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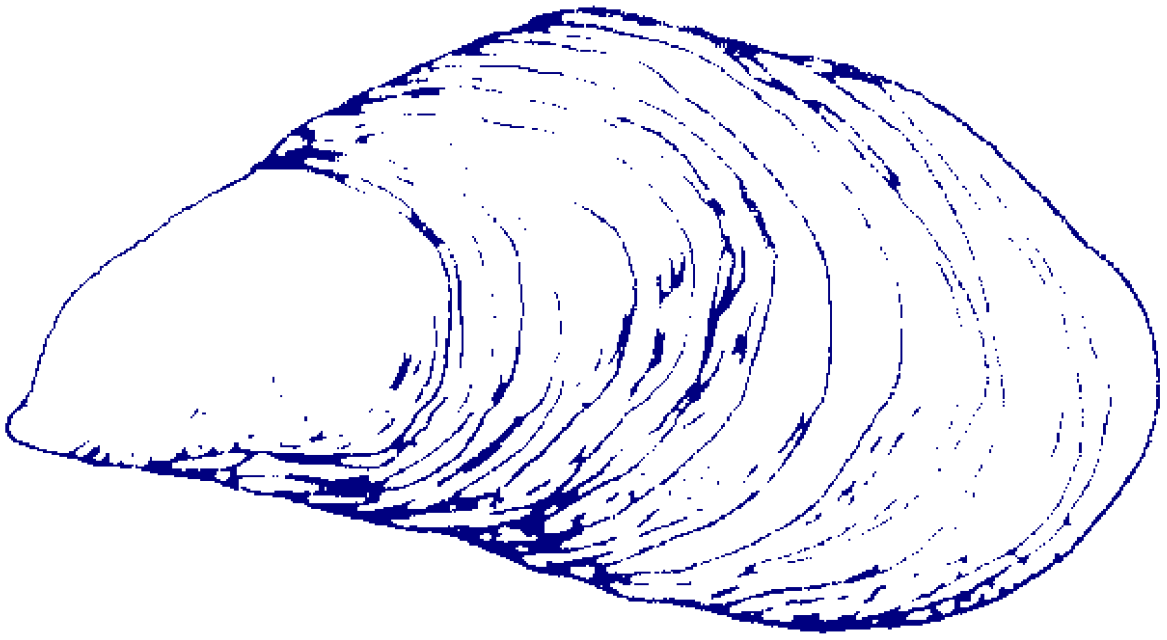
PRINCE WILLIAM SOUND RCAC

LONG-TERM ENVIRONMENTAL MONITORING PROGRAM

1998 - 1999 LTEMP MONITORING REPORT



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EXECUTIVE SUMMARY

The Long-Term Environmental Monitoring Program was designed to provide 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. These measurements provide a basis for the examination of spatial and temporal changes in hydrocarbon levels that are the result of both natural and man-induced inputs to the environment. The program focuses on sampling of intertidal mussels and nearby sediments to provide information on hydrocarbon levels that 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 during July 1998 and March 1999. Mussel samples were collected from indigenous (native) intertidal blue mussel populations for the analysis of hydrocarbons in tissues at all nine sites during this report period (Aialik Bay, Alyeska Marine Terminal, Disk Island, Gold Creek, Knowles Head, Sheep Bay, Shuyak Harbor, Sleepy Bay, and Windy Bay). Additional physical measurements of the mussels 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. Collection of intertidal sediment from adjacent areas was introduced into the program this year and performed at eight of the nine stations for the analysis of hydrocarbon concentrations and physical parameters to investigate baseline hydrocarbon concentrations in these areas. Sediment was collected at all of the existing stations except Sleepy Bay, where the beach substrate was too coarse to collect sediments.

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 that 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. Chemical analyses were performed using state-of-the art techniques following specific protocols to ensure the validity and integrity of the data. Analytical strategy for the 1998 - 1999 program was essentially the same as the last few years of the program except for the inclusion of aliphatic hydrocarbon analysis for tissues and the reporting of several other aliphatic hydrocarbon parameters for both tissues and sediments.

Hydrocarbons in the marine environment, particularly in the study area, can have a multitude of origins and include both human-induced and naturally-occurring inputs. 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 resident biota and sediments in Prince William Sound and the Gulf of Alaska. 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, residues from natural coal deposits, natural petroleum seeps from the eastern Gulf of Alaska area, and refined products such as diesel or Bunker C fuel oil. 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. Coal deposits in the Gulf of Alaska are now considered by some researchers to be the predominant source of naturally-occurring petrogenic hydrocarbons (or "background hydrocarbons") in the study area, and these also exhibit a distinctly different fingerprint from Alaska North Slope crude and other oils.

Examination of hydrocarbon data for both tissues and sediments indicated that hydrocarbons from a variety of sources can be identified in the 1998 - 1999 program. For many stations, these sources are similar to those identified in earlier program reports and by other researchers examining program data. However, it should be noted that 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.

The 1998 - 1999 data indicate that hydrocarbons in tissues in the study area vary between stations, and, to a lesser extent, over time. The polycyclic aromatic hydrocarbon levels in tissues were generally very low and at levels less than that seen in recent years. The apparent increasing trend in these compounds that had been seen in tissues over the last several years of the program was not apparent this year. The aliphatic hydrocarbon levels in tissues were considerably higher than the polycyclic aromatic hydrocarbon concentrations, as was expected due to the naturally-occurring compounds in these animals that interfere with the aliphatic hydrocarbon analyses. After reviewing the results, it appears that inclusion of this analysis for mussel tissues did not provide useful additional information. This agrees with earlier program data (1993 - 1994). Since this parameter had not been examined in tissues since 1994, no discussion of long-term trends was possible.

Although tissue PAH concentrations were low, PAH fingerprints from many stations exhibited a petrogenic hydrocarbon signal which could be attributed to several sources. As in many of the past surveys, hydrocarbons in the tissues at both the Alyeska Marine Terminal and Gold Creek stations during March 1999 were attributed to Alaska North Slope crude, with the most likely source identified as the Alyeska Marine Terminal and tanker operations. Lesser amounts of pyrogenic (combustion-sourced) hydrocarbons were also seen at these stations. In contrast to most past results, a background signature was also seen in the mussels collected at the Alyeska Marine Terminal during July 1998. This signature may have been visible due to the very low levels of PAH seen in July 1998, which may reflect normal ("non-contaminated") levels in these mussels (i.e., with no petroleum inputs from operations at the Alyeska Marine Terminal). Residues of *Exxon Valdez* spill oil were identified in tissues at Disk Island, a site heavily impacted during the 1989 spill, although hydrocarbon levels were very low at this site this year. This station also showed signs of background and pyrogenic inputs. Other stations exhibiting the background signature included Aialik Bay, Knowles Head, Sheep Bay, Sleepy Bay, Shuyak Harbor, and Windy Bay. Pyrogenic inputs were also apparent at some of these stations.

Levels of hydrocarbons in intertidal sediments were quite variable and ranged from quite low at most sites to extremely high at the Disk Island site where visibly oiled sediments were collected. Sediments collected at the Alyeska Marine Terminal also contained elevated levels of hydrocarbons relative to the other stations. Hydrocarbons at Disk Island were attributed to the *Exxon Valdez* spill while those at Alyeska were attributed to Alaska North Slope crude, although each station showed evidence of other inputs as well. Other stations showed very low levels of hydrocarbons with varying degrees of petrogenic, pyrogenic, and biogenic inputs. All of the intertidal sediments consisted of fairly coarse-grained materials, as was to be expected when sampling in the intertidal zone.

Sampling at the intertidal sediment stations this year provided valuable insights. First, it indicated that intertidal surficial sediments may be sampled in the area immediately adjacent to the mussel sampling areas at all but one of the existing sites. Second, it showed that even though these sediments are quite coarse, measurable quantities of hydrocarbons may still reside in them if hydrocarbons have been (or are being) released into the marine system, as seen at the Disk Island and Alyeska Marine Terminal sites. This means that should a spill event occur, these pre-existing sites could be sampled to determine potential spill impacts. Finally, the intertidal sediment data proved to support the use of the CRUDE index used by Payne et al. (1998) during their review of the 1993 - 1997 program. This index is a useful tool which helped to highlight petrogenic inputs in sediments.

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 sediments and indigenous (native) 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 development of a long-term comprehensive dataset that can be used to evaluate both temporal and spatial trends in hydrocarbon levels and to help determine potential impacts of oil transportation on the ecosystem. The program is 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 sixth year of the monitoring program. It includes results from the two LTEMP surveys performed during the RCAC=s 1998 - 1999 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; 1997a; 1997d; and 1998). For the reader's convenience, a Glossary and List of Acronyms is provided at the end of this document.

Intertidal indigenous blue mussel tissue samples and intertidal sediments were collected during two field surveys at LTEMP stations. Intertidal mussel samples were collected from pre-existing mussel stations for the analysis of polycyclic aromatic hydrocarbons (PAH); aliphatic hydrocarbons (AHC) which included the total resolved aliphatic hydrocarbons (TRAHC) and the unresolved complex mixture (UCM); and lipid content. Additional mussels were collected for measurement of gonadal index. Intertidal sediments were collected from newly-determined sites adjacent to the mussel sites for the analysis of PAH, AHC, particle grain size (PGS), and total organic carbon (TOC) content. This sampling was performed once to determine the viability of intertidal sediment sampling since oil spill impacts would be seen first in these areas.

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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. For the Mussel Watch Project, 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 1998 (Survey 12) and March 1999 (Survey 13). 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, AHC, and percent lipids. Twenty additional mussels were collected at each station for assessment of gonadal state.

In contrast to the subtidal sediment collection performed in the past for this program, intertidal sediments were collected during the program year reported here. Intertidal sediments were obtained from the beach areas immediately adjacent to each mussel sampling site at eight of the nine stations. Three replicate samples of surficial sediment (0 - 2 centimeters [cm]) from each intertidal 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 TRAHC and UCM). These parameters were used to assess hydrocarbon concentrations in both tissue and sediment. 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 (e.g., KLI, 1993c and 1993d), 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. The extent of the mussel population became particularly important in March 1999, when it was discovered that many of the mussels (and other intertidal organisms) at the LTEMP sites in the Gulf of Alaska sites had been subject to die-off, probably due to extreme winter temperatures.

Nine stations were sampled during LTEMP 1998 - 1999: 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, "L" for intertidal sediment). The sampling 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 Sleepy Bay, mussels and intertidal sediments were collected at each site during the 1998 - 1999 LTEMP. Sampling at Sleepy Bay included only mussel collection, as the beach at this site consists of cobble and boulders with very coarse-grained sediments found only below this armor. Table 2 provides sampling information such as average station height relative to Mean Lower Low Water (MLLW).

Table 1. 1998 – 1999 LTEMP Analytical Strategy.

Parameter/ Matrix	Description	Relevance
Polycyclic aromatic hydrocarbons (PAH)/ Mussel tissue and sediment	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	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)/ Mussel tissue and sediment	The aliphatic analysis this year includes the measure of hydrocarbons defined and undefined by the gas chromatographic technique, including the following: AHC – aliphatic hydrocarbons defined as 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 TRAHC – the total resolved aliphatic hydrocarbons, which includes the AHC analytes (n-C_{10} through n-C_{34} and pristane and phytane) plus other compounds such as plant waxes and lipids which are not individually identified or reported UCM – the unresolved complex 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 TRUAHC – the total area of resolved and unresolved aliphatic hydrocarbons represented by the total area of the GC run, whether or not these compounds have been identified	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
Percent lipid/ Mussel tissue	Lipid material in mussel tissue is primary storage area for hydrocarbons; gametes are mostly comprised of lipids	Useful in determining spawning state of mussels; hydrocarbon body burdens decrease when lipid-rich gametes are released
Gonadal index/ Mussel tissue and shell	Measure of shell length, shell volume, volume and weight of gonadal tissue, volume and weight of non-gonadal tissue	Useful in determining spawning state of mussels; hydrocarbon body burdens decrease when lipid-rich gametes are released
Particle grain size (PGS)/ Sediment	Percent gravel, sand, silt, and clay	Assessment of particle size distribution in sediments; potentially used to standardize organic parameters such as PAH and AHC
Total organic carbon (TOC)/ Sediment	Organic carbon	Assessment of organic carbon load in sediment; potentially used to standardize organic parameters (PAH and AHC)

Table 2. Station Locations and Sampling Information for the 1998 – 1999 LTEMP.

Station Location	Station Designation	Station Type	Sampling Date	Survey No.	Average Height (m) Above MLLW	GPS Coordinates	
						Latitude (N)	Longitude (W)
AIALIK BAY	AIB-B	Intertidal Mussel	7/29/98	12	1.49	59°52’43.8”	149°39’33.0”
			4/3/99	13	1.85	Not Available	Not Available
	AIB-L	Intertidal Sediment	7/29/98	12	1.63	59°52’45.3”	149°39’30.2”
ALYESKA MARINE TERMINAL	AMT-B	Intertidal Mussel	7/14/98	12	1.47	61°05’22.3”	146°24’32.4”
			3/18/99	13	2.14	61°05’26.3”	146°24’29.4”
	AMT-L	Intertidal Sediment	7/14/98	12	0.21	61°05’11.2”	146°24’08.4”
DISK ISLAND	DII-B	Intertidal Mussel	7/10/98	12	1.62	60°29’52.4”	147°39’41.2”
			3/17/99	13	1.86	Not Available	Not Available
	DII-L	Intertidal Sediment	7/10/98	12	2.30	60°29’51.7”	147°39’40.9”
GOLD CREEK	GOC-B	Intertidal Mussel	7/13/98	12	0.88	61°07’27.8”	146°29’47.8”
			3/18/99	13	0.61	61°07’21.7”	146°29’48.7”
	GOC-L	Intertidal Sediment	7/13/98	12	0.32	61°07’29.1”	146°29’50.0”
KNOWLES HEAD	KNH-B	Intertidal Mussel	7/12/98	12	2.64	60°41’28.4”	146°35’06.3”
			3/16/99	13	2.88	Not Available	Not Available
	KNH-L	Intertidal Sediment	7/12/98	12	0.21	60°41’25.5”	146°35’09.2”
SHEEP BAY	SHB-B	Intertidal Mussel	7/11/98	12	2.15	60°38’45.4”	145°59’50.4”
			3/16/99	13	2.34	Not Available	Not Available
	SHB-L	Intertidal Sediment	7/11/98	12	1.58	60°38’45.5”	145°59’50.3”
SHUYAK HARBOR	SHH-B	Intertidal Mussel	7/28/98	12	2.95	Not Available	Not Available
			4/3/99	13	2.95	Not Available	Not Available
	SHH-L	Intertidal Sediment	7/28/98	12	2.06	58°30’07.9”	152°37’38.6”
SLEEPY BAY	SLB-B	Intertidal Mussel	7/10/98	12	2.13	60°04’03.4”	147°49’57.9”
			3/17/99	13	2.41	60°04’01.2”	147°50’01.0”
WINDY BAY	WIB-B	Intertidal Mussel	7/29/98	12	1.94	59°13’06.0”	151°31’12.1”
			4/3/99	13	1.82	Not Available	Not Available
	WIB-L	Intertidal Sediment	7/29/98	12	2.14	59°13’07.5”	151°31’16.5”

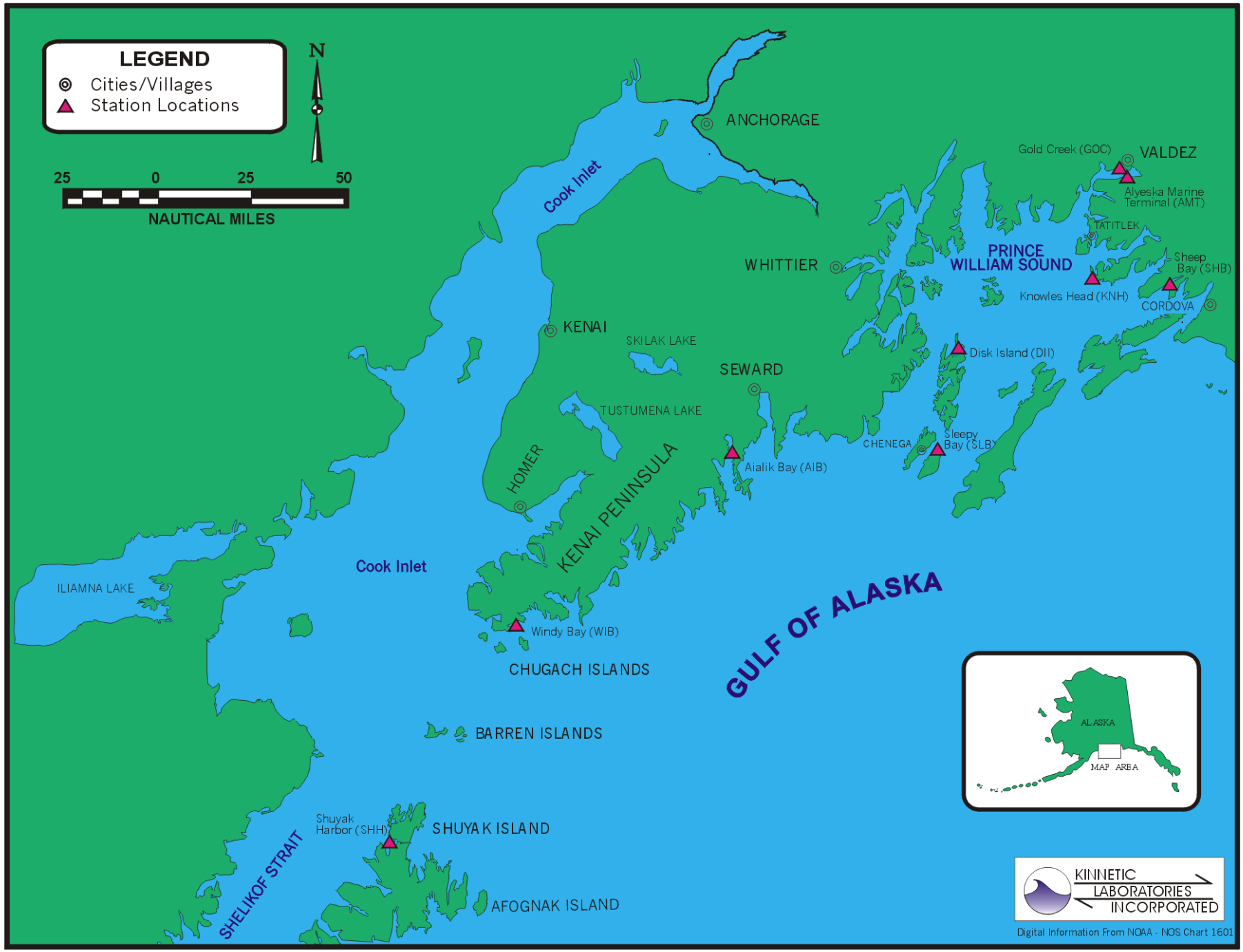

Figure 1. LTEMP Station Locations (Overall Study Area).

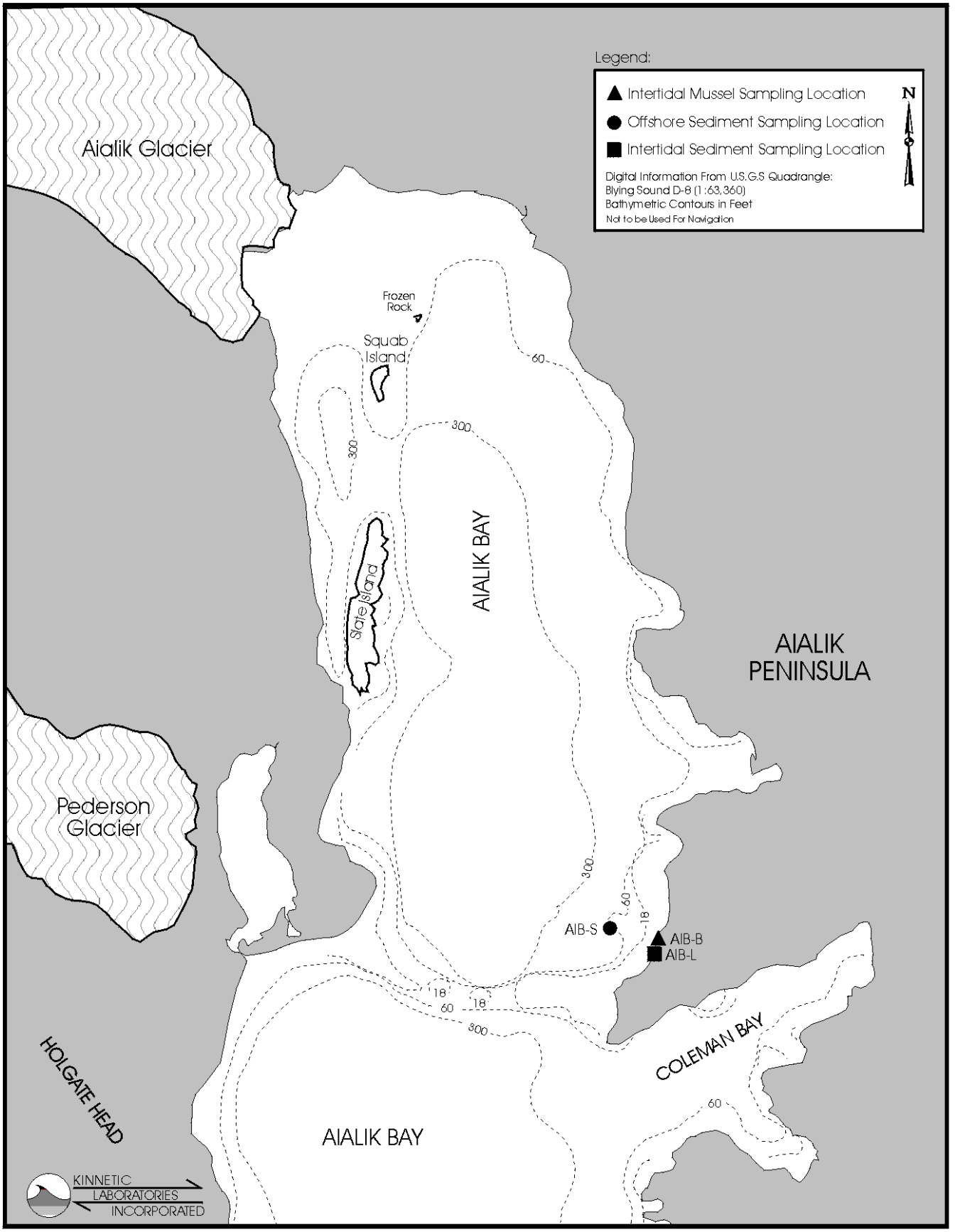

Figure 2. LTEMP Sampling Locations at the Aialik Bay Station.

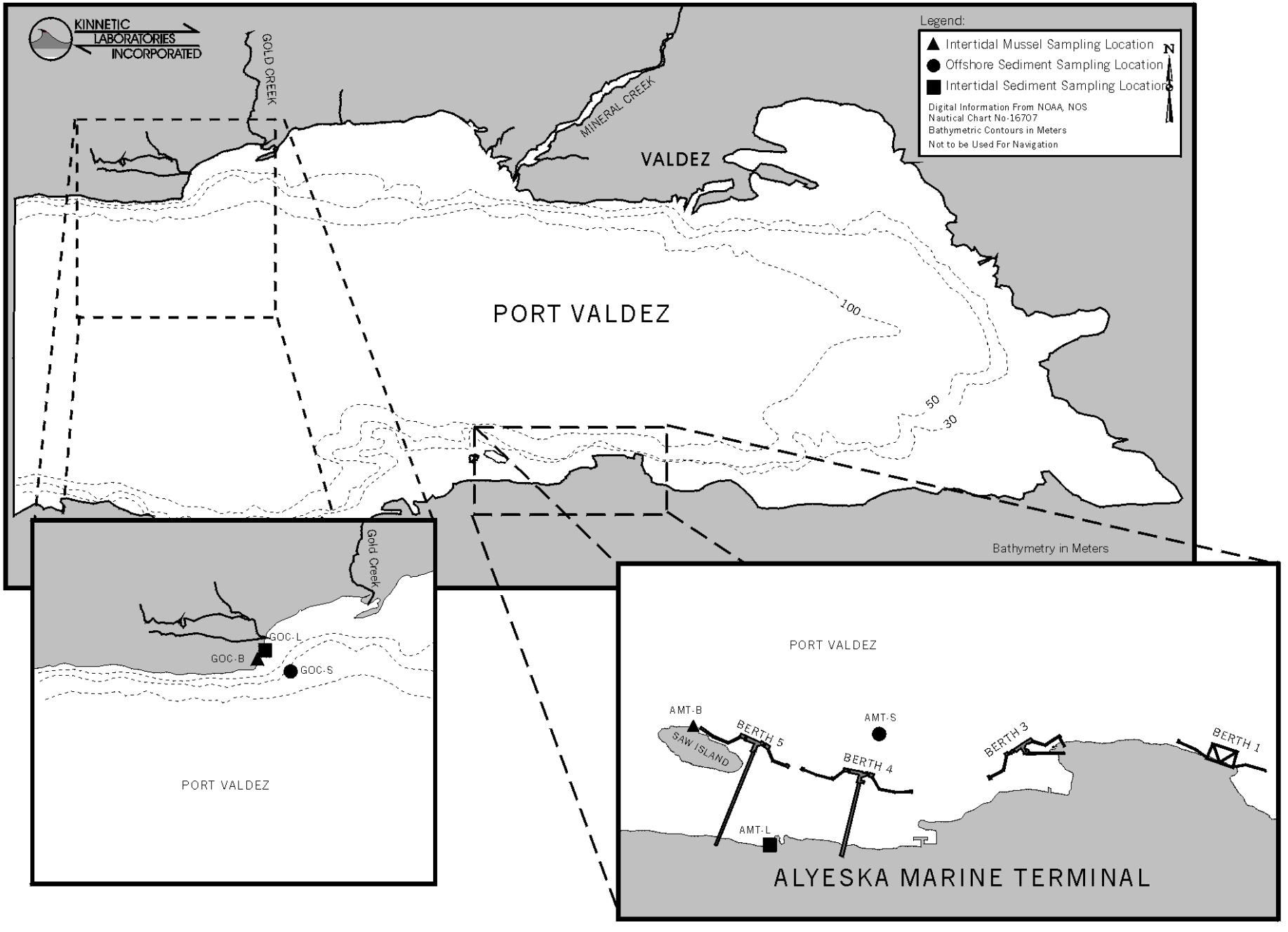

Figure 3. LTEMP Sampling Locations at the Alyeska Marine Terminal and Gold Creek Stations.

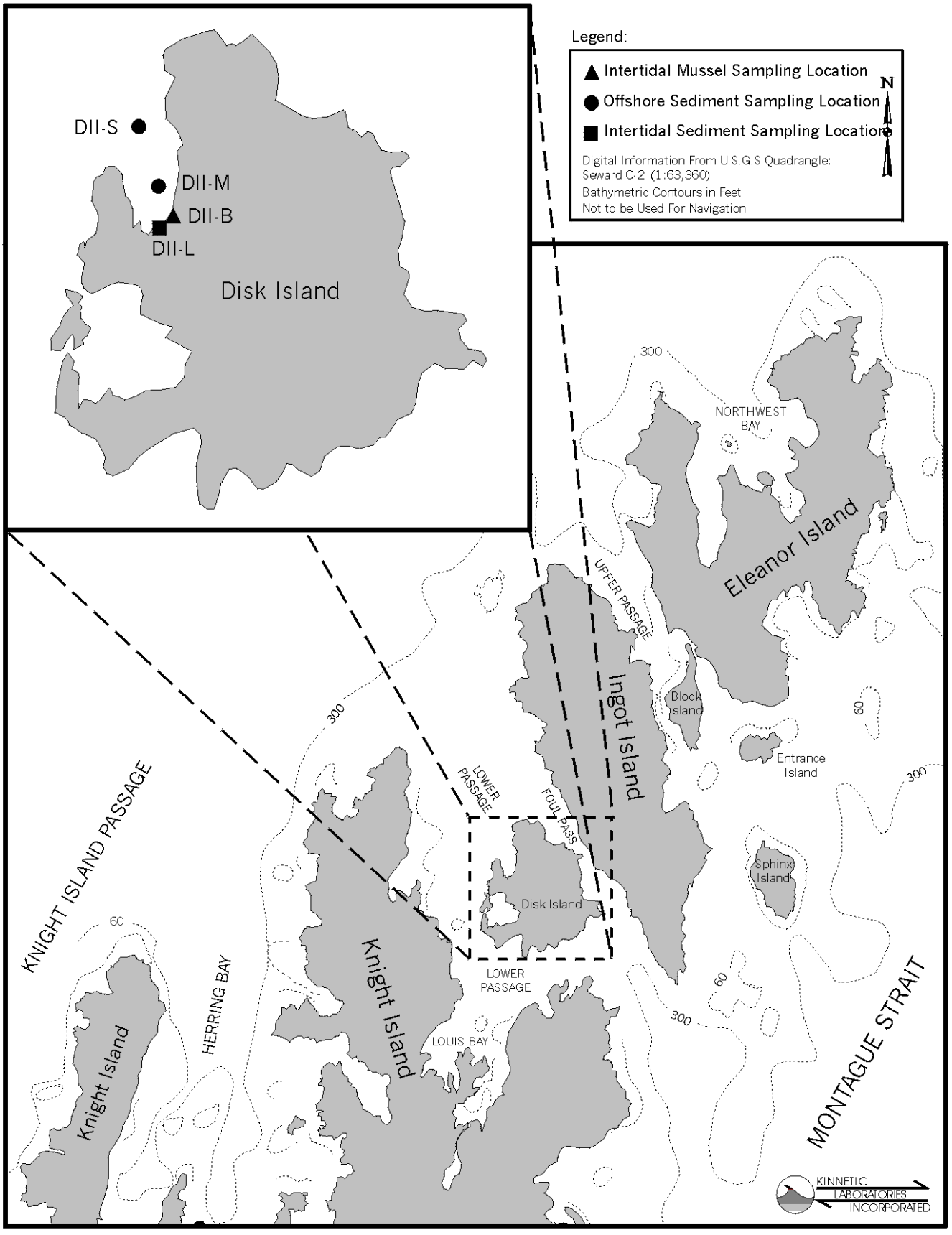

Figure 4. LTEMP Sampling Locations at the Disk Island Station.

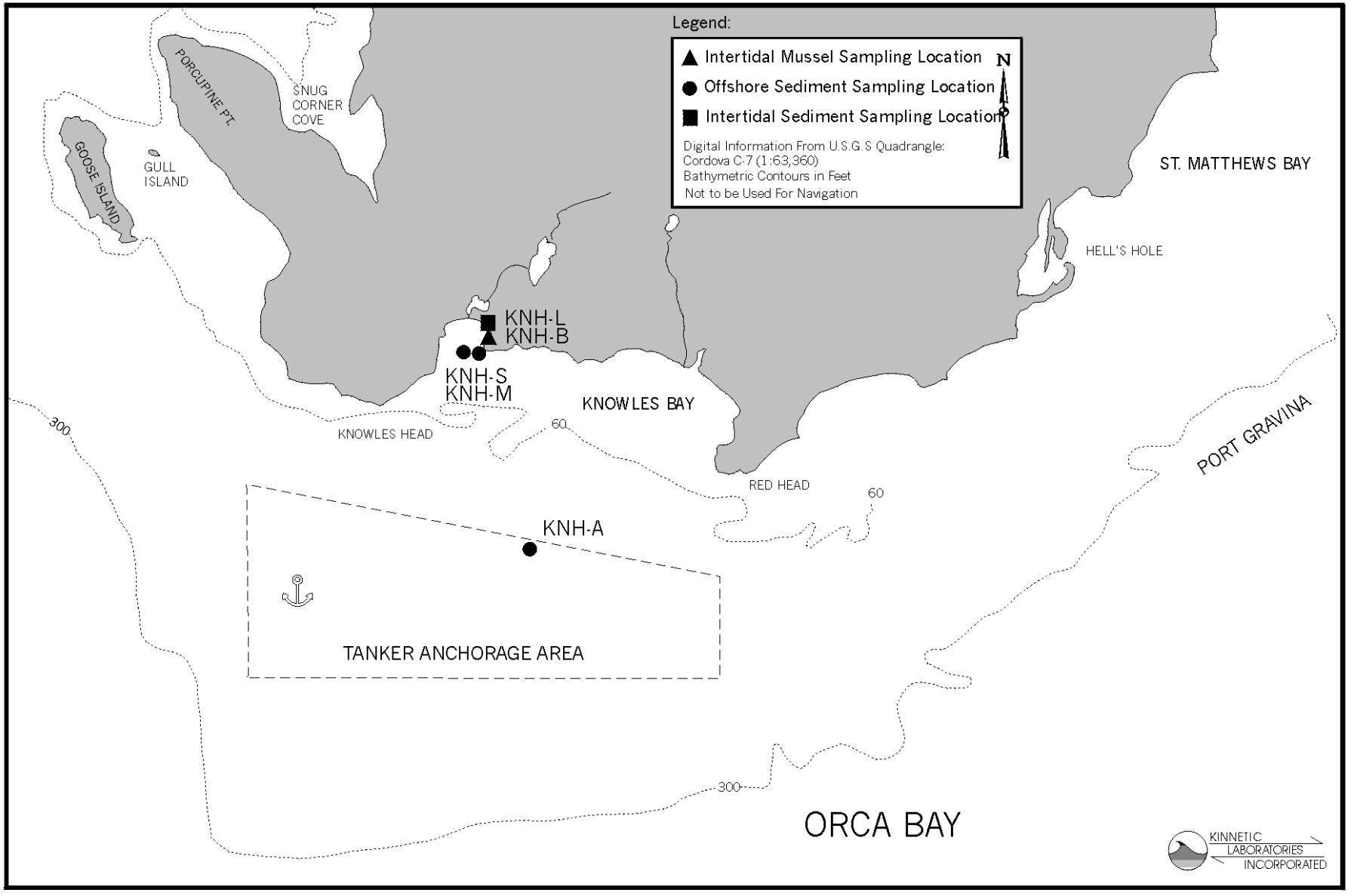

Figure 5. LTEMP Sampling Locations at the Knowles Head Station.

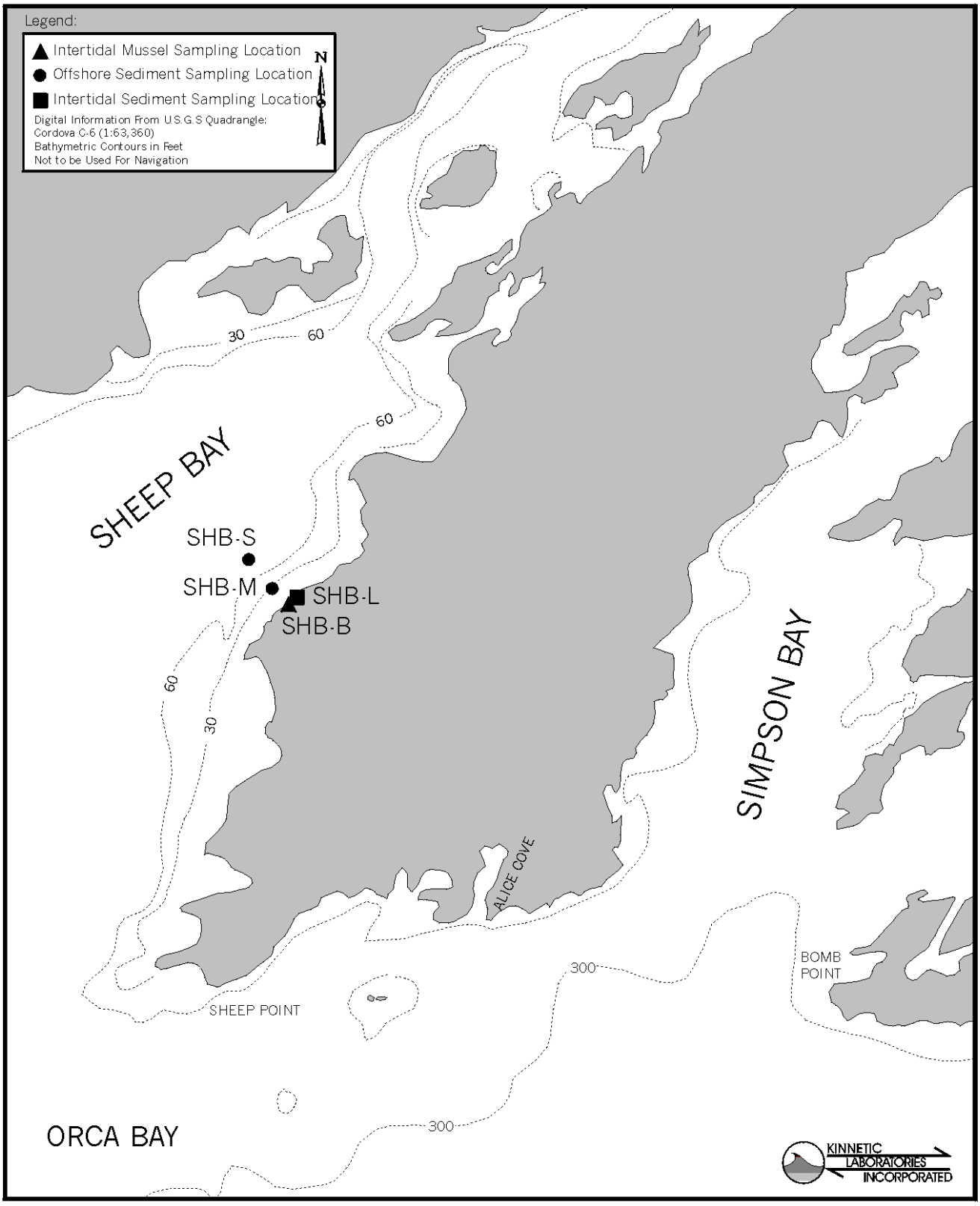

Figure 6. LTEMP Sampling Locations at the Sheep Bay Station.

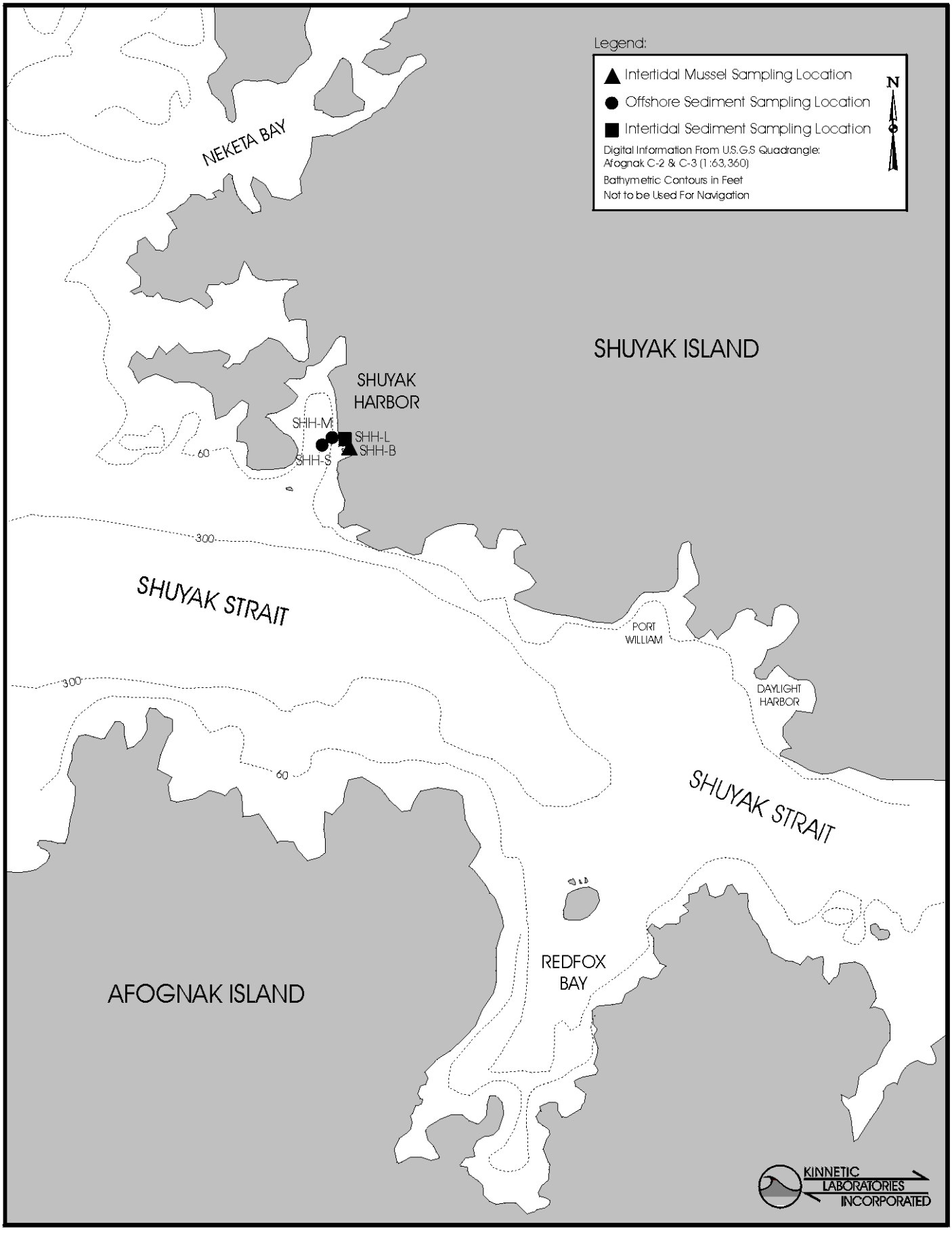

Figure 7. LTEMP Sampling Locations at the Shuyak Harbor Station.

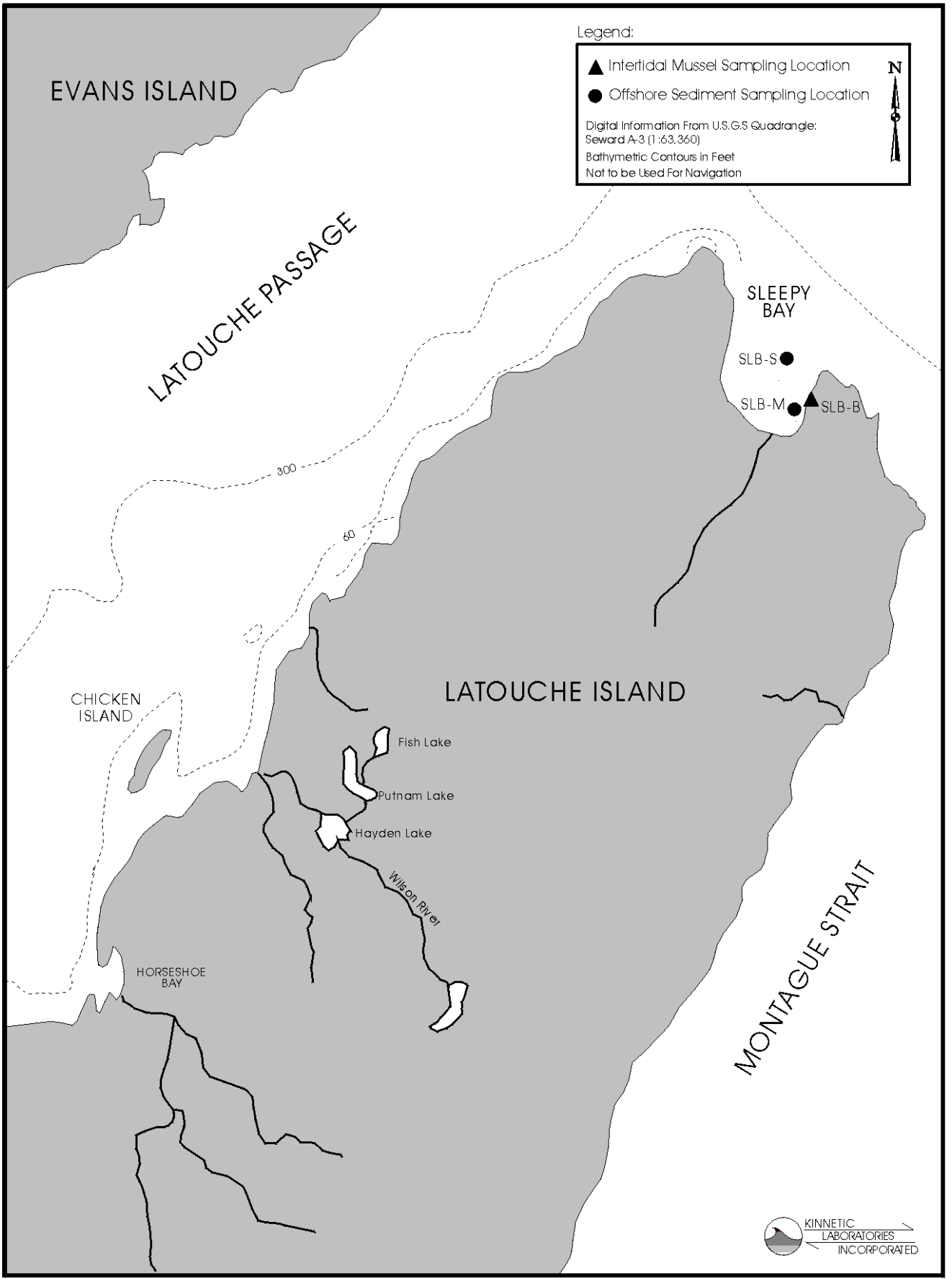

Figure 8. LTEMP Sampling Locations at the Sleepy Bay Station.

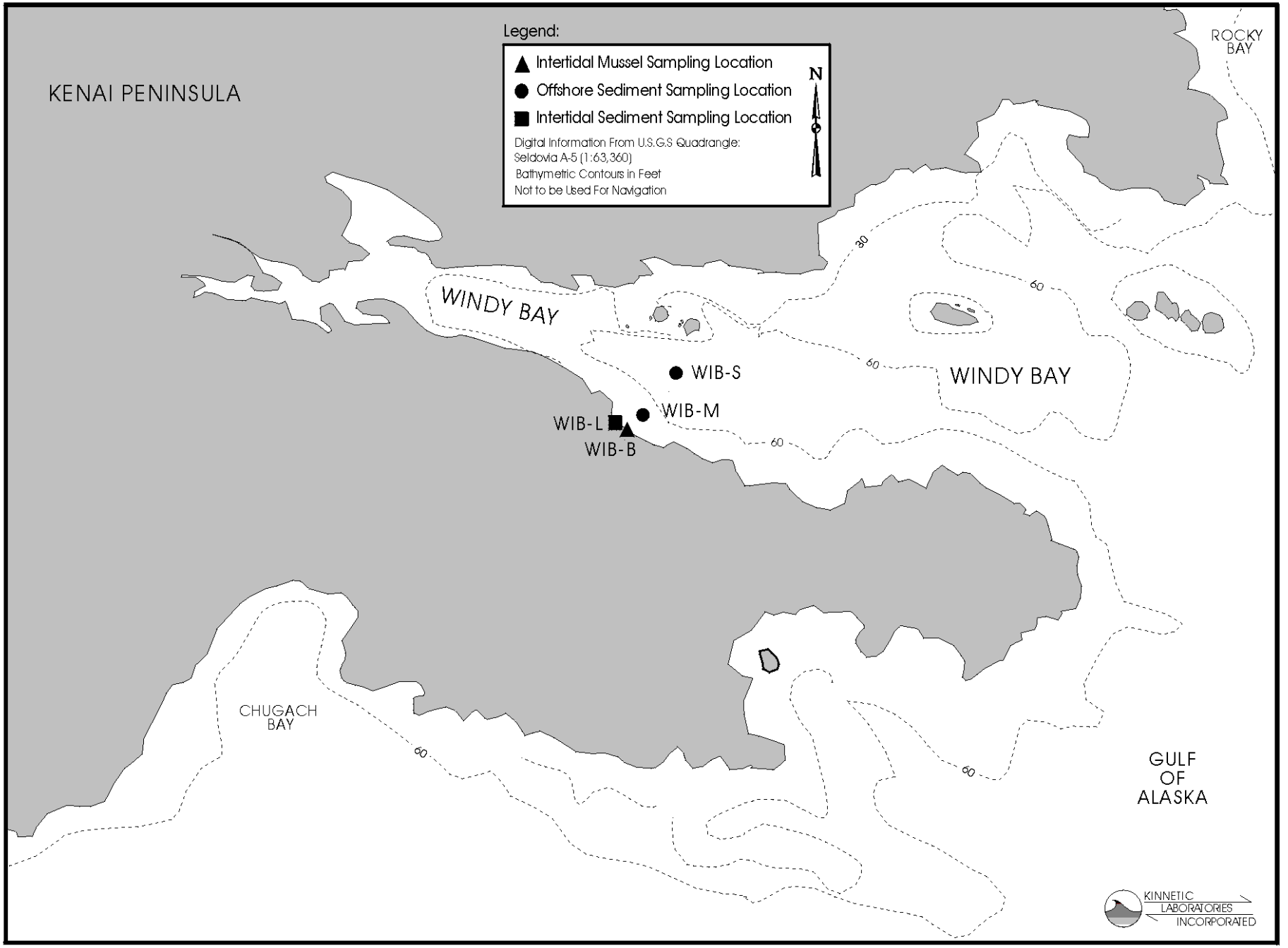

Figure 9. LTEMP Sampling Locations at the Windy Bay Station.

3.0 METHODOLOGY

3.1 Field Methods

Sampling and handling procedures followed those described in prior program reports (KLI, 1994a; 1995a; 1996a; 1997a; and 1998). 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.

Intertidal sediment sampling was performed using pre-cleaned stainless steel sampling spoons. Three discrete replicate sediment samples of surficial sediment (0 - 2 cm) were collected at each station where sediments were available. Samples were collected randomly from an area of the beach nearest the mussel site that appeared upon visual inspection to have reasonably fine sediment material. Surficial sediment was collected from a 1-m diameter area and placed into a composite pre-cleaned sample container for each of the three replicate samples collected for each analysis type.

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 intertidal stations when 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 or Great Northern Air Guides, both located in Anchorage.

3.2 Analytical Methods

Tissue samples were analyzed for PAH, AHC, 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. Intertidal sediment samples were analyzed for PAH, AHC, PGS, and TOC. 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 little substantive changes to the methods.

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[7]. 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 designated for PAH/AHC/TOC analysis were thoroughly homogenized by stirring with a clean stainless steel or Teflon[7] 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-9712). 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.

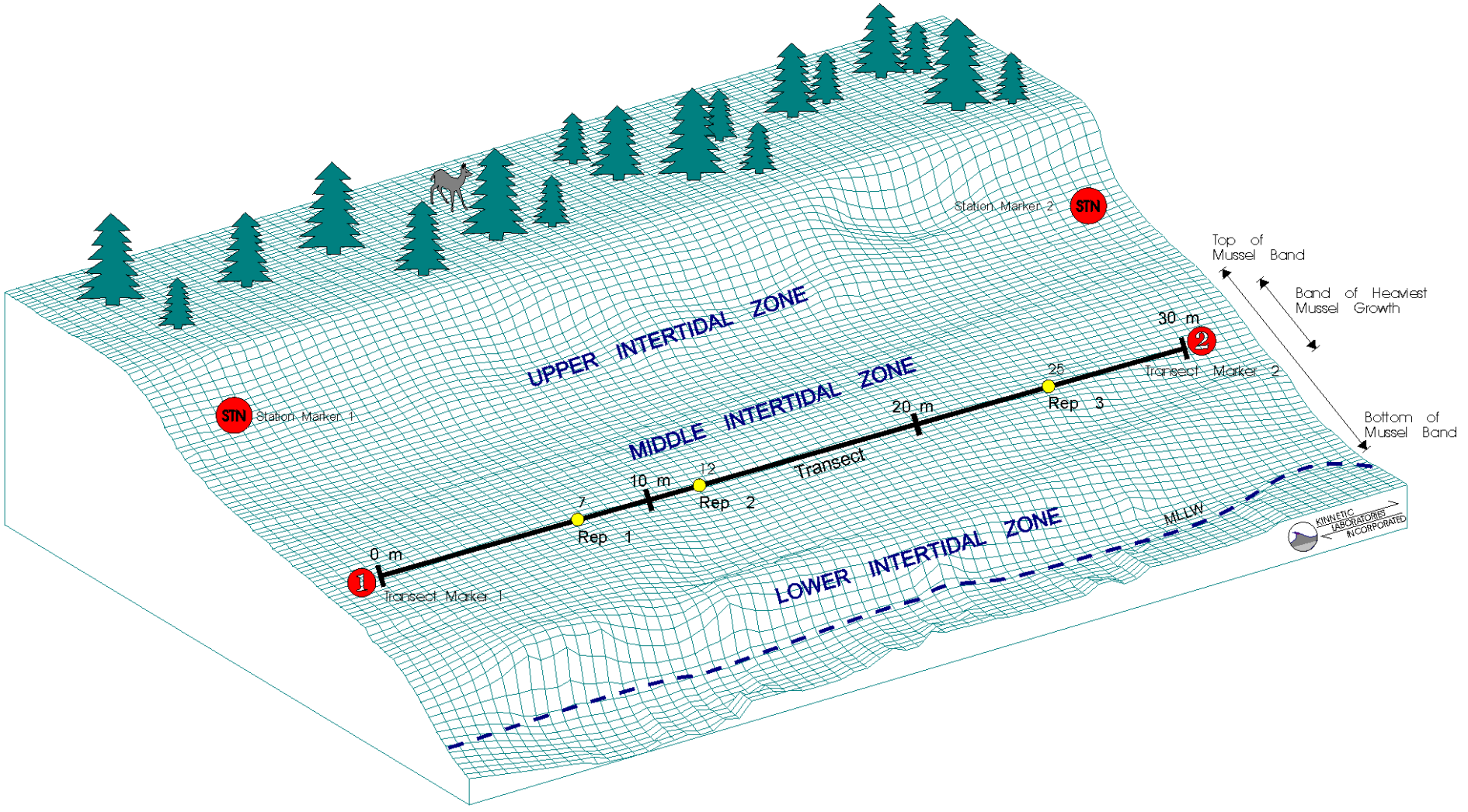

Figure 10. Diagram of LTEMP Intertidal Mussel Sampling Design with Example Replicates at 7, 12, and 25 Meters.

Table 3. List of Applicable Geochemical and Environmental Research Group Standard Operating Procedures used for the 1998 - 1999 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-9712 (replaces SOP-8902 and SOP-9419)
Extraction of tissue for hydrocarbon analysis	SOP-9807 (replaces SOP-8903)
Silica/alumina chromatography purification of tissues, AHC and PAH	SOP-9720
Gel permeation chromatography purification of tissues, PAH only	SOP-9724
Extraction of sediment for hydrocarbon analysis	SOP-8902
Alumina chromatography purification of sediments, AHC and PAH	SOP-9721
Polycyclic aromatic hydrocarbon determination	SOP-9733 (replaces SOP-8905 and SOP-9406)
Aliphatic hydrocarbon determination	SOP-8904
Weighing lipids (percent lipid determination)	SOP-9727 (replaces SOP-9231 and SOP-9414)
Particle grain size analysis	SOP-8908
Total organic carbon analysis	SOP-9730 (replaces 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.

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}. The PAH surrogate solution was added to each sample in the amount of 40 nanograms (ng) per sample for tissue and sediment matrices. The surrogate solution for AHC analysis was comprised of deuterated n-alkanes with 12, 20, 24, and 30 carbons. A total of 2 micrograms (μg) of AHC surrogate solution was added to each sample before extraction for tissue and sediment matrices.

3.2.2 Tissue Extraction Procedures

Extraction of tissue samples followed procedures outlined in GERG SOP-9807. Approximately 5 g (wet weight) of tissue was homogenized and then macerated in 100 milliliters (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 (US EPA, 1986), alumina/silica chromatography purification (GERG SOP-9720) and silica gel purification (GERG SOP-9724). The latter step was used as an additional cleanup step prior to analysis for PAH only to remove interfering lipids using high-performance liquid chromatography (HPLC) and a gel permeation column. 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 a modification of EPA Method 3611 alumina column purification (US EPA, 1986) to remove matrix interferences following GERG SOP-9721. 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 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-9733. This newer SOP is essentially identical to those used on prior LTEMP sediment samples (SOP-8905 and SOP-9406) except that the quality control requirements have been described more fully. As in GERG SOP-9406, the most recent SOP revision calls for the use of the deuterated perylene surrogate (perylene-d_{12}) only on an advisory basis. 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-9733 and summarized in the Mussel Watch procedural document (NOAA, 1993). Tissue and sediment PAH results were reported in ng/g (parts-per-billion [ppb]) dry weight.

Extracts were spiked prior to analysis with internal standard solutions comprised of fluorene-d_{10} and benzo(a)pyrene-d_{12}. An amount of 40 ng per sample was used for tissue and sediment matrices. In addition, spike standard solutions were used for matrix spike or laboratory blank spike samples, as described in Section 4.2.4. The matrix spike solution (100 ng per sample) 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 (1988) and described in Section 4.2.3. The MDLs listed in Table 5 for this reporting period were determined in Spring 1998 and 1999 for tissue and sediment PAH. 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 mathematically 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 rough measure of what portion of each sum *may* have fallen below the MDL. Individual TPAH values are not qualified with the “J” qualifier in this data set.

3.2.5 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. For this program year, the TRUAHC

Table 4. List of Target Analytes for the 1998 – 1999 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			
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	deuterated n-C_{30}		
Perylene-d_{12} (advisory only)		5			

Table 5. Method Detection Limits (Dry Weight in ng/g) Determined for the 1998 – 1999 LTEMP Hydrocarbon Analyses.

POLYCYCLIC AROMATIC HYDROCARBONS (PAH)				ALIPHATIC HYDROCARBONS (AHC)			
Analyte	Tissue July 1998	Tissue March 1999	Sediment July 1998	Analyte	Tissue July 1998	Tissue March 1999	Sediment July 1998
Naphthalene	10.9	2.6	1.6	n-C10	59.0	154.9	2.5
C1-Naphthalenes	21.5	6.0	1.6	n-C11	55.2	154.9	2.5
C2-Naphthalenes	13.6	3.4	1.3	n-C12	45.6	154.9	2.5
C3-Naphthalenes	8.2	2.9	1.6	n-C13	62.4	154.9	3.4
C4-Naphthalenes	8.2	2.9	1.6	n-C14	53.8	154.9	4.4
Biphenyl	7.5	1.3	0.5	n-C15	M 54	333.9	6.3
Acenaphthylene	4.3	0.7	0.4	n-C16	81.6	183.0	1.8
Acenaphthene	5.5	0.7	0.6	n-C17	161.3	206.7	1.4
Fluorene	5.3	2.1	0.8	Pristane	102.7	145.2	1.0
C1-Fluorenes	10.6	4.2	1.6	n-C18	59.0	56.6	10.2
C2-Fluorenes	10.6	4.2	1.6	Phytane	M 103	45.8	1.0
C3-Fluorenes	10.6	4.2	1.6	n-C19	34.6	68.1	0.6
Phenanthrene	6.8	2.3	0.4	n-C20	51.4	48.8	0.9
Anthracene	4.0	1.6	0.4	n-C21	M 51	77.3	0.9
C1-Phenanthrenes/Anthracenes	17.1	3.2	1.1	n-C22	39.4	77.3	1.2
C2-Phenanthrenes/Anthracenes	17.1	3.2	1.1	n-C23	56.6	77.3	2.1
C3-Phenanthrenes/Anthracenes	17.1	3.2	1.1	n-C24	21.1	77.3	1.5
C4-Phenanthrenes/Anthracenes	17.1	3.2	1.1	n-C25	103.2	77.3	2.3
Dibenzothiophene	6.8	1.2	0.5	n-C26	42.2	77.3	1.8
C1-Dibenzothiophenes	13.6	2.4	1.0	n-C27	104.2	77.3	3.5
C2-Dibenzothiophenes	13.6	2.4	1.0	n-C28	56.2	82.7	3.4
C3-Dibenzothiophenes	13.6	2.4	1.0	n-C29	204.5	128.2	7.4
Fluoranthene	5.6	1.9	0.5	n-C30	40.8	77.5	1.9
Pyrene	4.9	3.1	0.6	n-C31	41.0	77.5	6.5
C1-Fluoranthenes/Pyrenes	10.6	5.0	1.1	n-C32	62.9	62.1	6.1
Benzo(a)anthracene	2.3	2.4	0.3	n-C33	62.9	62.1	3.0
Chrysene	8.0	4.2	0.5	n-C34	63.0	61.0	4.0
C1-Chrysenes	16.0	8.5	1.0				
C2-Chrysenes	16.0	8.5	1.0	**Total AHC**	1872	2955	84
C3-Chrysenes	16.0	8.5	1.0				
C4-Chrysenes	16.0	8.5	1.0				
Benzo(b)fluoranthene	3.2	3.0	0.5				
Benzo(k)fluoranthene	2.2	2.6	0.2				
Benzo(e)pyrene	4.9	3.0	0.7				
Benzo(a)pyrene	4.3	2.5	1.4	M denotes matrix interference			
Perylene	12.9	1.5	3.1				
Indeno(1,2,3-c,d)pyrene	1.8	2.8	0.8				
Dibenzo(a,h)anthracene	1.4	2.2	0.7				
Benzo(g,h,i)perylene	2.3	2.0	0.6				
Total PAH (excluding perylene)	359	129	35				
1-Methylnaphthalene	12.3	2.5	0.7				
2-Methylnaphthalene	9.2	3.5	0.9				
2,6-Dimethylnaphthalene	6.8	1.7	0.6				
1,6,7-Trimethylnaphthalene	4.1	1.5	0.8				
1-Methylphenanthrene	8.5	4.6	0.5				

and TRAHC, as defined in Table 1, were also reported. Deviations from the SOP for the LTEMP included the reduction in amounts of surrogate, internal standard, and matrix spike solutions added to the 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.

Internal standard solutions consisting of deuterated n-C_{16}, (2 µg per sample) were added to each tissue and sediment extract. Matrix spiking solution consisting of alkanes from n-C_{10} to n-C_{34} and pristane were added to matrix spike and laboratory blank spike samples (10 µg per sample) for tissue and sediment 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 interference-free surrogate was used in the calculations. Data were generally reported on a dry weight basis in ng/g (ppb) for AHC and µg/g (parts-per-million [ppm]) for TRUAHC, TRAHC, and UCM. Quantitation followed standard procedures as provided in the GERG SOP-8904 and summarized in the Mussel Watch procedural document (NOAA, 1993).

Method detection limits for individual alkanes and isoprenoids (aliphatic compounds) are provided in Table 5. The MDLs were determined following procedures outlined in Section 4.2.3 during Spring 1994 and Spring 1999 for tissue AHC and Spring 1998 for sediment AHC. 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 TAHC, TRUAHC, and TRAHC values have not been qualified with the “J” in this data set.

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.

3.2.6 Percent Lipid Determination

Lipid content is defined by GERG SOP-9727 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.

3.2.7 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[7] 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.

3.2.8 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 (%) gravel, sand, silt, and clay on a dry weight basis.

3.2.9 Total Organic Carbon Analysis

Total organic carbon analysis was performed as described by GERG SOP-9730 using a 500-mg aliquot of freeze-dried sediment. This recent SOP describes quality control procedures more fully than the previously-used GERG SOP-8907. 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[7] Access[7] (Table 6). This relational database was used for all aspects of data storage, error checking, and reporting. Microsoft Excel[7] 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 laboratory QC samples
QCRESULT	analytical results on a by-sample, analysis type, and individual analyte basis, for laboratory QC samples
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 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 - 1999) has placed emphasis on the collection of more data rather than the statistical testing of those data. In addition, a separate program was performed in 1998 to evaluate the 1993 – 1997 LTEMP data and apply statistical testing (Payne et al., 1998).

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 1998 - 1999 program (Table 7). Polycyclic aromatic hydrocarbon parameters included TPAH and the fossil fuel pollution index (FFPI; Boehm and Farrington, 1984). Aliphatic hydrocarbon parameters included TAHC, TRAHC, 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. Finally, the CRUDE index (Payne et al., 1998), which incorporates both PAH and AHC parameters, has been calculated to further investigate the source of the hydrocarbons seen in the LTEMP samples.

While the summed parameters of TPAH and TAHC indicate the total level of hydrocarbon input at a site, they 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 a means of identifying the potential sources of the hydrocarbon inputs. Ratios such as the FFPI are extremely useful for determining potential sources of petroleum in sediments, but are considered 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. Nevertheless, these ratios have been calculated and reported for tissues this year because they are used in the CRUDE index calculation.

Additional parameters were analyzed so that they could be evaluated in terms of their correlation with hydrocarbon parameters, particularly important if hypothesis testing will be performed on these data. These include TOC and PGS in sediments and percent lipid in tissues. In addition, two measures of reproductive state were recorded to help evaluate the general condition and reproductive state 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 3.2.4, 3.2.5, and 4.2.3) is considered valid and useful, particularly when assessing low-level environmental contamination (US EPA, 1993). See prior program reports (e.g., 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 small replacement value (0.05 ng/g) 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 7. Hydrocarbon Parameters used in 1998 – 1999 LTEMP Data Analysis.

Parameter	Relevance
TPAH	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	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	Total AHC as defined for the LTEMP quantifies the total n-alkanes (n-C_{10} to n-C_{34}) plus pristane and phytane; represents the total resolved aliphatic hydrocarbons as determined by high resolution gas chromatography with flame ionization detection (GC/FID); includes both petrogenic and biogenic sources
TRAHC	The total resolved aliphatic hydrocarbons, which includes the historical LTEMP AHC analytes (n-C_{10} through n-C_{34} and pristane and phytane) plus other compounds such as plant waxes and lipids which are not individually identified or reported; includes both petrogenic and biogenic sources
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
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)
CRUDE Index	The CRUDE index incorporates the other indices to provide a single value which can be used as a relative indication of the probable presence of petroleum hydrocarbons (Payne et al., 1998) CRUDE = (TPAH x FFPI/100) + (TAHC/CPI^2) + UCM/1000 (where all concentrations are in the same units)

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 and the comprehensive documentation of sample collection and sample identification information.

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 samples 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.

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 to 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 8. Values that met QC criteria were not typically qualified in the data.

Table 8. 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 (1988). 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 (1993 - 1997), TPAH and 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, laboratory blank 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 9.

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 procedural blanks and matrix spike or laboratory blank 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 of reagent was run with each batch or at least once in 20 tissue and 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.

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. If insufficient sample material existed, a laboratory blank spike and laboratory blank spike duplicate were analyzed. This consisted of two laboratory blank material samples that were fortified with the spike material. The QC criteria for matrix spikes or laboratory blank 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 spike sample 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.

Table 9. 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)	T all samples and QC samples; 40 - 120 %	T all samples and QC samples; 40 - 120 %		
Procedural Blank (concentration)	T 1 in 20 samples or 1 per batch; < 3x MDL	T 1 in 20 samples or 1 per batch; < 3x MDL	T 1 in 20 samples or 1 per batch; < 3x MDL	
Matrix Spike/ Spike Duplicate or Lab Blank Spike/Spike Duplicate) (% recovery)	T 1 in 20 samples or 1 per batch; average of all compounds 40 - 120 %. See also duplicate (below)	T 1 in 20 samples or 1 per batch; average of all compounds 40 - 120 %. See also duplicate (below)		
Standard Reference Material (SRM)	T 1 in 20 samples or 1 per batch for sediment and tissue; < 30 % of the analytes should deviate more than "35 % from certified range; average values must fall within "30 of certified values %		T Reference material (LECO® pin and ring carbon standards) are used as calibration standard; values must fall within laboratory's calibration curve	
Reference Oil (concentration)	T 1 in 20 samples or 1 per batch; averages, standard deviations, and ranges are calculated to provide an estimate of precision	T 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])	T 1 in 20 samples or 1 per batch; used to assess laboratory performance	T 1 in 20 samples or 1 per batch; used to assess laboratory performance	T 1 in 20 samples or 1 per batch; "20 % for low level (<1.0 %) carbon samples and "10 % for normal/high carbon (>1.0 % carbon)	T 1 in 20 samples or 1 per batch; used for qualitative assessment of homogeneity of sediment

The SRMs used for the LTEMP were obtained from the National Institute of Standards and Technology (NIST). The SRMs analyzed for tissue PAH and AHC were NIST SRM 1974a and NIST SRM 2974, while NIST SRM 1941a was analyzed for sediment PAH, AHC, and TOC. 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. No certified or noncertified SRM values are available for AHC analyses using the GC/FID method, so while these analyses are reported, they are not used for QC purposes. For TOC, the reference material values must fall within the laboratory's calibration curve.

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 of each analytical batch by comparing results to the running average for the laboratory for all single analyte peaks. The control limits for each single component analyte is ±25 percent of the laboratory's running average. This material is also used to define the retention time windows for the alkylated PAH homologue clusters. Descriptive statistics calculated from these results included averages, standard deviations, and ranges. For the analysis of TOC, LECO[7] pin and ring carbon standards were run as reference materials and used essentially as calibration standards. For this type of quality control check, 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 if sufficient sample material existed. 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, laboratory blank 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.

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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 1998 and March 1999. 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 1998 - 1999 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.

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 consists of both a resolved and unresolved mixture of compounds, the TRAHC and the UCM, respectively. The TRAHC value, newly reported during this year of the program, gives additional sourcing information as it may provide a relative measure of biogenic contributions as compared to other sources. The presence and amount of the UCM can be an indicator of petroleum contamination, as it increases over time as petroleum is subject to biodegradation processes.

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 10. Summary of Samples Collected for the 1998 - 1999 LTEMP.

Station Location	Station Designation	Station Type	Analysis Type	Matrix	Survey 12 (7/98)	Survey 13 (3/99)
AIALIK BAY	AIB-B	Intertidal Mussel	PAH/AHC/lipids	Tissue	3	3
	AIB-B	Intertidal Mussel	Gonadal Index	Tissue	1	1
	AIB-L	Intertidal Sediment	PAH/AHC/TOC	Sediment	3	NA
	AIB-L	Intertidal Sediment	PGS	Sediment	3	NA
ALYESKA MARINE TERMINAL	AMT-B	Intertidal Mussel	PAH/AHC/lipids	Tissue	3	3
	AMT-B	Intertidal Mussel	Gonadal Index	Tissue	1	1
	AMT-L	Intertidal Sediment	PAH/AHC/TOC	Sediment	3	NA
	AMT-L	Intertidal Sediment	PGS	Sediment	3	NA
DISK ISLAND	DII-B	Intertidal Mussel	PAH/AHC/lipids	Tissue	3	3
	DII-B	Intertidal Mussel	Gonadal Index	Tissue	1	1
	DII-L	Intertidal Sediment	PAH/AHC/TOC	Sediment	3	NA
	DII-L	Intertidal Sediment	PGS	Sediment	3	NA
GOLD CREEK	GOC-B	Intertidal Mussel	PAH/AHC/lipids	Tissue	3	3
	GOC-B	Intertidal Mussel	Gonadal Index	Tissue	1	1
	GOC-L	Intertidal Sediment	PAH/AHC/TOC	Sediment	3	NA
	GOC-L	Intertidal Sediment	PGS	Sediment	3	NA
KNOWLES HEAD	KNH-B	Intertidal Mussel	PAH/AHC/lipids	Tissue	3	3
	KNH-B	Intertidal Mussel	Gonadal Index	Tissue	1	1
	KNH-L	Intertidal Sediment	PAH/AHC/TOC	Sediment	3	NA
	KNH-L	Intertidal Sediment	PGS	Sediment	3	NA
SHEEP BAY	SHB-B	Intertidal Mussel	PAH/AHC/lipids	Tissue	3	3
	SHB-B	Intertidal Mussel	Gonadal Index	Tissue	1	1
	SHB-L	Intertidal Sediment	PAH/AHC/TOC	Sediment	3	NA
	SHB-L	Intertidal Sediment	PGS	Sediment	3	NA
SHUYAK HARBOR	SHH-B	Intertidal Mussel	PAH/AHC/lipids	Tissue	3	3
	SHH-B	Intertidal Mussel	Gonadal Index	Tissue	1	1
	SHH-L	Intertidal Sediment	PAH/AHC/TOC	Sediment	3	NA
	SHH-L	Intertidal Sediment	PGS	Sediment	3	NA
SLEEPY BAY	SLB-B	Intertidal Mussel	PAH/AHC/lipids	Tissue	3	3
	SLB-B	Intertidal Mussel	Gonadal Index	Tissue	1	1
WINDY BAY	WIB-B	Intertidal Mussel	PAH/AHC/lipids	Tissue	3	3
	WIB-B	Intertidal Mussel	Gonadal Index	Tissue	1	1
	WIB-L	Intertidal Sediment	PAH/AHC/TOC	Sediment	3	NA
	WIB-L	Intertidal Sediment	PGS	Sediment	3	NA

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 as well as coal deposits. Potential sources of petrogenic PAH in the LTEMP study area include: Alaska North Slope (ANS) crude including EVOS oil residues; coal residue from natural coal deposits in the area; crude from Cook Inlet or other areas; Katalla, Yakataga, and other eastern Gulf of Alaska seep oil; oil products 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.

Earlier studies in PWS indicated that petroleum originating from natural seeps in the Gulf of Alaska contributed to the natural hydrocarbons (or "background hydrocarbons") in the study area (Page et al., 1995). Prior LTEMP reports also ascribed the background signature seen in some samples to these petroleum seep sources. The source of this background signature is currently the subject of controversy. Recent work has indicated that natural coal deposits rather than oil seeps may be the predominant source of petrogenic hydrocarbons in the study area (Short et al., 1999). An important distinction between these two potential sources is that coal residues are much less biologically available than those seen in petroleum. The researchers found that the PAH fingerprints were similar, but biomarker analyses revealed differences between the coal and petroleum seep sources. Work performed for the Minerals Management Service in Cook Inlet and Shelikof Strait indicated that while coal signatures exist in sediments from some areas of Cook Inlet, seep oil is responsible for the predominant background signature (Arthur D. Little, 1998).

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 bio-availability, 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) increased in tissue to a level state in about 20 days when the animals were exposed to contaminated resuspended sediments (Pruell et al., 1987).

Aliphatic hydrocarbon concentrations in tissues have been determined during the 1998 – 1999 program year after a four-year hiatus. A review of the LTEMP sampling and analytical program and evaluation of program data collected from 1993 – 1997 was performed in 1998 by J.R. Payne Environmental under a separate contract to PWS RCAC. One recommendation of this review was to re-institute the analysis of AHC in tissues (Payne et al., 1998). The report called for this analysis because AHC are much more abundant than PAH in crude oils and refined products. The authors believed that, since AHC are such a predominant part of crude oil, elevated levels would be easily seen in tissues in the event of a spill. Although this point is well taken, naturally-occurring compounds in the tissues themselves mimic the target analytes in terms of the chromatographic analysis and cause a matrix interference. The tissue AHC analyses had been omitted from the LTEMP after the first two years because the 1993 – 1994 data had indicated that matrix interferences were confounding interpretation. In addition, earlier LTEMP data indicated that the AHC fingerprints showed large seasonal variability that could be due to the reproductive state or seasonal feeding regime of the mussels, and the AHC concentrations in tissues did not correlate well with those seen in the corresponding sediments.

Nevertheless, AHC analyses were performed this year in mussel tissues, and results are reported below. In addition to the parameters historically reported for AHC, the TRAHC value has been included as recommended by the Payne report. This value is intended to offer further sourcing information as it provides an estimate of the resolvable aliphatic fraction that includes alkanes, pristane, phytane, biomarkers, and other compounds such as waxes and lipids. While these data have been reported along with the corresponding values of CPI ratio and UCM, interpretation in this report relies more closely on PAH data than AHC data for tissue body burden results.

5.2.1 Polycyclic Aromatic Hydrocarbons

Overall, tissue concentrations of PAH compounds were quite low at most stations during the 1998 - 1999 LTEMP. Concentrations of TPAH in each replicate were below the cumulative MDL at each station for July 1998 (359 ppb) and typically below the cumulative MDL in March 1999 (129 ppb; Table 11). As in the past, many individual PAH analytes were found to be at very low (below MDL) but still detectable concentrations (Appendix A). Nearly all of the individual analytes were below individual MDLs during July 1998. While March 1999 data showed relatively more individual analytes at above-MDL levels, unsurprising due to the lowered MDLs for this sample set, the majority of analytes were still reported at levels below the MDLs.

In the March 1999 (Survey 13) tissue samples, results reported for C_2-chrysene were problematic. While these values were mostly still below the MDL, they were clearly elevated and were identified with the "M" qualifier in the data to indicate a matrix interference. Unfortunately, investigation in the laboratory showed no clear justification for the elevation of this one analyte, and quality control samples performed with both sample batches for this survey were within normal limits for this analyte. This analyte was excluded from the TPAH calculations and the PAH fingerprint figures for this survey due to the matrix interference. It was also excluded from the FFPI and CRUDE index calculations.

Mean TPAH concentrations at many stations varied both within and between surveys (Tables 11 and 12; Figure 11). However, good agreement between replicates was shown at a number of stations, particularly during July 1998. Slightly higher within-station variability was seen during March 1999. The apparent increasing trend in tissue PAH that had been seen over the last several years of LTEMP was not apparent this year. In fact, a review of the historical data shows that many of the TPAH values have dropped to relatively low levels as compared to the overall station mean as depicted in Figure 11 and provided in Table 12.

The PAH concentrations at Station AIB had increased substantially during the prior three surveys of LTEMP (March 1997 - March 1998). The exact source of this contamination was unknown, but it was thought that it was likely to be diesel or gasoline (KLI, 1998). The mean TPAH levels at Station AIB, of particular concern because this station is considered a reference site, have now dropped to below the historical median of 126.0 ppb. Mean TPAH values

Table 11. LTEMP Tissue TPAH, FFPI, CRUDE Index, and Lipid Results for July 1998 and March 1999.

Station	TPAH (ng/g or ppb)							
	Survey 12 (July 1998)				Survey 13 (March 1999)			
	Rep. 1	Rep. 2	Rep. 3	Mean	Rep. 1	Rep. 2	Rep. 3	Mean
AIB-B	81.1	87.1	79.3	82.5	107.4	70.0	104.1	93.8
AMT-B	215.3	161.1	141.8	172.7	567.3	593.6	501.7	554.2
DII-B	50.7	63.6	52.2	55.5	63.7	120.4	139.8	108.0
GOC-B	138.4	157.2	171.4	155.7	276.0	266.6	216.2	252.9
KNH-B	92.4	102.5	120.2	105.0	145.7	152.2	87.7	128.5
SHB-B	61.7	91.5	93.4	82.2	186.7	89.9	117.1	131.2
SHH-B	92.1	78.2	102.1	90.8	249.9	128.2	109.6	162.6
SLB-B	181.9	79.2	127.0	129.4	103.8	123.2	126.0	117.7
WIB-B	74.1	59.0	76.4	69.8	92.7	67.7	104.8	88.4
Station	**FFPI (ratio)**							
	Survey 12 (July 1998)				Survey 13 (March 1999)			
	Rep. 1	Rep. 2	Rep. 3	Mean	Rep. 1	Rep. 2	Rep. 3	Mean
AIB-B	54.1	53.3	54.8	54.1	83.4	78.7	73.3	78.5
AMT-B	69.8	70.8	69.2	69.9	87.1	86.6	87.9	87.2
DII-B	64.5	69.6	69.1	67.7	66.9	78.4	82.4	75.9
GOC-B	71.5	66.6	73.7	70.6	68.9	73.8	72.4	71.7
KNH-B	66.1	67.3	70.8	68.1	77.6	80.9	77.9	78.8
SHB-B	71.0	65.0	67.3	67.8	85.1	80.4	84.4	83.3
SHH-B	64.4	63.2	66.3	64.7	79.7	84.5	84.5	82.9
SLB-B	53.8	70.2	70.8	64.9	73.7	73.6	71.3	72.9
WIB-B	66.0	64.9	61.4	64.1	81.2	81.7	84.9	82.6
Station	**CRUDE Index (ratio)**							
	Survey 12 (July 1998)				Survey 13 (March 1999)			
	Rep. 1	Rep. 2	Rep. 3	Mean	Rep. 1	Rep. 2	Rep. 3	Mean
AIB-B	7656.9	14214.1	3631.1	8500.7	2689.3	1024.4	3124.5	2279.4
AMT-B	8839.9	3738.9	4171.4	5583.4	15173.1	28981.0	30398.1	24850.7
DII-B	4789.2	6510.5	6362.0	5887.2	3814.6	26767.3	6587.4	12389.8
GOC-B	13759.5	22187.9	14912.8	16953.4	5459.2	13472.2	25189.6	14707.0
KNH-B	9697.5	15670.4	7340.4	10902.8	65806.7	31625.2	49543.5	48991.8
SHB-B	17261.4	19827.8	2479.5	13189.6	11367.8	23093.6	6980.8	13814.1
SHH-B	3324.9	6779.8	24962.3	11689.0	4115.2	5800.4	30248.3	13388.0
SLB-B	9917.3	9689.8	17157.2	12254.7	26377.9	9478.4	15812.7	17223.0
WIB-B	11146.4	6414.3	7830.5	8463.7	3006.8	2399.7	2799.5	2735.3
Station	**Lipids (%)**							
	Survey 12 (July 1998)				Survey 13 (March 1999)			
	Rep. 1	Rep. 2	Rep. 3	Mean	Rep. 1	Rep. 2	Rep. 3	Mean
AIB-B	6.0	2.5	5.9	4.8	7.7	4.7	8.7	7.0
AMT-B	1.4	3.5	4.6	3.2	15.5	7.9	16.9	13.4
DII-B	4.7	4.8	4.9	4.8	8.0	7.8	15.5	10.4
GOC-B	7.4	10.2	4.0	7.2	17.8	9.0	7.1	11.3
KNH-B	5.3	6.7	6.1	6.0	14.3	14.7	8.2	12.4
SHB-B	3.5	2.5	3.7	3.2	12.5	25.0	11.6	16.4
SHH-B	5.5	4.3	4.5	4.8	8.9	11.4	9.4	9.9
SLB-B	5.1	3.1	5.0	4.4	10.1	7.9	7.4	8.5
WIB-B	6.5	4.8	4.5	5.3	7.2	7.5	7.2	7.3

Table 12. Mean LTEMP Tissue Hydrocarbon Results by Station and Survey - 1993 through 1999.

Station (Survey)	TPAH (ng/g)	TAHC (ng/g)	TRAHC (µg/g)	UCM (µg/g)	Lipids (%)
AIB-B (3/93)	70.9	13008	NA	69.9	6.2
AIB-B (7/93)	104.5	33013	NA	0.8	5.9
AIB-B (3/94)	193.6	33529	NA	828.0	3.7
AIB-B (7/94)	126.0	17375	NA	18.6	8.4
AIB-B (3/95)	55.6	NA	NA	NA	4.7
AIB-B (7/95)	54.8	NA	NA	NA	7.0
AIB-B (3/96)	91.6	NA	NA	NA	4.2
AIB-B (7/96)	151.4	NA	NA	NA	10.7
AIB-B (3/97)	292.1	NA	NA	NA	4.7
AIB-B (7/97)	590.1	NA	NA	NA	6.0
AIB-B (3/98)	1012.1	NA	NA	NA	3.0
AIB-B (7/98)	82.5	11459	237.5	38.6	4.8
AIB-B (3/99)	93.8	4237	10.0	9.6	7.0
AMT-B (3/93)	325.0	24054	NA	297.6	7.6
AMT-B (7/93)	248.2	21144	NA	48.0	6.4
AMT-B (3/94)	797.3	20764	NA	964.0	3.8
AMT-B (ELS)	14351.2	131300	NA	1035.0	8.9
AMT-B (7/94)	1580.7	18013	NA	488.7	10.7
AMT-B (3/95)	517.1	NA	NA	NA	2.1
AMT-B (7/95)	87.3	NA	NA	NA	6.6
AMT-B (3/96)	241.6	NA	NA	NA	1.4
AMT-B (7/96)	229.2	NA	NA	NA	6.1
AMT-B (BWTP)	578.3	NA	NA	NA	4.7
AMT-B (3/97)	582.2	NA	NA	NA	3.8
AMT-B (7/97)	540.6	NA	NA	NA	7.6
AMT-B (3/98)	530.4	NA	NA	NA	2.4
AMT-B (7/98)	172.7	15008	396.6	56.9	3.2
AMT-B (3/99)	554.2	27862	183.6	838.8	13.4
DII-B (3/93)	107.0	18916	NA	326.8	4.5
DII-B (7/93)	92.1	33589	NA	18.1	6.8
DII-B (3/94)	290.4	26011	NA	151.7	6.5*
DII-B (7/94)	812.7	10066	NA	49.9	6.1
DII-B (3/95)	248.8	NA	NA	NA	3.1
DII-B (7/95)	113.3	NA	NA	NA	3.7
DII-B (3/96)	116.6	NA	NA	NA	0.8
DII-B (7/96)	120.3	NA	NA	NA	3.3
DII-B (3/97)	349.9	NA	NA	NA	3.0
DII-B (7/97)	291.4	NA	NA	NA	4.0
DII-B (3/98)	686.9	NA	NA	NA	2.3
DII-B (7/98)	55.5	12509	177.8	16.6	4.8
DII-B (3/99)	108.0	19691	155.7	312.3	10.4

Table 12. Mean LTEMP Tissue Hydrocarbon Results by Station and Survey - 1993 through 1999. (Continued)

Station (Survey)	TPAH (ng/g)	TAHC (ng/g)	TRAHC (µg/g)	UCM (µg/g)	Lipids (%)
GOC-B (3/93)	617.6	32585	NA	390.0	6.0
GOC-B (7/93)	127.1	10681	NA	2.8	7.0
GOC-B (3/94)	549.0	26338	NA	1023.8	4.1
GOC-B (7/94)	778.5	10875	NA	90.2	12.1
GOC-B (3/95)	644.5	NA	NA	NA	3.7
GOC-B (7/95)	77.5	NA	NA	NA	8.0
GOC-B (3/96)	151.0	NA	NA	NA	1.5
GOC-B (7/96)	132.7	NA	NA	NA	6.3
GOC-B (3/97)	391.2	NA	NA	NA	3.3
GOC-B (7/97)	423.8	NA	NA	NA	6.5
GOC-B (3/98)	472.2	NA	NA	NA	2.6
GOC-B (7/98)	155.7	27539	629.0	80.8	7.2
GOC-B (3/99)	252.9	18979	153.9	483.7	11.3
KNH-B (3/93)	72.4	47773	NA	141.0	4.4
KNH-B (7/93)	106.4	34056	NA	2.9	6.7
KNH-B (3/94)	411.1	37436	NA	255.2	4.9
KNH-B (7/94)	375.7	26759	NA	21.7	7.3
KNH-B (3/95)	137.5	NA	NA	NA	4.5
KNH-B (7/95)	100.9	NA	NA	NA	8.7
KNH-B (3/96)	144.8	NA	NA	NA	3.5
KNH-B (7/96)	365.2	NA	NA	NA	7.9
KNH-B (3/97)	472.8	NA	NA	NA	2.8
KNH-B (7/97)	832.7	NA	NA	NA	4.6
KNH-B (3/98)	844.1	NA	NA	NA	5.3
KNH-B (7/98)	105.0	23629	318.0	17.4	6.0
KNH-B (3/99)	128.5	32940	218.4	518.2	12.4
SHB-B (3/93)	44.1	16030	NA	217.3	5.0
SHB-B (7/93)	293.1	43433	NA	6.1	5.7
SHB-B (3/94)	96.9	23329	NA	49.0	6.4
SHB-B (7/94)	203.6	18158	NA	4.0	7.9
SHB-B (3/95)	66.2	NA	NA	NA	4.0
SHB-B (7/95)	77.6	NA	NA	NA	6.8
SHB-B (3/96)	111.2	NA	NA	NA	2.5
SHB-B (7/96)	320.6	NA	NA	NA	7.7
SHB-B (3/97)	390.7	NA	NA	NA	3.9
SHB-B (7/97)	988.9	NA	NA	NA	4.6
SHB-B (3/98)	306.1	NA	NA	NA	3.7
SHB-B (7/98)	82.2	25061	246.4	19.6	3.2
SHB-B (3/99)	131.2	12822	77.4	170.2	16.4

Table 12. Mean LTEMP Tissue Hydrocarbon Results by Station and Survey - 1993 through 1999. (Continued)

Station (Survey)	TPAH (ng/g)	TAHC (ng/g)	TRAHC (µg/g)	UCM (µg/g)	Lipids (%)
SHH-B (7/93)	58.0	23226	NA	11.4	7.3
SHH-B (3/94)	83.3	26386	NA	487.1	5.4
SHH-B (7/94)	67.5	18882	NA	8.8	9.5
SHH-B (3/95)	58.9	NA	NA	NA	7.3
SHH-B (7/95)	55.7	NA	NA	NA	6.0
SHH-B (3/96)	100.0	NA	NA	NA	3.2
SHH-B (7/96)	341.0	NA	NA	NA	9.0
SHH-B (3/97)	319.1	NA	NA	NA	1.7
SHH-B (7/97)	595.4	NA	NA	NA	3.9
SHH-B (3/98)	460.1	NA	NA	NA	3.9
SHH-B (7/98)	90.8	12201	297.5	49.5	4.8
SHH-B (3/99)	162.6	17583	23.2	2.2	9.9
SLB-B (3/93)	358.4	27757	NA	266.8	4.8
SLB-B (7/93)	91.6	34659	NA	19.2	6.7
SLB-B (3/94)	2209.3	44978	NA	1276.5	5.7*
SLB-B (7/94)	385.8	12862	NA	36.6	8.1
SLB-B (3/95)	623.5	NA	NA	NA	4.5
SLB-B (7/95)	162.3	NA	NA	NA	8.2
SLB-B (3/96)	129.8	NA	NA	NA	2.3
SLB-B (7/96)	124.7	NA	NA	NA	4.6
SLB-B (3/97)	298.8	NA	NA	NA	2.4
SLB-B (7/97)	795.1	NA	NA	NA	4.9
SLB-B (3/98)	509.7	NA	NA	NA	2.8
SLB-B (7/98)	129.4	18577	194.3	14.6	4.4
SLB-B (3/99)	117.7	15969	168.2	341.7	8.5
WIB-B (3/93)	64.6	37216	NA	152.8	5.1
WIB-B (7/93)	84.4	27376	NA	14.2	8.2
WIB-B (3/94)	125.6	22329	NA	521.1	6.3
WIB-B (7/94)	86.3	23124	NA	35.4	7.7
WIB-B (3/95)	62.0	NA	NA	NA	8.4
WIB-B (7/95)	52.8	NA	NA	NA	6.1
WIB-B (3/96)	112.0	NA	NA	NA	2.9
WIB-B (7/96)	148.7	NA	NA	NA	6.9
WIB-B (3/97)	559.3	NA	NA	NA	2.7
WIB-B (7/97)	343.8	NA	NA	NA	4.3
WIB-B (3/98)	482.6	NA	NA	NA	2.7
WIB-B (7/98)	69.8	7698	175.5	40.6	5.3
WIB-B (3/99)	88.4	4696	12.6	2.7	7.3

NA Not Analyzed

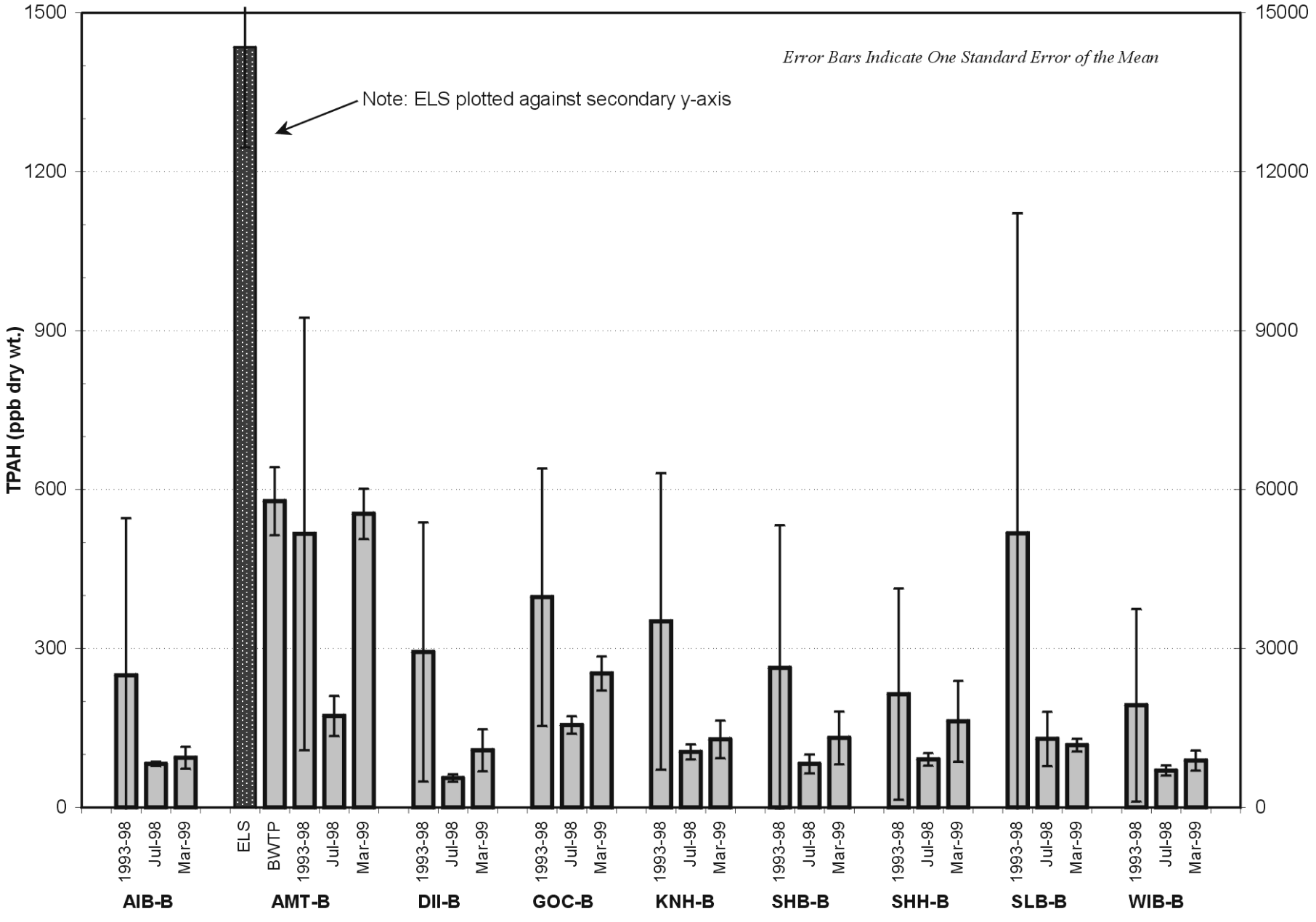

Figure 11. Mean LTEMP Tissue TPAH by Station and Survey - Historical, July 1998, and March 1999.

reported for this station were 82.5 and 93.8 ppb for the two surveys, as compared with the station mean of 1012.1 ppb in March 1998. Although the current PAH levels are very low, the fingerprints indicate a combination of background and pyrogenic sources. Pyrogenic inputs were more apparent during the July 1998 survey.

The PAH values reported for Station AMT were well within the range of values from earlier sampling events. The mean TPAH for July 1998 was quite low (172.7 ppb) compared to past results, while that seen during March 1999 (554.2 ppb) was in line with those seen during the prior three surveys (530.4 - 582.2 ppb; Tables 11 and 12, Figure 11). The PAH fingerprint for March 1999 at Station AMT is presented in Figure 12. The PAH signature at AMT for March 1999 was consistent with ANS crude as the source. The ratio of alkyl dibenzothiophenes to alkyl phenanthrenes was slightly greater 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. Also, the 5- and 6-ring PAH that are indicative of pyrogenic sources were almost absent in March 1999. The July 1998 fingerprint (not depicted) was more consistent with background sources and pyrogenic inputs. The PAH values during this survey were relatively low; in fact, the mean TPAH exhibited in July 1998 was one of the two lowest seen during the 15 sampling events reported to date at this site. These July 1998 concentrations may possibly reflect normal ("non-contaminated") levels in these mussels (i.e., with no petroleum inputs from operations at the Alyeska Marine Terminal), which is why the background fingerprint is apparent.

The mean tissue TPAH concentration of 55.5 ppb seen at Station DII during July 1998 was the lowest value reported to date at this station. The mean of 108.0 ppb reported for March 1999 was more typical, but still considerably lower than the values that had been seen in March and July 1997 and March 1998, which ranged from 291.4 to 686.9 ppb. The sources of the very low concentrations of PAH were likely to be a combination of EVOS/ANS, background, and pyrogenic compounds.

Mean TPAH values seen at Station GOC were 155.7 and 252.9 ppb for July 1998 and March 1999, respectively, fairly low compared to many of the historical values from this station. As depicted in Figure 12, the PAH fingerprint at Station GOC during the March 1999 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 for March 1999. These results are similar to that seen during many of the prior surveys.

Levels of PAH in mussel tissue from Station KNH collected during the 1998 - 1999 LTEMP were 105.0 and 128.5 ppb, considerably lower than the elevated levels seen during the prior two surveys (>833 ppb). Although not depicted, the fingerprints from these samples are similar to that seen in the past and exhibit patterns that are consistent with natural background for PWS.

The mean TPAH levels seen at Station SHB were within the historical range of the data at 82.2 and 131.2 ppb for the two surveys. The ratio of the phenanthrenes to dibenzothiophenes indicated a source other than ANS crude for this station. The fingerprint of the March 1999 SHB tissue samples indicated a large predominance of lower-end PAH such as naphthalenes and fluorenes (Figure 12). This type of signature would normally be indicative of a fairly fresh source of hydrocarbons, however, the natural background signature of coal has also been shown to have relatively high levels of naphthalenes and fluorenes (Short et al., 1999).

Station SHH showed mean TPAH values of 90.8 ppb (July 1998) and 162.6 ppb (March 1999), again considerably lower than that seen during the prior three surveys, which ranged from 319.1 to 595.4 ppb. The fingerprint at this station is similar to that seen at Stations KNH and SHB, indicating natural background hydrocarbon contributions.

Mean TPAH levels seen in tissues during 1998 - 1999 at Station SLB were 129.4 and 117.7 ppb. In contrast to the fingerprint from March 1998 (KLI, 1998), the fingerprint for July 1998 failed to show clear characteristics of weathered petroleum and an ANS crude source (Figure 12). The March 1999 fingerprint also indicated evidence of background inputs as well as pyrogenic hydrocarbons.

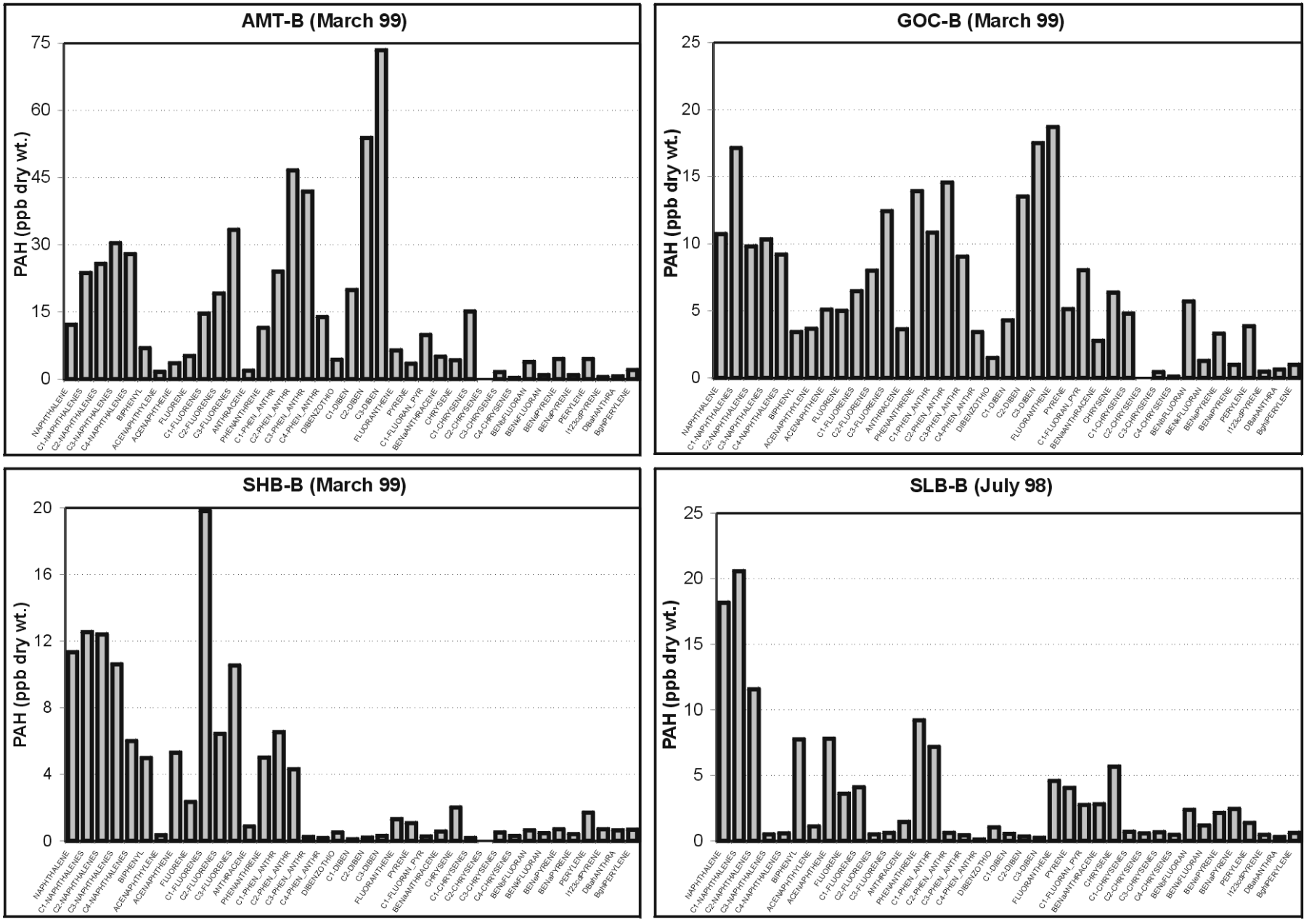

Figure 12. Mean LTEMP Tissue PAH Fingerprints - July 1998 and March 1999 Surveys, Stations AMT-B, GOC-B, SHB-B, and SLB-B.

Station WIB also showed considerably less PAH during this program year than during the prior three surveys. Mean TPAH was reported at 69.8 and 88.4 ppb for July 1998 and March 1999, respectively, as compared to values ranging from 343.8 to 559.3 3 ppb. The March 1999 fingerprint clearly exhibits the background signature, while the July 1998 fingerprint shows more evidence of pyrogenic inputs.

In addition to the petrogenic PAH seen at many of the 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 some locations. This pyrogenic material may come from combustion products (i.e., exhaust) or possibly creosote at some locations.

In contrast to some past surveys, the laboratory procedural artifact pattern was not apparent in this data set. This artifact occurs when values greater than zero were reported for each analyte that had a laboratory calibration standard. It 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. This was not apparent in this year's data because very few analytes were reported at the non-detect level.

In general, low (below MDL) PAH hydrocarbon body burdens were seen in resident mussel populations at most locations during the July 1998 and March 1999 surveys. Since most of the measured concentrations were qualified as estimates ("J"), care needs to be taken in drawing any conclusions from the data.

The calculated FFPI ratios for tissues are also provided in Table 11. It should be remembered that these calculations are based on very low PAH concentrations, with most analytes at estimated levels below the MDLs. In addition, the use of ratios such as these for tissue burden data is less valuable than for sediment data due to preferential uptake, depuration, and other biological factors discussed above. Mean FFPI ratios ranged from 54.1 at Station AIB during July 1998 to 87.2 at Station AMT during March 1999. As expected, many of the lowest FFPI ratios were seen at stations where the fingerprints exhibited a fairly clear indication of pyrogenic contributions (e.g., Stations AIB and WIB during July 1998). Higher mean FFPI values were seen during March 1999 than July 1998 at all stations. The highest value was seen at Station AMT during March 1999 (87.2), closely followed by Stations SHB, SHH, and WIB, all at approximately 83 (also during March 1999). While the fingerprints at Station AMT were indicative of ANS crude, those from Stations SHB, SHH, and WIB were ascribed to natural background sources.

5.2.2 Aliphatic Hydrocarbons

As expected, tissue concentrations of AHC were considerably higher than PAH levels (Tables 12 and 13; Figure 13). All of the sample results were well above the cumulative MDL values for this parameter (1872 ppb for July 1998 and 2955 for March 1999). Most of the individual AHC concentrations were reported at above MDL levels in the July 1998 data. Although more values fell below MDLs in the March 1999 data (due to increased MDLs for this survey), the majority of analytes were recorded at levels above the MDL for this survey.

Mean TAHC values ranged from approximately 7,698 ppb at Station WIB to 27,539 ppb at Station GOC for July 1998 and from 4,237 ppb at Station AIB to 32,940 ppb at Station KNH in March 1999. Stations AIB and WIB exhibited the lowest mean TAHC values across all stations and both surveys. Values reported for these two stations were considerably lower than those reported historically for 1993 – 1994 (Table 12). Some of the highest concentrations were seen at Station KNH, particularly for March 1999, which agrees with the historical data for this station.

Fingerprints for selected stations are depicted in Figure 14. Most of the stations exhibited similar fingerprints within season, although there was more variability seen in the July 1998 survey than the March 1999 survey. For example, Station AMT for July 1998 compared well with the mean fingerprint for this survey; this station was selected for visual comparison because it was expected to show a different signature, but it was essentially the same. The Station DII (March 1999) fingerprint mirrors the pattern for the mean fingerprint for this survey. The apparent differences between seasons was exhibited in the 1993 – 1994 data as well and was potentially due to spawning: it was thought that the release of lipid-rich gametes caused the fingerprint to shift from predominantly higher-end AHC in March to a more uniform distribution in July, as seen in Figure 14. Dietary influences may also contribute to this shift, since mussel feeding habits change throughout the year based on the seasonal availability of the plankton population.

Table 13. LTEMP Tissue TAHC, TRAHC, UCM, and CPI Results for July 1998 and March 1999.

Station	TAHC (ng/g or ppb)							
	Survey 12 (July 1998)				Survey 13 (March 1999)			
	Rep. 1	Rep. 2	Rep. 3	Mean	Rep. 1	Rep. 2	Rep. 3	Mean
AIB-B	9155.1	16639.1	8583.8	11459.3	4561.4	2452.7	5696.7	4236.9
AMT-B	15432.0	13279.0	16314.3	15008.4	26121.4	29033.1	28430.7	27861.7
DII-B	12544.1	13491.3	11492.0	12509.1	10211.7	39755.5	9106.9	19691.4
GOC-B	23892.3	38743.6	19982.5	27539.5	12413.6	12776.2	31746.7	18978.8
KNH-B	21631.9	26925.0	22330.4	23629.1	43754.9	24747.3	30318.4	32940.2
SHB-B	18541.5	32334.1	24306.3	25060.6	13418.0	13740.0	11307.1	12821.7
SHH-B	8787.5	7977.7	19838.1	12201.1	4863.7	7276.6	40608.7	17583.0
SLB-B	15565.7	17896.0	22270.5	18577.4	19208.9	8779.8	19917.1	15968.6
WIB-B	8971.3	5750.8	8373.3	7698.5	4116.2	4256.3	5715.1	4695.9
Station	TRAHC (µg/g or ppm)							
	Survey 12 (July 1998)				Survey 13 (March 1999)			
	Rep. 1	Rep. 2	Rep. 3	Mean	Rep. 1	Rep. 2	Rep. 3	Mean
AIB-B	205.2	344.0	163.4	237.5	10.1	7.9	12.1	10.0
AMT-B	383.6	386.1	420.1	396.6	170.8	179.2	200.7	183.6
DII-B	151.0	174.2	208.2	177.8	132.8	194.3	140.1	155.7
GOC-B	470.2	847.7	569.2	629.0	124.3	148.6	188.7	153.9
KNH-B	269.1	313.9	371.1	318.0	267.6	235.5	152.1	218.4
SHB-B	226.0	244.8	268.3	246.4	23.4	151.0	57.8	77.4
SHH-B	231.9	220.7	440.0	297.5	7.0	13.1	49.4	23.2
SLB-B	176.6	158.0	248.2	194.3	188.2	101.7	214.7	168.2
WIB-B	214.7	90.3	221.5	175.5	8.4	7.4	22.1	12.6
Station	UCM (µg/g or ppm)							
	Survey 12 (July 1998)				Survey 13 (March 1999)			
	Rep. 1	Rep. 2	Rep. 3	Mean	Rep. 1	Rep. 2	Rep. 3	Mean
AIB-B	39.3	60.5	16.1	38.6	10.1	5.7	13.0	9.6
AMT-B	48.7	50.0	72.0	56.9	936.1	665.5	914.7	838.8
DII-B	6.7	24.2	19.0	16.6	306.4	357.2	273.2	312.3
GOC-B	52.7	104.7	85.0	80.8	397.4	501.9	551.9	483.7
KNH-B	14.6	12.9	24.8	17.4	693.4	474.4	386.7	518.2
SHB-B	24.7	16.9	17.2	19.6	147.6	221.6	141.4	170.2
SHH-B	34.0	29.1	85.5	49.5	3.4	2.4	0.9	2.2
SLB-B	13.3	14.9	15.6	14.6	314.5	210.8	499.8	341.7
WIB-B	39.4	41.4	41.1	40.6	4.9	2.6	0.5	2.7
Station	CPI (ratio)							
	Survey 12 (July 1998)				Survey 13 (March 1999)			
	Rep. 1	Rep. 2	Rep. 3	Mean	Rep. 1	Rep. 2	Rep. 3	Mean
AIB-B	1.1	1.1	1.6	1.2	1.3	1.6	1.4	1.4
AMT-B	1.3	1.9	2.0	1.8	1.4	1.0	1.0	1.1
DII-B	1.6	1.4	1.3	1.5	1.7	1.2	1.2	1.4
GOC-B	1.3	1.3	1.2	1.3	1.6	1.0	1.1	1.2
KNH-B	1.5	1.3	1.8	1.5	0.8	0.9	0.8	0.8
SHB-B	1.0	1.3	3.2	1.8	1.1	0.8	1.3	1.1
SHH-B	1.6	1.1	0.9	1.2	1.1	1.1	1.2	1.1
SLB-B	1.3	1.4	1.1	1.3	0.9	1.0	1.1	1.0
WIB-B	0.9	1.0	1.0	1.0	1.2	1.3	1.5	1.3

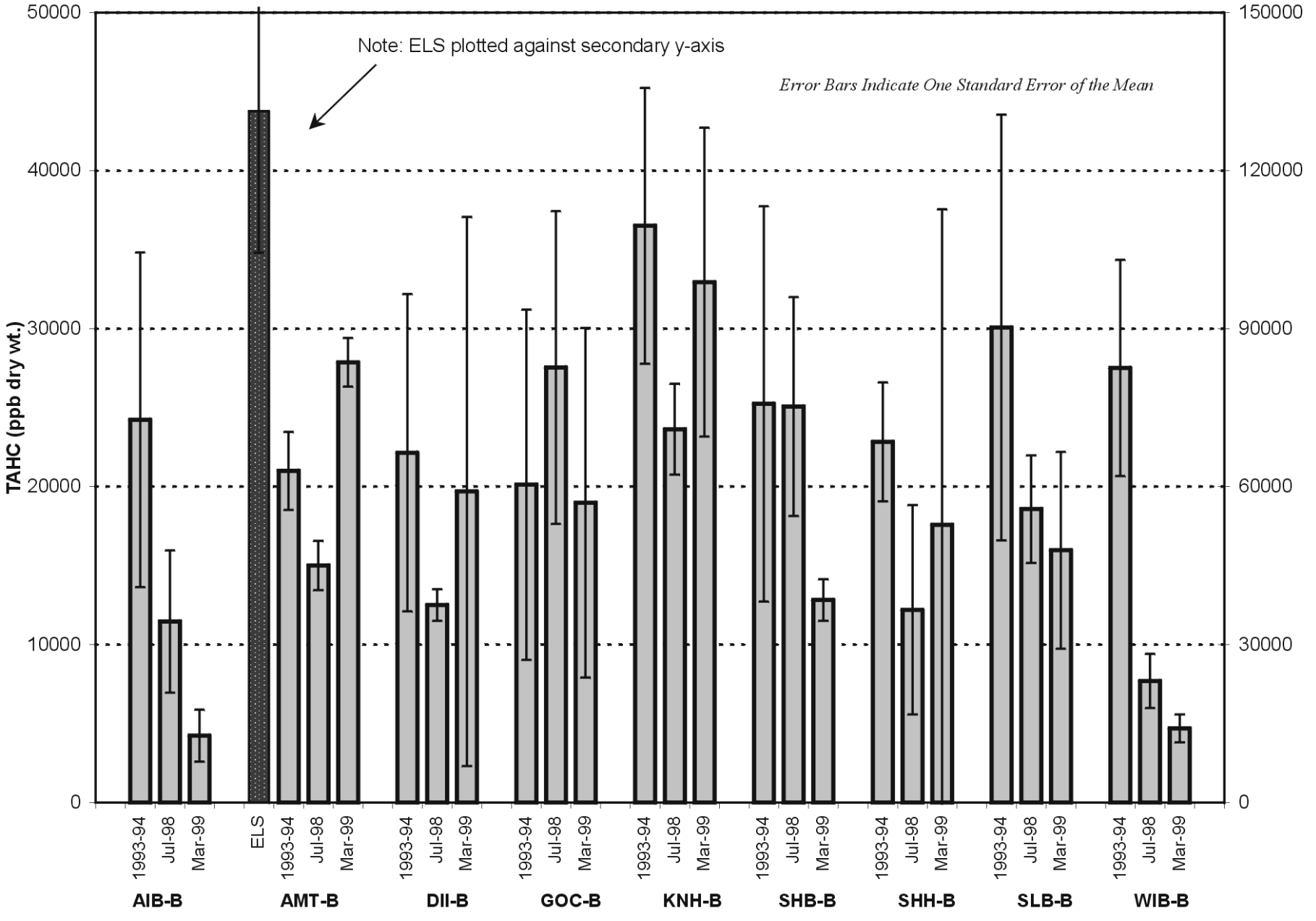

Figure 13. Mean LTEMP Tissue TAHC by Station and Survey - Historical, July 1998, and March 1999.

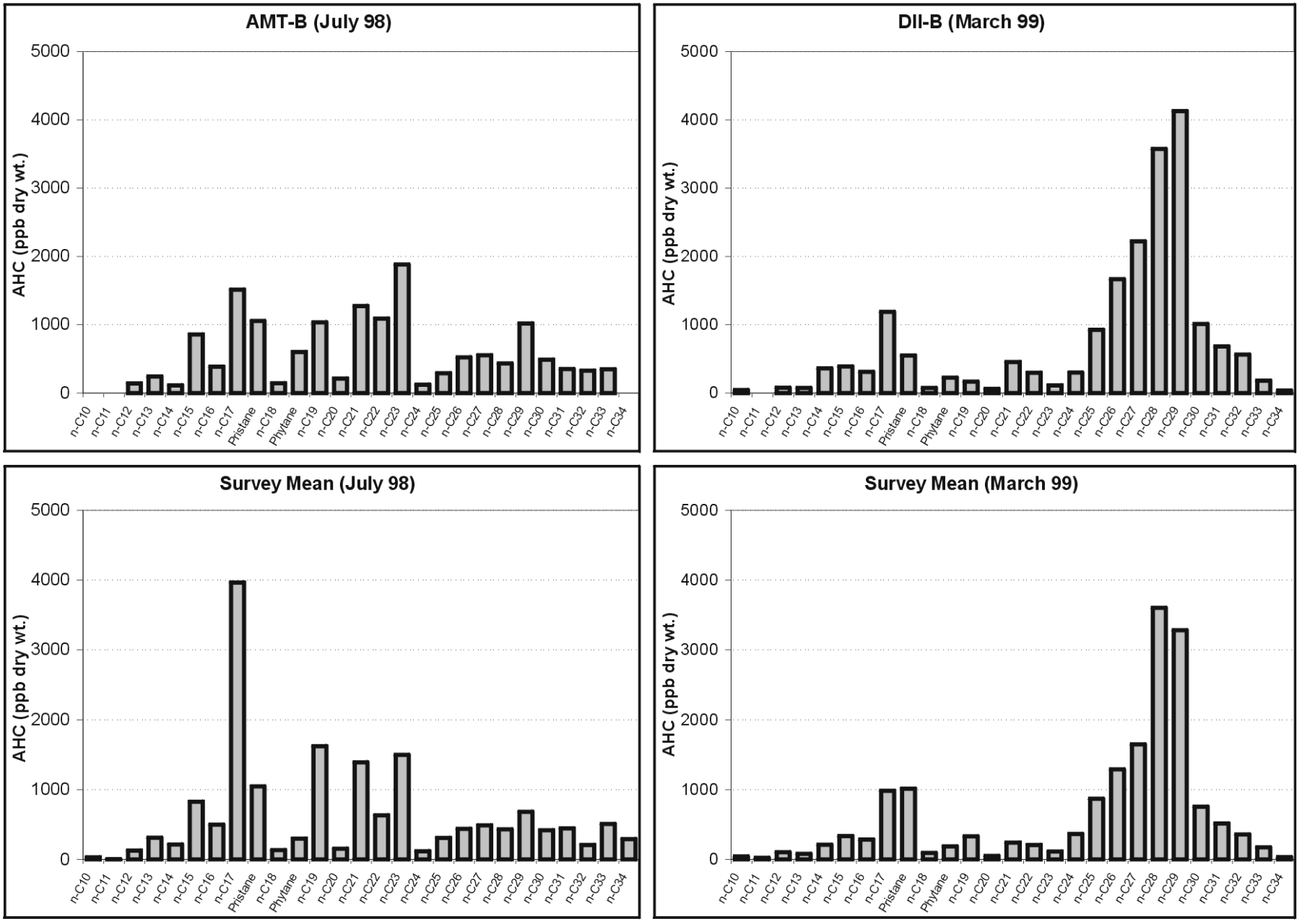

Figure 14. Mean LTEMP Tissue AHC Fingerprints - July 1998 and March 1999 Surveys, Stations AMT-B, DII-B, and Survey Means.

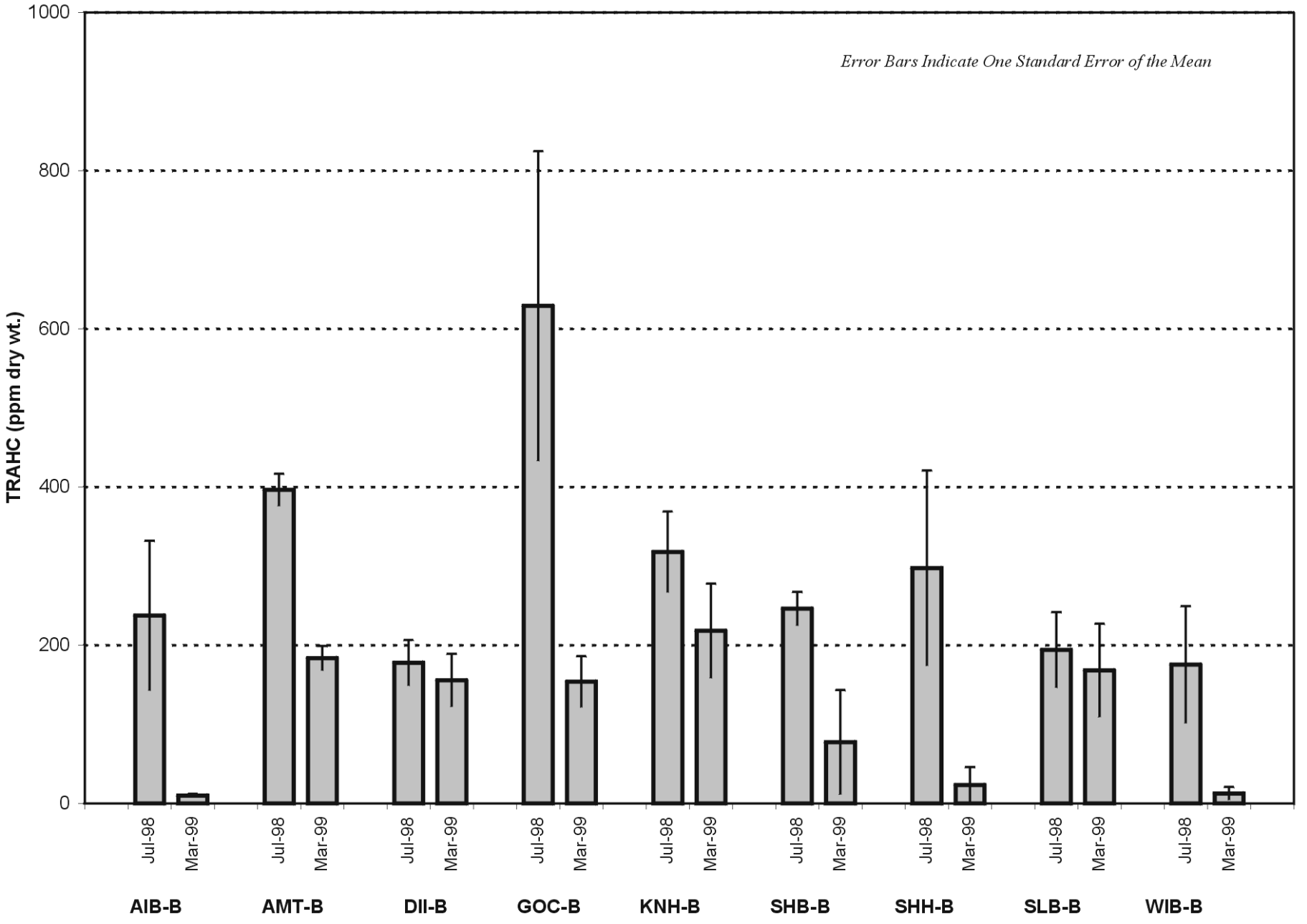

Figure 15. Mean LTEMP Tissue TRAHC by Station and Survey - July 1998 and March 1999.

The mean TRAHC concentrations were considerably higher within all stations during the July 1998 survey as compared to the March 1999 survey (Tables 12 and 13; Figure 15). The cause of this seasonal pattern was not determined; however, within station temporal variability may also be due to spawning or feeding as seen with the AHC concentrations. Values ranged from a mean of 175.5 ppm at Station WIB to 629.0 ppm at Station GOC in July 1998, and from 10.0 ppm at Station AIB to 218.4 at Station KNH in March 1999. Station GOC exhibited the highest mean TRAHC value in July 1998 as well as the highest mean TAHC seen during this survey, while Station WIB exhibited the lowest TRAHC and TAHC values for this survey. Good agreement between the minimum and maximum values for TRAHC and TAHC was also seen for March 1999 for Station AIB and KNH, respectively. This is not surprising as the TAHC concentration is a subset of the TRAHC value. As the concentration of TRAHC was not determined historically for LTEMP, no values are available for comparison.

The UCM values reported for the two 1998 – 1999 surveys showed a fairly high degree of between- and within-station variability (Tables 12 and 13; Figure 16). Mean UCM values ranged in July 1998 from 14.6 ppm at Station SLB to 80.8 ppm at Station GOC. Mean UCM values in March 1999 ranged from 2.2 ppm at Station SHH to 838.8 ppm at Station AMT. Inspection of Figure 16 indicates that this year's mean UCM values typically fell within the range of the 1993 – 1994 historical data. In contrast to that seen for TRAHC, the concentration of UCM were typically higher in March 1999 than those seen in July 1998. Exceptions to this seasonal trend included Stations AIB, SHH, and WIB, all of which exhibited extremely low mean UCM values in March 1999 (9.6, 2.2, and 2.7 ppm, respectively) compared to the July survey. These were also the same three stations that showed the lowest TRAHC concentrations for March 1999. Historically, the same seasonal trend of high UCM in the spring followed by low UCM in the summer was seen at all sites including Stations AIB, SHH, and WIB. These three sites are all located in the Gulf of Alaska where a large winter die-off of mussels and barnacles was observed during the March 1999 survey. The cause of this die-off was believed to be due to heavy icing and freezing conditions in some bays during January 1999. Many of the observed mussel beds in Windy Bay, including Station WIB, had been almost completely removed. Many of the mussels at Station SHH were still attached but were observed to be dead. Station AIB appeared to be visually healthy in comparison, but mussels at this site may also have been stressed by the extreme winter conditions. Therefore, the anomalously low UCM concentrations (and other AHC parameters) seen at these three stations during March 1999 can probably be attributed to factors that caused extreme stress to the populations.

As noted above, calculation of ratios such as the CPI are somewhat less viable for tissues than sediments because of the biological factors involved, particularly availability, preferential uptake, depuration, and bioaccumulation in lipid-rich tissues which may be expelled as gamete material during spawning. The mean CPI ratios ranged from 1.0 to 1.8 for July 1998 and 0.8 to 1.4 during March 1999 (Table 13). In sediment or water, CPI values close to one are an indication of petroleum, and higher values indicate biogenic input. However, for mussel tissues it is apparent that the CPI does not have the same direct correspondence due to matrix interference.

The CRUDE index values that were calculated after Payne et al. (1998) are reported in Table 11. The mean CRUDE index values ranged from 5,583 to 16,953 for July 1998 at Stations AMT and GOC, respectively. Mean values calculated for March 1999 were 2,279 at Station AIB and 48,992 at Station KNH. Because the AHC values reported for tissues are so elevated with respect to the PAH and UCM values, this index is probably not particularly helpful in assessing the petrogenic fraction of the hydrocarbons seen in the tissues. That is, the index does not provide any real new information due to the predominance of the AHC term in the calculation, which masks differences in the PAH and UCM terms that would normally be more indicative of source. This masking effect is apparent when Station KNH (March 1999) is examined, for example. This station exhibited the highest mean TAHC (32,940 ppb) and mean TRAHC (218 ppm) during this survey and showed a reasonably large mean UCM (518 ppm). The mean CRUDE index value for this station (48,992) was well above that seen at any other and nearly twice that seen at Station AMT for March 1999 (24,851). The PAH values for this station and survey, however, were quite low, with a mean of 128.5 ppb, and the PAH fingerprints indicated that background sources were the likely contributor for the hydrocarbons seen in these tissue samples. The fingerprint interpretation is similar to that seen in the past at this station, although pyrogenic sources have also been suggested in the past.

Analysis and reporting of AHC and associated parameters (TRAHC, UCM, and CPI) in mussel tissues did not appear to provide much useful information regarding hydrocarbon levels or sources other than confirming that large amounts of naturally-occurring compounds that are chromatographically indistinguishable from the target analytes exist in the mussel tissues. State-of-the-art purification steps are not sufficient in removing these interfering compounds

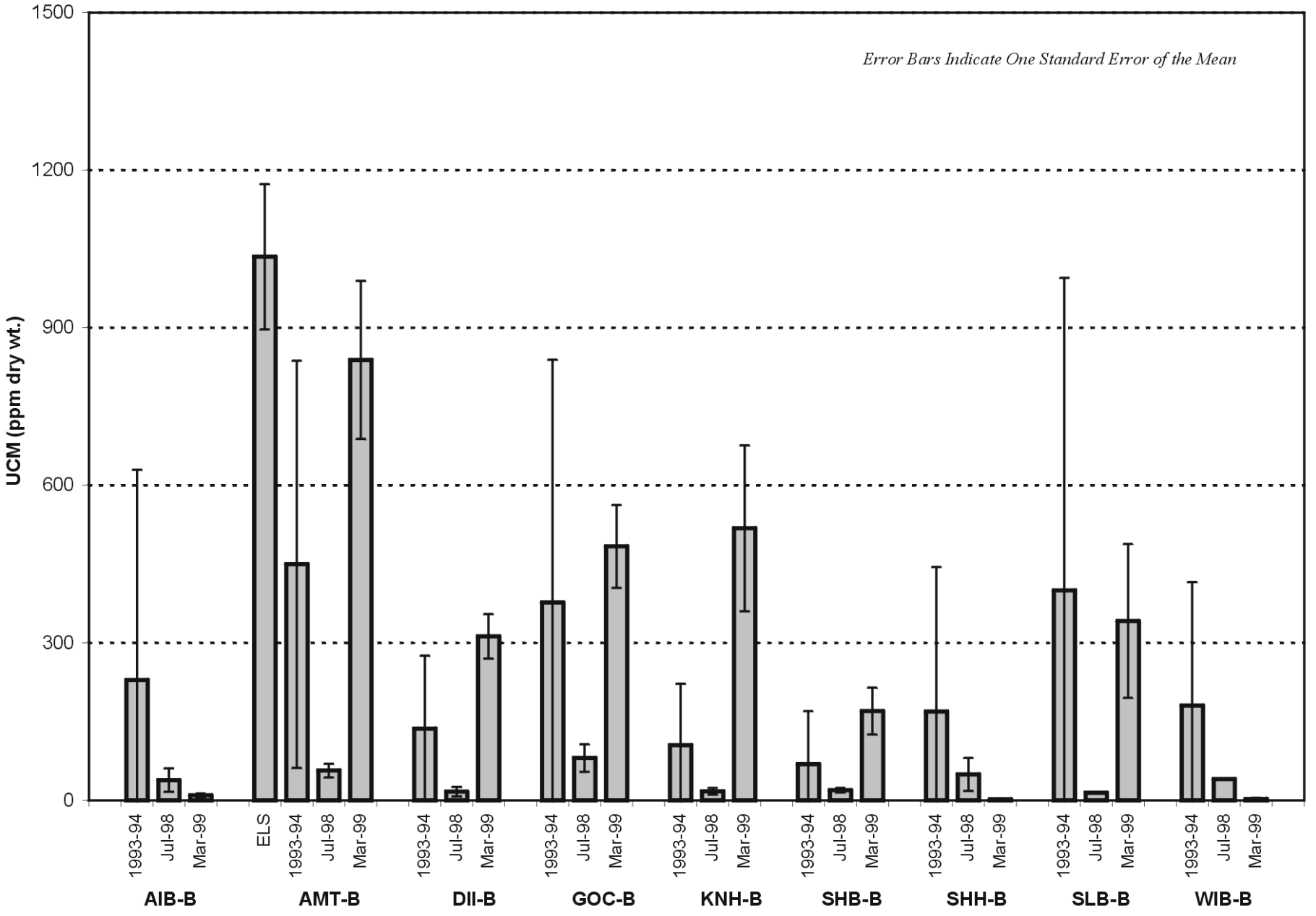

Figure 16. Mean LTEMP Tissue UCM by Station and Survey - Historical, July 1998, and March 1999.

without removing some of the target AHC themselves, thereby further confounding the results. In addition, while it is understood that AHC is a relatively large component of petroleum hydrocarbons in comparison to PAH, it is clear that PAH sampling in tissues has been sufficient to determine spill impacts in the past. For example, sampling at Station AMT in response to spill events has indicated that tissue PAH levels, although considerably lower than tissue AHC levels, can be used to pinpoint spill events as the TPAH became highly elevated after each spill. In fact, tissue PAH concentrations had increased 25 – 30 times during the ELS sampling event, as compared to tissue AHC concentrations which only increased by 5 – 6 times. In addition, the straight-chained AHC components in petroleum are easily weathered, whereas the PAH persist for much longer periods. This is exemplified in the EVOS-impacted sediment data for Station DII in July 1998 (discussed below), where the elevated TPAH level in one replicate was nearly 138,000 ppb as compared to a TAHC of approximately 8,000 ppb. The LTEMP data seem to invalidate the argument that AHC concentrations due to their proportionately larger presence are much more likely than PAH levels to allow identification of a spill event.

5.2.3 Percent Lipids

Tissue percent lipid concentrations showed a fairly high degree of variability among stations and among surveys (Tables 11 and 12; Figure 17). Mean concentrations of lipids in tissues during July 1998 ranged from 3.2 % at Stations AMT and SHB to 7.2 % at Station GOC. Mean lipid concentrations in March 1999 ranged from 7.0 % at Station AIB to 16.4 % at Station SHB. The historical trend at most sites of higher lipid concentrations during the summer surveys compared to the winter surveys may fail during the next program year, since March 1999 values were considerably higher than usual. Many of the stations showed March 1999 mean lipid results to be the maximum encountered to date.

Historically there has been was some indication of seasonal effects on gonadal development and spawning, although there is sufficient scatter in the data to suggest that the timing of these activities is variable among stations and years (Table 12). 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* (now referred to as *Mytilus trossulus*) 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.

5.2.4 Gonadal Index

In general, values of shell length and volume, gonadal tissue weight, and non-gonadal weights corresponded well (Table 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 outstanding differences were seen between either stations or surveys (Figures 18 and 19). 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. As in the past, mussels were largest overall at Stations AMT, GOC, SHH, and WIB, and smaller at the remaining stations, particularly Station KNH (Table 14). The size distribution of the LTEMP data will likely change given the winter die-off that occurred at Stations SHH and WIB in March 1999.

5.3 Sediment

Marine 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, is deposited in sediments, and is associated with fine-grained material. 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.

Intertidal sediments can also be considered a long-term repository of petroleum residues and are especially vulnerable to contamination during a spill or acute release to the marine environment. Due to their typically coarse-grained and fairly transient nature, however, intertidal sediments are not as prone to accumulation of long-term low-level chronic

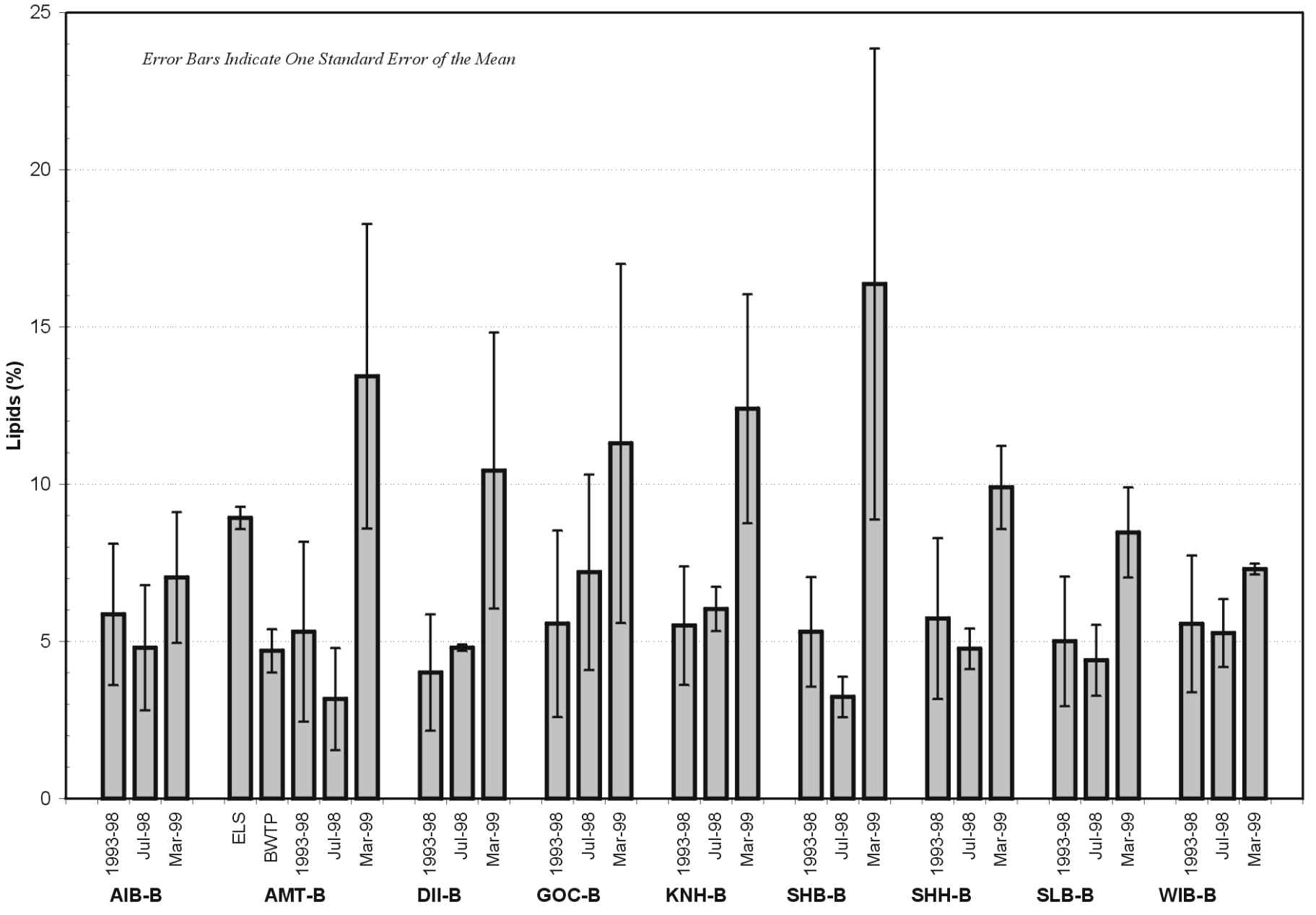

Figure 17. Mean LTEMP Tissue Percent Lipids by Station and Survey - Historical, July 1998, and March 1999.

Table 14. Mean LTEMP Gonadal Index Results by Station and Survey - 1993 through 1999.

Station (Survey)	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)	34	3.1	0.13	0.79	0.13	0.04
AIB-B (7/93)	31	2.4	0.05	0.61	0.08	0.02
AIB-B (3/94)	30	1.7	0.11	0.56	0.16	0.07
AIB-B (7/94)	37	3.1	0.14	0.95	0.13	0.05
AIB-B (3/95)	36	2.8	0.19	0.95	0.16	0.07
AIB-B (7/95)	38	3.7	0.46	1.40	0.24	0.12
AIB-B (3/96)	32	2.2	0.17	0.86	0.17	0.08
AIB-B (7/96)	34	2.9	0.28	1.06	0.20	0.10
AIB-B (3/97)	34	2.0	0.11	0.85	0.11	0.06
AIB-B (7/97)	35	2.7	0.24	0.99	0.18	0.09
AIB-B (3/98)	34	2.4	0.25	0.87	0.23	0.11
AIB-B (7/98)	34	2.7	0.11	0.82	0.12	0.04
AIB-B (3/99)	34	2.5	0.17	0.81	0.17	0.07
AMT-B (3/93)	42	5.7	0.40	1.55	0.20	0.07
AMT-B (7/93)	43	4.1	0.26	1.46	0.15	0.07
AMT-B (3/94)	41	4.4	0.32	1.22	0.19	0.07
AMT-B (ELS)	42	2.4	0.34	1.27	0.21	0.15
AMT-B (7/94)	40	3.7	0.22	1.21	0.15	0.06
AMT-B (3/95)	42	4.5	0.16	1.05	0.12	0.03
AMT-B (7/95)	42	4.4	0.47	1.88	0.20	0.11
AMT-B (3/96)	40	4.0	0.13	0.98	0.12	0.03
AMT-B (7/96)	42	4.4	0.42	1.61	0.20	0.10
AMT-B (BWTP)	42	4.2	0.26	1.34	0.16	0.06
AMT-B (3/97)	40	3.9	0.24	1.12	0.17	0.06
AMT-B (7/97)	42	4.9	0.38	1.64	0.19	0.08
AMT-B (3/98)	38	3.9	0.18	0.95	0.16	0.04
AMT-B (7/98)	41	4.0	0.18	1.07	0.14	0.05
AMT-B (3/99)	36	3.3	0.05	0.65	0.07	0.01
DII-B (3/93)	36	3.7	0.13	0.81	0.14	0.04
DII-B (7/93)	40	4.6	0.23	1.33	0.15	0.05
DII-B (3/94)	39	3.9	0.29	1.19	0.19	0.07
DII-B (7/94)	41	4.3	0.24	1.30	0.16	0.06
DII-B (3/95)	40	3.9	0.28	1.29	0.17	0.07
DII-B (7/95)	42	5.0	0.32	1.50	0.17	0.07
DII-B (3/96)	38	3.7	0.11	0.89	0.11	0.03
DII-B (7/96)	37	3.5	0.14	0.95	0.13	0.04
DII-B (3/97)	34	2.6	0.16	0.87	0.15	0.06
DII-B (7/97)	35	2.8	0.17	0.98	0.14	0.06
DII-B (3/98)	34	2.6	0.32	0.96	0.25	0.13
DII-B (7/98)	34	2.2	0.08	0.77	0.09	0.04
DII-B (3/99)	34	3.0	0.16	0.83	0.14	0.05

Table 14. Mean LTEMP Gonadal Index Results by Station and Survey - 1993 through 1999. (Continued)

Station (Survey)	Shell Length (mm)	Shell Volume (mL)	Gonadal Weight (g)	Non-Gonadal Weight (g)	Proportional Gonadal Weight (Ratio)	Gonadal Weight/ Shell Volume (Ratio)
GOC-B (3/93)	38	4.2	0.43	1.25	0.26	0.10
GOC-B (7/93)	41	4.9	0.25	1.47	0.14	0.05
GOC-B (3/94)	42	4.3	0.21	1.16	0.15	0.05
GOC-B (7/94)	43	4.3	0.31	1.66	0.16	0.07
GOC-B (3/95)	38	3.3	0.14	0.95	0.12	0.04
GOC-B (7/95)	41	4.2	0.41	1.64	0.20	0.10
GOC-B (3/96)	38	3.5	0.15	0.92	0.13	0.04
GOC-B (7/96)	40	3.6	0.42	1.54	0.21	0.12
GOC-B (3/97)	39	3.8	0.25	1.15	0.17	0.06
GOC-B (7/97)	41	4.0	0.34	1.56	0.17	0.08
GOC-B (3/98)	40	4.0	0.23	1.09	0.17	0.06
GOC-B (7/98)	40	3.3	0.15	1.23	0.11	0.05
GOC-B (3/99)	36	3.0	0.12	0.81	0.12	0.04
KNH-B (3/93)	30	2.2	0.08	0.52	0.13	0.04
KNH-B (7/93)	25	1.2	0.07	0.39	0.15	0.06
KNH-B (3/94)	28	1.1	0.12	0.46	0.16	0.13
KNH-B (7/94)	33	2.2	0.11	0.67	0.13	0.05
KNH-B (3/95)	31	2.2	0.09	0.66	0.11	0.04
KNH-B (7/95)	32	2.3	0.28	0.87	0.24	0.12
KNH-B (3/96)	30	2.2	0.11	0.63	0.15	0.05
KNH-B (7/96)	30	2.3	0.13	0.64	0.17	0.06
KNH-B (3/97)	29	1.9	0.09	0.50	0.15	0.05
KNH-B (7/97)	29	1.4	0.08	0.54	0.13	0.06
KNH-B (3/98)	27	1.4	0.08	0.48	0.15	0.06
KNH-B (7/98)	28	1.6	0.07	0.43	0.14	0.05
KNH-B (3/99)	31	1.9	0.09	0.51	0.16	0.06
SHB-B (3/93)	37	4.1	0.19	0.99	0.16	0.05
SHB-B (7/93)	37	3.7	0.19	1.03	0.15	0.05
SHB-B (3/94)	37	2.8	0.17	0.96	0.14	0.06
SHB-B (7/94)	37	3.1	0.11	0.97	0.10	0.04
SHB-B (3/95)	36	3.6	0.15	1.00	0.12	0.04
SHB-B (7/95)	34	2.6	0.21	0.92	0.19	0.08
SHB-B (3/96)	33	3.0	0.13	0.80	0.14	0.05
SHB-B (7/96)	33	2.6	0.19	0.74	0.20	0.07
SHB-B (3/97)	34	2.9	0.18	0.74	0.20	0.07
SHB-B (7/97)	34	2.5	0.12	0.83	0.12	0.05
SHB-B (3/98)	34	2.7	0.25	0.97	0.20	0.10
SHB-B (7/98)	33	2.3	0.09	0.68	0.12	0.04
SHB-B (3/99)	32	1.9	0.16	0.70	0.19	0.11

Table 14. Mean LTEMP Gonadal Index Results by Station and Survey - 1993 through 1999. (Continued)

Station (Survey)	Shell Length (mm)	Shell Volume (mL)	Gonadal Weight (g)	Non-Gonadal Weight (g)	Proportional Gonadal Weight (Ratio)	Gonadal Weight/ Shell Volume (Ratio)
	41	4.2	0.19	1.23	0.13	0.05
SHH-B (3/94)	39	4.0	0.33	1.30	0.20	0.08
SHH-B (7/94)	45	5.4	0.31	1.77	0.15	0.06
SHH-B (3/95)	39	3.6	0.33	1.34	0.19	0.09
SHH-B (7/95)	43	4.8	0.32	1.65	0.16	0.07
SHH-B (3/96)	41	3.7	0.28	1.37	0.17	0.07
SHH-B (7/96)	39	3.7	0.20	1.22	0.14	0.05
SHH-B (3/97)	40	4.0	0.20	1.10	0.15	0.05
SHH-B (7/97)	40	3.9	0.19	1.23	0.15	0.05
SHH-B (3/98)	36	2.5	0.14	0.94	0.12	0.05
SHH-B (7/98)	36	2.7	0.13	0.96	0.12	0.05
SHH-B (3/99)	36	3.4	0.31	1.07	0.22	0.09
SLB-B (3/93)	32	3.0	0.15	0.81	0.15	0.05
SLB-B (7/93)	30	2.0	0.09	0.59	0.13	0.05
SLB-B (3/94)	28	1.4	0.10	0.33	0.24	0.08
SLB-B (7/94)	37	3.2	0.20	1.07	0.16	0.06
SLB-B (3/95)	33	2.8	0.14	0.87	0.13	0.05
SLB-B (7/95)	34	3.0	0.17	0.88	0.15	0.05
SLB-B (3/96)	32	2.3	0.12	0.72	0.14	0.05
SLB-B (7/96)	32	2.5	0.12	0.77	0.14	0.05
SLB-B (3/97)	34	2.6	0.08	0.65	0.10	0.03
SLB-B (7/97)	33	2.2	0.15	0.87	0.15	0.08
SLB-B (3/98)	33	2.7	0.23	0.88	0.21	0.09
SLB-B (7/98)	34	2.3	0.05	0.58	0.07	0.02
SLB-B (3/99)	34	3.0	0.12	0.71	0.15	0.05
WIB-B (3/93)	35	3.8	0.11	0.84	0.10	0.03
WIB-B (7/93)	36	3.4	0.16	0.97	0.14	0.05
WIB-B (3/94)	37	3.2	0.14	0.94	0.13	0.04
WIB-B (7/94)	40	4.1	0.23	1.26	0.15	0.05
WIB-B (3/95)	36	2.8	0.13	0.92	0.12	0.05
WIB-B (7/95)	37	3.4	0.27	1.16	0.18	0.08
WIB-B (3/96)	39	3.7	0.17	1.15	0.13	0.04
WIB-B (7/96)	39	4.2	0.24	1.27	0.15	0.05
WIB-B (3/97)	40	3.3	0.11	1.09	0.08	0.03
WIB-B (7/97)	37	3.7	0.20	1.11	0.15	0.06
WIB-B (3/98)	38	2.9	0.29	1.20	0.20	0.10
WIB-B (7/98)	35	3.2	0.10	0.85	0.10	0.03
WIB-B (3/99)	32	2.3	0.13	0.87	0.12	0.05

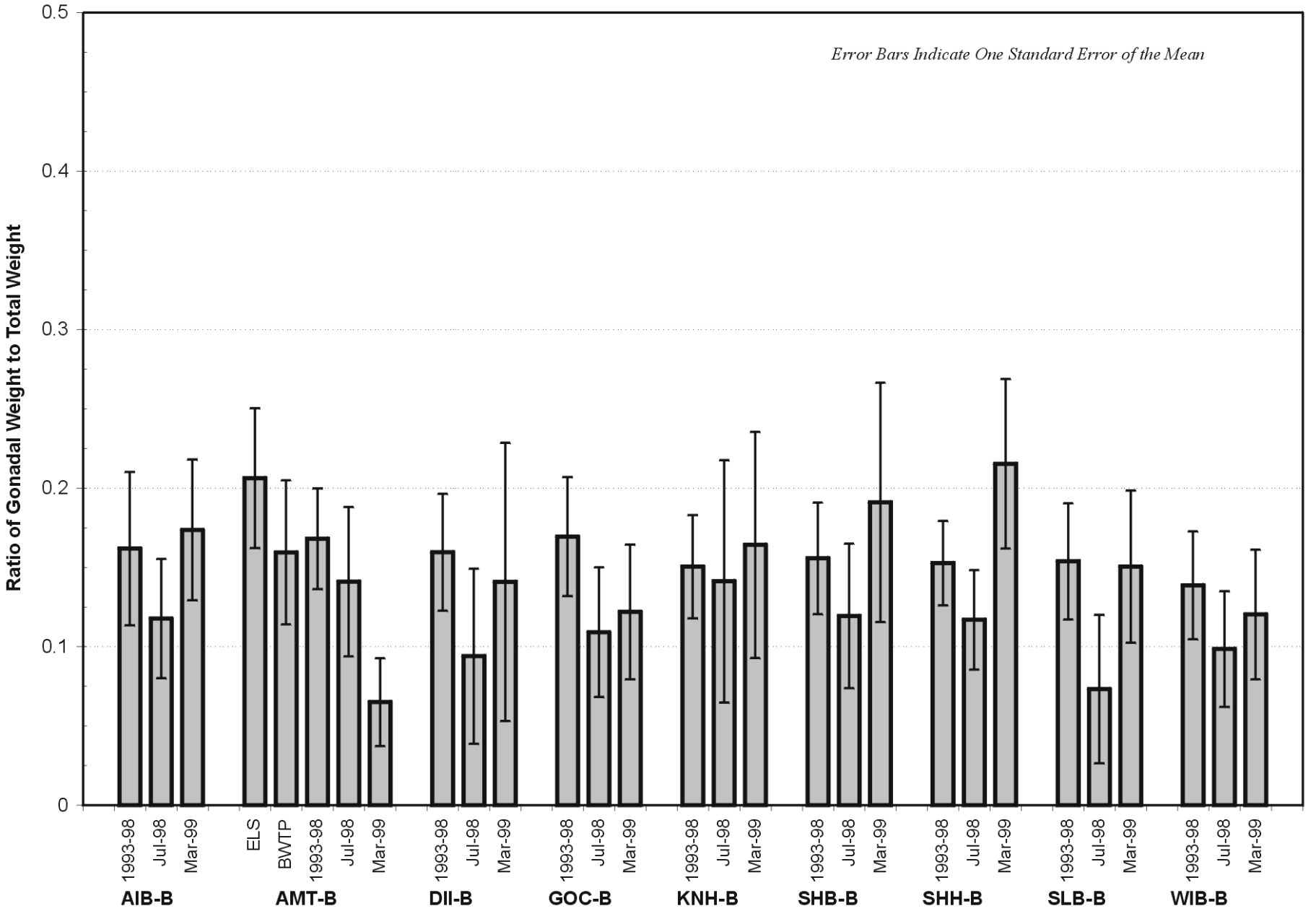

Figure 18. Mean LTEMP Proportional Gonadal Weight by Station and Survey - Historical, July 1998, and March 1999.

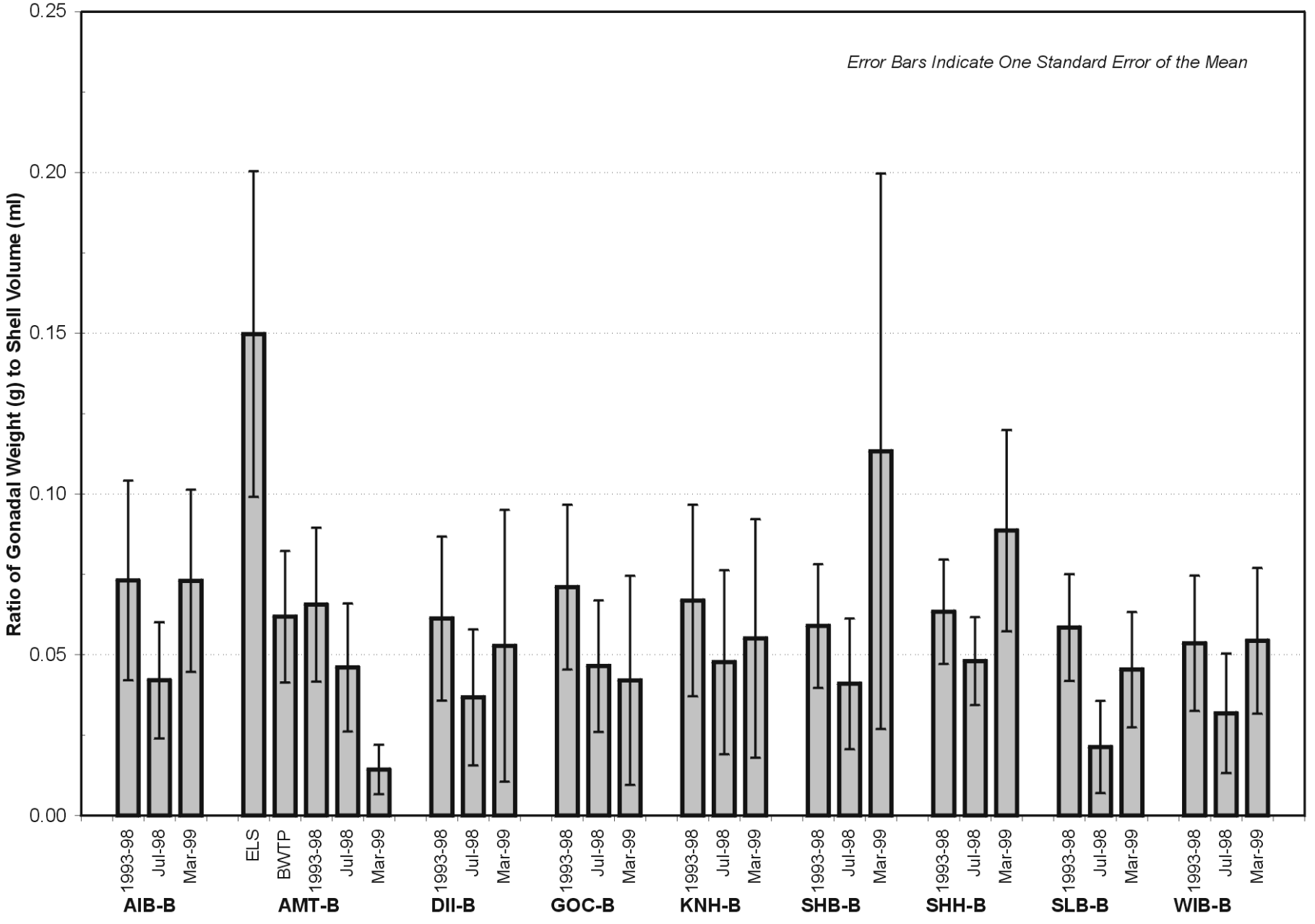

Figure 19. Mean LTEMP Gonadal Weight/Shell Volume by Station and Survey - Historical, July 1998, and March 1999.

hydrocarbon inputs. Based on the recommendations of reviewers over the course of the program, intertidal sediments were selected for study during this program year. During one survey in July 1998, LTEMP examined the intertidal sediments at each of the historic sampling sites. An attempt was made to locate the station close to the intertidal mussel site and also within a zone of fine-grained material. This combination proved impossible to achieve since the vast majority of sites in the PWS and Gulf of Alaska study areas consist of rock, cobble, or coarse-grained material. Therefore, most of the stations were located near the mussel sites and consisted of coarse material.

Aliphatic and polycyclic aromatic hydrocarbons were measured in sediments at each monitoring site except for Station SLB, where no suitable fine or coarse-grained material could be found without removing the cobble armor. As part of the original study design, three types of sites were sampled: (1) reference sites believed to be relatively remote from anthropogenic activities (Stations AIB, GOC and SHB), (2) sites previously identified as EVOS-impacted (Stations DII, SHH, 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

Intertidal sediment PAH chemistry results from the July 1998 LTEMP survey are summarized in Table 15. Individual sediment replicate data are provided in Appendix B. With the exception of the Station DII results, PAH concentrations in intertidal sediments were low. Only three of the eight stations sampled showed mean TPAH concentrations above the cumulative MDL of 35 ppb. Many individual analytes were estimated at concentrations below the MDLs and were qualified with the "J" qualifier. Concentrations of various analytes and indices calculated from these analyte concentrations varied considerably among stations.

Table 15. LTEMP Intertidal Sediment TPAH, FFPI, and CRUDE Index Results for July 1998.

Station	TPAH (ng/g or ppb)				FFPI (ratio)				CRUDE Index (ratio)			
	Rep. 1	Rep. 2	Rep. 3	Mean	Rep. 1	Rep. 2	Rep. 3	Mean	Rep. 1	Rep. 2	Rep. 3	Mean
AIB-L	4.7	12.3	9.0	8.7	80.4	82.4	84.8	82.5	15.0	29.7	17.7	20.8
AMT-L	25.6	38.0	123.2	62.3	63.6	69.8	62.8	65.4	77.2	41.0	249.8	122.7
DII-L	13784	137972	1737.4	51165	72.5	87.7	75.8	78.7	12749	129996	3365	48703
GOC-L	11.9	4.8	11.5	9.4	74.4	81.6	72.8	76.3	20.2	5.6	10.2	12.0
KNH-L	7.8	13.8	25.2	15.6	65.0	71.9	79.2	72.1	5.9	119.7	20.7	48.8
SHB-L	56.5	60.1	38.8	51.8	57.4	57.3	55.4	56.7	42.5	69.0	33.5	48.3
SHH-L	8.9	5.9	6.7	7.2	61.1	75.4	75.0	70.5	37.8	17.8	56.5	37.4
WIB-L	5.0	8.0	5.7	6.2	79.2	82.7	81.7	81.2	23.8	37.5	73.2	44.8

The overall mean concentration of TPAH in intertidal sediments ranged from 6.2 ppb at Station WIB to 51,165 ppb at Station DII (Table 15 and Figure 20). This high value at Station DII was expected because this sampling site still shows visible evidence of oil from the EVOS; samples were collected from visibly oily sediments just adjacent to the mussel sampling site. This is the same area that had been sampled opportunistically in the past, as reported in prior program reports (KLI, 1996a and 1997a). Sediment TPAH in single samples collected from this area were shown to be 101,377 ppb in July 1995 (Survey 6) and 109,555 ppb in July 1996 (Survey 8), compared to the replicate results of 13,784, 137,972, and 1,737 ppb in July 1998 (Survey 12).

The three stations that showed concentrations of mean TPAH above the cumulative MDL included Stations AMT (62.3 ppb), DII (51,165 ppb), and SHB (51.8 ppb). The next highest station was KNH at 15.6 ppb. Within-station variability was considerable at a number of these stations (AMT, KNH, and DII), as indicated by the large standard error bars depicted on Figure 20. This was expected due to the patchy nature of sediments in the intertidal area.

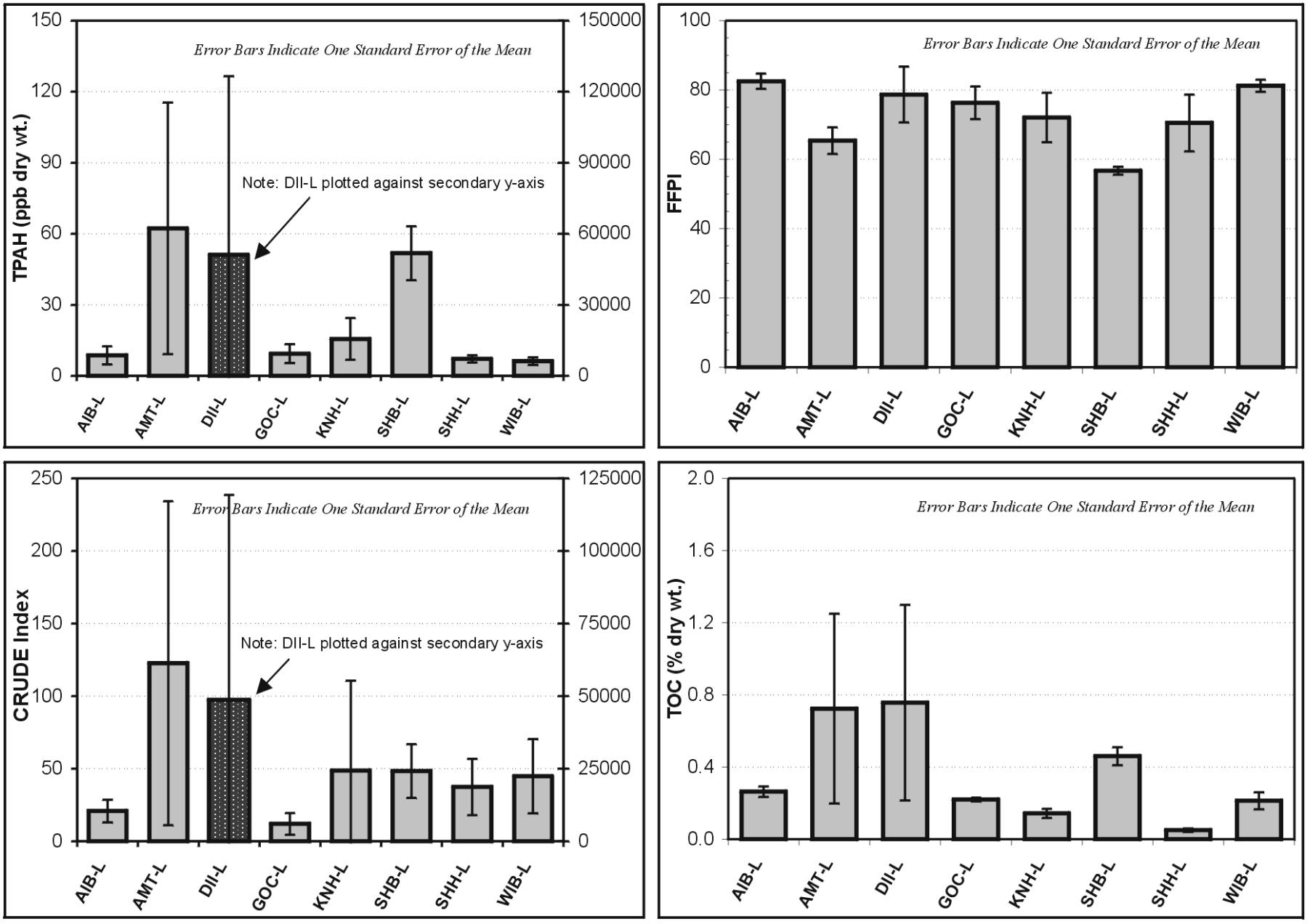

Figure 20. Mean LTEMP Intertidal Sediment TPAH, FFPI, CRUDE Index, and TOC by Station, July 1998.

Fingerprints for the four stations with the highest mean TPAH concentrations are provided in Figure 21. Station AMT exhibits an ANS crude type of signature with additional contributions of pyrogenics as seen by the relatively high molecular weight PAH concentrations. As in the past, the PAH signature in intertidal sediments from Station DII was indicative of weathered ANS as shown by the persistence of the alkylated homologues compared to their parent compounds, the ratio of the C_2- and C_3-dibenzothiophenes to phenanthrenes, and the relative lack of high molecular weight compounds (above C_3-dibenzothiophene). Station KNH showed background sources with a lesser pyrogenic component. Pyrogenic inputs were clearly evident at Station SHB which not only showed many of the high molecular weight PAH but also exhibited the typical pattern for pyrogenic PAH with high concentrations of the parent compounds compared to their alkylated homologues. The PAH at the remaining four stations, AIB, GOC, SHH, and WIB, were all very low (TPAH < 10 ppb) and exhibited the typical background signature. In addition, low levels of some pyrogenic constituents were seen at Station SHH.

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, this ratio was ~1 in intertidal sediments (Figure 21 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 indicates that if the source was ANS crude, the oil had weathered substantially. 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. The C_2-chrysene/C_2-phenanthrene ratio at Station DII was similar to the 0.5 value documented for EVOS crude by Bence and Burns in 1991, indicating that weathering of these components is proceeding very slowly at this EVOS site.

Mean values for FFPI in intertidal sediments collected during July 1998 ranged from 56.7 at Station SHB to 82.5 at Station AIB (Table 15 and Figure 20). Fairly low within-station variability was seen in this parameter, as indicated by the small standard error bars shown in Figure 20. The relatively low mean FFPI at Station SHB corresponds well with the fingerprint which clearly shows pyrogenic contributions. Other stations exhibited higher FFPI values in the 65.4 to 82.5 range. Station DII showed a mean FFPI of 78.7.

5.3.2 Aliphatic Hydrocarbons

Concentrations of 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 16. The concentrations of TAHC in sediments varied greatly among and within sites (Table 16 and Figure 22). Many of the TAHC values were below the cumulative MDL of 84 reported for this sample set, with many of the individual analytes estimated at below-MDL levels. Mean TAHC concentrations ranged from 20.0 ppb at Station AIB to 3,592 ppb at Station DII. Station AMT showed a relatively high TAHC concentration at 959.1 ppb. Aside from Stations DII and AMT, only Station SHB showed a mean TAHC above the cumulative MDL at 163.0 ppb. Other mean TAHC values fell below 49.0 ppb.

Visibly oiled sediments from Station DII yielded a mean TAHC result of 3,592 ppb with the three individual replicates ranging from 1,298.8 to 8,001.2 ppb (Table 16). These values may be compared with the single replicate samples taken in July 1995 (11,305 ppb) and July 1997 (1,406 ppb). This high concentration of TAHC seen in the second replicate taken at this station corresponds well with the high level of TPAH seen here, although this relationship is not clear in the other two replicates (i.e., the lowest TAHC value shows the mid-range TPAH value, and the mid-range TAHC value shows the lowest TPAH value). The mean AHC fingerprint for this station (Figure 23) indicates a weathered source with low levels of low molecular weight n-alkanes with peaks at some of the odd-numbered. Individual replicates at Station DII, however, were very different, with replicates 1 and 3 looking more like weathered oil, and replicate 2 indicating a stronger odd-to-even n-alkane preference which indicates a terrigenous source such as peat in the sample.

The mean AHC fingerprints from Stations AMT and SHB had an odd-carbon dominance in the n-C_{21} to n-C_{33} range of normal alkanes which was reflective of some biogenic input for the hydrocarbons (Figure 23). The CPI ratios at these sites, which appeared relatively high compared to the other stations in this sample set, were actually fairly low compared to the typical CPI values seen for biogenic inputs. This indicated a combination of biogenic and petrogenic inputs for these hydrocarbons, particularly at Station AMT, which also showed a relatively high UCM value (see below).

Table 16. LTEMP Intertidal Sediment TAHC, TRAHC, UCM, and CPI Results for July 1998.

Station	TAHC (ng/g or ppb)				TRAHC (mg/g or ppm)			
	Rep. 1	Rep. 2	Rep. 3	Mean	Rep. 1	Rep. 2	Rep. 3	Mean
AIB-L	24.3	19.9	15.9	20.0	0.2	1.1	0.7	0.7
AMT-L	254.1	131.0	2492.1	959.1	1.6	0.9	11.3	4.6
DII-L	1298.8	8001.2	1476.1	3592.0	28.8	38.9	10.1	25.9
GOC-L	51.6	13.9	26.2	30.6	0.3	0.3	0.3	0.3
KNH-L	5.0	47.6	82.5	45.0	0.1	0.3	0.5	0.3
SHB-L	89.7	248.0	151.4	163.0	0.4	0.8	0.7	0.6
SHH-L	41.7	35.9	69.5	49.0	0.9	0.2	7.7	2.9
WIB-L	16.9	18.9	64.4	33.4	1.4	0.7	0.3	0.8
Station	**UCM (mg/g or ppm)**				**CPI (ratio)**			
	Rep. 1	Rep. 2	Rep. 3	Mean	Rep. 1	Rep. 2	Rep. 3	Mean
AIB-L	1.2	0.8	0.4	0.8	1.6	1.0	1.3	1.3
AMT-L	6.2	5.7	27.0	13.0	2.2	3.9	4.1	3.4
DII-L	1461.6	5828.6	455.9	2582.0	0.1	1.6	1.0	0.9
GOC-L	0.0	0.0	1.0	0.3	2.1	2.9	5.7	3.6
KNH-L	0.0	0.0	0.0	0.0	2.5	0.7	10.4	4.5
SHB-L	0.0	0.0	0.0	0.0	3.0	2.7	3.5	3.1
SHH-L	3.6	2.3	3.2	3.0	1.2	1.8	1.2	1.4
WIB-L	0.2	1.4	0.2	0.6	0.9	0.8	1.0	0.9

Upon closer examination of Station AMT, it appears that a majority of the mean fingerprint can be attributed to replicate 3, which had the highest TPAH, TAHC, UCM, and TOC, and consisted of the highest proportion of fine-grained materials measured on the survey. See Section 5.3.4 for further information regarding the PGS results for the intertidal sediment sampling.

The fingerprint at Station WIB indicates a more clear petrogenic signal, although concentrations were very low (mean TAHC of 33.4 ppb). The odd-to-even preference seen at Stations AMT, DII, and SHB is not exhibited at this station, indicating biogenic contributions were minimal compared to the petrogenic contributions. Given the PAH signature at this intertidal station, it is likely that the AHC seen here are also background hydrocarbons.

Other stations exhibiting lower levels of AHC showed a variety of hydrocarbon sources. Station AIB, with the lowest mean TAHC, showed no clear signal that could be attributed to any particular source. Both petrogenic and biogenic signals were seen at Station GOC, which had noticeable differences between replicates. Station KNH exhibited mostly biogenic inputs, as seen by the high CPI value for this station. The Station SHH fingerprint showed more petrogenic inputs with some evidence of pyrogenics (based in part on the PAH signature). Little biogenic input was seen at this station.

The TRAHC values for intertidal sediments are provided in Table 16 and Figure 22. Mean TRAHC values ranged from 0.3 at Stations GOC and KNH to 25.9 at Station DII. A large degree of within-station variability was seen at

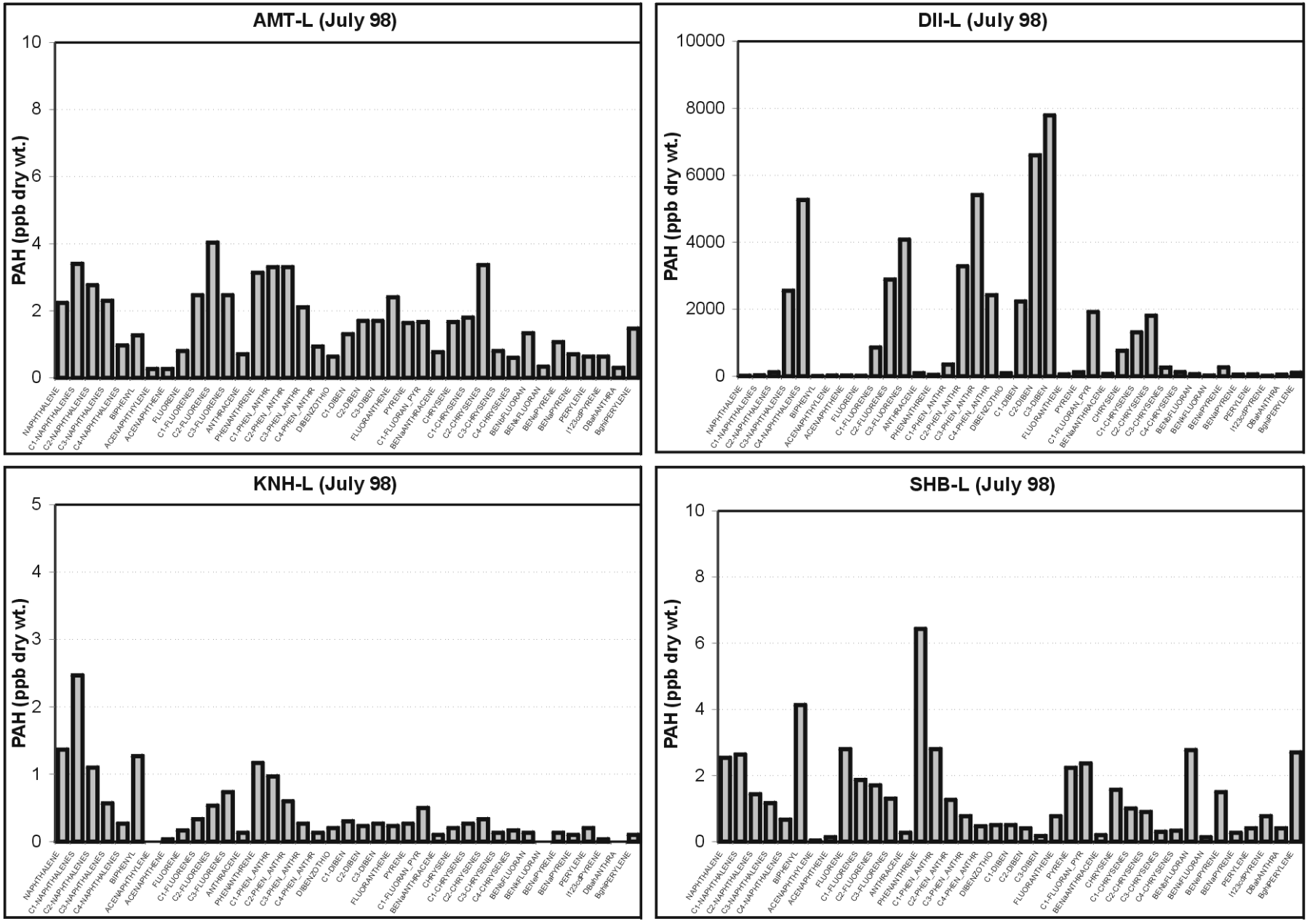

Figure 21. Mean LTEMP Intertidal Sediment PAH Fingerprints - July 1998 Survey, Stations AMT-L, DII-L, KNH-L, and SHB-L.

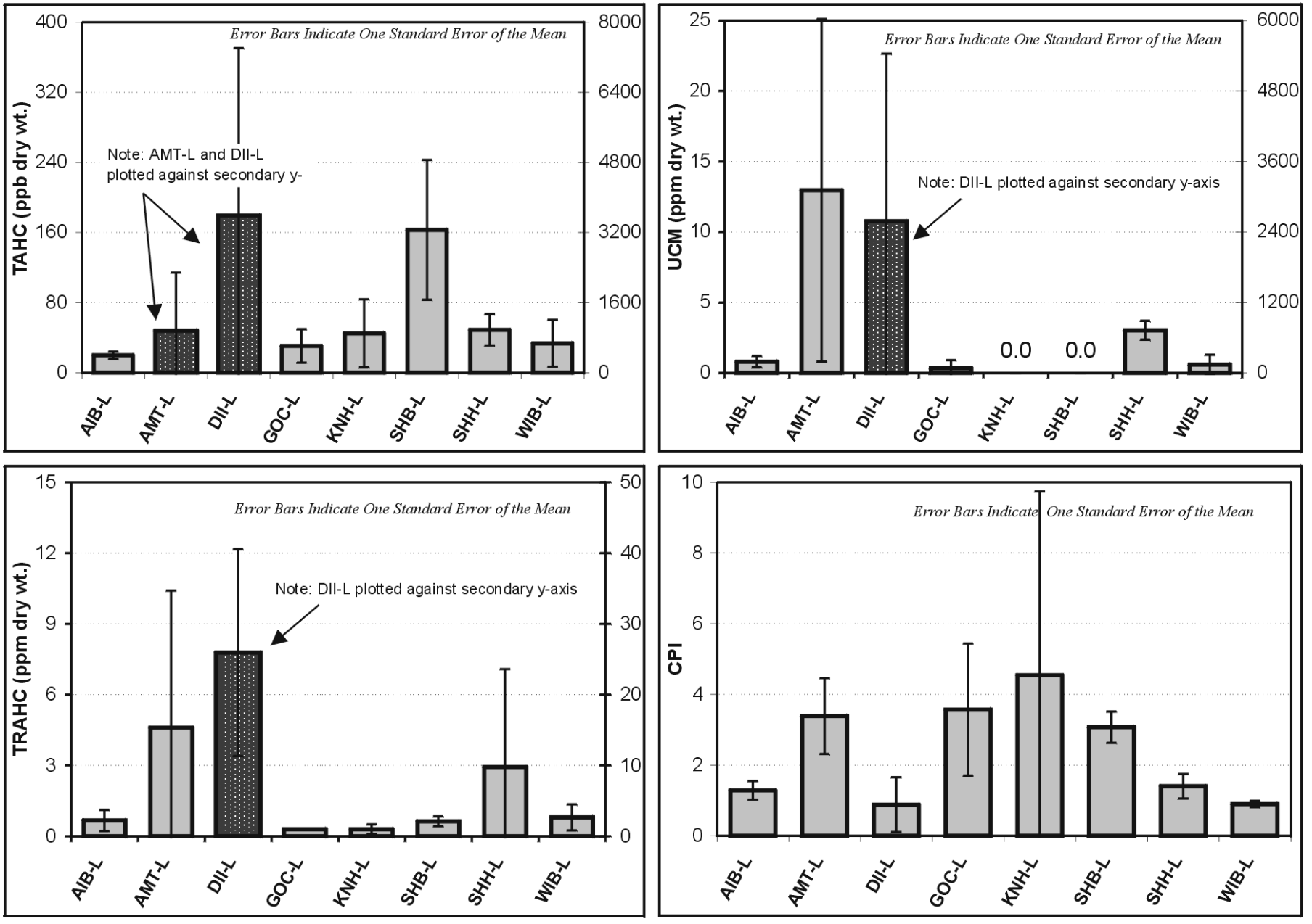

Figure 22. Mean LTEMP Intertidal Sediment TAHC, TRAHC, UCM, and CPI by Station, July 1998.

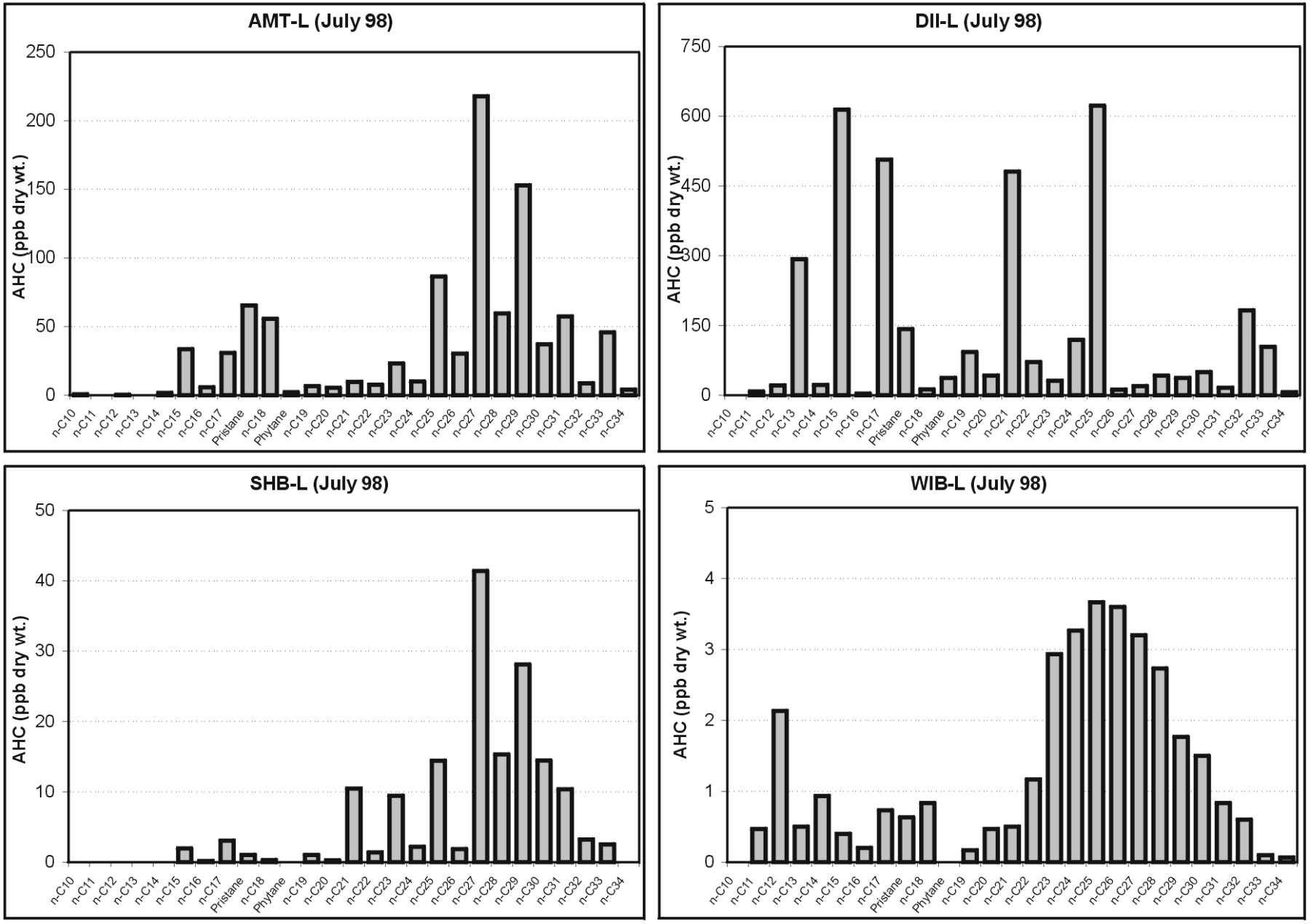

Figure 23. Mean LTEMP Intertidal Sediment AHC Fingerprints - July 1998 Survey, Stations AMT-L, DII-L, SHB-L, and WIB-L.

many of the stations. This parameter corresponds fairly well with the mean TAHC levels seen at these stations at the higher levels, with the two highest mean TRAHC values corresponding with the two highest mean TAHC values (Station AMT at 4.6 ppm and DII at 25.9 ppm). Relatively high concentrations of TRAHC were also seen at Station SHH (2.9 ppm).

A pattern similar to that seen in TRAHC was seen in the UCM values (Table 16 and Figure 22). The UCM values were highest at Station DII (2,582 ppm), followed by AMT (13.0 ppm) and SHH (3.0 ppm). Stations KNH and SHB showed no detectable levels of UCM, and the remaining stations were all less than 1 ppm. The extremely high UCM values at Station DII indicate the presence of weathered petroleum, as does the relatively elevated level (as compared to the other stations) seen at Station AMT.

The CPI ratios are provided in Table 16 and depicted in Figure 22. The CPI values ranged from 0.9 at Stations WIB and DII to 4.5 at Station KNH. The addition of petroleum to the marine environment in general lowers the CPI ratio, therefore sites with low CPI reflect primarily petrogenic hydrocarbon inputs, whereas those with high CPI values reflect biogenic inputs. Stations with relatively high values (> 3) were Stations AMT, GOC, KNH, and SHB, which indicated biogenic contributions to hydrocarbons in intertidal sediments at these sites.

The CRUDE index values calculated for intertidal sediments are provided in Table 15 and Figure 20. Mean values ranged from 12.0 at Station GOC to 48,703 at Station DII. As expected, the highest mean CRUDE index value was seen at Station DII, which exhibits clear EVOS contamination and showed the highest mean TPAH, TAHC, and UCM values. The next highest mean CRUDE index value, shown at Station AMT (122.7) was clearly elevated compared to the remaining stations, also indicating petroleum contamination. Unlike in the tissue samples, the CRUDE index does provide a useful tool for comparison between sediments. The calculation serves to normalize the concentrations against the sources so that actual petroleum contamination can be identified. The calculation magnifies petrogenic inputs relative to biogenic inputs in the AHC fraction, magnifies petrogenic inputs relative to pyrogenic inputs in the PAH fraction, and accounts for weathered petroleum in the UCM fraction. For example, Station SHB showed relatively high mean TPAH and TAHC values on the order of approximately three times that seen at Station KNH, SHH, and WIB, which initially made this station appear to be potentially contaminated with petroleum. However, this station exhibited a mean CRUDE index which was nearly identical to these three stations as a result of high biogenic and pyrogenic inputs and a non-detectable UCM fraction seen at this site. This indicated that the high levels of hydrocarbons seen at SHB were not the result of petroleum contamination.

5.3.3 Total Organic Carbon

Concentrations of TOC in sediments were variable among stations but fairly consistent within most stations (Table 17, Figure 20, and Appendix B). Mean TOC concentrations at the intertidal sites in July 1998 ranged from 0.05 % at Station SHH to 0.76 % at Station DII. The next highest TOC concentration was seen at Station AMT at 0.72 %. As mentioned previously, AMT and DII were also the two sites which exhibited the highest overall hydrocarbon concentrations. In general, mean TOC concentrations were very low at all of the intertidal sites and were substantially lower than those seen historically in the offshore sediments.

5.3.4 Particle Grain Size

As expected, the sediments encountered at the intertidal sampling sites were quite coarse as compared to subtidal sediments. Prior to the introduction of the intertidal sediment sampling, no gravel had been reported at any of the LTEMP subtidal sediment stations. Particle grain size results are provided in Table 17 and Appendix B. Sediment samples primarily consisted of sand and gravel rather than silt and clay. For ease of presentation, these have been grouped here into the coarser fraction (sand plus gravel) and the finer fraction (silt plus clay). Appendix B provides individual analyte data by replicate.

With the exception of Station AMT, mean sand plus gravel fraction was > 98 percent at all stations. Sediments were less coarse at Station AMT which exhibited the lowest mean sand plus gravel percentage (80.2) and therefore showed the highest silt plus clay fraction (19.8 percent). This station showed a large amount of variability between replicates

Table 17. LTEMP Intertidal Sediment PGS and TOC Results for July 1998.

Station	Sand + Gravel (%)				Silt + Clay (%)				TOC (%)			
	Rep. 1	Rep. 2	Rep. 3	Mean	Rep. 1	Rep. 2	Rep. 3	Mean	Rep. 1	Rep. 2	Rep. 3	Mean
AIB-L	100.0	100.0	100.0	100.0	0.0	0.0	0.0	0.0	0.28	0.23	0.28	0.26
AMT-L	97.1	91.0	52.4	80.2	2.9	9.0	47.6	19.8	0.40	0.44	1.33	0.72
DII-L	99.7	96.9	99.1	98.6	0.3	3.1	0.9	1.4	0.40	1.38	0.49	0.76
GOC-L	100.0	100.0	100.0	100.0	0.0	0.0	0.0	0.0	0.23	0.21	0.22	0.22
KNH-L	99.8	100.0	99.9	99.9	0.2	0.0	0.1	0.1	0.12	0.14	0.17	0.14
SHB-L	99.5	99.5	100.0	99.7	0.5	0.5	0.0	0.3	0.41	0.46	0.51	0.46
SHH-L	100.0	100.0	100.0	100.0	0.0	0.0	0.0	0.0	0.05	0.06	0.04	0.05
WIB-L	100.0	99.5	100.0	99.8	0.0	0.5	0.0	0.2	0.16	0.23	0.25	0.21

with replicate three showing the finest sediments (47.6 percent silt plus clay). This replicate showed the highest TPAH, TAHC, TRAHC, UCM, and TOC as compared to the other two replicates at this station. While it is known that hydrocarbons adhere to fine-grained particulates, examination of the data indicated that the elevated hydrocarbons at Station AMT are not simply a function of grain size.

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 8. A review of the QC data reported during the 1998 - 1999 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").

As described in Section 5.2.1, results reported for C_2-chrysene in the March 1999 (Survey 13) tissue samples were problematic. While these values were mostly still below the MDL, they were clearly elevated and were identified with the "M" qualifier in the data to indicate a matrix interference. Unfortunately, investigation in the laboratory showed no clear justification for the elevation of this one analyte, and quality control samples performed with both sample batches for this survey were within normal limits for this analyte. Very small sample tissue volumes were encountered during this survey, so re-analysis of the sample set was not possible. Due to this interference, C_2-chrysene was excluded from the TPAH calculations and the PAH fingerprint figures for this survey. It was also excluded from the FFPI and CRUDE index calculations.

5.4.1 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 QC 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 non-compliant recoveries (< 40 or > 120 percent) included deuterated n-C_{12} (three samples), deuterated n-C_{20} (four samples), and deuterated n-C_{30} (seven samples).

A number of surrogates were reported with the "D" qualifier indicating that the samples (intertidal sediment samples collected at Station DII in July 1998) required dilution and that the surrogate recoveries, which no longer related to loss of analytes during the extraction, were assumed to be 100 percent.

5.4.2 Procedural Blanks

Procedural blanks analyzed in conjunction with tissue and sediment analyses for the 1998 - 1999 LTEMP did not show PAH or AHC analytes at concentrations greater than three times the MDL. The 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 some of the 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.

5.4.3 Matrix Spike/Spike Duplicates and Laboratory Blank Spike/Spike Duplicates

Analyses of the 1998 - 1999 LTEMP samples included the analysis of matrix spike/spike duplicate or laboratory blank spike/spike duplicate pairs for PAH and/or AHC. Use of the laboratory spikes was required when insufficient sample material existed (as described in Section 4.2.4), as was the case for all tissues collected in March 1999.

While some individual analytes showed high percent recoveries and were qualified with a AQ@, most samples passed the QA criteria for average percent recovery and RPD. All matrix spike/spike duplicate (or laboratory blank spike/spike duplicate) analyses reported for PAH and AHC in tissue passed the QA criteria for average percent recovery and RPD. However, one blank spike duplicate (batch T1009 in March 1999) was lost in the laboratory during the extraction and cleanup, so no data are reported for this sample. All matrix spike/spike duplicate samples analyzed in conjunction with intertidal sediment batches for PAH and AHC passed the QA criteria for average percent recovery and RPD.

5.4.4 Reference Oil

Reference oil samples of EVOS oil were reported for PAH and AHC during the 1998 - 1999 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. Four of the reference oil samples run in conjunction with tissue analyses showed elevated levels of one or two individual analytes (n-C_{13}, n-C_{25}, n-C_{32}, and C_2-naphthalenes). The five individual analyte results showing values outside the acceptable limits were investigated, and each data point was appropriately qualified with the AQ@ qualifier. Overall, QA criteria were met for reference oil samples analyzed for the 1998 - 1999 LTEMP.

5.4.5 Standard Reference Materials

Standard Reference Materials (NIST 1974a and 2974 [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 in tissues were all less than 10 times the MDL and were properly qualified as such; no further action was required. Analytes exhibiting high recoveries in sediments, biphenyl and acenaphthylene, were checked for interferences and were properly qualified as "Q"; no further action was required. Also, reported PAH analytes having noncertified values were compared to laboratory acceptance limits and also appropriately qualified.

The AHC data reported for these samples are incidental as no certified or uncertified values exist for this method. These data are unqualified as no appropriate comparison values are available.

The four SRMs that were run for TOC were all within the laboratory's acceptance limits with recoveries more than 80 % of the certified value.

5.4.6 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 PWS98PGS0040 and PWS98PGS0050 (sand) showed low RPDs of 0.0 based on a 100 % sand fraction in both samples.

In addition, duplicate analyses were performed for both tissue and sediment PAH and AHC for the July 1998 samples. March 1999 tissue samples contained insufficient material to perform these analyses. Duplicate analyses for PAH and AHC can be compared with the original sample results to provide an estimate of precision, but specific QC criteria do not exist for these.

6.0 SUMMARY

The 1998 - 1999 LTEMP has added additional data to the information that has been collected since 1993. During the program year reported here (1998 - 1999), nine stations were sampled twice for intertidal mussels. In addition, eight newly-established intertidal sediment stations were sampled once during 1998. Analytical strategy for the 1998 - 1999 program was the same as the last few years of LTEMP except for the inclusion of AHC analysis for tissues and the reporting of several other AHC parameters for both tissues and sediments.

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, coal residues or natural oil seepage, and atmospheric fallout. Recent data presented by Short et al. (1999) and other sources indicate that the background signature previously attributed to natural oil seeps in the Katalla and Yakataga regions may actually originate in coal deposits. While the actual source of this signature is controversial at this time, LTEMP results at some stations clearly exhibit this background fingerprint. Examination of hydrocarbon data for both tissues and sediments indicated that hydrocarbons from a variety of these sources can be identified in the 1998 - 1999 data. For many stations, these sources are similar to those that had been identified in earlier program reports (KLI, 1993b; 1994a; 1995a; 1996a; 1997a, and 1998) and by other researchers examining LTEMP data (Payne et al., 1998).

The LTEMP data indicate that hydrocarbons in tissues in the study area vary between stations, and, to a lesser extent, over time. The PAH levels in tissues were generally very low and at levels less than that seen in recent years. Most individual analytes were reported at below-MDL levels. The apparent increasing trend in tissue TPAH that had been seen over the last several years of LTEMP was not apparent this year. In fact, a comparison of this year's data with the historical data shows that many of the mean TPAH values have dropped to relatively low levels as compared to the prior three surveys.

The AHC compounds in tissues were considerably higher than the PAH, as was expected due to the naturally-occurring compounds in mussel tissues that interfere with the AHC analysis. Since this parameter had not been examined in tissues since 1994, no comparison of long-term trends was possible. As in the 1993 - 1994 program, large seasonal differences in AHC distributions were seen at all stations; this is likely to be related to spawning or seasonal feeding factors, which makes interpretation of these data difficult. In addition, anomalously low AHC concentrations (and other AHC parameters such as UCM) were seen at the Gulf of Alaska stations (AIB, SHH, and WIB) during March 1999; these can probably be attributed to the extreme winter conditions that caused a die-off of mussels and other intertidal animals in the region.

Analysis and reporting of AHC and associated parameters (TRAHC, UCM, and CPI) in mussel tissues did not appear to provide useful additional information regarding hydrocarbon levels or sources. It did confirm that large amounts of naturally-occurring compounds chromatographically similar to the target analytes are present in the tissues. State-of-the-art purification steps are not sufficient in removing these interfering compounds without removing some of the target AHC themselves, thereby further confounding the results. In addition, while it is understood that AHC is a relatively large component of petroleum hydrocarbons in comparison to PAH, it is clear in the LTEMP dataset that PAH sampling in tissues has been sufficient to determine spill impacts in the past.

Although tissue PAH concentrations were low, PAH fingerprints from many stations exhibited a petrogenic hydrocarbon signal which could be attributed to several sources. As in many of the past surveys, hydrocarbons in the tissues at both Stations AMT and GOC during March 1999 were attributed to ANS crude, with the most likely source identified as the Alyeska Marine Terminal and tanker operations. Lesser amounts of pyrogenic hydrocarbons were also seen at both AMT and GOC. In contrast to most past results, a background signature was present in mussels at Station AMT during July 1998. The fact that this signature was visible may be due to the very low levels of PAH seen in July 1998, which may reflect normal ("non-contaminated") levels in these mussels (i.e., with no petroleum inputs from operations at the Alyeska Marine Terminal). Mussels at Station DII, a site heavily oiled during the EVOS, exhibited very low levels of PAH this year and showed inputs from a combination of factors, including EVOS/ANS crude, background, and pyrogenic sources. Other stations exhibiting background signatures included Station AIB, KNH, SHB, SHH, SLB, and WIB. Pyrogenic inputs were also apparent at Stations AIB, SLB, and WIB.

Levels of hydrocarbons in intertidal sediments were more variable. Both PAH and AHC levels ranged from quite low at most sites to extremely high at the Disk Island site (DII) where visibly oiled sediments were collected. Hydrocarbons at Station DII were attributed to EVOS/ANS crude. Sediments at Station AMT also contained elevated levels of both PAH and AHC relative to the other stations which were attributed to ANS crude and pyrogenic inputs. Both of these stations showed some evidence in the AHC fraction of biogenic inputs as well. Other stations showed very low levels of hydrocarbons with varying degrees of petrogenic, pyrogenic, and biogenic inputs. All of the intertidal sediments consisted of fairly coarse-grained materials; most were approximately 99 percent sand plus gravel and contained very little of the finer fraction (silt plus clay). Intertidal sediments at Station AMT were less coarse, with one replicate having nearly 48 percent fines. While it is known that hydrocarbons adhere to fine-grained particulates, examination of the data indicated that the elevated hydrocarbons at Station AMT were actual and not simply a function of grain size. Total organic carbon results were lower than those seen in the past for the subtidal sediment sampling.

Although the intertidal sediment sampling appears to add little to the LTEMP dataset in terms of actual hydrocarbon concentrations, it actually has provided critical information that may be useful in the future. First, it showed that, at eight of the nine pre-existing LTEMP sites, intertidal sediments may be sampled in the area immediately adjacent to the mussel sampling areas. Since sampling of intertidal sediments was not part of the initial program design, stations had not been located in areas that were necessarily amenable to this type of sampling. Intertidal sediment sampling at Sleepy Bay was not performed because of the cobble-armored beach that exists there. However, it should be noted that *subsurface* intertidal sediment could be collected there with the removal of some of the surface armor. Due to the porous nature of this type of beach, oil does reach the subsurface sediments and could potentially be documented there. Although these intertidal sediments are coarse and transient in nature due to the physical processes occurring along these beaches, it is possible to collect and analyze them for the same parameters historically used on the LTEMP. Second, it indicates that, although the sediments are coarse in nature, measurable quantities of hydrocarbons may still reside in them if hydrocarbons have been (or are being) released into the marine system, as seen at the Disk Island (DII) and Alyeska Marine Terminal (AMT) sites. This means that should a spill event occur, these pre-existing sites could be sampled to determine potential spill impacts. Finally, the intertidal sediment data proved to support the application for sediments of the CRUDE index used by Payne et al. (1998) during their review of the LTEMP 1993 - 1997 data. The CRUDE index calculation served to normalize the hydrocarbon concentrations against the sources so that actual petroleum contamination could be identified. This index is a useful tool which can be used to help identify petrogenic inputs in sediments.

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9.0 WEB SITE ACCESS

The PWS RCAC maintains a web site at which selected LTEMP reports and data can be accessed. The following reports and data are available for download:

- 1998 – 1999 Annual LTEMP Monitoring Report
- 1997 – 1998 Annual LTEMP Monitoring Report
- LTEMP Data Analysis of Hydrocarbons in Intertidal Mussels and Marine Sediments
- Monitoring Program Database (1993 –1998) and subsets

To download these documents and data, please visit the site at www.pwsrcac.org.

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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

CRUDE index - an index formulated by Payne et al. (1998) which serves to normalize the hydrocarbon concentrations against their sources so that actual petroleum contamination can be identified. Used to help determine relative petrogenic inputs and defined as follows:

$$CRUDE = (TPAH \times FFPI/100) + (TAHC/CPI^2) + UCM/1000$$

(where all concentrations are in the same units)

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.

Intertidal - the area on a marine beach between the high and low tide lines

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

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 gravel (if applicable), 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) - sum of the target aliphatic hydrocarbons

Total polycyclic aromatic hydrocarbons (TPAH) – sum of the target polycyclic aromatic hydrocarbons (excluding perylene)

Total revolved aliphatic hydrocarbons (TRAHC) - the sum of total resolved aliphatic hydrocarbons which includes the AHC analytes (n-C_{10} through n-C_{34} and pristane and phytane) plus other compounds such as plant waxes and lipids which are not individually identified or reported

Total resolved and unresolved aliphatic hydrocarbons (TRUAHC)- the total area of resolved and unresolved aliphatic hydrocarbons represented by the total area of the GC run, whether or not these compounds have been identified

TPAH - total polycyclic aromatic hydrocarbons

TRAHC - total resolved aliphatic hydrocarbons

TRUAHC - total resolved and unresolved aliphatic 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