LONG-TERM ENVIRONMENTAL MONITORING PROGRAM – FINAL REPORT:

2015 SAMPLING RESULTS AND INTERPRETATIONS

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C<small>ONTENTS</small>

List of Figures

List of Tables

Cover image – Tanker at Alyeska Marine Terminal Berth 5 as viewed from the LTEMP mussel sampling site on Saw Island. Photo by William B. Driskell.

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
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
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, 2015

ABSTRACT

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 mussels and sediments. This trend reflects a combination of reduced ballast-water-treatment-facility (BWTF) discharge volumes from historically decreased North Slope oil production, the transition to double-hulled tankers with segregated ballast tanks, and improved BWTF efficiency in removing particulate/oil-phase polycyclic aromatic hydrocarbons (PAH). As a result, over the last several years, mussel contamination has been generally shifting away from the terminal's petrogenic profiles to background dissolved-phase or pyrogenic PAH patterns.

Although historically, petrogenic hydrocarbons in mussels sampled from both the terminal and the background-reference site at Gold Creek (GOC) were commonly reported in hundreds of ng/g TPAH, by 2013, only very low, near method-detection-limit (MDL) traces of petrogenic components were found. From the July 2015 sampling, the character of the PAH patterns had further degraded to only dissolved-phase, background patterns at both locations. These were made up entirely of dissolved-phase hydrocarbons (naphthalenes) and just-above-MDL traces of combustion products. Average TPAH concentrations showed a modest increase between 2013 and 2015 (from 17 to 70 ng/g dry weight (DW) at AMT and from 20 to 43 ng/g DW at GOC) but based on the signatures, these changes most likely reflect variable or increased background inputs from local vessel traffic, runoff or aerial deposition. The saturated hydrocarbons (SHC) in mussel tissues at both locations exhibited only background biogenic components.

Likewise, in 2013, the sediment TPAH concentrations in the Port reached all-time lows (averaging 10 ng/g DW at AMT and 4 ng/g DW at GOC). In 2015, the TPAH concentrations increased to 30 ng/g DW at AMT, while at GOC they remained unchanged at 5 ng/g DW. The PAH patterns at AMT did not change significantly over this interval showing a mix of lower-molecular-weight petrogenic hydrocarbons augmented by higher relative concentrations of pyrogenic components. The SHC patterns at AMT show a mixture of marine and terrestrial biogenic components along with reduced levels of higher-molecular-weight petrogenic waxes. At GOC the PAH profiles during both 2013 and 2015 were dominated by dissolved-phase naphthalenes and combustion products with a relative shift to higher-molecular-weight pyrogenic hydrocarbons in 2015. At GOC, the SHC profiles continue to reflect only biogenic terrestrial plant waxes.

Oil biomarker analytes, relatively new to LTEMP sediment methods, show variable Alaska North Slope (ANS) residuals within in the Port. In 2013, ANS biomarkers were at quantifiable levels in the AMT sediments, but the concentrations were seven times lower at GOC with the profiles indicating mixtures with background sources. In 2015, the biomarkers again indicated the presence of ANS oil from BWTF operations only in the AMT sediments. The 2015 GOC biomarker concentrations and patterns were equivocal, suggesting mixed sources with little or no input from terminal operations.

Beyond the Port Valdez tanker operations area, Knowles Head (KNH) and Sheep Bay (SHB) mussels were also collected in 2015. At these two sites, background TPAH levels in mussels have modestly increased between the 2009 and 2015 collections (returning to 2002-2008 ranges, with current concentrations estimated at 29-46 ng/g

DW). The majority of this signal is due to traces of dissolved-phase naphthalenes and just-above MDL levels of pyrogenic phenanthrenes. As observed in both 2009 and 2013 sample sets, there is remarkable within-site fidelity (replicability) in PAH and SHC patterns at these stations. Although the samples each comprise only a few analytes, the components show a common complexity of dissolved and pyrogenic patterns that implies effects from a region-wide process. 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.

INTRODUCTION

PROJECT HISTORY

Under Federal and State statutes, the unregulated release of oil into the environment is strictly prohibited. To 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 program is to monitor impacts from oil transportation activities on the biota at selected sites from PWS and the Gulf of Alaska.

Alyeska's Ballast Water Treatment Facility (BWTF) treats and discharges oil-contaminated ballast water offloaded from tankers utilizing the terminal, so two stations – Alyeska Marine Terminal (AMT) adjacent to the offshore BWTF diffusers and Gold Creek (GOC) a reference station six km across the Port are of paramount interest to the program. Currently measured variables include polycyclic aromatic and saturated hydrocarbon levels (PAH and SHC) in mussel (*Mytilus trossulus*) tissues from the two stations within the Port, two stations in the eastern PWS area – Knowles Head (KNH) near the tanker anchorage and Sheep Bay (SHB) north of Cordova, and six stations, comprising the geographic reach of the *Exxon Valdez* oil spill (EVOS), sampled every five years between Valdez and Kodiak (Figure 1). Sediment samples from the two Port stations are analyzed for PAH, SHC, particle grain size, and total organic carbon content to monitor the site environments, and for the past three years, oil biomarkers have been added 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, background oil levels were higher, hot spots were identified, large and small spill events were visible in the data set, and identification of weathered sources was important (Table 5-1 in Payne et al. 1998). Subsequent to this assessment, the PWSRCAC reduced the scope of the program to biannual sampling of regional mussel tissues and Port Valdez sediments. Fall mussel sampling was added just in Port Valdez (AMT and GOC) to better track the terminal's discharge. Analyses of aliphatic hydrocarbons in mussel tissues that were dropped from the original program in 1995 due to results being confounded by lipid interference, were reinstated in 1998. Improved laboratory methods essentially eliminated interference issues.
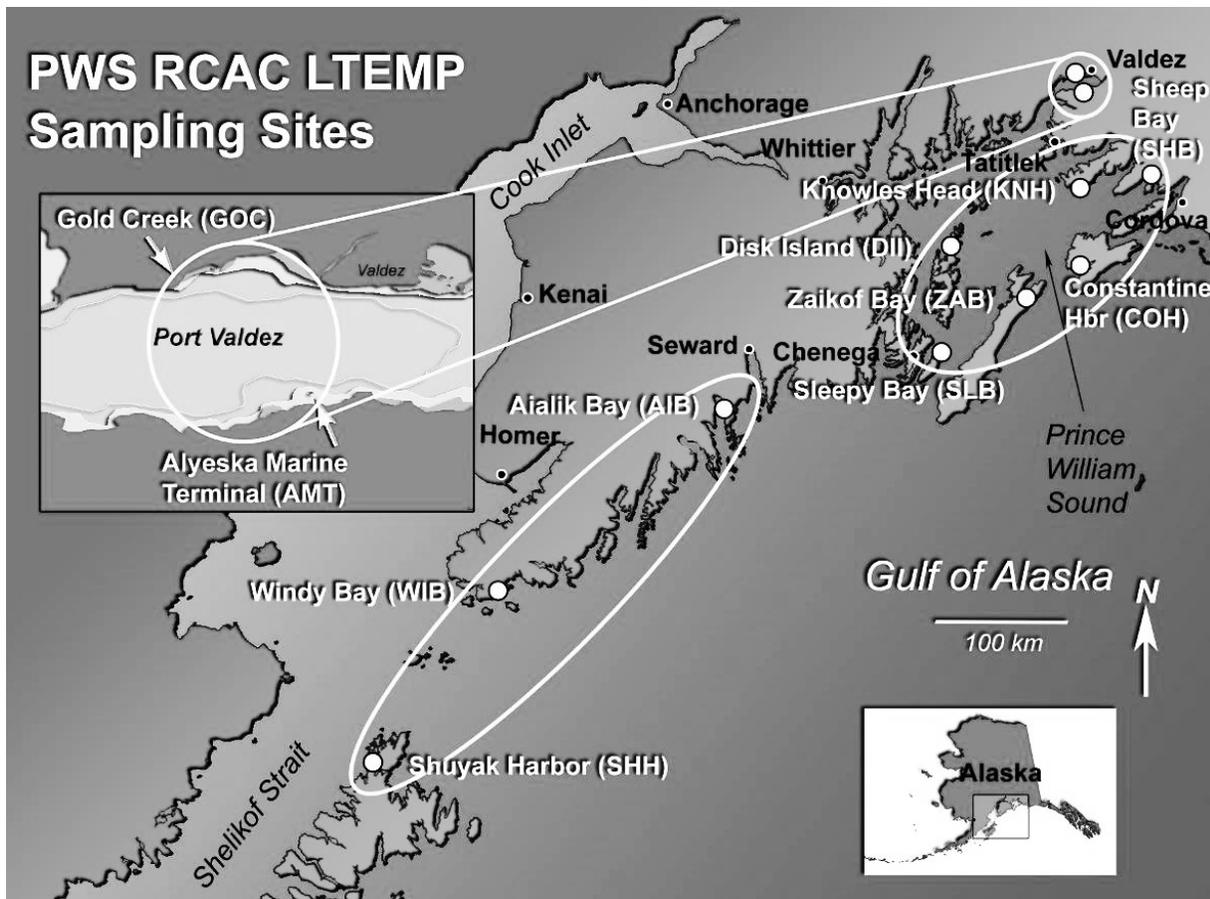
Figure 1. Map of the LTEMP sites. Circled regions represent sites with similar hydrocarbon signatures and events.

In 2001, another data evaluation and synthesis review was completed on just the LTEMP results from the Port Valdez sites (Payne et al., 2001). Data from AMT and the GOC control site suggested Alaska North Slope (ANS) crude oil residues from the terminal's ballast water treatment facility did accumulate in the intertidal mussels within the Port. However, the sediment and tissue (and the estimated water-column) PAH and SHC levels were very low. More importantly, the signatures allowed discrimination of particulate- (oil droplet) and dissolved-phase signals in the water column that correlated with seasonal uptake in mussels and, from other studies, with absorption in herring eggs. These findings gave new insight into the transport and exposure pathways in Port Valdez. The results also 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. The authors also 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., 2003a, 2005c).

In July 2002, PECI and the NOAA/NMFS Auke Bay Laboratory (ABL) began collecting and analyzing LTEMP samples. Detailed discussions of the transitional 2002/2003 LTEMP samples and inter-laboratory comparisons of split samples and Standard Reference Materials (SRMs) supplied by the National Institute of Standards and Technology (NIST) 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 are also published in *Marine Pollution Bulletin* (Payne at al., 2008b).

Recent years have brought change to the system as pipeline production has dropped from 2.03 million barrels per day at its peak in 1988 to current levels of 0.49 million barrels per day in 2015. Likewise, tanker regulations have instituted double-hulled tankers with segregated ballast. Aboard segregated-ballast vessels, empty cargo tanks are used for supplemental ballast only when operationally necessary (e.g., during winter storms). Treated-ballast water discharges to the Port have also changed from an average of about 10 million gallons per day (MGD) in 1978 to a maximum of around 15 MGD in 1990 to only 1.1 MGD in 2015. Facility operators estimate, and Discharge Monitoring Report data confirm, that more than half of the current discharge is treated 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 changes 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).

Prior to this report, all ten LTEMP sites were visited in July 2008, April 2009, and July 2013 (Figure 1); three NE sites in or near the Port to monitor terminal and tanker operations, six others to monitor the more remote sites for lingering 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. For the 2015 samplings, four of the ten LTEMP stations were visited and results interpreted in this report; Alyeska Marine Terminal, Gold Creek, Knowles Head and Sheep Bay (AMT, GOC, KNH, and SHB, respectively). As appropriate, the results are presented with the overall perspective/trend analysis from the inception of the monitoring program (1993).

METHODS

Collection and analytical methods have been described in previous LTEMP reports (Payne et al., 2003b; 2005a; 2006; 2008a, 2010a, 2015). Briefly, three replicates of mussels are collected by hand at each site while triplicate sediment samples are collected from the two locations within the Port using a modified Van Veen grab. Sampling protocols have remained the same, and the NMFS Auke Bay Laboratory has continued with the analytical chemistry measurements using their standard operating procedures (SOPs) as detailed in our previous reports. Along with the usual data for polycyclic aromatic hydrocarbons (PAH by modified Method 8270, GC/MS SIM) and saturated hydrocarbons (SHC by Method 8015, GC FID), beginning in 2011, Auke Bay also reports forty-eight petroleum biomarkers for the sediment samples. 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.

BIOMARKERS

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 was 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 only a perspective of "freshness" of the patterns plus tagging contributions from other sources. PAH compounds are more persistent, weathering slower in predictable

patterns and rates, both by molecular weight and within analyte groups, that can 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 changing and disappearing.

Biomarker analyses were done on sediments but not tissues. Compared to sediments, biomarkers from mussel tissues are generally not as effective for routine monitoring as mussels regularly purge and, currently, at most LTEMP stations, are only carrying trace-level, dissolved-phase PAH components. Water-insoluble biomarkers would only be detected in tissues when particulate oil was present (e.g., free oil droplets during a spill).

Technically, acquiring biomarker data is an extension of the EPA 8270 GC/MS method for PAH whereby four ions (191, 217, 218 and 231) are added to the mass spectrometer's list for selective ion monitoring (SIM). As a lab calibration standard, ABL normally runs a National Institute of Standards and Testing (NIST) certified standard reference material (SRM) of organics in marine sediments, either SRM 1944 or SRM 1941b. But these reference sediments have no certified values for biomarkers; for validation, we can only compare ABL results to other labs' results. Biomarker inter-lab calibrations were thus run using both ANS and Deepwater Horizon (DWH) oils (the later now a new NIST standard) (Payne et al., 2015).

Multiple approaches have been suggested for interpreting biomarker data but some degree of expert-guided pattern matching must be employed. Most approaches involve various diagnostic ratios (Wang and Stout, 2007) with several ratios normalized to the highly conservative $17\alpha(H),21\beta(H)$-hopane (also labeled T19 or C30 hopane and marked with golden fill color for visual reference in this report's 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. With 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 plus a suggested 22R homohopane (T22)/hopane ratios were used to confirm the visual similarities. The T6 triplets' ratio also would be added to the final diagnostics list for normal oil forensics but the lab has analytic issues with a co-eluting analyte. For this report, we simply present the overall patterns and an unexpected complication in their interpretations.

RESULTS AND DISCUSSION

LABORATORY QUALITY CONTROL

As in previous LTEMP reports, all analytes (Appendix 1) are reported on a blank-subtracted and surrogate-corrected, ng/g dry weight (DW) basis. Surrogates are novel or deuterated compounds added in known amounts to each raw sample in order to assess from their final percent recovery, the efficiency of extraction and analysis. In Auke Bay Laboratory SOPs (Larsen et al., 2003) surrogate recoveries are considered acceptable if they are between 30% and 120%, and if more than 10 recoveries from an entire string (analytic batch) fall outside the recovery targets, the string fails QA criteria and is reprocessed. If the majority of the failed recoveries occur in an individual sample, only that sample is reprocessed. Surrogate recovery standards were met for all PAH, biomarker and alkane surrogate hydrocarbons analyzed during the 2015 reporting period (Table 1). Laboratory method blanks for

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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.

Table 1. Surrogate recovery statistics from 2015 ABL analytic batches (n=2)

Analyte group	surrogate	average	min	max	n
PAH	NaphD8	61.9	30.1	101.1	33
	Acend10	75.4	43.3	101.2	33
	Phend10	88.9	46.5	101.6	33
	Chryd12	83.7	48.3	105.7	33
	Benad12	78.4	40.8	112.8	33
	Peryd12	79.2	42.4	110.6	33
alkanes	C12d26	60.1	45.3	64.7	31
	C16d34	86.5	69.5	101.6	31
	C20d42	66.9	53.7	81.5	31
	C24d50	56.5	45.9	67.0	31
	C30d64	57.6	42.3	78.5	31
biomarker	d-C20	97.5	85.2	103.3	13

each analytic sample batch demonstrated no significant background interference from analytical procedures, thus assuring that the analytes in the field samples represented environmental constituents and not analytical artifacts. Per ABL's standard reporting practices, the data are blank corrected.

METHOD DETECTION LIMITS

One lab-performance QC measure is the EPA-formulated, statistically-derived, analyte-specific, method detection limit (MDL). New MDLs assessed in 2010 dramatically improved the confidence in accurately quantifying low-level PAH. Dropping an order of magnitude below previously reported Auke Bay Lab MDLs, medians of PAH detection limits are now 0.02 ng/g wet weight in sediments and 0.07 ng/g wet weight in tissues (Table 2 and Appendix 2). Likewise, MDLs for SHC dropped to a median 0.26 ng/g wet weight in sediments and 1.9 ng/g wet weight in tissues. Wet weight to dry weight relationships are approximately 10:1 in tissues, 2:1 in sediments.

Table 2. Comparison of 1993-2010 Auke Bay Lab MDLs for all PAH analytes (see Appendix 2 for individual analyte MDLs).

	Tissue (ng/g wet)			Sediment (ng/g wet)		
	1993	1996	2010	1993	1996	2010
PAH						
min	0.35	0.57	0.03	0.17	0.16	0.01
max	2.20	3.69	1.86	2.15	1.29	0.10
median	0.65	1.67	0.07	0.60	0.29	0.02
SHC						
min	6.38	2.26	0.56	2.24	2.33	0.06
max	47.38	57.89	12.02	17.50	29.78	3.64
median	17.63	12.34	1.90	7.04	4.48	0.26
sample mass (g)	8	8	10	20	40	40

There are generally two views on use of MDLs; 1) censor all below-MDL data to some pre-decided level (which leads to further issues on how to deal with 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.

By definition, the USEPA 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 uncontrolled factors, lower results are not as reliable--they become estimates of lesser confidence. This reporting bulwark is certainly required when reviewing a crucial single-analyte analysis, e.g., water arsenic concentration, where the statistically determined MDL value serves its purpose of being a trustworthy limit necessary to ensure against toxic consequences. There are two differences between this example and the LTEMP dataset. First, there are no "critical values" involved in the 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. Generally, 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 PAHs appear 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 and 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 that those detected analytes 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 patterns were real and not false positives from lab or procedural artifacts. In these LTEMP data, MDLs mainly serve to tag when reported values have become, to some degree, estimated. Conversely, when an unrecognizable pattern 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.

PORT VALDEZ SEDIMENTS

ALYESKA MARINE TERMINAL
Average sediment TPAH concentrations at the 28-30 m deep Terminal Berth 4 site had plateaued since March 2005 at around 50-60 ng/g DW. These values were considerably lower than historical averages (Figure 2), but then in 2013, the concentrations dropped even further to all-time lows around 10 ng/g DW. Over this period, there has also been a shift in the PAH analyte patterns from generally petrogenic in 2008 to a mixed pattern where pyrogenic components became more dominant in 2011 and 2013. At the same time, the SHC profiles reflected more biogenic input as higher-molecular-weight petrogenic waxes generally disappeared (Figure 3). Specifically, in 2008 the petrogenic PAH patterns are characterized by the parent PAH (Ph, FL, PY, C) within each group being generally less than the C-2 or C-3 homologues yielding the hump patterns denoted by the red "tents" (Figure 3 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 (Figure 3 second panel). In the SHC plots, the 2008 alkanes were dominated by higher-molecular-weight petroleum waxes (Figure 3 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 3 second panel). In 2013, the largely pyrogenic PAH concentrations had dropped
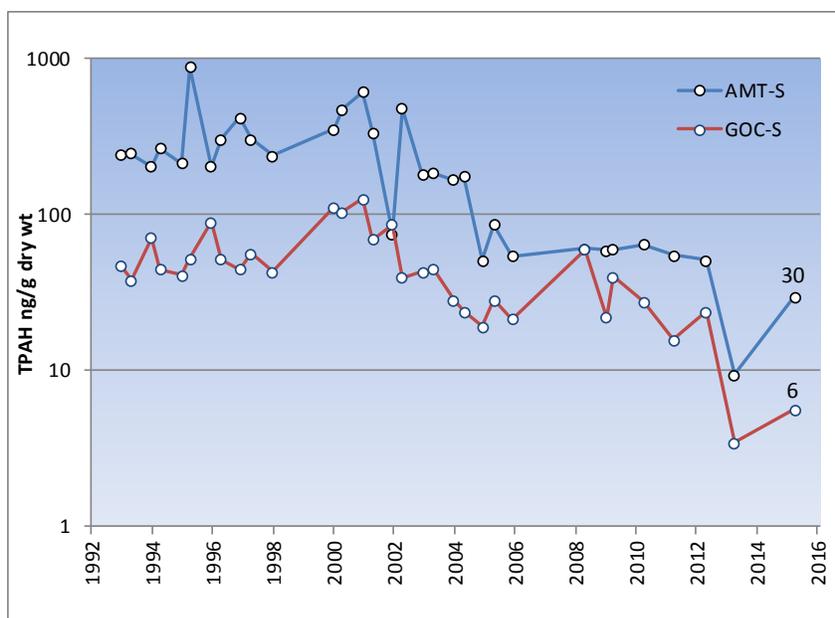
Figure 2. Time series of log(TPAH) in sediments at Alyeska Terminal and Gold Creek.

to a new low of 10 ng/g DW, and the SHC was dominated by biogenic constituents (Figure 3 third panel). In July 2015, the TPAH concentrations slightly increased again to around 30 ng/g DW, but there was very little change in the PAH and SHC profiles compared to 2013 (compare the third and bottom panels in Figure 3). Considering the very low levels in both years (although well above MDLs), the unchanging patterns are more relevant than the negligible difference in total concentrations.

GOLD CREEK

At the 68-72 m deep Gold Creek reference site (GOC), the sediments have consistently exhibited lower TPAH concentrations than AMT throughout the duration of the program (Figure 2). In 2013, the GOC samples showed record-low concentrations (as did AMT), but unlike the sediments at the terminal, the GOC sediment TPAH levels remained in single digits in 2015. With its patterns shifting earlier than AMT's, the PAH profiles at GOC have been dominated by pyrogenic components (Payne et al., 2008a,b; 2010a; 2015) since April 2000, and there appears to be a slight relative increase in higher-molecular-weight combustion products in 2015 (see Figure 4). In addition to the pyrogenics, GOC sediments also contain a moderate and invariant suite of N_0-N_4 naphthalenes that are believed to derive from glacial and riverine sediment input to the Port (Payne et al. 2010a,b). Similar naphthalene contents are 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. GOC sediment SHCs are almost exclusively dominated by biogenic sources from marine phytoplankton (n-C_{15}, n-C_{17}, pristane) and terrestrial plant waxes (odd-carbon-numbered n-alkanes between n-C_{23} and n-C_{33}).

In comparing the AMT and GOC sediment profiles, as petrogenic profiles at AMT disappear, by 2011 its signatures (Figure 3 second panel) begin to resemble the Gold Creek reference sediments (Figure 4). In 2013, only traces of the higher-molecular-weight petroleum waxes (> n-C_{32}) at AMT remain whereas they used to dominate the SHC profiles (Payne et al., 2008a,b; 2015). There are no higher-molecular-weight petroleum waxes present in the GOC sediments.

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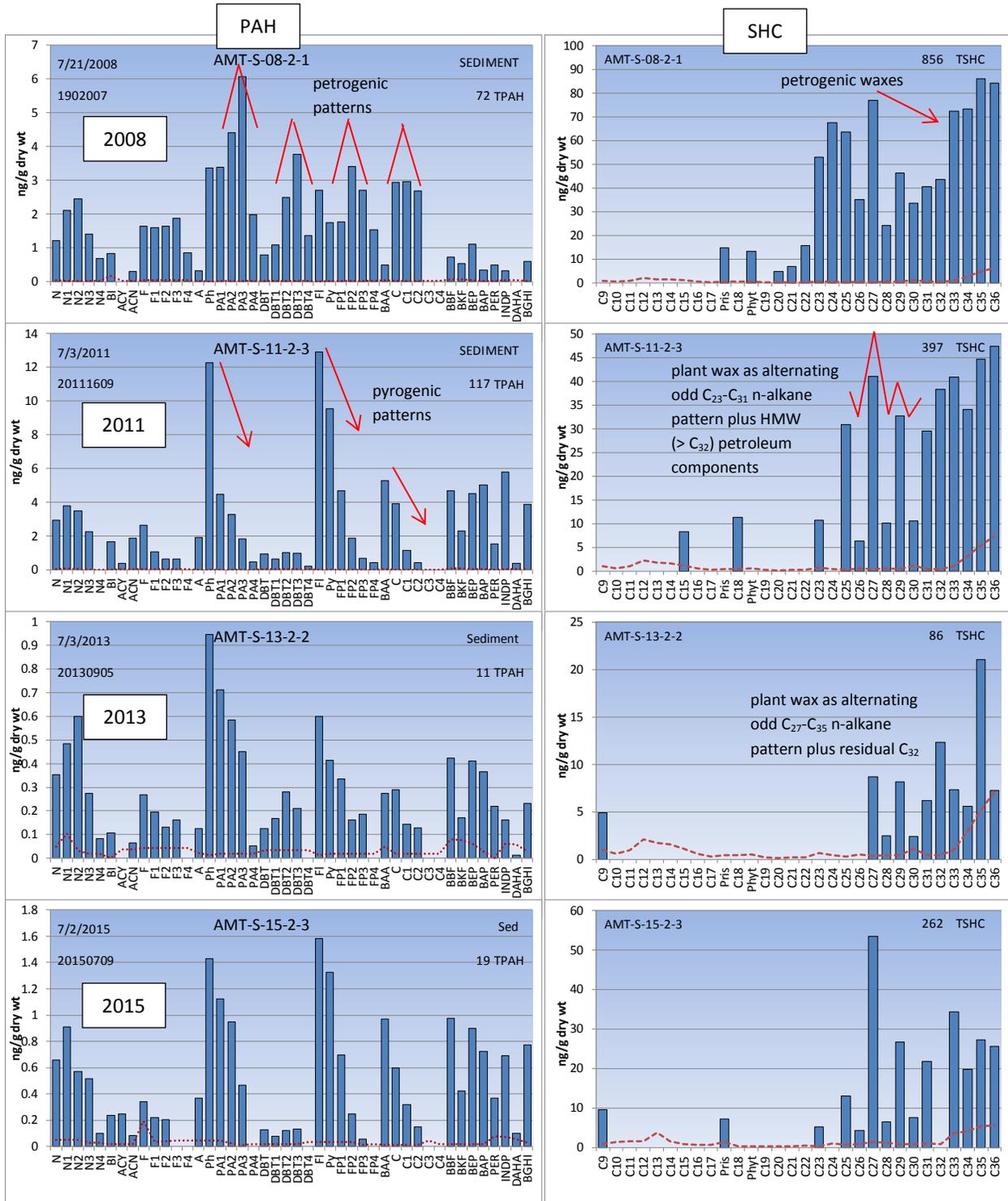
Figure 3. Representative PAH and SHC signatures of sediments at Alyeska Terminal between July 2008 and July 2015 showing the progression from a primarily petrogenic to a pyrogenic PAH signature with increasing terrestrial biogenic SHC and decreasing higher-molecular-weight n-alkane residuals (petrogenic waxes). Red dashed line is sample-specific MDL. Note graph scales reflect dropping TPAH and TSHC concentrations. All series replicate profiles are presented in Appendix 3.
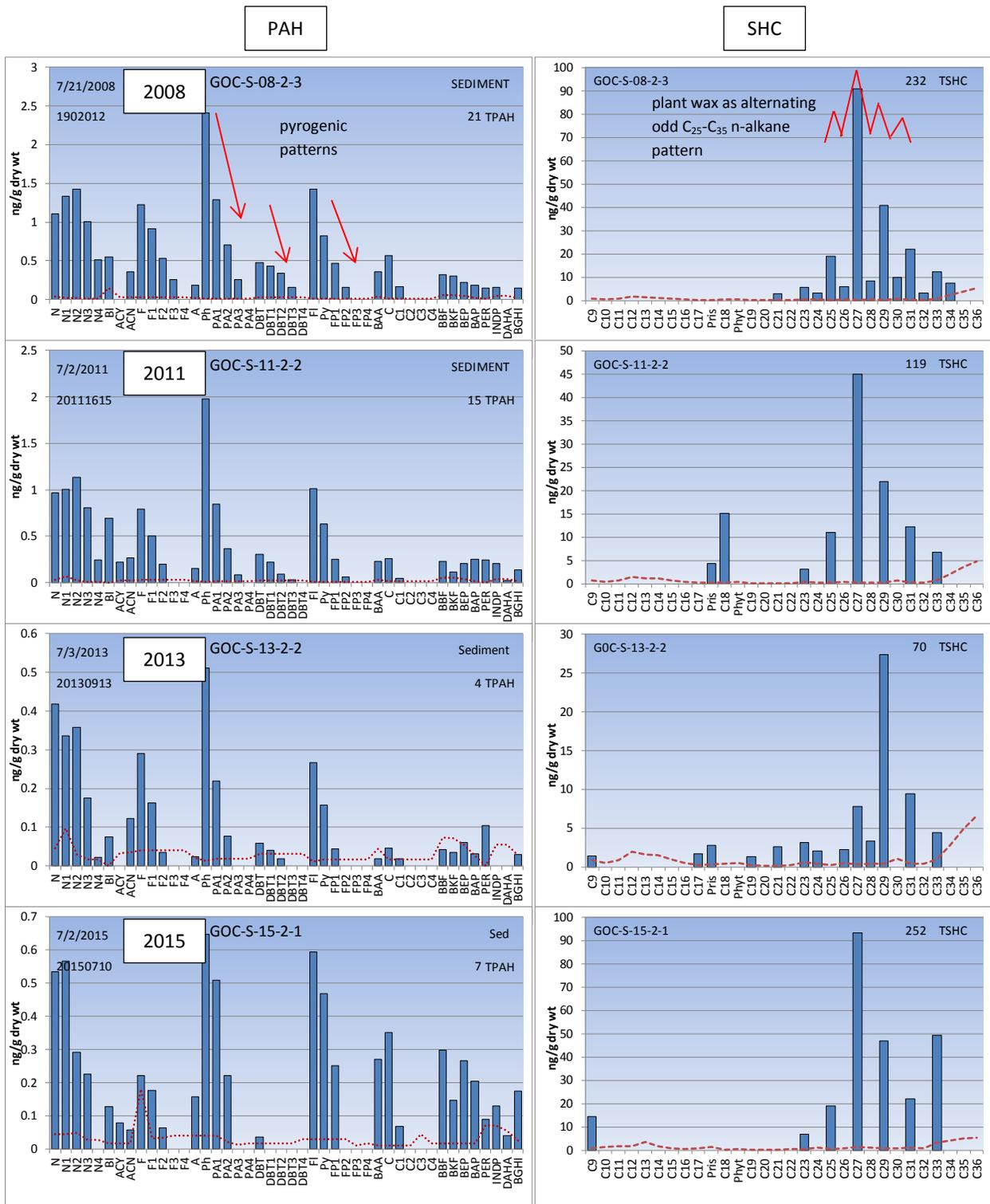
Figure 4. Representative PAH and SHC signatures of sediments at Gold Creek between July 2008 and July 2015 showing essentially invariant, background naphthalene components and pyrogenic, parent-dominated, PAH. SHC patterns reflect constant terrestrial and marine biogenic input. Red dashed line is sample-specific MDL. Note that while the patterns are all similar, the absolute concentrations are generally decreasing over time. All series replicate profiles are presented in Appendix 3.

SEDIMENT BIOMARKERS

As presented in our last report covering the 2013 data (Payne et al., 2015), there was a confirmed presence of low-level, weathered ANS oil in AMT sediments and equivocally at GOC. However, the degraded biomarkers now seen in three years of data suggest three hypotheses: the patterns (Figure 5) represent biomarkers either *weathered* in BWTF processing or by natural processes in the sediments or, more unlikely, that inputs to the BWTF may no longer be dominated by EVOS-era ANS oil residues, i.e., an amalgam of signatures.

As discussed in the 2015 report, biomarkers are persistent but not "ironclad;" they can be degraded (Frontera-Suau et al., 2002; Prince and Walters 2007). The observed "altered" LTEMP patterns could result from biological degradation within the terminal's Ballast Water Treatment Facility whereby the process adds nutrients, oxygenates, and strives to optimize hydrocarbon degradation prior to discharge. In these circumstances, the biomarker compounds can biologically and chemically degrade at rates varying with the abundance and efficacy of microbes specifically adapted to use them (e.g., some loss of hopane was noted in a 2004/2005 BWT study by Payne et al., 2005b,c). Alternatively, because data are not yet available to document the BWT's effect, the slightly weathered biomarkers may also be degrading in the sediments, i.e., natural degradation processes could occur in the continuously augmented water column or sedimentary environments near the outfall. Similar effects were seen in the Deepwater Horizon (DWH) and *Cosco Busan* data but involving just a few sterane compounds.

The third alternate hypothesis, that changing operating conditions at the Terminal with segregated ballast tankers may have shifted the nature of the effluent and that previously observed ANS oil signatures are not the patterns to expect, seems less probable. We would only expect a seasonal effect; tanker vessels now load extra ballast into cargo tanks as operationally required during heavy weather (usually winter). Ballast transfer logs from Terminal operations show that throughputs to the BWTF cycle seasonally, are at historic lows, and are shifting lower as the older predominant cargo-tank ballast users are replaced. With reduced ballast water volume, a more significant contribution to the BWTF comes from surface-water runoff collected at the terminal. In 2016, new dissolved-phase, particulate-(oil)-phase, and whole (unfiltered) samples of the BWTF effluent were collected to characterize the effluent hydrocarbons and confirm the appropriate hypothesis (report in progress).

With the current three years of biomarker data, the residual patterns at AMT, accepting the apparent losses of more labile compounds, show good fidelity to the three key diagnostic ratios (Figure 7) and are consistent with slightly degraded ANS petroleum biomarkers (Figure 5).
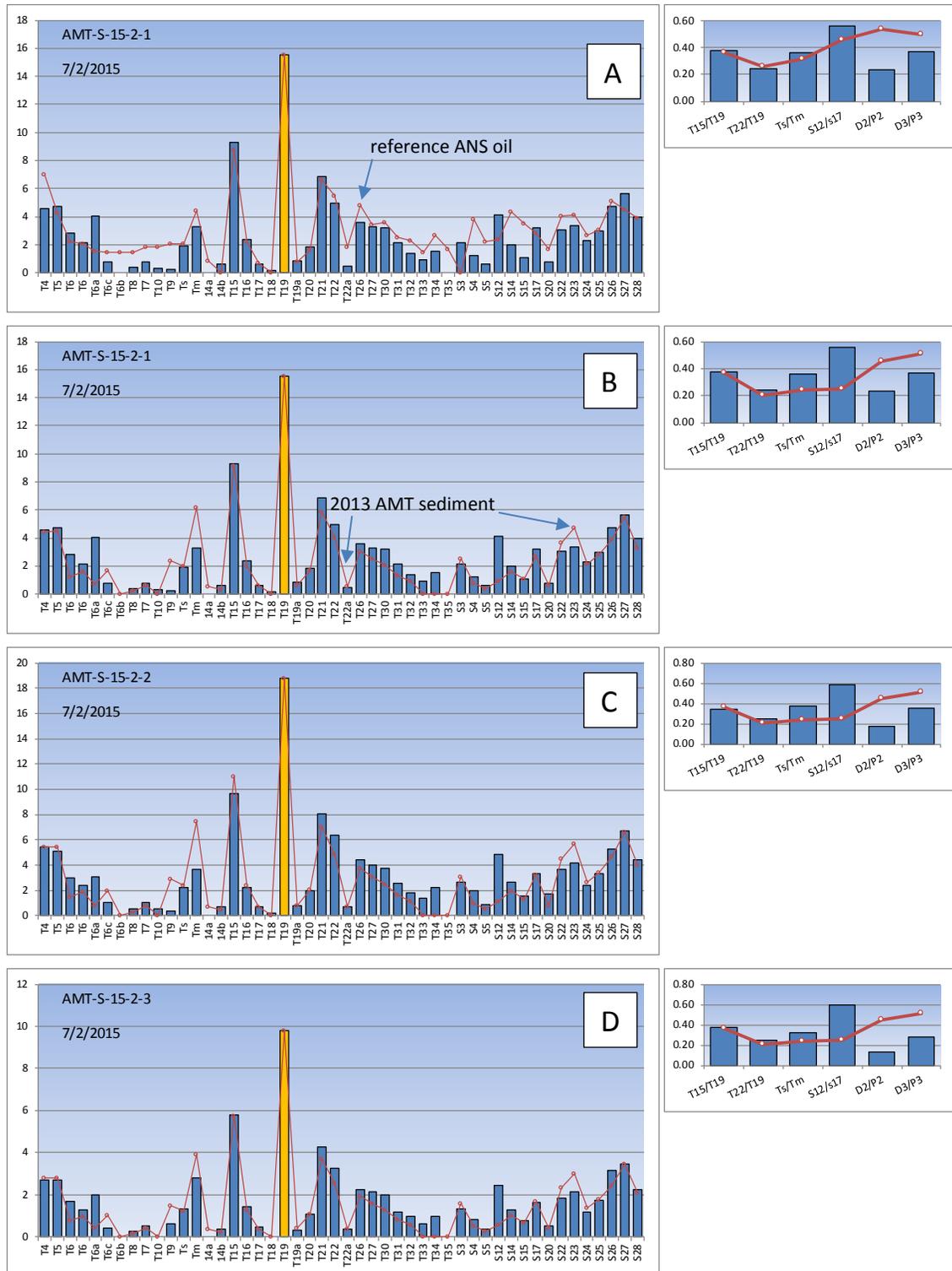
Figure 5. Biomarkers and diagnostic ratios from 2015 Alyeska Marine Terminal sediments. A) AMT sediment biomarkers plot compares ANS to this year's biomarkers; B, C, and D) AMT sediment biomarker replicates compared to 2013 sediment pattern (red overlay). Overlay is scaled by the sample's hopane (gold bar, T19).

In contrast, GOC biomarkers were much less abundant in previous years (relative to AMT) and essentially appear as residuals in the 2015 data. The current patterns have become even more tentative, and while some low level samples showed gapping analyte absences (weathered by BWTF and/or diluted by background sediments?), other parts of the profiles displayed a surplus (Figure 6), particularly in the steranes beginning around S22 (i.e., when normalized to hopane, their values exceed the red ANS reference line in the plots). These surpluses suggest another non-ANS source of hydrocarbons may be mixing with the GOC background hydrocarbons. Without knowing the actual weathered signature of ANS biomarkers as they exit the BWTF, it's difficult to parse out the presumably mixed, GOC background sources.

In summary, the biomarker patterns in AMT sediments can be tied to ANS discharge while GOC biomarkers that previously suggested low levels of ANS in a mixture with other background sources are now essentially absent.

Discussions in the previous LTEMP report 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). From Alyeska's annual monitoring program (EMP) sampling a 14 station design vs. LTEMP's two within Port Valdez, Shaw et al. (2005) concluded from the biomarker data comprising just hopane (T19) and norhopane (T15) 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. In 2008, in addition to the characteristic absence of oleanane, scatterplots of hopane and norhopane by year showed consistent ratios for all stations, which Blanchard et al. (2008) again concluded was due to the presence of ANS oil throughout the Port. Then in 2014 and again in 2015, their assessment was modified to suggest that while the consistent hopane ratios and absence of oleanane confirmed an ANS, BWTF-derived oil in shallow stations near the terminal, the reduced sediment hopane loads at deeper stations suggested a *refined* ANS source (plus pyrogenics) that did not derive from the BWTF effluent (Shaw and Blanchard, 2014, 2015). 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 hopane and norhopane, the target biomarkers (Bence et al. 1996, Stout and Wang, 2016). An alternative explanation might be that the low level biomarkers in the deeper sediments represent dilute, dispersed ANS crude inputs rather than refined products. The EMP conclusions cannot be confirmed from the abbreviated PAH and biomarker data available in the reports, but they generally agree with LTEMP's recent findings of low-level petrogenic plus pyrogenic patterns at AMT and pyrogenic-dominated patterns at GOC.
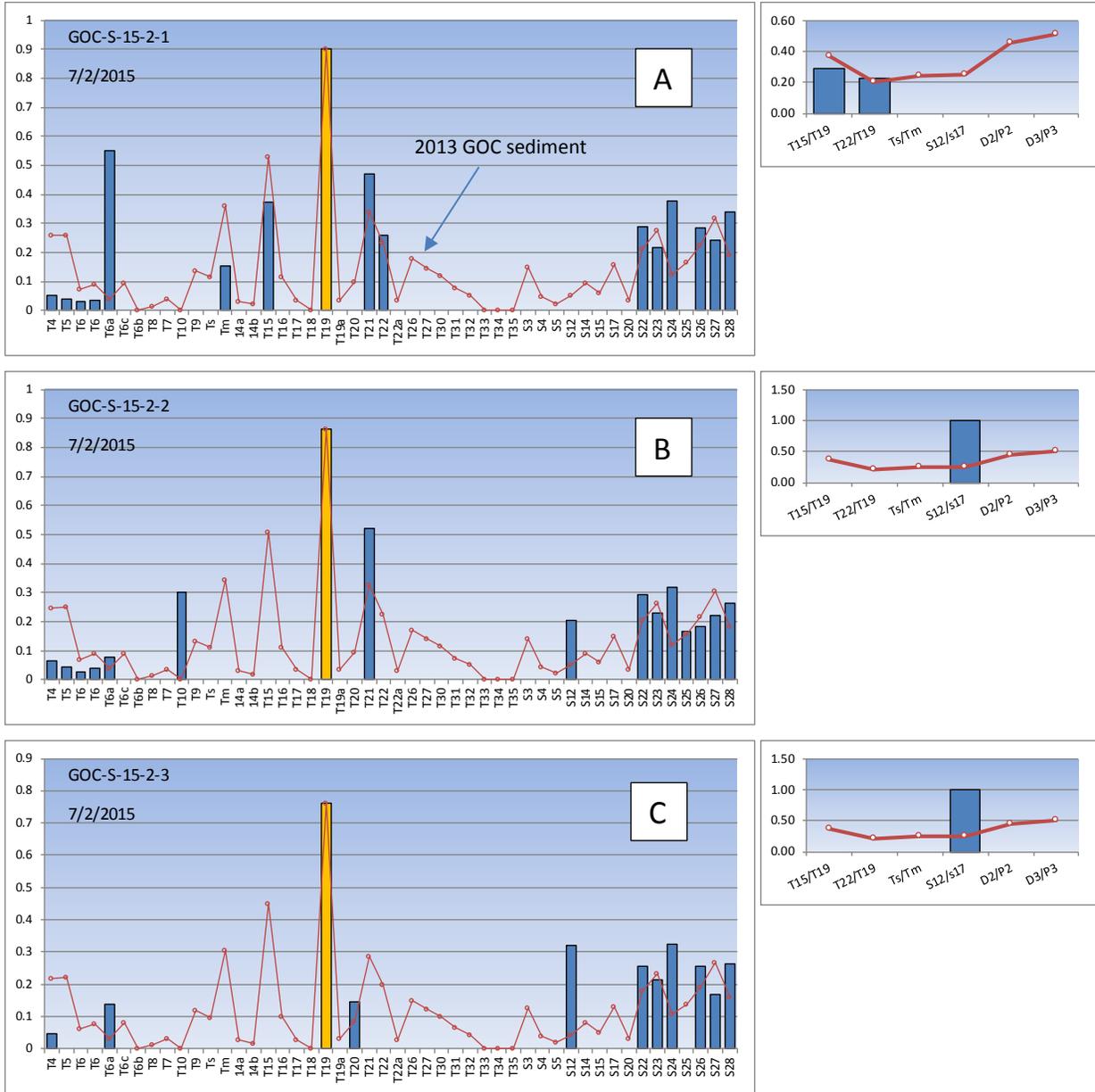
Figure 6. Biomarkers and diagnostic ratios from 2015 Gold Creek sediments, compared to 2013 GOC biomarker pattern (overlay in red), shows way fewer biomarkers than previously observed and impossible to affirm matching BWTF source. Overlay is scaled by the sample's hopane (gold bar, T19).
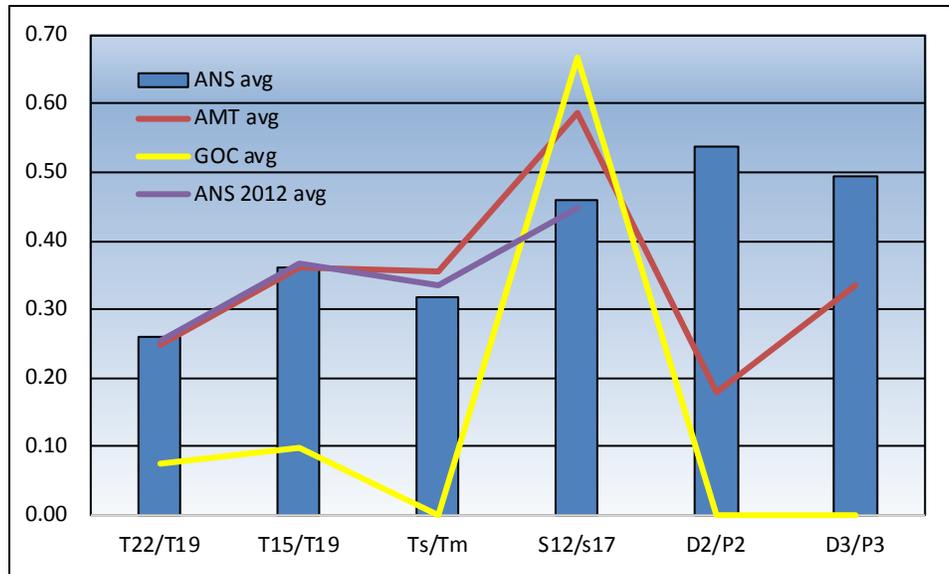
Figure 7. Comparison of average 2015 GOC and AMT diagnostic ratios with ABL's ANS references, original 1989 and 2012. Only the first three best-fitting ratios on the left of the figure were used for final evaluations.

SEDIMENT GRAIN SIZE

Sediment grain size samples are presented for all 2006-2015 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 8 and Table 3) and both sites show minor trends and outliers. In the 3D plots (Figure 9), note there are annual shifts at GOC (~70m depth) to higher sand content and back (albeit still a minor component, <20%) and with a return to original conditions in 2013. But in 2015, silt increased and clay decreased dramatically. At AMT (~30 m depth), there has been a cycle of increasing clay content through 2009 and then a decrease, returning to 2006 levels by 2015. The station 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. These grain-size component trends are presented with only modest confidence considering the non-rigorous collection methods, i.e., spooning up 250 mL of sample remnants after collecting the less consolidated surface floc for hydrocarbon analyses.
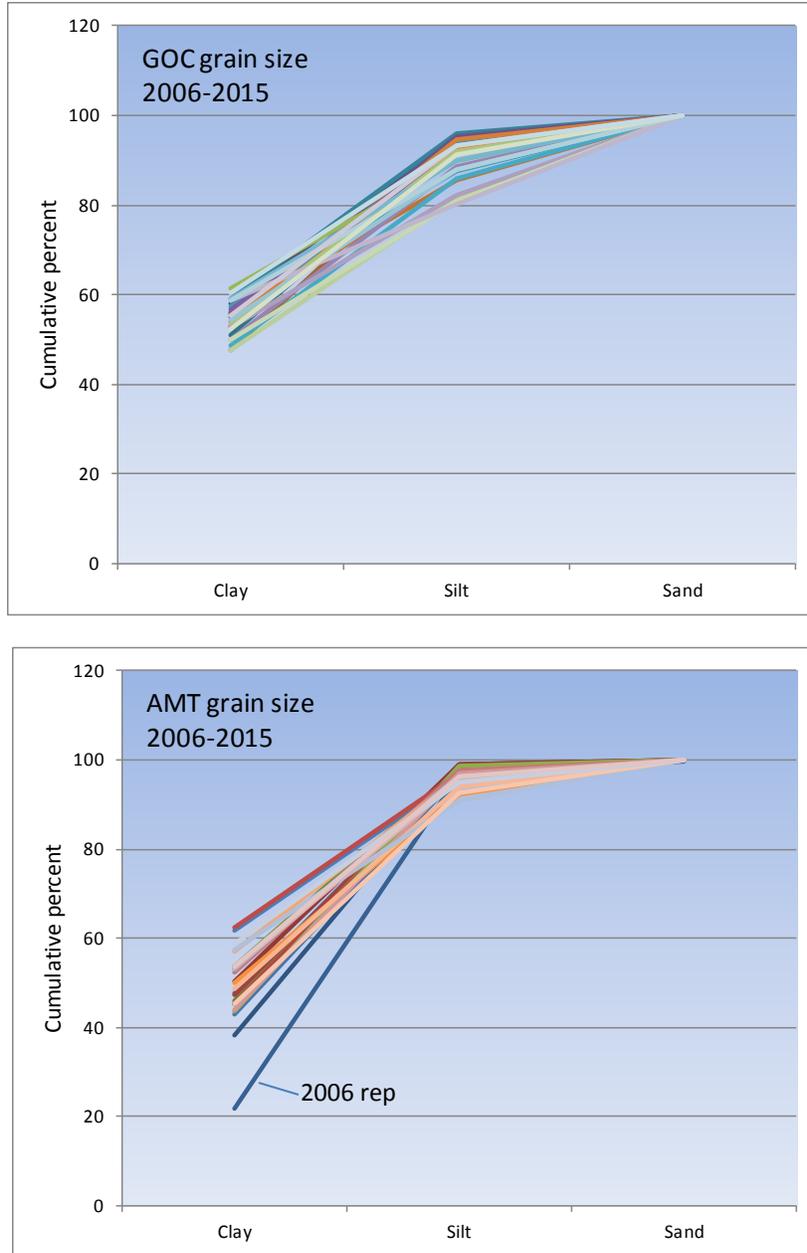
Figure 8. Cumulative grain size curves (%) for GOC and AMT, 2006-2015.

Table 3. Average grain size components for GOC and AMT, 2013-2015

	% Clay	% Silt	% Sand
AMT 2013	49.9	46.4	3.6
GOC 2013	54.0	36.2	9.8
AMT 2015	41.4	52.3	6.4
GOC 2015	28.0	64.3	7.7
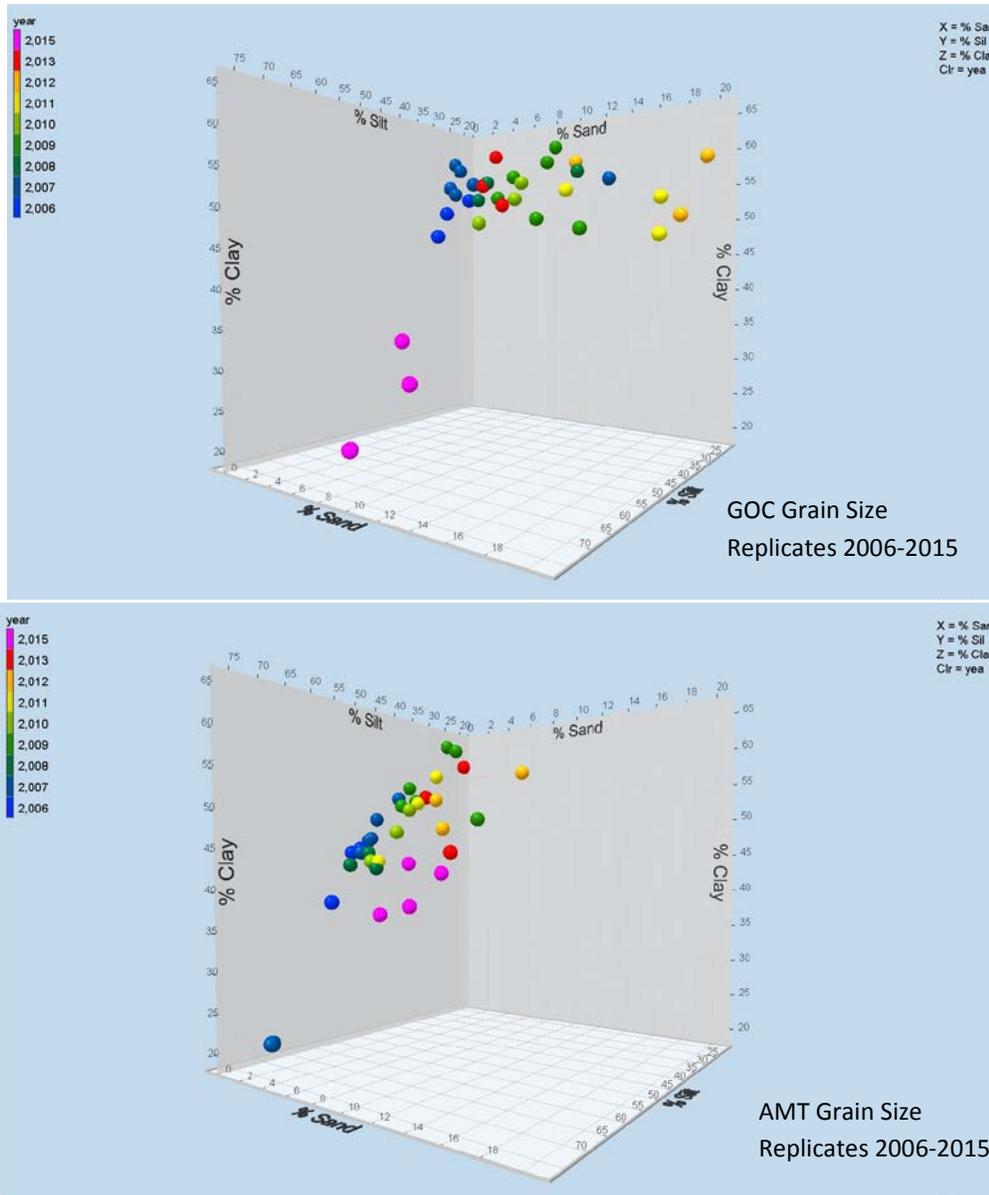
Figure 9. 3D plots of grain size components from GOC and AMT 2006-2015. Sampling years are color coded: blue to red, 2006-2013; pink, 2015. Note the clipped axes emphasize the shift in clay vs silt at GOC in 2015. Over the years, typically sand content has been most variable component at GOC, silt/clay at AMT.

17

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 is used to normalize contaminant concentrations in order to do site-to-site contaminant comparisons.

LTEMP TOC values showed seasonal cycles in the more frequent samplings early in the program but then show a slow increase in concentration until plateauing sometime around 2003 (Figure 10 and Table 4). There is an uptick at GOC in the previous two years of the program and mildly so in the previous year at AMT. Note that the data are not continuous and that sampling prior to 2002 was performed by KLI.
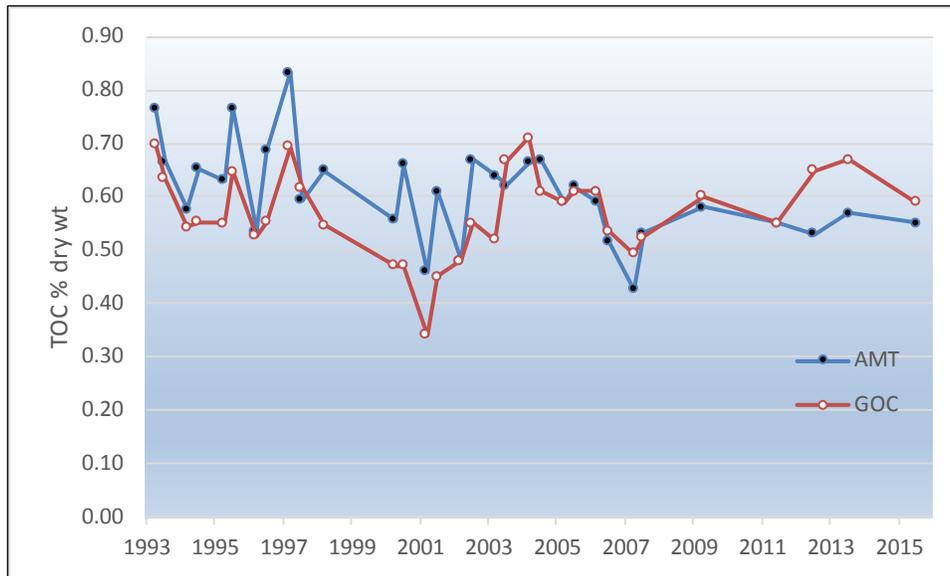
Figure 10. LTEMP Total Organic Carbon trends in AMT and GOC sediments (% dry wt), 1993-2015.

Table 4. LTEMP Total Organic Carbon in AMT and GOC sediments (% dry wt.)

Sample Date	AMT	GOC	Sample Date	AMT	GOC	Sample Date	AMT	GOC
Apr-93	0.77	0.70	Apr-00	0.56	0.47	Jul-05	0.62	0.61
Jul-93	0.67	0.63	Jul-00	0.66	0.47	Mar-06	0.59	0.61
Mar-94	0.58	0.54	Mar-01	0.46	0.34	Jul-06	0.52	0.54
Jul-94	0.65	0.55	Jul-01	0.61	0.45	Apr-07	0.43	0.49
Apr-95	0.63	0.55	Mar-02	0.48	0.48	Jul-07	0.53	0.53
Jul-95	0.77	0.65	Jul-02	0.67	0.55	Apr-09	0.58	0.6
Mar-96	0.54	0.53	Mar-03	0.64	0.52	Jun-11	0.55	0.55
Jul-96	0.69	0.55	Jul-03	0.62	0.67	Jul-12	0.53	0.65
Mar-97	0.83	0.69	Mar-04	0.66	0.71	Jul-13	0.57	0.67
Jul-97	0.59	0.62	Jul-04	0.67	0.61	Jul-15	0.55	0.59
Mar-98	0.65	0.55	Mar-05	0.59	0.59			

TISSUES IN PORT VALDEZ, KNOWLES HEAD AND SHEEP BAY

Average TPAH levels in AMT tissue samples have been steadily dropping since April 2007, and by 2010, they first approached all-time lows, estimated 17 ng/g DW (Figure 11 and Table **5**). At these trace concentrations, results must be qualified as estimates (many analytes are below MDL, Figure 12), but because of their patterns, they are not considered to be false positives. Although TPAH levels increased slightly in 2012, the majority of the PAH were pyrogenic not petrogenic in nature and thus, unlikely to be from changes in BWTF discharge. By 2013, TPAH levels were back down to an estimated 17 ng/g DW.   In 2013, the below-MDL phenanthrene/anthracenes (PA group) have a petrogenic pattern (Figure 12), as confirmed by the SHC fraction's petrogenic waxes, the higher-molecular-weight $n\text{-}C_{23}\text{-}n\text{-}C_{31}$ components that were also observed in 2011. In the 2011 sample, however, the PAH were only derived from combustion sources. Because these n-alkanes generally predominate over PAH in fresh crude and refined products, is possible that there were indeed traces of oil in the 2011 and 2013 mussels as suggested by the SHC patterns, but the PAH were simply below the MDL. Using SHC patterns alone to evaluate petrogenic sources is fraught with difficulties since the SHC are subject to rapid biodegradation, and in the majority (27 of 31) AMT tissues examined since 2008, the SHC have been dominated by biogenic constituents (e.g., $n\text{-}C_{15}$, $n\text{-}C_{17}$, and pristane) with only very rare observations of $n\text{-}C_{23}\text{-}n\text{-}C_{31}$ components (Payne et al., 2015). In the 2015 mussel samples from AMT, the TPAH levels are again slightly elevated at 70 ng/g DW, but they are exclusively background dissolved-phase naphthalenes with predominant biogenic SHC (Figure 12). The appearance of the 5-ringed PAH, perylene, in 2011, 2012 (not shown), and 2013 (Figure 12) is noted but not relevant to the interpretations. Perylene can occur naturally, generated by biologic processes or early stages of diagenesis in marine sediments (Bence et al., 2007) and thus, potentially being of non-petroleum origins, it is not included in TPAH summations. from non-oil matrices.

At GOC, average TPAH levels in mussel tissues during the early years (1993-2003) of the program were consistently lower or very close to those at AMT (except for the Fall 2004 diesel spill, cleared by the following July; Figure 11 and Table 5). Beginning in the 1990's, mixed dissolved-phase, petrogenic, and pyrogenic signals were common at this site, roughly trending with similar patterns or discharge events at AMT (Payne et al., 2008a,b; 2010a; 2015). Then after 2002, as TPAH levels in mussels at both AMT and GOC 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 (below-MDL dibenzothiophenes (DBTs) in 2008 and P/As in 2013) (Figure 11 and Figure 13). SHC patterns at GOC, with minor exceptions, have reflected mostly trace-level biogenic components (e.g., $n\text{-}C_{15}$, $n\text{-}C_{17}$, and pristane) over the 2008-2015 period (Figure 13). Exceptions included two of three replicates in April 2009, and one in 2011, each with traces of petrogenic $n\text{-}C_{24}\text{-}n\text{-}C_{30}$ SHC (see Appendix 4 in Payne et al., 2015). In none of these cases, however, were petrogenic sources suggested by the corresponding PAH profiles. Then, in 2013, when below-MDL petrogenic P/As were suggested in the PAH fraction in two of three replicates, no higher-molecular-weight $n\text{-}C_{24}$ to $n\text{-}C_{30}$ petrogenic waxes were observed (Payne et al., 2015). Because all of these concentrations are at such low levels, it is not surprising that the petrogenic signals sometimes suggested by the SHC patterns are not always reflected in the corresponding PAH profiles, and vice versa. Interestingly, perylene traces noted in the AMT mussels in 2011, 2012, and 2013 were also observed at GOC during 2012 and 2013, thus supporting the perylene's biogenic source. In the 2015 GOC collections, the slightly elevated (43 ng/g DW) TPAH were derived almost exclusively from dissolved-phase parent and C1-naphthalene (Figure 13), as also observed at AMT (Figure 12). In both instances the SHC patterns were dominated by marine biogenic components (e.g., $n\text{-}C_{15}$, $n\text{-}C_{17}$, and pristane) suggesting a common background source.
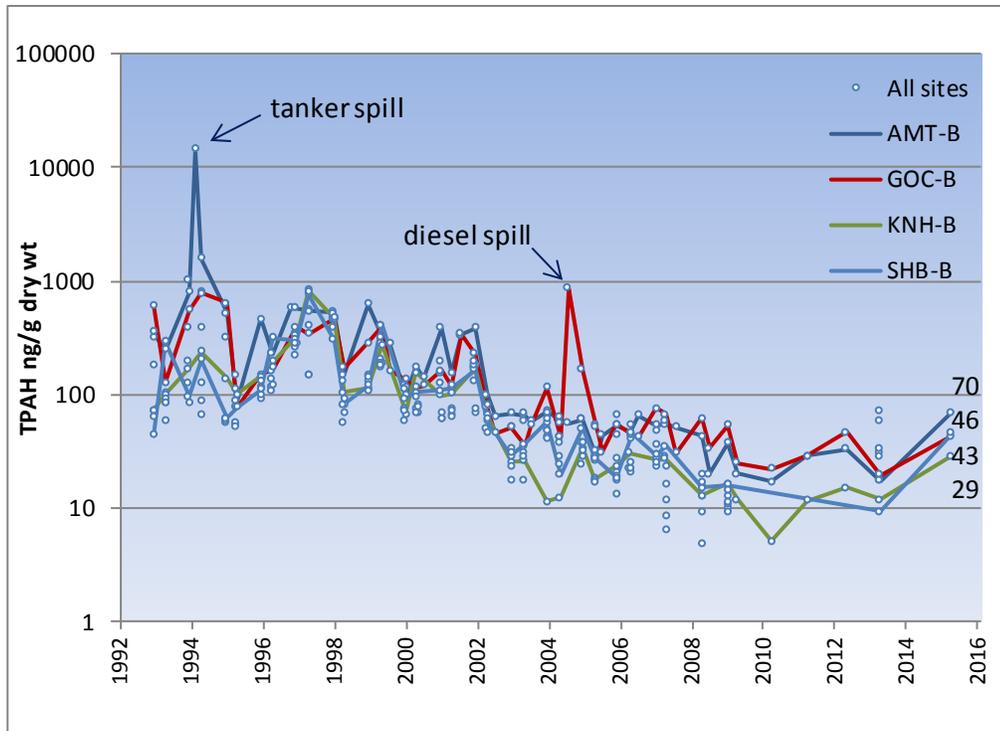
Figure 11. Time series of mean mussel log(TPAH) comparing 2015 Alyeska Terminal, Gold Creek, Knowles Head and Sheep Bay to prior LTEMP collections.

Table 5. Time series of mean TPAH (ng/g DW) from Alyeska Terminal, Gold Creek, and Knowles Head and Sheep Bay mussels, 2008-2015.

Sample Date	AMT	GOC	KNH	SHB
Jul-08	43	62	13	15
Sep-08	20	34		
Apr-09	38	54	17	16
Jul-09	20	25	12	
Jul-10	17	22	5	
Jul-11	29	29	12	
Jul-12	33	46	15	
Jul-13	17	20	12	9
Jul-15	70	43	29	46

The 2013 and 2015 PAH and SHC profiles for Knowles Head tanker anchorage (KNH) and Sheep Bay (SHB) are shown together (Figure 14 and Table 5) to facilitate comparisons of these two eastern-most PWS stations. KNH was originally selected because it was close to a known tanker anchorage/holding area when the terminal was more active, and SHB was intended as a non-EVOS-impacted reference site at the eastern-most end of PWS.
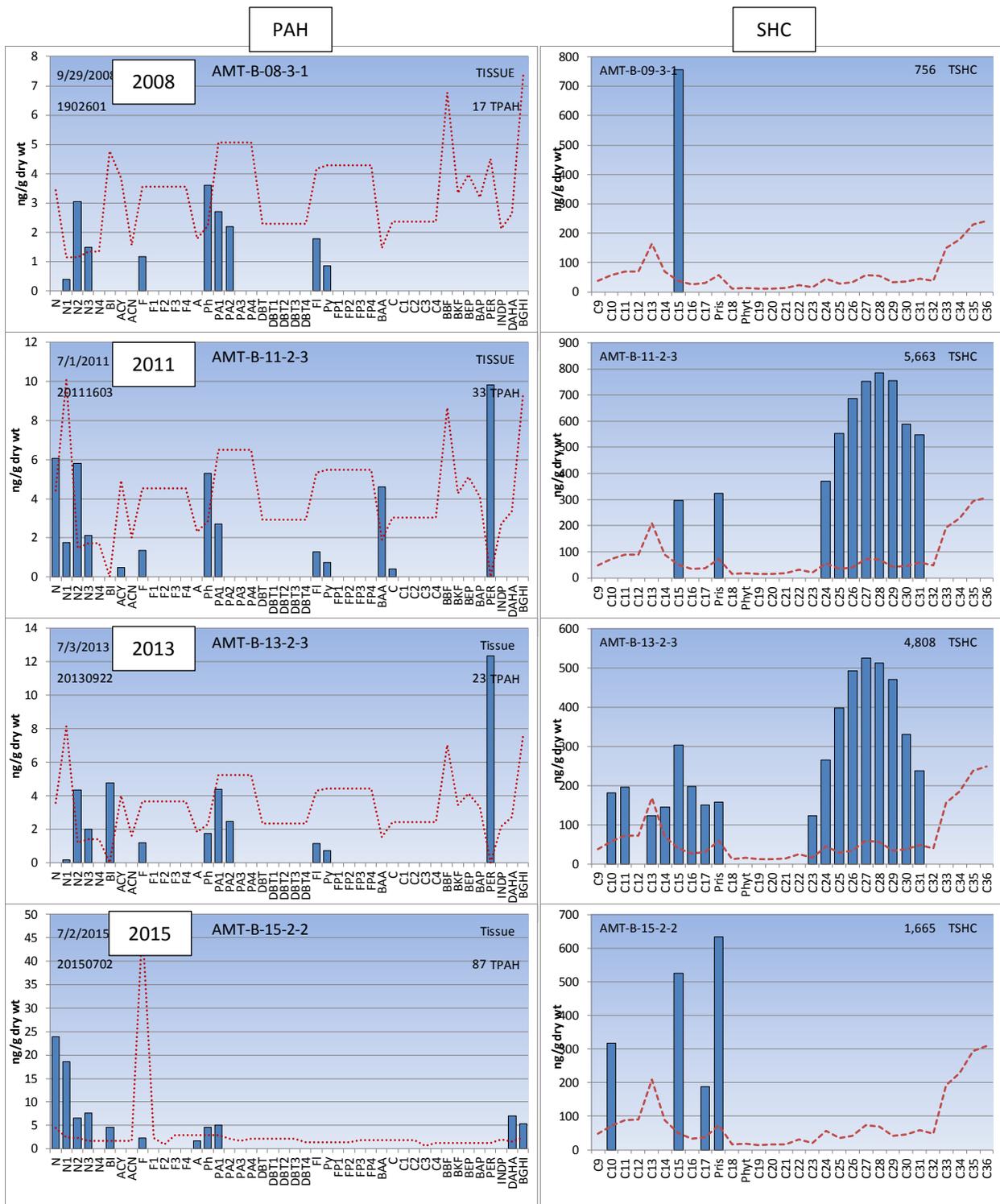
Figure 12. Examples of PAH and SHC profiles from AMT mussel tissues between July 2008 and July 2015 showing primarily below-MDL combustion product PAHs (except 2013 where the PAs appear petrogenic), perylene, and planktonic biogenic SHC (C_{15} and pristane) plus higher-molecular-weight C23-C31 petrogenic waxes in 2011 and 2013. Red dashed line is sample-specific MDL. All 2015 series replicate profiles are presented in Appendix 3.
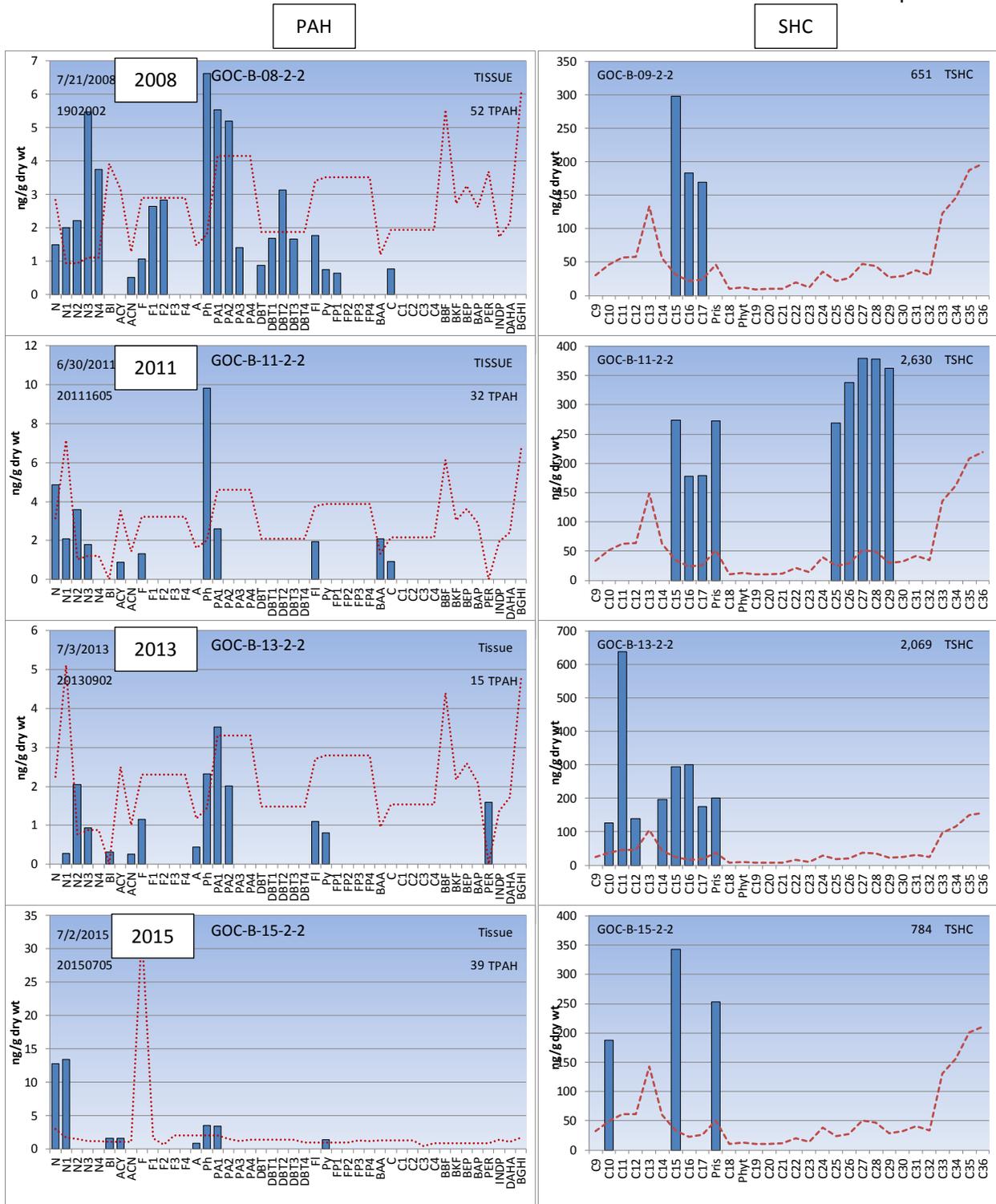
Figure 13. Examples of PAH and SHC profiles from GOC mussel tissues between July 2008 and July 2015 showing primarily combustion products (except 2013 where the less-than-MDL PAs appear petrogenic), perylene, and planktonic/terrestrial biogenic SHC plus higher-molecular-weight C_{23}-C_{31} petrogenic waxes in 2011. Red dashed line is sample-specific MDL. All 2015 series replicate profiles are presented in Appendix 3.
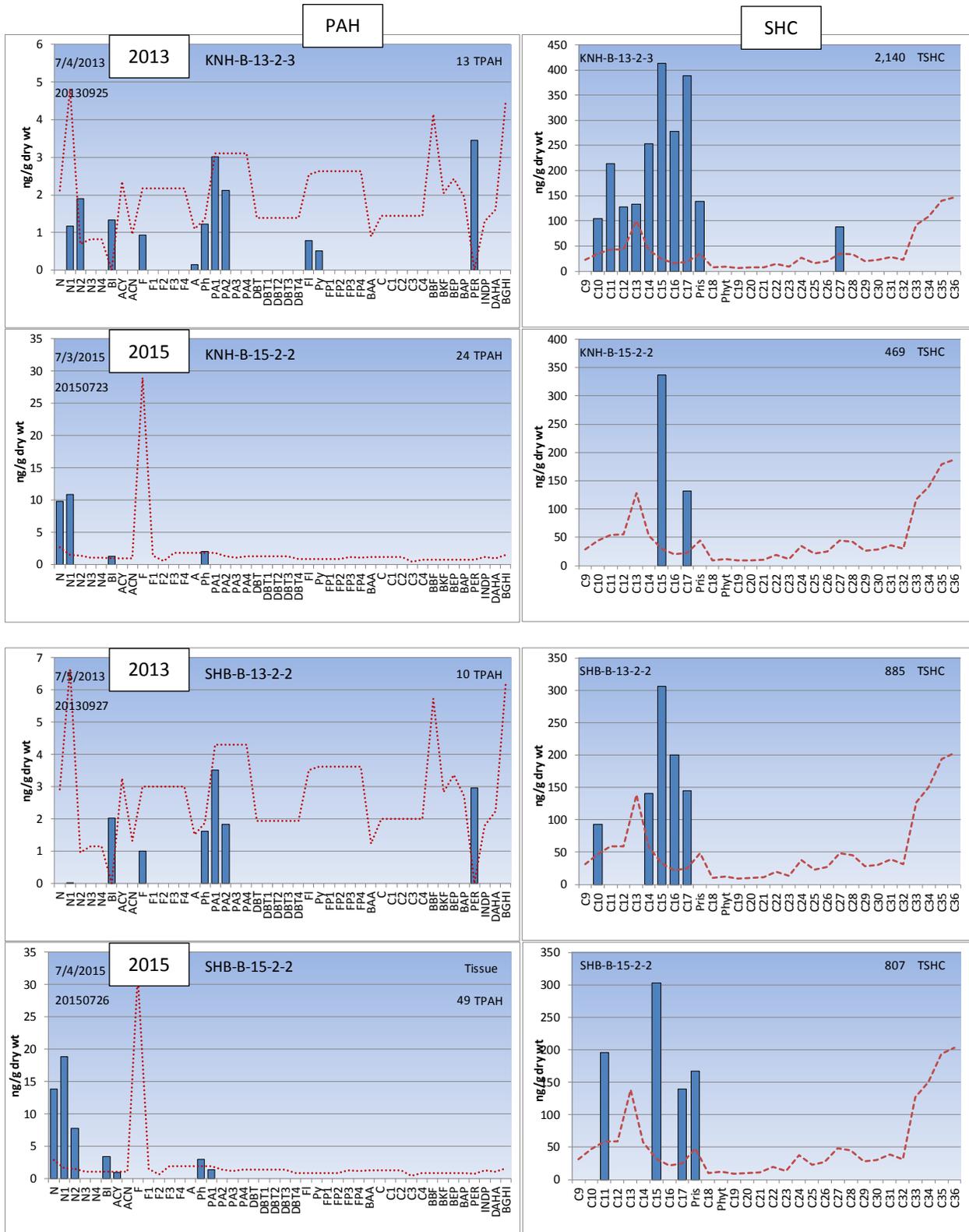
Figure 14. Examples of PAH and SHC profiles from 2013 and 2015 mussel collections at Knowles Head (KNH) and Sheep Bay (SHB) showing low-level dissolved PAH and mostly planktonic SHC. All 2015 series replicate profiles are presented in Appendix 3.

From KNH, average TPAH levels have been consistently low, ranging from an estimated 5-29 ng/g DW since March 2008 (Figure 11 and Table 5). With one exception, this site has been dominated by trace level (at or just-above MDL) naphthalenes and combustion-derived anthracenes/ phenanthrenes since July 1999. The exception in July 2004 showed a petrogenic PAH profile (Payne et al., 2008a,b; 2010a) and below-MDL petrogenic P/As in all three 2013 replicates (Figure 14) (Payne et al., 2015). In 2015, the site continued to be extremely clean with only parent and C1-naphthalene observed in the PAH profile, and the SHC fraction was dominated by marine biogenic components (n-C_{15} and n-C_{17}).

The TPAH concentrations at SHB also have been consistently low, ranging from 9-46 ng/g DW since 2008 (Figure 11 and Table 5). In 2015, the site continued to be extremely clean with only dissolved-phase (parent through C2-naphthalenes observed in the PAH profile, and the SHC fraction dominated by marine biogenic components (n-C_{15}, n-C_{17}, and pristane) (Figure 14). As shown by the trace-level (just above MDL) profiles (Figure 14), there was no evidence of any petroleum contamination at either of the KNH or SHB sites during the 2015 mussel collections although a trace was suggested at both sites in 2013. The naphthalene signals could be wind transported or may reflect dissolved phase naphthalenes from freshwater inputs during the spring melt, as seen in Cook Inlet river samples (unpublished ICIEMAP data, Sue Saupe, pers. comm., 2009).

TRENDS

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 mussels and sediments. This trend reflects a combination of reduced ballast-water-treatment-facility (BWTF) discharge volumes from historically decreased North Slope oil production, the transition to double-hulled tankers with segregated ballast tanks, and improved BWTF efficiency in removing particulate/oil-phase polycyclic aromatic hydrocarbons (PAH). As a result, over the last several years, mussel contamination has been generally shifting away from the terminal's earlier petrogenic profiles towards background dissolved-phase or pyrogenic PAH patterns.

Although historically, petrogenic hydrocarbons in mussels sampled from both the terminal and the background-reference site at Gold Creek (GOC) were commonly reported in hundreds of ng/g TPAH, by 2013, only very low, near method-detection-limit (MDL) traces of petrogenic components were found. From the July 2015 sampling, the character of the PAH patterns had further degraded at both locations to only background patterns made up entirely of dissolved-phase hydrocarbons (naphthalenes) and just-above-MDL traces of combustion products. Based on the signatures, these patterns suggest variable or increased background inputs from local vessel traffic, runoff or aerial deposition. The saturated hydrocarbons (SHC) at both locations exhibited only background biogenic components.

Like the mussels, Port Valdez sediment TPAH reached all-time lows in 2013 and then in 2015, marginally rebounded at AMT but remained essentially constant at GOC. The AMT PAH patterns currently comprise a mix of lower-molecular-weight petrogenic hydrocarbons and pyrogenic components while the SHC patterns show a mixture of marine and terrestrial biogenic components along with reduced levels of higher-molecular-weight petrogenic waxes. These results suggest continued input of weathered ANS oil plus combustion products. At GOC, the PAH profiles during both 2013 and 2015 showed little input from the terminal. Instead, they were dominated

by dissolved-phase naphthalenes and combustion products with a relative shift to higher-molecular-weight pyrogenic hydrocarbons in 2015. At GOC, the SHC profiles continue to reflect only biogenic terrestrial plant waxes. Oil biomarker analytes, relatively new to LTEMP sediment methods, show a variable presence of ANS oil from BWTF operations only in the AMT sediments. The 2015 GOC biomarker concentrations and patterns were equivocal, suggesting mixed sources with little or no input from terminal operations.

Beyond the Port Valdez tanker operations area, Knowles Head (KNH) and Sheep Bay (SHB) mussels were collected in 2015. At these two sites, background TPAH levels in mussels have modestly increased between the 2009 and 2015 collections with traces of dissolved-phase naphthalenes and just-above MDL levels of pyrogenic phenanthrenes. Noted in the 2009 and 2013 sample sets, although the samples each comprise only a few analytes, there was remarkable within-site fidelity in both PAH and SHC patterns at these stations. The components showed a common complexity of dissolved and pyrogenic patterns that implies effects from a region-wide process.

In previous years, it was easily assumed that pyrogenic trace patterns appearing at the otherwise clean sites across the region (Payne et. al, 2015) was due to the numerous seasonal wildfires depositing their combustion particulates. The current shift to dissolved naphthalenes plus petrogenic-appearing phenanthrene/anthracene and pyrogenic fluoranthene /pyrene (albeit below MDLs) is puzzling. We speculate that some atmospheric process or freshwater input(s) is the driver as again, the pattern appears at most sites and we know of no marine process that would produce this mixed pattern. Perhaps with warming tundra and melting permafrost, there is a release of PAH from the degrading vegetation? In Cook Inlet studies (Lees et al, 2000), we noted a naphthalene signal (and little else) in eroding peat samples, which seemed to be present in tissue samples. And ICIEMAP river data (Sue Saupe, pers. comm., 2009) show a possibility of freshwater inputs contributing local terrestrial-source PAH, primarily naphthalenes. If so, the use of the term "petrogenic" does not necessarily imply "oil" is present—some pattern components may have a notable oil-like aspect but clearly, there is no widespread trace of crude oil across the region (Payne et. al, 2015).

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. 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 (Table 6, 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 29-46 ng/g DW from the two 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 (Table 6 Figure 15) and 2008-2010 Alaskan sites (Figure 16) (now summing 38 parent and alkylated PAH homologues versus 44 LTEMP PAH analytes) show that average PAH concentrations in mussels for other West Coast sites are 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 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 6), the LTEMP results for the PWS and GOA sites demonstrate that these remote locations are still exceptionally clean.

Table 6. Current TPAH concentrations (2015) 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	2015	Port Valdez tissues		39-87
		PWS		19-46
	2013	Port Valdez tissues		17-20
		PWS		9-33
		GOA		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

PAHs

STATUS SUMMARY

Nation at a Glance:

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

REGIONAL SPECIES CHARACTERIZATION

NATIONAL CHARACTERIZATION

Concentration Ranges (ppb dry weight)

	Mussels	Zebra Mussels	Oysters
L	63 - 1187	128 - 389	47 - 828
M	1188 - 4434	390 - 1595	829 - 2511
H	4435 - 7561	1596 - 6519	2512 - 10717

Concentration Range (ppb dry weight)

L		47 - 1250
M		1251 - 4434
H		4435 - 10717

Regional Comparison of Concentration (%)

Great Lakes, Northwest, Northern California, Southern California, Western Gulf, Eastern Gulf, Southeast, Middle Atlantic, Lower Northeast, Upper Northeast

Figure 15. Status and trends result from national Mussel Watch data (Kimbrough et al., 2008). All Alaskan sites characterized as low concentrations (Figure 16).

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)

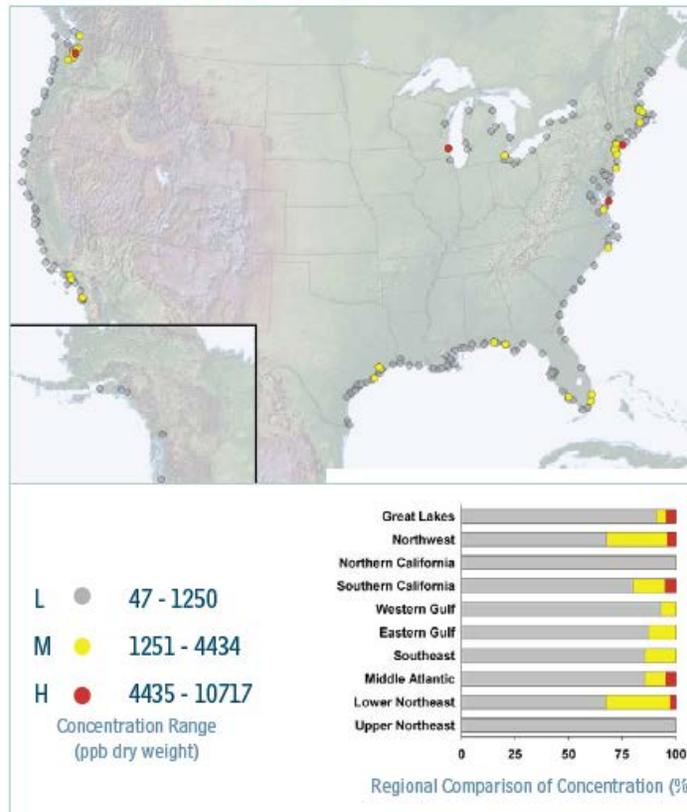| Sites	Spec	Butyltins	r	s	t	Chlordanes	r	s	t	DDTs	r	s	t	Dieldrins	r	s	t	PAHs	r	s	t	PCBs	r	s	t
KTMP	M	2.1				0.47				1.4				0.58				152				3.5			
NBES	M	3.7				2.7				2.2				0.98				316				7.7			
PVMC	M	7.3				2.6				1.7				0.31				441				6.4			
UISB	M	1.7				0.87				0.38				0.56				176				3.7			
CIHS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

Figure 16. Summary page of Alaska regional Mussel Watch results and trends based on 2004-05 report from Kimbrough et al., 2008.

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 very fresh to extensively degraded. 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. To address these residual deposits, the EVOS Trustee Council has sponsored various beach remediation studies and pilot projects (ADEC 2016).

CONCLUSIONS

Based on the sediment and mussel data, petrogenic hydrocarbon inputs from the Alyeska Marine Terminal and tanker operations suggest a slight rebound from 2013 all-time lows but in line with recent low level trends. As concluded in our previous LTEMP reports (Payne et al., 2010a; 2013, 2015), within Port Valdez, the low levels reflect a combination of reduced BTWF discharge volumes from decreased North Slope oil production, the transition to double-hulled tankers with segregated ballast tanks, and improved BWTF efficiency at removing particulate/oil-phase PAH. With the drop in oil discharge over the last few years, tissue collections at the Terminal, have changed from a mostly petrogenic pattern to a predominantly pyrogenic profile. Terminal sediments are also beginning to look more like Gold Creek's background-reference, low-level, pyrogenic profiles; however, biomarkers suggest continued inputs of ANS oil from the BWTF. The Terminal effluent will be resampled in 2016 to confirm the biomarker assessment. At GOC, biomarker concentrations are seven times lower than those at AMT and did not indicate ANS oil. Shaw and Blanchard (2016) draw similar conclusions regarding ANS sources in their sediment collections throughout the Port. Based on LTEMP signatures, the pyrogenic components now dominating the patterns likely reflect variable or increased background inputs from local vessel traffic, runoff or aerial deposition.

In 2015, mussels were collected from two eastern PWS locations, Knowles Head (KNH) near the tanker anchorage and Sheep Bay (SHB) north of Cordova. PAH signals there were very similar to those observed in 2013, reflecting only dissolved-phase naphthalenes and just-below-MDL traces of combustion-derived phenanthrenes while SHC patterns showed only biogenic background inputs. Recall that the April 2013 mussel collections from all central PWS and GOA sites had similar trace patterns of dissolved-phase naphthalenes and just-above-MDL petrogenic phenanthrenes/anthracenes whose commonalities in pattern details suggested region-wide sources with local geographic similarities (Payne et al., 2015).

Compared to 2004-05 West Coast Mussel Watch data and the more recent Alaskan Mussel Watch sites, the LTEMP results for the PWS and GOA stations demonstrate that the region is exceptionally clean (excluding the few remaining sequestered oil sites).

NEW METHODS, TECHNOLOGY AND FUTURE DIRECTIONS

At this point in LTEMP monitoring, we feel the most pressing need is to obtain and analyze a sample of the BWTF effluent for PAH and biomarkers--a deficiency in the current LTEMP data set. After coordinating with Alyeska, an effluent sample was collected in July 2016 (report in progress). Also, in 2016, passive sampling devices (PSD) were deployed just offshore at the Port Valdez mussel collection locations (plus a third site at Jackson Point, east of Terminal 2). This project will be led by Dr. Sarah Allan but closely coordinated with the LTEMP field efforts. The PSD devices comprise caged polyethylene strips hung submerged in shallow water to absorb passing hydrocarbons. The PAH and biomarker data, analyzed at Oregon State, will be compared with the co-sampled mussel results. New to the project will be a short list of oxygenated hydrocarbon analyses using GC/MS methods.

Other trending topics in oil fate are tracking polar compounds using alternative mass spectrometry instruments. These newer instruments exceed the resolving range of traditional GC/MS revealing previously un-tracked

compounds including the more polar, hetero-atomic hydrocarbons (containing oxygen, sulfur or nitrogen). These analytes are confounded in the "unresolved complex mixture" (UCM) of (or excluded by extraction for) GC/MS analyses (Liu and Kujawinski, 2015, Ruddy et al., 2014). They were previously considered the "lost" weathered components that had been selectively transformed/consumed by microbes or removed as natural oil fate. Notably, more than 30 thousand compounds have been identified in fresh DWH oil samples by FT-ICR methods (McKenna et al., 2013). In 2016, the Gulf of Mexico Research Initiative is actively supporting this approach, funding a project looking at weathering (including biodegradation) of DWH oil using GC x GC, LCMS and FT-ICR methods. For LTEMP, an interesting study would be to assess ballast water signatures through the BWTF, out the discharge and then perhaps to track the oxygenated-HC plume through the Port. Relevant toxicity data for these previously enigmatic compounds are currently minimal (reviewed in Fingas and Banta, 2016); however, potential net toxicity appears to be limited considering benthic monitoring results from EMP and casual observations of LTEMP intertidal populations.

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

ANALYTES	Abbreviation	Internal Standard	Surrogate Standard
PAH			
Naphthalene	N	A	1
C1-Naphthalene	N1	A	1
C2-Naphthalene	N2	A	2
C3-Naphthalene	N3	A	2
C4-Naphthalene	N4	A	2
Biphenyl	BI	A	2
Acenaphthylene	AC	A	2
Acenaphthene	AE	A	2
Fluorene	F	A	2
C1-Fluorenes	F1	A	2
C2-Fluorenes	F2	A	2
C3-Fluorenes	F3	A	2
Dibenzothiophene	D	A	3
C1-Dibenzothiophene	D1	A	3
C2-Dibenzothiophene	D2	A	3
C3-Dibenzothiophene	D3	A	3
C4-Dibenzothiophene	D4	A	3
Anthracene	A	A	3
Phenanthrene	P	A	3
C1-Phenanthrene/Anthracene	PA1	A	3
C2-Phenanthrene/Anthracene	PA2	A	3
C3-Phenanthrene/Anthracene	PA3	A	3
C4-Phenanthrene/Anthracene	PA4	A	3
Fluoranthene	FL	A	3
Pyrene	PYR	A	3
C1-Fluoranthene/Pyrene	FP1	A	3
C2-Fluoranthene/Pyrene	FP2	A	3
C3-Fluoranthene/Pyrene	FP3	A	3
C4-Fluoranthene/Pyrene	FP4	A	3
Benzo(a)Anthracene	BA	A	4
Chrysene	C	A	4
C1-Chrysenes	C1	A	4
C2-Chrysenes	C2	A	4
C3-Chrysenes	C3	A	4
C4-Chrysenes	C4	A	4
Benzo(b)fluoranthene	BB	A	5
Benzo(k)fluoranthene	BK	A	5
Benzo(e)pyrene	BEP	A	5
Benzo(a)pyrene	BAP	A	5

ANALYTES	Abbreviation	Internal Standard	Surrogate Standard
Perylene	PER	A	6
Indeno(1,2,3-cd)pyrene	IP	A	5
Dibenzo(a,h)anthracene	DA	A	5
Benzo(g,h,i)perylene	BP	A	5
Total PAH	**TPAH**		**5**

Saturated hydrocarbons (SHC or n-alkanes)

n-Decane	C10	B	7
n-Undecane	C11	B	7
n-Dodecane	C12	B	7
n-Tridecane	C13	B	7
n-Tetradecane	C14	B	8
n-Pentadecane	C15	B	8
n-Hexadecane	C16	B	8
n-Heptadecane	C17	B	8
Pristane	Pristane	B	8
n-Octadecane	C18	B	9
Phytane	Phytane	B	9
n-Nonadecane	C19	B	9
n-Eicosane	C20	B	9
n-Heneicosane	C21	B	9
n-Docosane	C22	B	10
n-Tricosane	C23	B	10
n-Tetracosane	C24	B	10
n-Pentacosane	C25	B	10
n-Hexacosane	C26	B	10
n-Heptacosane	C27	B	10
n-Octacosane	C28	B	10
n-Nonacosane	C29	B	11
n-Triacontane	C30	B	11
n-Hentriacontane	C31	B	11
n-Dotriacontane	C32	B	11
n-Tritriacontane	C33	B	11
n-Tetratriacontane	C34	B	11
Total n-Alkanes	TALK		
Calibrated analytes are identified by boldface. Internal standards: A = hexamethylbenzene; B = dodecylcyclohexane. Surrogate standards: 1 = naphthalene-d8, 2 = acenaphthene-d10, 3 = phenanthrene-d10, 4 = chrysene-d12, 5 = benzo[a]pyrene-d12, 6 = perylene-d12, 7 = dodecane-d26, 8 = hexadecane-d34, 9 = eicosane-d42, 10 = tetracosane-d50, and 11 = triacontane-d62.			

Petroleum Biomarkers

Class	Biomarker	Abbrev
Terpanes	C23 tricyclic terpane	T4
	C24 tricycilic 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),17â(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 Hydrocarbon Method Detection Limits (MDL) at Auke Bay Laboratory.

All values in ng/g dry weight (based on average 2008-2012 wet wt/dry wt measurements).

Analyte	Abbrev	Tissue				Sediment		
		1993	1996	2010		1993	1996	2010
naphthalene	N	24.4	19.1	1.9		0.98	2.48	0.06
2-methylnaphthalene		11.0	12.1	1.1		0.90	1.44	0.06
1-methylnaphthalene		14.6	31.4	1.0		1.98	1.08	0.06
2,6-dimethylnaphthalene		7.8	6.3	0.8		1.88	0.71	0.04
2,3,5-trimethylnaphthalene		4.7	7.6	0.7		0.90	0.37	0.02
biphenyl*	BI	8.3	26.6	20.7		4.13	0.90	0.19
acenaphthylene	AC	6.3	21.3	1.0		2.40	0.73	0.04
acenaphthene	AE	6.0	8.7	0.4		1.17	0.54	0.04
fluorene	F	5.6	19.7	1.3		1.75	1.31	0.04
dibenzothiophene	DBT	3.9	12.7	0.6		0.92	0.44	0.04
phenanthrene	P	9.2	12.3	0.8		1.29	0.71	0.02
1-methylphenanthrene		6.2	28.1	0.9		2.62	0.56	0.02
anthracene	A	7.2	9.9	0.9		3.19	0.50	0.02
fluoranthene	FL	13.1	23.1	0.8		0.88	0.44	0.02
pyrene	PYR	10.9	23.8	0.8		1.00	0.38	0.02
benzo(a)anthracene	BAA	4.8	8.2	0.3		0.33	0.31	0.04
chrysene	C	6.1	13.1	0.6		2.54	0.81	0.02
benzo(b)fluoranthene	BBF	6.7	37.6	0.6		1.17	0.46	0.08
benzo(k)fluoranthene	BKF	8.7	18.6	0.9		0.77	0.35	0.08
Benzo(e)pyrene	BEP	9.1	22.1	0.7		1.15	0.60	0.06
Benzo(a)pyrene	BAP	7.2	17.8	1.1		3.10	0.44	0.02
Perylene	PER	10.4	25.0	5.1		1.12	0.98	0.02
Indeno(1,2,3-cd)pyrene	IND	4.9	11.8	0.4		0.65	0.38	0.06
dibenzo(a,h)anthracene	DBA	4.2	14.7	0.3		0.48	0.35	0.06
benzo(ghi)perylene	BGHI	6.1	41.0	0.6		0.90	0.77	0.02
						0.00	0.00	0.00
min		3.9	6.3	0.3		0.33	0.31	0.02
max		24.4	41.0	20.7		4.13	2.48	0.19
median		7.2	18.6	0.8		1.15	0.56	0.04
extracted sample mass (g wet weight)		10	8	10		20	40	40

|								
n-nonane	C9			20				0.97
n-decane	C10	186	643	31		5.9	6.7	0.52
n-undecane	C11	109	523	39		4.3	7.9	0.90
n-dodecane	C12	71	305	39		6.4	7.7	2.10
n-tridecane	C13	143	211	91		5.5	13.3	1.69
n-tetradecane	C14	272	284	38		4.3	15.5	1.58
n-pentadecane	C15	251	214	21		19.4	16.6	1.06
n-hexadecane	C16	394	168	14		8.5	18.7	0.58
n-heptadecane	C17	526	166	16		10.9	17.5	0.27
pristane	Prist	283	159	32		20.2	15.5	0.38
n-octadecane	C18	204	99	7		23.3	27.3	0.44
phytane	Phyt	204	98	8		23.3	19.2	0.50
n-nonadecane	C19	240	76	6		5.3	6.9	0.23
n-eicosane	C20	274	56	7		10.4	8.1	0.12
n-heneicosane	C21	201	38	7		9.1	8.1	0.19
n-docosasne	C22	75	60	13		6.0	8.3	0.21
n-tricosane	C23	149	52	9		21.3	8.1	0.62
n-tetracosine	C24	172	49	24		33.7	10.4	0.44
n-pentacosane	C25	101	25	15		7.3	8.6	0.27
n-hexacosane	C26	104	84	18		20.4	6.3	0.50
n-heptacosane	C27	196	78	32		16.4	5.1	0.31
n-octacosane	C28	179	137	30		13.5	16.9	0.44
n-nonacosane	C29	332	111	18		14.7	7.7	0.40
n-triacontane	C30	219	175	20		17.9	4.5	1.10
n-hentriacontane	C31	0	0	26		0.0	0.0	0.40
n-dotriacontane	C32	153	394	21		23.3	11.6	0.42
n-tritriacontane	C33	0	0	83		0.0	0.0	0.98
n-tetratriacontane	C34	89	407	99		13.9	57.3	2.92
n-pentatriacontane	C35	0	0	127		0.0	0.0	5.15
n-hexatriacontane	C36	0	0	134		0.0	0.0	7.00
min		71	25	6		4.3	4.5	0.12
max		526	643	134		33.7	57.3	7.00
median		196	137	21		13.5	8.6	0.50
extracted sample mass (g wet weight)		8	8	10		20	40	40

* Biphenyl is sometimes encountered as a laboratory artifact (as it was during the MDL study) thereby elevating the MDL for this constituent compared to the other analytes. It is not utilized to a great extent in the LTEMP data analysis.

Appendix 3. Histogram Plots For 2015 Field Samples And Blanks
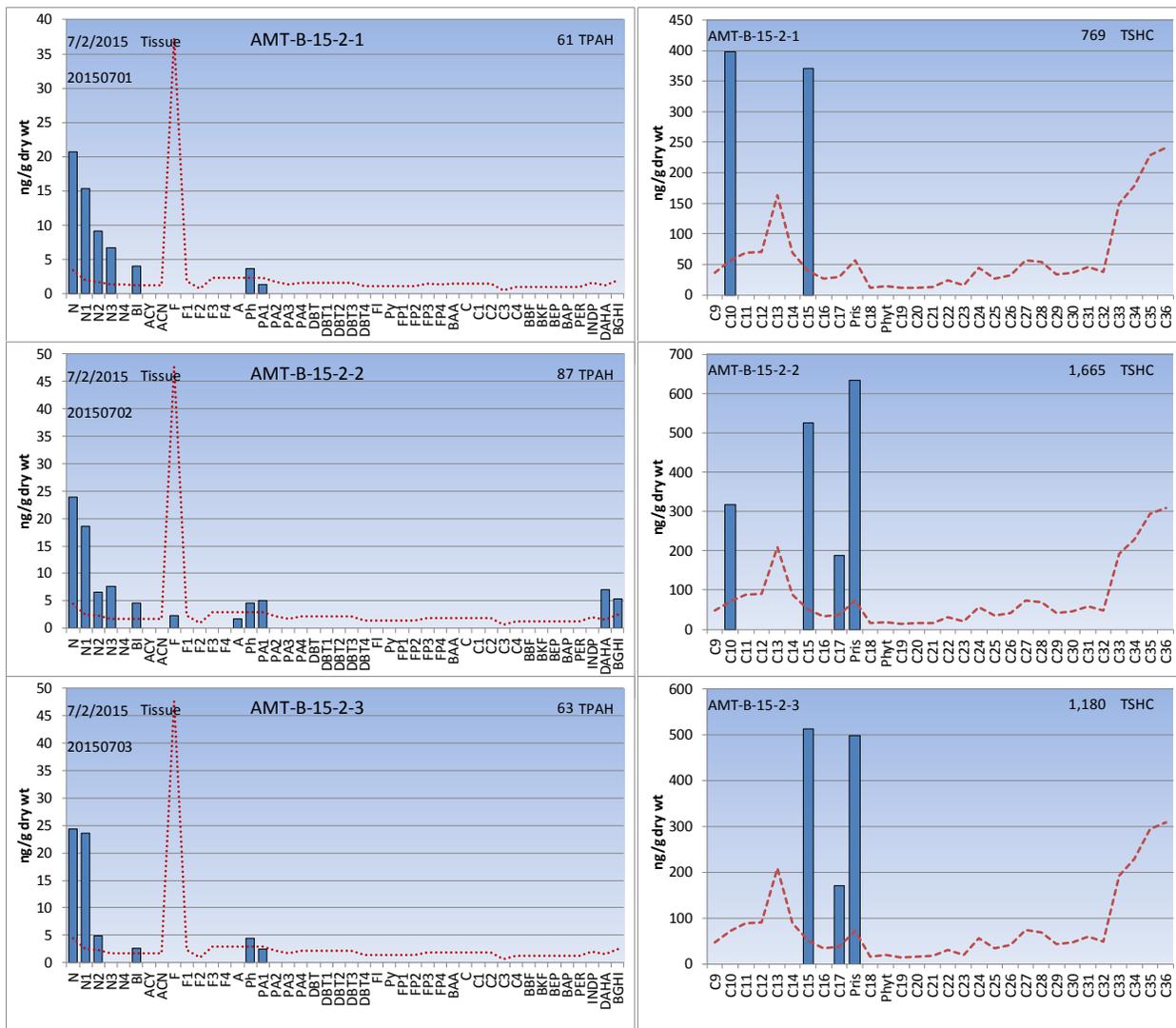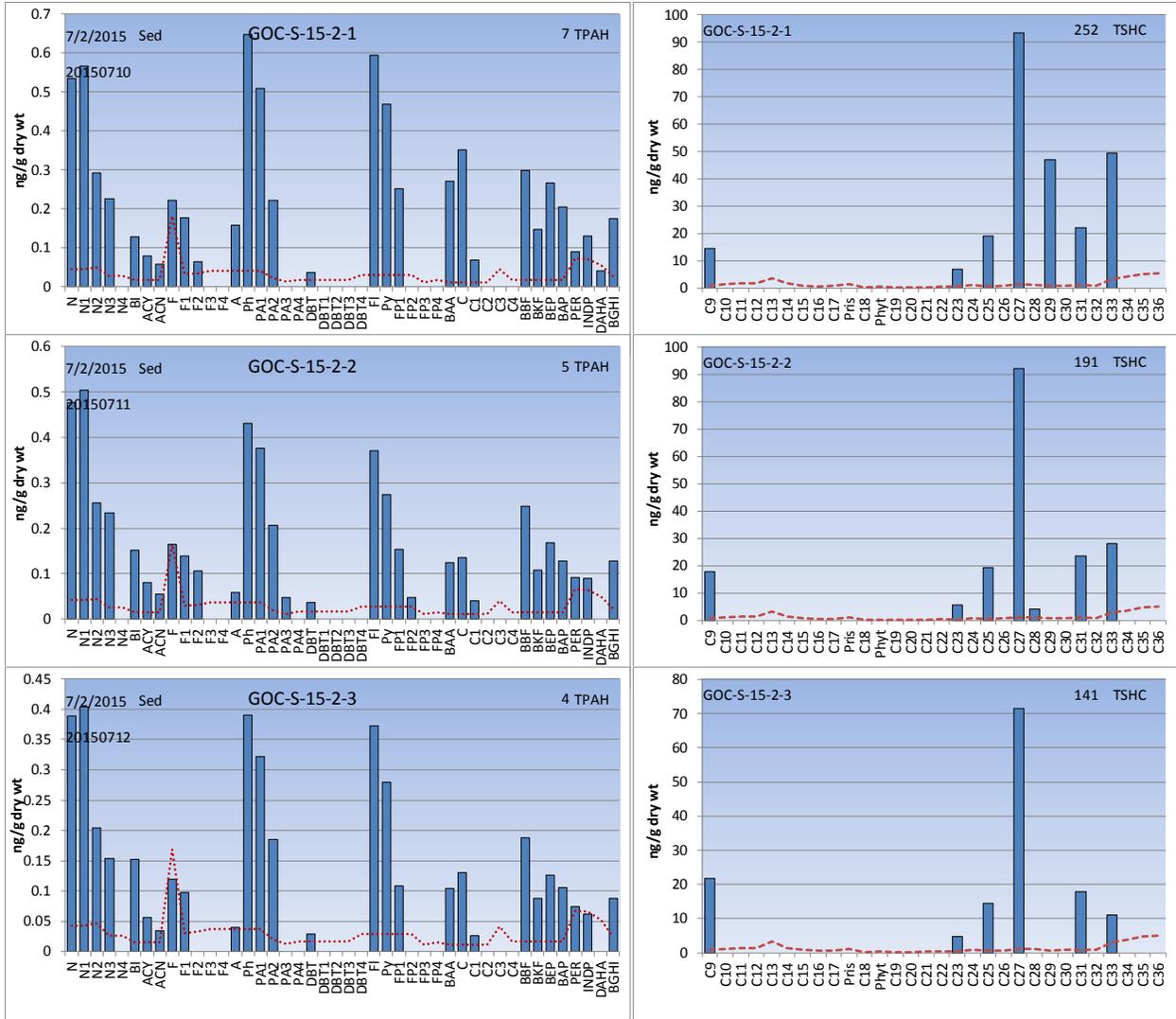

PAH and SHC plots of replicate mussel tissue samples from AMT, July 2015. Dotted red line represents lab method detection limits.
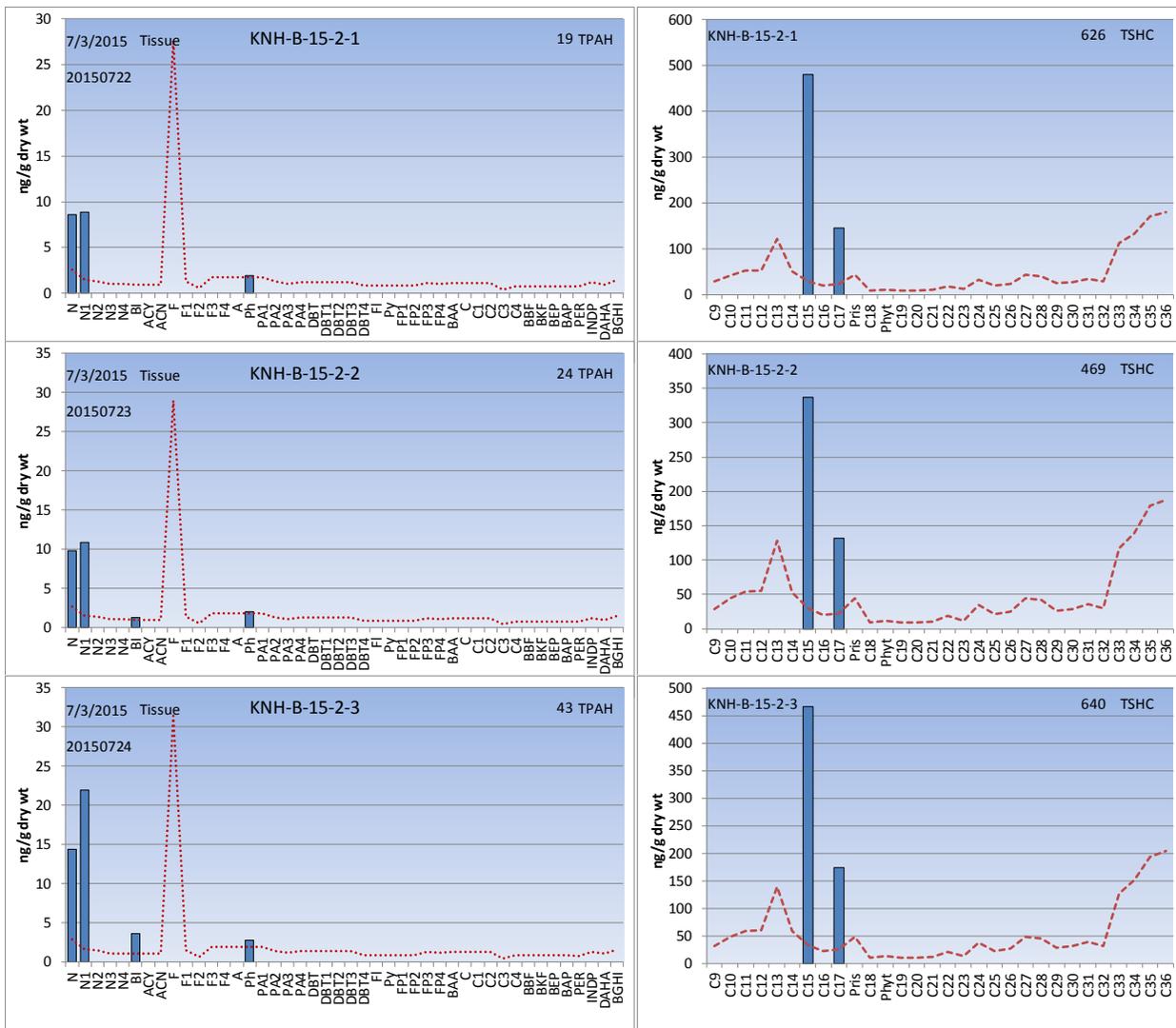
PAH and SHC plots of replicate mussel tissue samples from GOC, July 2015.   Dotted red line represents lab method detection limits.
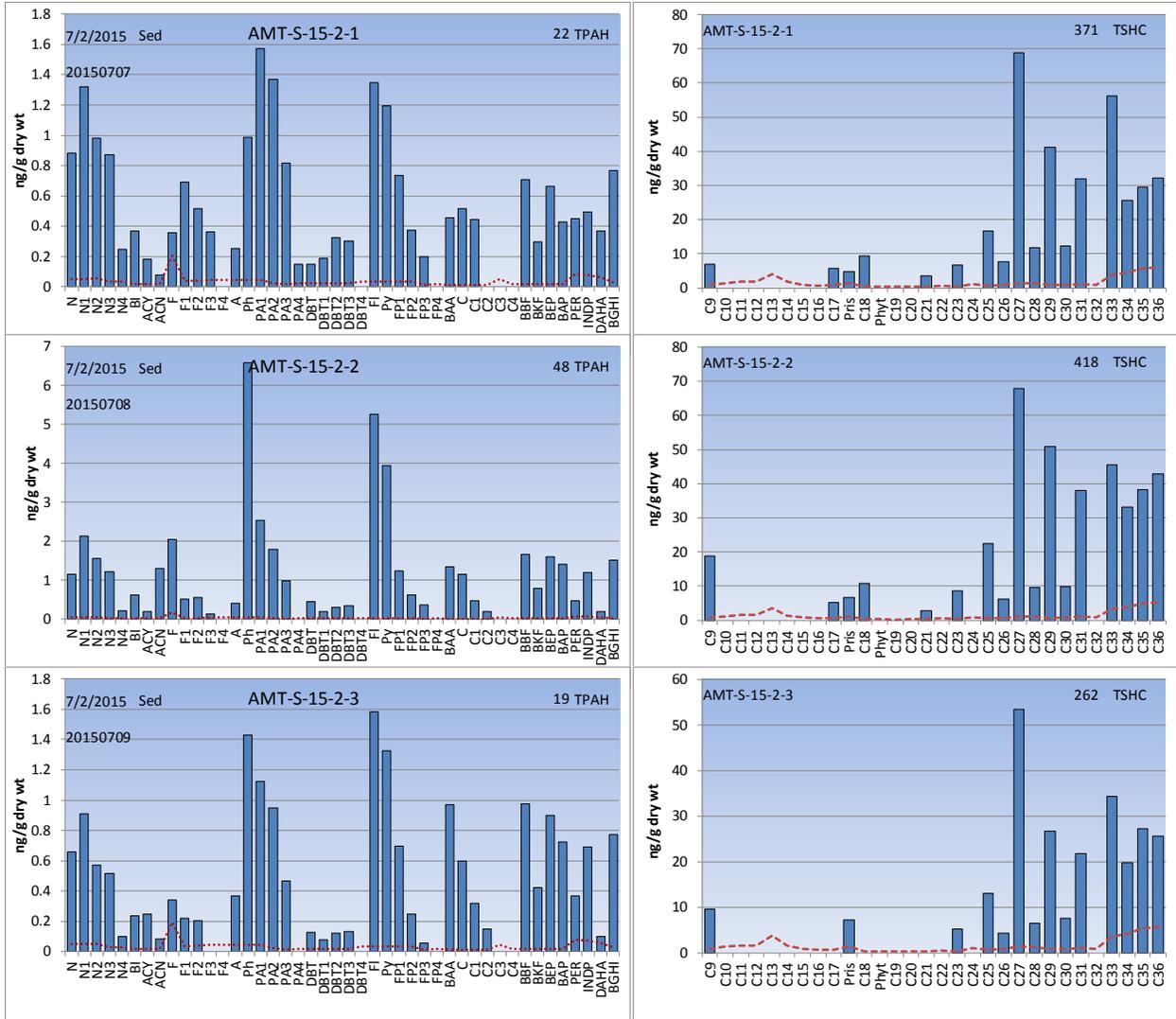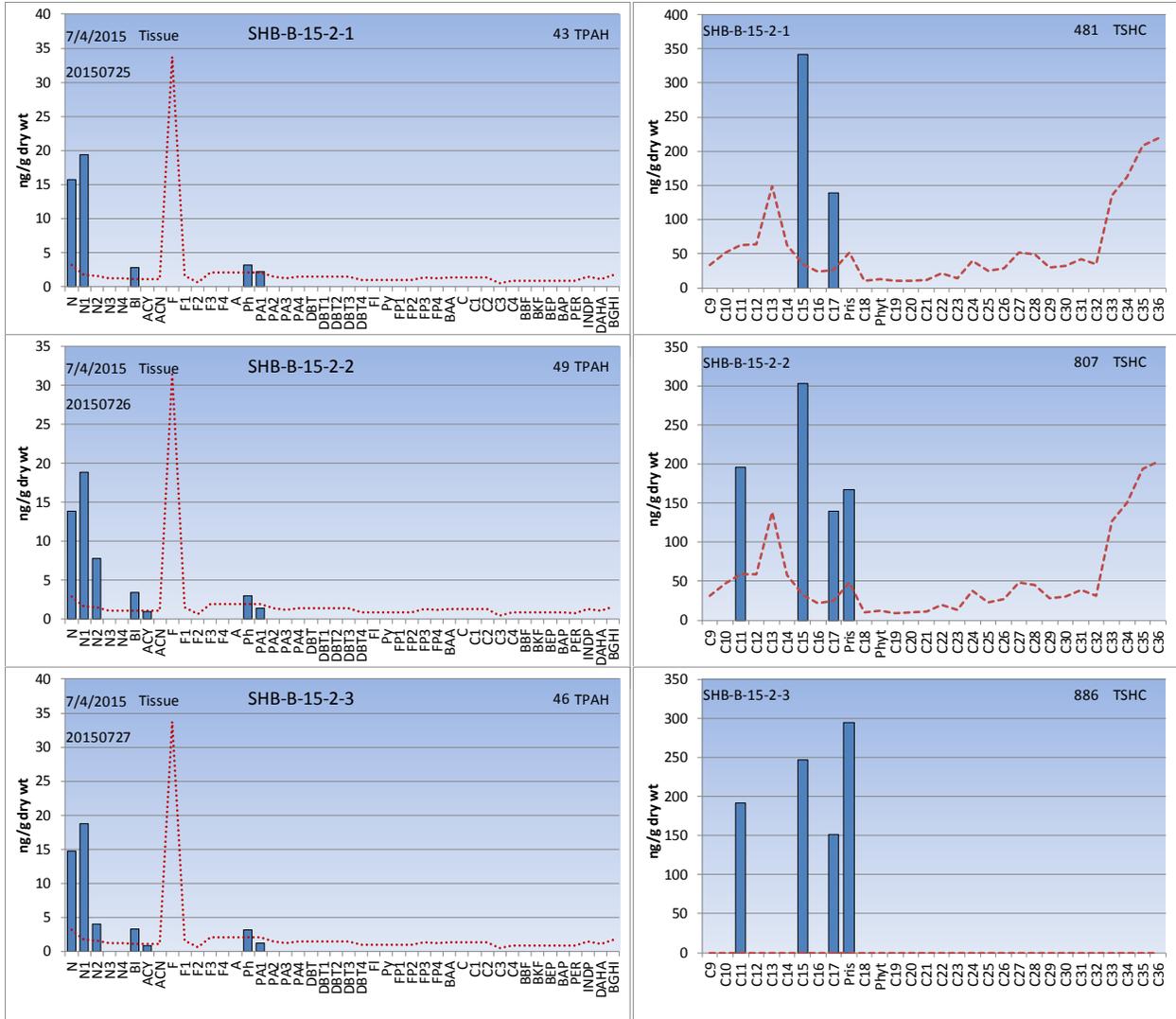
PAH and SHC plots of replicate sediment samples from AMT, July 2015. Dotted red line represents lab method detection limits.

PAH and SHC plots of replicate sediment samples from GOC, July 2015.   Dotted red line represents lab method detection limits.

PAH and SHC plots of replicate mussel tissue samples from Knowles Head (KNH), July 2015. Dotted red line represents lab method detection limits.

PAH and SHC plots of replicate mussel tissue samples from Sheep Bay (SHB), July 2015. Dotted red line represents lab method detection limits.
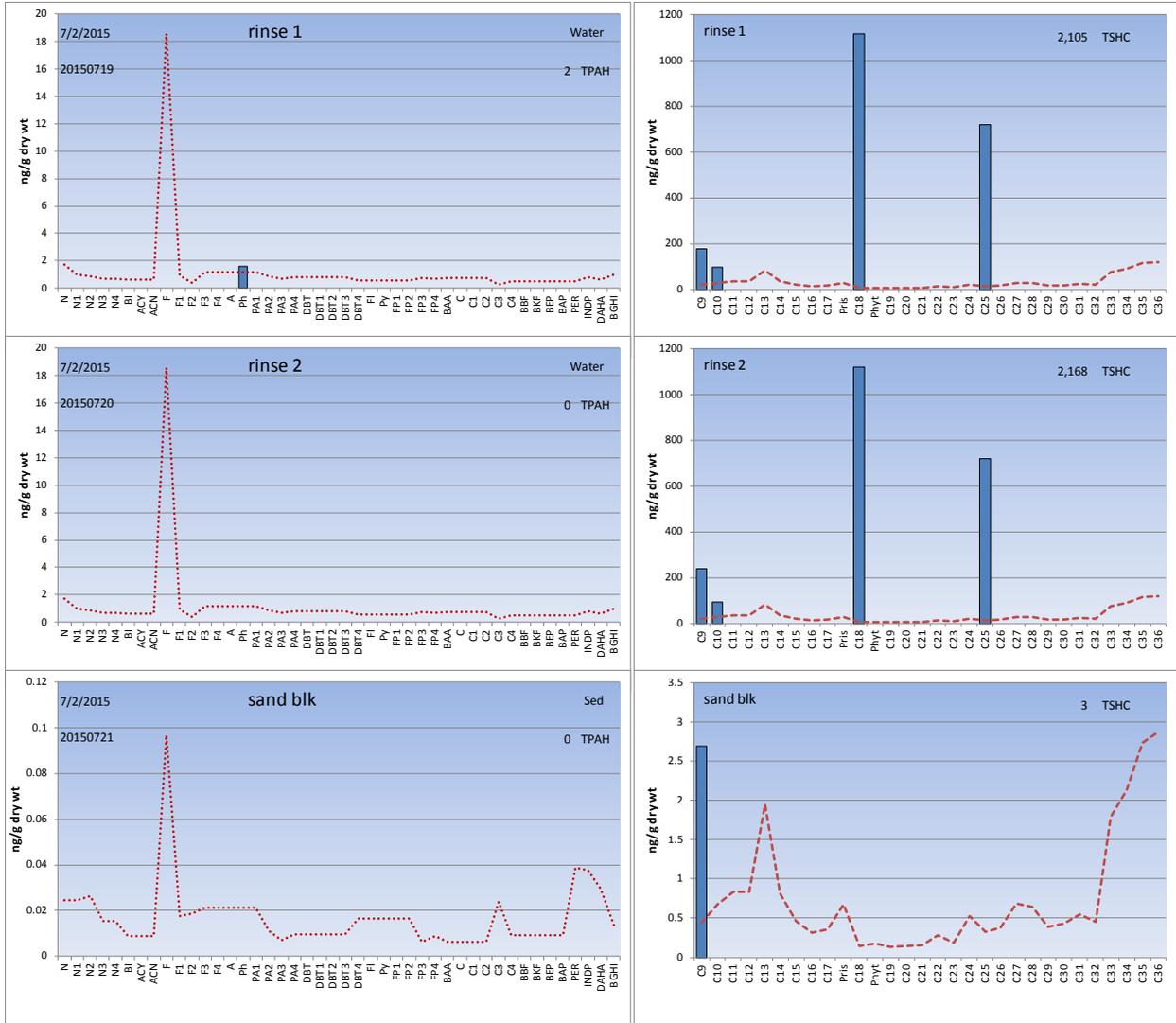
PAH and SHC plots of field quality control rinse and trip blank samples, July 2015. Dotted red line represents lab method detection limits