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PRINCE WILLIAM SOUND RCAC

LONG-TERM ENVIRONMENTAL MONITORING PROGRAM

2003-2004 LTEMP Monitoring Report

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Regional Citizens' Advisory Council

April 18, 2005

PWSRCAC Contract 951.04.1

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cover photo from original by Lisa Ka'aihue, 2004

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LIST OF ABBREVIATIONS

Stations:

AMT	Alyeska Marine Terminal, Port Valdez
AIB	Aialik Bay, west of Seward
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
ANS	Alaskan North Slope
BWTF	Alyeska Terminal's Ballast Water Treatment Facility
CPI	carbon preference index
CRUDE	crude oil index
EVOS	*Exxon Valdez* oil spill
FFPI	fossil fuel pollution index
GC/FID	gas chromatography/flame ionization detector
GC/MS	gas chromatography/mass spectrometry
GERG	Geochemical and Environmental Research Group, Texas A&M
KLI	Kinnetic Laboratories, Inc., Anchorage AK
MDL	analytic method detection limit
MPI	Mytilus pollution index
MSD	mass selective detector
NIST	National Institute of Standards and Technology
NMFS	National Marine Fisheries Service
NOAA	National Oceanographic and Atmospheric Administration
PAH	polycyclic (or polynuclear) aromatic hydrocarbons
PDR	particulate/dissolved ratio
PECI	Payne Environmental Consultants, Inc., Encinitas, CA
PGS	particle grain size
PWS	Prince William Sound
SHC	saturated hydrocarbons (n-alkanes + pristane and phytane)
SIM	selected ion monitoring
SRM	NIST standard reference material
TAHC	total AHC
TALK	total n-alkanes
TIC	total inorganic carbon
TOC	total organic carbon
TPAH	total PAH
TSHC	total saturated hydrocarbons (essentially the same as TALK)
UCM	unresolved complex mixture

1 Executive Summary

The overall results from this year are very similar to last year's. After reviewing the current LTEMP 2003-2004 results, we have concluded that the intertidal sites monitored by the LTEMP program are still extremely clean. With the exception of the Alyeska Marine Terminal site and, to a lesser extent, the Gold Creek site in Port Valdez, the regional sites do not show elevated concentrations of hydrocarbons from either Terminal operations and discharges, or oil transportation activities within Prince William Sound (PWS). Even at Alyeska Marine Terminal and Gold Creek, where PAH and AHC contaminants from the Alyeska Marine Terminal Ballast Water Treatment Facility (BWTF) are detected, the currently measured concentrations are small and suggest that PWS is not heavily contaminated from ongoing anthropogenic activities.

As noted last year, the monitoring aspect is functioning smoothly. In general, when actual spills or other episodic hydrocarbon inputs occurred, the LTEMP mussel tissue and sediment results detected the event; for example, after the 1994 *T/V Eastern Lion* oil spill, the 1997 BWTF sheening event, the 1994 mussel-bed cleaning activities on Disk Island and sediment-cleansing-trials at Sleepy Bay. At the other survey sites, the background levels were extremely low and generally near or below the laboratory method detection limits (MDL). When the signal levels are so low, it is easy to pick up spurious noise (real or artifacts) from the clean samples. To a small degree, there have been problems with laboratory artifacts with the historic LTEMP data (discussed in depth last year).

With last year's comprehensive, all-sample critical-review under our belt, this year, we were able to pick additional patterns out of the data. Specifically, we found that where there are spikes or increases in sediment total polycyclic aromatic hydrocarbon (TPAH) burdens at Gold Creek, they are often due to inclusion of combustion products, and that they are not directly attributable to activities at the terminal, 6 km away. Sediment spikes at Alyeska Marine Terminal are from petrogenic and pyrogenic sources. Both Gold Creek and Alyeska Marine Terminal also show evidence of biogenic saturated hydrocarbon (SHC) sources, including one pattern from copepods, and an odd–carbon-number pattern from terrestrial plant waxes. In general, the data from both TPAH and CRUDE Index plots for Alyeska Marine Terminal sediments show declines in petroleum hydrocarbon contamination from the BWTF starting in March 2001 and continuing through the latest collections in March 2004. The TPAH and CRUDE Index values for Gold Creek are substantially lower and have shown a generally decreasing trend over this same time frame. Additional analyses of steranes, hopanes, and other biological marker compounds would be needed to determine if the trace-level petroleum constituents in the sediments at Gold Creek are from the BWTF or other sources (boat traffic, sewage disposal from the city of Valdez, street runoff, or natural sources such as Gold or Mineral Creeks).

Tissue hydrocarbon burdens as reflected by TPAH concentrations remain very low at all stations, and yet, it is still possible to detect a finite but declining petroleum hydrocarbon signal from the BWTF at Alyeska Marine Terminal and Gold Creek within Port Valdez. The winter vs. summer particulate-phase vs. dissolved-phase pattern has reappeared at

Gold Creek after being largely absent between October 2000 and April 2002. This pattern has always been present at Alyeska Marine Terminal. The tissue SHC patterns at both stations show contributions from marine biogenic sources (e.g., from phytoplankton, marine algae, and copepods) and from terrestrial plant waxes. In addition, the SHC patterns in the mussel tissues at Alyeska Marine Terminal clearly show the influence of particulate/oil-phase components and a chromatographically unresolved complex mixture (UCM) from the BWTF, but as noted above, both Alyeska Marine Terminal and Gold Creek have shown declines in the oil contamination signal since October 2001 and March 2002.

TPAH concentrations in mussel tissues at the outlying stations throughout PWS are uniformly low (generally less than 100-200 ng/g dry weight) and reflect a primarily dissolved-phase signal or source. The SHC profiles from recent years at these outer stations reflect an almost exclusive biogenic source. Because the typical hydrocarbon contaminant concentrations measured in mussel tissues outside Port Valdez are so low (often at or below method detection limits), detailed trend analyses are confounded by background levels, spurious events, and historic data-quality issues. Nevertheless, portions of the historic dataset are internally consistent with known pollution events, observed seasonal changes, and plausible transitions to the current low oiling levels.

The LTEMP program appears to be on-track with high-quality, high-sensitivity data with a good record of detected events. These are the hallmarks of a good monitoring program. The LTEMP data have also proven invaluable as a corroborating data set in acquiring a much more in-depth perspective of the trends and behavior of oil contaminants in the region. Taken together, the TPAH and TSHC values and the associated histogram plots (or fingerprints) do not show the “ubiquitous” background contamination reported throughout much of PWS by Exxon’s consultants (Boehm et al., 2003). The station locations from the Exxon studies and LTEMP are from different areas, but clearly, the LTEMP data in no way suggest that PWS is heavily contaminated from past and ongoing anthropogenic activities.

2 LTEMP Oil Primer

Prior to the usual introductory portion of the report, this section is included as background material for those readers unfamiliar with oil chemistry or the oil contaminants found in Prince William Sound and central Alaskan coastal regions.

2.1 Regional Sources

In the LTEMP regional environment, oil hydrocarbons arrive from numerous and varied sources. Topping the list would be Alaskan North Slope (ANS) crude including lingering residues from the *Exxon Valdez* oil spill (EVOS); oil products from the Alyeska Marine Terminal (not necessarily ANS); coal, peat and organic-rich shales from vast local and regional deposits; Cook Inlet crude oil; and refined petroleum products that have made their way into the marine environment.

Of primary interest to LTEMP is, of course, ANS crude oil. This crude actually consists of a blend of petroleum from the production fields on the Alaskan North Slope, including Prudhoe Bay, Kuparuk, Endicott, and Lisburne, that together exhibit a chemical fingerprint that is quite distinct from that of oil found in other geographic areas. The EVOS of March 1989 consisted of ANS crude, which over time has weathered to produce a significantly different fingerprint than that of fresh ANS crude. Petroleum that originates from organic-rich shales (or hydrocarbon "source rock") and coal deposits in the Gulf of Alaska also contribute significantly to the natural (or “background") hydrocarbons in the study area, and these also exhibit a distinctly different fingerprint. Recent work shows the source rock signature to be particularly widespread in the deep sediments of PWS, and indeed, appears unchanged in coastal sediments from upstream of the Copper River past the Outer Kenai and through Shelikof Straits (unpublished data, Susan Saupe). Fortunately, animals exposed to these sediments do not seem to accumulate hydrocarbons because these contaminants are not bioavailable. Natural terrestrial oil seeps have also been invoked as hydrocarbon sources, but recent work indicates input from these seeps is insignificant compared with the other sources.

Other petroleum products that may have been introduced into the marine environment in Prince William Sound (PWS) include oil products from source locations other than Alaska. For example, the Great Alaskan Earthquake of 1964 and the resultant tsunamis washed fuel oil and asphalt made from California source oils into Port Valdez, and subsequently into PWS (Kvenvolden et al. 1995). These authors noted that tarballs from these California-sourced products have been found throughout the northern and western parts of PWS. Most recently, hydrocarbons from historic anthropogenic activities (long-abandoned mines, logging operations, camp sites, and fish canneries) in addition to current settlements within PWS have been hypothesized as being additional sources of background hydrocarbon signals (Boehm et al. 2003).

2.2 Oil Chemistry, Source Allocations, and Weathering Behavior

Chemically, oil is a complex mixture of decayed ancient organic matter broken down and modified under geologic heat and pressure. Each deposit is a unique blend but there are commonalities. Hydrocarbons are by far the most abundant compounds in crude oil,

accounting for 50-98% of the volume. And in various proportions, all crude blends contain "lighter fractions" of hydrocarbons (similar to gasoline), "intermediate fractions" like diesel or fuel oil, heavier tars and wax-like hydrocarbons, and ultimately residual materials like asphalt. For purposes of the LTEMP chemical analyses, crude oil is identified by its signature blend of just two compositional hydrocarbon groups, the polycyclic aromatic hydrocarbons (PAH) and the saturated (or aliphatic) hydrocarbons (SHC), also referred to as n-alkanes. These two compositional groups encompass the intermediate, heavier tars, and wax-like fractions. As shown by the histogram plots in Figure 1, we work with approximately 40 PAH compounds and 26 SHC components to identify a hydrocarbon source. (Names and abbreviations of the individual analytes shown in this and all following figures are presented in Table 2 in Section 4.2 - Analytical Methods.) These PAH typically account for 2-5% of petroleum by weight (and about 3% of ANS crude).

For source identifications, it is useful to distinguish between five main families of PAH components. In order from light to heavy (left to right in the histogram plots), they are: naphthalenes (N), fluorenes (F), phenanthrenes/anthracenes (P/A), dibenzothiophenes (D), and chrysenes (C).

The naphthalenes are two-ring aromatics (i.e., two 6-carbon rings linked together) and are less persistent in the environment compared to the other higher-molecular-weight groups. They typically disappear from spilled oil by evaporation and dissolution weathering and as such, they may or may not be present in the histogram plots of oil residues or oil-contaminated sediment samples. Because they dissolve slowly and to a limited extent in water, they can also be detected moving directly from the water column into exposed organisms. The fluorenes, anthracenes, and phenanthrenes (which are all three-ring aromatics) are each more persistent in the environment, and as such, they can act as markers to help differentiate among different oil sources. The dibenzothiophenes (another three-ring compound that also contains sulfur) are important, because they are substantially more abundant in Alaskan North Slope crude oil than in other oil deposits in the region such as Cook Inlet or Katalla crude oil. Finally, the heavier four- and five-ring aromatics (including, the chrysenes (C) through benzo(g,h,i)perylene (BP)) are important because: 1) they can help distinguish between crude oils and refined products (such as diesel oil) that may have been produced from a particular crude oil; and 2) they are also representative of combustion by-products.

Chemists have developed a nomenclature to distinguish the various members of each family. The simple parent compounds in each of the five PAH families are referred to as "C_0" (e.g., C_0-naphthalene, here abbreviated simply as "N"). Their other family members, known to chemists as alkyl-substituted homologues, are adorned with an alkyl molecule ($-CH_3$) in a named position around the margin of the PAH ring. These homologues thus become known by their sequence name, e.g., C1-naphthalene (abbreviated as N1), C2-naphthalene (N2), and so on (N3 and N4) (see Figure 1).

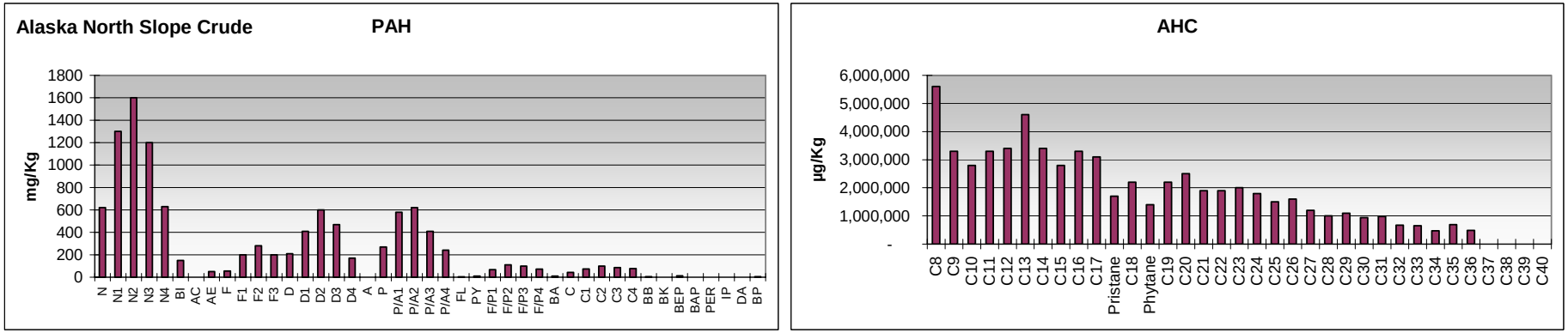

Figure 1. Example histograms of ANS PAH and SHC (also referred to as AHC) components.

Regarding the family structure, it is important to note that petrogenic (petroleum-derived) PAHs have a characteristic fingerprint whereby the parent compounds in each of the five PAH families (e.g., the parent C_0-naphthalene, abbreviated as "N") are usually at lower concentrations than their other family members (see Figure 1). With evaporation/dissolution weathering, these lower-molecular-weight components are more easily eliminated, thus generating a characteristic "water-washed profile" with the levels of $C_0<C_1<C_2<C_3$ within each PAH group. Eventually, with continued weathering, only the most persistent alkylated phenanthrenes/anthracenes, dibenzothiophenes, and chrysenes are seen, and typically at very characteristic, source-specific ratios in the remaining oil residues (Figure 2).

Likewise, in the SHC fraction, the n-alkanes also clearly show the effects of evaporation weathering with losses of all components with molecular weights below n-C_{14} apparent after several weeks (Figure 2). With continued microbial degradation, the remaining n-alkanes will be selectively removed leaving only the branched compounds, pristane and phytane, which are also removed but at a much slower rate over time. Incidentally, phytoplankton make n-C_{15} and n-C_{17} which mussels can accumulate by feeding on the phytoplankton. Substantial concentrations of pristane are also naturally present in some zooplankton; they biosynthesize it from chlorophyll ingested with the phytoplankton they eat. Therefore, all three compounds can show up in mussel and sediment samples as a result of marine biogenic input. In a spring plankton bloom, these natural aliphatic hydrocarbons can easily dominate the SHC fraction. Phytane, on the other hand, is almost exclusively associated with oil, so its presence in samples can also be used as another indicator of petroleum contamination.

Pyrogenic PAHs come from combustion sources including atmospheric fallout and surface runoff from the burning of fossil fuels (diesel, heating oil, gasoline, etc.) and from other pyrogenic sources such as forest fires and camp fires. Creosote, which is used to preserve wood pilings, is also usually included in this category. Pyrogenic PAHs are characterized by high molecular weight PAHs greater than C_3-dibenzothiophene (D3), and by high concentrations of the parent compounds compared to their alkyl homologues. A typical pattern for pyrogenic PAHs is decreasing concentration with increasing alkyl substitution and molecular weight within a group, i.e., $C_0>C_1>C_2>C_3>C_4$, opposite the trend seen in crude oil and distillate products.

For the aliphatic hydrocarbons, the nomenclature strategy changes. The abbreviation for the aliphatic compound, n-C_{10}, now refers to 10 carbon atoms linked in a straight chain (no cyclic rings). In contrast to the PAHs, aliphatic hydrocarbons can account for more than 70 percent of petroleum by weight. Also, as noted above, aliphatic hydrocarbons can be synthesized by organisms (both planktonic and terrestrial), and may be present as degradation products in some bacteria. As shown in Figure 1, crude petroleum contains a homologous series of n-alkanes ranging from one to more than 30 carbons with odd- and even-numbered n-alkanes present in nearly equal amounts. In contrast, biogenic hydrocarbons (produced by living organisms) preferentially contain specific suites of

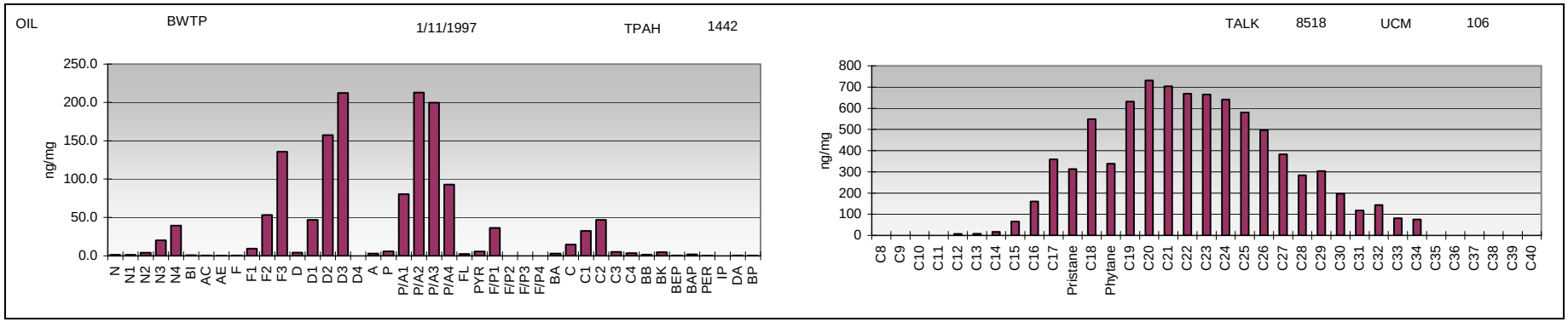

Figure 2. Histogram of weathered ANS from LTEMP 11/97.

normal alkanes with mainly odd-numbered carbons between n-C_{15} and n-C_{33}. In addition to the example of n-C_{15}, n-C_{17}, and pristane from marine plankton cited above, terrestrial plants contribute a predominant odd-numbered carbon pattern including n-C_{25}, n-C_{27}, n-C_{29}, n-C_{31}, and n-C_{33}. These so-called "plant waxes" are commonly observed in marine sediments in depositional areas receiving significant amounts of terrestrial runoff.

Petroleum also contains a complex mixture of branched and cyclic compounds generally not found in organisms. This complex mixture can include oxygenated compounds that produce an "unresolved complex mixture" of compounds (the UCM) on the gas chromatographic chart. The UCM appears proportionally more prominent in analyses as additional oxygenated compounds are introduced to oil by bacterial and photochemical processes. Thus, the presence and amount of the UCM can be a diagnostic indicator of heavily-weathered petroleum contamination.

Once in water, a crude oil signature can be modified by several processes including evaporation and dissolution weathering, and microbial degradation. We've recently identified another twist in tracking an oil source, the dissolved versus particulate fractions. As a droplet of oil enters water, the more readily-dissolvable components, particularly the naphthalenes, are removed from the droplet thus leaving behind a particulate (or oil droplet) fraction with the "water-washed pattern" mentioned above (low on the parent stock). The receiving water then has the dissolved components signature. In essence, one source produces two signatures in water. This process is readily apparent in the discharge into Port Valdez from the Ballast Water Treatment Facility (BWTF) at the Alyeska Marine Terminal.

Figure 3 presents histograms of the PAH and SHC associated with this discharge (Payne et al. 2001; Salazar et al. 2002). In this case, the PAH pattern associated with the colloidal/particulate (oil-droplet) phase shows the depletion of naphthalene (N) and methylnaphthalene (N1) compared to higher alkylated homologues (N2, N3, and N4), and, to a lesser extent, this same "water-washed pattern" is observed for the fluorenes (F's), dibenzothiophenes (D's), and phenanthrenes/anthracenes (P/A's). The SHC (n-alkane) distribution from the BWTF discharge still shows the presence of minute oil droplets (the water insoluble components that do not dissolve). In addition to evaporation weathering, there is evidence of enhanced microbial degradation from the biological treatment tanks at the BWTF as shown by the depleted concentrations of the n-alkanes compared to pristane and phytane (compare the SHC patterns in Figures 1 and 3).

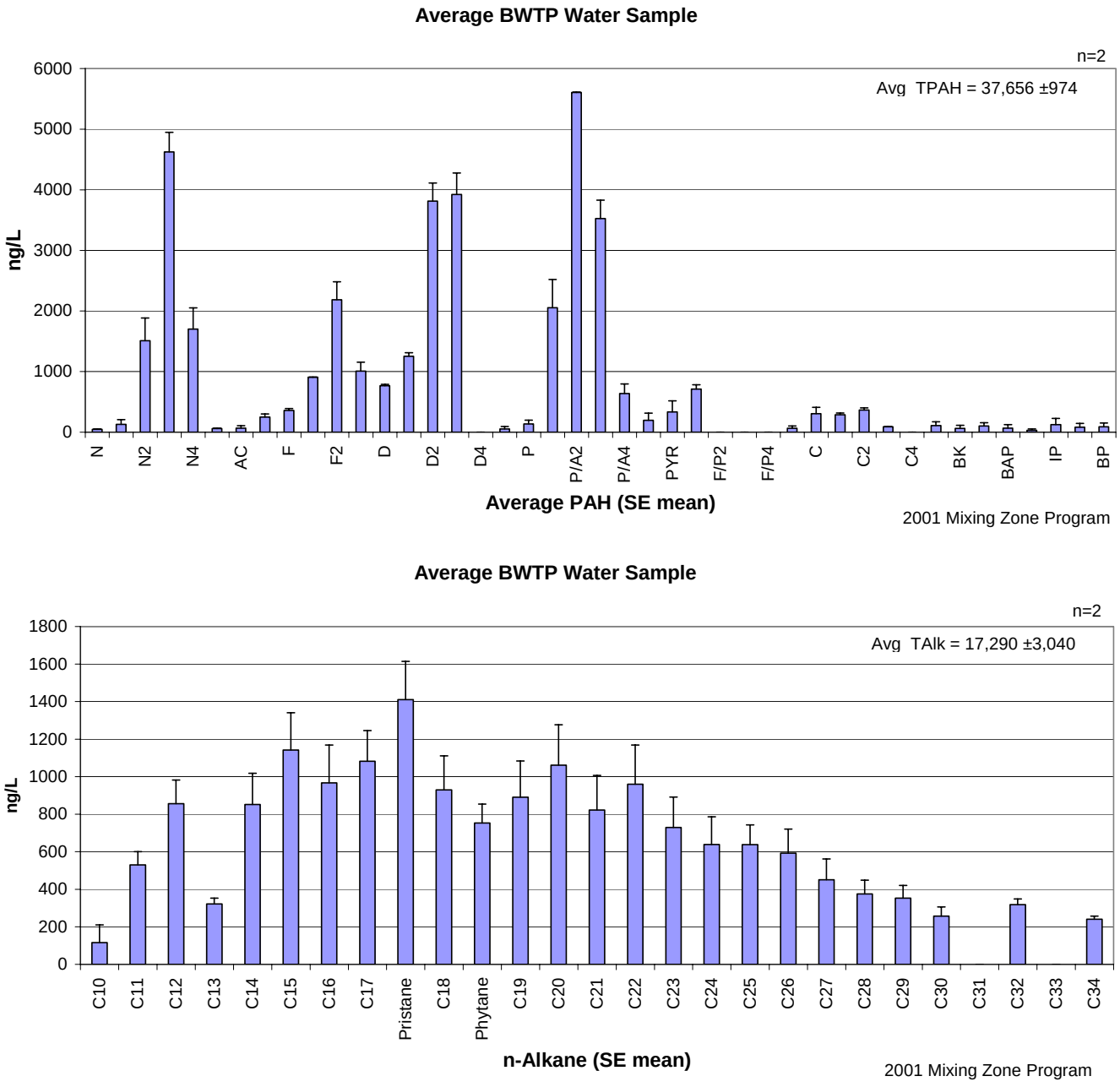

Figure 3. PAH and SHC histograms of effluent from the Alyeska Marine Terminal BWTF (from Salazar et al. 2002).

2.3 Mussels as Indicator Organisms

When analyzing the mussel tissue samples collected as part of LTEMP, it is important to recognize that as filter feeders, mussels can accumulate oil from both the dissolved and particulate/oil-droplet phases. Figure 4 (from Payne et al. 2001) presents examples of mussels collected from oiled areas of Cabin Bay, Naked Island in Prince William Sound in May 1989 immediately after the *Exxon Valdez* oil spill and again in May/June in 1990 and 1991. In 1989, the mussels clearly accumulated PAH and aliphatic hydrocarbons from both the dissolved and particulate phases to which they were exposed; however, the particulate (dispersed oil droplet phase) was the predominant source for the accumulated higher-molecular-weight PAH (C_2-dibenzothiophenes (D2) through higher alkylated homologues of the phenanthrenes/anthracenes and chrysenes) and the aliphatics (phytane plus the even distribution of n-alkanes from n-C_{19} through n-C_{34}). As noted above, these higher-molecular-weight components have only limited water solubilities and have long been associated with the whole oil (droplet) phase. In the post-spill 1990 and 1991 data, the mussels accumulated primarily dissolved-phase PAH (at significantly reduced overall concentrations) from the more water-soluble hydrocarbons still leaching from the contaminated intertidal zone. This is manifest in the histogram plots at the bottom of Figure 4 by the predominant naphthalene and alkyl-substituted naphthalene homologues in greater relative abundance compared to the other PAH. Likewise, the SHC profile for the mussel samples in 1990-1991 is characterized primarily by lower molecular weight biogenic components (n-C_{15}, n-C_{17}, and pristane) with little or no contribution of higher molecular weight n-alkanes from dispersed oil droplets.

This series of histogram plots are presented as examples of what should be considered in the report that follows and specifically kept in mind when reviewing the data generated during the past 12 years of the LTEMP. The histogram profiles in Figure 4 are particularly important, because they also illustrate typical patterns of oil contamination (from both particulate and dissolved phases) in the absence of other confounding factors, such as lipid interference.

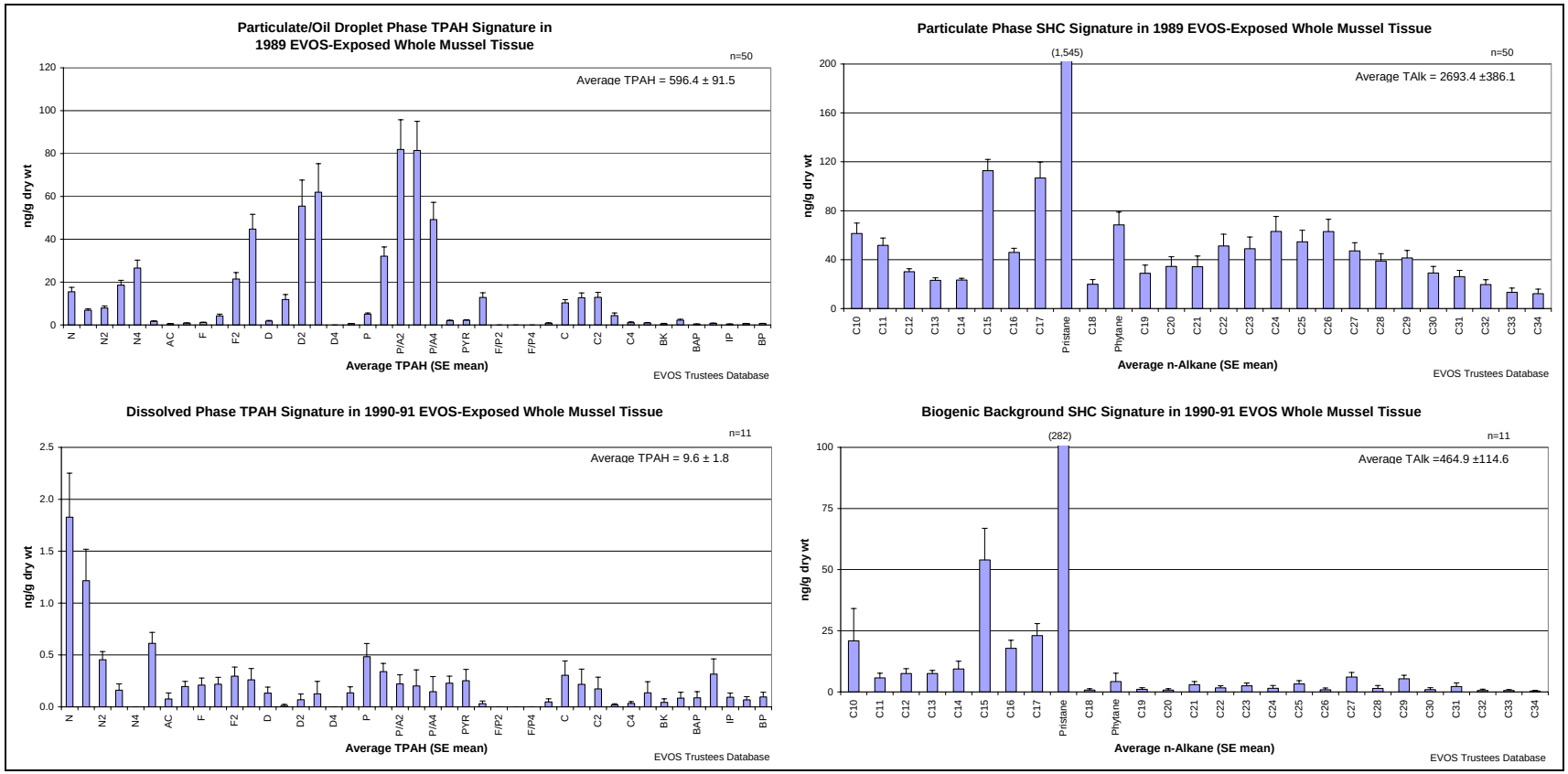

Figure 4. Average PAH and SHC histograms of whole mussel extracts from samples collected from oiled areas of Cabin Bay, Naked Island in Prince William Sound in May 1989 after the Exxon Valdez oil spill (EVOS) and again in May/June 1990 and 1991. The number of samples contributing to each composite is denoted by "n" (from Payne et al. 2001; data from NOAA EVTHD database).

3 Introduction

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 rules, the unregulated release of oil into the environment is strictly prohibited; the LTEMP data serve as an independent quality control for Alyeska Terminal and for tanker operations throughout the region.

Currently measured variables include polycyclic (or polynuclear) aromatic and saturated (or aliphatic) hydrocarbon levels (PAH and SHC) in mussel (*Mytilus trossulus*) tissues from ten stations between Valdez and Kodiak and sediments from two stations in Port Valdez. The Port Valdez sediment samples are also analyzed for particle grain size and total organic carbon content. Sampling and analytical methods are patterned after the protocols developed by the National Oceanic and Atmospheric Administration (NOAA) Status and Trends Mussel Watch Program as fully detailed in the annual Monitoring Reports prepared by Kinnetic Laboratories, Inc. (KLI) and the Geochemical and Environmental Research Group (GERG).

Since the program's inception in 1993, LTEMP samples have been collected by KLI and analyzed by GERG. In July 2002, Payne Environmental Consultants, Inc (PECI) and the NOAA/NMFS Auke Bay Laboratory (ABL) began conducting the program. The LTEMP results were last reviewed in a synthesis paper (Payne et al. 1998) covering the 1993-97 results. 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. The authors recommended several changes to the existing program at that time, including:

- adjusting the sampling plan to include more sites,
- modifying the statistical criteria,
- adding intertidal sediment samples,
- rectifying method detection limit (MDL) problems in the laboratory analyses,
- paying closer attention to field and procedural blank contamination problems,
- reinstating aliphatic hydrocarbon analyses in mussel tissue samples,
- tightening field sample procedures regarding sampling depth and mussel size,
- dropping lipid corrections, seasonal sampling, and unnecessary shell measurements from the mussel sampling, and
- sampling and analyzing potential background sources with common laboratory methods.

The RCAC subsequently made several changes reducing the scope of the program and resulting in the current biannual sampling program of regional mussel tissues and Port Valdez sediments. In recent years, in addition to the early spring and mid-summer samplings, another set of mussel samples, taken in the fall just in Port Valdez (Alyeska Marine Terminal and Gold Creek), was added to the sample design. Analysis of aliphatic

hydrocarbons in mussel tissues, dropped from the original program in 1995 due to results confounded from lipid interference, was reinstated in 1998.

In 2001, another data evaluation and synthesis review was completed on just the LTEMP results from the Port Valdez sites (Payne et al. 2001). Review of the data from Alyeska Marine Terminal and the Gold Creek control site suggests Alaska North Slope (ANS) crude oil residues from the terminal's ballast water treatment facility (BWTF) have accumulated in the intertidal mussels within the port. As noted above, PAH and SHC levels measured in sediments and mussel tissues (and the estimated water-column levels) continue to be low and unlikely to cause deleterious effects. From the signature of analytes, however, we were able to 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 give new insight into the transport and exposure pathways in Port Valdez. The results also suggest a surface microlayer mechanism may be responsible for seasonal transport of ANS weathered oil residues from the BWTF diffuser to intertidal zones to the north and west of the terminal. Payne et al. (2001) concluded that the possibility of concentrated contaminants in a surface microlayer combined with the potential for photo-enhanced toxicity should be considered in future investigations of potential impacts in Port Valdez.

This report examines the current and historic results of 700 tissue and 120 sediment samples collected from within Prince William Sound and the surrounding region (Figure 5a) in addition to the laboratory quality control results. Other sampling depths or locations in the original sample design that are no longer occupied are not included in this review. Not included in this year's report are reviews of related studies, chiefly, Alyeska's environmental monitoring program, 2002 regional EMAP data (unreleased), and NMFS studies of retained oil in PWS beaches.

4 Methods

4.1 Sampling Design

For both the tissue and sediment collections, the current sample design followed the previous years' efforts (KLI 2002) with slight modifications. As noted above, mussel tissues are sampled at ten sites and sediments from two sites in Port Valdez on a biannual basis (March-April and July-August) (Figure 5b). Mussel tissues are also collected from the two Port Valdez sites in October.

For tissues, three replicates were taken from random locations along the transect at each site but forgoing the prescribed randomization, detailed documentation, and beach-freezing procedures used by KLI. In a more streamlined procedure, a replicate of 25-30 mussels was collected by hand using Nitrile gloves, wrapped in aluminum foil, Ziplock® bagged, labeled, double-bagged and kept chilled until reaching the nearest freezer. The collection site was photographed and GPS coordinates recorded for chain-of-custody documentation. The entire trip collection was eventually air-freighted frozen to the NOAA/NMFS Auke Bay Laboratory in Juneau.

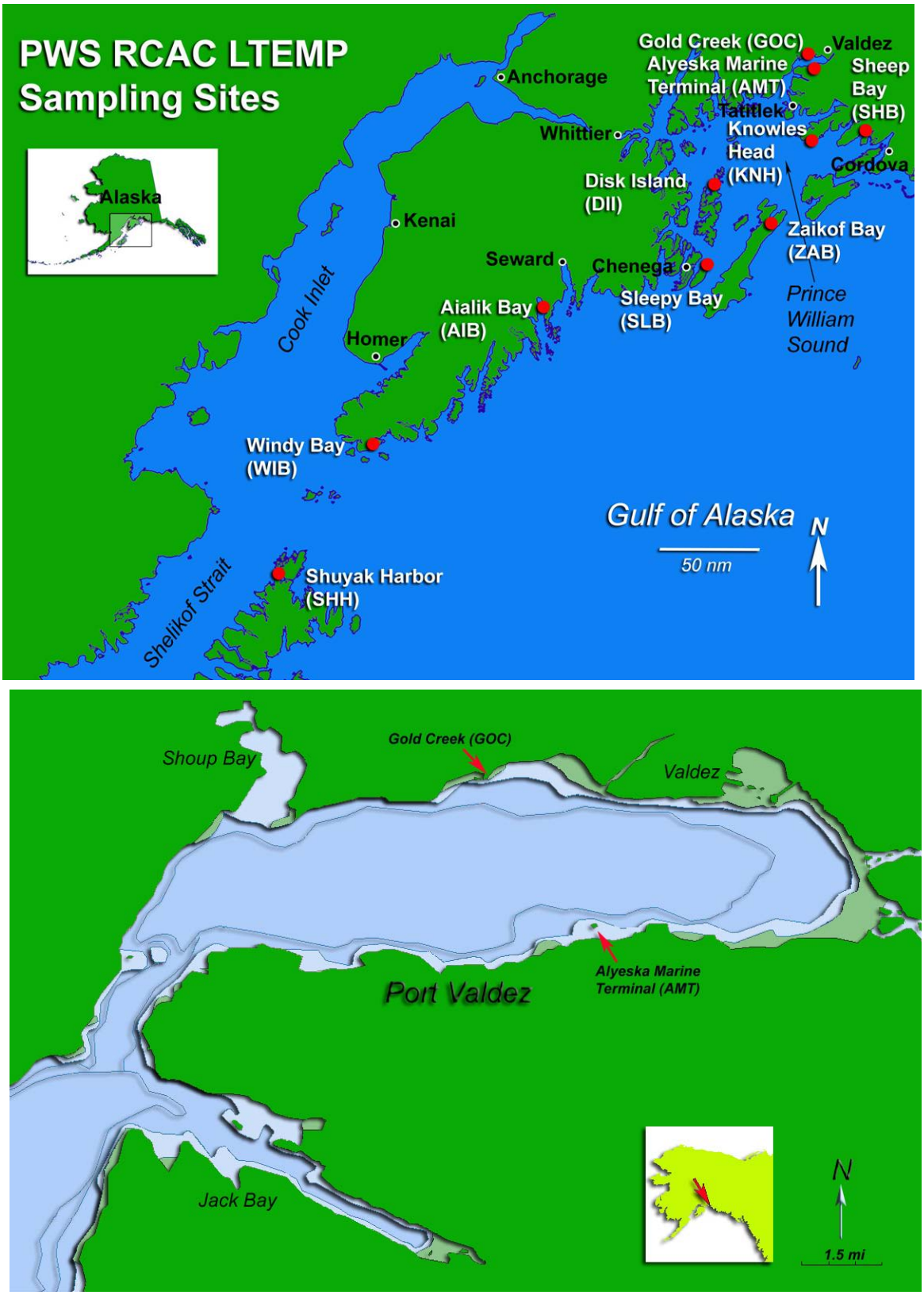

Figure 5. Map of LTEMP sites with close-up of Port Valdez.

Sediments were collected using the general techniques instituted by KLI but again some procedures varied. For example, in July 2002 and March 2003, a standard Van Veen grab was used rather than KLI's modified Van Veen; the standard version lacks a stabilization frame that encircles the grab. A modified Van Veen sampler (identical to the one previously used by KLI) was purchased by PECI and used during the July 2003 and all subsequent sediment sampling efforts. Data from a comparison trial of the two sampler versions, conducted in July 2003, are included in this report. Another significant change was replacing KLI's multi-solvent decontamination procedure with a simple seawater hose rinse. In low-oil-level environments such as PWS, a non-solvent rinse is less prone to picking up secondary contamination (e.g., from ship's oils and lubricants or airborne diesel particulates and combustion products). A review of trip and equipment blanks have confirmed the effectiveness of the sea-water rinse procedures.

Both LTEMP contractors have used a combination of vessel and float plane to access the sampling sites. Typically, the PECI field trips used the *M/V Auklet* for the Port Valdez and Knowles Head stations and a float plane to sample all other sites.

Table 1. LTEMP Stations 2003-2004

Station Location	Station Code	Sample Type	Sampling Date	Average Station Depth	Global Positioning System (GPS) Coordinates Latitude (N)	Longitude (W)
Aialik Bay	AIB-B	Intertidal Mussel	8/1/03		59° 52.753'	149° 39.593'
			3/20/04		59° 52.752'	149° 39.588'
Alyeska Marine Terminal	AMT-B	Intertidal Mussel	7/27/03		61° 5.408'	146° 24.502'
			10/7/03		61° 5.420'	146° 24.500'
			3/21/04		61° 5.408'	146° 24.502'
	AMT-S	Subtidal Sediment	7/27/03	67m	61° 5.400'	146°23.673'
			3/23/04	72m	61° 5.388'	146°23.711'
Disk Island	DII-B	Intertidal Mussel	7/29/03		60° 29.904'	147° 39.668'
			3/17/04		60° 29.908'	147° 39.641'
Gold Creek	GOC-B	Intertidal Mussel	7/27/03		61° 7.454'	146° 29.763'
			10/7/03		61° 7.442'	146° 29.777'
			3/21/04		61° 7.454'	146° 29.763'
	GOC-S	Subtidal Sediment	7/27/03	32m	61° 7.455'	146°29.591'
			3/23/04	32m	61° 7.419'	146°29.603'
Knowles Head	KNH-B	Intertidal Mussel	7/28/03		60° 41.449'	146° 35.141'
			3/23/04		60° 41.431'	146° 35.159'
Sheep Bay	SHB-B	Intertidal Mussel	7/28/03		60° 38.769'	145° 59.847'
			3/17/04		60° 38.763'	145° 59.857'
Shuyak Harbor	SHH-B	Intertidal Mussel	8/1/03		58° 30.076'	152° 37.657'
			3/15/04		58° 30.076'	152° 37.657'
Sleepy Bay	SLB-B	Intertidal Mussel	7/29/03		60° 4.037'	147° 49.999'
			3/17/04		60° 4.051'	147° 49.989'
Windy Bay	WIB-B	Intertidal Mussel	8/1/03		59° 13.096'	151° 31.210'
			3/15/04		59° 13.084'	151° 31.191'
Zaikof Bay	ZAB-B	Intertidal Mussel	7/29/03		60° 15.918'	147° 5.117'
			3/17/04		60° 15.912'	147° 5.120'

4.2 Analytic Methods

Sediment samples (50 g wet weight) or mussel samples (10 g wet weight) were spiked with a suite of 5 aliphatic and 6 aromatic perdeuterated hydrocarbon surrogate standards (identified in Table 2) and then extracted with dichloromethane at 100°C and 2,000 psi for 10 min in a Dionex ASE 200 accelerated solvent extractor. The dichloromethane solutions were exchanged with hexane over steam, and separated into aliphatic and aromatic fractions by column chromatography (10 g 2%-deactivated alumina over 20 g 5%-deactivated silica gel; columns for sediments also contained 20 g granular elemental copper and 8 g anhydrous sodium sulfate for removal of sulfur and water, respectively). Aliphatics eluting with 50 mL pentane were analyzed by gas chromatography with a flame ionization detector (GC/FID) following concentration to ~ 1 mL hexane over steam and addition of dodecylcyclohexane as an internal standard to evaluate recoveries of the surrogate standards. PAH constituents from the sample extracts were further purified by gel-permeation high performance liquid chromatography (HPLC). The injection volume was 0.5 mL into dichloromethane flowing at 7 mL/min through two size-exclusion gel columns (Phenomenex, phenogel, 22.5 mm x 250 mm, 100 Å pore size) connected sequentially. The initial 110 mL eluate was discarded, and the following 50 mL was concentrated over a 60–70^{o} C water bath and exchanged with hexane to a final volume of *ca*. 1 mL, then spiked with hexamethylbenzene as an internal standard for estimating recoveries of the initially added perdeuterated aromatic hydrocarbon surrogate standards.

PAHs in extracts were separated and analyzed with a Hewlett-Packard 6890 gas chromatograph equipped with a 5973 mass selective detector (MSD). The injection volume was 1 µL into a splitless injection port at 300° C. The initial oven temperature was 60° C, increasing at 10° C per minute immediately following injection to a final temperature of 300° C, then held for 12 min. The chromatographic column was a 25 m fused silica capillary (0.20 mm ID) coated with 5% phenyl methyl silicone. The helium carrier gas was maintained at 70 kPa inlet pressure.

The gas chromatographic column eluted into the 70 eV electron impact MSD through a 240° C transfer line. The ionizer temperature and pressure were 240° C and 10^{-5} torr, respectively. The MSD was operated in the selected-ion-monitoring (SIM) mode. The MSD was tuned with mass 69, 102, and 512 fragments of perfluorotributylamine before each batch of samples was analyzed.

Calibrated PAHs were identified based on retention time and ratio of two mass fragment ions characteristic of each hydrocarbon. Calibrated PAHs are identified by bold typeface in Table 2, and include dibenzothiophene and the aromatic hydrocarbons in Standard Reference Material (SRM) supplied by the National Institute of Standards and Technology (NIST). Chromatographic peaks were identified as a calibrated aromatic hydrocarbon if both ions were co-detected at retention times within ±0.15 minutes (9 seconds) of the mean retention time of the hydrocarbon in the calibration standards, and if the ratio of the confirmation ion to the quantification ion was within ±30% of the expected ratio.

Table 2. Polycyclic aromatic hydrocarbon (PAH) and saturated hydrocarbon (SHC) analytes measured in this study, along with analyte abbreviations, internal and surrogate standards.

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	P/A1	A	3
C2-Phenanthrene/Anthracene	P/A2	A	3
C3-Phenanthrene/Anthracene	P/A3	A	3
C4-Phenanthrene/Anthracene	P/A4	A	3
Fluoranthene	FL	A	3
Pyrene	PYR	A	3
C1-Fluoranthene/Pyrene	F/P1	A	3
C2-Fluoranthene/Pyrene	F/P2	A	3
C3-Fluoranthene/Pyrene	F/P3	A	3
C4-Fluoranthene/Pyrene	F/P4	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
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

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 = hexamethyl benzene; 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.

Uncalibrated PAHs include the alkyl-substituted isomers of naphthalene (except the methyl-substituted homologues), fluorene, dibenzothiophene, phenanthrene/anthracene, fluoranthene/pyrene, and chrysene listed in Table 2. Uncalibrated PAHs were identified by the presence, within a relatively wide retention time window, of a single mass fragment ion that is characteristic of the uncalibrated PAH sought. Wider retention time windows were necessary for the uncalibrated PAH because of the range of retention times of the various isomers that are included in an uncalibrated PAH homologue grouping (e.g. C3-phenanthrene).

Concentrations of calibrated PAHs in extracts were estimated by a method employing multiple internal standards and a five-point calibration curve for each calibrated PAH. The deuterated surrogate standards that were initially spiked into each sample are treated as internal standards, where each surrogate compound is associated with one or more calibrated PAHs (see Table 2). A calibration curve for each calibrated PAH and batch of samples analyzed was based on five different hexane dilutions of the PAH standard run before each sample batch or "laboratory string." Each calibration curve was derived from linear regression of (1) the ratio of MSD/SIM quantification ion response of the calibrated PAH and the associated deuterated surrogate standard and (2) the ratio of the amount of calibrated PAH and the amount of deuterated surrogate in the calibration standards.

Concentrations of uncalibrated PAHs in extracts were determined with calibration curves and procedures for the most similar calibrated PAH. The MSD/SIM response to the quantification ion of each uncalibrated PAH homologue isomer were summed; this sum was used in place of the calibrated PAH response in the procedure described above for calculating concentrations of calibrated PAHs. For example, the fluorene calibration curve and procedure was used for all the alkyl-substituted fluorenes identified, but 2,6-dimethylnaphthalene, 2,3,5-trimethylnaphthalene and 1-methylphenanthrene calibration curves were used for C2-naphthalenes, C3-naphthalenes and for all the alkyl-substituted phenanthrenes, respectively.

Alkanes in extracts were separated and analyzed with a Hewlett-Packard 5890 gas chromatograph equipped with a flame ionization detector (FID). The injection volume was 1 µL into a splitless injection port at 300° C. The 60° C initial oven temperature was maintained for 1 minute, then increased at 6° C per minute to a final temperature of 300° C, then held for 25 min. The detector temperature was 320° C. The chromatographic column was the same as that used for PAH analysis (see above). The helium carrier gas flow rate was 0.80-2.0 mL per minute, and the column effluent was combined with 34 mL per minute nitrogen make-up gas before entering the FID. The FID was operated with hydrogen- and air-flow rates of approximately 33 and 360-410 mL per minute, respectively. Alkane hydrocarbons were identified based on their retention times. Any peak detected above the integrator threshold within ±0.25% of the mean retention time of an alkane in the calibration standards was identified and quantified as that alkane.

Concentrations of calibrated alkanes (listed in Table 2) were determined by an internal-standard method employing a five-point calibration curve for each alkane. The deuterated surrogate standards that were initially spiked into each sample were treated as internal standards, where each surrogate compound was associated with a group of calibrated alkanes (see Table 2). A calibration curve for each calibrated alkane and batch of samples analyzed was based on five different hexane dilutions of the alkane standards. Each calibration curve was derived from linear regression of (1) the ratio of FID response of the alkane and the associated deuterated surrogate standard, and (2) the ratio of the amount of calibrated alkane and the amount of deuterated surrogate in the calibration standards.

Amounts of uncalibrated alkane hydrocarbons and the cumulative amount of hydrocarbons in the unresolved complex mixture (UCM) were based on detector responses and the calibration curve for hexadecane. Flame ionization detector response due to the UCM was determined as the difference of the total FID response and the response due to distinguishable peaks using valley-to-valley baseline integrations.

4.3 Quality Assurance

Quality control samples were analyzed with each batch of 12 samples to assess the accuracy and precision of the analysis, and to verify the absence of laboratory contaminants introduced during analysis. Two quality control samples for accuracy assessment were prepared from hydrocarbon standards prepared by NIST (for PAH) or by ABL (for aliphatics), and run with each batch. Precision was assessed by analysis of two NIST standard reference material (SRM) samples analyzed with each batch: SRM 1974a for mussels and SRM 1944 for sediments. The mussel reference is especially appropriate for these analyses because the PAH concentrations are quite low, with many of the PAH analytes present at concentrations near the method detection limits (MDLs). Absence of laboratory contaminants was verified by analysis of one method blank sample with each batch.

Method detection limits were estimated for each calibrated alkane and PAH analyte following the procedure described in Appendix B, 40 Code of Federal Regulations, Part 136. Method detection limits for uncalibrated PAHs were not experimentally determined. Consequently, detection limits for these analytes were arbitrarily assumed as the MDL of the most closely related calibrated PAH analyte.

4.4 Determination of Moisture Content

Weighed aliquots of wet mussel homogenates or of sediments were dried at 100^{o} C for 24 h and re-weighed to determine the moisture content, and the ratio of these wet and dry weights was used to convert PAH and SHC concentrations to a dry weight basis.

4.5 Particle Grain Size Determination

Determination of the distribution of particle grain sizes in the sediment samples was determined by a combination of sieving and pipette methods based on the procedures given by Folk (1974). Implementation of these procedures at ABL (Larsen and Holland 2004) is almost identical with the method described in SOP-8908 at GERG. The ABL procedure differs from the GERG procedure in the sample pre-treatment. At ABL, a somewhat smaller sample aliquot is used (8 – 12 g instead of 15 – 20 g sediment), the minimum amount of hydrogen peroxide is used to oxidize organic matter (typically 30 – 60 ml of 30% H_2O_2 instead of 50 – 100 ml), the sample is not washed with distilled water to remove soluble salts at ABL because of the risk of loosing sediment fines, and only ~ 100 ml of sodium hexametaphosphate solution is used to disperse the sample at ABL instead of 400 ml at GERG. These changes were implemented at ABL because they were specifically optimized for the samples analyzed for the LTEMP program. The effects of these minor procedural differences on the estimates of particle grain size distributions in comparison with results produced at GERG are almost certainly negligible.

4.6 Determination of Total Organic and Total Carbon

Analytical measurements of total organic and total carbon are determined on oven dried and pulverized sediment samples using a Dohrmann DC-85A TOC catalytic combustion (oxygen at 200 ml/min and cobalt oxide on alumina) furnace. The carbon dioxide produced is passed through an acidified liquid sparger (scrubs out entrained water vapor and corrosive species), two scrubbers (copper and tin) and linearized non-dispersive infrared detection, by comparison with results from a calibration curve based on potassium acid phthalate. Total organic carbon (TOC) and total carbon (TC) are determined on samples treated with and without 10% HCl in methanol. Total inorganic carbon is calculated as the difference between TC and TOC.

4.7 Data Analysis

The LTEMP program was designed to determine baseline conditions and help identify potential future impacts of oil transportation in the study area. In the conception of this project, the sample design was configured to facilitate inferential testing of null hypotheses. For example, the number of replicates was assessed to ensure that the desired power would be obtained in testing three primary hypotheses. Following the project review in 1998 (Payne et al. 1998), this emphasis was relegated to lesser priority. It was realized at that time that there was more information available in the individual samples than in simply looking at trends of averaged indices. A more cogent story could be told by subjectively assessing the chemical composition and levels of the analytes than could be garnered from evaluating the trends in means and variances. Over the past five years, we have also developed new analytic tools and insights into the behavior and fate of oil in the regional environment (Payne et al. 2001). Following last year's data quality

review of all LTEMP tissue and sediment data (Payne et al. 2003a), this year, the analyses and interpretations focused on looking closely at trends and assessing the performance of the two models of grab samplers.

Several indices have been developed and used in prior LTEMP studies. KLI has diligently reported these values during recent years. For the current report, we utilize a number of these where needed, namely, the TPAH, TAHC, CRUDE, MPI and PDR indices plus one additional, the pyrogenic index. The goal here is to quantify, as much as possible, the subjective task of source identification and to provide supporting evidence for suppositional trends and scenarios, including the identification of laboratory artifacts. Should they be required, these ratios may also be useful in developing testable null hypotheses.

The indices used for this report are presented in Table 3; their function and composition have been explained in earlier reports. A new index developed this year is the Pyrogenic Index. In reviewing the CRUDE Index plots for the sediments analyzed over the 11 years of the program, we noted that whenever there was a spike in the CRUDE Index value or when the standard error bars for a particular season's collection were unusually large, the cause could usually be attributed to one sample exhibiting a different PAH profile. Often, the outlier exhibited elevated levels of PAH that clearly were derived from combustion sources. To help identify those samples that contained unusually high concentrations of combustion products, we developed the Pyrogenic Index, which is essentially the sum of those PAH that are characteristic of combustion (as opposed to petroleum) sources normalized to the total PAH (TPAH) signal. We found this approach to be useful in screening sediment samples for combustion vs. petrogenic sources and in presenting an overview without resorting to detailed analyses of individual histogram plots.

Table 3. Hydrocarbon Parameters Used in the LTEMP Data Analysis (adapted partially from KLI, 1997).

Parameter	**Relevance**
CPI (sediments)	The Carbon Preference Index represents the relative amounts of odd and even chain alkanes within a specific boiling range and is defined as follows: $CPI = 2(C_{27} + C_{29})/(C_{26} + 2C_{28} + C_{30})$ Odd and even numbered n-alkanes are equally abundant in petroleum but have an odd numbered preference in biological material; a CPI close to 1 is an indication of petroleum and higher values indicate biogenic input (Farrington and Tripp 1977)

CRUDE Index (sediments)	A summation of TPAH, TSHC and UCM weighted to assess the petrogenic fractions (derived from FFPI and CPI indices). $CRUDE = (TPAH \times FFPI/100) + (TSHC/CPI^2) + UCM$
FFPI (sediments)	The Fossil Fuel Pollution Index is the ratio of fossil-derived PAHs to TPAH and is defined as follows: $FFPI = [(N + F + P + D)/TPAH] \times 100$ where: N (Naphthalene Series) = C_0-N + C_1-N + C_2-N + C_3-N + C_4-N F (Fluorene series) = C_0-F + C_1-F + C_2-F + C_3-F P (Phenanthrene/Anthracene series) = C_0-A +C_0-P + C_1-P/A + C_2-P/A + C_3-P/A + C_4-P/A D (Dibenzothiophene Series) = C_0-D + C_1-D + C_2-D + C_3-D FFPI is near 100 for petrogenic PAH; FFPI for pyrogenic PAH is near 0 (Boehm and Farrington 1984)
Marine Biogenic Index (mussel tissues)	Mussels and copepods accumulate selected aliphatic hydrocarbons from their phytoplankton diets. Marine Biogenic index = (C_{15} + C_{17} + pristane)/TSHC
MPI (mussel tissues)	The Mytilus Petrogenic Index isolates the FFPI fraction of TPAH MPI = TPAH X FFPI/100
PDR (mussel tissues and sediments)	The Particulate/Dissolved Ratio identifies a sample as containing the dissolved or particulate (oil droplet) PAH fractions of oil. PDR = (Phenanthrenes_Anthracenes + Dibenzothiophenes + Chrysenes)/Naphthalenes Samples having PDR values less than 1.0 are dissolved oil fractions, greater than 2.0 are particulate/oil droplet fractions, between 1 and 2 are blends of the fractions.
Plant Wax Index (sediments)	The Plant Wax Index is the sum of aliphatic hydrocarbons typical of naturally-occurring terrestrial plant wax compounds Plant Wax Index = (C_{25} + C_{27} + C_{29} + C_{31})/TSHC

Pyrogenic Index	The Pyrogenic Index is the sum of those parent (unsubstituted) PAH components that typically predominant in samples with significant combustion product sources normalized to the TPAH Pyrogenic Index = (A + P + FL + PY + C + BB + BK + BEP + BAP + IP + DA + BP)/TPAH
TPAH (mussel tissue and sediments)	Total PAH as determined by high resolution GC/MS with quantification by selected ion monitoring; defined as the sum of 2 to 5-ring polycyclic aromatic hydrocarbons: Naphthalene + fluorene + dibenzothiophene + phenanthrene/anthracene + chrysene, and their alkyl homologues + other PAHs (excluding perylene); useful for determining TPAH contamination and the relative contribution of petrogenic, pyrogenic, and diagenic sources
TSHC (sediments)	Total Saturated Hydrocarbons quantifies the total n-alkanes (n-C_{10} to n-C_{34}) + pristane and phytane; represents the total resolved hydrocarbons as determined by high resolution gas chromatography with flame ionization detection (GC/FID); includes both petrogenic and biogenic sources
UCM (sediments)	Unresolved Complex Mixture – petroleum compounds represented by the GC-FID signal for total resolved peaks plus unresolved area minus the total area of the resolved peaks quantified with valley-to-valley baseline integration; a characteristic of some fresh oils and most weathered oils.
Upper Aliphatic Hump (mussel tissues)	The modal group of analytes termed the Upper Aliphatic Hump is thought to be a laboratory artifact of lipid or other interference that over-reports these values. This index is used in screening for SHC data quality. Upper Aliphatic Hump = Sum of C_{22} to C_{32}/TAHC

The Upper Aliphatic Hump is a relative quantification of the C_{22} to C_{32} mode in the aliphatic compounds. This modal group is thought to possibly be an artifact of lipid interference in measuring the SHC during earlier years of the LTEMP. This cluster was ubiquitous in many mussel samples across all stations and seasons in the early years of the program, and it made up anywhere from 50-90% of the total SHC (TSHC) signal when samples were being analyzed at GERG (Payne et al. 2003a). Despite an appearance that was temptingly close to the homologous series of even and odd higher-molecular-weight n-alkanes characteristic of heavily weathered fuel oils, it did not correlate with individual or total PAH (TPAH) concentrations in any of the samples and therefore could not be associated with oil. In an effort to try and tease out meaningful SHC data against this background signal during last year's data analysis, the Upper Aliphatic Hump was used to plot its frequency of appearance and in various other attempts to define quantitative correlations among it and other variables (Payne et al. 2003a). In this year's program we have noted ultra-trace levels of n-alkanes in this molecular-weight range showing up in selected tissue samples, but the concentrations are

orders-of-magnitude lower than those associated with the lipid interference problem. As such, they are believed to possibly be due to traces of weathered oil or tarballs (but at concentrations too low for associated PAH to be detected) or to possible bacterial sources associated with the mussel tissues (Davis 1968; Han and Calvin 1969). The plant wax and the marine biogenic indices are based upon the well-known attribution of specific aliphatic hydrocarbons to these sources. These indices quantify the portion of the TSHC that come from these specific sources. Terrestrial plant waxes add to the C_{25}, C_{27}, C_{29} and C_{31} values. Sediments heavy in terrestrial deposits will spike the plant-wax constituents. From their diets of phytoplankton and detrital organic matter, mussels accumulate C_{15}, $C_{17,}$ and pristane.

For this program, we find the CRUDE Index very effective for evaluating hydrocarbons in sediments; however, the CRUDE Index is not calculated for LTEMP tissues. Due to missing aliphatic data and problems with lab results; the MPI is used instead.

Data analysis for this project relies heavily on reviewing the histogram plots of each sample. To facilitate this effort, an Excel application was developed to plot each sample from a station in replicate groups (by station and sampling date) with lab method detection limits (MDLs) superimposed on the histogram and the relevant lab method blank adjacent to the group. For example, from Aialik Bay, 64 tissue PAH samples were plotted three to a row plus the lab blank for that batch. The SHC samples were plotted in the same manner. This method provides a quick comparative review of replicate trends at a station. For a more detailed comparison, another application could graph both PAH and SHC analytes with relevant indices from any two samples plus a reference standard (e.g., BWTF outfall or ANS crude). Finally, individual graphs of select indices or pairings of indices were used for evaluating trends at particular sites.

4.8 Data Management

Last year, data received in spreadsheet format from ABL were combined with historic data from KLI Microsoft Access database archives. Slight modifications were made to the historic data to standardize chemical compound names and abbreviations. This year's data will be amended to the same database, metadata updated and the product delivered to the EVOS Trustees data archives. Microsoft Excel pivot tables were used for most data compilations. Graphing and data processing routines (described above) were then custom programmed for Excel using Microsoft Visual Basic for Applications (VBA) code.

5 Results and Discussion

5.1 Grab Sampler Comparison

When the PECI/ABL team took over the LTEMP study from KLI/GERG in 2002, an unmodified Van Veen grab from ABL's inventory was used for sediment sampling rather than the modified grab that KLI used (Figure 6). A modified Van Veen has a self-leveling, stability-ring framework that ensures the grab penetrates perpendicular to the

Figure 6. Modified (left) and unmodified (right) models of Van Veen grabs used in sampling method comparisons. The clam-shell buckets are cocked open on the left model and closed on the right.

sediment surface—a factor important to obtaining quantitative volumes of infauna but not of concern to the LTEMP study. Still, valid questions arose as to whether the change in grabs would affect the reproducibility of the "KLI standard" sample and that the time series data might thus be compromised. In order to forestall such issues, PECI purchased a modified Van Veen to use for this program. Thus, one objective of this year's program was to assess any differences in the performance of the two grabs. In July 2003, three replicates were taken with each grab at both Gold Creek and Alyeska Marine Terminal sites.

The most critical assessments in comparing the performance of the two grab samplers would be to detect any significant differences among the replicate samples either in grain size or chemistry results. Because both samplers, PECI's modified and ABL's unmodified Van Veen, employ the same grabbing method, the most likely difference would manifest from the respective bow pressure wave created from the descending grab washing or blowing away the unconsolidated sediment surface layer. Because oil micro-droplets tend to agglomerate onto suspended particulate material (SPM), the surface layer of unconsolidated-to-consolidated SPM is the matrix of interest. Particle grain size comparisons are thus highly relevant as is the TPAH signature from whole sedimented oil/SPM agglomerates.

In the field, we found that the newly-built, modified Van Veen was too efficient in sampling the soft muds of Port Valdez. Frequently, a sample was compromised and rejected when the grab penetrated too deeply, overfilling the grab bucket and allowing the sediment surface to touch the upper access doors. Ironically, we found out after the cruise that KLI had added baffle plates to the bottom of the stabilizing ring on their sampler to reduce its penetration (and consequentially, create a larger bow pressure wave) (pers comm., David Janka). For the March 2004 cruise, we too, added small baffle plates to two sides of the stabilizing ring of the PECI sampler to adapt to Port Valdez's soft sediments and better duplicate KLI's methods.

5.1.1 Particle Grain Size

Normally, only a single PGS sample is taken per station and analyzed to represent the entire grab sampling event. For the purposes of this comparative study, separate PGS samples were analyzed for all collected sediments thus producing triple replicates from the actual chemistry samples. As described below, this approach proved so useful in identifying outlier samples that we are recommending a procedure change to collect triplicate PGS samples.

From July's Alyeska Marine Terminal samples, results from the ABL and PECI grab samplers show that any differences were indistinguishable from normal variation; the samples were remarkably similar in both grain size and chemical composition (upper Figure 7). The site seems quite homogeneous. In contrast, the July Gold Creek samples (lower Figure 7) had one outlier, replicate 3 from the modified (PECI) grab (Table 4), which retrieved an unusual sample with a trace of gravel and substantially more sand and less silt than most other samples. Often during field operations, the Gold Creek site can be a difficult location to sample; the optimal location lies atop an underwater knoll, which between spring tidal currents and surface breezes, is sometimes problematic to stay positioned over. Obviously, the one atypical sample from July came from a slightly coarser matrix (i.e., includes gravel) suggesting the replicate variance was due to spatial substrate changes (even though the GPS readings confirm the retrieval location was within the normal cluster of sampling stations) rather than grab performance issues. Because the other two July PECI replicates are within the variation of the site's grain-size composition, the data suggest the ABL and PECI grabs sampled with indiscernible differences.

In the March grain size analyses, Gold Creek replicate 2 contained a dramatically higher amount of sand than the other replicates, (18% versus 9% and 12%). Again, the GPS positions reflect a reasonably tight sampling cluster so these results support Gold Creek's spatial sediment heterogeneity interpretation rather than equipment issues.

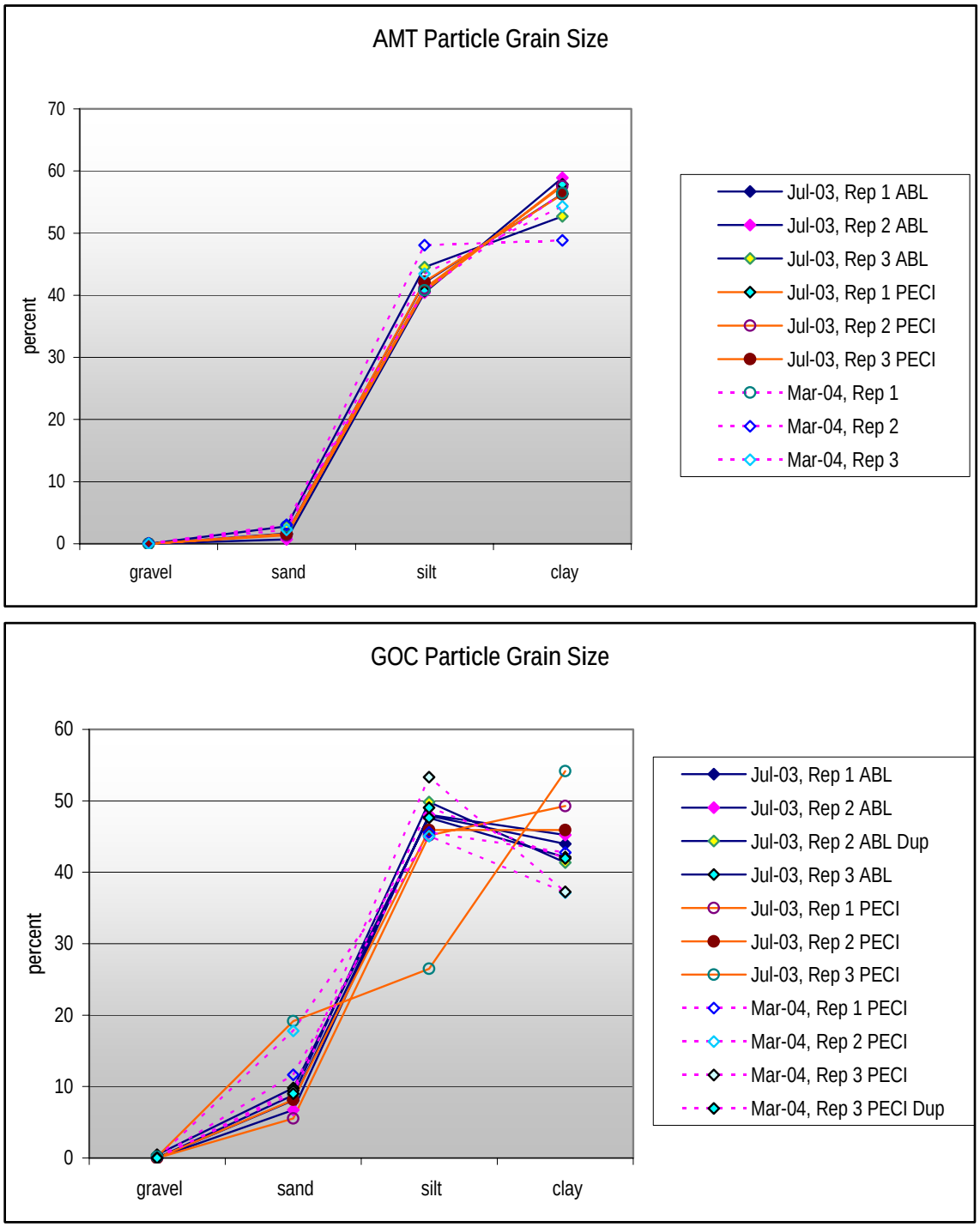

Figure 7. Sediment grain size distribution from Alyeska Marine Terminal and Gold Creek in July 2003 and March 2004.

Table 4. Relative sediment grain size distribution from Gold Creek and Alyeska Marine Terminal sample, July 2003 and March 2004. Outlier samples with higher amounts of sand are bold highlighted.

		Relative amounts			
Date	**Sample**	**Gravel**	**Sand**	**Silt**	**Clay**
7/27/2003	AMT-S-2-03-1A		1.64	42.06	56.30
	AMT-S-2-03-2A		0.71	40.39	58.90
	AMT-S-2-03-3A		2.78	44.52	52.70
	AMT-S-2-03-1P		1.54	40.65	57.81
	AMT-S-2-03-2P		1.35	41.10	57.54
	AMT-S-2-03-3P		1.58	42.18	56.24
	GOC-S-2-03-1A		8.10	47.91	44.00
	GOC-S-2-03-2A		6.71	48.06	45.23
	GOC-S-2-03-2ADup		8.80	49.83	41.37
	GOC-S-2-03-3A	0.48	9.80	47.61	42.12
	GOC-S-2-03-1P		5.54	45.17	49.28
	GOC-S-2-03-2P		8.15	45.93	45.93
	GOC-S-2-03-3P	0.19	**19.16**	26.48	54.16
3/21/2004	GOC-S-1-04-1		11.64	45.57	42.78
	GOC-S-1-04-2		**17.80**	45.05	37.15
	GOC-S-1-04-3		9.43	53.33	37.24
	GOC		9.02	49.05	41.93
3/23/2004	AMT-S-1-04-1		2.80	40.76	56.44
	AMT-S-1-04-2	0.06	3.02	48.07	48.84
	AMT-S-1-04-3		2.25	43.44	54.30

5.1.2 Chemistry Comparisons

With one exception, the chemistry data show no significant or systematic differences in aliphatic or PAH composition or quantitative totals when collected with either the ABL or PECI grab samplers. Figure 8 illustrates nearly identical PAH profiles (and measured TPAH) for all six samples collected at Alyeska Marine Terminal. With the Gold Creek sediments, the PAH profiles (and TPAH) were nearly identical in 5 of 6 replicates, and the one sample that showed a different PAH profile (and a significantly higher TPAH value) was also the same outlier (July 03, PECI-Rep 3) that exhibited higher relative sand and lower silt content compared to the other five replicates.

The PAH profiles for all six Alyeska Marine Terminal samples (Figure 8) were characterized by higher-molecular-weight components that represent a mixture of weathered oil droplet/SPM-phase petroleum plus combustion products. This pattern is fairly typical of those observed at Alyeska Marine Terminal.

In five of the six samples collected at Gold Creek, the PAH profiles showed a mixture of lower-molecular-weight, naphthalene-dominated components, which could be derived from dissolved-phase PAH interacting with suspended particulate material, plus combustion products represented by the parent-PAH-dominated series for phenanthrenes, dibenzothiophenes, fluoranthene, and chrysene. There are also very low traces of combustion products in the benzo(b)fluoranthene (BB) through benzo(a)pyrene (BAP) range. The one outlier (also with the different PGS distribution) exhibited higher relative concentrations of all of the higher-molecular-weight PAH compared to the naphthalenes, and this was particularly true for the phenanthrenes and anthracenes. In addition, the majority of the TPAH was due to a single component, chrysene (C) at 30 ng/g dry weight.

This difference in composition for the one outlier at Gold Creek (as determined by PGS and PAH) was not reflected in the aliphatic hydrocarbon distribution (Figure 9). All six samples collected at Gold Creek reflected a primarily biogenic n-alkane pattern dominated by odd-carbon numbered higher molecular weight plant waxes, with a trace of n-C_{12} to n-C_{21} aliphatics indicative of weathered petroleum hydrocarbons. Likewise, there were no differences noted in the aliphatic patterns for any of the sediments samples collected with either grab sampler at Alyeska Marine Terminal. The patterns reflected higher-molecular-weight n-alkanes derived from weathered ANS crude oil with a modest contribution from terrestrial plant wax components. In addition to the qualitative similarities between samplers, the quantitative total SHC (TSHC) values were also within the range of historic values measured at these sites; there were no differences related to grab sampler performance.

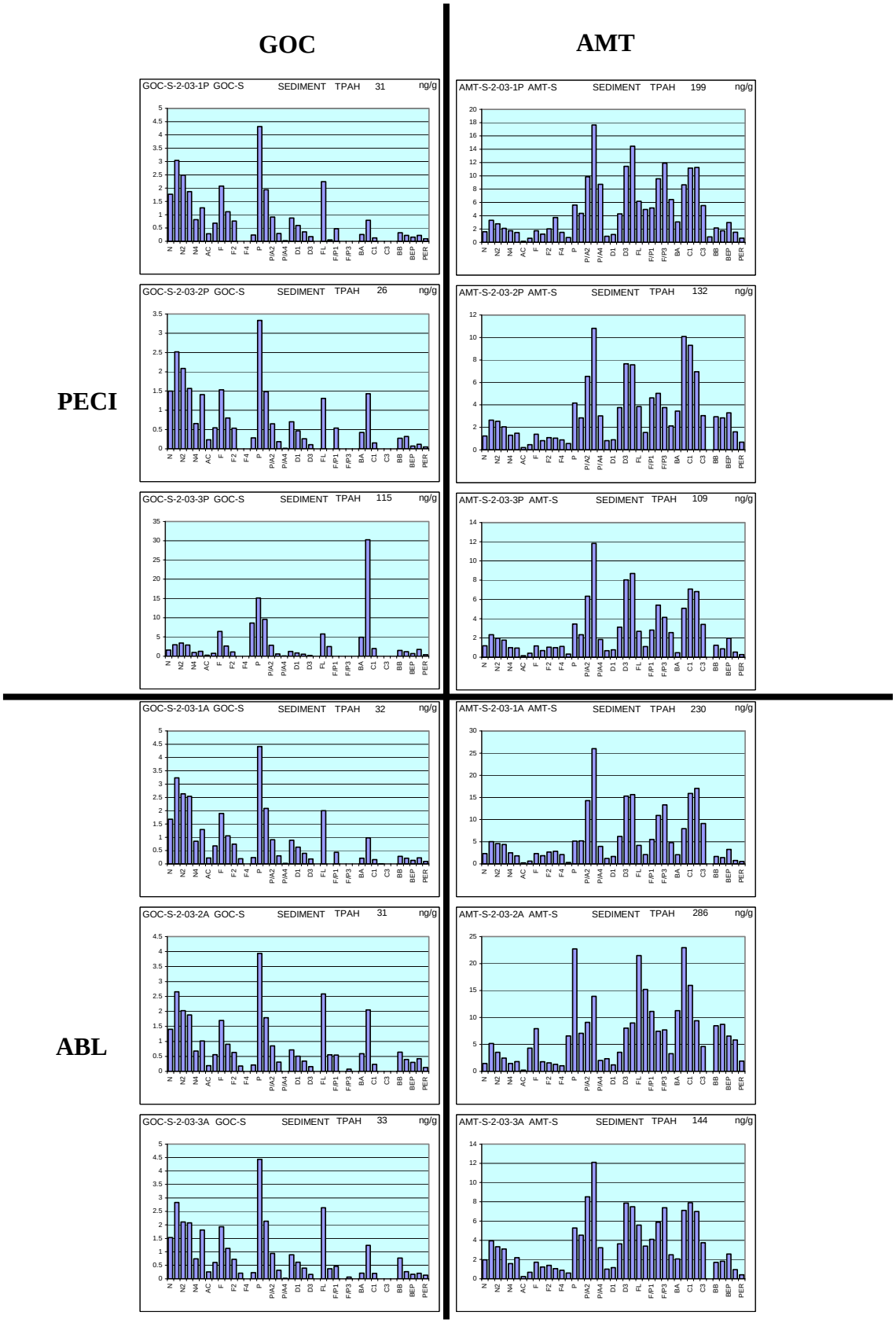

Figure 8. PAH histograms from Gold Creek and Alyeska Marine Terminal sediment replicates using modified (PECI) and unmodified (ABL) Van Veen grabs. Note Gold Creek PECI rep 3 was a particle grain size outlier.

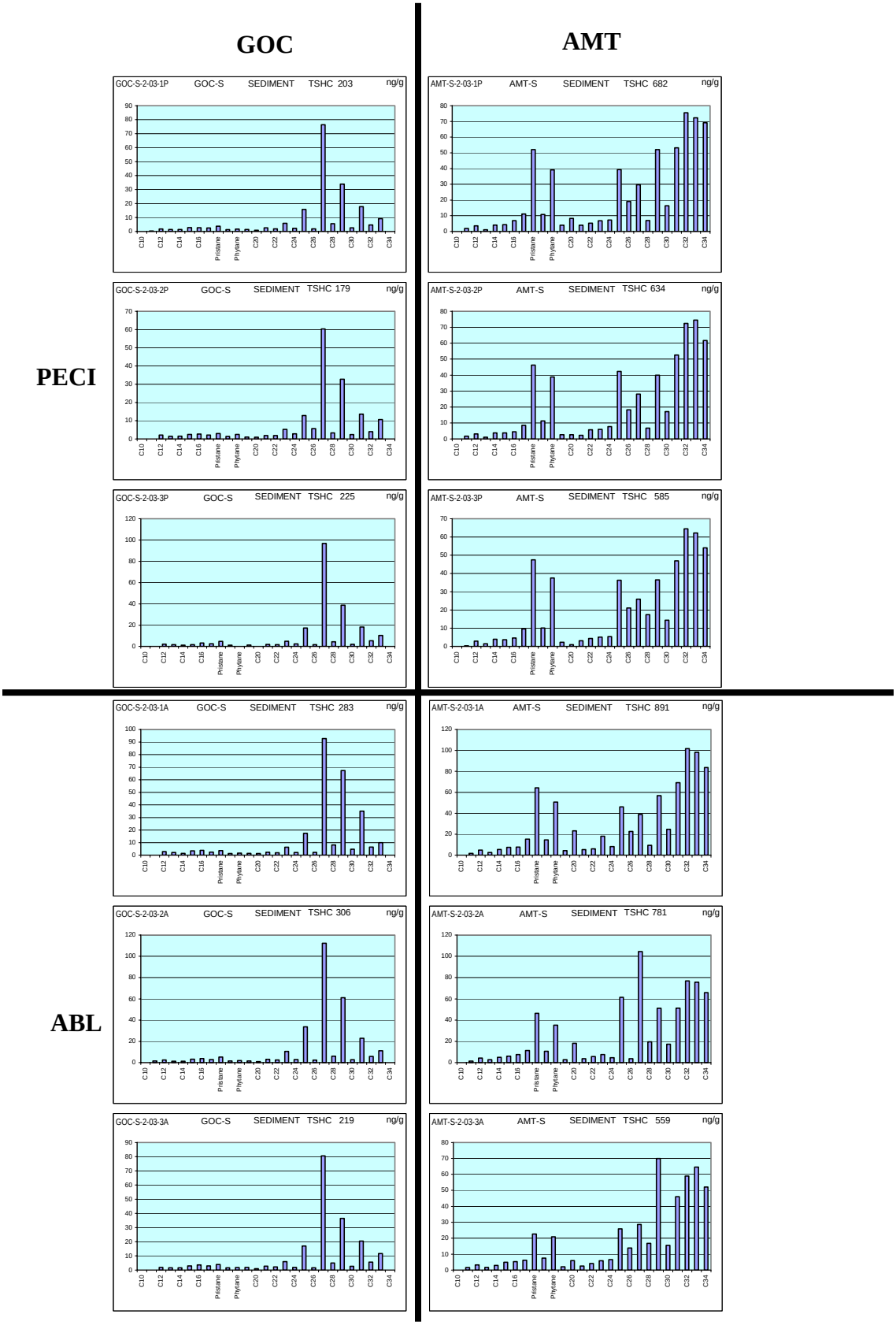

Figure 9. SHC histograms from Gold Creek and Alyeska Marine Terminal sediment replicates using modified (PECI) and unmodified (ABL) Van Veen grabs. Note Gold Creek PECI rep 3 was a particle grain size outlier.

5.2 Analysis of Field Samples

5.2.1 ABL Quality Assurance Results

For the 2003-2004 field samples, all the hydrocarbon analytes listed on Table 2 were lower than respective MDLs by at least a factor of six in the method blanks analyzed with each batch of samples for this report, verifying the absence of positive interferences introduced at the laboratory. Analysis of the sixteen accuracy-check samples (i.e. SRM 1491 or the ABL aliphatic standard) indicated that accuracy for the calibrated compounds ranged from 92% to 116% of certified or expected values except for 2,3,5-trimethyl naphthalene, which had a mean value of 130% of the certified value in these samples. The median precision of the PAH (including the uncalibrated PAH) in the eight SRM 1974b samples analyzed for the mussel batches, expressed as the coefficient of variation, was 19%. The precision ranged from 9% to 147%, and was less than 40% for all but seven analytes, which included biphenyl, C-3 and C-4 dibenzothiophenes, C-3 and C-4 phenanthrenes/anthracenes, C-2, C-3 and C-4 fluoranthenes/pyrenes, and C-3 chrysenes, most of which (C-3 phenanthrene/anthracenes excepted) are present in this SRM at concentrations that are near or below their detection limits. Precision of aliphatics was not evaluated for this SRM because aliphatics were usually below MDLs, and because certified values are not available. The median precision of the PAH (including the uncalibrated PAH) in the four SRM 1944 samples analyzed for the sediment batches, expressed as the coefficient of variation, was 14%. The precision ranged from 2.8% to 116%, and was less than 40% for all but three analytes, which included C-2 fluorene, C-3 fluoranthenes/pyrenes, and C-4 chrysenes.

Recoveries of surrogate standards were between 32% and 126% for all of the surrogate hydrocarbons monitored.

5.2.2 Sediments

5.2.2.1 Particle Grain Size

Sediment grain size plots (Figure 10) show that sediment compositions from the last two samplings are within the variance of previous years. Last year's report (Payne et al. 2003a) discusses sources and relevance of this variance. To summarize, the PGS data serve two main purposes to the LTEMP program. First, they ensure that the monitored location has not undergone drastic changes, e.g., slope failures, dredge spoils deposits, etc. Secondly, the silt + clay value allows a rough confirmation or calibration of TPAH levels should it ever become necessary. From the past and current data, we have noted outlier samples (and the effect on the chemistry data), but conclude that the outliers represent spatial heterogeneity rather than site changes and more importantly, have not affected the trends nor the interpretation of results.

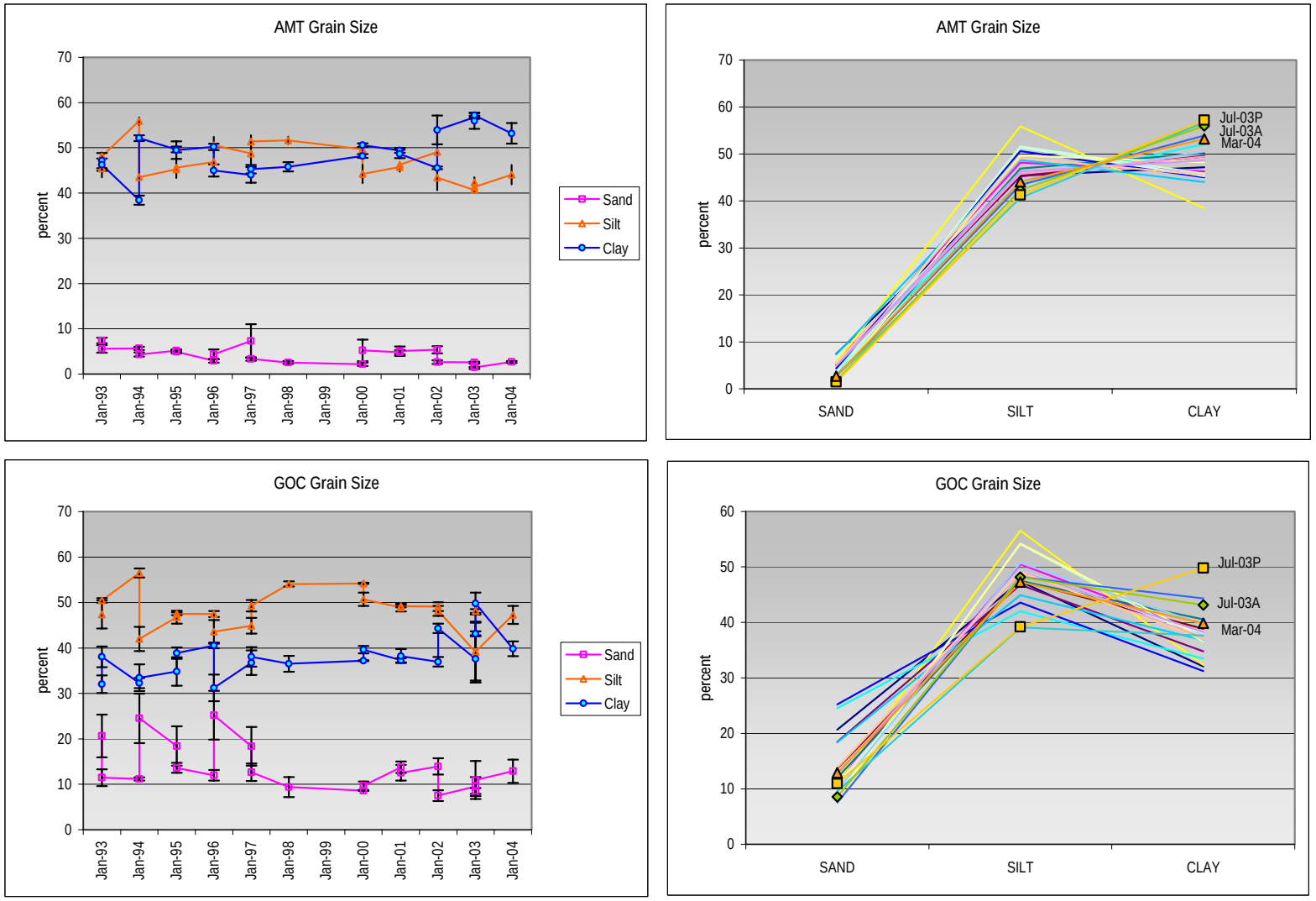

Figure 10. Time series and time overlays of grain size composition at Alyeska Marine Terminal and Gold Creek, 1993-2004

5.2.2.2 Chemistry Data Quality

Overall data quality was reasonably good for ABL-analyzed sediment samples as reflected by deuterated surrogate recoveries, the lack of significant interference by target analytes and other unknown components in procedural blanks, acceptable precision in duplicate samples, and as measured by comparison to specific calibrated PAH analytes in SRMs. Surrogate recoveries for deuterated PAH ranged from 32 to 126 percent at ABL, and 99% fell within 40 – 110%. These values are within the accepted ranges published in the standard operating procedures (SOP's) for the ABL laboratory and those recommended in NOAA Status and Trends protocols. In accordance with those protocols and to be consistent with procedures utilized at GERG, all individual and total PAH and SHC concentrations have been corrected for surrogate recoveries.

In laboratory-batch-associated procedural blanks, target analytes were consistently below MDLs. When target analytes were observed in the procedural blanks, they were generally less than 10 percent of the values observed in the associated field samples. Furthermore, when PAH or SHC components in the blanks exceeded those observed in the field samples, the overall patterns were sufficiently different to ensure that the samples truly represented field conditions and were not just the result of laboratory artifacts or contamination. Figure 11 presents representative PAH and SHC histograms plots from field samples and associated blanks from Alyeska Marine Terminal) and Gold Creek in March 2004. Method detection limits (adjusted for sample size) are shown by the blue diamonds and solid blue line in each figure. These plots illustrate that although numerous components are often at or below MDLs (particularly for Gold Creek), reasonable precision among the field replicates was obtained and substantially different patterns were generated in field samples and associated procedural blanks.

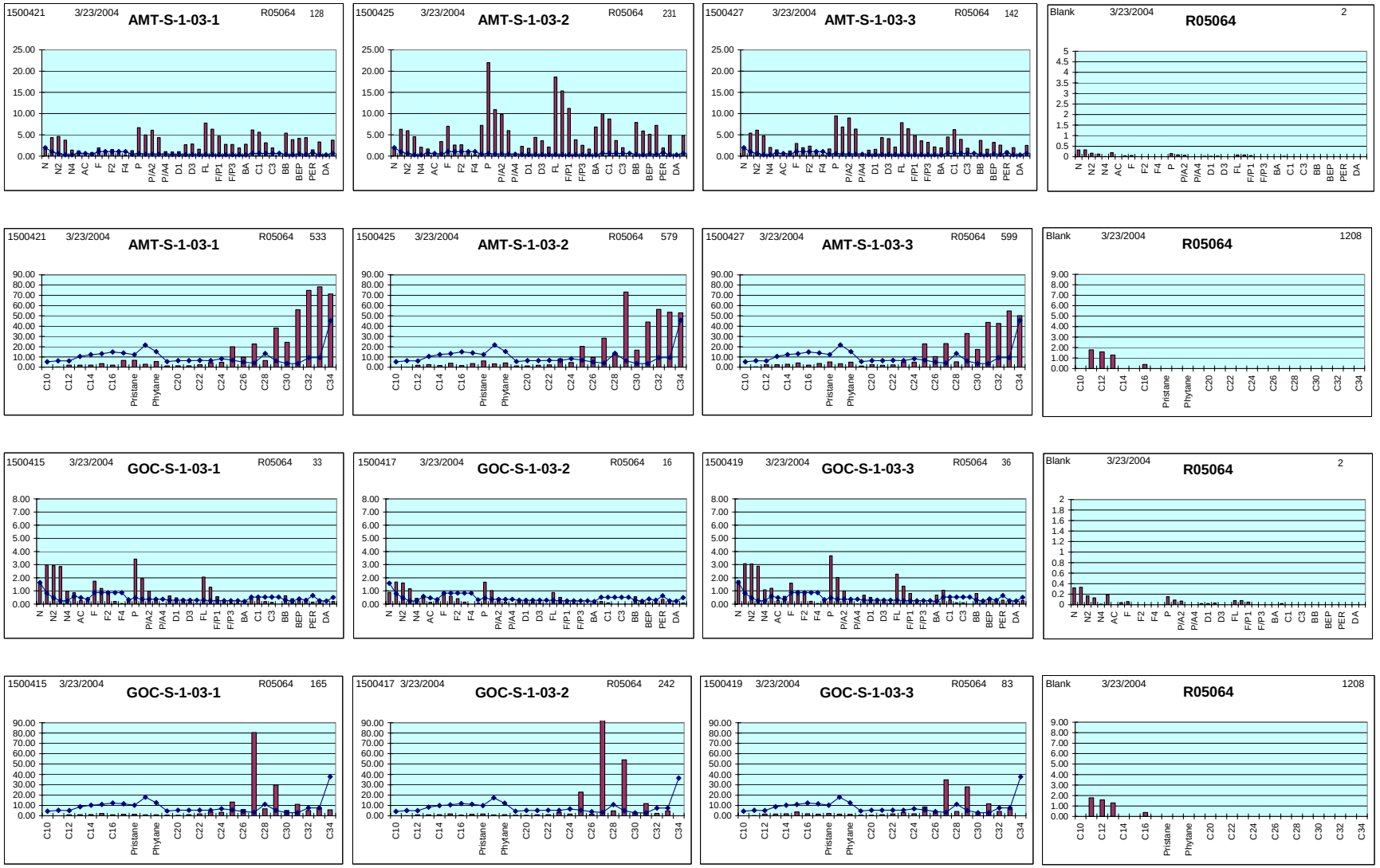

Figure 11. PAH and SHC histograms from Alyeska Marine Terminal and Gold Creek in March 2004 showing typical low oil, combustion product, and biogenic hydrocarbon levels and the relative differences in fingerprint patterns and concentrations measured in the associated procedural blanks.

5.2.2.3 Sediment Hydrocarbon Concentration Trends and Source Analyses

For historic recap of the sediment trends, Appendix A-1 presents the total SHC and PAH values of individual samples, seasonal averages, and the associated coefficients of variation for the replicate measurements completed between 1993 and 2004. The TPAH values in the sediments from Gold Creek are uniformly low, ranging from a low of 16 ng/g dry wt. (ave. 28 ng/g dry wt.) in March 2004 to a maximum of only 156 ng/g dry wt. (ave. 89 ng/g dry wt.) in March 1996. The sediments obtained at Alyeska Marine Terminal exhibit more variability and ranged from a low of 10 ng/g dry wt. (ave. 76 ng/g dry wt.) measured in March 2002 to a high of 1,650 ng/g dry wt. (ave. 880 ng/g dry wt.) observed in July 1995.

Figure 12 presents the mean TPAH concentrations (and associated standard error of the mean) measured in the sediments as a function of time. This figure illustrates the temporal variability and shows that the TPAH concentrations in the sediments at the two sites do not appear to be related.

Figures 13 and 14 present the average sediment PAH and SHC histogram profiles for both Port Valdez stations and allows comparison between the stations by season and intertidal versus subtidal sample location. The PAH concentrations in the intertidal stations are substantially lower than the subtidal samples at both locations; however, the compositions are slightly different. The Alyeska Marine Terminal intertidal site collected in July 1998 appears to have both a dissolved- and particulate-phase petroleum signal, while the Gold Creek intertidal sample exhibits characteristics from both a petrogenic and pyrogenic signal.

There does not seem to be a seasonal PAH pattern observed in the subtidal sediments at either Alyeska Marine Terminal or Gold Creek, although the variability is higher at Alyeska Marine Terminal in the summer. Likewise, the SHC profiles look very similar in both seasons, with the only major difference being increased relative concentrations of pristane (copepod related) in the summer samples.

Figure 15 plots the sediment CRUDE index values for both stations over the eleven years of the program to date. The CRUDE index combines into a single value many of the numerous individual factors and characteristic ratios that have been used for oil data analysis by chemists and environmental scientists in the past (see Table 3). With this single-value approach emphasizing the petrogenic over the pyrogenic and biogenic signals, several additional details and trends that are not apparent in examining TPAH data alone can be resolved. Note that the y-axis scales in Figure 15 go from 1 – 3,000 for Alyeska Marine Terminal and only 0 – 300 at Gold Creek where the petroleum hydrocarbon influence is much smaller. More detailed source allocations, time-series trend analyses, and investigations of the apparent within-season variability at both sites are discussed more fully in the sections that follow.

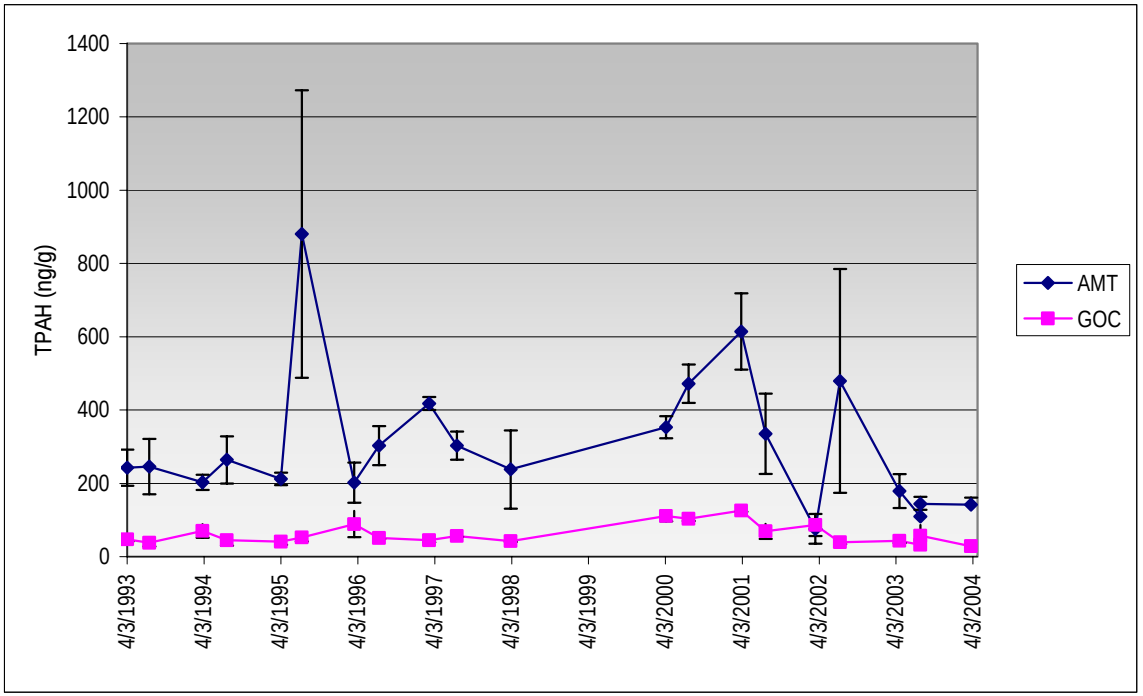

Figure 12. Time series mean sediment TPAH concentrations (and standard error of the mean) measured from March 1993 through March 2004 at Alyeska Marine Terminal and Gold Creek.

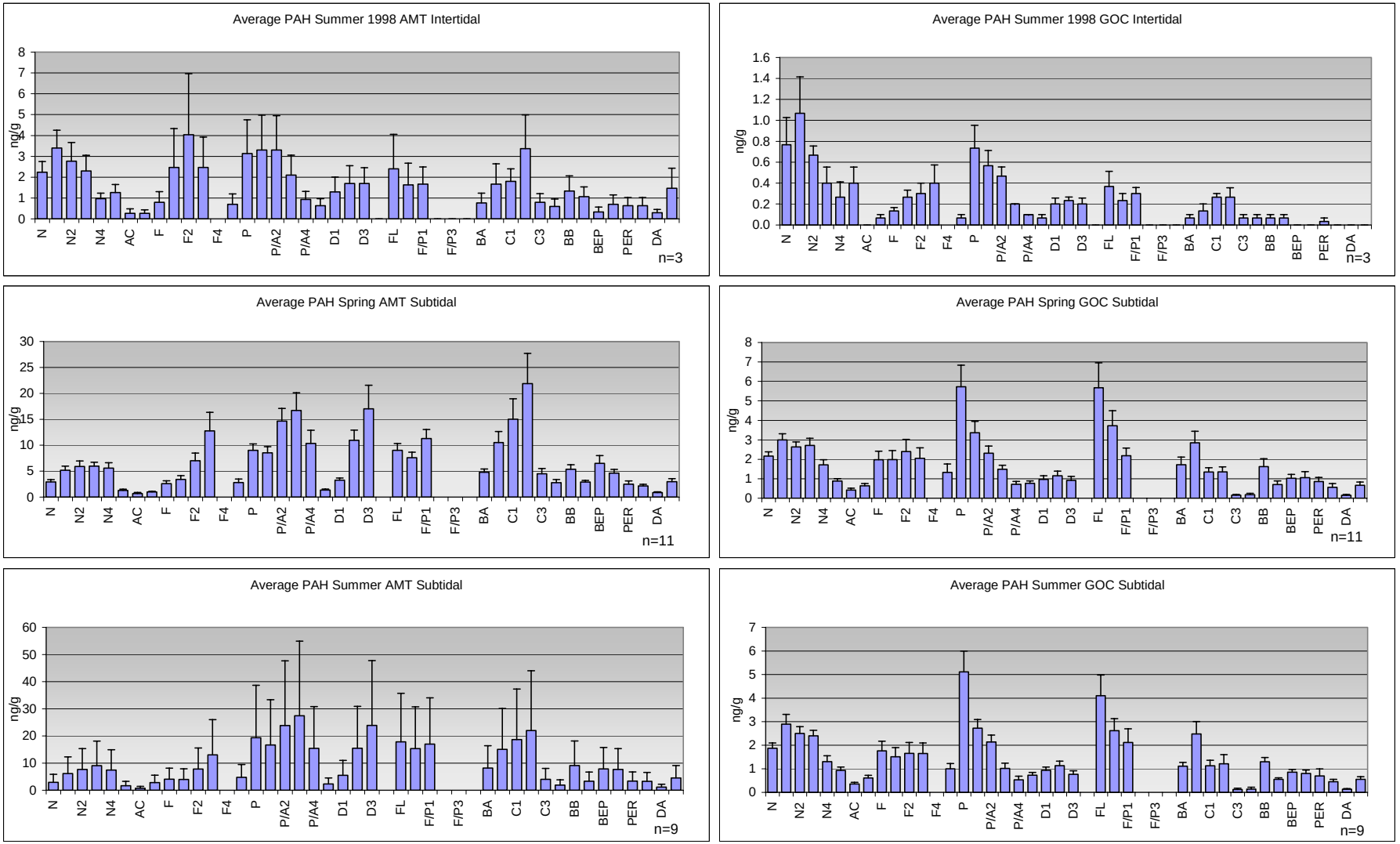

Figure 13. Average PAH histograms comparing intertidal and seasonal subtidal sediments samples from Alyeska Marine Terminal and Gold Creek stations. Error bars represent the standard error of mean; n indicates the number of samples (intertidal) or cruises (subtidal) contributing to each average.

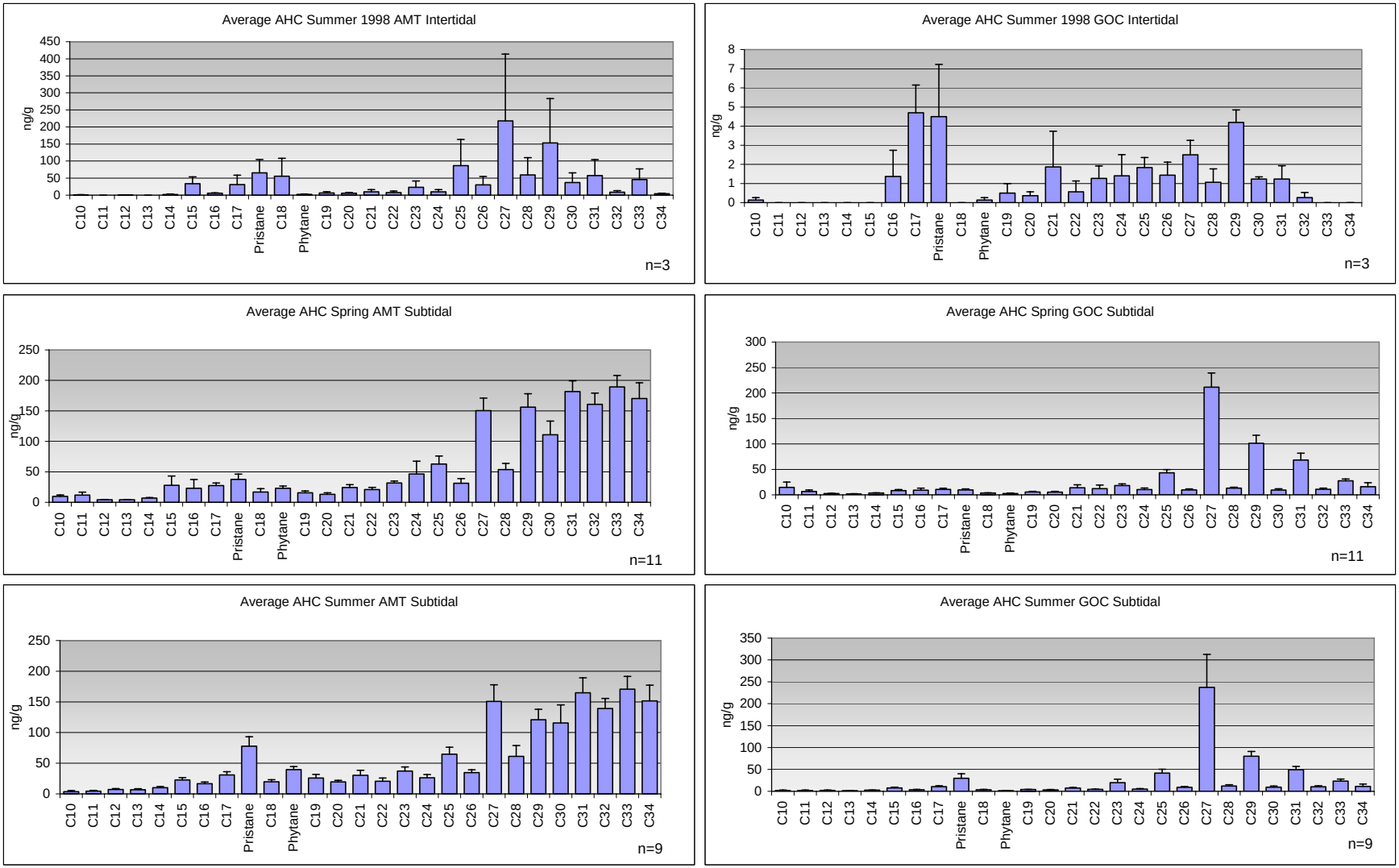

Figure 14. Average SHC histograms comparing intertidal and seasonal subtidal sediments samples from Alyeska Marine Terminal and Gold Creek stations. Error bars represent the standard error of mean; n indicates the number of samples (intertidal) or cruises (subtidal) contributing to each average.

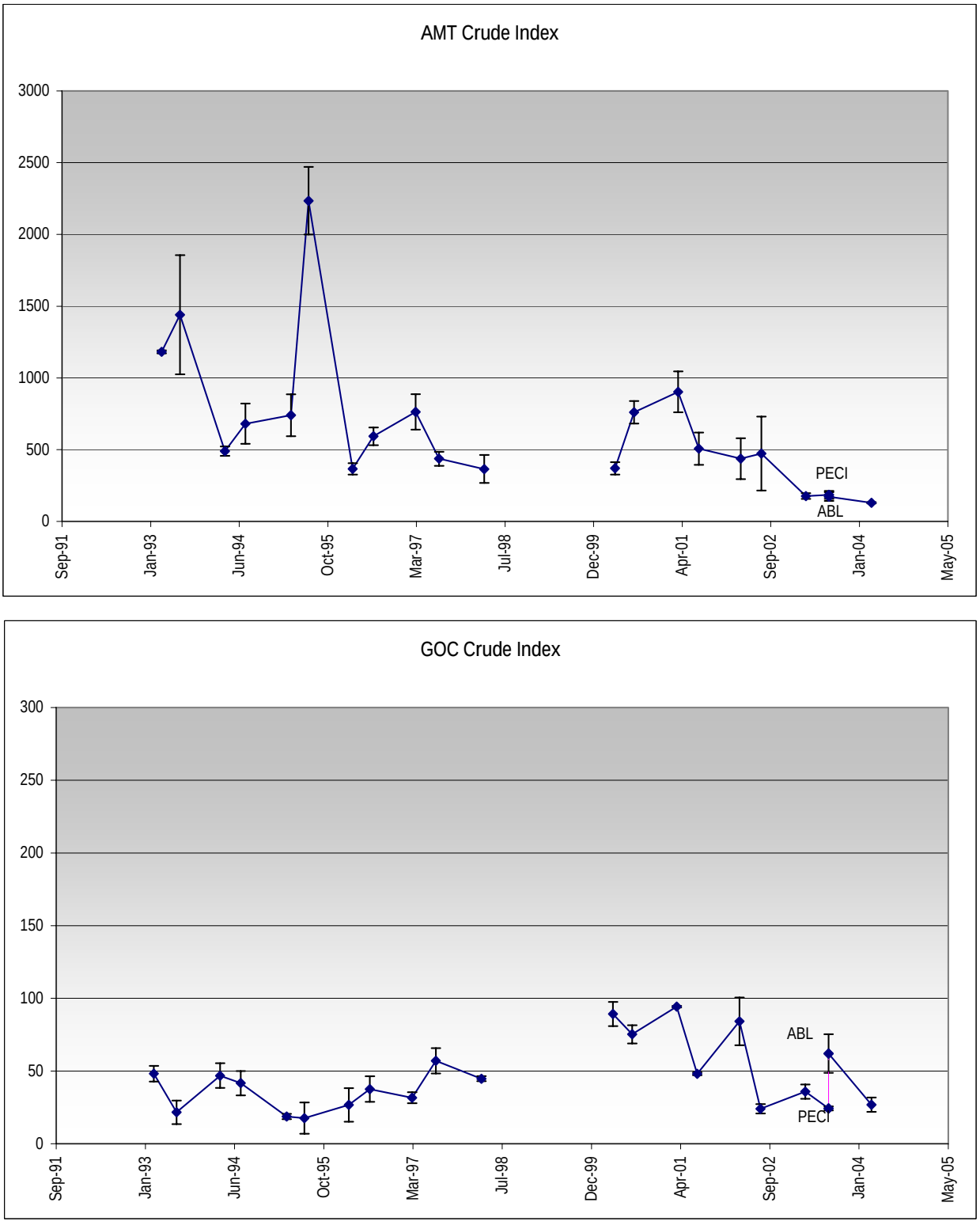

Figure 15. CRUDE Index values for Alyeska Marine Terminal and Gold Creek sediments samples collected between March 1993 and March 2004 (sediments were not analyzed between July 1998 and March 2002). Error bars represent the standard error of the mean.

The plots demonstrate order-of-magnitude higher concentrations at Alyeska Marine Terminal compared to Gold Creek. With the exception of two elevated values in the July 1993 and 1995 collections (discussed in more detail below), the values at Alyeska Marine Terminal appear to be relatively constant (ranging from around 300 to 900) with low standard errors from April 1996 through July 2002. Within that range, however, there is clearly a decreasing trend in the Alyeska Marine Terminal sediments beginning in April 2001 through the most recently collected samples from March 2004. In contrast, the values at Gold Creek are uniformly low, ranging from a low of 18 in July 1995 to a high of only 94 in March 2001.

There are several higher CRUDE index values at each station over time (Figure 15) and often these higher values display larger standard error bars suggesting more variability in that particular suite of samples. To determine if these higher CRUDE index samples were due to some specific change in hydrocarbon fingerprint in one or more of the triplicate samples collected during each cruise, we selectively printed the PAH and SHC histograms (along with the associated procedural blanks) for each sample set with either unusually high (or low) CRUDE index values and those replicates exhibiting larger standard error bars for a single season's collection. These plots are shown in Figures 16 through 26 for Alyeska Marine Terminal and Figures 27 through 33 for Gold Creek (specific findings discussed below). Fortunately, although there are trace-level constituents present in the method blanks associated with most of the samples, their composition and concentrations are not such that they interfered with analysis of the field samples.

5.2.2.3.1 Alyeska Marine Terminal Sediments

As shown in Figure 15, the first suite of samples at Alyeska Marine Terminal with relatively higher variance was collected in July 1993. As shown in Figure 16, the saturated (aliphatic) hydrocarbon profiles for all three samples showed essentially identical patterns with the absolute values for TSHC varying by about a factor of 2-3. The SHC pattern suggests a mixture of well-weathered petroleum components (as reflected by the n-C_{17}/pristane and n-C_{18}/phytane ratios) in the intermediate to higher-molecular-weight range, plus contributions from odd-carbon number predominated plant waxes in the n-C_{25}, n-C_{27}, and-n-C_{29} range. This pattern is very typical of the aliphatic patterns observed at Alyeska Marine Terminal throughout the 11 years of LTEMP data considered in this report. The PAH data show much more variability, and this is believed to be responsible for the larger standard error bars shown for this sample set in Figure 15. Two of the three replicates show a similar pattern reflecting lower-molecular-weight PAH clearly derived from ANS crude oil (naphthalenes, fluorenes, phenanthrenes/anthracenes, and dibenzothiophenes). For each of these PAH homologous suites, there is a water-washed pattern with increasing concentrations for higher-alkylated components within each suite. In the third replicate (PWS93PAT0045), however, the oil derived PAH pattern (which in fact is just at or below the laboratory method detection limit in all three samples) is dwarfed by combustion-sourced phenanthrenes/anthracenes and fluoranthenes. Because of the contributions of these combustion products, the total PAH in the third replicate is two times greater than that observed in the other two.

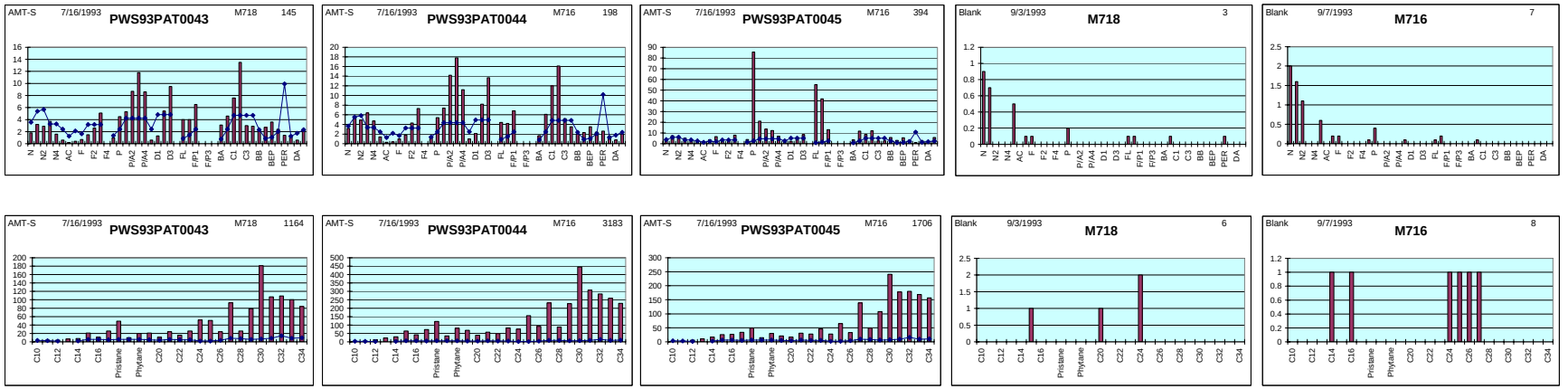

Figure 16. July 1993 sediment PAH (upper) and SHC profiles (lower) from Alyeska Marine Terminal and associated procedural blanks. These samples illustrate intermediate CRUDE values due to weathered ANS oil and one replicate (PWS93PAT0045) with higher levels of combustion products.

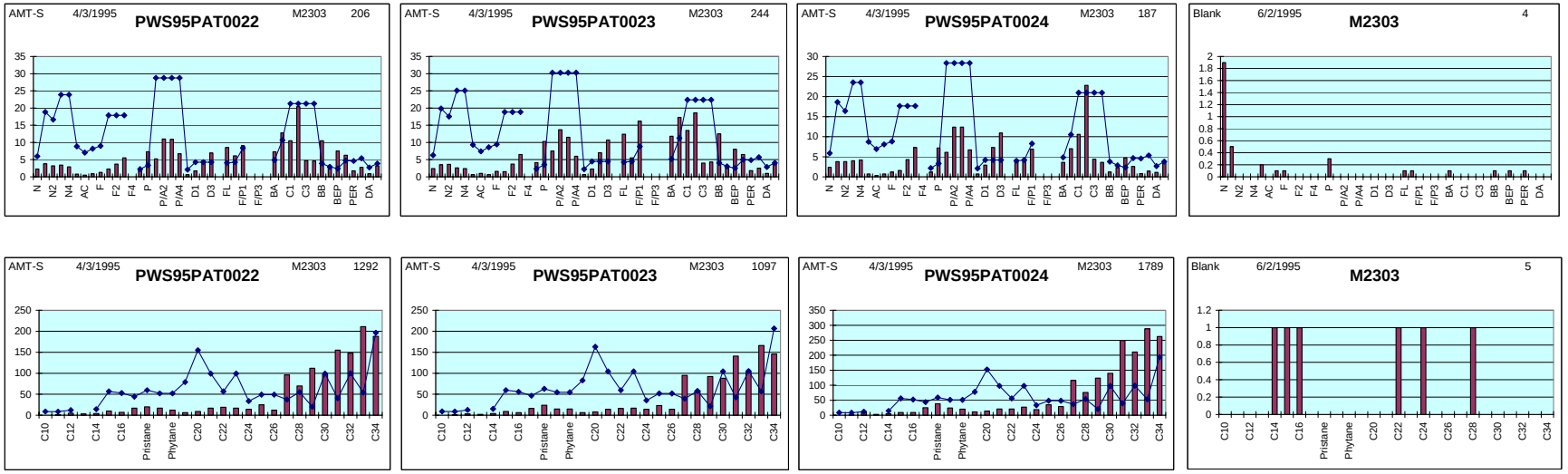

Figure 17. April 1995 sediment PAH and SHC profiles from Alyeska Marine Terminal and associated procedural blanks. These profiles represent weathered crude oil, before the big jump in the CRUDE Index value in July 1995.

Figure 17 shows a more typical pattern from April 1995 that is characteristic of most of the sediments from Alyeska Marine Terminal (also see Figures 13 and 14). As shown by the data in Figure 15 and the histogram profiles in Figure 17, the precision among the replicates is reasonably tight. All three samples are characterized by a well-weathered petroleum signal plus contributions from higher-molecular-weight combustion products, and they are included to illustrate the typical pattern of intermediate-level PAH concentrations before the big increase in the CRUDE Index values shown in Figure 15 for July 1995.

The histogram plots in Figure 18 illustrate that the spike in the CRUDE Index value (Figure 15) for the July 1995 samples (and the associated higher standard error bars) is due to the presence of much higher concentrations of combustion products (in addition to the lower level petroleum constituents) in one of the three replicates. This variability is not reflected in the aliphatic hydrocarbon patterns; however, it can be observed in the PAH histogram profile for the first replicate (PWS95PAT0028) in Figure 18. That sample has higher absolute concentrations of phenanthrenes/anthracenes, fluorenes, chrysenes and benzo(b)fluoranthene, and the greater abundance of the parent PAH relative to the alkyl-substituted homologues confirms the combustion source. If the single sample with the combustion derived components were eliminated, the composition and concentrations of observed PAH in the other two samples would be in line with most of the other samples analyzed from Alyeska Marine Terminal over the course of the program.

The next "spike" in the CRUDE Index values at Alyeska Marine Terminal occurs in March 1997; however, as shown by the standard error bars in Figure 15, there is much lower variability associated with the sample. The PAH and SHC histogram plots shown in Figure 19 clearly show the pattern derived from heavily-weathered (water-washed and microbial degraded) crude oil with very little or only minor contributions from higher-molecular-weight combustion products. As before, the SHC pattern reflects a combination of bacterially degraded crude oil components plus higher-molecular-weight odd-carbon-numbered plant waxes.

The next sample set showing elevated variability in the CRUDE Index occurred in March 1998 (Figure 15). The histogram plots in Figure 20 clearly show the presence of weathered petroleum hydrocarbons at similar and lower concentrations in two of the three replicates (yielding a lower CRUDE Index value); however sample PWS98PAT0017 appears to contain higher relative concentrations of phenanthrenes/anthracenes, dibenzothiophenes, fluoranthenes, and chrysenes. The aliphatic hydrocarbon pattern for this particular sample is also slightly elevated compared to the other two, and we suspect that these differences simply reflect the inclusion of a finite oil droplet in the sample. The increased variability in the CRUDE Index value is believed to be due to the fluoranthenes in sample PWS98PAT0017.

CRUDE Index data in Figure 15 show maxima for the samples collected in July 2000 and March 2001, and both samples show slightly increased standard error bars. The histogram plots in Figure 21 show similar TPAH values, but there are significant differences in the

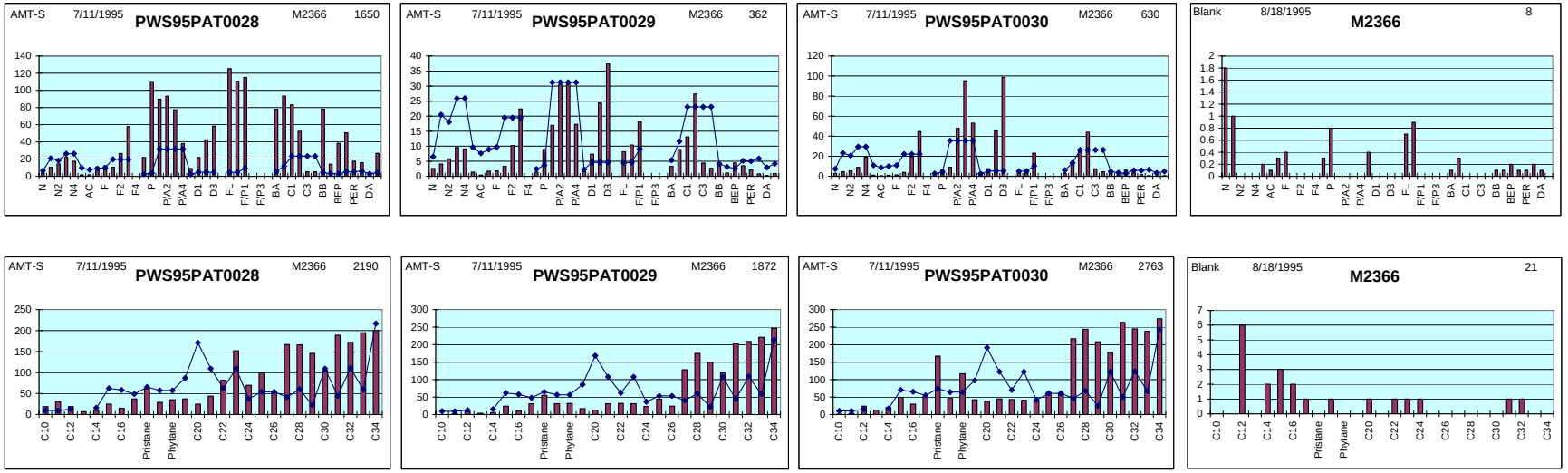

Figure 18. July 1995 sediment PAH and SHC profiles from Alyeska Marine Terminal and associated procedural blanks. These samples exhibited high variability and the greatest CRUDE Index value observed in the program. Two of the replicates show variable weathered oil signals and one outlier (PWS95PAT0028) exhibits an elevated combustion-derived PAH signal.

Figure 19. March 1997 sediment PAH and SHC profiles from Alyeska Marine Terminal and associated procedural blanks. The PAH fractions clearly depict a classic weathered oil signal with very little variability, and the SHC profiles show a mixture of weathered oil and higher-molecular-weight terrestrial plant wax signals.

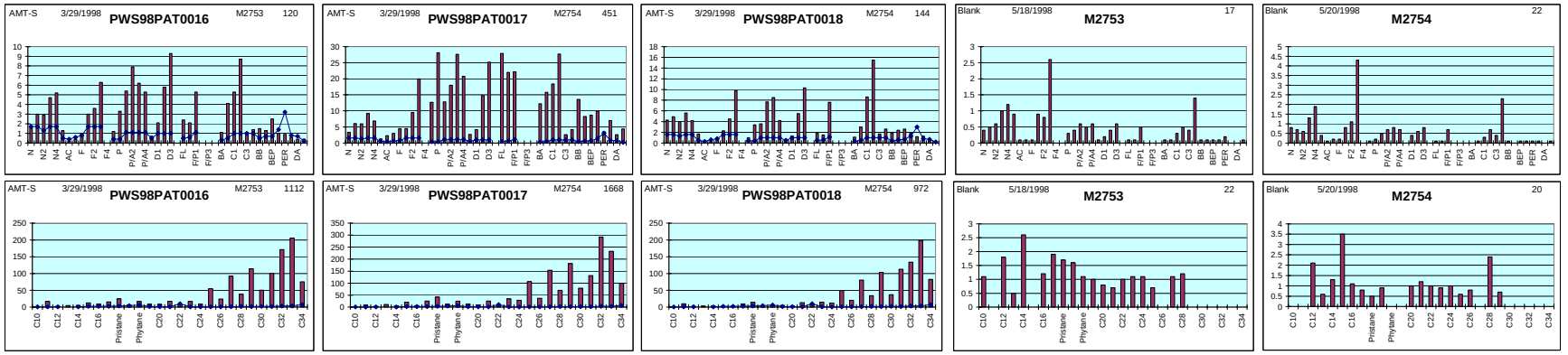

Figure 20. March 1998 sediment PAH and SHC profiles from Alyeska Marine Terminal and associated procedural blanks. The PAH fractions clearly depict lower and somewhat variable weathered oil signals (yielding a lower CRUDE Index value), and the SHC profiles show a mixture of weathered oil and higher-molecular-weight terrestrial plant wax signals.

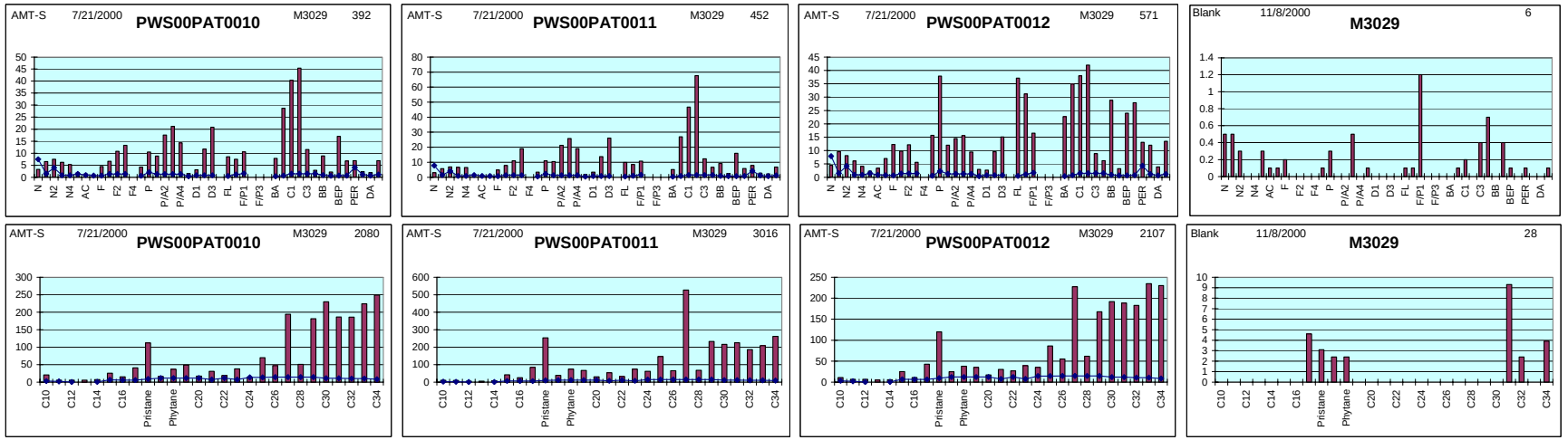

Figure 21. July 2000 sediment PAH and SHC profiles from Alyeska Marine Terminal and associated procedural blanks. These samples yielded a slighter higher CRUDE Index value (761) and revealed slightly different compositions, but the patterns definitely reflected weathered crude oil, combustion products, and marine and terrestrial biogenic components.

PAH profile for sample PWS00PAT0012 compared to the other two replicates. In this case, that sample appears to also contain combustion-derived PAH in addition to the weathered petroleum signal. These samples yielded a slighter higher CRUDE Index value (761) and reflected weathered crude oil, combustion products, and marine and terrestrial biogenic components. In the March 2001 samples, however, the histogram profiles (see Figure 22) for the three samples are essentially identical showing a heavily weathered crude oil pattern (CRUDE Index 903), and the variability in Figure 15 is simply due to different concentrations of petroleum derived hydrocarbons in the three samples.

The time-series data in Figure 15 show a drop in the CRUDE Index value (to 501) in July 2001, but the standard error bars again suggest fairly high variability in the sediments collected at that time. In this instance the data in Figure 23 suggest that this variability is due to different absolute concentrations of TPAH and highly variable compositions. In one of the three replicates, the PAH are at or just below the method detection limit and represent a mix of petroleum and combustion products. In the second replicate (sample PWS01PAT0011) the PAH profile is clearly dominated by combustion products, and in the third sample (PWS01PAT0012) the PAH profile reflects contributions from relatively fresh but water-washed ANS crude oil. This is also represented by the SHC profile for the sample. Presumably this reflects inclusion of a relatively fresh oil droplet in the sediment grab.

The CRUDE Index value for the March 2002 samples is low compared to the three previous sample sets (Figure 15); however, the standard error bars associated with this measurement are relatively high for such a low value. The histogram plots shown in Figure 24 demonstrate that this variability is due to significant heterogeneity among the three samples collected. These samples were among the last analyzed by KLI/GERG and the profiles show very clean and highly variable oil, combustion- product and biogenic sources. One sample (PWS02PAT0004) contained only very low concentrations of naphthalenes and traces of phenanthrene (all well below the method detection limit), while the second replicate contained low-level water-washed PAH of petroleum origin and several combustion products (all at or just below method reporting limits). The third replicate (PWS02PAT0006) had a similar PAH composition profile to the intermediate concentrations sample, however, the total PAH concentration was two times higher. The aliphatic profiles for all three samples were essentially identical.

Figure 15 shows somewhat higher variability again in the July 2002 replicates, which were from the first suite of samples collected after PECI/ABL took over the program. In this instance, the data in Figure 25 demonstrate that two of the three replicates contained a mixture of relatively low concentrations of oil-derived naphthalenes and fluorenes, with higher relative concentrations of oil and combustion-derived higher-molecular-weight PAH. The third sample (Alyeska Marine Terminal-S-2-02-2) was characterized by order-of-magnitude higher concentrations of total PAH (TPAH) with the source most likely being due to inclusion of a finite oil droplet in the sample. The pattern is clearly that of water-washed crude oil with no evidence of contributions from combustion products. The

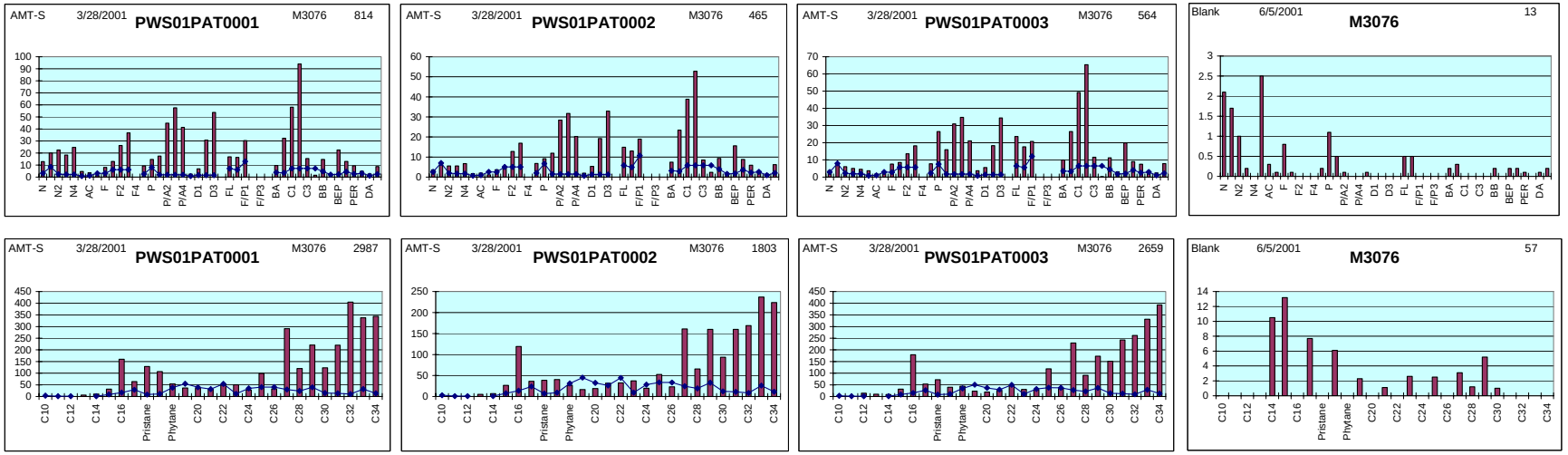

Figure 22. March 2001 sediment PAH and SHC profiles from Alyeska Marine Terminal and associated procedural blanks. These samples yielded a higher CRUDE Index value (903) and exhibited variable concentrations but the same heavily weathered oil compositional pattern. The SHC profiles reflect weathered crude oil plus marine and terrestrial biogenic components.

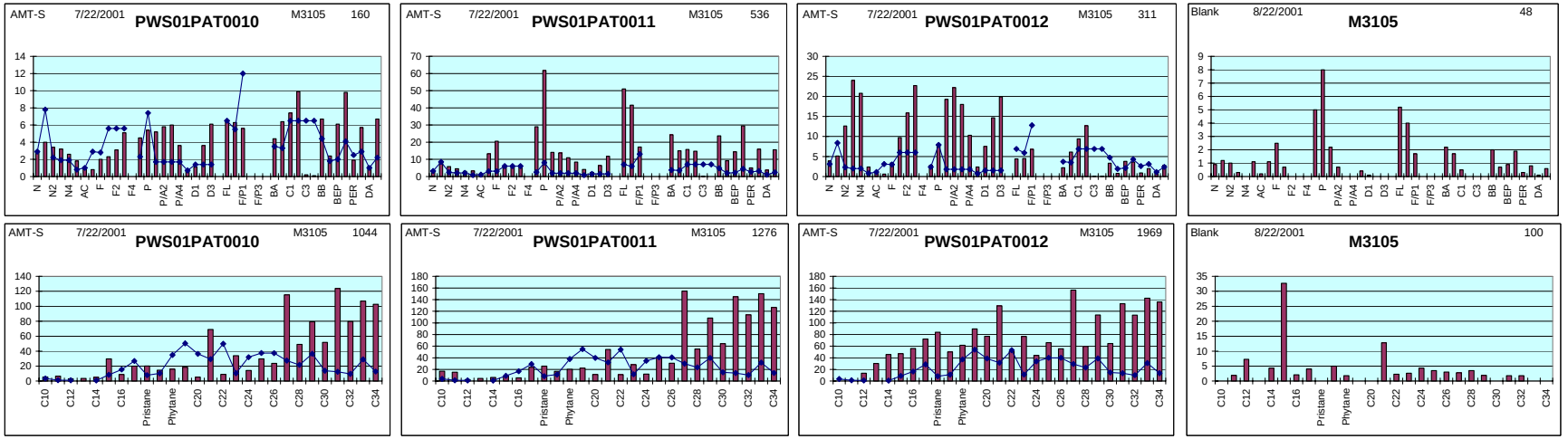

Figure 23. July 2001 sediment PAH and SHC profiles from Alyeska Marine Terminal and associated procedural blanks. These samples yielded in intermediate CRUDE Index value (501) and exhibited highly variable and differing amounts of oil and combustion products.

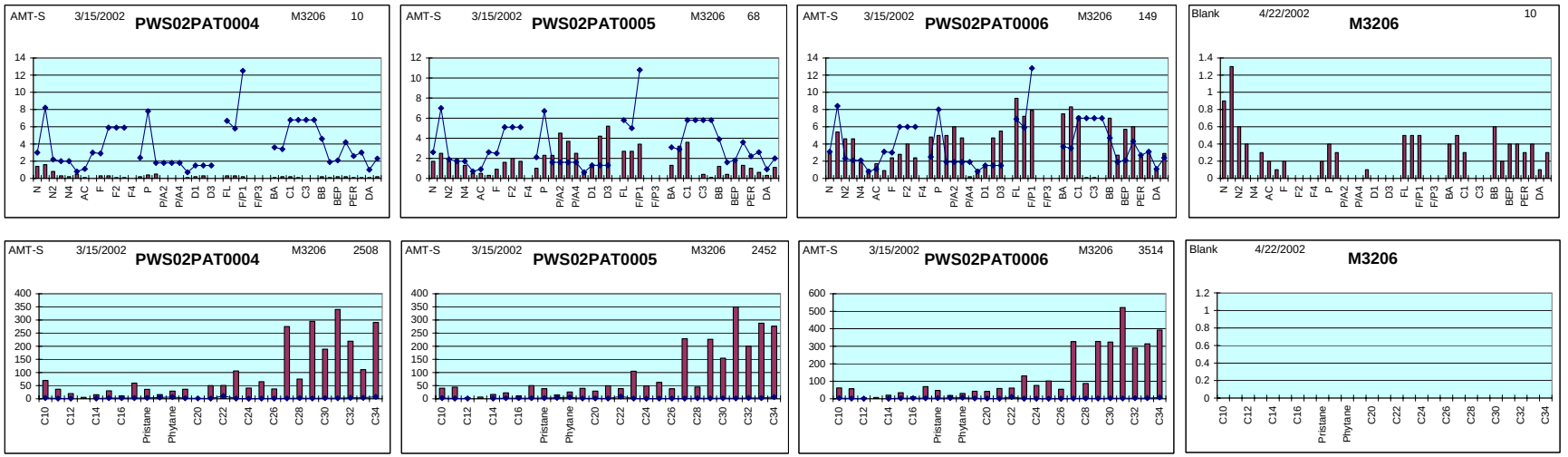

Figure 24. March 2002 sediment PAH and SHC profiles from Alyeska Marine Terminal and associated procedural blanks. These samples were among the last analyzed by KLI/GERG and the profiles show very clean and highly variable oil, combustion product and biogenic sources.

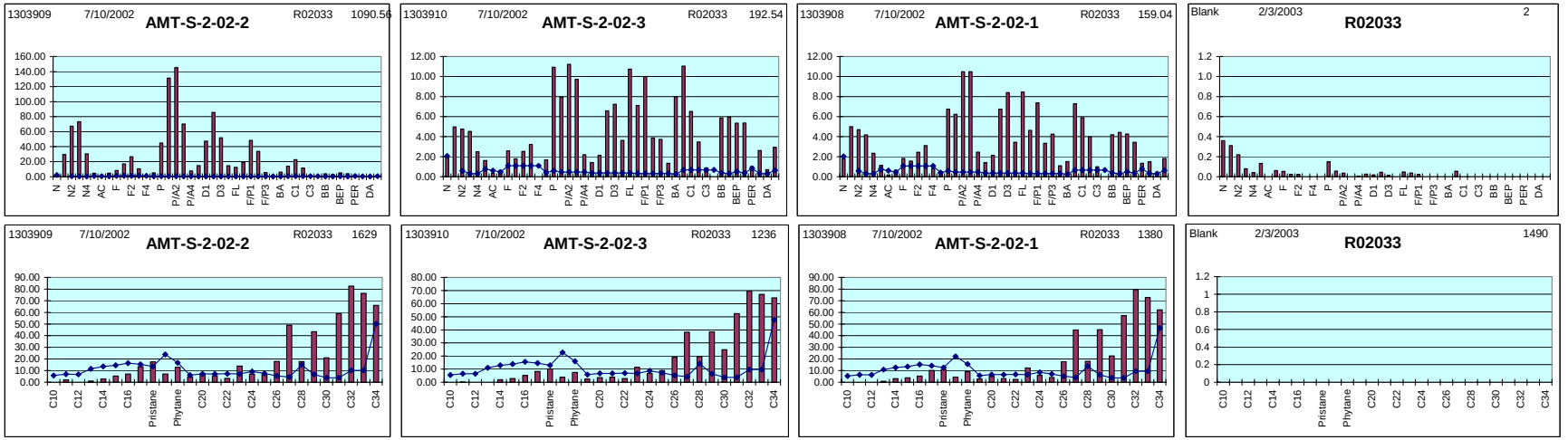

Figure 25. July 2002 sediment PAH and SHC profiles from Alyeska Marine Terminal and associated procedural blanks. These samples were among the first analyzed by PECI/ABL. Two of the samples showed low-level PAH from weathered oil and combustion products, and the third (AMT-S-2-02-2) showed order-of-magnitude higher PAH from weathered oil only. All three SHC fractions showed a mixture of weathered oil and biogenic sources.

aliphatic fractions for all three replicates had similar compositional patterns, but the total SHC (TSHC) in one sample (PWS02PAT0006) was about 1.4 times higher than the other two.

The CRUDE Index plot in Figure 15 shows the lowest overall value (129) for any suite of samples collected during the 11 years of the program in March 2004. The precision of the triplicate measurements was very tight as reflected by the standard error bars shown in Figure 15, and the PAH and SHC histograms shown in Figure 26 demonstrate a mixture of lower-molecular-weight naphthalenes and phenanthrenes from petroleum sources with higher-molecular-weight phenanthrene/anthracenes, fluoranthenes, and chrysenes reflecting combustion sources. In addition, all three samples contain benzo(b)fluoranthene (BB) through benzo(g,h,i)perylene (PB) components clearly reflecting combustion sources. The aliphatic fractions from March 2004 showed below MDL concentrations of petroleum components in the n-C_{12} through n-C_{22} range plus a mixture of higher-molecular-weight petroleum components and odd-carbon-number terrestrial plant waxes in the n-C_{23} to n-C_{34} range.

5.2.2.3.2 Gold Creek Sediments

As shown by the different concentration scales in Figure 15 for the CRUDE Index values associated with the Gold Creek sediments, the CRUDE index values were uniformly and significantly lower than those observed for the Alyeska Marine Terminal sediments. With one or two exceptions the precision about the measurements was also tighter. There do appear to be three spikes in CRUDE Index values in the early years of the program (in July 1993, March 1994 and July 1997), and then a jump in CRUDE Index values with the resumption of sediment analyses in April 2000, followed by a variable but generally decreasing trend in CRUDE Index values from that period through March 2004. The causes for these observed trends and the variance associated with the triplicate measurements were investigated by examining the specific PAH and SHC profiles for the samples.

Figure 27 presents the PAH and SHC histogram plots for the triplicate sediment samples collected in July 1993. The individual PAH are all below the laboratory method detection limit and they reflect a combination of lower-molecular-weight PAH from crude oil or distillate products and intermediate molecular weight PAH from combustion sources. The precision among the triplicate measurements is remarkably tight, particularly in light of the very low concentrations measured. The SHC profiles reflect the dominance of higher-molecular-weight odd carbon numbered n-alkanes (n-C_{25}, n-C_{27} , n-C_{29}, and n-C_{31}) associated with terrestrial plant waxes. This pattern is in fact present in the SHC fractions for all sediment samples collected at Gold Creek.

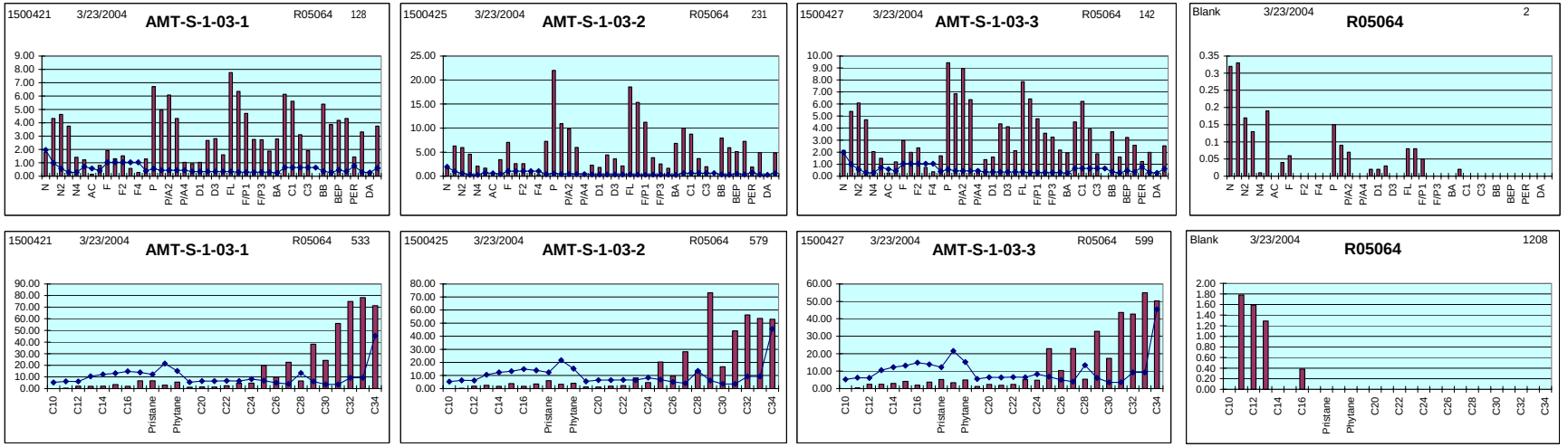

Figure 26. March 2004 sediment PAH and SHC profiles from Alyeska Marine Terminal and associated procedural blanks. These samples had very low PAH concentrations with significant combustion sources in addition to weathered oil. The SHC fractions showed below MDL traces of petroleum components plus significant levels of terrestrial plant wax components. The precision among the replicates was very tight as reflected by the non-existent standard error bars in Figure 15.

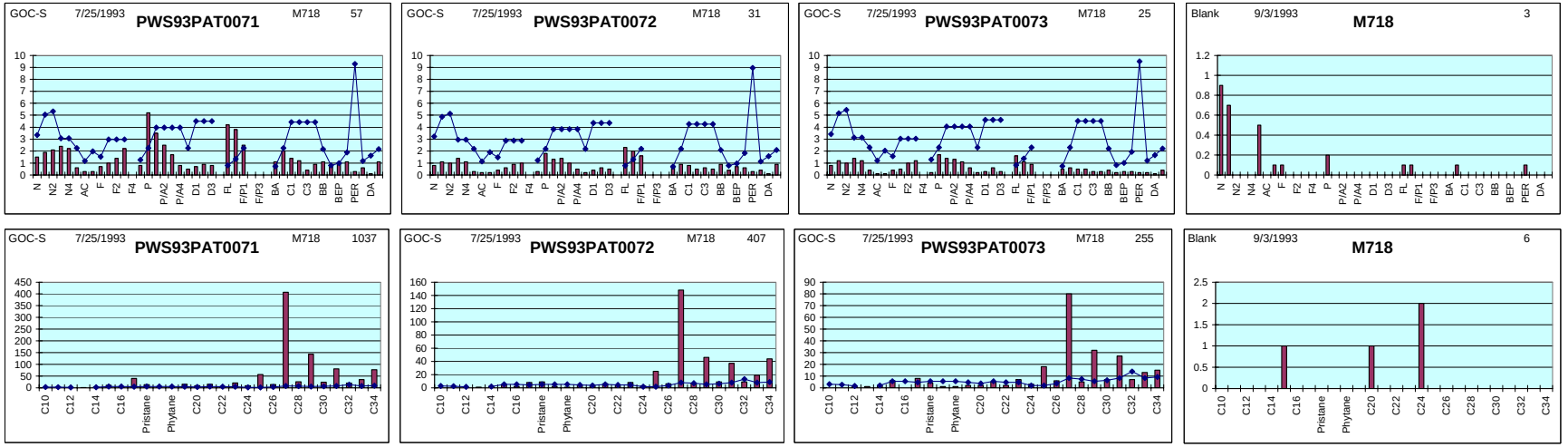

Figure 27. July 1993 sediment PAH (upper) and SHC profiles (lower) from Gold Creek and associated procedural blanks. These samples had very low (below MDL) PAH concentrations that represented a mixture of weathered oil or distillate products plus significant combustion sources. The SHC fractions showed no evidence of petroleum components, but instead reflected a mixture of marine and terrestrial biogenic components.

The CRUDE index plot in Figure 15 suggests a slightly elevated value for the March 1994 samples along with larger standard error bars associated with those measurements. As shown by the PAH histogram data in Figure 28, this apparent increase is really just due to slightly elevated concentrations of fluoranthenes and higher-molecular-weight combustion products in the benzo(b)fluoranthene (BB) through benzo(g,h,i)perylene (BP) range. With the exception of the fluoranthenes in one replicate (PWS94PAT0024), all of these components were below the laboratory method reporting limit, so the apparent increase is not considered to be environmentally significant. The SHC profiles represent purely biogenic sources.

The apparent increase in the standard error associated with the March 1996 samples is due to high concentrations of phenanthrene and fluoranthenes (presumably from combustion sources) in one sample (PWS96PAT0002) and elevated levels of fluoranthenes relative to the other PAH in another sample (PWS96PAT0001) (Figure 29). In both cases the apparent source of these PAH is believed to be from combustion sources. The SHC fraction reflects purely marine and terrestrial biogenic components.

Sediment sampling and analyses were discontinued at the beginning of the July 1998 LTEMP program, and they were not initiated again until spring 2000. As shown in Figure 15, at that time there was an apparent increase in the CRUDE Index values reported for the sediments at Gold Creek (going from around 50 before sediment analyses were discontinued to near 100 with their resumption in April 2000). This increase is reflected in the PAH profiles shown in Figure 30. Beginning with that suite of samples the method reporting limit for the laboratory was reduced, and higher finite concentrations of all of the PAH were reported. It is not known, however, if this may or may not reflect a change in instrumentation or integration procedures associated with the laboratory measurements (Payne et al. 2003a). The data in the histogram plots suggest a mixture of petroleum or distillate product components in the naphthalene and fluorene suite, with combustion-derived contributions from the phenanthrenes/anthracenes, fluoranthenes, and chrysenes. In addition there were traces of combustion products in the benzo(b)fluoranthene (BB) through benzo(g,h,i)perylene (BP) range. The SHC fraction reflects purely marine and terrestrial biogenic components.

The overall CRUDE Index values decreased in the July 2001 samples and then increased again in March 2002 with a concomitant increase in the standard error bars associated with those measurements. The PAH and SHC profiles shown in Figure 31 for the March 2002 samples reflect contributions from intermediate but highly variable levels of both oil and combustion products. The increase variability is due to the contributions of fluoranthenes and chrysenes, which were more variable among the samples. This suite of samples was also among the first to show traces of petroleum hydrocarbon contamination in the aliphatic fractions, although, the predominant SHC components were still derived from biogenic terrestrial plant waxes.

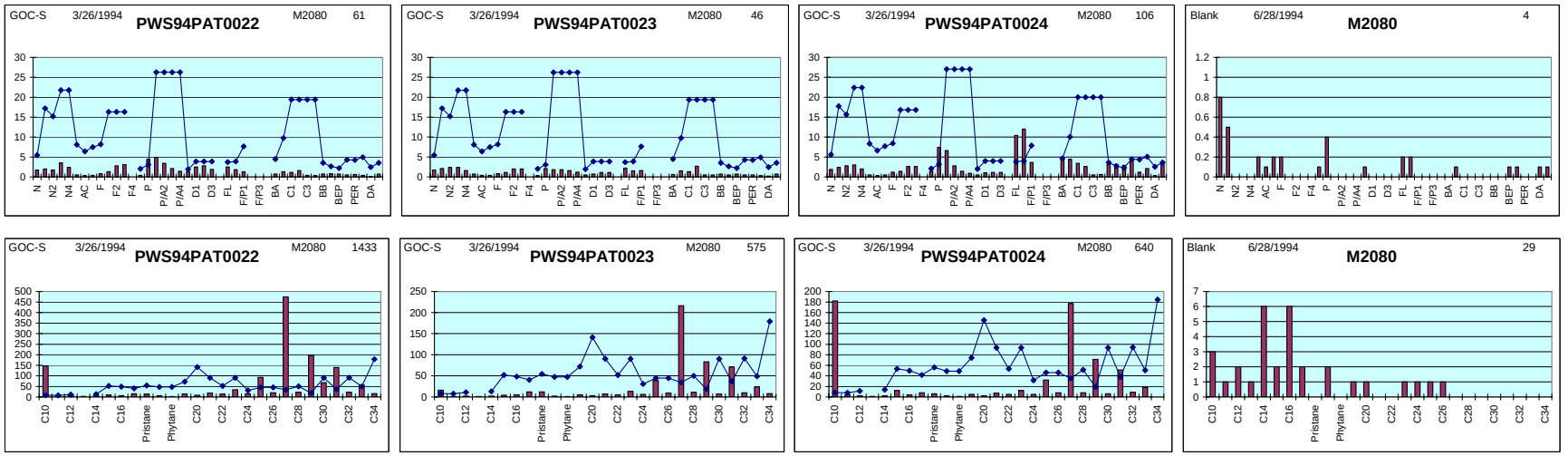

Figure 28. March 1994 sediment PAH and SHC profiles from Gold Creek and associated procedural blanks. These samples had very low TPAH levels but yielded a slightly higher and more variable CRUDE Index value due to the fluoranthenes and higher-molecular-weight combustion products in replicate PWS94PAT00024. The SHC fractions were purely biogenic.

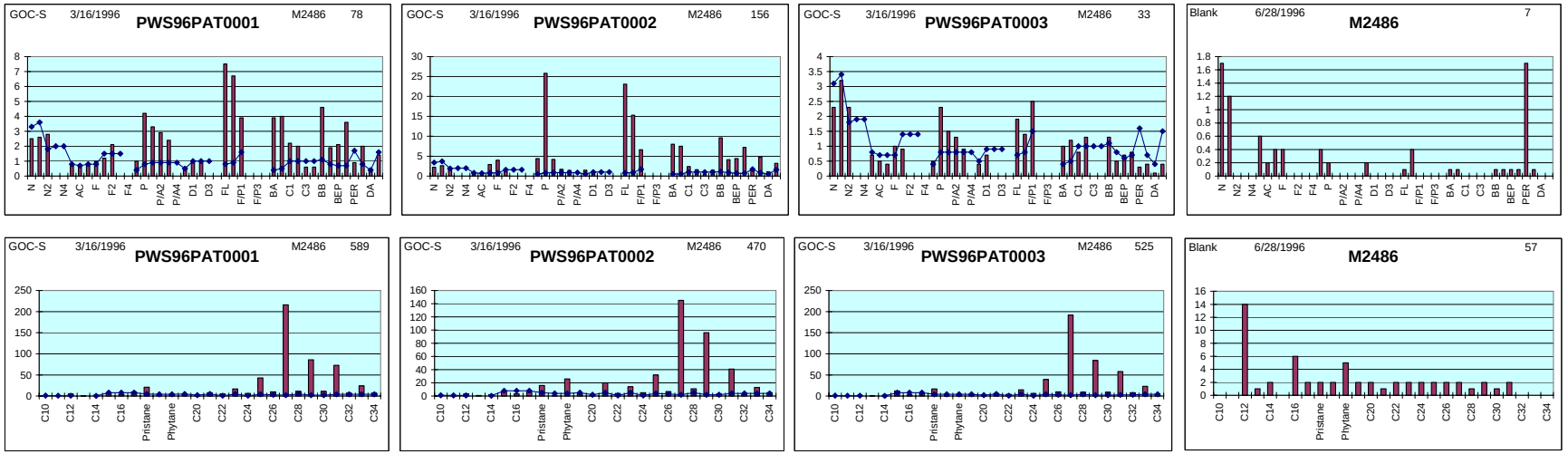

Figure 29. March 1996 sediment PAH and SHC profiles from Gold Creek and associated procedural blanks. These samples reflected low, but highly variable PAH (particularly phenanthrene and the fluoranthenes) derived primarily from combustion sources. The SHC fraction reflected purely marine and terrestrial biogenic components.

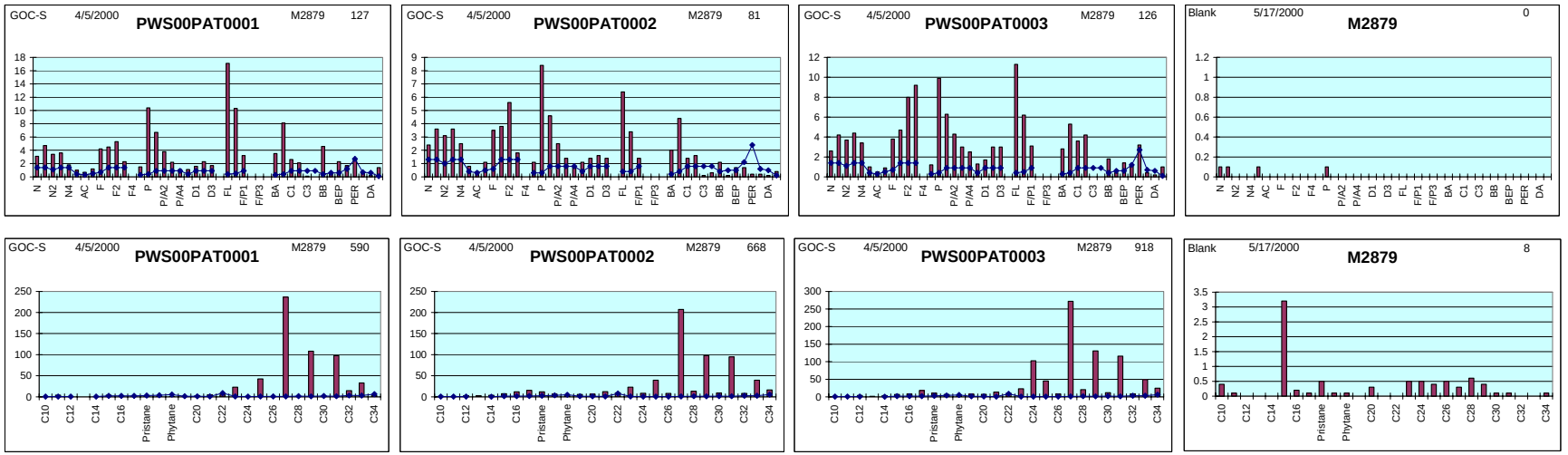

Figure 30. April 2000 sediment PAH and SHC profiles from Gold Creek and associated procedural blanks. These samples were among the first after sediment analyses were resumed again and reflected the highest and least variable TPAH measured at GOLD CREEK. PAH sources included traces of distillate products and higher levels of combustion products (particularly phenanthrene/anthracenes and fluoranthenes). The SHC fraction reflected purely marine and terrestrial biogenic components.

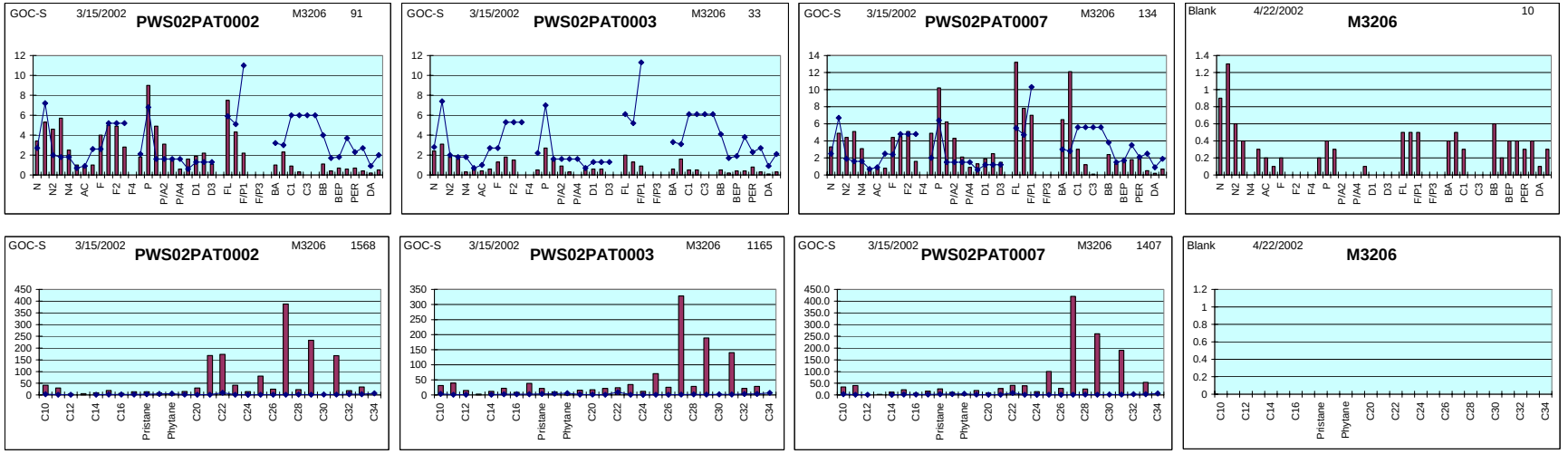

Figure 31. March 2002 sediment PAH and SHC profiles from Gold Creek and associated procedural blanks. These samples exhibited highly variable PAH profiles from oil or refined products and combustion products. The SHC fractions were less variable and reflected primarily marine and terrestrial biogenic sources.

The CRUDE Index values dropped again in July 2002 and March 2003, and they remained low in five of six replicate samples collected in July 2003 (see discussion of ABL versus PECI grab samples in Section 5.1). The July 2002 samples were among the first collected by the PECI/ABL team, and Figure 32 illustrates the presence of alkylated naphthalenes and fluorenes from petroleum sources with greater contributions of combustion products in the phenanthrene/anthracene, fluoranthene, and chrysenes suites. This same pattern was observed in March 2003 except the BB thru BP signal was missing. The aliphatic profiles also suggest trace-levels (all below the MDLs) of petroleum components in addition to much higher concentrations of biogenic terrestrial plant wax components. The precision associated with these low-level measurements is considered to be very good as reflected by the small standard error bars shown in Figure 15.

The CRUDE Index values remain low in March 2004, and the precision associated with the replicate measurements was again very tight. As shown by the histogram data in Figure 33, the PAH hydrocarbons were among the lowest observed to date in the LTEMP, and they derived from a mixture of petroleum distillate or crude oil sources in the naphthalene and fluorene range with slightly elevated contributions of combustion products in the phenanthrene/anthracene and fluoranthene range. These patterns were essentially identical to those observed in July 2002, March 2003, and five of six replicates in July 2003. As in the majority of all the other SHC profiles from Gold Creek, the patterns reflect primarily terrestrial plant waxes plus a trace of marine biogenic components.

5.2.2.3.3 Summary of Sediment Analyses

From examination of all the PAH data from both of these sites, it is clear that the Alyeska Marine Terminal subtidal sediments are primarily contaminated by a weathered ANS oil signal, which would be consistent with BWTF-diffuser-sourced, dispersed oil-droplet/suspended-particulate-material (SPM) interactions and resulting sedimentation (Payne et al. 1989; 2003a,b). The Gold Creek sediments, on the other hand, show PAH contamination from a low-level petrogenic source with slightly greater relative input from combustion (pyrogenic) sources. The pyrogenic signal at Gold Creek may be slightly greater in the spring, but it is probably not statistically significant. It is not possible to tell if the low-level petroleum source in the subtidal sediments at Gold Creek is from the BWTF and other activities at Alyeska Marine Terminal, or other sources (boat traffic, sewage and wastewater discharges from the City of Valdez). It may be possible to identify this source through sterane/triterpane analyses of Gold Creek sediments and comparisons to Alyeska Marine Terminal sediments and Alyeska BWTF discharges as part of future LTEMP or other PWS RCAC research activities, especially the sediment core project.

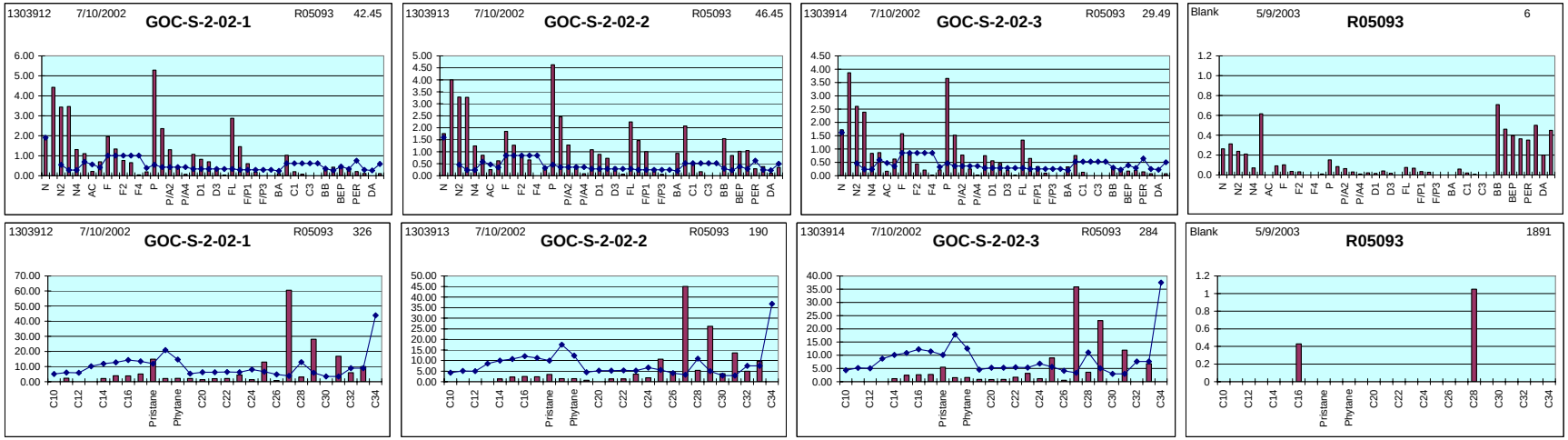

Figure 32. July 2002 sediment PAH and SHC profiles from Gold Creek and associated procedural blanks. These were among the first samples collected by PECI/ABL. They exhibited very low and nearly identical PAH profiles reflecting a trace of diesel or other distillate product (as indicated by the naphthalenes) plus a predominant combustion-derived signal. This same pattern was observed in March 2003 except the BB thru BP signal was missing.

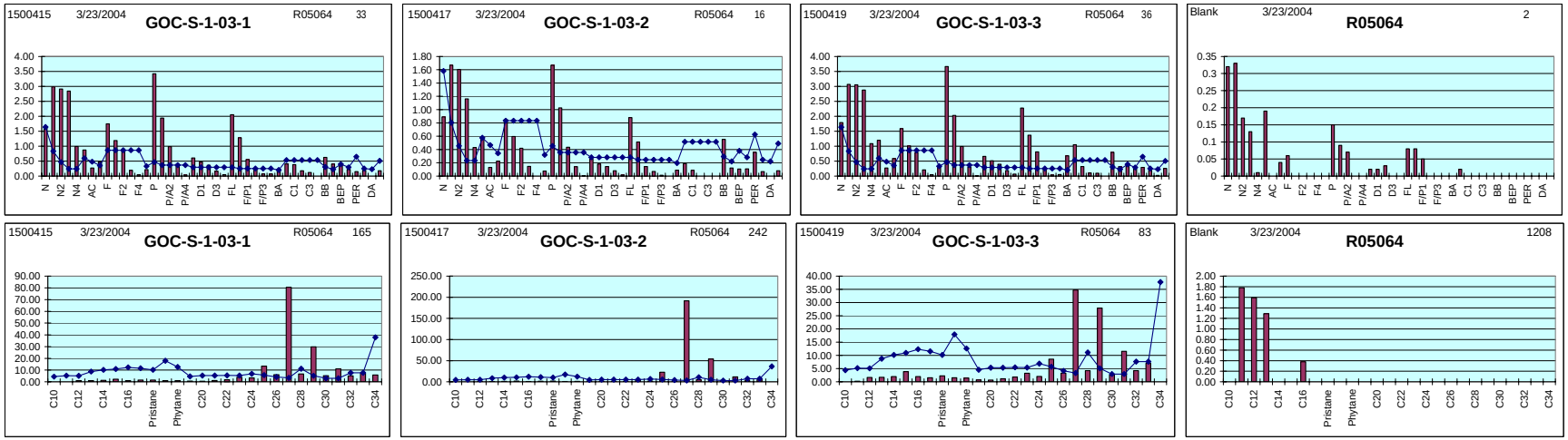

Figure 33. March 2004 sediment PAH and SHC profiles from Gold Creek and associated procedural blanks. These are among the lowest and least variable PAH measurements observed in the LTEMP to date, and the patterns reflect a mixture of a distillate product plus a very distinct combustion product profile from the fluorenes, phenanthrenes/anthracenes, fluoranthenes, and chrysenes, plus the BB to BP suite. The SHC profiles reflect primarily terrestrial plant waxes plus a trace of marine biogenic components.

The SHC patterns presented in Figure 14 show a predominantly biogenic signal in the two intertidal samples with significant variability observed among the replicates at each site. The subtidal sediments at Alyeska Marine Terminal show a combination of biogenic and very weathered ANS oil signals, again consistent with terrestrial and marine copepod fecal-pellet sources along with substantial oil-droplet/SPM interactions given the elevated levels of dispersed oil droplets introduced to region from the BWTF diffuser (Payne et al. 2001; Salazar et al. 2002). The SHC signals in the subtidal sediments at Gold Creek show a combination of marine and terrestrial biogenic input, with very little weathered-oil signal in keeping with the extremely low CRUDE Index values observed at the site.

In going through all the historic PAH and SHC histogram plots and reconciling the profiles with the absolute CRUDE Index values and associated standard errors, we were struck with the observation that often the elevated CRUDE Index values for a particular sample set included one or more samples that also contained elevated PAH from combustion sources. Although the CRUDE Index was designed to minimize the contributions from combustion products (none of the components in the benzo(b)fluoranthene (BB) through benzo(g,h,i)perylene (BP) range are included), it does include parent (unsubstituted) PAH from the naphthalenes, fluorenes, phenanthrenes/anthracenes, and dibenzothiophenes (see Table 3). While alkylated PAH homologues from each of these latter suites of PAH are clearly indicative of petrogenic sources, the unsubstituted parent PAH are often present in greater abundance compared to the alkylated homologues within each suite when the source is derived from combustion products. Therefore, we created a Pyrogenic Index to tease out this combustion signal in samples that exhibited an elevated- or extremely-variable CRUDE Index signal. As shown in Table 3, the Pyrogenic Index is defined as:

$$\text{Pyrogenic Index} = (A + P + FL + PY + C + BB + BK + BEP + BAP + IP + DA + BP)/TPAH$$

Thus, it only contains the sum of those components largely associated with combustion products (the parent PAH from the phenanthrene/anthracene, fluoranthene, pyrene, and chrysene groups plus the individual higher molecular weight components in the benzo(b)fluoranthene through benzo(g,h,i)perylene range that are more traditionally associated with combustion sources).

Figure 34 presents the individual CRUDE Index values observed for all replicate sediment samples analyzed in the program along with the associated Pyrogenic Index values for each sample. In general, the Pyrogenic Index values are more variable at Alyeska Marine Terminal compared to Gold Creek, but both sites exhibit a number of spikes with values above 0.4. When the PAH histogram plots for those samples with Pyrogenic Index values above 0.4 were examined, we found that those samples generally represented the outliers with higher concentrations of combustion products contributing to the elevated or variable CRUDE Index value for that station. This was particularly true at Gold Creek, where the overall PAH concentrations were significantly lower compared to Alyeska Marine

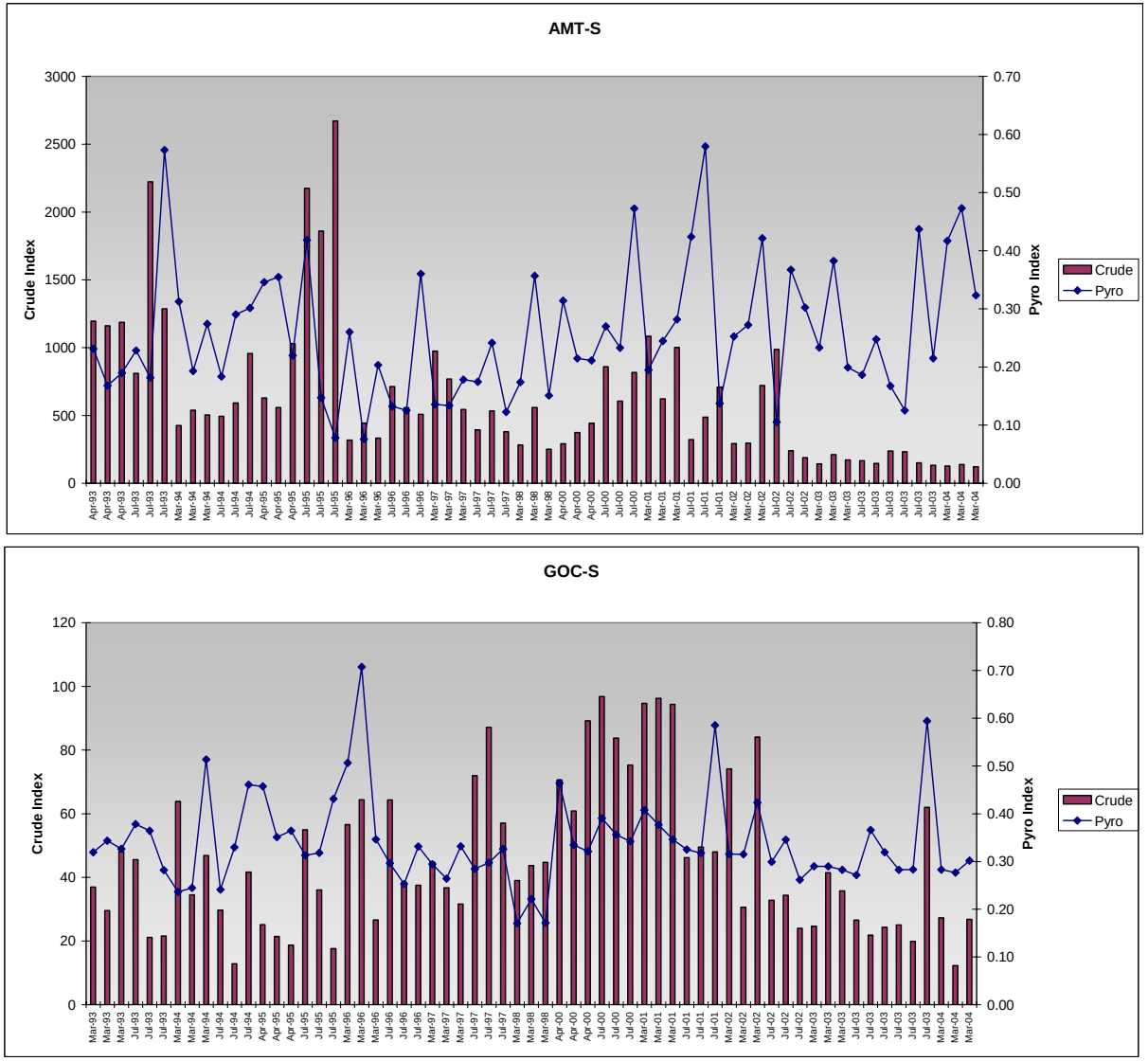

Figure 34. Individual sediment sample CRUDE Index and associated Pyrogenic Index values for all Alyeska Marine Terminal and Gold Creek sediments, 1993-2004.

Terminal, such that the presence of combustions products had more of an impact on the overall PAH pattern. Parametric correlation analyses found no significant relationships between CRUDE and Pyrogenic Indices at either station. Autocorrelations of the respective time series also found no interpretable patterns.

Historically, double ratio plots of C-2 dibenzothiophene/C-2 phenanthrene versus C-3 dibenzothiophene/C-3 phenanthrene (D2/P2 vs. D3/P3) have been used to help identify ANS crude-derived sources (Brown et al. 1980; Overton et al. 1981; Boehm et al. 1989; Sauer and Boehm 1991; Brown and Boehm 1993; Page et al. 1993; Page et al. 1995; Douglas et al. 1996, Payne and Driskell, 2001). Figure 35 presents the D2/P2 vs. D3/P3 double ratio plot for all of the Alyeska Marine Terminal & Gold Creek sediments analyzed to date. The samples are color- and shape-coded to reflect the sampling location including four weathered ANS crude oil samples from the Alyeska Ballast Water Treatment Facility (BWTF) effluent (Salazar et al. 2002, Payne et al., 2001, 2004 BTT Progress reports). Quite clearly, most of the Alyeska Marine Terminal sediments cluster around the ANS source signals, although some of the Alyeska Marine Terminal samples also trend into the background signals observed at Gold Creek. The figure also distinguishes those samples that exhibited Pyrogenic Index values above 0.4, also color-coded by site. For these data, however, the samples with Pyrogenic Indices > 0.4 cluster much closer together showing a source that is not strongly correlated with ANS crude oil. For reference, an NIST reference sample for combustion soot is also presented on the figure. Not surprisingly, this combustion product profile is more closely associated with the samples from the background sediments collected at Gold Creek where the influence from the marine terminal is seldom observed.

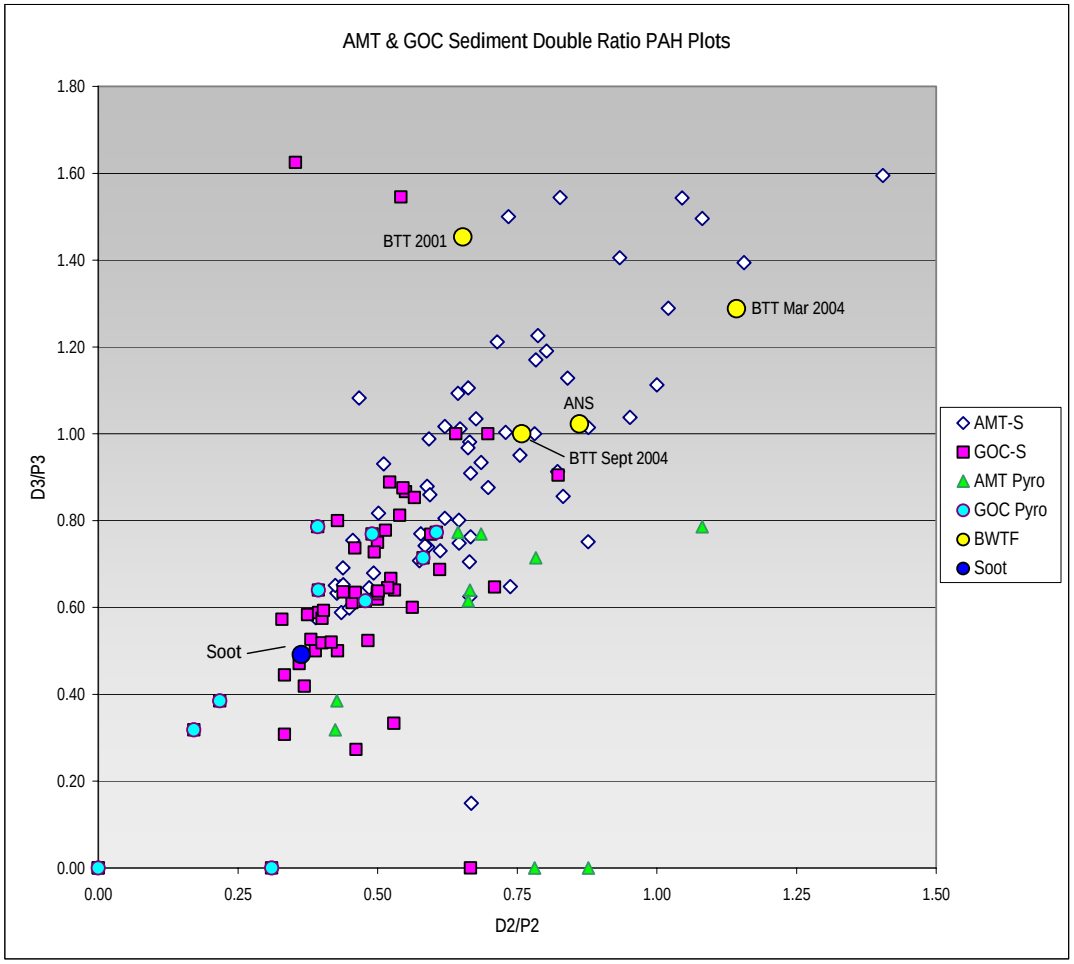

Figure 35. Double-ratio plot of C-2 dibenzothiophene/C-2 phenanthrene vs. C-3 dibenzothiophene/C-3 phenanthrene (D2/P2 vs. D3/P3) for Alyeska Marine Terminal & Gold Creek sediment samples, 1993-2004.

5.2.3 Tissues

5.2.3.1 Mussel Populations

One issue of moderate concern is the availability of mussels at some of the sites (Table 5). Some locations have but patchy remnants of former colonies so boldly obvious in earlier KLI photos. At most sites, there is normal attrition in the dominant 6-7 year old mussel age class (based on growth rings) with a 3-4 year old class maturing to fill the space. There are also new 0-3 year old recruits at most locations. The size and robustness of mussels differ substantially among the sampling sites, most likely natural variation from available food resources. The Sleepy Bay site is the most impoverished location and is definitely in a transition state. Recruitment is poor and adults are mostly scattered or absent. If current trends persist, this site may have to be relocated.

5.2.3.2 Tissue Chemistry Data Quality

Problems with lipid interference in samples analyzed at GERG were alluded to in our report last year (Payne et al. 2003a) when discussing interlaboratory inter-calibration exercises, and they have been referred to in numerous KLI/GERG reports, particularly with regard to saturate hydrocarbon (SHC) analyses in tissues. Lipid interference occurs when naturally occurring fats in living tissues are extracted along with the hydrocarbon components of interest but not adequately separated from the target SHC and PAH components during sample extract fractionation and cleanup (by silica gel (SiO_2) column chromatography and/or HPLC) procedures employed by the laboratory. This flaw results in additional and interfering peaks due to the lipids eluting from the gas chromatographic instrumentation used in the target analyte measurements. Although most of these interfering components can be eliminated by the selected ion monitoring (SIM) GC/MS procedures used for the PAH analyses, there are evidently some lipids that elute at the same time and generate similar ions to those used to identify and quantify specific components, and this appeared to be particularly problematic with the alkylated fluorenes (Payne et al., 2003a). With the SHC analyses, which are done by FID/GC, <u>any</u> lipid or other material that elutes from the GC at the same time or close to the target analytes will interfere or generate a false positive, because the detector does not have the discriminating power to distinguish between hydrocarbons and lipids.

Thus, tissue samples, due to their higher lipid content, are particularly prone to the over-reporting certain analytes. For example, the anomalous fluorene (F1, F2, and F3) pattern observed in GERG's analysis of NIST SRM as part of the laboratory inter-calibration program discussed at length in last year's report (Payne et al. 2003a) is likely due to lipid interference. In the SRM SHC data, lipid interference also led to anomalously high levels of C_{20}, C_{25}, C_{29}, C_{30}, and C_{32} (compared to values reported by ABL). In the inter-laboratory split-tissue samples, the problem manifest itself again in the PAH data as anomalous alkylated fluorene (F, F1, F2, F3) and possibly, alkylated phenanthrenes/anthracenes (P/A1, P/A2, P/A3, P/A4).

Table 5. Field notes on mussel populations.

Station	Field notes – March 2004
Aialik Bay	Very good population. Dense, 5-6 yr old, plump and healthy crop of recruits. Few predators visible.
Alyeska Marine Terminal	Denser population and not as patchy as Gold Creek.
Disk Island	Healthy, plump, vivid blue shells. No mussels in mid-transect swale.
Gold Creek	Colony in eroded patchy strips, slippery, silt-covered with reduced shell volume. Suboptimal niche?
Knowles Head	Mussels dense but small. Good crop of 3-4 yr old recruits.
Sheep Bay	Harvestable mussels discontinuous in mid transect. Shells small (<2 cm) but still 6-7 yr old. Distinct zone in KLI photos no longer visible. 3-4 yr old recruits appearing on upper surfaces.
Shuyak Harbor	Mussels patchy near right end. But healthy and aged 5-6 yr old. Less patchy near left end but slightly smaller. Good recruitment.
Sleepy Bay	Mussels are only in broken shale above the marker and at left end beyond marker. Mostly very small 3-5 yr olds. No mussels in mid-section. Small healthy group found on back side of outcrop beyond left end marker. This site may be in jeopardy.
Windy Bay	Good site. Beds dense and continuous. Mussels healthy, plump and aged. Good recruitment.
Zaikof Bay	Very dense, medium-sized population.

In the SHC data for the inter-calibration tissue samples, lipid interference manifest itself as excessively large (two and three order of magnitude greater) contributions of C_{21}, C_{23}, C_{29}, C_{30}, and C_{31} n-alkanes compared to the other components. For example, fairly good agreement was obtained between GERG and ABL for the lower molecular weight ($C_{12} - C_{16}$) n-alkanes that were measured in the range of 100-500 ng/g dry wt. in both the Alyeska Marine Terminal and Gold Creek tissue split intercalibration samples (just as they were in the NIST SRM samples). But GERG also reported concentrations of heaver-molecular-weight n-alkanes that ranged from 2,000 to 90,000 ng/g dry wt., while these components were essentially not detected by ABL.

These observations prompted us to go back last year and look at the historical database to see if there were anomalous concentrations of higher molecular weight n-alkanes in the SHC profiles, and whether or not the observed SHC profiles could be correlated with station locations, sampling, dates, percent lipid, or petroleum hydrocarbon contamination when it appeared in PAH profiles (Payne et al. 2003a). In undertaking the analyses of the tissue data for the 2003-2004 program, we again kept these lipid interference issues in mind, as discussed in the following sections.

5.2.3.3 Tissue Indices

In our 2001 report summarizing LTEMP results for Port Valdez (Payne et al. 2001), we presented evidence for a dissolved vs. particulate/oil-droplet signal in the mussels at both Alyeska Marine Terminal and Gold Creek. The seasonal dependence of these signals led us to hypothesize a water-column stratification-controlled transport mechanism to explain the observations (Payne et al. 2001). During our data analysis for the 2002-2003 LTEMP (Payne et al. 2003a), we expanded upon that approach and developed the Particulate to Dissolved Ratio (PDR) to quantify the observed qualitative differences in the PAH histograms of particulate/oil-droplet vs. dissolved components. Essentially, the PDR is simply the ratio of the higher molecular weight PAH that have lower water solubilities and are generally associated with finite oil droplets to the sum of the more water soluble alkylated naphthalenes (e.g., Table 3 and Figure 4 in the Oil Primer at the beginning of this report). Careful correlation of the PDR values with visual examination of the mussel PAH histograms from all stations over all seasons has confirmed that if a sample exhibits a PDR value greater than 2, the PAH pattern will show an accumulation by the mussel of predominately the higher molecular weight alkylated phenanthrene/anthracene (P/A), dibenzothiophene (D), and chrysene (C) components associated with particulate (finite) oil droplets, while a PDR value less than 1 will come from a sample where the naphthalenes (N) predominate. Samples with PDR values between 1 and 2 contain a mixture of components from both the dissolved and particulate phases.

PDR values are also plotted for each station in Figure 36, which compares the average TPAH time-series values for all ten LTEMP stations over the 11 years of the program. To assist with additional source characterization, the figure, and the significance of the observed values along with selected PAH and SHC histograms are discussed on a site-specific basis in the following sections and Appendix A-3.

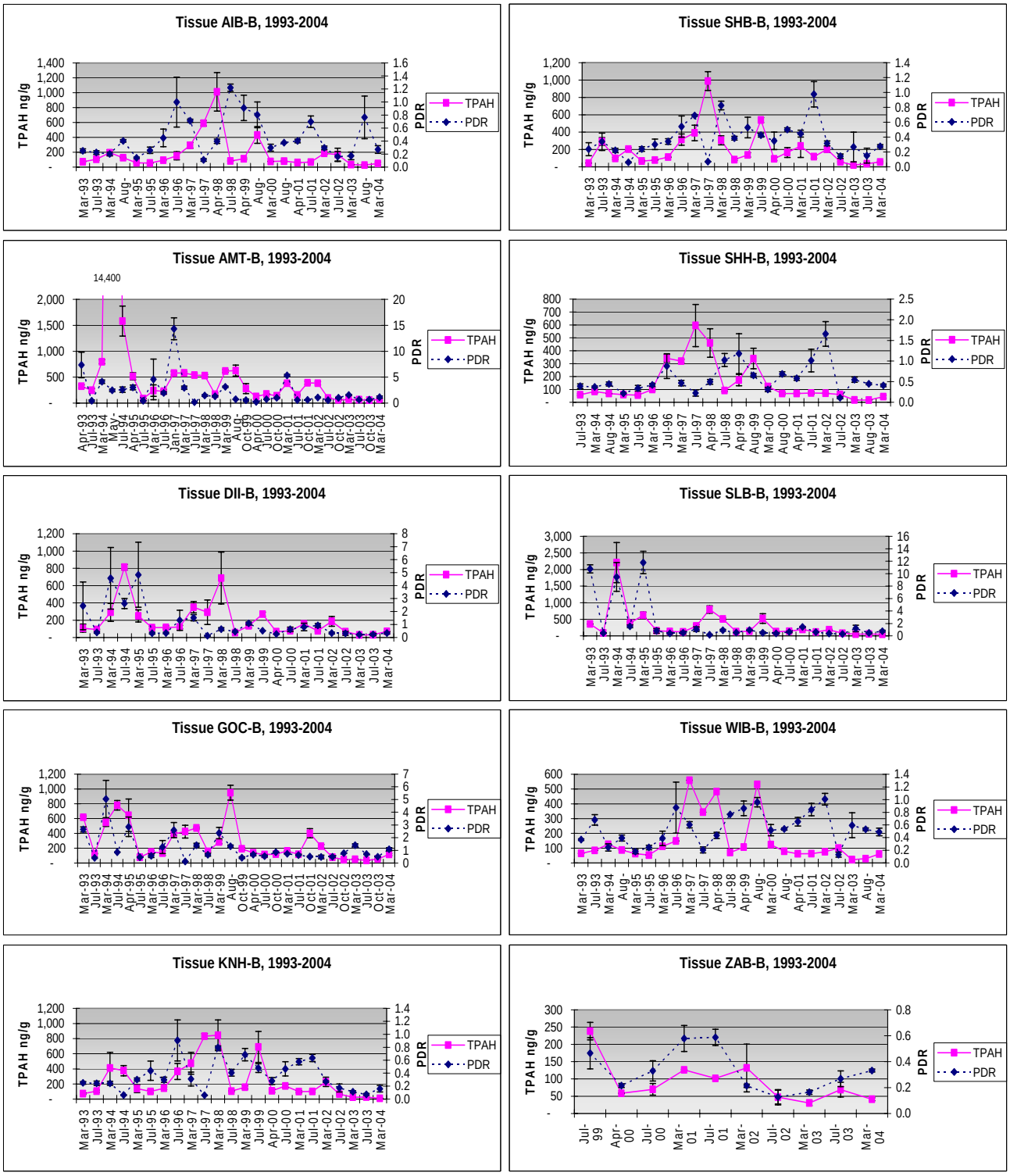

Figure 36. Total PAH (TPAH) and Particulate to Dissolved Ratio (PDR) data for all tissue samples analyzed in the 1993-2004 LTEMP.

In general, the measured TPAH concentrations are very low, ranging from 11 to 14,350 ng/g dry wt across all stations. Not surprisingly, the concentrations at Alyeska Marine Terminal are the highest, and ranged from 59 to 1,581 ng/g dry wt., excluding the samples collected after the *T/V Eastern Lion* oil spill. The mussel samples collected at Alyeska Marine Terminal following the *T/V Eastern Lion* oil spill in May 1994 exhibited exceptionally high TPAH concentrations, with values reaching 14,350 ng/g dry wt. In general, the measured TPAH values measured elsewhere are quite low (usually < 600 ng/g dry weight) for most sample collections with occasional spikes to concentrations approaching 1,000 ng/g dry weight. These exceedances are discussed further on a site-specific basis in the following sections and in Appendix A-3. Different concentration scales are used for each station presented in Figure 36 to accentuate the wide ranges observed within a given site over time, so care should be taken to note the individual concentration scales when comparing the TPAH data among sites. Several sites appear to have a primary or secondary TPAH maximum in July 1997 (Sheep Bay, Shuyak Harbor, Sleepy Bay, and Knowles Head), while Aialik Bay and Disk Island peak in March 1998, and Windy Bay appears to be high in both March 1997 and March 1998. Alyeska Marine Terminal TPAH concentration peaks in July 1994 (as does Gold Creek) and this clearly reflects PAH input from the *T/V Eastern Lion* oil spill in the Port. Zaikof Bay has the lowest TPAH values of any site and shows only moderate variability with neither spring nor summer collections showing a consistent trend.

In our 1998 review of the LTEMP (Payne et al. 1998), we introduced the Mytilus Petrogenic Index (MPI), which is essentially, a total rather than a relative FPPI. It is very similar to the TPAH, except that pyrogenic PAH are excluded, summing instead only the petrogenic PAH components (fluorenes, phenanthrene/anthracenes, dibenzothiophenes and chrysenes). In this way, the contribution from petroleum hydrocarbon contamination in the absence of combustion byproducts is emphasized (see Table 3).

Figure 37 presents the individual MPI plots for each station along with the average PDR values generated for each sample set. The data in the figure suggest that the apparent summer-dissolved vs. winter/spring-particulate signal observed at Gold Creek and to a lesser extent at Alyeska Marine Terminal seems to break down after the spring of 2000, when lower overall MPI (and TPAH) values are observed, although it did begin to manifest itself again in the 2003 and 2004 collections at these sites. Also, the other sites do not show the same seasonal pattern as that observed within Port Valdez, and at most of the outer PWS stations, the signal is primarily driven by dissolved components as reflected by the PDR values that are generally less than one. There are seasonal fluctuations to be sure, but at some of the other stations, the PDR is higher in summer (indicating a mixture of dissolved and particulate/oil-droplet phases) and lower in winter and just the opposite at others. What is common among most stations is the tendency for the apparent MPI maxima in the 1997-1998 time frame to be largely derived from a dissolved-phase signal of primarily naphthalene(s), with an absolute minimum PDR (maximum naphthalene signal) observed at all stations in July 1997.

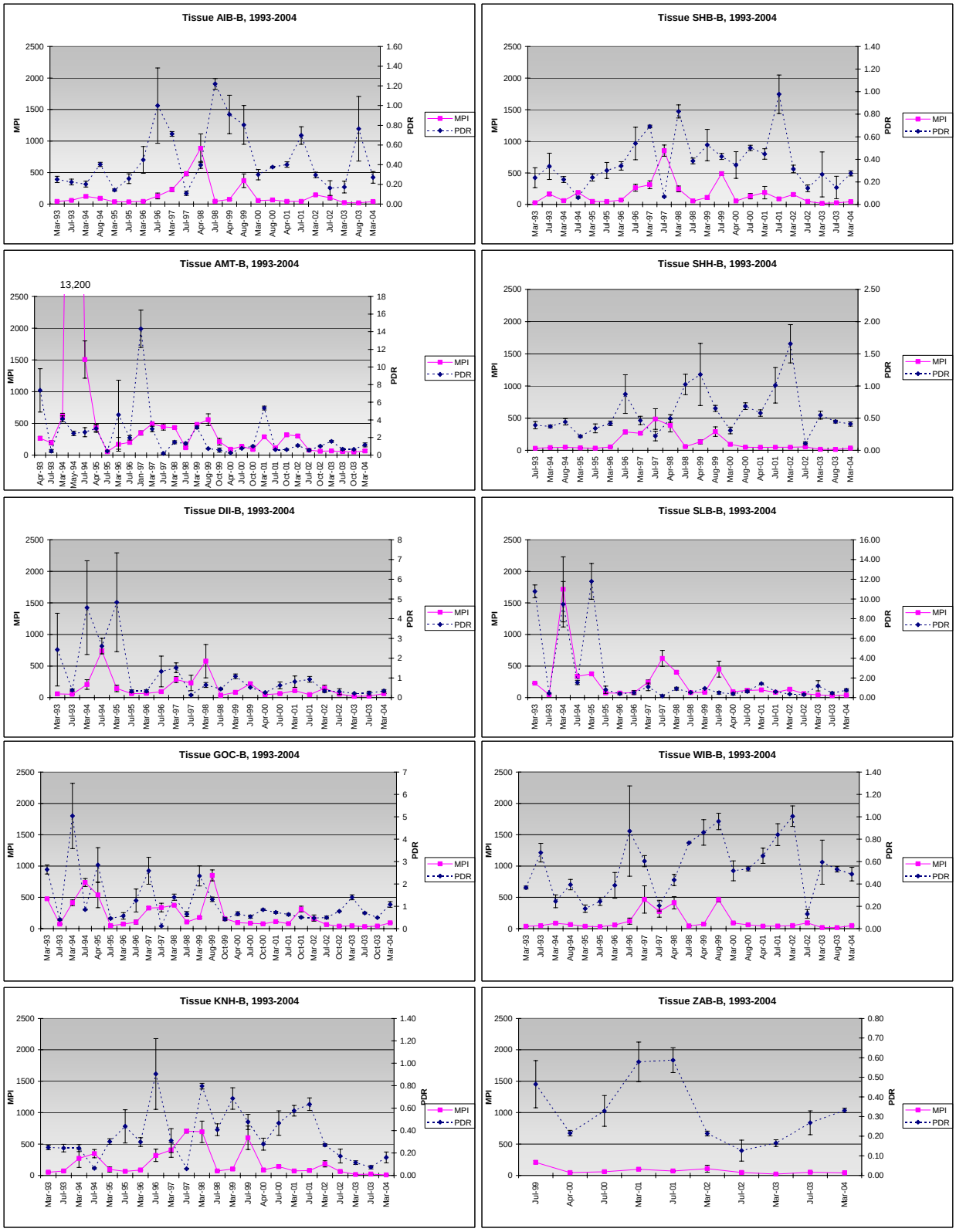

Figure 37. Mytilus Petrogenic Index (MPI) and Particulate to Dissolved Ratio (PDR) data for all tissues analyzed during the 1993-2004 LTEMP.

As discussed in the 2002-2003 LTEMP Report (Payne et al. 2003a), we can only speculate about the apparent across-the-board TPAH and MPI increase in the July 1997 to March 1998 time frame. The BWTF spill in January 1997 might be the cause for the increase at Gold Creek and Alyeska Marine Terminal, but the apparent increases at Aialik Bay, Sheep Bay, Shuyak Harbor, Disk Island, Windy Bay, and Knowles Head are more difficult to explain. There are synchronous increases at some stations in 1997 while others peak in 1998. Yet it is obvious that an event has occurred during the 1997-98 period before the sites fall into their more predictable behavior of recent years.

In an effort to explain these apparent trends, we re-examined the PAH histogram plots for all of the samples to see if there was an obvious dissolved vs. particulate/oil-droplet phase signature or other commonality that would explain the data. For this effort, we also considered the available SHC data, although there were no SHC data from 1995-1998, and most of the remaining data were compromised because of lipid interference.

While it is conceivable that there could be some explanation for an across-the-region increase in a predominantly dissolved-phase signal between March 1997 and March 1998, we found it hard to believe that it could occur in an area as large and diverse as Port Valdez and Prince William Sound (including Kodiak Island). Therefore, we began to look for some other systematic bias or difference in collection or analytical procedures that might explain the observations. For example, we ruled out the possibility that the apparent MPI (and TPAH) increase might have been due to lipid interference, because the maxima occurred during a period when the anomalous fluorene pattern and percent lipids measured in the tissues were at a minimum.

During our investigation for the 2002-2003 LTEMP Report (Payne et al. 2003a), we learned from Dr. Guy Denoux at GERG (personal communication, 8/7/03), that the laboratory installed new GC/MS instrumentation and integration software in the early 1997 timeframe, and that this resulted in increased sensitivity (lower detection limits) and a greater number of alkylated PAH homologues being routinely integrated with the automated integration software. The potential ramifications of this procedural change are discussed in the following paragraphs.

Figures 38 and 39 present the PAH histogram plots of field samples and associated procedural blanks from Aialik Bay (near Seward) collected and analyzed between March 1993 and November 1997. It should be noted that the PAH patterns were almost identical throughout the early 1993-1996 timeframe, and although the absolute concentrations were usually ten times higher in the field samples, an identical pattern was obtained in the procedural blanks. During the initial years of the LTEMP program, the software with GERG's GC/MS instrumentation did not automatically integrate all the alkylated PAH homologues, and as a result, PAH patterns similar to those observed in Figures 38 and 39 were often obtained on samples from the cleaner areas. Integration of the remaining C_2-, C_3-, and C_4-alkylated homologues had to be done manually by the GC/MS operator, and then only when a recognizable signal was observed. When there

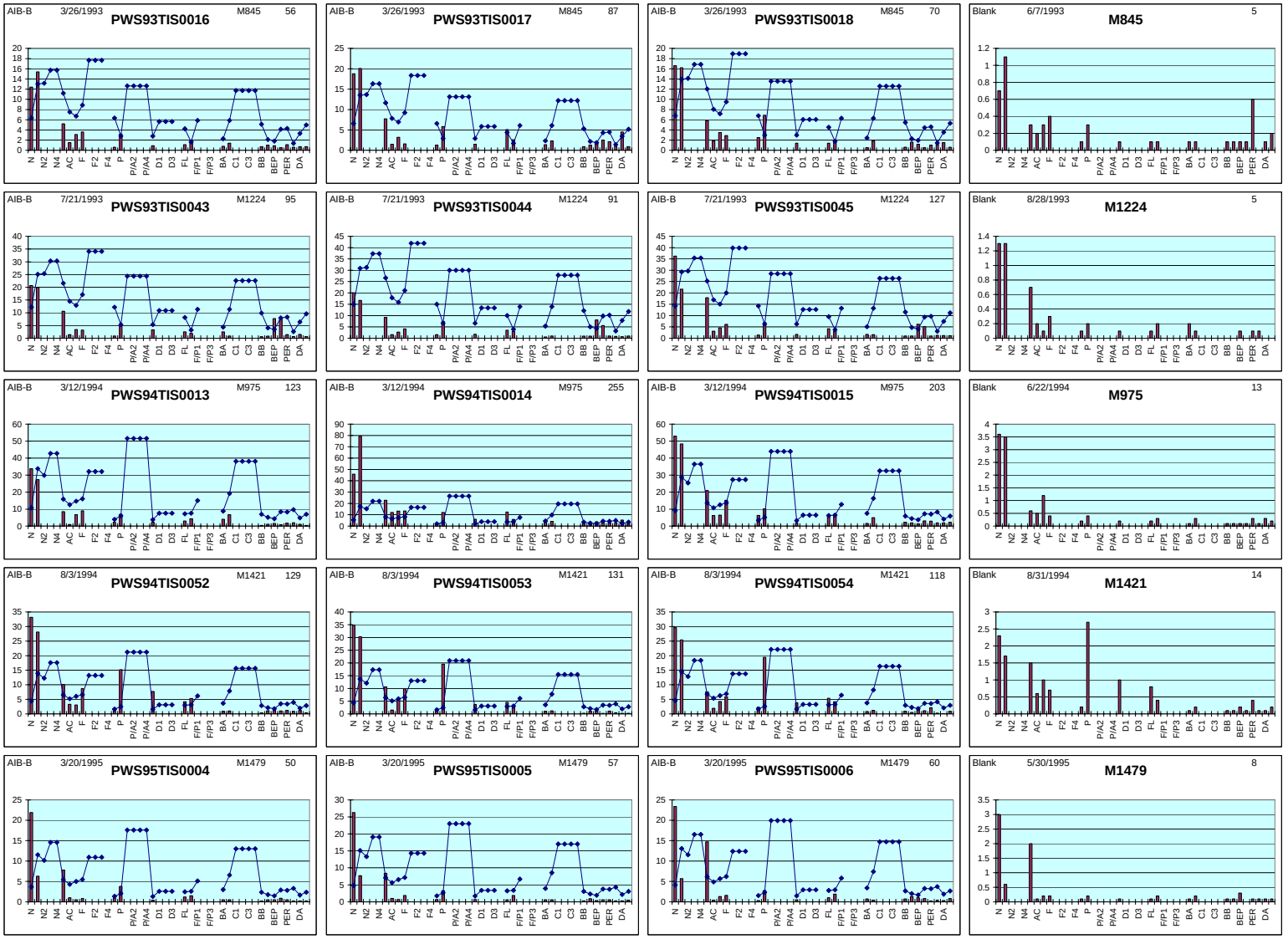

Figure 38. PAH histograms of Aialik Bay mussel samples and associated procedural blanks showing the typical background artifact pattern obtained with the initial GC/MS instrumentation used for the 1993-1995 analyses.

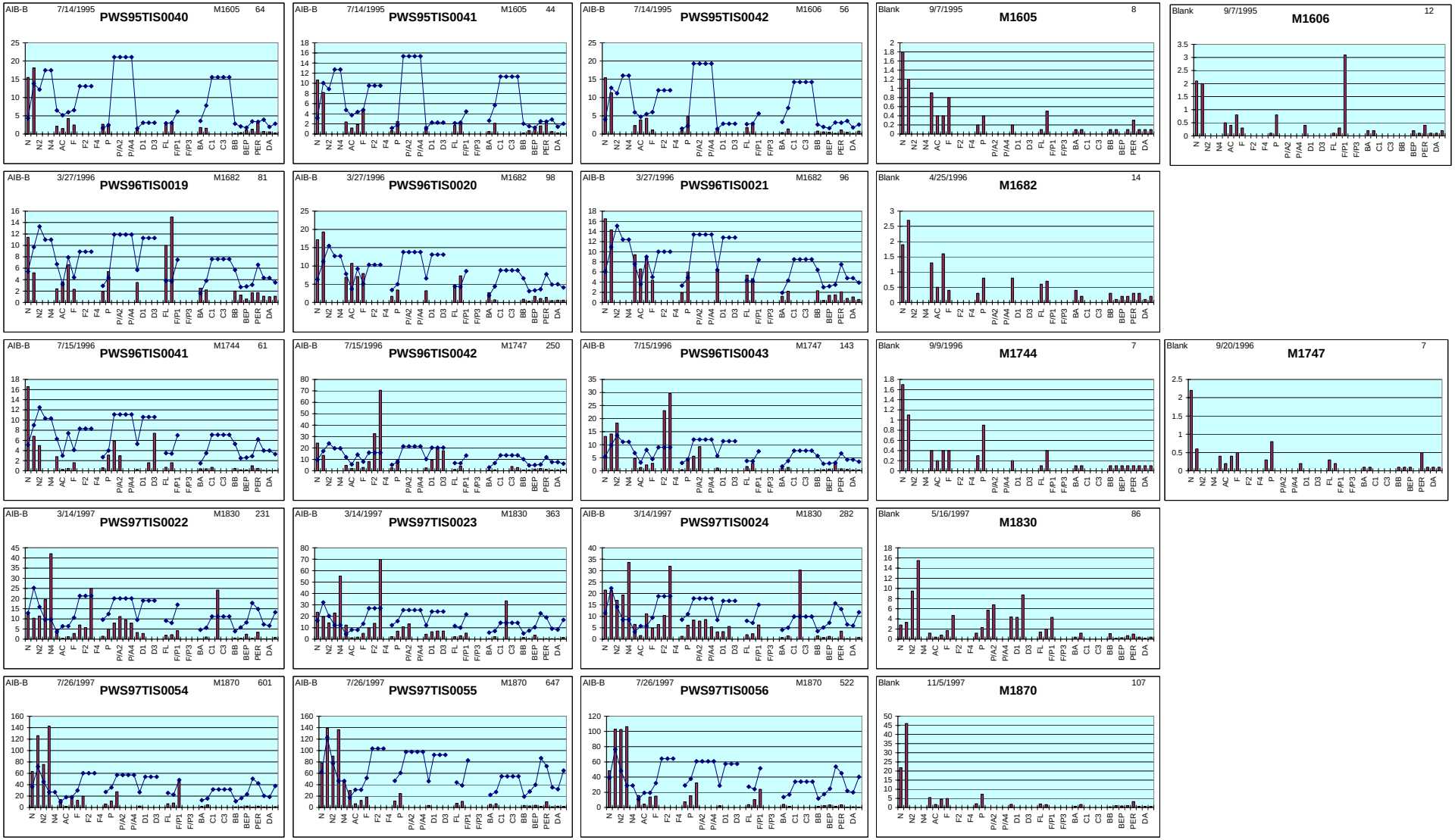

Figure 39. PAH histograms of Aialik Bay mussel samples 1995-1997 and associated procedural blanks showing the increasingly complex background pattern obtained with the change in GC/MS instrumentation at GERG beginning with the 1997 analyses.

was significant oil contamination (such as at the Alyeska Marine Terminal and Gold Creek sites after the *T/V Eastern Lion* oil spill in 1994), the instrumentation was sensitive enough to detect the signal from the remaining alkylated homologues, and they were manually integrated. The rest of the time, however, profiles closer to those shown in Figure 38 were obtained.

When a new Mass Selective Detector (MSD) and updated integration software were installed at GERG sometime in 1997, the sensitivity of the GC/MS system used for the LTEMP samples was increased, and automated integration of the previously missing alkylated PAH homologues was initiated. The result was higher TPAH values and much more complex looking PAH profiles, such as those shown from the March and July 1997 Aialik Bay samples in Figure 39 (rows four and five) were observed in all the samples examined in the program. Note the appearance in row four (March 1997 samples) of more peaks from homologues of naphthalene, fluorene, dibenzothiophenes, and the first appearance of C_2-chrysenes (C2). In the bottom row (July 1997), the peaks diminish, reflecting a more dissolved-fraction signature; however, the complexity of the lighter (left end) analytes is still apparent.

With the available data, it is impossible to say if the apparent increase in all the samples across the study region in the 1997-1998 period was the result of the instrumentation and software changes, or if there really was some event in Port Valdez and PWS that was the cause. Certainly there were some subtle differences among the samples and stations with regard to the MPI and PDR values (see Figure 37), and these signals did not all track together with time Nevertheless, the possibility of a systematic error or laboratory bias cannot be completely ruled out.

Because of the significant differences in the MPI and PDR signals during the *T/V Eastern Lion* event (before the 1997-1998 period), we believe that the data probably accurately reflect the conditions in the study region at that time. Likewise, the observed MPI and PDR differences noted among the stations since 1998, suggest that if there was a systematic laboratory bias, it has probably been addressed, and the data from 1998 on are representative of the conditions in Port Valdez and PWS. It is just the 1997-1998 period that has us concerned. If the noted region-wide increases are in fact real, then additional research will be required to try and track down the cause. In Figure 37, all the MPI values have been plotted on the same concentration scale to facilitate comparisons among stations. At this concentration range, the MPI values are off-scale in May 1994 for Alyeska Marine Terminal, and as noted before, the significantly elevated MPI values at Alyeska Marine Terminal and Gold Creek in July 1994 have been attributed to the influence of the *T/V Eastern Lion* oil spill in Port Valdez. We previously reported that we believed the Disk Island and Sleepy Bay maxima in July 1994 were the result of mussel-bed and beach-cleaning operations completed at Disk Island and Sleepy Bay that summer (Payne et al. 1998; 2003a). These and other site-specific trends in the data are discussed further Appendix A-3.

The use of the MPI and PDR allow real-trend and dissolved- vs. particulate/oil-droplet source analyses, but as noted before, lipid interference problems have precluded establishing any correlations between MPI (and TPAH) and the saturated hydrocarbon (SHC) data for most of the mussel tissues analyzed thus far in the program. This has been corrected with better lipid separation during the sample cleanup after July 2002, and seasonal trends since then are discussed in Appendix A-3 on a site-specific basis. As demonstrated by the paired PAH and AHC histogram plots in the Oil Primer (Section 2), a tremendous amount of additional information about the state of hydrocarbon contamination can be obtained from this information. For the sake of data completeness, Figure 40 presents the total SHC (TSHC) data for all stations over the full eleven years of the program, even though we have serious reservations about much of the tissue SHC data (particularly before July 2002).

The mode of hydrocarbon incorporation (particulate or dissolved) into the sentinel organisms is important, because other species and developmental stages are affected differently by dissolved and particulate oil fractions. If the LTEMP is truly going to be used to monitor the impacts of the Alyeska Marine Terminal operations and hydrocarbon transport through Port Valdez and Prince William Sound, this mechanism of exposure must also be delineated, and better SHC analyses can be important in this process.

5.2.3.4 Summary of Tissue Results

From the detailed individual station accounts (Appendix A-3), the tissue hydrocarbons burdens (as reflected by TPAH) remain very low at all stations, and yet, it is still possible to detect a finite but declining petroleum hydrocarbon signal from the BWTF at Alyeska Marine Terminal and Gold Creek within Port Valdez. The winter vs. summer particulate-phase vs. dissolved-phase pattern seems to be reappearing at Gold Creek after being largely absent between October 2000 and April 2002. This pattern has always been present at Alyeska Marine Terminal. The tissue SHC patterns at both stations show contributions from marine biogenic sources (e.g., n-C_{15}, n-C_{17}, and pristane from phytoplankton, marine algae, and copepods) and higher-molecular weight odd–carbon-number n-alkanes in the n-C_{23} to n-C_{33} range from terrestrial plant waxes. In addition, the SHC patterns in the mussel tissues at Alyeska Marine Terminal clearly show the influence of particulate/oil-phase components and a chromatographically unresolved complex mixture (UCM) from the BWTF, but as noted above, both Alyeska Marine Terminal and Gold Creek have shown declines in the oil contamination signal since October 2001 and March 2002.

TPAH concentrations at the outlying stations throughout PWS are uniformly low (generally less than 100-200 ng/g dry weight) and reflect a primarily dissolved-phase signal or source. The SHC profiles from recent years at these outer stations reflect an almost exclusive biogenic source. Because the typical hydrocarbon contaminant concentrations measured in mussel tissues outside Port Valdez are so low (often at or below method detection limits), detailed trend analyses are confounded by background

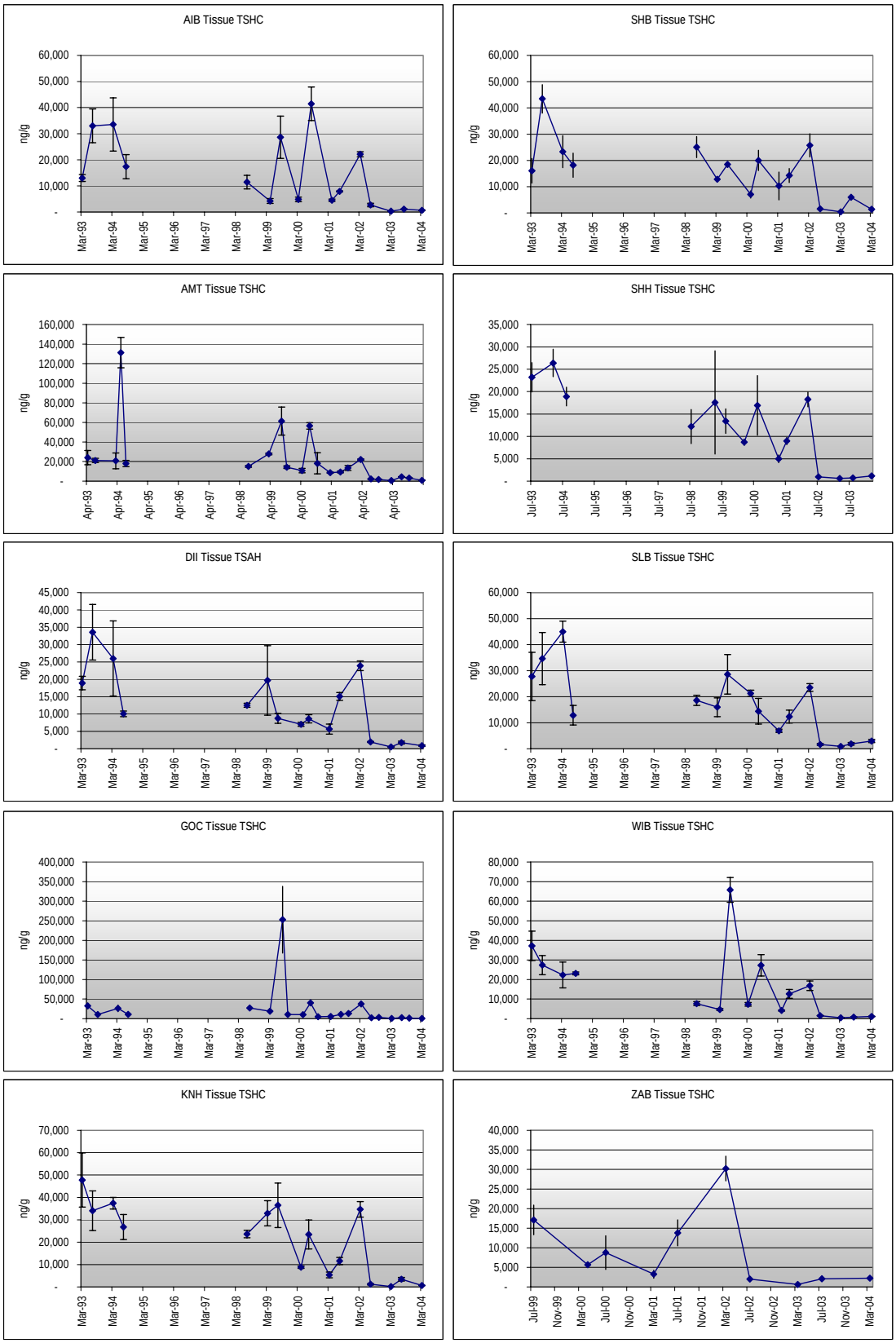

Figure 40. Total saturated hydrocarbon (TSHC) values for all LTEMP tissue samples. Note, tissue SHC analyses were discontinued between July 1994 and July 1998.

levels, spurious events, and historic data-quality issues. Nevertheless, portions of the historic dataset are internally consistent with known pollution events, observed seasonal changes, and plausible transitions to the current low oiling levels.

Taken together, the TPAH and TSHC values and the associated histogram plots (or fingerprints) do not show the "ubiquitous" background contamination reported throughout much of PWS by Exxon's consultants (Boehm et al., 2003). The station locations from the Exxon studies and LTEMP are from different areas, but clearly, the LTEMP data in no way suggest that PWS is heavily contaminated from past and ongoing anthropogenic activities. Furthermore, from the 2002 EMAP project (unpublished data, Susan Saupe), the background contamination signature appears identically in subtidal coastal samples from the Copper River past the Outer Kenai and through the lower Shelikof Straits (West Nagai Strait). Significantly, the signature retains its "fresh" naphthalene appearance implying the PAH is not degrading en route but is instead bound up in the matrix material and not bioavailable.

6 Conclusions

With the exception of identifiable pollution events, most of the LTEMP study sites remain remarkably free of hydrocarbon contaminants from anthropogenic or natural sources, most of the time. The most important hydrocarbon pollution sources evident in samples from these stations may be related to 1) the *T/V Eastern Lion* oil spill in Port Valdez in 1994; 2) a sheen event from the Ballast Water Treatment Facility of the Alyeska Marine Terminal in Port Valdez; and 3) oil from the 1989 *Exxon Valdez* oil spill occasionally evident at two stations that were heavily impacted. Apart from stations affected by these events, concentrations derived from petrogenic sources are usually near or below the analytical detection limits of the methods used for their analysis, typically in the low parts per billion for individual PAH.

Standard versus modified Van Veen grab sampler comparisons show no differences in the composition or concentrations of hydrocarbons in sediments collected by the two samplers. Likewise the comparative PGS data showed no systematic bias or differences. An expanded protocol will include collection of separate PGS samples with each sediment grab (as opposed to a single composite from triplicate grabs). Sediment samples will continue to be collected with PECI's new, modified Van Veen grab (currently stored in Valdez and dedicated to LTEMP).

Analytically, the low concentrations of hydrocarbons usually encountered in LTEMP samples present substantial challenges to the hydrocarbon analysis laboratories. Despite state of the science methods, outstanding quality assurance programs and exemplary performance track records, the accuracies of some of the hydrocarbon analytes from earlier years of the program may have been compromised at various times, causing relatively small biases in some of the reported results. The compounds most vulnerable include some of the higher-molecular-weight alkanes, the alkylated fluorenes, and the alkylated phenanthrenes.

Perusal of the historic and current results suggest occasional positive interferences from incomplete lipid removal in some samples analyzed at GERG, and possibly a somewhat lowered sensitivity (~ -30%) for alkylated phenanthrenes analyzed at ABL. Because of these interferences, it remains unclear whether the slight increase in PAH observed at regional stations (beyond Port Valdez) during 1997 and 1998 reflect actual changes in the sampled environment, or are the result of artifacts introduced during analysis in the laboratory. Through detailed examination of all PAH and SHC histogram plots for all stations and seasons, it was possible to screen the data for the confounding effects from obvious lipid interference, and it appears that this problem did not drastically change the overall conclusions with regard to low-level PAH contamination in mussels across all sites.

Sediment TPAH concentrations at Alyeska Marine Terminal are low (generally below 600 ng/g dry wt.) but highly variable, and the PAH and SHC histogram profiles continue to indicate the accumulation of PAH and SHC components from the BWTF (and presumably other terminal operations). Additional hydrocarbon sources at Alyeska Marine Terminal include combustion products (which may or may not be related to terminal activities) and biogenic marine and terrestrial SHC components. At Gold Creek, the PAH components in the sediments are generally 5-10 times lower than those at Alyeska Marine Terminal, and they do not show the same degree of petrogenic contamination or variability compared to the Alyeska Marine Terminal site. The PAH in Gold Creek sediments are derived primarily from combustion products.

It is not possible to determine if the low-but-discernible petrogenic hydrocarbons in the Gold Creek sediments are from the BWTF and/or other activities at the Alyeska Marine Terminal, or if they represent input from other sources, including boat traffic; sewage and wastewater effluent; and surface/stormwater runoff from the city of Valdez. The SHC pattern in the Gold Creek sediments clearly includes marine biogenic input and terrestrial-sourced plant wax components.

The historic tissue data demonstrate that the sampled mussels have accumulated hydrocarbons and show PAH patterns that can be clearly associated with known spill events such as the *T/V Eastern Lion* oil spill in 1994 and the BWTF sheening incident in 1997. In addition, they can pick up petrogenic hydrocarbons from other activities such as the beach cleaning operations at Disk Island in the summer of 1994 and possibly the release of buried *Exxon Valdez* oil in Sleepy Bay during the winter and spring periods of 1993, 1994, and 1995 (see Appendix A-3). The open northeast fetch makes the latter site particularly susceptible to storm-wave turbulence and resulting beach disturbance following strong northerly winds. There do not appear to be significant releases of buried oil since March 1998, and Sleepy Bay now appears to be on a par with other clean sites within PWS. The mussel tissue TPAH burdens at Sleepy Bay have been consistently below 100 ng/g dry weight since July 2002.

Tissue PAH concentrations as reflected in TPAH and MPI plots appear to have declined at both Alyeska Marine Terminal and Gold Creek since October 2001 and March 2002, and this trend appears to be continuing with the 2003-2004 samples. Although the

concentrations are low, the data from Alyeska Marine Terminal continue to indicate the accumulation of dissolved and particulate/oil-phase PAH components from the BWTF that are seasonally controlled by water-column stratification. In the 2003 LTEMP final report (Payne et al. 2003a), we reported that this pattern appeared to be breaking down at Gold Creek after March 2000 with the overall decline in TPAH and MPI levels at the site. The 2003-2004 data suggest, however, that water-column stratification-controlled transport of dissolved PAH and particulate/oil-droplets may have returned at this site, although the dissolved-phase pattern still clearly predominates.

The TPAH and MPI plots for the regional PWS and Gulf of Alaska stations (including Kodiak Island) are generally very low (< 200 ng/g wt.) and appear to have declined at most stations since March 2002 reflecting an almost exclusively dissolved-phase signal (PDR < 1). The apparent increase across the region (Port Valdez and PWS, including Kodiak Island) in TPAH and MPI in mussels during the 1997-1998 timeframe might be related to a systematic change in laboratory procedures implemented at that time. However, it is impossible to definitively state whether or not the trend was real (reflecting a region-wide input of primarily dissolved-phase PAH components) or a laboratory artifact without additional laboratory data (Total-Ion-Current profiles and hardcopy FID gas chromatographic profiles for all tissue samples).

7 Recommendations

- To facilitate evaluation of lipid interferences we recommend in the future that analytical laboratories supply and evaluate hard and electronic copies of total ion current chromatograms for the GC/MS analyses and the detector response for GC/FID analyses, to facilitate evaluation of lipid interferences. These products would provide conclusive evidence for the presence of positive interferences in these analyses.
- The elimination of the lipid measurements beginning with the 2002 mussel collections was perhaps a mistake. The lipid measurements became very helpful in investigating the earlier problems with laboratory artifacts during the 2002-2003 data analysis (Payne et al. 2003a), and it may be prudent to re-introduce this measurement back into the program.
- It is not possible to tell if the low-level petroleum source in the subtidal sediments at Gold Creek is from the BWTF and other activities at Alyeska Marine Terminal or other sources (boat traffic, sewage and wastewater discharges from the City of Valdez). This source may be identified through a limited set of sterane/triterpane analyses of Alyeska Marine Terminal and Gold Creek sediments for comparison to Alyeska BWTF discharges as part of future LTEMP or other PWS RCAC research activities. We recommend a limited series of sterane/triterpane analyses in sediment samples at both Alyeska Marine Terminal and Gold Creek starting with the March 2005 sample collections.
- All the tissue and sediment samples collected during the LTEMP program have been archived by the respective laboratories. We recommend retrieving and reanalyzing individual archived samples from Aialik Bay collected in April 1998, Sheep Bay from July 1997, Shuyak Harbor from July 1997, Windy Bay in March

1997, and Knowles Head from March 1998. If the samples are reanalyzed by the Auke Bay Laboratory and elevated PAH levels are still observed, then we will know that the apparent trends observed in the TPAH and PDR plots for the 1997-1998 time frame are in fact real and not the result of a laboratory bias. If on the other hand, lower TPAH values in line with those observed earlier and later in the LTEMP program are obtained, then the apparent region-wide increases in the period of July 1997 through April 1998 can be identified as nothing more than laboratory error.

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Appendices

Appendix A- 1 TPAH and TSHC summary table for all Alyeska Marine Terminal and Gold Creek sediment samples.

Appendix A- 2 Summary of tissue TPAH and TSHC for 2002-2003 program.

Appendix A-3 Station Accounts for Tissue Samples

Appendix A-1 TPAH and TSHC summary table for Alyeska Marine Terminal and Gold Creek sediment samples.

Date	Sample ID	Total SHC	Mean	Std Dev	CV	Total PAH	Mean	Std Dev	CV
Alyeska Marine Terminal Subtidal Sediments (AMT-S)									
3-Apr-93	PWS93PAT0040	1868				196			
3-Apr-93	PWS93PAT0041	2533				341			
3-Apr-93	PWS93PAT0042	1873	2091	383	18.3	191	243	85	35.1
16-Jul-93	PWS93PAT0043	1164				146			
16-Jul-93	PWS93PAT0044	3183				198			
16-Jul-93	PWS93PAT0045	1707	2018	1045	51.8	394	246	131	53.2
26-Mar-94	PWS94PAT0025	1047				202			
26-Mar-94	PWS94PAT0026	1698				167			
26-Mar-94	PWS94PAT0027	1675	1473	369	25.1	239	203	36	17.8
20-Jul-94	PWS94PAT0031	1425				174			
20-Jul-94	PWS94PAT0032	1242				230			
20-Jul-94	PWS94PAT0033	1922	1530	352	23.0	389	264	112	42.2
3-Apr-95	PWS95PAT0022	1291				206			
3-Apr-95	PWS95PAT0023	1093				244			
3-Apr-95	PWS95PAT0024	1785	1390	356	25.6	186	212	29	13.9
11-Jul-95	PWS95PAT0028	2189				1650			
11-Jul-95	PWS95PAT0029	1872				362			
11-Jul-95	PWS95PAT0030	2763	2275	452	19.9	629	880	680	77.2
16-Mar-96	PWS96PAT0004	1109				160			
16-Mar-96	PWS96PAT0005	1578				311			
16-Mar-96	PWS96PAT0006	1100	1262	273	21.7	135	202	95	47.1
12-Jul-96	PWS96PAT0025	2265				326			
12-Jul-96	PWS96PAT0026	1782				201			
12-Jul-96	PWS96PAT0027	1602	1883	343	18.2	381	303	92	30.5
6-Mar-97	PWS97PAT0001	2203				417			
6-Mar-97	PWS97PAT0002	1980				449			
6-Mar-97	PWS97PAT0003	2929	2371	496	20.9	388	418	31	7.3
17-Jul-97	PWS97PAT0029	1124				246			
17-Jul-97	PWS97PAT0030	1477				377			
17-Jul-97	PWS97PAT0031	1892	1498	384	25.7	288	303	67	22.0
29-Mar-98	PWS98PAT0016	1112				120			
29-Mar-98	PWS98PAT0017	1668				451			
29-Mar-98	PWS98PAT0018	972	1251	368	29.4	144	238	185	77.6
5-Apr-00	PWS00PAT0004	1465				313			
5-Apr-00	PWS00PAT0005	1575				335			
5-Apr-00	PWS00PAT0006	1568	1536	62	4.0	412	353	52	14.7
21-Jul-00	PWS00PAT0010	2080				392			
21-Jul-00	PWS00PAT0011	3016				452			
21-Jul-00	PWS00PAT0012	2107	2401	533	22.2	571	472	91	19.4
28-Mar-01	PWS01PAT0001	2987				814			
28-Mar-01	PWS01PAT0002	1803				465			

28-Mar-01	PWS01PAT0003	2659	2483	611	24.6	564	614	180	29.3
22-Jul-01	PWS01PAT0010	1044				160			
22-Jul-01	PWS01PAT0011	1276				536			
22-Jul-01	PWS01PAT0012	1969	1429	481	33.7	311	335	189	56.4
15-Mar-02	PWS02PAT0004	2508				10			
15-Mar-02	PWS02PAT0005	2452				68			
15-Mar-02	PWS02PAT0006	3514	2825	598	21.2	149	76	70	92.2
10-Jul-02	AMT-S-2-02-1	473				192			
10-Jul-02	AMT-S-2-02-2	504				158			
10-Jul-02	AMT-S-2-02-3	551	509	39	7.7	1089	480	528	110.2
18-Mar-03	AMT-S-1-03-1	654				134			
18-Mar-03	AMT-S-1-03-2	694				271			
18-Mar-03	AMT-S-1-03-3	594	648	51	7.8	131	179	80	44.7
27-Jul-03	AMT-S-2-03-1P	604				199			
27-Jul-03	AMT-S-2-03-2P	564				132			
27-Jul-03	AMT-S-2-03-3P	522	563	41	7.3	109	147	47	31.7
27-Jul-03	AMT-S-2-03-1A	791				230			
27-Jul-03	AMT-S-2-03-2A	701				286			
27-Jul-03	AMT-S-2-03-3A	496	663	151	22.8	144	220	71	32.4
23-Mar-04	AMT-S-1-03-1	451				128			
23-Mar-04	AMT-S-1-03-2	417				231			
23-Mar-04	AMT-S-1-03-3	352	407	50	12.3	142	167	56	33.6
Alyeska Marine Terminal Intertidal Sediments (AMT-L)									
14-Jul-98	PWS98PAT0043	254				26			
14-Jul-98	PWS98PAT0044	131				38			
14-Jul-98	PWS98PAT0045	2492	959	1329	138.6	123	62	53	84.8
Gold Coast Subtidal Sediments (GOC-S)									
19-Mar-93	PWS93PAT0001	941				47			
19-Mar-93	PWS93PAT0002	436				36			
19-Mar-93	PWS93PAT0003	1460	946	512	54.1	58	47	11	23.4
25-Jul-93	PWS93PAT0071	1036				57			
25-Jul-93	PWS93PAT0072	408				31			
25-Jul-93	PWS93PAT0073	256	567	413	73.0	25	38	17	45.2
26-Mar-94	PWS94PAT0022	1429				60			
26-Mar-94	PWS94PAT0023	571				45			
26-Mar-94	PWS94PAT0024	638	879	477	54.3	106	70	32	45.2
19-Jul-94	PWS94PAT0028	385				47			
19-Jul-94	PWS94PAT0029	378				18			
19-Jul-94	PWS94PAT0030	737	500	205	41.1	68	44	25	56.6
3-Apr-95	PWS95PAT0019	463				57			
3-Apr-95	PWS95PAT0020	322				34			
3-Apr-95	PWS95PAT0021	528	438	105	24.1	31	41	14	35.0
11-Jul-95	PWS95PAT0025	750				67			
11-Jul-95	PWS95PAT0026	598				59			
11-Jul-95	PWS95PAT0027	444	597	153	25.6	31	52	19	36.1
16-Mar-96	PWS96PAT0001	588				78			
16-Mar-96	PWS96PAT0002	470				156			
16-Mar-96	PWS96PAT0003	523	527	59	11.2	33	89	62	69.9

12-Jul-96	PWS96PAT0028	541				56			
12-Jul-96	PWS96PAT0029	440				45			
12-Jul-96	PWS96PAT0030	629	537	95	17.6	52	51	6	10.9
6-Mar-97	PWS97PAT0004	624				54			
6-Mar-97	PWS97PAT0005	431				39			
6-Mar-97	PWS97PAT0006	441	499	109	21.8	40	44	8	18.9
17-Jul-97	PWS97PAT0026	514				53			
17-Jul-97	PWS97PAT0027	788				55			
17-Jul-97	PWS97PAT0028	552	618	148	24.0	60	56	3	5.7
29-Mar-98	PWS98PAT0013	341				42			
29-Mar-98	PWS98PAT0014	301				48			
29-Mar-98	PWS98PAT0015	352	331	27	8.1	38	43	5	11.6
5-Apr-00	PWS00PAT0001	590				126			
5-Apr-00	PWS00PAT0002	668				81			
5-Apr-00	PWS00PAT0003	918	725	171	23.6	126	111	26	23.4
20-Jul-00	PWS00PAT0007	966				105			
20-Jul-00	PWS00PAT0008	753				111			
21-Jul-00	PWS00PAT0009	912	877	111	12.7	92	103	10	9.3
28-Mar-01	PWS01PAT0004	904				125			
28-Mar-01	PWS01PAT0005	833				131			
28-Mar-01	PWS01PAT0006	901	879	40	4.6	120	126	5	4.2
21-Jul-01	PWS01PAT0007	311				40			
21-Jul-01	PWS01PAT0008	506				59			
21-Jul-01	PWS01PAT0009	2993	1270	1495	117.8	108	69	35	50.8
15-Mar-02	PWS02PAT0002	1568				91			
15-Mar-02	PWS02PAT0003	1165				33			
15-Mar-02	PWS02PAT0007	1407	1380	203	14.7	134	86	51	59.1
10-Jul-02	GOC-S-2-02-1	188				42			
10-Jul-02	GOC-S-2-02-2	147				46			
10-Jul-02	GOC-S-2-02-3	117	151	36	23.9	29	39	9	22.4
18-Mar-03	GOC-S-1-03-1	291				31			
18-Mar-03	GOC-S-1-03-2	368				52			
18-Mar-03	GOC-S-1-03-3	280	313	48	15.4	45	43	11	24.7
27-Jul-03	GOC-S-2-03-1P	203				31			
27-Jul-03	GOC-S-2-03-2P	179				26			
27-Jul-03	GOC-S-2-03-3P	225	202	23	11.4	115	57	50	87.9
27-Jul-03	GOC-S-2-03-1A	283				32			
27-Jul-03	GOC-S-2-03-2A	306				31			
27-Jul-03	GOC-S-2-03-3A	219	269	45	16.8	33	32	1	2.1
23-Mar-04	GOC-S-1-03-1	193				33			
23-Mar-04	GOC-S-1-03-2	316				16			
23-Mar-04	GOC-S-1-03-3	132	214	94	43.8	36	28	11	38.7
Gold Creek Intertidal Sediments (GOC-L)									
13-Jul-98	PWS98PAT0040	52				12			
13-Jul-98	PWS98PAT0041	14				5			
13-Jul-98	PWS98PAT0042	26	31	19	63.3	12	10	4	41.8

Appendix A-2 Tissue TPAH and TSHC summary for LTEMP 2003-2004.

Sample ID	Sample Date	TPAH	Mean	Std Dev	CV	TSHC	Mean	Std Dev	CV
AIB-B-2-03-1	8/1/2003	12				1136			
AIB-B-2-03-2	8/1/2003	21				1129			
AIB-B-2-03-3	8/1/2003	47	26.64	17.92	67.27	989	1084.59	83.20	7.67
AMT-B-2-03-1	7/27/2003	90				860			
AMT-B-2-03-2	7/27/2003	61				433			
AMT-B-2-03-3	7/27/2003	45	65.20	22.58	34.63	347	546.64	275.06	50.32
DII-B-2-03-1	7/29/2003	19				258			
DII-B-2-03-2	7/29/2003	44				130			
DII-B-2-03-3	7/29/2003	30	30.88	12.42	40.22	502	296.58	188.86	63.68
GOC-B-2-03-1	7/27/2003	30				485			
GOC-B-2-03-2	7/27/2003	39				456			
GOC-B-2-03-3	7/27/2003	36	35.05	4.47	12.76	574	505.18	61.71	12.21
KNH-B-2-03-1	7/28/2003	26				195			
KNH-B-2-03-2	7/28/2003	20				230			
KNH-B-2-03-3	7/28/2003	32	26.17	6.16	23.54	3428	1284.32	1856.52	144.55
SHB-B-2-03-1	7/28/2003	67				539			
SHB-B-2-03-2	7/28/2003	15				456			
SHB-B-2-03-3	7/28/2003	27	36.35	27.25	74.96	372	455.65	83.56	18.34
SHH-B-2-03-1	8/1/2003	15				786			
SHH-B-2-03-2	8/1/2003	21				514			
SHH-B-2-03-3	8/1/2003	16	17.44	2.70	15.50	920	739.86	206.49	27.91
SLB-B-2-03-1	7/29/2003	35				140			
SLB-B-2-03-2	7/29/2003	65				0			
SLB-B-2-03-3	7/29/2003	75	57.86	20.83	36.01	0	46.60	80.71	173.21
WIB-B-2-03-1	8/1/2003	23				889			
WIB-B-2-03-2	8/1/2003	42				836			
WIB-B-2-03-3	8/1/2003	23	29.05	11.02	37.95	738	821.18	76.94	9.37
ZAB-B-2-03-1	7/29/2003	42				0			
ZAB-B-2-03-2	7/29/2003	54				132			
ZAB-B-2-03-3	7/29/2003	111	68.89	37.17	53.95	360	163.98	182.23	111.13
AMT-B-3-03-1	10/7/2003	46				310			
AMT-B-3-03-2	10/7/2003	64				311			
AMT-B-3-03-3	10/7/2003	66	58.68	10.91	18.58	406	342.14	55.05	16.09
GOC-B-3-03-1	10/7/2003	72				358			
GOC-B-3-03-2	10/7/2003	45				412			
GOC-B-3-03-3	10/7/2003	46	54.26	15.56	28.69	282	350.29	65.35	18.65
AIB-B-1-04-1	3/20/2004	83				3933			
AIB-B-1-04-2	3/20/2004	40				57			
AIB-B-1-04-3	3/20/2004	21	48.16	31.54	65.49	0	1330.20	2254.38	169.48
AMT-B-1-04-1	3/21/2004	120				94			
AMT-B-1-04-2	3/21/2004	53				0			
AMT-B-1-04-3	3/21/2004	39	70.92	43.48	61.31	24	39.27	48.98	124.71
DII-B-1-04-1	3/17/2004	69				89			
DII-B-1-04-2	3/17/2004	70				117			
DII-B-1-04-3	3/17/2004	72	70.20	1.61	2.29	42	82.71	37.73	45.61

GOC-B-1-04-1	3/21/2004	139				78			
GOC-B-1-04-2	3/21/2004	91				107			
GOC-B-1-04-3	3/21/2004	118	116.01	23.76	20.48	100	95.03	15.15	15.94
KNH-B-1-04-1	3/23/2004	7				144			
KNH-B-1-04-2	3/23/2004	17				99			
KNH-B-1-04-3	3/23/2004	10	11.37	4.95	43.49	45	96.21	49.51	51.46
SHB-B-1-04-1	3/17/2004	44				281			
SHB-B-1-04-2	3/17/2004	74				249			
SHB-B-1-04-3	3/17/2004	51	56.57	15.76	27.86	187	239.03	47.85	20.02
SHH-B-1-04-1	3/15/2004	23				131			
SHH-B-1-04-2	3/15/2004	64				213			
SHH-B-1-04-3	3/15/2004	42	43.11	20.50	47.56	200	181.53	43.80	24.13
SLB-B-1-04-1	3/17/2004	56				202			
SLB-B-1-04-2	3/17/2004	36				265			
SLB-B-1-04-3	3/17/2004	53	48.33	11.08	22.93	376	281.27	88.21	31.36
WIB-B-1-04-1	3/15/2004	92				276			
WIB-B-1-04-2	3/15/2004	44				118			
WIB-B-1-04-3	3/15/2004	45	60.34	27.60	45.74	176	189.88	79.56	41.90
ZAB-B-1-04-1	3/17/2004	44				212			
ZAB-B-1-04-2	3/17/2004	33				43			
ZAB-B-1-04-3	3/17/2004	47	41.22	7.04	17.08	222	159.09	100.36	63.08

Appendix A-3 Station Accounts for Tissue Samples

A-3.1 Alyeska Marine Terminal (AMT)

During the early years of the LTEMP program, tissue hydrocarbon burdens at Alyeska Marine Terminal (AMT) were highly variable and reflected both particulate-phase (oil droplet) and dissolved-phase signals (Figures 38 and 39). TPAH concentrations between April 1993 and July 1996 ranged from a low of less than 100 ng/gram dry weight to a high of over 14,400 ng/gram dry weight in May 1995 (Figure 36), with the latter occurrence due to the ANS crude oil released during the *Eastern Lion* oil spill at the terminal. Elevated residues of particulate/oil-phase ANS crude oil (averaging over 1500 ng/gram dry weight) were still observed in July 1994.

Particulate-to-dissolved ratio (PDR) values during the early years suggested the seasonally-controlled input of primarily oil-droplet/particulate-phase hydrocarbons during the winter months and dissolved-phase hydrocarbons during the summer months (Payne et al. 2001; 2003a). During the interval from January 1997 through August 1999, TPAH concentrations at the terminal were relatively constant around 500 ng/gram dry weight (with the exception of July 1998 when the overall concentrations decreased again). Note: there is an overall drop in TPAH concentrations at all sites throughout the program in July 1998 (Figure 36); however, it is not known if this reflects some procedural artifact or if it may be due to a region-wide perturbation. The PDR values during this time suggested primarily a particulate/oil phase signal, with generally higher PDR ratios during the March sampling periods. Beginning in October 1999, the TPAH values dropped to between 100 and 200 ng/gram dry weight and they remained at these lower levels until March 2001. The PDR value of 5 for that sample suggested a strong particulate/oil phase signal, as confirmed by the PAH histogram plots (Figure 41) showing weathered oil droplets containing alkylated phenanthrenes/anthracenes and dibenzothiophenes. Intermediate TPAH values (200-450 ng/gram dry weight) were observed in October 2001 and March 2002 with the typical seasonally-controlled PDR values suggesting more of a particulate/oil phase signal during the winter months. Beginning in July 2002 the TPAH values have been consistently very low (less than 100 ng/gram dry weight) through March 2004. The PDR values again suggest the predominance of a particulate/oil-phase sample during the winter, with dissolved-phase signals predominating in the summer and fall.

As described above and in Payne et al. (2003a), there were numerous problems with lipid interference in the aliphatic hydrocarbon analyses completed during the early years of the LTEMP program. This was particularly problematic in low-level samples. An exception to this occurred in May 1994 after the *Eastern Lion* oil spill when higher concentrations of petroleum derived SHC were clearly observed due to the recently spilled oil (Figure 42). Even in this instance, however, exceptionally high values of pristane (80,000, 55,000, 90,000 ng/gram dry weight) were reported, and this single component is responsible for most of the spike in TSHC shown at that time in Figure 40. These values were higher than any others observed during the LTEMP program and the possibility of a laboratory artifact or lipid interference cannot be completely eliminated. Nevertheless, the presence of

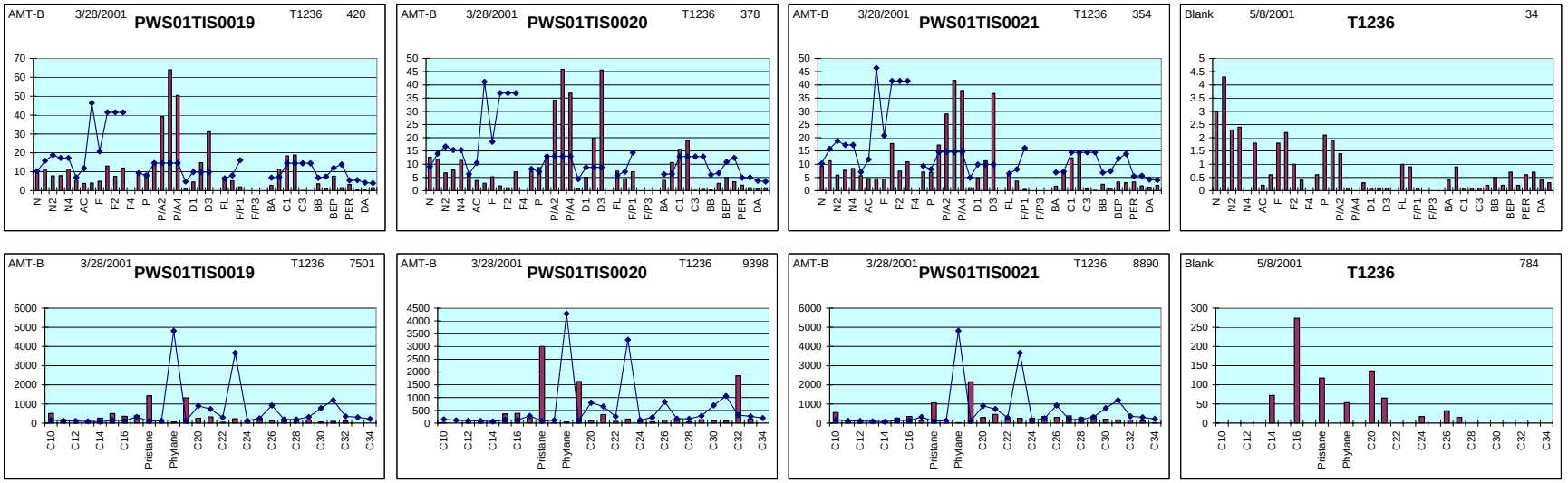

Figure 41. PAH and SHC histograms for mussel tissues at AMT in March 2001 showing a particulate/oil-phase PAH signal and a primarily biogenic SHC pattern.

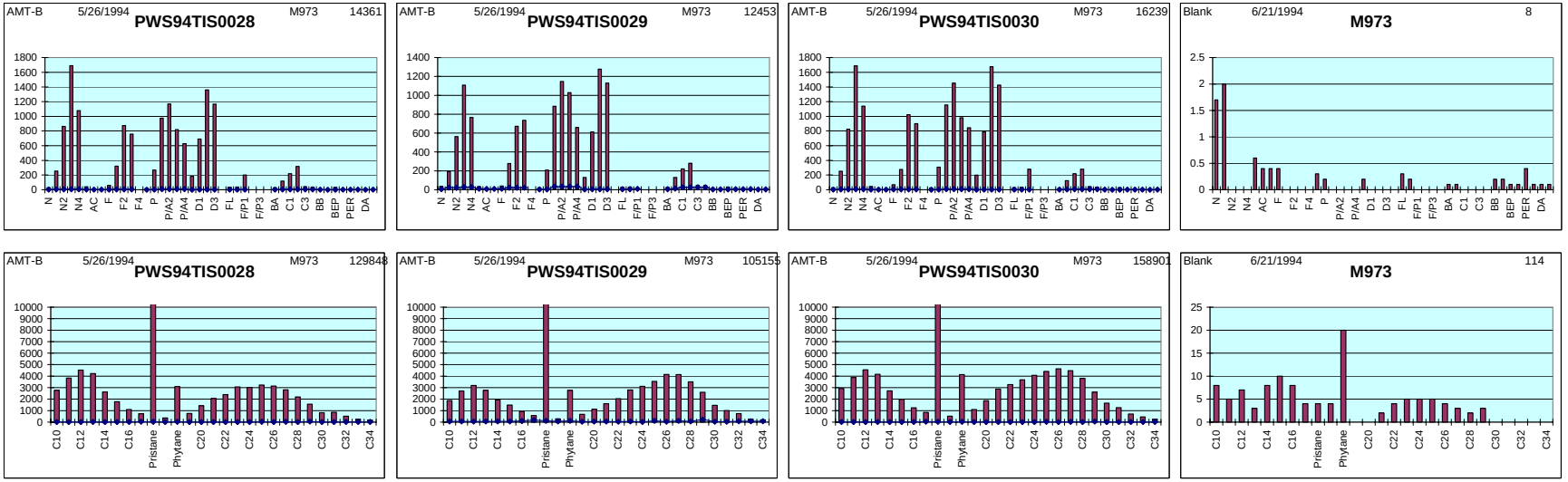

Figure 42. PAH and SHC histograms for mussel tissues at AMT in May 1994 after the *Eastern Lion* oil spill. Note, pristane is off scale in all three SHC plots at 80,000, 55,000, and 90,000 ng/g dry wt. Both the PAH and SHC profiles reflect whole oil droplets.

phytane and the bimodal distribution of even and odd n-alkanes is clearly demonstrative of whole-oil droplets, in agreement with the PDR values for the PAH components discussed above. Whole-oil droplet residues continued to be reflected in the SHC patterns obtained in July 1994, and the PDR value for the measured PAH also reflected particulate-phase oil. Saturated hydrocarbon analyses were discontinued at the request of the analytical laboratory in spring 1995 because of the aforementioned lipid interference problem. Saturated hydrocarbon analyses were initiated again during the summer of 1998, however, continued lipid interference problems plagued the analytical program as described in the 2002/2003 LTEMP final report (Payne et al. 2003a). As a result of these problems, unrealistically high total saturated hydrocarbon (TSHC) concentrations were often reported, and we have little faith in the tissue SHC data between the period of July 1998 and March 2002. With the initiation of analyses by the Auke Bay laboratory in July 2002, more realistic SHC profiles and overall concentrations were obtained. Since that time, the TSHC values at Alyeska Marine Terminal have trended in the range of around 800-4300 ng/gram dry weight (Figure 40), and the precision associated with the triplicate measurements has been very tight. For the most part, biogenic components (n-C_{15}, n-C_{17}, and pristane derived from marine algae and copepods) are typically observed at or just above the laboratory method reporting limit during the spring collections (Figure 43). Occasionally, phytane and higher-molecular-weight components (n-C_{22} through n-C_{33}) indicative of weathered ANS crude oil residues have been observed (July and October 2003) as shown in Figure 44. Even in these instances, however, the individual n-alkanes are just barely above the method reporting limits, and taken in total, the TSHC values were in the range of only 3,200-4,400 ng/gram dry weight. In March 2004, the TSHC values were significantly reduced and ranged from only 747-852 ng/gram dry weight, with little evidence of significant petroleum-hydrocarbon contamination. At that time, the signals suggested a mixture of biogenic components of both marine and terrestrial origin.

Based on the general decreasing trend of TPAH over this 11 year period and the appearance of the SHC profiles over the last 2 years, it appears that operations at the BWTF are improving, such that significantly lower concentrations of TPAH and petroleum-derived SHC components are seen. This is particularly true for the particulate/oil-droplet-phase signals. Surrogate recoveries for both deuterated PAH and SHC have continued to be good, so these observed decreases are not due to a laboratory or procedural artifact, and instead reflect actual changes in the field. This improvement may theoretically reflect lowered daily effluent volumes from the BWTF or operational improvements in the removal efficiency of dissolved and particulate/oil-phase residues from the BWTF effluent.

A-3.2 Gold Creek (GOC)

At Gold Creek (GOC), the TPAH values for the mussel tissues (Figure 36) are consistently lower than those observed at AMT. There is greater seasonal variability during the earlier years of the program, but there is clearly particulate-phase oil contamination observed in March 1993 (PDR = 2.65). The concentrations dropped dramatically in July 1993, and then increased again in March and July 1994. The PDR value of 5.04 for the March 1994

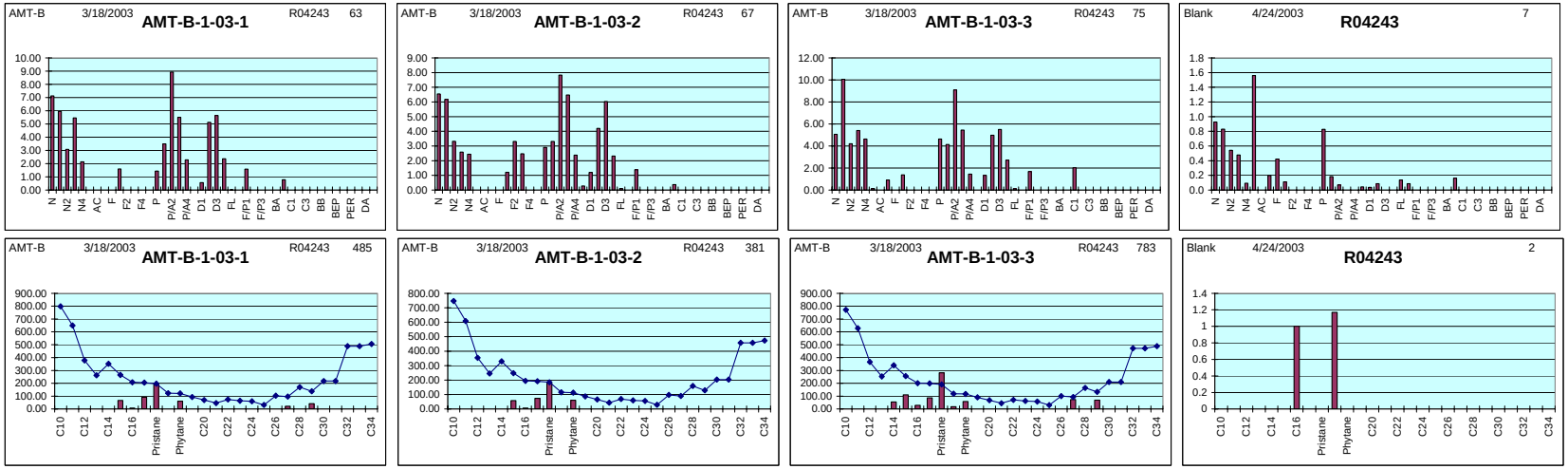

Figure 43. PAH and SHC histograms for mussel tissues at AMT in March 2003. A mixture of dissolved and particulate/oil-phase hydrocarbon sources in the PAH profiles (1.7 PDR), while the SHC are primarily marine biogenic with a trace of whole oil phytane.

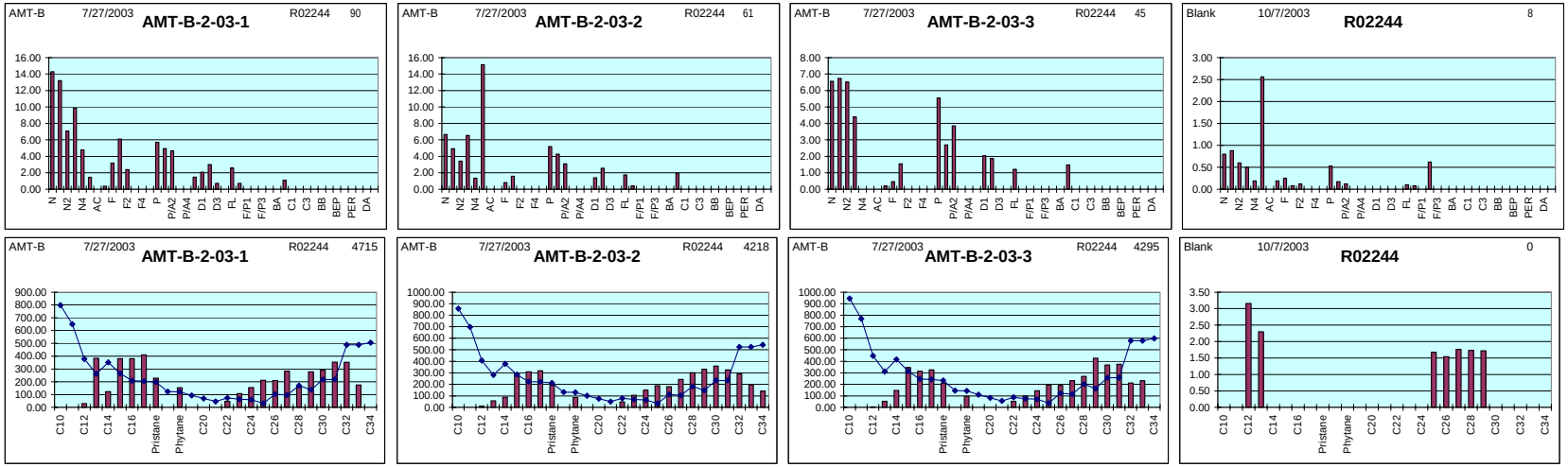

Figure 44. PAH and SHC histograms for mussel tissues at AMT in July 2003. The PAH suggest a dissolved-phase signal (0.7 PDR) while the SHC reflects particulate oil (or possibly bacterial sources).

samples clearly shows the presence of particulate-phase oil in the PAH histogram plots (Figure 45). The apparent increase from the July 1994 samples has been previously attributed to residues from the *Eastern Lion* oil spill at the Alyeska Marine Terminal in May 1994. Interestingly, the PDR value of 0.85 for the July 1994 samples (where the TPAH value was the highest) suggests primarily a dissolved-phase signal; however, this is not reflected in the PAH profiles, which clearly show a particulate/oil-phase pattern (Figure 46). The reason for the anomalously low PDR value is due to the fact that fluorenes are omitted in the PDR calculation to compensate for the lipid interference problems later in the program (particularly in July 1999). In this case, the PAH profiles in Figure 46 clearly show a water-washed fluorene pattern that is consistent with weathered ANS oil. If the fluorenes are included in the PDR calculation for these three samples, an average revised PDR value of 2.15 is obtained, which clearly reflects the particulate/oil-phase signal from the *Eastern Lion* oil spill in those samples. Slightly elevated TPAH values are suggested during the interval from March 1997 through March 1999 (particularly during the spring samplings); however, as described above and in Payne et al. (2003a), this apparent increase in TPAH values may reflect a procedural artifact associated with increased sensitivity from GC/MS instrumentation changes at the analytical laboratory during that time interval. The apparent increase in TPAH value to nearly 1,000 ng/gram dry weight in August 1999 appears to be an artifact due to exceptionally-high fluorene concentrations due to incomplete separation of lipids during sample cleanup at the laboratory (see Payne et al. 2003a). TPAH concentrations are then reduced significantly to less than 200 ng/gram dry weight between October 1999 and July 1991. There is an apparent increase in TPAH concentrations in October 2001 and March 2002, however, the PDR values clearly suggests that the source of these TPAH are from the dissolved-phase, and as a result, accurate source identification is not possible. Overall TPAH concentrations have remained extremely low (generally less than 100 ng/gram dry weight) at Gold Creek since July 2002. The PDR values suggest the reappearance of the seasonally controlled particulate/oil-phase versus dissolved phase signal during this time period; however, most of the PAH are below the laboratory method reporting limit.

The same lipid interference problems described above compromised many of the early low-concentration SHC profiles for Gold Creek; however, the samples collected in July 1994 (Figure 46) clearly reflected a recognizable pattern due to a mixture of marine biogenic (n-C_{15}, n-C_{17}, and pristane) components in addition to petroleum (phytane, plus somewhat equivocal n-C_{23} through n-C_{33}) residues, which presumably came from the *Eastern Lion* oil spill at the terminal. As noted above, SHC analyses were discontinued from March 1995 through March 1998. Continued lipid interference problems between July 1998 and July 2002 rendered much of those data useless, but occasionally biogenic patterns at Gold Creek could be recognized. Still, there was little or no evidence of significant petroleum-hydrocarbon contamination in agreement with the TPAH measurements and PDR values obtained during that time frame. Since the initiation of analyses at ABL in July 2002, there has been no reoccurrence of the lipid interference problem, and profiles reflecting primarily low-level biogenic inputs have been observed. The only exceptions are trace-level biogenic and very minor petrogenic signals in July and

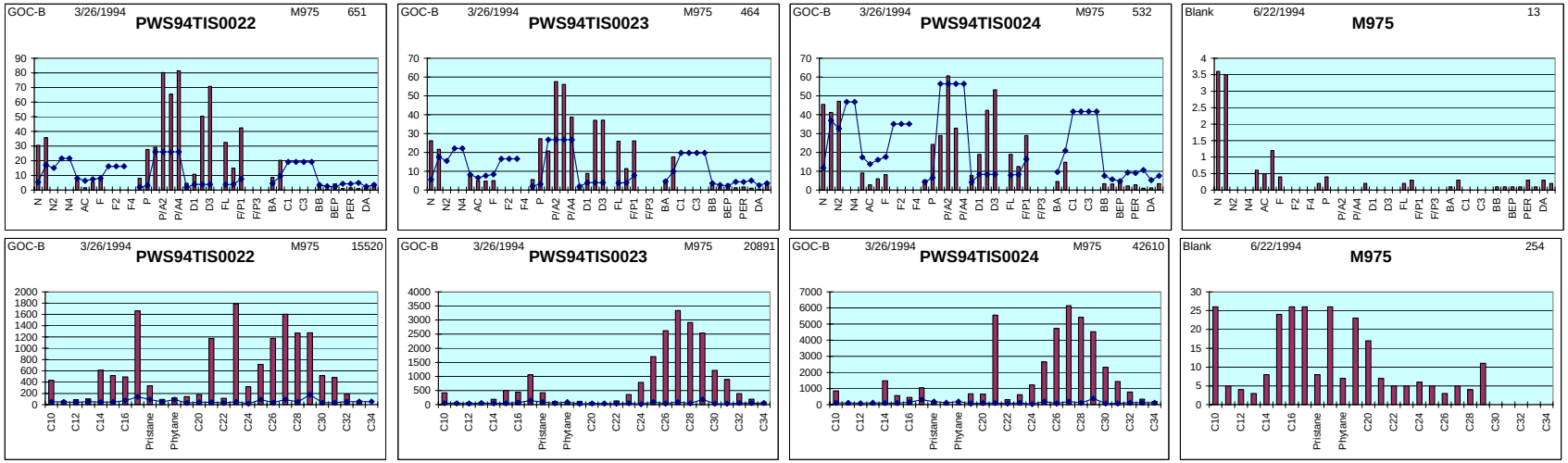

Figure 45. PAH and SHC histograms for mussel tissues at GOC in March 1994. The PAH patterns suggest a primarily particulate/oil-phase signal while the SHC patterns show marine biogenic components and the n-C_{24} to n-C_{32} lipid interference pattern.

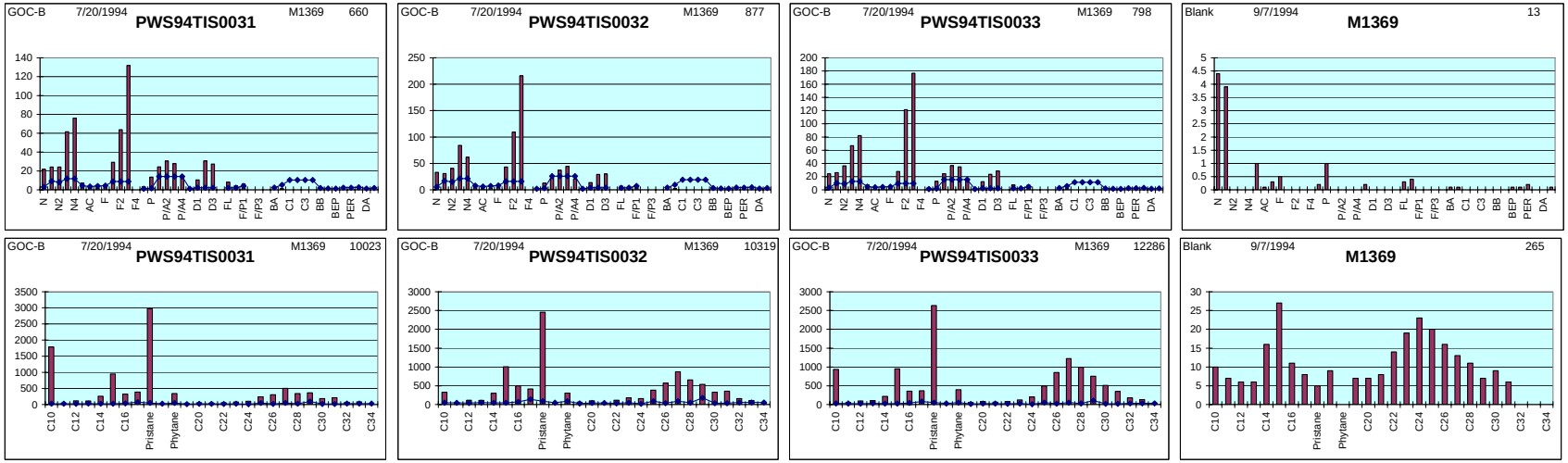

Figure 46. PAH and SHC histograms for mussel tissues at GOC in July 1994 showing residual contamination from the *Eastern Lion* oil spill. The presence of phytane in the SHC profiles confirms the presence of particulate-phase oil, although the n-C_{24} to n-C_{32} pattern may or may not be associated with petroleum contamination as it might also be due to lipid interference.

October 2003 (TPAH < 100 ng/g dry weight) and March 2004 (Figure 47). Although the TPAH values associated with these latest samples are low (less than 150 ng/gram dry weight) the PDR values show a slight increase in complexity reflecting both a dissolved and a particulate/oil-phase source in agreement with the SHC profiles.

A-3.3 Aialik Bay (AIB)

The TPAH values measured at this site were consistently low from 1993 through March 1997 (Figure 36), and for the most part, the PAH histogram plots suggest that what was reported came primarily from procedural artifacts (see Figures 38 and 39 and Payne et al. 2003a). Beginning in July 1997 through April 1998 there was an apparent increase in TPAH, although the PDR values clearly suggested predominantly a dissolved-phase signal. As mentioned previously (Payne et al. 2003a), this apparent increase during this time frame also may be due to increased instrument sensitivity introduced by a newer GC/MS installed in the laboratory during this time frame. Beginning in July 1998 the TPAH values have been consistently low (with one sample set in August 1999 (Figure 48) showing relatively higher TPAH concentrations and greater variability).

Close examination of the PAH histogram plots for the August 1999 samples, however, reveals fluorene contamination due to inadequate lipid cleanup in the laboratory (see discussion in Payne et al. 2003a), so this apparent increase in the overall trend line is not believed to reflect conditions in the field. Since March 2000, the TPAH values have been consistently very low (generally less than 100 ng/gram dry weight), and the PDR values clearly show the predominance of the dissolved-phase signal throughout this time frame (Figure 36). The majority of PAH are below the method reporting limit, and in some instances reflect patterns similar to those observed (albeit at lower concentrations) in laboratory blanks. This site is currently very clean, and the most recent set of PAH profiles do not reflect any petroleum hydrocarbon contamination at this time.

Like most of the other cleaner LTEMP sites, the SHC measurements during the early years of the program were confounded by excessively high levels of lipid interference. As a result, much of the higher-molecular-weight (n-C_{22} through n-C_{32}) SHC data are of no value. It is possible to make out just-above-the method detection limit concentrations of n-C_{15}, n-C_{17}, and pristane (suggesting marine biogenic sources) in many of the samples. Based on these data, the general absence of phytane, and the PAH profiles, there doesn't appear to be any petroleum hydrocarbon contamination at this site through at least August 1994. As at the other sites, SHC analyses were discontinued between March 1995 and March 1998. After SHC analyses were initiated again, the data continued to be somewhat erratic (Figure 40) and equivocal, with continued interference from lipids plus low-level biogenic hydrocarbons noted. As such, the SHC patterns do not help to confirm the presence of petroleum leading to the apparent increase in TPAH in the July 1997 and April 1998 timeframe noted in Figure 36. Since the initiation of SHC analyses at the Auke Bay Laboratory in July 2002, there have been no lipid interference problems, and all of the histogram plots suggest only near MDL levels of marine-biogenic hydrocarbons (n-C_{15}, n-C_{17}, and pristane) and no evidence petroleum-hydrocarbon contamination in agreement with the PAH profiles for the site.

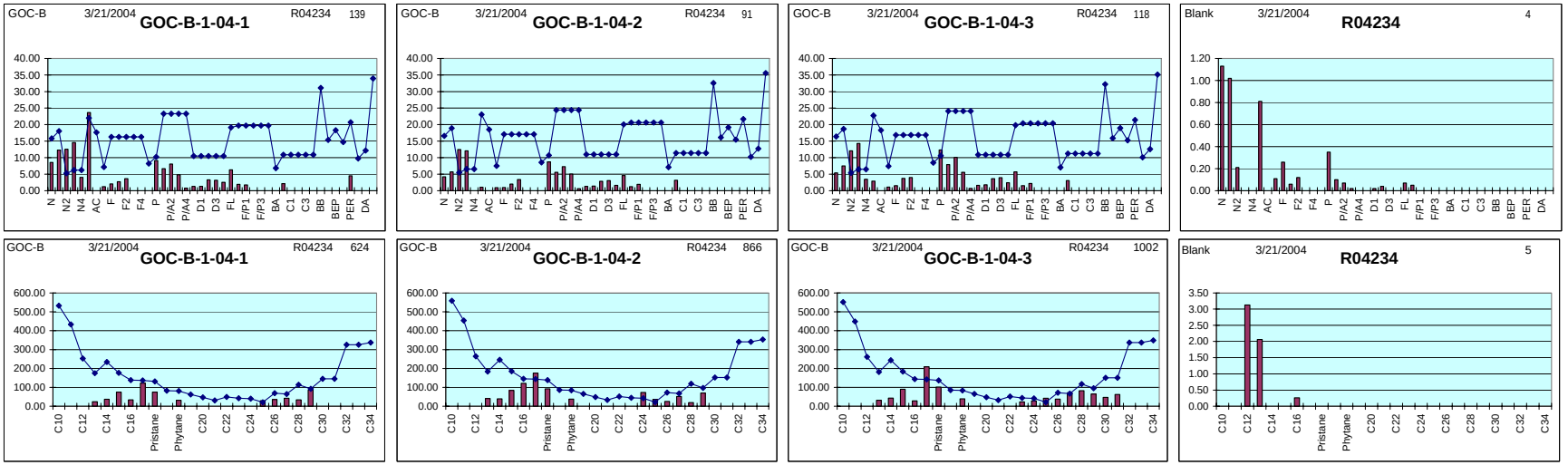

Figure 47. PAH and SHC histograms for mussel tissues at GOC in March 2004 showing a predominately dissolved-phase PAH signal (PDR = 1.08) and a marine biogenic SHC pattern with a trace of phytane from particulate-phase oil and terrestrial plant waxes.

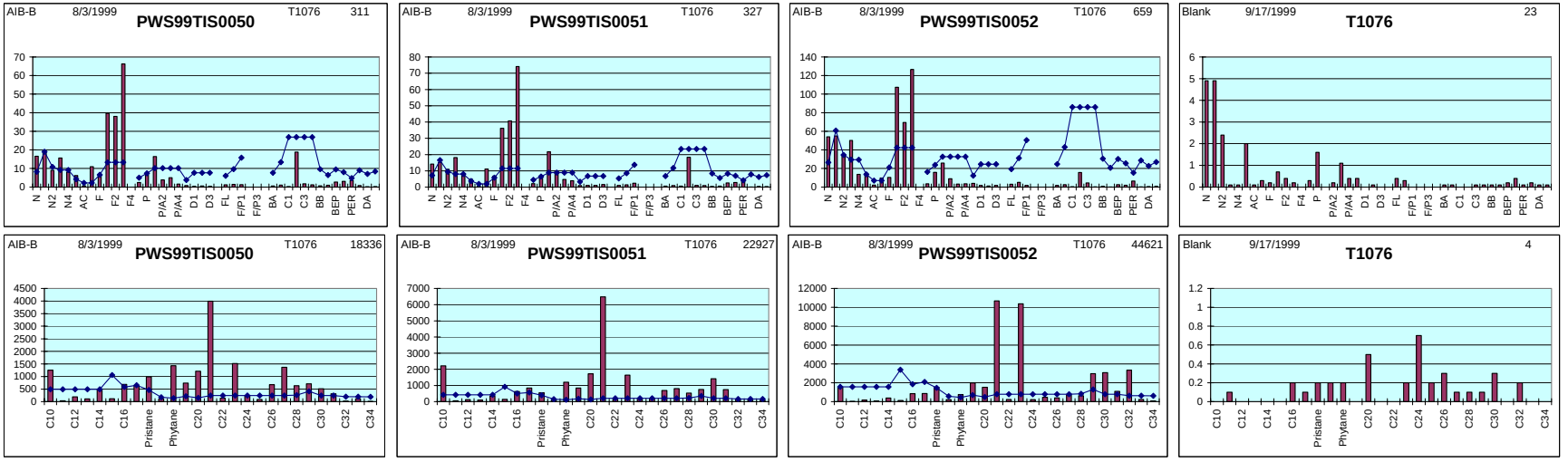

Figure 48. PAH and SHC histograms for mussel tissues at AIB in August 1999. The anomalous fluorene pattern (F1, F2, F3) from interfering lipids is clearly apparent against a background of primarily dissolved-phase PAH, and the SHC profiles are dominated by n-C_{21} and n-C_{23} (at concentrations in the 4,000 – 10,000 ng/g dry weight range) due to inadequate sample cleanup in the laboratory.

A-3.4 Disk Island (DII)

The TPAH and PDR plots in Figure 36 for Disk Island (DII) show several interesting trends over time that can largely be explained by beach cleaning operations in the early 1990s to remove residual *Exxon Valdez* oil. The initial samples collected in March 1993 and July 1993 were extremely clean, and reflected only the low-level laboratory procedural artifact pattern in five of the six samples. One of the three replicates collected in March 1993 showed evidence of higher-molecular-weight particulate/oil-phase alkylated phenanthrenes/anthracenes and chrysenes, and this is reflected in the relatively high PDR value and larger standard error bars associated with the PDR value for that sample. In March 1994 two of the three replicates reflected particulate/oil-phase PAH contamination causing the observed increase in TPAH and PDR values (also note the larger standard error bars associated with the PDR value). During the summer of 1994 beach cleaning operations were undertaken, and the oil released during these efforts is clearly reflected in the PAH profiles shown in Figure 49 and the elevated TPAH values (800 ng/gram dry weight) and the PDR value of 2.6 suggesting a primarily particulate/oil-phase source. The overall TPAH values dropped by March 1995; however, two of the three replicates showed significant particulate/oil-phase PAH components as reflected by the elevated PDR value of 4.8. By July 1995 all of the previously observed petroleum hydrocarbon contamination was gone with total PAH concentrations of less than 200 ng/gram dry weight reported for the July 1995 and March 1996 samples. In fact, close examination of the PAH profiles generated during this time frame revealed that none of these PAH were due to petroleum contamination, and instead they reflected the pattern ascribed to laboratory artifacts. This laboratory artifact pattern persisted in two of the three samples collected in July 1996, while one sample reflected particulate/oil-phase petroleum hydrocarbon contamination. In March 1997 all three replicates exhibited elevated TPAH levels and contributions primarily from alkylated-phenanthrenes/ anthracenes, dibenzothiophenes, and chrysenes derived from the particulate/oil-phase. TPAH concentrations were still relatively high in July 1997 and March 1998, however most of the constituents were derived from dissolved phase sources as shown by the PDR values in Figure 36. After July 1998 the TPAH values have been consistently low and derived almost exclusively from dissolved-phase sources. The one apparent exception to this in July 1999 (where elevated TPAH values were reported) is due to contributions from alkylated fluorenes that are believed to be due to lipid interference in those samples. In recent years the TPAH values at this site have generally been below 50-100 ng/g dry weight, and there have been no samples exhibiting any evidence of significant petroleum hydrocarbon contamination (Figure 50).

As that the other sites in the early years of the LTEMP program the tissue SHC data from Disk Island (DII) cannot be used to confirm the presence of petroleum hydrocarbon residues. Most of the samples reflect low-level biogenic aliphatics of marine origin plus significantly higher levels of n-alkanes in the n-C_{22} through n-C_{32} range that are believed to be due to lipid interference. This is particularly unfortunate because the TPAH and PDR values clearly suggest particulate/oil-phase hydrocarbon contamination in July 1994, and this was attributed to beach cleaning operations at the site. From this standpoint, it

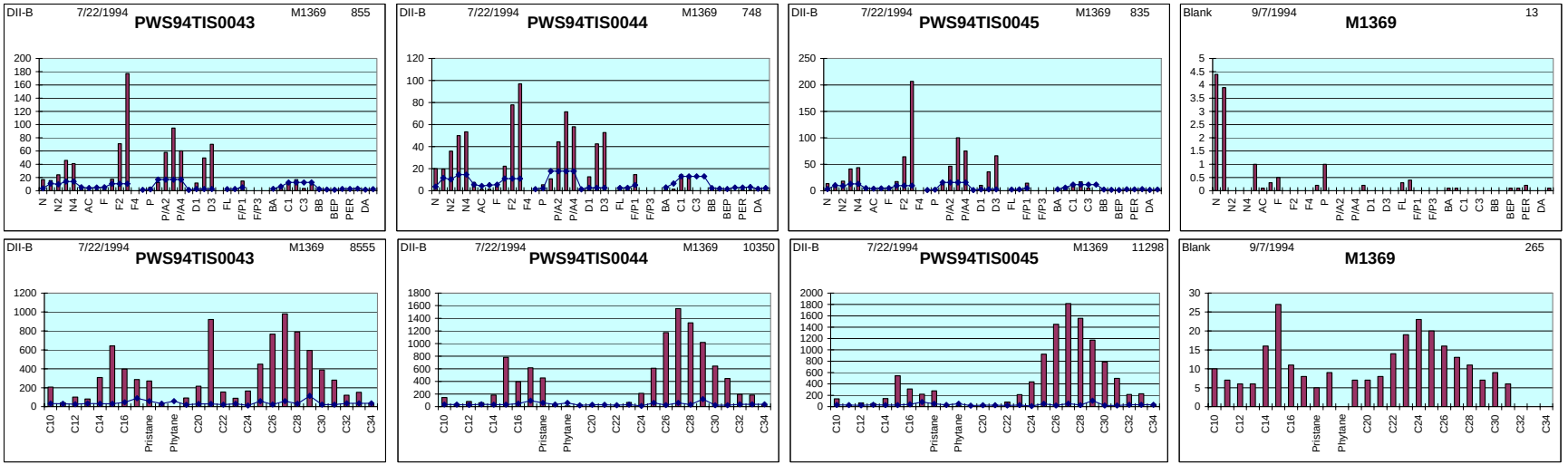

Figure 49. PAH and SHC histograms for mussel tissues at DII in July 1994. The PAH profiles clearly show heavily weathered particulate/oil-phase components released during beach-cleaning operations, but this is not reflected in the SHC profiles, which show little or no phytane, and only marine biogenic components plus interference from n-alkanes due to incomplete lipid removal.

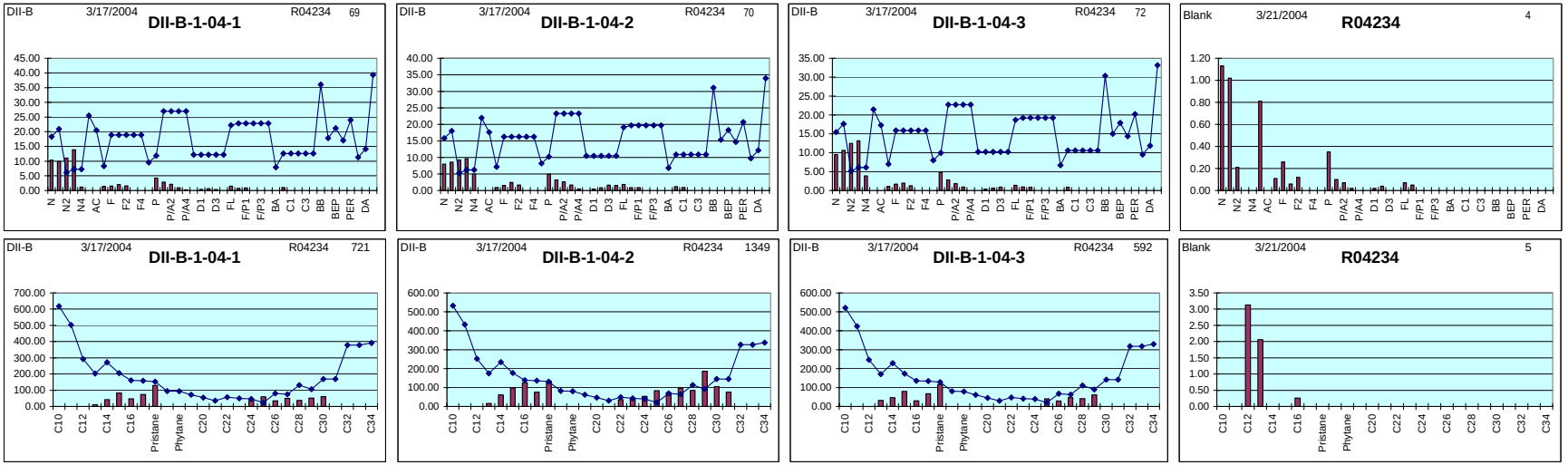

Figure 50. PAH and SHC histograms for mussel tissues at DII in March 2004. The PAH reflect < MDL dissolved-phase signals, while the SHC plots show <MDL contributions from copepods, terrestrial plant waxes, and possibly microbial sources.

would have been nice to obtain confirmatory evidence of biodegraded aliphatic compounds of petroleum origin in the SHC profiles, but as shown in Figure 49 this simply wasn't observed. When SHC hydrocarbon analyses were initiated again in July 1998 the observed patterns reflected primarily marine biogenic sources and occasional lipid interference. In July 1999 when the TPAH signal appeared to suggest increased PAH levels, the SHC profile reflected only biogenic pattern from marine and possibly terrestrial sources. In April 2000 phytane was detected in two of the three replicates suggesting possible particulate-phase oil; however, this was not reflected in either the TPAH or PDR values reported on those samples. Thus, there again appears to be a disconnect between the SHC and PAH analyses, and no meaningful trends can be defined between July 2000 and March 2002. After tissue analyses were undertaken by the Auke Bay Laboratory in July 2002, the lipid interference problems were eliminated and only marine biogenic sources were noted through March 2004. As in the samples at Sheep Bay (SHB) and Shuyak Harbor (SHH), there appeared to be just above-the-MDL traces of higher-molecular-weight n-alkanes of microbial origin in two of the three samples collected in July 2003 and one of the three replicates collected in March 2004 (Figure 50). Based on the low levels of the TPAH and PDR values discussed above, none of these higher-molecular-weight n-alkanes are believed to be due to petrogenic sources.

A-3.5 Knowles Head (KNH)

The TPAH and PDR plots in Figure 36 for Knowles Head (KNH) show what appears to be low but variable total PAH levels during the first four years of the program (March 1993 through March 1996). Closer examination of the PAH profiles generated during this period, however, reveals nothing more than the pattern attributed to low-level procedural artifacts in the majority of the samples. Most of the constituents are below the laboratory reporting limit, and with the possible exception of the July 1994 samples (Figure 51), there is little or no evidence of any petroleum hydrocarbon contamination at this site during this period. Furthermore, in the July 1994 samples, naphthalenes and alkylated fluorenes make up most of the TPAH, so it is not a typical oil profile. This is corroborated by the SHC plots described below -- the 3 replicate samples from this time period show only low-level marine biogenic patterns plus lipid interference. The apparent increase in TPAH levels in July 1996 looks like it might possibly be from a particulate/oil-phase source (as reflected in the increased PDR value) with a continuing increase in total PAH in March 1997 through July 1997, but there is a shift towards a much more dissolved-phase signal over this timeframe (Figure 36). Figure 52 presents the PAH histogram plots for mussel tissues at this station from July 1996 through July 1998. The subtle changes in PAH patterns (reflecting a change in the particulate versus dissolved phase of the source) suggests that the observed profiles are real and not just due to increased sensitivity associated with the GC/MS instrumentation change implemented at the laboratory over this period. Unfortunately, there were no SHC analyses completed at this time to provide additional insight on these samples. The sudden drop in TPAH levels in July 1998 and March 1999 (and slight increase in complexity as noted by the change in the PDR values) corresponds to similar shifts at Windy Bay, Shuyak Harbor, Sheep Bay, and Aialik Bay (although at Aialik Bay the PDR complexity decreased). This type of across-region shift is believed to

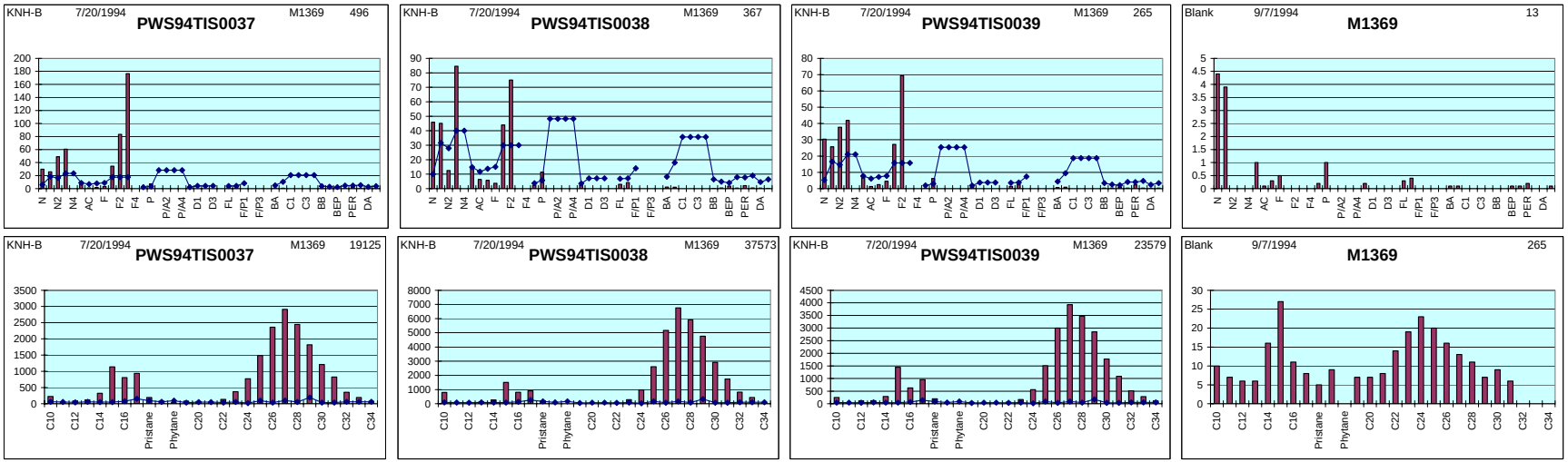

Figure 51. PAH and SHC histogram plots for mussel tissue at KNH in July 1994. The PAH profiles show elevated TPAH, but the major contribution is from alkylated fluorenes and naphthalenes suggesting a primarily dissolved-phase source. The SHC plots show only marine biogenic components, no phytane, and possible higher-molecular-weight lipid interference.

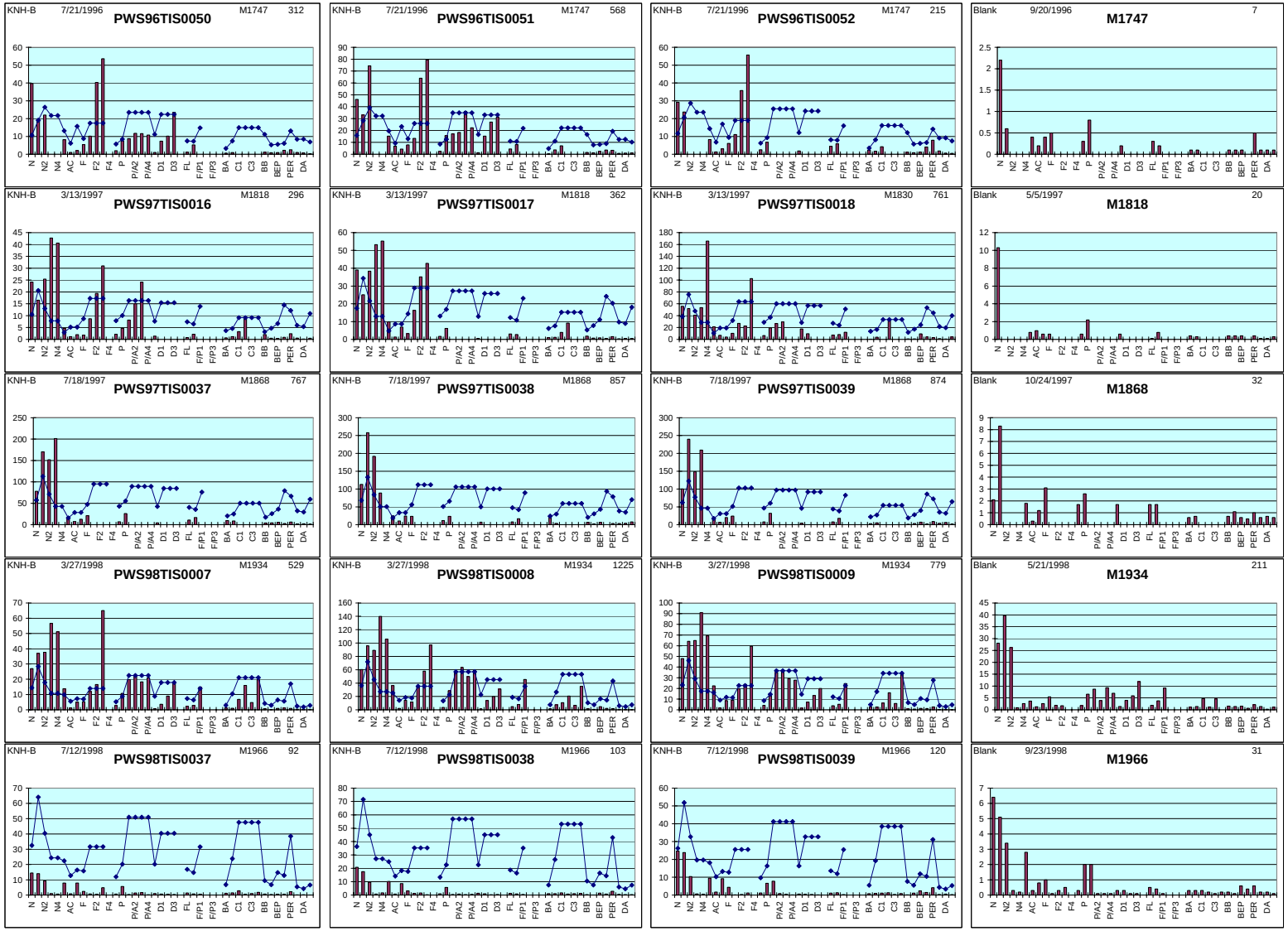

Figure 52. PAH histogram plots for mussel tissue at KNH from July 1996 through July 1998. These profiles show the shift in phase from a mixed particulate/oil-phase plus dissolved signal in July 1996 to a dissolved-phase signal over this time interval along with the significant drop in TPAH in July 1998. There are no corresponding SHC profiles for these samples.

be unlikely, and as discussed by Payne et al. (2003a), may reflect some procedural bias. It was not observed at Alyeska Marine Terminal, Disk Island, Sleepy Bay, however, so it may in fact be real. The PAH profiles for the July 1998 samples are certainly cleaner than those obtained from the March 1998 collection, although the profile was very similar to that observed in the laboratory procedural blank run with this suite of samples. The samples run in March 1999 show slightly greater complexity as reflected in the increased TPAH and PDR values in Figure 36, but the apparent increase in TPAH for the July 1999 samples again reflects significant contributions from alkylated fluorenes (due to interference from incomplete lipid removal), and as such the samples are not believed to reflect increased petroleum hydrocarbon contamination. After April 2000 the overall TPAH levels are generally quite low (below 200 ng/gram dry weight), and most of the individual PAH are below the respective laboratory method reporting limits. The absence of any higher-molecular-weight PAH suggests a primarily dissolved-phase signal as reflected in the very low PDR values; however, the individual PAH concentrations are so low that little more can be said about the source. Also, a similar suite of lower-molecular-weight PAH (at significantly lower concentrations) was observed in the procedural blanks run with the samples. From these data can be concluded that there has been no significant petroleum hydrocarbon contamination at Knowles Head since March 1998, although here again the procedural blank associated with the March 1998 samples was fairly contaminated (Figure 52).

As in most of the other cleaner sites examined in the early years of the LTEMP program, the SHC profiles generated between March 1993 and July 1994 reflected primarily marine biogenic signals and probable interference from higher-molecular-weight lipids. These observations would corroborate the lack of petrogenic signals observed in the PAH analyses. As noted above, the possible presence of petroleum-derived PAH in the July 1994 samples was not supported by the SHC data. Unfortunately no SHC data are available between July 1994 and July 1998, so it is not possible to corroborate the possible petroleum hydrocarbon signal seen in the PAH analyses in July 1997 and March 1998. When SHC analyses were resumed in July 1998, only marine biogenic hydrocarbons and traces of possible terrestrial biogenic hydrocarbons were observed. In March 1999 an unusual n-C_{24} through n-C_{32} pattern was observed, but it too could have been due to lipid interference, and the TPAH values were low at less than 200 ng/gram dry weight. Thus, there didn't appear to be any petroleum hydrocarbon contamination at that time. In the July 1999 samples the SHC profiles were characterized by high levels of n-C_{21}, n-C_{23}, and n-C_{29}, but these were believed to reflect lipid interference due to the high fluorene signals in the PAH analyses. All three replicates collected in April 2000 had SHC profiles that suggested a mixture of marine biogenic hydrocarbons and possibly at-method-detection-limit petroleum components. The total SHC value was significantly lower than earlier samples, however, and the PAH profiles did not corroborate the presence of petroleum. In July 2000, one of the three replicates showed high concentrations of phytane and higher-molecular-weight (n-C_{24} through n-C_{33}) components that suggest hydrocarbon contamination; however, this was not reflected in the PAH patterns discussed above. Unusually high concentrations of phytane were observed in two of three replicates in March 2002; however, the rest of the SHC components did not resemble fresh or weathered petroleum. The TPAH levels were slightly elevated (around 200 ng/gram dry weight) compared to samples collected both before and after that time period, but the PDR

values dropped to around 0.27 suggesting primarily a dissolved-phase signal in the PAH profiles. This lack of agreement between the SHC and PAH profiles from the March 2002 samples makes it impossible to determine if, in fact, there really was trace level hydrocarbon contamination at that time or not. After July 2002, when the Auke Bay Laboratory began analyses of the tissue samples, there was no evidence of petroleum hydrocarbon contamination, and only a marine biogenic signal was observed in July 2002 and March 2003. In July 2003, the SHC pattern was again derived from marine biogenic components; however, there was also possible evidence of trace-level (two times the method detection limit) concentrations of higher-molecular-weight n-C_{22} through n-C_{33} components, which are believed to be possibly introduced from microbial sources (bacterial contamination of the mussel tissues). This same pattern was observed in March 2004, but the concentrations were an order of magnitude lower. In any event, there is no evidence of significant petroleum hydrocarbon contamination in agreement with the PAH profiles discussed above.

A-3.6 Sheep Bay (SHB)

During the early years of the program, TPAH concentrations at Sheep Bay (SHB) were consistently very low (generally less than 100-200 ng/gram dry weight – see Figure 36), and with the possible exception of samples collected during July 1994, the histogram profiles from March 1993 through March 1996 reflected the pattern identified as that resulting from procedural artifacts (e.g., see Figure 38 and Payne et al. 1998; 2003a). In March and July 1997, there was an apparent increase in TPAH (derived primarily from a dissolved-phase signal); however, it is again possible that this apparent trend is result of increased sensitivity of the GC/MS instrumentation used in laboratory. The TPAH signal apparently decreases in July 1998 and April 1999 (and the PDR values suggest a mixture of particulate/oil-phase and dissolved-phase constituents). With the exception of one sample set in July 1999, the samples collected after July 1998 are consistently very low (less than 200 ng/gram dry weight) and reflect primarily a dissolved-phase signal. The apparent increase in TPAH for the July 1999 samples is due primarily to the presence of alkylated fluorenes, which in fact, were misidentified due to interference from lipids that were not successfully removed during sample cleanup at the laboratory. With the few exceptions noted above, the hydrocarbon levels at this site are exceptionally low, and they do not reflect significant petroleum contamination. Since July 2002, measured dissolved-phase PAH are at or below the laboratory method reporting limits, and in several instances, are similar to components measured at significantly lower concentrations in laboratory blanks.

Most of the SHC analyses undertaken at this site are confounded by lipid interference problems, although it is possible to make out below method detection limit contributions from marine biogenic algae in many of the samples. In agreement with the early PAH data, there is no significant evidence of petroleum-hydrocarbon contamination in any of the samples analyzed through July 1994. The July 1997 samples (which contained the anomalous fluorene pattern due to lipid interference) were characterized by exceedingly high concentrations of n-C_{17} and n-C_{19} at concentrations that were almost 10 times higher than other more natural biogenic components. After that, the SHC patterns were fairly random with evidence of marine biogenic components and continued lipid interference

problems. The April 2000 samples contained below-MDL levels of components that might be associated with petroleum contamination, but this was not supported by the TPAH or PDR values discussed above. Since the Auke Bay Laboratory undertook tissue analyses (July 2002), most samples have exhibited only a marine biogenic profile. In July 2003, there was, however, a cluster of above-method-detection-limit n-alkanes from n-C_{22} through n-C_{34} (Figure 53). Unlike the lipid interference profiles observed at GERG (where individual n-alkanes were reported at concentrations of several thousand ng/gram dry weight), these alkanes were only 2-3 times above the MDL, there was no phytane or no significant UCM, and they are believed to possibly be due to marine bacteria (Davis, 1968; Han and Calvin, 1969). There was no supporting PAH evidence to suggest petroleum contamination, and this higher-molecular-weight cluster had decreased significantly again by March 2004.

A-3.7 Shuyak Harbor (SHH)

At Shuyak Harbor (SHH), TPAH values are consistently low from July 1993 through March 1996 (Figure 36), when the reported concentrations are believed to be procedural artifacts as identified and described by Payne et al. (1998; 2003a) and shown in Figure 38. The apparent increases in TPAH over the July 1996 through April 1998 period reflect what appears to be an increases in dissolved-phase, lower-molecular-weight hydrocarbons; however, this time period also coincides with the change in GC/MS instrumentation at the laboratory. Nevertheless, the PAH histogram plots generated during this time frame appear to be real. There is a significant decrease in the TPAH signal in July compared to April 1998 (Figure 54) while the PDR values suggest a mixture of dissolved-phase constituents with traces of higher-molecular-weight particulate-phase/oil components. The apparent secondary maxima in TPAH concentrations in August 1999 is largely driven by increased levels of alkylated fluorenes, which are again believed to be a laboratory artifact due to lipid interference. Beginning with the March 2000 collection (Figure 36), the TPAH values are uniformly low (all below 100 ng/gram dry weight), and while all components are below the laboratory method reporting limits, the PDR values for July 2001 and March 2002 suggest mixed particulate/oil-phase and dissolved-phase sources. Similar trends are observed at Knowles Head and Windy Bay. All of the remaining samples analyzed since July 2002 reflect an exclusively dissolved-phase signal; however, this pattern may also be due to laboratory artifacts because similar dissolved-phase components were observed (at significantly lower concentrations) in the associated laboratory blanks. Because most of the measured components are below the laboratory reporting limits, it is abundantly clear that this site is extremely clean and not subject to significant petroleum hydrocarbon contamination.

The SHC data for this site (like the other cleaner areas) are confounded by what appears to be higher-molecular-weight lipid interference. During the early years of the program, however, biogenic hydrocarbons of marine origin can be identified in the lower-molecular weight range where lipid interference wasn't a problem. With the reinstatement of SHC analyses in July 1998, lipid interference continued on a sporadic basis through March 2002. During this time there were several instances when traces of petrogenic contamination might have been suggested by the presence of phytane (July 1998, April

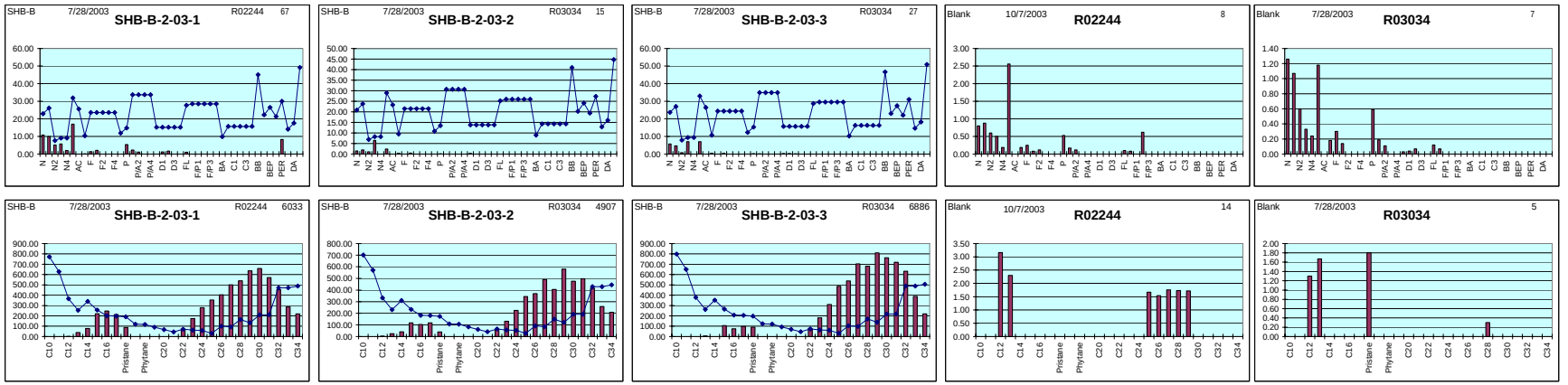

Figure 53. PAH and SHC histograms for mussel tissues at SHB in July 2003. The dissolved-phase PAH are well below the MDL in all three replicates, while the SHC profiles show marine biogenic components (n-C_{15}, n-C_{17}, and pristane) presumably derived from copepods plus n-C_{22} to n-C_{34} alkanes believed to be due to marine bacteria. The absence of phytane and ultra-low PAH profiles suggest no particulate/oil-phase contamination.

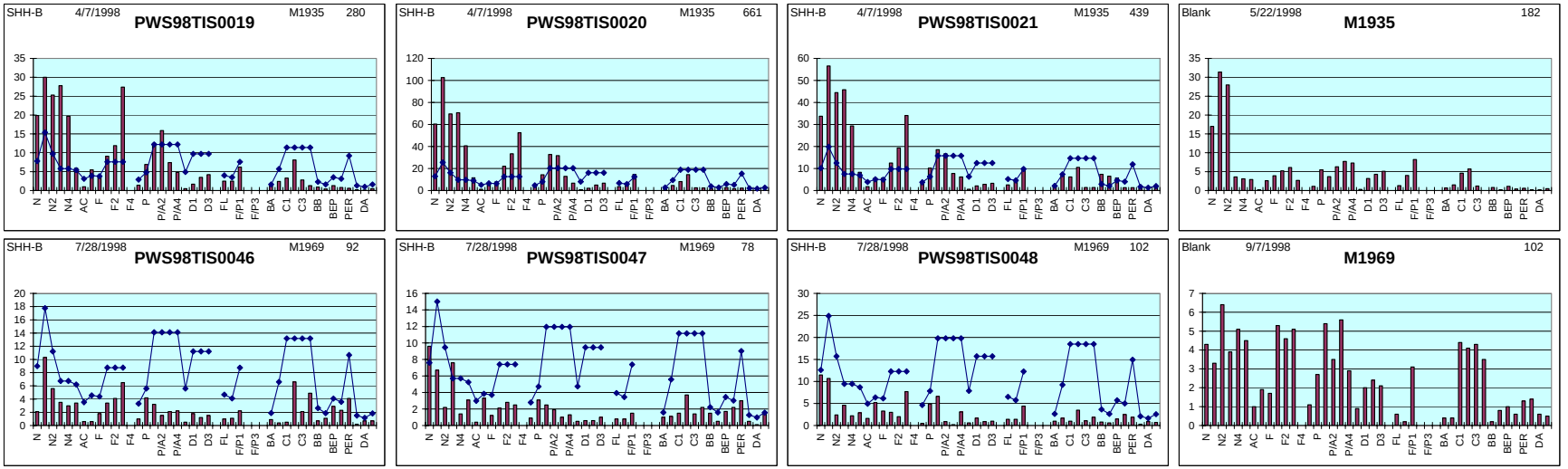

Figure 54. PAH histograms for mussel tissues at SHH in April and July 1998. There are no SHC data for the April samples and the July 1998 data are not shown. These profiles reflect a decreasing trend in dissolved-phase PAH and fairly constant pyrogenic components over the time-interval sampled. Unfortunately, the procedural blanks for both sets of samples were pretty contaminated.

1999, August 1999, and March 2000), and while the apparent TPAH values increased between July 1998 and August 1999 (largely due to fluorene artifacts), they dropped significantly again in March 2000 when a more complex SHC patterns were noted (Figure 55). Thus, the SHC and PAH profiles don't track together at these extremely low concentrations as one might expect if the site had been truly subject to petroleum hydrocarbon contamination. Furthermore, in March 2000 when the SHC pattern was at its most complex, the PDR value for this site was less than 0.5 reflecting a predominant dissolved-phase source for the PAH in direct contrast to the SHC profiles (see Figure 55). Then, between August 2000 and March 2002 when the PDR values increased in a systematic manner suggesting increased complexity (see Figure 36), the SHC profiles exhibited little or no evidence of particulate-phase hydrocarbons, and the TPAH levels remained low and constant (less than 100 ng/gram dry weight). Thus, there doesn't appear to be any correlation between the SHC profiles and the PAH measurements completed at this site. During most of this time, the SHC profiles reflected a combination of biogenic hydrocarbons in the lower-molecular weight (n-C_{15} through n-C_{17}) range plus lipid interference. This biogenic pattern without the lipid interference continued after Auke Bay Laboratory began analyses in July 2002 through March 2004, with no evidence of petroleum hydrocarbon contamination in agreement with of the TPAH and PDR values discussed above. The March 2004 samples shown in Figure 56 suggest at or below-MDL traces of higher-molecular-weight n-alkanes between n-C_{22} and n-C_{31}. The same pattern was observed at Sheep Bay (SHB) in July 2003 (e.g., see Figure 53) and to a lesser extent in March 2004 at that location, and at this time it is believed to possibly reflect input from microbial sources (Davis, 1968; Han and Calvin, 1969). It was not present in the August 2003 samples from SHH analyzed at the time, so it is not believed to be a laboratory artifact. There is no evidence of petroleum hydrocarbon contamination (because the absence of phytane) although a bimodal distribution of below-MDL level n-alkanes was apparent. The TPAH concentrations throughout this period were all below 100 ng/gram dry weight.

A-3.8 Sleepy Bay (SLB)

The TPAH and PDR plots in Figure 36 for Sleepy Bay (SLB) show significant variability and elevated TPAH concentrations during the early years of the LTEMP program (March 1993 through July 1995). The PDR plots show significant particulate/oil-phase contributions in the spring (March) samples, while the summer (July) samples collected during this interval suggest a dissolved or possibly mixed particulate/oil-phase and dissolved-phase signal. As will be shown below, with the exception of the July 1994 samples, these other summer profiles were actually nothing more that procedural artifacts. Like the samples collected at Disk Island (DII), the elevated TPAH levels and significant particulate/oil-phase signals in July 1994 are believed to reflect beach cleaning operations to remove residual *Exxon Valdez* oil. The elevated mussel tissue burdens in the other samples (March 1993, March 1994, and March 1995) may be attributed to natural cleansing and release of particulate/oil-phase residues during winter and spring storm events. Sleepy Bay is exposed to a considerable fetch of open water to the northeast (east of Knight Island), and as such, it would be subject to considerable storm activity and wave

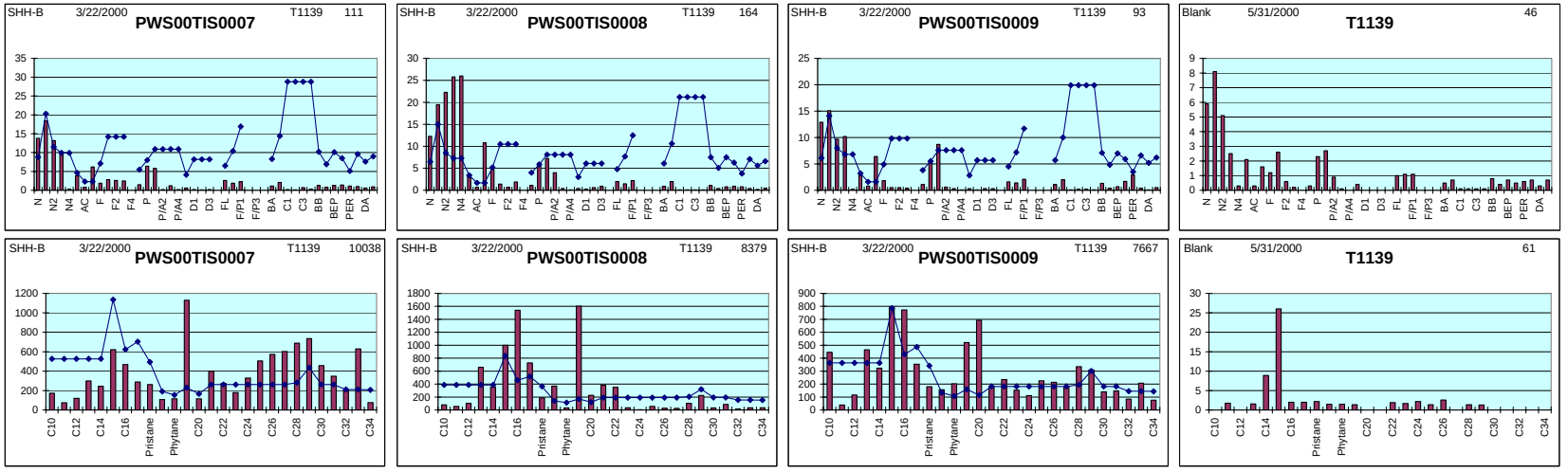

Figure 55. PAH and SHC histograms for mussel tissues at SHH in March 2000. The PAH profiles clearly reflect a dissolved-phase pattern while the SHC patterns suggest particulate/oil-phase sources. Apparently the PAH and SHC are not coupled at these extremely low levels.

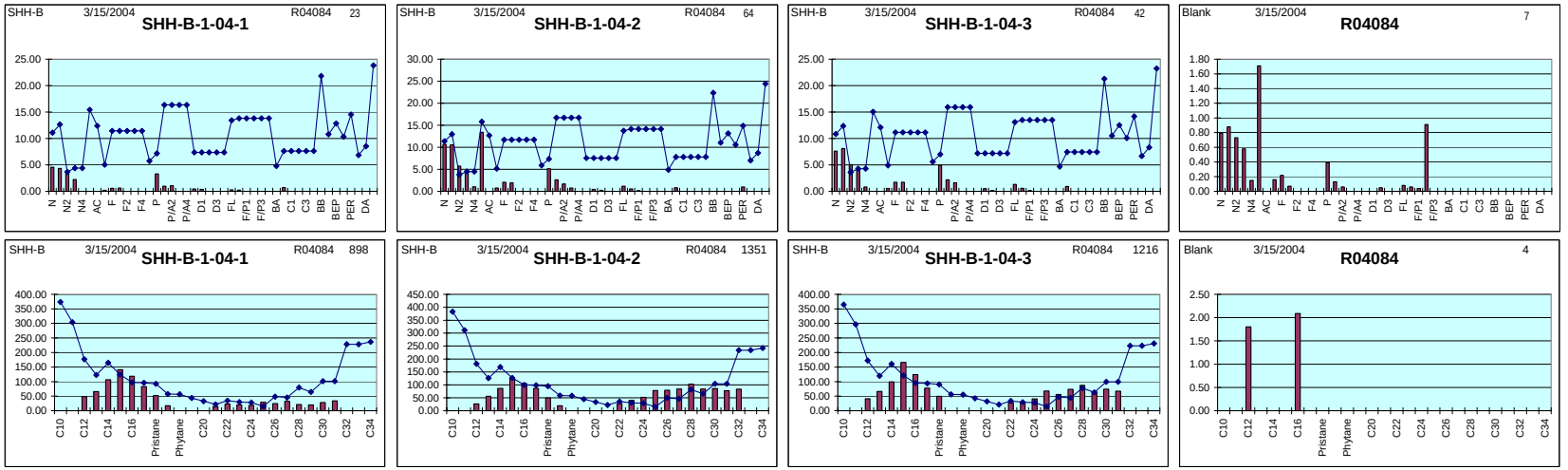

Figure 56. PAH and SHC Histograms for mussel tissues at SHH in March 2004. The PAH profiles show < MDL traces of dissolved-phase components while the SHC plots reflect < MDL traces of marine biogenic, terrestrial plant wax, and possibly microbial sources.

turbulence introduced during northerly spring winds, and release of buried oil may be showing up in the tissue samples collected at those times. As shown by the compiled PAH histograms shown in Figure 57, the TPAH values obtained for March 1993, March 1994, July 1994, and March 1995 all reflect real and significant petroleum hydrocarbon contamination at the site. In contrast, the July 1993 samples, and the majority of samples collected from July 1995 through July 1996 showed no evidence of petroleum hydrocarbon contamination, and the only PAH detected could be ascribed to procedural artifacts. Figure 36 suggests that slightly elevated TPAH values were observed again in July 1997 and March 1998. The PDR value of 0.17 for the July 1997 samples reflected a primarily dissolved-phase source (exclusively naphthalenes), while the PDR value of 0.91 for the March 1998 samples suggested a little more complexity from naphthalenes plus other higher-molecular-weight PAH constituents in the particulate/oil phase as confirmed by the PAH profiles shown in Figure 58. By July 1998, the TPAH values were below 200 ng/gram dry weight and they reflected a primarily dissolved-phase signal. The slightly elevated TPAH values noted in July 1999 are due to the inclusion of fluorenes (from lipid interference) in this sample set, and in fact, the TPAH values from the field (without the fluorenes) are probably significantly lower and reflect an exclusive dissolved-phase source. After April 2000, the TPAH values are extremely low (generally less than 200 ng/gram dry weight), and although most of the individual components are below laboratory method reporting limits, the PAH histogram patterns suggest an almost exclusively dissolved-phase signal. Because the individual PAH concentrations are generally below the laboratory reporting limits, and similar to patterns observed (at significantly lower concentrations) in laboratory procedural blanks, it appears that the site has not been exposed to significant petroleum hydrocarbon contamination since March 1998.

Like the SHC patterns for most of the other sites in the early years of the program, the aliphatic hydrocarbon analyses at Sleepy Bay are confounded by high levels of lipid interference. Most of the samples reflect only biogenic aliphatics of marine origin, although, one of the samples from March 1994 contains traces of what appear to be petroleum hydrocarbons (including phytane) in addition to marine biogenic sources and the ubiquitous n-C_{23} to n-C_{34} lipid pattern. This at least corroborates the high TPAH and PDR values obtained for this site at this time. By July 1994, however, the evidence for weathered petroleum hydrocarbons in the SHC fractions was again absent. When SHC analyses were initiated again in July 1998 there were continued problems with lipid interference, although traces of petrogenic hydrocarbons were suggested by the SHC patterns in March 1999 and April 2000. Unfortunately, these did not correspond to elevated TPAH or PDR values measured at the same time (see Figure 36), so again the trace level aliphatic signals did not appear to be coupled to the aromatic hydrocarbons measured in these samples. After the Auke Bay Laboratory began analyses of tissue samples in July 2002, there were no more instances of lipid interference and the SHC profiles suggested a predominance of marine biogenic components (n-C_{15}, n-C_{17}, and pristane) derived from copepods. There did appear to be a minor contribution (at or 1-2 times above the MDL) of what are believed to be microbial derived n-alkanes in the n-C_{23} through n-C_{34} range in one of three replicates from the July 2003 samples and two of three replicates in the March 2004 samples (Figure 59). Notwithstanding a trace of phytane in two of the three replicates from the March 2004 collections, the remaining n-alkanes are

Figure 57. Compiled PAH histograms from Sleepy Bay (SLB) showing the presence of particulate/oil-phase PAH in March 1993, March 1994, July 1994, and March 1995 and the absence of oil-phase contamination reflected only by laboratory procedural artifacts in July 1993 and July 1995 through July 1996.

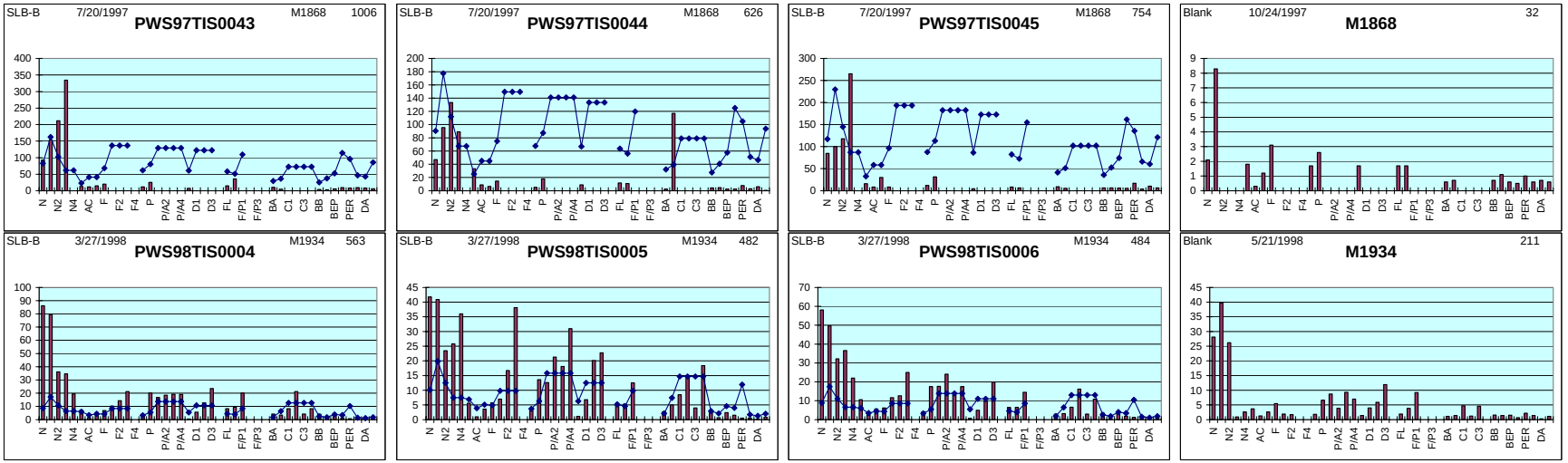

Figure 58. PAH histogram plots for mussel tissues at SLB in July 1997 and March 1998. The data show a primarily dissolved-phase signal (0.2 PDR) in the summer samples with a more complex mixture of dissolved and particulate/oil-phase signals (0.9 PDR) in the spring possibly reflecting release of buried oil residues during winter/spring storms.

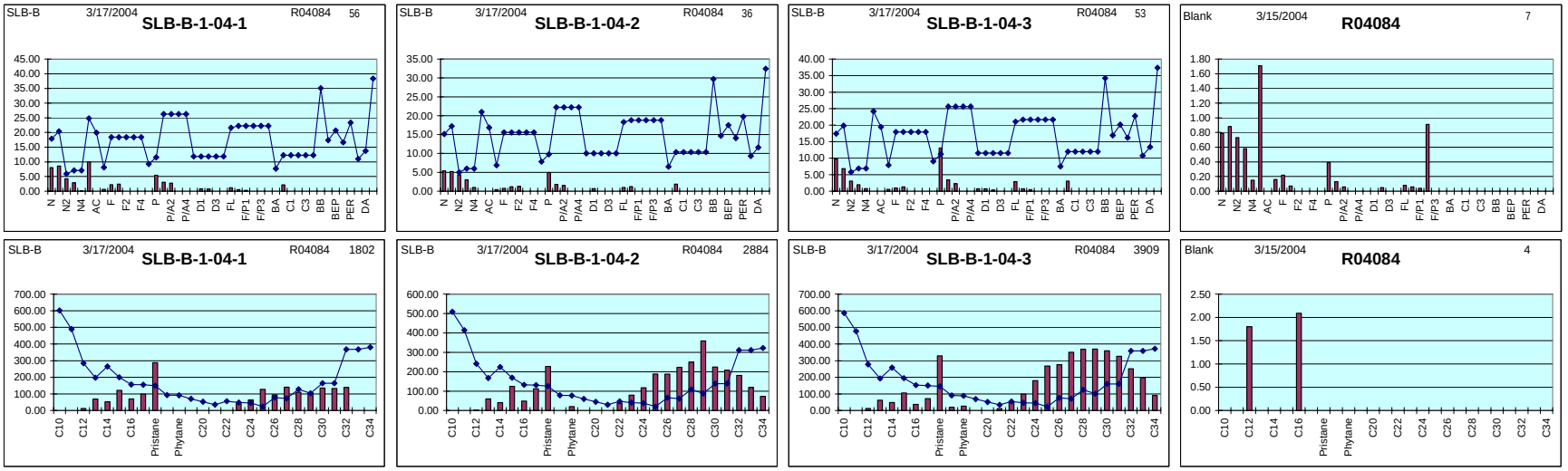

Figure 59. PAH and SHC histograms for mussel tissues at SLB in March 2004. The PAH profiles clearly reflect a dissolved-phase signal, while the SHC plots show evidence of copepod-sourced lipids, a trace of phytane, and either weathered oil or bacterial alkanes.

not believed to be of petroleum origin because of the absence of elevated TPAH or PDR signals with these samples. Alternatively, the March 2004 samples were collected immediately after 4 days of intense northerly winds, and the signals might just reflect traces of residual buried *Exxon Valdez* oil released by storm waves just before they were collected. Unfortunately, the PAH concentrations are too low for any definitive source identification.

A-3.9 Windy Bay (WIB)

The TPAH and PDR plots in Figure 36 for Windy Bay (WIB) suggest extremely low-level (generally less than 100 ng/gram dry weight) total PAH for the first four years of the program (March 1993 through March 1996). Like many of the other cleaner sites, detailed examination of the histogram plots for these samples reveals, that the reported PAH were actually nothing more than laboratory procedural artifacts. The apparent increase in TPAH concentrations during March and July 1997 and April 1998 might be real; however, this was also when the new GC/MS instrumentation was introduced at the laboratory so the apparent trend may just reflect increased instrumental sensitivity. Also, there was considerable contamination in the procedural blank (with a similar PAH profile and comparable concentrations) run with the April 1998 samples. Figure 60 presents a composite plot of all the PAH histograms and associated blanks on the samples collected between July 1996 and March 2000. The significant drop in the TPAH signal in July 1998 and April 1999 appears to be real, and it is believed to reflect actual PAH concentrations in the field. As discussed above, this same pattern was observed at Aialik Bay, Knowles Head, and Shuyak Harbor. The apparent increase in TPAH concentrations to levels above 500 ng/gram dry weight in August 1999 is believed to be a laboratory artifact caused by significant concentrations from alkylated fluorenes as a result of incomplete lipid separation. After March 2000, the TPAH values are generally less than 100 ng/gram dry weight (Figure 36), and although most of the individual constituents are well below the laboratory reporting limits, the PAH patterns suggest a primarily dissolved-phase signal with slightly increasing contributions from higher-molecular-weight particulate/oil phase PAH in the August 2000 through March 2002 time frame. This conclusion has to be tempered by the observation, however, that similar lower-molecular weight PAH patterns were observed in many of the laboratory procedural blanks (although at lower concentrations) run with most of these samples. After July 2002, most of the individual PAH are well below the laboratory method reporting limit and the signal appears to be exclusively derived from the dissolved phase. As before, however, similar lower-molecular weight PAH (naphthalene through C_4-naphthalenes) were observed at lower concentrations in the blanks run with these samples (see Figure 61). Overall, this site appears to be extremely clean with little or no apparent petroleum hydrocarbon contamination observed since March 1997 (and/or possibly April 1998).

The early SHC profiles from samples collected at Windy Bay show only biogenic hydrocarbons of marine origin and higher-molecular-weight n-alkane patterns due to lipid interference. This general pattern did not change with the resumption of tissue SHC analyses in July 1998, and there was no evidence of petroleum hydrocarbon contamination through March 2002 (the last sample set collected and analyzed by the KLI/GERG team).

Figure 60. Composite PAH histograms for tissue samples at WIB between July 1996 and March 2000. The increase in complexity in the 1997 samples is apparent, and the drop in PAH burden between April and July 1998 can be observed. The influence fluorene pattern artifact on the TPAH values in the August 1999 samples is readily apparent, and the characteristic dissolved-phase signal in all three samples from March 2000 can be seen.

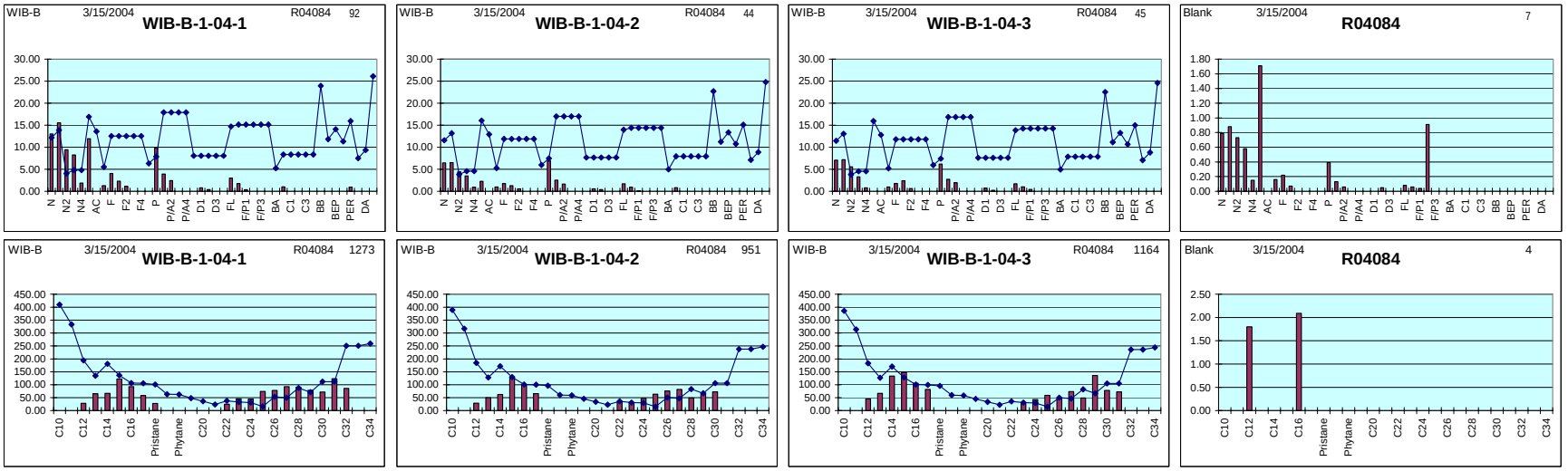

Figure 61. PAH and SHC histogram plots for mussel tissue at WIB in March 2004. The < MDL PAH profile reflects a predominantly dissolved phase signal, and the < MDL SHC plots show marine lipids from copepods plus possible bacterial sources, but no phytane.

The SHC profiles for the August 1999 samples (where the fluorene levels were so high in these and other samples due to insufficient lipid removal) reflected primarily n-C_{21} at concentrations ranging from 35,000-50,000 ng/gram dry weight. After Auke Bay Laboratory initiated tissue analyses in July 2002, all of the samples reflected a biogenic signal of marine origin (n-C_{15}, n-C_{17} and pristane) and occasional traces of higher-molecular-weight plant waxes. There appeared to be at- or just- below-MDL traces of higher-molecular-weight n-C_{22} through n-C_{30} alkanes from microbial sources in all three replicates from the March 2004 sampling period (Figure 61).

A-3.10 Zaikof Bay (ZAB)

Samples have only been collected at this site since July 1999, and as shown by the TPAH and PDR data in Figure 36, very low and consistent TPAH values have been observed at this site over time. The highest TPAH values observed at the site occurred in July 1999, but as with all the other tissue samples analyzed for that collection, a significant fraction of the TPAH came from alkylated fluorenes that are believed to be due to lipid interference. Discounting that initial higher TPAH value, the remaining TPAH values have been relatively low and constant over time. The PDR values suggest primarily dissolved-phase constituents with maybe a little bit more higher-molecular-weight complexity in March (Figure 62) and July 2001. Note that similar increased PDR values were also observed in this time-frame at Knowles Head, and Windy Bay; however, examination of individual histogram plots from these additional sites failed to reveal any systematic patterns that could be readily attributed to laboratory procedures. Since March 2002, the TPAH values at Zaikof Bay have been all less than 100 ng/gram dry weight, and almost exclusively derived from alkyl substituted naphthalenes. Traces of alkylated phenanthrenes/anthracenes were observed in the July 2003 and March 2004 (Figure 63) samples contributing to the slightly increased PDR values for those samples. As with many of the other samples examined in recent years, the naphthalenes and phenanthrene/anthracenes are also present in the procedural blanks, but at significantly lower levels compared to the field samples. Overall there is no evidence of significant petroleum hydrocarbon contamination at Zaikof Bay during this period of the study.

The SHC profiles generated between July 1999 and March 2002 were highly variable, both compositionally and with regard to total saturated hydrocarbons (TSHC) as shown in Figure 40. There appeared to be problems with lipid interference in some, but not all samples, and phytane (suggesting possible petroleum contamination) was observed at below method detection limit concentrations in April 2000, but it didn't correspond to elevated TPAH levels. After Auke Bay Laboratory initiated analyses in July 2002, only marine biogenic hydrocarbons were noted in July 2002 and March 2003. These constituents were augmented in July 2003 with at-method detection limit concentrations of what are believed to be microbial-sourced n-C_{23} through n-C_{32} n-alkanes. This pattern appeared again in two of three replicates analyzed in March 2004 (Figure 63), and in this instance the microbial-sourced n-alkanes were present at approximately two times the

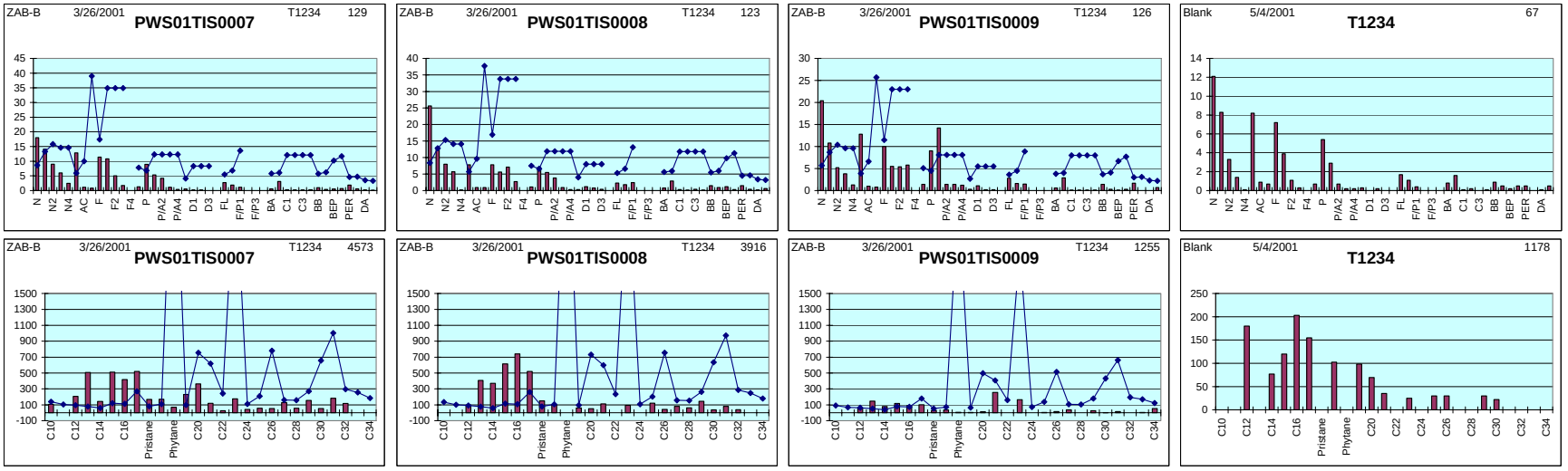

Figure 62. PAH and SHC histograms for mussel tissues at ZAB in March 2001. The presence of the alkylated P/A contributed to a slightly elevated PDR (0.58) compared to earlier samples, but the pattern is still derived from the dissolved phase. One of the SHC replicates showed a trace of phytane, but the major contributors are marine biogenic lipids and terrestrial plant waxes.

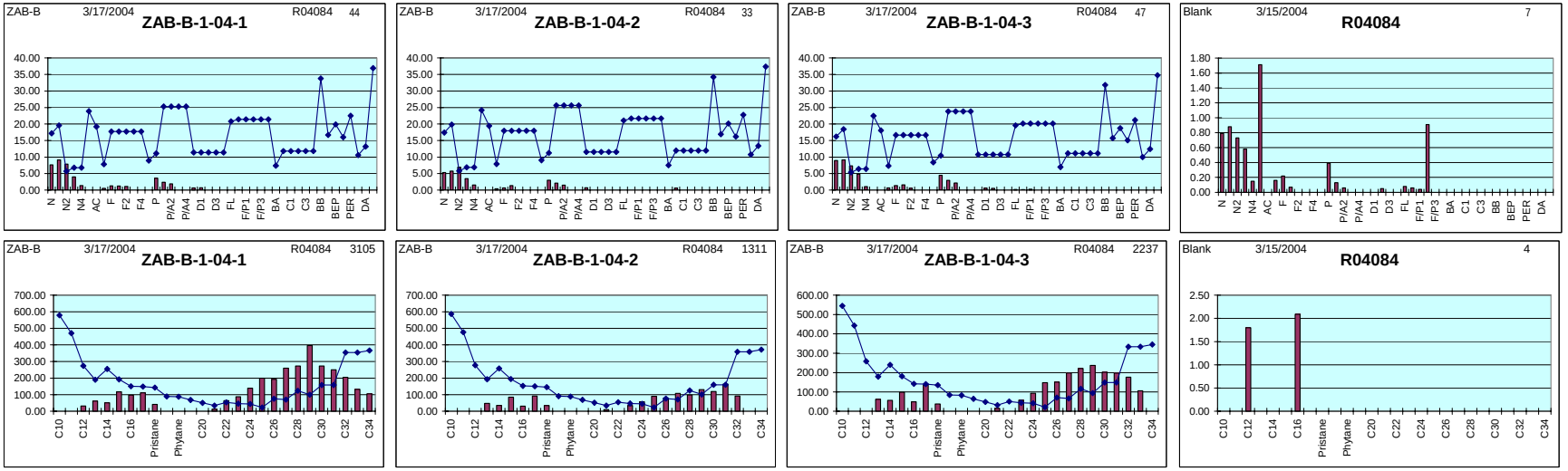

Figure 63. PAH and SHC histograms for mussel tissues at ZAB in March 2004. The PAH profiles reflect a dissolved-phase signal (PDR = 0.33), while the SHC plots show a mix of marine biogenic lipids plus possible microbial n-C_{22} to n-C_{34} alkanes.

method detection limit. As noted above, there were traces of what appeared to be below-MDL combustion-derived alkylated phenanthrenes/anthracenes in these same samples, which also contributed to slightly higher average PDR values. There were no traces of phytane in either the July 2003 or March 2004 sample sets, however, so we do not believe that the higher-molecular-weight n-alkanes discussed above are from petroleum. Therefore, we concluded that they represent possible bacteriological contamination of the mussels collected at those times.

This pattern of trace-level n-C_{23} through n-C_{32} n-alkanes was observed in the chromatographic profiles from numerous sites in the July 2003 and March 2004 collections. When it was observed on the chromatograms, the n-alkane pattern was represented by one half to one cm high peaks at the highest instrument sensitivity when the lowest level standards and surrogates were well off scale (> 10 cm). In all cases these individual n-alkanes were well below the lowest calibration standard, and as often as not, they were at or just slightly above the MDL. They were not observed in any of the laboratory procedural blanks or field blanks collected with the samples. Because they generally did not correlate with PAH components derived from petroleum, we concluded that they may be the result of marine bacteria present in the mussels (Davis 1968; Han and Calvin 1969). This microbial pattern was observed at the following sites: Sheep Bay (July 2003 and just a trace in March 2004); Shuyak Harbor (July 2003); Disk Island (July 2003); Sleepy Bay (both July 2003 and March 2004); Windy Bay (March 2004); Knowles Head (July 2003 and a trace in March 2004); Zaikof Bay (both July 2003 and March 2004). It was not observed at Aialik Bay, Alyeska Marine Terminal (where it would have been masked by both petroleum and biogenic hydrocarbons which were readily apparent), or Gold Creek (where terrestrially derived odd-carbon numbered higher-molecular-weight biogenic n-alkanes were noted). This pattern was obviously not observed in any of the samples analyzed at GERG because of the many order-of-magnitude higher levels of biological lipids present in the majority of the samples.