
LONG-TERM ENVIRONMENTAL MONITORING PROGRAM

RESULTS AND INTERPRETATIONS FROM SAMPLING, 2008-2013



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June 2015



PWSRCAC Contract No.

951.10.01

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Cover image – sediment sampling at the Gold Creek (GOC) reference site from the *M/V Auklet*, July 2006. Photo by Chris Boswell.

ABBREVIATIONS**Stations:**

AMT	Alyeska Marine Terminal, Port Valdez
AIB	Aialik Bay, west of Seward
COH	Constantine Harbor, Hinchinbrook Entrance, PWS
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
EVOS	<i>Exxon Valdez</i> 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
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, 2008-2013

ABSTRACT

In recent years, petrogenic hydrocarbon inputs from the Alyeska Marine Terminal (AMT) and tanker operations have been declining in both mussels and sediments as reflected in total polycyclic aromatic hydrocarbon (TPAH) concentrations for Port Valdez. This trend reflects a combination of reduced ballast-water-treatment-facility (BWTF) 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 polycyclic aromatic hydrocarbons (PAH). Additionally, over the last several years, mussel contamination has been generally shifting away from the terminal's petrogenic profiles to background pyrogenic PAH patterns; however, in 2013, there were suggestions of petrogenic traces at both the terminal and background-reference site at Gold Creek (GOC). The concentrations are still extremely low; estimated (with below-detection-limit caveats) at 17-20 ng/g dry weight (DW). TPAH concentrations in the Port sediments are now at all-time lows (4-10 ng/g DW), and the AMT sediments are now beginning to look more like the background-reference, pyrogenic profiles that have been observed for years at GOC. Even the saturated hydrocarbon (SHC) profiles in the AMT sediments are reflecting a mixture of petrogenic and terrestrial, biogenic inputs. Oil biomarker analytes, relatively new to LTEMP sediment methods, show low-level ANS oil traces in the Port sediments. At GOC, the biomarker concentrations are seven times lower than those in AMT sediments, with the profiles indicating mixtures with background sources. Outside the Port, near the tanker anchorage at Knowles Head, mussels continue to show clean, trace-level patterns, although petrogenic traces of phenanthrenes/anthracenes and SHC were suggested in 2013.

Beyond the tanker operations area, in the central Prince William Sound (PWS) and Gulf of Alaska (GOA) stations, TPAH levels in mussels have modestly increased between the 2009 and 2013 collections (current range estimated at 9-73 ng/g DW). The majority of this change is due to traces of dissolved-phase naphthalenes and a subtle shift from pyrogenic to petrogenic phenanthrenes/anthracenes with slightly higher concentrations at all but two stations. In both 2009 and 2013 sample sets there is remarkable within-site fidelity (replicability) in PAH and SHC patterns. Although the samples each comprise only a few analytes, the components show a common complexity of dissolved, petrogenic, and pyrogenic patterns that implies effects from a region-wide process. Compared to the most recent West Coast Mussel Watch data (2004-05) and the more recent 2008-10 Alaskan Mussel Watch sites, LTEMP results demonstrate that the region is exceptionally clean. Any lingering *Exxon Valdez* oil spill (EVOS) deposits are not appearing in LTEMP mussel samples.

INTRODUCTION

PROJECT HISTORY

The primary objective of the ongoing Long-Term Environmental Monitoring Program (LTEMP) is to collect "...standardized measurements of hydrocarbon background in the EVOS region as long as oil flows through the pipeline." Under Federal and State statutes, the unregulated release of oil into the environment is strictly prohibited; the LTEMP data serve as a sentinel indicator and independent quality control check for Alyeska Marine Terminal and tanker operations throughout the region.

The Ballast Water Treatment Facility (BWTF) at the Terminal treats and discharges oil-contaminated ballast water offloaded from tankers utilizing the Port, so two stations – Alyeska Marine Terminal (AMT) adjacent to the 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 and eight stations 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 recently 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 the current 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, dropped from the original program in 1995 due to results being confounded from lipid interference, were reinstated in 1998. Improved laboratory methods have essentially eliminated interference issues at this time.

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 had accumulated in the intertidal mussels within the Port. Payne et al. (2001) concluded, however, that the PAH and SHC levels measured in sediments and mussel tissues (and the estimated water-column levels) were very low and unlikely to cause deleterious effects. From the analyte signatures, they were able to further discriminate between particulate- (oil droplet) and dissolved-phase signals in the water column and then correlate those signals with seasonal uptake of hydrocarbons in mussels and with absorption in herring eggs (from other studies). 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. They concluded 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).

In July 2002, Payne Environmental Consultants, Inc. (PECI) and the NOAA/NMFS Auke Bay Laboratory (ABL) began conducting LTEMP operations. Detailed discussions of the transitional 2002/2003 LTEMP samples and interlaboratory 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 et 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 day levels of 0.5 million barrels per day in 2015. Likewise, tanker regulations have instituted double-hulled tankers with segregated ballast. On segregated-ballast vessels, 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 0.6 MGD in 2015. Less tanker traffic, cleaner ballast, and a new ballast-water-treatment configuration at 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, which, for the last two permit renewal cycles, PWSRCAC submitted detailed reviews of concerns (Payne et al., 2003c and 2012).

For this report, all ten LTEMP stations were visited in July 2008, April 2009, and July 2013; three sites were in or near the Port to monitor terminal and tanker operations, and seven to monitor the more remote sites for lingering EVOS impacts. To more thoroughly monitor Port operations, collections were taken annually at the two Port sites and nearby Knowles Head. This report summarizes findings for July 2008 through July 2013, a period comprising the previous contract's final year (2008-2009) for visiting all sites plus the final 2013 grand sampling event. As appropriate, the results are presented with the overall perspective/trend analysis from the inception of the monitoring program (1993).

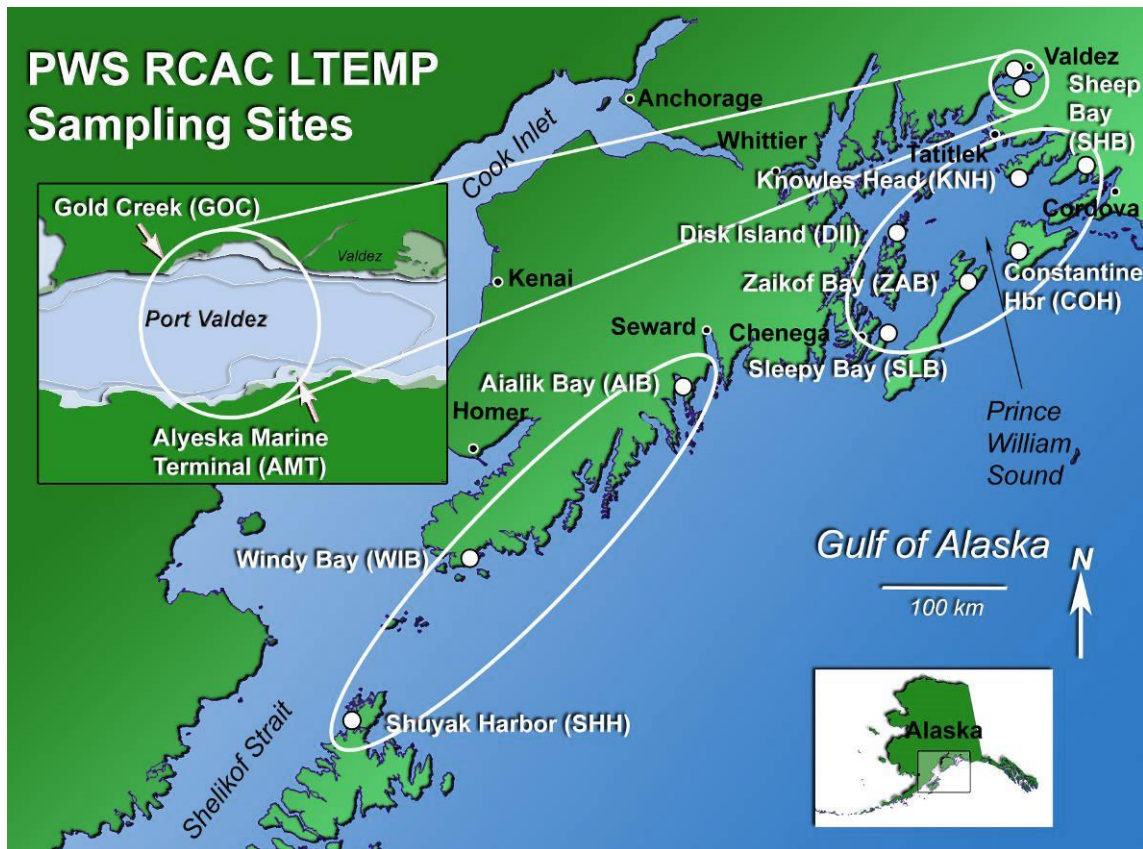


Figure 1. Map of the LTEMP sites. Circled regions represent sites with similar hydrocarbon signatures and events.

METHODS

Collection and analytical methods have been described in previous LTEMP reports (Payne et al., 2003b; 2005a; 2006; 2008a, 2010a). Briefly, three replicates of mussels are collected by hand at each site while triplicate sediment samples are collected from 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 polycyclic aromatic hydrocarbons (PAH by modified Method 8270, GC/MS SIM) and saturated hydrocarbon (SHC by Method 8015, GC FID) data, recently added to this contract are petroleum biomarkers for sediment samples. In 2011, Auke Bay Laboratory (ABL) modified their analytical procedures but realizing the information potential, expanded beyond the contractual list to report a more complete suite (Appendix 1, n=48), one more practical for oil spill forensics (Wang and Stout, 2007). Technically, acquiring biomarker data is an extension of the 8270 method for PAH whereby four ions (191, 217, 218 and 231), are added to the mass spectrometer's list for selective ion monitoring (SIM).

BIOMARKERS

Petroleum biomarkers are conservative, weathering-resistant, hydrocarbon compounds, unique to an oil formation and that, for LTEMP, can facilitate and confirm detection of AMT-derived, Alaska North Slope (ANS) 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 sources¹. 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., during a spill).

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).

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 α (H),21 β (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 overlaid ANS reference 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. Normally, the T6 triplets' ratio also would be added to the final diagnostics list but not when the lab is having analytic issues (one analyte is co-eluting). For this report, we simply report the patterns and the unexpected complication in their interpretations.

¹ For readers who are not familiar with oil-spill fingerprinting or forensics, see Appendix 6 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.

RESULTS AND DISCUSSION

LABORATORY QUALITY CONTROL

As in previous LTEMP reports, all analytes 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 98.8% of all PAH and 100% for alkane surrogate hydrocarbons analyzed during the 2013 reporting period. For the biomarker analytes, mean surrogate recovery was slightly high, 128 vs. 120% for the three runs of 2011-13 analyses, but the data were considered usable because of good agreement within the inter-laboratory comparison exercise and the fact that all the biomarker analytes are compared to a common surrogate. Laboratory method blanks for 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 QC performance 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 previous MDLs, PAH limits are now down to medians of 0.02 ng/g wet weight in sediments and 0.07 ng/g wet weight in tissues (Table 1 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 1. 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

The best use of these MDL values is debatable. 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 is certainly required when reviewing a single-analyte analysis, e.g., water arsenic concentration, where this 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 rational, predictable results, i.e., one does not have to place all reliance on knowledge-blind expectations from a Gaussian curve (from a statistical perspective, additional knowledge is analogous to Bayesian priors). Such is the case with LTEMP data. Oil weathers in predictable patterns (see Appendix 6) and if a sample’s PAHs appear to the forensics-expert data interpreter to represent a rational pattern, then applying the statistically established, single-analyte, MDLs (censuring the data) would be more conservative than necessary. For example, if a sample’s phenanthrenes (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 (see analyte patterns in Figure 2 and Appendix 6), there would be sufficient confidence that those analytes were not false positives and that the values had been reasonably estimated. This added-confidence attribute is further bolstered in LTEMP data by seeing higher-level patterns of within-site fidelity and regional-wide commonalities that changed uniquely 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. From the opposite view, when an irrational pattern appears, it’s 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 a lab, sampling or field anomaly.

In summary, 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 this study, it is felt that option two best serves the purpose of the program. For the readers and our benefit in reviewing data, individual analyte MDLs (adjusted to sample weight) appear on PAH and SHC plots as red dotted lines.

SOURCE STANDARDS

With known changes in ANS reservoir output since the 1970’s, it seemed prudent to reanalyze a fresh sample of the pipeline source oil for comparison to LTEMP results. A 2012 sample sent from Alyeska to Environment Canada was split for intercalibration with Auke Bay Lab. Results from the two labs are mostly similar (Figure 2) with minor exceptions to C2- and C3-naphthalenes (N2 & N3), C3-fluorene (F3), C3-dibenzothiophene (DBT3) and the chrysenes (C-C2). In comparing the two 2012 samples, there would be no problem forensically identifying ANS oil analyzed at either lab. There are more significant differences in comparing the 1989 ANS cargo from the *Exxon Valdez* tanker hold (ABL ANS 1989) with the Environment Canada 2002 sample (ENVC ANS 2002) (Figure 2).

Overall, there were some differences in the freshness of naphthalenes but naphthalenes are highly volatile; the differences were likely due to field and lab handling procedures and tenure of the samples. For unknown reason(s), there is also unexpected variability in the dibenzothiophenes (DBT) that don’t follow a time trend. Since both labs agree on the 2012 DBT values, the possibility of lab differences diminishes but an actual change in ANS-oil sulfur content is possible. Or perhaps the production blend is not as constant as we presume. In the Gulf of Mexico, subtle variations in sulfur-containing PAH are noted trending spatially across the seeps from the Macondo reservoir. Alyeska’s blends may reflect similar differences. For LTEMP, the answer is uncertain and not resolvable from only 3 samples. Still, the temporal changes in PAH patterns suggests the ANS oil biomarkers, too, may show similar compositional variability across years.

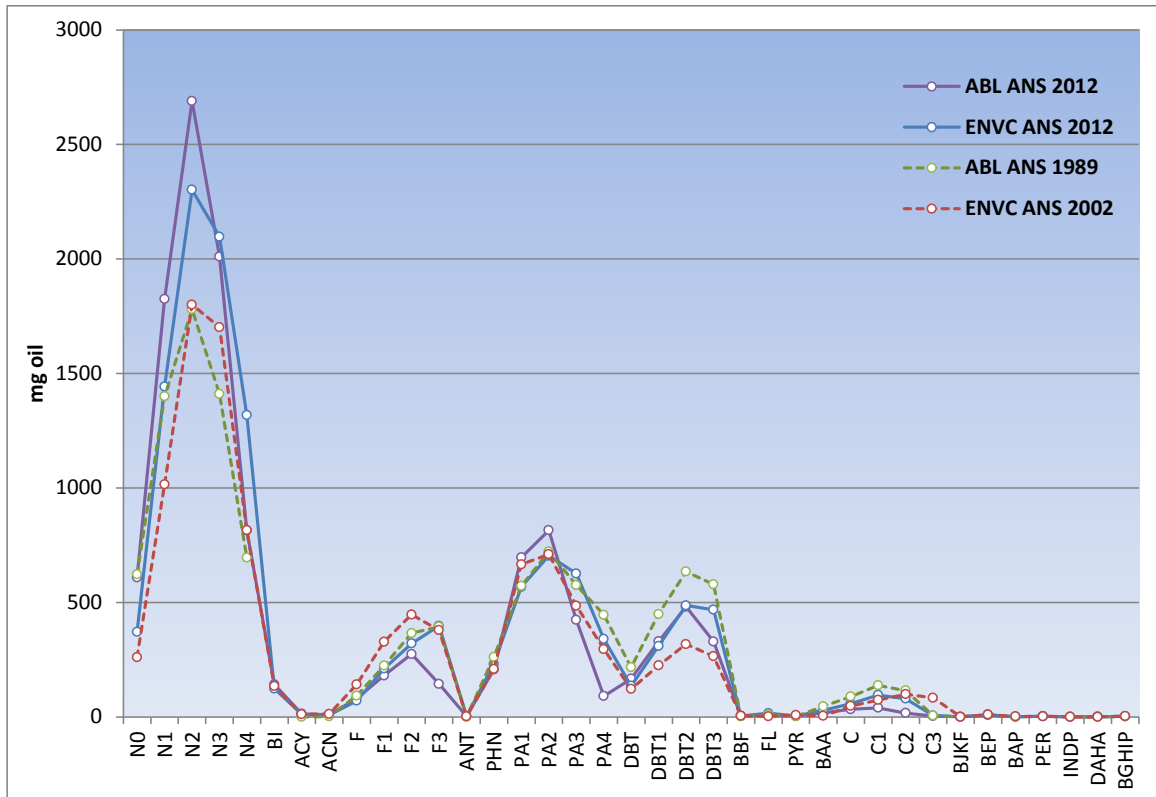
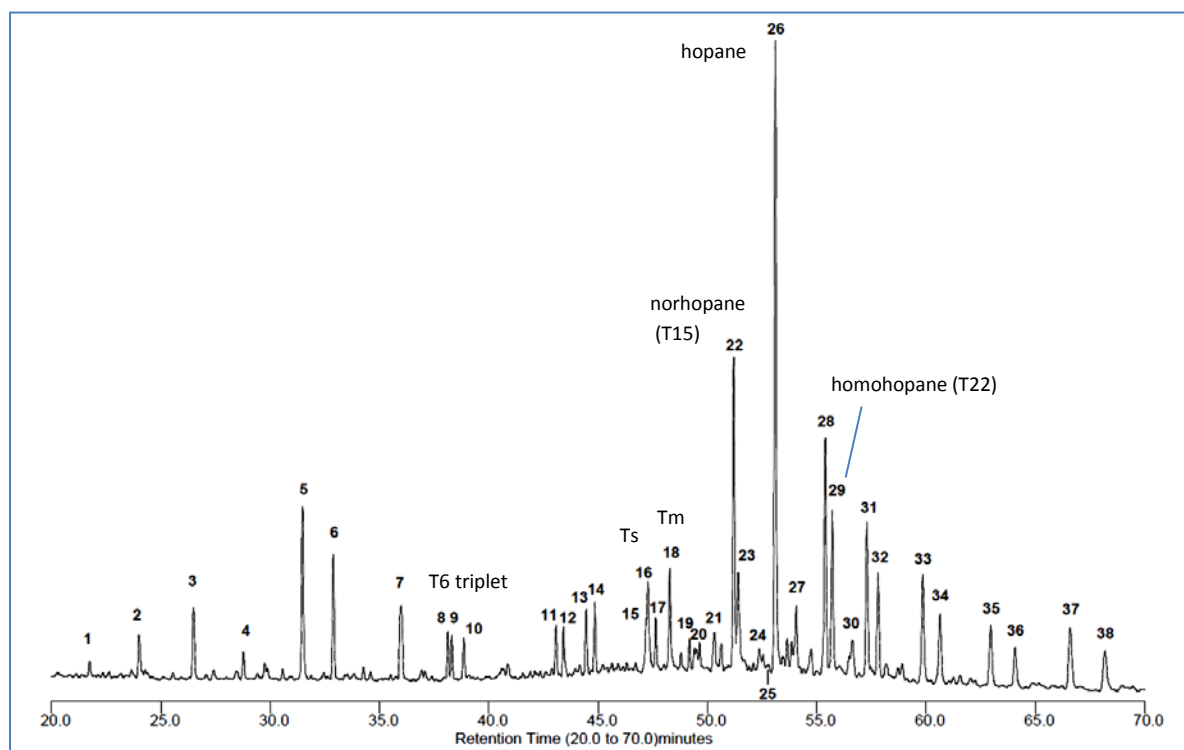
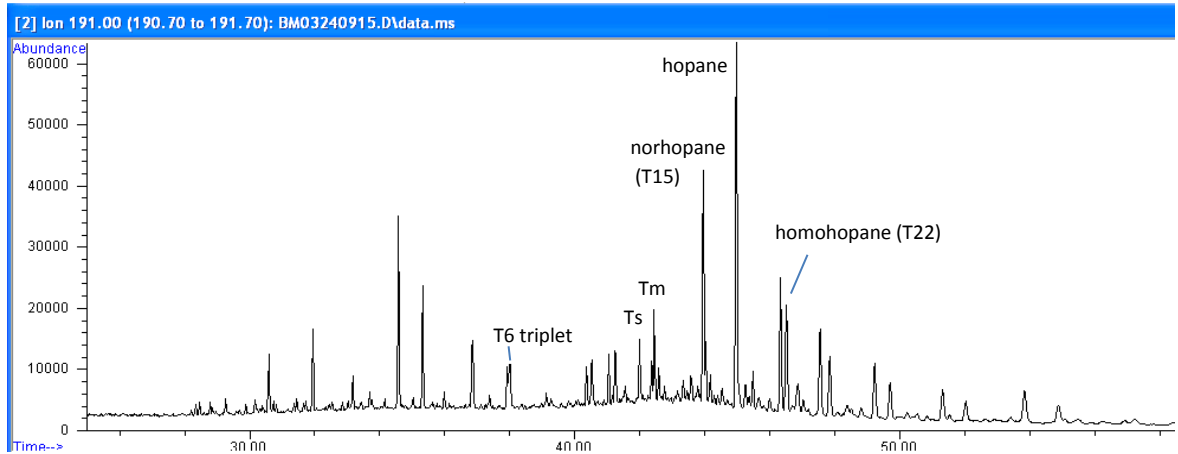


Figure 2. Inter-lab comparison of 2012 ANS oil PAH from Environment Canada and Auke Bay Lab versus earlier ANS oil standards.

BIOMARKER INTERCALIBRATION

ABL's ANS reference-oil biomarker results compared quite well with published results (Figure 3); however, the lab had issues separating the triplet T6 terpane compounds, T6a, T6b and T6c (identified as peaks 8, 9 & 10 [Figure 3 center]). This is unfortunate since these triplets are often used as one of the diagnostic source markers. In ABL's initial 2011-12 field samples, the quantified plots had deficits in mid-range terpane analytes but with such a small number of samples (n=6) analyzed from only two locations and only two analytic lab runs, it was difficult to know if these results reflected actual environmental conditions or analytic artifacts. Another possibility was that the ANS oil patterns had changed over the years from the 1989 standard as several North Slope fields are currently blended into the pipeline product. To resolve this concern, a sample of 2012 production ANS oil from Alyeska and split with Environment Canada was used to assess the current PAH and biomarker composition. These analyses would also serve as a biomarker inter-lab calibration exercise between Environment Canada (Bruce Hollebhone's lab) and Auke Bay.



1	C19 Tricyclic terpene	14	C29 [22R] Tricyclic terpene	27	17b21a Moretane [C30]
2	C20 Tricyclic terpene	15	C30 [22S] Tricyclic terpene	28	22S Homohopane [C31]
3	C21 Tricyclic terpene	16	18a Trisnorneohopane [C27 Ts]	29	22R Homohopane [C31]
4	C22 Tricyclic terpene	17	C30 [22R] Tricyclic terpene	30	Gammacerane [C30]
5	C23 Tricyclic terpene	18	17a Trisnorneohopane [C27 Tm]	31	22S Bishomohopane [C32]
6	C24 Tricyclic terpene	19	C31 [22S] Tricyclic terpene	32	22R Bishomohopane [C32]
7	C25 Tricyclic terpene	20	C31 [22R] Tricyclic terpene	33	22S Trishomohopane [C33]
8	C26 [22S] Tricyclic terpene	21	Bisnorhopane [C28]	34	22R Trishomohopane [C33]
9	C26 [22R] Tricyclic terpene	22	Norhopane [C29]	35	22S Tetrakishomohopane [C34]
10	C24 Tetracyclic terpene	23	18a Neonorhopane [C29]	36	22R Tetrakishomohopane [C34]
11	C28 [22S] Tricyclic terpene	24	17b21a Normoretane [C29]	37	22S Pentakishomohopane [C35]
12	C28 [22R] Tricyclic terpene	25	Oleanane [C30]	38	22R Pentakishomohopane [C35]
13	C29 [22S] Tricyclic terpene	26	Hopane [C30]		

Figure 3. GC/MS m/z 191 ion traces of terpanes and hopanes for 1989 ANS reference oil from Auke Bay Laboratory (upper plot) and a similar North Slope oil (lower plot) (Lilis et al., 1998) demonstrating comparability of detection.

Biomarker inter-lab calibration results were slightly inconclusive as the Environment Canada lab doesn't analyze the full suite of biomarkers reported by ABL (Figure 4). In 2015, they will report new results from a 2015 sample with the full suite, and have offered to provide older data from individual North Slope production fields from 2005 but they were not available for review at this time (B. Hollebhone, pers comm, 2015). In the limited current data, terpanes and hopanes (up through H35R) were recognizably close between labs but, for unknown reasons, the few steranes reported were divergent. Seeking a second and fuller confirmation, attempts to have Alpha Analytical, the premier lab used for NOAA NRDA efforts on the BP oil spill (DWH), participate in the inter-lab exercise were declined by lab management. Instead, indirect biomarker comparisons were made between ABL and Alpha labs using the DWH MC252 source oil, now a certified reference standard (NIST SRM) run with every DWH sample batch. Results are good (Figure 5). While there appear to be systematic quantification differences, they don't compromise the essential patterns or diagnostic ratios for forensic purposes. Looking at just terpanes (T4 to T19, hopane), comparing ABL's MC252 results to control oil averages from four BP contract labs (obtained from BP's Gulf Science Data public website) and Alpha (from NOAA NRDA public data), ABL results fall mid-group and thus, demonstrates its adequacy in quantifying biomarkers (Figure 6). The only note is that the T15 norhopane values are proportionately slightly lower than other labs. Self-referentially, the diminished T15 will not affect forensic interpretations when assessing ABL biomarkers. Comparing ABL results to other labs, e.g., Shaw's results in Alyeska Environmental Reports, will require an adjustment.

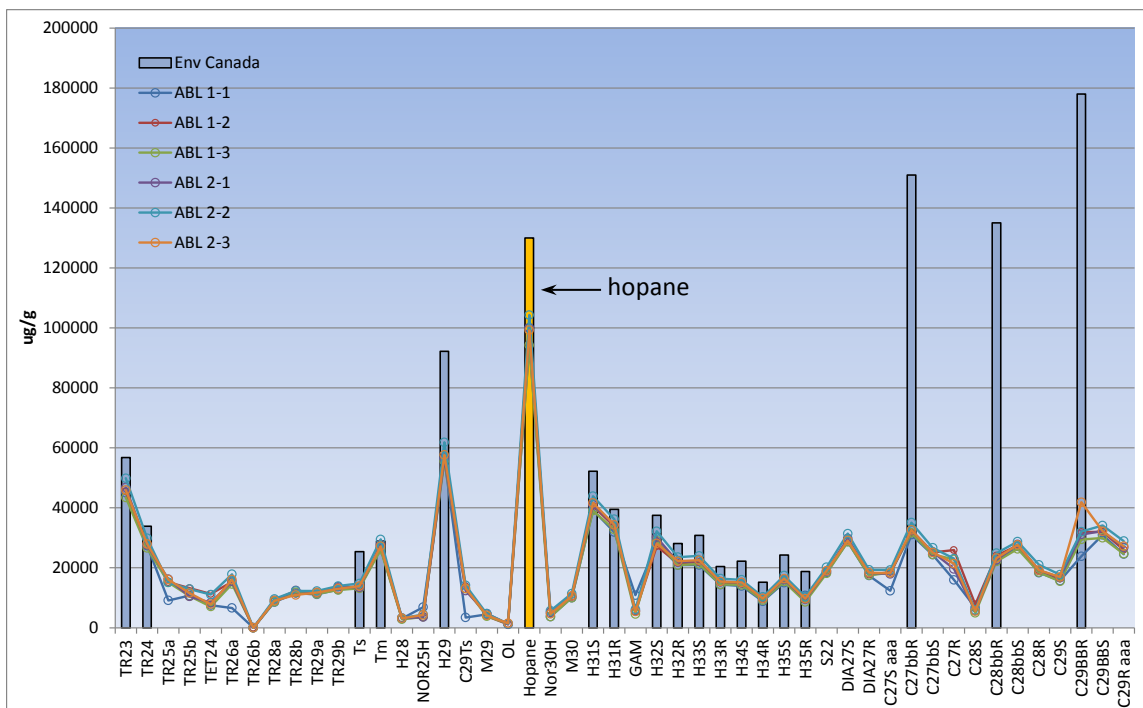


Figure 4. Inter-lab calibration results between ABL (6 reps) and Environment Canada (average of 3 reps) of biomarkers for 2012 ANS oil. Note that Environment Canada reported only a partial suite of biomarkers and the three steranes (right side of plot) are reported summed rather than as separate R and S epimers.

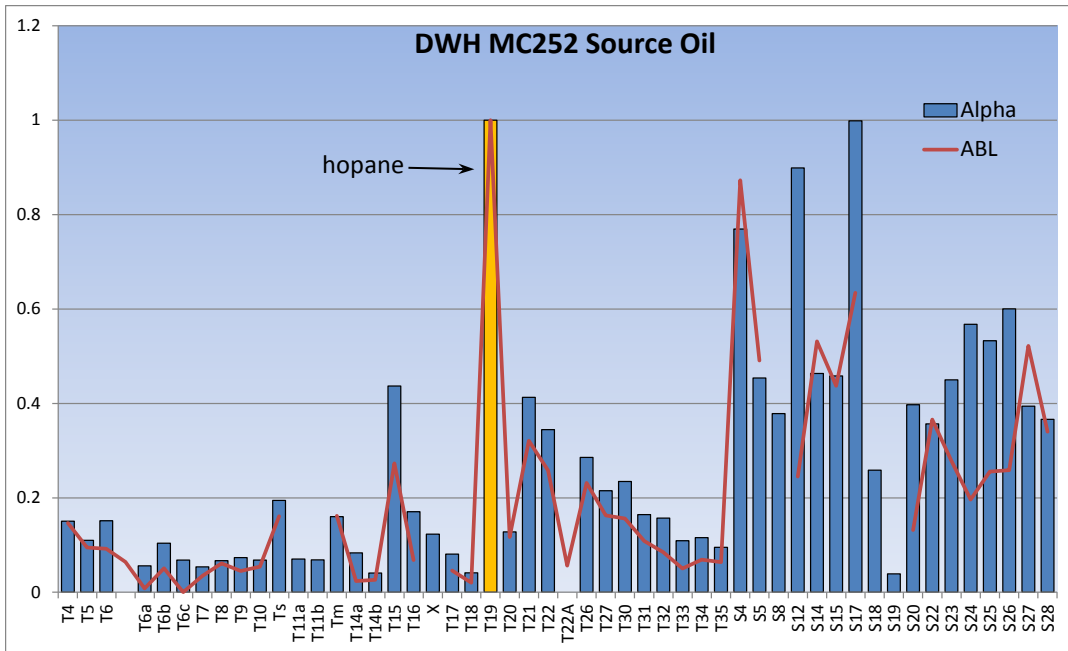


Figure 5. Inter-lab comparison of DWH reference oil biomarkers between Alpha and ABL, 2012.

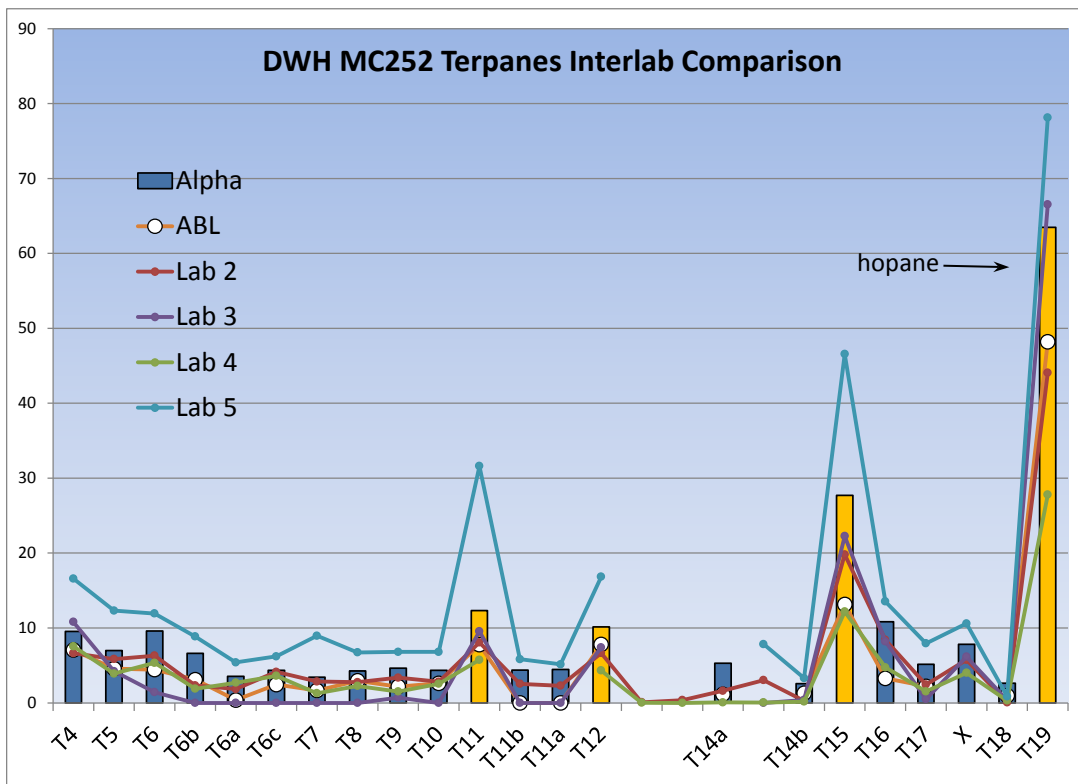


Figure 6. Interlab comparison of MC252 terpane biomarkers. Values represent averages of control oil runs by BP contract labs and NOAA NRDA's Alpha Lab versus ABL's single run. Labeling gaps are terpanes that do not have a common "T" abbreviated name.

PORT VALDEZ SEDIMENTS

ALYESKA MARINE TERMINAL

At the terminal, average sediment TPAH concentrations at the Berth 4 site had plateaued since March 2005 at around 50-60 ng/g DW, which were very low compared to historic levels (Figure 7). But in 2013, they dropped dramatically into near single-digit values (above MDLs). There has also been a shift in the PAH analyte patterns from generally petrogenic in 2008 to pyrogenic in 2011 and 2013 while the SHC profiles reflected more biogenic input over this period (Figure 8; all samples shown in Appendix 4). 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 8 top). Beginning in July 2009, the PAH patterns (Figure 8, second panel) suggested more of a mixed pyrogenic and petrogenic pattern in that the parent PAHs were greater than the remaining PAH within each homologue group, but there was still a hint of the PAH “hump” pattern in the remaining PAH that reflected a residual petrogenic influence. 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 8 third and bottom panel). In the SHC plots, the 2008 and 2009 alkanes were dominated by higher-molecular-weight petroleum waxes (Figure 8 top and second panel), but by July 2011, the SHC exhibited a mix of biogenic n-alkanes and higher-molecular-weight C₃₂-C₃₆ petroleum waxes (Figure 8 third panel). In 2013, the largely pyrogenic PAH concentrations had dropped to a new low of 10 ng/g DW, and the SHC was dominated by biogenic constituents (Figure 8 bottom).

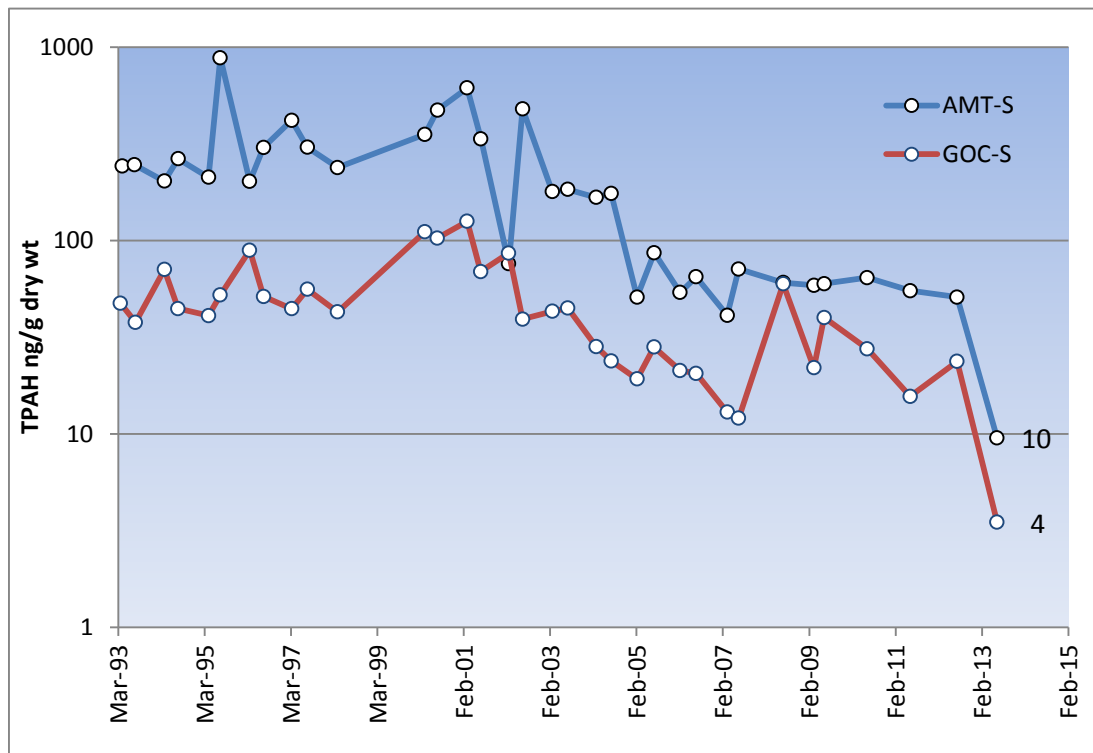


Figure 7. Time series of TPAH in sediments at Alyeska Terminal and Gold Creek.

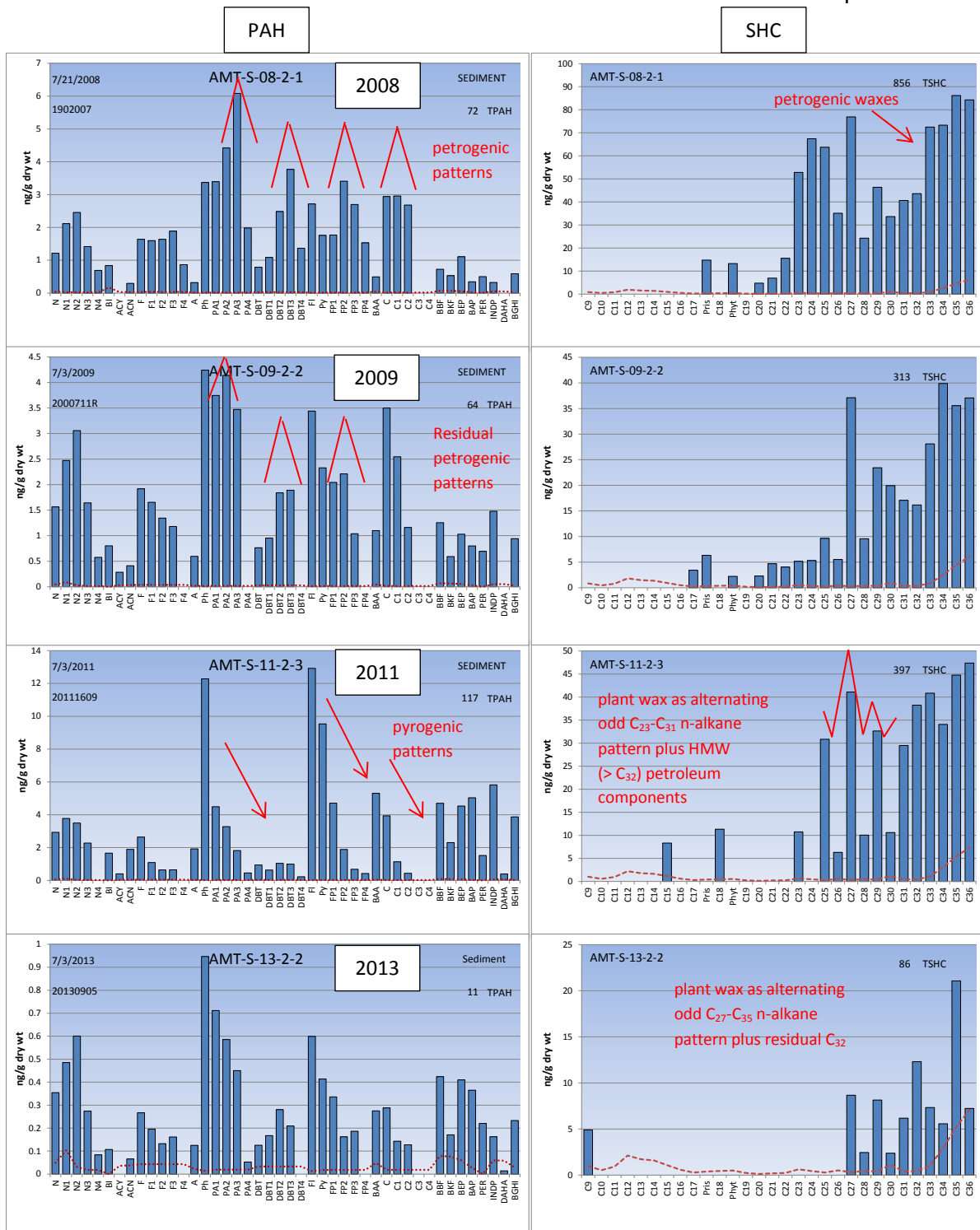


Figure 8. Representative PAH and SHC signatures of sediments at Alyeska Terminal between July 2008 and July 2013 showing the progression from a primarily petrogenic to a pyrogenic PAH signature with increasing terrestrial biogenic SHC and decreasing higher-molecular-weight n-alkane residuals (petrogenic 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 4.

GOLD CREEK

At the Gold Creek reference site (GOC), the sediments had consistently lower TPAH concentrations than AMT throughout the duration of the program (Figure 7). And like AMT, the most recent sampling reported record-low concentrations, now dipping into single digits. With its patterns shifting earlier than AMT's, the PAH profiles have been dominated by pyrogenic components (Payne et al., 2008a,b; 2010a) since April 2000 (see Figure 9 and Appendix 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 8 second from bottom) begin to resemble the Gold Creek reference sediments (Figure 9). 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).

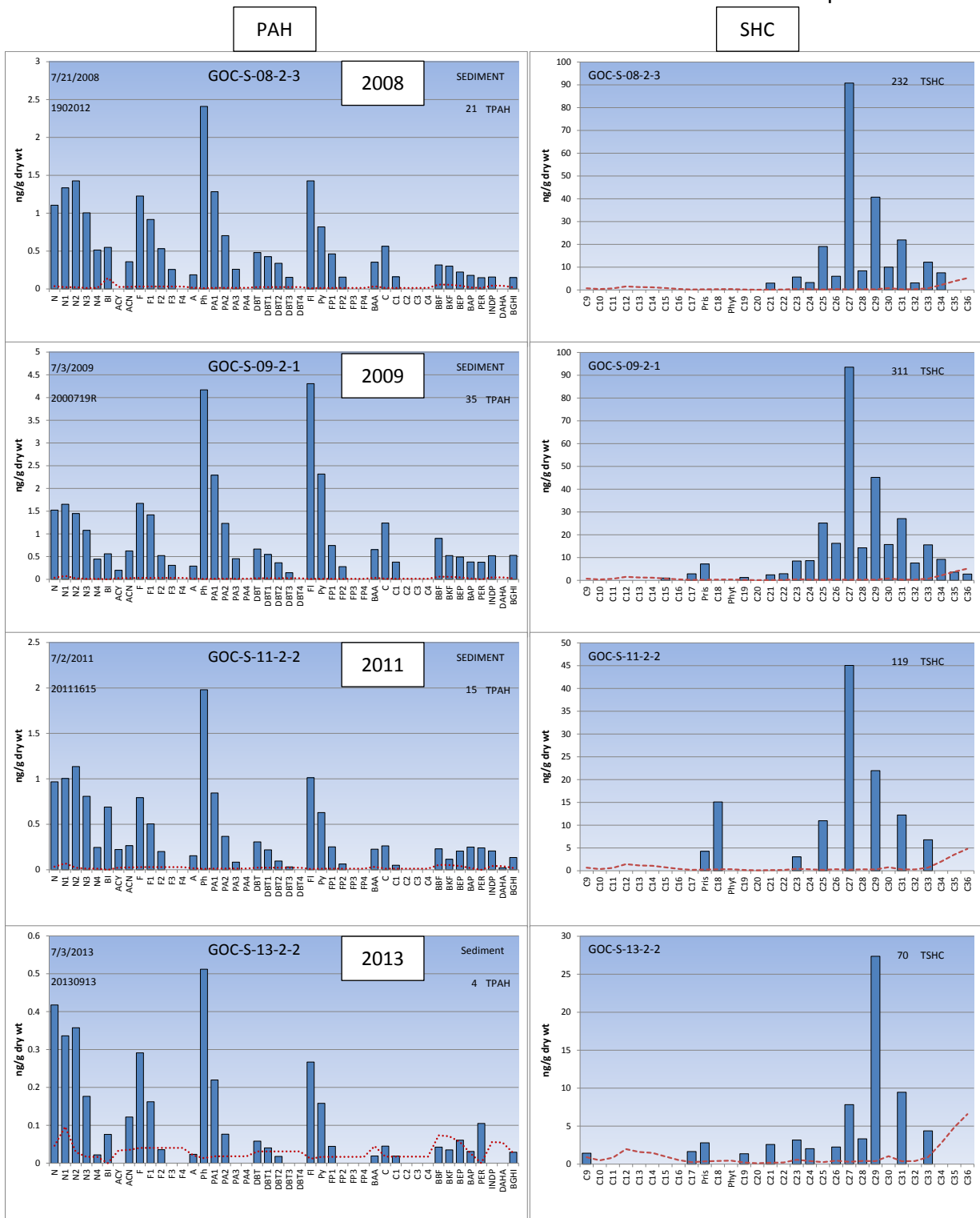


Figure 9. Representative PAH and SHC signatures of sediments at Gold Creek between July 2008 and July 2013 showing essentially invariant, background naphthalene components and pyrogenic, parent-dominated, PAH. SHC patterns reflect constant terrestrial and marine biogenic input. Red dashed line is sample-specific MDL. Note that while the patterns are all similar, the absolute concentrations are decreasing over time. All series replicate profiles are presented in Appendix 4.

SEDIMENT BIOMARKERS

In our last report through the 2012 collections (Payne et al., 2013), the sparse or missing biomarkers in field samples were puzzling. With the most recent 2013 results showing the lab is capable of producing consistent, precise biomarker results, the data suggest something else is happening. Not only is any petrogenic PAH signature weathered to near extinction but the biomarkers, too show evidence of degradation. A weathered ANS-like signature suggests two scenarios: we now hypothesize that either the patterns (Figure 10) represent biomarkers *weathered* in BWTF processing or, more unlikely, that inputs to the BWTF may no longer be dominated by ANS oil residues.

Biomarkers are persistent but not “ironclad,” they can be degraded. In other spills and studies, there has been evidence that under certain circumstances, microbes can use biomarker hydrocarbons as a food source (Frontera-Suau et al., 2002; Prince and Walters 2007). The observed “altered” LTEMP patterns most likely 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 (Payne et al., 2005b,c). In these circumstances, the biomarker compounds can biologically degrade at rates varying with the abundance and efficacy of microbes specifically adapted to use them. Similar effects were seen in the DWH and *Cosco Busan* data to a much smaller degree and involving just a few sterane compounds. But those events were occurring in nature rather than in a process tank engineered to consume hydrocarbons.

An alternative hypothesis is that changing operating conditions at the Terminal with segregated ballast tankers may have shifted the nature of the effluent and that ANS oil signatures are not the patterns to expect. 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 ballast users are replaced.

But do the LTEMP sediment patterns at the Terminal look like ANS oil? The residual patterns at AMT, accepting the apparent losses of more labile compounds, are not inconsistent with ANS petroleum biomarkers (Figure 10) and show good fidelity to the three key diagnostic ratios (Figure 11). In summary, the biomarker patterns in AMT sediments can be tentatively tied to ANS discharge. Analyzing a sample from the BWTF effluent would confirm this hypothesis.

In contrast, GOC biomarkers were much less abundant and the patterns more tentative, and while some low level samples showed gapping analyte absences, other parts of the profiles displayed a surplus (Figure 10), 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 data suggest another non-ANS source of hydrocarbons is likely 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, GOC biomarkers suggest low levels of ANS in a mixture with other background sources. Again, a BWTF sample would be pivotal in confirming the assessment.

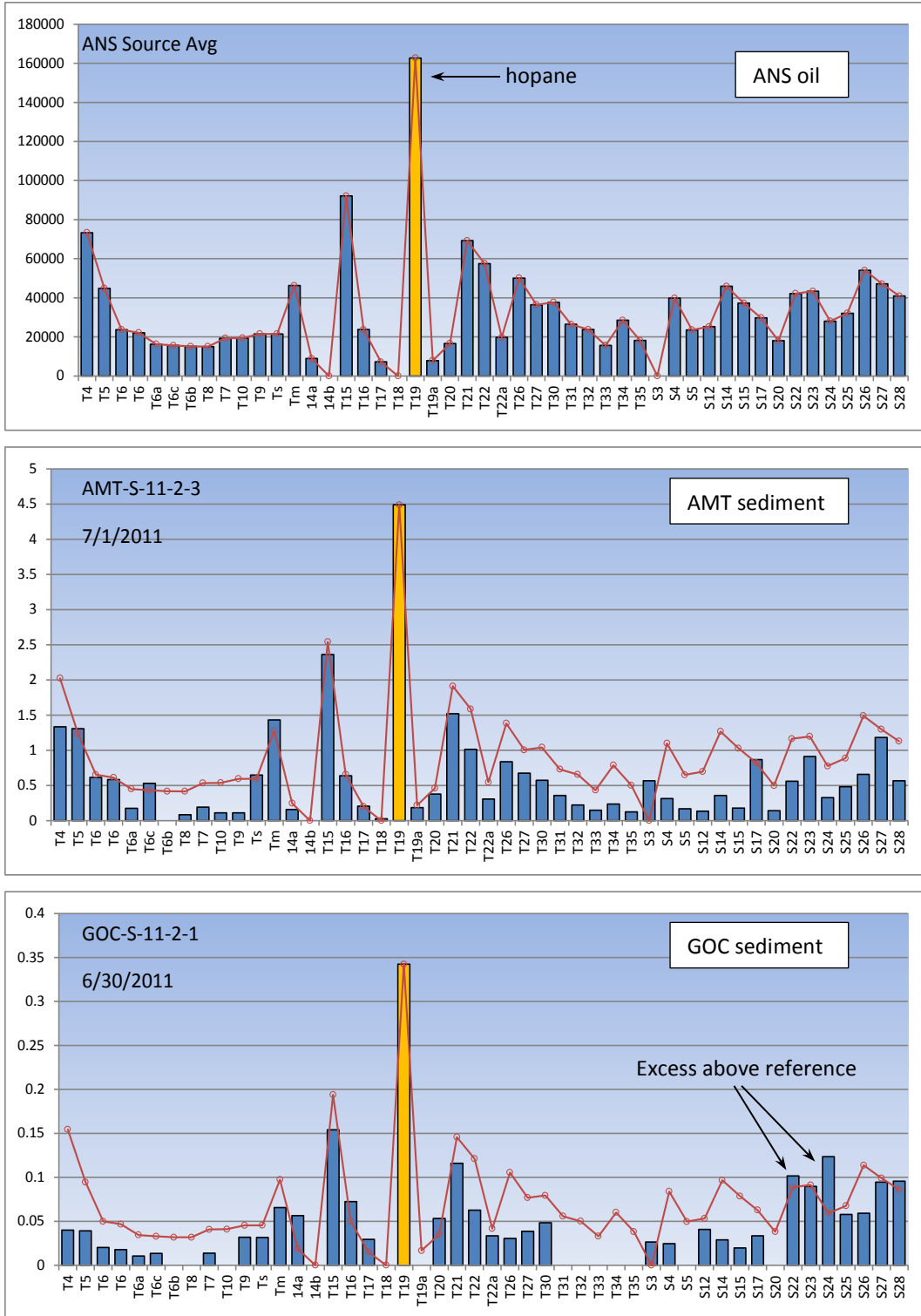


Figure 10. Representative ABL-quantified biomarker plots of EVOS (ANS) Crude Oil standard (top), AMT sediments from July 2011 (center), and GOC sediments from July 2011 (bottom). Red line denotes ANS reference normalized to the sample's hopane (highlighted in gold). Note the AMT sample shows only losses below the ANS reference suggesting only weathering effects, while the GOC sample shows a weaker signal but with excess S22-S24, suggesting an additional source(s).

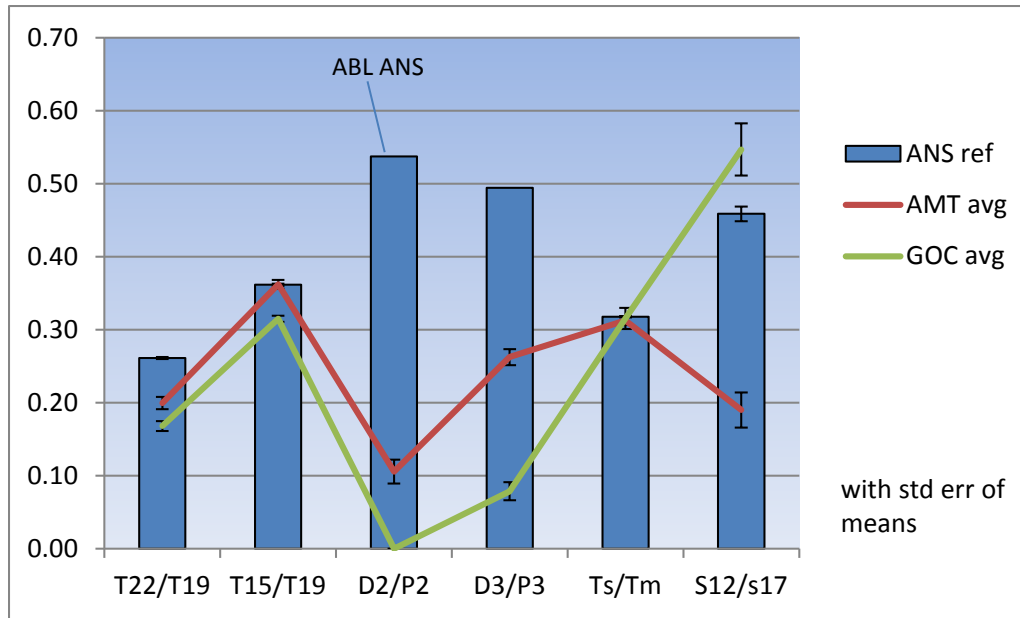


Figure 11. Comparison of average GOC and AMT diagnostic ratios with ANS reference. Only the three best-fitting ratios were used for final evaluations.

Overall, these biomarker profiles are significantly different from two other petrogenic sources found in the Sound, Katalla source rock and Monterey oil. As depicted by Bence et al. (1996) (Figure 12), the ANS-origin EVOS oil differs from Katalla and Yakataga regional sources east of PWS, primarily by the absence of the oleanane biomarker (T18 seen just before the C30 hopane) plus various subtler differences (e.g., note Ts and Tm proportions in all non-EVOS plots). In the Gulf of Alaska, the Katalla/Yakataga, source rock materials, an oil-containing matrix, become finely fragmented and are transported westward by Gulf currents with some deposited in the PWS basin to become the much disputed (during EVOS-era) PWS background.

In 2002, EPA, AK DEC and others (with CIRCAC's Susan Saupe as chief scientist) collected sediments and biota across coastal Gulf of Alaska from Copper River to the southern tip of the Alaskan Peninsula for the AK EMAP program. In the sediments was a nearly continuous trace of particulate petrogenic hydrocarbons that originated as source rock in the Katalla region. The patterns confirmed transport of the material into the depths of PWS, along the Kenai outer coast and into Shelikof Straits. Local sources sometimes dominated, as in Cook Inlet and the Katmai coast but the signal proceeds down to Chignik. The persistent pattern suggests the PAH are locked within the matrix and therefore not bioavailable. Of interest to LTEMP is the occurrence of the pattern throughout the PWS basin, even up into College Fjord—but not into Port Valdez. Since neither LTEMP nor the Alyeska EMP collections are encountering oleanane, Port Valdez hydrocarbon inputs must be locally sourced. The depths of Port Valdez may be sheltered from the coastal inputs by its bathymetry and currents or perhaps the glacial sediments from Mineral Creek and Shoup Glacier dominate any inputs from the Sound.

The other source found in intertidal regions of the Sound are tarballs from Monterey formation oil (Kvenvolden et al., 1995), remnants of oil spilled during the major 1964 earthquake. Brought to Alaska in the pre-pipeline era from California, Monterey oil is distinct from ANS oil by its inclusion of both oleanane and 28,30-bisnorhopane (T14a or H28, eluting just before norhopane Figure 12). Oleanane comes from the flowering angiosperms which only appeared in the later Triassic formations; the North Slope deposits formed earlier and missed the bloom (era). In only one of the eighteen LTEMP sediment samples, a trace level of oleanane was detected.

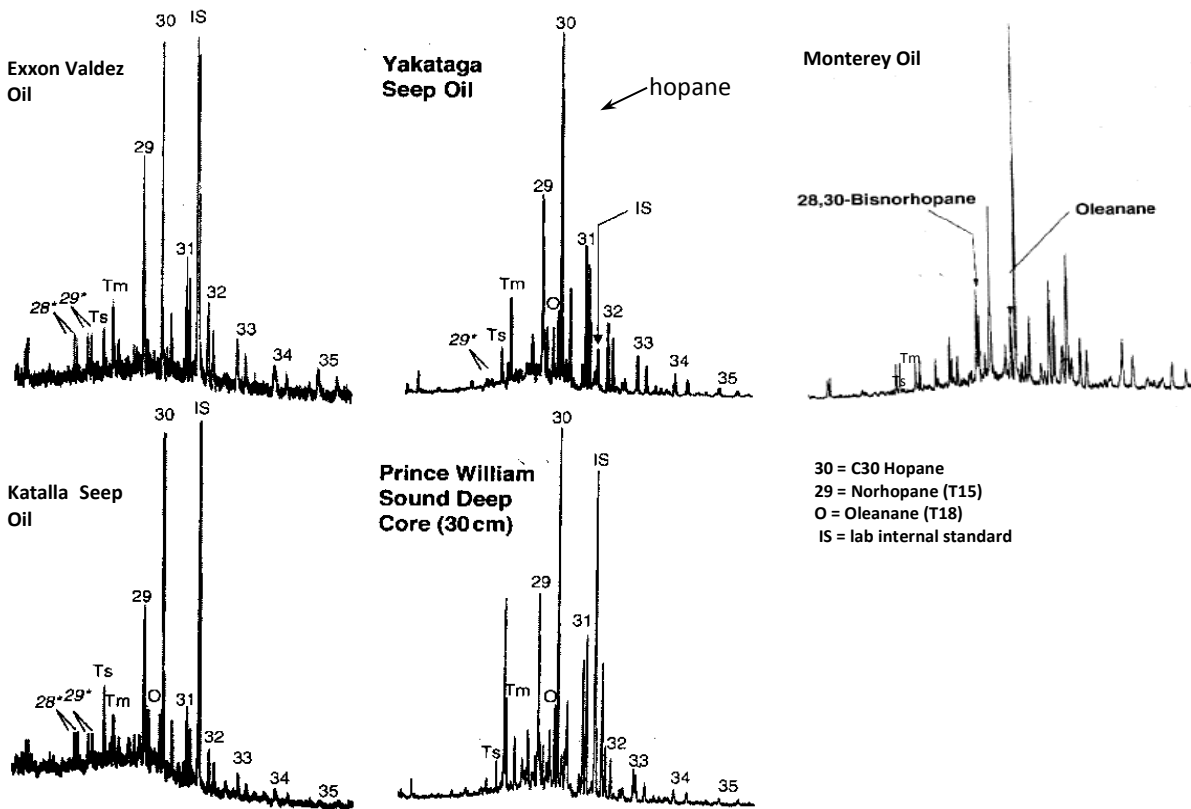


Figure 12. Ion traces of hydrocarbon sources found in PWS. Adapted from Wang and Stout, 2007.

Shaw (2009) also reports one sample in 2005 Port Valdez sediments showed a trace of oleanane. We suggest that bioturbation in the sediments could theoretically resurface traces of the spilled Monterey product. These results again confirm that the biomarker patterns represent mixtures with other background biomarker sources, particularly away from the terminal and BWTF outfall.

Shaw et al. (2005) concluded from their 2005 EMP biomarker data comprising just hopane and norhopane that EMP Stations 40 and 50 (near Gold Creek but at greater depths in the Port) contained petrogenic components derived from Alaska North Slope crude oil. In 2008, in addition to the 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. In 2014, their assessment was modified to suggest that although the absence of oleanane and expected hopane ratios confirmed an ANS, BWTF-derived oil in shallow stations near the terminal, the sediment hopane loads were reduced at deeper stations. That depletion suggested to them a refined ANS source with pyrogenics was present at the deep stations but not from the BWTF (Shaw and Blanchard, 2014). We can't confirm these conclusions from the available abbreviated PAH and biomarker data but find no conflict with recent LTEMP pyrogenic-dominated patterns at GOC and AMT.

SEDIMENT GRAIN SIZE

Sediment grain size samples were recently analyzed for all 2006-2013 collections. These data are presented 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 13

and Table 2) and both sites show minor trends and outliers. In the 3D plots (Figure 14), note there are annual shifts to higher sand content at both locations albeit still a minor component (<10%) and with a return to original conditions at GOC in 2013. More dramatically, at AMT, there has been a steady increase in clay content. The station locations occupy 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 we get off-site at GOC, we begin to see gravel tell-tales in the grab. These grain-size component trends are addressed 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 hydrocarbons.

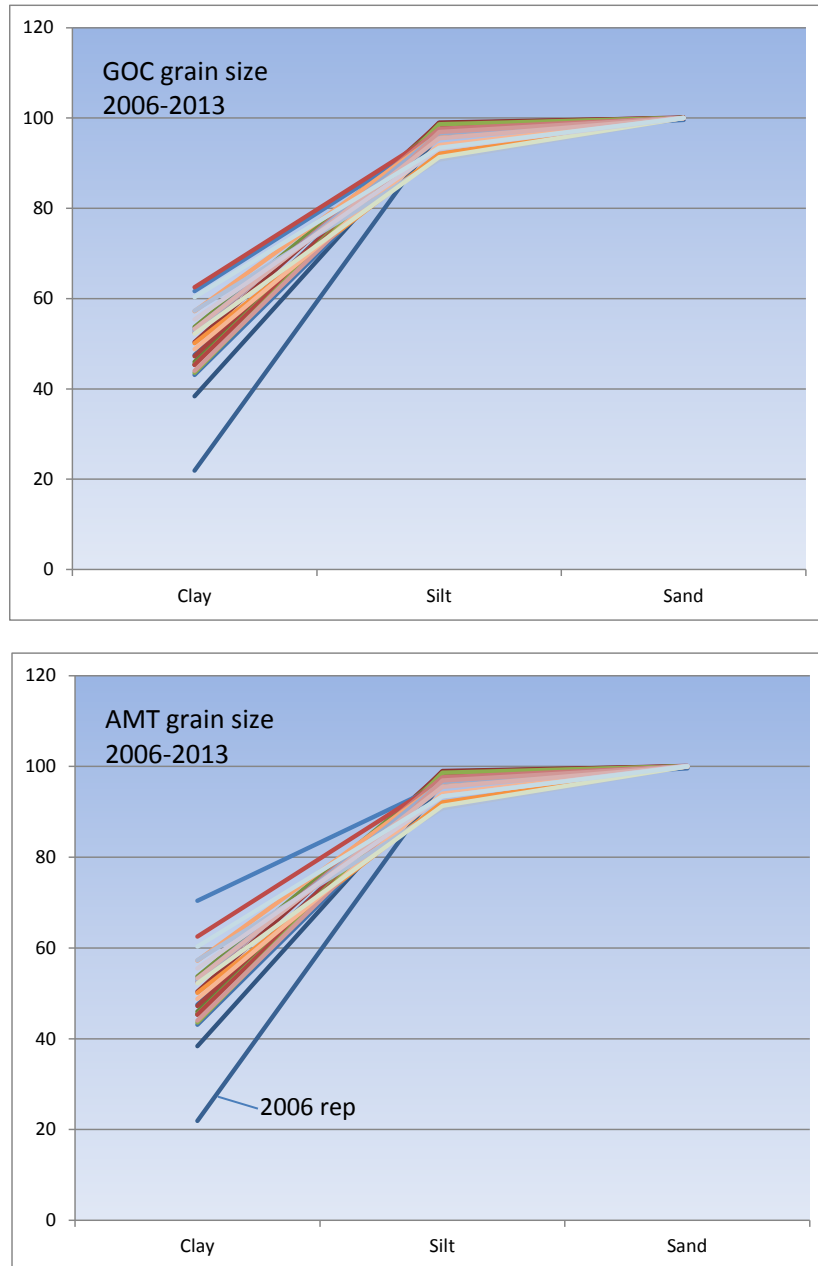


Figure 13. Cumulative grain size curves (%) for GOC and AMT, 2006-2013.

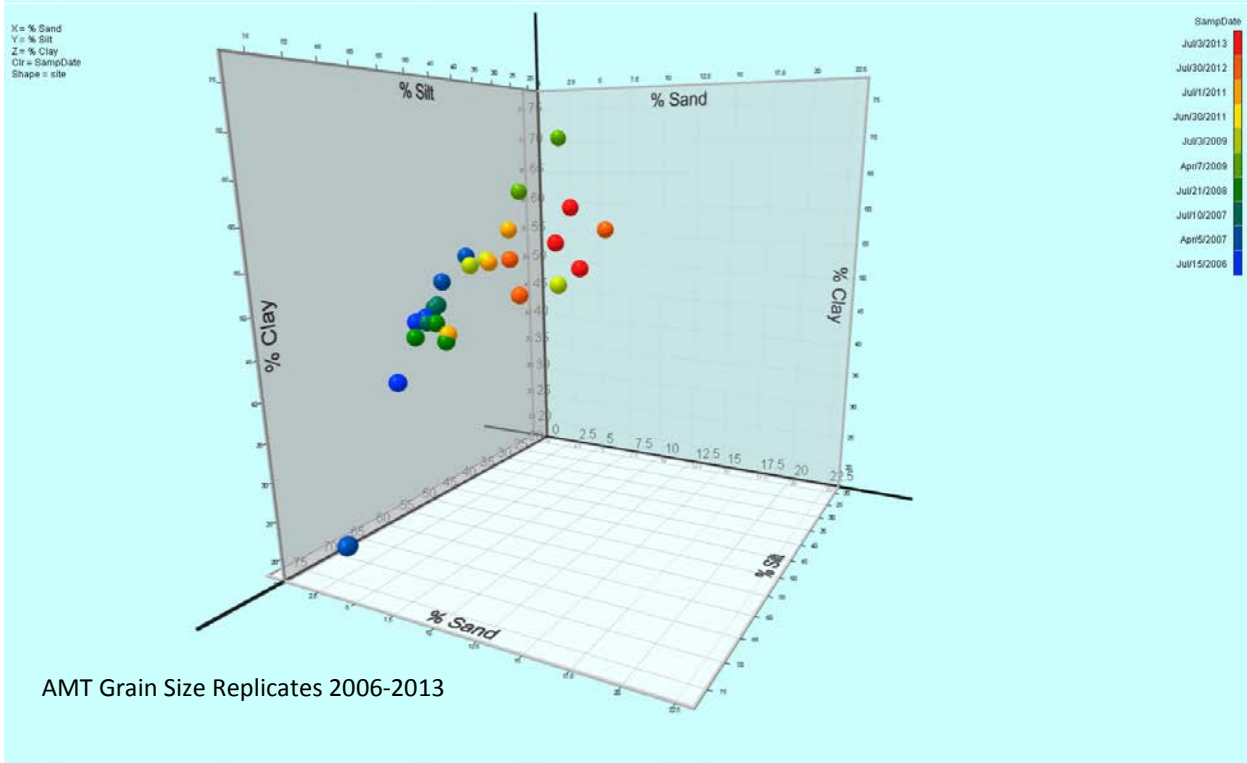
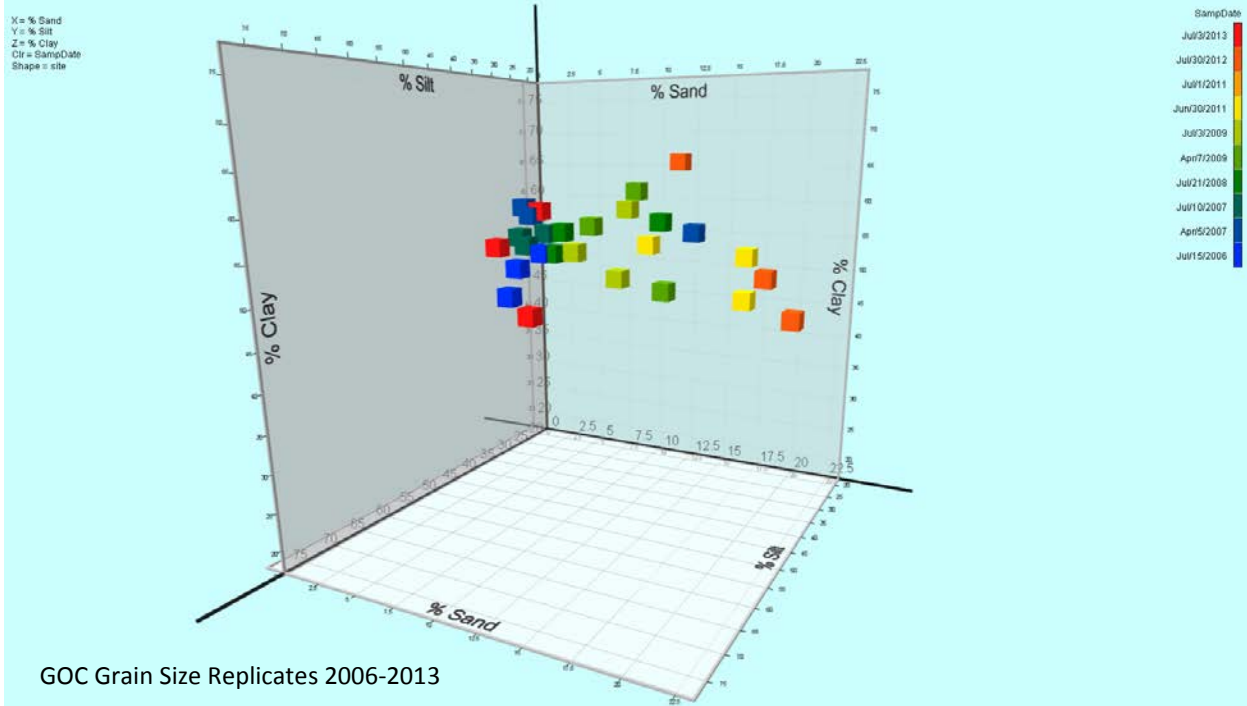


Figure 14. 3D plots of grain size components from GOC and AMT 2006-2013. Sampling years color coded (blue 2006, red 2013). Note shifts to higher clay content at AMT plus higher sand content at both and then retro-shift in 2013 GOC samples back to original 2006 cluster.

Table 2. Average grain size components for GOC and AMT, 2006-2013

	% Clay	% Silt	% Sand
AMT 2013	49.9	46.4	3.6
GOC 2013	54.0	36.2	9.8

SEDIMENT TOC

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

LTEMP values appeared to have yearly cycles within a limited range and a slow increase in concentration until plateauing sometime around 2003 (Figure 15 and Table 3). There is an uptick at GOC in the last two years of the program and in the last year at AMT. Note that the data are not continuous and that sampling prior to 2002 was performed by KLI.

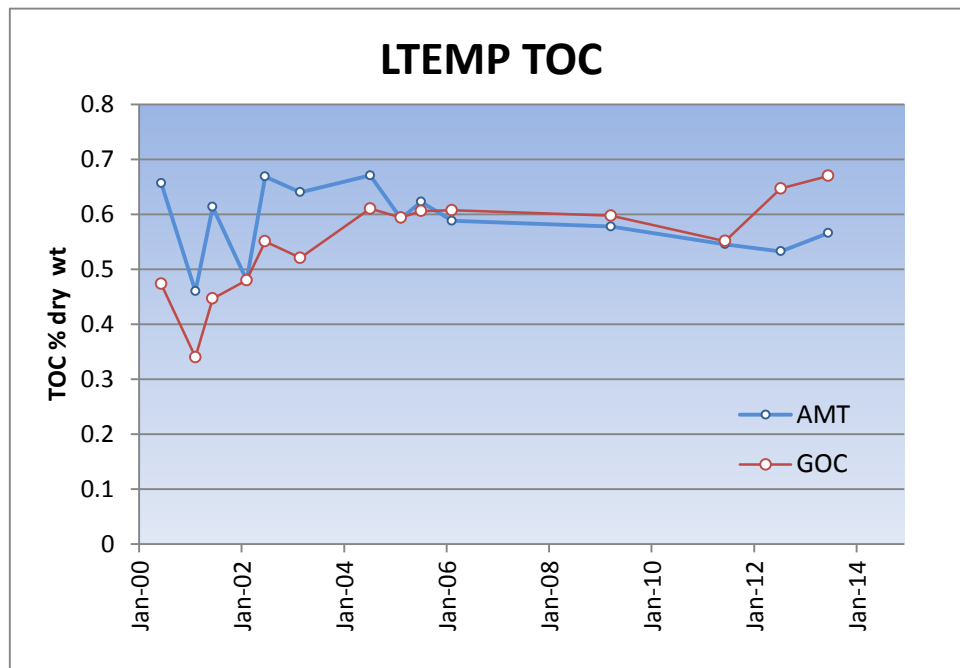


Figure 15. LTEMP Total Organic Carbon trends in AMT and GOC sediments (% dry wt)

Table 3. LTEMP Total Organic Carbon trends in AMT and GOC sediments (% dry wt)

SampDate	AMT	GOC	SampDate	AMT	GOC
Jul-00	0.66	0.47	Mar-05	0.59	0.59
Mar-01	0.46	0.34	Jul-05	0.62	0.61
Jul-01	0.61	0.45	Mar-06	0.59	0.61
Mar-02	0.48	0.48	Apr-09	0.58	0.60
Jul-02	0.67	0.55	Jun-11	0.55	0.55
Mar-03	0.64	0.52	Jul-12	0.53	0.65
Jul-04	0.67	0.61	Jul-13	0.57	0.67

TISSUES IN PORT VALDEZ AND KNOWLES HEAD

Average TPAH levels in AMT tissue samples have been steadily dropping since April 2007, and by 2010 first approached all-time lows, estimated 17 ng/g DW (Figure 16 and Table 4). At these trace concentrations, results must be qualified as estimates (most analytes are below MDL) but because of their patterns, are not considered to be false positives. Although they increased slightly in 2012, the majority of the PAH are pyrogenic not petrogenic in nature and thus, unlikely to be from changes in BWTF discharge (Figure 17 and other profiles in Appendix 4). By 2013 they were back down to an estimated 17 ng/g DW. Also, note the appearance of perylene in 2011, 2012, and 2013 (Figure 17). This is a naturally occurring PAH generated by biologic processes or early stages of diagenesis in marine sediments (Bence et al., 2007) and, potentially being either petrogenic or pyrogenic PAH, is not included in TPAH calculations. In 2013, the below-MDL phenanthrene/anthracenes (P/As) have a petrogenic pattern (Figure 17), as confirmed by the SHC fraction's petrogenic waxes, the higher-molecular-weight n-C₂₃-n-C₃₁. Throughout this period, however, most of AMT tissues' SHC were dominated by biogenic constituents (e.g., n-C₁₅, n-C₁₇, and pristane). A possible petrogenic input appeared in two replicates' SHC in 2011 but were not reflected in the PAH patterns (Appendix 4).

Average TPAH levels in GOC mussel tissues have consistently been lower or very close to those at AMT except for the Fall 2004 diesel spill (cleared by the following July; Figure 16). 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). Between March 2003 and 2013, with the exception of the aforementioned diesel spill, the signals became largely pyrogenic with occasional petrogenic components (below-MDL dibenzothiophenes (DBTs) in 2008 and P/As in 2013) (Figure 18). From July 2005 to present, the TPAH concentrations have consistently been in the 26-62 ng/g DW range, and just slightly higher than the levels observed at AMT due primarily to elevated pyrogenic P/As (Figure 16 and Figure 18). With minor exceptions, SHC patterns at this site over the 2008-2013 period have been mostly trace-level biogenic (e.g., n-C₁₅, n-C₁₇, and pristane). Exceptions included two of three replicates in April 2009, and one in 2011, each with traces of petrogenic n-C₂₄-n-C₃₀ SHC (Appendix 4). In none of these cases, however, were petrogenic sources suggested by the 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-C₂₄-n-C₃₀ petrogenic waxes were observed (see Appendix 4). 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 visa 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 a biogenic source.

From the Knowles Head tanker anchorage (KNH), average TPAH levels have been consistently low, ranging from an estimated 5-32 ng/g DW since March 2005 (Figure 16). 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 19 and Appendix 4). Note the perylene that was also observed in the mussels at AMT and GOC in 2012 and 2013. Presumably, this reflects some region-wide marine event. The SHC patterns at KNH between July 2008 and 2013 were almost exclusively biogenic (e.g., n-C₁₅, n-C₁₇, and pristane) (Figure 19). In 2013, a mixed signal was seen where, just like the 2013 GOC mussels, below-MDL petrogenic P/As are suggested in the PAH patterns from two of three replicates but without petrogenic waxes in the SHC profile (Figure 19 and Appendix 4).

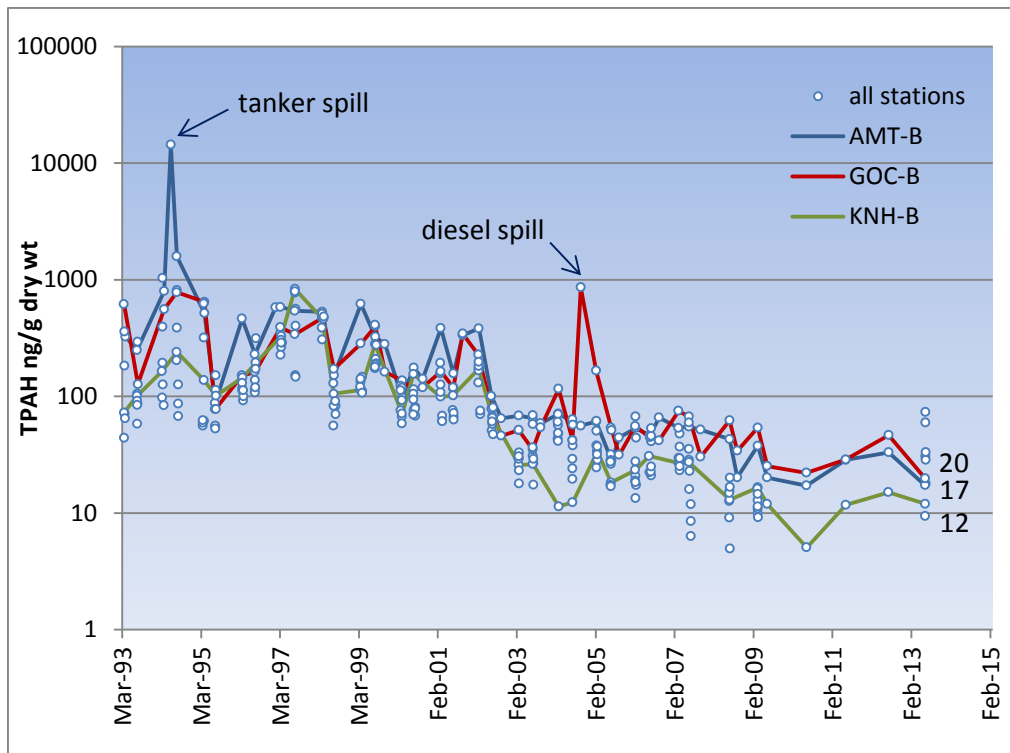


Figure 16. Time series of mussel tissues TPAH from Alyeska Terminal, Gold Creek and Knowles Head sites.

Table 4. Recent mussel tissue mean TPAH (ng/g DW) from Alyeska Terminal, Gold Creek, and Knowles Head sites.

Samp Date	AMT-B	GOC-B	KNH-B
Jul-08	43	62	13
Sep-08	20	34	
Apr-09	38	54	17
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

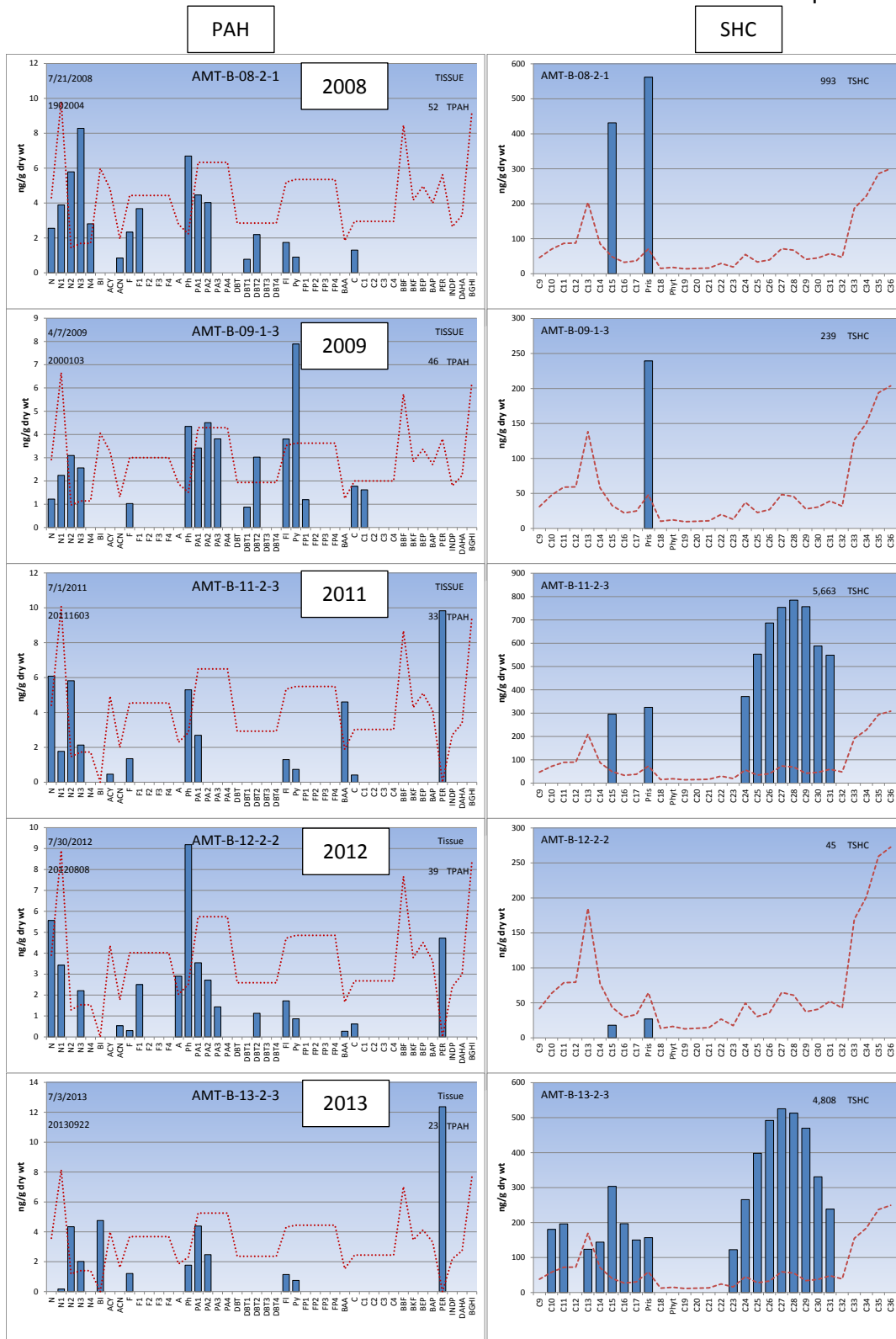


Figure 17. Representative PAH and SHC profiles from AMT mussel tissues between July 2008 and July 2013 showing primarily below-MDL combustion product PAHs (except 2013 where the P/As appear petrogenic), perylene, and planktonic biogenic SHC (C15 and pristane) and higher-molecular-weight C₂₃-C₃₁ petrogenic waxes in 2011 and 2013. Red dashed line is sample-specific MDL.

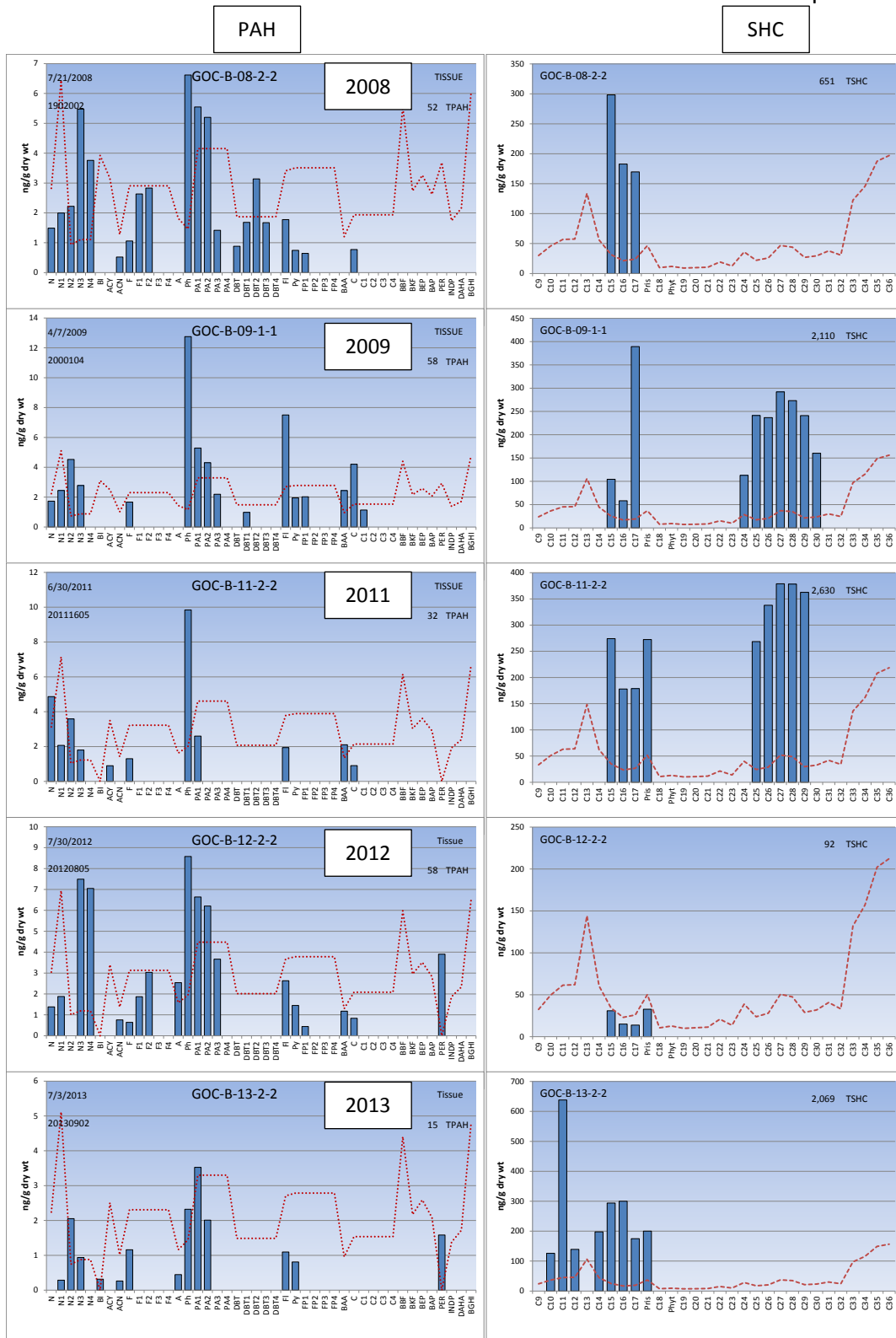


Figure 18. Representative PAH and SHC profiles from GOC mussel tissues between July 2008 and July 2013 showing primarily combustion products (except 2013 where the less-than-MDL P/As appear petrogenic), perylene, and planktonic/terrestrial biogenic SHC plus higher-molecular-weight C₂₃-C₃₁ petrogenic waxes in 2009 and 2011. Red dashed line is sample-specific MDL.

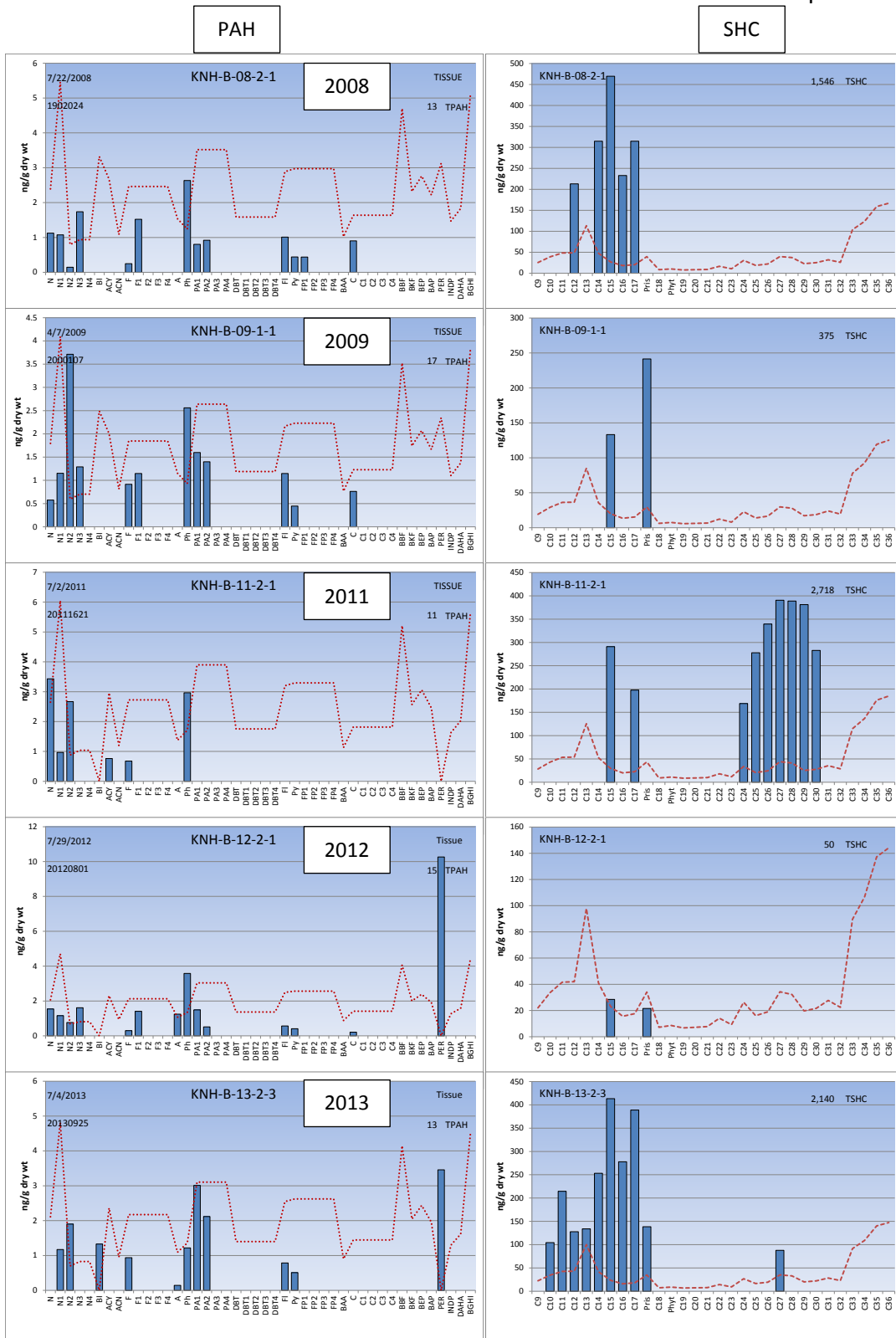


Figure 19. Representative PAH and SHC profiles from KNH mussel tissues between July 2008 and July 2013 showing primarily trace-level PAH combustion products (except 2013 where the less-than-MDL P/As appear petrogenic), perylene, and planktonic/terrestrial biogenic SHC plus higher-molecular-weight C₂₄-C₃₀ petrogenic waxes in 2011. Red dashed line is sample-specific MDL.

PRINCE WILLIAM SOUND AND GOA MUSSEL TISSUES

In the five-year interim since the last samples were collected in the outer Prince William Sound (PWS) and Gulf of Alaska (GOA) stations, TPAH concentrations show modest increases at six of the ten LTEMP sites (Figure 20 and Table 5). Again, from MDL concerns, these results must be qualified as estimates but because of their consistent patterns, are not considered to be false positives. Notably, only the four eastern-most stations (AMT, GOC, KNH, and SHB) show recent TPAH decreases, and while the outer PWS and GOA site concentrations increased by a factor of roughly 2 to 8, they are still considered to comprise low background levels. As seen in the combined average PAH profiles for all stations (Figure 21) and the individual PAH and SHC histogram plots (Appendix 4), most of these increases in 2013 are due to markedly higher concentrations of naphthalenes (note that perylene (PER) is not included in the TPAH summation). In addition, most of the trace-level, higher-molecular-weight PAH in 2009 were pyrogenic in origin (parent-dominated), and, at least for the PAs, have switched to a petrogenic pattern and increased slightly in six of the PWS and GOA stations in 2013. Only AIB and SLB continued to show trace levels of pyrogenic PAs in 2013. At the same time, pyrogenic FL/PY and C all decreased significantly between 2009 and 2013 while PER increased (Figure 21).

In 2009, naphthalenes were present at all stations but only in above-MDL concentrations near the tanker anchorage at Knowles Head (KNH) (Figure 21). In 2013, above-MDL-levels of naphthalenes were observed at each of the PWS and GOA stations except KNH, and the rest of the PAH, previously mostly pyrogenic, were now primarily petrogenic (Figure 21 and Table 5). These shifts may be partially explained by seasonal differences (collections in April 2009 vs. July 2013) but trace-level sources are enigmatic. The naphthalene signals could be wind transported or may reflect particulate naphthalenes from increased freshwater inputs during the spring melt, as seen in Cook Inlet river samples (unpublished ICIEMAP data, 2009).

In our last “all-sites” report, we noted within-site fidelity and regional pattern similarities for the 2009 tissue collections (Payne et al., 2013). In the current data, excellent within-station replicability (albeit low-level) is again observed but differs from the earlier patterns with the addition of naphthalene spikes and variable phenanthrenes/anthracenes (Figure 21 and Figure 22). This improbable reoccurrence of being regionally similar but different in the five year interval reinforces that these trace-level signals are real and not laboratory or procedural artifacts nor uncontrolled values. Method blanks were clean, primarily showing only below-MDL traces of biphenyl. Appendix 3 presents the individual PAH histogram plots for all the 2009 and 2013 collections arranged by site similarities within geographic regions.

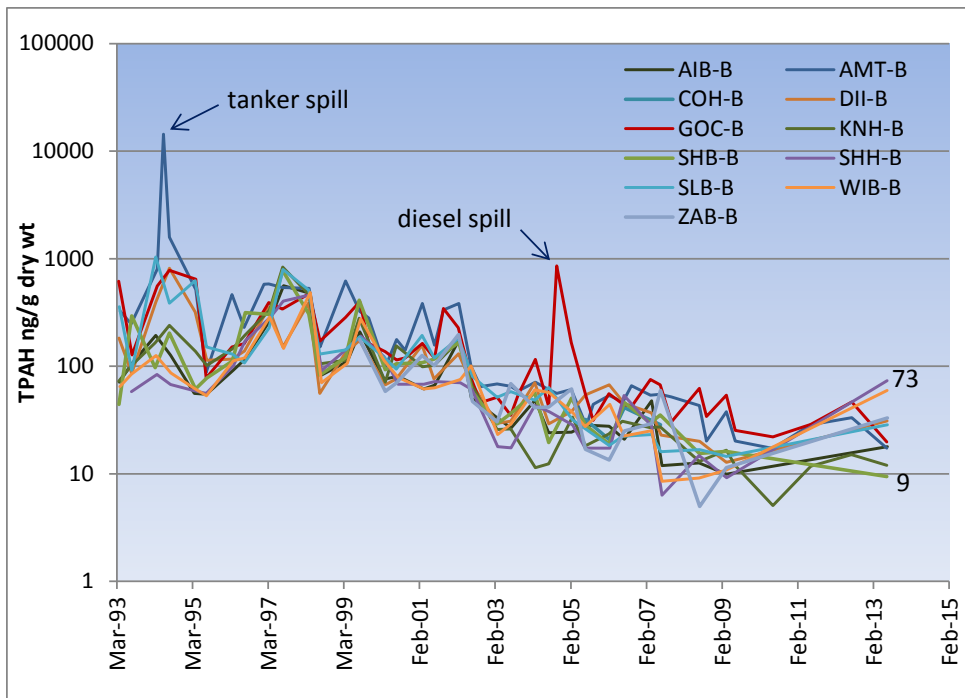


Figure 20. Mussel-tissue TPAH time series for all stations (1993-2013).

Table 5. Mussel-tissue TPAH concentrations (ng/g dry wt) and dominant pattern type 2008, 2009 and 2013

ID	Region	TPAH (ng/g dry wt)			Dominant PAH Pattern	
		2008	2009	2013	2009	2013
AIB	GOA	13	10	18	Pyrogenic	Pyrogenic
AMT	Port Valdez	43	38	17	Mixed pyrogenic & petrogenic	Petrogenic
DII	Central PWS	20	13	30	Mixed pyrogenic & petrogenic	Petrogenic
GOC	Port Valdez	62	54	20	Pyrogenic	Petrogenic
KNH	Eastern PWS	13	17	12	Pyrogenic	Petrogenic
SHB	Eastern PWS	15	16	9	Pyrogenic	Petrogenic
SHH	GOA	15	9	73	Pyrogenic	Petrogenic
SLB	Central PWS	17	15	28	Pyrogenic	Pyrogenic
WIB	GOA	9	11	59	Pyrogenic	Petrogenic
ZAB	Central PWS	5	11	33	Petrogenic	Petrogenic

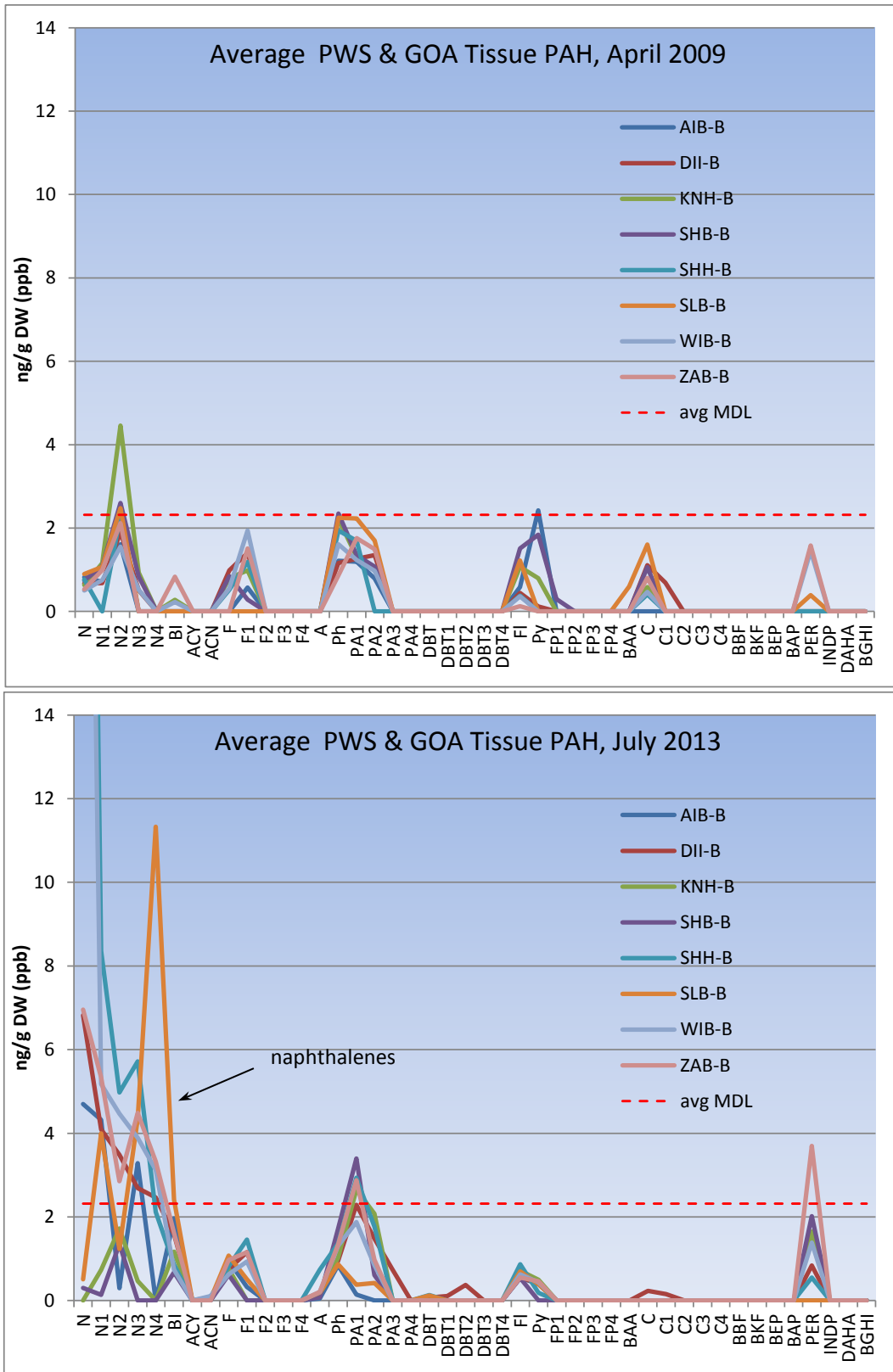


Figure 21. Average PAH tissue patterns showing regional commonalities at all stations , Apr 2009 and July 2013, (n= 3 reps /station). Average MDL = 2.3 ng/g DW.

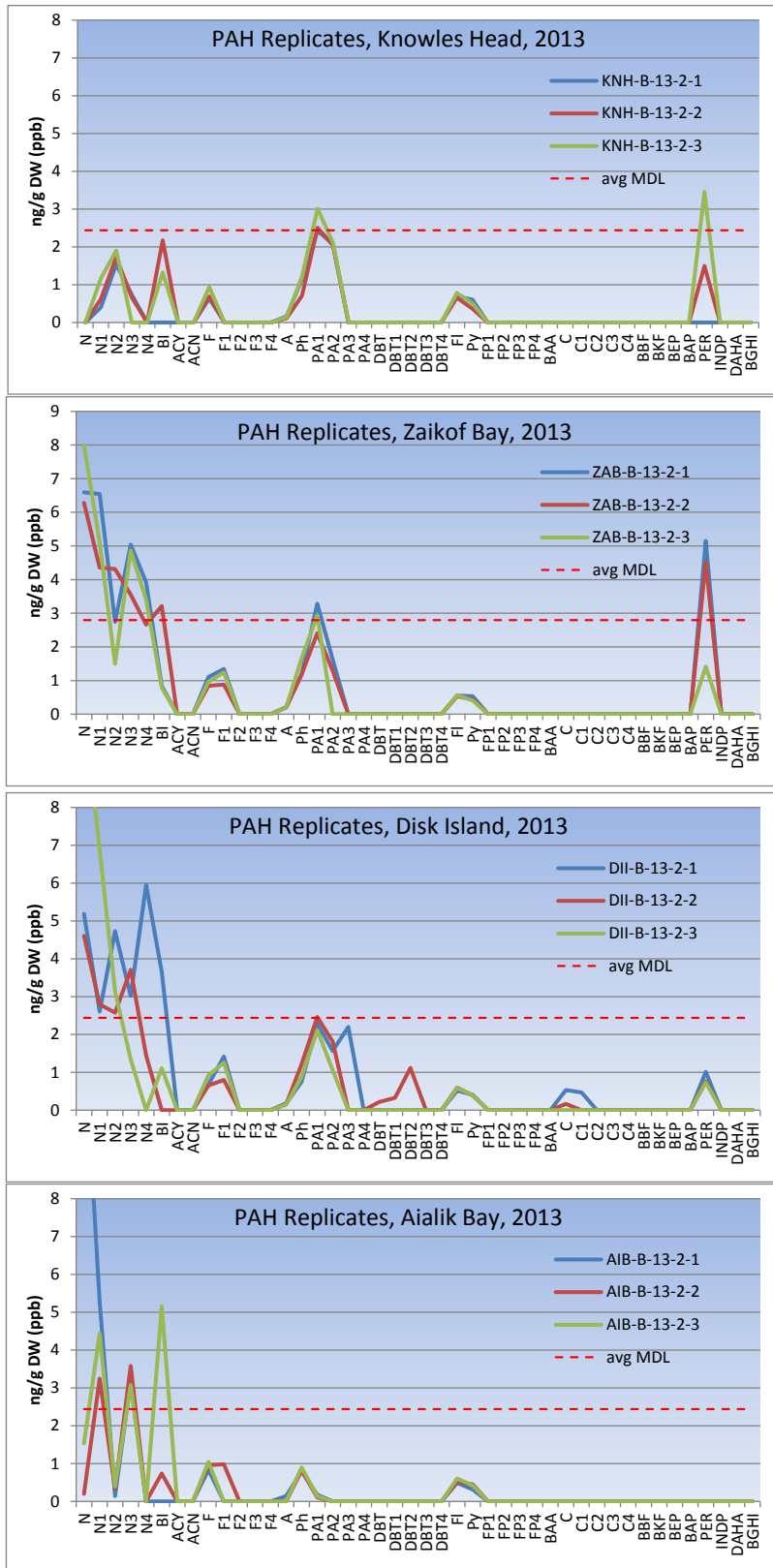


Figure 22. Example PAH patterns from 2013 stations showing within-site fidelity.

TRENDS

In the Sound, with the bulk of EVOS oil either dissipated or the remnants buried and sequestered, the regional sites are currently looking very clean. Although there have been some rebounds, they are still low TPAH values, driven mostly by the ubiquitous naphthalenes and below-MDL concentrations of petrogenic phenanthrenes/anthracenes (Appendix 3 and Figure 21). In our previous report, we hypothesized that “It could easily be the case that the LTEMP data are currently tracking subtle variations in the background PAH, and that they are near or at the minimum.” Current trends continue to support that statement: background TPAH levels in the region appear primarily to be between single digits and ~35 ng/g DW with some unknown process-driven excursions to modestly higher levels.

In previous years, it was easily assumed that pyrogenic trace patterns appearing at the otherwise clean sites across the region 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 bioavailable. And ICIEMAP river data (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.

How do these levels compare with other Alaskan sites? Unfortunately, comparable studies are scarce and existing data are becoming dated but the 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 and similar to the 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 below 20-30 ng/g DW. Reaching farther, data from the 2004-2005 National Status and Trends, Mussel Watch Program (Table 6, Figure 23) and 2008-2010 Alaskan sites (Figure 24) (now summing 38 parent and alkylated PAH homologues versus 44 LTEMP PAH analytes) show that PAH concentration in mussels for other West Coast sites is 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.

- 1 Table 6. Current TPAH concentrations in regional mussel tissues (ppb, ng/g DW) relative to 2004-2010 NOAA Mussel Watch
- 2 monitoring data and a recovered Alaskan oil-spill event.

LTEMP	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
	2009	Port Valdez	Gold Creek	31
		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
	Nanwalek		Nanwalek	194
	Port Graham		Port Graham	376
	Port Graham		Murphy's Slough	428
			Seldovia Bay	Powder Island
M/V Kuroshima (1997)	Unalaska	2004 followup	25-85	

4

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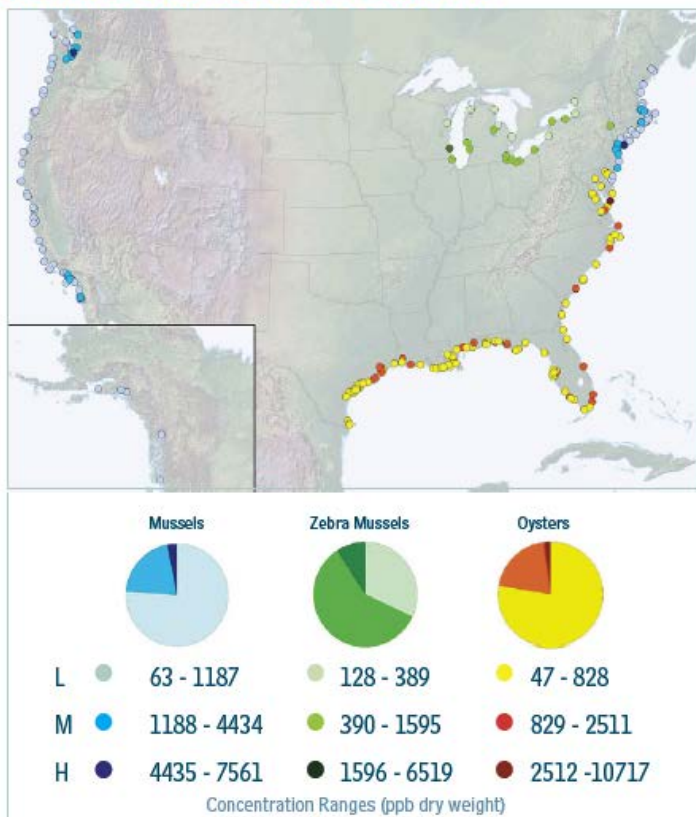
PAHs

Nation at a Glance:

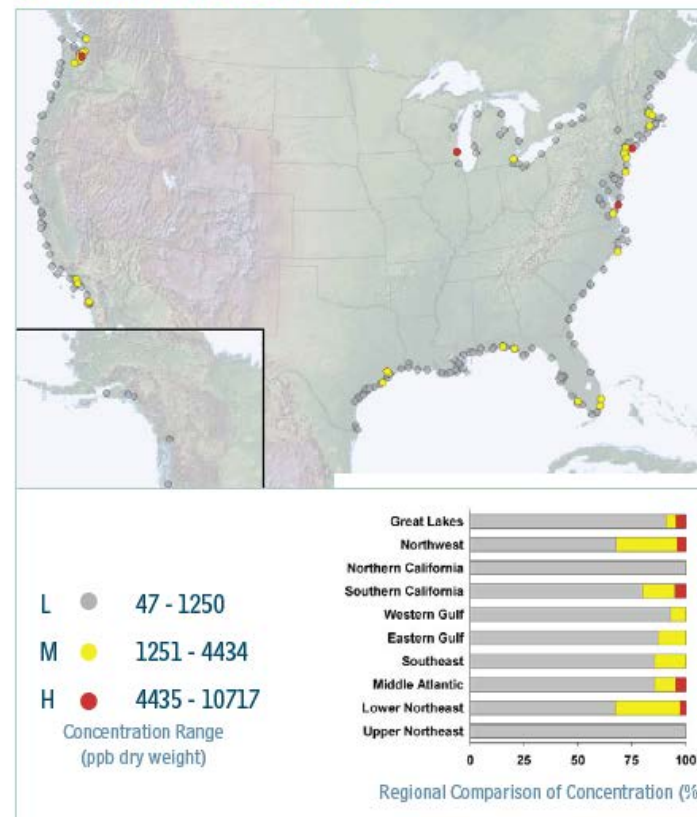
STATUS SUMMARY

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

REGIONAL SPECIES CHARACTERIZATION



NATIONAL CHARACTERIZATION



6

7 Figure 23. 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) Status (s) Trend (t)
 Mussels (M) National Status National Trend
 ● Medium ● Medium ▼ Decreasing
 ● High ● High ▲ Increasing

Zebra Mussels (ZM)
 ● Medium
 ● High

Oysters (O)
 ● Medium
 ● High

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

Concentrations derived from 2004-2005 data.

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

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 24. Summary page of Alaska regional Mussel Watch results and trends based on 2004-05 data 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, EVOS Trustees have sponsored a number of beach remediation projects.

CONCLUSIONS

Based on the sediment and mussel data, petrogenic hydrocarbon inputs from the Alyeska Marine Terminal and tanker operations continue to decline. As concluded in our last LTEMP reports (Payne et al., 2010a; 2013), within Port Valdez, the decrease reflects 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. The sediments, too, are beginning to look more like Gold Creek's background-reference, low-level, pyrogenic profiles. However, the mussel tissues at both AMT and GOC, while very low, still exhibited a slight petrogenic pattern at both stations in 2013.

Biomarker data from the Port sediments show evidence of low-level, very weathered ANS oil but the assessment is tentative pending a new sample of the treated ballast effluent. At GOC, biomarker concentrations are seven times lower than those at AMT and the profiles indicate mixing with background sources. Shaw and Blanchard (2014) draw similar conclusions regarding deep basin sediments.

Beyond the Port, with the April 2013 mussel collections at the central PWS and GOA sites, the overall TPAH levels have gone up since 2009 but the increases are largely attributable to traces of dissolved-phase naphthalenes and just-above-MDL petrogenic phenanthrenes/anthracenes. All of the PAH levels measured in the April 2009 and July 2013 samples are extremely low (mostly near or just below even the new MDLs), yet remarkable site fidelity exists within the PAH and SHC patterns for each stations' replicates for each year's collections. These pattern consistencies within stations and regions, and yet different between years makes the trace data convincing and not just lab noise or other procedural artifacts. The SHC patterns at all of these sites are mostly derived from biogenic sources but there appears to be sporadic indications of petrogenic SHC (n-C₂₃-n-C₃₁) but generally little evidence of oil contamination. Again, the data showed remarkable site fidelity at most of the stations.

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

From our experience on the BP Deepwater Horizon spill, we've become aware of two innovative methods that may help inform the PWSRCAC and regulatory agencies about conditions in Port Valdez. In a prior study for PWSRCAC that attempted to track the BWTF discharge plume, the effort was haphazard at best, collecting water and deploying mussel cages with little assurance of encountering the plume (Salazar et al., 2002). During 2010-2011 on a similar task albeit larger scale, Dr. Payne served as chief scientist on nine sampling cruises in the Gulf of Mexico in efforts to track and sample the deep oil plume released from the ruptured wellhead. The adaptive sampling methods were eventually fine-tuned to incorporate CTD, dissolved oxygen (DO) and fluorescence sensors on either a rosette of GoFlo samplers or when available, on a remote-operated vehicle (ROV). The most effective

strategy was to have direct readings of depth, DO and fluorescence on a downcast and then plan sampling on the upcast where any DO sags or fluorescence spikes suggested the presence of oil. Should a subsurface plume (e.g., a sunken fish-processor vessel) need to be sampled in the future, this enhanced instrument method is recommended.

Other trending topics in oil fate are alternative mass spectrometry instruments. Using a two-dimensional, GC x GC MS enhances some abilities to better discriminate and detect subtle changes in the PAH, SHC, and biomarkers. Its utility has been demonstrated in tracking weathering changes and resolving subcomponents (with much of the oil work coming out of Chris Reddy's WHOI lab) (Frysiner et al., 2002, Aeppli et al., 2012). Another new instrument accruing spectacular resolution but only reporting elemental composition is the Fourier Transform-Ion Cyclotron Resonance Mass Spectrometer (FT-ICR MS). This instrument is able to see beyond the resolving range of GC/MS and has identified in excess of 30 thousand compounds in DWH oil samples (McKenna et al., 2013). These compounds include the more polar, oxygenated and hetero-atomic hydrocarbons lost in the "unresolved complex mixture" (UCM) of (or extraction for) GC/MS resolution. Studies are showing at least some of these compounds are likely microbial degradation products—what were previously considered the "lost" weathered components consumed or removed as natural oil fate. They weren't lost, they just weren't visible to the older instrument methods. An interesting study would be to assess ballast water signatures through the BWTF, out the discharge and then to track the plume through the port. Toxicity data for these previously enigmatic compounds is currently minimal to non-existent; they have never been measured in whole-oil tox tests.

And as a side note, using FT-ICR methods, a team at the National High Magnetic Laboratory-Future Fuels Consortium has been able to identify the persistent, fresh-core-preserving, outer crust of lingering EVOS mousse (Irvine et al, 1999, 2006, 2007) as primarily comprised of the above-mentioned oxygenated hydrocarbons (Rogers, pers comm, 2015).

For 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.

ACKNOWLEDGEMENTS

This success of this project reflects the efforts of many more individuals than currently appear in the author's list. From our stalwart vessel operator, tireless supporter and colleague, Dave Janka (and Annette Janka), our primary pilots, Terry Kennedy and Jose DeCreft, our former and current colleagues at Auke Bay Lab (including the project newbie, Dr. L. Schaufler), our project managers, Lisa Ka'aihue and Joe Banta, our many prior and current SAC advisors, and the every-ready folks on RCAC staff...and our families...for the years of Alaskan adventures and productive science--BIG THANKS!

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