LONG-TERM ENVIRONMENTAL MONITORING PROGRAM:
2017 SAMPLING RESULTS AND INTERPRETATIONS

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

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Cover image – Outbound tanker as viewed from Sheep Bay. Photo by William Driskell.

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ABBREVIATIONS

Stations:

AMT	Alyeska Marine Terminal, 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	NOAA/NMFS Auke Bay Laboratory, Juneau AK
AHC	aliphatic hydrocarbons (same as saturated hydrocarbons – SHC)
ANS	Alaskan North Slope
BWTF	Alyeska Terminal's Ballast Water Treatment Facility
DW	Dry Weight
DWH	*Deepwater Horizon* (oil spill)
EVOS	*Exxon Valdez* oil spill
FT-ICR	Fourier Transform-Ion Cyclotron Resonance mass spectrometer
GC/FID	gas chromatography/flame ionization detector
GC/MS	gas chromatography/mass spectrometry
GERG	Geochemical and Environmental Research Group, Texas A&M University
KLI	Kinnetic Laboratories, Inc., Anchorage AK
LCMS	liquid chromatography/mass spectrometry
MDL	analytic method detection limit
NIST	National Institute of Standards and Technology
NMFS	National Marine Fisheries Service
NOAA	National Oceanographic and Atmospheric Administration
PAH	polycyclic (or polynuclear) aromatic hydrocarbons
PECI	Payne Environmental Consultants, Inc., Encinitas, CA
PGS	particle grain size
PSD	passive sampling device (polyethylene samplers that accumulate dissolved-phase hydrocarbons from seawater)
PWS	Prince William Sound
RCAC	Regional Citizens' Advisory Council
SAC	Scientific Advisory Committee for PWSRCAC
SHC	saturated hydrocarbons (same as AHC: n-alkanes + pristane and phytane)
SIM	selected ion monitoring
SRM	NIST standard reference material
TOC	total organic carbon
TPAH	total PAH
TSHC	total saturated hydrocarbons (same as total alkanes)
UCM	unresolved complex mixture

RESULTS AND INTERPRETATIONS FROM LTEMP SAMPLING, 2017

ABSTRACT

This annual report examines the hydrocarbon chemistry data from Port Valdez sediments and mussel tissues with the goal of monitoring for impacts from oil transportation activities on the environment at selected sites from Prince William Sound (PWS) and the Gulf of Alaska (GOA). The data are viewed from two perspectives: 1) characterizing the chemical profiles as to the likely source and degradation of the hydrocarbons, plus 2) the concentration of the oil contaminants. There are three groups of oil hydrocarbons analyzed for this data set: polycyclic aromatic hydrocarbon (PAH), saturated hydrocarbons (SHC) and oil biomarkers.

Overall, the petrogenic hydrocarbon (oil) inputs into Port Valdez from the Alyeska Marine Terminal (AMT) and tanker operations have been declining over the last two decades as reflected in total polycyclic aromatic hydrocarbon (TPAH) concentrations in both mussels and sediments. This trend reflects 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 PAH.

As a result, over the last several years, contamination in mussels at AMT has been generally shifting away from the terminal's petrogenic profiles to background dissolved-phase or pyrogenic (combustion-derived) PAH patterns. In contrast, the Gold Creek (GOC) reference site mussels have generally shown only low-level dissolved-phase and pyrogenic PAH profiles since 2006 but in 2016, traces of a diesel spill were observed. In the July 2017 GOC collections, there was no evidence of residual hydrocarbons from the 2016 diesel spill as the PAH pattern reverted to the trace-level dissolved-phase and pyrogenic profile.

Although TPAH concentrations in mussels historically sampled from both AMT and GOC were commonly reported in hundreds of ng/g dry weight (DW), by 2013, only very low (< 20 ng/g) traces of mostly pyrogenic components were found. By 2017, the total PAH concentrations were less than 10 ng/g, and the composition reflected primarily dissolved-phase background and particulate-phase combustion products. Individual-component method detection limits (MDLs) for these most recent samples were generally less than 0.4 ng/g.—None of the observed PAH patterns in tissues at either AMT or GOC matched those of the July 2016 or March 2017 treated ballast waters, but recall that the treated ballast water discharge signals showed major seasonal differences in which the bulk of the dissolved-phase hydrocarbons are actually discharged during winter operations when more ballast water is being treated. Sampling the effluent in March 2017 showed a two-fold increase in dissolved-phase TPAH compared to July 2016. The observed single-digit summer tissue results correlate with low concentration discharges. The saturated hydrocarbons (SHC) in mussels from both locations during 2008-2015 exhibited primarily background biogenic components with the exception of a petrogenic signal at AMT in 2013. Quantified mussel SHC data were not available for 2016 or 2017.

Like the mussels, Port Valdez sediment TPAH reached all-time lows in 2013 and then marginally rebounded at both AMT and GOC. The 2016 and 2017 AMT sediment PAH patterns have shifted from a dominant pyrogenic pattern in earlier samples to a mix of pyrogenic and weathered petrogenic components from the BWTF effluent. AMT sediment biomarkers from 2011 through 2017 also confirm that the source is BWTF effluent. The 2017 sediment SHC patterns at the terminal show a mixture of marine and terrestrial biogenic components along with higher-molecular-weight (C_{31}-C_{40}) petrogenic waxes at similar levels compared to 2016. Based on the signatures, these patterns suggest

variable or increased inputs of weathered ANS oil plus combustion products from local vessel traffic, runoff, or aerial deposition.

At the GOC reference site, the sediment PAH profiles since 2000 have shown a pyrogenic pattern with little or no input from the terminal. Instead, they are dominated by ubiquitous low-level naphthalenes and combustion products. The 2017 sediment PAH patterns and concentrations are essentially identical to the 2016 data. Nevertheless, the overall TPAH concentrations are still detectible in a just-above-MDL range. The SHC profiles in GOC sediments continue to be biogenic, reflecting only background inputs of terrestrial plant waxes. From the more extensive biomarker data reported in 2016 and 2017, it appears that, in addition to natural background biomarkers, low-level traces of some ANS-derived biomarkers are accumulating in the GOC sediments. While the GOC sedimentary biomarker data are sparse (with many missing components), the observed constituents and diagnostic ratios are now unequivocal. However, despite the presence of the less degradable, ANS-derived biomarkers, there is no evidence of BWTF-derived PAH or SHC accumulation at that site.

Compared to the most recent West Coast Mussel Watch data (2004-05) and the more recent 2008-10 Alaskan Mussel Watch sites, the 2017 LTEMP results continue to demonstrate that the sampled region is exceptionally clean.

INTRODUCTION

PROJECT HISTORY

Under Federal and State statutes, the unregulated release of oil into the environment is strictly prohibited. Towards this purpose, the Long Term Environmental Monitoring Program (LTEMP) data serve as a sentinel indicator and independent quality control check for Alyeska Marine Terminal and tanker operations throughout the Prince William Sound (PWS) and Gulf of Alaska (GOA) region. The primary goal of the 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 the Gulf of Alaska.

At the Alyeska's terminal, the Ballast Water Treatment Facility (BWTF) treats and discharges oil-contaminated ballast water offloaded from tankers utilizing the terminal, so sampling at two traditional stations, Alyeska Marine Terminal (AMT) adjacent to the offshore BWTF discharge diffusers and Gold Creek (GOC), a reference station six km across the Port, was intended to assess impacts from the effluent (Figure 1). Currently measured variables include polycyclic aromatic and saturated hydrocarbon levels (PAH and SHC) and oil biomarkers in mussel (*Mytilus trossulus*) tissues from the two stations within the Port and two stations in the eastern PWS area – Knowles Head (KNH) near the tanker anchorage and Sheep Bay (SHB) north of Cordova. Six additional stations, comprising the geographic reach of the *Exxon Valdez* oil spill (EVOS), are now sampled every five years between Valdez and Kodiak (Figure 2). 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). Their results effectively documented higher background oil levels while identifying hot spots and both large and small spill events. Subsequent to this assessment, the PWSRCAC reduced the scope of the program from triannual to biannual sampling of regional mussel tissues and Port Valdez sediments. Fall mussel sampling was then re-added just in Port Valdez (AMT and GOC) 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.

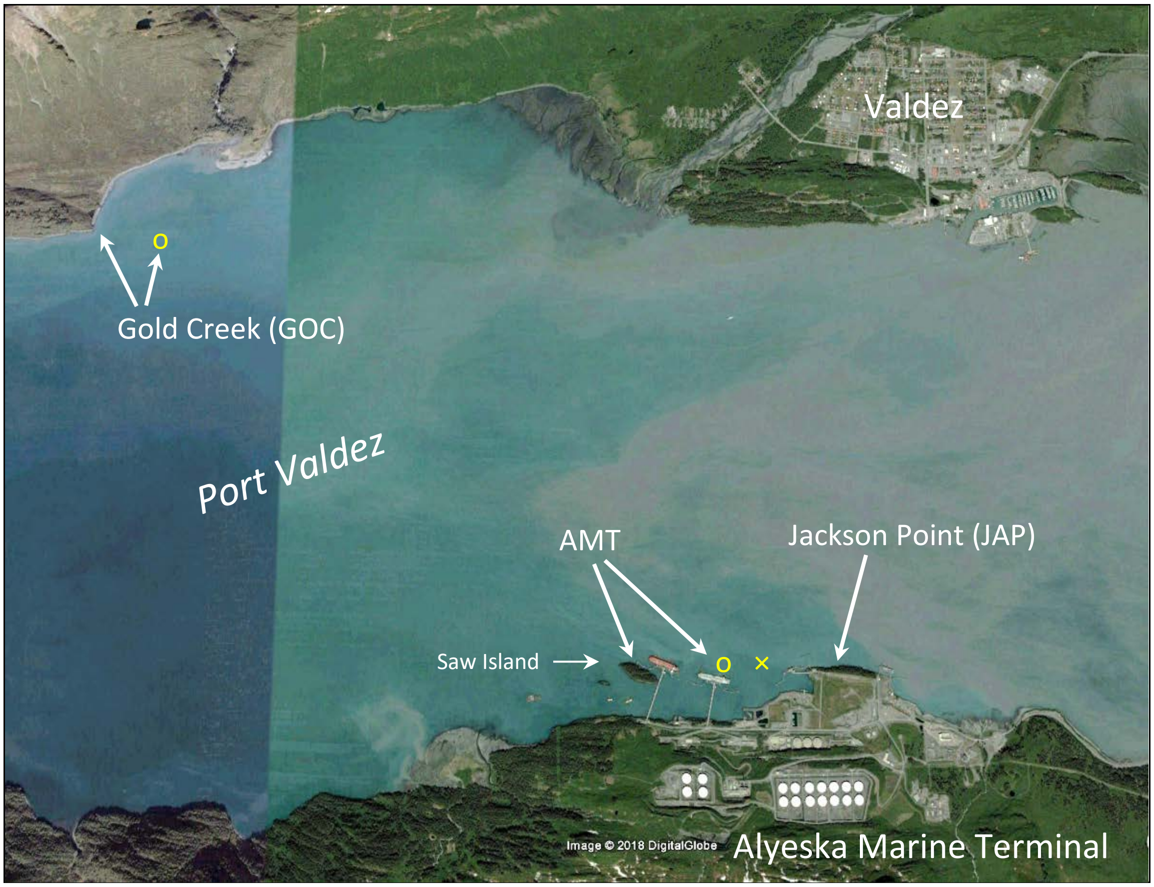

Figure 1. LTEMP sampling stations in Port Valdez adjacent to (AMT and JAP) and 6 km northwest (GOC) of the Alyeska Marine Terminal. Satellite image from Google Earth shows tankers docked at both Berth 4 and 5. The yellow "x" denotes the offshore location of the BWTF BTT diffuser; yellow "o" indicates sediment grab locations at AMT and GOC. The Jackson Point (JAP) station was added in summer 2016.

In 2001, another comprehensive data evaluation and synthesis was completed on just the LTEMP results from the Port Valdez sites (Payne et al., 2001). From AMT and the GOC reference site, Alaska North Slope (ANS) crude oil residues from the terminal's ballast water treatment facility 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 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. Stratified waters formed during the milder seasonal winds of late-spring/summer kept the particulate oil-phase from the discharge plume subsurface 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).

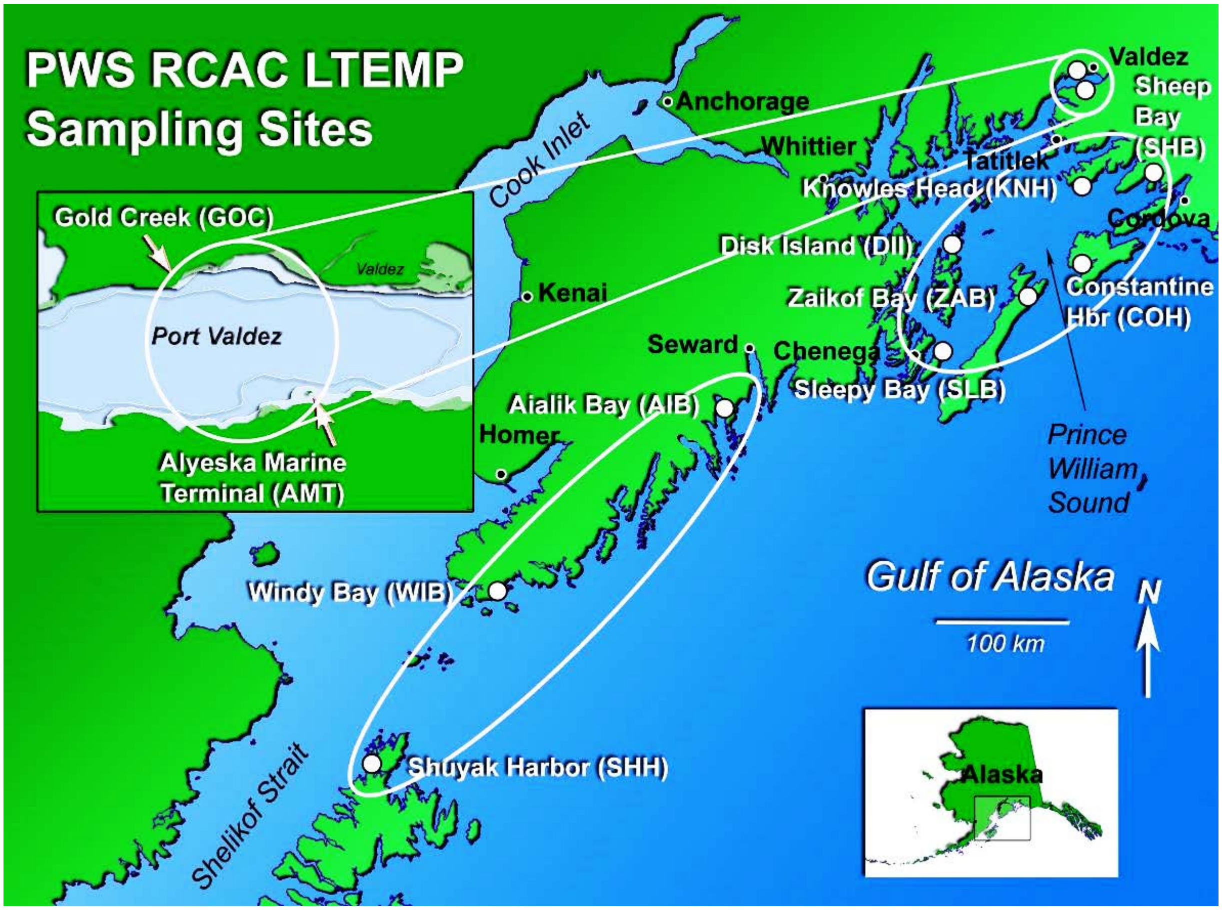

Figure 2. Map of the LTEMP sites. Circled regions represent sites with similar hydrocarbon signatures and events.

In July 2002, PECI and the NOAA/NMFS Auke Bay Laboratory (ABL) began collecting and analyzing 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 *Marine Pollution Bulletin* (Payne at al., 2008b).

Recent years have brought change to both the system and the environment as pipeline production has dropped from 2.03 million barrels per day at its peak in 1988 to current levels of 0.53 million barrels per day (Table 1). 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 ballast waters are uncontaminated seawater that do not require treatment. Treated-ballast water discharges to the Port have also swung from an average of about 10 million gallons per day (MGD) in 1978 to a maximum of around 15 MGD in 1990 to currently only 0.88 MGD (Table 1). Facility operators estimate, and Discharge Monitoring Report data confirm, that more than half of the current discharge is from the terminal's stormwater runoff (Rich Loftin, pers. comm., 2016). In summary, less tanker traffic, cleaner ballast, and a new ballast-water-treatment configuration at the Alyeska terminal have resulted in substantial reductions in detected hydrocarbon concentrations and composition in the field samples. All discharges are made under a National Pollution Discharge Elimination System (NPDES) Permit for which PWSRCAC submitted detailed reviews during the last two permit renewal cycles (Payne et al., 2003c and 2012).

Table 1. Recent average throughout of Alyeska Pipeline and ballast water treatment

	2015	2016	2017	
Pipeline throughput	0.49	0.52	0.53	M barrels/day
BWTF throughput	1.10	1.00	0.88	M gal/day

Prior to this report, all ten LTEMP sites were most recently visited in July 2008, April 2009, and then, beginning the reduced effort, 5-year cycle concept, in July 2013 (Figure 2). Visits included three NE sites in or near the Port to monitor terminal and tanker operations, six others to monitor the more remote sites for lingering *Exxon Valdez* Oil Spill (EVOS) impacts, and the eastern-most one to serve as a non-EVOS-impacted control (SHB). Initially, to more thoroughly monitor Port operations, LTEMP collections had been taken tri-annually at the two Port sites and nearby Knowles Head but efforts were later reduced to annual sampling. In 2015 sampling occurred at four of the ten LTEMP stations (Alyeska Marine Terminal, Gold Creek, Knowles Head and Sheep Bay (AMT, GOC, KNH, and SHB, respectively) (Payne et al., 2016). In 2016, another mussel sampling site was added at Jackson Point (JAP) within the terminal port (Figure 1) but east of the active berths and the traditional station at Saw Island (AMT). This site was meant to evaluate a potential PAH gradient to either side of the BWTF outfall and to correlate tissue data with trial passive-sampling devices (PSDs) that were concurrently deployed subsurface at the same terminal locations (Minick and Allan, 2016, Long-Term Environmental Monitoring Program – Supplemental Report on monitoring for Polycyclic Aromatic Hydrocarbons using Passive Samplers: 2016 Sampling Results and Interpretation). In 2017, only these three Port Valdez sites were sampled.

The 2016 program also included a change in analytical services when NOAA Auke Bay Laboratory (ABL) closed its hydrocarbon facilities in Juneau, Alaska. This 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 tissues samples, all with independent, third-party QC validation as part of that litigation-sensitive effort. The LTEMP lab transition also involved performance-based round-robin intercalibration programs in which both Auke Bay and Alpha/NewFields participated to demonstrate they could generate comparable data with known precision, accuracy, method detection limits, and representativeness.

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). Briefly, three replicates of mussels are collected by hand at each site while triplicate sediment samples are collected from the two Port locations (AMT and GOC) using a modified Van Veen grab. Sampling protocols have remained the same but as noted above, 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, 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 EPA Method 8270. 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 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, saturated hydrocarbons in sediments 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 samples is also provided. However, due to contractual omissions along with concerns that potential lipid interference and anticipated below-MDL-concentration issues might occur with GC/FID, SHC analyses of tissues were not performed by Alpha Analytical on the 2016 and 2017 tissue samples. However, later examination of selected-ion-monitoring (SIM) plots of *m/z* 85 ions acquired during tissue biomarker analyses demonstrated that the aliphatic hydrocarbons actually were present at high enough concentrations to allow GC/FID measurement. But PWSRCAC subsequently elected not to pursue the analyses. For comprehensive interpretation and continuity with earlier LTEMP results and to further evaluate a diesel spill at GOC in 2016, we reported 2016 tissue SHC using secondary evidence, the unquantified *m/z* 85 plots *in lieu* of quantified GC/FID SHC data (Payne and Driskell, 2017b). Through contractual omission, tissue SHC data were also not quantified in 2017.

BIOMARKERS

A recent addition to the LTEMP suite of analytes, petroleum biomarkers are conservative, weathering-resistant, hydrocarbon compounds, unique to each oil formation and that, for LTEMP, can facilitate and confirm detection of AMT-derived, Alaska North Slope crude-oil constituents in Port sediments, even when the PAH are degraded. The objective of using biomarkers is to look at the hydrocarbon signatures using less degradable analytes than the SHC and PAH. In the environment, the SHC are quickly consumed by microbes, giving forensic reviewers a perspective of “freshness” of crude oil patterns while also distinguishing petroleum distillates (diesel vs. fuel oil vs. crude oil, etc.) plus tagging contributions from other (primarily biogenic) sources. PAH compounds are more persistent, weathering slower in predictable patterns and rates, which serve to track longer-term fate, behavior, and mixing with other sources[1]. 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.

In 2016, biomarkers were analyzed on both sediments and tissues. For routine monitoring, however, mussel tissues biomarkers are generally less effective than sediments as the mussels regularly purge and, currently, at most LTEMP stations, only carry trace-level, dissolved-phase and combustion-derived PAH components. Water-insoluble biomarkers 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).

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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 Alaska North Slope 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).

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 marked with a golden fill color for visual reference in bar plots). 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 screened PAH and biomarker results graphically with an ANS 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 analytes (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 busts would require batch reanalysis. Surrogate recovery standards were met for all PAH, biomarker and alkane surrogate hydrocarbons analyzed during the 2017 reporting period excepting one tissue sample with marginally low naphthalene recovery (Table 2). Laboratory method blanks for each analytic sample batch demonstrated no significant laboratory or analytic background interference, thus assuring that the analytes in the field samples represented environmental constituents. There were, however, some matrix interferents noted in 2017 lab qualifiers (flags) with several sediment biomarkers (moretane, T26, T31 and T33). As obvious spike anomalies, they were ignored for data-pattern interpretations. Per our standard forensic reporting practices, the data discussed herein are neither blank-corrected nor surrogate-corrected and are reported as raw data (with below-MDL values flagged as estimated). All of the PAH, biomarker, and SHC profiles presented in Appendix 2 have the sample-specific MDLs overlaid on the histogram profiles.

Table 2. Surrogate recovery statistics by matrix from 2017 Alpha Laboratory analyses.

Matrix	Surrogate	Average (%)	Max	Min	Count
Sediment	Naphthalene-d8	94	99	88	8
	Phenanthrene-d10	112	116	107	8
	Benzo[a]pyrene-d12	101	119	84	8
	5B(H)Cholane	103	110	98	8
	ortho-Terphenyl	102	106	96	8
	d50-Tetracosane	101	105	95	8
Tissue	Naphthalene-d8	65	79	35	10
	Phenanthrene-d10	80	83	69	10
	Benzo[a]pyrene-d12	89	95	78	10
	5B(H)Cholane	101	110	96	10

METHOD DETECTION LIMITS

One lab-performance QC measure is the EPA-formulated, statistically-derived, analyte-specific, method detection limit (MDL) that EPA defines as “the minimum measured concentration of a substance that can be reported with 99% confidence that the measured concentration is distinguishable from method blank results.” Alpha Analytical Laboratory’s MDLs for hydrocarbon fall within the accepted norms 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 (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	n.a.	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 them 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 on single-sample PAH and SHC plots as red dotted lines 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-percent 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. 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 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 more conservative than necessary. 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. This added-confidence attribute is further bolstered in near-trace LTEMP data by seeing higher-level patterns of within-site fidelity and regional-wide commonalities that collectively changed between years—which could only occur if the

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

patterns were real 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.

Alyeska Marine Terminal Ballast Water Treatment Facility (BWTF) Effluent Sampling and Analyses

The primary source of oil contamination in Port Valdez has historically been the partially degraded discharge from the Alyeska Marine Terminal's Ballast Water Treatment Facility (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 high value that reflects the collected runoff from the terminal and smaller tanker ballast volumes requiring treatment during the calmer summer months. Anticipating less runoff and more ballast water in the system during winter operations, effluent samples were again collected in March, 2017.

Compared to the winter samples, summer effluent had lower TPAH values (2,885 ng/L vs. 7,605 ng/L), and were more highly weathered and biodegraded relative to initially fresh Alaska North Slope (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 are present in the effluent (Figure 4) at similar concentrations and with essentially identical degrees of weathering. At the same time, the winter BTT effluent has a much higher proportion of bioavailable, dissolved-phase components (Figure 5).

Lower-molecular-weight SHC are subject to both dissolution/evaporation losses and microbial degradation (NAS 1975, 1985, and 2003). Microbial processes can be tracked as decreases in more easily assimilated n-alkanes, n-C_{17} and n-C_{18}, relative to the branched-chain isoprenoids, pristane and phytane. SHC are well degraded by the combined abiotic and microbial processes in the BWTF's biological treatment tank and to a greater extent in summer vs. winter (Figure 4, Table 4).

Typically for this report, the summer effluent reference profile or ANS source is overlaid on the sample's profile. MDL overlays are shown for selected time-series data profiles, and they are shown for all 2017 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 presented in Appendix 2 of last year's report (Payne and Driskell, 2017b).

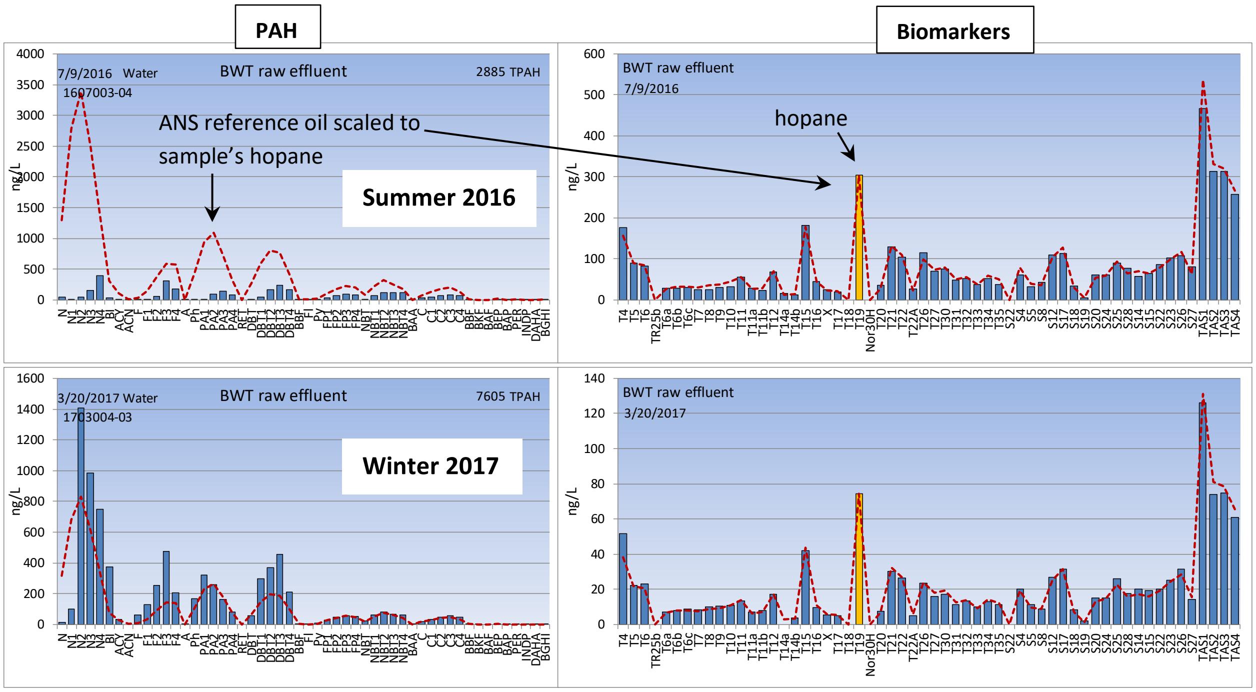


Figure 3. PAH and biomarker profiles of raw (unfiltered) BTT effluent samples from July 2016 (upper plots) and March 2017 (lower plots). The dotted red line represents an overlay of fresh Alaska North Slope (ANS) crude oil normalized (scaled) to hopane (colored gold in the biomarker profiles). Excess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

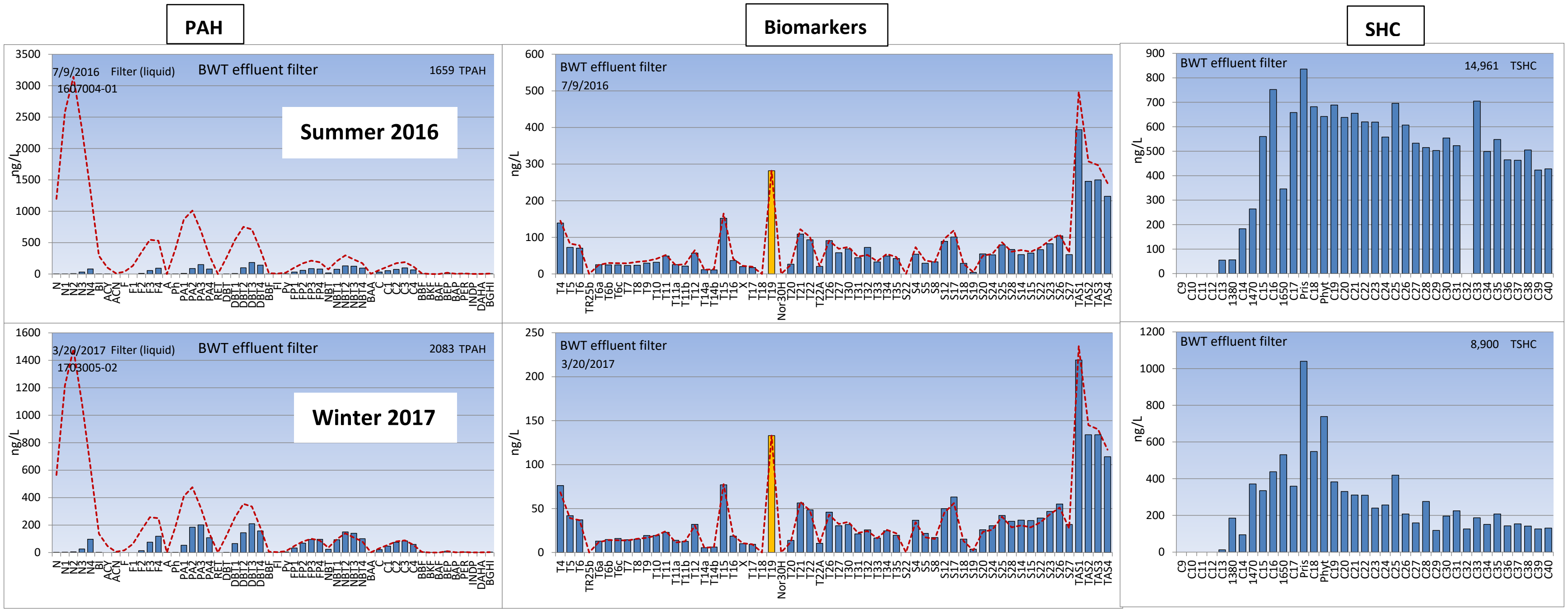


Figure 4. PAH, biomarker, and SHC profiles of the particulate/oil-phase droplets in the BWTF-BTT effluent. The red line overlay represents fresh ANS scaled to the sample's hopane (colored gold in the biomarker plots). The gaps between the measured PAH and the overlay portrays the extent of abiotic and biotic weathering. The TPAH concentrations are very similar but there is additional loss of the higher-molecular-weight (FPs, NBTs, and Cs) due to biodegradation in the summer. Biomarkers show essentially no degradation relative to fresh ANS (middle plots). SHC show losses of lower-molecular-weight C_9 through C_{15} components due to a combination of evaporation and dissolution processes as well as selective straight-chain n-alkane microbial degradation relative to branched-chain isoprenoids (Table 4).

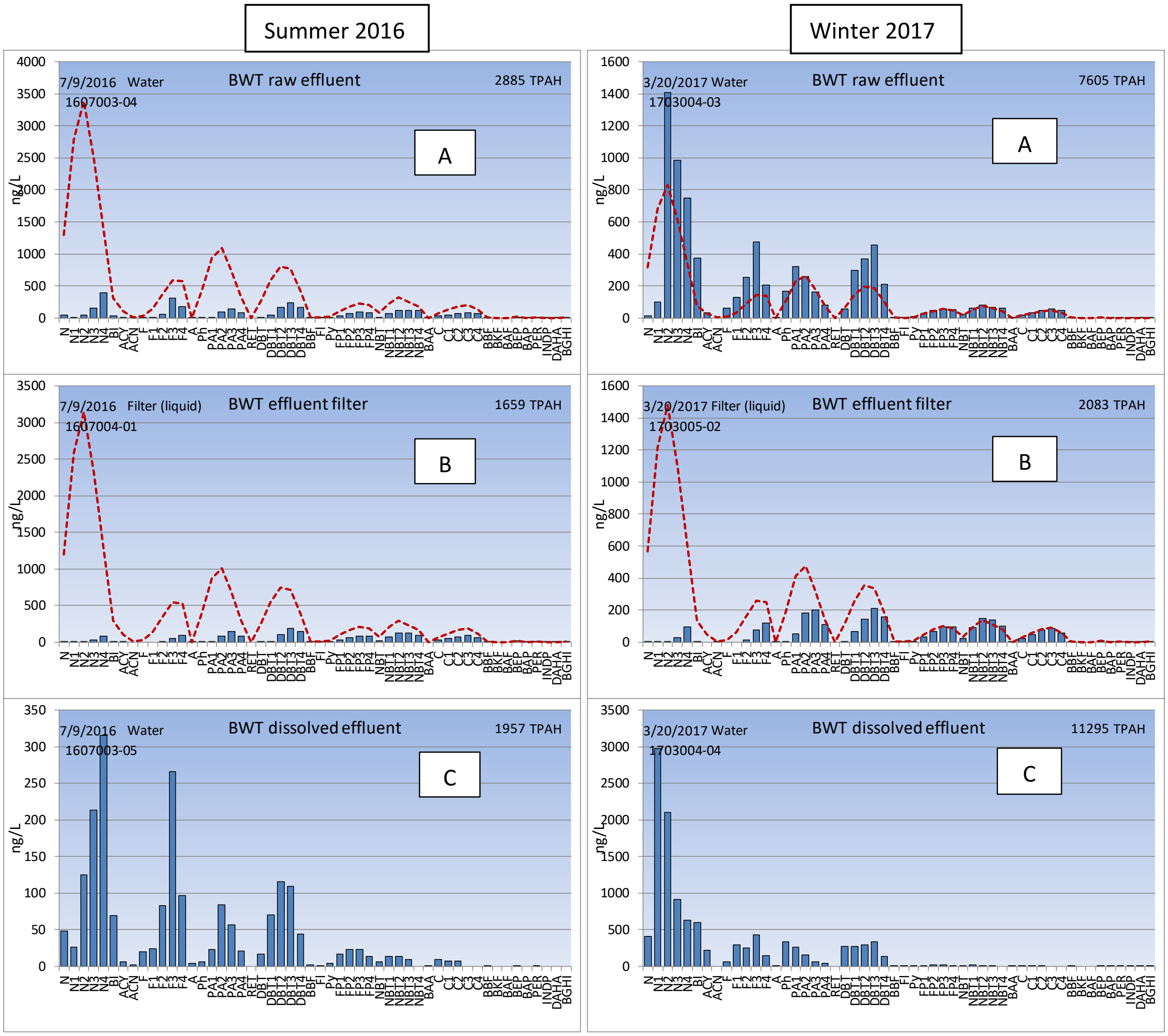


Figure 5. PAH profiles of Biological Treatment Tank (BTT) effluent samples collected under summer (July 2016) and late winter (March 2017) conditions: A) whole unfiltered sample; B) particulate/oil phase trapped on the glass-fiber-filter; and C) dissolved phase. The dotted red line in A and B represents fresh ANS crude oil PAH profile normalized to hopane to show evaporation and dissolution effects on lower-molecular-weight PAH (C is all dissolved and doesn't have a reference pattern overlay on it).

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).

	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

TPAH TRENDS

Note that while we consider TPAH 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, it is presented here. With TPAH levels dropping from historic highs between 1992 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 had plateaued at around 50-60 ng/g (DW) from March 2005 through April 2012 (Figure 6, Table 5). 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 in July 2015, the TPAH concentrations rebounded slightly to around 30 ng/g and further up to around 56 ng/g in 2016 and 75 ng/g in 2017.

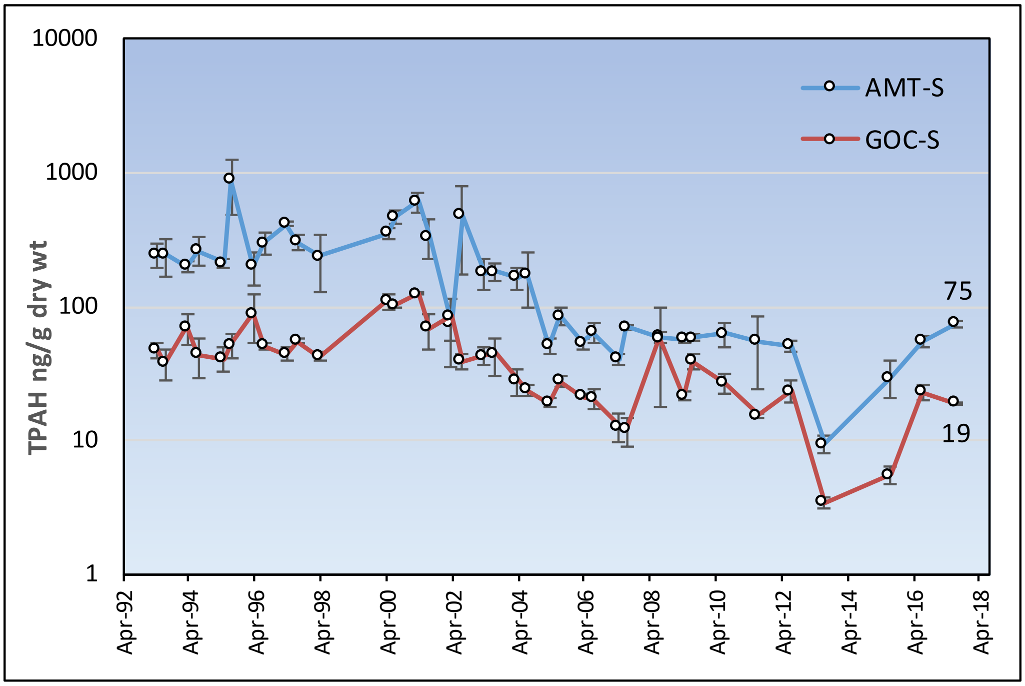


Figure 6. Time series of log(TPAH) in sediments at Alyeska Terminal (AMT) and Gold Creek (GOC). Error bars are ± SE of means.

USING SEDIMENT BIOMARKER DATA

Biomarkers' persistence in the BTT 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 weathering of the SHC and PAH continue. In an example profile, when the PAH are plotted with a fresh ANS overlay scaled to the sample's hopane (Figure 7, top), the individual components almost completely disappear suggesting almost complete loss of PAH due to *in situ* weathering during or after sedimentation. And while there is some degradation of the biomarkers as shown by the small gaps between the hopane-normalized ANS profile and the individual components, a sufficient profile exists to still positively assign the signal to the BWTF effluent. The biomarker losses are consistent with microbial degradation and abiotic dissolution weathering/dilution on particulate-phase oil droplets released from the diffusers. Similar losses, including microbial degradation of selected C_{28} and C_{29} tricyclic terpanes, S4 and S5 diasteranes, S14 and S15 steranes, plus (previously unknown) abiotic dissolution weathering of the triaromatic steranes (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, 2018a). For demonstration, when the PAH and biomarker data are re-scaled to the measured NBT2 rather than the hopane in the sample (Figure 7, bottom plots), an excess of biomarkers appear above the fresh ANS overlay, demonstrating the proportion of accumulated, more recalcitrant biomarkers and the higher-alkylated NBT and chrysene homologues in the near-diffuser sediments over time.

Table 5. Historic average sediment TPAH values, 2010-2017. (ng/g DW)

	AMT-S	GOC-S		AMT-S	GOC-S
Apr-00	353	111	Mar-06	54	21
Jul-00	472	103	Jul-08	61	60
Mar-01	614	126	Apr-09	59	22
Jul-01	335	69	Jul-09	60	40
Mar-02	76	86	Jul-10	64	28
Jul-02	480	39	Jul-11	55	16
Mar-03	179	43	Jul-12	51	24
Jul-03	184	45	Jul-13	9	3
Mar-04	167	28	Jul-15	30	6
Jul-04	175	24	Jul-16	56	23
Mar-05	51	19	Jul-17	75	19
Jul-05	86	28			

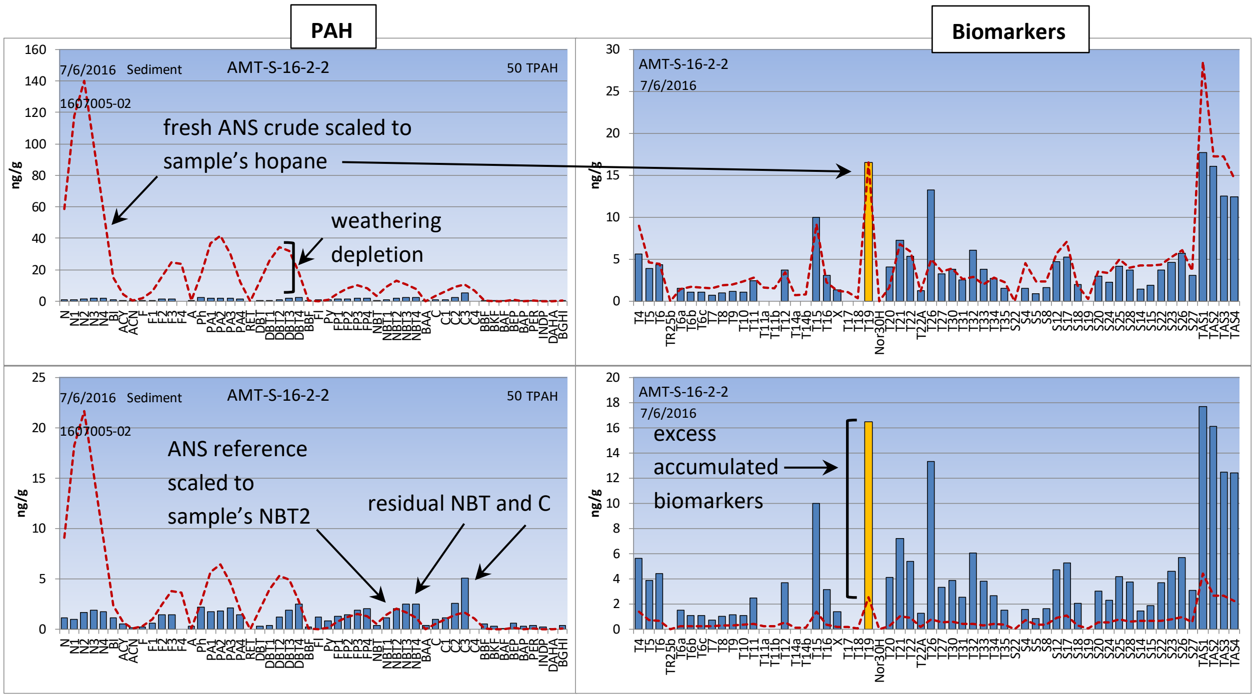


Figure 7. PAH and biomarker profiles of a representative 2016 AMT sediment sample overlaid with fresh ANS crude oil reference (dotted red lines) when alternatively scaled by the highly conservative biomarker, hopane (upper plots), versus the less recalcitrant PAH, NBT2 (lower plots). In the lower plot, the biomarker analytes 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. In this lower profile there is also an accumulation of a few of the more recalcitrant PAH including higher-alkylated NBT and chrysene homologues. The replicate 2017 AMT sediment profiles are essentially identical to this example (Figure 8).

ALYESKA MARINE TERMINAL

Looking at just the 2017 AMT sediment replicates, both profile patterns and concentrations were very tight (Figure 8). Despite their heavily weathered PAH profiles, all replicates confirmed the presence of ANS crude oil derived from the BWTF effluent. The SHC patterns show a mix of trace-level marine planktonic alkanes (C_{15}, C_{17}, pristane), odd-carbon numbered terrestrial plant wax components (C_{25}, C_{27}, C_{29}, C_{31}), and residual higher-molecular-weight C_{33}-C_{40} petrogenic waxes (Payne et al., 2015, 2016; Payne and Driskell, 2017b).

As suggested above, more relevant than the TPAH-trend perspective are the changes in the PAH and SHC patterns reflecting the different sources and concentration-dependent weathering behavior between 2008 and 2017 (Figure 9). Over this period, there has been a shift in PAH profiles from generally petrogenic in 2008 to a mixed pattern where pyrogenic components became more dominant from 2011 through 2015 (not shown; see Payne and Driskell, 2017b for more details). At the same time, the SHC profiles reflected more biogenic input as higher-molecular-weight petrogenic waxes generally disappeared (Figure 9).

Specifically, in 2008, the petrogenic PAH patterns were characterized by the parent PAH (PH, FL, PY, C) within each group being generally less than the C-2 or C-3 alkyl-substituted homologues yielding the hump patterns denoted by the red “tents” (Figure 9, top). By 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, second panel). In the SHC plots, the 2008 alkanes were dominated by higher-molecular-weight petroleum waxes (Figure 9, top panel) but, by July 2011, the SHC exhibited a mix of biogenic n-alkanes and higher-molecular-weight C_{32}-C_{36} petroleum waxes (Figure 9, second panel). By 2015 (not shown), there had been a trend of decreasing oil concentrations accompanied by a higher portion of combustion products in the AMT sediment but this was reversed in 2016 and 2017 with more and higher concentrations of petrogenic components observed.

Most of the TPAH increase in 2016 and 2017 AMT sediments was due to water-washed petrogenic components (Figure 9, bottom two panels). Specifically, the 2016 and 2017 AMT sediment patterns are almost identical, with the exception of parent phenanthrene exceeding the C1-C4 alkylated homologues suggesting a mixed combustion-product source for these constituents in 2017. In both 2016 and 2017 AMT sediments, the higher-molecular-weight (BBF to BGHI) pyrogenic combustion products were much lower than the petrogenic components (i.e., compared to 2011). The 2016 and 2017 AMT SHC patterns were very similar, although the elevated C_{32} in 2016 is believed to be a laboratory artifact. Considering the very low but higher-trending (and above-MDL) PAH levels since 2013 (Figure 6), the transitions from petrogenic to pyrogenic patterns between 2008 and 2015 and then back to petrogenic in 2016 and 2017 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 is over two-times lower (see next section), tanker and workboat exhaust while at or maneuvering near the berths is the likely source of the pyrogenics. The biomarker patterns over this timeframe (Figure 10) show a continued accumulation of BWTF-derived ANS components as the PAH patterns reflect extensive weathering and the variable introduction of additional combustion sources.

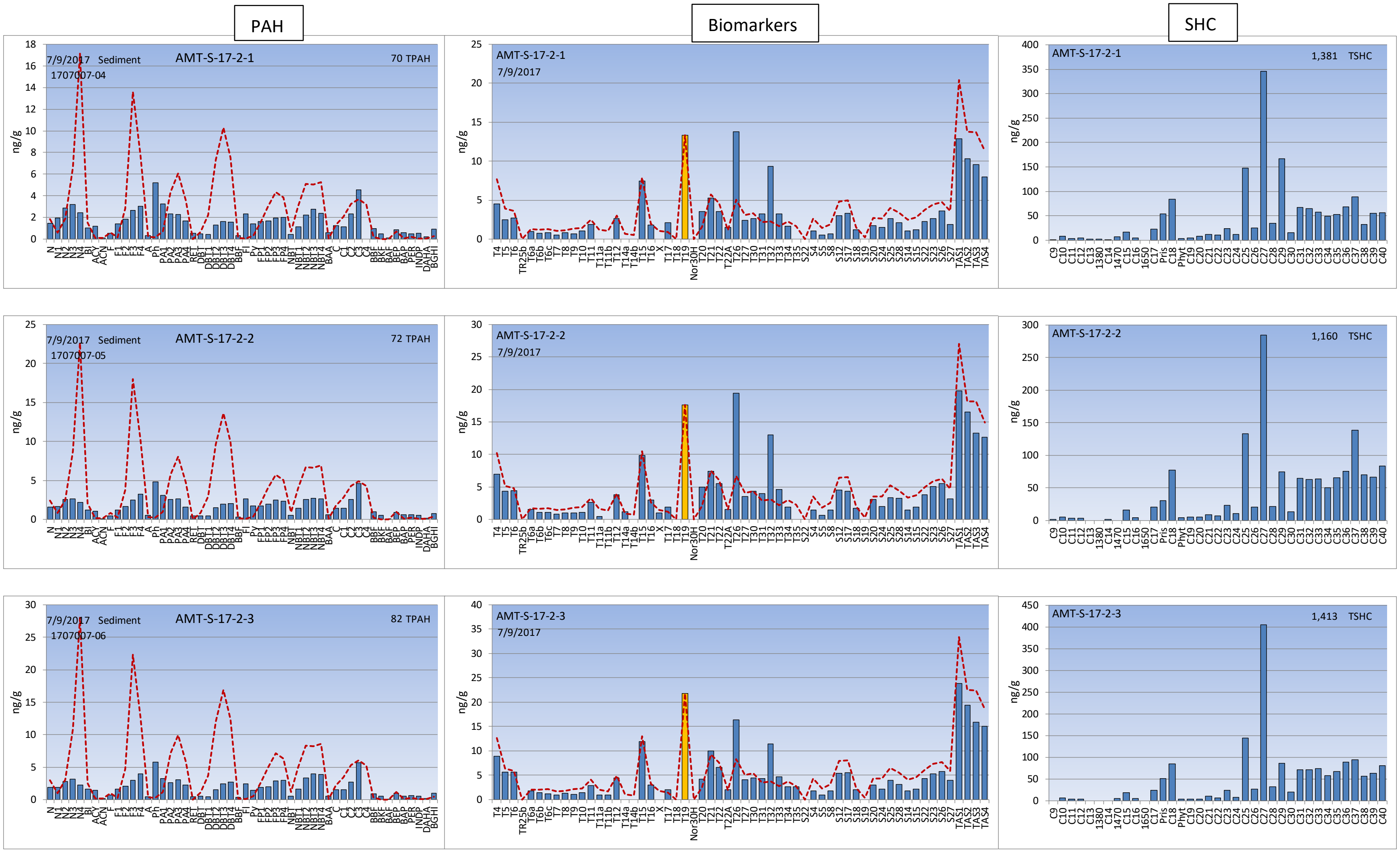


Figure 8. PAH, biomarker, and SHC concentrations and profiles of 2017 AMT sediment replicates. The dotted red line in the PAH and biomarker profiles is the July 2016 raw BWTF effluent (Figure 3) normalized against the sample's hopane. Biomarkers confirm the presence of a weathered ANS profile in the PAH.

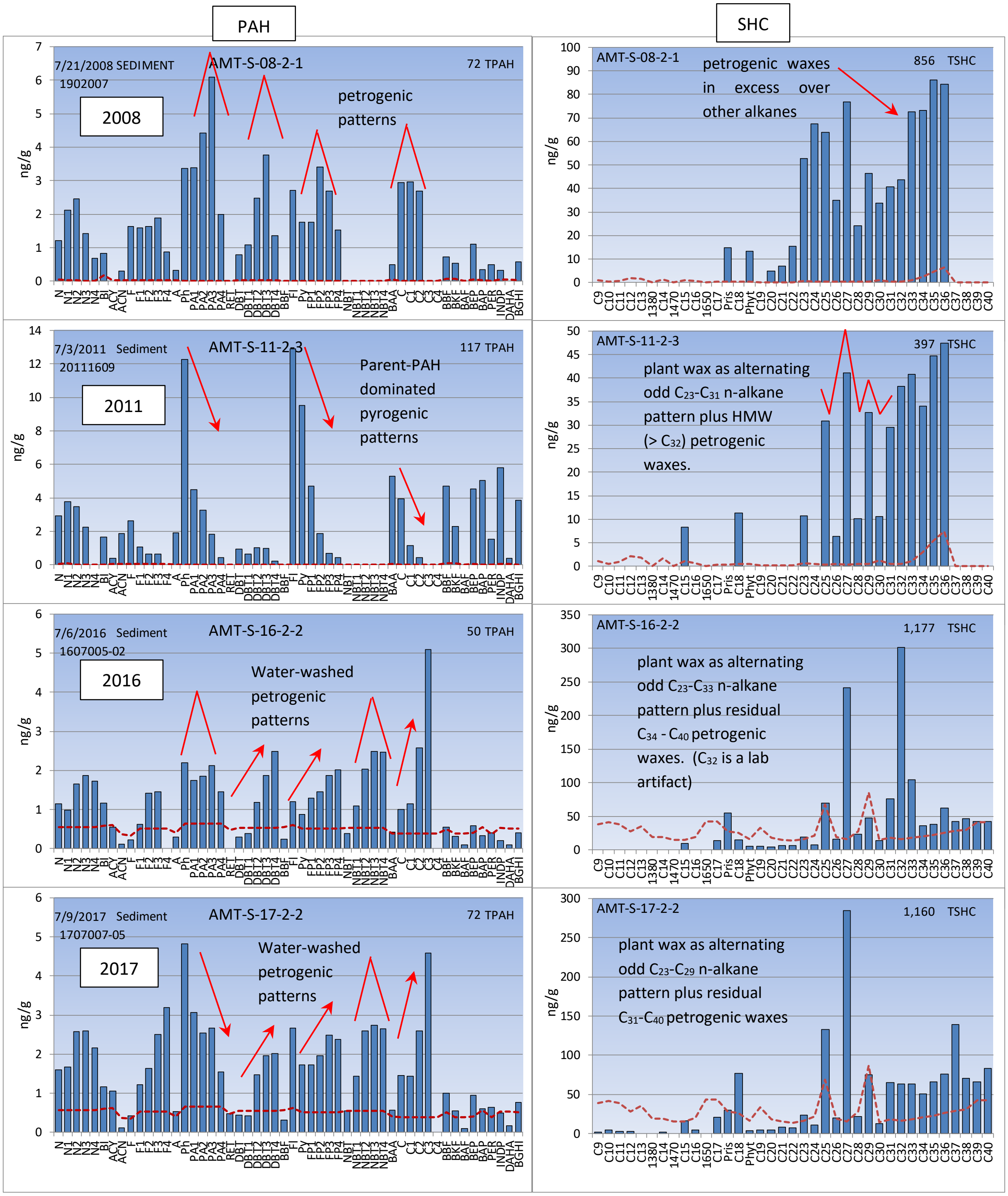


Figure 9. Representative PAH and SHC signatures of sediments at Alyeska Terminal between July 2008 and July 2017 showing the progression from a primarily petrogenic to a pyrogenic PAH signature with increasing terrestrial biogenic SHC and decreasing higher-molecular-weight n-alkane residuals (petrogenic waxes) through 2017. In July 2016, the PAH pattern became more of a water-washed petrogenic signal with higher relative TPAH concentrations compared to higher-molecular-weight combustion products (BBF through BGHI). This pattern was unchanged in 2017 with the exception of the P/As appearing more pyrogenic. The 2016 SHC remained largely biogenic (C_{32} spike is a lab artifact) and this pattern was unchanged in 2017. Red dashed line is sample-specific MDL.

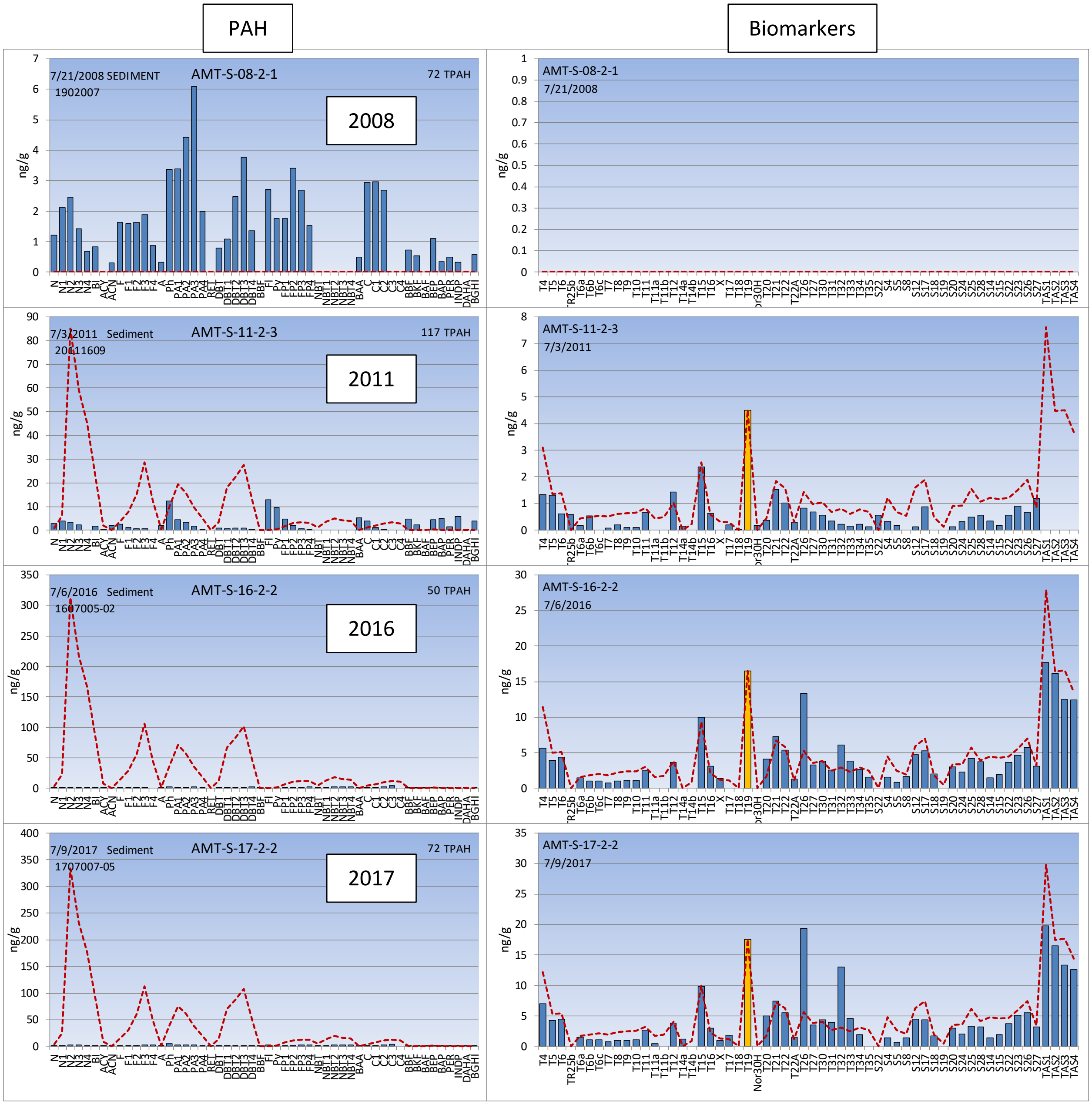


Figure 10. Time-series AMT sediment PAH profiles from 2008, 2011, 2016 and 2017 along with the biomarker profiles obtained after introducing those analyses to LTEMP in 2011. The dotted red line denotes the PAH and biomarker profiles from the July 2016 raw ballast water sample normalized to hopane (see Figure 3 and Figure 7). No biomarker data are available from 2008, and ABL did not report triaromatic steranes (TAS compounds) in their pre-2016 sediment analyses.

GOLD CREEK

Sediments at the 28-30m deep, Gold Creek reference site (GOC) have consistently exhibited lower TPAH concentrations than AMT throughout the duration of the program (Figure 6). In 2013, the GOC samples showed record-low concentrations (as did AMT) but unlike the sediments at the terminal, the 2015 levels remained in single digits (2014 samples were not collected due to a program hiatus). The TPAH concentrations then increased from 5.6 in 2015 to 23 and 19 ng/g DW in 2016 and 2017, respectively. Although this represents a roughly 4-fold increase, the values are still quite low (see ±SE data presented in Figure 6 demonstrating a tight precision about the measurements). Just like the similarities observed in the 2017 AMT sediment replicates, remarkable fidelity in profile and concentration was observed again in the three 2017 GOC sediment grabs (Figure 11). The PAH profiles are clearly derived from parent-dominated combustion products while the SHC patterns show a mix of trace-level marine planktonic alkanes (C_{15}, C_{17}, pristane) plus odd-carbon-numbered, terrestrial-plant-wax components (C_{25}, C_{27}, C_{29}, C_{31}) but no residual higher-molecular-weight C_{33}-C_{40} petrogenic waxes (Payne et al., 2015, 2017b).

The 2017 GOC replicate PAH, SHC, and biomarker patterns were also essentially superimposable (Figure 11), and identical to those observed in 2016 (Figure 12 and Figure 13). Because these patterns were observed in all three GOC sediment replicates collected in 2016 and 2017 and were similar to Auke Bay results from 2011, it appears that trace-level accumulations of biomarkers associated with the BWTF effluent (Figure 3) are accumulating in GOC sediments. The concentrations are very low, and there are numerous missing components but the norhopane (T15) to hopane (T19) ratios are appropriate (Figure 11 and Figure 13) and there are low-level S17 to S27 steranes plus triaromatic steranes (TAS) similar to the 2016-2017 effluent. There are also other components (T20, moretane; T26, bishomohopane; and T32 and T33 tetrakishomohopanes), but these either were noted as matrix interferents or suggest additional sources that were not in the BWTF effluent nor observed in AMT sediments. As noted above, the petrogenic biomarker compounds are much more resistant to weathering, and as such, they can be observed even when PAH and SHC associated with the terminal operations are not detected.

With the GOC patterns shifting from petrogenic to pyrogenic earlier than AMT's, the PAH profiles at the reference site have been dominated by pyrogenic components since April 2000 (Payne et al., 2008a,b; 2010a; 2015; and Payne and Driskell 2017b) and were accompanied by the overall drop in TPAH concentrations (Figure 6). The similarity in the time series plots of PAH and SHC profiles at GOC (Figure 12) further supports the relative stability in a common source over time. Over the nine-year period between 2008 and 2017, the PAH are primarily derived from parent-dominated combustion products with little change in the patterns. The overall 2016 PAH patterns appear to be slightly more complex but that is due to the inclusion of C3- and C4-alkylated homologues that were not always reported by the Auke Bay laboratory (Figure 12). In this context, however, the five-ring BBF through BGHI background pyrogenic components are consistently reported in the 0.3-0.4 ng/g DW range by both laboratories throughout this period, and they are significantly lower than the mid-range PAH. In addition to the pyrogenic components, GOC sediments also contain a moderate and relatively invariant suite of N_0-N_4 naphthalenes (Figure 12). These are believed to derive from glacial and riverine sediment input to the Port (Payne et al. 2010a, 2010b). Similar naphthalene contents were seen in varying degrees in all ten major Cook Inlet rivers surveyed during the ICIEMAP program (Susan Saupe, pers. comm., 2009) and in Cook Inlet sediments (Lees et al, 2000) where there is a tentative link to peat inputs.

As noted above, the SHC profiles (Figure 12) show no hint of ANS oil from the Terminal. Over the last nine years, the GOC sediment SHCs have been almost exclusively dominated by biogenic sources from marine phytoplankton and terrestrial plant waxes, and there is no evidence of the higher-molecular-weight petrogenic waxes observed in the terminal sediments (Figure 9) between 2008 and 2011.

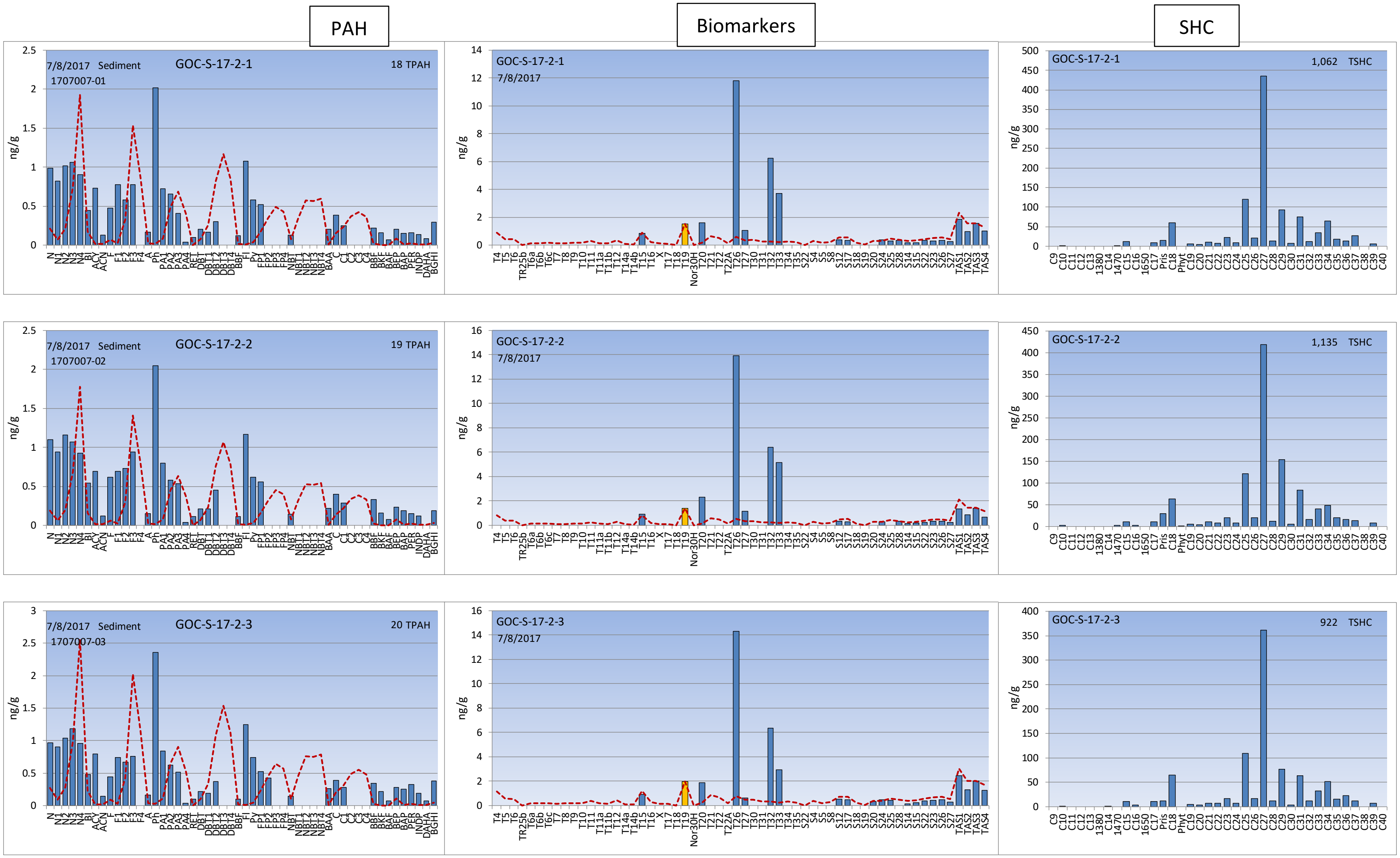


Figure 11. PAH, biomarker, and SHC concentrations and patterns of 2017 GOC sediment replicates. The dotted red line is July 2016 BWTF effluent (Figure 3) normalized against the sample's hopane.

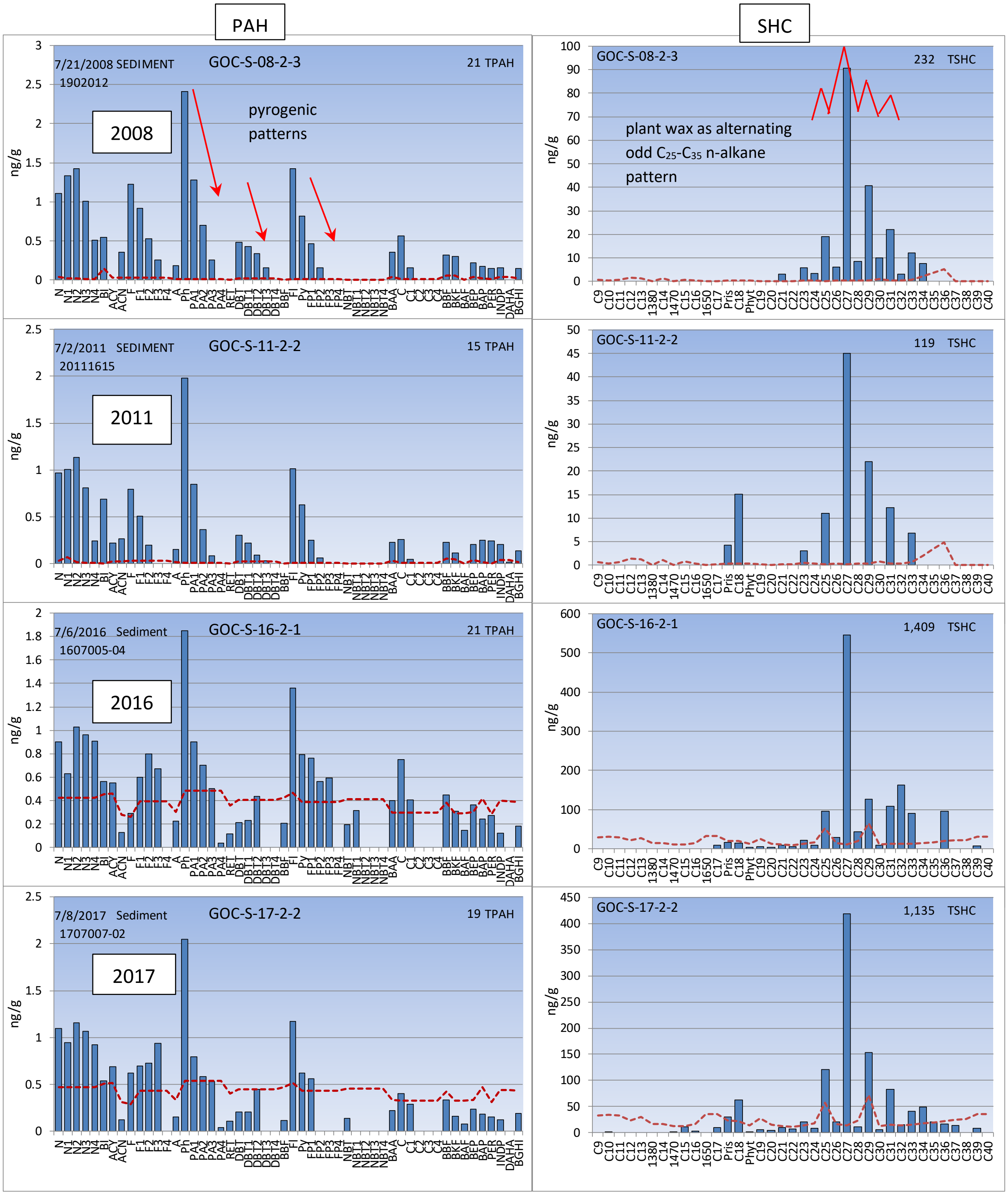


Figure 12. Representative PAH and SHC from Gold Creek sediments between July 2008 and July 2017 showing very similar, background naphthalene components and pyrogenic, parent-dominated, PAH. The 2016 PAH pattern is slightly more complex with more resolved peaks but still reflecting a dominant pyrogenic source. SHC patterns all reflect constant terrestrial and marine biogenic inputs. Red dashed line is sample-specific MDL.

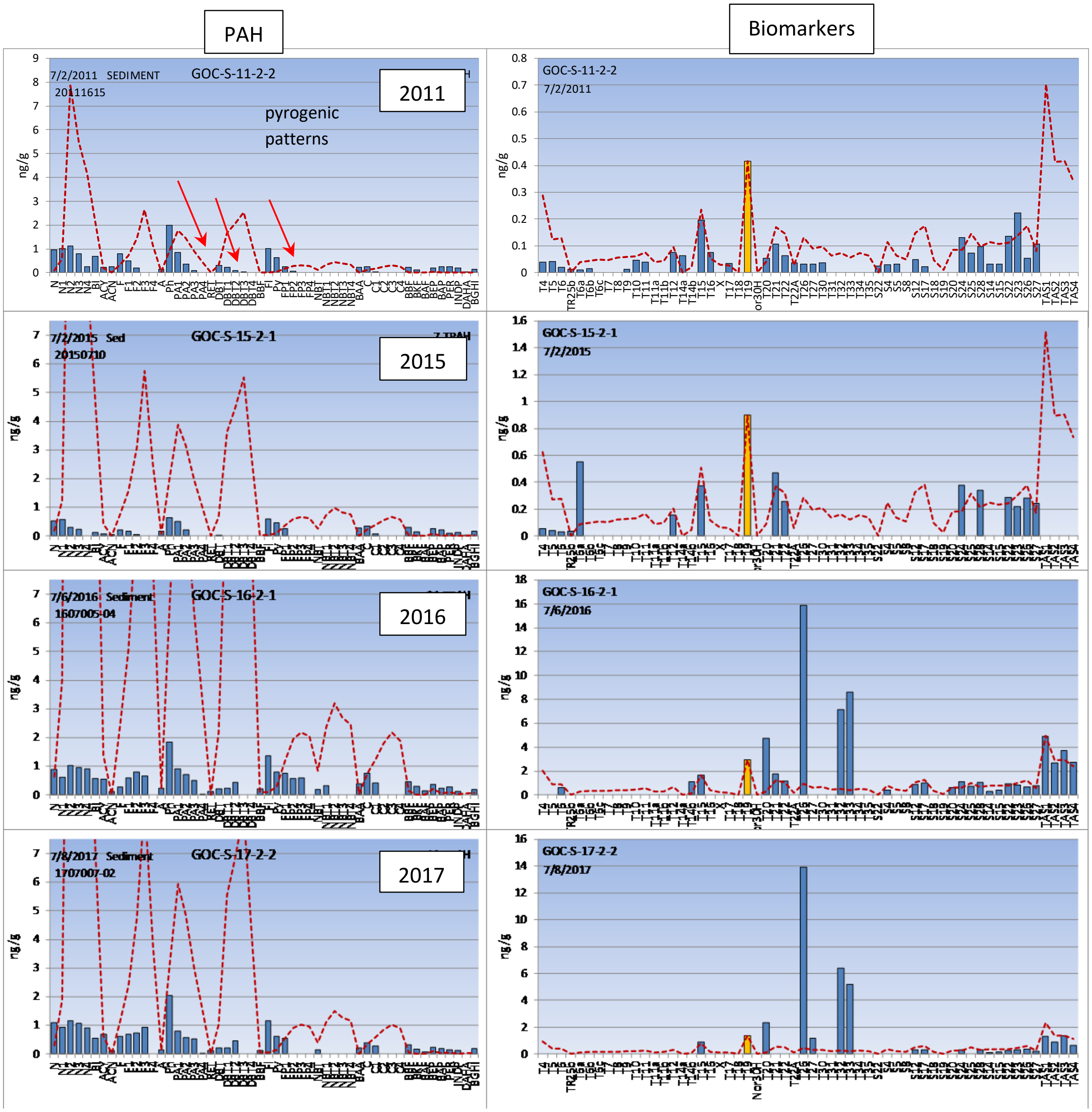


Figure 13. GOC sediment PAH and biomarker profiles from 2011, 2015, 2016 and 2017. The dotted red line denotes the July 2016 raw ballast water sample normalized to the sample's hopane. Analyses in 2011 and 2015 by ABL but they did not include the triaromatic steranes (TAS) in their suite of biomarker analytes. Analyses in 2016 and 2017 by Alpha/NewFields.

ALYESKA'S SEDIMENT MONITORING

Discussions in previous LTEMP reports demonstrate how the PAH, SHC and biomarker chemical profiles preclude other broad-scale hydrocarbon sources from within and outside the Sound (Payne et al., 2015; Payne and Driskell 2017b). Alyeska's NPDES-required, Environmental Monitoring Program (EMP) annually samples sediments in a 14 station design vs. LTEMP's two within Port Valdez stations. Shaw and Blanchard (2016, 2017) recently concluded from their EMP sediment biomarker data comprising just hopane (T19), norhopane (T15) and oleanane (T18) that all stations in the port, including deep-water EMP Stations 40 and 50 (along the midline of Port Valdez), contained petrogenic components derived from Alaska North Slope crude oil. Scatterplots of hopane and norhopane by year showed consistent ratios for all stations, which Shaw and Blanchard again concluded was due to the presence of ANS oil throughout the Port.

Beginning in 2014, their assessment was modified to suggest 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 (Shaw and Blanchard, 2016, 2017). The attribution to a refined ANS seems puzzling since the most abundant refined ANS source would likely be marine diesel or gasoline fuels but the distillation points required in refining these fuels typically eliminate the EMP target biomarkers, hopane and norhopane (Bence et al. 1996, Stout and Wang, 2016). Furthermore, if refined fuels had retained their biomarkers we would expect them to have an altered norhopane/hopane ratio due to differential loss from volatility during distillation, yet the EMP ratios are fairly constant in all samples. An alternative explanation might be that the low level biomarkers in the deeper sediments represent dilute, dispersed ANS crude inputs rather than refined products. LTEMP biomarker data at GOC supports this suggestion.

Also note that herein we document enhanced biomarker levels at AMT; biomarkers initially accumulate in normal proportion relative to the PAH components but, with slower degradation, subsequently become residuals of the weathered ANS inputs accumulating in excess to expected proportions (Figure 7). EMP sites near the diffuser would be prone to acquire similarly "enhanced" biomarker profiles. As a forensic exercise, we note that scaling the BWTF source profile to fit the PAH in Alyeska EMP, near-diffuser, sediment sample, 145A (adjusting the source to match the sample's most conservative PAH, chrysene) (Figure 14) required re-scaling the ANS overlay to roughly half of the hopane in ANS (hopane being the normal scalar of choice). In other words, there appears to be a two-fold excess portion of hopane biomarkers in this sediment sample relative to the PAH; half of the accumulated PAH have been weathered away. This biomarker "enhancement" generally agrees with LTEMP's nearby AMT sample which showed a weathered PAH profile that has accumulated approximately 2.7-fold excess hopane; i.e., two-thirds of the expected PAH have degraded.

Another point made by Shaw and Blanchard suggesting non-ANS inputs relates to the established notion that ANS oil is from formations lacking in oleanane (absent due to the geologic age of the formation, Kvenvolden et al., 1995). Reporting oleanane in most of their 2015-16 samples logically suggested that there must be a non-ANS source and thus, some additional non-BWTF contributions to the sediment background. Their conclusions are logically correct but our data from sample splits of pipeline-sourced ANS crude collected in 2012 and analyzed by both Auke Bay and Alpha laboratories did find very low level amounts of oleanane (~1-2% relative to hopane) in the oil stock. But these levels were nowhere near the higher amounts Shaw and Blanchard report (0-70%, median 4%). We would need to see a detailed lab report in order to confirm these findings.

The 2017 EMP results were not available for this report but, surmising from the 2016 results, the EMP conclusions cannot be corroborated from the abbreviated PAH and biomarker data available in their reports. Nevertheless, it can be said that the EMP conclusions generally agree with LTEMP's recent findings of low-level petrogenic plus pyrogenic patterns in the sediments at AMT and pyrogenic-dominated patterns with traces of BWTF-derived biomarkers (but not PAH or SHC) at GOC.

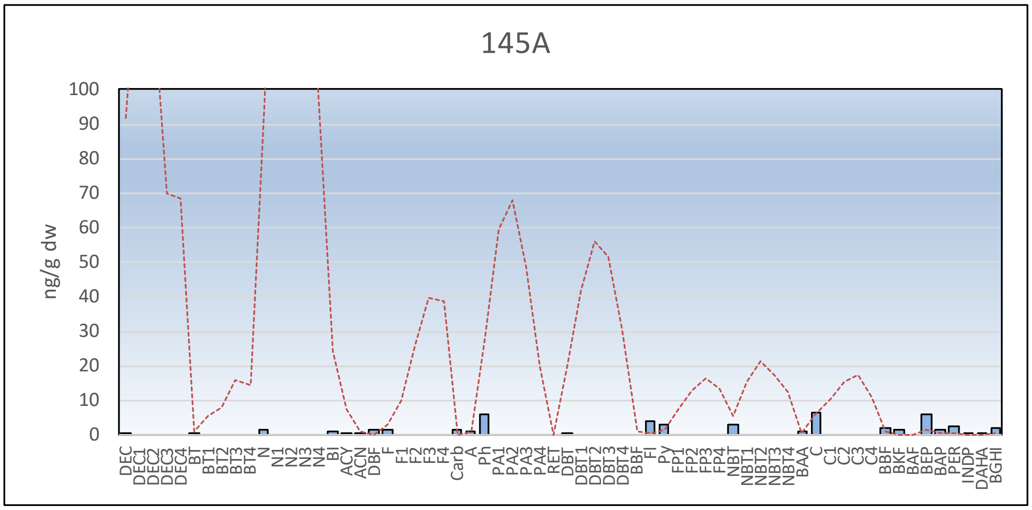
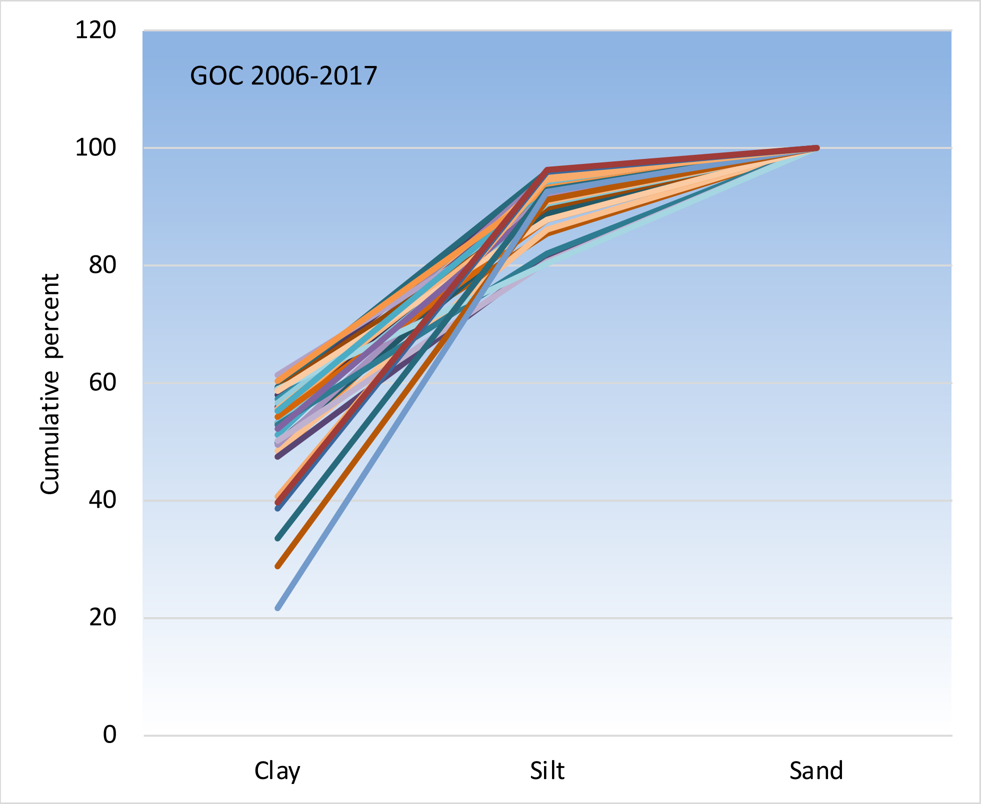


Figure 14. PAH profile of 2016 Alyeska EMP, near-diffuser, sediment sample 145A (showing Alyeska's abbreviated analyte reporting list). Red overlay represents a fresh ANS oil profile scaled to the recalcitrant chrysene (C). Alternatively, scaling to hopane inflates the overlay (not shown) and suggests that based on the amount of chrysene present, the sample should have only half of the reported hopane. These data imply that the two-fold surplus of biomarkers are residuals from degraded previous inputs of ANS.

SEDIMENT GRAIN SIZE

The LTEMP sediment-sampling locations comprise a heterogeneous slope and a sediment shelf in a fjord dynamically swept by tidal currents (and prop wash at AMT), 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, 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 grain-size samples are presented for all 2006-2017 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 15 and Table 6) and with both sites showing minor trends and outliers. In the 3D plots (Figure 16), note there are annual shifts at GOC (~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 and 2017, there was further return towards a clay-dominant substrate. At AMT (~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 (Table 6).



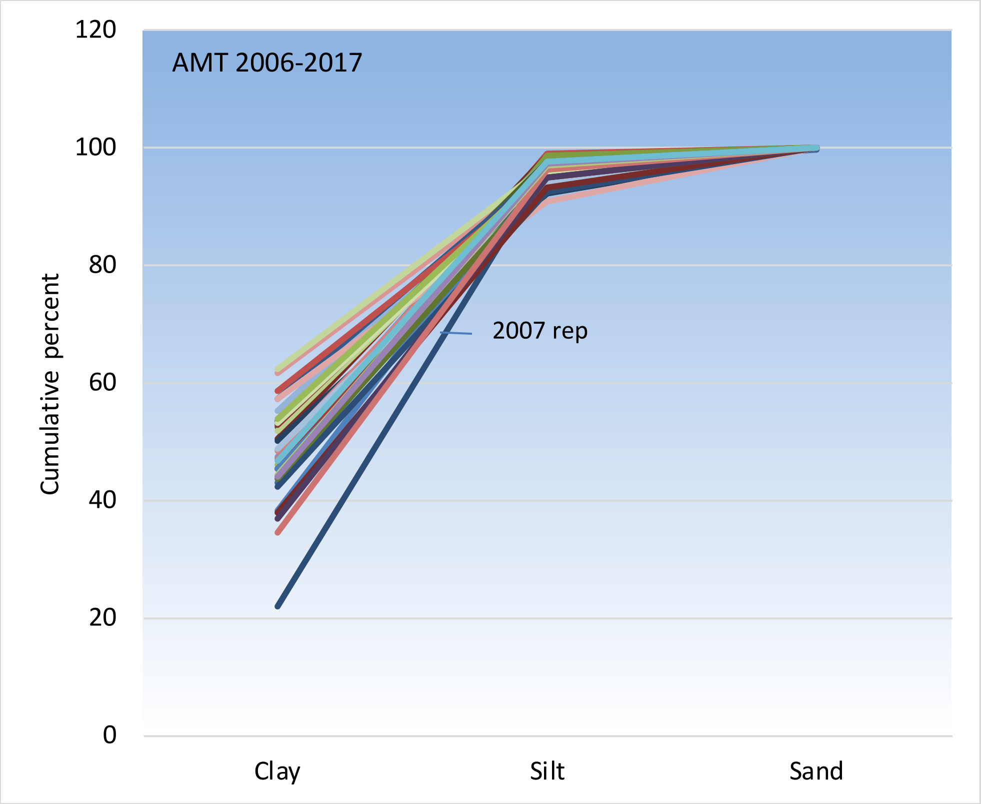


Figure 15. Individual replicate cumulative grain-size curves (%) for GOC and AMT, 2006-2017.

Table 6. Average grain size components for GOC and AMT, 2006-2016

AMT				GOC			
Year	% Sand	% Silt	% Clay	Year	% Sand	% Silt	% Clay
2006	1	55	43	2006	6	44	51
2007*	2	54	44	2007*	7	37	56
2008	2	54	44	2008	9	36	55
2009*	4	40	56	2009*	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
avg	3.4	48.2	48.4	avg	8.6	41.3	50.1

- Combines two seasons of sampling

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.

LTEMP TOC values showed seasonal cycles during the more frequent samplings early in the program but then showed a slow increase in concentration until plateauing sometime around 2003 (Figure 17 and Table 7). There was an uptick at GOC in 2012 and 2013 and mildly so at AMT in 2013. Since then, GOC TOC levels have dropped in 2015-2017 while AMT shows a modest upward trend 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. Also, note that the data are not continuous, that sampling prior to 2002 was performed by KLI, and that 2016 incorporates the third laboratory change for the project.

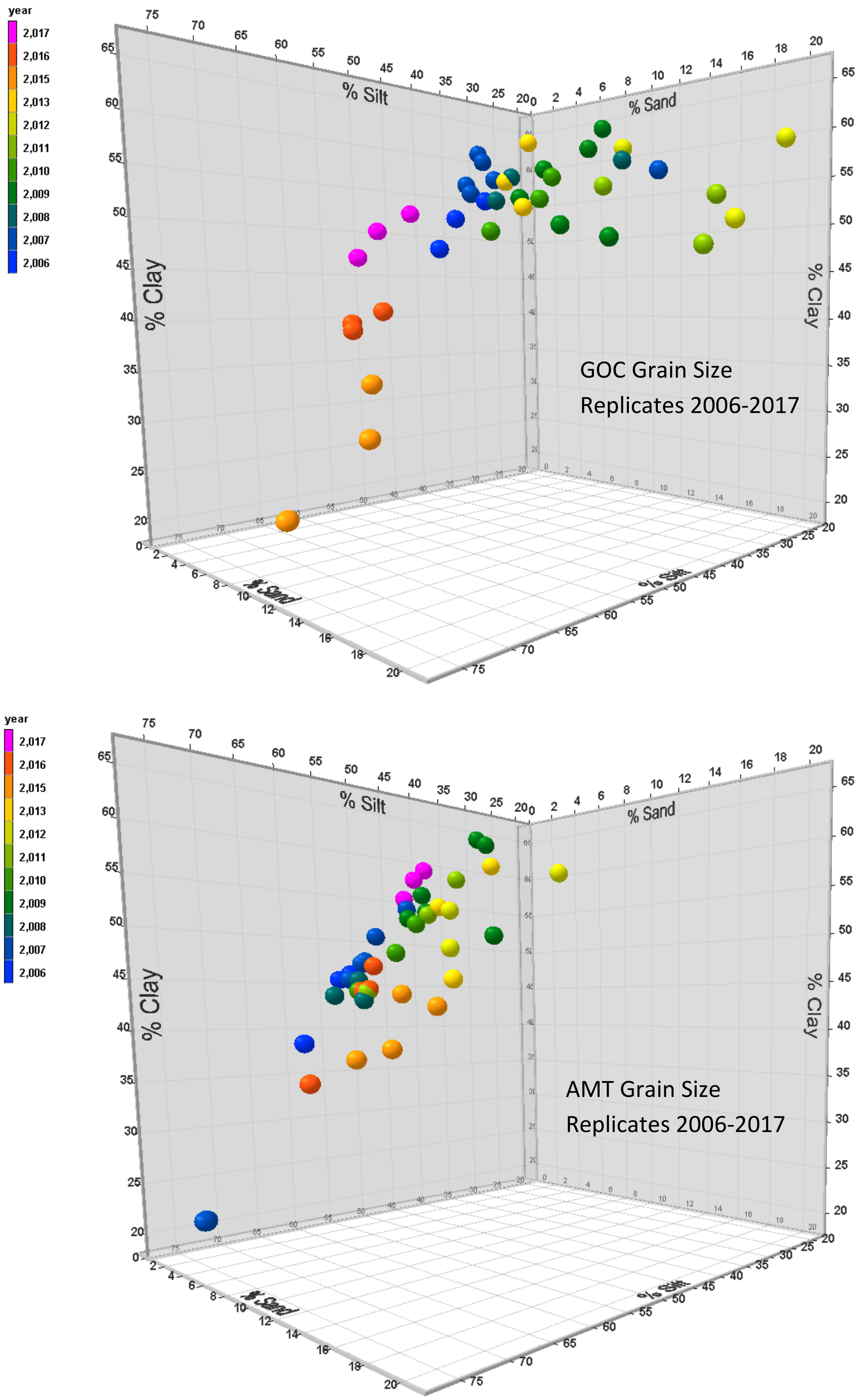


Figure 16. 3D plots of grain size components from GOC and AMT 2006-2017. Sampling years are color coded: blue to red, 2006-2016; pink, 2017. Note the clipped axes emphasize a decreasing shift in clay vs silt at GOC in 2015. Over the years, typically sand content has been most variable component at GOC, silt/clay at AMT.

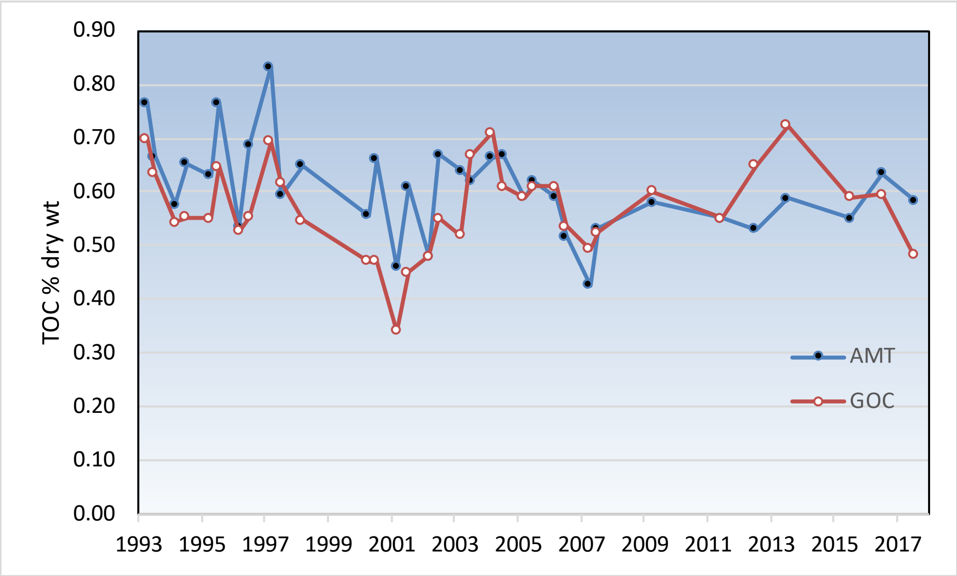


Figure 17. LTEMP Total Organic Carbon trends in AMT and GOC sediments (% DW.), 1993-2017.

Table 7. LTEMP Total Organic Carbon in AMT and GOC sediments (% DW.)

Sample Date	AMT	GOC	Sample Date	AMT	GOC	Sample Date	AMT	GOC
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			
Apr-00	0.56	0.47	Mar-06	0.59	0.61			

PORT VALDEZ MUSSEL TISSUES

TPAH TRENDS

Although historically, TPAH concentrations in mussels sampled from both the Alyeska Marine Terminal (AMT) and the background-reference site at Gold Creek (GOC) were commonly reported in hundreds of ng/g dry weight (DW), in 2002 the concentrations dropped to ~8-80 ng/g DW levels (Figure 18). The exception to this post-2002 range occurred with a diesel spill at GOC in the summer of 2004 when elevated TPAH concentrations were approaching 1,000 ng/g DW. The GOC TPAH concentrations were back in the pre-spill range by summer 2005, and continued to fall at both locations until summer 2013 when only very low, near method-detection-limit (MDL) traces of petrogenic components were found. No mussel samples were collected in 2014 but, in 2015, the tissue burdens at both locations increased slightly while the character of the PAH patterns further degraded to primarily dissolved-phase, background patterns (discussed below). Mussel TPAH concentrations in 2016 remained essentially the same at GOC (~27 ng/g DW) but they dropped to all-time lows at AMT (Figure 18). In 2017, the TPAH levels at AMT, JAP, and GOC had decreased again into single digits, and as shown in Table 8, the standard errors of the mean are very tight.

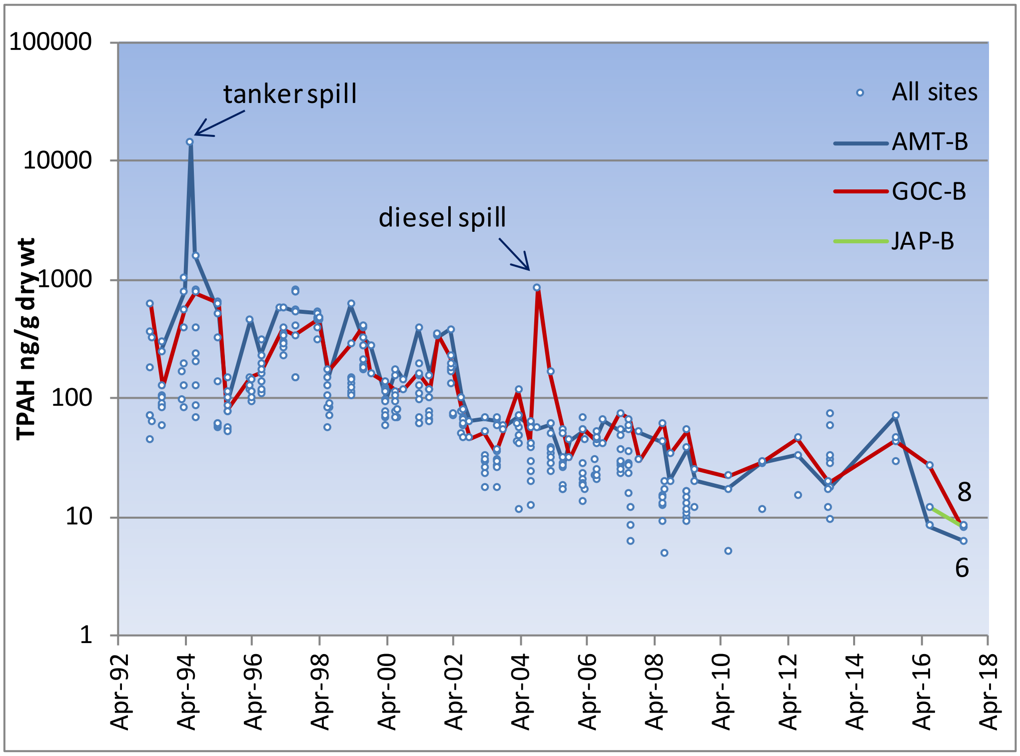


Figure 18. Time series of mean mussel log(TPAH) comparing 2017 Alyeska Terminal and Gold Creek to prior LTEMP collections at other regional sites. See standard errors of mean in Table 8.

Table 8. Time series of mean TPAH (ng/g DW) from Alyeska Terminal, Gold Creek, and Jackson Point mussels, 2008-2017.

	Jul-08	Sep-08	Apr-09	Jul-09	Jul-10	Jul-11	Jul-12	Jul-13	Jul-15	Jul-16	Jul-17
Mean TPAH											
AMT	43	20	38	20	17	29	33	17	70	8	6
GOC	62	34	54	25	22	29	46	20	43	27	8
JAP										12	8
± SE of means											
AMT	5.8	1.9	6.8	0.8	0.9	2.2	3.1	2.9	8.6	1.8	0.2
GOC	6.3	3.5	2.8	1.2	1.4	3.3	6.6	2.4	3.6	13.3	0.4
JAP										1.6	2.6

ALYESKA MARINE TERMINAL AND JACKSON POINT

The PAH and biomarker patterns and concentrations at both the Terminal's AMT and JAP sites in 2017 showed only trace levels of dissolved-phase naphthalenes, and variable combustion products plus perylene (Figure 19 and Figure 20). The profiles for the two adjacent sites were nearly identical, and neither site had any evidence of PAH or biomarker accumulation from the BTT effluent. The TPAH concentrations in the replicates from both sites were very low (Table 8), and between the two stations, the patterns at AMT showed slightly greater within-site fidelity (Figure 19). One of the JAP replicates had slightly higher fluorenes (Fs) compared to the other two (Figure 20).

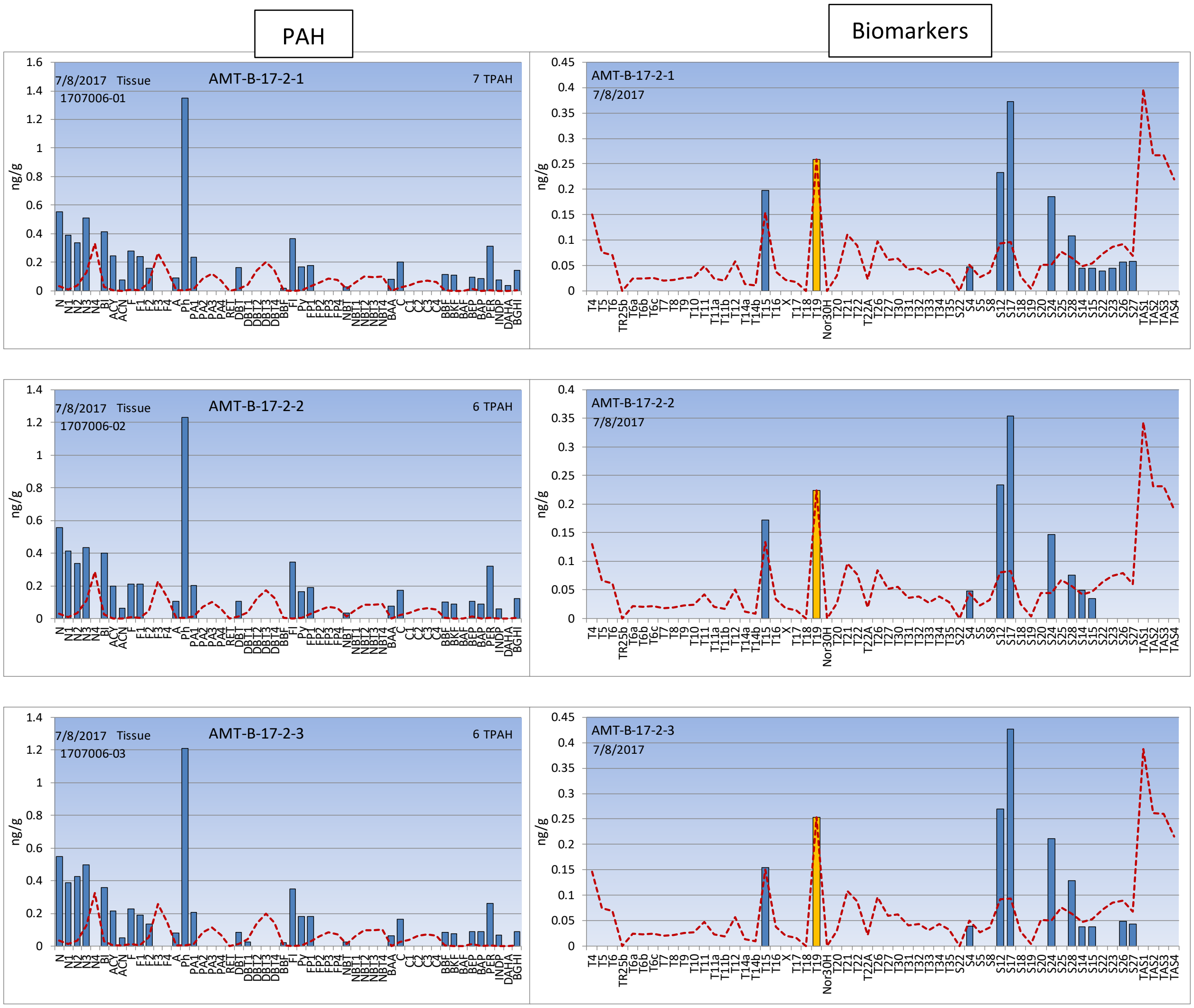


Figure 19. Replicate 2017 AMT (Saw Island) mussel samples presented together to allow direct comparison of absolute PAH and biomarker concentrations and patterns. The dotted red line in the PAH and biomarker profiles is July 2016 BWTF effluent normalized against the sample's hopane. No evidence of PAH or biomarker accumulation from the BWTF effluent is observed in any of the replicates.

Historical PAH data for the traditional AMT site (Figure 21) suggest the presence of dissolved-phase naphthalenes in 2008, 2015, and 2017 plus at- or below-MDL traces of combustion products in most of the samples. At these trace concentrations, results must be qualified as estimates (many analytes are below MDL – Figure 21) but

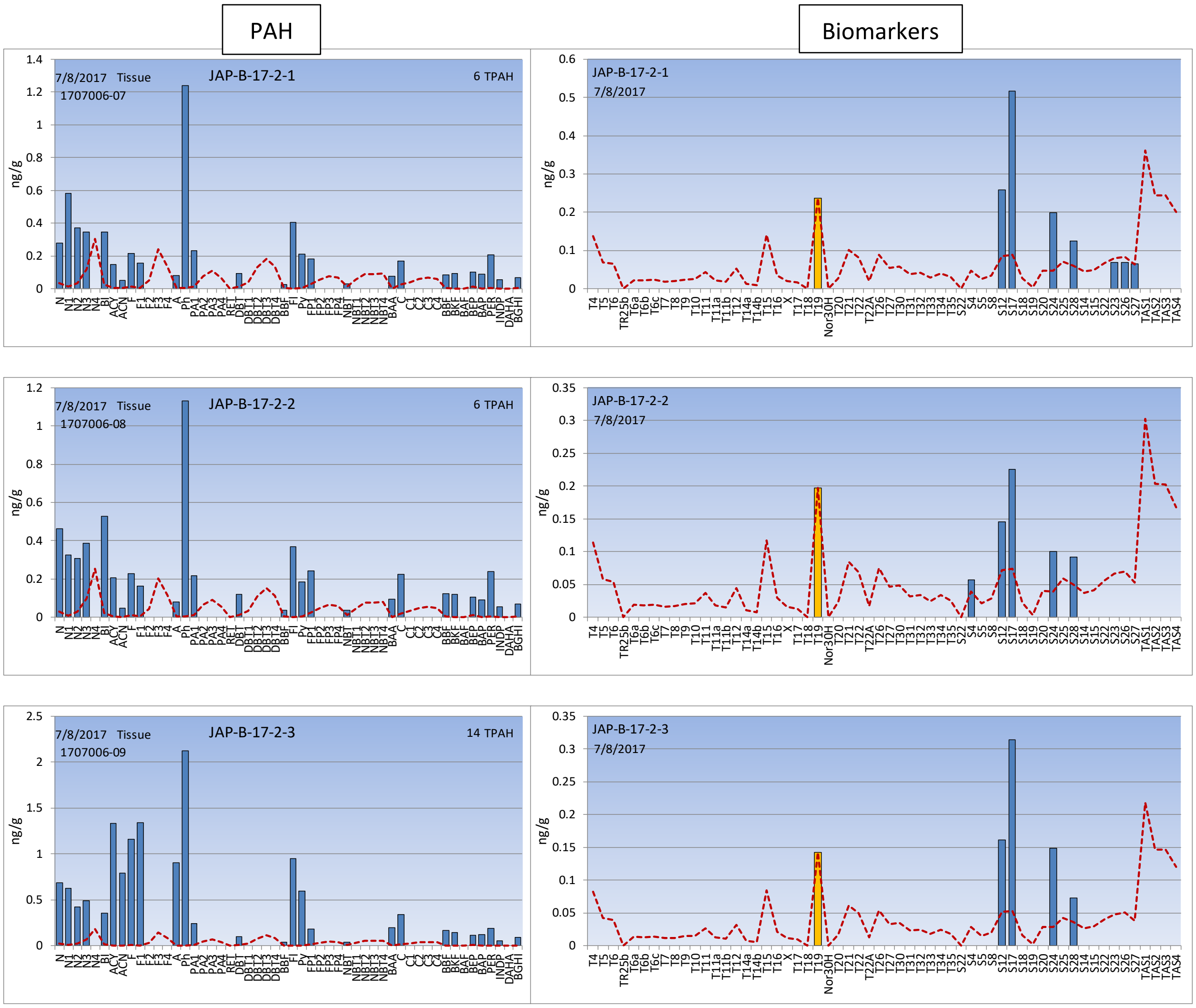


Figure 20. PAH and biomarkers from replicate 2017 Jackson Point (JAP) mussel samples. The dotted red line in the PAH and biomarker profiles is July 2016 BWTF effluent normalized against the sample's hopane. No evidence of PAH or biomarker accumulation from the BWTF effluent is observed in any of the replicates.

because of their patterns, they are not considered to be false positives. Although TPAH levels increased slightly in 2015 (Figure 18), the majority of the PAH were dissolved-phase naphthalenes, which also were observed to a lesser extent at GOC (Figure 24). Recall that the source of dissolved-phase PAH cannot be definitively determined just from their profiles. These, however, did not match the pattern associated with BWTF effluent, so presumably they were derived from another unknown source. In addition to the dissolved-phase components and parent-PAH dominated combustion products (e.g., phenanthrenes (P) and fluoranthenes/pyrenes (FL/PY), perylene (PER) is occasionally observed. 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. The SHC data for 2008 and 2015 AMT samples show contributions from marine biogenic sources (Payne et al., 2015), and in the majority (27 of 31) AMT tissues examined since 2008, the SHC have been dominated by biogenic constituents (e.g., n-C$_{15}$, n-C$_{17}$, and pristane) with only very rare observations of petrogenic components (Payne et al., 2015). Quantified SHC data are not available for 2016 and 2017 mussels (see GOC tissue discussion below).

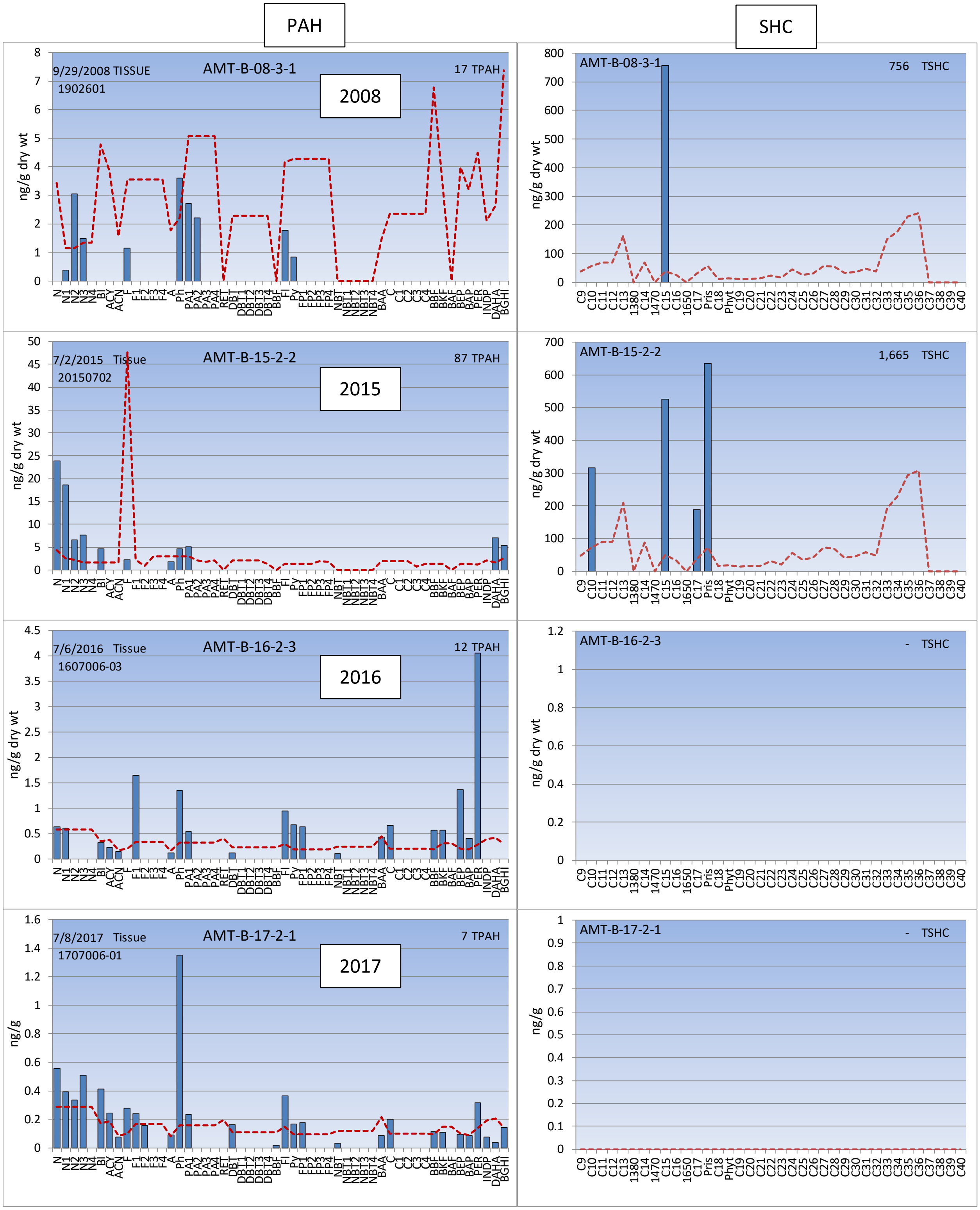


Figure 21. Time-series PAH and SHC profiles of mussels collected at AMT in 2008, 2015, 2016, and 2017 showing primarily dissolved-phase naphthalenes in 2015 and trace-level combustion-product PAHs, perylene, and planktonic biogenic SHC (n-C$_{15}$ and pristane) in other years. Quantified SHC data are not available for 2016 and 2017 mussel samples. The dotted red line denotes the sample-specific MDL as neither hopane nor NBT2 were present for scaling.

Because mussel samples were only collected from Jackson Point starting in 2016, prolonged time-series data are not available. But comparisons of representative samples from 2016 and 2017 (Figure 22) show similar trace-level combustion-derived PAH and presumably biogenic steranes whereby the constituent patterns do not correspond with the BWTF effluent.

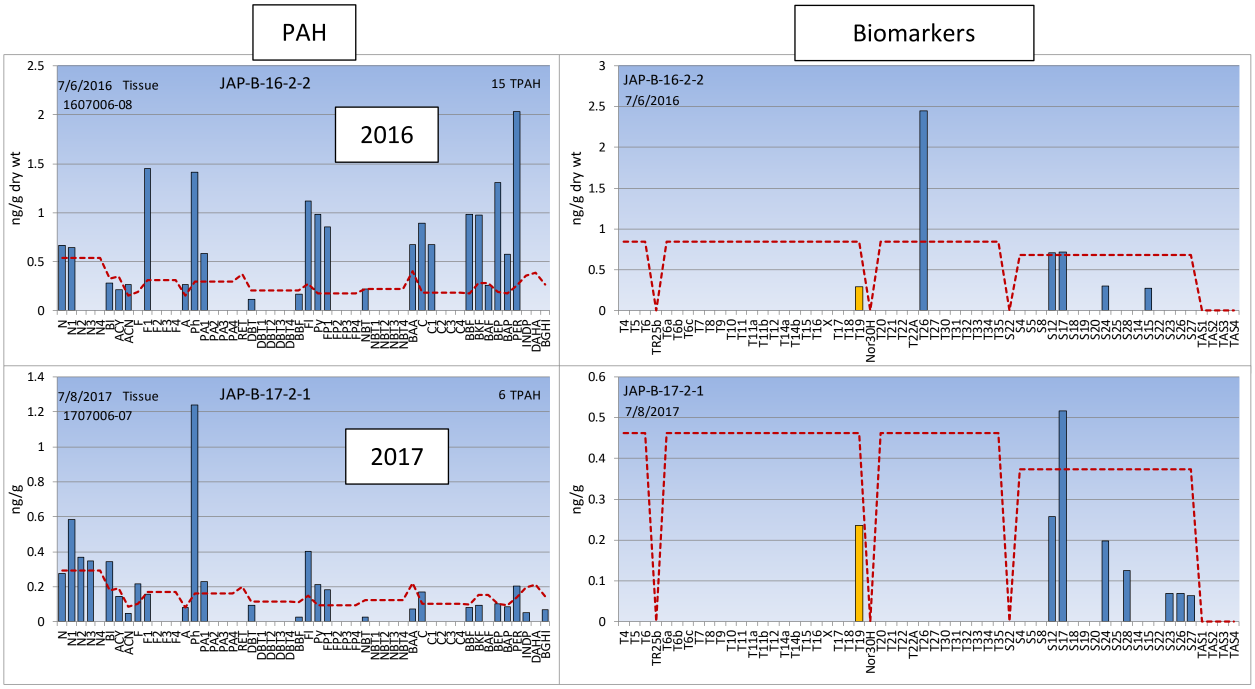


Figure 22. Time-series PAH and S/T profiles of mussels collected at JAP in 2016 and 2017 showing primarily trace-level dissolved-phase naphthalenes, combustion product PAHs (Ph, FL, PY, C, BBF, BKE, BEP), and perylene (PER). Traces of hopane (T19) but not norhopane (T15) are observed along with other steranes, presumably of biogenic origin. Quantified SHC data are not available for 2016 and 2017 mussel samples. The dotted red line denotes the sample-specific MDL as neither hopane nor NBT2 were present for scaling.

Gold Creek Reference Station

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 (Figure 18 and Table 8). In GOC profiles of that era, mixed dissolved-phase, petrogenic, and pyrogenic signals were common and roughly trending with similar phase patterns or discharge events at AMT (Payne et al., 2008a,b; 2010a; 2015). After 2002, as TPAH levels in mussels at both stations trended lower, the signals at GOC have been close to or just slightly above those at AMT, largely due to pyrogenic and occasional petrogenic components. An exception to this mostly parallel trend occurred in 2004 when the PAH and SHC profiles at GOC showed evidence of a fresh diesel spill (Figure 18). The diesel signal had largely cleared by summer 2005, and then the TPAH levels again generally tracked with AMT through July 2015. In July 2016, the GOC TPAH concentrations dropped back to 27 ng/g DW while the corresponding levels at AMT dropped to all-time lows at 8 ng/g DW. In 2017, the TPAH at GOC and AMT were both in single digits at 8 and 6 ng/g DW, respectively.

Interpreting the 2017 profiles, the replicate GOC mussel sample samples (Figure 23) showed no evidence of input from the BWTF discharges. Also, all evidence of the 2016 diesel spill (presumed related to a fisheries opening) described in detail last year (Payne and Driskell, 2017b) had disappeared.

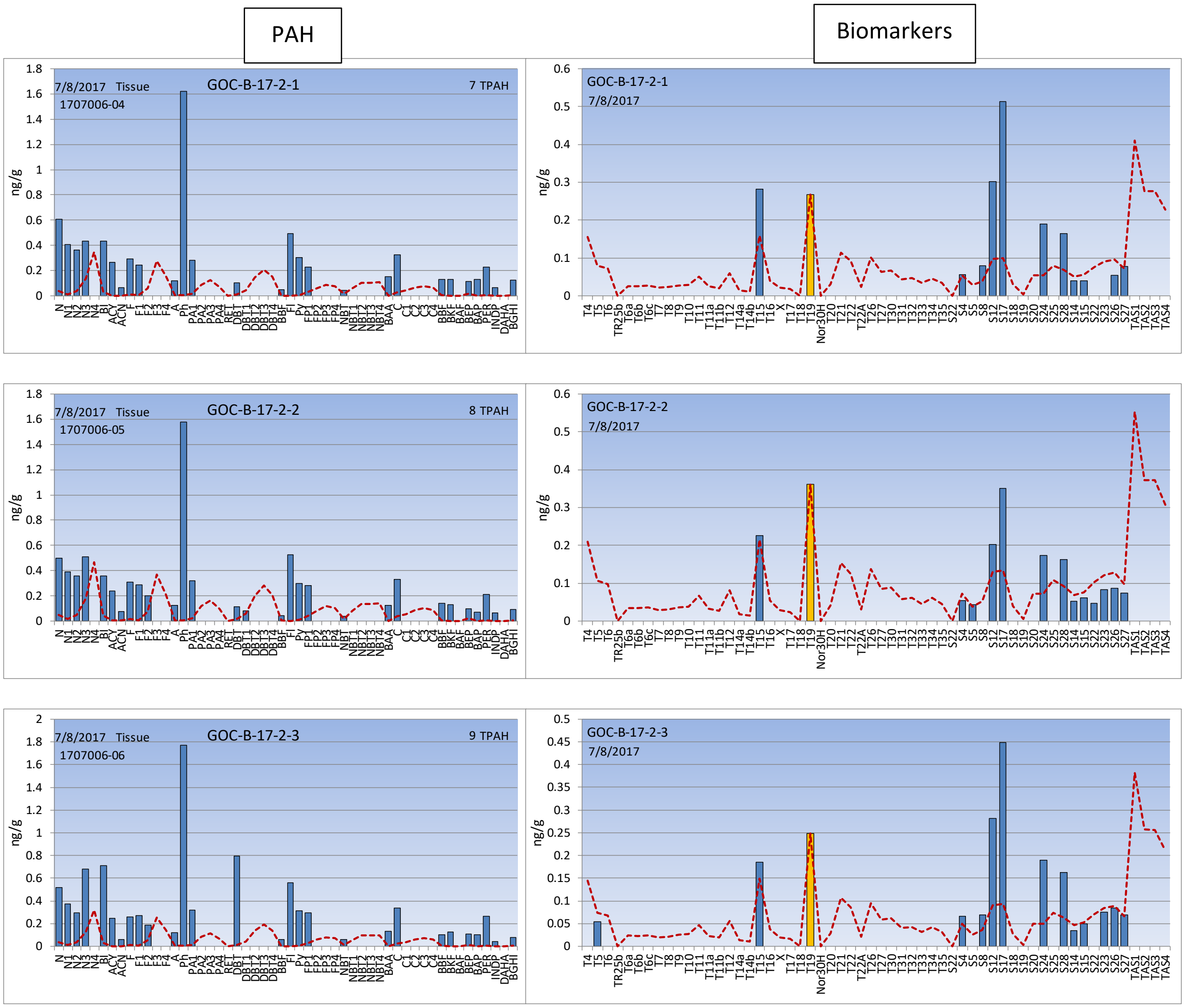


Figure 23. Replicate 2017 Gold Creek (GOC) mussel samples presented together to allow direct comparison of absolute PAH and biomarker concentrations and patterns. The dotted red line is BWTF effluent normalized against the sample's hopane. No evidence of PAH or biomarker accumulation from the BWTF effluent is observed in any of the replicates, and the PAH, biomarker, and SHC patterns from the diesel spill described in last year's report (Payne and Driskell, 2017b) are no longer visible (see Figure 24 and Figure 25).

The time-series PAH plots from Gold Creek (Figure 24) show dissolved-phase naphthalenes plus combustion products in 2008, and dissolved-phase naphthalenes along with at- or below-method detection limit (MDL) traces of combustion products in the 2015 samples. By 2016, the PAH pattern shows a well-defined, above-MDL, alkylated fluorene (F) and phenanthrene/anthracene (PA) pattern indicative of diesel contamination plus background combustion products and perylene. There was no evidence of residual PAH from the 2016 GOC diesel spill in the 2017 samples. Perylene, can occur naturally, generated by biologic processes or early stages of diagenesis in marine sediments (Bence et al., 2007). Hence, it was no surprise that perylene traces seen in the AMT mussels in 2016 (Figure 21) were also observed at GOC at the same times (Figure 24), thus supporting a ubiquitous biogenic-source concept. SHC in 2008 and 2015 are mostly trace-level biogenic components (e.g., n-C_{15},

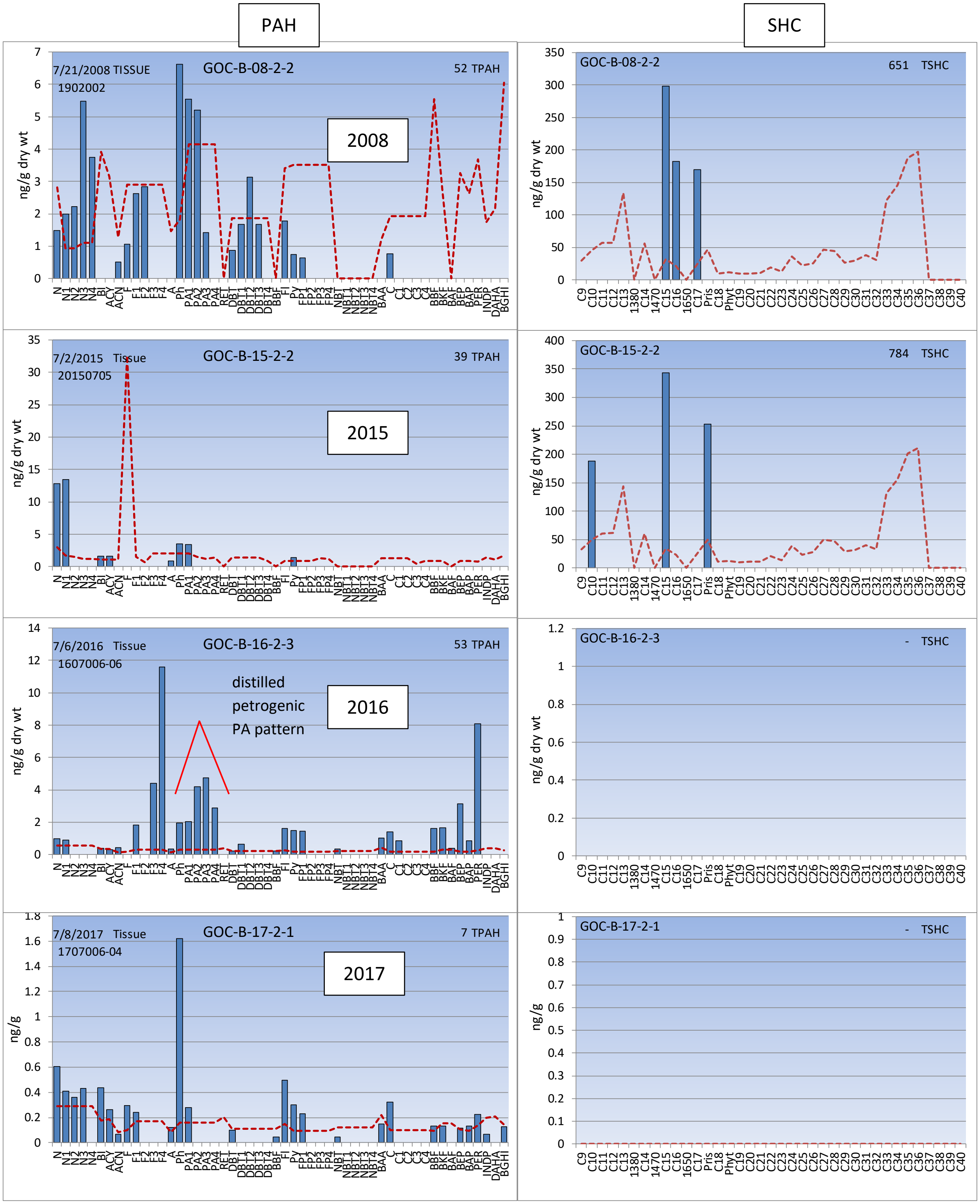
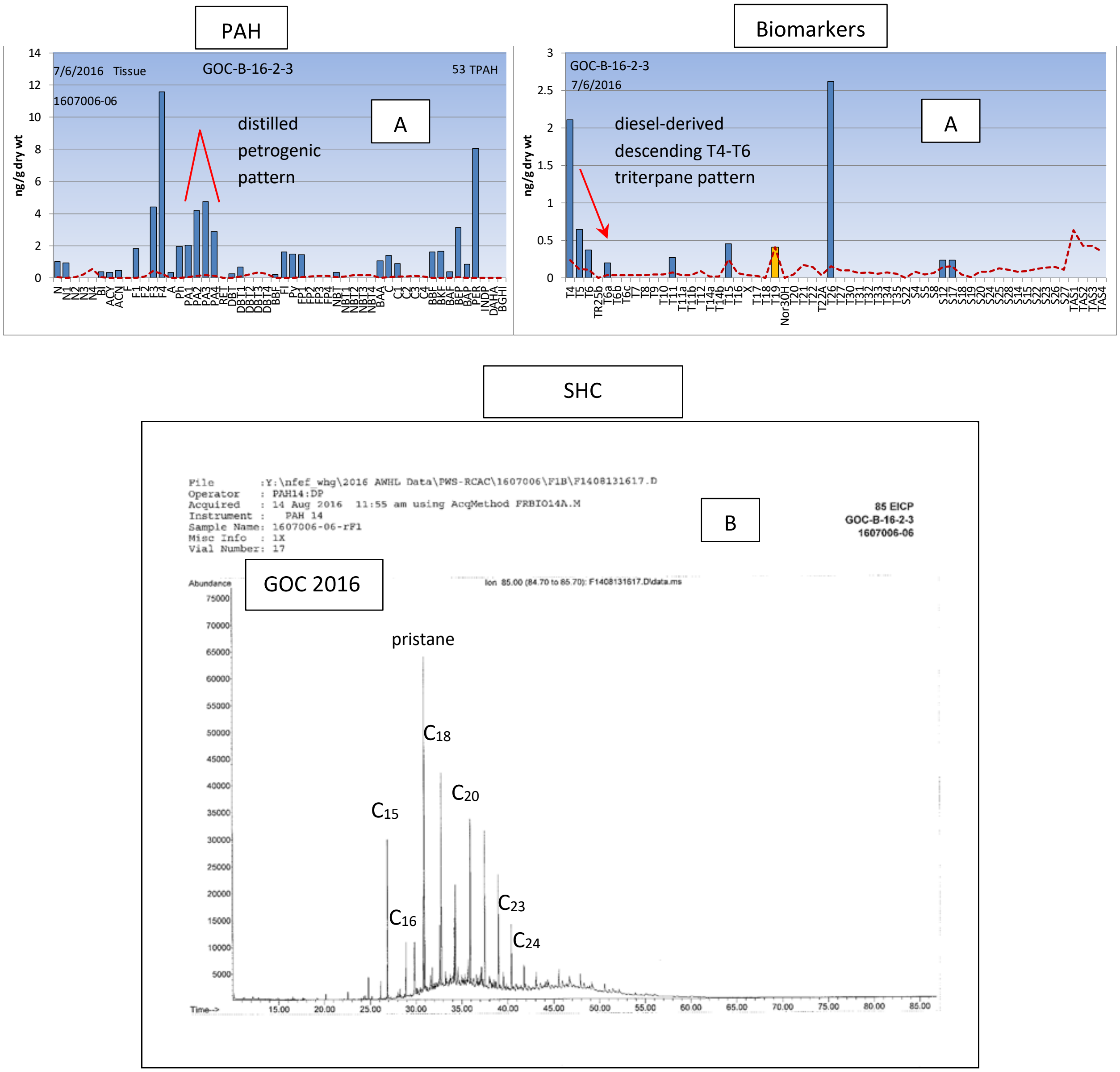


Figure 24. Time-series PAH and SHC profiles of mussels collected at GOC. Dotted red line denotes the sample-specific MDLs. PAH profiles suggest dissolved-phase naphthalenes plus combustion products in 2008, dissolved-phase naphthalenes in the 2015, and petrogenic fluorenes (F1, F3 and F4) and C1-C4 alkylated PA from a diesel spill in 2016. There is no evidence of BWTF effluent or residual diesel in 2017. SHC in 2008 and 2015 are derived from marine phytoplankton, and copepods. GC/FID SHC data are not available for 2016 and 2017 but SIM *m/z* 85 data were used to identify the diesel signal in 2016 (see Figure 25).

n-C_{17}, and pristane) derived from marine phytoplankton, algae, and copepods (Payne et al., 2015). No SHC data were obtained in 2016 or 2017 but as described in Payne and Driskell (2017b), SIM *m/z* 85 GC/MS profiles (Figure 25) confirmed the presence of low-level diesel contamination.



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Acquired    : 14 Aug 2016  11:55 am using AcqMethod FRBIO14A.M
Instrument  :   PAH 14
Sample Name: 1607006-06-rF1
Misc Info   : 1X
Vial Number: 17
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Figure 25. PAH, Biomarker and SHC plots documenting the 2016 diesel spill at Gold Creek: A) 2016 GOC mussel tissue PAH and biomarker patterns with red tent over the PA pattern and descending T4, T5 and T6 triterpanes (red arrow) over the biomarkers derived from recent diesel input. The dotted red line in the upper plots is BWTF effluent normalized against the sample's hopane; B) Reconstructed ion chromatogram (*m/z* 85) of GOC tissue with biogenic C_{15} and pristane plus the characteristic C_{16}-C_{24} (odd/even ratio = 1) n-alkane pattern from weathered diesel oil. No evidence of PAH, biomarker or SHC accumulation from the BWTF effluent is observed but the data show unequivocal evidence of a recent diesel spill.

PASSIVE SAMPLING DEVICES

Passive sampling devices (PSD) were deployed at the three Port Valdez sites in 2016 to sample concurrent with the mussel collections (Minick and Allan, 2016). Generally, a passive sampler device will only sample a fraction of the total analyte present; freely dissolved species and labile complexes as well as conjugated species that diffuse into the membrane. For LTEMP, the devices were deployed for a month and were expected to sample dissolved and oxygenated hydrocarbons. After processing and analysis at OSU, the resulting PSD data were ambiguous. The expected oxygenated forms were not detected and without the full suite of alkylated PAH analyses and biomarkers, forensic insights were limited. Minick and Allan suggest a pyrogenic naphthalene signature but considering the sampling device, it's more likely from dissolved naphthalenes. The reported presence of two insoluble hopanes suggest the device and analyses were seeing particulate hydrocarbons, too. From GOC, they showed slightly elevated parent phenanthrene (compared to AMT and JAP) but there was no discernible evidence of the diesel spill.

SUMMARY TRENDS

- In 2016 and 2017, our forensics understanding was greatly improved by analyses (PAH, SHC, and biomarker) of phase-separated, seasonal effluent samples from the Biological Treatment Tank (BTT) at Alyeska's Ballast Water Treatment Facility (BWTF). 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 sample.
- 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, oil inputs into Port Valdez from the Alyeska Marine Terminal and tanker operations, permitted oil inputs to the Port have been declining in recent years.
- TPAH concentrations in mussels at AMT, JAP and GOC are now reaching all-time, single-digit lows (ng/g DW, ppb).
    - At AMT, mussel PAH contamination over the last ten-plus years has been shifting away from the earlier petrogenic profiles towards trace-level background, dissolved-phase or pyrogenic patterns.
    - GOC mussels have generally shown only low-level pyrogenic PAH profiles since 2006 but in 2016, evidence of a diesel spill was observed. All evidence of the previous year's spill had disappeared by 2017.
    - The 2008-2015 saturated hydrocarbons (SHC) in mussels from all locations exhibited primarily background biogenic components with the exception of a petrogenic signal at AMT in 2013. Quantified mussel SHC data were not available for 2016 or 2017.
- 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, the 2016 and 2017 AMT sediment PAH patterns are nearly identical but have shifted from a dominant pyrogenic pattern in recent samples (2011–2015) to a mix with highly weathered petrogenic components derived from the BWTF effluent. Biomarker profiles from 2011 through 2017 strongly confirm the linkage to the BWTF effluent. SHC patterns show a mixture of marine and terrestrial biogenic components along with higher-molecular-weight petrogenic waxes at reduced levels compared to earlier years. Based on the signatures, these patterns suggest variable or increased background inputs of weathered ANS oil plus combustion products from local vessel traffic, runoff, or aerial deposition.

- At the GOC 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 terrestrial plant waxes. With the additional biomarker constituents now being reported, it appears that trace-level accumulations of biomarkers associated with the BWTF effluent are indeed accumulating in GOC sediments and have been since biomarkers were first reported in 2011. The concentrations are very low (at or just above the reporting limit), and there are numerous missing components but key diagnostic biomarkers are present and similar to the BWTF effluent in most samples. Because these petrogenic biomarker components are much more resistant to weathering compared to PAH and SHC, they can be observed and attributed to the Terminal even when PAH and SHC are largely absent or dominated by combustion sources.

BEYOND LTEMP

Other than 2017 LTEMP results, there have been no new data from other studies to report for relevant comparisons. This section thus repeats from last year's report but is included for interest of new readers.

How do these levels compare with other Alaskan sites? Unfortunately, comparable studies are scarce, no longer current, and variable about which analytes are actually summed but the earlier reported values still seem reasonable (Table 9). 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 compares favorably and 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 2013's 18-73 ng/g DW levels at Gulf of Alaska sites (overall average 50 ng/g DW). These data also suggest a natural dissolved-phase background TPAH somewhere around 20-30 ng/g DW.

Reaching farther, data from the 2004-2005 National Status and Trends, Mussel Watch Program (Figure 26) and 2008-2010 Alaskan sites (Figure 27) (now summing only 38 parent and alkylated PAH homologues versus 44 LTEMP PAH analytes) show that average TPAH concentrations in mussels for other West Coast sites have been nearly 66 times higher at 825 ng/g DW. 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 Alaskan 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 (Table 9), the LTEMP results for Port Valdez, PWS, and GOA sites demonstrate that these remote locations are still exceptionally clean.

Finally, a 2005 EVOS Trustees Program, Long-Term Monitoring of Anthropogenic Hydrocarbons in the *Exxon Valdez* Oil Spill Region, examined ten 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. Rates of disappearance had diminished to an estimated 4% yr^{-1}. If left undisturbed, Short et al. (2007) predicted they would be there for decades. Revisiting the sites in 2015, Auke Bay researchers found mostly unchanged conditions since 2001 (Lindeberg et al., 2018).

Table 9. Current TPAH concentrations (2017) in regional mussel tissues (ppb, ng/g DW) relative to 2004-2010 NOAA Mussel Watch monitoring data and a recovered Alaskan oil-spill event.

LTEMP	2017	Port Valdez tissues	AMT, JAP & GOC	6-19
	2016	Port Valdez tissues	AMT, JAP & GOC	6-53
	2015	Port Valdez tissues	AMT & GOC	39-87
		PWS (KNH & SHB)	KNH & SHB	19-46
	2013	Port Valdez tissues	AMT & GOC	17-20
		PWS	Six stations (see Figure 2)	9-33
		GOA	Three stations (see Figure 2)	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	2008	Cook Inlet	Bear Cove	119
		Cook Inlet	Homer Spit	208
		Port Valdez	Alyeska Marine Terminal	52
		Port Valdez	Gold Creek	31
	2009	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
	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
M/V Kuroshima (1997)		Unalaska	2004 followup	25-85

Lindeberg et al. again concluded that the estimated 0.6% *Exxon Valdez* oil would remain sequestered and not bioavailable 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).

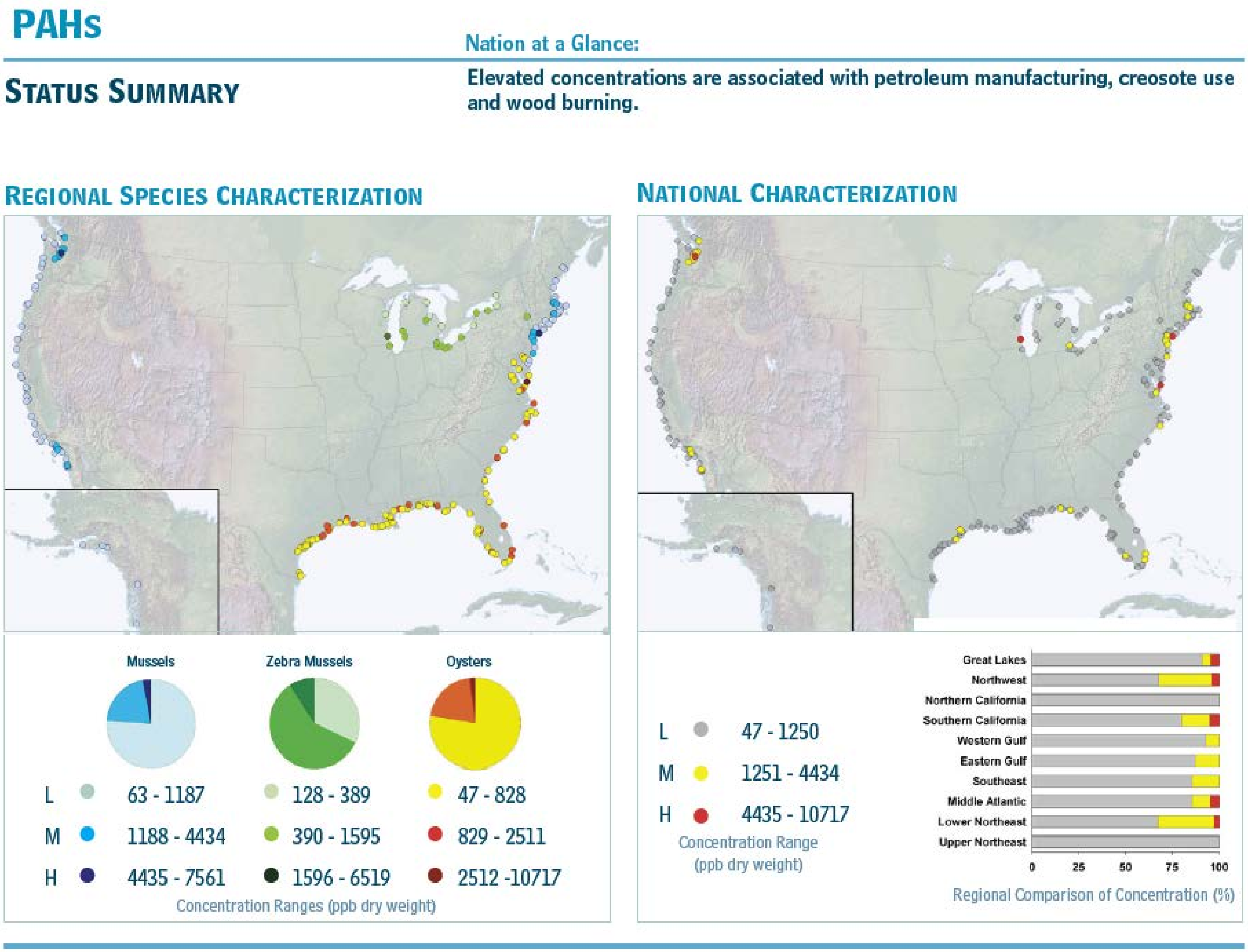
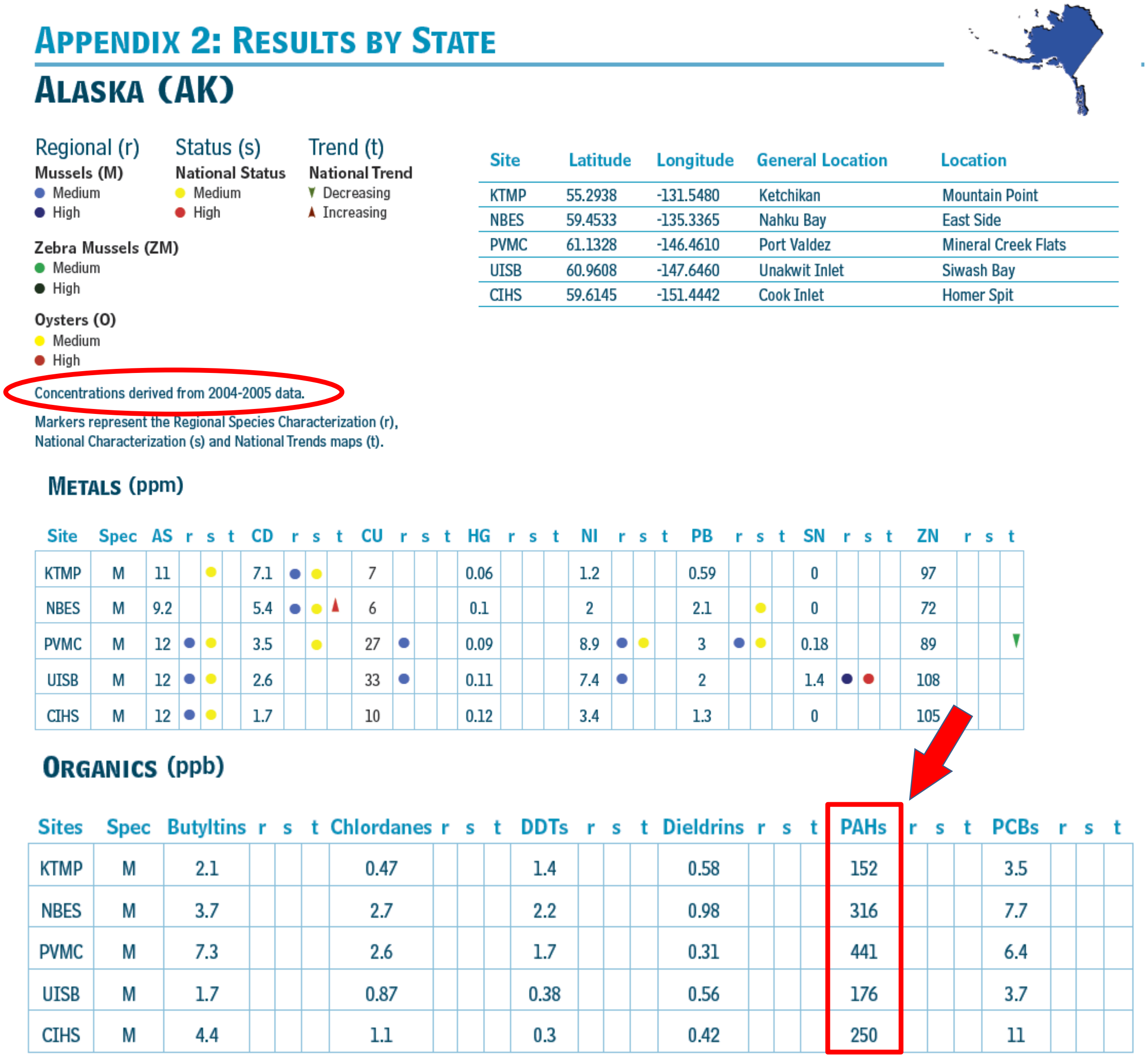


Figure 26. Status and trends result from National Mussel Watch data (Kimbrough et al., 2008). All Alaskan sites characterized as low concentrations.



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

CONCLUSIONS

In recent years, the petrogenic hydrocarbon (oil) inputs into Port Valdez from the Alyeska Marine Terminal (AMT) and tanker operations have been declining as reflected in total polycyclic aromatic hydrocarbon (TPAH) concentrations in both sediments and mussels. As concluded in our earlier reports, this trend reflects 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 PAH.

In 2016, our forensics' approach to tracking Alaska North Slope (ANS) oil was greatly improved by the collection and detailed analyses of effluent samples from the Biological Treatment Tank (BTT) at Alyeska's Ballast Water Treatment Facility (BWTF).

In 2016 and 2017, the AMT sediment PAH reverted back to a mix of low-level petrogenic components that showed significant additional hydrocarbon weathering compared to the recently sampled BWTF effluent. The biomarker profiles from 2011 through 2017 AMT sediments, however, strongly confirm that the source is directly linked to the BWTF effluent. The sediment SHC patterns at the terminal show a mixture of marine and terrestrial biogenic components along with higher-molecular-weight petrogenic waxes at reduced levels compared to earlier years. Based on the signatures, these patterns suggest variable or increased inputs of weathered ANS oil plus combustion products from local vessel traffic, runoff, or aerial deposition.

At the GOC reference site, the sediment PAH profiles are dominated by low-level naphthalenes and combustion products. The SHC profiles in GOC sediments continue to be biogenic, reflecting only background inputs of terrestrial plant waxes. With the more extensive Alpha/Newfields biomarker data set in 2016 and 2017, it appears that in addition to natural background biomarkers, near- or above-MDL-traces of some ANS-derived biomarkers are accumulating in the GOC sediments. While the GOC sedimentary biomarker data are sparse (with many missing components), the observed constituents and hopane to norhopane ratios are now unequivocal. However, there is no evidence of BWTF-derived PAH or SHC accumulation at that site.

The 2016 addition of mussel collections at Jackson Point (JAP) within the terminal port but east of the traditional AMT station at Saw Island was meant to correlate tissue data with trial passive-sampling devices (PSD) being deployed subsurface at the same terminal locations and to evaluate a potential PAH gradient to either side of the BWTF outfall. Both locations showed very similar tissue PAH and biomarker profiles but with no suggestion of BWTF-derived uptake. No gradient was found. PSD data appear in a separate report.

The Gold Creek (GOC) reference site mussels have generally shown only low-level pyrogenic PAH profiles since 2006 but in 2016, evidence of a diesel spill was observed. By 2017, all traces of the diesel spill had disappeared. The 2008-2015 saturated hydrocarbons (SHC) in mussels from both locations exhibited primarily background biogenic components with the exception of a petrogenic signal at AMT in 2013. Unfortunately, SHC data were not measured by GC-FID in 2016 but the laboratory did analyze for *m/z* 85 ions as part of the tissues' SIM GC/MS biomarker analyses, and those data (while technically not quantifiable) along with the tissue biomarker profiles, confirmed the presence of trace-level n-alkanes characteristic of diesel oil at GOC in 2016.

By comparison, analysis of the PSDs deployed at GOC during the preceding month and recovered during the mussel sampling in July 2016 showed slightly elevated parent phenanthrene (compared to AMT and JAP) but without the benefit of alkylated PAH analyses and biomarkers, there was no discernible evidence of the diesel spill. PSD data for the 2017 collections were not available at the time of this writing.

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

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

ANALYTES	**Abbreviation**
PAH	
Naphthalene	N
C1-Naphthalene	N1
C2-Naphthalene	N2
C3-Naphthalene	N3
C4-Naphthalene	N4
Biphenyl	BI
Acenaphthylene	ACY
Acenaphthene	AEN
Fluorene	F
C1-Fluorene	F1
C2-Fluorene	F2
C3-Fluorene	F3
Anthracene	A
Phenanthrene	Ph
C1-Phenanthrene/Anthracene	PA1
C2-Phenanthrene/Anthracene	PA2
C3-Phenanthrene/Anthracene	PA3
C4-Phenanthrene/Anthracene	PA4
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	BA
Chrysene	C
C1-Chrysene	C1
C2-Chrysene	C2
C3-Chrysene	C3
C4-Chrysene	C4

Benzo(b)fluoranthene	BBF
Benzo(k)fluoranthene	BKF
Benzo(a)fluoranthene	BAF
Benzo(e)pyrene	BEP
Benzo(a)pyrene	BAP
Perylene	PER
Indeno(1,2,3-cd)pyrene	INDP
Dibenzo(a,h)anthracene	DAHA
Benzo(g,h,i)perylene	BGHI
Total PAH	TPAH

Saturated hydrocarbons (SHC or n-alkanes)

n-Decane	C10
n-Undecane	C11
n-Dodecane	C12
n-Tridecane	C13
n-Tetradecane	C14
n-Pentadecane	C15
n-Hexadecane	C16
n-Heptadecane	C17
Pristane	Pristane
n-Octadecane	C18
Phytane	Phytane
n-Nonadecane	C19
n-Eicosane	C20
n-Heneicosane	C21
n-Docosane	C22
n-Tricosane	C23
n-Tetracosane	C24
n-Pentacosane	C25
n-Hexacosane	C26
n-Heptacosane	C27
n-Octacosane	C28
n-Nonacosane	C29
n-Triacontane	C30
n-Hentriacontane	C31
n-Dotriacontane	C32
n-Tritriacontane	C33
n-Tetratriacontane	C34
Total n-Alkanes	TALK
Calibrated analytes are boldfaced.	

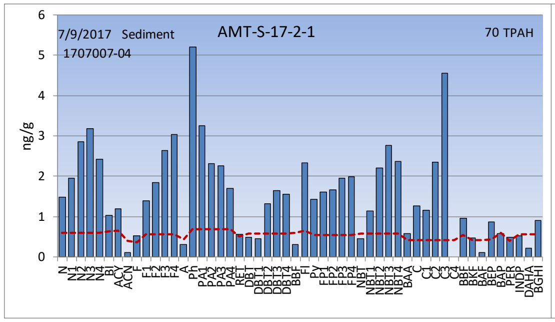
Petroleum Biomarkers

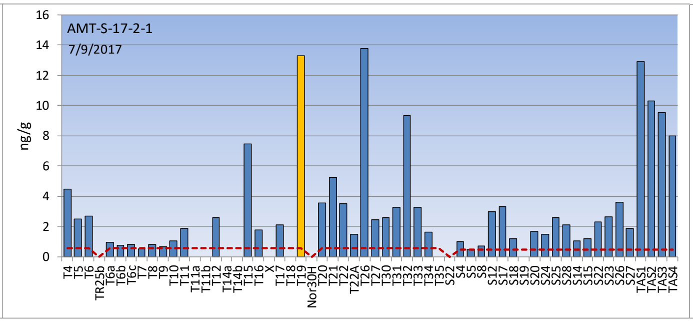
Class	Biomarker	Abbrev
Terpanes	C23 tricyclic terpane	T4
	C24 tricyclic terpane	T5
	C25 tricyclic terpane (a)	T6
	C25 tricyclic terpane (b)	T6
	C24 tetracyclic terpane	T6a
	C26 tricyclic terpane (a)	T6c
	C26 tricyclic terpane (b)	T6b
	C28 tricyclic terpane (a)	T8
	C28 tricyclic terpane (b)	T7
	C29 tricyclic terpane (a)	T10
	C29 tricyclic terpane (b)	T9
Hopanes	18α(H),21β(H)-22,29,30-trisnorhopane	Ts
	17α(H),21β(H)-22,29,30-trisnorhopane	Tm
	17α(H),18α(H),21β(H)-28,30-bisnorhopane	14a
	17α(H),21β(H)-25-norhopane	14b
	17α(H),21β(H)-30-norhopane	T15
	18α(H),21β(H)-30-norneohopane	T16
	17β(H),21α(H)-30-norhopane (normoretane)	T17
	18α(H) and 18β(H)-oleanane	T18
	17α(H),21β(H)-hopane	T19
	17α(H)-30-nor-29-homohopane	
	17β(H),21α(H)-hopane (moretane)	T20
	22S-17α(H),21β(H)-30-homohopane	T21
	22R-17α(H),21β(H)-30-homohopane	T22
	Gammacerane	T22a
	22S-17α(H),21β(H)-30,31-bishomohopane	T26
	22R-17α(H),21β(H)-30,31-bishomohopane	T27
	22S-17α(H),21β(H)-30,31,32-trishomohopane	T30
	22R-17α(H),21β(H)-30,31,32-trishomohopane	T31
	22S-17α(H),21β(H)-30,31,32,33-tetrakishomohopane	T32
	22R-17α(H),21β(H)-30,31,32,33-tetrakishomohopane	T33
	22S-17α(H),21β(H)-30,31,32,33,34-pentakishomohopane	T34
	22R-17α(H),21β(H)-30,31,32,33,34-pentakishomohopane	T35
Steranes	C22 5α(H),14β(H),17α(H)-sterane	
	C27 20S-13β(H),17α(H)-diasterane (diacholestane)	S4
	C27 20R-13β(H),17α(H)-diasterane (diacholestane)	S5
	C27 20S-5α(H),14α(H),17α(H)-cholestane	S12
	C27 20R-5α(H),14β(H),17β(H)-cholestane	S14
	C27 20S-5α(H),14β(H),17β(H)-cholestane	S15

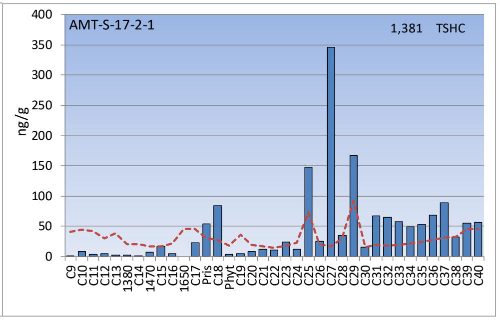
	C27 20R-5α(H),14α(H),17α(H)-cholestane	S17
	C28 20S-5α(H),14α(H),17α(H)-ergostane (methylcholestane)	S20
	C28 20R-5α(H),14β(H),17β(H)-ergostane (methylcholestane)	S22
	C28 20S-5α(H),14β(H),17β(H)-ergostane (methylcholestane)	S23
	C28 20R-5α(H),14α(H),17α(H)-ergostane (methylcholestane)	S24
	C29 20S-5α(H),14α(H),17α(H)-stigmastane (ethylcholestane)	S25
	C29 20R-5α(H),14β(H),17β(H)-stigmastane (ethylcholestane)	S26
	C29 20S-5α(H),14β(H),17β(H)-stigmastane (ethylcholestane)	S27
	C29 20R-5α(H),14α(H),17α(H)-stigmastane (ethylcholestane)	S28

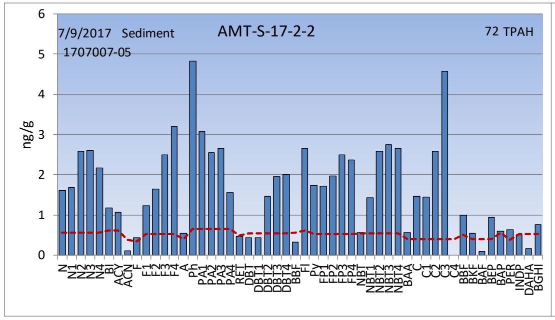
APPENDIX 2. Analytic Results for 2017 Field Samples and Blanks

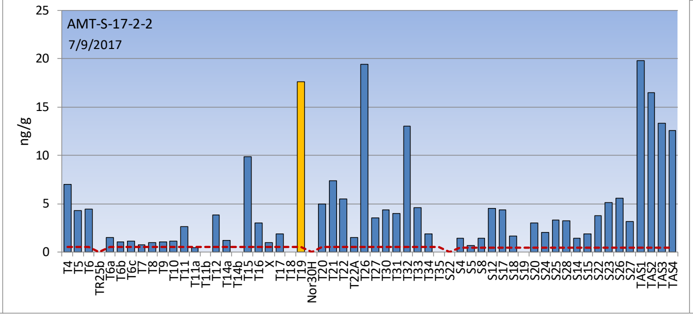
2017 AMT Sediments (PAH, Biomarkers, and SHC)

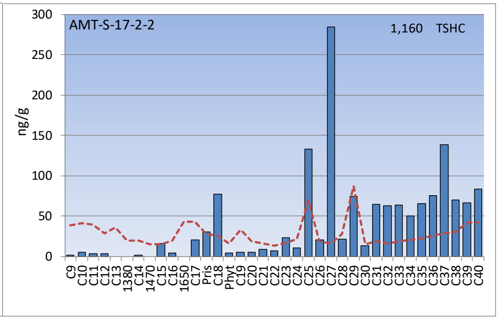


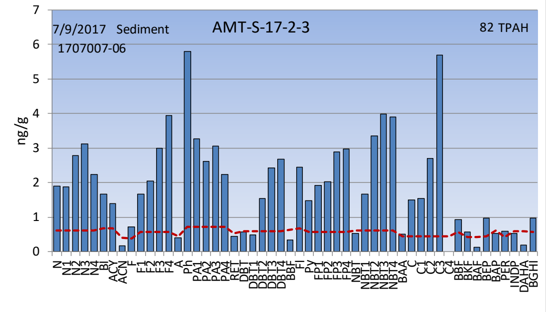


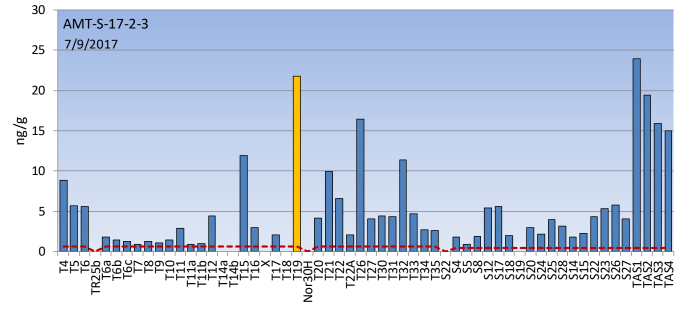


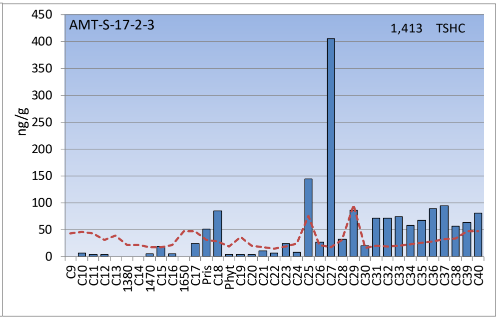






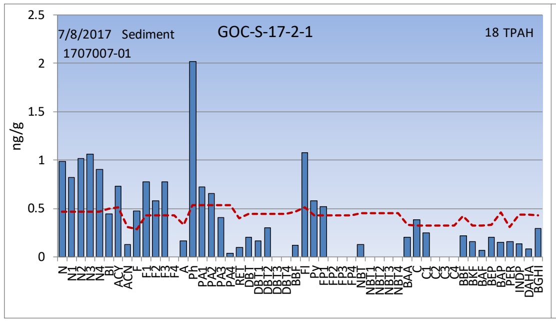


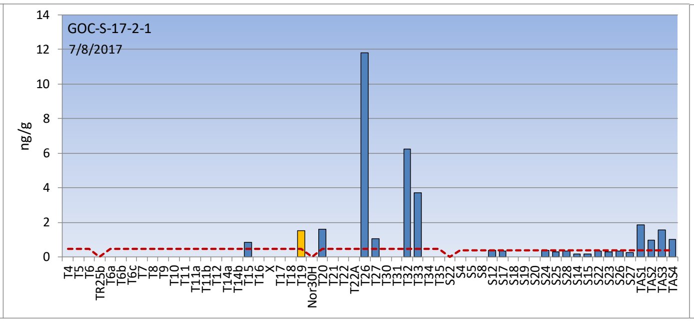


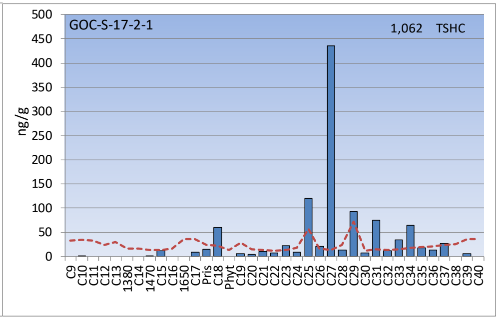


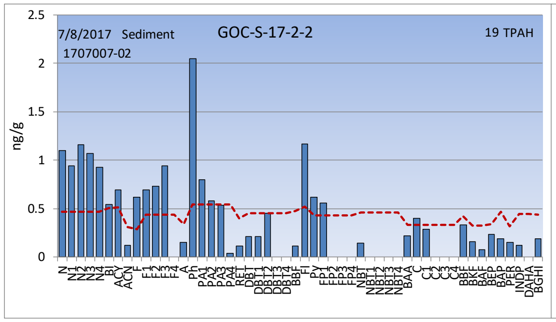
The dotted red line represents the sample-specific MDL for PAH and SHC and the Reporting Limit (RL) for biomarkers.

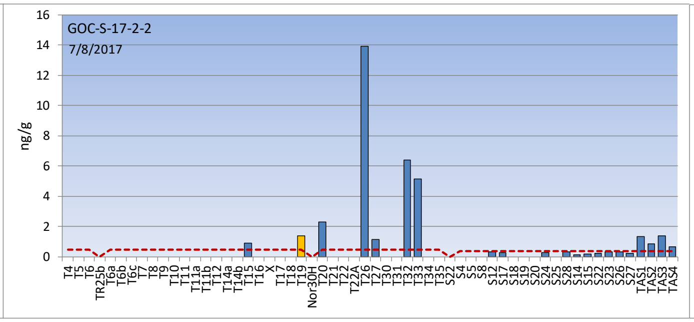
2017 GOC Sediments (PAH, Biomarkers, and SHC)

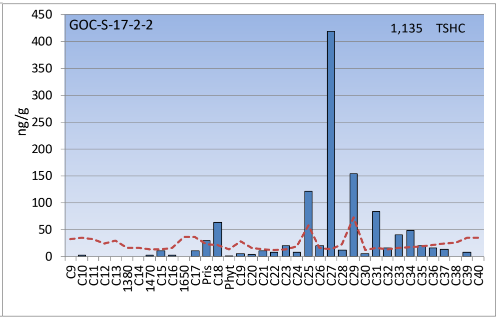


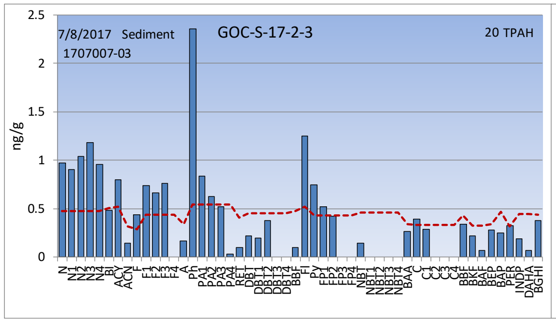


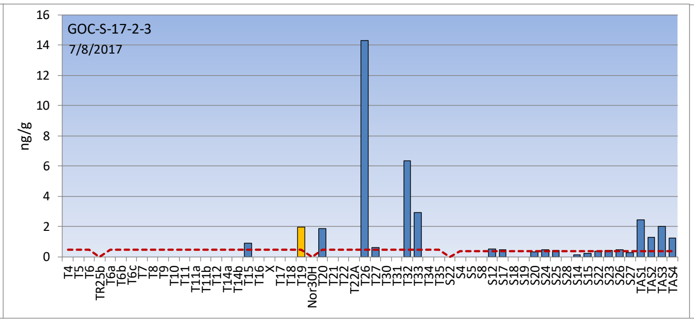


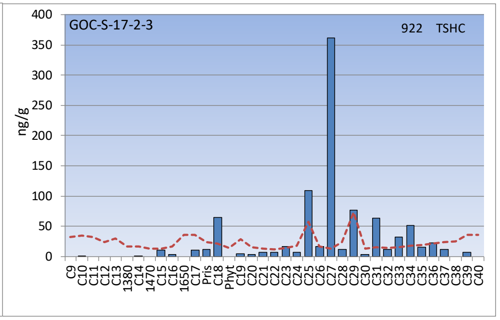






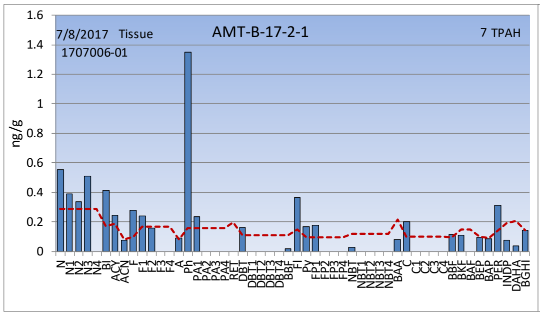


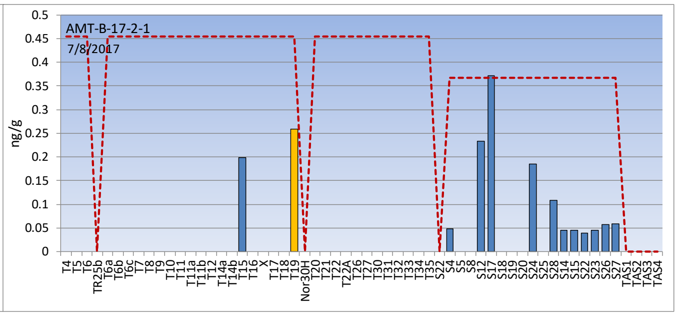


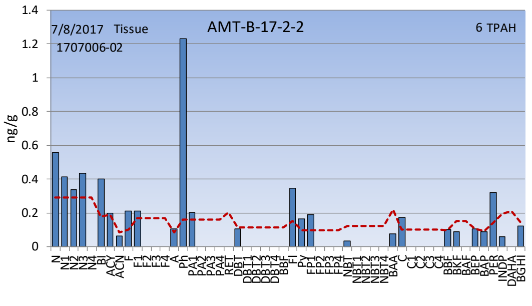


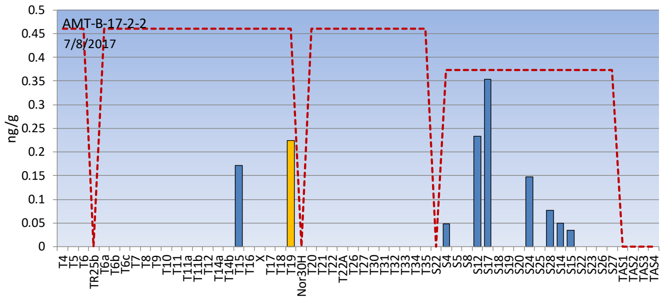
The dotted red line represents the sample-specific MDL for PAH and SHC and the Reporting Limit (RL) for biomarkers.

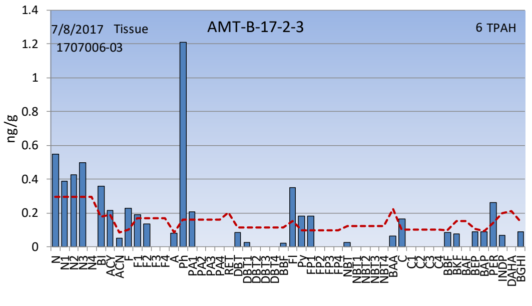
2017 AMT Tissues (PAH and Biomarkers)

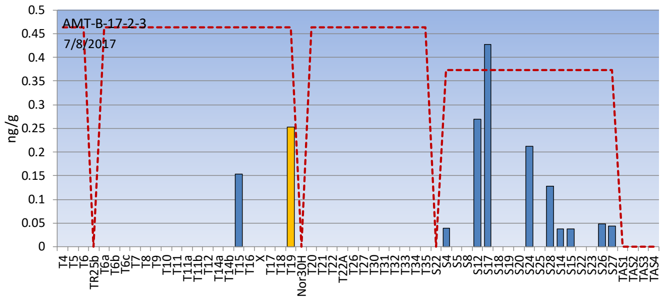






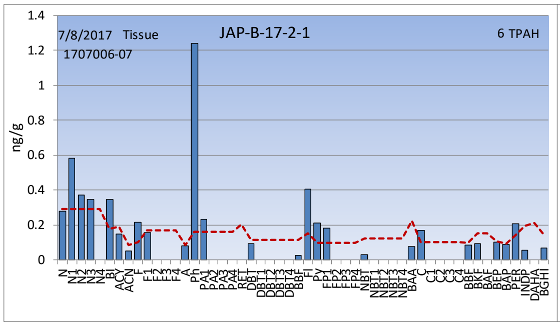


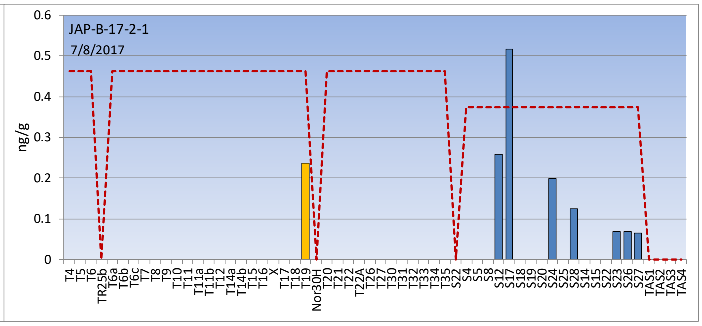


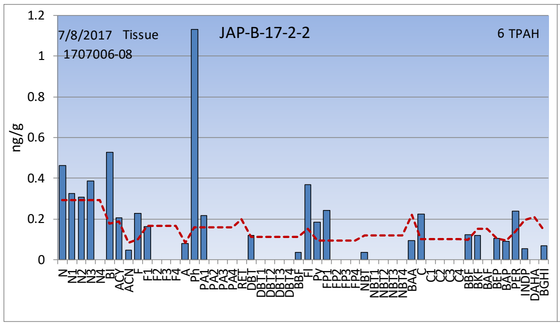


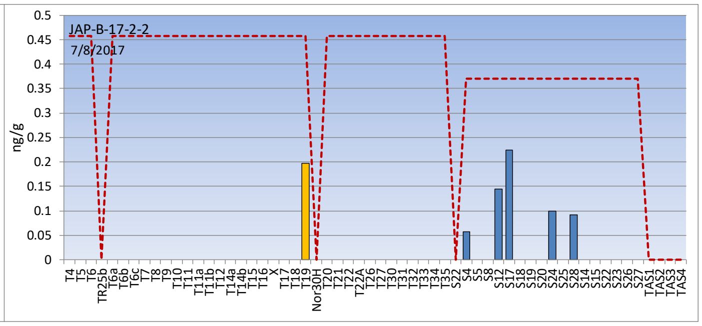
The dotted red line represents the sample-specific MDL for PAH and Reporting Limit (RL) for biomarkers.

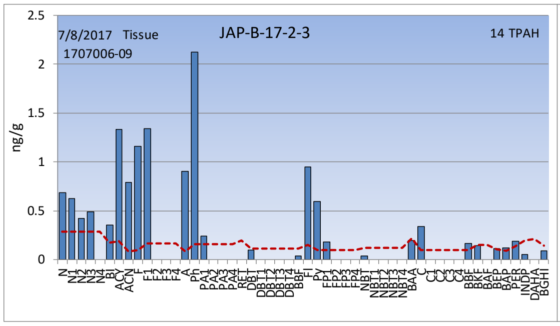
2017 JAP Tissues (PAH and Biomarkers)

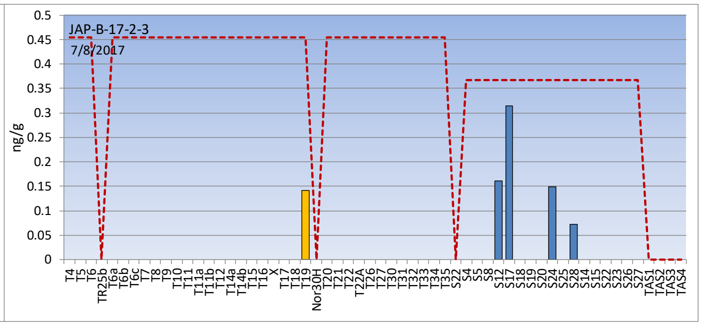






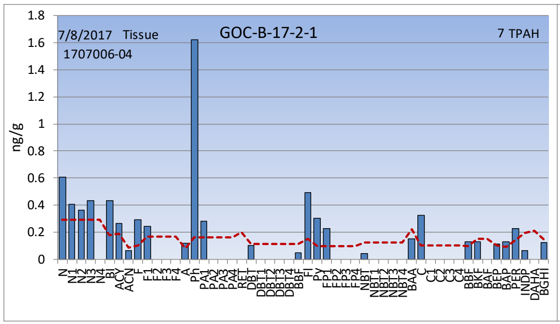


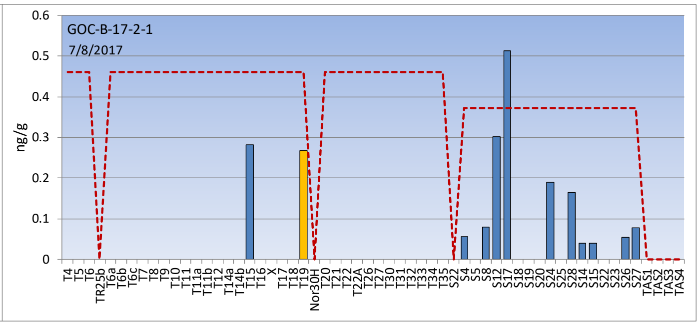


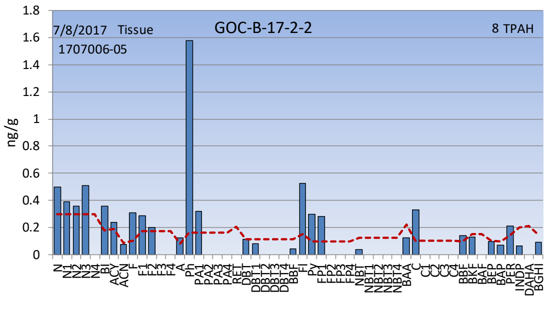


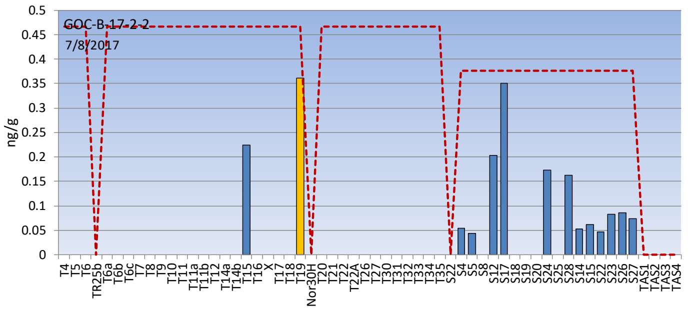
The dotted red line represents the sample-specific MDL for PAH and Reporting Limit (RL) for biomarkers.

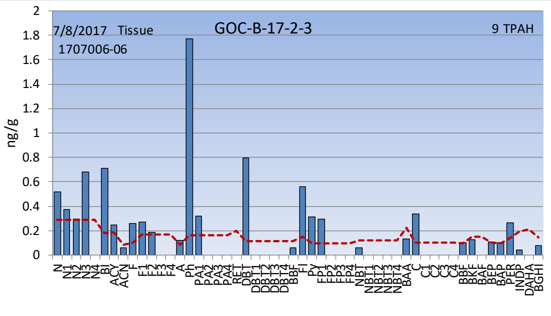
2017 GOC Tissues (PAH and Biomarkers)

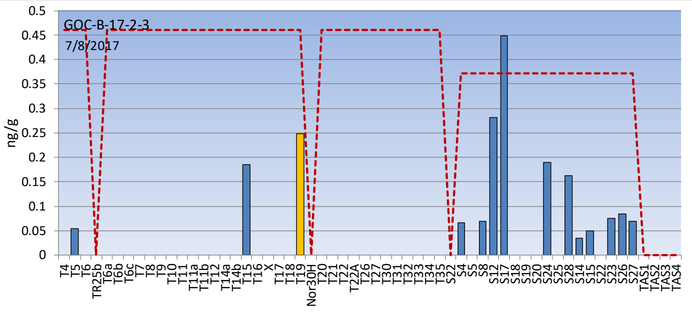








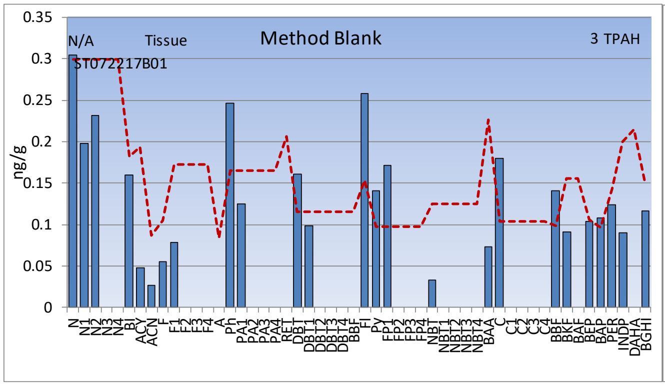


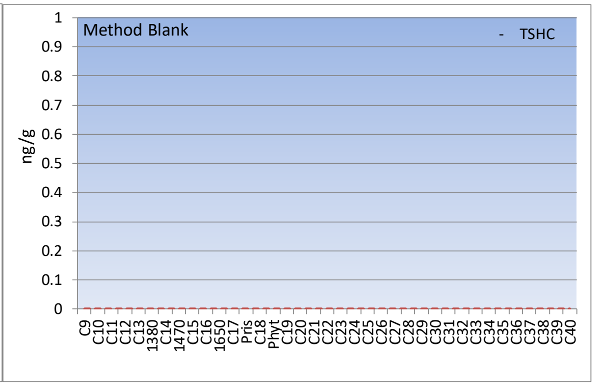


The dotted red line represents the sample-specific MDL for PAH and Reporting Limit (RL) for biomarkers.

2017 Matrix Lab Method Blanks with MDL overlay

Tissue





Sediment