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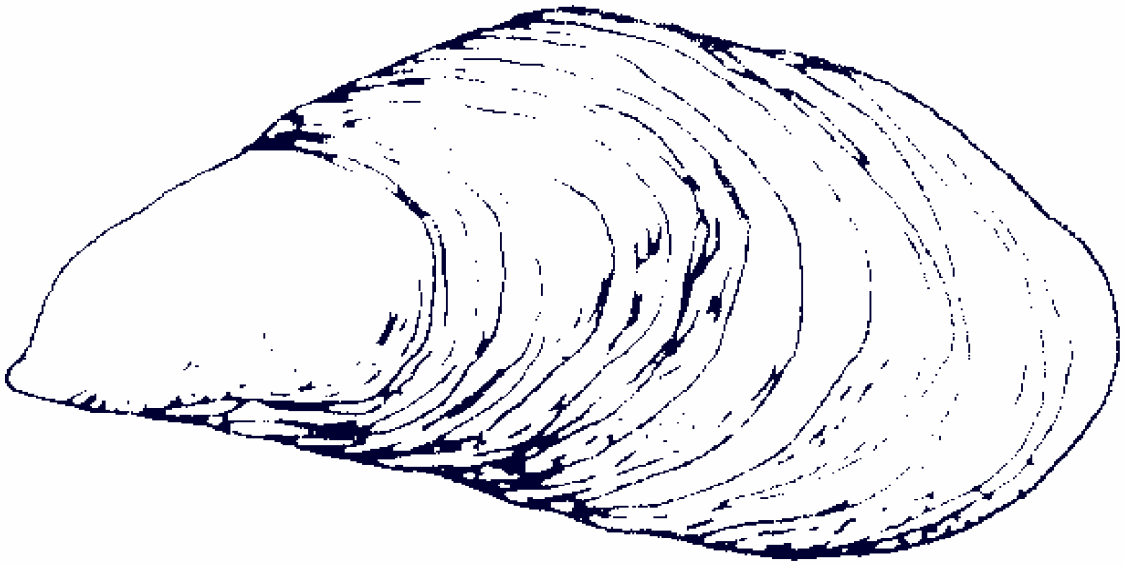
PRINCE WILLIAM SOUND RCAC

LONG-TERM ENVIRONMENTAL MONITORING PROGRAM

1997 - 1998 LTEMP MONITORING REPORT



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EXECUTIVE SUMMARY

The Long-Term Environmental Monitoring Program was designed to provide baseline measurements of hydrocarbon concentrations and sources at program sites within areas of Prince William Sound and the Gulf of Alaska under the auspices of the Prince William Sound Regional Citizens' Advisory Council. The program focuses on sampling of subtidal sediments and intertidal mussels to provide information on hydrocarbon levels that currently exist in the study area. The program is being conducted by Kinnetic Laboratories, Inc. under the administration of the Council's Scientific Advisory Committee.

This monitoring report includes data collected at nine stations during July 1997 and March 1998. Mussel samples were collected from indigenous (native) intertidal blue mussel populations for the analysis of hydrocarbons in tissues. Additional measurements of lipid content, tissue weights and volumes, and shell characteristics were made to indicate the reproductive state of the animals because spawning can directly affect the amount of hydrocarbons that are concentrated in their tissues. Subtidal sediment was collected for the analysis of hydrocarbon concentrations and physical parameters, such as particle grain size and total organic carbon. Chemical analyses were performed using state-of-the art techniques following specific protocols to ensure the validity and integrity of the data.

Chemical analyses were performed for a number of parameters that are indicative of possible petroleum contamination. These include various components of petroleum, such as polycyclic aromatic hydrocarbons, aliphatic hydrocarbons, and the unresolved complex mixture which contains compounds that cannot be identified using currently-available techniques. These parameters provide information on the levels of hydrocarbons in marine sediments and mussel tissue. Various types of hydrocarbon ratios were also used to help determine the potential source of hydrocarbons found in the sediment samples.

Because of the physical and biological variability in nature, a large amount of baseline data reflecting existing conditions is required before man-made changes to the environment can be identified or assessed. These man-induced changes could include, for example, large releases of petroleum to the environment via a spill or long-term input due to industrial or commercial activities such as oil transportation, fishing, forestry, and mining. The results presented in this report are intended to present a picture of what might be occurring at the program stations in terms of hydrocarbon levels and sources. The 1997 - 1998 program has added additional data to the time-series baseline information that has been collected since 1993. During the program year reported here, shallow subtidal sediment was collected at six stations (Disk Island, Knowles Head, Sheep Bay, Shuyak Harbor, Sleepy Bay, and Windy Bay), and deeper subtidal sediment was sampled at two sites (Alyeska Marine Terminal and Gold Creek). Intertidal mussel tissue was collected at all nine sites during this report period.

Program data indicate that hydrocarbons in tissues and sediments in the study area vary between stations, and, to a lesser extent, over time. Hydrocarbon levels in tissues were generally low, although they were higher than those seen during past surveys at some sites. Levels in sediments were more variable, with some stations exhibiting background levels and others showing anthropogenic influences. Many of the concentrations reported here are at or below method detection limits that have been determined using the same procedures and instruments used to analyze the samples. Put simply, these detection limits are based on a statistical method that is used to indicate how reliable the data may be. Values below these limits, while still valid, are less reliable, and this fact should be taken into account when reviewing the data and discussion presented in this report.

Hydrocarbons in the marine environment, particularly in the study area, can have a multitude of origins. These include the release of oil through man's activities such as the T/V *Exxon Valdez* oil spill in March 1989, operations at the Alyeska Marine Terminal, or other oil transportation activities; combustion sources such as stack exhaust or forest fires; boating and ship activities; natural oil seepage or coal deposits; biological processes from bacteria or other organisms; and atmospheric fallout. Natural events such as earthquakes can also result in the release of hydrocarbons. All of these may contribute hydrocarbons to sediments and resident biota in Prince William Sound and the Gulf of Alaska. Examination of hydrocarbon data from both tissues and sediments indicated that hydrocarbons from a variety of sources can be identified in the 1997 - 1998 program.

For purposes of this report, hydrocarbons were classified as having several distinct sources. Hydrocarbons resulting from biological processes were classified as biogenic, while those from a combustion source, such as boat exhausts or industrial emissions, were classified as pyrogenic. Hydrocarbons of a petroleum (petrogenic) nature that might be found in the study area include Alaska North Slope crude, *Exxon Valdez* oil spill residues, natural petroleum seeps from the eastern Gulf of Alaska area, refined products such as diesel or Bunker C fuel oil, and petroleum from other regions, such as the Cook Inlet area. Alaska North Slope crude consists of a mixture of petroleum from the various production fields on the Alaskan North Slope, and exhibits a fingerprint that is quite distinct from that of oil found in other geographic areas. The *Exxon Valdez* spill consisted of Alaska North Slope crude, which over time has weathered to produce a slightly different fingerprint than that of fresh crude. Petroleum that ordinates from natural seeps in the Gulf of Alaska contribute to the natural hydrocarbons (or "background hydrocarbons") in the study area, and these also exhibit a distinctly different fingerprint.

Mussel tissue from stations at Alyeska Marine Terminal, Disk Island, Gold Creek, and Sleepy Bay exhibited a strong petrogenic hydrocarbon signal, particularly during March 1998. A larger proportion of individual analytes at levels above the detection limit were seen in March 1998 samples as compared to earlier surveys, resulting in clearer polycyclic aromatic hydrocarbon fingerprints. As in the past, hydrocarbons in March 1998 tissue samples at Alyeska Marine Terminal and Gold Creek were attributed to Alaska North Slope crude, with the most likely source identified as the Alyeska Marine Terminal and tanker operations. Residues of *Exxon Valdez* spill oil were identified in tissues at Disk Island and Sleepy Bay, two of the sites known to have been heavily impacted during the spill. The station in Windy Bay, also heavily impacted by the spill, showed fingerprints that were not attributable to Alaska North Slope crude or the spill but more closely resembled background sources. During March 1998, clear petrogenic fingerprints were seen at stations at Aialik Bay, Knowles Head, Sheep Bay, and Shuyak Harbor which was ascribed to natural background sources. Tissues from Aialik Bay may have been contaminated with fuel which accounted for the relatively high levels of polycyclic aromatic hydrocarbons seen at this site (compared to historical data). Lesser pyrogenic inputs were also noted at many of these stations, particularly Alyeska Marine Terminal, Gold Creek, and Sleepy Bay.

Sediment results also indicated a number of probable sources of petroleum hydrocarbons. Sediments collected at the deeper subtidal stations (Alyeska Marine Terminal and Gold Creek) showed petrogenic as well as pyrogenic inputs. Sediments at the Alyeska Marine Terminal continued to show clear Alaska North Slope crude contamination. Hydrocarbons seen at this location are the result of long-term (chronic) inputs. The petrogenic and pyrogenic polycyclic aromatic hydrocarbons seen at Gold Creek were not attributed to Alaska North Slope crude. Sediments at the shallow Disk Island site also showed petroleum hydrocarbons primarily of a background nature with a possible *Exxon Valdez* spill oil component.

Shallow subtidal sediments from Sleepy Bay also showed a mixture of petrogenic and pyrogenic hydrocarbons. The polycyclic aromatic hydrocarbon fingerprints indicate that the hydrocarbons are largely of a pyrogenic nature, with lesser amounts of possible Alaska North Slope crude/*Exxon Valdez* spill oil and seep-derived hydrocarbons. Two additional sites that had been impacted by the spill, Shuyak Harbor and Windy Bay, showed a combination of sources. Petrogenic hydrocarbons were attributed to seep-derived background and spill oil. Both of these stations showed a substantial pyrogenic component, and the Windy Bay station also showed a large amount of biogenic input which may be due in part to logging activities. Hydrocarbons found in shallow subtidal sediments at the Knowles Head and Sheep Bay stations were ascribed to natural background. Some evidence of pyrogenic inputs was also seen at these stations.

1.0 INTRODUCTION

The Prince William Sound Regional Citizens' Advisory Council (RCAC) is an independent organization that was formed in 1989 in response to the T/V *Exxon Valdez* oil spill (EVOS). The RCAC was later certified under the Federal Oil Pollution Act of 1990. Operating under a contract with Alyeska Pipeline Service Company, the RCAC acts to minimize the environmental impacts associated with the terminal and the oil transportation tanker fleet. The RCAC's mission includes the performance of research designed to help understand and evaluate environmental impacts associated with oil transportation, including baseline research conducted prior to another spill event.

The purpose of the Long-Term Environmental Monitoring Program (LTEMP), implemented in 1993, is to provide long-term baseline measurements of hydrocarbon levels and sources in subtidal sediments and indigenous blue mussels at program sites within areas of Prince William Sound (PWS) and the Gulf of Alaska represented by the RCAC. The program objective has been modified over the course of the program to provide emphasis on the collection of baseline data that can be used to determine future potential impacts of oil transportation on the ecosystem. The program is being performed by Kinnetic Laboratories, Inc. (KLI) in Anchorage, Alaska, under the administration of the RCAC's Scientific Advisory Committee. Chemical analyses were performed by the Geochemical and Environmental Research Group (GERG) of Texas A&M University in College Station, Texas.

The purpose of this report is to present data from the fifth year of the monitoring program. It includes results from the last two LTEMP surveys performed during the RCAC's 1997 - 1998 fiscal year. Only limited data from prior program years are provided or discussed in this report; for more information concerning prior data, the reader is referred to earlier program reports (e.g., KLI, 1993a; 1993b; 1994a; 1994d; 1995a; 1995b; 1996a; and 1997a). For the reader's convenience, a Glossary and List of Acronyms is provided at the end of this document.

Subtidal sediment and/or intertidal indigenous (native) blue mussel tissue samples were collected during two field surveys at nine stations. Sediments were collected from shallow subtidal zone at depths of six to ten meters (m) by diver (six stations) and from deeper areas (approximately 24 to 68 m) using a sediment grab (two stations).

Subtidal sediment was collected for the analysis of polycyclic aromatic hydrocarbons (PAH); aliphatic hydrocarbons (AHC) which included the unresolved complex mixture (UCM); total organic carbon (TOC); and particle grain size (PGS). Intertidal mussel samples were collected for the analysis of PAH and lipid content. Additional mussels were collected for measurement of gonadal index.

2.0 STUDY DESIGN AND APPROACH

2.1 Sampling Design

As discussed in earlier program documents, the basic sampling approach for the LTEMP is consistent with the National Oceanographic and Atmospheric Administration's (NOAA) National Mussel Watch Project where native populations of sedentary organisms are utilized as bioindicators of chemical contamination, and nearby sediments are used to evaluate trends in contamination in the marine environment (NOAA, 1989a). A full description of sampling methods may be found in earlier program documents (e.g., KLI, 1993a; 1994a; 1995a; 1996a; and 1997a).

Sampling reported here was performed in July 1997 (Survey 10) and March 1998 (Survey 11). Indigenous mussel samples designated for hydrocarbon analysis were collected by hand from the mid-intertidal zone of each station using a stratified random sampling design. Three replicates of 30 individuals each were collected from three randomly-selected points along a 30-m transect. Replicate mussel samples were analyzed for PAH and percent lipids. Twenty additional mussels were collected at each station for assessment of gonadal state.

Shallow subtidal sediments (6 - 10 m) were collected by diver at six of the nine LTEMP sites, while a Van Veen sediment grab was used to collect deeper sediments (24 - 68 m) at two sites. Three replicate samples of surficial sediment (0 - 2 centimeters [cm]) from each sediment station were analyzed for PAH, AHC, PGS, and TOC.

Analytical strategy is summarized in Table 1; analytical methods are described in Section 3.2. Analytical approach included the use of compound-specific measurements for organic parameters such as PAH and AHC (including UCM). These parameters were used to assess hydrocarbon concentrations in both tissue (PAH only) and sediment (PAH and AHC). Additional parameters analyzed for tissues included percent lipids and gonadal index. Additional parameters examined in sediments included PGS and TOC, which are typically analyzed to evaluate their correlation with the hydrocarbon parameters.

2.2 Site Selection Criteria

As indicated in the initial study plan (KLI, 1993a) and program survey reports (KLI, 1993c; 1993d; 1994b; 1994c; 1995c; 1995d; 1996b; 1996c; 1997b; 1997c; and 1998), individual sampling sites were selected on the basis of several criteria. These included presence or absence of known or potential sources of hydrocarbon contamination, including the T/V *Exxon Valdez* oil spill (EVOS), the Alyeska Marine Terminal in Port Valdez, and the Knowles Head tanker anchorage area; the extent of native intertidal mussel populations; geographic features such as rocky benches in the intertidal area; and nearshore bathymetry and soft-bottom sediment to allow subtidal sediment collection.

Nine stations were sampled during LTEMP 1997 - 1998: Aialik Bay (AIB), Alyeska Marine Terminal (AMT; Saw Island), Disk Island (DII), Gold Creek (GOC), Knowles Head (KNH), Sheep Bay (SHB), Shuyak Harbor (SHH), Sleepy Bay (SLB), and Windy Bay (WIB; Table 2; Figures 1 - 9). Station designations used throughout this report are provided in Table 2 and include a station abbreviation followed by a station type code ("B" for intertidal mussel, "M" for shallow subtidal sediment, and "S" or "A" for deep subtidal sediment). The sites can be separated into three groupings based on potential or known hydrocarbon contamination: (1) reference sites believed to be relatively remote from oil industry activities (Stations AIB, GOC, and SHB), (2) sites previously identified as EVOS-impacted (Stations DII, SHH, SLB, and WIB), and (3) sites related to the marine terminal operations in Port Valdez and tanker operations (Stations AMT and KNH).

With the exception of Aialik Bay, mussels and subtidal sediments were collected at each site during the 1997 - 1998 LTEMP. Sampling at Aialik Bay included only mussel collection, as shallow sediment collection by diver was omitted from this site due to zero visibility conditions. Table 2 provides sampling information such as average station depth (sediment) or height (mussel samples) relative to Mean Lower Low Water (MLLW). Additional sampling information is provided in individual reports from each survey (KLI, 1997c and 1998).

Table 1. LTEMP Analytical Strategy.

Parameter	Description	Matrix	Relevance
Polycyclic aromatic hydrocarbons (PAH)	2 to 6-ring polycyclic aromatic hydrocarbon compounds; includes homologous series of aromatic hydrocarbons consisting of unsubstituted (parent) compounds, such as naphthalene, and substituted compounds, which are similar structures with alkyl side chains that replace hydrogen ions, such as C_1-naphthalene	Mussel tissue, sediment, and water (blanks)	Useful for determining hydrocarbon contamination and the relative contribution of petrogenic, pyrogenic, and diagenic sources; useful in source identification and determination of weathering rates
Aliphatic hydrocarbons (AHC)	Fully saturated normal alkanes (paraffins) and branched alkanes, n-C_{10} to n-C_{34}; includes the isoprenoid compounds pristane (C_{19}) and phytane (C_{20}) that are often the most abundant isoprenoids in petroleum hydrocarbons	Sediment and water (blanks)	Useful for determining hydrocarbon contamination and the relative contribution of petrogenic and biogenic sources; useful in determination of weathering rates and rates of oil degradation
Unresolved complex mixture (UCM)	A mixture of hydrocarbons of undefined structure that are not separated by gas chromatographic techniques; represented by the total resolved plus unresolved area minus the total area of all peaks that have been integrated; a characteristic of some fresh oils and most weathered oils	Sediment and water (blanks)	Useful for determining hydrocarbon contamination and the relative contribution of petrogenic, pyrogenic, and diagenic sources; useful in source identification and determination of weathering rates
Percent Lipid	Lipid material in mussel tissue is primary storage area for hydrocarbons; gametes are mostly comprised of lipids	Mussel tissue	Useful in determining spawning state of mussels; hydrocarbon body burdens decrease when lipid-rich gametes are released during spawning
Gonadal Index	Measure of shell length, shell volume, volume and weight of gonadal tissue, volume and weight of non-gonadal tissue	Mussel tissue and shell	Useful in determining spawning state of mussels; hydrocarbon body burdens decrease when lipid-rich gametes are released during spawning
Particle Grain Size (PGS)	Percent sand, silt, and clay	Sediment	Assessment of particle size distribution in sediments; potentially used to standardize organic parameters such as PAH and AHC
Total Organic Carbon (TOC)	Organic carbon	Sediment	Assessment of organic carbon load in sediment; potentially used to standardize organic parameters (PAH and AHC)

Station Location	Station Designation	Station Type	Sampling Date	Survey No.	Average Depth (m) (Above or Below MLLW)	GPS Coordinates	
						Latitude (N)	Longitude (W)
AIALIK BAY	AIB-B	Intertidal	7/26/97	10	1.5	59º52'46.5"	149º39'33.5"
			4/11/98	11	1.6	59º52'44.4"	149º39'37.7"
ALYESKA MARINE TERMINAL	AMT-B	Intertidal	7/17/97	10	1.5	61º05'21.8"	146º24'34.6"
			3/29/98	11	1.4	61º05'24.4"	146º24'29.1"
	AMT-S	Subtidal	7/17/97	10	-67	61º05'22.0"	146º23'43.0"
			3/29/98	11	-68	61º05'24.6"	146º23'39.4"
DISK ISLAND	DII-B	Intertidal	7/21/97	10	1.5	60º29'53.8"	147º39'40.0"
			3/25/98	11	1.6	60º29'52.6"	147º39'42.3"
	DII-M	Shallow Subtidal	7/21/97	10	-10	60º29'58.4"	147º39'44.2"
			3/25/98	11	-11	60º29'57.6"	147º39'44.6"
GOLD CREEK	GOC-B	Intertidal	7/17/97	10	1.2	61º07'27.5"	146º29'44.2"
			3/29/98	11	0.9	61º07'26.5"	146º29'45.2"
	GOC-S	Subtidal	7/17/97	10	-24	61º07'22.9"	146º29'37.7"
			3/29/98	11	-29	61º07'27.0"	146º29'37.3"
KNOWLES HEAD	KNH-B	Intertidal	7/18/97	10	2.5	60º41'23.4"	146º35'11.1"
			3/27/98	11	2.6	60º41'25.7"	146º35'07.9"
	KNH-M	Shallow Subtidal	7/18/97	10	-8	60º41'12.8"	146º35'43.7"
			3/27/98	11	-9	60º41'12.3"	146º35'49.2"
SHEEP BAY	SHB-B	Intertidal	7/19/97	10	2.1	60º38'47.5"	145º59'52.1"
			3/28/98	11	2.3	60º38'47.6"	145º59'47.6"
	SHB-M	Shallow Subtidal	7/19/97	10	-10	60º38'49.4"	145º59'55.5"
			3/28/98	11	-9	Not Available	Not Available
SHUYAK HARBOR	SHH-B	Intertidal	7/25/97	10	2.4	58º30'05.2"	152º37'39.5"
			4/7/98	11	2.8	58º30'04.0"	152º37'35.5"
	SHH-M	Shallow Subtidal	7/25/97	10	-10	Not Available	Not Available
			4/7/98	11	-10	Not Available	Not Available
SLEEPY BAY	SLB-B	Intertidal	7/20/97	10	2.0	60º04'02.4"	147º49'59.7"
			3/27/98	11	2.2	60º04'00.0"	147º49'58.1"
	SLB-M	Shallow Subtidal	7/20/97	10	-9	60º04'02.9"	147º50'02.9"
			3/27/98	11	-10	Not Available	Not Available

Station Location	Station Designation	Station Type	Sampling Date	Survey No.	Average Depth (m) (Above or Below MLLW)	GPS Coordinates	
						Latitude (N)	Longitude (W)
WINDY BAY	WIB-B	Intertidal	7/26/97	10	1.8	59º13'06.0"	151º31'13.5"
			4/11/98	11	2.2	59º13'06.3"	151º31'12.0"
	WIB-M	Shallow Subtidal	7/26/97	10	-6	Not Available	Not Available
			4/11/98	11	-9	Not Available	Not Available

Table 2. Station Locations and Sampling Information for the 1997 - 1998 LTEMP

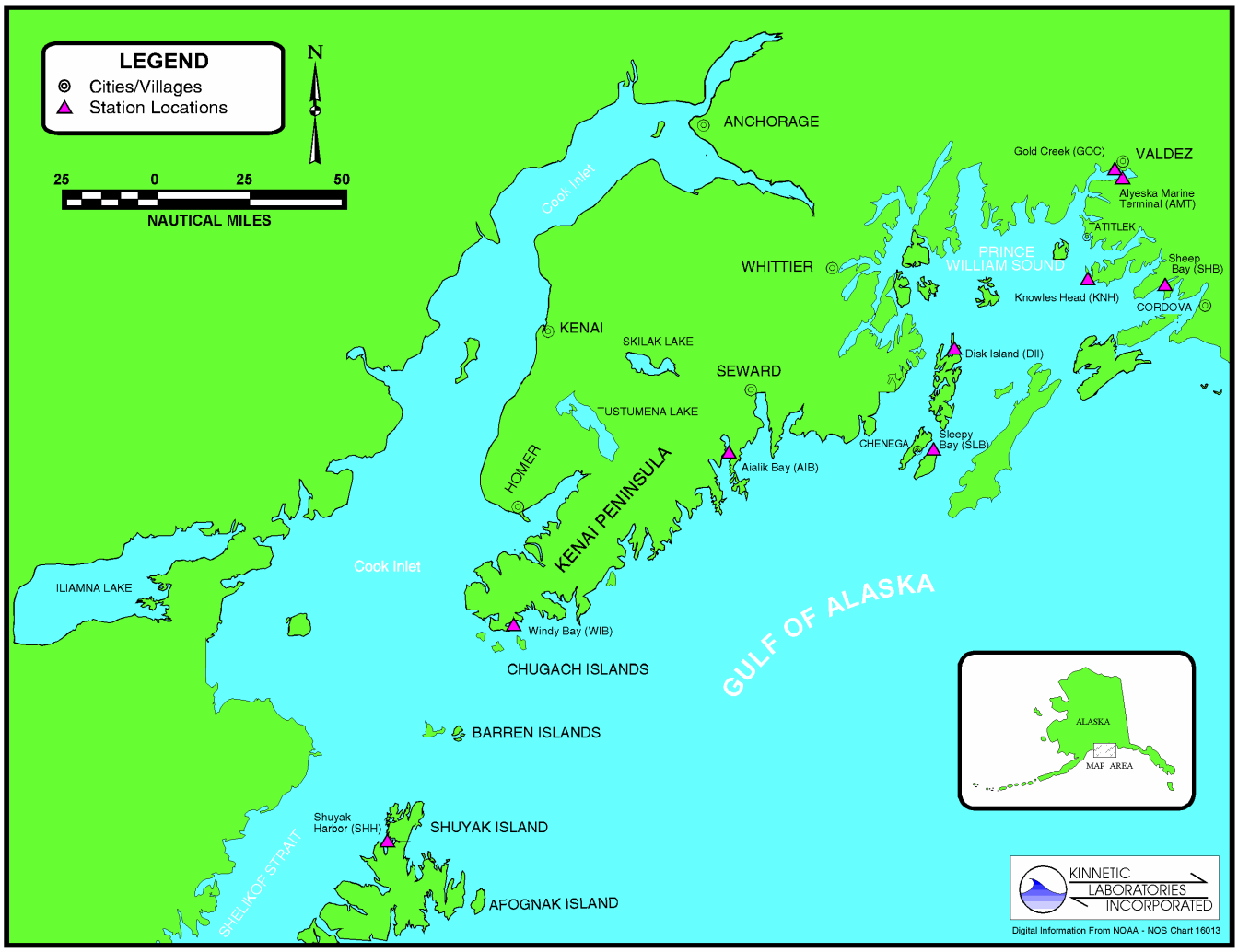

Figure 1. LTEMP Station Locations (Overall Study Area).

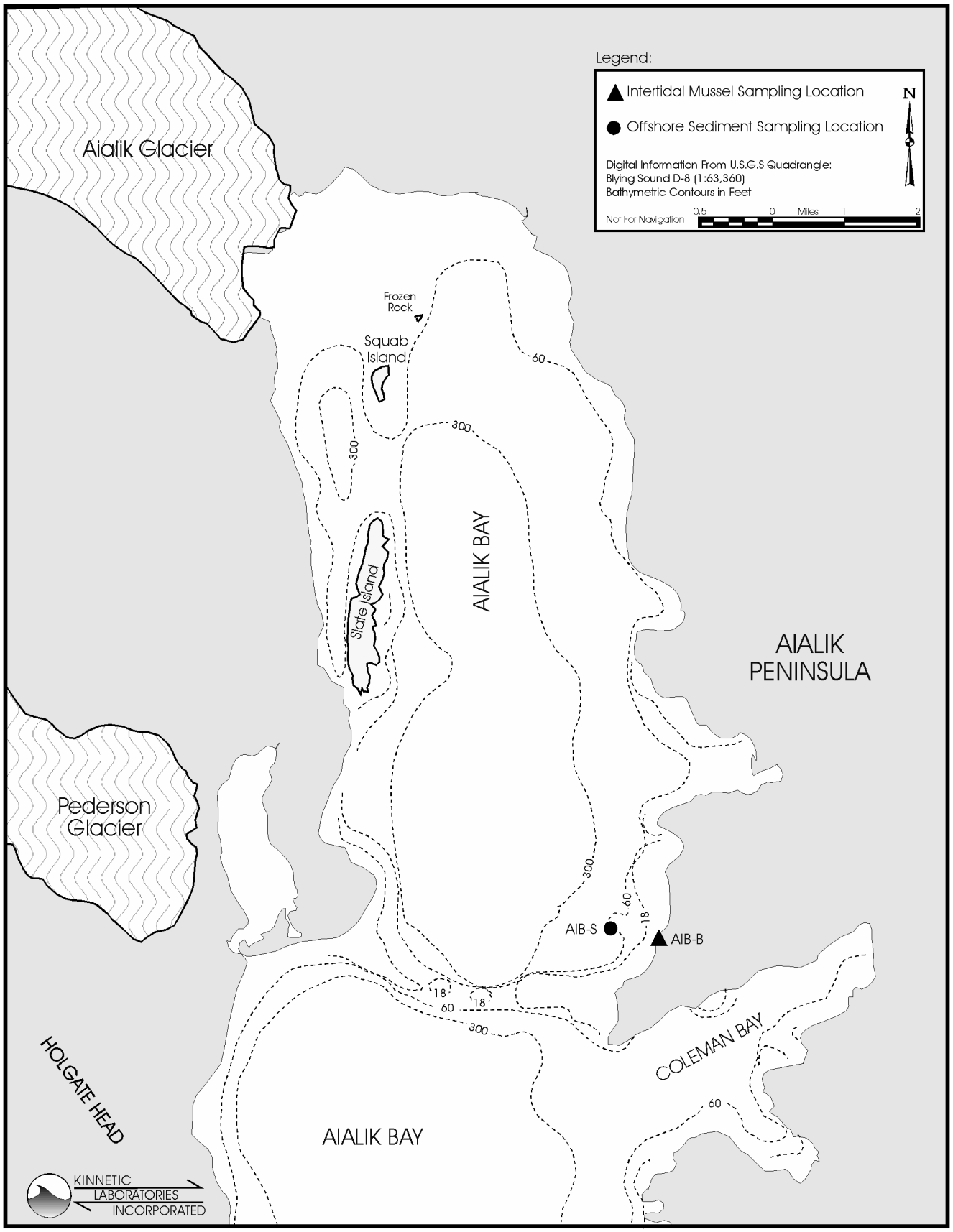

Figure 2. LTEMP Sampling Locations at the Aialik Bay Station.

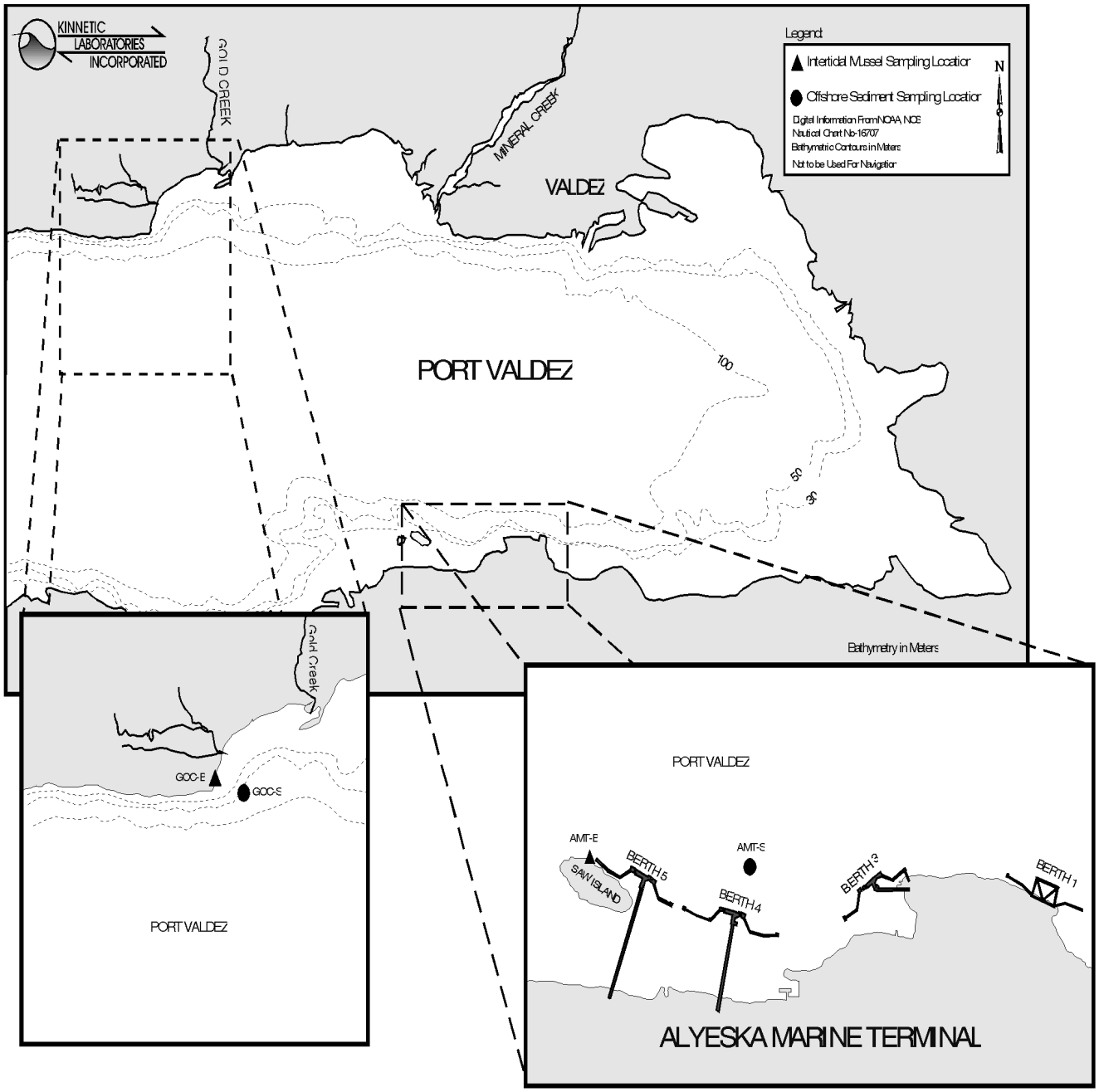

Figure 3. LTEMP Sampling Locations at the Alyeska Marine Terminal and Gold Creek Stations.

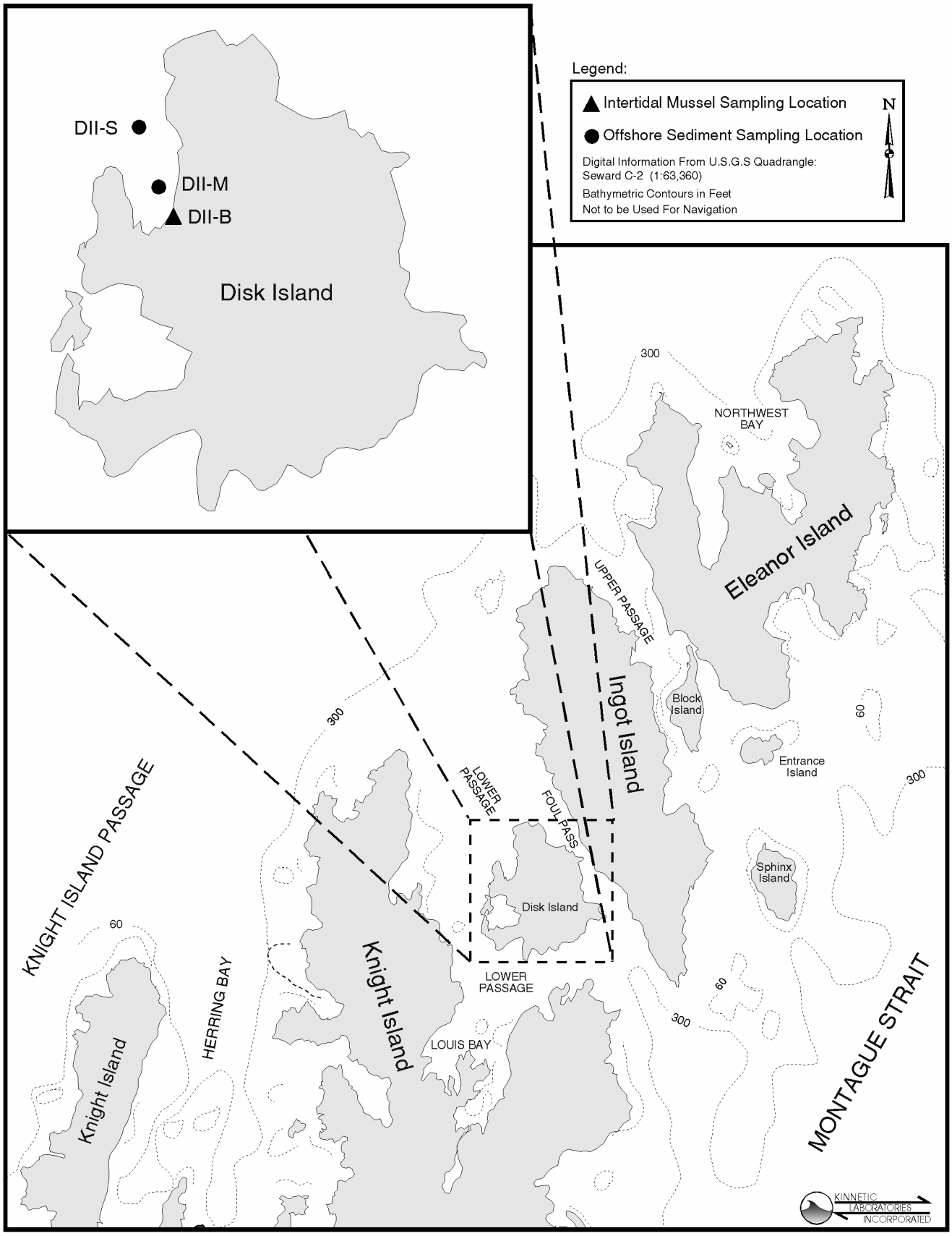

Figure 4. LTEMP Sampling Locations at the Disk Island Station.

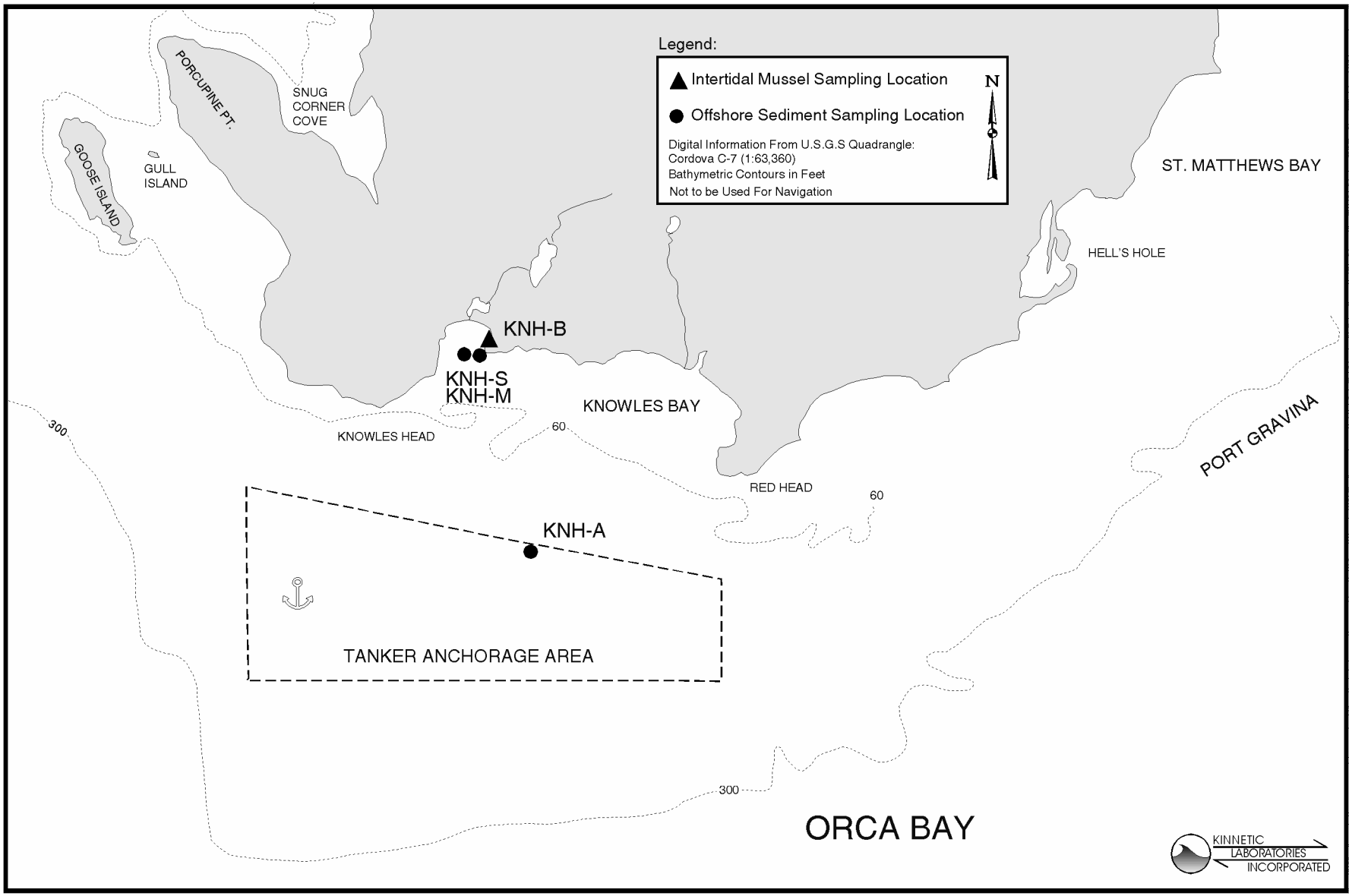

Figure 5. LTEMP Sampling Locations at the Knowles Head Station.

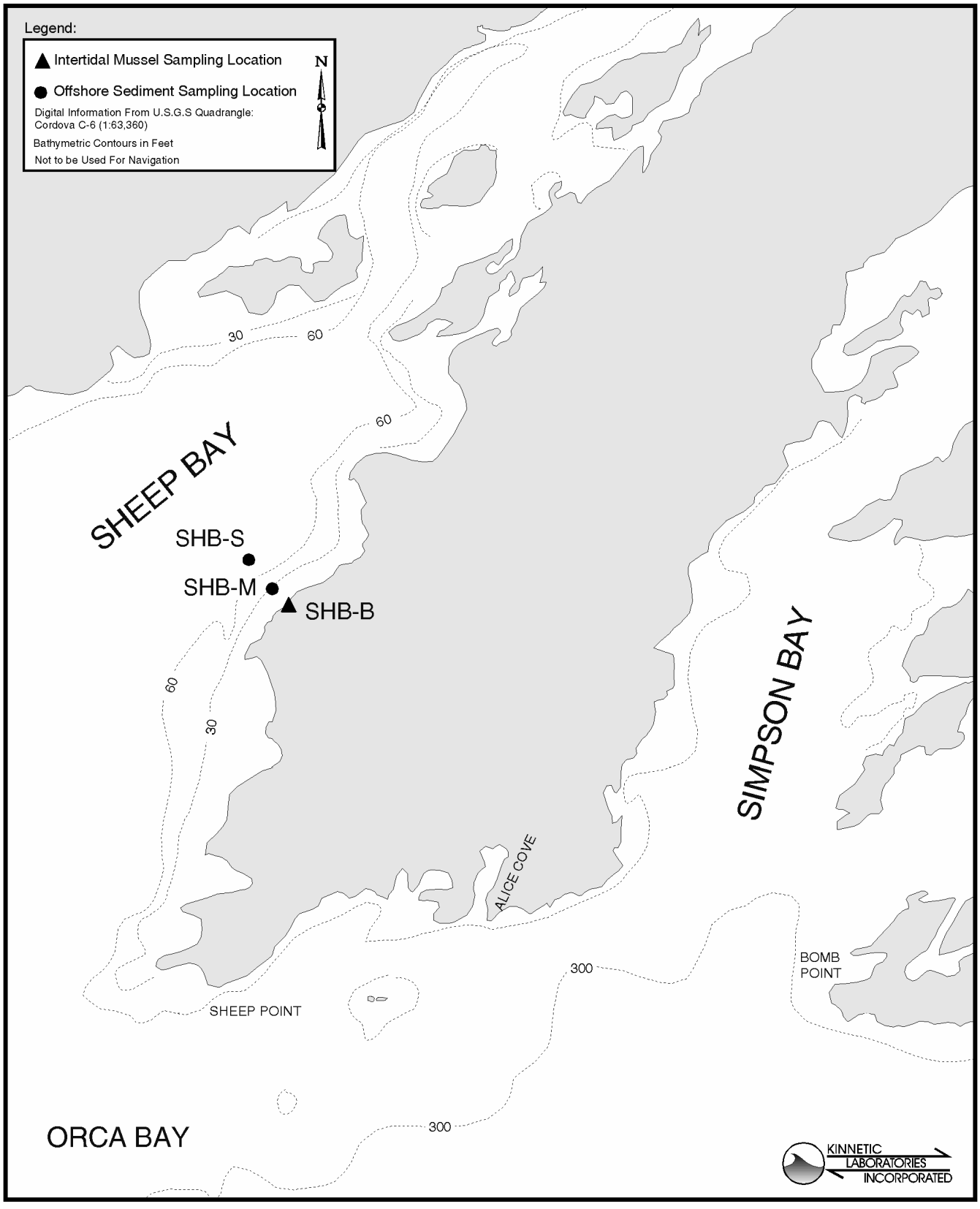

Figure 6. LTEMP Sampling Locations at the Sheep Bay Station.

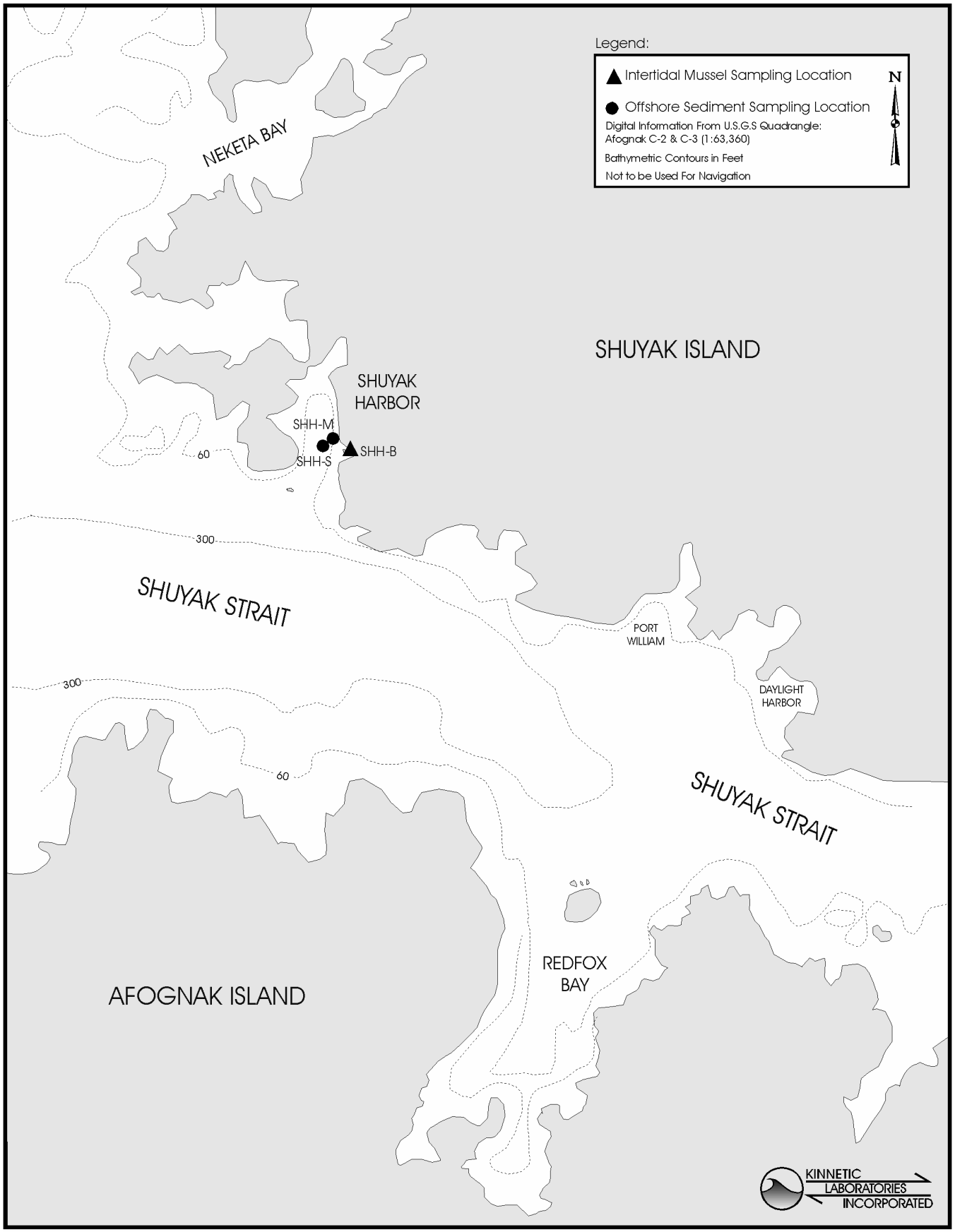

Figure 7. LTEMP Sampling Locations at the Shuyak Harbor Station.

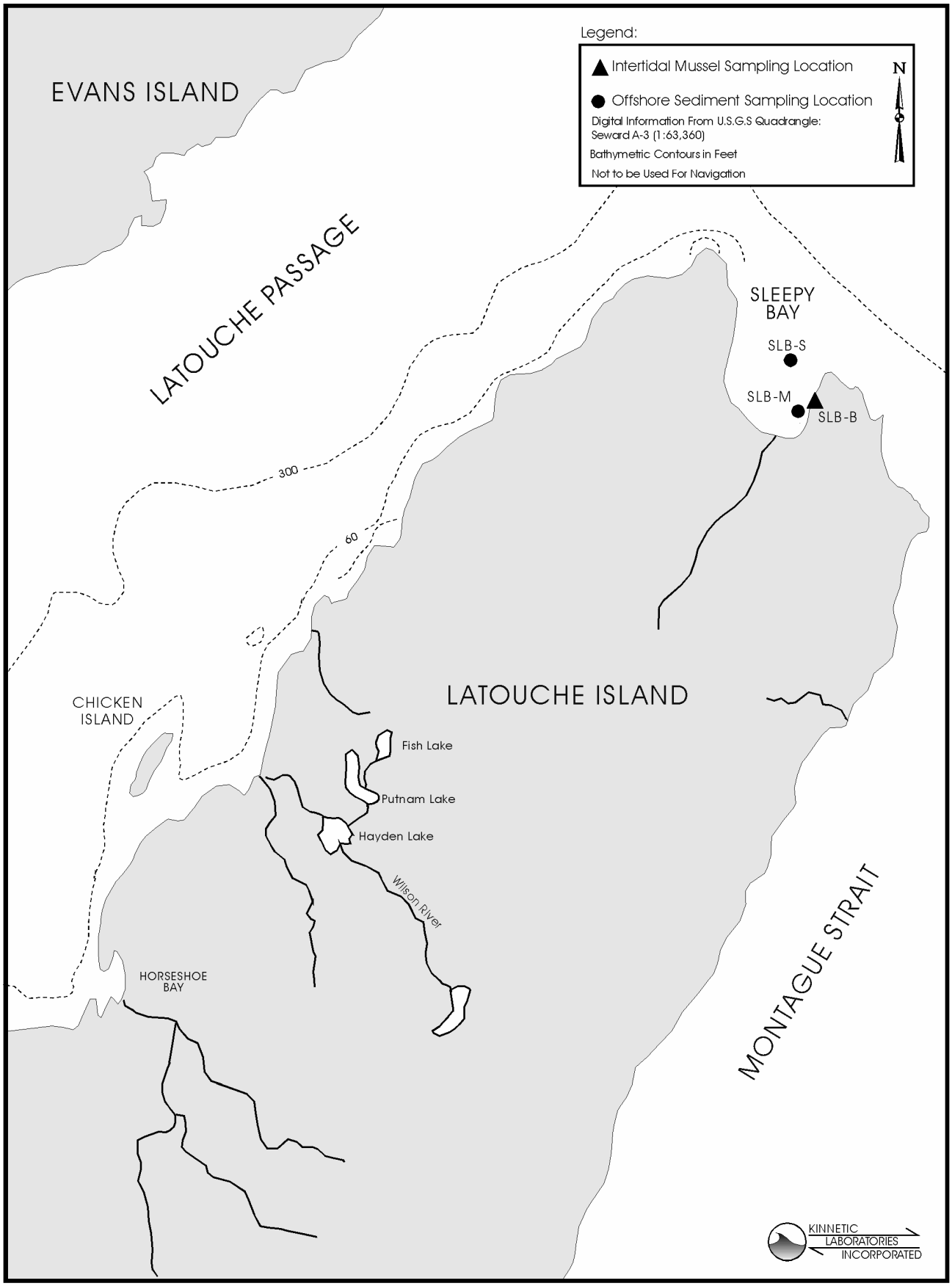

Figure 8. LTEMP Sampling Locations at the Sleepy Bay Station.

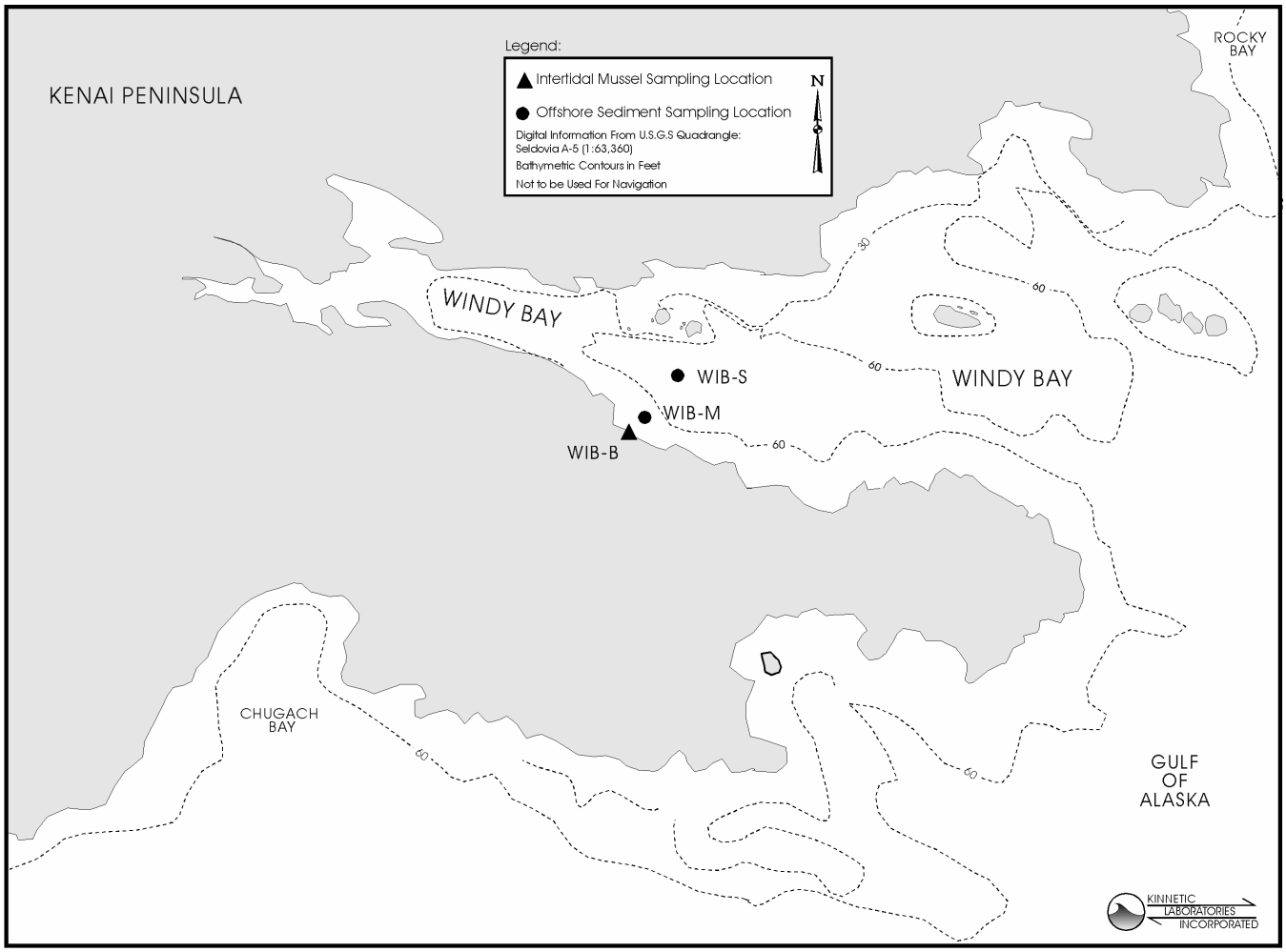

Figure 9. LTEMP Sampling Locations at the Windy Bay Station.

3.0 METHODOLOGY

3.1 Field Methods

Sampling and handling procedures followed those described in prior program reports (KLI, 1994a; 1995a; 1996a; and 1997a). Intertidal mussel samples were collected using a stratified random sampling design as depicted in Figure 10. Each transect was divided into three zones (0-10 m, 11-20 m, and 21-30 m), and one replicate of 30 individual mussels (*Mytilus trossulus*, formerly *M. edulis*) was collected from within each of these zones using random numbers to determine placement. Additional mussels were collected from each transect for gonadal index determination.

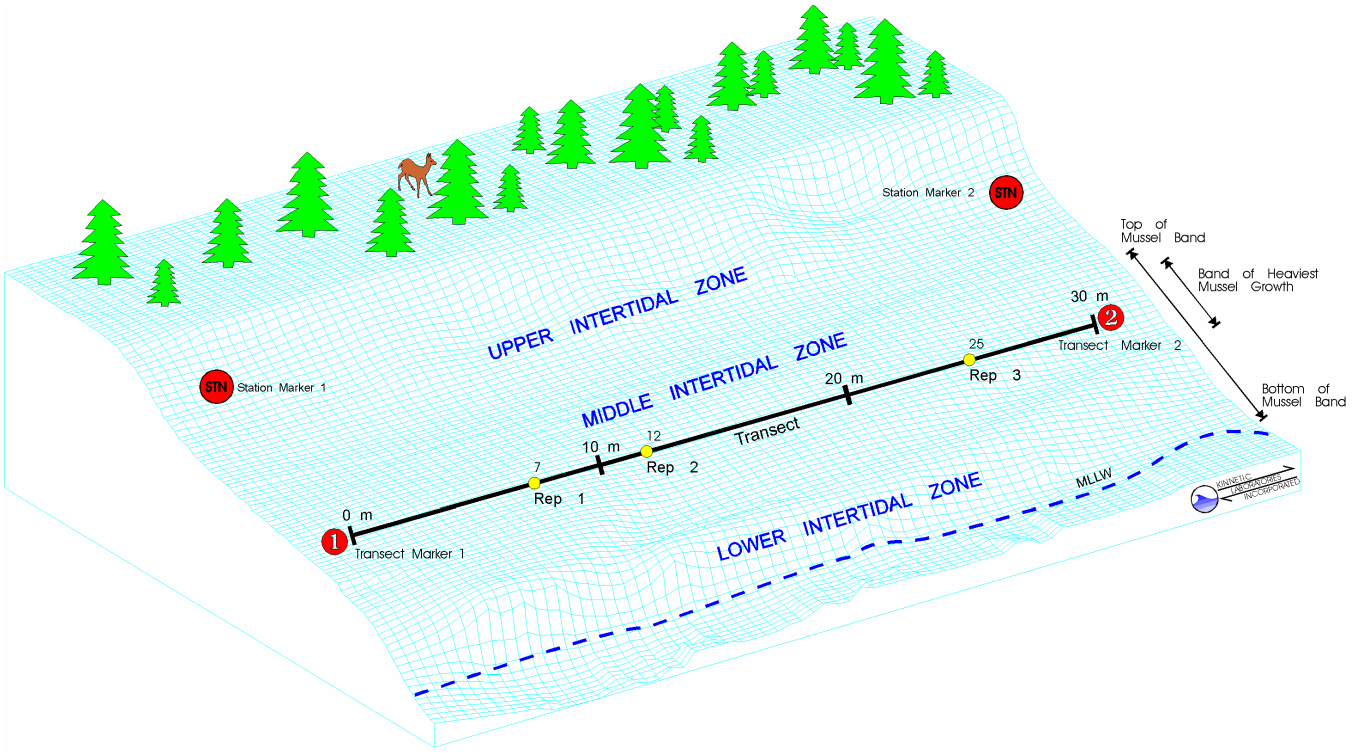

Figure 10. Diagram of LTEMP Intertidal Sampling Design with Example Replicates at 7, 12, and 25 Meters.

Subtidal sediment sampling was performed using a Teflon®-coated modified Van Veen grab (0.1 m^2) or by diver following previously described LTEMP procedures. Deeper sediment sampling was performed at the Alyeska Marine Terminal (AMT) and Gold Creek (GOC) stations, and shallow subtidal sediments were collected at six of the remaining stations by diver (Disk Island [DII], Knowles Head [KNH], Sheep Bay [SHB], Shuyak Harbor [SHH], Sleepy Bay [SLB], and Windy Bay [WIB]). Three discrete replicate sediment samples of surficial sediment (0 - 2 cm) were collected at each station. Quality control samples were also collected as described in Section 4.

Sample documentation followed procedures outlined in prior program reports and included the use of project-specific log forms, labels, and chain of custody forms. Sample identification and integrity were ensured by a rigidly-enforced chain of custody program.

Navigation and station location included the use of nautical charts and a global positioning system (GPS). A hand-held GPS was used to obtain the coordinates of both intertidal and subtidal stations whenever possible.

The M/V *Auklet* out of Cordova was used for sampling within PWS. Stations in the Gulf of Alaska were sampled from a float plane chartered through Jim Air of Anchorage.

3.2 Analytical Methods

Tissue samples were analyzed for PAH and lipid content. In addition to the tissue samples designated for chemical analysis, a separate sample of mussels was collected at each station for the determination of gonadal index. Subtidal sediment samples were analyzed for the following parameters: PAH, AHC, PGS, and TOC. Field and equipment rinsate blanks were analyzed for PAH and AHC. With the exception of gonadal index which was determined in the field or at KLI Anchorage, all samples were analyzed at the Geochemical and Environmental Research Group (GERG) of Texas A&M University.

Sample receipt, preparation, and analyses followed procedures outlined in earlier program reports and described by GERG Standard Operating Procedures (SOPs; Table 3). New SOP numbers provided in the table generally reflect revision of the old SOPs to include more detail, with no substantive changes to the methods. The exception to this is provided in Section 3.2.5 below, where PAH determination is described.

3.2.1 Sample Preparation and Percent Moisture Determination

Tissue samples arrived at the laboratory whole and were rinsed with reagent water to remove extraneous material as necessary. Mussels were shucked and dissected with solvent-rinsed tools. Tissue was homogenized using a Tekmar Tissumizer®. A 1 - 5 gram (g) aliquot of tissue was removed and weighed for percent moisture determination (GERG SOP-9415). After drying at 50° C, the tissue was reweighed and percent moisture calculated. Remaining tissue material was stored in the dark at -20° C.

Sediment samples for PAH/AHC/TOC were thoroughly homogenized by stirring with a clean stainless steel or Teflon® utensil, and representative subsamples were then removed as required for the individual analyses. An aliquot (≈1 g wet weight) for dry weight determination was removed, weighed, freeze-dried, and reweighed to determine percent moisture (GERG SOP-9419). A 30 g wet weight aliquot for PAH/AHC analysis was placed in a labeled pre-combusted jar for chemical drying with sodium sulfate until the sample was dry, free-flowing, and homogeneous. Remaining sediment was also dried for archival.

Table 3. List of Applicable Geochemical and Environmental Research Group Standard Operating Procedures used for the 1997 - 1998 LTEMP.

Procedure	GERG SOP No.
Sample receipt/sample preparation	SOP-9225
Percent moisture determination (tissue)	SOP-9415 (replaces SOP-8903)
Percent moisture determination (sediment)	SOP-9419 (replaces SOP-8902)
Extraction of tissue for hydrocarbon analysis	SOP-8903
Extraction of sediment for hydrocarbon analysis	SOP-8902
Extraction of water for hydrocarbon analysis	SOP-8901
Polycyclic aromatic hydrocarbon determination	SOP-9406 (replaces SOP-8905)
Aliphatic hydrocarbon determination	SOP-8904
Weighing lipids (percent lipid determination)	SOP-9414 (replaces SOP-9231)
Particle grain size analysis	SOP-8908
Total organic carbon analysis	SOP-8907

Sediment samples designated for particle grain size analysis were homogenized and subsampled prior to analysis (GERG SOP-8908). Excess PGS sediment was archived at 4°C. Water samples were stored in the dark at or below 4°C until extraction. No further processing was required for these samples.

Just prior to extraction, all hydrocarbon samples and quality control samples were spiked with surrogate solutions. The PAH surrogate solution contained naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, and perylene-d_{12}. Sufficient PAH surrogate solution was added to each sample to provide a final concentration (of extract volume) of 40 nanograms/milliliter (ng/mL) for sediment, tissue, and water matrices. The surrogate solution for AHC analysis was comprised of deuterated n-alkanes with 12, 20, 24, and 30 carbons. Sufficient AHC surrogate solution was added to each sample before extraction to provide a final concentration (of extract volume) of 2 micrograms/milliliter (µg/mL) for sediment and water matrices.

3.2.2 Tissue Extraction Procedures

Extraction of tissue samples followed procedures outlined in GERG SOP-8903. Approximately 5 g (wet weight) of tissue was homogenized and then macerated in 100 mL of methylene chloride and 50 g of sodium sulfate for chemical drying. The sample was then concentrated to 2.0 mL and purified to remove non-hydrocarbon material using a combination of EPA Methods 3611 and 3630, alumina column purification and silica gel purification, respectively (US EPA, 1986). A fraction of the extract was subjected to an additional cleanup step using high-performance liquid chromatography (HPLC) prior to analysis for PAH. Extracts were stored at or below 4° C.

3.2.3 Sediment Extraction Procedures

Extraction procedures followed those described in GERG SOP-8902. Thirty g (wet weight) of chemically-dried sediment was extracted using a Soxhlet extractor with methylene chloride. The extract was concentrated and then purified using EPA Method 3611 alumina column purification (US EPA, 1986) to remove matrix interferences. This clean-up step removes non-hydrocarbons that might otherwise cause interference during analysis. The aliphatic and aromatic fractions were collected in a single fraction and concentrated to 0.5 mL, and aliquots of this were used for analysis of PAH and

AHC. Extracts were stored at or below 4° C prior to and after analysis.

3.2.4 Water Extraction Procedures

Equipment and field blanks were processed using procedures described in GERG SOP-8901. The acidified water samples were serially extracted with methylene chloride. After being concentrated, the extract from each sample was used for PAH and AHC analyses. Extracts were stored at or below 4°C.

3.2.5 Determination of Polycyclic Aromatic Hydrocarbons

Polycyclic aromatic hydrocarbons and their alkylated homologues listed in Table 4 were determined using a gas chromatograph/mass spectrometry (GC/MS) technique in the selected ion monitoring (SIM) mode as described by GERG SOP-9406. This newer SOP is essentially identical to that used on prior LTEMP sediment samples (SOP-8905) except that the deuterated perylene surrogate (perylene-d_{12}) has been made an advisory surrogate only. This has little effect on the LTEMP due to the fact that perylene, which is largely biogenic in nature, is reported but has been excluded from the calculation of total PAH (TPAH).

Gas chromatographic (GC) separation was accomplished on a fused-silica capillary column with a DB-5 bond phase. The GC column fed directly into the ion source of the mass spectrometer (MS) operating in the SIM and electron-impact ionization mode. A computer system interfaced with the MS continuously acquired and stored all mass-spectral data during the analysis. This system also allowed display of a GC/MS data file for ions of specific mass and plotting ion abundances versus time or scan number. Quantitation followed standard procedures as provided in the GERG SOP-9406 and summarized in the Mussel Watch procedural document (NOAA, 1993). Sediment PAH results were reported in ng/g (parts-per-billion [ppb]) dry weight. Equipment blank quantitation was based on 15 g dry sediment, and PAH results were reported in ng/g (ppb).

Extracts were spiked with internal standard solutions prior to analysis. Sufficient internal standards comprised of fluorene-d_{10} and benzo(a)pyrene-d_{12} were used to provide a final concentration (of extract volume) of 40 ng/mL for sediment, tissue, and water matrices. In addition, matrix spike standard solutions were used for matrix spike samples, as described in Section 4.2.4. The matrix spike solution consisted of 2- to 5-ring PAH shown in Table 4.

The method detection limit (MDL) for each analyte, defined as the lowest concentration of analyte that a method can reliably detect, was calculated by performing analyses on pre-extracted sediment and fresh biological tissue following procedures outlined in the Federal Register 40 CFR Part 136, Appendix B (1986). The MDLs for this reporting period listed in Table 5 were determined in Spring 1997 and Spring 1998 as described in Section 4.2.3 below. For data reporting, the MDL was adjusted to account for actual sample size used for the analysis. Analyte concentrations falling below the calculated MDL but above zero (0) were considered estimates and were qualified with the "J" qualifier (see Section 4.2.1). Concentrations equal to zero (0) were not measured and were qualified with the "ND" code for non-detect.

For summed parameters such as TPAH, the cumulative MDLs reflected in Table 5 are the sum of individual MDLs for all the analytes within that parameter. This excludes perylene and the five specific isomers listed at the bottom of the table. Because there is no widely-accepted standard concerning the calculation of the MDL for summed parameters, this cumulative value is intended to provide a measure of what portion of each sum may have fallen below the MDL.

3.2.6 Determination of Aliphatic Hydrocarbons

Aliphatic hydrocarbon (AHC) concentrations for analytes provided in Table 4 were determined utilizing high resolution capillary gas chromatography with flame ionization detection (GC/FID) as described by GERG SOP-8904. The method, based on modification of EPA Method 8100 (US EPA, 1986), is typically used for the analysis of environmental samples for normal alkanes, pristane and phytane, and the UCM. Deviations from the SOP included the reduction in amounts of surrogate, internal standard, and matrix spike solutions added to the sediment samples or extracts prior to analysis.

Gas chromatographic (GC) separation was similar to that described for PAH and used a column that provided baseline resolution of alkanes (n-C_{10} to n-C_{34}), pristane/n-C_{17}, phytane/n-C_{18}, surrogates, and internal standards. The flame ionization output was collected and processed by a data acquisition package.

Table 4. List of Target Analytes for LTEMP Hydrocarbon Analyses.

Polycyclic Aromatic Hydrocarbons (PAH)			Aliphatic Hydrocarbons (AHC)		
Analyte	**Internal Standard Reference**	**Surrogate Reference**	**Analyte**	**Internal Standard Reference**	**Surrogate Reference**
Naphthalene	A	1	**Normal Alkanes**		
C_1-Naphthalenes	A	1	n-C_{10}	A	1
C_2-Naphthalenes	A	2	n-C_{11}	A	1
C_3-Naphthalenes	A	2	n-C_{12}	A	1
C_4-Naphthalenes	A	2	n-C_{13}	A	1
Biphenyl	A	2	n-C_{14}	A	1
Acenaphthylene	A	2	n-C_{15}	A	1
Acenaphthene	A	2	n-C_{16}	A	1
Fluorene	A	2	n-C_{17}	A	1
C_1-Fluorenes	A	2	n-C_{18}	A	1
C_2-Fluorenes	A	2	n-C_{19}	A	1
C_3-Fluorenes	A	2	n-C_{20}	A	1
Phenanthrene	A	3	n-C_{21}	A	1
Anthracene	A	3	n-C_{22}	A	1
C_1-Phenanthrenes/Anthracenes	A	3	n-C_{23}	A	1
C_2-Phenanthrenes/Anthracenes	A	3	n-C_{24}	A	1
C_3-Phenanthrenes/Anthracenes	A	3	n-C_{25}	A	1
C_4-Phenanthrenes/Anthracenes	A	3	n-C_{26}	A	1
Dibenzothiophene	A	3	n-C_{27}	A	1
C_1-Dibenzothiophenes	A	3	n-C_{28}	A	1
C_2-Dibenzothiophenes	A	3	n-C_{29}	A	1
C_3-Dibenzothiophenes	A	3	n-C_{30}	A	1
Fluoranthene	B	3	n-C_{31}	A	1
Pyrene	B	3	n-C_{32}	A	1
C_1-Fluoranthenes/Pyrenes	B	3	n-C_{33}	A	1
Benzo(a)anthracene	B	4	n-C_{34}	A	1
Chrysene	B	4			
C_1-Chrysenes	B	4	**Isoprenoid Hydrocarbons**		
C_2-Chrysenes	B	4	Pristane	A	1
C_3-Chrysenes	B	4	Phytane	A	1
C_4-Chrysenes	B	4			
Benzo(b)fluoranthene	B	4			
Benzo(k)fluoranthene	B	4			
Benzo(e)pyrene	B	4			
Benzo(a)pyrene	B	4			
Perylene	B	5 advisory only			
Indeno(1,2,3-c,d)pyrene	B	4			
Dibenzo(a,h)anthracene	B	4			
Benzo(g,h,i)perylene	B	4			
Specific Isomers					
1-methylnaphthalene	A	1			
2-methylnaphthalene	A	1			
2,6-dimethylnaphthalene	A	2			

Polycyclic Aromatic Hydrocarbons (PAH)			Aliphatic Hydrocarbons (AHC)		
Analyte	**Internal Standard Reference**	**Surrogate Reference**	**Analyte**	**Internal Standard Reference**	**Surrogate Reference**
1,6,7-trimethylnaphthalene	A	2			
1-methylphenanthrene	A	3			
Internal Standards			**Internal Standards**		
Fluorene-d_{10}	A		deuterated n-c_{16}	A	
Benzo(a)pyrene-d_{12}	B				
Surrogates			**Surrogates**		
Naphthalene-d_8		1	deuterated n-C_{20}		1
Acenaphthene-d_{10}		2	deuterated n-C_{12}	Other surrogates for aliphatics are monitored to insure performance of the method; if deuterated n-C_{20} exhibits a matrix interference, the closest surrogate not exhibiting an interference is used for calculations.	
Phenanthrene-d_{10}		3	deuterated n-C_{24}		
Chrysene-d_{12}		4			
Perylene-d_{12} (advisory only)		5	deuterated n-C_{30}		

Table 5. Method Detection Limits (Dry Weight in ng/g) Determined for the 1997 - 1998 LTEMP Hydrocarbon Analyses.

Polycyclic Aromatic Hydrocarbons (PAH)					Aliphatic Hydrocarbons (AHC)		
	Tissue		Sediment			Sediment	
Analyte	July 1997	March 1998	July 1997	March 1998	Analyte	July 1997	March 1998
Naphthalene	7.0	10.9	0.7	1.6	n-C_{10}	3.3	2.5
C_1-Naphthalenes	13.7	21.5	0.5	1.6	n-C_{11}	3.6	2.5
C_2-Naphthalenes	8.6	13.6	0.6	1.3	n-C_{12}	0.7	2.5
C_3-Naphthalenes	5.2	8.2	0.2	1.6	n-C_{13}	0.8	3.4
C_4-Naphthalenes	5.2	8.2	0.2	1.6	n-C_{14}	0.8	4.4
Biphenyl	1.9	7.5	0.3	0.5	n-C_{15}	11.2	6.3
Acenaphthylene	3.5	4.3	0.2	0.4	n-C_{16}	3.0	1.8
Acenaphthene	3.5	5.5	0.1	0.6	n-C_{17}	3.5	1.4
Fluorene	5.8	5.3	0.2	0.8	n-C_{18}	4.1	10.2
C_1-Fluorenes	11.5	10.6	0.4	1.6	n-C_{19}	3.9	0.6
C_2-Fluorenes	11.5	10.6	0.4	1.6	n-C_{20}	3.9	0.9
C_3-Fluorenes	11.5	10.6	0.4	1.6	n-C_{21}	2.7	0.9
Phenanthrene	6.7	6.8	0.1	0.4	n-C_{22}	1.8	1.2
Anthracene	5.2	4.0	0.1	0.4	n-C_{23}	1.4	2.1
C_1-Phenanthrenes/Anthracenes	10.9	17.1	0.3	1.1	n-C_{24}	1.0	1.5
C_2-Phenanthrenes/Anthracenes	10.9	17.1	0.3	1.1	n-C_{25}	1.6	2.3
C_3-Phenanthrenes/Anthracenes	10.9	17.1	0.3	1.1	n-C_{26}	0.9	1.8
C_4-Phenanthrenes/Anthracenes	10.9	17.1	0.3	1.1	n-C_{27}	2.5	3.5
Dibenzothiophene	5.1	6.8	0.2	0.5	n-C_{28}	1.1	3.4
C_1-Dibenzothiophenes	10.3	13.6	0.3	1.0	n-C_{29}	4.7	7.4
C_2-Dibenzothiophenes	10.3	13.6	0.3	1.0	n-C_{30}	1.5	1.9
C_3-Dibenzothiophenes	10.3	13.6	0.3	1.0	n-C_{31}	9.2	6.5
Fluoranthene	4.9	5.6	0.1	0.5	n-C_{32}	2.1	6.1
Pyrene	4.3	4.9	0.1	0.6	n-C_{33}	6.8	3.0
C_1-Fluoranenes/Pyrenes	9.2	10.6	0.1	1.1	n-C_{34}	4.1	4.0
Benzo(a)anthracene	2.5	2.3	0.1	0.3			
Chrysene	3.0	8.0	0.2	0.5			
C_1-Chrysenes	6.1	16.0	0.4	1.0	Pristane	1.0	1.0
C_2-Chrysenes	6.1	16.0	0.4	1.0	Phytane	1.6	1.0
C_3-Chrysenes	6.1	16.0	0.4	1.0			
C_4-Chrysenes	6.1	16.0	0.4	1.0			
Benzo(b)fluoranthene	2.1	3.2	0.1	0.5			
Benzo(k)fluoranthene	7.2	2.2	0.3	0.2			
Benzo(e)pyrene	4.4	4.9	0.1	0.7			
Benzo(a)pyrene	9.6	4.3	0.2	1.4			
Perylene	8.1	12.9	1.1	3.1			
Indeno(1,2,3-c,d)pyrene	3.9	1.8	0.2	0.8			
Dibenzo(a,h)anthracene	3.6	1.4	0.3	0.7			
Benzo(g,h,i)perylene	3.1	2.3	0.1	0.6			
Total PAH (excluding perylene)	262.6	359.1	10.2	35.4	Total AHC	82.8	84.1
1-methylnaphthalene	7.8	12.3	10.2	0.7			
2-methylnaphthalene							

Polycyclic Aromatic Hydrocarbons (PAH)					Aliphatic Hydrocarbons (AHC)		
	Tissue		Sediment			Sediment	
Analyte	July 1997	March 1998	July 1997	March 1998	Analyte	July 1997	March 1998
	5.8	9.2	8.4	0.9			
2,6-dimethylnaphthalene	4.3	6.8	9.1	0.6			
2,3,5-trimethylnaphthalene	2.6	4.1	0.1	0.8			
1-methylphenanthrene	5.4	8.5	0.2	0.5			

Internal standard solution consisted of deuterated n-C_{16}, with a sufficient amount added to obtain a final concentration (of extract volume) of approximately 2 µg/mL for sediment and water matrices. Matrix spiking solution consisting of alkanes from n-C_{10} to n-C_{34} and pristane were added to matrix spike extracts at a concentration sufficient to provide a final concentration of 10 µg/mL for sediment and water matrices.

Analyte concentrations were determined based on the concentration of deuterated n-C_{20} surrogate added before extraction. If this surrogate failed to comply with quality control criteria due to a matrix interference, the closest surrogate not exhibiting an interference was used in the calculations. Sediment data were generally reported in ng/g (ppb) and µg/g (parts-per-million [ppm]) on a dry weight basis for AHC and UCM, respectively. Quantitation followed standard procedures as provided in the GERG SOP-8904 and summarized in the Mussel Watch procedural document (NOAA, 1993). Field and equipment blank quantitation was based on 15 g dry sediment, and results were reported in ng/g (ppb) and µg/g (ppm) for AHC and UCM, respectively.

Method detection limits for individual alkanes and isoprenoids (aliphatic compounds) are provided in Table 5. The MDLs were determined in Spring 1997 and Spring 1998 following procedures outlined in Section 4.2.3. For data reporting, the MDL was adjusted to account for actual sample size used for the analysis. The cumulative MDL for the summed parameter of total AHC (TAHC) reflected in the table is the sum of individual MDLs for all the analytes within that parameter. As there is no widely-accepted standard concerning the MDL for summed parameters, this cumulative value is intended to provide a measure of what portion of each sum may have fallen below the MDL.

Individual AHC analyte concentrations falling below the calculated MDL but above zero (0) are considered estimates and are qualified with the "J" qualifier (see Section 4.2.1). Concentrations equal to zero (0) are not measured and are qualified with the "ND" code for non-detect.

3.2.7 Percent Lipid Determination

Lipid content is defined by GERG SOP-9414 as the weight of material extracted from tissue samples with methylene chloride. Percent lipid material was calculated in tissue extracts by diluting to a known volume, removing an aliquot, evaporating the aliquot to dryness, and weighing the dried material. The weight was then corrected for volume and divided by the sample weight to determine percent lipid.

3.2.8 Gonadal Index Determination

Reproductive state of the mussels was determined for a discrete sample of 20 individual mussels collected from each station during each survey. For each individual mussel collected, four separate measurements were obtained: shell length, shell volume, weight of gonadal tissue, and weight of non-gonadal tissue (excluding byssal threads). After dissection of the bivalves, shell length was measured using metric calipers and recorded to the nearest millimeter (mm). Shell volumes were calculated by measuring the amount of water required to fill the shell and were recorded to the nearest 0.1 mL. Weights of gonadal and non-gonadal tissue were determined using a Mettler® E200 electronic balance and recorded with precision of 0.01 g. After all individual mussels had been measured, gonadal tissue from all individuals was pooled for the measurement of total gonad volume, which was accomplished by measuring the volume of displacement in a graduated cylinder. Non-gonadal tissue was pooled and measured in the same manner. Each total volume measurement was recorded to the nearest 0.5 mL. In addition to these measurements, visual observations concerning shell characteristics,

gonad or body appearance, or other distinguishing factors were recorded as appropriate.

3.2.9 Particle Grain Size Determination

The determination of PGS was performed using a method adapted from Folk (1974), as described by GERG SOP-8908. Sediment samples were homogenized and a subsample of 15 - 20 g removed for analysis. The subsample was treated with 30 percent hydrogen peroxide for 12 hours to oxidize organic matter and washed with distilled water to remove soluble salts. After the addition of dispersant and shaking for approximately 24 hours, this sediment solution was sieved to separate the gravel/sand fraction from the silt/clay fraction. Dry-sieve techniques were used to determine the sand and gravel fractions. Silt and clay fractions were determined by a pipetting technique. Results were reported in percent (%) sand, silt, and clay on a dry weight basis.

3.2.10 Total Organic Carbon Analysis

Total organic carbon analysis was performed as described by GERG SOP-8907 using a 500-mg aliquot of freeze-dried sediment. The sediment was placed in an induction furnace designed to burn samples in an oxygen atmosphere. Gases produced by the combustion were processed and put through an infrared detector for quantification of carbon dioxide. Total organic carbon was determined after sample acidification. Carbonate carbon (inorganic carbon) was determined as the difference between total carbon and total organic carbon. Results were reported in percent TOC and percent total inorganic carbon (TIC, or carbonate carbon) on a dry weight basis.

3.3 Data Management and Analysis

3.3.1 Data Management

Data handling and management followed procedures outlined in prior LTEMP reports. The LTEMP data reside in a relational database consisting of eleven tables in Microsoft® Access® (Table 6). This relational database was used for all aspects of data storage, error checking, and reporting. Microsoft Excel® was also used for data entry, data verification, and calculation of summary statistics.

Table 6. Tables in the LTEMP Database.

Table	Contents
STATION	field sampling information on a by-station basis
SAMPLE	field sampling and sample shipment information on a by-sample basis
ANALYSIS	analytical method and handling data on a by-sample and analysis basis, for field-collected samples
RESULT	analytical results on a by-sample, analysis type, and individual analyte basis, for field-collected samples
QCANAL	analytical method and handling data on a by-sample and analysis basis, for quality control samples originating in the laboratory
QCRESULT	analytical results on a by-sample, analysis type, and individual analyte basis, for quality control samples originating in the laboratory
GONINF	field sampling information for pooled gonadal index measurements (gonadal and non-gonadal tissue volume)
GONIND	gonadal index data on a by-mussel basis (shell length, shell volume, non-gonadal weight, and gonadal

Table	Contents
	weight)
COC	chain of custody (COC) data on a COC basis
COC_XFER	COC information on a COC, relinquish date, and time basis
VALIDVAL	provides valid values that may be found for different types of fields in the other tables (a look-up table)

3.3.2 Statistical Design

As indicated in prior LTEMP reports, the program was designed to determine baseline conditions and help identify potential future impacts of oil transportation in the study area. It was also designed to provide sufficient data to test three null hypotheses addressing differences in chemical and physical characteristics among sampling sites and through time. The initial program applied statistics to test these hypotheses, and the results were reported in annual reports. More recent work on the program (1994 - 1998) has placed emphasis on the collection of more baseline data rather than the statistical testing of those data.

3.3.3 Data Analysis

A number of PAH and AHC parameters indicative of possible petroleum contamination were utilized for summarizing the results of the 1997 - 1998 program (Table 7). These same parameters were used for hypothesis testing in 1993 and 1994 and could be appropriate for use in future hypothesis testing. Polycyclic aromatic hydrocarbon parameters included TPAH and the fossil fuel pollution index (FFPI; Boehm and Farrington, 1984). Aliphatic hydrocarbon parameters included TAHC and the carbon preference index (CPI; Farrington and Tripp, 1977), also known as the odd-even preference index. The UCM was also used as a diagnostic indicator of petroleum contamination and is indicative of petroleum products that have been extensively biodegraded.

Table 7. Hydrocarbon Parameters used in LTEMP Data Analysis.

Parameter	Relevance
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 + chrysene, and their alkyl homologues + other PAH (excluding perylene); useful for determining TPAH contamination; includes petrogenic, pyrogenic, and diagenic sources
FFPI (sediments)	The fossil fuel pollution index is the ratio of fossil-derived PAH to TPAH and is defined as follows: FFPI = (N + F + P + D)/TPAH x 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 + C_2-P + C_3-P + C_4-P 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)
TAHC (sediments)	Total aliphatic 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

Parameter	Relevance
UCM (sediments)	Petroleum compounds represented by the total resolved plus unresolved area minus the total area of all peaks that have been integrated; a characteristic of some fresh oils and most weathered oils
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)

TPAH and TAHC indicate the total level of hydrocarbon input at a site but provide no information on the possible sources (i.e., contamination of petrogenic, biogenic, pyrogenic, or diagenic origin; see glossary). The other parameters described by Table 7 provide information concerning the potential sources of the inputs. While these types of ratios such as the FFPI are useful for determining potential sources of petroleum in sediments, they are less appropriate for tissue analyses because levels of tissue contamination are affected by factors such as preferential uptake of hydrocarbons, bioaccumulation rates, depuration, and other biological processes. Therefore, FFPI ratios have not been discussed for tissues in this report.

In addition, TOC and PGS data were collected as concomitant parameters to hydrocarbons in sediments. In the event of future hypothesis testing, these data would be analyzed to evaluate their correlation with the other sediment parameters. Percent lipid data were reported due to their potential correlation with tissue hydrocarbon parameters. In addition, two measures of reproductive state recorded could be used for hypothesis testing to help evaluate the general conditions of the mussels. These included the ratios of gonadal weight to total body tissue weight (proportional gonadal weight) and gonadal weight to shell volume.

Certain conventions were used in preparing the data for analysis. All data were reported, including values below MDL. Use of data below the MDL (as defined for this program in Sections 3.2.5, 3.2.6, and 4.2.3) is considered valid and useful, particularly when assessing low-level environmental contamination (US EPA, 1993). See prior program reports (KLI, 1996a and 1997a) for further discussion concerning the use of uncensored data for this program. When calculating summed or ratio parameters, all values and estimated values (below MDL, indicated with a "J" qualifier) were used. For parameters where individual analytes were used for calculating summed parameters (TPAH and TAHC) and indices (FFPI, CPI, and gonadal ratios), non-detect concentrations represented with a zero (0) value and/or the "ND" qualifier were assigned a value of zero. For calculation of ratios based on individual analyte values, non-detect or zero values were assigned a value as shown in Table 8 in order to avoid division by zero errors. This method has been shown to cause less bias in estimating population parameters than several alternative methods (Gilbert, 1987).

Table 8. Replacement Values for Zero (0) or Non-Detect (ND) Results in LTEMP Calculations.

Parameter	Tissue		Sediment	
	Minimum Value	Replacement Value	Minimum Value	Replacement Value
PAH analytes	0.1 ng/g	0.05 ng/g	0.1 ng/g	0.05 ng/g
AHC analytes	Not Applicable	Not Applicable	1.0 ng/g	0.5 ng/g

UCM	Not Applicable	Not Applicable	0.1 µg/g	0.05 µg/g

4.0 QUALITY ASSURANCE/QUALITY CONTROL

Since program inception in 1993, the LTEMP has included a comprehensive quality assurance/quality control (QA/QC) program that encompassed all aspects of the project, from initial sample collection through laboratory analysis and data analysis to reporting. The objectives of the QA/QC program were to fully document the field and laboratory data and to maintain data integrity. The QA/QC program has been more fully described by prior program reports (e.g., KLI, 1994a and 1997a) and was designed to allow the data to be assessed by the following parameters:

- Precision
- Accuracy
- Comparability
- Representativeness
- Completeness.

These parameters are controlled by adhering to documented methods and procedures and by the analysis of quality control (QC) samples on a routine basis.

4.1 Field Quality Control

Quality control activities in the field included adherence to documented procedures, including those in the study plan; comprehensive documentation of sample collection and sample identification information; and the collection of quality control samples (equipment and field blanks).

Sampling procedures used for this program have been fully documented in the study plan and prior annual reports. They have also been successfully used on a large number of scientific programs. The use of documented and well-known procedures provided for greater likelihood of obtaining sediment uncontaminated by sampling procedures or apparatus. It also helped ensure that data collected over the course of the program are comparable and that the study results are representative of conditions existing at the sampling sites.

Use of extensive field documentation provided a paper trail that existed for each sample and ensured credibility of the data. In addition, sample integrity and identification were ensured by a rigidly-enforced chain of custody program. The chain of custody procedure documented the handling of a sample from the time the sample was collected to the arrival of the sample at the laboratory.

Equipment rinsate blanks were collected once during each 1997 - 1998 survey for the analysis of PAH and AHC. Equipment blanks consisted of a de-ionized (DI) water rinse of the grab after it had been decontaminated. These blanks helped to assess comparability and representativeness of the data, providing information to determine if the grab and sampling utensils were being adequately cleaned by the decontamination process.

Field blanks were collected once at Station AMT during Survey 11 (March 1998) for the analysis of PAH and AHC. Field blanks consisted of HPLC-grade DI water poured from the DI stock dispenser into the appropriate sampling container. Field blank analysis was used to assess the accuracy, comparability, and representativeness of the data by determining if atmospheric contaminants such as boat exhaust or tanker emissions were present during sampling.

4.2 Laboratory Quality Control

Analytical quality control for this program included adherence to documented procedures, particularly SOPs; calibration of analytical instruments; determination of method detection limits; and use of quality control samples, internal standards, and surrogate solutions.

4.2.1 Adherence to Documented Procedures

The analytical laboratory, GERG, operates under a quality assurance (QA) program described in their QA management plan and an overall QA project plan. This program involves the participation of qualified and trained personnel; the use of standard operating procedures for analytical methodology and procedures; a rigorous system of documenting and validating measurements; maintenance and calibration of instruments; and the analysis of QC samples for precision and accuracy tracking.

Documentation in the laboratory included finalizing the original chain of custody forms and generating the internal documents that track samples through the laboratory, as outlined in GERG SOP-9225. The paper trail included the records of various steps of analysis, including calibration and maintenance of equipment, preparation and analyses of samples, and storage conditions (e.g., refrigerator logs).

Analytical procedures were documented by the GERG SOPs listed in Table 3. Any deviations from the SOPs were documented in the GERG project files. Data affected by such deviations were appropriately qualified as described in Section 4.2.4. The SOPs are comprehensive and typically provide information concerning proper sample collection, storage, and preservation; required apparatus and materials; analytical procedure; standardization and calibration techniques; quality control samples required; methods of calculating values and assessing data quality; and reporting and performance criteria.

The laboratory followed specific procedures when the data results did not meet acceptable quality criteria, as outlined in the appropriate SOPs. This included the re-analysis of samples, if necessary, due to matrix interferences or other problems. All sample results that did not meet QC criteria, if any, were qualified as falling outside QC limits using data qualifiers provided in Table 9. Values that met QC criteria were not typically qualified in the data with the exception that some values were qualified with the "Y" code for internal laboratory use.

Table 9. Qualifiers for LTEMP Data Reporting.

Data Code	Description
B	Analyte reported in blank
D	Sample diluted in order to analyze, therefore surrogate is diluted
J	Quantity below the MDL
ND	Not detected (not measured above zero)
NA	Not applicable
M	Matrix interference
N	Values identified as not within QC criteria
Q	Does not meet QA criteria
Y	Values identified as within QC criteria

4.2.2 Instrument Calibration

Calibration is an integral part of any instrumental analysis. Calibration requirements for each type of analysis used on this program are fully described in the appropriate GERG SOP. Typically, instrument calibration was performed daily and on a per batch basis. For example, for AHC analysis, the gas chromatograph calibration was performed with at least five standards with different concentrations, one of which was near the method detection limit. This initial calibration was verified by the measurement of a calibration standard every six to eight samples.

4.2.3 Determination of Method Detection Limits

The MDLs for the PAH and AHC analyses provided in Table 5 were determined following the method detailed in the Federal Register 40 CFR Part 136, Appendix B (1986). The MDL is defined as the lowest concentration of analyte that a method can reliably detect. The MDLs were determined by calculating results of seven replicate measurements of one low-level or spiked sample. The results of a Student's t-test at the 99 percent confidence level was multiplied by the standard deviation of the seven replicates to obtain the lowest possible concentration that is quantifiable at this 99 percent confidence limit (i.e., that is not considered an estimate). The MDL determinations for the LTEMP were based on 1 g dry weight for tissues with a final extract volume of 1.0 mL and 15 g dry weight for sediment with a final extract volume of 0.5 mL.

MDLs were estimated for analytes not available in the spike solution or in the actual matrix (i.e., biological tissue) by using the closest-related compound. For alkylated homologues such as C_2-naphthalene, MDLs were estimated as twice that of a similar authentic compound. As called for by the procedure, analyte levels greater than 10 times the historical MDL were not used to calculate MDLs; for analytes exhibiting this matrix interference, the MDL was estimated using the closest related compound.

The MDL was adjusted for sample size for each individual sample and each individual analyte for reporting purposes. Analyte concentrations that fell below the calculated MDL but above zero (0) were considered estimates and were qualified with the "J" qualifier. Concentrations equal to zero (0) were not measured and were qualified with the "ND" code for non-detect.

During prior LTEMP reporting periods, TPAH or TAHC values were qualified with the "J" if the qualifier was used on all but two of the individual analytes within that summed parameter. This practice has been discontinued by GERG as it provides no information about how much of the total value actually falls above or below the MDL and is somewhat misleading. Therefore, the summed parameters of TPAH and TAHC do not include qualifiers in this report.

4.2.4 Internal Quality Control Checks

Internal laboratory QC checks included the use of surrogate solutions and QC samples such as procedural blanks, matrix spike/spike duplicates, standard reference materials (SRMs), reference oils, and duplicates. Results from these QC samples allow the assessment of quality assurance parameters such as accuracy and precision of the data. A summary of the QC and acceptable results criteria is provided in Table 10.

Surrogate compounds, described in Section 3.2.1, were spiked into all PAH/AHC samples prior to extraction to measure individual sample matrix effects which are associated with sample preparation and analysis. This included QC samples such as field-collected blanks, procedural blanks, and matrix spike samples. Surrogate compound analyses were reported in percent recovery. If a surrogate could not be measured because the sample required dilution, the surrogate recovery was appropriately qualified ("D"). All surrogate percent recoveries must fall within 40 to 120 percent. If the surrogate recoveries were outside these limits, the laboratory took corrective actions, such as rechecking calculations, ensuring the purity of internal standards and surrogate solutions, verifying instrument performance, or other appropriate steps. If a matrix interference or other problem was identified, the data were appropriately qualified. If investigative and corrective actions failed to identify a problem, the extract was re-injected on the gas chromatograph and the surrogate recoveries again compared to the acceptable limits of 40 to 120 percent. If the surrogate recoveries fell within these limits, the reanalysis data were reported. If QC standards were still not met, the sample may have been re-extracted (if sufficient volume existed) and analyzed. If insufficient volume existed, the data were reported but designated as outside acceptable QC limits. Surrogates that co-eluted with interferences were appropriately qualified and an alternative, closest-eluting surrogate exhibiting no interferences was used for calculations.

A procedural blank consisting of HPLC water was run with each batch of field-collected QC blanks for PAH and AHC. A procedural blank of reagent was run with each batch or at least once in 20 tissue and/or sediment samples for PAH, AHC, and TOC analyses. Procedural blanks were subject to the entire analytical procedure. Procedural blank levels less than

three times the MDL were acceptable for PAH, AHC, and TOC. If blank levels for any component were greater than three times the MDL, the procedure and instruments were investigated to identify sources of contamination. The sample set was typically re-extracted and re-analyzed. Should insufficient sample material be available, the data may be reported with the appropriate qualifier. An analyte exhibiting levels at greater than three times the MDL in the blank would be qualified with the "B", as would the same analyte in the samples in that analytical batch showing that analyte at a level of less than 10 times the MDL. For samples within that batch showing that analyte at concentrations of greater than 10 times the MDL, no qualifier was necessary.

Table 10. Schedule of Internal Quality Control (QC) Checks and Acceptance Criteria for Each Analysis Performed for the LTEMP.

Type of QC (reporting method)	Type of Analysis			
	PAH	**AHC**	**TOC**	**PGS**
Surrogate Spike Solution (% recovery)	all samples and QC samples; 40 - 120 %	all samples and QC samples; 40 - 120 %		
Procedural Blank (concentration)	1 in 20 samples or 1 per batch; < 3x MDL	1 in 20 samples or 1 per batch; < 3x MDL	1 in 20 samples or 1 per batch; < 3x MDL	
Matrix Spike/Matrix Spike Duplicate (% recovery)	1 in 20 samples or 1 per batch; average of all compounds 40 - 120 %. See also duplicate (below)	1 in 20 samples or 1 per batch; average of all compounds 40 - 120 %. See also duplicate (below)		
Standard Reference Material (SRM)	1 in 20 samples or 1 per batch for sediment and tissue PAH; < 30 % of the analytes should deviate more than ±35 % from certified range		Reference material used as calibration standard; values must fall within laboratory's calibration curve	
Reference Oil (concentration)	1 in 20 samples or 1 per batch; averages, standard deviations, and ranges are calculated to provide an estimate of precision	1 in 20 samples or 1 per batch; averages, standard deviations, and ranges are calculated to provide an estimate of precision		
Duplicate (concentration or relative percent difference [RPD])	1 in 20 samples or 1 per batch; used to assess laboratory performance	1 in 20 samples or 1 per batch; used to assess laboratory performance	1 in 20 samples or 1 per batch; ±20 % for low level (<1.0 %) carbon samples and ±10 % for normal/high carbon (>1.0 %	1 in 20 samples or 1 per batch; used for qualitative assessment of homogeneity of sediment

			carbon)	

Matrix spike and matrix spike duplicates were also run with each batch or for every 20 PAH and AHC samples, whichever was more frequent. For this type of quality control analysis, a sample was randomly chosen and split into three subsamples. Two of these subsamples were fortified with the matrix spike solutions. All three subsamples were analyzed following routine procedure, and the fortified samples were reported in percent recovery of the matrix spike solution. The QC criteria for matrix spikes for both PAH and AHC were that the average recoveries for all compounds must fall between 40 and 120 percent. If these criteria were not met, the matrix spike was re-injected on the GC. If the results met the criteria, they were reported. If the re-injection results failed, the entire batch of samples was resubmitted for extraction (if sufficient sample material was available). If insufficient sample existed, the data were reported but designated as falling outside the QC criteria.

The SRMs used for the LTEMP were obtained from the National Institute of Standards and Technology (NIST) and were typically analyzed only for PAH and TOC in sediments (NIST SRM 1941a). For PAH analyses, average values must fall within ±30 percent of the certified values. In addition, less than 30 percent of the analytes having certified values of greater than 10 times the laboratory MDL should exceed ±35 percent of the certified range of values. If these criteria are not met but all other quality control criteria are in control, no corrective action is required, and the data are qualified with the "Q" qualifier code. For TOC, the reference material values must fall within the laboratory's calibration curve. The SRM data provided during this reporting period (Survey 10 only) for AHC do not have certified or consensus values and data are for internal laboratory use.

Additional SRMs were analyzed for tissue PAH (NIST SRM 1974a). Values for this SRM had been reported in the past (pre-1997) as consensus values because the SRM had not yet been certified by NIST; however, certification of this standard occurred in late 1995, and values reported in this data set are compared to the certified values.

Laboratory reference oils consisting of laboratory-prepared *Exxon Valdez* crude oil standards were analyzed with each batch of PAH and AHC. Results of the reference oil analyses were used to provide an estimate of precision over the course of the analysis. Descriptive statistics calculated from these results included averages, standard deviations, and ranges. For the analysis of TOC, LECO® pin and ring carbon standards were run as reference materials and used essentially as calibration standards. Sample results must fall within the laboratory's calibration curve.

Duplicate samples were analyzed for the PAH, AHC, TOC, and PGS parameters at a rate of each batch or one in every 20 samples. Samples were split into two subsamples or duplicates and analyzed following normal protocol. Total organic carbon duplicates must fall within ±20 percent for low level samples (<1.0 percent carbon) and ±10 percent for normal and high level samples (>1.0 percent carbon). Duplicate results for PAH, AHC, and PGS do not have formal acceptance criteria and are used as a more qualitative measure of laboratory performance or sediment homogeneity. In addition, relative percent difference (RPD) criteria were applied to the matrix spike/spike duplicate and sample/duplicate results as a measure of precision. All RPD results recorded at the laboratory are charted to ensure that 95 percent of the points are within two standard deviations of the mean. Separate charts are maintained for each matrix and analyte. For analytes having concentrations of greater than 10 times the MDL, an average RPD of less than 25 is generally considered optimal. In calculating the RPD, the value of half the MDL was used for any analyte where the concentration fell below the MDL.

5.0 RESULTS AND DISCUSSION

5.1 Introduction

The purpose of the LTEMP is to provide long-term baseline measurements of hydrocarbon levels and sources in mussels and sediments at program sites within areas of PWS and the Gulf of Alaska represented by the RCAC. These data may then be used to determine future potential impacts of petroleum industry activities on these measurable aspects of the ecosystem. This report primarily presents results from surveys performed during July 1997 and March 1998. Where pertinent, summary data from prior years of the LTEMP have been included for comparison. This includes depiction of the historical station means (mean of all replicates collected over time) and error bars representing variability of the survey means.

A summary of samples collected during 1997 - 1998 is provided in Table 11. Appendices A and B provide sampling information as well as analytical results for each sample collected and analyzed. This section provides an overview and discussion of analytical results. Where data from prior program years have been included in the text or summarized in tables or figures, the reader is referred to prior reports for additional information as required.

All hydrocarbon parameters include analyte values as well as estimated concentrations (i.e., those that were qualified as below the MDL). Therefore, results and discussion presented in this report are based on data that have not been censored by removing concentrations below the MDL. The reader is referred to the appendices for the full data, including individual analyte values and data qualifiers. The low levels of some of the analytes and the prevalence of estimated concentrations (values below MDL) should be kept in mind while reading this report. Also, lower PAH MDLs were achieved for the July 1997 sample set as compared to earlier LTEMP surveys as well as the March 1998 survey (Table 5). Although the same laboratory procedures were followed, improved instrument sensitivity effectively lowered the baseline above which the signal of hydrocarbons could be seen, so smaller concentrations could be determined, including many of the PAH alkylated homologues that were previously non-detectable in tissue samples. As a result, clearer PAH fingerprints were exhibited for some sites, particularly for tissues where concentrations were generally very low. This was less obvious for the sediments, since sediment PAH concentrations have typically been higher (above MDLs) and many of the alkyl homologues had been detected previously. The MDLs reported for sediment AHC for the July 1997 sample set were also somewhat lower than those reported in the past, but the effect this has on the data was negligible, since concentrations have typically been above MDLs. The MDLs reported for the March 1998 sample set were more comparable to those MDLs reported in prior years of the program, so apparent increases in concentrations at some sites for this survey are likely to be real.

Hydrocarbons are an important constituent of petroleum, with PAH and AHC accounting for more than 70 percent of petroleum by weight. While hydrocarbons are ubiquitous in the marine environment, petroleum-derived hydrocarbons can be used to trace petroleum contamination (Brassell et al., 1978; Boehm and Requejo, 1988; Kennicutt and Comet, 1992). Aliphatic hydrocarbons can also be synthesized by planktonic and terrestrial organisms.

Petroleum contains a homologous series of n-alkanes with one to more than 30 carbons with odd and even n-alkanes present in nearly equal amounts, whereas organisms preferentially produce specific suites of normal alkanes with odd numbers of carbons from 15 to 33. Petroleum also contains a complex mixture of branched and cycloalkanes generally not found in organisms, although the latter may be found as degradation products in bacteria. This complex mixture can produce a chromatographically unresolved complex mixture of compounds (the UCM) when petroleum is extensively biodegraded. The presence and amount of the UCM can be an indicator of petroleum contamination.

Petroleum contains monoaromatic and polycyclic aromatic hydrocarbons (PAH), both of which can be toxic to organisms. Monoaromatic hydrocarbons such as benzene, toluene, and xylene are highly volatile and are quickly lost through evaporative processes. These compounds do not persist in the marine environment for long periods of time and have not been measured in this study. Petroleum contains an extensive suite of PAH, and the amount and composition of the PAH fraction can be effectively used as a tracer of petroleum contamination. PAH are also toxic and serve as an indication of exposure in organisms. In general, PAH are more resistant to microbial breakdown than many aliphatic hydrocarbons and thus tend to persist in the environment longer. Based on consideration of the petroleum chemistry, biological occurrences of hydrocarbons (i.e., interferences), and toxicological effects, aliphatic hydrocarbons (AHC) and PAH were chosen as the

preferred organic tracers of potential future petroleum contamination in PWS.

Table 11. Summary of Samples Collected for the 1997 - 1998 LTEMP.

Station Location	Station Designation	Station Type	Analysis Type	Matrix	Number of Replicates	
					Survey 10 (7/97)	Survey 11 (3/98)
AIALIK BAY	AIB-B	Intertidal	PAH/lipids	Tissue	3	3
	AIB-B	Intertidal	Gonadal Index	Tissue	1	1
ALYESKA MARINE TERMINAL	AMT-B	Intertidal	PAH/lipids	Tissue	3	3
	AMT-B	Intertidal	Gonadal Index	Tissue	1	1
	AMT-S	Subtidal	PAH/AHC	Water blank	1EB	1EB 1FB
	AMT-S	Subtidal	PAH/AHC/TOC	Sediment	3	3
	AMT-S	Subtidal	PGS	Sediment	3	3
DISK ISLAND	DII-B	Intertidal	PAH/lipids	Tissue	3	3
	DII-B	Intertidal	Gonadal Index	Tissue	1	1
	DII-I[a]	Intertidal	PAH/lipids	Tissue	1[b]	NA
	DII-I[a]	Intertidal	PAH/AHC/TOC	Sediment	1[b]	NA
	DII-I[a]	Intertidal	PGS	Sediment	1[b]	NA
	DII-M	Shallow Subtidal	PAH/AHC/TOC	Sediment	3	3
	DII-M	Shallow Subtidal	PGS	Sediment	3	3
GOLD CREEK	GOC-B	Intertidal	PAH/lipids	Tissue	3	3
	GOC-B	Intertidal	Gonadal Index	Tissue	1	1
	GOC-S	Subtidal	PAH/AHC/TOC	Sediment	3	3
	GOC-S	Subtidal	PGS	Sediment	3	3
KNOWLES HEAD	KNH-B	Intertidal	PAH/lipids	Tissue	3	3
	KNH-B	Intertidal	Gonadal Index	Tissue	1	1
	KNH-M	Shallow Subtidal	PAH/AHC/TOC	Sediment	3	3
	KNH-M	Shallow Subtidal	PGS	Sediment	3	3
SHEEP BAY	SHB-B	Intertidal	PAH/lipids	Tissue	3	3
	SHB-B	Intertidal	Gonadal Index	Tissue	1	1
	SHB-M	Shallow Subtidal	PAH/AHC/TOC	Sediment	3	3

Station Location	Station Designation	Station Type	Analysis Type	Matrix	Number of Replicates	
					Survey 10 (7/97)	Survey 11 (3/98)
	SHB-M	Shallow Subtidal	PGS	Sediment	3	3
SHUYAK HARBOR	SHH-B	Intertidal	PAH/lipids	Tissue	3	3
	SHH-B	Intertidal	Gonadal Index	Tissue	1	1
	SHH-M	Shallow Subtidal	PAH/AHC/TOC	Sediment	3	3
	SHH-M	Shallow Subtidal	PGS	Sediment	3	3
SLEEPY BAY	SLB-B	Intertidal	PAH/lipids	Tissue	3	3
	SLB-B	Intertidal	Gonadal Index	Tissue	1	1
	SLB-I[a]	Intertidal	PAH/lipids	Tissue	1[b]	NA
	SLB-I[a]	Intertidal	PAH/AHC/TOC	Sediment	1[b]	NA
	SLB-I[a]	Intertidal	PGS	Sediment	1[b]	NA
	SLB-M	Shallow Subtidal	PAH/AHC/TOC	Sediment	3	3
	SLB-M	Shallow Subtidal	PGS	Sediment	3	3
WINDY BAY	WIB-B	Intertidal	PAH/lipids	Tissue	3	3
	WIB-B	Intertidal	Gonadal Index	Tissue	1	1
	WIB-M	Shallow Subtidal	PAH/AHC/TOC	Sediment	3	3
	WIB-M	Shallow Subtidal	PGS	Sediment	3	3

a Opportunistic Sample

b Archived (Not Analyzed)

EB Equipment Blank

FB Field Blank

NA Not Applicable

Polycyclic aromatic hydrocarbons are generally divided into three main sources: biogenic, petrogenic, and pyrogenic. Biogenic PAH are those formed by biological processes or those formed during the early stages of diagenesis. Biogenic PAH that are synthesized by organisms can be easily differentiated from those in petroleum. Most abundant of these is perylene, which is believed to be formed during the bacteriological breakdown of organic matter in marine sediments by a process called early diagenesis (Venkatesan, 1988). Since perylene is not found in petrogenic PAH, it has been excluded from the summation of TPAH in this report.

Petrogenic PAH include crude oil and its refined products. Potential sources of petrogenic PAH in the LTEMP study area include: Alaska North Slope (ANS) crude including EVOS oil residues; Cook Inlet crude; Katalla, Yakataga, and other eastern Gulf of Alaska seep oil; oil product from the Alyeska Marine Terminal; and refined petroleum products that have made their way into the marine environment. Alaska North Slope crude consists of a mixture of petroleum from the various production fields on the Alaskan North Slope, including Prudhoe Bay, Kuparuk, Endicott, and Lisburne, and

exhibits a fingerprint that is quite distinct from that of oil found in other geographic areas. The EVOS of March 1989 consisted of Alaska North Slope crude, which over time has weathered to produce a slightly different fingerprint than that of fresh crude. Petroleum that originates from natural seeps in the Gulf of Alaska contribute to the natural hydrocarbons (or "background hydrocarbons") in the study area, and these also exhibit a distinctly different fingerprint. Other petroleum products that may have been introduced into the marine environment in PWS include oil products from source-rock in locations other than Alaska. For example, the Great Alaskan Earthquake of 1964 and the resultant tsunamis caused the introduction of fuel oil and asphalt made from California source oils into Port Valdez, and subsequently into PWS (Kvenvolden et al., 1995). These authors noted that residues of these California-sourced products have been found throughout the northern and western parts of PWS, typically in the form of tar balls found on beaches at the high tide line.

Petrogenic PAH have a characteristic fingerprint where the parent compounds (i.e., C_0-naphthalenes, fluorenes, phenanthrenes, dibenzothiophenes, and chrysenes) are usually at lower concentrations than their alkyl homologues. With weathering, this feature becomes more prominent since the more soluble parent compound (C_0) disappears before the alkyl homologue (C_1), which in turn disappears more quickly than C_2, and so on. This characteristic weathering fingerprint is termed a 'water-washed profile' when the $C_0<C_1<C_2<C_3$ within each PAH group.

Pyrogenic PAH sources include 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 usually included in this category also. Pyrogenic PAH are characterized by high molecular weight PAH, greater than C_3-dibenzothiophene, and by high concentrations of the parent compounds compared to their alkyl homologues. A typical pattern for pyrogenic PAH is decreasing concentration with molecular weight within a group, i.e., $C_0>C_1>C_2>C_3>C_4$. It has been noted, however, that the PAH in diesel soot has primarily a petrogenic signature (Bence and Burns, 1995).

5.2 Tissue

Polycyclic aromatic hydrocarbon concentrations in tissues have been widely used to assess the level of exposure to petroleum contamination. However, tissue contaminants may not directly reflect environmental levels due to several factors including preferential uptake, bioaccumulation, detoxification, metabolism, and depuration. These confounding factors can obscure the relationship between body burden and actual exposure. The uptake and ability to eliminate contaminants is dependent on species, with invertebrates such as mussels generally less capable of elimination than vertebrates such as fish. Mussels and other molluscs have been shown to adjust to changes in ambient conditions in 90 days or less (NOAA, 1989b), which means that contaminants in their body tissues are likely to indicate fairly recent exposure. For example, researchers have shown that concentrations of PAH and polychlorinated biphenyls (PCBs) increase in tissue to a level state in about 20 days when the animals were exposed to contaminated resuspended sediments (Pruell et al., 1987).

5.2.1 Polycyclic Aromatic Hydrocarbons

Overall, tissue concentrations of PAH compounds remained relatively low at most stations during the 1997 - 1998 LTEMP. Concentrations of TPAH in each replicate were generally above their cumulative MDLs at each station for each of the two surveys: 263 ppb for July 1997 and 359 ppb for March 1998 (Table 12). However, many individual PAH analytes were found to be at low (below MDL) or non-detectable concentrations at most locations during the two 1997 - 1998 surveys (Appendix A). In general, the July 1997 survey had a much greater percentage of non-detectable PAH analytes as compared to the March 1998 survey. This apparent difference does not appear to be due to higher instrument sensitivity for the March 1998 survey, the data for which were reported using higher MDLs than the July 1997 sample set and lower MDLs than those for past years. This apparent recent increase in PAH was seen at many sites as indicated by mean TPAH levels reported for all LTEMP surveys (Table 13 and Figure 11). In fact, a review of the historical data indicates that many of the stations have shown elevated levels of TPAH during the past two to three surveys when compared to prior surveys. Stations AIB, KNH, SHB, and SHH all showed elevated mean TPAH values during at least one of the last two surveys as compared to all other surveys.

Table 12. Summary of 1997 - 1998 LTEMP Tissue TPAH and Percent Lipid Results.

Station	TPAH (ppb)						Lipid (%)					
	Survey 10 (7/97)			Survey 11 (3/98)			Survey 10 (7/97)			Survey 11 (3/98)		
	Rep. 1	Rep. 2	Rep. 3	Rep. 1	Rep. 2	Rep. 3	Rep. 1	Rep. 2	Rep. 3	Rep. 1	Rep. 2	Rep. 3
AIB-B	601.0	647.2	522.1	1213.7	499.0	1323.7	6.2	4.3	7.4	3.0	3.0	2.9
AMT-B	613.6	485.8	522.5	554.4	546.8	490.0	8.4	8.2	6.3	2.9	2.3	1.9
DII-B	572.4	158.1	143.7	378.8	1287.0	394.8	2.7	4.5	4.7	2.9	2.3	1.6
GOC-B	590.6	310.2	370.6	478.8	450.7	487.2	5.1	6.7	7.7	2.4	3.1	2.4
KNH-B	766.8	857.0	874.2	528.7	1224.5	779.1	4.7	4.3	4.9	4.0	6.8	5.0
SHB-B	1100.9	1093.9	771.8	408.1	257.6	252.5	4.2	4.5	5.2	2.8	4.2	4.1
SHH-B	920.1	401.6	464.5	280.4	661.3	438.5	4.1	4.3	3.3	4.3	3.1	4.3
SLB-B	1005.6	625.8	754.0	562.7	482.0	484.3	5.3	4.5	4.9	3.2	2.4	2.9
WIB-B	354.1	146.1	531.2	436.8	693.0	318.1	4.2	3.4	5.2	2.6	2.5	3.0

Table 13. Mean LTEMP Tissue Results by Station and Survey - 1993 through 1998.

Station (Survey)	TPAH (ppb)	Lipid (%)	Shell Length (mm)	Shell Volume (mL)	Gonadal Weight (g)	Non-Gonadal Weight (g)	Proportional Gonadal Weight (Ratio)	Gonadal Weight/ Shell Volume (Ratio)
AIB-B (3/93)	70.9	6.2	34	3.1	0.13	0.79	0.13	0.04
AIB-B (7/93)	104.5	5.9	31	2.4	0.05	0.61	0.08	0.02
AIB-B (3/94)	193.6	3.7	30	1.7	0.11	0.56	0.16	0.07
AIB-B (7/94)	126.0	8.4	37	3.1	0.14	0.95	0.13	0.05
AIB-B (3/95)	55.6	4.7	36	2.8	0.19	0.95	0.16	0.07
AIB-B (7/95)	54.8	7.0	38	3.7	0.46	1.40	0.24	0.12
AIB-B (3/96)	91.6	4.2	32	2.2	0.17	0.86	0.17	0.08
AIB-B (7/96)	151.4	10.7	34	2.9	0.28	1.06	0.20	0.10
AIB-B (3/97)	292.1	4.7	34	2.0	0.11	0.85	0.11	0.06
AIB-B (7/97)	590.1	6.0	35	2.7	0.24	0.99	0.18	0.09
AIB-B (3/98)	1012.1	3.0	34	2.4	0.25	0.87	0.23	0.11
AMT-B (3/93)	325.0	7.6	42	5.7	0.40	1.55	0.20	0.07
AMT-B (7/93)	248.2	6.4	43	4.1	0.26	1.46	0.15	0.07

Station (Survey)	TPAH (ppb)	Lipid (%)	Shell Length (mm)	Shell Volume (mL)	Gonadal Weight (g)	Non-Gonadal Weight (g)	Proportional Gonadal Weight (Ratio)	Gonadal Weight/ Shell Volume (Ratio)
AMT-B (3/94)	797.3	3.8	41	4.4	0.32	1.22	0.19	0.07
AMT-B (ELS)	14351.2	8.9	42	2.4	0.34	1.27	0.21	0.15
AMT-B (7/94)	1580.7	10.7	40	3.7	0.22	1.21	0.15	0.06
AMT-B (3/95)	517.1	2.1	42	4.5	0.16	1.05	0.12	0.03
AMT-B (7/95)	87.3	6.6	42	4.4	0.47	1.88	0.20	0.11
AMT-B (3/96)	241.6	1.4	40	4.0	0.13	0.98	0.12	0.03
AMT-B (7/96)	229.2	6.1	42	4.4	0.42	1.61	0.20	0.10
AMT-B (BWTP)	578.3	4.7	42	4.2	0.26	1.34	0.16	0.06
AMT-B (3/97)	582.2	3.8	40	3.9	0.24	1.12	0.17	0.06
AMT-B (7/97)	540.6	7.6	42	4.9	0.38	1.64	0.19	0.08
AMT-B (3/98)	530.4	2.4	38	3.9	0.18	0.95	0.16	0.04
DII-B (3/93)	107.0	4.5	36	3.7	0.13	0.81	0.14	0.04
DII-B (7/93)	92.1	6.8	40	4.6	0.23	1.33	0.15	0.05
DII-B (3/94)	290.4	6.5[a]	39	3.9	0.29	1.19	0.19	0.07
DII-B (7/94)	812.7	6.1	41	4.3	0.24	1.30	0.16	0.06
DII-B (3/95)	248.8	3.1	40	3.9	0.28	1.29	0.17	0.07
DII-B (7/95)	113.3	3.7	42	5.0	0.32	1.50	0.17	0.07
DII-B (3/96)	116.6	0.8	38	3.7	0.11	0.89	0.11	0.03
DII-B (7/96)	120.3	3.3	37	3.5	0.14	0.95	0.13	0.04
DII-B (3/97)	349.9	3.0	34	2.6	0.16	0.87	0.15	0.06
DII-B (7/97)	291.4	4.0	35	2.8	0.17	0.98	0.14	0.06
DII-B (3/98)	686.9	2.3	34	2.6	0.32	0.96	0.25	0.13
GOC-B (3/93)	617.6	6.0	38	4.2	0.43	1.25	0.26	0.10
GOC-B (7/93)	127.1	7.0	41	4.9	0.25	1.47	0.14	0.05
GOC-B (3/94)	549.0	4.1	42	4.3	0.21	1.16	0.15	0.05
GOC-B (7/94)	778.5	12.1	43	4.3	0.31	1.66	0.16	0.07
GOC-B (3/95)	644.5	3.7	38	3.3	0.14	0.95	0.12	0.04
GOC-B (7/95)	77.5	8.0	41	4.2	0.41	1.64	0.20	0.10
GOC-B (3/96)	151.0	1.5	38	3.5	0.15	0.92	0.13	0.04
GOC-B (7/96)	132.7	6.3	40	3.6	0.42	1.54	0.21	0.12
GOC-B (3/97)	391.2	3.3	39	3.8	0.25	1.15	0.17	0.06

Station (Survey)	TPAH (ppb)	Lipid (%)	Shell Length (mm)	Shell Volume (mL)	Gonadal Weight (g)	Non-Gonadal Weight (g)	Proportional Gonadal Weight (Ratio)	Gonadal Weight/ Shell Volume (Ratio)
GOC-B (7/97)	423.8	6.5	41	4.0	0.34	1.56	0.17	0.08
GOC-B (3/98)	472.2	2.6	40	4.0	0.23	1.09	0.17	0.06
KNH-B (3/93)	72.4	4.4	30	2.2	0.08	0.52	0.13	0.04
KNH-B (7/93)	106.4	6.7	25	1.2	0.07	0.39	0.15	0.06
KNH-B (3/94)	411.1	4.9	28	1.1	0.12	0.46	0.16	0.13
KNH-B (7/94)	375.7	7.3	33	2.2	0.11	0.67	0.13	0.05
KNH-B (3/95)	137.5	4.5	31	2.2	0.09	0.66	0.11	0.04
KNH-B (7/95)	100.9	8.7	32	2.3	0.28	0.87	0.24	0.12
KNH-B (3/96)	144.8	3.5	30	2.2	0.11	0.63	0.15	0.05
KNH-B (7/96)	365.2	7.9	30	2.3	0.13	0.64	0.17	0.06
KNH-B (3/97)	472.8	2.8	29	1.9	0.09	0.50	0.15	0.05
KNH-B (7/97)	832.7	4.6	29	1.4	0.08	0.54	0.13	0.06
KNH-B (3/98)	844.1	5.3	27	1.4	0.08	0.48	0.15	0.06
SHB-B (3/93)	44.1	5.0	37	4.1	0.19	0.99	0.16	0.05
SHB-B (7/93)	293.1	5.7	37	3.7	0.19	1.03	0.15	0.05
SHB-B (3/94)	96.9	6.4	37	2.8	0.17	0.96	0.14	0.06
SHB-B (7/94)	203.6	7.9	37	3.1	0.11	0.97	0.10	0.04
SHB-B (3/95)	66.2	4.0	36	3.6	0.15	1.00	0.12	0.04
SHB-B (7/95)	77.6	6.8	34	2.6	0.21	0.92	0.19	0.08
SHB-B (3/96)	111.2	2.5	33	3.0	0.13	0.80	0.14	0.05
SHB-B (7/96)	320.6	7.7	33	2.6	0.19	0.74	0.20	0.07
SHB-B (3/97)	390.7	3.9	34	2.9	0.18	0.74	0.20	0.07
SHB-B (7/97)	988.9	4.6	34	2.5	0.12	0.83	0.12	0.05
SHB-B (3/98)	306.1	3.7	34	2.7	0.25	0.97	0.20	0.10
SHH-B (7/93)	58.0	7.3	41	4.2	0.19	1.23	0.13	0.05
SHH-B (3/94)	83.3	5.4	39	4.0	0.33	1.30	0.20	0.08
SHH-B (7/94)	67.5	9.5	45	5.4	0.31	1.77	0.15	0.06
SHH-B (3/95)	58.9	7.3	39	3.6	0.33	1.34	0.19	0.09
SHH-B (7/95)	55.7	6.0	43	4.8	0.32	1.65	0.16	0.07

Station (Survey)	TPAH (ppb)	Lipid (%)	Shell Length (mm)	Shell Volume (mL)	Gonadal Weight (g)	Non-Gonadal Weight (g)	Proportional Gonadal Weight (Ratio)	Gonadal Weight/ Shell Volume (Ratio)
SHH-B (3/96)	100.0	3.2	41	3.7	0.28	1.37	0.17	0.07
SHH-B (7/96)	341.0	9.0	39	3.7	0.20	1.22	0.14	0.05
SHH-B (3/97)	319.1	1.7	40	4.0	0.20	1.10	0.15	0.05
SHH-B (7/97)	595.4	3.9	40	3.9	0.19	1.23	0.15	0.05
SHH-B (3/98)	460.1	3.9	36	2.5	0.14	0.94	0.12	0.05
SLB-B (3/93)	358.4	4.8	32	3.0	0.15	0.81	0.15	0.05
SLB-B (7/93)	91.6	6.7	30	2.0	0.09	0.59	0.13	0.05
SLB-B (3/94)	2209.3	5.7[b]	28	1.4	0.10	0.33	0.24	0.08
SLB-B (7/94)	385.8	8.1	37	3.2	0.20	1.07	0.16	0.06
SLB-B (3/95)	623.5	4.5	33	2.8	0.14	0.87	0.13	0.05
SLB-B (7/95)	162.3	8.2	34	3.0	0.17	0.88	0.15	0.05
SLB-B (3/96)	129.8	2.3	32	2.3	0.12	0.72	0.14	0.05
SLB-B (7/96)	124.7	4.6	32	2.5	0.12	0.77	0.14	0.05
SLB-B (3/97)	298.8	2.4	34	2.6	0.08	0.65	0.10	0.03
SLB-B (7/97)	795.1	4.9	33	2.2	0.15	0.87	0.15	0.08
SLB-B (3/98)	509.7	2.8	33	2.7	0.23	0.88	0.21	0.09
WIB-B (3/93)	64.6	5.1	35	3.8	0.11	0.84	0.10	0.03
WIB-B (7/93)	84.4	8.2	36	3.4	0.16	0.97	0.14	0.05
WIB-B (3/94)	125.6	6.3	37	3.2	0.14	0.94	0.13	0.04
WIB-B (7/94)	86.3	7.7	40	4.1	0.23	1.26	0.15	0.05
WIB-B (3/95)	62.0	8.4	36	2.8	0.13	0.92	0.12	0.05
WIB-B (7/95)	52.8	6.1	37	3.4	0.27	1.16	0.18	0.08
WIB-B (3/96)	112.0	2.9	39	3.7	0.17	1.15	0.13	0.04
WIB-B (7/96)	148.7	6.9	39	4.2	0.24	1.27	0.15	0.05
WIB-B (3/97)	559.3	2.7	40	3.3	0.11	1.09	0.08	0.03
WIB-B (7/97)	343.8	4.3	37	3.7	0.20	1.11	0.15	0.06
WIB-B (3/98)	482.6	2.7	38	2.9	0.29	1.20	0.20	0.10

[a] Mean of Replicates 1 and 2 only; Replicate 3 lost during processing.

[b] Mean of Replicates 2 and 3 only; Replicate 1 lost during processing.

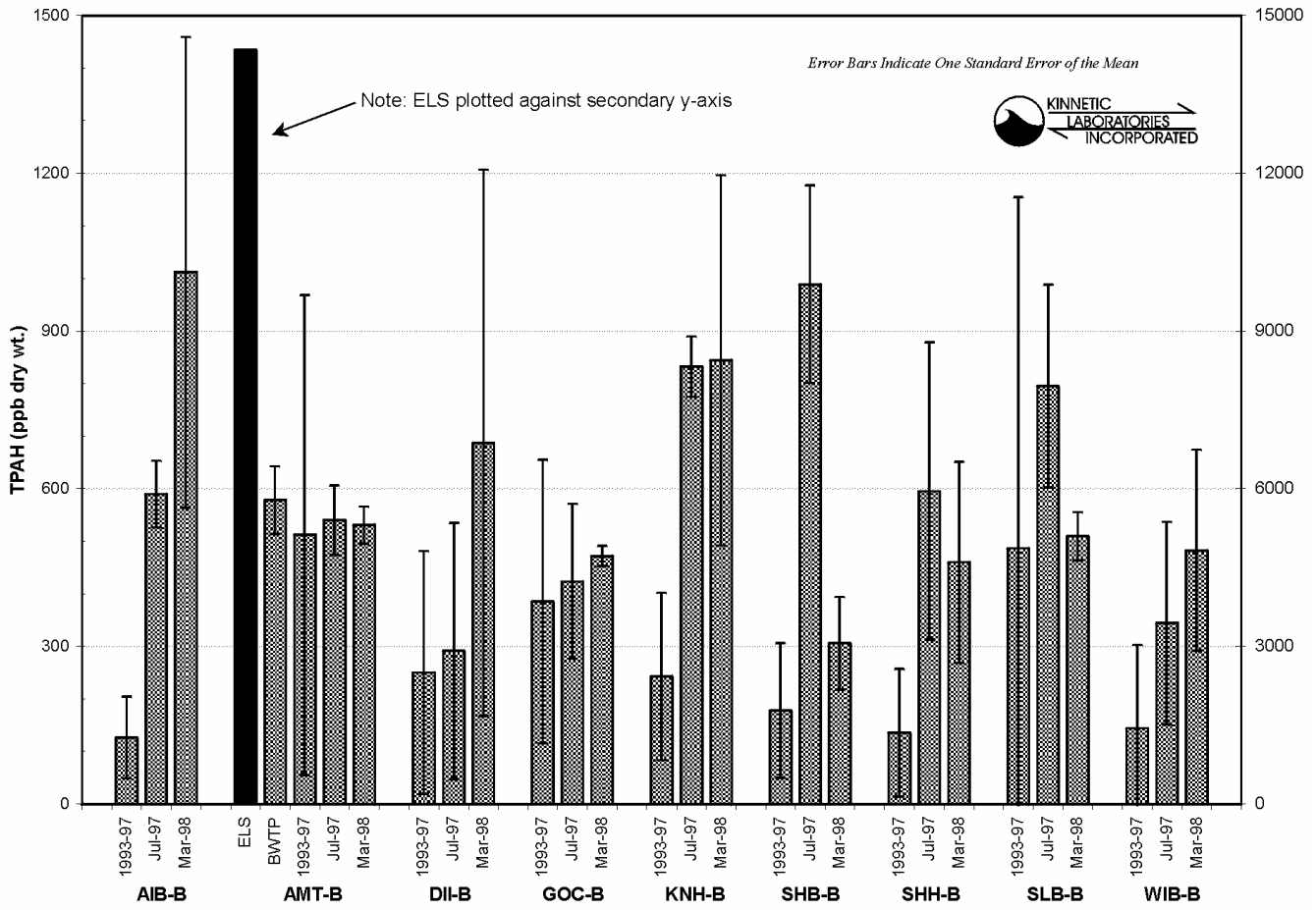

Figure 11. Mean LTEMP Tissue TPAH by Station and Survey - Historical, July 1997, and March 1998.

Mean TPAH concentrations at most of the stations varied greatly both within and between surveys (Tables 12 and 13; Figure 11). Exceptions were Stations AMT and GOC, which had similar TPAH concentrations between replicates for both the July 1997 and March 1998 surveys. Other stations, such as AIB for the March 1998 survey, show relatively large intra-station variability (i.e., relatively large differences between replicates). Station AIB is a reference site and showed a mean TPAH range of approximately 56 to 194 ppb over the course of the first eight surveys. The last survey (March 1998) showed an elevated mean TPAH concentration of 1,012 ppb, with individual replicates at 1,213.7, 499.0, and 1,323.7 ppb. Part of this elevated TPAH trend appears to be due to lowered MDLs reported for the last three surveys, however some of the changes such as those seen at Station AIB are too large to be explained by this alone. Some of the elevated TPAH values seen during the 1997 - 1998 LTEMP were the result of one elevated replicate at each station, and this considerable within-station variability is reflected by the large error bars depicted on Figure 11 and presented in Table 12.

The PAH fingerprint for Station AIB from the March 1998 survey is presented in Figure 12. The PAH concentrations at Station AIB have increased substantially over the past six surveys, however the exact source of this contamination is unknown. The high TPAH seen in the individual replicates from this survey were partially the result of elevated naphthalenes in the samples with respect to the other analytes. The fact that low molecular weight naphthalenes were still relatively abundant would indicate a fairly fresh source. It is possible that the source of PAH was from either diesel or gasoline which may be due to vessel activity in the area; however, the presence of low-level chrysenes would indicate other sources as well. The alkyl phenanthrenes were found to be much higher in concentration relative to that of the alkyl dibenzothiophenes, which would indicate that the source was not from ANS feed stock.

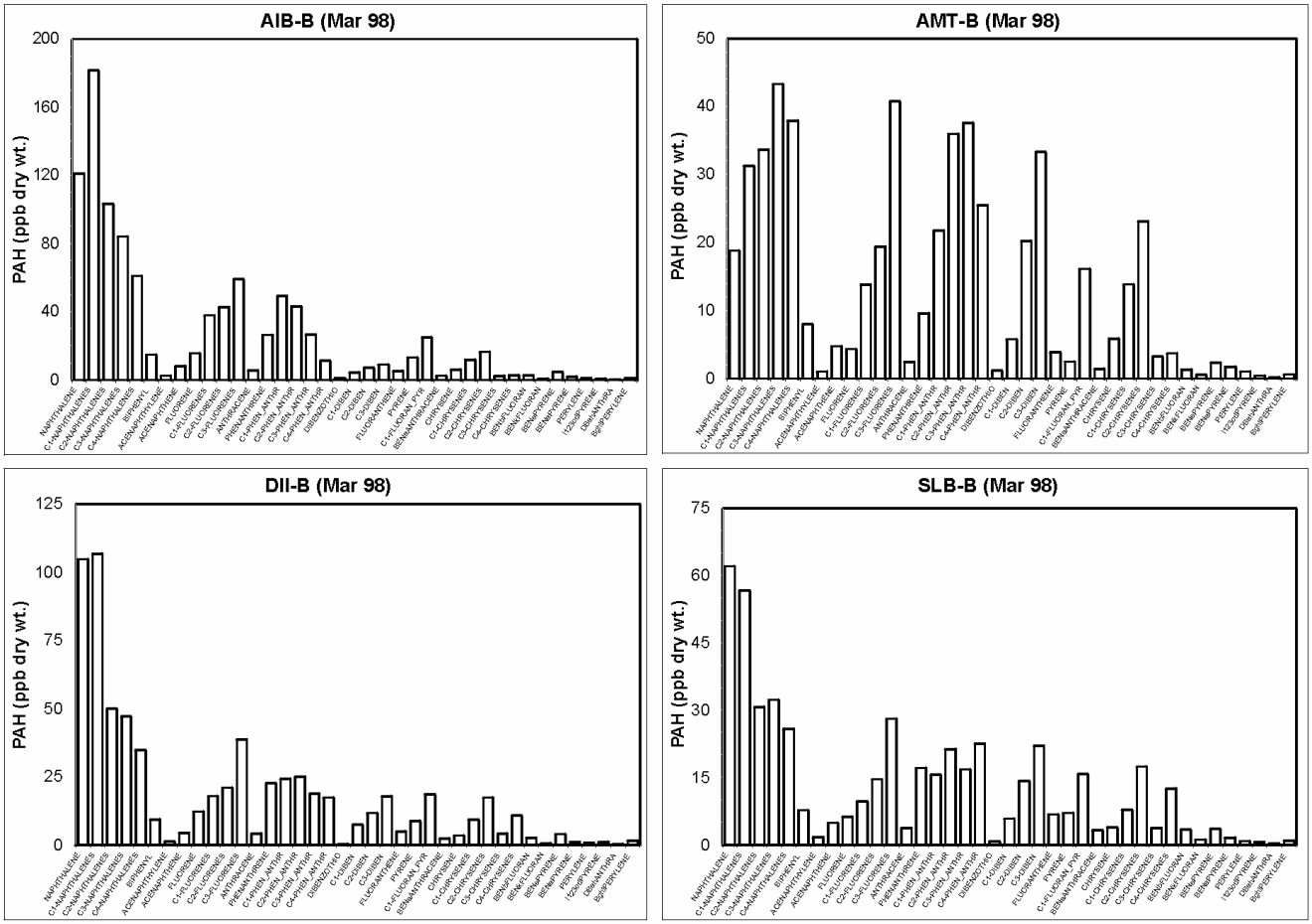

Figure 12. Mean Tissue PAH Values for LTEMP - March 1998 Survey, Stations AIB-B, AMT-B, DII-B, and SHB-B.

The elevated mean TPAH exhibited at Station AMT after the T/V *Eastern Lion* spill (ELS) of May 1994 had apparently subsided, with surveys conducted from July 1995 to July 1996 (Surveys 6 - 8) showing the lowest mean TPAH concentrations encountered at that station. The Alyeska Ballast Water Treatment Plant (BWTP) spill sampling in January 1997 and the subsequent sampling showed somewhat elevated TPAH levels, although these values were again within the range of historical values seen at this site. As reported elsewhere, statistical comparisons of the BWTP spill sampling with historical data from this site failed to show significant differences between sampling times, nor were the fingerprints from tissues from the BWTP sampling indicative of contamination from the spilled oil (KLI, 1997d). Mean TPAH concentrations from the last four surveys were similar in concentration and ranged from 530.4 to 582.2 ppb, well within the range of values historically seen at this site (Table 13 and Figure 11). The PAH fingerprint for March 1998 at Station AMT is presented in Figure 12. The PAH signature at AMT was consistent with ANS crude as the source. The ratio of alkyl dibenzothiophenes to alkyl phenanthrenes was slightly less than 1 and alkyl chrysenes were present, which would indicate that the contamination was not the result of diesel fuel. Naphthalenes and fluorenes were also abundant in the samples, indicating a fairly fresh, unweathered source.

The mean tissue TPAH concentration at Station DII was 686.9 ppb during March 1998, the second highest value seen at this site over time (Table 13). Mean TPAH in July 1997 was 291.4 ppb. The tissue PAH fingerprints from Station DII during the March 1998 indicate hydrocarbons of a petrogenic nature (Figure 12). Ratios of C_2-dibenzothiophene/C_2-phenanthrene and C_3-dibenzothiophene/C_3-phenanthrene in the tissue sample closely approached those described for EVOS oil (Bence and Burns, 1995). The C_2-chrysene/C_2-phenanthrene ratio of approximately 0.8 indicates that this oil has undergone some weathering when compared to earlier surveys. Prior surveys found a ratio of about 0.2 which indicates that the source was relatively fresh and similar to both fresh EVOS oil and Katalla Seep oil (approximately 0.2;

Bence and Burns, 1995). The PAH signature in the tissue sample appeared to be slightly more weathered than seen previously as evidenced by the relatively higher levels of chrysenes; however, the pattern was still consistent with EVOS oil as the source.

Mean TPAH values seen at Station GOC were 423.8 and 472.2 ppb for July 1997 and March 1998, respectively. Although not depicted, the PAH fingerprint at Station GOC during the March 1998 survey was typical of ANS crude with the alkyl phenanthrenes similar in concentration to that of the alkyl dibenzothiophenes and with lower levels of alkyl chrysenes. Naphthalenes were also abundant indicating a fairly fresh, unweathered source. A comparison of PAH fingerprints from Stations GOC and AMT indicated a very similar pattern at the two stations. These results are similar to that seen during most of the prior surveys.

Levels of PAH in mussel tissue from Station KNH collected during the 1997 - 1998 LTEMP were relatively high at 832.7 and 844.1 ppb. The March 1998 samples exhibited the highest mean TPAH seen at this station to date (844.1 ppb), but the fingerprint from this station exhibits a pattern that is consistent with natural background for PWS. The level of alkyl phenanthrenes as compared to the alkyl dibenzothiophenes indicates that the petroleum is not sourced from ANS crude. The March 1998 survey yielded a clearer fingerprint with a greater number of reported concentrations for individual PAH analytes as compared to prior surveys; however, most individual analyte concentrations were still below their respective MDLs for the survey.

Mean TPAH levels seen during 1997 - 1998 at Station SLB were 795.1 and 509.7 ppb. The PAH fingerprint for March 1998 at this station exhibited a signature that is characteristic of weathered petroleum (Figure 12). The fluorenes, phenanthrenes, dibenzothiophenes, and chrysenes all have developed a 'water-washed profile', where the distribution of the parent (C_0) to the alkyl homologues is $C_0<C_1<C_2<C_3$. The ratio of alkyl dibenzothiophenes to phenanthrenes was nearly 1, and the degree of weathering indicated that EVOS oil was the likely source since this site had been heavily oiled during the spill.

In addition to the petrogenic PAH seen at these sites discussed above, small amounts of pyrogenic hydrocarbons consisting of fluoranthene, pyrene, and an assortment of 5- and 6-ring PAH were also found to be present at most locations. This pyrogenic material may come from combustion products (i.e., exhaust) or possibly creosote at some locations.

The majority of fingerprints from the other stations (SHB, SHH, and WIB) during the March 1998 survey indicated a signature that was consistent with the natural background and seeps in the region. In the July 1997 survey, many of the mussel tissues show the typical laboratory procedural artifact pattern where values greater than zero were reported for each analyte that had a laboratory calibration standard. This artifact is due to the fact that parent analytes with calibration standards have much lower MDLs than their alkylated homologues, so these parent analytes are typically reported while their homologues may not be detected.

In general, low (below MDL) or non-detectable PAH hydrocarbon body burdens were seen in resident mussel populations at most locations during the July 1997 and March 1998 surveys with a greater percentage of non-detectable PAH occurring in July 1997. Even with these low concentrations, however, there was an apparent increase in TPAH concentrations at some locations during July 1997 and March 1998 compared to the long-term average. It appeared that many of the alkylated homologues that were previously non-detectable were found in these samples at estimated concentrations (i.e., below the MDL). Overall, since many of the measured concentrations were qualified as estimates, care needs to be taken in drawing any conclusions from data other than those discussed above.

5.2.2 Percent Lipids

Tissue percent lipid concentrations were similar among stations and among surveys (Tables 12 and 13). Mean concentrations of lipids in tissues during July 1997 ranged from 3.9 % at Station SHH to 7.6 % at Station AMT. Mean lipid concentrations in March 1998 ranged from 2.3 % at Station DII to 5.3 % at Station KNH. The apparent general trend at most sites of higher lipid concentrations during the summer surveys compared to the winter surveys continued for the recent two surveys (Figure 13; Table 13). These differences are attributed to the reproductive state and maturity of the mussel populations that were sampled.

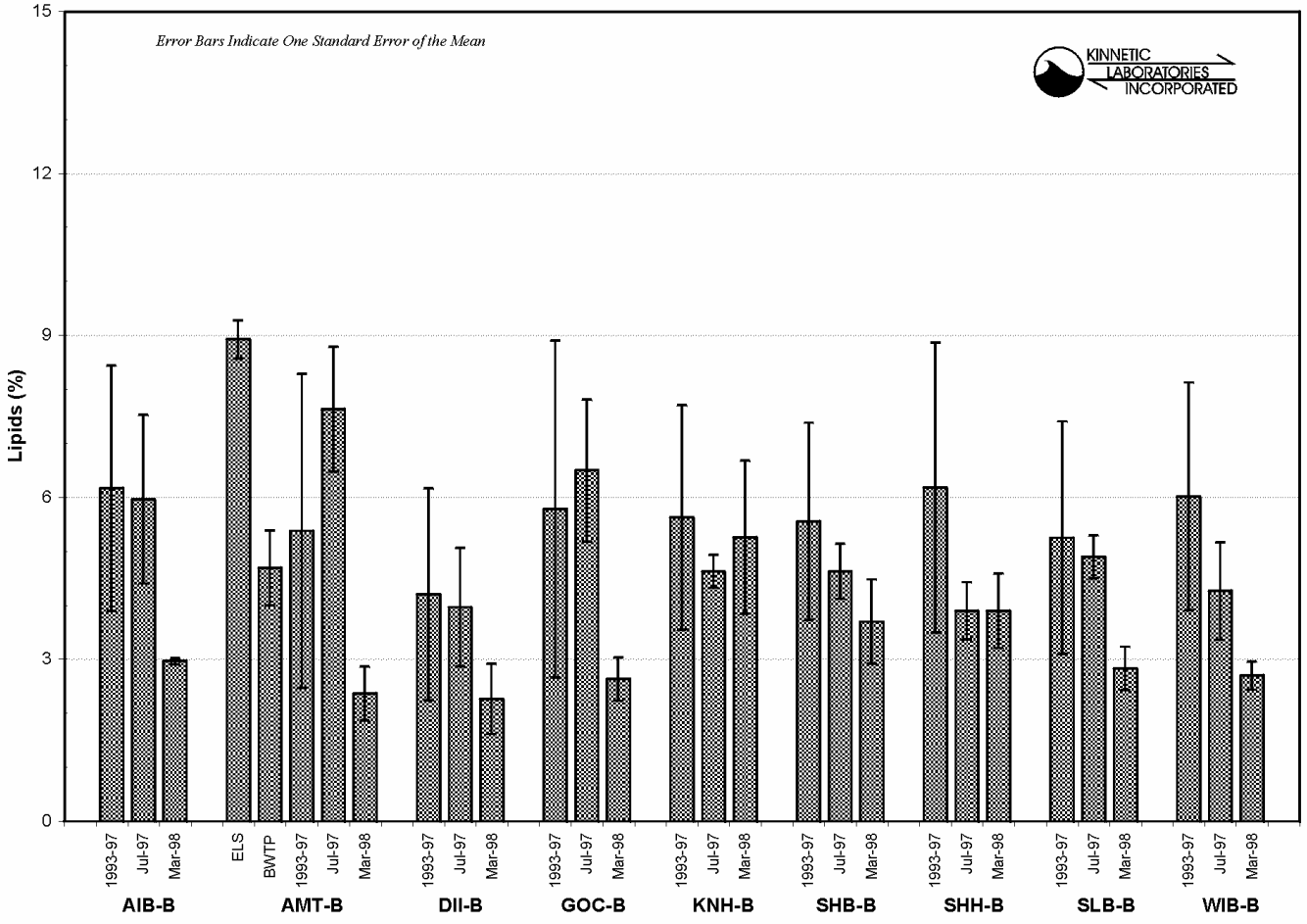

Figure 13. Mean LTEMP Tissue Percent Lipids by Station and Survey - Historical, July 1997, and March 1998.

Although there was some indication of seasonal effects on gonadal development and spawning, there was sufficient scatter in the data to suggest that the timing of these activities is variable among stations and years (Table 13). However, it seems fairly certain that gonadal development occurs in the winter and early spring and that spawning occurs at least once in the late spring or early summer. This is supported by observations by Keiser (1978) of *Mytilus edulis* in Port Valdez, and is in contrast with those of Suchanek (1979) for Washington State and other areas (by reference). Although *Mytilus* apparently spawns in late winter to early spring in temperate areas, spawning may be retarded in more northern areas due to longer more intense winters.

5.2.3 Gonadal Index

In general, values of shell volume, gonadal tissue weight, and non-gonadal weights corresponded well (Tables 13 and 14; Appendix A), indicating that differences in these raw values were related more to the size of the mussels at a station than to the relative health or reproductive state of individuals among stations. When the gonadal data were evaluated using ratios of the gonadal weight to the total weight or to the shell volume, few differences were seen between either stations or

surveys (Figures 14 and 15). Although there was some variability, these attributes were generally similar at a given station among surveys. This suggests that there have been no major population shifts and that minor variations reflect somewhat patchy distributions of size classes. Mussels were largest overall at Stations AMT, GOC, SHH, and WIB, and smaller at the remaining stations, particularly Station KNH (Table 14).

Table 14. Summary of Mean 1997 - 1998 LTEMP Gonadal Index Results.

Station	Shell Length (mm)		Shell Volume (mL)		Non-Gonadal Weight (g)		Gonadal Weight (g)		Proportional Gonadal Weight (Ratio)		Gonadal Weight/Shell Volume (Ratio)	
	Survey 10 (7/97)	Survey 11 (3/98)	Survey 10 (7/97)	Survey 11 (3/98)	Survey 10 (7/97)	Survey 11 (3/98)	Survey 10 (7/97)	Survey 11 (3/98)	Survey 10 (7/97)	Survey 11 (3/98)	Survey 10 (7/97)	Survey 11 (3/98)
AIB-B	35	34	2.7	2.4	0.99	0.87	0.24	0.25	0.18	0.23	0.09	0.11
AMT-B	42	38	4.9	3.9	1.64	0.95	0.38	0.18	0.19	0.16	0.08	0.04
DII-B	35	34	2.8	2.6	0.98	0.96	0.17	0.32	0.14	0.25	0.06	0.12
GOC-B	41	40	4.0	4.0	1.56	1.09	0.34	0.23	0.17	0.17	0.08	0.06
KNH-B	29	27	1.4	1.4	0.54	0.48	0.08	0.08	0.12	0.15	0.06	0.06
SHB-B	34	34	2.5	2.7	0.83	0.97	0.12	0.25	0.12	0.20	0.05	0.10
SHH-B	40	36	3.9	2.5	1.28	0.94	0.19	0.14	0.13	0.102	0.05	0.05
SLB-B	33	33	2.2	2.7	0.87	0.88	0.15	0.23	0.15	0.21	0.08	0.09
WIB-B	37	38	3.7	2.9	1.11	1.20	0.20	0.29	0.15	0.20	0.06	0.10

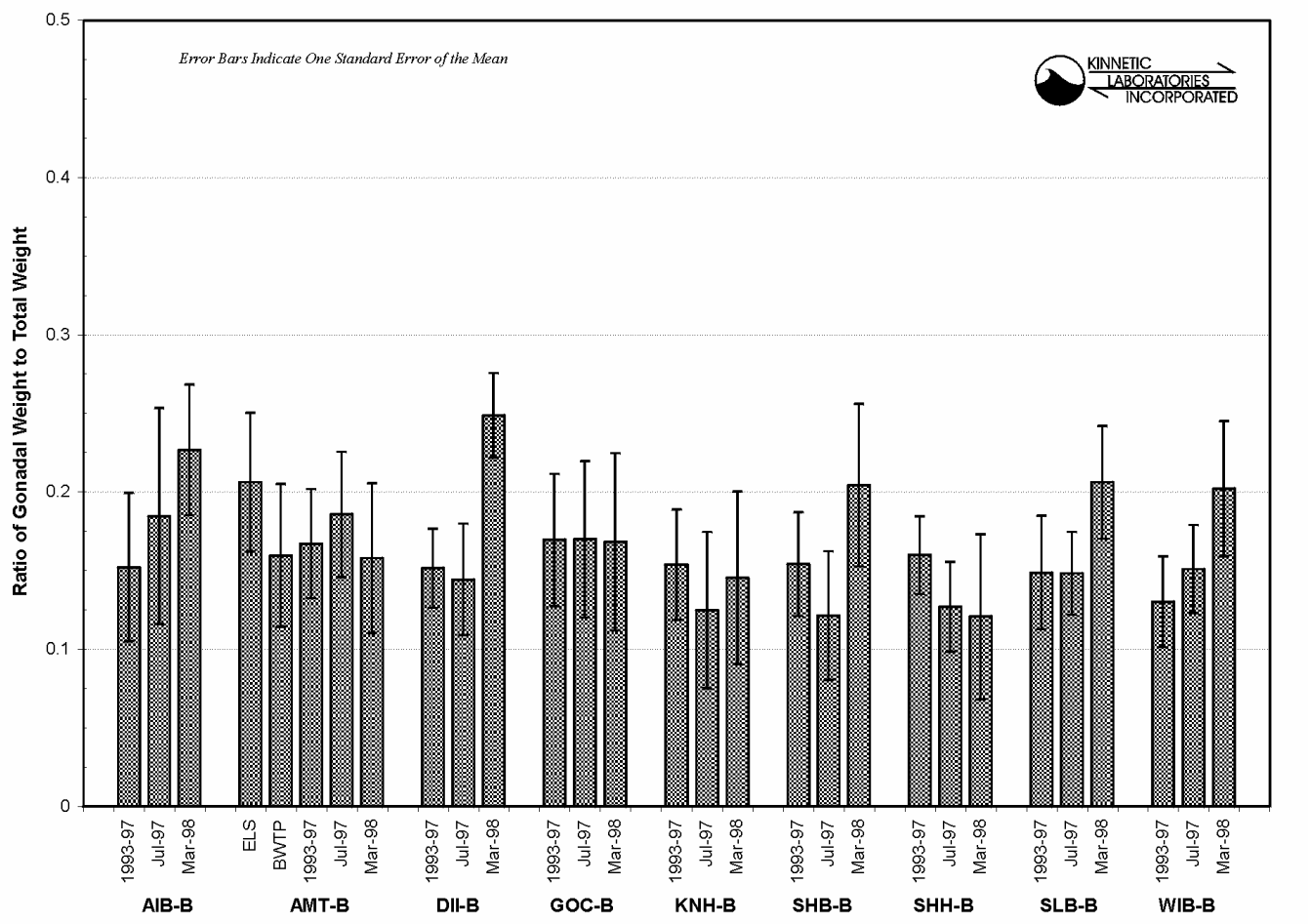

Figure 14. Mean LTEMP Proportional Gonadal Weight by Station and Survey - Historical, July 1997, and March 1998.

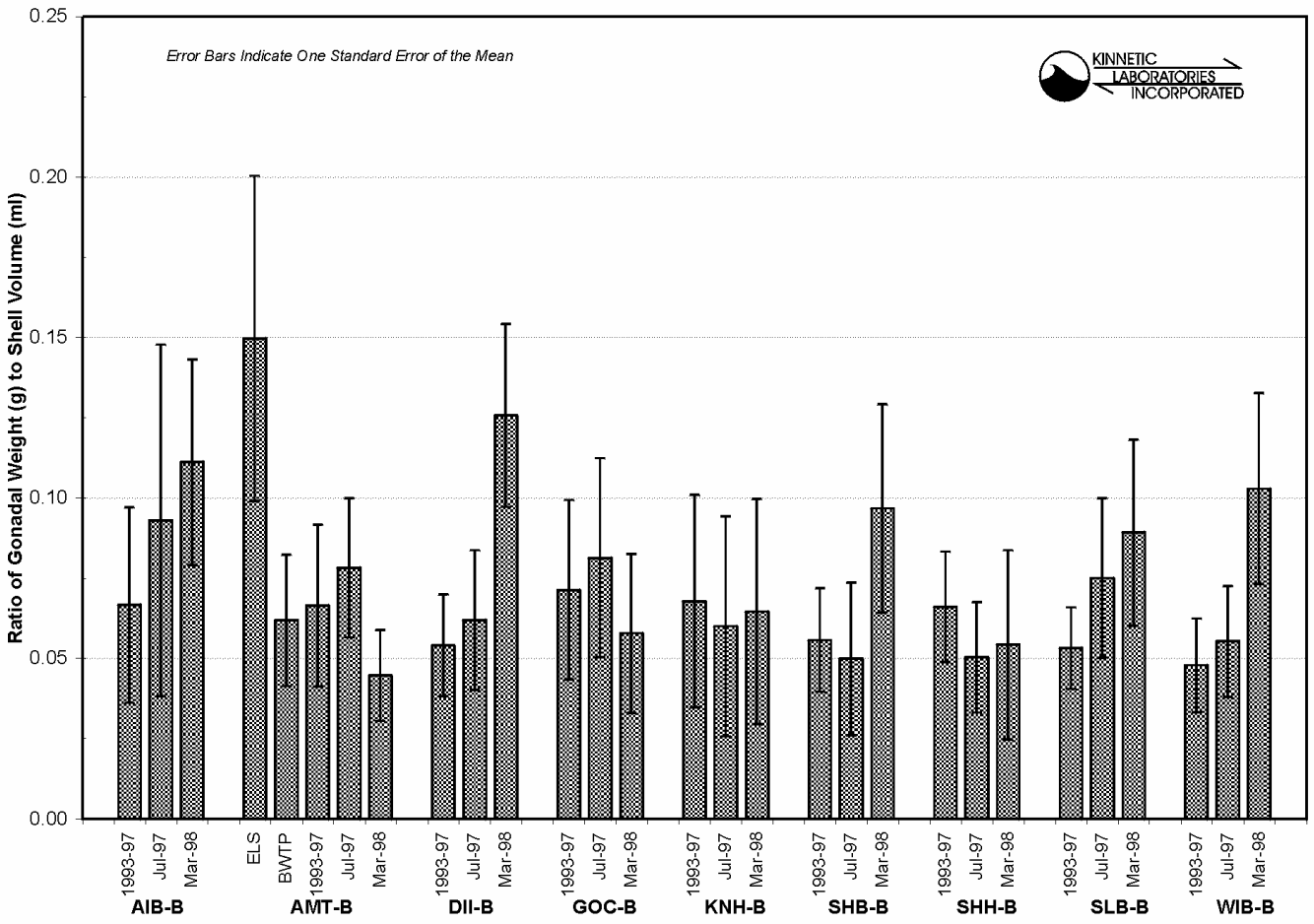

Figure 15. Mean LTEMP Gonadal Weight/Shell Volume by Station and Survey - Historical, July 1997, and March 1998.

5.3 Sediment

Subtidal sediments are a long-term repository of the residues of petroleum released to the marine environment. Petroleum in the offshore environment can be altered by natural dispersion, evaporation, dissolution, photo-oxidation, and microbial degradation. It tends to adhere to particulates and is deposited in sediments. The presence and composition of petroleum contaminants in sediment are a record of the long-term, chronic accumulation of contaminants thus reflecting the potential for exposure of the resident biota.

Based on these considerations, aliphatic and polycyclic aromatic hydrocarbons were measured in sediments at each monitoring site except for Station AIB, where shallow sediments have not been sampled by diver due to the zero visibility condition of this site. As part of the study design, three types of sites were sampled: (1) reference sites believed to be relatively remote from anthropogenic activities (Stations GOC and SHB), (2) sites previously identified as EVOS-impacted (Stations DII, SHH, SLB, and WIB), and (3) sites related to the marine terminal operations in Port Valdez and tanker operations (Stations AMT and KNH).

5.3.1 Polycyclic Aromatic Hydrocarbons

Sediment PAH chemistry results from the July 1997 and March 1998 LTEMP surveys are summarized in Tables 15 and 16. Individual sediment replicate data are provided in Appendix B. Concentrations of various analytes and indices calculated from these analyte concentrations varied considerably among stations. The overall mean concentration of TPAH in subtidal sediments during July 1997 ranged from 10.6 ppb at Station KNH-M to 303.2 ppb at Station AMT-S (Table 16 and Figure 16). Mean TPAH concentrations from March 1998 showed a similar range at the sediment sites, with Stations

KNH-M and SLB-M at 10.9 and 282.3 ppb, respectively. The high mean TPAH concentration seen at Station SLB-M during the March 1998 survey was the result of one high replicate with a concentration of 714.3 ppb (Table 15) as indicated by the large standard error bars in Figure 16.

Table 15. Summary of 1997 - 1998 LTEMP Sediment TPAH and FFPI Results.

Station	TPAH (ppb)						FFPI (Ratio)					
	Survey 10 (7/97)			Survey 11 (3/98)			Survey 10 (7/97)			Survey 11 (3/98)		
	Rep. 1	Rep. 2	Rep. 3	Rep. 1	Rep. 2	Rep. 3	Rep. 1	Rep. 2	Rep. 3	Rep. 1	Rep. 2	Rep. 3
AMT-S	245.3	376.4	287.9	119.6	450.8	143.5	58.2	64.1	61.4	64.8	51.5	59.7
DII-M	37.6	23.8	14.7	30.9	20.5	15.0	44.7	59.8	61.0	57.4	67.3	62.3
GOC-S	53.3	54.4	59.4	41.8	47.5	37.9	63.4	57.6	55.2	73.9	67.2	74.1
KNH-M	10.8	9.3	11.7	10.5	8.5	13.8	64.2	74.1	71.4	71.0	69.0	68.5
SHB-M	104.5	114.1	99.5	61.2	56.7	92.0	66.0	63.2	65.2	65.1	72.2	74.3
SHH-M	37.8	74.6	108.7	116.9	104.2	125.4	49.5	40.9	53.2	61.2	71.6	64.8
SLB-M	42.6	44.1	36.9	50.0	82.7	714.3	39.6	47.9	46.3	45.1	30.4	27.9
WIB-M	122.1	7.5	7.2	48.4	53.1	53.0	23.3	70.4	61.4	79.2	78.5	79.4

Table 16. Mean LTEMP Sediment Results by Station and Survey - 1993 through 1998.

STATION (SURVEY)	TPAH (ng/g)	FFPI (ratio)	TAHC (ng/g)	UCM (mg/g)	CPI (ratio)	TOC (%)	Sand (%)	Silt+Clay (%)
AMT-S (3/93)	242.6	60.8	2091	122.2	1.5	0.77	7.43	92.60
AMT-S (7/93)	246.0	56.4	2018	120.6	1.3	0.67	5.57	94.40
AMT-S (3/94)	202.5	53.9	1473	98.8	2.3	0.58	5.70	94.33
AMT-S (7/94)	264.4	57.9	1530	93.2	1.9	0.65	4.33	95.66
AMT-S (3/95)	212.0	45.7	1390	98.7	1.6	0.63	5.17	94.86
AMT-S (7/95)	880.2	62.9	2275	134.2	1.2	0.77	4.93	95.07
AMT-S (3/96)	201.8	57.9	1262	101.8	3.1	0.54	2.93	97.07
AMT-S (7/96)	302.5	62.3	1883	108.5	2.5	0.69	4.37	95.60
AMT-S (3/97)	417.8	63.0	2370	1.0	2.3	0.83	7.30	92.77
AMT-S (7/97)	303.2	61.2	1498	89.6	4.1	0.59	3.33	96.67
AMT-S (3/98)	238.0	58.7	1251	61.7	3.8	0.65	2.57	97.43
DII-M (7/94)	22.0	54.4	103	3.6	7.2	0.29	94.60	5.40
DII-M (3/95)	15.3	63.4	93	3.3	4.5	0.20	98.20	1.83
DII-M (7/95)	9.6	41.6	97	0.3	3.7	0.19	98.13	1.87
DII-M (3/96)	16.1	48.3	143	17.6	2.8	0.22	94.60	5.40

STATION (SURVEY)	TPAH (ng/g)	FFPI (ratio)	TAHC (ng/g)	UCM (mg/g)	CPI (ratio)	TOC (%)	Sand (%)	Silt+Clay (%)
DII-M (7/96)	24.1	73.4	156	12.5	3.6	0.37	96.67	3.37
DII-M (3/97)	23.0	66.4	161	1.9	2.2	0.40	96.97	3.03
DII-M (7/97)	25.4	55.2	136	4.2	17.6	0.29	98.03	1.97
DII-M (3/98)	22.1	62.3	231	20.0	3.0	0.27	97.63	2.37
GOC-S (3/93)	47.3	61.0	946	6.2	15.9	0.70	20.63	79.43
GOC-S (7/93)	37.7	58.5	567	3.7	12.1	0.63	11.47	88.54
GOC-S (3/94)	70.6	59.2	879	3.3	14.1	0.54	11.20	88.80
GOC-S (7/94)	44.4	55.4	500	2.7	18.8	0.55	24.53	75.47
GOC-S (3/95)	40.6	50.9	438	0.7	18.5	0.55	18.43	81.57
GOC-S (7/95)	52.1	53.2	597	4.2	13.1	0.65	13.63	86.40
GOC-S (3/96)	89.1	40.5	527	14.3	14.7	0.53	12.00	88.03
GOC-S (7/96)	51.1	61.8	537	13.1	39.5	0.55	25.20	74.80
GOC-S (3/97)	44.1	63.1	499	1.7	7.9	0.69	18.37	81.67
GOC-S (7/97)	55.7	58.8	618	18.3	9.2	0.62	12.65	87.35
GOC-S (3/98)	42.4	71.7	331	1.4	8.9	0.55	9.40	90.60
KNH-M (3/95)	6.9	81.4	30	12.0	17.6	0.16	97.67	2.36
KNH-M (7/95)	6.8	71.2	47	0.1	2.2	0.18	98.63	1.40
KNH-M (3/96)	8.6	83.5	49	0.0	1.9	0.15	94.37	5.63
KNH-M (7/96)	9.0	77.4	35	0.0	5.6	0.24	98.33	1.67
KNH-M (3/97)	6.3	59.7	66	0.3	3.2	0.27	97.23	2.77
KNH-M (7/97)	10.6	69.9	51	11.1	9.1	0.21	97.14	2.86
KNH-M (3/98)	10.9	69.5	67	5.2	1.7	0.23	98.93	1.07
SHB-M (7/94)	37.2	74.7	167	1.3	11.4	0.86	90.03	9.97
SHB-M (3/95)	46.5	67.7	159	8.3	8.7	0.77	94.37	5.70
SHB-M (7/95)	56.6	58.0	254	1.1	3.1	0.86	94.73	5.23
SHB-M (3/96)	52.9	75.3	197	6.0	4.7	0.66	93.60	6.40
SHB-M (7/96)	70.5	76.0	392	3.2	2.7	0.72	89.93	10.13
SHB-M (3/97)	119.9	73.3	685	4.2	2.4	1.52	70.43	29.53
SHB-M (7/97)	106.0	64.8	587	13.8	8.6	1.32	82.84	17.16
SHB-M (3/98)	70.0	70.6	400	5.0	5.3	0.97	90.53	9.47
SHH-M (3/95)	80.6	59.5	402	2.3	7.4	0.85	84.07	15.94
SHH-M (7/95)	48.4	58.1	251	7.1	3.7	0.33	94.40	5.60
SHH-M (3/96)	61.7	68.2	274	2.3	3.8	0.85	96.27	3.80
SHH-M (7/96)	60.5	69.3	350	5.3	3.4	0.91	83.17	16.83
SHH-M (3/97)	127.8	66.5	351	1.2	3.9	1.20	83.73	16.30
SHH-M (7/97)	73.7	47.8	251	2.4	9.9	0.56	93.98	6.02

STATION (SURVEY)	TPAH (ng/g)	FFPI (ratio)	TAHC (ng/g)	UCM (mg/g)	CPI (ratio)	TOC (%)	Sand (%)	Silt+Clay (%)
SHH-M (3/98)	115.5	65.9	298	9.5	4.6	0.94	87.23	12.77
SLB-M (7/94)	252.1	43.9	384	32.8	2.4	0.99	88.40	11.66
SLB-M (3/95)	664.5	30.7	688	81.0	1.9	1.33	87.97	12.07
SLB-M (7/95)	537.1	33.9	1693	118.8	2.0	2.22	88.63	11.37
SLB-M (3/96)	427.3	35.5	934	121.6	7.9	1.34	84.83	15.20
SLB-M (7/96)	481.6	33.1	1020	74.2	6.8	1.45	90.80	9.20
SLB-M (3/97)	109.7	43.1	218	10.6	5.4	0.79	95.27	4.73
SLB-M (7/97)	41.2	44.6	130	8.3	6.1	0.70	97.37	2.63
SLB-M (3/98)	282.3	34.5	384	26.4	4.6	0.69	97.10	2.97
WIB-M (3/95)	12.8	78.5	143	0.3	12.4	0.51	98.17	1.87
WIB-M (7/95)	7.5	66.0	232	0.0	8.2	0.57	81.73	18.23
WIB-M (3/96)	6.5	81.9	99	0.0	6.2	0.22	97.73	2.30
WIB-M (7/96)	8.2	63.0	155	0.1	17.3	0.74	97.50	2.50
WIB-M (3/97)	38.2	66.5	160	0.5	8.5	0.60	94.53	5.50
WIB-M (7/97)	45.6	51.7	125	1.4	7.1	0.48	98.03	1.97
WIB-M (3/98)	51.5	79.0	284	4.3	8.0	0.74	95.10	4.93

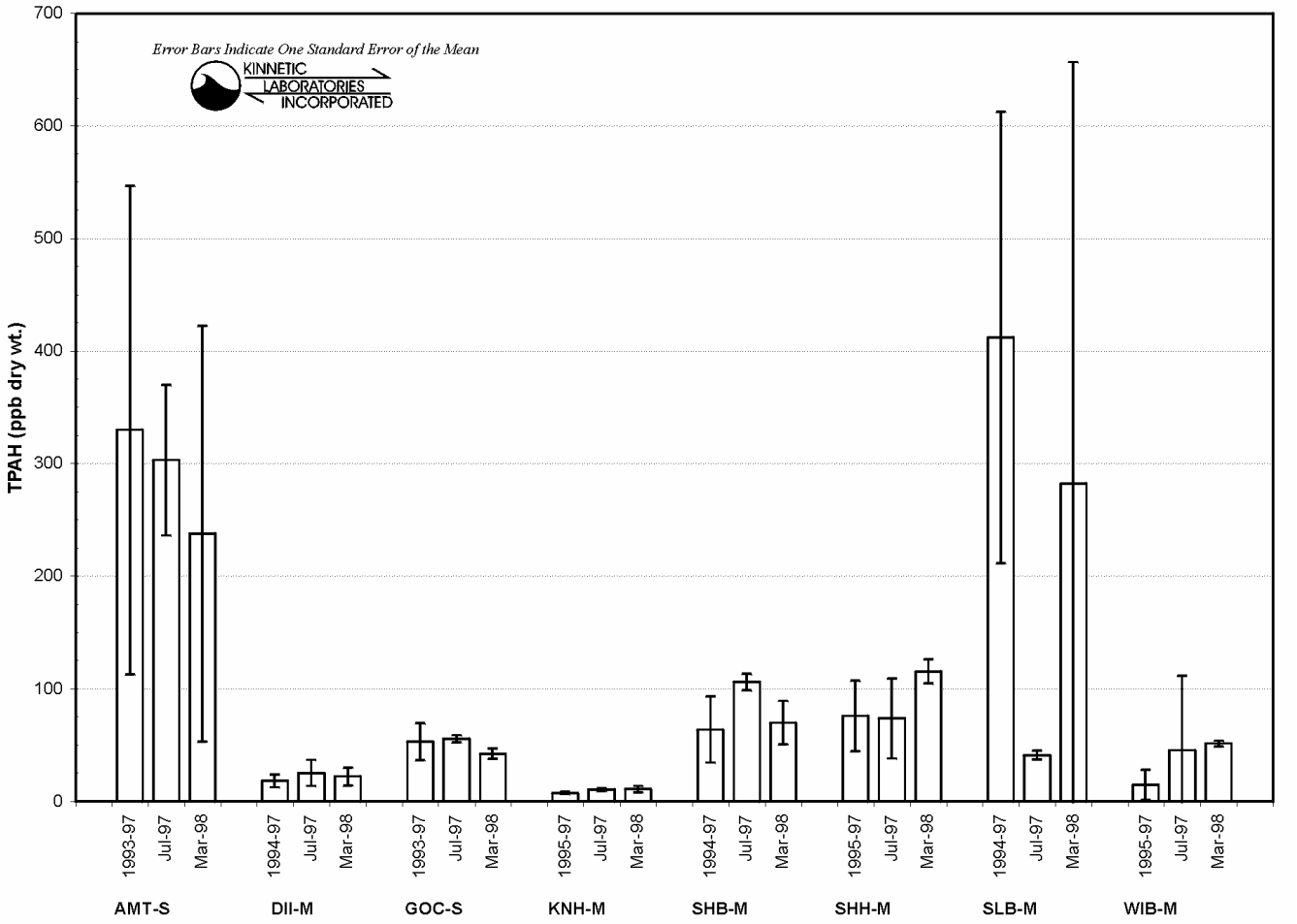

Figure 16. Mean LTEMP Sediment TPAH by Station and Survey - Historical, July 1997, and March 1998.

With the exception of Station SLB-M during the March 1998 survey, TPAH levels from the shallow subtidal stations have been quite low (< 128 ppb) during all surveys (Table 16 and Figure 16). The TPAH levels at the two deeper sites (AMT-S and GOC-S) have been much more variable between locations but have been fairly consistent at individual sites through time. Station AMT-S, however, showed a four-fold increase during July 1995 (Survey 6) from the previous five surveys.

The last five surveys have shown further variability at this site, with mean TPAH concentrations ranging from 201.8 to 417.8 ppb. July 1997 and March 1998 surveys showed mean TPAH concentrations of 303.2 and 238.0, respectively.

Mean values for FFPI in sediments collected during July 1997 ranged from 44.6 at Station SLB-M to 69.9 at Station KNH-M (Table 16 and Figure 17). March 1998 values ranged from 34.5 at Station SLB-M to 79.0 at Station WIB-M. As seen during prior surveys, the FFPI during the 1997 - 1998 LTEMP surveys was consistently the lowest at Station SLB-M. This site has the lowest FFPI ratios as a result of the heavy weathering (i.e., low naphthalenes and fluorenes) and relatively high levels of chrysenes and pyrogenic PAH (Figure 18).

Stations DII-M, GOC-S, KNH-M, and WIB-M exhibited low levels of PAH. Concentrations of PAH at Station KNH-M were very low and for the most part below MDLs, but this station did exhibit a petrogenic fingerprint as evidenced by the predominance of naphthalenes, fluorenes, and phenanthrenes. This is reflected in the high FFPI for all surveys (Table 16 and Figure 17). Mean TPAH concentrations at Station KNH-M for the seven surveys were all less than 11 ppb. These low concentrations probably reflect low-level long-term input from the Katalla and other seeps in the eastern Gulf of Alaska. Page et al. (1995) suggests that a portion of the background in both PWS and the Gulf of Alaska is due to these natural seeps of petroleum which adhere to fine-grained suspended sediment and are transported into the area by westerly flowing coastal currents. Prior surveys indicated that the deeper more fine-grained sediments at KNH had much higher

concentrations of PAH that also had the same 'background signature'.

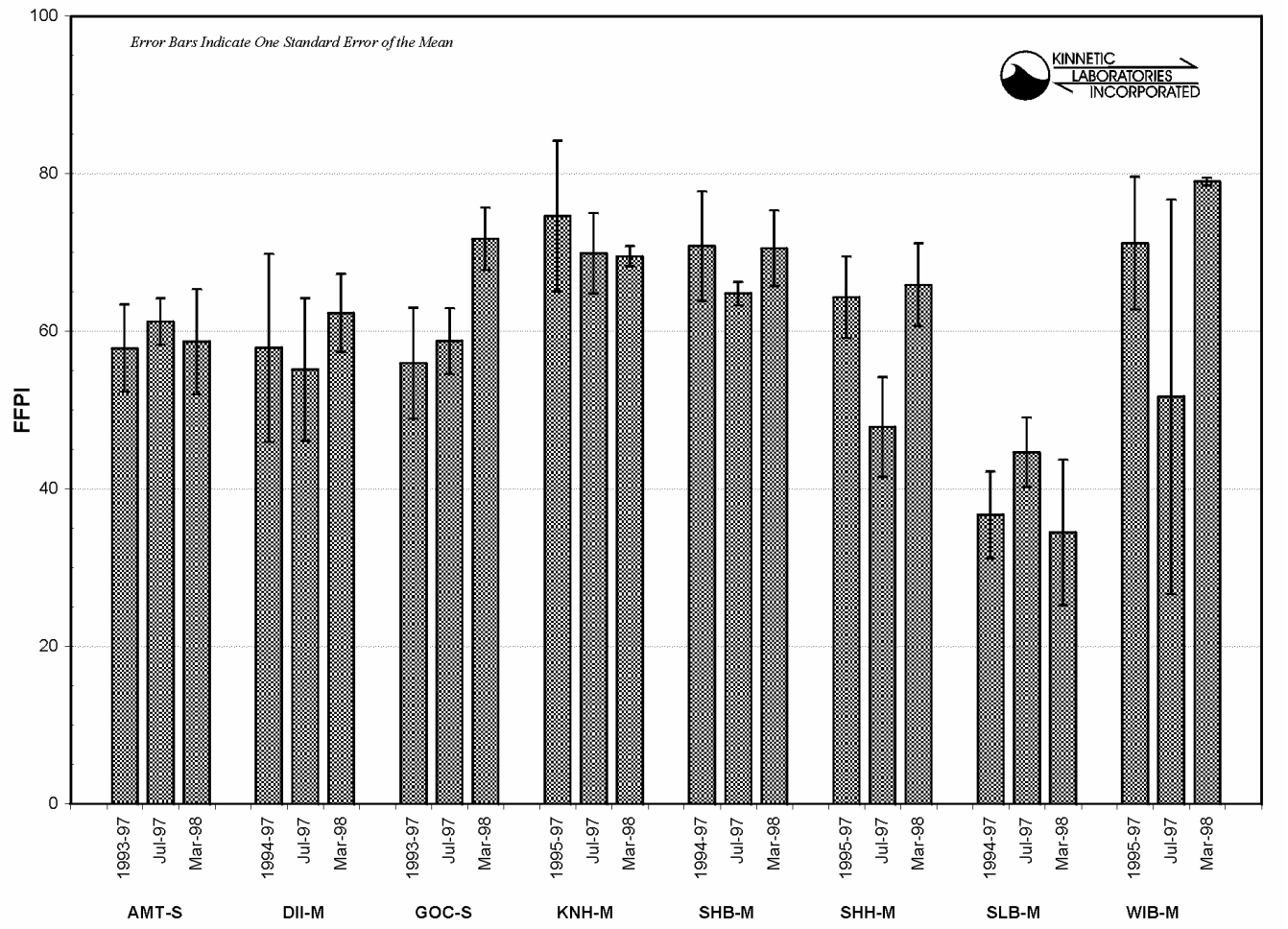

Figure 17. Mean LTEMP Sediment FFPI by Station and Survey - Historical, July 1997, and March 1998.

Concentrations of PAH in sediments were somewhat higher at Station SHB-M with mean TPAH of 106.0 and 70.0 for the July 1997 and March 1998 surveys, respectively. The PAH fingerprint at Station SHB-M was also indicative of low-level petrogenic inputs (Figure 18); this was supported by relatively high mean FFPI values of 64.8 and 70.6 for the two surveys (Table 16 and Figure 17). Most of this PAH appears to be a low-level petrogenic signature in PWS and is not traceable to ANS crude or the EVOS oil. The ratio of alkyl dibenzothiophenes to alkyl phenanthrenes was found to be relatively low (<0.2), which confirms the non-EVOS oil source for these hydrocarbons (refer to Appendix B for individual analyte concentrations). Page et al. (1995) found the C_2-dibenzothiophene/C_2 -phenanthrene ratio to be 1.08 ± 0.14 for both ANS crude/diesel and EVOS crude oil, and a ratio of 0.15± 0.02 for PWS background which is consistent with Katalla and other Gulf of Alaska seeps. Recent work by the Minerals Management Service in Lower Cook Inlet and Shelikof Strait indicates that in some areas this background signature can be traced to coal deposits as their source (Arthur D. Little, 1998). They found that the PAH fingerprints were similar, but additional biomarker analyses revealed differences between the coal and seep sources.

In addition to petrogenic hydrocarbons, low levels of pyrogenic hydrocarbons which were near the MDLs were also present at Station SHB-M and consisted of fluoranthene, pyrene, and an assortment of 5- and 6-ring PAH which may be sourced in combustion products (i.e., exhaust). Low levels of naphthalenes and fluorenes were also seen at Station SHB-M which is characteristic of the unweathered background levels of hydrocarbons that have been seen in PWS including the deep cores that were taken in conjunction with the LTEMP in 1995 (KLI, 1995b).

The PAH concentrations at Station GOC-S were at low background levels near the MDLs (Appendix B) during both the July 1997 and March 1998 surveys, with TPAH concentrations of 55.7 and 42.4 ppb, respectively. The PAH signature was primarily petrogenic but smaller amounts of pyrogenic hydrocarbons consisting of fluoranthene, pyrene, and an assortment of 5- and 6-ring PAH were also seen in the sediments. Biogenic inputs were low as evidenced by the low levels of perylene.

Sediments at Station AMT-S exhibited a PAH fingerprint typical of petroleum along with low levels of 5- and 6-ring PAH suggesting an input of pyrogenic hydrocarbons that have a combustion or creosote origin (Figure 18). Mean TPAH concentrations at Station AMT-S were 303.2 ppb during July 1997 and 238.0 ppb during March 1998. These concentrations were clearly higher than all other sites except the March 1998 survey for SLB-M. The C_2-dibenzothiophene/C_2-phenanthrene and C_3-dibenzothiophene/C_3-phenanthrene ratios for Station AMT-S were near 1 which is consistent with ANS/EVOS oil (Figure 18). As described above, the ratio of C_2-dibenzothiophene/C_2-phenanthrene was found to be ≈1.08 for EVOS oil as compared to ≈0.15 for Katalla Seep oil and background concentrations in the sediments of PWS (Page et al., 1995). These same authors also reported C_3-dibenzothiophene/C_3-phenanthrene ratios of 1.19 ± 0.08 for EVOS oil and 0.16 ± 0.07 for natural background conditions in PWS. The relatively high levels of chrysenes at this station rule out diesel fuel as the source.

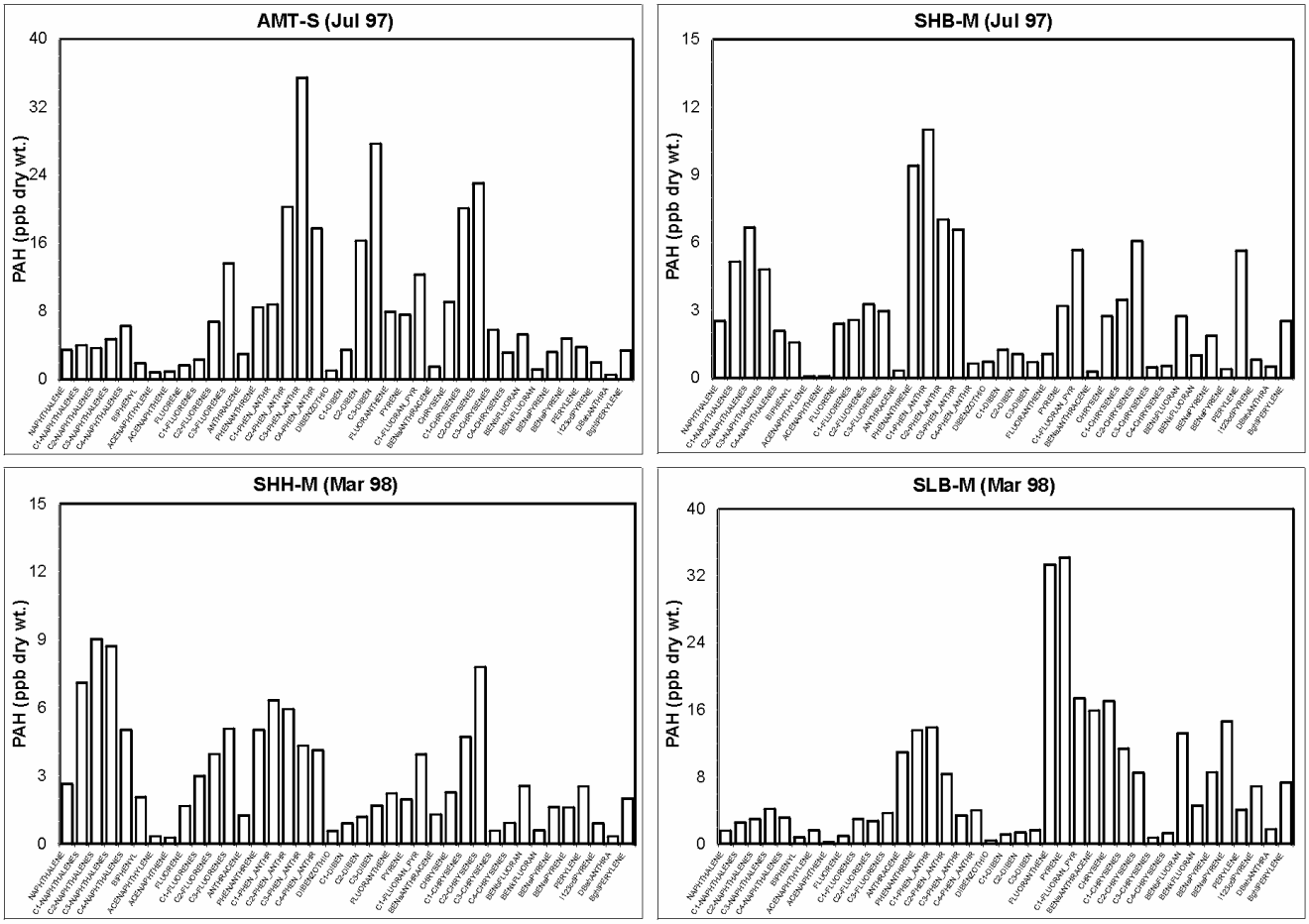

Figure 18. Mean Sediment PAH Values for LTEMP - July 1997 and March 1998 Surveys, Stations AMT-S, SHB-M, SHH-M, and SLB-M.

The average ratio of C_2-chrysene to C_2-phenanthrene can be used as a indication of the degree of weathering. With weathering, the ratio increases since the alkyl phenanthrenes are degraded more quickly than the alkyl chrysenes. At Station AMT-S, this ratio was ~1 for the two recent surveys (Figure 18 and Appendix B). This ratio was found to be

around 0.2 for EVOS crude oil just after the spill in 1989 and had increased to 0.5 in 1991 (Bence and Burns, 1995). The C_2-chrysene/C_2-phenanthrene ratio at Station AMT-S indicates that if the source was ANS crude, the oil had weathered substantially and was probably the result of low input from the Alyeska Marine Terminal and tanker activity over a period of years. If the source had been diesel fuel, this ratio would have been very small since the high molecular weight chrysenes are not found in diesel fuel.

Sites previously identified as EVOS-impacted contained hydrocarbon concentrations that were similar in value to those seen at the reference sites, however source identification from the PAH fingerprints was often different. Polycyclic aromatic hydrocarbon concentrations at these EVOS sites located at Stations DII-M, SHH-M, SLB-M, and WIB-M varied somewhat between locations but were usually fairly consistent between surveys (Tables 15 and 16; Figure 16). An exception was Station SLB-M which had a substantially higher mean TPAH concentration of 282.3 ppb for the March 1998 survey compared to 41.2 ppb for the July 1997 survey. This high concentration at SLB-M was the result of one replicate that had a TPAH concentration of 714.3 (Table 15). Even with this high concentration, however, the mean TPAH concentration for the March 1998 survey was still lower than four of the seven prior surveys (Table 16).

Hydrocarbon PAH fingerprints from Stations SLB-M were primarily made up of pyrogenic hydrocarbons with lesser amounts from petrogenic sources (Figure 18); this was supported by the fact that this station had the lowest FFPI ratios of any location (refer to Table 16 and Figure 18). The PAH fingerprint was dominated by concentrations of fluoranthene, pyrene, and 5- and 6-ring PAH which are indicative of pyrogenic inputs. Also, pyrogenic PAH are characterized by high concentrations of the parent compounds compared to their alkyl homologues, where a typical pattern is decreasing concentrations with molecular weight within a series (i.e., $C_0>C_1>C_2>C_3>C_4$). This characteristic pyrogenic pattern can be seen in the phenanthrene and chrysene series at this station. The C_2- and C_3-dibenzothiophene-phenanthrene ratios suggest that the petrogenic hydrocarbons at these two stations are predominantly of a background or Katalla-like origin and are similar to hydrocarbons at the reference sites with lesser amounts of residual EVOS oil input (Figure 18).

Hydrocarbon concentrations at Station WIB-M were found to be very low with mean TPAH concentrations of 45.6 and 51.5 ppb for the last two surveys (Table 16 and Figure 16). Hydrocarbon concentrations at WIB-M were either very low or below MDL for most analytes. The fingerprints from the two surveys were very different. The July 1997 survey consisted of pyrogenic PAH whereas the March 1998 survey was primarily petrogenic with a fairly large biogenic input as indicated by the perylene levels (refer to Appendix B). Petrogenic inputs from Katalla-like sources are indicated by the ratios of the alkylated dibenzothiophenes to phenanthrenes.

Concentrations of mean TPAH at Station SHH-M were 73.7 and 115.5 ppb for the July 1997 and March 1998 surveys, respectively (Table 16 and Figure 16). An examination of the fingerprints at SHH-M indicated that the PAH in the shallow sediments were dominated by petrogenic PAH with lesser amounts of fluoranthene, pyrene, and 5- and 6-ring PAH indicative of pyrogenic inputs (Figure 18). These pyrogenic inputs were found to be greater during the July 1997 survey as compared to the March 1998 survey (refer to Appendix B). Biogenic inputs were low as evidenced by the relatively low levels of perylene. The petrogenic signal was characteristic of Katalla, Cook Inlet crude oil, or coal signatures as evidenced by the ratio of dibenzothiophenes to phenanthrenes and the presence of unweathered lower molecular weight naphthalenes and fluorenes.

Sediment PAH levels from the Disk Island shallow subtidal station (DII-M) were found to be very low. Mean concentrations of TPAH at DII-M were found to be 25.4 and 22.1 ppb for the two 1997 - 1998 surveys (Table 16 and Figure 16). The PAH fingerprint from Station DII-M was primarily petrogenic with smaller amounts of fluoranthene, pyrene, and 5- and 6-ring pyrogenic PAH (refer to Appendix B). The C_2 and C_3-dibenzothiophene/phenanthrene ratios fall between EVOS oil and Katalla sources which would indicate a combination of the two inputs. Prior surveys indicated that the beach at Disk Island still contained pockets of relatively unweathered EVOS oil (KLI, 1996a and 1997a). It appeared from the beach samples that were collected during these surveys that Disk Island still had some pockets of relatively unweathered EVOS oil that was being transported into the subtidal region by wave and current activity.

5.3.2 Aliphatic Hydrocarbons

Aliphatic hydrocarbons that were measured for the LTEMP consisted of the series of odd and even chain n-alkanes (n-C_{10} to n-C_{34}) plus pristane and phytane. Concentrations of these individual aliphatic hydrocarbons by station and replicate are presented in Appendix B. The TAHC consists of the sum of the individual analytes and is summarized by station and replicate in Table 17. The overall mean concentrations of TAHC in sediments varied greatly among sites but was fairly consistent within a site over time (Table 16 and Figure 19). During July 1997, mean TAHC concentrations ranged from 51 ppb at Station KNH-M to 1498 ppb at Station AMT-S. Mean TAHC during March 1998 ranged from 67 ppb at Station KNH-M to 1251 ppb at Station AMT-S. The highest TAHC concentrations seen during each survey have been at Station AMT-S since the beginning of the LTEMP program in 1993. A relatively high mean TAHC concentration of 1693 ppb was also seen at Station SLB-M during July 1995 (Table 16).

Table 17. Summary of 1997 - 1998 LTEMP Sediment TAHC, UCM, and CPI Results.

Station	Survey 10 (7/97)			Survey 11 (3/98)		
	Rep. 1	Rep. 2	Rep. 3	Rep. 1	Rep. 2	Rep. 3
TAHC (ng/g or ppb)						
AMT-S	1124	1477	1892	1111.6	1668.4	972.4
DII-M	108	154	146	303.5	225.0	165.2
GOC-S	514	788	552	341.1	300.9	352.2
KNH-M	36	53	64	104.0	48.2	48.1
SHB-M	603	584	573	435.6	375.3	388.8
SHH-M	134	171	447	282.1	319	292.5
SLB-M	157	110	122	390.3	273.7	489.0
WIB-M	74	87	213	312.9	225.1	314.9
UCM (µg/g or ppm)						
AMT-S	78.9	90.6	99.4	55.1	77.8	52.1
DII-M	4.2	5.2	3.1	34.4	16.1	9.5
GOC-S	27.0	15.6	12.2	1.5	1.7	1.0
KNH-M	16.4	10.1	6.9	8.8	4.3	2.5
SHB-M	15.1	13.9	12.5	6.3	6.2	2.5
SHH-M	0.6	0.7	5.9	16.2	3.5	8.8
SLB-M	8.8	8.0	8.0	28.8	19.3	31.1
WIB-M	1.5	1.9	0.7	5.5	3.7	3.7
CPI (Ratio)						
AMT-S	3.4	3.4	5.4	3.6	3.6	4.0
DII-M	9.1	18.9	24.9	2.8	3.0	3.1
GOC-S	10.9	6.4	10.2	11.0	8.1	7.5
KNH-M	2.7	7.1	17.5	1.5	1.7	2.0
SHB-M	8.0	9.5	8.1	5.1	7.1	3.6
SHH-M	11.8	6.1	11.7	4.0	5.8	3.9

SLB-M	7.4	6.1	4.8	3.7	3.6	6.5
WIB-M	8.1	10.2	2.9	11.7	5.3	7.1

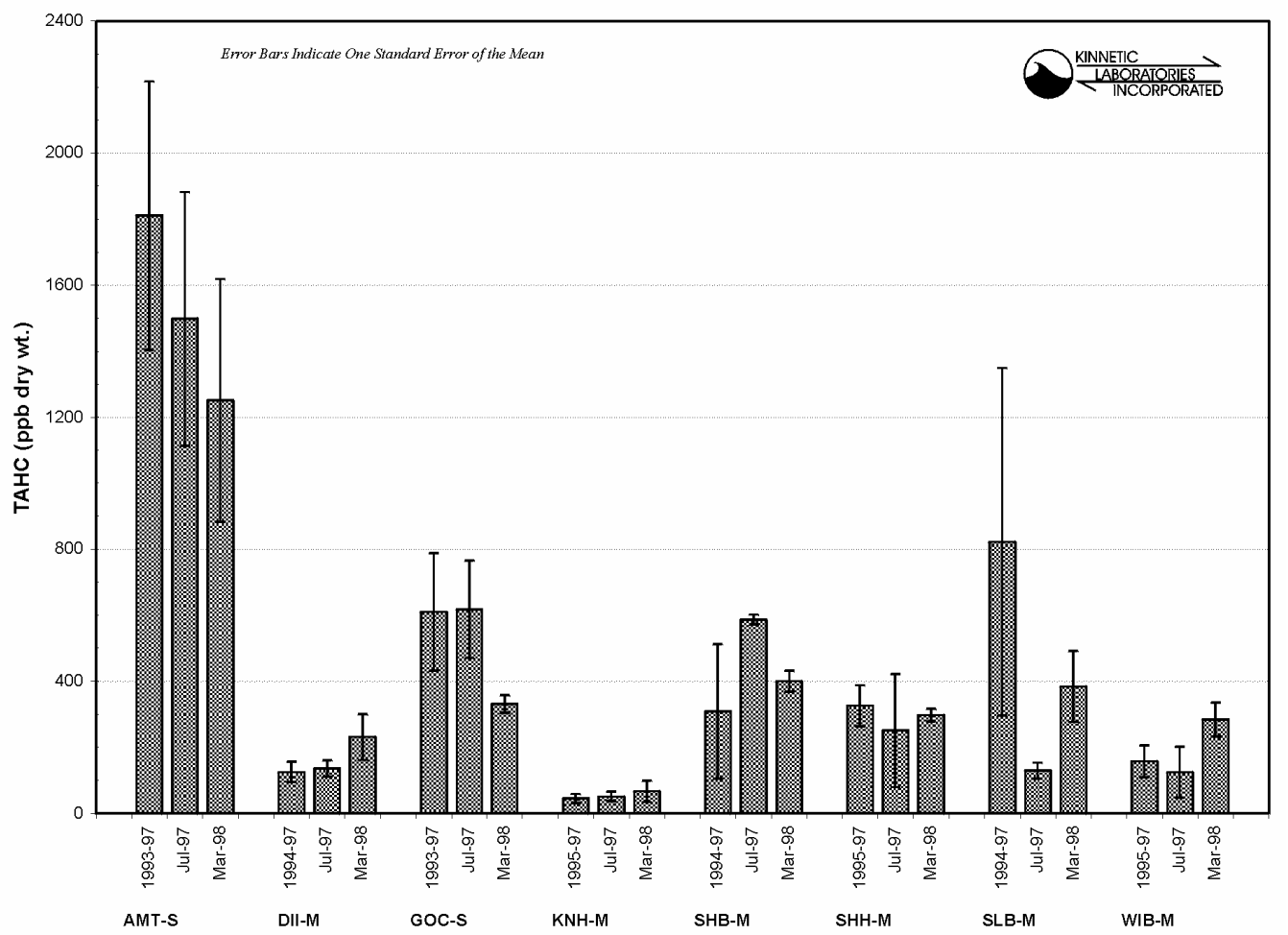

Figure 19. Mean LTEMP Sediment TAHC by Station and Survey - Historical, July 1997, and March 1998.

The CPI represents the ratio of the relative amounts of odd and even alkanes within a specific boiling range (n-C_{26} to n-C_{30}). High CPI values are characteristic of biogenic inputs from terrestrial sources such as plants, whereas low CPI values are the result of equally abundant even and odd alkanes that are characteristic of petrogenic inputs. For the LTEMP, the CPI varied substantially between sites but was fairly consistent at individual sites between surveys with few exceptions (Tables 16 and 17; Figure 20). Mean values of CPI in sediments during the 1997 - 1998 LTEMP ranged from 1.7 at Station KNH-M in March 1998 to 17.6 at Station DII-M in July 1997. The most noticeable difference in CPI at a site occurred at Station DII-M which showed a value of 3.0 during March 1998 versus 17.6 during July 1997. Station KNH-M also showed fairly large variability between the July 1997 and March 1998 surveys at 9.1 and 1.7, respectively. High CPI values at other stations (GOC-S, SHB-M, SHH-M (July 1997), and WIB-M) were the result of high terrestrial inputs from runoff or, in the case of Station WIB-M, potential inputs from logging operations. Low CPI values were seen at stations that had petrogenic inputs from natural seeps, Alyeska Marine Terminal operations, or EVOS oil, such as Stations AMT-S, DII-M (March 1998), SHH-M (March 1998), and SLB-M.

The UCM fraction in sediments varied considerably among stations and between surveys (Tables 16 and 17; Figure 21). Mean values for the July 1997 and March 1998 surveys ranged from approximately 1.4 ppm at Stations GOC-S and WIB-M to 89.6 ppm at Station AMT-S. In general, concentrations of UCM have historically been higher at Stations AMT-S and SLB-M than at any of the other stations.

Individual aliphatic hydrocarbon concentrations were in general above their MDLs for each sample, however, there still were a large number of estimated concentrations (Appendix B). The highest AHC concentrations were seen at Station AMT-S during both the July 1997 and March 1998 LTEMP surveys. The AHC fingerprint at Station AMT-S was characterized by hydrocarbons that were highly biodegraded and predominantly consisted of long-chain (n-C_{25}) alkanes or higher (Figure 22). The distribution of even and odd alkanes were similar, which is indicative of petrogenic inputs. Also, the sediments at the Station AMT-S exhibited a relatively large UCM of hydrocarbons when compared to other stations. A large UCM relative to TAHC is generally a feature of weathered petroleum. This petrogenic hydrocarbon input and the fact that the samples showed a high degree of weathering was confirmed by the PAH analysis discussed earlier.

The AHC fingerprint at Station GOC-S had an odd carbon dominance in the n-C_{23} to n-C_{31} range of normal alkanes which is reflective of a biogenic origin for the hydrocarbons (Figure 22). The CPI at this site was one of the highest measured, indicating predominately terrestrial biogenic input. The addition of petroleum to the marine environment in general lowers the CPI ratio, therefore sites with low CPI reflect petrogenic hydrocarbon inputs. Also, the UCM at Station GOC-S has historically been very low with the highest mean concentration being 18.3 ppm. The low UCM and high CPI at Station GOC-S relative to Station AMT-S helps substantiate the fact that the source of relatively high AHC levels at Station GOC-S was biogenic rather than petrogenic. Runoff from the rivers in this area may contribute to this biogenic source.

A fingerprint of AHC for March 1998 at Station SLB-M, an EVOS-impacted station, is also presented in Figure 22. The similar distribution of odd-to-even alkanes illustrated by the low CPI is indicative of a petroleum source. The relatively large number of short chain (low alkanes) compared to long chain (high alkanes) at Station SLB-M indicate that the petroleum source was not heavily weathered. Also, the ratios of pristane to n-C_{17} and phytane to n-C_{18}, both indicators of biodegradation, were relatively low compared to other locations, which would indicate a low degree of weathering. In unweathered petroleum, n-C_{17} is relatively abundant compared to pristane, and n-C_{18} is relatively abundant compared to phytane. Biodegradation causes an increase in these ratios due to the selective depletion of straight chain and single methyl-branched (n-alkanes) relative to highly-branched aliphatic hydrocarbons (i.e., isoprenoids - pristane and phytane). Unweathered EVOS oil has a pristane/n-C_{17} ratio of less than 1 (refer to Appendix C for EVOS reference oil data). For the phytane/C_{18} ratio, unweathered EVOS oil is approximately 0.5. A comparison of these ratios as seen in the AHC fingerprints indicate that the hydrocarbons in the subtidal sediment at Station SLB-M were relatively unweathered compared to those sampled at Station AMT-S. A similar pattern to that seen at SLB-M was also evident at DII-M for March 1998 (refer to Appendix B).

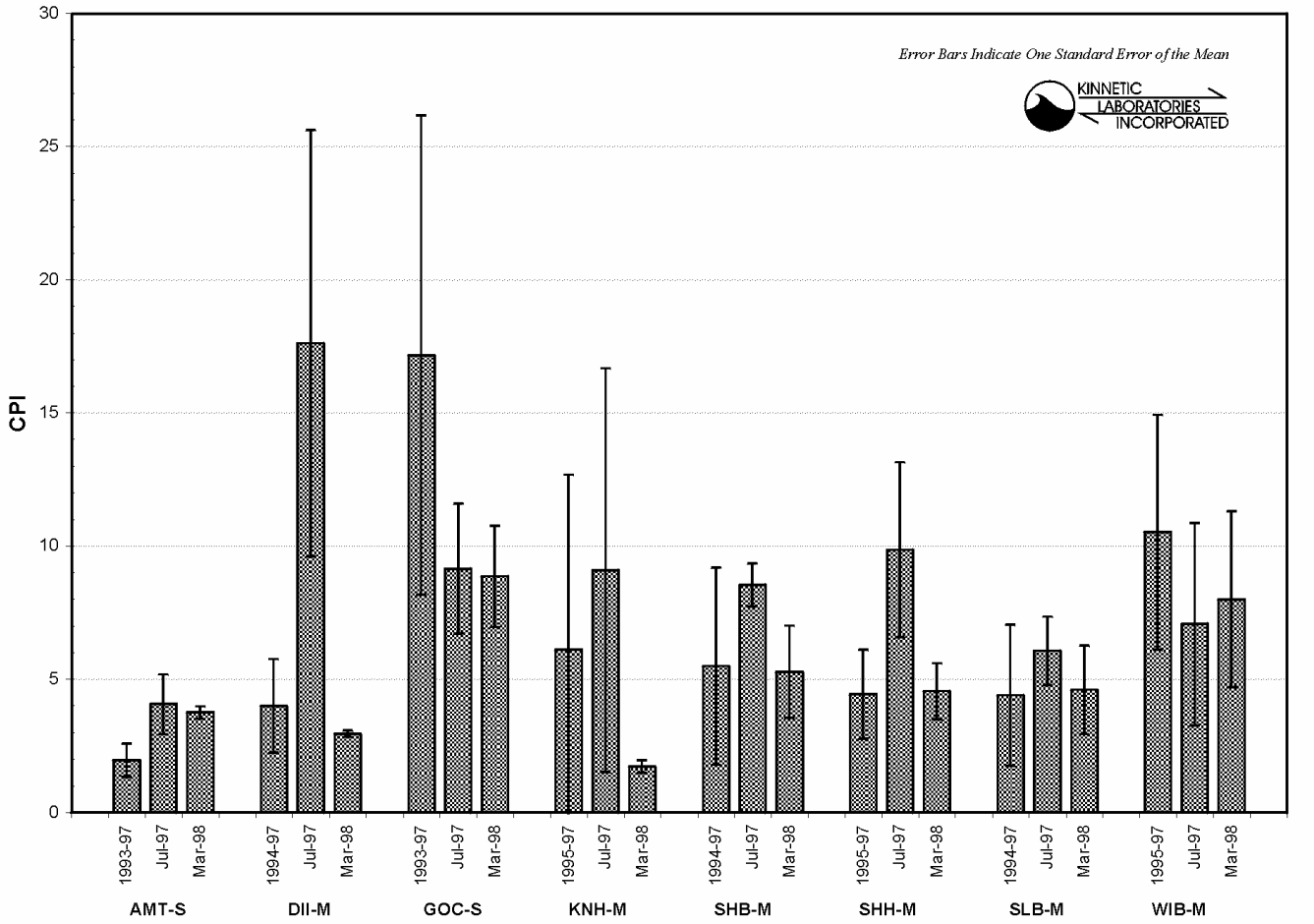

Figure 20. Mean LTEMP Sediment CPI by Station and Survey - Historical, July 1997, and March 1998.

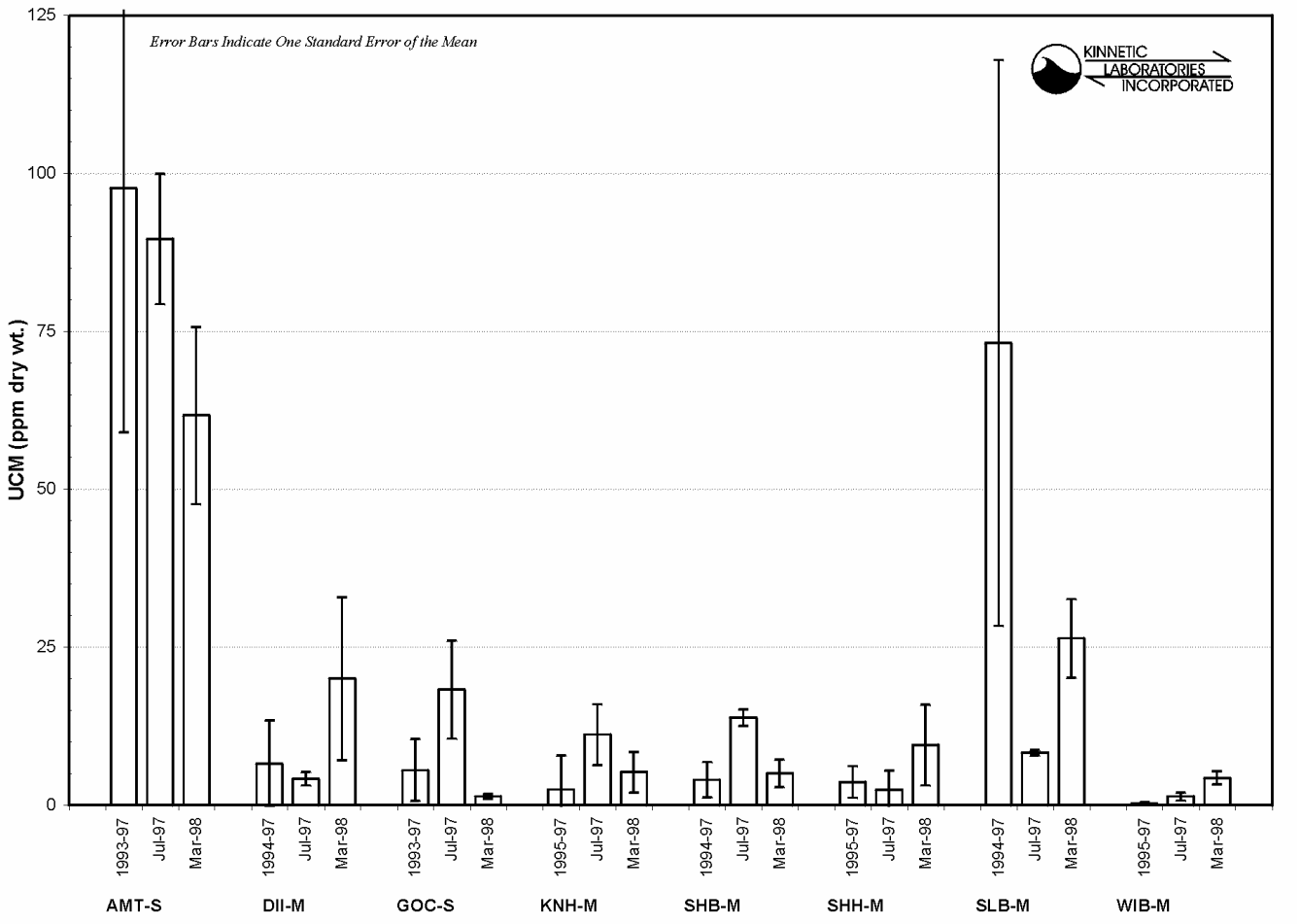

Figure 21. Mean LTEMP Sediment UCM by Station and Survey - Historical, July 1997, and March 1998.

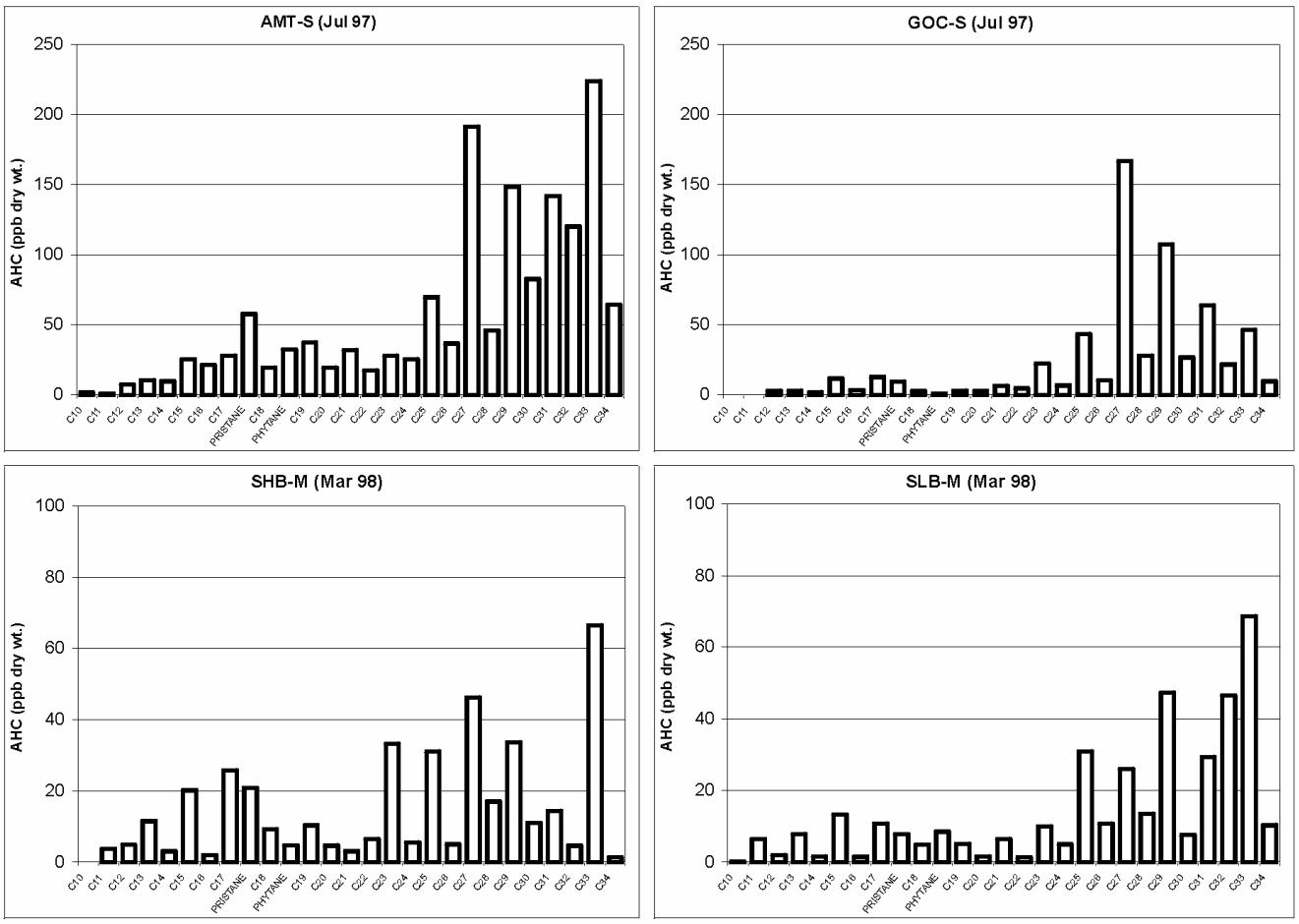

Figure 22. Mean Sediment AHC Values for LTEMP - July 1997 and March 1998 Surveys, Stations AMT-S, GOC-S, SHB-M, and SLB-M.

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Other sites previously identified as EVOS-impacted contained aliphatic hydrocarbon concentrations that were actually less than those seen at the reference sites. Concentrations of TAHC were similar at all of these locations between surveys. Most of these sites exhibited a UCM indicative of biodegraded oil and generally had similar CPIs compared to the reference locations. However, the source of these petrogenic inputs could not be determined from the aliphatic signature and could be either anthropogenic or due to natural seeps in the area. As noted in a special supplemental study conducted by the RCAC, AHC measured in deep sediments within PWS in 1995 were found to have CPIs of less than 2 and exhibited a hydrocarbon signature that was attributed to natural background hydrocarbon inputs (KLI, 1995b).

The AHC signature from Station SHB-M indicates a combination of sources. The relatively large number of short chain (low alkanes) compared to long chain (high alkanes) when compared to other locations would indicate a petroleum source that was not heavily weathered. Also, the relatively low CPIs indicates a combination of biogenic and petrogenic inputs. The overall TAHC level is somewhat higher than most of the other stations. Also, the ratios of pristane to n-C_{17} and phytane to n-C_{18}, both indicators of biodegradation, were relatively low which would indicate recent inputs with a low degree of weathering.

Sediment collected at Station WIB-M exhibited similar biogenic patterns to that seen at Station GOC-S with no noticeable petrogenic hydrocarbons in the AHC signature. The low UCM and high CPI ratios at these stations indicates biogenic inputs as the main source of AHC (Table 16). Hydrocarbons in the sediments inshore of the tanker anchorage (KNH-M) were very low and primarily of a biological origin with no petroleum hydrocarbon input exhibited during the July 1997 or March 1998 surveys.

5.3.3 Total Organic Carbon

Concentrations of TOC in sediments were variable among stations but fairly consistent within stations (Tables 16 and 18; Figure 23; Appendix B). Mean TOC concentrations July 1997 ranged from 0.21 % at Station KNH-M to 1.32 % at Station SHB-M. March 1998 mean concentrations ranged from 0.23 to 0.97 %, with the low and high values at the same two stations as in July 1997. In general, mean TOC concentrations have been fairly consistent within a location over time (Table 16).

Table 18. Summary of 1997 - 1998 LTEMP Sediment TOC and Silt Plus Clay Results.

Station	TOC (%)						Silt + Clay (%)					
	Survey 10 (7/97)			Survey 11 (3/98)			Survey 10 (7/97)			Survey 11 (3/98)		
	Rep. 1	Rep. 2	Rep. 3	Rep. 1	Rep. 2	Rep. 3	Rep. 1	Rep. 2	Rep. 3	Rep. 1	Rep. 2	Rep. 3
AMT-S	0.51	0.66	0.61	0.65	0.72	0.58	97.1	97.1	95.9	96.9	97.3	98.1
DII-M	0.27	0.30	0.31	0.29	0.30	0.23	1.2	2.5	2.2	1.9	2.7	2.5
GOC-S	0.60	0.61	0.64	0.59	0.56	0.49	89.8	88.7	83.5	91.5	86.4	93.9
KNH-M	0.22	0.20	0.22	0.27	0.21	0.20	3.5	2.0	3.1	1.3	1.6	0.3
SHB-M	1.41	1.28	1.26	0.97	0.99	0.94	12.3	20.6	18.5	11.7	10.2	6.5
SHH-M	0.32	0.32	1.03	0.78	0.88	1.16	4.0	4.2	9.9	13.3	13.2	11.8
SLB-M	0.72	0.79	0.58	0.69	0.62	0.75	2.9	2.4	2.6	3.1	2.2	3.6
WIB-M	0.43	0.46	0.54	0.67	0.74	0.81	1.5	1.4	3.1	2.7	6.1	6.0

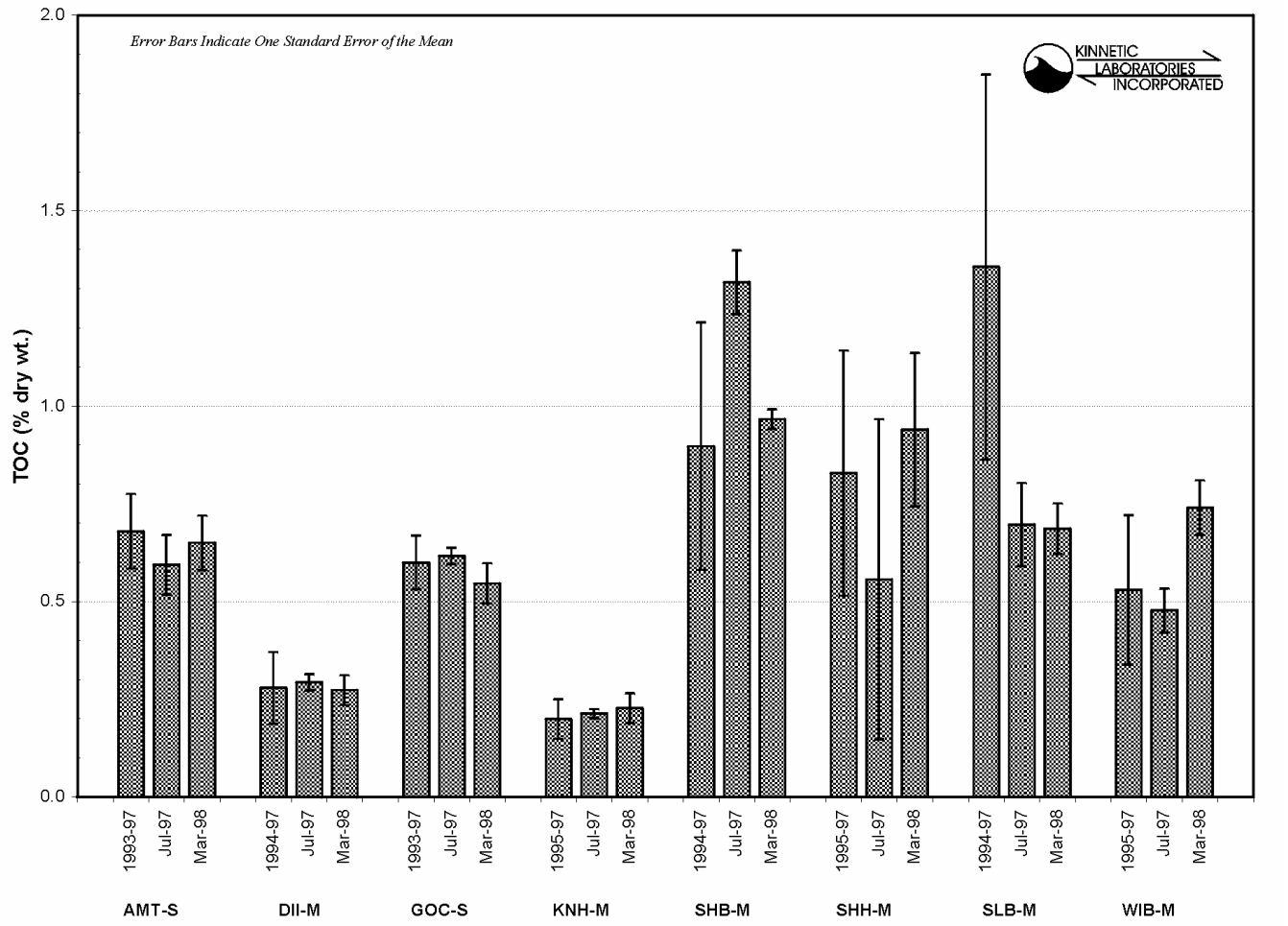

Figure 23. Mean LTEMP Sediment TOC Composition by Station and Survey - Historical, July 1997, and March 1998.

5.3.4 Particle Grain Size

The percentage of silt and clay in samples varied considerably among stations, but were comparatively similar at a given station through time (Tables 16 and 18; Figure 24). Individual replicate data are provided in Appendix B. Over all stations, sediment texture ranged from mostly sand to very fine silt and clay. No gravel has been reported at any of the LTEMP stations to date. The proportion of mean silt plus clay grain size fraction in July 1997 varied from 1.97 % at Stations DII-M and WIB-M to 96.67 % at Station AMT-S. March 1998 values ranged from 1.07 % at Station KNH-M to 97.43 % at Station AMT-S. The two deep stations, AMT-S and GOC-S, clearly showed the finest sediments when compared to the shallow subtidal locations (Table 16 and Figure 24). As expected, shallow subtidal stations were typically more coarse-grained than the deeper stations due to wave and current activity.

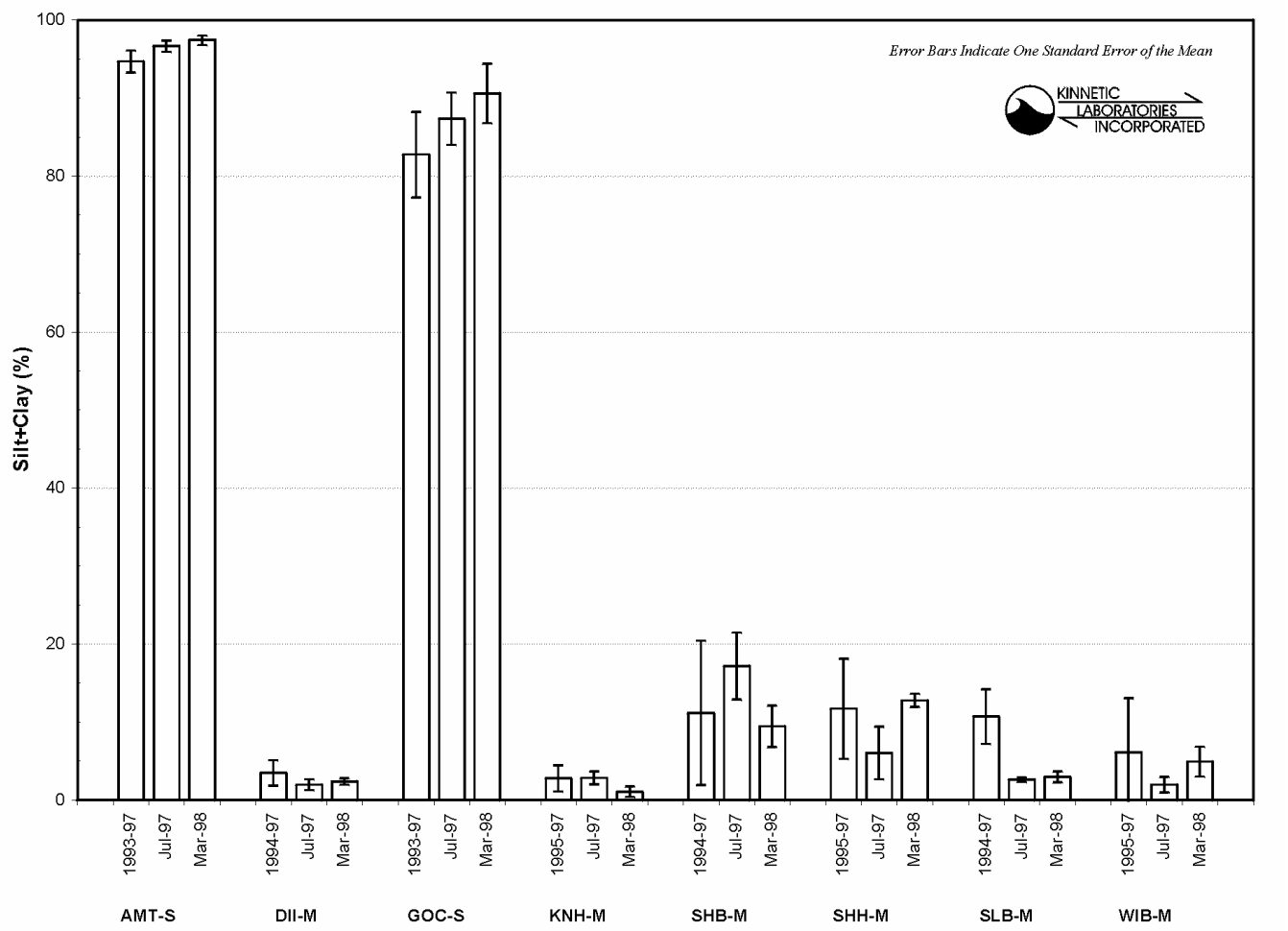

Figure 24. Mean LTEMP Silt+Clay Composition by Station and Survey - Historical, July 1997, and March 1998.

5.4 Quality Control Results

Quality control results are provided in Appendix C and briefly summarized in this section. The reader is referred to the appropriate appendix to review individual sample and QC sample results, including all data qualifiers. As described above, any data that did not meet QC criteria were qualified using the codes provided in Table 9. A review of the QC data reported during the 1997 - 1998 LTEMP indicates less than one percent of the data values required a qualifier code to indicate a matrix interference ("M"), analytes present in the procedural blank ("B"), and/or results failing the quality acceptance criteria for other reasons ("Q").

5.4.1 Equipment and Field Blanks

Two equipment blanks and one field blank were collected during the 1997 - 1998 LTEMP. Each of the equipment and field blanks showed very low levels of PAH and AHC, and UCM values were below MDL. Most of the individual analytes fell below MDLs and were qualified with the "J" qualifier.

5.4.2 Surrogate Compounds

Review of surrogate recoveries reported for LTEMP sample analyses indicated that the majority met acceptance criteria of recoveries of 40 to 120 percent. Those that failed to meet acceptance criteria were appropriately qualified. The surrogate perylene-d_{12} was low (less than 40 percent) for a few samples. As reported in the past, this is typical for this surrogate, which is now considered an advisory surrogate that is only used to calculate the concentration of perylene. This low

recovery is not problematic for LTEMP because perylene is a biogenic hydrocarbon that has not been included in TPAH values for this program. Other surrogates that were qualified because they exhibited high recoveries (greater than 120 percent), including deuterated n-C_{30} (four samples), deuterated n-C_{20} (one sample), naphthalene-d_8 (one sample), and acenaphthene-d_{10} (two samples).

5.4.3 Procedural Blanks

With few exceptions, procedural blanks contained negligible concentrations of PAH and AHC analytes and carbon (for TOC) at levels less than the acceptance criteria (less than three times the MDL). Many of these concentrations were qualified as ND or below the MDL ("J"), and many of these samples also exhibited the laboratory artifact pattern. As described above, this artifact is due to parent analytes with calibration standards having much lower MDLs than their alkylated homologues, so these parent analytes are typically reported while their homologues may not be detected.

Procedural blanks analyzed in conjunction with tissue analyses for the 1997 - 1998 LTEMP did not show PAH analytes at concentrations greater than three times the MDL. One of the procedural blanks (Q15388) analyzed in conjunction with July 1997 sediment samples (batch M2660) showed one analyte at a level above this limit: benzo(g,h,i)perylene at 0.7 ng/g as compared to an MDL of 0.2 ng/g. Benzo(g,h,i)perylene values were qualified with a “B” in the blank and in samples and QC samples in this batch with concentrations of less than 10 times the MDL. No further action was taken. Other procedural blanks analyzed for PAH and AHC in conjunction with sediments showed no analytes at greater than three times the MDL. One procedural blank (Q15378) analyzed in conjunction with July 1997 field-collected water blank samples showed n-C_{23} at levels above the limit (132 ng/L compared to an MDL of 15 ng/L); this analyte was also qualified with a “B” in the blank. Since the concentration of this analyte in the one sample in this batch (PWS97PAB0003) was above 10 times the MDL, no qualifier code was necessary. No other analytes in these procedural blanks were documented at concentrations greater than three times the MDL.

5.4.4 Matrix Spike/Matrix Spike Duplicates

Analyses of the 1997 - 1998 LTEMP samples included the analysis of matrix spike/matrix spike duplicate pairs for PAH and/or AHC. While some individual analytes showed high percent recoveries and were qualified with a “Q”, most samples passed the QA criteria for average percent recovery and RPD. All matrix spike/matrix spike duplicate analyses for PAH in tissue passed the QA criteria for average percent recovery and RPD. One matrix spike duplicate of sample PWS98PAT0016 (Survey 11 sediment, batch M2753) showed an average percent recovery of 141.1, exceeding the QC criteria of 120. After further investigation, it was determined that there was non-homogeneity in the sample matrix and that the alkylated phenanthrenes and chrysenes in the matrix spike duplicate sample were elevated. Data for this sample were qualified with a “Q”; no further action was taken. All matrix spike/matrix spike duplicate samples analyzed in conjunction with other sediment batches for PAH and AHC passed the QA criteria for average percent recovery and RPD. Blank spike and blank spike duplicate analyses performed in conjunction with the field-collected equipment and field blanks also fell within acceptable limits.

5.4.5 Reference Oil

Reference oil samples of EVOS oil were reported for PAH and AHC during the 1997 - 1998 LTEMP. Analysis of these samples was performed in conjunction with each hydrocarbon sample batch regardless of matrix. Most reference oil samples passed the laboratory requirements. Two of the references oil samples showed elevated levels of one or two individual analytes in each sample (n-C_{13}, C_2-naphthalenes, and dibenzothiophene), and one sample showed much lower levels of one analyte (phytane) than expected. All analytes showing values outside the acceptable limits were investigated, and each data point was appropriately qualified with the “Q” qualifier. Overall, QA criteria were met for all reference oil samples analyzed for the 1997 - 1998 LTEMP.

5.4.6 Standard Reference Materials

Standard Reference Materials (NIST 1974a [tissue] or 1941a [sediment]) were analyzed with each batch of samples to

provide an estimate of accuracy. Results for PAH were compared with certified values to determine percent difference. Although high recoveries were noted in some instances, no interferences were noted by the analysts. Analytes exhibiting these high recoveries were properly qualified with a "Q"; no further action was required.

The AHC data reported for these samples (i.e., Survey 10 sediments) are incidental as no certified values exist for these samples. Also, reported PAH analytes having no certified values (e.g., biphenyl) were compared to laboratory acceptance limits and also appropriately qualified, although no certified SRM values exist.

5.4.7 Duplicate Analyses

Duplicate analyses performed for TOC met the acceptance criteria of RPD between duplicates of ±20 for low carbon content samples (<1.0 percent) and ±10 for high carbon samples (>1.0 percent).

No strict acceptance criteria exist for PGS duplicates. Instead, duplicate analyses are intended to provide an estimate of the homogeneity of the samples. The duplicate analysis performed for samples PWS97PGS0047 (silt) and PWS98PGS0012 and PWS98PGS0024 (clay) showed high RPDs exceeding 25. However, the silt and clay concentrations for these samples were each less than 1 percent; no further action was required.

In addition, duplicate analyses were performed for both tissue and sediment PAH and AHC. These duplicate analyses can be compared with the original sample results to provide an estimate of precision, but specific QC criteria do not exist for duplicate samples.

6.0 SUMMARY

The 1997 - 1998 LTEMP has added additional data to the baseline information that has been collected since 1993. During the program year reported here (1997 - 1998), nine stations were sampled for intertidal mussels. In addition, six shallow subtidal sediment stations were sampled along with the two deeper subtidal sediment stations.

The LTEMP data indicate that hydrocarbons in tissues and sediments in the study area vary between stations, and, to a lesser extent, over time. Hydrocarbon levels in tissues were generally low, although they were higher than those seen during past surveys at some sites. Levels in sediments were more variable, with some stations exhibiting background levels and others showing anthropogenic influences.

Hydrocarbons in PWS can have a multitude of origins, including both natural and anthropogenic sources, such as those from the EVOS or Alyeska Marine Terminal-related activity, biological activity, combustion sources, vessel activities, natural oil seepage, coal deposits, and atmospheric fallout. Examination of hydrocarbon data for both tissues and sediments indicated that hydrocarbons from a variety of these sources can be identified in the 1997 - 1998 data. For many stations, these sources are the same that have been identified in earlier program reports (KLI, 1993b; 1994a; 1995a; 1996a; and 1997a) and by other researchers examining LTEMP data (Payne et al., 1998).

Mussel tissue from Stations AMT, DII, GOC, and SLB exhibited a strong petrogenic hydrocarbon signal, particularly during March 1998. A larger proportion of individual analytes at levels above the detection limit were seen in March 1998 samples as compared to earlier surveys, resulting in clearer PAH fingerprints. As in the past, hydrocarbons in March 1998 tissue samples at Stations AMT and GOC were attributed to ANS crude, with the most likely source identified as the Alyeska Marine Terminal and tanker operations. Residues of EVOS oil were identified in tissues at Stations DII and SLB, two of the LTEMP sites known to have been heavily impacted during the EVOS. Station WIB, also heavily impacted by the EVOS, showed PAH fingerprints that were not attributable to ANS/EVOS but more closely resembled background sources. During March 1998, a clear petrogenic fingerprint seen at Stations AIB, KNH, SHB, and SHH was ascribed to natural background sources. Station AIB tissues may have been contaminated with fuel which accounted for the relatively high levels of PAH seen at this site (compared to historical data). Lesser pyrogenic inputs were also noted at many of these stations, particularly Stations AMT, GOC, and SLB.

Sediment results also indicated a number of probable sources of petroleum hydrocarbons. Sediments collected at the deeper subtidal stations (AMT-S and GOC-S) showed petrogenic as well as pyrogenic inputs. Sediments at the Alyeska Marine Terminal (AMT-S) continued to show clear ANS crude contamination. Hydrocarbons seen at this location are the result of long-term (chronic) inputs, as shown by the PAH and AHC weathering ratios and the high UCM levels seen at this site. The petrogenic and pyrogenic PAH seen at Station GOC were not attributed to ANS. Sediments at the shallow Disk Island site (Station DII-M) also showed petroleum hydrocarbons with a probable combination of EVOS oil and background sources. Fingerprints in the sediments differ from those seen in tissue at this site; tissues here have typically shown ANS/EVOS patterns.

Sediments at Station SLB-M also showed a mixture of petrogenic and pyrogenic hydrocarbons. The PAH fingerprints indicate that the hydrocarbons are largely of a pyrogenic nature, with lesser amounts of possible ANS/EVOS oil and seep-derived background hydrocarbons. Two additional EVOS-impacted sites, Stations SHH-M and WIB-M, showed a combination of sources. Petrogenic hydrocarbons were attributed to seep-derived background and EVOS oil. Both of these stations showed a substantial pyrogenic component. Station WIB-M also showed a large amount of biogenic input which may be due in part to logging activities.

Hydrocarbons found in sediments at Stations KNH-M and SHB-M were ascribed to natural background. Some evidence of pyrogenic inputs were also seen at these stations.

7.0 ACKNOWLEDGMENTS

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GLOSSARY and LIST OF ACRONYMS

A

AIB - Aialik Bay

AHC - aliphatic hydrocarbons

Aliphatic hydrocarbons (AHC) - Fully saturated normal alkanes (paraffins) and branched alkanes, n-C_{10} to n-C_{34}; includes the isoprenoid compounds pristane (C_{19}) and phytane (C_{20}) that are often the most abundant isoprenoids in petroleum hydrocarbons

AMT - Alyeska Marine Terminal

ANS - Alaska North Slope (refers to origin of petroleum products)

Anthropogenic - Resulting from the influence of human activities. (Refers to hydrocarbon input.)

B

Biogenic - Synthesized by plants and animals, including microbiota. (Refers to hydrocarbon input.)

BWTP - Ballast Water Treatment Plant at Alyeska Marine Terminal

C

Carbon preference index (CPI) - 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).

COC - Chain of Custody

CPI - see carbon preference index

D

DI - De-ionized water

Diagenic - Resulting from alteration by microbial or chemical processes. (Refers to hydrocarbon input.)

DII - Disk Island

E

ELS - T/V *Eastern Lion* spill (May 1994)

Electron-impacted ionization mode - An ionization method that utilizes electrons to impact the analyte mixture to facilitate ionization.

EVOS - *Exxon Valdez* oil spill

F

FFPI - fossil fuel pollution index

Fossil fuel pollution index (FFPI) - The fossil fuel pollution index is the ratio of fossil-derived PAH to total PAH as follows:

FFPI = (N + F + P + D)/TPAH x 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 + C_2-P + C_3-P + C_4-P
D (Dibenzothiophene series) = C_0-D + C_1-D + C_2-D + C_3-D

An FFPI is near 100 for petrogenic PAH; FFPI for pyrogenic PAH is near 0 (Boehm and Farrington, 1984).

G

Gas chromatography with flame ionization detection (GC/FID) - The process in which the components of a mixture are separated from one another according to their ionization time when heated.

Gas chromatography with mass spectrometry detection (GC/MS) - The process in which the components of a mixture are separated from one another according to their mass.

GC/FID - gas chromatography with flame ionization detection

GC/MS - gas chromatography with mass spectrometry detection

GERG - Geochemical and Environmental Research Group of Texas A&M University

GI - gonadal index

GOC - Gold Creek

Gonadal index (GI) - Measure of shell volume, shell length, volume and weight of gonadal and non-gonadal tissue.

GPS - Global Positioning System. Satellite based navigation system.

H

High-performance liquid chromatography (HPLC) - An analytical method based on separation of the components of a mixture in solution by selective adsorption.

Homogeneous - Uniform in structure or composition.

HPLC - high performance liquid chromatography

I

Indigenous - Native or naturally occurring.

K

KLI - Kinnetic Laboratories, Inc.

KNH - Knowles Head

L

LTEMP - Long-Term Environmental Monitoring Program

LLD - Lower Limit of Detection

Lower Limit of Detection - a detection limit, generally lower than the MDL, which is considered a typically achievable detection limit based on the sample set being analyzed.

M

Macrofauna - Non-microscopic animals

Macroflora - Non-microscopic plants

MDL - method detection limit

Mean Lower Low Water (MLLW) - The average height of the daily lower low waters occurring over a 19 year period.

Method detection limit (MDL) - The lowest concentration of an analyte that a method can reliably detect.

MLLW - Mean Lower Low Water

MS - Mass spectrometer

Mytilus edulis - blue mussel (believed now to be found only outside of Alaska)

Mytilus trossulus - blue mussel (Alaskan species)

N

ND - Not detected

NIST - National Institute of Standards Technology

NOAA - National Oceanic and Atmospheric Administration

P

PAH - polycyclic aromatic hydrocarbons

Particle grain size (PGS) - Percent sand, silt, and clay.

PCBs - Polychlorinated biphenyls

Percent lipid - Concentration of lipid as a fraction of the total tissue weight. Lipid material in mussel tissue is the primary storage area for hydrocarbons; gametes are mostly comprised of lipids.

Petrogenic - Resulting from natural geologic processes which originally form petrochemicals. (Refers to petroleum hydrocarbon input)

PGS - particle grain size

Polycyclic aromatic hydrocarbons (PAH) - 2 to 6-ring polycyclic aromatic hydrocarbon compounds; includes homologous series of aromatic hydrocarbons consisting of unsubstituted (parent) compounds, such as naphthalene, and substituted compounds, which are similar structures with alkyl side chains that replace hydrogen ions, such as C_1-naphthalene.

ppb - parts-per-billion or ng/g

ppm - parts-per-million or µg/g

PWS - Prince William Sound

Pyrogenic - Resulting from the activity of fire or very high temperature. (Refers to hydrocarbon input from high temperature, incomplete combustion of fossil fuels, or creosote.)

Q

QA - quality assurance

QC - quality control

Qualifier code - Character used to qualify data based on method detection limits, matrix interference, or other performance parameter.

R

RCAC - Prince William Sound Regional Citizens' Advisory Council

RPD - Relative percent difference

S

Selected ion monitoring (SIM) - A gas chromatograph operating mode in which the detection range is limited to include only the masses of the desired analytes.

SHB - Sheep Bay

SHH - Shuyak Harbor

SIM - selected ion monitoring

SLB - Sleepy Bay

SOP - Standard operating procedure

Soxhlet extractor - A laboratory apparatus consisting of a glass flask and condensing unit used for continuous reflux extraction of alcohol- or ether-soluble components.

SRM - Standard Reference Material

Standard Reference Material (SRM) - A certified known concentration of a compound that is analyzed in conjunction with samples for Quality Assurance/Quality Control (QA/QC) purposes.

T

TAHC - total aliphatic hydrocarbons

TOC - total organic carbon

Total organic carbon (TOC) - The percentage by dry weight of organic carbon in a sediment sample.

Total aliphatic hydrocarbons (TAHC) - see Aliphatic Hydrocarbons

Total polycyclic aromatic hydrocarbons (TPAH) - see Polycyclic Aromatic Hydrocarbons

TPAH - total polycyclic aromatic hydrocarbons

U

UCM - unresolved complex mixture

Unresolved complex mixture (UCM) - Petroleum compounds represented by the total resolved plus unresolved area minus the total area of all peaks that have been integrated; a characteristic of some fresh oils and most weathered oils

USGS - U.S. Geological Survey

V

Van Veen grab - Device used for collection of subtidal marine sediments.

W

WIB - Windy Bay