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PRINCE WILLIAM SOUND RCAC

LONG-TERM ENVIRONMENTAL MONITORING PROGRAM

2000 - 2002 LTEMP MONITORING REPORT

Presented to:

Regional Citizens' Advisory Council
Scientific Advisory Committee
3709 Spenard Road
ANCHORAGE, AK 99503
(907) 277-7222 FAX 277-4523

Presented by:

KINNETIC LABORATORIES INCORPORATED
403 West 8th Avenue Anchorage, AK 99501
(907) 276-6178 FAX 278-6881
e-mail: kinnetic@alaska.net

With Analytical Services and
Technical Support Provided by:

GERG TEXAS A&M UNIVERSITY
The Geochemical and Environmental Research Group

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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 human-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 performed by Kinnetic Laboratories, Inc. under the administration of the Council's Scientific Advisory Committee.

This monitoring report includes data collected during six surveys performed during the period of July 2000 through March 2002. Mussel samples were collected from indigenous (native) intertidal blue mussel populations for the analysis of hydrocarbons in tissues at ten sites during four of the surveys (July 2000, March and July 2001, and March 2002). Stations sampled included Aialik Bay, Alyeska Marine Terminal (Saw Island), Disk Island, Gold Creek, Knowles Head, Sheep Bay, Shuyak Harbor, Sleepy Bay, Windy Bay, and Zaikof Bay. In addition to the mussels, subtidal sediments were collected at the two Port Valdez Alyeska Marine Terminal and Gold Creek stations during these surveys. Two additional mussel sampling surveys were completed at these two Port Valdez stations during October 2000 and 2001 to increase temporal coverage of these stations.

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 mussel tissues and marine sediments. 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 current program was the same as the prior year of the program.

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 human activities such as the T/V *Exxon Valdez* oil spill in March 1989, operations at the Alyeska Marine Terminal, and oil transportation activities such as tanker and oil spill response operations; 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 2000 - 2002 data. For many stations, these sources are similar to those identified in earlier LTEMP reports and by other researchers examining LTEMP data. It should be noted, however, that many of the concentrations reported here are at or below method detection limits. These detection limits are based on a statistical method used to determine the lowest concentration that a method can accurately quantify. Values below these limits are useful for interpretation but are statistically less accurate than those above detection limits, and this should be taken into account when reviewing the data and discussion presented in this report.

Data presented in this report indicate that hydrocarbons in tissues in the study area vary considerably between stations and over time. The polycyclic aromatic hydrocarbon levels in tissues were generally low, and all were within the historical range of concentrations seen at each site. The increasing trend in tissue total polycyclic aromatic hydrocarbon levels that had been seen prior to March 1998 has not been evident since that time, with more recent surveys generally showing very low tissue concentrations. This reversal of an apparent trend underlines the intrinsic value of a long-term dataset such as that being generated by the LTEMP. A collection of long-term temporal data allows the evaluation of apparent trends in terms of the natural variability seen in the environment. Without this long-term data, impacts cannot be separated from natural variability.

Although tissue polycyclic aromatic hydrocarbon concentrations were low, fingerprints from many stations exhibited a petrogenic hydrocarbon signal which could be attributed to several sources. As in many past surveys, PAH in the tissues at the Alyeska Marine Terminal stations were attributed to a combination of natural background and pyrogenic sources, and for at least two of the six sampling events reported here, Alaska North Slope crude. As reported earlier for March 2000 and July 1998, the background signature was present in mussels at this station during several surveys in this reporting period, perhaps visible due to the very low levels of polycyclic aromatic hydrocarbons seen for these surveys. These signatures may reflect normal ("background") levels in these mussels (i.e., with no petroleum inputs from terminal operations). In contrast, no evidence of crude inputs was seen at the Gold Creek station, with background and pyrogenic sources being responsible for the low-level concentrations seen here. Mussels collected at the other program stations (Aialik Bay, Disk Island, Knowles Head, Sheep Bay, Shuyak Harbor, Sleepy Bay, Windy Bay, and Zaikof Bay) typically showed inputs from primarily background sources with lesser pyrogenic or biogenic inputs. In March 2001, the station at Sleepy Bay also showed evidence of increased pyrogenic contributions as well as possible crude contamination.

The aliphatic hydrocarbon levels in tissues were considerably higher than the polycyclic aromatic hydrocarbon concentrations, as was expected due to the naturally-occurring lipid compounds in these animals that interfere with the aliphatic hydrocarbon analyses. As in earlier results, it appears that inclusion of this analysis for mussel tissues did not provide additional information that was helpful in assessing hydrocarbon contamination or potential sources. Extremely high levels of aliphatics seen at some stations and for some analytes have been attributed to lipid interference that is inherent in this type of analysis in tissues. A large component of the aliphatic hydrocarbons documented in tissues was not attributable to petroleum and these were considered to be naturally-occurring materials that probably originated in the planktonic food source of the mussels.

Polycyclic aromatic hydrocarbons levels in subtidal sediments collected from the Alyeska Marine Terminal and Gold Creek stations were quite low. In fact, the data seen during this sampling period at the Alyeska station constituted the lowest mean total polycyclic aromatic hydrocarbon value seen to date here. While the range for the Gold Creek station was extended upward during this reporting period, levels seen here were still quite low.

Sediments at the Alyeska station exhibited polycyclic aromatic hydrocarbon signatures which indicated petroleum sources, including weathered Alaska North Slope crude, along with some lesser pyrogenic inputs for each of the surveys. As in the past, several of the surveys (July 2000 and March 2001) showed fingerprints that exhibited signatures typical of a weathered Alaska North Slope petroleum source along with additional input of pyrogenic hydrocarbons that may have had a combustion or creosote origin. The fingerprint from July 2001 exhibited a combination of sources, including background sources, Alaska North Slope crude, and pyrogenic sources. Although overall concentrations were relatively low compared to the prior two surveys, a weathered profile was still apparent. March 2002 concentrations were very low but showed a similar pattern. In contrast, the fingerprints at the Gold Creek station showed a petrogenic background and pyrogenic signature with a predominance of pyrogenic inputs for all four surveys.

Aliphatic hydrocarbon levels in sediments during this reporting period were higher than historical levels at both the Alyeska Marine Terminal and Gold Creek stations, extending upward the range of mean values seen to date. As noted for the tissues, there was some evidence of elevated concentrations of some analytes being due to influences of plant lipids on the aliphatic analysis, particularly at the Gold Creek station. The aliphatic fingerprints at the Alyeska station indicated inputs of primarily a petrogenic nature with a weathered source along with smaller amounts of biogenic inputs. In contrast, the fingerprints at Gold Creek showed a predominance of alkanes which are associated with plant material (a biogenic source).

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 last two years of the monitoring program. It includes results from the six LTEMP surveys between July 2000 and March 2002. 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; 1998; 1999; and 2000). For the reader's convenience, a Glossary and List of Acronyms is provided at the end of this document. In addition, information on web site access to LTEMP information is provided in Section 9.0 of this report.

2.0 STUDY DESIGN AND APPROACH

2.1 Sampling Design

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

Sampling reported here was performed in July 2000 (Survey 17), October 2000 (Survey 18), March 2001 (Survey 19), July 2001 (Survey 20), October 2001 (Survey 21), and March 2002 (Survey 22). For convenience, these surveys are referred to using the survey number or the first month during which samples were collected for that survey (e.g., Survey 17 or July 2000). Indigenous mussel samples 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 polycyclic aromatic hydrocarbons (PAH); aliphatic hydrocarbons (AHC) which included the total resolved aliphatic hydrocarbons (TRAHC) and the unresolved complex mixture (UCM); and percent lipid content. Twenty additional mussels were collected at each station for assessment of gonadal state.

Sediments were obtained during winter and summer surveys from the nearshore subtidal areas immediately adjacent to the mussel sampling site at two stations (Alyeska Marine Terminal and Gold Creek). Three replicate samples of surficial sediment (0 - 2 centimeters [cm]) from each subtidal sediment station were collected using a modified Van Veen grab, as described in earlier program reports. These sediment samples were analyzed for PAH, AHC, TRAHC, and UCM; total organic carbon (TOC); and particle grain size (PGS).

Analytical strategy is summarized in Table 1; analytical methods are described in Section 3.2. The analytical approach included the use of compound-specific measurements for organic parameters such as PAH and AHC to allow the assessment of hydrocarbon concentrations in tissue and sediment. Mussels were also analyzed for 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. These sites had begun to recover and be re-colonized in July 1999, but sampling at Windy Bay had to be shifted by 30 m at one time to obtain the mussel samples because the original transect no longer contained mussels large enough to sample.

Ten stations were sampled during LTEMP 2000 – 2002 (Table 2; Figures 1 – 10). These are Aialik Bay (AIB), Alyeska Marine Terminal (AMT; at Saw Island), Disk Island (DII), Gold Creek (GOC), Knowles Head (KNH), Sheep Bay (SHB), Shuyak Harbor (SHH), Sleepy Bay (SLB), Windy Bay (WIB), and Zaikof Bay (ZAB).

Table 1. 2000 - 2002 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 2000 - 2002 LTEMP.

Station Location	Station Designation	Station Type	Sampling Date	Survey No.	Average Height (m) Above or Below MLLW	Global Positioning System (GPS) Coordinates	
						Latitude (N)	Longitude (W)
AIALIK BAY	AIB-B	Intertidal Mussel	8/6/00	17	1.4	59°52'44.1"	149°39'35.7"
			4/12/01	19	1.6	59°52'44.1"	149°39'35.9"
			7/25/01	20	1.3	59°52'44.3"	149°39'35.7"
			3/30/02	22	1.6	59°52'44.3"	149°39'36.0"
ALYESKA MARINE TERMINAL	AMT-B	Intertidal Mussel	7/21/00	17	1.4	61°05'24.9"	146°24'29.7"
			10/12/00	18	2.0	61°05'27.1"	146°24'29.3"
			3/28/01	19	2.0	NA	NA
			7/22/01	20	1.4	61°05'24.6"	146°24'30.3"
			10/17/01	21	1.3	61°05'24.9"	146°24'30.0"
			3/15/02	22	1.9	61°05'25.0"	146°24'30.3"
	AMT-S	Subtidal Sediment	7/21/00	17	-66	61°05'23.5"*	146°23'40.9"*
			3/28/01	19	-68	61°05'23.5"*	146°23'41.2"*
			7/22/01	20	-68	61°05'22.8"*	146°23'41.3"*
			3/15/02	22	-66	61°05'23.9"*	146°23'41.2"*
DISK ISLAND	DII-B	Intertidal Mussel	7/20/00	17	2.9	60°29'54.2"	147°39'40.4"
			3/24/01	19	1.1	60°29'54.3"	147°39'40.2"
			7/18/01	20	1.7	60°29'54.3"	147°39'40.4"
			3/12/02	22	1.8	60°29'54.4"	147°39'40.4"
GOLD CREEK	GOC-B	Intertidal Mussel	7/21/00	17	1.2	61°07'27.4"	146°29'45.9"
			10/12/00	18	1.0	61°07'27.8"	146°29'45.7"
			3/28/01	19	1.1	61°07'27.5"	146°29'46.2"
			7/22/01	20	0.7	61°07'27.4"	146°29'46.9"
			10/17/01	21	1.2	61°07'27.4"	146°29'46.1"
			3/10/02	22	1.3	NA	NA
	GOC-S	Subtidal Sediment	7/20/00	17	-29	61°07'26.7"*	146°29'35.0"*
			3/28/01	19	-25	61°07'25.3"*	146°29'36.2"*
			7/21/01	20	-25	61°07'25.3"*	146°29'34.7"*
			3/15/02	22	-26	61°07'26.3"*	146°29'35.9"*
KNOWLES HEAD	KNH-B	Intertidal Mussel	7/18/00	17	2.7	60°41'25.7"	146°35'08.4
			3/27/01	19	2.6	60°41'26.3"	146°35'08.7"
			7/20/01	20	2.3	60°41'26.5"	146°35'08.7"
			3/14/02	22	2.3	60°41'26.4"	146°35'09.2"
SHEEP BAY	SHB-B	Intertidal Mussel	7/18/00	17	3.6	60°38'45.9"	145°59'50.7"
			3/27/01	19	2.1	60°38'45.9"	145°59'51.0"
			7/20/01	20	1.9	60°38'46.3"	145°59'51.0"
			3/14/02	22	2.6	60°38'46.0"	145°59'51.0"
SHUYAK HARBOR	SHH-B	Intertidal Mussel	8/6/00	17	2.4	58°30'05.3"	152°37'38.7"
			4/11/01	19	2.0	58°30'05.2"	152°37'39.1"
			7/25/01	20	2.2	58°30'05.2"	152°37'38.9"
			3/30/02	22	2.4	58°30'04.8"	152°37'39.2"
SLEEPY BAY	SLB-B	Intertidal Mussel	7/19/00	17	2.4	60°04'02.3"	147°50'00.1"
			3/25/01	19	2.2	60°04'02.1"	147°49'59.9"
			7/19/01	20	2.4	60°04'02.3"	147°50'00.0"
			3/13/02	22	2.4	60°04'02.3"	147°50'00.0"
WINDY BAY	WIB-B	Intertidal Mussel	8/6/00	17	2.6	59°13'05.3"	151°31'11.3"
			4/12/01	19	1.8	59°13'05.8"	151°31'12.9"
			7/25/01	20	1.8	59°13'05.2"	151°31'11.6"
			3/30/02	22	2.0	59°13'05.7"	151°31'13.0"
ZAIKOF BAY	ZAB-B	Intertidal Mussel	7/18/00	17	2.1	60°15'54.6"	147°05'06.8
			3/26/01	19	1.9	60°15'54.7"	147°05'07.2"
			7/19/01	20	2.3	60°15'54.5"	147°05'07.1"
			3/13/02	22	2.0	60°15'54.7"	147°05'07.0"

NA Not Available * Differential Global Positioning System (DGPS) used to document station position

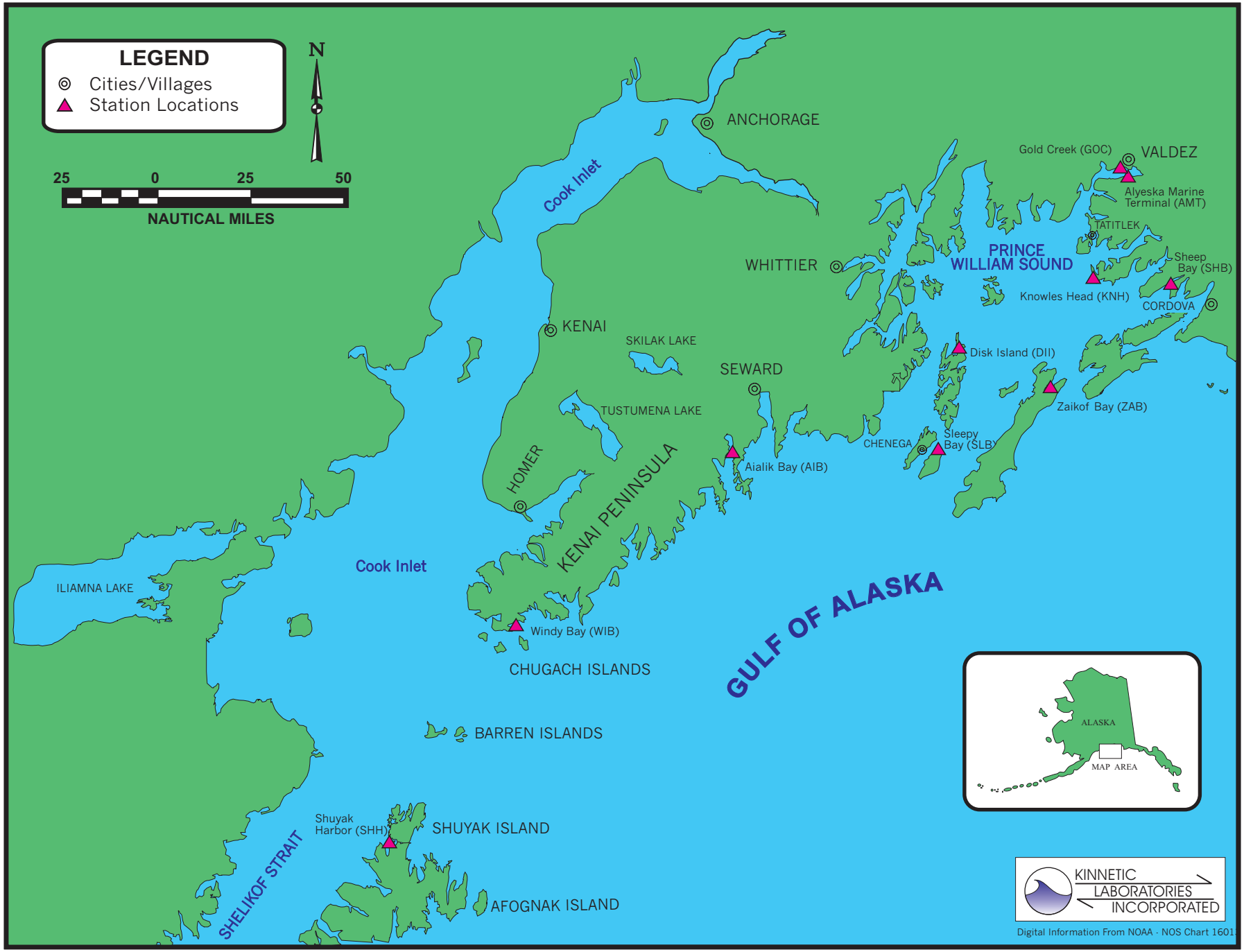


Figure 1. LTEMP Station Locations (Overall Study Area).

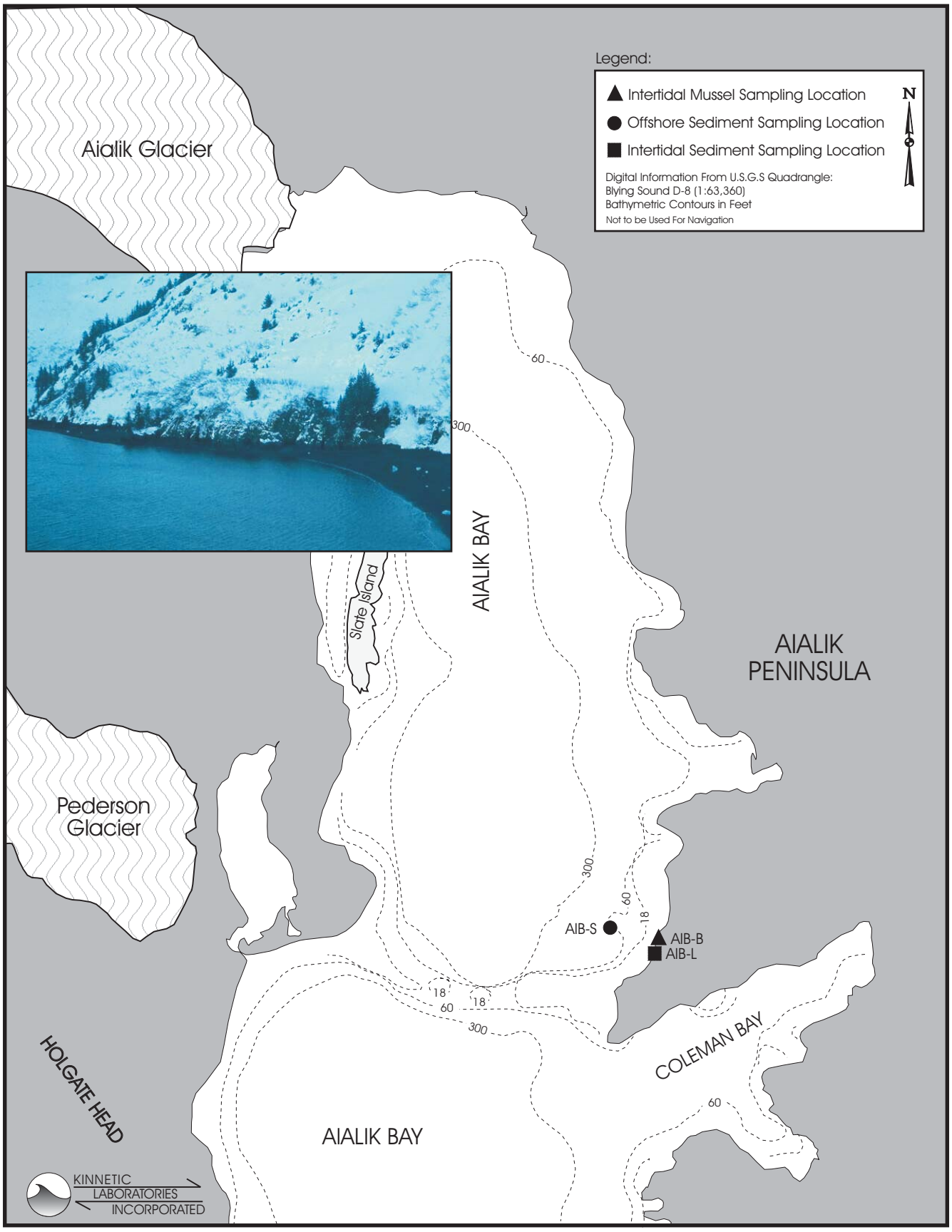


Figure 2. LTEMP Sampling Locations at the Aialik Bay Station.

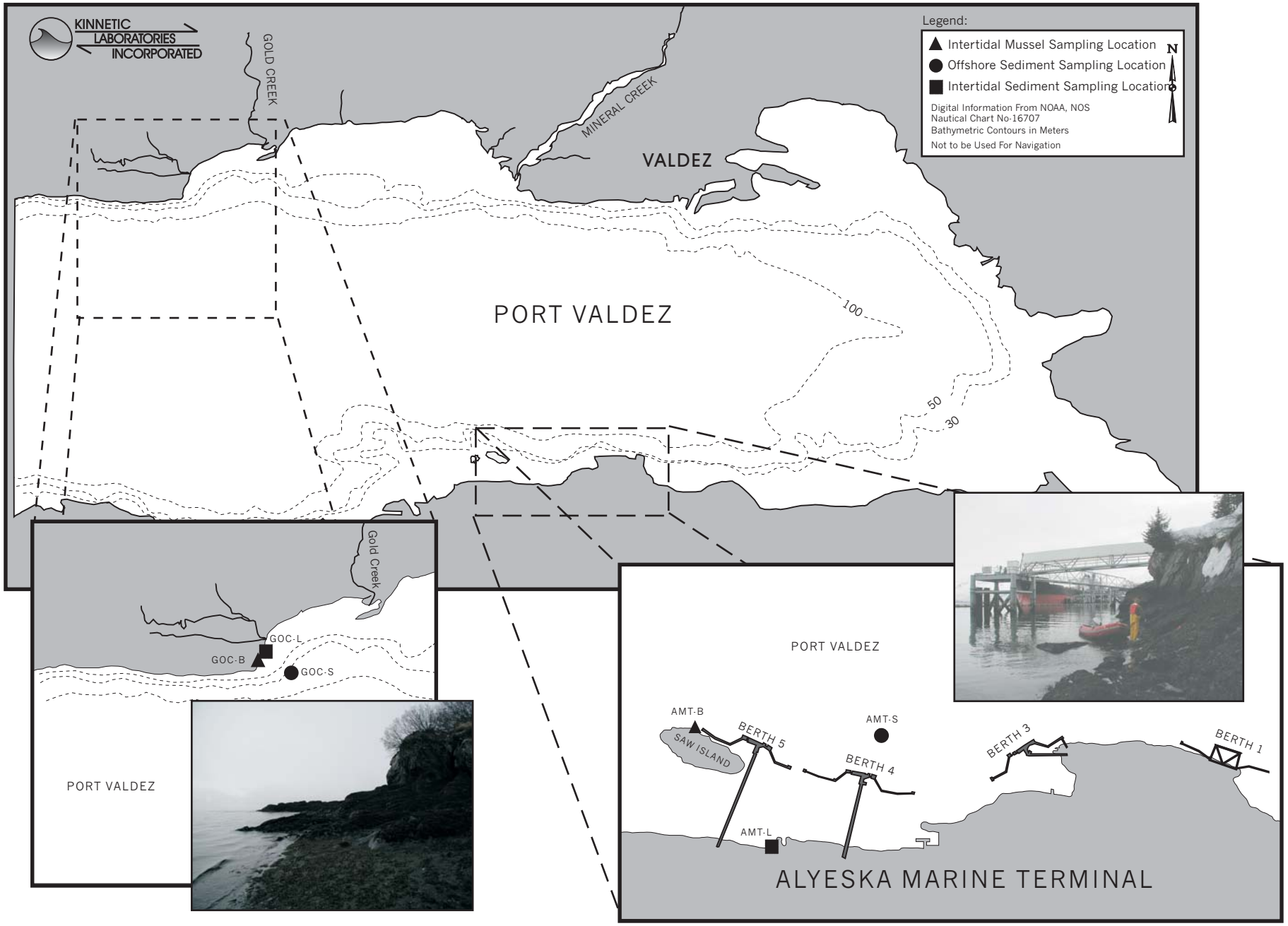


Figure 3. LTEMP Sampling Locations at the Alyeska Marine Terminal and Gold Creek Stations.

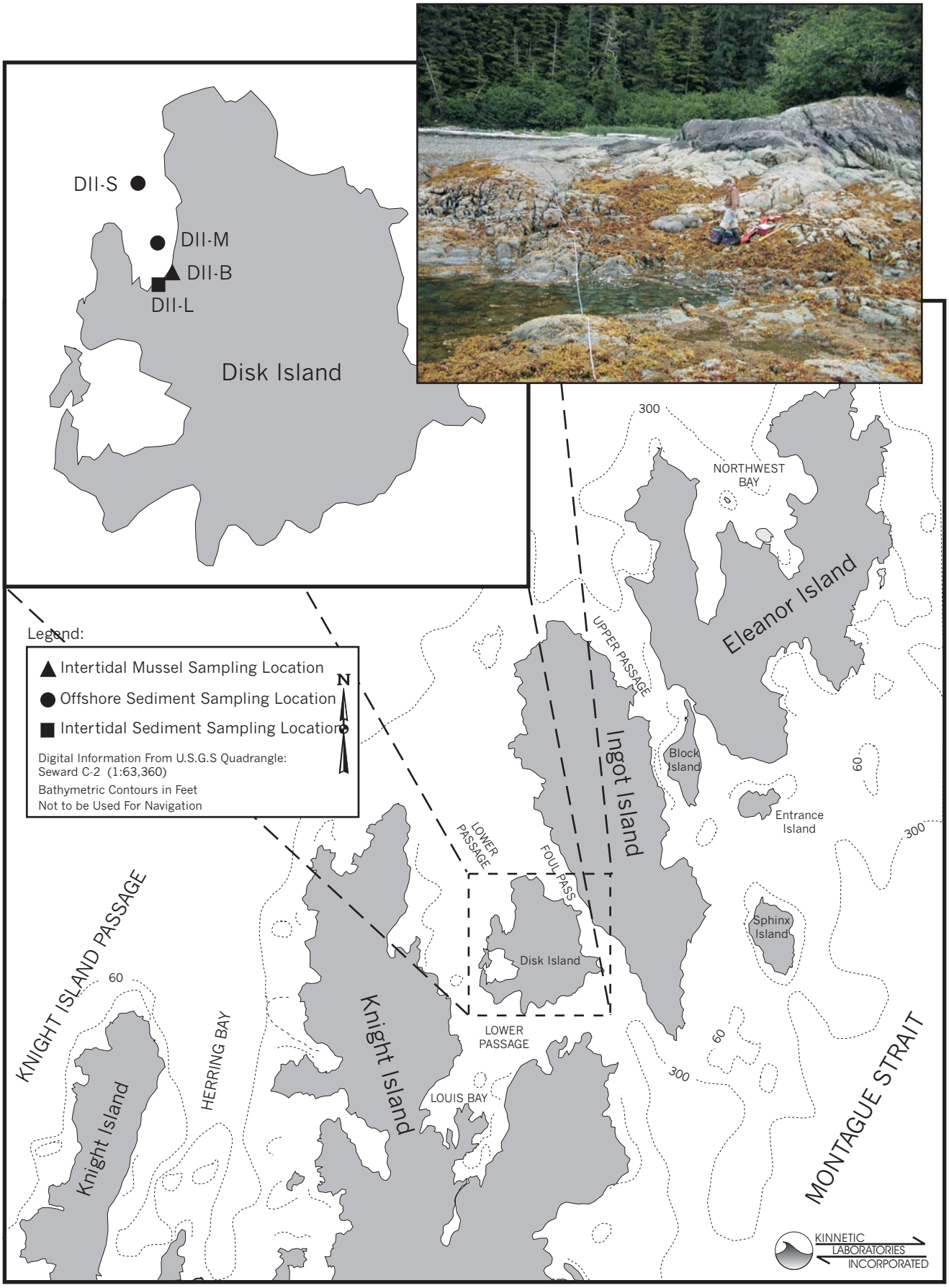


Figure 4. LTEMP Sampling Locations at the Disk Island Station.

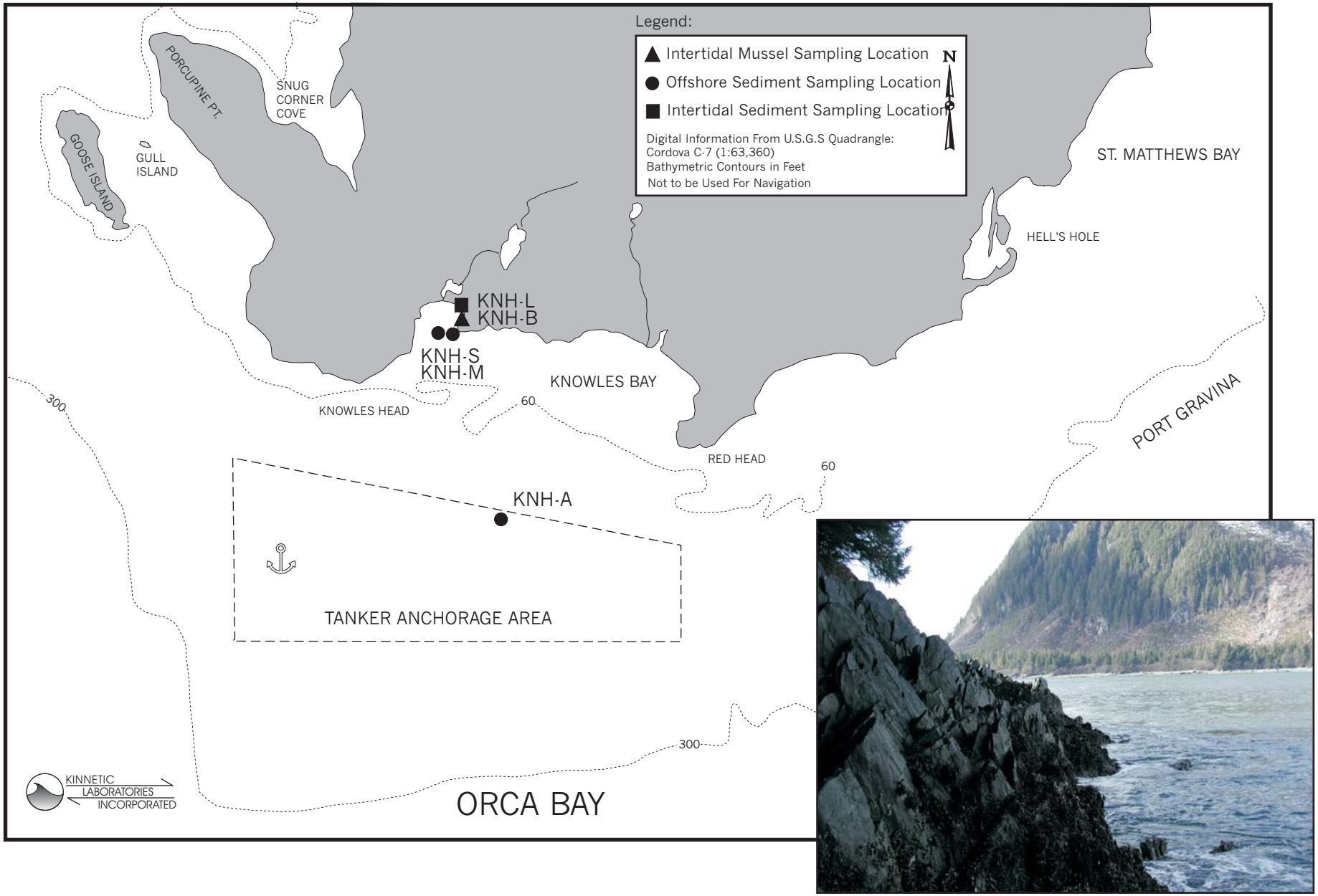


Figure 5. LTEMP Sampling Locations at the Knowles Head Station.

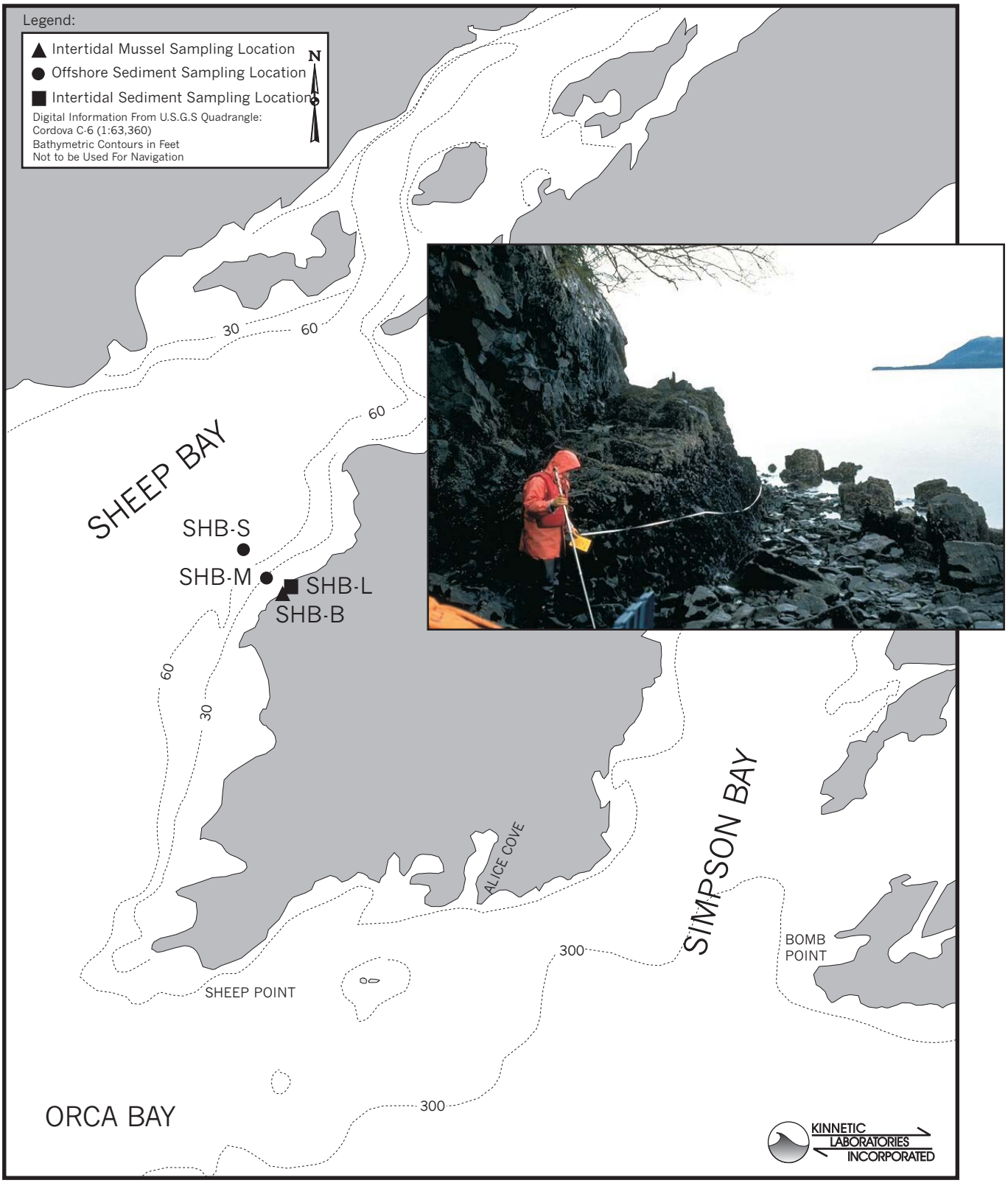


Figure 6. LTEMP Sampling Locations at the Sheep Bay Station.

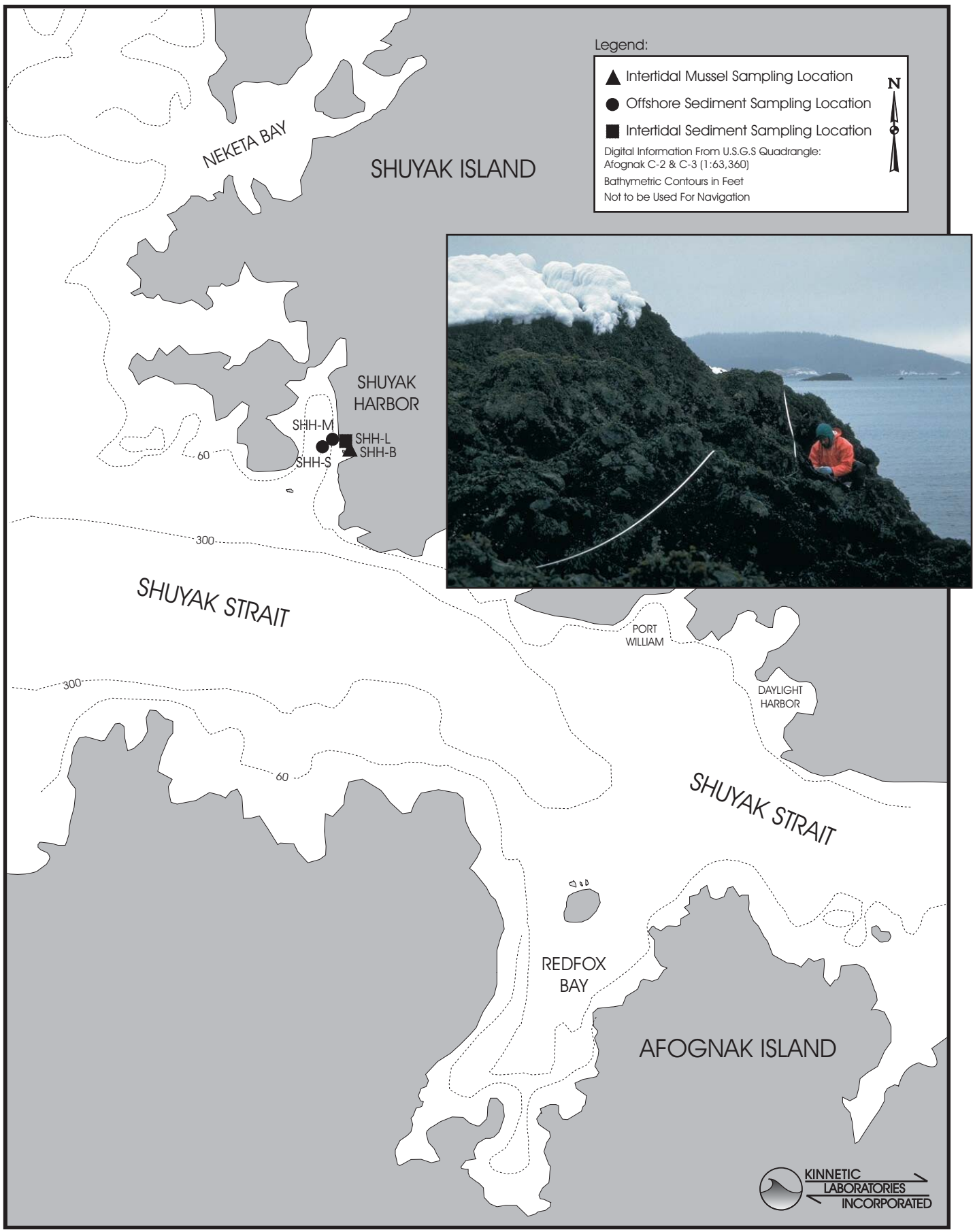


Figure 7. LTEMP Sampling Locations at the Shuyak Harbor Station.

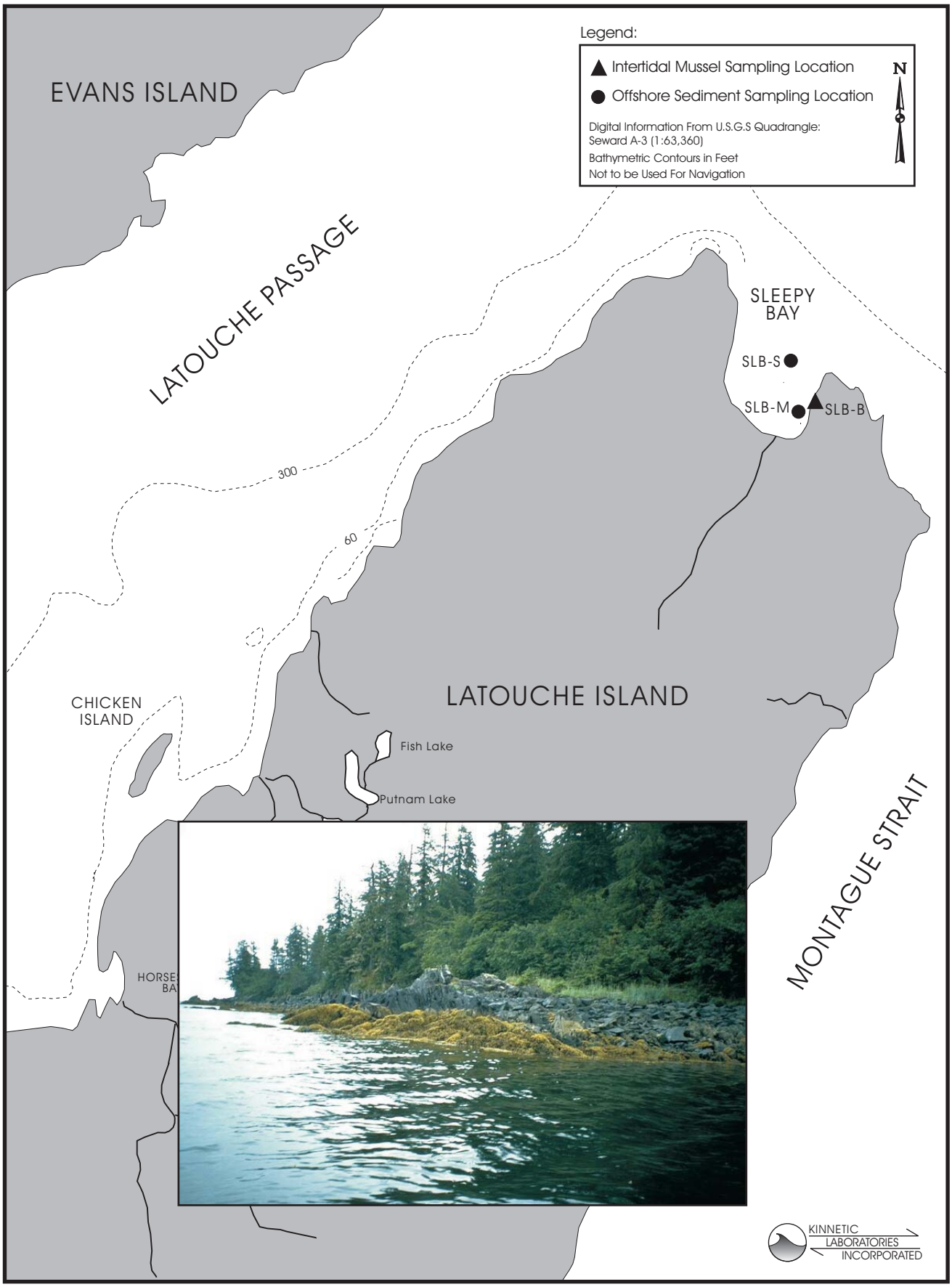


Figure 8. LTEMP Sampling Locations at the Sleepy Bay Station.

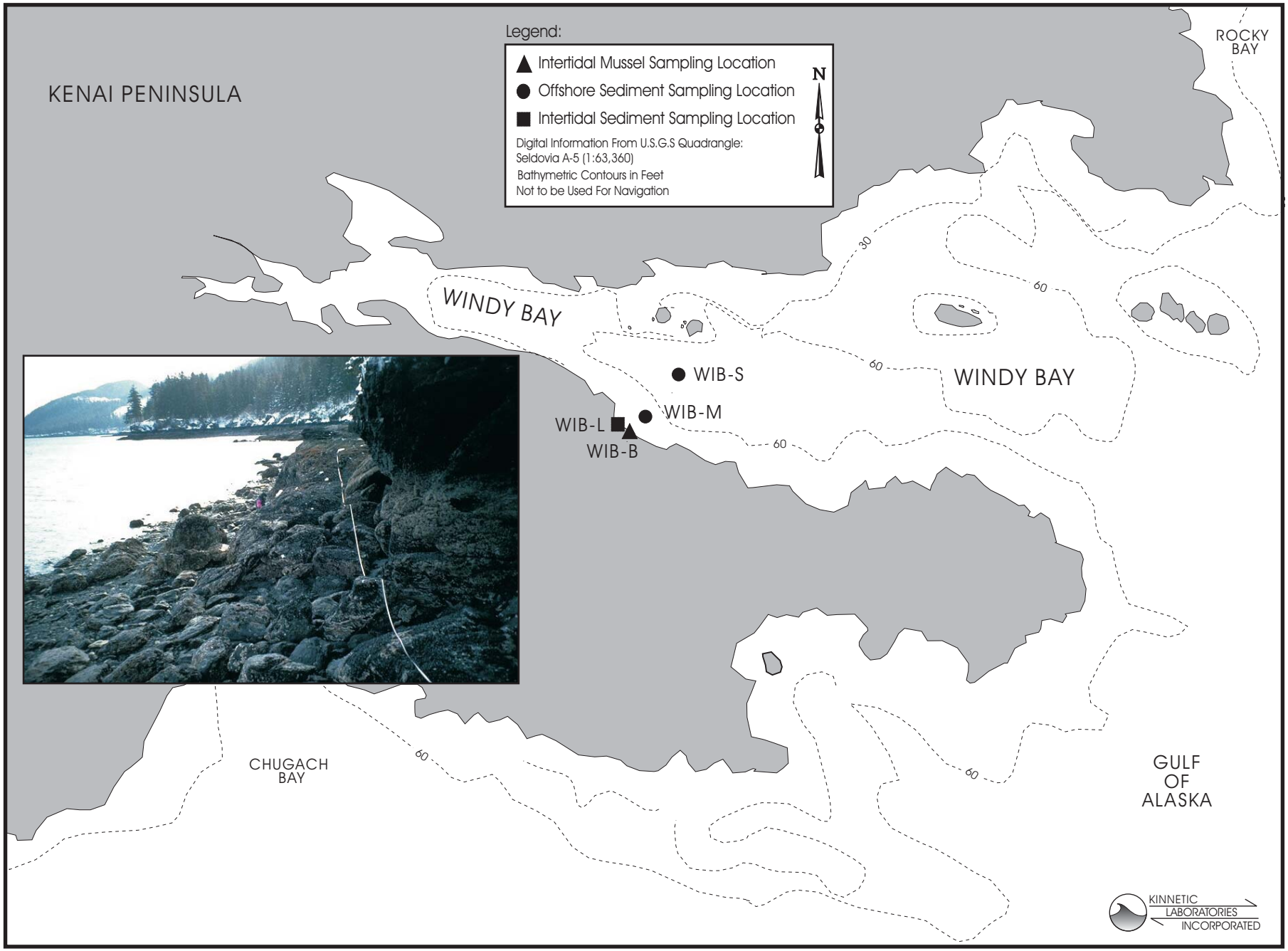


Figure 9. LTEMP Sampling Locations at the Windy Bay Station.

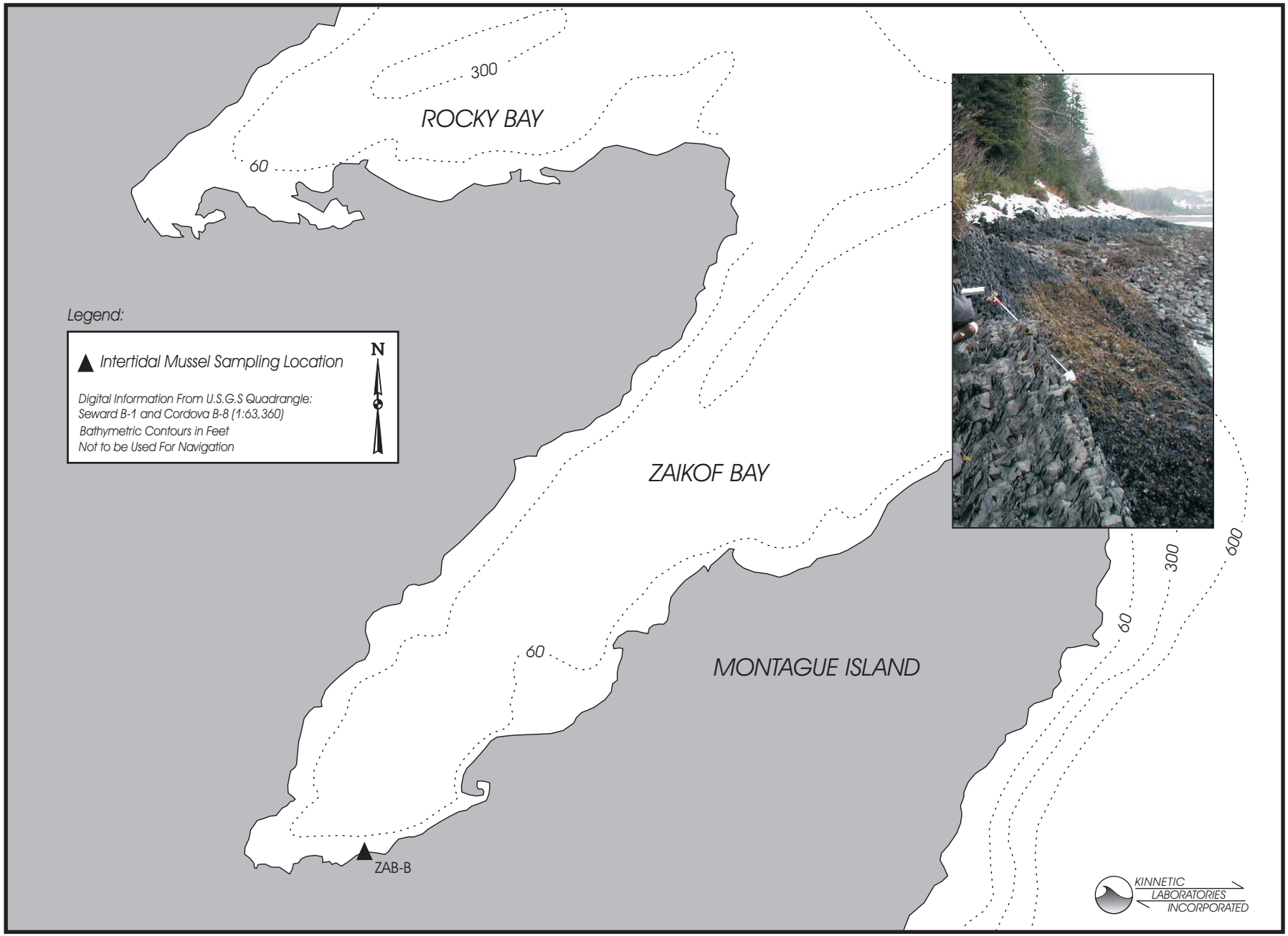


Figure 10. LTEMP Sampling Location at the Zaikof Bay Station.

Station designations used throughout this report as provided in Table 2 include a station abbreviation followed by a station type code ("B" for intertidal mussel, "S" for subtidal sediment, "I" for an opportunistic intertidal station). 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, KNH, and ZAB). Table 2 provides sampling information for each survey.

3.0 METHODOLOGY

3.1 Field Methods

Sampling and handling procedures followed those described in prior program reports (KLI, 1994a; 1995a; 1996a; 1997a; 1998; 1999; and 2000). Intertidal mussel samples were collected using a stratified random sampling design as depicted in Figure 11. Each transect was divided into three zones (0-10 m, 11-20 m, and 21-30 m), and one replicate of a minimum of 30 individual mussels (*Mytilus trossulus*, formerly *M. edulis*) was collected from within each of these zones using random numbers to determine placement. Due to lack of tissue material in some prior surveys, additional mussels were collected at some sites where the mussels were smaller to ensure sufficient material for chemical analysis. Up to 60 mussels may have been collected for each replicate. Additional mussels were collected from each transect for gonadal index determination.

Subtidal sediment collection was performed using a modified Van Veen grab as described in earlier program reports. Three discrete replicate sediment samples of surficial sediment (0 - 2 cm) were collected from the grab at the two Port Valdez stations (AMT-S and GOC-S) during winter and summer surveys in 2000 and 2001. Sediment samples were not collected during the October surveys.

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. A differential GPS system (DGPS) was used whenever possible after March 2000 to accurately document the location of the subtidal sediment sampling sites in Port Valdez. Differential GPS was not typically used for the intertidal stations, which were permanently marked. In addition, the curtailing of the selective availability feature (which decreased the accuracy of the GPS coordinates for national security reasons) in the United States after May 2000 resulted in increased accuracy of the non-differential GPS coordinate system.

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. Subtidal 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's Anchorage office, 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®. 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.

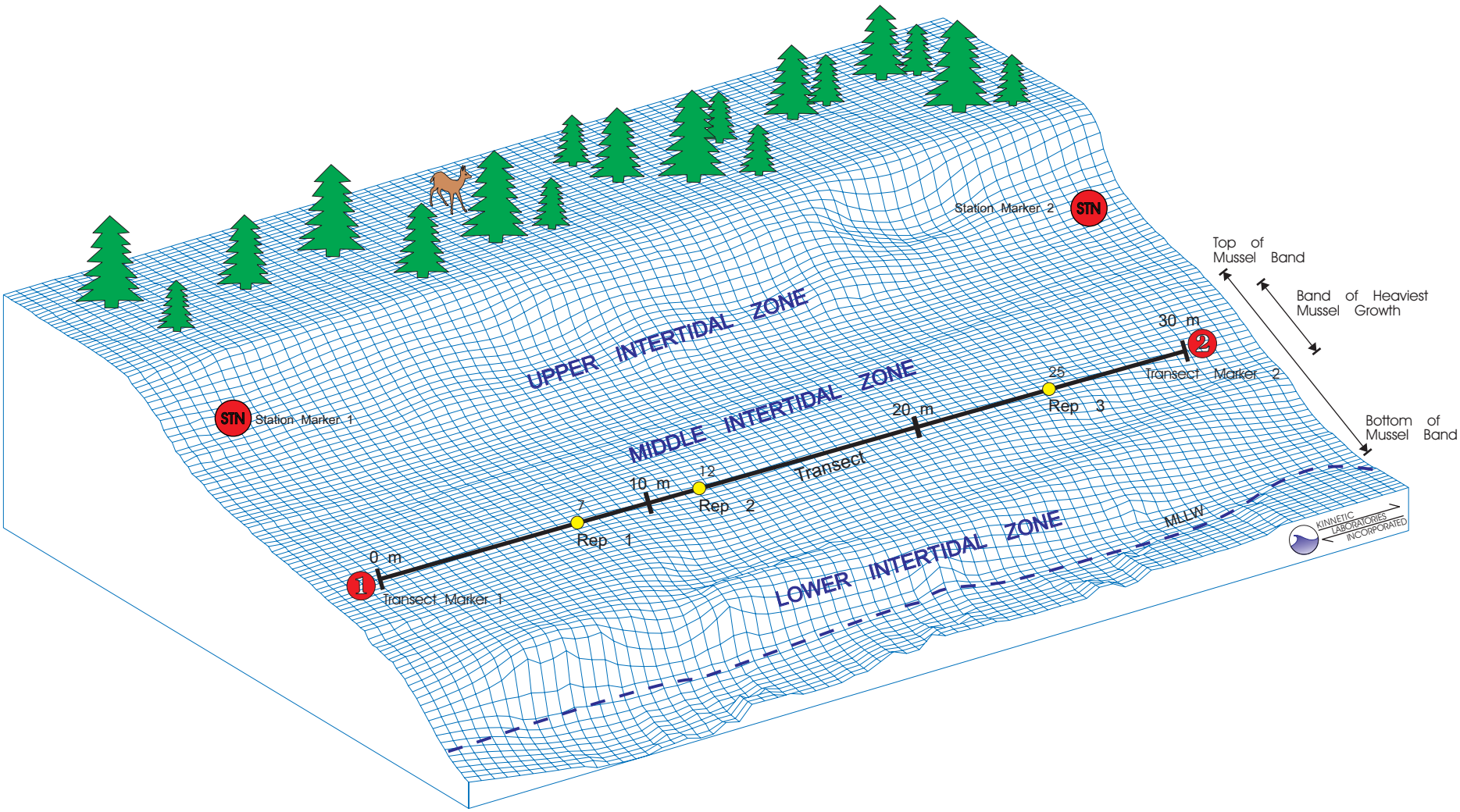


Figure 11. Diagram of LTEMP Intertidal Mussel Sampling Design with Example Replicates at 7, 12, and 25 Meters.

Table 3. List of Applicable Geochemical and Environmental Research Group Standard Operating Procedures used for the 2000 - 2002 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-9804 (replaces 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 PAH/AHC/TOC analysis were thoroughly homogenized by stirring with a clean stainless steel or Teflon® utensil, and representative subsamples were then removed as required for the individual analyses. An aliquot (≈1 g wet weight) for dry weight determination was removed, weighed, freeze-dried, and reweighed to determine percent moisture (GERG SOP-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.

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-9804, which further describes procedures earlier documented by 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). Identification of the analyte peaks in the chromatograms of the sample extracts was performed by comparing them with the target retention times in the calibration curve for single analyte compounds or the analyte retention times in the chromatogram of the GERG reference oils (GERG Standard Check) for the multiple analyte groups. 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 4 for this reporting period were determined in Spring 2000 and 2001 for tissue and sediment. 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 4 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

Table 4. Target Analytes and Method Detection Limits for LTEMP 2000 – 2002 PAH Analyses.

Polycyclic Aromatic Hydrocarbons (PAH)			Method Detection Limits (MDLs; dry weight in ng/g))			
			Tissues		Sediment	
Analyte	Internal Standard Reference	Surrogate Reference	July 2000 October 2000	March 2001 July 2001 October 2001 March 2002	July 2000 March 2001 July 2001	March 2002
Naphthalene	A	1	5.8	7.0	5.3	2.0
C_1-Naphthalenes	A	1	4.7	10.8	1.0	5.4
C_2-Naphthalenes	A	2	9.3	12.8	2.8	1.5
C_3-Naphthalenes	A	2	7.3	11.8	0.6	1.3
C_4-Naphthalenes	A	2	7.3	11.8	0.6	1.3
Biphenyl	A	2	4.7	4.8	1.0	0.5
Acenaphthylene	A	2	3.8	8.1	0.6	0.7
Acenaphthene	A	2	5.9	31.6	0.5	2.0
Fluorene	A	2	5.2	14.1	0.5	1.9
C_1-Fluorenes	A	2	10.3	28.3	1.0	3.9
C_2-Fluorenes	A	2	10.3	28.3	1.0	3.9
C_3-Fluorenes	A	2	10.3	28.3	1.0	3.9
Phenanthrene	A	3	3.5	5.5	1.5	5.1
Anthracene	A	3	3.5	6.3	0.4	1.6
C_1-Phenanthrenes/Anthracenes	A	3	5.9	10.0	0.9	1.2
C_2-Phenanthrenes/Anthracenes	A	3	5.9	10.0	0.9	1.2
C_3-Phenanthrenes/Anthracenes	A	3	5.9	10.0	0.9	1.2
C_4-Phenanthrenes/Anthracenes	A	3	5.9	10.0	0.9	1.2
Dibenzothiophene	A	3	1.4	3.4	0.3	0.5
C_1-Dibenzothiophenes	A	3	2.8	6.7	0.6	1.0
C_2-Dibenzothiophenes	A	3	2.8	6.7	0.6	1.0
C_3-Dibenzothiophenes	A	3	2.8	6.7	0.6	1.0
Fluoranthene	B	3	2.6	4.4	0.3	4.4
Pyrene	B	3	2.4	5.5	0.8	3.8
C_1-Fluoranthenes/Pyrenes	B	3	5.1	11.0	1.1	8.2
Benzo(a)anthracene	B	4	3.7	4.7	0.3	2.4
Chrysene	B	4	3.5	4.9	0.5	2.2
C_1-Chrysenes	B	4	7.0	9.9	1.0	4.5
C_2-Chrysenes	B	4	7.0	9.9	1.0	4.5
C_3-Chrysenes	B	4	7.0	9.9	1.0	4.5
C_4-Chrysenes	B	4	7.0	9.9	1.0	4.5
Benzo(b)fluoranthene	B	4	2.3	4.6	0.6	3.0
Benzo(k)fluoranthene	B	4	2.5	5.0	0.4	1.2
Benzo(e)pyrene	B	4	2.4	8.2	0.5	1.4
Benzo(a)pyrene	B	4	2.6	9.5	0.5	2.8
Perylene	B	5	2.0	3.7	2.9	1.7
Indeno(1,2,3-c,d)pyrene	B	4	1.2	3.8	0.8	2.0
Dibenzo(a,h)anthracene	B	4	1.1	2.8	0.5	0.7
Benzo(g,h,i)perylene	B	4	1.6	2.7	0.8	1.5
Total PAH (Cumulative MDL, excluding perylene)			184.4	379.6	34.7	94.3
Specific Isomers						
1-methylnaphthalene	A	1	2.3	5.9	2.1	2.3
2-methylnaphthalene	A	1	2.4	4.9	4.5	3.1
2,6-dimethylnaphthalene	A	2	4.6	6.4	1.4	0.7
1,6,7-trimethylnaphthalene	A	2	3.6	5.9	0.3	0.7
1-methylphenanthrene	A	3	2.9	5.0	0.4	0.6
Internal Standards						
Fluorene-d_{10}	A					
Benzo(a)pyrene-d_{12}	B					
Surrogates						
Naphthalene-d_8		1				
Acenaphthene-d_{10}		2				
Phenanthrene-d_{10}		3				
Chrysene-d_{12}		4				
Perylene-d_{12}		5				

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 5 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 reporting period, the TRUAHC 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. Analyte peaks in the chromatograms were identified by comparing them with the analyte retention times in the chromatograms of the reference mixture (GERG Standard Check).

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 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 also provided in Table 5. The MDLs were determined following procedures outlined in below in Section 4.2.3 during Spring 1999 and 2000 for tissue and Spring 2000 and 2001 for sediment. 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.

Table 5. Target Analytes and Method Detection Limits for LTEMP 2000 - 2002 AHC Analyses.

Aliphatic Hydrocarbons (AHC)			Method Detection Limits (MDLs; dry weight in ng/g)			
			Tissue		Sediment	
Analyte	Internal Standard Reference	Surrogate Reference	July 2000 October 2000	March 2001 July 2001 October 2001 March 2002	July 2000 March 2001 July 2001	March 2002
Normal Alkanes						
n-C_{10}	A	1	154.9	39.8	4.6	5.7
n-C_{11}	A	1	154.9	29.7	4.3	10.5
n-C_{12}	A	1	154.9	27.3	4.3	18.4
n-C_{13}	A	1	154.9	22.6	6.5	5.3
n-C_{14}	A	1	154.9	17.3	8.3	7.0
n-C_{15}	A	1	333.9	34.3	8.3	23.9
n-C_{16}	A	1	183.0	32.0	8.3	34.5
n-C_{17}	A	1	206.7	77.4	8.3	24.9
n-C_{18}	A	1	56.6	31.2	8.3	34.0
n-C_{19}	A	1	68.1	28.0	9.8	21.8
n-C_{20}	A	1	48.8	69.3	9.8	25.7
n-C_{21}	A	1	77.3	69.3	10.1	25.6
n-C_{22}	A	1	77.3	69.3	10.1	18.8
n-C_{23}	A	1	77.3	69.3	10.1	14.8
n-C_{24}	A	1	77.3	31.6	10.1	25.0
n-C_{25}	A	1	77.3	59.7	8.0	9.4
n-C_{26}	A	1	77.3	59.7	8.0	8.6
n-C_{27}	A	1	77.3	46.2	7.2	6.5
n-C_{28}	A	1	82.7	45.3	7.2	19.9
n-C_{29}	A	1	128.2	77.5	6.0	8.7
n-C_{30}	A	1	77.5	77.5	6.0	25.9
n-C_{31}	A	1	77.5	77.5	6.2	10.1
n-C_{32}	A	1	62.1	84.7	6.2	21.3
n-C_{33}	A	1	62.1	73.3	3.8	4.8
n-C_{34}	A	1	61.0	52.8	3.8	26.3
Isoprenoid Hydrocarbons						
Pristane	A	1	145.2	23.3	5.2	20.1
Phytane	A	1	45.8	23.3	5.2	7.2
Total AHC (Cumulative MDL)			2955	1349	194	465
Internal Standards						
deuterated n-C_{16}	A					
Surrogates						
deuterated n-C_{20}		1				
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.					
deuterated n-C_{24}						
deuterated n-C_{30}						

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 recorded to the nearest 0.1 mL. Weights of gonadal and non-gonadal tissue were determined using a Ohaus Scout II® Model SC2020 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 Access® (Table 6). This relational database was used for all aspects of data storage, error checking, and reporting. Microsoft Excel® was also used for data entry, data verification, and calculation of summary statistics.

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 - 2000) 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).

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)

3.3.3 Data Analysis

A number of PAH and AHC parameters indicative of possible petroleum contamination were utilized for summarizing the results of the 2000 - 2002 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. The CRUDE calculation serves to normalize the concentrations against the sources so that actual petroleum contamination can be identified by magnifying petrogenic inputs relative to biogenic inputs in the AHC fraction, magnifying petrogenic inputs relative to pyrogenic inputs in the PAH fraction, and accounting for weathered petroleum in the UCM fraction.

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

Table 7. Hydrocarbon Parameters used in the 2000 - 2002 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)

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).

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, but in some cases, a "Y" or "<3xMDL" qualifier may have been used.

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
I	Interference noted in sample results
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
<3xMDL	Values at concentrations greater than MDL but less than three times the MDL and within QC criteria (used for procedural blanks)

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 Tables 4 and 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 some 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 the more recent years of the program, including those data provided 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

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

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.

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 was 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 non-certified 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* ("GERG STD Check") or other crude oil standard ("STD OIL 2000") were analyzed with each batch of PAH and AHC. These samples are analyzed as an instrument standard check solution with each analytical batch. This material is also used to define the retention time windows for the alkylated PAH homologue clusters. 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. Descriptive statistics calculated from these results included averages, standard deviations, and ranges. For the analysis of TOC, LECO® pin and ring carbon standards were run as reference materials and used essentially as calibration standards. 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 one per 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. All duplicate sample analyses must show concentrations at levels above 10 times the MDL in order for valid percent recoveries to be calculated. 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.

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 the period of July 2000 through March 2002. Summary data from prior years of the LTEMP have been included for comparison where pertinent. This includes information in some of the tables as well as 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 2000 - 2002 is provided in Table 10. 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. In some tables and most of the text, values have been rounded to the nearest integer for ease of presentation.

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, added to the program during a prior reporting period, can give 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 2000 - 2002 LTEMP.

Station Location	Station Designation	Station Type	Analysis Type	Matrix	July 2000 Survey 17	October 2000 Survey 18	March 2001 Survey 19	July 2001 Survey 20	October 2001 Survey 21	March 2002 Survey 22
AIALIK BAY	AIB-B	Intertidal Mussel	PAH/AHC/lipids	Tissue	3	NC	3	3	NC	3
	AIB-B	Intertidal Mussel	Gonadal Index	Tissue	1	NC	1	1	NC	1
ALYESKA MARINE TERMINAL	AMT-B	Intertidal Mussel	PAH/AHC/lipids	Tissue	3	3	3	3	3	3
	AMT-B	Intertidal Mussel	Gonadal Index	Tissue	1	1	1	1	1	1
	AMT-S	Subtidal Sediment	PAH/AHC/TOC/PGS	Sediment	3	NC	3	3	NC	3
DISK ISLAND	DII-B	Intertidal Mussel	PAH/AHC/lipids	Tissue	3	NC	3	3	NC	3
	DII-B	Intertidal Mussel	Gonadal Index	Tissue	1	NC	1	1	NC	1
GOLD CREEK	GOC-B	Intertidal Mussel	PAH/AHC/lipids	Tissue	3	3	3	3	3	3
	GOC-B	Intertidal Mussel	Gonadal Index	Tissue	1	1	1	1	1	1
	GOC-S	Subtidal Sediment	PAH/AHC/TOC/PGS	Sediment	3	NC	3	3	NC	3
KNOWLES HEAD	KNH-B	Intertidal Mussel	PAH/AHC/lipids	Tissue	3	NC	3	3	NC	3
	KNH-B	Intertidal Mussel	Gonadal Index	Tissue	1	NC	1	1	NC	1
SHEEP BAY	SHB-B	Intertidal Mussel	PAH/AHC/lipids	Tissue	3	NC	3	3	NC	3
	SHB-B	Intertidal Mussel	Gonadal Index	Tissue	1	NC	1	1	NC	1
SHUYAK HARBOR	SHH-B	Intertidal Mussel	PAH/AHC/lipids	Tissue	3	NC	3	3	NC	3
	SHH-B	Intertidal Mussel	Gonadal Index	Tissue	1	NC	1	1	NC	1
SLEEPY BAY	SLB-B	Intertidal Mussel	PAH/AHC/lipids	Tissue	3	NC	3	3	NC	3
	SLB-B	Intertidal Mussel	Gonadal Index	Tissue	1	NC	1	1	NC	1
WINDY BAY	WIB-B	Intertidal Mussel	PAH/AHC/lipids	Tissue	3	NC	3	3	NC	3
	WIB-B	Intertidal Mussel	Gonadal Index	Tissue	1	NC	1	1	NC	1
ZAIKOF BAY	ZAB-B	Intertidal Mussel	PAH/AHC/lipids	Tissue	3	NC	3	3	NC	3
	ZAB-B	Intertidal Mussel	Gonadal Index	Tissue	1	NC	1	1	NC	1

NC Not Collected

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 includes 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 or petroleum source rock formations; 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. One method of determining an ANS source is to compare the relative concentrations of the C_2- and C_3-dibenzothiophenes and phenanthrenes; for ANS crude, both of these ratios approximate 1, while the ratio for background sources is closer to 0.2 (Page et al., 1995).

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 hydrocarbons in 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. However, other researchers contend that petroleum seeps and eroding petroleum source rock formations are the predominant source of hydrocarbons in the area. 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 shows 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 were determined in mussel tissue to help assess the level of exposure of these native organisms to petroleum contamination. The determination of PAH in tissues has been widely used to assess the level of exposure to petroleum and other contamination. However, it is important to note that 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 were also determined in tissues during this reporting period, as required by the program contract. The tissue AHC analyses had been omitted from the LTEMP after the first two years of the program because the 1993 – 1994 data had indicated that matrix interferences caused by naturally-occurring compounds in the tissues themselves 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. However, a review of the LTEMP 1993 – 1997 was performed in 1998 under a separate contract to PWS RCAC (Payne et al., 1998). This report did not examine the tissue AHC data collected during the 1993-1994 LTEMP, but called for re-instituting the analysis of this parameter 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 lipids in the tissues themselves mimic the target analytes in terms of the chromatographic analysis and cause a matrix interference that makes these data virtually unusable unless a spill event has occurred. While cleanup of the extracts removes significant portions of the fatty acids, phospholipids, and other compounds, these and other classes of lipids may remain. These fatty acid esters and other compounds cannot be fully removed from the sample extracts without removing the target alkanes themselves, which would render the analytical results even less valuable. These naturally-occurring compounds elute next to and co-elute with the n-alkanes that are measured during the aliphatic analysis (Table 5), making it difficult to quantify the alkanes since the chromatographic separation is problematic.

In addition to the parameters historically reported for AHC (TAHC and UCM), the TRAHC value was also included in the analytical strategy, as recommended in 1998 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. It should be noted that a major component of the TRAHC concentrations are the lipids that are still present in the extract. The TRAHC will show seasonal shifts in the make up of the lipids classes even if the total percent lipids remains fairly constant. While these AHC and corresponding 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.

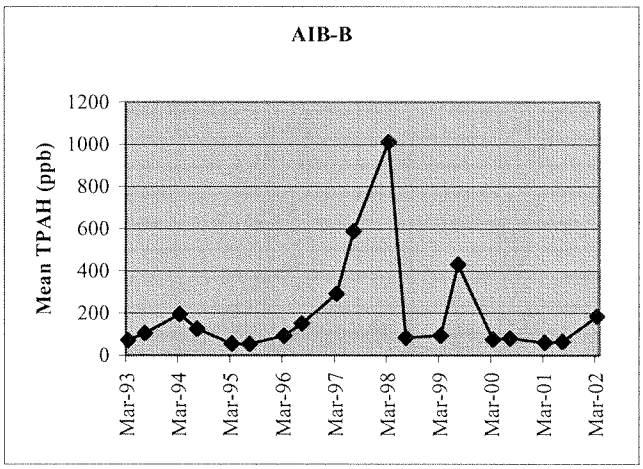
5.2.1 Polycyclic Aromatic Hydrocarbons

Overall, tissue concentrations of PAH compounds continued to be quite low at most stations during the 2000 - 2002 LTEMP. Individual TPAH replicate values ranged from 1.4 at Station ZAB-B (March 2002) to 526 at Station GOC-B (October 2001). The majority of TPAH concentrations were below the cumulative MDLs (184 ppb for July and October 2000 and 380 ppb for March 2001 through March 2002) at each of the LTEMP stations sampled (Table 11). As in the past, the majority of individual PAH analytes (about 80 %) were found to be at very low (below MDL) but still detectable concentrations (Appendix A). Mean TPAH concentrations at many stations varied both within and between surveys (Tables 11 and 12; Figure 12). Good agreement between replicates was shown at a number of stations, while other stations showed more variability.

Table 11. LTEMP Tissue TPAH Results for July 2000 through March 2002.

Station	TPAH (ng/g or ppb)											
	Survey 17 (July 2000)				Survey 18 (October 2000)				Survey 19 (March 2001)			
	Rep. 1	Rep. 2	Rep. 3	Mean	Rep. 1	Rep. 2	Rep. 3	Mean	Rep. 1	Rep. 2	Rep. 3	Mean
AIB-B	78.5	63.0	99.7	80.4	NC	NC	NC	NC	56.3	81.2	46.3	61.3
AMT-B	160.8	179.5	188.7	176.3	148.5	104.7	169.3	140.8	419.7	378.0	354.3	384.0
DII-B	83.1	80.2	64.4	75.9	NC	NC	NC	NC	154.8	140.4	176.4	157.2
GOC-B	102.9	128.6	111.6	114.4	97.7	136.4	123.6	119.2	150.3	171.3	167.6	163.1
KNH-B	173.7	212.9	135	173.9	NC	NC	NC	NC	106.4	72.8	117.0	98.7
SHB-B	104.8	278.4	112.8	165.3	NC	NC	NC	NC	107.7	NC	373.0	240.4
SHH-B	48.0	78.3	76.9	67.7	NC	NC	NC	NC	78.1	70.3	54.6	67.7
SLB-B	129.0	93.6	196.7	139.8	NC	NC	NC	NC	209.9	218.7	150.0	192.9
WIB-B	58.5	74.1	101.9	78.2	NC	NC	NC	NC	56.3	61.2	65.9	61.1
ZAB-B	99.8	42.5	66.3	69.5	NC	NC	NC	NC	129.3	122.6	125.8	125.9
Station	**TPAH (ng/g or ppb)**											
	Survey 20 (July 2001)				Survey 21 (October 2001)				Survey 22 (March 2002)			
	Rep. 1	Rep. 2	Rep. 3	Mean	Rep. 1	Rep. 2	Rep. 3	Mean	Rep. 1	Rep. 2	Rep. 3	Mean
AIB-B	61.3	85.0	53.7	66.7	NC	NC	NC	NC	217.9	167.7	167.3	184.3
AMT-B	186.4	144.3	139.2	156.6	449.4	384.8	340.2	391.5	405.5	318.2	424.2	382.6
DII-B	85.2	72.3	69.8	75.8	NC	NC	NC	NC	138.0	299.0	122.6	186.5
GOC-B	120.8	110.1	126.0	119.0	340.6	339.7	526.3	402.2	254.3	245.6	182.1	227.3
KNH-B	91.6	129.5	84.5	101.9	NC	NC	NC	NC	338.2	217.2	127.7	227.7
SHB-B	99.6	96.9	152.4	116.3	NC	NC	NC	NC	155.4	276.0	176.6	202.7
SHH-B	69.0	89.0	57.6	71.9	NC	NC	NC	NC	73.4	61.0	75.8	70.1
SLB-B	119.5	101.6	135.0	118.7	NC	NC	NC	NC	141.8	183.9	218.9	181.5
WIB-B	62.4	52.8	73.8	63.0	NC	NC	NC	NC	87.1	68.7	69.5	75.1
ZAB-B	99.7	99.2	104.7	101.2	NC	NC	NC	NC	237.2	1.4	156.2	131.6

NC Not Collected



The mean PAH concentrations at Station AIB-B ranged from 61 ppb (March 2001) to 184 ppb (March 2002) during this reporting period, well within the lower range of historical values seen at this station. The overall station minimum was 55 ppb seen in July 1995, while the historical maximum was the elevated level of 1,012 ppb seen in March 1998. The median mean TPAH seen at this station over all sampling periods was 94 ppb. An elevated mean TPAH value of 432 ppb was seen in July 1999 of which nearly half was comprised of the alkylated fluorenes, as discussed in the last report. Elevated PAH concentrations had been seen here between March 1997 and March 1998. In March 1998 (1,012 ppb), the source of this PAH contamination was unknown, but it was thought that it was likely to be diesel or gasoline from a vessel release in the area. This site has been of particular concern in the past because it is a reference site. It is, however, subject to fairly heavy recreational use which may result in contamination from refined products.

The PAH fingerprints for this station continued to exhibit a background-type signature showing a combination of petrogenic with lesser amounts of pyrogenic PAH. The four surveys showed a similar pattern, with very low concentrations of individual PAH analytes. The March 2002 survey showed increased naphthalenes relative to the prior three surveys; this may be due to increased background input, particularly coal where the naphthalenes and other

Table 12. Mean LTEMP Tissue Hydrocarbon Results by Station and Survey - 1993 through 2002.

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
AIB-B (7/99)	432.2	28628	391.6	585.0	10.6
AIB-B (3/00)	75.6	4816	89.9	146.3	5.7
AIB-B (7/00)	80.4	41443	316.8	177.9	7.5
AIB-B (3/01)	61.3	4519	157.5	210.0	6.3
AIB-B (7/01)	66.7	7915	122.0	105.3	10.6
AIB-B (3/02)	184.3	22139	181.2	244.2	7.7
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
AMT-B (7/99)	627.5	61377	646.8	199.6	8.0
AMT-B (10/99)	280.3	14208	72.0	253.4	7.7
AMT-B (3/00)	127.3	10772	356.8	219.0	7.0
AMT-B (7/00)	176.3	56440	465.2	234.9	10.7
AMT-B (10/00)	140.8	18193	286.5	89.5	1.3
AMT-B (3/01)	384.0	8596	144.2	216.4	4.7
AMT-B (7/01)	156.6	9422	161.4	235.6	10.4
AMT-B (10/01)	391.5	13428	97.0	112.1	11.6
AMT-B (3/02)	382.6	22055	209.1	336.6	7.6
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
DII-B (7/99)	269.1	8744	99.3	120.0	5.1
DII-B (3/00)	66.9	7022	209.1	352.6	6.2
DII-B (7/00)	75.9	8610	140.3	51.7	6.9
DII-B (3/01)	157.2	5665	49.3	52.0	7.2
DII-B (7/01)	75.8	15065	149.0	220.6	9.0
DII-B (3/02)	186.5	23911	149.3	105.8	4.0

Table 12. Mean LTEMP Tissue Hydrocarbon Results by Station and Survey - 1993 through 2002. (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
GOC-B (7/99)	949.2	252815	2546.5	191.4	11.3
GOC-B (10/99)	191.1	10537	52.0	252.9	5.6
GOC-B (3/00)	136.3	10393	385.1	171.4	7.8
GOC-B (7/00)	114.4	40384	376.6	148.5	7.4
GOC-B (10/00)	119.2	5263	75.8	41.1	1.2
GOC-B (3/01)	163.1	5404	90.2	114.2	5.2
GOC-B (7/01)	119.0	11062	199.0	188.7	9.4
GOC-B (10/01)	402.2	13295	77.5	109.2	8.0
GOC-B (3/02)	227.3	37836	163.8	109.9	6.0
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
KNH-B (7/99)	689.4	36497	218.6	52.9	4.7
KNH-B (3/00)	110.3	8806	230.5	184.7	6.6
KNH-B (7/00)	173.9	23429	304.8	140.1	9.3
KNH-B (3/01)	98.7	5377	179.0	132.7	7.8
KNH-B (7/01)	101.9	11587	218.9	437.6	12.4
KNH-B (3/02)	227.7	34695	281.4	108.3	5.0
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
SHB-B (7/99)	539.4	18461	148.0	79.1	2.5
SHB-B (3/00)	92.4	7064	148.6	159.9	5.6
SHB-B (7/00)	165.3	20002	305.6	151.0	7.2
SHB-B (3/01)	240.4**	10267**	86.9**	169.2**	14.9**
SHB-B (7/01)	116.3	14236	276.4	404.1	11.4
SHB-B (3/02)	202.7	25713	203.6	201.2	6.5

Table 12. Mean LTEMP Tissue Hydrocarbon Results by Station and Survey - 1993 through 2002. (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
SHH-B (7/99)	338.7	13405	195.8	313.5	7.7
SHH-B (3/00)	122.5	8695	107.3	101.5	5.6
SHH-B (7/00)	67.7	16921	312.7	112.3	10.0
SHH-B (3/01)	67.7	4985	134.2	102.4	6.0
SHH-B (7/01)	71.9	8969	164.6	136.0	7.8
SHH-B (3/02)	70.1	18280	149.7	228.6	5.7
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
SLB-B (7/99)	523.6	28592	104.2	246.5	4.9
SLB-B (3/00)	128.5	21262	379.4	468.4	5.0
SLB-B (7/00)	139.8	14399	191.2	62.1	5.1
SLB-B (3/01)	192.9	6853	123.9	72.1	6.0
SLB-B (7/01)	118.7	12345	211.2	387.3	8.8
SLB-B (3/02)	181.5	23521	157.8	111.8	5.2
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
WIB-B (7/99)	530.9	65764	952.1	276.4	12.3
WIB-B (3/00)	124.1	7319	104.8	101.0	6.6
WIB-B (7/00)	78.2	27250	459.5	203.7	9.4
WIB-B (3/01)	61.1	4139	101.5	98.1	6.0
WIB-B (7/01)	63.0	12650	256.7	148.1	6.7
WIB-B (3/02)	75.1	16859	160.9	273.2	7.1

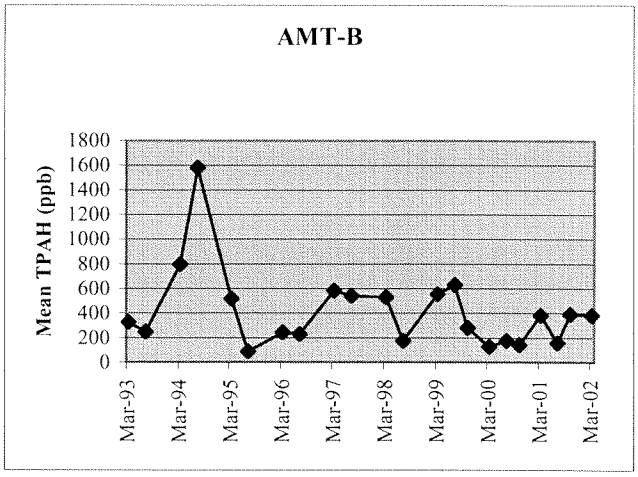
Table 12. Mean LTEMP Tissue Hydrocarbon Results by Station and Survey - 1993 through 2002. (Continued)

Station (Survey)	TPAH (ng/g)	TAHC (ng/g)	TRAHC (µg/g)	UCM (µg/g)	Lipids (%)
ZAB-B (7/99)	238.1	17105	131.2	310.1	3.1
ZAB-B (3/00)	58.2	5658	155.9	228.0	5.5
ZAB-B (7/00)	69.5	8773	86.4	78.9	7.1
ZAB-B (3/01)	125.9	3248	24.4	37.0	6.1
ZAB-B (7/01)	101.2	13811	213.8	305.0	8.6
ZAB-B (3/02)	131.6	30234	164.4	83.9	5.0

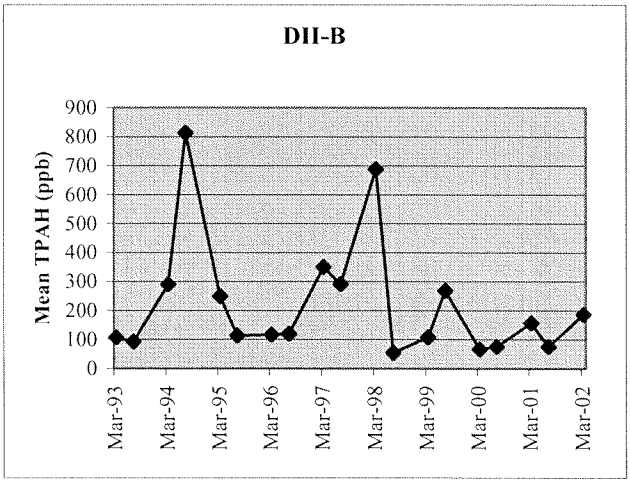
NA Not Analyzed * Mean of 2 reps., one rep. lost during processing ** Collected only 2 reps. due sparseness of mussels

and other lower-molecular weight compounds are present but not available for natural weathering processes as they would be when coming from other petrogenic sources, or possibly from some contamination of refined product.

The AMT-B station has been sampled three times per year since 1999 (in March, July, and October). The mean TPAH values reported for Station AMT-B were well within the range of values seen during earlier sampling events (Figure 12). The mean TPAH concentrations for this station ranged from 127 to 392 ppb for this period, with a fair amount of within-station variability (Table 11; Figure 12). The overall range of values at this station was 87 to 1,581 ppb (Table 12), with a median of 354 ppb. This range excludes the T/V *Eastern Lion* sampling event (May 1994) which exhibited a mean TPAH concentration of 14,351 ppb. It includes the regular summer sampling event which occurred two months afterwards (July 1994) and exhibited the highest value seen here (1,581 ppb).



The PAH fingerprints at Station AMT-B varied between surveys. Mean fingerprints from July and October 2000 and July 2001 showed lower levels of PAH and exhibited background inputs with lesser amounts of pyrogenics. The October 2000 survey showed some possible evidence of crude input, as the ratios of C_2- and C_3-dibenzothiophenes to C_2- and C_3-phenanthrenes were slightly elevated compared to those seen in July 2000 and 2001; however, PAH concentrations were very low. In contrast, March 2001 (Figure 13) and March 2002 exhibited predominantly crude signatures, with March 2002 showing increased naphthalenes. The October 2001 results were similar in concentration to March 2001, but were predominantly background with a C_1-fluorene peak.



The tissue TPAH concentrations at Station DII-B ranged from 67 to 187 ppb during this period, in the low range of those historically seen at this station (55 – 813 ppb). The median for all sampling events was 120 ppb. There was good agreement between replicates for most surveys this period, with the highest intra-station variability seen during March 2002 where replicate values ranged from 127 to 299 ppb. In general, all mean TPAH values at this station have been quite low compared to the extremely elevated values in visibly oiled opportunistic tissue samples (single replicates) taken at the same location in July 1995 and 1996 which had TPAH values of 8,156 and 2,058, respectively. Another oiled sample collected in July 1999 showed a concentration of 930 ppb.

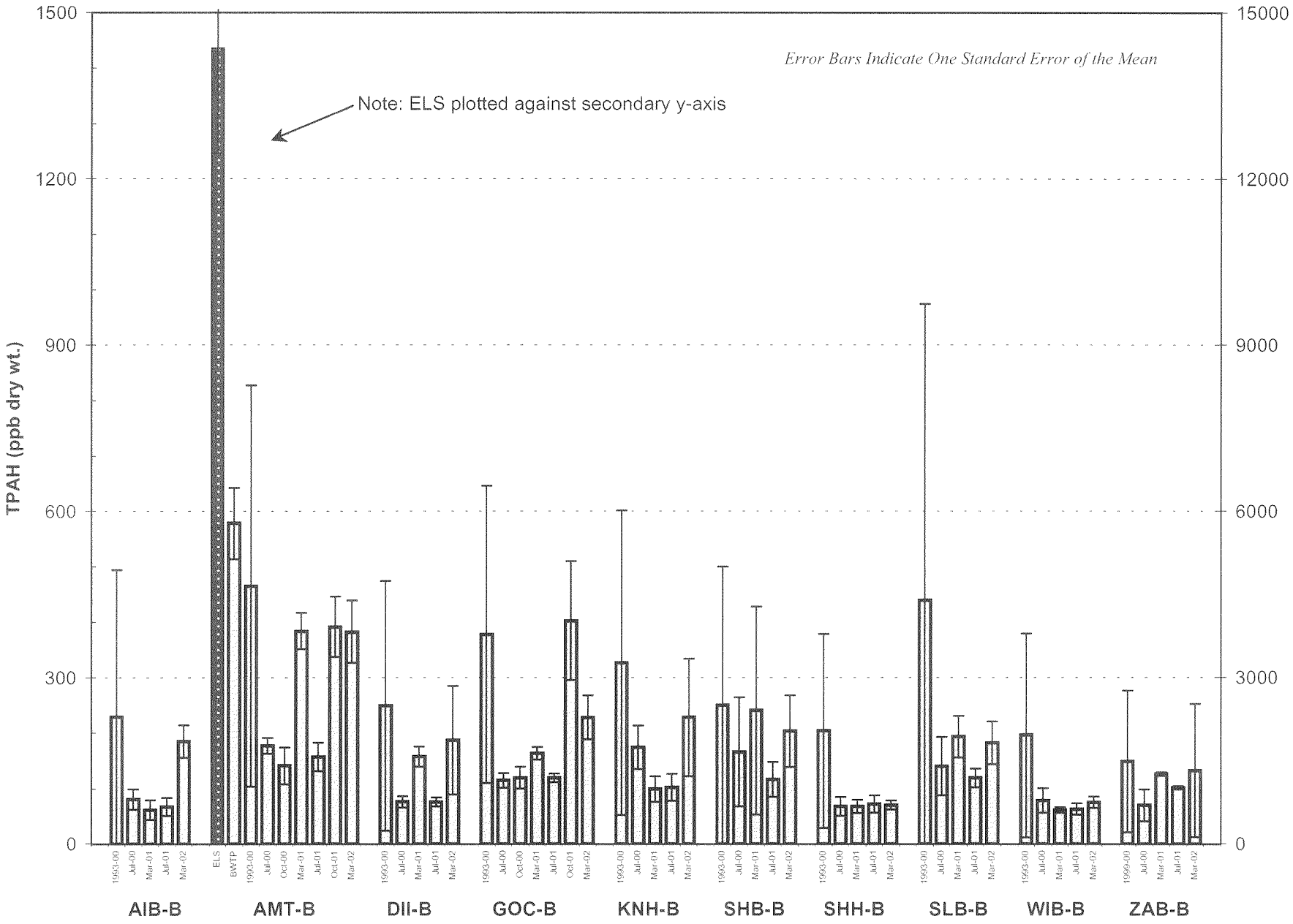


Figure 12. Mean LTEMP Tissue TPAH by Station and Survey - Historical and July 2000 to March 2002.

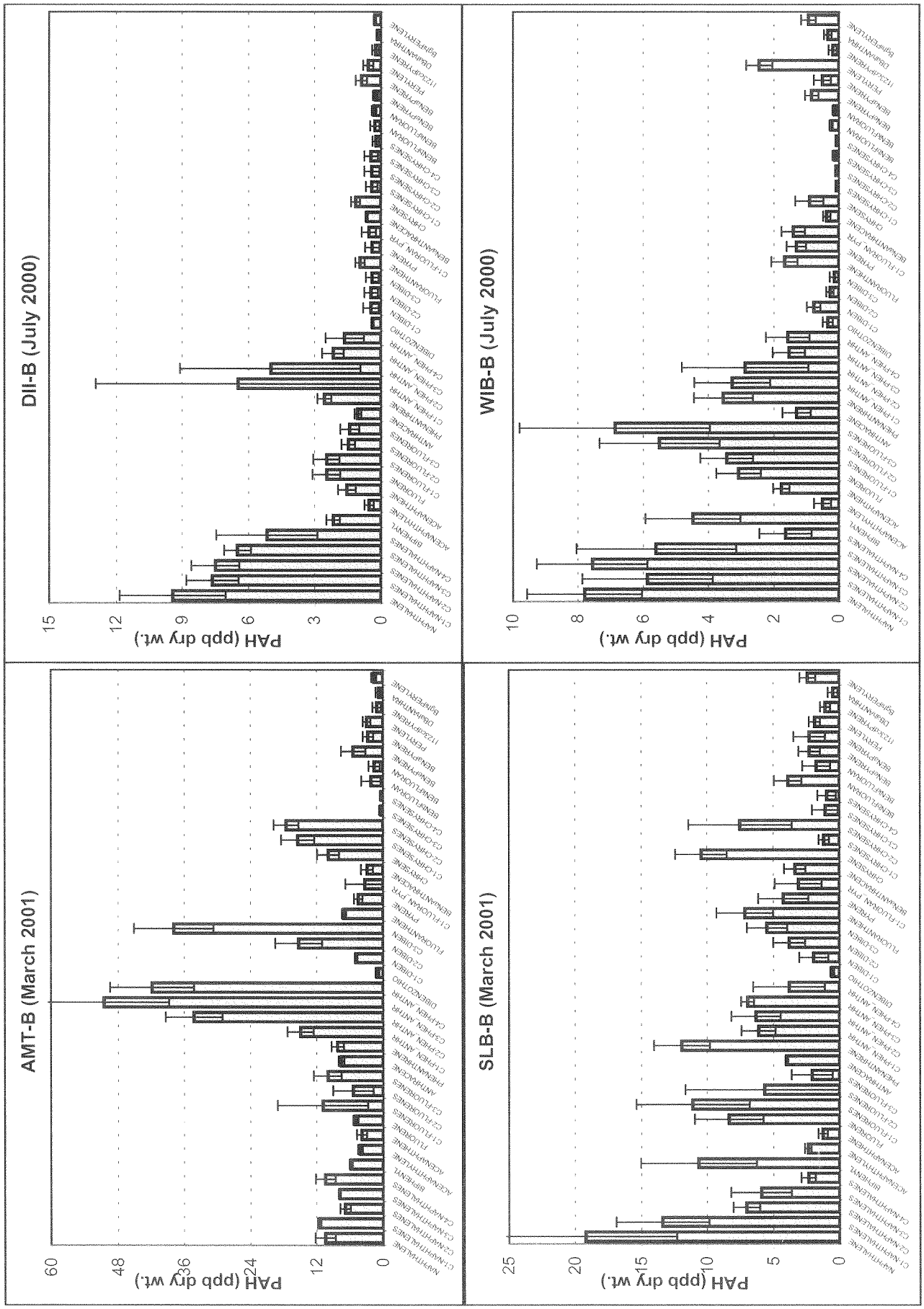
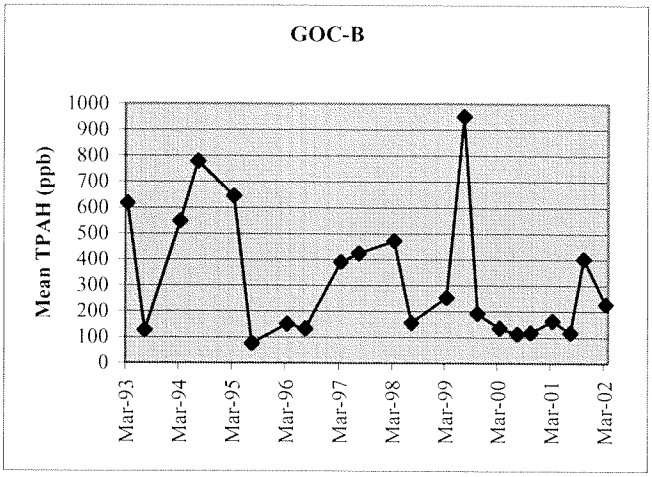


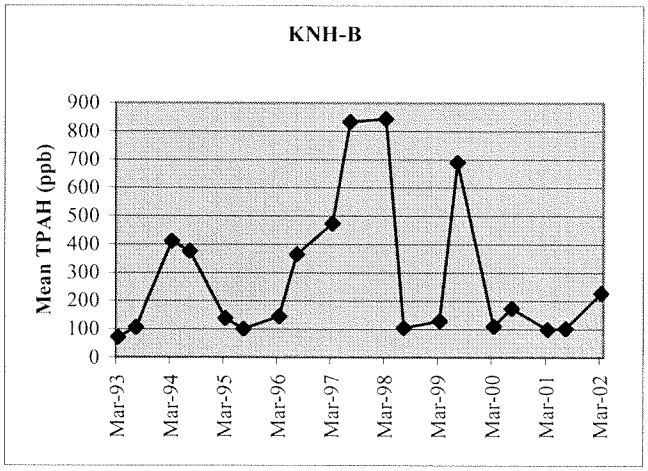
Figure 13. Mean LTEMP Tissue PAH Fingerprints - July 2000 and March 2001 Surveys, Stations AMT-B, DII-B, SLB-B, and WIB-B.

The PAH fingerprints from Station DII-B for July 2000 (Figure 13) showed predominant background sources with varying amounts of pyrogenic PAH. The other three surveys showed higher levels of PAH and a combination of background and lesser pyrogenic- inputs, as seen in the past. If an EVOS/ANS component does exist at this station, as seen here in the past, it is now relatively small. As discussed in earlier reports, opportunistic tissue samples collected from a visibly oiled area nearby clearly indicated elevated PAH levels and an EVOS/ANS signature.

Mean TPAH values seen at Station GOC-B ranged from 114 to 402 ppb for this period. The highest mean TPAH value was seen in October 2001 at 402 ppb. Approximately 20 % of this was accounted for by C_1-fluorene. The overall range for mean TPAH at GOC-B was 77 to 950 ppb, while the median was 209 ppb. Intra-station variability was highest in October 2001, where replicate values ranged from 340 to 526 ppb. Note that the relatively high TPAH values documented in July 1999 were attributed to high levels of the alkylated fluorenes, as discussed earlier.



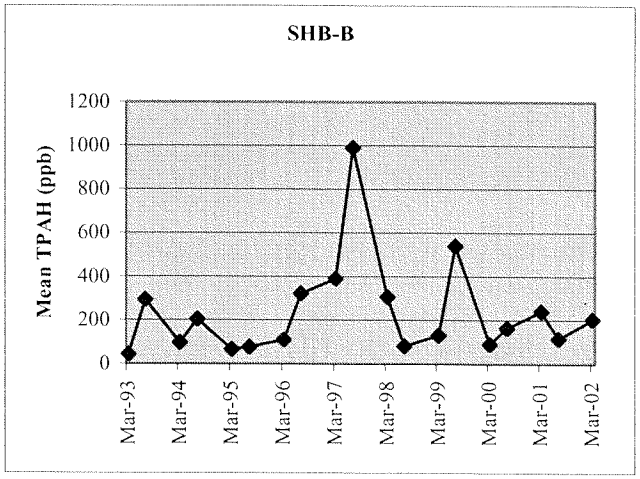
Fingerprints for Station GOC-B showed primarily background and pyrogenic signatures. This contrasts with some data at this station from the past, where an ANS crude signature was apparent (e.g., October 1999).



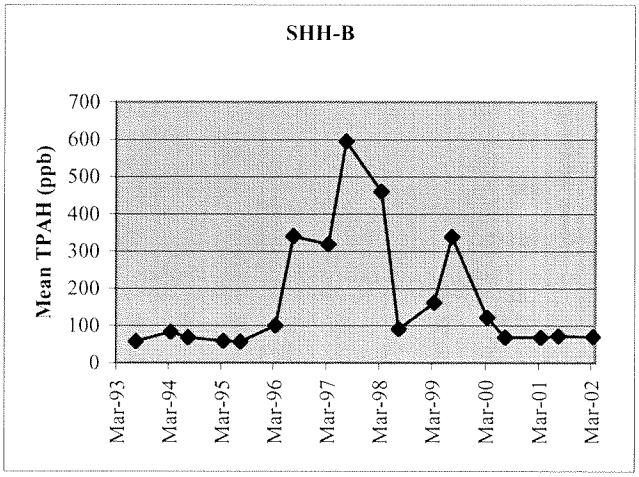
Levels of mean TPAH in mussel tissue from Station KNH-B during the latest sampling period were again quite low, ranging from 99 to 228 ppb as compared to the overall range of 72 to 844 ppb. The overall median for mean TPAH at this station was 145 ppb (Figure 12 and Table 12). Good agreement was seen between replicates in March 2001 and July 2001. July 2000 and March 2002 showed increased variability.

As in the past, the fingerprints of all four surveys at Station KNH-B exhibited patterns consistent with natural background for PWS. These showed a predominance of lower-end PAH. This could be indicative of a fairly fresh hydrocarbon source; however, the natural background signature also demonstrates this.

The mean TPAH levels seen at Station SHB-B ranged from 92 to 240 ppb. The overall range of mean TPAH at this station was 44 – 989 ppb, with a median of 165 ppb (Tables 11, 12; Figure 12). This station showed considerable intra-station variability. The mussel band at this station has become much more sparsely populated in recent years of the LTEMP. In March 2001, only two replicates were collected at this station due to a nearly complete lack of mussels longer than the required 2 cm in the mid-portion of the transect. Means for the March 2001 survey were calculated from only two replicates.



As at Station KNH-B, the fingerprints at Station SHB-B exhibited low PAH levels and a natural background signature.

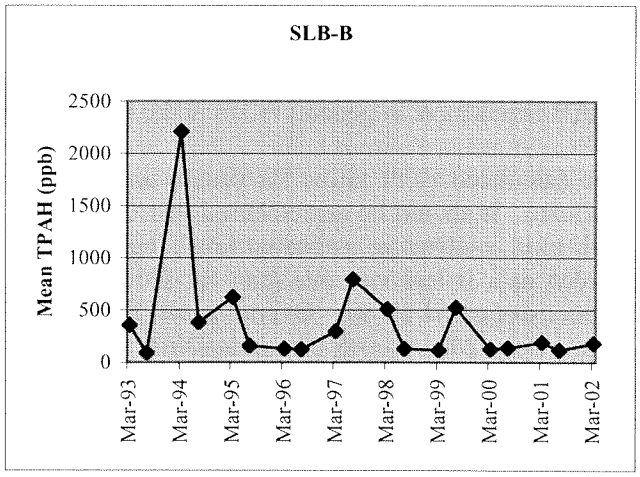


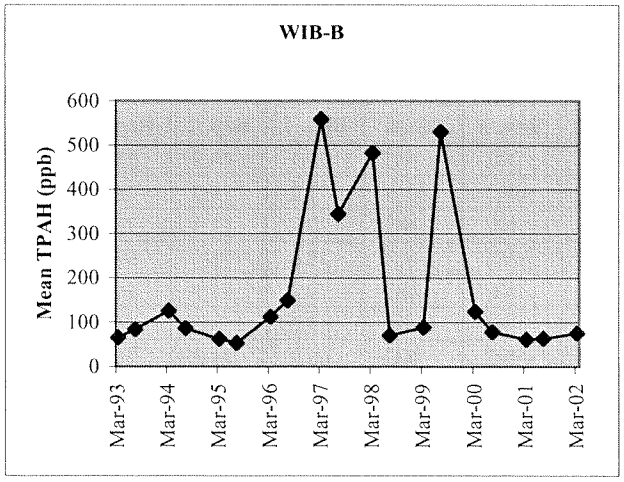
Sampling at this station began in July 1993. Station SHH-B showed extremely low mean TPAH values ranging from 68 to 72 ppb during this reporting period. Intra-station variability was quite low at this station during the latest survey events. The mean TPAH at this station exhibited a historical range of 56 – 595 ppb, with a median of 87 ppb.

As in the past, the fingerprints at this station were similar to that seen at Stations KNH-B and SHB-B, indicating natural background contributions. Individual PAH were very low, with some predominance of the lower weight PAH which has been ascribed by some researchers to coal.

Mean TPAH levels seen in tissues at Station SLB-B during this period were quite low and ranged from 119 to 193 ppb. The overall range for this station was 92 to 2209 ppb. The extreme for this station was seen during March 1994. The median for this station was 182 ppb.

As in the 1998 – 2000 programs, fingerprints from the most recent surveys indicated background with lesser amounts of pyrogenic contributions. The March 2001 survey showed higher level of pyrogenic inputs compared to the prior three surveys (Figure 13). Also, the ratios of C_2- and C_3-dibenzothiophenes to C_2- and C_3-phenanthrenes were elevated compared to the other three surveys which may indicate some crude contribution.

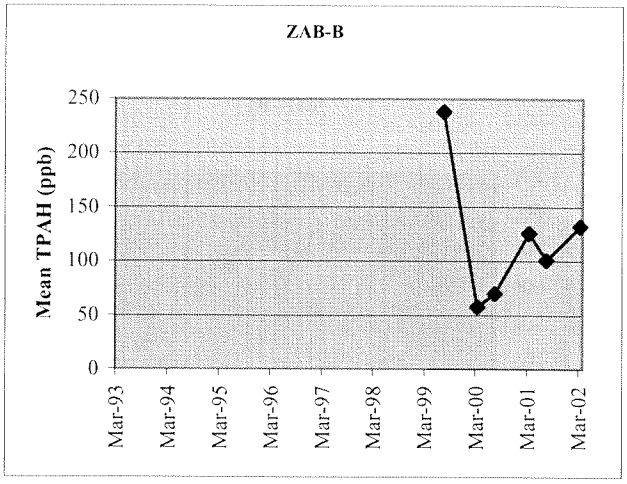




Station WIB-B also showed extremely low mean TPAH values ranging from 61 to 78 ppb. All the recent surveys showed fairly low intra-station variability, with July 2000 showing the highest variability. The overall range of mean TPAH at this station was 53 to 559 ppb. The median at WIB-B was 86 ppb (Tables 11 and 12, Figure 12).

Fingerprints from Station WIB-B indicated the background signature, with two of the four surveys showing relatively high perylene concentrations indicating biogenic inputs as well (Figure 13). Lower levels of pyrogenics PAH were also seen during all four surveys. These fingerprints show good agreement with historical data where low levels were documented.

Sampling at Station ZAB-B was initiated during July 1999, so only six sampling events exist for this station. The overall range of mean TPAH seen here was 58 to 238 ppb (Table 11). The median seen at this station was 114 ppb. March 2002 data at this station showed an extreme degree of variability with a range of 1.4, 156, and 237 ppb seen in the three replicates analyzed.



Fingerprints from the last four surveys were indicative of low level background sources (Figure 13). This agrees with the fingerprints from the former two surveys. Again, high levels of naphthalene were seen here relative to the other PAH compounds.

In summary, low (below MDL) PAH hydrocarbon body burdens were seen in resident mussel populations at most locations during the 2000 - 2002 program. Since the majority of the measured concentrations were qualified as estimates ("J"), care needs to be taken in drawing any conclusions from the data. In terms of overall trends, the apparently increasing levels of tissue PAH that had been seen leading up to March 1998 were no longer apparent in July 1998 and March 1999 data previously reported. While generally high values were again reported in July 1999, they were within the range of concentrations previously seen at each site at all but one station (Station GOC-B). In addition, as reported in the last LTEMP report, relatively elevated values seen in July 1999 were often ascribed to lipids and the feeding regime of the mussels. Elevated values seen during that survey were not due to increases of petroleum hydrocarbons in the environment. During the last two years of data reported here, TPAH levels have in general fallen in the lower range of historical values encountered to date at each station.

The calculated FFPI ratios for tissues are also provided in Table 12 as means and in Table 13 by individual replicate. It should be remembered that these calculations are typically 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. Overall mean FFPI ratios ranged from approximately 64 (Stations AIB-B and DII-B during July 2001) to 85 (Stations DII-B and ZAB-B during July 2000) during this reporting period. A large amount of variability was seen within some stations over time, while others were less variable. For example, Station AIB-B mean FFPI ranged from 64 to 81, while Station GOC-B ranged from 70 to 80. Mean FFPI at Station AMT-B ranged from 68 to 84,and Station SHH-B ranged from 69 to 74.

Table 13. LTEMP Tissue FFPI Results for July 2000 through March 2002.

Station	FFPI (ratio)											
	Survey 17 (July 2000)				Survey 18 (October 2000)				Survey 19 (March 2001)			
	Rep. 1	Rep. 2	Rep. 3	Mean	Rep. 1	Rep. 2	Rep. 3	Mean	Rep. 1	Rep. 2	Rep. 3	Mean
AIB-B	83.2	80.3	79.5	81.0	NC	NC	NC	NC	70.1	70.9	73.0	71.3
AMT-B	75.8	83.3	82.8	80.6	61.8	71.8	69.3	67.6	77.2	74.7	78.1	76.7
DII-B	84.9	85.3	83.9	84.7	NC	NC	NC	NC	72.3	71.3	72.0	71.9
GOC-B	78.4	81.6	79.8	79.9	71.8	64.8	69.5	68.7	77.8	75.6	68.5	74.0
KNH-B	76.9	87.0	79.5	81.1	NC	NC	NC	NC	79.4	77.9	66.8	74.7
SHB-B	79.4	78.4	85.9	81.2	NC	NC	NC	NC	83.6	NC	78.0	80.8
SHH-B	78.6	65.6	78.2	74.1	NC	NC	NC	NC	68.2	71.3	75.0	71.5
SLB-B	80.4	80.0	86.8	82.4	NC	NC	NC	NC	66.6	60.9	69.3	65.6
WIB-B	77.2	80.7	80.8	79.6	NC	NC	NC	NC	68.7	77.7	66.8	71.1
ZAB-B	84.7	86.2	83.7	84.9	NC	NC	NC	NC	77.9	79.0	78.3	78.4

Table 13. LTEMP Tissue FFPI Results for July 2000 through March 2002. (Continued)

Station	FFPI (ratio)											
	Survey 20 (July 2001)				Survey 21 (October 2001)				Survey 22 (March 2002)			
	Rep. 1	Rep. 2	Rep. 3	Mean	Rep. 1	Rep. 2	Rep. 3	Mean	Rep. 1	Rep. 2	Rep. 3	Mean
AIB-B	66.6	66.5	58.2	63.8	NC	NC	NC	NC	82.6	81.1	77.6	80.4
AMT-B	75.4	76.6	77.3	76.5	83.5	81.8	85.3	83.5	77.5	82.4	81.0	80.3
DII-B	70.6	53.6	69.0	64.4	NC	NC	NC	NC	76.8	84.0	74.2	78.3
GOC-B	73.9	73.6	74.1	73.9	85.6	77.9	78.0	80.5	73.3	73.6	67.0	71.3
KNH-B	73.9	75.8	79.7	76.5	NC	NC	NC	NC	81.3	83.5	80.1	81.6
SHB-B	70.3	75.9	79.7	75.3	NC	NC	NC	NC	80.6	74.9	82.4	79.3
SHH-B	72.3	65.4	69.9	69.2	NC	NC	NC	NC	73.4	65.5	72.9	70.6
SLB-B	75.2	66.8	72.6	71.5	NC	NC	NC	NC	73.2	72.7	76.2	74.1
WIB-B	71.7	65.2	68.6	68.5	NC	NC	NC	NC	66.7	72.5	65.8	68.4
ZAB-B	60.5	73.2	73.4	69.0	NC	NC	NC	NC	81.4	66.1	81.9	76.5

NC Not Collected

5.2.2 Aliphatic Hydrocarbons

As expected, tissue concentrations of AHC were considerably higher than PAH levels (Tables 12 and 14; Figure 14). Replicate TAHC values ranged from approximately 1,255 ppb at Station ZAB-B (March 2001) to 61,766 ppb at Station AMT-B (July 2000) for this reporting period. All but one of the individual sample results were above the cumulative MDL values for TAHC (2955 ppb for July and October 2000; 1349 ppb for March 2001 – March 2002; Table 5). As in the past, many of the individual AHC concentrations (about 32 %) were reported at below-MDL levels.

Table 14. LTEMP Tissue TAHC Results for July 2000 through March 2002.

Station	TAHC (ng/g or ppb)											
	Survey 17 (July 2000)				Survey 18 (October 2000)				Survey 19 (March 2001)			
	Rep. 1	Rep. 2	Rep. 3	Mean	Rep. 1	Rep. 2	Rep. 3	Mean	Rep. 1	Rep. 2	Rep. 3	Mean
AIB-B	43637	51346	29345	41443	NC	NC	NC	NC	5216	4627	3714	4519
AMT-B	61766	57131	50423	56440	39781	6762	8035	18193	7501	9398	8890	8596
DII-B	10807	6749	8274	8610	NC	NC	NC	NC	5134	3474	8387	5665
GOC-B	39125	37991	44035	40384	4257	4064	7468	5263	3766	4461	7985	5404
KNH-B	19183	36121	14984	23429	NC	NC	NC	NC	4390	3826	7914	5377
SHB-B	19445	26939	13621	20002	NC	NC	NC	NC	4978	NC	15556	10267
SHH-B	9516	11037	30210	16921	NC	NC	NC	NC	6711	4255	3989	4985
SLB-B	14545	5787	22864	14399	NC	NC	NC	NC	5651	7006	7903	6853
WIB-B	20888	22793	38071	27250	NC	NC	NC	NC	4075	3761	4582	4139
ZAB-B	17368	4485	4468	8773	NC	NC	NC	NC	4573	3916	1255	3248
Station	**TAHC (ng/g or ppb)**											
	Survey 20 (July 2001)				Survey 21 (October 2001)				Survey 22 (March 2002)			
	Rep. 1	Rep. 2	Rep. 3	Mean	Rep. 1	Rep. 2	Rep. 3	Mean	Rep. 1	Rep. 2	Rep. 3	Mean
AIB-B	8084	8184	7477	7915	NC	NC	NC	NC	20529	21947	23941	22139
AMT-B	10789	7563	9914	9422	11692	10202	18391	13428	22899	20656	22609	22055
DII-B	17051	14969	13175	15065	NC	NC	NC	NC	25309	25265	21160	23911
GOC-B	9012	8111	16062	11062	14127	12687	13072	13295	39802	43738	29969	37836
KNH-B	10226	14794	9742	11587	NC	NC	NC	NC	35800	40107	28180	34695
SHB-B	9619	14283	18808	14236	NC	NC	NC	NC	32107	27818	17214	25713
SHH-B	8358	10532	8016	8969	NC	NC	NC	NC	21338	15685	17817	18280
SLB-B	16105	7650	13280	12345	NC	NC	NC	NC	21436	22747	26382	23521
WIB-B	11901	16892	9158	12650	NC	NC	NC	NC	21599	15320	13659	16859
ZAB-B	11346	20351	9737	13811	NC	NC	NC	NC	35742	30080	24881	30234

NC Not Collected

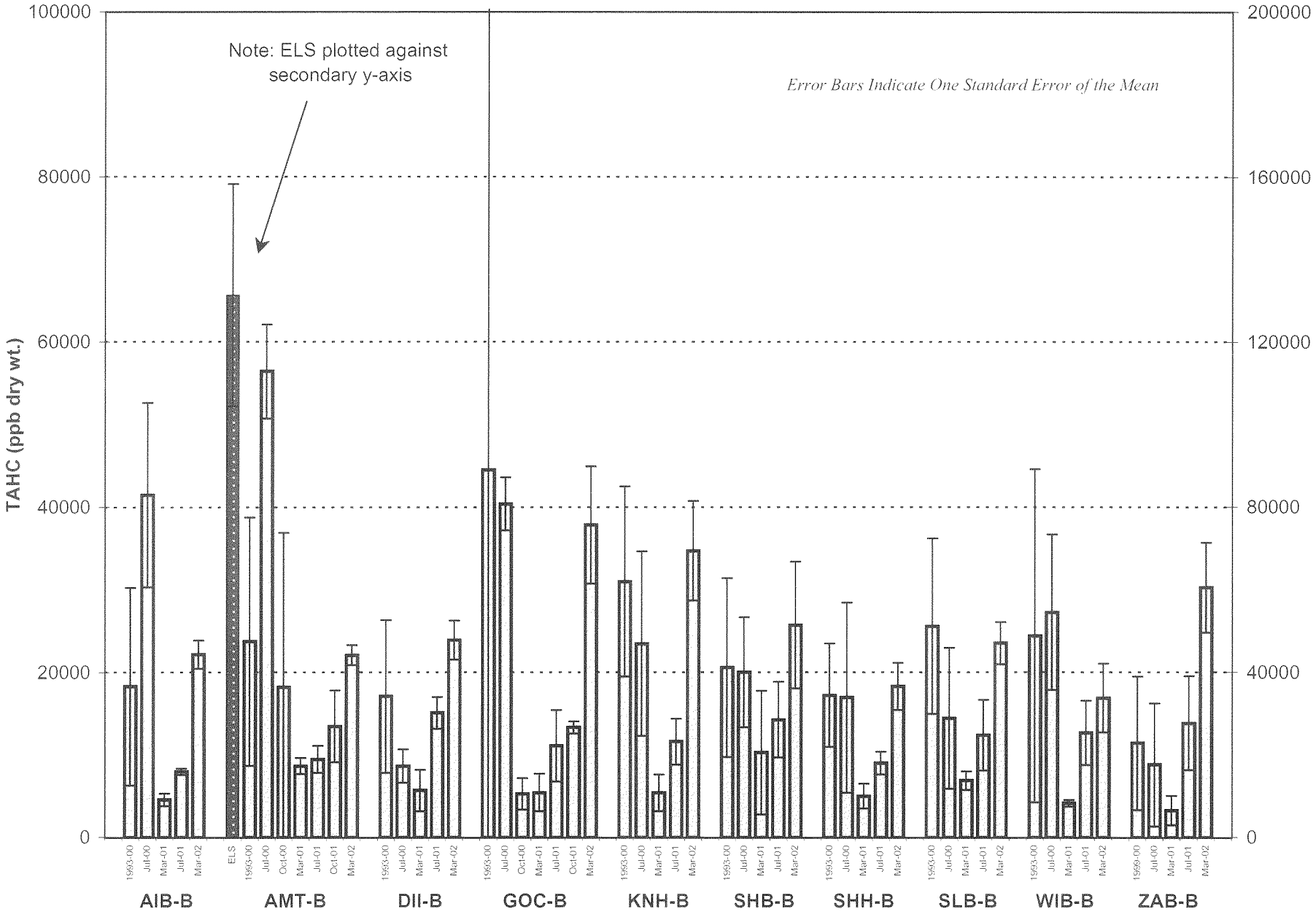


Figure 14. Mean LTEMP Tissue TAHC by Station and Survey - Historical and July 2000 to March 2002.

Striking peaks in TAHC levels during summer sampling periods relative to winter sampling occurred at most stations during summer surveys in 1999 and 2000, but this did not continue into 2001, when the summer survey failed to show such strikingly elevated concentrations (Figure 15). Also, in March 2002, TAHC values were higher than the previous summer's concentrations, so it is unclear whether this pattern may continue. As in the past, intra-station variability was generally higher for TAHC than for TPAH. Extremely elevated AHC values seen at some stations (as discussed below) were typically subject to additional review by the analytical laboratory, which confirmed that the large values seen for some compounds were due to lipid interferences, most likely from plant materials. For example, during July 2000, elevated concentrations of n-C_{29} were seen at a number of stations, accounting for more than 50 % of the TAHC at these stations. As noted above, these lipids cannot be removed from the sample extract without removing some of the target n-alkanes themselves. As in the past, the data suggest that a large portion of the AHC seen in the tissue analysis during this reporting period was actually lipid material that eluted with the target n-alkanes on the gas chromatogram. This matrix interference makes these data difficult to interpret.

As in the past, most of the stations exhibited similar AHC fingerprints within a survey, although each survey shows a different pattern of peaks. These seasonal differences between surveys could potentially be due to spawning, when the release of lipid-rich gametes may cause the fingerprints to shift, or dietary influences, since mussel feeding habits change throughout the year based on the availability of the plankton population. It has been noted by GERG scientists that there is dominance in the lipids with a carbon number of around 20 in the summer samples, which would be similar to the lipids contained in phytoplankton (the primary food source for the mussels). This was seen both historically and during this reporting period in surveys performed in July 2000, October 2000, and July 2001. Elevated levels of n-C_{21} and n-C_{23} were seen in these surveys that were ascribed to lipid interference which was likely the result of feeding on a particular species of phytoplankton that was available during that time, typically during the plankton bloom in summer.

Due to the inherent limitation in the aliphatic results in tissues, although AHC levels are briefly summarized in this report, these data have not been discussed in depth here, nor have AHC fingerprints or ratios been used for source identification as it is clear that a significant portion of the TAHC is not from hydrocarbon sources. All individual replicate AHC data are provided in Appendix A.

Mean TAHC values at Station AIB-B ranged from 4,519 to 41,443 ppb during this reporting period (Table 14; Figures 14 and 15). The high value reported in July 2000 was the overall maximum encountered at this station. The elevated levels of TAHC during this survey were the result of an elevated level of n-C_{29} from plant lipids, as noted above, which accounted for approximately 65 % of the TAHC. A similar peak was seen at Stations AMT-B, GOC-B, and WIB-B during this survey. The overall median of mean TAHC seen at this station was 15,192 ppb.

Station AMT-B exhibited mean TAHC values ranging from 8,596 to 56,440 ppb during this period. The minimum mean TAHC encountered in March 2001 was the overall minimum seen here. The overall station maximum was 61,377 ppb (July 1999), while the overall median was 18,193 ppb.

Mean TAHC at Station DII-B ranged from 5,665 to 23,911 ppb during this reporting period as compared to the overall station range of 5,665 to 33,589 ppb. The overall station minimum was shown here during March 2001. The overall median for this station was 13,787 ppb.

Station GOC-B mean TAHC values ranged from 5,263 to 40,384 ppb during this reporting period. The overall station range was 5,263 ppb (October 2000) to 252,815 ppb (July 2000). The overall median was 13,295 ppb.

The mean TAHC seen at Station KNH-B ranged from 5,377 to 34,695 ppb for this reporting period and from 5,377 to 47,773 for all sampling events. The minimum value was exhibited in March 2001 as were the minimum values for this parameter at several other stations. The median value for this station was 29,850 ppb.

Station SHB-B showed mean TAHC values ranging from 7,064 to 25,713 ppb this reporting period. The lowest values were exhibited in March 2000, while the highest were again seen in March 2002. The overall range for this station was 7,064 ppb (March 2000) to 43,433 ppb (July 1993). The overall median was 18,310 ppb. As

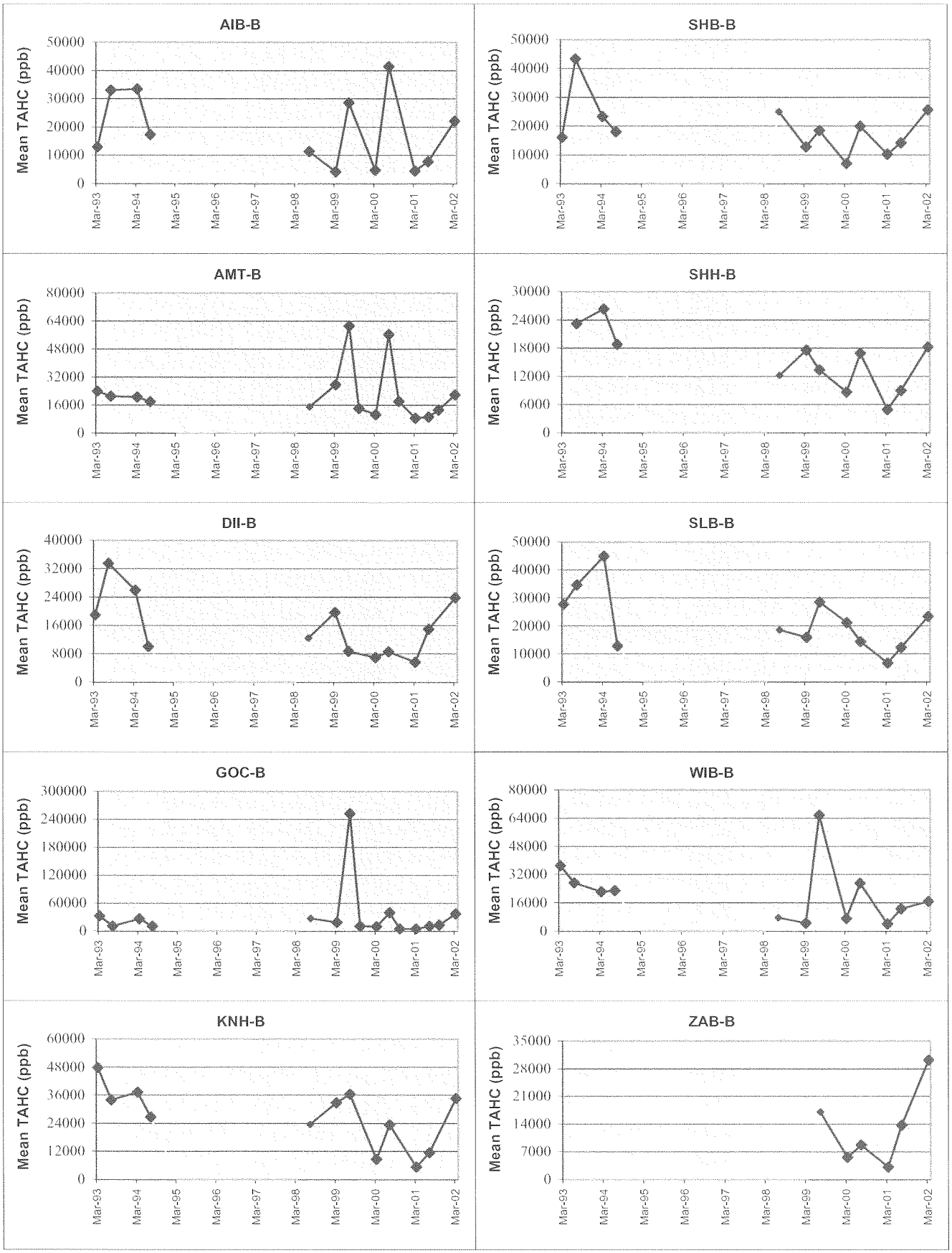


Figure 15. Mean LTEMP Tissue TAHC Time-Series for all Stations, March 1993 - March 2002.

noted for the TPAH, only two replicates were collected here in March 2001; means for this survey were calculated from only two replicates.

The mean TAHC at Station SHH-B ranged from 4,985 ppb (March 2001) to 18,280 ppb (March 2002). The overall station range was from 4,985 ppb to 26,386 ppb, with a median of 16,921 ppb.

Station SLB-B mean TAHC values ranged from 6,853 to 23,521 ppb for this period. This low value was seen in March 2001 and was the lowest encountered to date at this station. The overall station maximum was 44,978 ppb (March 1994), and the median was 19,920 ppb.

The mean TAHC shown at Station WIB-B ranged from 4,139 to 27,250 ppb, again with the minimum seen during the March 2001 sampling. This compares with the overall station range of 4,139 to 65,764 ppb, with a median of 19,594 ppb.

Station ZAB-B exhibited a mean TAHC range of 3,248 to 30,324 ppb during this sampling period. This low value of mean TAHC was the lowest encountered at any LTEMP station to date. The one other sampling event which had occurred at this site was in July 1999, which showed a mean TAHC of 17,105 ppb. The overall median for this site was 11,292 ppb.

The mean TRAHC concentrations were found to show a fair degree of variability both within station and over time. During this reporting period, the mean TRAHC values appear to correspond fairly well with fluctuations in TAHC concentrations for most surveys at most stations (Tables 12 and 15; Figure 16). They corresponded less well during the March 2002 survey where stations with relatively high TAHC values (compared to other surveys) did not show elevated TRAHC concentrations. The cause of these differences were likely due to the greater lipid

Table 15. LTEMP Tissue TRAHC Results for July 2000 through March 2002.

Station	TRAHC (µg/g or ppm)											
	Survey 17 (July 2000)				Survey 18 (October 2000)				Survey 19 (March 2001)			
	Rep. 1	Rep. 2	Rep. 3	Mean	Rep. 1	Rep. 2	Rep. 3	Mean	Rep. 1	Rep. 2	Rep. 3	Mean
AIB-B	336.3	378.7	235.3	316.8	NC	NC	NC	NC	173.2	173.4	126.0	157.5
AMT-B	376.4	595.5	423.8	465.2	612.5	106.0	141.0	286.5	142.7	129.5	160.4	144.2
DII-B	143.7	130.9	146.4	140.3	NC	NC	NC	NC	24.0	80.1	43.9	49.3
GOC-B	258.9	430.8	440.2	376.6	74.2	66.7	86.5	75.8	113.1	90.6	67.1	90.2
KNH-B	353.1	344.9	216.4	304.8	NC	NC	NC	NC	181.0	163.6	192.5	179.0
SHB-B	269.8	381.4	265.6	305.6	NC	NC	NC	NC	74.1	NC	99.8	86.9
SHH-B	179.9	255.6	502.5	312.7	NC	NC	NC	NC	163.7	98.1	140.9	134.2
SLB-B	131.7	169.9	271.9	191.2	NC	NC	NC	NC	84.2	136.7	150.7	123.9
WIB-B	343.5	527.3	507.6	459.5	NC	NC	NC	NC	94.2	117.4	92.8	101.5
ZAB-B	241.9	7.9	9.5	86.4	NC	NC	NC	NC	52.3	9.9	11.1	24.4
Station	TRAHC (µg/g or ppm)											
	Survey 20 (July 2001)				Survey 21 (October 2001)				Survey 22 (March 2002)			
	Rep. 1	Rep. 2	Rep. 3	Mean	Rep. 1	Rep. 2	Rep. 3	Mean	Rep. 1	Rep. 2	Rep. 3	Mean
AIB-B	117.5	123.9	124.6	122.0	NC	NC	NC	NC	185.3	159.6	198.7	181.2
AMT-B	174.1	139.0	171.2	161.4	82.2	94.6	114.3	97.0	217.5	181.8	228.0	209.1
DII-B	176.1	137.8	133.1	149.0	NC	NC	NC	NC	148.5	144.1	155.2	149.3
GOC-B	168.5	153.7	274.8	199.0	76.1	80.9	75.4	77.5	120.2	207.1	164.2	163.8
KNH-B	206.5	264.6	185.5	218.9	NC	NC	NC	NC	366.9	251.7	225.8	281.4
SHB-B	232.0	233.5	363.8	276.4	NC	NC	NC	NC	211.6	308.5	90.7	203.6
SHH-B	149.3	190.2	154.2	164.6	NC	NC	NC	NC	178.6	124.3	146.1	149.7
SLB-B	245.6	149.4	238.6	211.2	NC	NC	NC	NC	148.7	142.0	182.8	157.8
WIB-B	164.4	437.7	168.0	256.7	NC	NC	NC	NC	182.3	162.4	138.0	160.9
ZAB-B	169.0	272.6	199.7	213.8	NC	NC	NC	NC	182.0	168.9	142.4	164.4

NC Not Collected

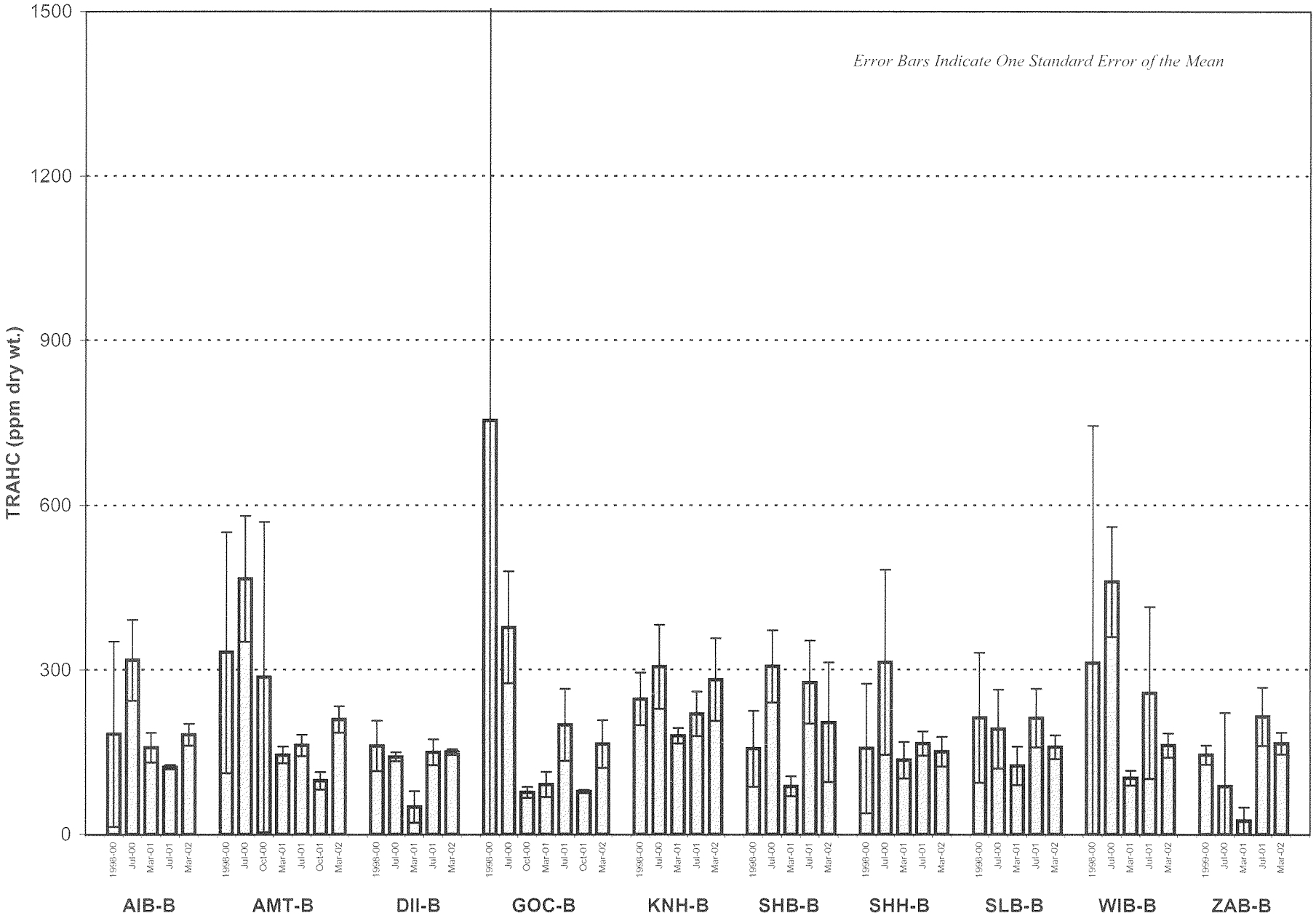


Figure 16. Mean LTEMP Tissue TRAHC by Station and Survey - Historical and July 2000 to March 2002.

and plant wax content that is measured by the TRAHC parameter; some within-station temporal variability was probably due to spawning or feeding as seen with the TAHC concentrations. Mean TRAHC values ranged from 24 ppm (March 2001, Station ZAB-B) to 465 ppm (July 2000, Station AMT-B).

The UCM values reported for the 2000 – 2002 period showed a fairly high degree of between- and within-station variability (Tables 12 and 16; Figure 17). Inspection of the data indicates that these mean UCM values typically fell within the range of the 1993 - 1994 and 1998 - 2000 historical data.

Individual UCM values ranged from 20 ppm (Station ZAB-B, March 2001) to 567 ppm (Station SHB-B, July 2001). Mean UCM values ranged in July 2000 from 52 ppm (Station DII-B) to 235 ppm (Station AMT-B). Mean UCM concentrations for the October 2000 sampling were at 90 and 41 ppm for AMT-B and GOC-B, respectively. Mean UCM values in March 2001 ranged from about 37 ppm (Station ZAB-B) to 216 ppm (Station AMT-B). In July 2001 they were considerably higher and ranged from 105 to 438 ppm at Stations AIB-B and KNH-B, respectively. Mean UCM concentrations for the October 2001 sampling were at 112 and 109 ppm for Stations AMT-B and GOC-B, respectively. The final sampling in March 2002 showed a range of 84 ppm (Station ZAB-B) to 337 ppm (Station AMT-B). In contrast to past data, the seasonal trend of high UCM in the spring and low UCM in the following summer was not seen in this reporting period (Table 12).

Table 16. LTEMP Tissue UCM Results for July 2000 through March 2002.

Station	UCM (µg/g or ppm)											
	Survey 17 (July 2000)				Survey 18 (October 2000)				Survey 19 (March 2001)			
	Rep. 1	Rep. 2	Rep. 3	Mean	Rep. 1	Rep. 2	Rep. 3	Mean	Rep. 1	Rep. 2	Rep. 3	Mean
AIB-B	197.8	186.9	149.1	177.9	NC	NC	NC	NC	193.0	234.4	202.7	210.0
AMT-B	229.2	259.7	215.7	234.9	109.1	63.6	95.8	89.5	247.9	223.6	177.7	216.4
DII-B	49.7	47.7	57.6	51.7	NC	NC	NC	NC	46.4	28.3	81.4	52.0
GOC-B	115.3	137.1	193.0	148.5	44.1	54.3	24.9	41.1	71.7	62.5	208.4	114.2
KNH-B	174.8	159.0	86.4	140.1	NC	NC	NC	NC	111.7	106.7	179.6	132.7
SHB-B	131.6	168.9	152.5	151.0	NC	NC	NC	NC	111.9	NC	226.5	169.2
SHH-B	69.3	118.4	149.2	112.3	NC	NC	NC	NC	120.0	93.5	93.8	102.4
SLB-B	52.2	63.2	70.9	62.1	NC	NC	NC	NC	36.3	54.3	125.7	72.1
WIB-B	133.5	220.0	257.6	203.7	NC	NC	NC	NC	119.6	94.5	80.3	98.1
ZAB-B	119.3	54.6	62.8	78.9	NC	NC	NC	NC	53.8	37.5	19.9	37.0
Station	**UCM (µg/g or ppm)**											
	Survey 20 (July 2001)				**Survey 21 (October 2001)**				**Survey 22 (March 2002)**			
	Rep. 1	**Rep. 2**	**Rep. 3**	**Mean**	**Rep. 1**	**Rep. 2**	**Rep. 3**	**Mean**	**Rep. 1**	**Rep. 2**	**Rep. 3**	**Mean**
AIB-B	111.6	104.6	99.8	105.3	NC	NC	NC	NC	219.5	248.4	264.7	244.2
AMT-B	290.8	222.8	193.2	235.6	56.5	53.2	226.7	112.1	375.5	269.9	364.5	336.6
DII-B	199.0	227.0	235.9	220.6	NC	NC	NC	NC	124.6	121.9	70.8	105.8
GOC-B	161.9	165.9	238.3	188.7	41.5	80.3	205.7	109.2	54.1	131.5	144.0	109.9
KNH-B	423.0	471.6	418.1	437.6	NC	NC	NC	NC	90.0	132.2	102.7	108.3
SHB-B	321.1	324.1	567.2	404.1	NC	NC	NC	NC	114.2	299.3	190.0	201.2
SHH-B	137.2	134.2	136.5	136.0	NC	NC	NC	NC	233.3	206.6	245.9	228.6
SLB-B	415.7	448.5	297.8	387.3	NC	NC	NC	NC	89.7	118.2	127.5	111.8
WIB-B	144.7	171.3	128.4	148.1	NC	NC	NC	NC	342.4	239.8	237.6	273.2
ZAB-B	247.7	375.8	291.6	305.0	NC	NC	NC	NC	117.0	70.7	64.1	83.9

NC Not Collected

As noted above, calculation of ratios such as the CPI are somewhat less viable for tissues than sediments because of the biological factors such as availability, preferential uptake, lipid interference, depuration, and bioaccumulation in lipid-rich tissues which may be expelled as gamete material during spawning. In addition, extremely low or non-detect values seen for some analytes disproportionately skew the CPI ratio, making interpretation difficult. In sediment or water, CPI values close to 1.0 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 and other factors.

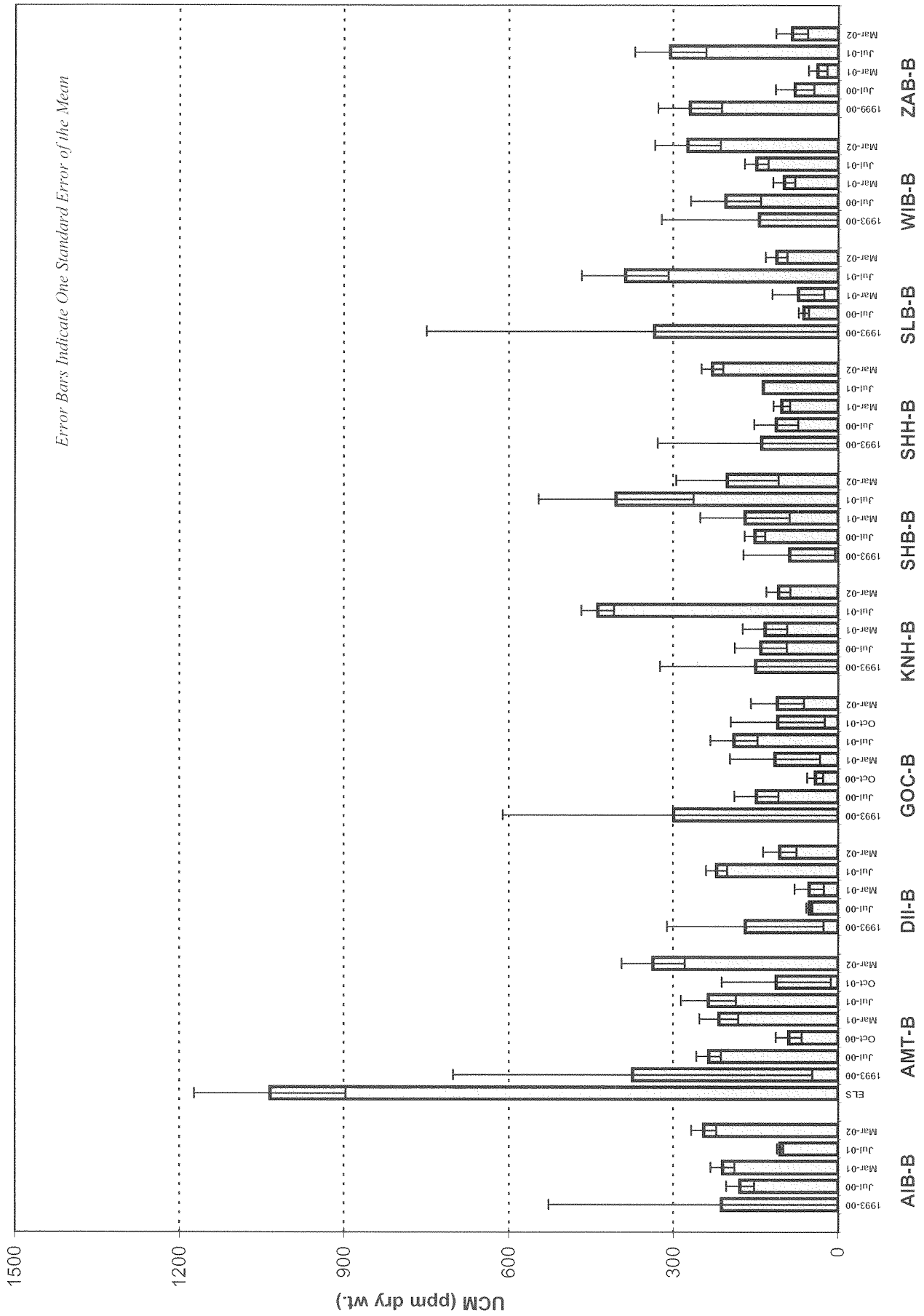


Figure 17. Mean LTEMP Tissue UCM by Station and Survey - Historical and July 2000 to March 2002.

Individual CPI ratios ranged from 0.0 to 1710 during this reporting period. The mean CPI ratios ranged from 0.9 (Station SHH-B) to 16.2 (Station AMT-B) in July 2000 (Table 17). In March 2001, mean CPI values ranged from 1.7 (Station AMT-B) to 572 (Station SHH-B, due to non-detect concentrations in one replicate). Discarding this outlier, the range was 1.7 to 13.0. Mean CPI ratios ranged from 0.4 (Station AMT-B) to 279 (Station AIB-B) for the July 2001 sampling, with the anomalously high value again attributed to non-detect concentrations prevalent in one replicate. The range without that outlier was 0.4 to 3.3. During March 2002, the mean CPI ranged from 5.3 (Station SHB-B) to 9.7 (Station AMT-B). During the October 2000 sampling, the mean CPI values were 3.3 and 4.7 for Stations AMT-B and GOC-B, respectively. October 2001 showed lower mean values at 0.8 and 2.1 for the two respective Port Valdez stations.

Table 17. LTEMP Tissue CPI Results for July 2000 through March 2002.

Station	CPI (ratio)											
	Survey 17 (July 2000)				Survey 18 (October 2000)				Survey 19 (March 2001)			
	Rep. 1	Rep. 2	Rep. 3	Mean	Rep. 1	Rep. 2	Rep. 3	Mean	Rep. 1	Rep. 2	Rep. 3	Mean
AIB-B	14.5	15.8	9.7	13.3	NC	NC	NC	NC	4.4	5.0	2.5	4.0
AMT-B	21.7	14.9	12.1	16.2	1.8	1.3	6.7	3.3	1.8	1.9	1.4	1.7
DII-B	1.4	1.3	1.3	1.3	NC	NC	NC	NC	2.4	3.3	1.4	2.4
GOC-B	17.6	11.5	14.7	14.6	7.3	4.9	1.9	4.7	3.4	8.1	4.5	5.4
KNH-B	1.5	1.2	1.3	1.3	NC	NC	NC	NC	4.0	2.8	3.0	3.3
SHB-B	1.2	1.9	1.2	1.5	NC	NC	NC	NC	5.6	NC	7.8	6.7
SHH-B	0.8	0.9	1.1	0.9	NC	NC	NC	NC	4.9	1.2	1710	572
SLB-B	2.7	1.7	1.5	2.0	NC	NC	NC	NC	4.2	1.3	1.7	2.4
WIB-B	0.7	0.8	10.4	4.0	NC	NC	NC	NC	8.2	16.1	14.7	13.0
ZAB-B	1.3	1.2	1.3	1.3	NC	NC	NC	NC	2.6	2.2	7.0	3.9
Station	**CPI (ratio)**											
	Survey 20 (July 2001)				**Survey 21 (October 2001)**				**Survey 22 (March 2002)**			
	Rep. 1	**Rep. 2**	**Rep. 3**	**Mean**	**Rep. 1**	**Rep. 2**	**Rep. 3**	**Mean**	**Rep. 1**	**Rep. 2**	**Rep. 3**	**Mean**
AIB-B	837	0.5	0.4	279	NC	NC	NC	NC	6.6	5.4	5.6	5.9
AMT-B	0.0	0.7	0.5	0.4	0.6	1.3	0.4	0.8	9.9	8.2	11.1	9.7
DII-B	0.4	0.4	0.6	0.5	NC	NC	NC	NC	4.7	6.3	5.8	5.6
GOC-B	0.7	1.6	7.6	3.3	1.4	3.5	1.5	2.1	7.2	8.7	7.1	7.7
KNH-B	0.9	0.9	1.7	1.2	NC	NC	NC	NC	9.7	8.9	9.1	9.2
SHB-B	1.0	2.2	2.5	1.9	NC	NC	NC	NC	6.4	2.8	6.6	5.3
SHH-B	1.1	1.4	0.7	1.1	NC	NC	NC	NC	7.5	5.9	5.4	6.3
SLB-B	1.0	1.0	2.2	1.4	NC	NC	NC	NC	8.7	8.8	8.0	8.5
WIB-B	2.9	2.7	1.1	2.3	NC	NC	NC	NC	9.1	3.6	9.9	7.5
ZAB-B	0.8	1.3	0.6	0.9	NC	NC	NC	NC	7.3	8.1	8.6	8.0

NC Not Collected

The CRUDE index values as defined in Table 7 were calculated although these values are 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. Because the AHC values reported for tissues are so elevated with respect to the PAH and UCM values, and because they are so subject to lipid and plant material interference, this index is not very useful for assessing hydrocarbon source in tissues.

The mean CRUDE index values ranged from 445 (Station GOC-B) to 26,026 (Station WIB-B) for July 2000 (Table 18). In March 2001, mean CRUDE values ranged from 173 (Station WIB-B) to 3,721 (Station AMT-B). Mean CRUDE ratios ranged from 3,885 to approximately 1.5 billion (1.51E+09) for Stations WIB-B and AMT-B, respectively, during July 2001. This high value reflects the anomalous CPI resulting from non-detect AHC values for this station. Discarding this outlier, the maximum mean value encountered in July 2001 was 67,787 at Station DII-B. During March 2002, the mean CRUDE ranged from 575 (Station SLB-B) to 1,905 (Station SHB-B).

Table 18. LTEMP Tissue CRUDE Index Results for July 2000 through March 2002.

Station	CRUDE (ratio)											
	Survey 17 (July 2000)				Survey 18 (October 2000)				Survey 19 (March 2001)			
	Rep. 1	Rep. 2	Rep. 3	Mean	Rep. 1	Rep. 2	Rep. 3	Mean	Rep. 1	Rep. 2	Rep. 3	Mean
AIB-B	471	443	541	485	NC	NC	NC	NC	499	475	836	603
AMT-B	483	668	714	621	12221	3893	390	5501	2789	3129	5247	3721
DII-B	5411	4281	4761	4818	NC	NC	NC	NC	1052	452	4293	1932
GOC-B	322	527	487	445	194	315	2236	915	505	260	712	492
KNH-B	8984	26560	8456	14667	NC	NC	NC	NC	465	640	1146	750
SHB-B	13015	7527	9170	9904	NC	NC	NC	NC	361	NC	771	566
SHH-B	15937	12432	27065	18478	NC	NC	NC	NC	449	3138	135	1241
SLB-B	2109	2109	10599	4939	NC	NC	NC	NC	495	4576	3072	2714
WIB-B	42959	34423	691	26024	NC	NC	NC	NC	218	157	145	173
ZAB-B	10012	3146	2759	5305	NC	NC	NC	NC	835	935	144	638
Station	**CRUDE (ratio)**											
	Survey 20 (July 2001)				**Survey 21 (October 2001)**				**Survey 22 (March 2002)**			
	Rep. 1	**Rep. 2**	**Rep. 3**	**Mean**	**Rep. 1**	**Rep. 2**	**Rep. 3**	**Mean**	**Rep. 1**	**Rep. 2**	**Rep. 3**	**Mean**
AIB-B	152	31961	42302	24805	NC	NC	NC	NC	869	1130	1152	1050
AMT-B	4.54E+09	14369	42017	1.51E+09	28257	6852	93917	43009	925	840	893	886
DII-B	90316	80061	32984	67787	NC	NC	NC	NC	1387	1006	789	1061
GOC-B	17644	3392	607	7214	7425	1370	6365	5054	1003	896	861	920
KNH-B	13365	20424	3858	12549	NC	NC	NC	NC	746	818	547	704
SHB-B	9908	3449	3726	5694	NC	NC	NC	NC	1016	3966	732	1905
SHH-B	7249	5683	15218	9383	NC	NC	NC	NC	670	697	911	759
SLB-B	18058	8970	3026	10018	NC	NC	NC	NC	475	545	704	575
WIB-B	1561	2478	7616	3885	NC	NC	NC	NC	664	1472	423	853
ZAB-B	20241	11911	25964	19372	NC	NC	NC	NC	988	529	528	682

NC Not Collected

During the October 2000 sampling, the mean CRUDE values were 5,501 and 915 for Stations AMT-B and GOC-B, respectively. October 2001 showed mean values of 43,009 and 5,054 for the two respective Port Valdez stations.

In summary, as noted in the prior LTEMP reports and in this discussion, analysis and reporting of AHC and associated parameters (TRAHC, UCM, CPI, and CRUDE index) in mussel tissues does not appear to provide much useful information regarding hydrocarbon levels or potential anthropogenic sources. It does confirm, however, 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 without removing some of the target n-alkanes themselves, thereby further confounding the AHC 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, such as was seen during the ELS event.

5.2.3 Percent Lipids

Tissue percent lipid concentrations continued to show a fairly high degree of variability among stations and among surveys (Tables 12 and 19; Figure 18). Mean concentrations of lipids in tissues during July 2000 ranged from 5.1 % at Station SLB-B to 10.7 % at Station AMT-B. Mean lipid concentrations in March 2001 ranged from 4.7 % at Station AMT-B to 14.9 % at Station SHB-B. July 2001 showed a range of 6.7 % (Station WIB-B) to 12.4 (Station KNH-B), while March 2002 showed a minimum of 4.0 (Station DII-B) and a maximum of 7.7 (Station AIB-B). October 2000 values were 1.3 and 1.2 % at Stations AMT-B and GOC-B, respectively, while October 2001 values were higher at 11.6 and 8.0 %, respectively.

Table 19. LTEMP Tissue Lipid Results for July 2000 through March 2002.

Station	Lipids (%)											
	Survey 17 (July 2000)				Survey 18 (October 2000)				Survey 19 (March 2001)			
	Rep. 1	Rep. 2	Rep. 3	Mean	Rep. 1	Rep. 2	Rep. 3	Mean	Rep. 1	Rep. 2	Rep. 3	Mean
AIB-B	7.7	7.7	7.1	7.5	NC	NC	NC	NC	5.9	6.0	6.9	6.3
AMT-B	7.8	13.0	11.2	10.7	1.5	1.3	1.0	1.3	4.8	4.2	5.2	4.7
DII-B	7.3	7.7	5.7	6.9	NC	NC	NC	NC	7.0	4.7	9.9	7.2
GOC-B	5.3	8.5	8.3	7.4	1.5	1.1	1.1	1.2	4.7	7.2	3.8	5.2
KNH-B	11.0	8.2	8.8	9.3	NC	NC	NC	NC	8.4	6.2	8.9	7.8
SHB-B	7.0	8.4	6.3	7.2	NC	NC	NC	NC	5.3	NC	24.4	14.9
SHH-B	6.6	9.7	13.7	10.0	NC	NC	NC	NC	7.1	5.6	5.3	6.0
SLB-B	4.2	6.4	4.6	5.1	NC	NC	NC	NC	4.9	5.9	7.1	6.0
WIB-B	6.7	10.6	11.0	9.4	NC	NC	NC	NC	5.6	6.2	6.2	6.0
ZAB-B	7.3	6.3	7.6	7.1	NC	NC	NC	NC	5.4	5.4	7.6	6.1
Station	**Lipids (%)**											
	Survey 20 (July 2001)				Survey 21 (October 2001)				Survey 22 (March 2002)			
	Rep. 1	Rep. 2	Rep. 3	Mean	Rep. 1	Rep. 2	Rep. 3	Mean	Rep. 1	Rep. 2	Rep. 3	Mean
AIB-B	10.2	10.7	11.0	10.6	NC	NC	NC	NC	7.8	7.1	8.3	7.7
AMT-B	12.6	8.4	10.2	10.4	9.1	12.1	13.6	11.6	8.5	5.2	9.1	7.6
DII-B	9.6	9.5	7.9	9.0	NC	NC	NC	NC	5.7	3.0	3.4	4.0
GOC-B	10.2	8.8	9.2	9.4	4.8	10.6	8.6	8.0	7.8	7.2	3.1	6.0
KNH-B	11.4	13.4	12.5	12.4	NC	NC	NC	NC	3.8	7.9	3.4	5.0
SHB-B	10.7	8.8	14.7	11.4	NC	NC	NC	NC	6.2	7.0	6.3	6.5
SHH-B	8.9	7.6	6.9	7.8	NC	NC	NC	NC	5.0	6.1	5.9	5.7
SLB-B	12.2	6.6	7.6	8.8	NC	NC	NC	NC	3.0	5.4	7.1	5.2
WIB-B	7.2	5.1	7.8	6.7	NC	NC	NC	NC	7.9	8.2	5.3	7.1
ZAB-B	8.3	9.4	8.2	8.6	NC	NC	NC	NC	7.1	3.6	4.2	5.0

NC Not Collected

The historical pattern of higher concentrations during the summer surveys compared to the winter surveys appears to continue at most stations in this data set. This pattern was not exhibited in 1999 when higher than usual mean lipid values seen in March 1999 led to decreased concentrations at most stations in July 1999. Historically there has been 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 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

Values of shell length and volume, gonadal tissue weight, and non-gonadal weights are presented in Table 20 and Appendix A. As in the past, mussels were largest overall at Stations AIB-B, AMT-B, GOC-B, ZAB-B, SHH-B and DII-B. During this reporting period, Station KNH-B has regained the position of having the smallest mussel lengths; this position was held for a short time by Station WIB-B where the mussel band had undergone radical change in the prior reporting period. In general, gonadal weight to shell volume and, to a lesser extent, proportional gonadal weights were fairly low at almost all stations during March 2002, which may have been a spawning effect that is not normally seen (Figures 19 and 20). Otherwise, although there was some variability, the proportional gonadal weight ratios were generally similar at a given station among surveys, whereas much greater variability was seen in the gonadal weight to shell volume ratio. This suggests that there have been no major population shifts and that minor variations reflect somewhat patchy distributions of size classes (Table 20). These parameters have not proven to be particularly useful over the course of the LTEMP in assessing the condition of the mussel populations nor the reproductive state of the mussels.

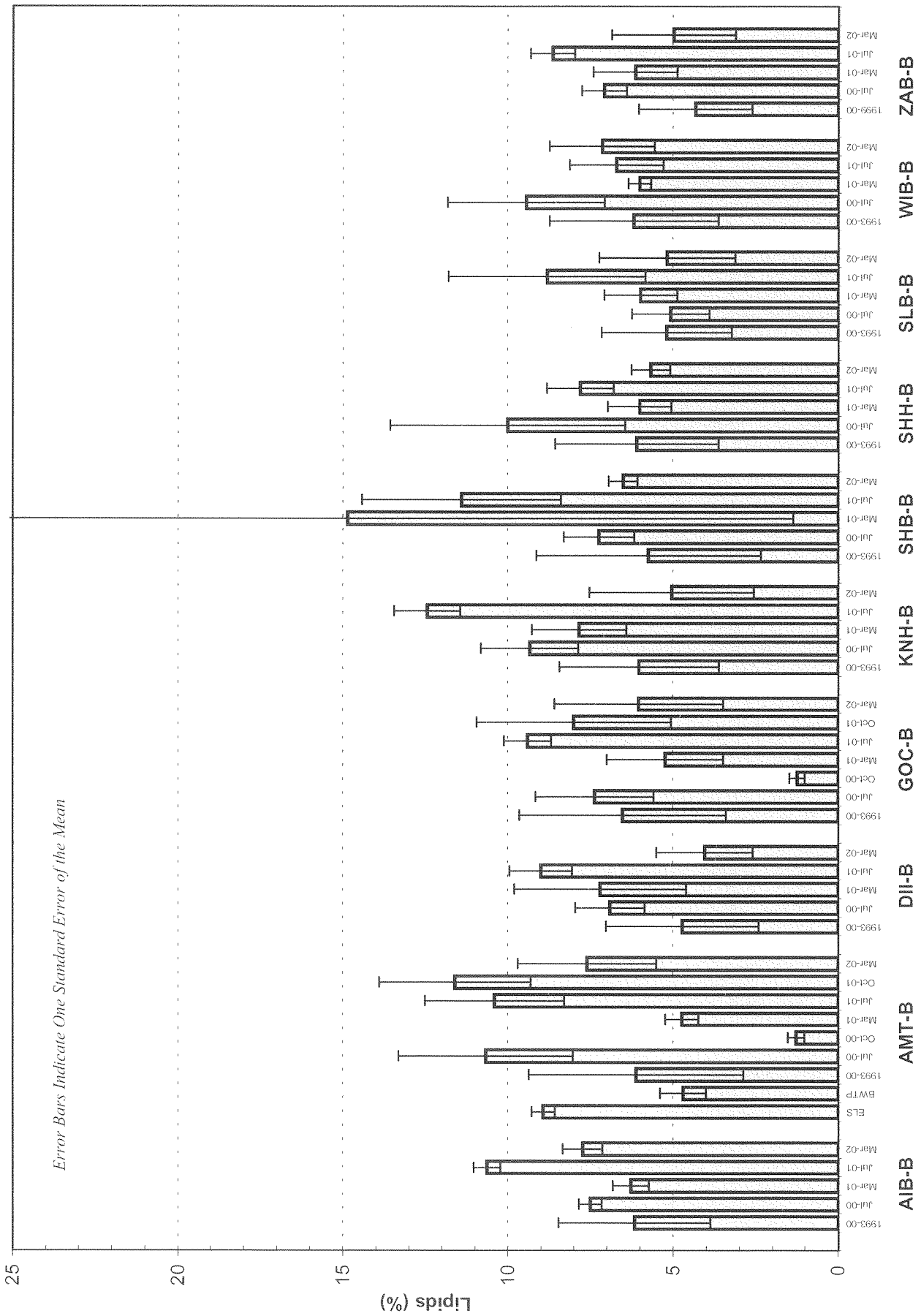


Figure 18. Mean LTEMP Tissue Percent Lipids by Station and Survey - Historical and July 2000 to March 2002.

Table 20. Mean LTEMP Gonadal Index Results by Station and Survey - 1993 through 2002.

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
AIB-B (7/99)	36	3.3	0.23	1.09	0.17	0.07
AIB-B (3/00)	36	3.0	0.23	0.99	0.19	0.08
AIB-B (7/00)	36	3.3	0.21	1.04	0.17	0.07
AIB-B (3/01)	38	3.6	0.23	1.20	0.16	0.07
AIB-B (7/01)	42	2.5	0.48	1.53	0.23	0.20
AIB-B (3/02)	40	4.6	0.24	1.26	0.15	0.05
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
AMT-B (7/99)	42	4.9	0.12	1.05	0.10	0.03
AMT-B (10/99)	41	4.2	0.18	1.12	0.13	0.04
AMT-B (3/00)	36	3.2	0.15	0.92	0.14	0.04
AMT-B (7/00)	38	3.2	0.23	1.22	0.16	0.07
AMT-B (10/00)	38	3.1	0.22	1.14	0.16	0.07
AMT-B (3/01)	40	3.7	0.23	1.16	0.16	0.06
AMT-B (7/01)	40	2.1	0.20	1.12	0.14	0.09
AMT-B (10/01)	39	3.9	0.10	0.86	0.10	0.03
AMT-B (3/02)	39	4.3	0.11	0.80	0.11	0.02
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
DII-B (7/99)	34	3.0	0.14	0.87	0.13	0.05
DII-B (3/00)	34	3.1	0.13	1.00	0.11	0.04
DII-B (7/00)	35	2.9	0.17	0.95	0.15	0.06
DII-B (3/01)	35	2.6	0.14	0.86	0.13	0.06
DII-B (7/01)	37	1.5	0.16	1.08	0.13	0.12
DII-B (3/02)	38	3.6	0.19	1.16	0.14	0.05

Table 20. Mean LTEMP Gonadal Index Results by Station and Survey - 1993 through 2002. (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
GOC-B (7/99)	40	5.0	0.18	1.31	0.12	0.04
GOC-B (10/99)	38	4.4	0.18	1.02	0.15	0.04
GOC-B (3/00)	37	3.2	0.15	0.93	0.14	0.05
GOC-B (7/00)	38	3.6	0.20	1.12	0.15	0.07
GOC-B (10/00)	37	2.9	0.20	1.12	0.15	0.07
GOC-B (3/01)	40	3.7	0.25	1.37	0.15	0.07
GOC-B (7/01)	44	2.7	0.26	1.27	0.16	0.10
GOC-B (10/01)	40	4.1	0.13	0.97	0.11	0.03
GOC-B (3/02)	40	4.1	0.08	0.82	0.07	0.02
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
KNH-B (7/99)	30	1.9	0.16	0.63	0.20	0.08
KNH-B (3/00)	33	2.2	0.13	0.79	0.14	0.06
KNH-B (7/00)	26	0.7	0.05	0.42	0.09	0.08
KNH-B (3/01)	29	1.9	0.09	0.58	0.13	0.05
KNH-B (7/01)	30	0.8	0.11	0.60	0.14	0.14
KNH-B (3/02)	32	2.1	0.06	0.59	0.09	0.03
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
SHB-B (7/99)	34	3.0	0.18	0.95	0.16	0.06
SHB-B (3/00)	34	2.7	0.16	0.93	0.14	0.06
SHB-B (7/00)	34	1.5	0.13	0.88	0.13	0.09
SHB-B (3/01)	36	3.0	0.13	0.77	0.13	0.05
SHB-B (7/01)	32	1.0	0.15	0.68	0.17	0.16
SHB-B (3/02)	32	2.4	0.08	0.63	0.10	0.03

Table 20. Mean LTEMP Gonadal Index Results by Station and Survey - 1993 through 2002. (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)
SHH-B (7/93)	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
SHH-B (7/99)	41	4.0	0.23	1.31	0.15	0.06
SHH-B (3/00)	38	3.6	0.21	1.11	0.16	0.06
SHH-B (7/00)	38	3.6	0.19	1.13	0.14	0.05
SHH-B (3/01)	35	2.7	0.14	0.82	0.14	0.05
SHH-B (7/01)	38	1.8	0.17	1.09	0.13	0.11
SHH-B (3/02)	37	3.8	0.20	1.04	0.16	0.05
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
SLB-B (7/99)	33	2.4	0.09	0.68	0.11	0.04
SLB-B (3/00)	31	2.0	0.07	0.70	0.08	0.03
SLB-B (7/00)	32	1.3	0.08	0.67	0.10	0.07
SLB-B (3/01)	30	1.8	0.05	0.49	0.09	0.03
SLB-B (7/01)	31	1.1	0.05	0.57	0.08	0.05
SLB-B (3/02)	34	2.8	0.09	0.71	0.09	0.03
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
WIB-B (7/99)	28	1.4	0.13	0.67	0.16	0.10
WIB-B (3/00)	27	1.8	0.24	0.72	0.25	0.13
WIB-B (7/00)	32	2.1	0.09	0.78	0.10	0.04
WIB-B (3/01)	31	1.8	0.10	0.68	0.12	0.06
WIB-B (7/01)	35	1.2	0.12	0.83	0.12	0.11
WIB-B (3/02)	33	2.9	0.07	0.70	0.09	0.02
ZAB-B (7/99)	37	3.3	0.16	0.94	0.15	0.05
ZAB-B (3/00)	37	3.3	0.18	1.04	0.15	0.05
ZAB-B (7/00)	35	1.4	0.15	0.86	0.15	0.11
ZAB-B (3/01)	38	3.6	0.17	0.95	0.15	0.05
ZAB-B (7/01)	41	2.5	0.18	1.15	0.12	0.07
ZAB-B (3/02)	38	3.7	0.09	0.85	0.09	0.02

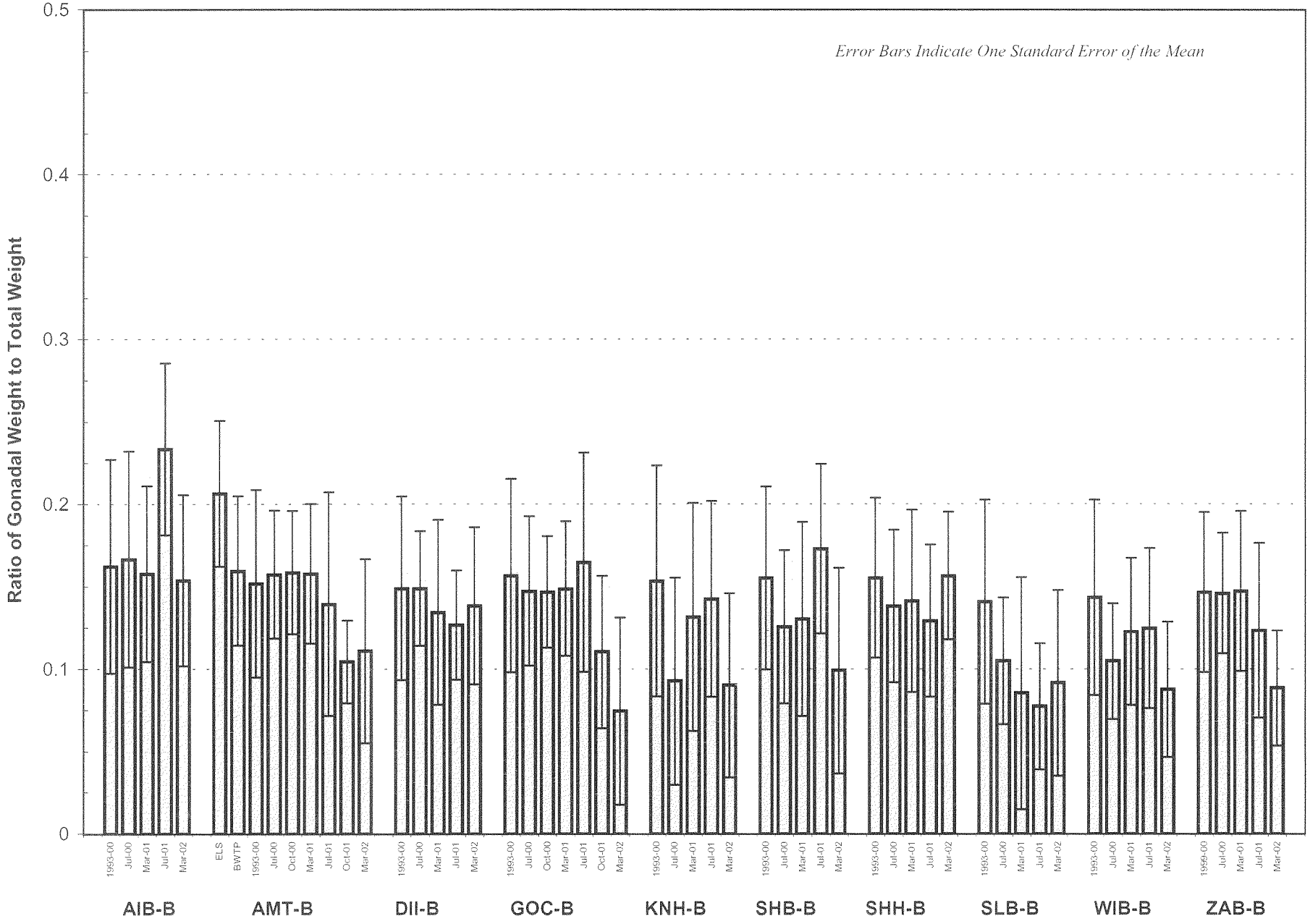


Figure 19. Mean LTEMP Proportional Gonadal Weight by Station and Survey - Historical and July 2000 to March 2002.

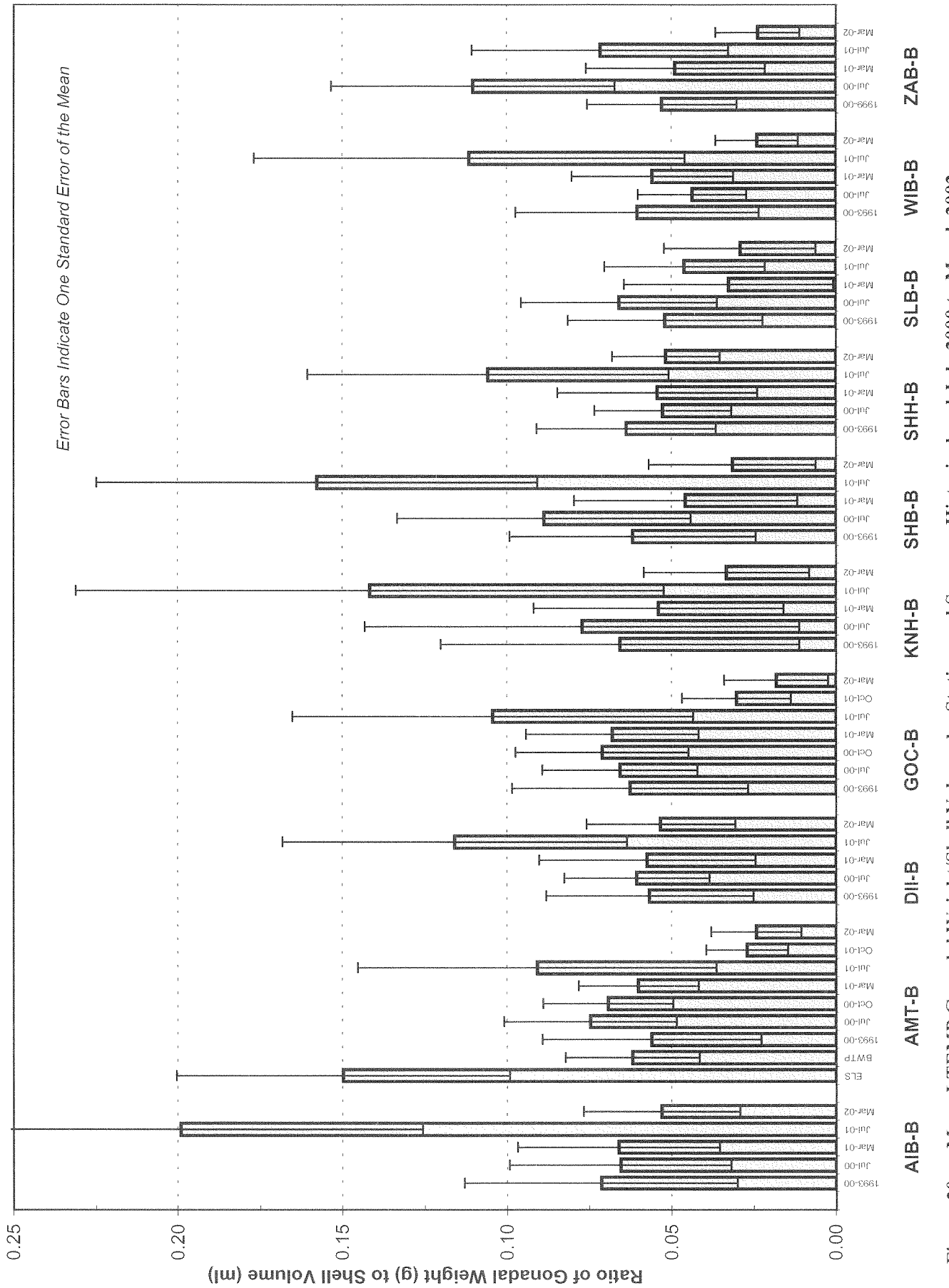


Figure 20. Mean LTEMP Gonadal Weight/Shell Volume by Station and Survey - Historical and July 2000 to March 2002.

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.

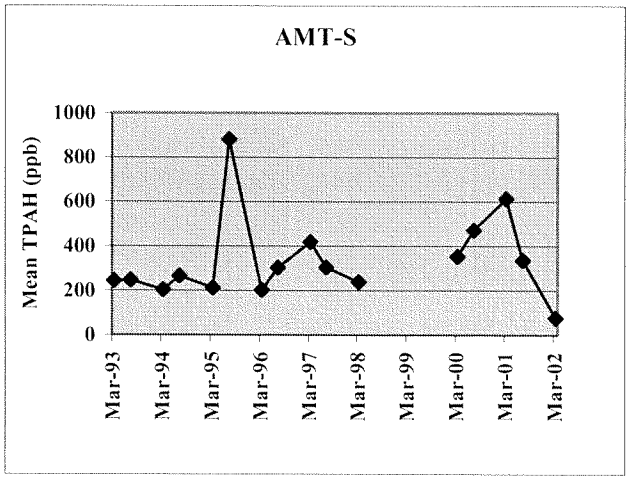
Aliphatic and polycyclic aromatic hydrocarbons were measured in subtidal sediments at the two Port Valdez LTEMP stations (AMT-S and GOC-S) during the surveys which were performed in March and July of each sampling year. No sediment samples were collected at these stations during the October surveys and no other LTEMP sediment stations were sampled during this reporting period.

5.3.1 Polycyclic Aromatic Hydrocarbons

Individual PAH analyte sediment replicate data are provided in Appendix B. The majority of individual PAH analytes were seen at levels above MDLs for all sediment samples. The TPAH values reported were well above the cumulative MDL of 35 ppb for July 2000, March 2001, and July 2001 (Table 21). In March 2002, two of the three replicates collected at each of the two stations were below the cumulative MDL of 94 ppb for TPAH, and many of the individual analytes were seen at below-MDL levels in these replicates.

Table 21. LTEMP Subtidal Sediment TPAH Results for July 2000 through March 2002.

Station	TPAH (ng/g or ppb)							
	Survey 17 (July 2000)				Survey 19 (March 2001)			
	Rep. 1	Rep. 2	Rep. 3	Mean	Rep. 1	Rep. 2	Rep. 3	Mean
AMT-S	391.8	452.0	571.4	471.7	814.4	464.4	563.3	614.0
GOC-S	104.6	110.6	92.1	102.4	125.3	130.6	120.2	125.4
Station	**TPAH (ng/g or ppb)**							
	Survey 20 (July 2001)				Survey 22 (March 2002)			
	Rep. 1	Rep. 2	Rep. 3	Mean	Rep. 1	Rep. 2	Rep. 3	Mean
AMT-S	159.8	535.8	310.5	335.4	9.6	67.8	148.3	75.2
GOC-S	39.8	59.0	108.3	69.0	91.2	32.5	133.8	85.8



Individual replicate TPAH at Station AMT-S ranged from an extremely low value of approximately 10 ppb (March 2002) to 814 ppb (March 2001). Mean TPAH values for Station AMT-S ranged from 75 (March 2002) to 614 ppb (March 2001; Table 21). As shown in Figure 21 and Table 22, there was a fair amount of variability between sampling periods as well as between replicates. The mean TPAH values seen during this reporting period were within the historical range of values seen at this station (202 - 880 ppb), except for the March 2002 survey, which showed a mean TPAH of 75 ppb (replicate values of 10, 68, and 148 ppb). The extremely low value seen at Replicate 1 was questioned by the laboratory (without knowing the station location) and re-injected for re-analysis, but sample results remained unchanged. All of the values for this replicate were estimated (below MDL) or non-detect. Replicate 2 at this station was also considerably lower than most seen in the past at this station, with many analytes at below-MDL levels, while Replicate 3 was more in line with the lower range of values seen in the past here. A review of the

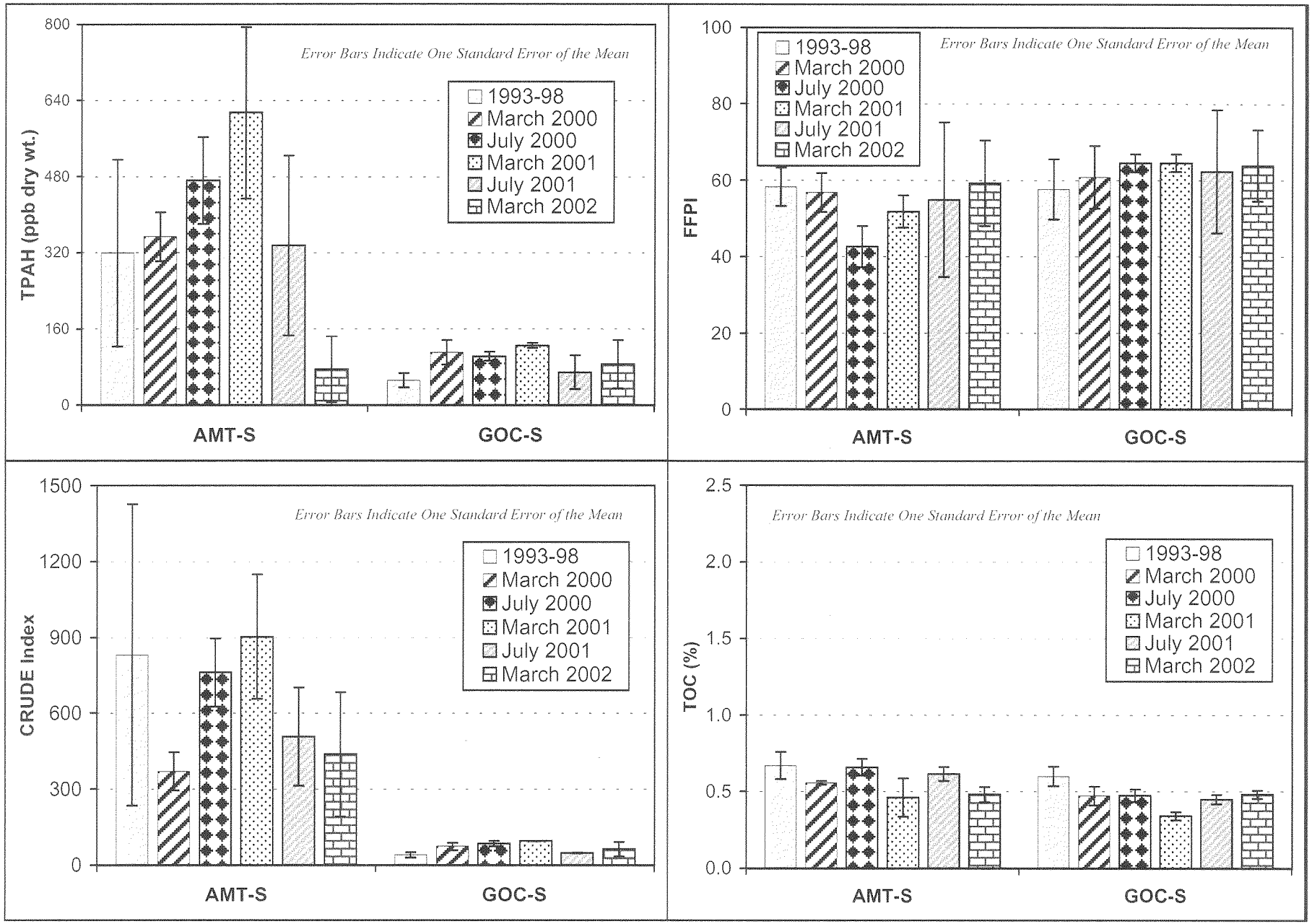


Figure 21. Mean LTEMP Subtidal Sediment TPAH, FFPI, CRUDE Index, and TOC by Station, Historical and March 2000 to March 2002.

Table 22. Mean LTEMP Subtidal Sediment Results at Stations AMT-S and GOC-S – 1993 through 2002.

STATION (SURVEY)	TPAH (ng/g)	FFPI (ratio)	TAHC (ng/g)	CPI (ratio)	TRAHC (μg/g)	UCM (μg/g)	CRUDE* (ratio)	TOC (%)	Silt+ Clay (%)
AMT-S (3/93)	242.6	60.8	2091	1.5	NA	122.2	1199.2	0.77	92.6
AMT-S (7/93)	246.0	56.4	2018	1.3	NA	120.6	1453.5	0.67	94.4
AMT-S (3/94)	202.5	53.9	1473	2.3	NA	98.8	486.5	0.58	94.3
AMT-S (7/94)	264.4	57.9	1530	1.9	NA	93.2	670.0	0.65	95.7
AMT-S (3/95)	212.0	45.7	1390	1.6	NA	98.7	738.4	0.63	94.9
AMT-S (7/95)	880.2	62.9	2275	1.2	NA	134.2	2267.5	0.77	95.1
AMT-S (3/96)	201.8	57.9	1262	3.1	NA	101.8	350.0	0.54	97.1
AMT-S (7/96)	302.5	62.3	1883	2.5	NA	108.5	598.3	0.69	95.6
AMT-S (3/97)	417.8	63.0	2370	2.3	NA	1.0	712.3	0.83	92.8
AMT-S (7/97)	303.2	61.2	1498	4.1	NA	89.6	365.8	0.59	96.7
AMT-S (3/98)	238.0	58.7	1251	3.8	NA	61.7	290.2	0.65	97.4
AMT-S (3/00)	353.2	56.8	1536	4.9	4.7	103.3	366.8	0.56	97.9
AMT-S (7/00)	471.7	42.6	2401	2.6	7.8	156.4	760.6	0.66	94.8
AMT-S (3/01)	614.0	51.8	2482	2.5	7.9	157.2	902.4	0.46	95.2
AMT-S (7/01)	335.4	54.9	1429	2.4	5.3	64.2	506.5	0.61	94.9
AMT-S (3/02)	75.2	53.9	2824	2.9	0.8	17.0	436.7	0.48	94.6
GOC-S (3/93)	47.3	61.0	946	15.9	NA	6.2	38.7	0.70	79.4
GOC-S (7/93)	37.7	58.5	567	12.1	NA	3.7	29.7	0.63	88.5
GOC-S (3/94)	58.5	59.2	879	14.1	NA	3.3	49.5	0.54	88.8
GOC-S (7/94)	44.4	55.4	500	18.8	NA	2.7	28.7	0.55	75.5
GOC-S (3/95)	40.6	50.9	438	18.5	NA	0.7	22.6	0.55	81.6
GOC-S (7/95)	52.1	53.2	597	13.1	NA	4.2	35.4	0.65	86.4
GOC-S (3/96)	89.1	40.5	527	14.7	NA	14.3	52.9	0.53	88.0
GOC-S (7/96)	51.1	61.8	537	39.5	NA	13.1	45.0	0.55	74.8
GOC-S (3/97)	44.1	63.1	499	7.9	NA	1.7	37.5	0.69	81.7
GOC-S (7/97)	55.7	58.8	618	9.2	NA	18.3	58.4	0.62	87.4
GOC-S (3/98)	42.4	71.7	331	8.9	NA	1.4	36.0	0.55	90.6
GOC-S (3/00)	110.9	60.8	725	104.7	2.6	4.1	71.6	0.47	91.4
GOC-S (7/00)	102.4	64.5	877	10.4	2.3	10.6	84.9	0.47	90.3
GOC-S (3/01)	125.4	64.6	879	13.2	2.5	8.9	94.9	0.34	86.2
GOC-S (7/01)	69.0	62.3	1270	30.2	2.7	0.6	47.8	0.45	87.4
GOC-S (3/02)	85.8	63.9	1380	15.8	0.6	4.0	62.8	0.48	86.1

* CRUDE Index values for March 1993 to March 1998 are calculated from station and survey means rather than individual replicate data.

NA Not Analyzed

navigation data for this survey by individual replicate compared to the other surveys failed to indicate any problems with vessel positioning that might have potentially accounted for these low TPAH values. The lowest individual replicate value that had been seen here in the past was 120 ppb during March 1998. In comparison with the March 2002 data, the TPAH levels documented during March 2001 were quite high. Individual replicates here exhibited 464, 563, and 814 ppb, which were among the highest seen to date. The overall median for mean TPAH at this station was 284 ppb.

Mean PAH example fingerprints for Stations AMT-S and GOC-S (for March 2001) are provided in Figure 22. As in the past, July 2000 and March 2001 PAH fingerprints at Station AMT-S exhibited signatures typical of the

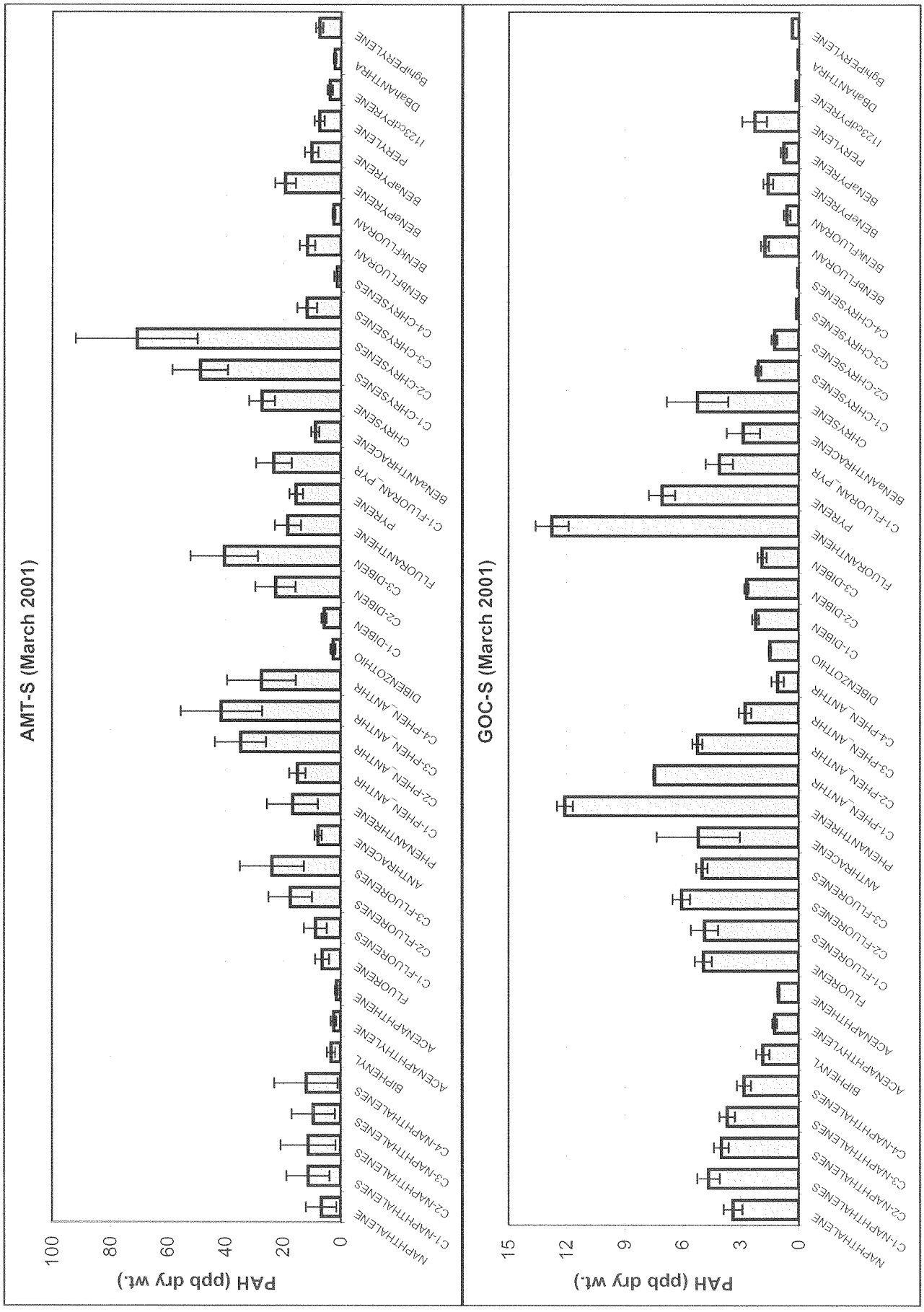


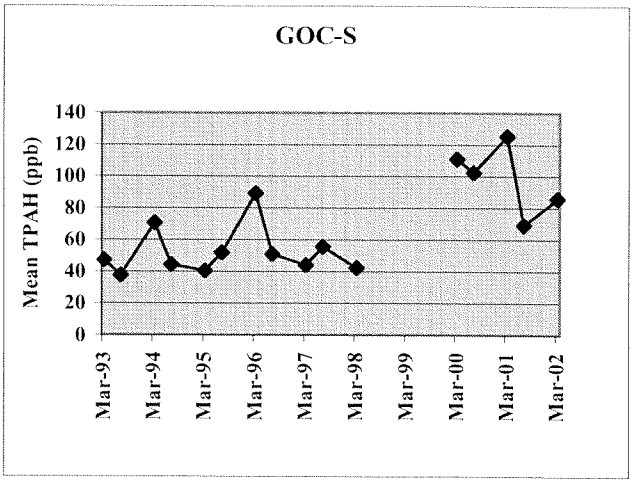
Figure 22. Mean LTEMP Subtidal Sediment PAH Fingerprints - March 2001 Survey, Stations AMT-S and GOC-S.

signatures had a petroleum along with low levels of 5- and 6-ring PAH (above C_3-dibenzothiophene), suggesting some additional input of pyrogenic hydrocarbons that may have had a combustion or creosote origin. The petroleum component pattern that was typical of weathered ANS crude. The weathering is shown by the persistence of the alkylated homologues compared to their parent compounds as seen in the fluorene, phenanthrene/anthracene, dibenzothiophene, and chrysene series, where $C_0<C_1<C_2<C_3<C_4$. ANS is indicated by the ratio of the C_2- and C_3-dibenzothiophenes to phenanthrenes (most values ~1). Previous work in the area by numerous investigators has shown the natural background PAH signature in the Prince William Sound region to have a ratio of ~ 0.2 for C_2- and C_3-dibenzothiophenes to phenanthrenes and ANS to have a value near 1.0. This difference clearly indicates that the PAH in the subtidal sediments seen at this location are not from natural background sources but are more likely due to the tanker operations and/or the ballast water discharge from the BWTP. The fact that the chrysenes are present would indicate an ANS crude rather than ANS diesel fuel as the source of the hydrocarbon input.

The PAH fingerprint from July 2001 exhibited a combination of sources, including background sources, ANS crude, and pyrogenic sources. Although overall concentrations were relatively low compared to the prior two surveys, a weathered profile was still apparent. March 2002 concentrations were very low, particularly Replicates 1 and 2, but Replicate 3 showed a similar pattern.

The average ratio of C_2-chrysene to C_2-phenanthrene can be used as a indication of the degree of weathering. With weathering, this ratio increases since the alkyl phenanthrenes are degraded more quickly than the alkyl chrysenes. 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). In Station AMT-S sediments during July 2000 and March 2001 respectively, the mean C_2-chrysene/C_2-phenanthrene ratio were 2.9 and 2.0 (Figure 22 and Appendix B). This ratio indicates that if the source was ANS crude, the oil had weathered substantially, which is consistent with past LTEMP data from this location. 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.

Individual replicate TPAH at Station GOC-S ranged from approximately 33 to 134 ppb. Mean TPAH at this station ranged from 69 to 125 ppb for this sampling period, extending the maximum from the previous range of historical values (38 to 111 ppb). March 2001 proved to be the overall high for this station and showed good agreement between replicates at 120, 125, and 131 ppb. The overall median for mean TPAH at this station was 54 ppb.



Station GOC-S also showed both petrogenic and pyrogenic inputs with a predominance of pyrogenic components for all four surveys. The fingerprints show patterns of high concentrations of the parent compound compared to their alkyl homologues in the naphthalene, phenanthrene/anthracene, and chrysene series, indicating pyrogenic inputs (Figure 22). 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 pyrogenic pattern is the $C_0>C_1>C_2>C_3>C_4$. Also, the phenanthrene series were in general much higher in concentration than the dibenzothiophene series, which would indicate a background signature rather than ANS crude.

The individual replicate FFPI ratios at Station AMT-S ranged from 36 to 78, while mean FFPI ratios ranged from 43 to 59 (Table 23). The historical range for this station was 46 to 63. This value for the July 2000 survey extended the overall range downward. This low mean FFPI during this survey was mainly due to Replicate 3, which showed increased levels of compounds greater than C_3-dibenzothiophene, which is characteristic of pyrogenic sources. As shown in Figure 21, most FFPI values showed a fair amount of intra-station variability, especially during the July 2001.

The FFPI ratios at Station GOC-S ranged from 44 to 73 for these four surveys, with mean FFPI tightly grouped at 62 to 65. This compared to a historical mean FFPI range of 41 to 72. Again, a fair amount of variability was seen between replicates, particularly in July 2001, but the station mean for this survey was very similar to the others.

Table 23. LTEMP Subtidal Sediment FFPI Results for July 2000 through March 2002.

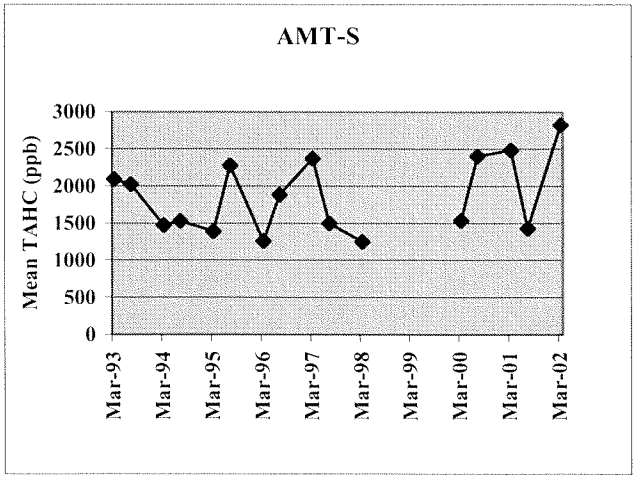
Station	FFPI (ratio)							
	Survey 17 (July 2000)				Survey 19 (March 2001)			
	Rep. 1	Rep. 2	Rep. 3	Mean	Rep. 1	Rep. 2	Rep. 3	Mean
AMT-S	45.4	45.9	36.4	42.6	56.6	50.2	48.6	51.8
GOC-S	61.9	66.1	65.5	64.5	63.7	62.8	67.2	64.6
Station	FFPI (ratio)							
	Survey 20 (July 2001)				Survey 22 (March 2002)			
	Rep. 1	Rep. 2	Rep. 3	Mean	Rep. 1	Rep. 2	Rep. 3	Mean
AMT-S	44.2	42.2	78.2	54.9	68.3	62.8	46.7	59.3
GOC-S	69.9	73.1	43.8	62.3	72.3	65.4	53.9	63.9

5.3.2 Aliphatic Hydrocarbons

Concentrations of individual aliphatic hydrocarbons in sediments by station and replicate are presented in Appendix B. The TAHC consists of the sum of the individual alkanes, pristane, and phytane (Table 5) and is summarized by station and replicate in Table 24 for this sampling period. Although some of the individual analytes fell below their MDLs, especially at Station GOC-S where lower AHC levels were documented, the majority was above MDLs, and all of the TAHC values were above the cumulative MDLs reported for this sample set (Table 5).

Table 24. LTEMP Subtidal Sediment TAHC Results for July 2000 through March 2002.

Station	TAHC (ng/g or ppb)							
	Survey 17 (July 2000)				Survey 19 (March 2001)			
	Rep. 1	Rep. 2	Rep. 3	Mean	Rep. 1	Rep. 2	Rep. 3	Mean
AMT-S	2080	3016	2107	2401	2987	1803	2658	2483
GOC-S	966	753	912	877	904	833	901	879
Station	TAHC (ng/g or ppb)							
	Survey 20 (July 2001)				Survey 22 (March 2002)			
	Rep. 1	Rep. 2	Rep. 3	Mean	Rep. 1	Rep. 2	Rep. 3	Mean
AMT-S	1044	1275	1969	1429	2508	2452	3514	2824
GOC-S	311	505	2993	1270	1568	1165	1407	1380



The concentrations of individual replicate TAHC at Station AMT-S ranged from approximately 1,044 to 3,514 ppb (Table 24). Mean TAHC ranged from 1,429 to 2,824 ppb for the four surveys reported here (Tables 22 and 24), as compared to the historical range of 1,251 to 2,370 ppb. Three of the four surveys reported here exhibited mean TAHC above the historical maximum, extending the overall range. March 2002 was particularly elevated, with replicates ranging from 2,452 to 3,514 ppb. This was in contrast to the mean TPAH where an all-time low was recorded for this survey. As seen in Figure 23, there was a fair amount of intra-station variability within this station except for the March 2000 sampling, which showed less scatter. The overall median for the station was 1,710 ppb.

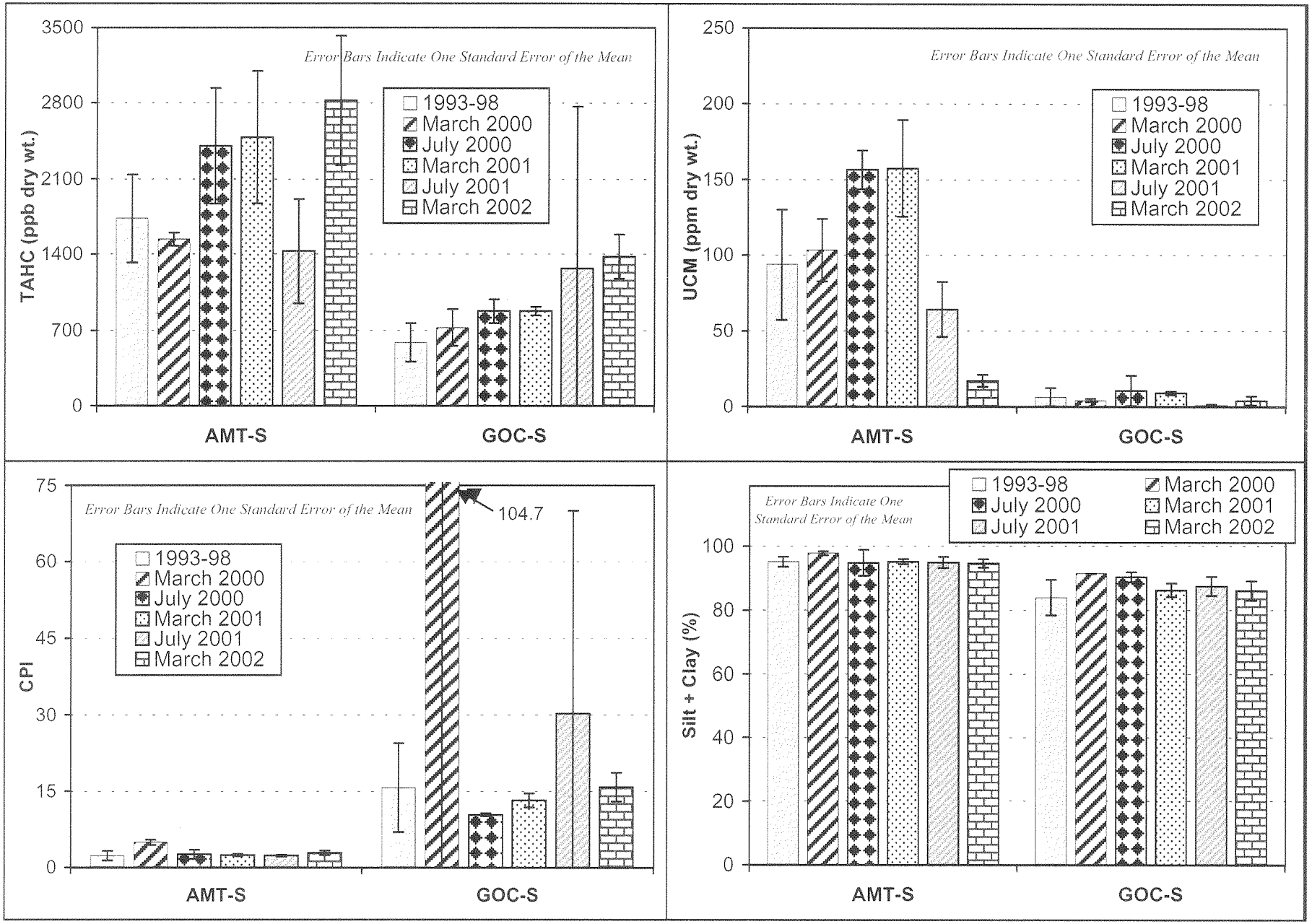
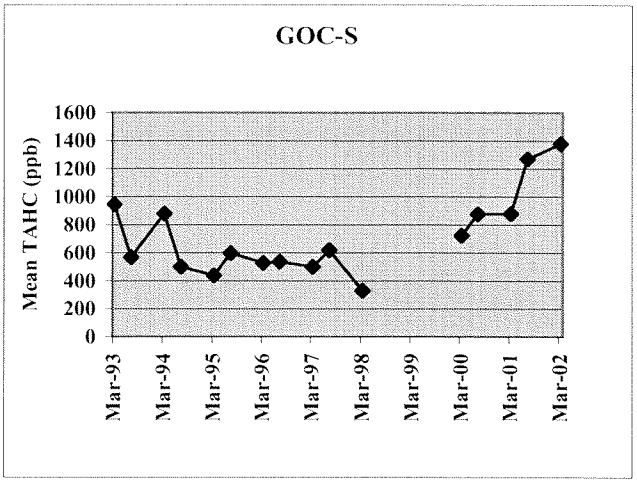


Figure 23. Mean LTEMP Subtidal Sediment TAHC, UCM, CPI, and Silt+Clay by Station, Historical and March 2000 to March 2002.

The AHC fingerprints at Station AMT-S indicated a much higher predominance of higher molecular weight aliphatic hydrocarbons as compared to the lower weight compounds, which would indicate a weathered source. In general, the odd alkanes were slightly higher but still similar in concentration to the even alkanes. This would indicate petrogenic hydrocarbons as the primary source with smaller amounts of biogenic inputs (Figure 24).

Individual replicate TAHC values at Station GOC-S ranged between 311 and 2,993 ppb (Table 24). Mean TAHC values ranged from 877 to 1,380 ppb for the four surveys compared to a historical range of 331 to 946 ppb (Table 22). As at Station AMT-S, the last two surveys extended the upper range of mean TAHC values. This is in contrast to the PAH data and was accounted for by elevated concentrations of n-C_{27} in most replicates. As noted below in the discussion of CPI, these high n-C_{27} concentrations were due to a greater influence of plant materials (lipids) on this odd peak in the aliphatic analysis. The July 2001 survey showed considerable intra-station variability with the three replicates at ranging from 311 to 2,993 ppb (Figure 23). The overall median for mean TAHC at Station GOC-S was 608 ppb.



The AHC fingerprints at Station GOC-S had a predominance of odd alkanes, especially n-C_{25}, n-C_{27}, n-C_{29}, and n-C_{31}. This indicates a biogenic source which contrasts with that seen at Station AMT-S. Also, the predominance of the higher end molecular weight compounds was indicative of a weathered source.

The individual replicate CPI ratios at Station AMT-S ranged from 2.0 to 3.6, while mean CPI ratios ranged from 2.4 to 2.9 (Table 25). The historical range of mean CPI for this station was 1.2 to 4.9, and the overall station median of mean CPI was 2.4 (Table 22). As shown in Figure 23, most CPI values were tightly replicated and all from this sampling period fell within historical range. Pure petrogenic sources are characterized by a CPI that is approximately 1. The fairly low CPI values reported at this station over time indicate a combination of both petrogenic and biogenic inputs.

The individual replicate CPI ratios at Station GOC-S ranged from 4.1 to 76.0 during this reporting period, with mean CPI ranging from 10.4 to 30.2. An extremely high value calculated for Replicate 3 during July 2001 resulted in these extreme maxima. This high CPI value resulted from an extremely elevated level of n-C_{27} in this sample, which was re-checked at the laboratory for confirmation before reporting. This high concentration was due to the influence of plant materials (lipids) on this odd peak in the aliphatic analysis. However, since the data point could not be excluded as it met all required analytical guidelines, it was reported as n-C_{27}. This high n-C_{27} value resulted in an extremely high CPI result. The relatively high CPI values seen at Station GOC-S are fairly typical of biogenic inputs, as biological material is indicated by the predominance of odd alkanes in the n-C_{21} to n-C_{33} range of normal alkanes.

Table 25. LTEMP Subtidal Sediment CPI Results for July 2000 through March 2002.

Station	CPI (ratio)							
	Survey 17 (July 2000)				Survey 19 (March 2001)			
	Rep. 1	Rep. 2	Rep. 3	Mean	Rep. 1	Rep. 2	Rep. 3	Mean
AMT-S	2.0	3.6	2.1	2.6	2.6	2.6	2.2	2.5
GOC-S	10.0	10.5	10.5	10.4	13.8	11.5	14.1	13.2
Station	**CPI (ratio)**							
	Survey 20 (July 2001)				Survey 22 (March 2002)			
	Rep. 1	Rep. 2	Rep. 3	Mean	Rep. 1	Rep. 2	Rep. 3	Mean
AMT-S	2.2	2.6	2.3	2.4	3.0	3.2	2.4	2.9
GOC-S	4.1	10.5	76.0	30.2	17.4	12.5	17.4	15.8

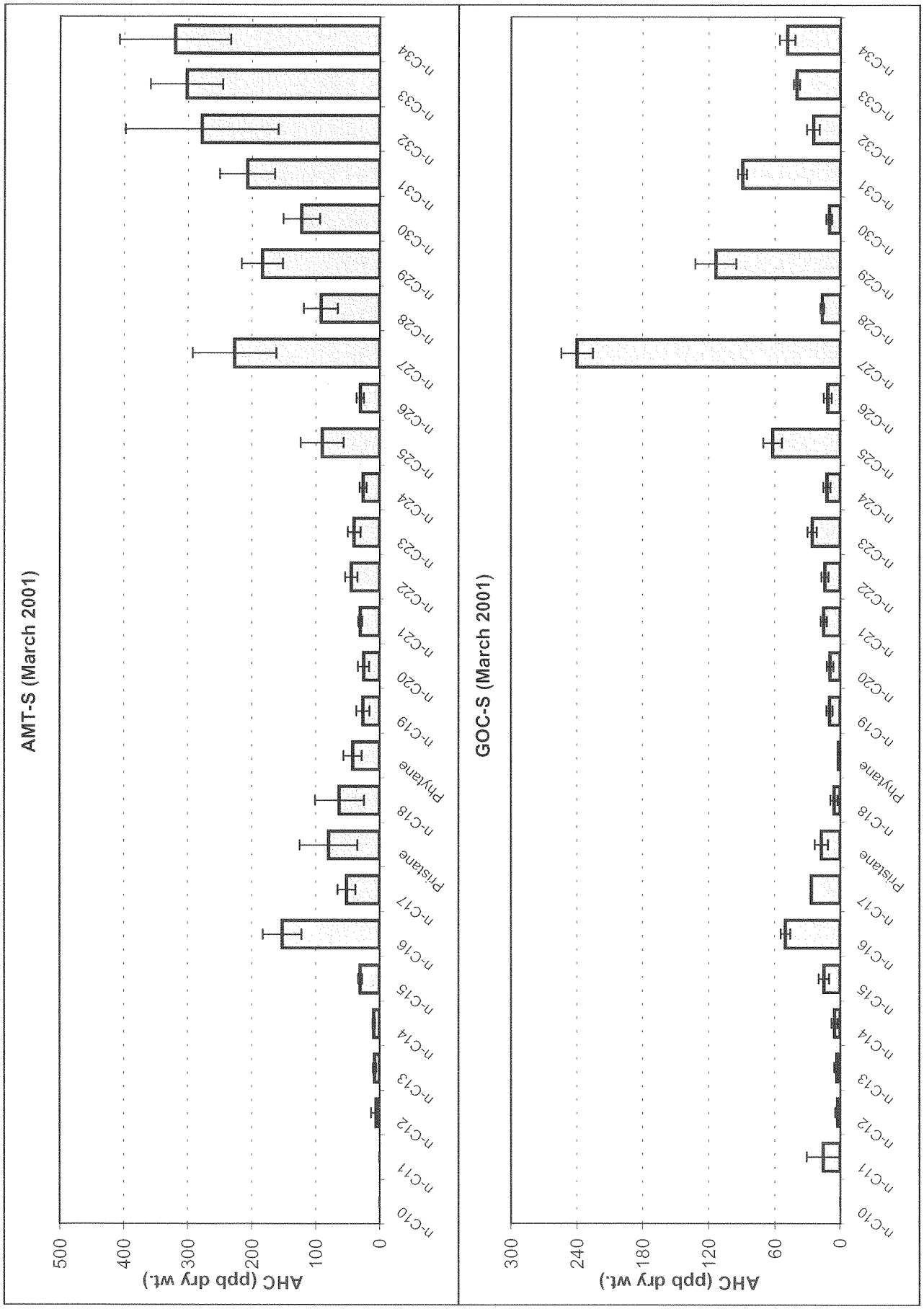


Figure 24. Mean LTEMP Subtidal Sediment AHC Fingerprints - March 2001 Survey, Stations AMT-S and GOC-S.

The replicate UCM values at Station AMT-S ranged from approximately 12 to 176 ppm, with mean concentrations ranging from 17 to 157 ppm (Table 26). This compared to a historical range of 1 to 134 ppm for mean UCM at this station (Table 22). The relatively high values seen in July 2000 and March 2001 extend the overall maximum seen at this station, as can be seen in Figure 23. The overall median for mean UCM at Station AMT-S was 100 ppm. Historically, Station AMT-S has always exhibited a high UCM compared to other LTEMP subtidal sediment stations, including Station GOC-S. A large UCM relative to TAHC is generally a feature of weathered petroleum. This petrogenic input at Station AMT-S and the fact that the samples showed a high degree of weathering was confirmed by the PAH analysis discussed earlier. The individual UCM at Station GOC-S ranged from non-detect to 22 ppm for the four surveys. The mean UCM concentrations ranged 0.6 to approximately 11 ppm as compared to a historical range of 0.7 to 18 ppm. The median for mean UCM for all surveys was 4 ppm.

Table 26. LTEMP Subtidal Sediment UCM Results for July 2000 through March 2002.

Station	UCM (µg/g or ppm)							
	Survey 17 (July 2000)				Survey 19 (March 2001)			
	Rep. 1	Rep. 2	Rep. 3	Mean	Rep. 1	Rep. 2	Rep. 3	Mean
AMT-S	151.8	170.8	146.6	156.4	175.9	120.5	175.2	157.2
GOC-S	22.1	3.4	6.4	10.6	10.0	7.7	8.9	8.9
Station	**UCM (µg/g or ppm)**							
	Survey 20 (July 2001)				**Survey 22 (March 2002)**			
	Rep. 1	**Rep. 2**	**Rep. 3**	**Mean**	**Rep. 1**	**Rep. 2**	**Rep. 3**	**Mean**
AMT-S	44.4	67.8	80.4	64.2	12.4	19.7	19.0	17.0
GOC-S	0.0	1.7	0.2	0.6	2.9	1.8	7.3	4.0

The TRAHC values for subtidal sediments are provided in Table 27. Individual replicate TRAHC values ranged from 0.7 to 9.2 ppm at Station AMT-S. Mean TRAHC values ranged from 0.8 to 7.9 ppm at this station. Individual replicate TRAHC values ranged from 0.4 ppm to 5.5 ppm at Station GOC-S. Mean TRAHC values ranged from 0.6 to 2.7 ppm for this station. The within-station variability was fairly low during most surveys at these two locations. This parameter corresponds fairly well with the mean TAHC levels seen at these stations, with concentrations at Station AMT-S approximately twice as high as those seen at Station GOC-S.

Table 27. LTEMP Subtidal Sediment TRAHC Results for July 2000 through March 2002.

Station	TRAHC (µg/g or ppb)							
	Survey 17 (July 2000)				Survey 19 (March 2001)			
	Rep. 1	Rep. 2	Rep. 3	Mean	Rep. 1	Rep. 2	Rep. 3	Mean
AMT-S	7.1	9.2	7.2	7.8	9.0	6.3	8.3	7.9
GOC-S	1.8	1.8	3.4	2.3	2.5	2.6	2.4	2.5
Station	**TRAHC (µg/g or ppb)**							
	Survey 20 (July 2001)				**Survey 22 (March 2002)**			
	Rep. 1	**Rep. 2**	**Rep. 3**	**Mean**	**Rep. 1**	**Rep. 2**	**Rep. 3**	**Mean**
AMT-S	3.6	4.0	8.2	5.3	0.7	0.8	0.8	0.8
GOC-S	1.2	1.5	5.5	2.7	0.6	0.4	0.8	0.6

The CRUDE index values calculated for the two locations for the four surveys are provided in Table 28. Individual replicate values ranged from 293 to 1,084 at Station AMT-S with the means ranging from 437 to 902. The historic range for mean CRUDE values was 290 to 2,268 for this station. The overall median value was 634. Station GOC-S CRUDE values were much lower and ranged from 31 to 96 for individual replicates, with means ranging from 48 to 95. The historic range for mean CRUDE was 23 to 74 for this station; this range was extended by several surveys during this latest sampling period. The overall median value of mean CRUDE for Station GOC-S was 46.

Table 28. LTEMP Subtidal Sediment CRUDE Results for July 2000 through March 2002.

Station	CRUDE (ratio)							
	Survey 17 (July 2000)				Survey 19 (March 2001)			
	Rep. 1	Rep. 2	Rep. 3	Mean	Rep. 1	Rep. 2	Rep. 3	Mean
AMT-S	858.8	605.9	817.1	760.6	1084.0	622.2	1001.0	902.4
GOC-S	96.4	83.3	75.1	84.9	94.5	96.0	94.2	94.9
Station	**CRUDE (ratio)**							
	Survey 20 (July 2001)				Survey 22 (March 2002)			
	Rep. 1	Rep. 2	Rep. 3	Mean	Rep. 1	Rep. 2	Rep. 3	Mean
AMT-S	322.2	487.8	709.6	506.5	292.8	296.8	720.6	436.7
GOC-S	46.0	49.4	48.1	47.8	74.0	30.5	84.0	62.8

Comparisons of historic CRUDE index values to those seen in these surveys indicate that the index was within the range seen historically at Station AMT-S (Table 22 and Figure 21). At Station GOC-S, the CRUDE index was slightly higher than those seen historically. The higher CRUDE values at Station GOC-S for these surveys can be traced to the TPAH concentrations which were somewhat higher than those seen historically, as discussed above. The AHC contribution to the CRUDE index at GOC-S was small due to the high CPI values. As expected, the highest mean CRUDE index value was seen at Station AMT-S, which exhibits clear ANS crude petroleum contamination and showed the highest mean TPAH, TAHC, and UCM values. The CRUDE index does provide a useful tool for comparison in sediments, although it is not useful in tissues. The calculation serves to normalize the concentrations against the sources so that actual petroleum contamination can be identified by magnifying petrogenic inputs relative to biogenic inputs in the AHC fraction, magnifying petrogenic inputs relative to pyrogenic inputs in the PAH fraction, and accounting for weathered petroleum in the UCM fraction. For example in the CRUDE calculation, an initially heavy indication of potential petroleum contamination caused by a relatively high mean TPAH or TAHC value is reduced by a low FFPI (pyrogenic inputs) or high CPI (biogenic inputs).

5.3.3 Total Organic Carbon

Concentrations of mean TOC in sediments ranged from 0.46 to 0.66 % for Station AMT-S and from 0.34 to 0.48 % at Station GOC-S (Table 29 and Figure 21; Appendix B). Mean TOC data from this period extended the range downward for both stations (Table 22). A fair degree of within-station variability was seen at Station AMT-S during the March 2001 survey, but other surveys showed good agreement between replicates.

Table 29. LTEMP Subtidal Sediment TOC Results for July 2000 through March 2002.

Station	TOC (%)							
	Survey 17 (July 2000)				Survey 19 (March 2001)			
	Rep. 1	Rep. 2	Rep. 3	Mean	Rep. 1	Rep. 2	Rep. 3	Mean
AMT-S	0.63	0.72	0.62	0.66	0.60	0.36	0.42	0.46
GOC-S	0.48	0.43	0.51	0.47	0.35	0.36	0.31	0.34
Station	TOC (%)							
	Survey 20 (July 2001)				Survey 22 (March 2002)			
	Rep. 1	Rep. 2	Rep. 3	Mean	Rep. 1	Rep. 2	Rep. 3	Mean
AMT-S	0.66	0.57	0.61	0.61	0.48	0.43	0.53	0.48
GOC-S	0.48	0.44	0.42	0.45	0.51	0.47	0.46	0.48

5.3.4 Particle Grain Size

A summary of particle grain size results is provided in Table 30 and Figure 23; historical data are provided in Table 22. Appendix B provides individual analyte data by replicate. Sediment samples primarily consisted of silt plus clay at both subtidal locations. The silt/clay fractions at Station AMT-S ranged between 90 and 97 % with survey means ranging all around 95 %, which compares well with an overall median of 95 % for this station. Silt/clay fractions at Station GOC-S were typically more variable and ranged between 83 and 92 %, with means ranging from 86 to 90 %. This compares to an overall median of 87 %.

Table 30. LTEMP Subtidal Sediment Silt + Clay Results for July 2000 through March 2002.

Station	Silt + Clay (%)							
	Survey 17 (July 2000)				Survey 19 (March 2001)			
	Rep. 1	Rep. 2	Rep. 3	Mean	Rep. 1	Rep. 2	Rep. 3	Mean
AMT-S	97.3	90.1	97.0	94.8	94.6	94.8	96.1	95.2
GOC-S	91.8	88.6	90.6	90.3	83.8	87.9	86.9	86.2
Station	Silt + Clay (%)							
	Survey 20 (July 2001)				Survey 22 (March 2002)			
	Rep. 1	Rep. 2	Rep. 3	Mean	Rep. 1	Rep. 2	Rep. 3	Mean
AMT-S	92.9	95.5	96.4	94.9	95.4	93.1	95.4	94.6
GOC-S	89.4	88.9	84.0	87.4	83.3	89.4	85.5	86.1

5.4 Quality Control Results

Quality control results are provided in Appendix C (tissue) and Appendix D (sediment) 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 data reported during the 2000 - 2002 LTEMP indicates that 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 noted in Section 5.3.2, tissue AHC results showed elevated levels of the several of the odd alkanes in the n-C_{21} to n-C_{33} range, which are fairly typical of biogenic inputs that can not be removed by the extraction and cleaning process. Although it is clear that plant lipid material is co-eluting with the aliphatic hydrocarbons in some cases, since these analytical peaks meet the laboratory's guidelines for aliphatic peak identification and quantification, they have not been removed from the data. This is particularly true for tissues but can come into play even with sediments, as described above.

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. In all cases where non-compliant surrogate recoveries were noted, the peak integrations and calculations for each sample were checked. The values for these samples were annotated with an appropriate qualifier (Table 8) before reporting.

The surrogate perylene-d_{12} fell outside the acceptance criteria for a number of samples and QC samples and was appropriately qualified with the "Q". 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 qualified recovery is not problematic for LTEMP because not only is this surrogate considered advisory only, perylene is a biogenic hydrocarbon that has not been included in TPAH values for this program.

One deuterated acenaphthene-D_{10} QC sample had low surrogate recovery; this was denoted with the "Q" qualifier. Two samples and three QC samples showed low surrogate recoveries for deuterated naphthalene-D_8 and were labeled with the "Q" qualifier after further investigation indicated the loss of this surrogate was not significant to the data. No further action was required.

The values for the surrogate deuterated n-C_{12} were qualified on six samples and four quality control samples because they exhibited low, non-compliant recoveries. Deuterated n-C_{24} exhibited high surrogate recoveries in three samples. The values for these samples were qualified with an "M" to denote matrix interference or a "Q" indicating the QC variance. In one QC sample, the deuterated n-C_{24} exhibited slightly low recoveries; this value was qualified with the "M" qualifier, and no further action was required.

The values for deuterated n-C_{30} were qualified on many tissue and a few sediment QC samples. Recoveries in most of these cases were high. After further investigation, the values for most of these samples were qualified with an "M" to denote matrix interference; two were qualified with a "Q" indicating the QC variance. No further action was required.

5.4.2 Procedural Blanks

With the exception of two samples, the procedural blanks analyzed in conjunction with tissue and sediment analyses for the 2000 - 2002 LTEMP contained negligible concentrations of PAH and AHC analytes and carbon (for TOC) at levels less than the maximum acceptance criteria (i.e., less than three times the MDL). Many of these concentrations were qualified as ND or below the MDL ("J"). Two procedural blanks (Q19836 and Q19850) associated with the July 2001 tissue samples exhibited interference with n-C_{15}, which was identified as a silicone peak which sometimes appears as an instrumental artifact of the GC. This can sometimes interfere with n-C_{15} but not with other alkanes. These values were qualified with the "B" and "Q" qualifiers and no further action was required. As in the past, some of the procedural blanks 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

Analyses of the 2000 - 2002 LTEMP samples included the analysis of matrix spike/spike duplicate pairs for PAH and AHC. Use of the laboratory spikes due to insufficient sample material was not required during this sample set except for one batch where additional spikes were needed for another sample run to complete duplicate analyses on tissues for March 2002. While some individual analytes showed low or high percent recoveries falling outside the 40 to 120 % acceptance criteria, all matrix spike/spike duplicate samples (and lab spike/spike duplicate samples) passed the QA criteria for average percent recovery and RPD. Peaks for all individual analytes falling outside the criteria were checked and, since no improvements could be made and the overall QA objectives had been met in all cases, these analytes were qualified with a "Q". No further action was required. For the October 2000 survey, one tissue matrix spike and one matrix spike duplicate sample (Q19161 and Q19162) had

invalid spike results for n-C_{21} as the native concentration in the sample exceeded the spike amount. For the March 2001 survey, several PAH analytes were spiked at levels less than the native concentrations in the samples and were therefore invalid. These analytes were qualified in the data and no further action was required.

5.4.4 Reference Oil

Reference oil samples of petroleum oil (GERG STD Check or STD OIL 2000) were reported for PAH and AHC during the 2000 - 2002 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. Five analytes failed to meet QC (showing elevated levels) in reference oil samples associated with tissue analyses (July 2000 and October 2000) and sediment analyses (July 2000 and March 2002). The five individual analyte results (for n-C_{10}, fluorene, and C_1-fluorenes) showing values outside the acceptable limits were investigated, with the peak integration being checked and the calibration verified. Since no interferences were found and the overall QA criteria were met, each data point was appropriately qualified with the "Q" qualifier. No further action was required.

5.4.5 Standard Reference Materials

Standard Reference Materials (NIST 1941A, 1974, 2974, or 2978 [tissue] or 1944 [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. Reported PAH analytes having non-certified values were compared to laboratory acceptance limits and also appropriately qualified. Although non-compliant recoveries were noted in fifteen instances for acenaphthylene, anthracene, benzo(a)pyrene, fluoranthene, and pyrene, no interferences were noted by the analysts upon investigation by re-checking these peaks, and overall QC criteria were met in all these samples. These individual analytes falling outside the acceptance range were appropriately qualified and no further action was required.

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

The SRM analysis performed in conjunction with TOC analysis was also performed on NIST 1944. The six SRMs that were run for TOC for this reporting period exhibited recoveries that were within the laboratory's acceptance limits.

5.4.6 Duplicate Analyses

Duplicate analyses were performed for both tissue and sediment PAH and AHC for the 2000 - 2002 LTEMP. Duplicate analyses for PAH and AHC were compared with the original sample results to provide an estimate of precision, but specific QC criteria do not exist for these samples. Rather, RPD results are charted at the laboratory for comparison purposes. For several duplicate samples, no concentrations were measured at levels above 10 times the MDL, so the duplicate analysis was not valid for calculation of percent recovery. This included July 2000 sediment (AHC), March 2001 tissue samples (PAH and AHC), July 2001 tissue and sediment samples (PAH and AHC), and March 2002 sediment (PAH and AHC). July 2000 sediment PAH duplicates met requirements.

For March 2002 tissue, most PAH and AHC analytes fell below the 10 times MDL level. Three analytes for sample PWS02TIS0024 showed valid concentrations. Two of these exceeded the QC criteria. It was determined that these were lipids that were not removed from the extract during the cleanup process rather than alkanes. No further action was taken. The same case was seen for July 2000 and October 2000 aliphatics, where a few analytes exceeded the QC criteria. These peaks were also identified as probable lipids. These QA variances underscore the difficulties inherent in interpreting AHC analyses in tissues, which contain naturally-occurring lipids that are difficult to remove from the samples without removing alkanes and are also difficult to distinguish chromatographically. The PAH duplicate analyses for these surveys met laboratory criteria.

For October 2001, the overall QC criteria for duplicates as the average RPD for AHC was within the QC limits. One individual analyte that was high was qualified to denote this variance. The duplicate for PAH passes all QC criteria.

During the March 2001 sample analysis, sediment duplicates met the criteria for average RPD. Although some individual analytes were high, they failed to show concentrations above 10 times the MDL so were invalid for comparison.

Three sets of duplicate analyses performed for TOC met the acceptance criteria of RPD between duplicates of <20 for low carbon content samples (< 1.0 percent). No duplicate analysis for TOC was run for the July 2000 survey. Total carbon was duplicated rather than total organic carbon due to a laboratory error. While these data did meet laboratory requirements, total carbon is not target parameter of the LTEMP.

No strict acceptance criteria exist for PGS duplicates. Instead, duplicate analyses are intended to provide an estimate of the homogeneity of the samples. The four duplicate sample pair analyses for PGS analysis exhibited RPDs ranging from 0.2 to 7.

6.0 SUMMARY

The 2000 - 2002 LTEMP has added additional data to the information that has been collected since 1993. During the sampling period reported here, ten stations were sampled four times for intertidal mussels. The two existing LTEMP stations in Port Valdez were also sampled for intertidal mussels twice during fall sampling events to augment the temporal coverage of this area. In addition, subtidal sediment sampling at the two Port Valdez stations was performed four times during this reporting period. Analytical strategy for the 2000 – 2002 program was the same as the prior reporting period for LTEMP.

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, natural oil seepage, and atmospheric fallout. Data presented by Short et al. (1999) and other researchers indicate that the background signature previously attributed to natural oil seeps in the Katalla and Yakataga regions may actually originate in coal deposits. 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 2000 - 2002 data. For many stations, these sources are similar to those that had been identified in earlier program reports (KLI, 1993b; 1994a; 1995a; 1996a; 1997a, 1998, 1999, and 2000) and by other researchers examining LTEMP data (Payne et al., 1998).

The LTEMP data indicate that hydrocarbons in tissues in the study area vary considerably between stations and over time. The PAH levels in tissues were generally low, and all were within the historical range of levels seen at each site. Many individual analytes were reported at below-MDL levels, and TPAH frequently fell below cumulative MDLs. The increasing trend in tissue TPAH that had been seen prior to March 1998 has not been evident since that time, and more recent surveys have generally shown very low tissue TPAH concentrations.

As in the past, although tissue PAH concentrations were generally low, PAH fingerprints from many stations exhibited a petrogenic signal which could be attributed to several sources. As in many of the past surveys, PAH in the tissues at Station AMT-B were attributed to a combination of natural background and pyrogenic sources, and for at least two of the six sampling events here, ANS crude. As reported earlier for March 2000 and July 1998, the background signature was present in mussels at Station AMT-B during several surveys in this reporting period, perhaps visible due to the very low levels of PAH seen for these surveys. These signatures may reflect normal ("non-contaminated") levels in these mussels (i.e., with no petroleum inputs from operations at the Alyeska Marine Terminal). In contrast, no evidence of crude inputs was seen at Station GOC-B, with background and pyrogenic sources being responsible for the low level PAH concentrations seen here.

Mussels at Station DII-B, a site heavily oiled during the EVOS, exhibited very low levels of PAH and showed inputs from primarily background and pyrogenic sources. In contract to some earlier results, including those from opportunistic samples collected nearby from the still-visibly oiled beach area, no clear signature of crude was seen.

The other mussel tissue stations (AIB-B, KNH-B, SHB-B, SHH-B, SLB-B, WIB-B, and ZAB-B) primarily exhibited background petrogenic signatures, with varying amounts of pyrogenics seen at most stations. As in the past, biogenic inputs were also present at many stations, particularly Station WIB-B, which exhibited extremely high perylene levels during some surveys. During the March 2001 survey, Station SLB-B showed a higher level of pyrogenics compared to the prior three surveys. Also, the C_2- and C_3-dibenzothiophenes to C_2- and C_3-phenanthrenes ratios were elevated as compared to the other surveys which may indicate some crude contribution.

The AHC compounds in tissues were considerably higher than the PAH, as was expected due to the naturally-occurring compounds in mussel tissues that co-elute with the individual aliphatic analytes and interfere with the AHC analysis. Extremely high levels of aliphatics seen at some stations and for some analytes have been attributed to lipid interference with the analysis, most likely originating in the planktonic food source of the mussels. As in the 1993 - 1994 and 1998 - 2000 programs, large, apparently seasonal differences in AHC distributions (fingerprints) were seen at all stations; these were likely to be related to spawning or seasonal feeding factors, which makes interpretation of these data difficult. As in the last two reports, analysis and reporting of AHC and associated parameters (TRAHC, UCM, CPI, and CRUDE) in mussel tissues did not appear

to provide useful additional information regarding hydrocarbon levels or sources. It did confirm that large amounts of natural lipid compounds that are 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.

As in tissue, PAH in subtidal sediments collected from Stations AMT-S and GOC-S were quite low. In fact, the data seen during this sampling period at Station AMT-S constituted the lowest mean TPAH encountered to date at this station. The station maximum for mean TPAH was extended upward at Station GOC-S during this reporting period, but in general, PAH levels seen here were still quite low. As in the past, and in contrast to the tissue results, the majority of individual PAH analytes were seen at levels above MDL for all sediment samples, with the TPAH above the cumulative MDL for all surveys but March 2002, where PAH concentrations were very low.

Station AMT-S exhibited PAH signatures which indicated petroleum sources, including weathered ANS, along with some lesser pyrogenic inputs for each of the surveys. As in the past, several of the surveys (July 2000 and March 2001) showed PAH fingerprints that exhibited signatures typical of a weathered ANS petroleum source along with additional input of pyrogenic hydrocarbons that may have had a combustion or creosote origin. The PAH fingerprint from July 2001 exhibited a combination of sources, including background sources, ANS crude, and pyrogenic sources. Although overall concentrations were relatively low compared to the prior two surveys, a weathered profile was still apparent. March 2002 concentrations were very low, particularly Replicates 1 and 2, but Replicate 3 showed a similar pattern. In contrast, the fingerprints at Station GOC-S showed a petrogenic background and pyrogenic signature with a predominance of pyrogenic inputs for all four surveys.

Total AHC results were higher than historical levels during this reporting period for sediments, raising the overall maximums for mean TAHC at both Station AMT-S and GOC-S. Although some of the individual analytes fell below their MDL, especially at Station GOC-S where lower AHC levels were documented, the majority of analytes were above MDLs, and all of the TAHC values were above the cumulative MDLs reported for this sample set.

At Station AMT-S, three of the four surveys reported here exhibited mean TAHC above the historical maximum. March 2002 was particularly elevated. This was in contrast to the mean TPAH where an all-time low was recorded for this survey at this station. The AHC fingerprints at Station AMT-S indicated a much higher predominance of higher molecular weight aliphatic hydrocarbons as compared to the lower weight compounds, which would indicate a weathered source. In general, the odd alkanes were slightly higher but still similar in concentration to the even alkanes. This would indicate petrogenic hydrocarbons as the primary source with smaller amounts of biogenic inputs.

Results from Station GOC-S during the last two surveys have extended the upper range of mean TAHC values seen. This can be accounted for by elevated concentrations of n-C_{27} in most of these replicates. As noted below in the discussion of CPI, these high concentrations of n-C_{27} were due to a greater influence of plant materials (lipids) on this odd peak in the aliphatic analysis. The AHC fingerprints at Station GOC-S had a predominance of odd alkanes, especially n-C_{25}, n-C_{27}, n-C_{29}, and n-C_{31}. This indicates to a biogenic source which contrasts with that seen at Station AMT-S. Also, the predominance of the higher-end molecular weight compounds were indicative of a weathered source.

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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:

- 1999 – 2000 Annual LTEMP Monitoring Report
- 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.

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, n-C_{10} through n-C_{34} plus pristane and phytane

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

Z

ZAB - Zaikof Bay