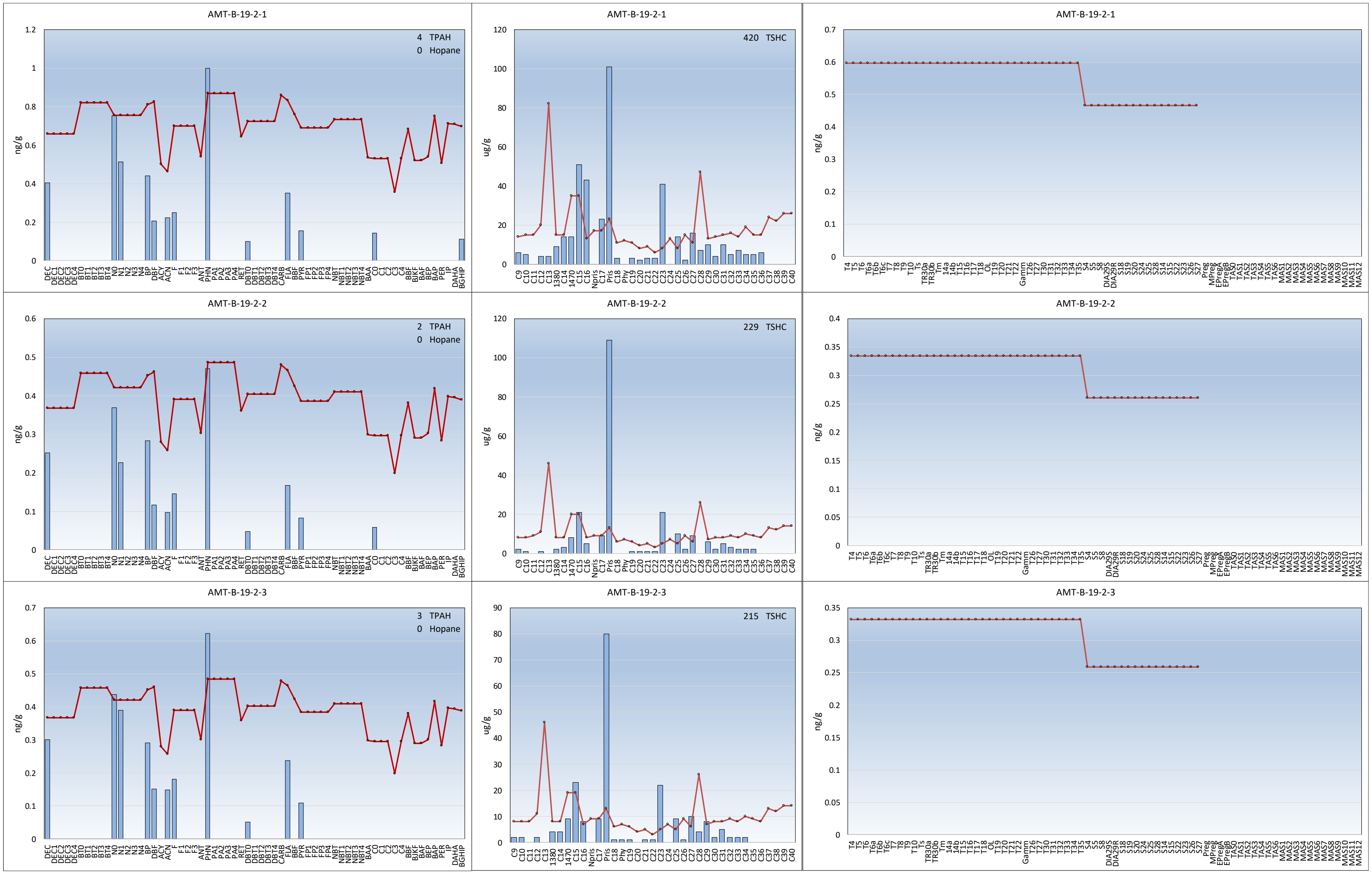
The dotted red line represents the sample-specific MDL for PAH, SHC, and biomarkers.

2019 GOC Sediments (PAH, SHC, and Biomarkers)



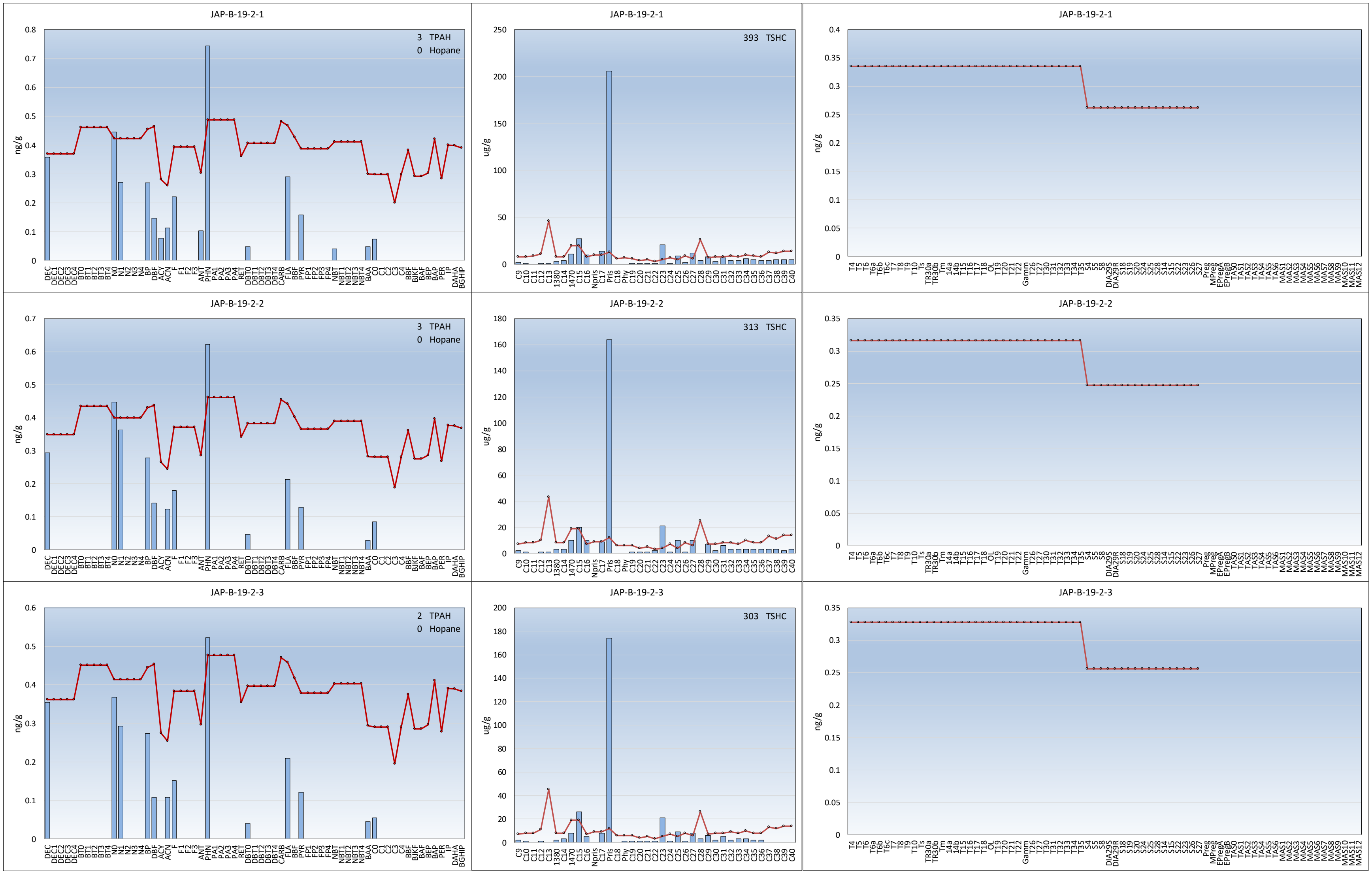
The dotted red line represents the sample-specific MDL for PAH, SHC, and biomarkers.

2019 AMT Tissues (PAH, SHC, and Biomarkers)



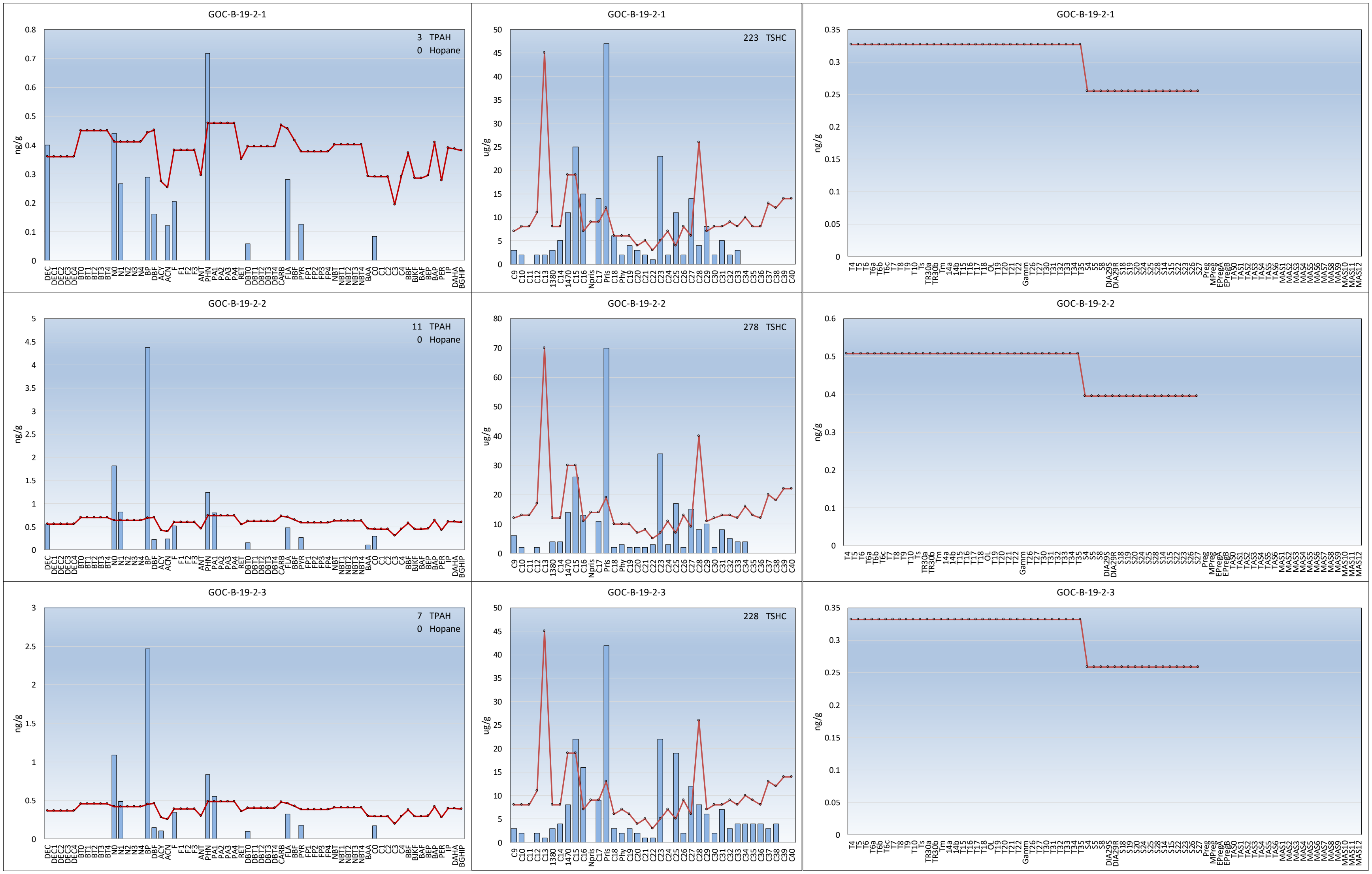
The dotted red line represents the sample-specific MDL for PAH, SHC, and biomarkers.

2019 JAP Tissues (PAH, SHC, and Biomarkers)



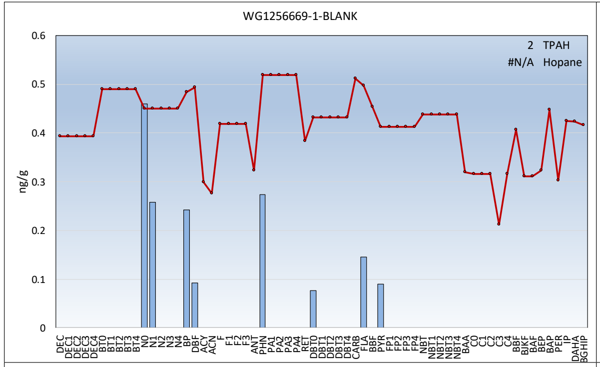
The dotted red line represents the sample-specific MDL for PAH, SHC, and biomarkers.

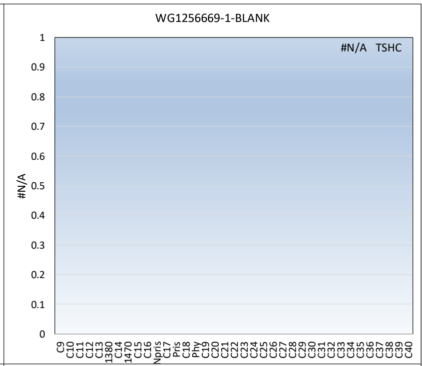
2019 GOC Tissues (PAH, SHC, and Biomarkers)

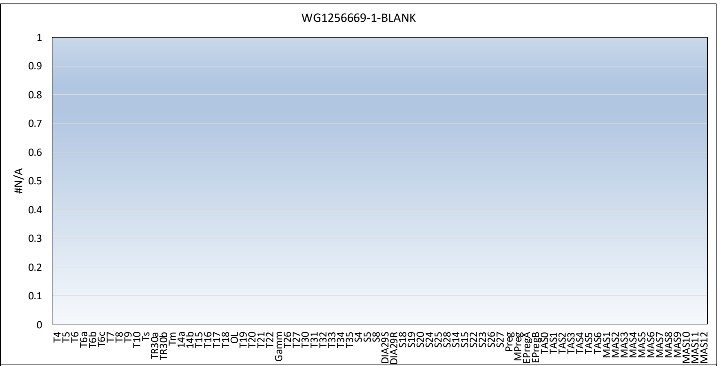


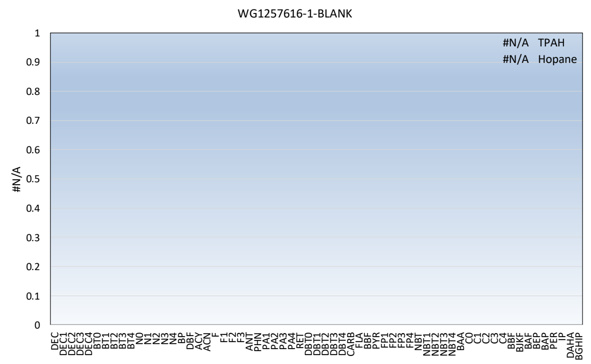
The dotted red line represents the sample-specific MDL for PAH, SHC, and biomarkers.

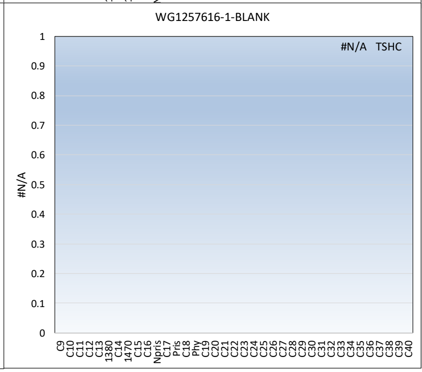
2019 Tissue Lab Method Blanks with MDL overlay

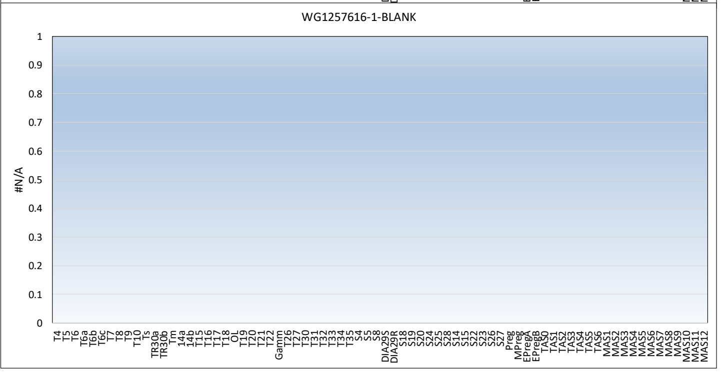




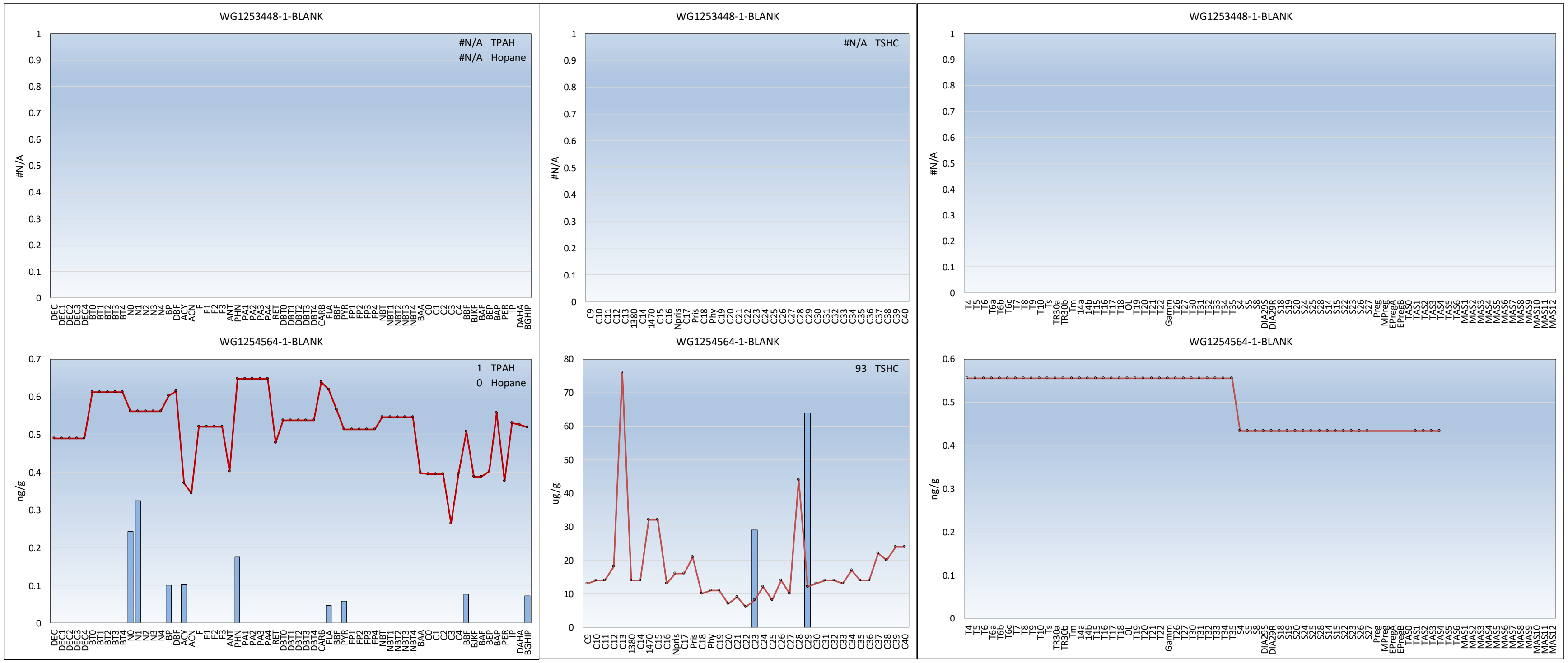








2019 Sediment Lab Method Blank with MDL overlay



The dotted red line represents the sample-specific 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, so 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 33) 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 34, Table 10).

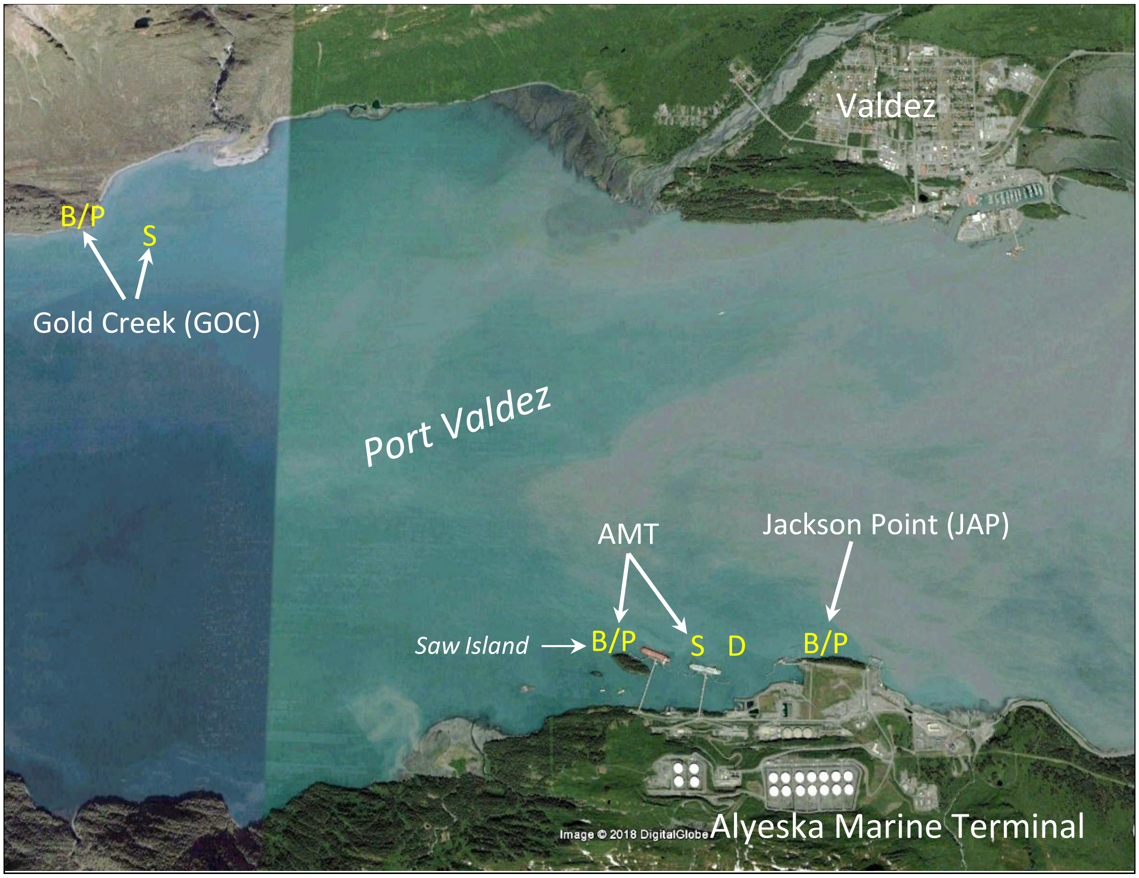


Figure 33. LTEMP sampling stations in Port Valdez adjacent to (AMT-B, AMT-S, and JAP) and 6 km northwest (GOC) of the VMT. This Google Earth image shows tankers docked at both Berth 4 and 5. The yellow "D" denotes the offshore location of the BWTF outfall diffuser; yellow "S" indicates sediment grab locations and "B/P" for biological tissue and PSD samples. The JAP station was added in summer 2016.

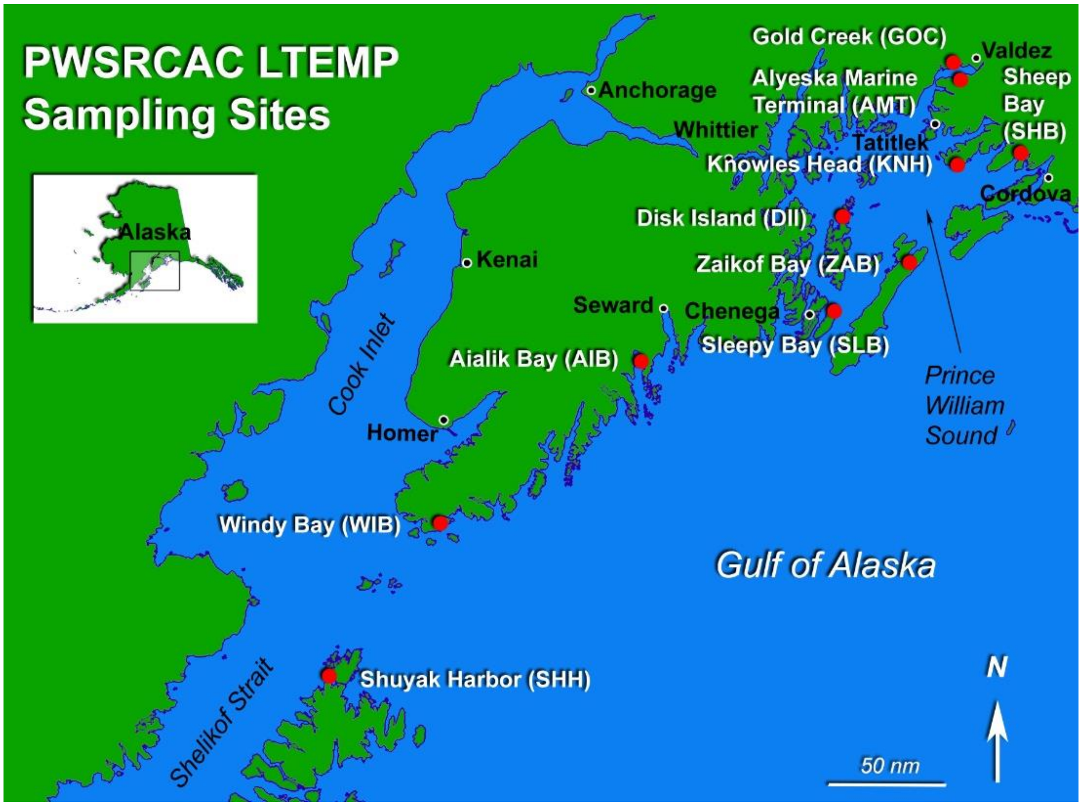


Figure 34. Map of the LTEMP sites with station abbreviations.

Table 10. 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									

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.

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 10). 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, just the 3 Port Valdez sites were visited.

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 20.6 MGD (Figure 35). 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 0.8 MGD (Table 11). 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).

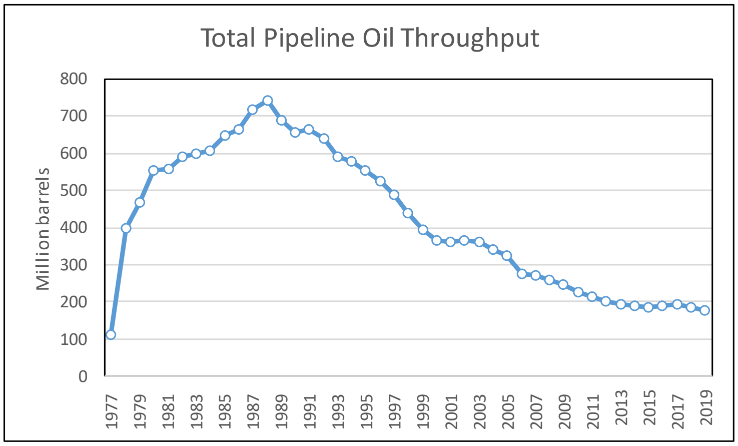


Figure 35. Annual pipeline oil throughput (M barrels) from Alyeska statistics, *https://alyeska-pipe.com/TAPS/PipelineOperations/Throughput*

Table 11. Recent average daily throughput of Alyeska Pipeline and ballast water treatment (MGD).

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

APPENDIX 4. 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. Follow-up 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 9-33 ng/g DW inside the Sound but similar to 19-46 ng/g DW from the two PWS sites in 2015 and also similar to the 2013 levels of 18-73 ng/g DW at GOA sites (overall average 50 ng/g DW). 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 below 5 ng/g DW.

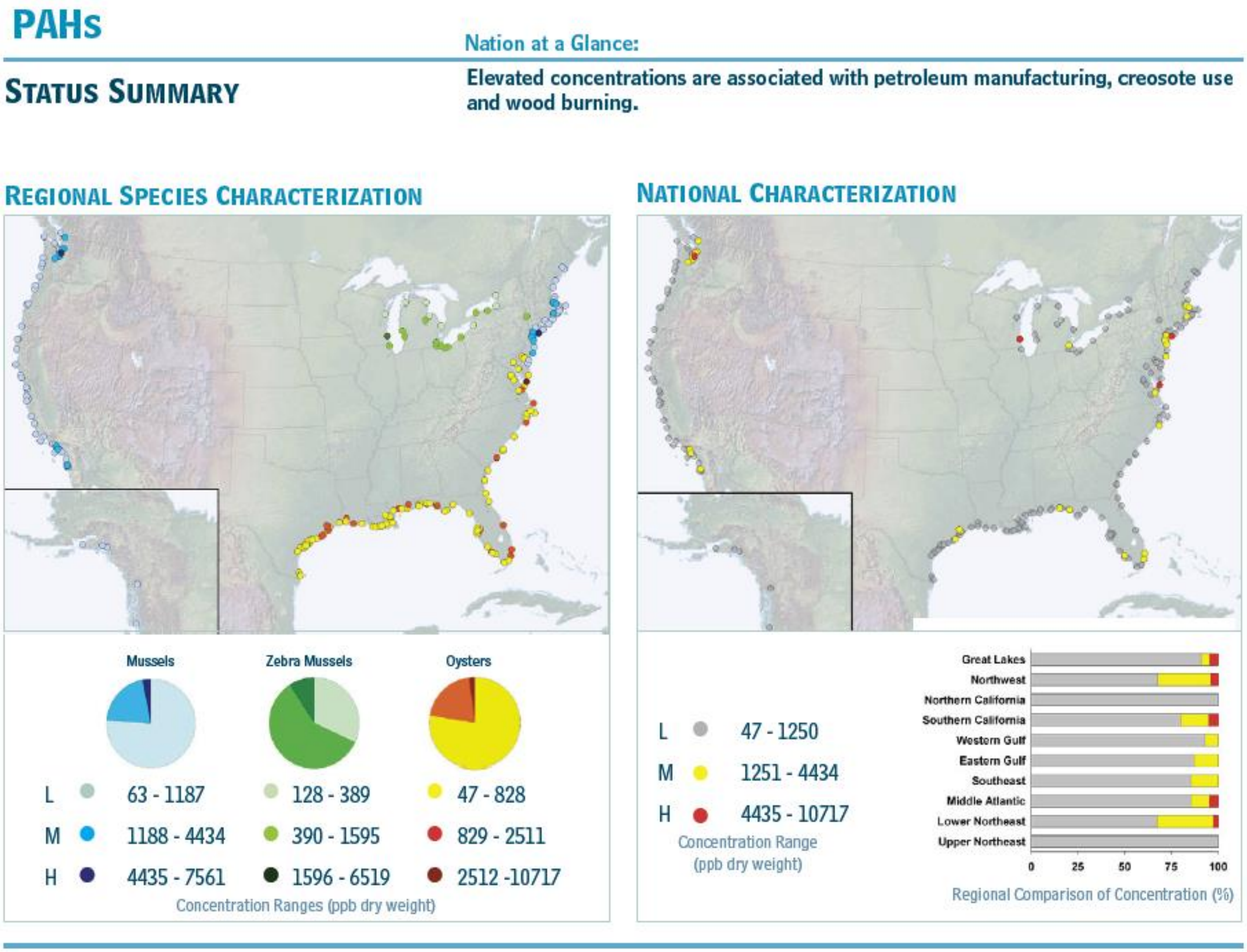
Reaching farther, data from the 2004-2005 National Status and Trends, Mussel Watch Program and 2008-2010 Alaska sites (Table 12) (now summing only 38 parent and alkylated PAH homologues versus 43 LTEMP PAH analytes) show that average TPAH concentrations in mussels for other West Coast sites have been nearly 66 times higher (825 ng/g DW) than LTEMPs. 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 2004-5, 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). 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 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 (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.

The extremely low 2018 TPAH 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 28) 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 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).

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 2019	Port Valdez tissues	AMT-B, JAP & GOC	3-7
2018	Port Valdez tissues	AMT-B, JAP & GOC	4-6
2017	Port Valdez tissues	AMT-B, JAP & GOC	6-19
2016	Port Valdez tissues	AMT-B, JAP & GOC	6-53
2015	Port Valdez tissues	AMT-B & GOC	39-87
2013	Port Valdez tissues	AMT-B & GOC	17-20
2018	PWS	Five stations	4-5
	GOA	Three stations	4-5
2015	PWS (KNH & SHB)	KNH & SHB	19-46
2013	PWS	Six stations	9-33
	GOA	Three stations	18-73
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



PAHs

STATUS SUMMARY

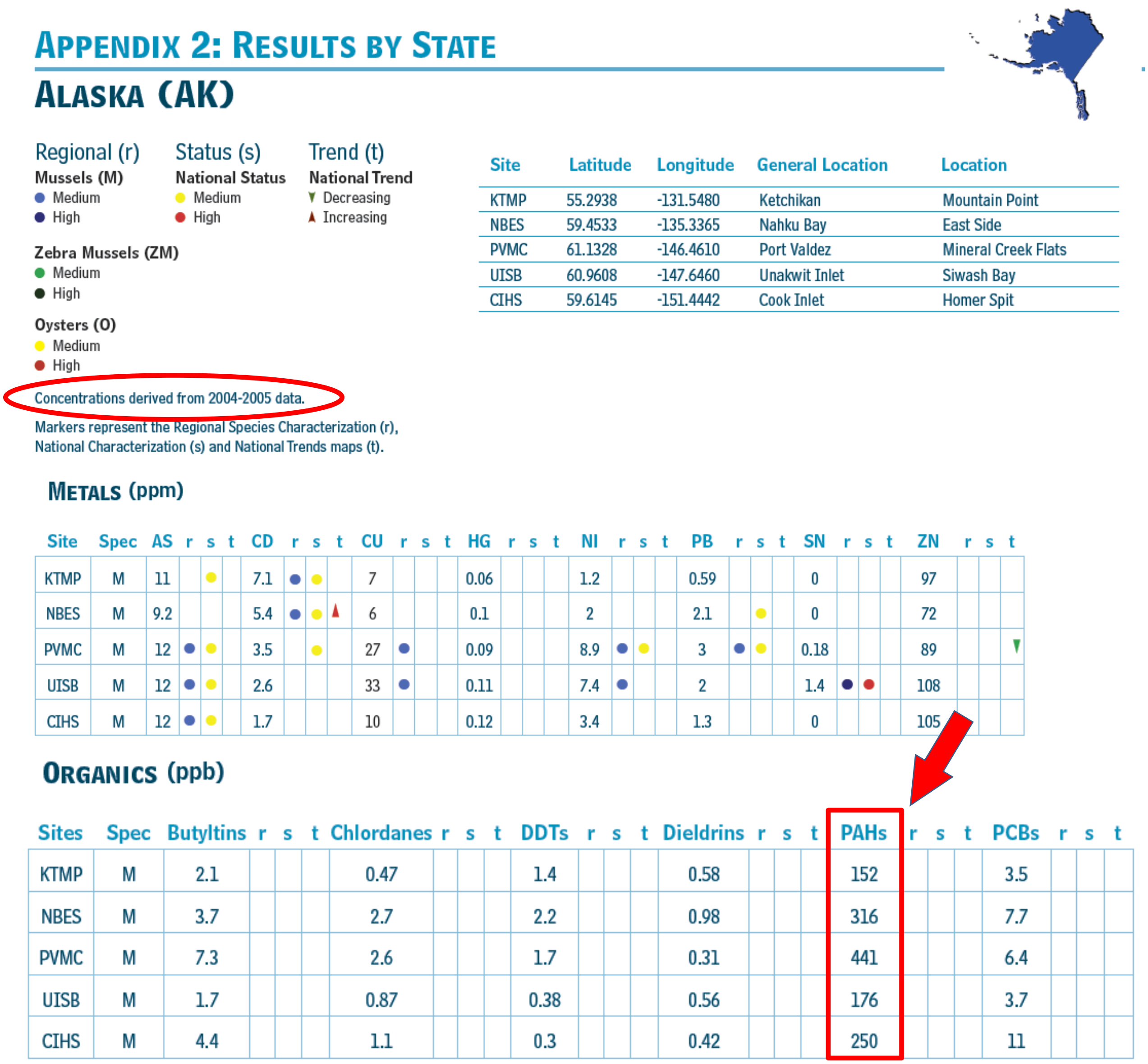
Nation at a Glance:

Elevated concentrations are associated with petroleum manufacturing, creosote use and wood burning.

REGIONAL SPECIES CHARACTERIZATION

NATIONAL CHARACTERIZATION

Figure 36. 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 37. Summary page of Alaska regional Mussel Watch results and trends based on 2004-05 report from Kimbrough et al., 2008.