NOAA Technical Memorandum NMFS-NWFSC-12

Volume I:
Survey of Alaskan Subsistence Fish, Marine Mammal, and Invertebrate Samples Collected 1989-91 for Exposure to Oil Spilled from the *Exxon Valdez*

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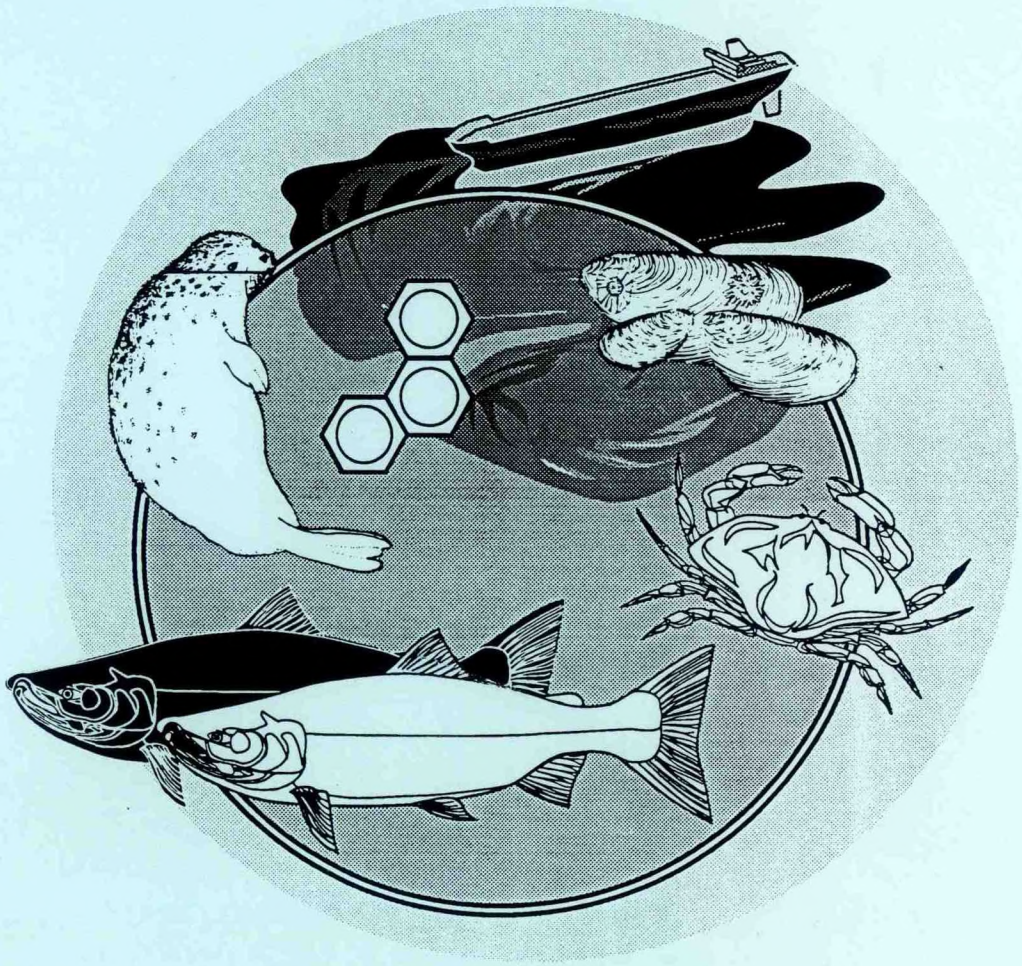

U.S. DEPARTMENT OF COMMERCE
National Oceanic and Atmospheric Administration
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NOAA Technical Memorandum NMFS

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Survey of Alaskan Subsistence Fish, Marine Mammal, and Invertebrate Samples Collected 1989-91 for Exposure to Oil Spilled from the *Exxon Valdez*

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EXECUTIVE SUMMARY

The *Exxon Valdez* ran aground on Bligh Reef, Prince William Sound, Alaska on March 24, 1989, spilling millions of gallons of Prudhoe Bay crude oil (PBCO). During the weeks following the spill, large amounts of oil flowed towards southwestern Prince William Sound, and as a result, many shorelines were oiled. The spreading of spilled oil raised concerns of native Alaskans that their subsistence seafoods (fish, marine mammals, and invertebrate organisms) were contaminated by the spilled petroleum. At the request of native Alaskans, a study was conducted as a cooperative effort among NOAA, Exxon, and the Alaska Department of Fish and Game to assess the degree of contamination of subsistence organisms by PBCO. In this study, edible flesh of fish, marine mammals, and shellfish from 22 native subsistence food collection areas and from two reference areas (Angoon and Yakutat) were analyzed for aromatic compounds (ACs). Vertebrates can readily biotransform ACs to metabolites that are concentrated in bile for excretion. This process greatly limits the accumulation of ACs in tissues such as edible flesh. Thus, for fish and marine mammals, bile was first analyzed for the presence of fluorescent aromatic compounds (FACs) as an indication of exposure to petroleum.

Based on the concentrations of FACs in bile, it was evident that pink salmon, halibut, and Pacific cod from the Chenega area had been exposed to ACs during 1989, as were pink salmon from Tatitlek, Kodiak, and Old Harbor. The bile method was useful because it quickly identified those fish that were relatively unexposed to ACs and, therefore, of less immediate interest for analysis by the more detailed method for ACs in tissue.

As expected, most fish muscle samples were not contaminated with ACs (<10 ng/g). In fact, the highest concentration of ACs found in muscle samples of fish caught during this study was 100 ng/g in a pink salmon caught near Kodiak (city) in 1989. In contrast, two samples of smoked salmon obtained from Tatitlek and Old Harbor contained 23,000 and 8,100 ng/g ACs, respectively.

Bile and tissue samples were collected from 33 harbor seals and 10 sea lions in 1989 and 1990. As with fish, the concentrations of FACs in bile of harbor seals varied considerably. Nine of the 12 bile samples with the highest concentrations of FACs were from animals collected in 1989 that were visibly oiled. With two minor exceptions, samples of muscle, liver, and kidney from harbor seals and sea lions, as well as blubber from sea lions, were not contaminated (<10 ng/g) with ACs. Samples of blubber from 12 of the harbor seals were minimally contaminated (10 to 99 ng/g), and samples of blubber from 4 harbor seals were moderately contaminated with ACs (100 to 1,000 ng/g).

Invertebrates from most of the sampling areas were not contaminated or were minimally contaminated by ACs (<100 ng/g). Therefore, results are presented for only those few stations where higher concentrations of ACs were found. Molluscs from some stations at the Chenega, Windy Bay, Kodiak, and Old Harbor sampling areas were moderately or highly contaminated (>100 ng/g) with ACs. For example, some of the mollusc samples from 4 of the 12 stations in the Chenega area (CHE1, CHE7, CHE10, CHE24) were moderately or highly contaminated with ACs. Mollusc samples from Windy Bay stations WNB1 and WNB3 contained concentrations of ACs as high as 18,000 ng/g; 34 of 106 invertebrate samples contained concentrations of ACs greater than 100 ng/g. The only two stations on Kodiak Island where mollusc samples had mean concentrations of ACs (by year for individual species) greater than 100 ng/g (moderately or highly contaminated) were KOD3 and OHA4. Most of the mollusc samples (26 of 30) from station KOD3 (located on Near Island about 1/4 mile from Kodiak's boat harbor) were moderately or heavily contaminated with ACs (>100 ng/g). Station OHA4 was adjacent to the village of Old Harbor near the boat harbor, and the concentrations of ACs in molluscs collected at this site in 1989 and 1990 were just within the moderately contaminated category or lower.

Aromatic compounds were present in molluscs at concentrations high enough to evaluate in terms of temporal trends only at some stations. For example, the concentrations of ACs declined significantly with time in mussels at: 1) Chenega stations CHE9 and CHE10 (1990 to 1991), and 2) at the combined Windy Bay stations WNB1/WNB3 (1989 to 1991). The degree of contamination of invertebrates from WNB1 and WNB3 stations varied with sampling year and by species.

Specifically, some of the mussel samples from Windy Bay station WNB1 (1989) and from WNB3 (1990) were highly contaminated (>1,000 ng/g), whereas the concentrations of ACs in mussels from these stations in 1991 were minimally to moderately contaminated (10 ng/g to 1,000 ng/g). The decline in concentrations of ACs in these molluscs probably related to decreased exposure which resulted from weathering of the spilled oil at the particular stations. The concentrations of ACs in molluscs at some other stations did not decline significantly with time. For example, the concentrations of ACs in butter clams from Kodiak station KOD3 did not consistently decline over four sampling periods during 1990.

The relative concentrations of the hundreds of different ACs in various petroleums and petroleum products can vary considerably. The patterns of these concentrations can be useful for purposes of comparison. The patterns of some ACs (phenanthrenes and dibenzothiophenes) in selected mollusc samples from Chenega area stations CHE1 and CHE10 and Windy Bay stations WNB1 and WNB3 were similar to that of weathered PBCO. Because the overall patterns of ACs in molluscs did not exactly match that of PBCO, other observations were also important in considering sources. For example, following the spill, oil was observed in the area of station CHE1 and at CHE10, a tar mat about 1 m wide extended the length of the beach at the high tide line. Also, stations WNB1 and WNB3 were observed to be moderately to heavily oiled. Thus, based on the patterns of ACs in molluscs and the known proximity of the spilled oil to these areas, oil from the *Exxon Valdez* may have been the source of ACs in mollusc samples from CHE1, and most likely was the source of ACs in mollusc samples from CHE10, WNB1, and WNB3. The patterns of ACs in selected samples from Kodiak Island stations KOD3 and OHA4 were also similar to those for mollusc samples from CHE1, CHE10, WNB1, and WNB3. However, the presence of naphthalenes in the patterns was more prominent in the samples from KOD3 and OHA4 than in the Chenega and Windy Bay samples. This finding implies exposure of the KOD3 and OHA4 molluscs to a less weathered source of ACs. Therefore, the ACs in molluscs from KOD3 and OHA4 are suspected to be from a local continuing source of petroleum. Additional support for this conclusion includes: 1) KOD3 and OHA4 were near active boat harbors which could be a source of ACs, 2) the spilled oil was not observed to impact these areas, and 3) the concentrations in molluscs at KOD3 did not continually decline over four

samplings during 1990. Based on patterns, PBCO was probably a minor source of the ACs in mollusc samples from station CHE7. The pattern of ACs implied that the source of these compounds in selected molluscs from CHE7 was due to exposure to creosote (perhaps from the creosoted pilings located near the sampling station) and/or products of combustion. Based on the patterns of ACs in selected samples, PBCO was probably not a source, or only a minor source of the ACs in molluscs from Tatitlek station T1. More likely, the source of the ACs in mollusc samples from T1 was products of combustion processes.

Interestingly, of the ACs found in fish muscle, unsubstituted ACs predominated, which was probably due to the more rapid metabolism of alkylated ACs than of unsubstituted ACs by fish liver. Conversely, molluscs, which have little ability to metabolize ACs, had both alkylated and unsubstituted ACs, and the patterns of ACs in molluscs more closely resembled that for petroleum components. Furthermore, in the blubber samples from harbor seals with elevated concentrations of ACs, the concentrations of alkyl-substituted ACs were similar to or greater than the concentrations of the corresponding nonsubstituted ACs. This pattern is similar to what was found in PBCO and molluscs, and generally the opposite of what was observed in fish.

In conclusion, the finding of elevated concentrations of FACs in some bile samples from fish and marine mammals was clear evidence of their exposure to petroleum. Generally, ACs were not found in muscle tissue of fish, harbor seals, and sea lions. Some harbor seal blubber samples did contain ACs; however, the concentration of ACs in most blubber samples was less than 100 ng/g. Smoked salmon contained higher concentrations of ACs (8,000 to 20,000 ng/g) than any of the untreated subsistence samples. The concentrations of ACs were less than 100 ng/g in approximately 90% of the more than 1,000 mollusc samples from 80 sampling beaches. The concentrations of ACs were elevated in some mollusc samples (as high as 18,000 ng/g), and the concentrations of ACs exceeded 1,000 ng/g in 24 samples.

The results to date provide important information on the level of contamination of subsistence fish, shellfish, and marine mammals from fishing areas of native Alaskan villages in and near Prince William Sound. In an advisory opinion, the Food

and Drug Administration has indicated that little risk is involved in the consumption of the nonsmoked subsistence foods studied. Subsistence food gatherers were advised not to collect or consume food if oil was observed to be present. The results also show that in future oil spills, shellfish tissues should be given the highest priority for analysis, whereas rapid screening of bile from fish and marine mammals should be sufficient to provide information on level of exposure.

CONTENTS

PREFACE

The Environmental Conservation (EC) Division of the Northwest Fisheries Science Center conducts investigations on the fate and effects of organic contaminants in the marine environment and in seafoods consumed by humans. Often, trace levels of toxic chemicals are analyzed, and because the chemical composition of marine environments can be extremely complex, sensitive and reliable analytical methods are needed to produce data with confidence and reproducibility. The EC Division's analytical chemistry program for trace organics and toxic elements has, since the mid-1970s, provided NOAA with advanced analytical capabilities that were not otherwise readily available. This resulted in the development of state-of-the-art analytical techniques to measure trace organics, their metabolites, and metals in sediment and tissue samples. Much of the analytical methodology needed for NOAA's environmental projects was developed over the past decade and a half by the Division's researchers, with funding support coming from the National Marine Fisheries Service, other NOAA elements, and agencies outside NOAA.

During the last decade and a half, the EC Division conducted thousands of sophisticated analyses of marine samples for trace levels of petroleum hydrocarbons and other chemical contaminants. Early success in studies conducted in Puget Sound and in the New York Bight laid the foundations for the Division's present prominent role in NOAA's long-term National Status and Trends Program, NOAA's Coastal Ocean Program, and the National Marine Fisheries Service's Marine Mammal Health and Stranding Response Program and Seafood Quality and Safety Program. At the same time, the EC Division has conducted several interlaboratory comparisons for analyses of marine samples. Over the years, through efforts instituted by the EC Division, precision among experienced laboratories improved many folds. Moreover, in response to the need to analyze large numbers of environmental samples with greater speed, EC Division scientists replaced two lengthy manual cleanup procedures with a single high performance liquid chromatography, cutting cleanup time and solvent consumption by two-thirds. Division scientists also developed methods to test for petroleum by rapidly screening fish bile for aromatic hydrocarbon metabolites and sediment for the aromatic hydrocarbons. These screening techniques have ensured the rapid acquisition of data and early assessment for detailed priority analyses. With these improved methods, the EC Division is in an excellent position to continue timely and quality analyses on subsistence samples potentially impacted by the *Exxon Valdez* oil spill.

INTRODUCTION

The *Exxon Valdez* ran aground on Bligh Reef, Prince William Sound (PWS), Alaska, on March 24, 1989, spilling more than 10 million gallons of Prudhoe Bay crude oil (PBCO). During the 2 weeks following the spill, large amounts of floating oil spread to southwest PWS, resulting in heavy oiling of several shorelines (Galt et al. 1991). As the PBCO spilled from the *Exxon Valdez* and spread from PWS along the outer Kenai Peninsula, shoreline oiling was variable. Shorelines of some eastward-facing bays along the Gulf of Alaska such as Windy Bay received moderate to heavy oiling. By the time the oil reached Kodiak Island and the Alaska Peninsula, shoreline oiling was generally lighter because the oil was in the form of widely scattered patches of tar balls and mousse. The village of Tatitlek, which is only a few miles east of where the spill occurred, did not seem to receive any direct shoreline oiling as the oil moved south and west.

The spreading of spilled oil raised concerns among native Alaskans that their subsistence seafood (fish, marine mammals, and invertebrate organisms) was contaminated by the spilled petroleum. In response to their concerns, NOAA entered into memoranda of understanding (MOU) with Exxon and subsequently with the Alaska Department of Fish and Game (ADF&G) to analyze subsistence seafoods sampled from sites used by native Alaskans, and from reference areas for selected aromatic compounds (ACs) found in spilled oil (Varanasi et al. 1990).

Petroleum, such as PBCO, contains many hundreds of organic compounds, generally classified into groups including aliphatic and polycyclic aromatic hydrocarbons and compounds that contain sulfur, oxygen, and nitrogen. Aromatic hydrocarbons and dibenzothiophenes comprise the group of ACs that are known for their toxicity, and these compounds can be monitored in biota as indicators of exposure to petroleum-related ACs (Table 1). Previous laboratory studies have shown that fish and mammals efficiently biotransform ACs to polar derivatives that are concentrated in their bile for excretion (Statham et al. 1976, Varanasi and Gmur 1981, Stein et al. 1984, Varanasi et al. 1989b). As a result of this biotransformation, ACs may not readily accumulate in the edible flesh of fish or marine mammals. Thus, to quickly measure the exposure of fish and marine mammals to ACs, a sensitive method for screening bile for the presence of

fluorescent aromatic compounds (FACs) which are characteristic of petroleum ACs was utilized. This semiquantitative procedure for measuring FACs utilizes high performance liquid chromatography (HPLC) with fluorescence detection (Krahn et al. 1984, 1986b). This method has been employed previously to evaluate exposure of fish to ACs from an oil spill on the Columbia River (Krahn et al. 1986a) and in a variety of other laboratory and field studies. The results of biliary FACs analyses were used to prioritize corresponding samples of edible fish tissue for analyses of individual ACs.

Individual ACs in selected tissue samples from invertebrates, fish, marine mammals, and other tissue types (e.g., herring roe on kelp) were analyzed using gas chromatography/mass spectrometry (GC/MS). This procedure is much more labor and time intensive than the measurement of FACs in bile. However, recent important improvements in, and automation of, the extract cleanup procedure (Krahn et al. 1988a) and the use of a special sequenced selected-ion monitoring (SSIM) GC/MS program (Burrows et al. 1990) enabled us to provide high quality analytical data for low concentrations (<1 ng/g wet weight) of ACs in tissue samples quickly and efficiently. The GC/MS method also detects sulfur-containing ACs such as the dibenzothiophenes, which can be useful markers for oil contamination.

In addition to organic compounds, petroleum contains certain metals (e.g., nickel and vanadium). Metals were not analyzed as part of the study because of very low concentrations of these metals relative to hydrocarbon components in PBCO and the lack of information about the bioavailability processes of metals in various marine biota (including those sampled in this study).

This report presents the results of analyses of bile for FACs and tissue samples for ACs from subsistence species collected in 1989, 1990, and 1991. The results were evaluated both in terms of geographical distribution and temporal changes.

This report is divided into two volumes. The second volume contains supplemental data too voluminous to be included as Appendices to the primary report. These data are available on request as NOAA Technical Memorandum NMFS-NWFSC-13, Volume II: Supplemental Information Concerning a Survey of

Alaskan Subsistence Fish, Marine Mammal, and Invertebrate Samples Collected 1989-91 for Exposure to Oil Spilled from the *Exxon Valdez*. Volume II includes the following sections: A - Concentrations of Metabolites of Fluorescent Aromatic Compounds in Fish Bile; B - Concentrations of Aromatic Compounds in Edible Tissue of Fish; C- Concentrations of Metabolites of Fluorescent Aromatic Compounds in Bile from Marine Mammals; D - Concentrations of Aromatic Compounds in Edible Tissues of Marine Mammal Samples; E - Concentrations of Aromatic Compounds in Invertebrate Samples; and F - Quality Assurance.

METHODS

Following the spill in March 1989, the goal was to organize and implement a program to determine if subsistence seafoods were contaminated by the petroleum. In 1990, the program was expanded to include sampling more areas, especially for shellfish, and to collect more samples in selected sampling areas. In 1991, the study focused exclusively on shellfish stations in the Chenega Bay sampling area and Windy Bay islands. The reasons for this exclusive focus were that the southwestern area of PWS in the general vicinity of the village of Chenega Bay was potentially the most impacted by oil from the spill, several stations in the Chenega sampling area showed elevated concentrations in 1990, and the Windy Bay islands were the most heavily-oiled stations in the study and were important for assessing temporal trends.

Details of protocols for the field sampling, chemical analyses, and statistical evaluation are outlined below.

Sample Collection

Samples of marine biota were collected under two programs using similar protocols. Exxon sponsored collections by its contractor, Dames and Moore, in 1989, 1990, and 1991. The ADF&G sponsored collections in 1990 and 1991. A NOAA Hazardous Materials Response and Assessment Division representative also participated in the sample collections. Invertebrate samples were collected over a 3-year period with at least three collection cycles each year. Fish and marine mammal samples were collected in 1989 and 1990. In most cases, the

sampling areas and stations were selected by area residents because they were important subsistence collection areas.

Fish and Shellfish

In 1989, comparable numbers of shellfish and fish samples were collected from each village. The target invertebrate species included mussels (*Mytilus edulis*), butter clams (*Saxidomus giganteus*), littleneck clams (*Protothaca staminea*), and chitons (order *Neoloricata*). Fish species included pink salmon (*Oncorhynchus gorbuscha*), coho salmon (*O. kisutch*), sockeye salmon (*O. nerka*) chum salmon (*O. keta*), chinook salmon (*O. tshawytscha*), halibut (*Hippoglossus stenolepis*), and Pacific cod (*Gadus macrocephalus*). Marine mammals, including harbor seals (*Phoca vitulina*) and Steller sea lions (*Eumetopias jubatus*), were also sampled. Three sampling cycles were conducted during the summer of 1989 (July, August, and September) in subsistence areas associated with villages in PWS (Tatitlek and Chenega Bay); Lower Cook Inlet (including the Outer Kenai Peninsula villages of Port Graham and English Bay, Kasitsna Bay, and Windy Bay); and Kodiak Island (city of Kodiak, Chiniak, Larsen Bay, Karluk, Akhiok, Old Harbor, Ouzinkie, and Port Lions) (Figs. 1-13).

In 1990, all of the above-mentioned areas were sampled at least once and the number of samples for each species from each sampling area was increased compared to 1989. In addition, samples were collected from other areas in southwestern PWS near the village of Chenega Bay and from areas on the Kenai Peninsula as requested by villagers (Port Chatham, Sadie Cove, Point Bede, Port Dick, Chugach Bay) (Figs. 4-6), and from four village areas on the Alaska Peninsula (Chignik, Ivanof Bay, Kashvik, and Perryville) (Figs. 1, 14-15). The focus during the second year was on collecting larger numbers of invertebrate species at each sampling station.

In 1991, the project focused primarily on areas in southwestern PWS and Lower Cook Inlet (areas near Chenega Bay and Windy Bay). Some shorelines in both of these areas were heavily oiled in 1989 and thus would be areas at which temporal changes in levels of ACs in invertebrate subsistence species could possibly be evaluated over the 3-year sampling period.

Selection of sample stations and the subsistence resources to be sampled was done in cooperation with village representatives. Sampling at each village area usually included two beaches for intertidal invertebrates. Salmon and bottomfish were collected from stations designated by village fishermen as ones generally fished. Hence, sample collection represented the approach of subsistence collectors rather than random or statistical sampling. No attempt was made to avoid or seek out oiled areas for sampling of fish or invertebrates. If oil was observed on a beach or in the vicinity of a sample collection area, it was noted in the sampling log. Since the habitat requirements vary for different species, individual stations sometimes encompassed a relatively large beach area over a range of tidal elevations in order to collect several species. For example, mussels were collected from higher tidal elevations than clams, while chitons were collected from rocky, lower intertidal areas.

In most cases, an individual from each village participated in sample collections conducted in areas adjacent to his/her village, except for marine mammal samples. Field collection protocols were followed to minimize the possibility of external contamination of samples. Tools used in sampling (e.g., shovels) were washed with soap and water and a new pair of surgical gloves was worn between sample collections. Intertidal shellfish were collected by hand or shovel. A minimum of four to six individual animals of each invertebrate species was collected at each station as one sample. Gear used in the fish collections included hook-and-line and gill nets for salmon, and hook-and-line and longline for halibut and bottomfish. Bile taken from fish was placed in solvent rinsed 4-mL vials and frozen as soon as possible for analysis for FACs. Fillets or whole fish were double wrapped in aluminum foil (which had been pre-baked at 350° F for 1 hour), placed in Zip-Loc® freezer bags and placed in ice coolers. Samples were shipped frozen and stored at -80°C at the laboratory until analyzed. Bile and tissue samples from fish were sampled and maintained as individual samples, whereas the invertebrate organisms that comprised a sample were packaged together in the field. Chain-of-custody forms were used and were signed by both parties when samples were transferred from sample collectors to laboratory personnel.

The number of fish and mollusc samples collected by site and year is shown in Table 2.

Marine Mammals

Marine mammals were collected under two programs with different objectives. Samples collected by ADF&G were from animals and areas with expected high exposure to spilled oil. Samples were collected from animals harvested by subsistence hunters in 1990 by Dr. Paul Becker of NOAA as part of the Marine Mammal Tissue Archival Program, Office of Protected Resources. Harbor seals and Steller sea lions that were collected both by ADF&G and NOAA in 1989 and 1990 were from sites that were oiled during the *Exxon Valdez* spill or that were adjacent to oiled areas. Samples were collected from 33 harbor seals and 10 Steller sea lions. Chain-of-custody procedures and bile and tissue sample procedures were the same as for fish samples (described above). Bile from 29 harbor seals and the 10 sea lions was analyzed for FACs, and samples from all the harbor seals and sea lions were analyzed for ACs in tissues.

Bile Analyses

The concentrations of FACs in bile were determined using a Waters HPLC equipped with a Perkin-Elmer HC-ODS/ PAH column (0.26 X 25 cm), an automatic injector, and Perkin-Elmer model 40 fluorescence (UV-F) detectors connected in series (Krahn et al. 1986b). Thawed bile was injected directly into the HPLC and eluted through the column using a linear gradient from 100% solvent A (water containing 5 mg/L of acetic acid) to 100% solvent B (methanol) over 15 minutes. The flow rate was 1 mL/min and the column temperature was 50°C. All solvents were degassed with helium. The UV-F responses were recorded at the wavelength pairs for naphthalene (NPH) and phenanthrene (PHN), prominent constituents of ACs in PBCO (Table 1). The fluorescence of NPH metabolites was monitored using excitation and emission wavelength pairs of 290 and 335 nm, respectively. Fluorescence of PHN metabolites was monitored using excitation and emission wavelength pairs of 260 and 380 nm, respectively.

The total integrated area from each detector was then converted to corresponding equivalents of either NPH or PHN standards that would give the same integrated response. Concentrations of FACs in bile are reported on the basis of bile weight and biliary protein. The levels of protein in bile samples were determined by the method of Lowry et al. (1951).

Analyses of Aromatic Compounds in Tissue (Edible Flesh)

The results of the bile analyses were used to estimate the exposure of fish to ACs and to rank the exposure as low, medium, or high. Fish samples were then selected for analysis of edible flesh for the ACs found in PBCO by the more quantitative and costly GC/MS technique. Edible flesh samples from the same fish species from a sampling area were analyzed as individual samples or as composites of individuals which had similar FACs levels in their bile. Samples of flesh from fish (collected in 1989) with relatively low levels of bile FACs were generally analyzed as composites. Some of the samples of fish collected in 1990 that had relatively low levels of FACs in their bile were not analyzed. Tissue samples from marine mammals were not composited for analysis.

Edible flesh of fish, marine mammals, and invertebrate samples were analyzed for the ACs listed in Table 1 using the procedures of Sloan et al. (1993), Krahn et al. (1988a) and Burrows et al. (1990). Summaries of the analytical protocols are given below and consisted of four major steps: a) extraction; b) HPLC cleanup; c) analyte determination by GC/MS; and d) quality assurance. In addition, samples of petroleum and related products were weighed, dissolved in methylene chloride, and analyzed, starting with the HPLC cleanup.

Extraction of Aromatic Compounds

The edible tissues of invertebrates that comprised a sample were homogenized and a 5-g portion of the homogenized tissue was analyzed for ACs. Fish and marine mammal tissue samples were taken for analysis by cutting back the surface layer of tissue and then taking 5 g of tissue that had not been in contact with the foil wrapping. When tissue samples from more than one fish were to be composited for analysis, the individual 5-g samples were combined and homogenized and a 3- to 5-g portion of the homogenate was used for analysis for ACs. The 3- to 5-g sample of homogenate was added to a centrifuge tube containing sodium sulfate and methylene chloride. The method internal standards (surrogate standards) for ACs were added and the mixture macerated with a Tekmar Tissumizer®. The resulting extract was filtered through a column of silica and alumina and the extract concentrated to 1 mL for cleanup by HPLC.

Fractionation of Extract to Isolate Aromatic Compounds

The ACs were isolated using a Spectra-Physics (Mountain View, California) model 8800 HPLC equipped with an ultraviolet detector (254 nm), an automatic injector, and a fraction collector. Two 22.5 x 250-mm stainless-steel preparatory size columns containing Phenogel 100-Å size-exclusion packing (Phenomenex, Rancho Palos Verdes, California) were used in series with a 2-µM Rheodyne model 7302 filter and a 7.8 x 50-mm guard column containing the same Phenogel packing. The HPLC pre-column and column were connected to a six-port valve that allowed the guard column to be backflushed to remove extraneous materials after cleanup of a set of samples (n ~ 10).

Methylene chloride was used as the solvent and was pumped at a flow rate of 7 mL/min for 20 minutes at ambient temperature. The HPLC solvent was degassed by bubbling helium through it. The helium was delivered via a regulator equipped with a stainless-steel diaphragm and was passed through an in-line charcoal filter (200-cc hydrocarbon trap, Alltech Assoc., Deerfield, Illinois), then through a high-purity heated trap (Supelco Inc., Bellefonte, Pennsylvania), and an oxygen indicating trap (Alltech Assoc.) to eliminate compounds which could be transferred to the HPLC solvent by the helium.

A 250-µL portion of a 1 mL extract was injected onto the HPLC column and the fraction containing the ACs collected according to Sloan et al. (1993) and Krahn et al. (1988b). The solvent in the HPLC fraction was exchanged into hexane as the volume was reduced by evaporation to approximately 1 mL. Further evaporation, and then the addition of standards, brought the final volume to ca. 120 µL for analysis by capillary column GC with mass spectrometric quantification.

Aromatic Compound Determinations by Gas Chromatography/Mass Spectrometry - Sequenced Selected Ion Monitoring

The ACs were determined according to MacLeod et al. (1985) by GC/MS quantification as outlined by Burrows et al. (1990). A 30-m x 0.25-mm DB-5 capillary column (J & W Scientific) was used in a Hewlett-Packard (HP) model 5890 GC. The GC sample (3 µL) was injected splitless, and the split valve opened

after 30 seconds (split ratio 20:1). The oven temperature of 50°C was held for 1 minute and then programmed to increase at 4°C/min to 300°C, where the temperature was held for 10 minutes. The GC/MS analyses were accomplished using either a Finnigan Incos 50B or HP 5970 MSD mass spectrometer with the appropriate data system and an HP autosampler. A SSIM scan descriptor that included 10 groups of about 20 ions each was used.

Statistical Methods

Results of chemical analyses of samples of fish and shellfish from stations within each sampling area were compared using GT2 comparison-interval graphs (in cases where an analyte was not detected, it was assigned a value of zero for statistical treatment). The GT2 comparison intervals are similar in appearance to confidence intervals, but they actually present the results of analysis of variance followed by a multiple-range test. The GT2 comparison interval for each mean is calculated based on the number of samples for that mean, the variability about that mean, and the number of means being compared (Gabriel 1978, Sokal and Rohlf 1981).

The advantage of using comparison intervals is that they provide a graphical way of depicting significant differences between means (e.g., when comparison intervals overlap they are not significantly different ($p \leq 0.05$)). When the number of samples for the means of interest are unequal, it is desirable to use the GT2 method (Gabriel 1978, Sokal and Rohlf 1981) for calculating the comparison intervals because the span of a comparison interval depends on the within-group variability in the entire data set and on the number of samples in each category.

RESULTS AND DISCUSSION

Aromatic Compounds in Petroleum and Petroleum Products

Petroleum contains a wide variety of hydrocarbons and their derivatives, including a large number of ACs. The composition of the ACs varies among different petroleums (Clark and Brown 1977). Prudhoe Bay crude oil was analyzed at the beginning of the study to determine the composition of the ACs that could be present in samples of subsistence foods. The chromatogram from the GC/MS analysis of the ACs in PBCO (Fig. 16A) shows the presence of a large number of peaks, each representing one or possibly more compounds. The availability of several substitution sites on parent ACs can result in many different isomers consisting of substituted alkyl groups containing one to four carbon atoms (denoted respectively as C1, C2, C3, etc., Table 1). For example, naphthalene, phenanthrene, pyrene, and the 12 isomers of C2-substituted naphthalenes (C2NPHs) are shown in Figure 17; the C2NPHs are identified in Figure 16B. Thus, the reported value of C2NPHs in PBCO represents the sum of the concentrations of the individual C2NPH isomers. Accordingly, the 35 nonsubstituted and alkyl-substituted ACs (Table 1) were comprised of some 270 individual components.

For discussion purposes, it is convenient to divide the ACs listed in Table 1 into the low-molecular-weight ACs (LACs) and the high-molecular-weight ACs (HACs). This has the convenience of dividing the ACs approximately into: a) the more water-soluble and acutely toxic compounds, LACs; and b) the less water-soluble and more chronically toxic compounds, HACs (National Research Council 1985). The LACs are more prone to dissolution, evaporation, and bacterial degradation and, hence, their levels in the environment generally would decline as the spilled oil weathered. The HACs, on the other hand, are more resistant to dissolution, evaporation, and bacterial degradation and tend to persist in the environment. It is also evident from Table 3 that the LACs comprised about 97% of the ACs in PBCO (generally those components to the left of fluoranthene in Fig. 18).

The pattern of selected components in petroleum, petroleum products, combustion products (from an urban marine sediment), and other materials such as

creosote (from coal tar) that may have been associated with the spill sites were compared (Figs. 18-21). The selected ACs are graphed with the peak areas normalized to one selected alkyl-substituted phenanthrene (C2PHN) component. Comparing the different graphs, one can see that the relative concentrations of the more volatile components, such as naphthalene, and the less volatile components, such as benzo[a]pyrene, varied in the different products. For example, the PBCO collected from the sea surface 11 days following the spill had lost some of the more volatile (and water-soluble) components (e.g., naphthalenes) compared to the C2PHN component in fresh PBCO (Fig. 18). The composition of ACs in a sample collected from a patch of oil from the beach at Snug Harbor, PWS in July 1990, about 15 months after the *Exxon Valdez* spill (Fig. 19), was quite similar to the 11-day weathered PBCO except for lower levels of naphthalene, C1- and C2-naphthalenes. The lack of continued weathering could have been due to several factors; for example, the formation of an outer layer or crust could have sealed the material from further weathering, or the tar mat may have been in the high intertidal zone and thus less exposed to wave action and other degradation processes.

The pattern of ACs in two other crude oils, Cook Inlet crude oil (CICO) and Kuwaiti crude oil was evaluated and found to be similar to that in the PBCO except for the dibenzothiophenes (DBTs). Prudhoe Bay crude oil contained a considerably larger number and amount of DBTs relative to the C2PHN component; the DBTs were mostly absent in the CICO, but higher in Kuwaiti crude than in PBCO (Fig. 19). The No. 2 fuel-oil pattern (Fig. 20) appeared somewhat similar to PBCO even though No. 2 fuel-oil is basically comprised of a distillation fraction of the crude oil. Bunker fuel, a heavy distillate fraction of petroleum (that generally is diluted with No. 2 fuel-oil to obtain the desired viscosity) contains more of the less volatile components of crude oil (Fig. 20). A pattern of creosote is included (Fig. 21) because molluscs were collected from one station near creosoted pilings and the question was raised if the ACs in those samples were from creosote. Three major components of creosote (phenanthrene, fluoranthene, pyrene), a coal tar distillate, are also major components in combustion products as shown in an extract of marine sediment from an urban area (Duwamish III sediment, Fig. 21), but are not major components in PBCO. These patterns will be important in subsequent sections for comparisons to patterns from analyses of shellfish. It is important to note that when comparing patterns, only similarities or differences can

be pointed out. Generally, a pattern should not be linked to a particular source unless the study was appropriately designed and the ambiguities (such as those above) considered.

Fluorescent Aromatic Compounds in Bile of Fish

Bile was analyzed for FACs by high-performance liquid chromatography/ ultraviolet fluorescence (HPLC/UV-F) at PHN and NPH wavelength pairs to estimate the exposure of fish to ACs. The concentrations of FACs at the two wavelength pairs were highly correlated ($r = 0.91$, $p = 0.0001$); thus only the concentrations measured at the PHN wavelength pair ($FACs_{PHN}$) are discussed and will be denoted as FACs. The results of analyses of bile for FACs from salmon and bottomfish collected in 1989 and 1990 are summarized in Tables 4 and 5, respectively. Results of concentrations of biliary FACs and protein in individual fish are summarized in Vol. II, Section A.

As discussed earlier, the main utility of bile analyses was to quickly assess exposure of fish to ACs and then to use those results to set priorities for corresponding samples of edible tissue for more comprehensive analysis for individual ACs by GC/MS. Prioritization was done using bile concentrations reported on the basis of bile weight, allowing the selection of edible tissues samples for GC/MS analysis from fish that had elevated concentrations of FACs in their bile. Conversely, fish which exhibited low concentrations of biliary FACs were probably less exposed to ACs and thus were of lower immediate interest.

In this report, the concentrations of biliary FACs in fish will be compared using results based on bile protein. Excretion of metabolites of ACs into bile of fish can be affected by many factors, such as species, age, and feeding status. Previous laboratory studies have shown marked increases in protein concentrations in bile of nonfeeding fish compared to feeding fish (Collier and Varanasi 1987). Moreover, it was shown in these studies that the variation between concentrations of biliary FACs in some fish from the same area were reduced when differences in bile protein were taken into account. In the subsistence study, pink salmon were sampled from a number of areas (e.g., Chenega Bay, Chiniak, Old Harbor, Port Lions, Tatitlek) that included fish being caught upstream in rivers and from the open sea. Results of bile analyses showed significant differences in concentrations

of biliary FACs and protein between pink salmon caught in open water compared to pink salmon caught in streams from the same area. For example, at Chenega Bay in 1989, significantly higher mean concentrations of biliary FACs and protein were found in pink salmon caught upstream (220,000 ng PHN equiv./g bile and 36 mg bile protein/g bile, respectively) compared to concentrations in pink salmon from the open sea (7,700 ng PHN equiv./g bile and 1.5 mg bile protein/g bile, respectively, Vol. II, Section A). However, when FACs were normalized for protein, similar concentrations of biliary FACs were observed in pink salmon sampled from the stream (6,400 ± 3,600 ng PHN equiv./mg bile protein) and open sea (4,600 ± 1,900 ng PHN equiv./mg bile protein) and were not significantly different ($p = 0.40$).

Biliary $FACs_{PHN}$ in Salmon

A wide range of FACs (260 to 6,000 ng PHN equiv./mg bile protein) was measured in bile of salmonids sampled from subsistence fishing grounds in 1989 and 1990, indicating that those fish with FACs concentrations in the higher end of the concentration range were exposed to petroleum-related ACs (Table 4). In 1989, the highest concentrations of biliary FACs were in pink salmon from Chenega Bay (6,000 ng PHN equiv./mg bile protein), a site heavily impacted by the spilled oil, and Kodiak (2,800 ng PHN equiv./mg bile protein). In 1989, the concentrations of biliary FACs in pink salmon from Chenega Bay were significantly higher than concentrations in fish from all other subsistence sites, except in fish from Kodiak, as indicated by GT2 comparison interval plots (Fig. 22). Additionally, concentrations of biliary FACs in pink salmon from most sites, except in fish from Chenega Bay, Kodiak, and Old Harbor, were not statistically different than in fish from Tatitlek. Tatitlek was not in the path of the oil spill, but was very close to the spill site and fish enroute to the Tatitlek area may have passed through heavily oiled areas. For pink salmon sampled in 1989, no significant differences were observed when comparing the concentrations of FACs in fish from all other areas to fish from Angoon, the reference site. This was due to a single pink salmon having a biliary FACs concentration (12,000 ng PHN equiv./mg bile protein) that was 4- to 20-fold higher than concentrations in the other three pink salmon (1,800 ± 1,300 ng PHN equiv./mg bile protein) sampled from Angoon. The finding of an elevated level of FACs in one pink salmon from Angoon is not understood. In 1990, no significant differences were observed among concentrations of biliary $FACs_{PHN}$ in pink salmon from the subsistence sites sampled.

In 1989, coho salmon were sampled from a number of sites to allow statistical evaluation of the concentrations of FACs in their bile. The results of concentrations of biliary $FACs_{PHN}$ in coho salmon are summarized in Figure 23. Levels of biliary FACs based on bile protein were significantly higher in coho salmon from Ouzinkie, Akhiok, and Tatitlek than concentrations in fish from Angoon, the reference site. Salmon, a pelagic species, can migrate over large distances, thus the finding of elevated concentrations of FACs in Tatitlek fish may be due to these salmon passing through contaminated waters near the site of the oil spill before capture. Insufficient numbers of bile samples from other species of salmon (e.g., sockeye, chum) were sampled to be able to compare FACs between 1989 and 1990.

In 1990, sufficient numbers of chum and sockeye salmon were collected from some areas to allow site comparisons of the concentrations of FACs found in bile of these fish. Mean concentrations of FACs in bile of sockeye salmon from Karluk and Larsen Bay in 1990 were not significantly different from concentrations in sockeye salmon from Yakutat, the designated reference site (Fig. 24). In addition, concentrations of FACs in bile of chum salmon from Old Harbor and Port Graham in 1990 were similar (760 and 750 ng PHN equiv./mg bile protein, respectively), but were significantly lower than concentrations in chum salmon from Ouzinkie (Fig. 25).

Biliary $FACs_{PHN}$ in Bottomfish

A wide range of FACs (92 to 9,700 ng PHN equiv./mg bile protein) was also measured in bile of bottomfish sampled in 1989 and 1990, indicating that some of these fish were exposed to petroleum-related ACs (Table 5). In 1989, the highest concentrations of biliary FACs measured in each species of bottomfish (e.g., halibut, Pacific cod, rockfish), as with salmon, were from Chenega Bay or Kodiak. For example, in Pacific cod, a demersal species, the highest mean concentrations of FACs were found in fish (5,200 ng PHN equiv./mg bile protein) from Chenega Bay. Moreover, one of the highest mean concentrations of $FACs_{PHN}$ found in halibut (4,100 ng PHN equiv./mg bile protein), a benthic species, was also from Chenega Bay. Only one halibut sample (7,400 ng PHN equiv./mg bile protein) from Kodiak contained a higher biliary FACs level than Chenega Bay halibut.

In 1989, concentrations of $FACs_{PHN}$ in bile of halibut from Chenega Bay, Ouzinkie, and Port Lions were significantly higher according to GT2 comparison intervals than concentrations in bile of halibut from Angoon, the reference site (Fig. 26). Statistical comparisons of bile analyses of halibut collected in 1990 were not possible because of insufficient sample size. Moreover, statistical comparisons of bile analyses of other species of bottomfish shown in Table 5 were not possible because bottomfish were rarely sampled from more than three sites, making even qualitative comparisons difficult.

In 1989, concentrations of FACs in bile of Pacific cod from Chenega Bay were significantly higher according to GT2 comparison intervals than concentrations in bile of Pacific cod from Larsen Bay (Fig. 27). Although statistical comparisons could not be made with Pacific cod from Angoon, the reference site, because only one fish was collected, the level of FACs in bile of this fish (480 ng PHN equiv./mg bile protein) was much lower than concentrations in bile of Pacific cod from Chenega Bay. In 1990, no significant differences were found among concentrations of FACs in bile of Pacific cod from all the subsistence sites.

Temporal Changes in Biliary FACs in Salmon

Elevated concentrations of FACs in bile generally relate to recent exposure. When the source of exposure to ACs is removed, the FACs concentrations in bile will decline. For example, the half life of ACs in fish can be estimated to be on the order of 2 to 4 weeks (Collier and Varanasi 1991). Pink salmon was the only species collected in sufficient numbers from several subsistence sites in both sampling years to allow evaluation of temporal changes (Fig. 22). Temporal comparisons for other salmon species and for bottomfish species sampled were not possible because of small sample size or lack of corresponding data from 1989. Pink salmon from Chenega Bay showed the most significant change from 1989 to 1990. The tenfold decrease in concentrations of FACs observed in bile of pink salmon sampled at Chenega Bay in 1990 relative to those sampled in 1989 (6,000 $\pm$ 3,400 to 490 $\pm$ 230 ng PHN equiv./mg bile protein), indicates a substantial decrease in exposure to ACs compared to the previous year. The concentrations of FACs in bile of pink salmon from Kodiak, however, did not change from 1989 to 1990, indicating that exposure of these fish to ACs did not change substantially.

Aromatic Compounds in Edible Flesh of Fish

As described earlier, samples of edible flesh of fish were selected for analysis based on the concentrations of FACs in bile. Volume II, Section B includes the results for the ACs listed in Table 1 for the edible flesh of samples of fish according to village areas, species, laboratory sample number, and collector, and these data are summarized in Table 6. The results from comparable samples collected at Angoon and Yakutat, Alaska, which are designated reference sites, are included in Vol. II, Section B. For discussion, the concentrations of ACs in tissue samples will be categorized as follows:

1.	not contaminated by ACs	<10 ng/g wet weight
2.	minimally contaminated by ACs	10 to 99 ng/g wet weight
3.	moderately contaminated by ACs	100 to 1,000 ng/g wet weight
4.	highly contaminated by ACs	>1,000 ng/g wet weight

Based on the mean concentrations of ACs in edible flesh of fish, all samples would be included in category 1 (not contaminated by ACs) except for the samples of pink salmon and sockeye salmon from the Kodiak area and the two samples of smoked salmon analyzed in this study (Table 6). Even the mean concentrations of ACs in the pink salmon and sockeye salmon from the Kodiak area were very low (<34 ng/g). A major point from Table 6 is that a majority of the mean concentrations of ACs were less than 1 ng/g, which further validates previous studies that ACs taken up by fish are readily converted to metabolites and excreted in their bile and, hence, do not get stored in tissue (Stein et al. 1984, 1987).

On the basis of individual fish samples, excluding the smoked salmon samples, only one sample of fish muscle was moderately contaminated with ACs (Table 7) and only 3 samples had concentrations between 50 and 99 ng/g (category 2). The concentrations exceeded 10 ng/g (category 1) in only 16 samples of fish, the majority of which were collected in 1989. The concentrations of ACs in the edible flesh of the other fish samples were less than 10 ng/g and were generally comparable to the concentrations detected in the same or related species from the

reference sites, Angoon and Yakutat. Pink salmon was the only species sampled at several sites in both years, but for the most part, only a small number of samples was collected. The small number of samples and low concentrations of ACs in most samples makes it difficult to evaluate temporal trends of ACs in fish muscle.

In contrast to the samples of fresh fish, samples of smoked salmon from Old Harbor and Tatitlek contained 8,100 and 23,000 ng/g of ACs, respectively (Table 7). The concentrations of benzo[a]pyrene (a carcinogenic HAC) in these samples were 6 ng/g (Old Harbor) and 18 ng/g (Tatitlek), which are low values but are still higher than in any of the other fish collected in this study. It is well known that the smoking process results in the accumulation of ACs in the tissue, hence more samples of smoked fish should be analyzed so that better comparisons can be drawn among the different smoking procedures. Such information should be valuable to subsistence hunters.

Fluorescent Aromatic Compounds in Bile of Marine Mammals

Bile samples were collected from 29 harbor seals and 10 Steller sea lions in 1989 and 1990 (Tables 8 and 9). The harbor seals collected in 1989 were part of the Natural Resources Damage Assessment program and hence were selected for their degree of external oiling. Of the 19 harbor seals collected in 1989, 13 were visibly oiled and 6 showed no external oiling. All 11 of the harbor seals collected from PWS in the spring-summer of 1989 were visibly heavily oiled. Because of molting, the harbor seals that were visibly oiled in the spring or summer of 1989 would not still be oiled by the fall of 1989. In 1990, six seals were collected from previously heavily oiled areas in PWS, but they did not show any visible oiling. Steller sea lions were collected in 1989 from The Needle in PWS, the Gulf of Alaska, and the Barren Islands in Lower Cook Inlet. None of the sea lions showed signs of visible oiling. In 1990, samples were collected from seven harbor seals in Prince William Sound by Chenega Bay subsistence hunters and one Steller sea lion from Flat Island along the Outer Kenai (Lower Cook Inlet) taken by subsistence hunters from the village of English Bay. None of these animals collected in 1990 showed any sign of external oiling.

In contrast to fish, we have not determined whether biliary protein can be used as a normalizing factor to account for differences in the composition of bile of

marine mammals. Thus, the concentrations of FACs in these pinnipeds are expressed as ng PHN equivalents per gram bile. The levels of biliary protein in bile of these marine mammals, however, were measured and are given in Tables 8 and 9. As with fish, the range of concentrations of FACs was wide (170-210,000) ng PHN equiv./g of bile. Even though oil was observed to be present on 13 harbor seals at the time samples were collected, the concentrations of FACs varied widely in those animals indicating that many factors, including the degree of absorption/ ingestion of oil, metabolism, and excretion determine the levels of metabolites in bile. Hence, considerable caution should be used in comparing the presence of oil on the exterior of the animals with FACs in bile. For example, it would not be known when or how the animal came in contact with the oil. However, 9 of the 12 bile samples with the highest concentrations of $FACs_{PHN}$ ($\geq$8,000 ng/g) were from animals that were visibly oiled. Only 4 of the 14 bile samples from harbor seals with concentrations of $FACs_{PHN}$ less than 8,000 ng/g were from animals that were visibly oiled.

Samples from nine Steller sea lions were collected in 1989 and one in 1990; five were collected from PWS and five from the Gulf of Alaska. The concentrations of FACs in bile from Steller sea lions were generally much lower than the concentrations of FACs in bile from harbor seals (except for one sample, concentrations of FACs in bile from sea lions were <5,000 ng/g bile). None of the sea lions sampled were visibly oiled. Sea lions did not seem to avoid oil, as some were observed swimming in oiled areas. The results for FACs in marine mammals are detailed in Vol. II, Section C.

Temporal trends in concentrations of FACs in bile of mammals were not statistically evaluated due to an insufficient number of samples.

Aromatic Compounds in Edible Flesh of Marine Mammals

Tissues from most of the harbor seals and sea lions sampled were analyzed for ACs. Since there was no data base regarding the correlation of FACs in bile with marine mammal exposure to ACs, all blubber samples were analyzed. Bile FACs were used to select tissue samples other than blubber for analysis for ACs. High concentrations of FACs in bile was used to select animals for analyzing muscle, liver, and kidney tissues. The mean concentrations of ACs (Table 10),

were highest in blubber of harbor seals from Herring Bay and Bay of Isles sampled in 1989. The mean concentrations of ACs in these blubber samples were in the moderately contaminated category (category 3), whereas most of the blubber samples from the other areas were not contaminated. Blubber samples of seals from Herring Bay and Bay of Isles sampled in 1990 were only minimally contaminated (category 2) with ACs. With the exception of blubber from one animal from Flat Island that contained 17 ng/g ACs, blubber samples from Steller sea lions had concentrations of ACs in category 1. With the exception of one harbor seal muscle sample from Seal Island, 1989, the concentrations of ACs in liver, muscle, and kidney samples from harbor seals and sea lions were also in category 1 (Vol. II, Section D).

On an individual tissue sample basis, the concentrations of ACs were greater than 10 ng/g in 18 tissue samples from 16 harbor seals, 16 of which were blubber samples (Table 11). Of these 16 blubber samples, four were moderately contaminated with ACs (category 3) and all four were from visibly oiled animals collected from the heavily oiled areas of Herring Bay and Bay of Isles, PWS in 1989. Blubber samples from 10 of the 13 visibly oiled harbor seals (Vol. II, Section D) had concentrations of ACs in categories 2 and 3. The only sample of muscle tissue that exceeded 10 ng/g (16 ng/g) was collected from a visibly heavily-oiled harbor seal pup in Seal Bay in 1989. The only sample of liver tissue that exceeded 10 ng/g (15 ng/g) was collected from a harbor seal in Herring Bay in 1990. The kidney samples that were analyzed had category 1 concentrations of ACs (concentrations were <10 ng/g). Tissue samples collected from seven harbor seals harvested by subsistence hunters in PWS in 1990 had AC concentrations less than 10 ng/g. The concentrations of ACs in edible tissue (blubber, liver, kidney, and muscle) from the marine mammals are detailed in Vol. II, Section D by species, site, and year sampled.

The limiting factors for statistical comparison of FACs in bile samples from animals with ACs in tissues include the small number of samples and the lack of control studies. As the data base for ACs in marine mammals expands, we will be able to better establish the correlation of FACs in bile with ACs in tissue.

In the blubber samples with elevated concentrations of ACs, the concentrations of alkyl-substituted ACs were similar to or greater than the

concentrations of the corresponding nonsubstituted AC (e.g., the ratios of the concentrations of C1PHN to PHN in sample numbers 60-1325 and 60-1412 (duplicate with 60-1424) were 1.7 and 1.8, respectively, Vol. II, Section D). A similar ratio was found in PBCO (e.g., C1PHN to PHN = 2.1) and generally these ratios were opposite of what was observed in the very few fish in this study where ACs were detected in their muscle tissue. Laboratory studies have shown that the alkyl-substituted ACs are more readily metabolized by fish than the nonalkyl substituted components (Schnell et al. 1980). Also, the ratios of LACs/HACs in harbor seals that had greater than 100 ng/g of ACs in their blubber were very high (e.g., 1,000 for sample 60-1325, and 270 for duplicate samples 60-1412/1424, compared to ca. 400 for PBCO). These patterns of ACs in blubber may correspond to the oil these two animals were exposed to because both were collected in 1989, and both were visibly oiled.

As noted earlier, FACs in bile of fish are indicative of relatively recent exposure to ACs, because ACs that are taken up by the animal are readily metabolized and excreted in their bile. Further, metabolites of ACs in bile of fish have been correlated to exposure to ACs in laboratory and field studies (Stein et al. 1987); however, much less is known about metabolism and excretion of ACs in marine mammals. The limited data available on biotransformation enzyme systems and metabolite profiles of ACs in marine mammals suggest that the extent of metabolism of xenobiotic compounds in marine mammals is intermediate between terrestrial mammals and fish (Boon et al. 1992, Norstrom et al. 1992). Their results suggest that the metabolic capability of cetaceans (e.g., whales) is similar to fish, while the metabolic capability of pinnipeds (e.g., harbor seals, Steller sea lions) is greater than fish or cetaceans, but less than terrestrial mammals. Thus, the marked differences in ACs profiles between pinniped blubber and fish muscle would not appear to be due solely to differences in biotransformation capacities. Differences in kinetics of uptake of ACs, route of exposure, and lipid content of the tissues may all contribute to the differences in ACs profiles observed; however, additional studies are needed to determine the physiological basis for the observed differences.

Aromatic Compounds in Invertebrates

Invertebrates were collected from July 1989 through August 1991 from a variety of sampling areas (Table 12). Analyses of more than 1,000 samples of

invertebrate tissues were performed, with mussels, butter clams, littleneck clams, and chitons being the primary target invertebrate species. In total, 22 sampling areas were chosen for sampling, along with two reference areas (Table 12). The largest number of samples was collected from the Chenega Bay and Windy Bay sampling areas (194 and 187, respectively) and these were the only 2 areas sampled during 1991. At most sampling areas, more than one sampling station (beach area) was chosen for collecting invertebrate samples (Table 13). The numbers of samples of each of these species collected are presented in Table 13 by sampling area and year to show the major part of the sampling for invertebrate samples. The mean concentrations of ACs and standard deviation from each sampling station by year are also included. It is readily seen from this data that the highest concentrations of ACs were found in samples from stations CHE7, CHE10, WNB1, WNB3, and KOD3. It is also evident that the mean concentrations of ACs in samples from many areas were less than 100 ng/g and that the concentrations of ACs covered a very large range. Therefore, it was convenient to divide the concentrations into four categories of ranges as described earlier (page 16), with category 4 being the most contaminated (>1,000 ng/g) and category 1 being uncontaminated.

In this section, those samples that were moderately or highly contaminated (category 3 or 4) will be discussed. The 14 stations that had one or more invertebrate samples with concentrations of ACs in categories 3 or 4 are included in Table 14, and this table shows that stations CHE7, WNB1, WNB3, and KOD3 had the most samples in categories 3 and 4.

Comparison of ACs in Molluscs by Area

The Tatitlek area (east of the spill) is closest to Bligh Reef where the spill occurred, but direct oiling of beaches was not observed in this area. Only two invertebrate samples (both from station T1) out of 45 collected from the sampling stations in the Tatitlek sampling area had concentrations of ACs that exceeded 100 ng/g (Tables 12, 14), and, as explained in a later section, the ACs in these two samples probably were not related to the spilled oil.

The Chenega Bay sampling area was the first subsistence collection area in the path of the spilled oil and included a large geographic area in southwestern

PWS (Fig. 3). Due to the concerns of the community and the potential for shoreline oiling, 12 sampling stations for invertebrates were established. Oil was observed in the area or on the beach at 3 of the sampling stations (CHE1, CHE 10, CHE24), and 4 of the 12 Chenega sampling stations (CHE1, CHE7, CHE10, CHE24) had samples (41 out of 194) with concentrations of ACs that exceeded 100 ng/g. Thirty-one of the 41 samples that were in category 3 or 4 were from CHE7, although the spilled oil may not have been the main source of ACs at this site. This issue will be discussed in a later section. Oil was observed in the area of station CHE1 in 1989 following the spill (this station was located adjacent to the village of Chenega Bay). Booms were put in place to prevent oiling of the beach which received little or no direct oiling. Six of 38 invertebrate samples from CHE1 had concentrations of ACs greater than 100 ng/g (category 3 or 4). At CHE10, there was a tar mat about 1 m wide that extended most of the length of the beach. Oil was also observed on the beach at station CHE24, where one mussel sample of 10 collected had a concentration of ACs in category 3. The high, low, and median concentrations of ACs in the target mollusc samples from CHE1, CHE7, and CHE10 (Fig. 28) demonstrate the wide range of concentrations found in these samples.

One of the next subsistence seafood sampling areas in the path of the spilled oil was Windy Bay on the southwestern part of the Kenai Peninsula. All of the Windy Bay sampling stations were oiled, but two stations (stations 1 and 3, two small islands in the mouth of Windy Bay) were moderately to heavily oiled. During the three sampling years, 106 invertebrate samples were collected from these 2 stations. Of the 106 samples, only 34 contained concentrations of ACs that exceeded 100 ng/g (Tables 12, 14). Only 3 of the 81 invertebrate samples collected from the other 3 Windy Bay stations located at the head of Windy Bay had concentrations of ACs that were greater than 100 ng/g (Tables 13, 14). As stated above, the high, low, and median concentrations (Fig. 29) show that the concentrations varied considerably for the target mollusc samples at the most contaminated Windy Bay sampling stations. The mean concentrations of ACs in molluscs from the other sampling stations on the Kenai Peninsula (Lower Cook Inlet, Table 13) were mostly in the not contaminated category.

The spilled oil was carried along Kodiak Island and southward along the Alaska Peninsula. Several areas in this region were selected for invertebrate

sampling, however, invertebrate samples from only five stations (K7, KOD3, OHA4, CHG1, CHG3) had concentrations of ACs greater than 100 ng/g (Table 14). At K7, only 1 sample of 4 had concentrations of ACs greater than 100 ng/g; at OHA4, 4 of 26; at CHG1, 2 of 9; and at CHG3, 3 of 10 had concentrations of ACs greater than 100 ng/g. However, at station KOD3, 26 of 30 samples had concentrations of ACs greater than 100 ng/g, 9 of which were greater than 1,000 ng/g (Figs. 7, 8, 14). The high, low, and median concentrations of ACs in mussel and clam samples from station KOD3 (Fig. 29) were similarly high in 1989 and 1990, and all were moderately or highly contaminated. Station KOD3 is located on Near Island about a quarter of a mile from Kodiak's boat harbor; therefore, the potential source of the ACs in the samples from KOD3 may have been from boating activity (also see page 32). Station OHA4 is near the village of Old Harbor and within 1/4 mile of a boat harbor. Five samples from the Chignik sampling area (stations CHG1 and CHG3, Fig. 14) were moderately contaminated; however, the concentrations of ACs in these samples were just over 100 ng/g wet weight. The mean concentrations of ACs in molluscs from the Kodiak Island and Alaska Peninsula sampling stations, other than the five discussed here, were mostly in the not contaminated category (<10 ng/g, Table 13) and were comparable to reference area values.

Comparison of ACs in Molluscs by Species

Aromatic Compounds in Mussels

The majority of the mussel samples were not contaminated with ACs, including the samples from the reference areas. Of all of the invertebrates sampled, mussels comprised one of the most intensely sampled species; hence it is possible to compare concentrations of ACs in this species from various sites. Thirty-one of the mussel samples from Chenega Bay station CHE10 (1990), Windy Bay stations WNB1 (1989), WNB3 (1990), and Kodiak station KOD3 (1989) fell into category 4 (highly contaminated by ACs) based on the mean concentrations of ACs (Table 13). Mussels from Chenega Bay stations CHE1 (1989) and CHE7 (1990), Windy Bay station WNB3 (1991), Kodiak station KOD3 (1990) and Old Harbor station OHA4 (1990) were moderately contaminated with ACs (category 3). Mussels from the other samplings were not contaminated or were only minimally contaminated (Table 13).

The concentrations of total ACs that exceeded 100 ng/g in mussel samples are listed in order of decreasing concentration by station in Table 15. The highest concentrations of ACs in individual mussel samples were from Windy Bay stations WNB1 (1989) and WNB3 (1990), 18,000 and 5,500 ng/g, respectively. Only 15 mussel samples of 367 were highly contaminated (those with >1,000 ng/g of ACs) and they were from the Chenega Bay, Windy Bay, and Kodiak sampling areas. Forty-seven mussel samples were moderately contaminated (100 to 1,000 ng/g) and were from the three areas above plus the Old Harbor and Chignik sampling areas. It is notable that of these 47 mussel samples, many were in the low end of the moderately contaminated category (i.e., the concentrations of ACs were <200 ng/g in 28 of the 47 samples). Even at the more contaminated Windy Bay stations WNB1 and WNB3, only 15 of the 32 moderately or highly contaminated mussel samples had concentrations greater than 200 ng/g. Furthermore, four samples from each of two sample collections from WNB3 (March 1990 and July 1990) were from the upper intertidal or splash zone and the presence of oil was noted during the March 1990 sample collection. These eight samples were highly contaminated, whereas none of the other mussel samples from WNB3 had concentrations of ACs in concentration category 4.

Aromatic Compounds in Butter Clams

The only butter clams that were highly contaminated (category 4) based on the mean concentrations of ACs (Table 13) were from Kodiak (station KOD3, 1990). The only butter clams that were moderately contaminated with ACs were from Kodiak station KOD3 (1989, only one sample was collected), Chenega Bay station CHE7 (1990 and 1991), and from Old Harbor station OHA4 (1989). The mean concentrations of ACs in butter clams were mostly in the not-contaminated category or in the low end of the minimally contaminated category.

Based on the concentrations of ACs in individual samples (208 total), nine samples of butter clams (eight from the Kodiak station KOD3 sampling site collected in 1990 and one from Chenega Bay station CHE7) were highly contaminated with ACs (Table 16). Only 18 samples of butter clams were moderately contaminated with ACs, all of which were from Tatitlek, Chenega Bay, Kodiak, and Old Harbor sampling areas.

Aromatic Compounds in Littleneck Clams

None of the littleneck clam samples were highly contaminated with ACs (Table 17). Only 21 samples of littleneck clams out of a total of 175 were moderately contaminated with ACs. Many of the littleneck clam samples were not contaminated with ACs, with concentrations similar to those from Yakutat, the reference area.

Aromatic Compounds in Chitons

Only one sample of chitons (183 total) was highly contaminated with ACs (the sample was from Windy Bay station WNB1, 1989; Table 18) and only two samples were moderately contaminated (samples from Kodiak station KOD3, 1989). The mean concentrations of ACs in all the other chiton samples were in the not-contaminated category, similar to the ones for Yakutat, the reference area (Table 13).

Aromatic Compounds in Other Invertebrate Species and Miscellaneous Samples

One hundred thirty-three samples of a variety of other tissues and invertebrate samples, including clam species other than those discussed above, crab, limpets, sea urchins, snails, shrimp, kelp, and herring roe on kelp, were analyzed for ACs. Of these samples, most (95) were not contaminated with ACs, 35 samples were minimally contaminated with ACs, 3 were moderately contaminated with ACs (2 snail samples and 1 macoma clam sample from Windy Bay), and none fell into category 4 (highly contaminated with ACs).

In summary, the sampling design for this study did not include sample collections to explain species differences in concentrations of ACs in mussels, clams, or chitons. The differences in concentrations observed may be relative to exposure but could be due to other factors as well (e.g., uptake and depuration). Only 25 of the more than 1,000 invertebrate samples analyzed were considered highly contaminated (>1,000 ng/g). Of these 25 samples, all were mussels or clams except for one sample of chitons, and all 25 samples were from three

sampling areas (Chenega Bay, Windy Bay, Kodiak Island). Invertebrate samples that were either moderately or highly contaminated were primarily from some stations at Chenega Bay (CHE1, CHE7, CHE10, CHE24), Windy Bay (WNB1, WNB3), Kodiak (KOD3), and Old Harbor (OHA4). Even so, the concentrations of ACs in many of the invertebrate samples from the above stations were in the not-contaminated category, and most of the mean concentrations of ACs in these samples fell in either the not-contaminated or minimally-contaminated categories.

Temporal Changes in the Concentrations of Aromatic Compounds in Molluscs

The concentrations of ACs in mussels and clams from Chenega Bay, Windy Bay, Kodiak, and Old Harbor were further evaluated using GT2 comparison interval graphs to determine statistically if the concentrations of ACs declined during the period of this study. When the comparison-interval bars do not overlap, the concentrations of ACs being compared are significantly different. For Chenega Bay, the concentrations of ACs in mussels collected from CHE1 in March 1990 were significantly lower than for samples collected either in August 1989 or June 1991 (Fig. 30). The concentrations of ACs in mussels from CHE7 in June 1991 were significantly lower than those in samples collected in July 1990, but not for those collected in April 1990. At both CHE1 and CHE7, the lack of a continued decline in concentrations may have been related to the sampling conditions (e.g., the stage of the tidal cycle, the lack of resampling at the sampling location, or the existence of a continual source of ACs). The concentrations of ACs were significantly lower in mussel samples collected in 1991 from CHE9 and CHE10 compared to 1990. Furthermore, it is important to note that both the limited number of sampling cycles, and the small number of samples collected during each cycle, hampered our ability to draw strong conclusions about temporal trends from the data.

The GT2 plots show that mussel samples from WNB1 collected in April 1991 had significantly lower concentrations of ACs than those collected in 1989 (Fig. 31). The eight mussel samples from the higher part of the tidal zone of the WNB3 station (discussed on page 25) were the most contaminated with ACs. The concentrations of ACs in these eight samples from the two collections were not significantly different, however, the concentrations of ACs in all of the other

mussel samples from WNB3 were significantly lower than those eight samples, and the remaining samples from WNB3 were only minimally or moderately contaminated with ACs. The concentrations of ACs were significantly lower in mussels from WNB3 collected in 1991 compared to those collected in July 1990, but not significantly lower than those collected in March or April 1990. Thus, it is difficult to see a declining trend in concentrations of ACs at WNB3. At WNB2, the concentrations of ACs were not significantly lower in mussels collected in 1991 compared to those collected in 1990. As at Chenega Bay, evaluation of temporal trends in the concentrations of ACs was limited by the sampling scheme (e.g., a limited number of samples).

Most butter clam samples from Chenega Bay station CHE1 were minimally contaminated or not contaminated with ACs (Fig. 32). The concentrations of ACs in all of these samples were not significantly different. The concentrations of ACs in butter clams from CHE7 were moderately or highly contaminated with ACs and were significantly lower in samples collected in April 1990 and June 1991 than in those collected in February 1990. The concentrations of ACs in the samples collected in June 1990 were not significantly different from those collected in February 1990. Also, the concentrations of ACs were significantly lower in butter clams from CHE10 collected in August 1991 than those collected in 1990, with the concentrations being low in all of the samples.

The concentrations of ACs in butter clams from Kodiak station KOD3 did not decline significantly over the four sampling events in 1990 and the majority of the mean concentrations of ACs were in the highly contaminated category (Fig. 33). Moreover, the concentrations of ACs were consistent for three of the four sampling events.

Most butter clams from Old Harbor station OHA3 were not contaminated with ACs (Fig. 34). In fact, this is a good example of where the concentrations of ACs in samples are so low that they should not be compared statistically. As noted earlier, only two butter clams collected from Old Harbor station OHA4 in 1989 were moderately contaminated with ACs (Table 16). However, all of the other samples collected from this station during 1989 and 1990 had concentrations of ACs that were in category 1 or the lower part of category 2.

Overall, most of the littleneck clam samples were not contaminated or minimally contaminated and the concentrations of ACs did not differ significantly (Fig. 35). The concentrations of ACs in littleneck clams from station CHE1 were consistently near the low end of the minimally contaminated category and there was no significant decline in the concentrations of ACs in these samples over time. The concentrations of ACs in littleneck clams from station CHE7 were near the 100-ng/g level and were consistent over the 2 years of sampling. Possible reasons for this will be addressed in a later section. The concentrations of ACs in littleneck clams from CHE10 collected in August 1991 were significantly lower than for those collected in April 1990 and June 1991. Littleneck clams from the two sample collections from Kodiak station KOD3 were moderately contaminated and the concentrations of ACs were not significantly different. Again, as for butter clams from KOD3, additional investigation is needed to determine the source of the ACs. The concentrations of ACs were significantly lower in littleneck clams from Windy Bay station WNB4 in April 1991 than for those collected in July 1990.

Patterns of Aromatic Compounds in Invertebrates

Comparing patterns of ACs from samples of biota, petroleums, and other sources (e.g., combustion products) provides useful information about possible sources of contamination. However, certain limitations of such techniques become apparent when comparing patterns of ACs in samples to patterns in sources. As shown earlier, ACs may come from a variety of sources including petroleum, petroleum products such as the different fuel oils, and products of combustion, and there are distinct differences in the patterns of ACs in many of these materials. In addition, when released into the environment, all of these materials undergo a variety of changes (e.g., evaporation, dissolution in water, bacterial degradation, photooxidation). Moreover, biogenic processes such as bioaccumulation, metabolism, and depuration of ACs can also influence both the levels and patterns of ACs present in marine organisms. Furthermore, in this study, samples of the oil or sediment were not collected from the beach at the time the molluscs were collected; therefore, the source of the ACs that the mussels were being exposed to could not be fully known. Thus, relating the presence of ACs in biota such as molluscs to sources is complicated by the above factors. Even though a thorough treatment of the data relative to patterns and possible sources is beyond the original

scope of this program and report, comparison of patterns of ACs can provide valuable clues to the sources of contamination.

The samples that were used for pattern comparison generally were randomly selected from those with the higher concentrations of ACs from the stations of interest. For example, examination of the patterns of ACs in selected mussel samples from Chenega Bay station CHE1 and Windy Bay station WNB1 (Fig. 36) show that they are almost identical, suggesting a common source of contamination. These two chromatographic patterns contain many of the alkyl-substituted components typical of petroleum, and, as would be expected, they show considerable losses of the more volatile and more water-soluble components of the LACs (the components to the left of phenanthrene, Fig. 18) when compared to the patterns obtained with PBCO.

As noted earlier, Windy Bay stations WNB1 and WNB3 could be considered to be one station. Temporal comparison of the patterns of ACs in mussels from Windy Bay stations WNB1 and WNB3 from 1989, 1990, and 1991 shows a continuing increase in the relative concentrations of some of the HACs and dibenzothiophenes (Figs. 36 and 37), otherwise, these three patterns for ACs in mussels from stations WNB1 and WNB3 are very similar to each other. Petroleum from the *Exxon Valdez* spill was known to impact stations WNB1 and WNB3, and Chenega Bay station CHE1, thus the spilled petroleum was probably the source of the ACs in the molluscs, even though the patterns in the fresh PBCO and the molluscs are not identical.

The pattern of ACs in mollusc samples from Chenega Bay station CHE10 was somewhat different than the pattern for molluscs from CHE1. For example, a mussel sample from CHE10 (Fig. 38) contained many of the same alkyl-substituted components as those in the mussels from stations CHE1, WNB1, and WNB3. However, the pattern also contained ACs suggestive of combustion products (e.g. phenanthrene, fluoranthene, pyrene, and benz[a]anthracene) when compared to the patterns of ACs in an urban sediment from Puget Sound, Washington (Fig. 21). There was a tar mat on the beach at CHE10 assumed to be from the spilled oil, which could account for the petroleum pattern in the mollusc sample. However, the source of the combustion products pattern in this sample is not clear.

The concentrations of ACs were high in some invertebrates from sampling stations that were not observed to have been exposed to the spilled PBCO. In some of these samples (e.g., Chenega Bay station CHE7) the ratio of LACs/HACs was considerably lower than in samples that probably were exposed to the spilled oil (e.g., WNB3 samples). The pattern of ACs in a butter clam from Chenega station CHE7 (Fig. 38) was similar in some ways to that for the mussel sample from CHE10, but it contained less of the C3PHN, C1DBT, C2DBT, and C3DBT components. The pattern for ACs in the butter clam sample from CHE7 also had similarities to the patterns for combustion products in the urban sediment extract described above and to creosote (Fig. 21). Alkyl-substituted ACs suggestive of petroleum were also present in the butter clam sample, but appear to be a minor component in this example. Creosoted pilings were noted to be in the CHE7 area where the butter clam samples were collected; however, in the absence of a carefully designed sampling and analysis study, it would be difficult to say that the ACs in the clams were from the creosoted pilings. The comparison of patterns shows that caution is important when correlating patterns to potential sources. At the same time, these comparisons show that, if used judiciously, pattern comparison may provide an in-depth look into the potential sources of exposure.

Tatitlek station T1 also was not suspected to have been exposed to the spilled PBCO, even though samples from these stations contained ACs. The patterns of ACs in butter clams from Tatitlek station T1 (Fig. 39) contain the ACs indicative of combustion products, but they were relatively free of the alkyl-substituted phenanthrenes and dibenzothiophenes found in PBCO and in the Windy Bay mussels.

As noted earlier, molluscs from two Kodiak Island stations (KOD3 and OHA4) were moderately or highly contaminated with ACs. The patterns of ACs in a mussel sample from each station (Fig. 40) were very similar to the patterns of ACs in mussel samples from WNB3 (Fig. 37), except for the higher relative amounts of the more volatile and water-soluble components of the LACs in the KOD3 and OHA4 samples. Higher concentrations of ACs typical of combustion products were present in the OHA4 sample, including fluoranthene, pyrene, and benz[a]anthracene. The pattern of ACs in a sample of butter clams collected from station KOD3 in March 1990 (Fig. 41) was nearly identical to that for mussels

collected at the same station in April 1990 (Fig. 40). Also, for butter clams collected at three different times in 1990 at KOD3 (March, May, and September), the pattern of the ACs typical of petroleum in these samples remained consistent over the relatively short period of time, even though the ACs typical of combustion products relative to the C2-phenanthrene peaks appeared to decrease (Figs. 41 and 42). The consistent pattern of petroleum-related ACs in these samples implies that the clams were being continually exposed to the same source of these ACs over time (probably a local source of ACs, not the *Exxon Valdez* oil spill). Furthermore, the pattern of ACs in littleneck clams collected from KOD3 in April 1990, (Fig. 41) was nearly the same as that in butter clams from the same station collected in March 1990 (Fig. 41). These patterns suggest that the mussels and the two clam species collected from station KOD3 were all exposed to a similar source(s) of ACs.

The preceding examples of pattern comparison illustrate the need to utilize a thorough and ongoing sampling scheme and to consider the many ambiguities involved when comparing the patterns of ACs in biological samples to the patterns in sources. Also, these pattern comparisons show that the proper use of pattern comparison can be a powerful asset for identifying sources of contamination by ACs.

CONCLUSIONS

Many of the fish, marine mammals, and invertebrates sampled during the subsistence study were exposed to petroleum-related ACs. The best evidence for exposure of fish and marine mammals was the concentrations of metabolites of ACs (FACs) found in their bile because the ACs taken up by fish and mammals are readily metabolized and excreted in their bile. The concentrations of FACs in bile of fish indicated that many species, including water column and bottom feeding species, had been exposed to ACs in petroleum. The highest concentrations of FACs were found in the bile of pink salmon from Chenega Bay, Kodiak, and Old Harbor in 1989. Generally, lower concentrations of FACs were found in bile of other salmon species, and in that of halibut and cod. With only a few exceptions, the edible tissue of fish was not contaminated with ACs (concentrations were <10 ng/g) because of efficient metabolism and excretion of ACs via hepatobilliary systems which prevented deposition of ACs into extrahepatic tissues. The highest

concentration of ACs in edible tissue of fish was 100 ng/g (in a pink salmon sample from Kodiak). Also, the ratio of the concentrations of alkyl substituted ACs to non-alkyl substituted ACs was higher in PBCO and in molluscs than in edible tissue of fish. This would be predicted because fish more readily metabolize the alkyl-substituted ACs, whereas molluscs have minimal ability to metabolize ACs.

The concentrations of FACs in the bile from harbor seals indicated varying degrees of exposure of these animals to ACs typical of petroleum, whereas the concentrations of FACs in bile from Steller sea lions indicated modest exposure. The highest concentrations of FACs in harbor seals were found in bile of visibly oiled animals from heavily oiled areas of PWS in 1989. Blubber from four harbor seals from PWS was moderately contaminated with ACs (concentrations ranged from 130 ng/g to 810 ng/g), blubber from 12 harbor seals was minimally contaminated (<100 ng/g) with ACs, and blubber from the other 15 harbor seals was not contaminated with ACs. The blubber from sea lions was not contaminated with ACs except for one sample that contained only 17 ng/g. Most of the muscle, liver, and kidney samples analyzed from harbor seals and Steller sea lions were not contaminated with ACs.

Most invertebrates from the 22 village areas (ca. 80 sampling stations) and the two reference areas, Angoon and Yakutat, were not contaminated or were minimally contaminated with ACs. However, several of the mollusc samples from some stations at Chenega Bay, Windy Bay, Kodiak, and Old Harbor sampling areas were in category 3 and 4 (moderately to highly contaminated (>100 ng/g)). Mollusc samples from four stations in the Chenega Bay sampling area and three stations at Windy Bay were moderately or highly contaminated with ACs and the GC-MS patterns were indicative of petroleum. The pattern of ACs in a mollusc sample from a different station at Chenega Bay (CHE7) suggested that the main source of ACs may not have been from petroleum. Aromatic compounds present in samples from two Kodiak Island stations were indicative of petroleum exposure, but no time related decline suggested the source of exposure may not have been from the *Exxon Valdez* spill.

Tissue samples from several species of marine invertebrates from the vicinity of the spill were moderately or highly contaminated with ACs similar to

those in petroleum. However, these elevated concentrations of ACs in invertebrate samples were substantially lower than the concentrations of ACs in a sample of smoked salmon obtained from a resident at Tatitlek (23,000 ng/g).

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TABLES

Table 1. Aromatic contaminants (ACs: aromatic hydrocarbons and dibenzothiophenes) determined in edible tissue in the Exxon/Alaska Department of Fish and Game/NOAA subsistence fish, marine mammal, and shellfish studies. Lower molecular weight ACs = LACs; higher molecular weight ACs = HACs. C1-, C2-, etc. are abbreviations for methyl-, dimethyl/ethyl-, etc., respectively.

2- and 3-ring aromatic compounds LACs	4- to 6-ring aromatic compounds HACs
naphthalene (NPH)	fluoranthene (FLA)
C1-naphthalenes (C1NPH)	pyrene (PYR)
C2-naphthalenes (C2NPH)	C1-fluoranthenes/pyrenes (C1FLA)
C3-naphthalenes (C3NPH)	benz[a]anthracene (BAA)
C4-naphthalenes (C4NPH)	chrysene (CHR)
acenaphthylene (ACY)	C1-chrysenes/benz[a]anthracenes (C1CHR)
acenaphthene (ACE)	C2-chrysenes/benz[a]anthracenes (C2CHR)
fluorene (FLU)	C3-chrysenes/benz[a]anthracenes (C3CHR)
C1-fluorenes (C1FLU)	C4-chrysenes/benz[a]anthracenes (C4CHR)
C2-fluorenes (C2FLU)	benzo[b]fluoranthene (BbF)
C3-fluorenes (C3FLU)	benzo[k]fluoranthene (BkF)
phenanthrene (PHN)	benzo[a]pyrene (BAP)
C1-phenanthrenes/anthracenes (C1PHN)	indeno[1,2,3-cd]pyrene (IDP)
C2-phenanthrenes/anthracenes (C2PHN)	dibenz[a,h]anthracene (DBA)
C3-phenanthrenes/anthracenes (C3PHN)	benzo[ghi]perylene (BZP)
C4-phenanthrenes/anthracenes (C4PHN)	
dibenzothiophene (DBT)	
C1-dibenzothiophenes (C1DBT)	
C2-dibenzothiophenes (C2DBT)	
C3-dibenzothiophenes (C3DBT)	

Table 2. Summary of sample collection of major species by site, year, and number of samples. Name abbreviations used in other figures and tables are shown in parentheses.

Village sampling site	Year	Number of samples collected					
		Mussels	Butter clams	Littleneck clams	Chitons	Salmon species	Bottomfish
Angoon (AGN)	1989	2	1		2	6	2
Yakutat (YAK)	1990	6	6	6	6	6	6
Tatitlek (T or TAT)	1989	7			2	13	5
	1990	14	16	6			9
Chenega Bay (CHE)	1989	5	2			20	11
	1990	21	24	24	8	3	14
	1991	44	17	25	17		
Port Graham/English Bay (PTG)	1989	10		1	3	10	4
	1990	24		2	33	5	11
Windy Bay (WNB)	1989	3		1	2		
	1990	38		5	12	2	
	1991	61		8	17		
Port Dick (PTD)	1990	1		6			
Chugach Bay (CHG)	1990				7		
Port Chatham (PTC)	1990	2		5	9		
Point Bede (BED)	1990				7		
Kasitsna Bay (KAS)	1989	2	1		1		
	1990			6			
Sadie Cove (SAD)	1990	2		5			
Kodiak (K or KOD)	1989	1	1	2	2	12	4
	1990	7	16	8	8	3	
Chiniak (CHI)	1989	2	7	3	5	16	3
	1990	16	8	4	4		
Old Harbor (OHA)	1989	1	10	2	3	20	5
	1990	10	20	10	7	8	1
Akhiok (AKH)	1989	2	3	1	1	4	
	1990	8	3	6			3
Karluk (KAR)	1989	4	1		2	6	
	1990	8	4	4		7	
Larsen Bay (LAB)	1989	1	7		3	20	7
	1990	4	14	7	1	3	1
Port Lions (PTL)	1989		7	2	5	16	5
	1990	14	11	14	4	3	2
Ouzinkie (OUZ)	1989	1	4	2	2	18	5
	1990	9	22	10	9	9	3
Chignik (CHG)	1990	19					
Ivanof Bay (IVB)	1990	9	3				
Perryville (PER)	1990	9			1	2	3
Kashvik Bay (KAT)	1990						

Table 3. Concentrations, µg/g wet weight, of aromatic contaminants (ACs) in oil.

ACs	Sample:	*Exxon Valdez* fresh oil 1989	Snug Harbor oil *
	Lab no.:	60-300	59-321
naphthalene		830	2
C1-naphthalenes		2,000	11
C2-naphthalenes		2,800	300
C3-naphthalenes		2,500	850
C4-naphthalenes		1,300	650
acenaphthylene		1	nd
acenaphthene		11	1
fluorene		110	12
C1-fluorenes		250	100
C2-fluorenes		430	240
C3-fluorenes		120	230
phenanthrene		340	16
C1-phenanthrenes/anthracenes		720	120
C2-phenanthrenes/anthracenes		820	330
C3-phenanthrenes/anthracenes		620	280
C4-phenanthrenes/anthracenes		140	110
dibenzothiophene		320	43
C1-dibenzothiophenes		580	200
C2-dibenzothiophenes		840	510
C3-dibenzothiophenes		710	490
Sum of lower molecular weight ACs (LACs)		15,000	4,500
fluoranthene		15	5
pyrene		16	8
C1-fluoranthenes/pyrenes		88	54
benz[a]anthracene		2	nd
chrysene		55	26
C1-chrysenes/benz[a]anthracenes		81	41
C2-chrysenes/benz[a]anthracenes		98	13
C3-chrysenes/benz[a]anthracenes		52	6
C4-chrysenes/benz[a]anthracenes		nd	3
benzo[b]fluoranthene		7	4
benzo[k]fluoranthene		nd	nd
benzo[a]pyrene		1	1
indeno[1,2,3-cd]pyrene		nd	nd
dibenz[a,h]anthracene		nd	nd
benzo[ghi]perylene		nd	nd
Sum of higher molecular weight ACs (HACs)		420	160
LACs/HACs		37	28

* Sample was collected in 1990 from seepage from an excavated beach area at Snug Harbor.
nd = not detected.
See Table 1 for explanation of LACs, HACs, C1, C2, etc.

Table 4. Concentrations (mean ± standard deviation) of fluorescent aromatic compounds measured at phenanthrene wavelengths ($FACs_{PHN}$ (ng phenanthrene equivalents)) in bile of salmon collected during the 1989 and 1990 studies. The number of samples analyzed is in parentheses.

Species	Village sampling site, year	FACs (ng PHN eq./g bile)	FACs (ng PHN eq./mg bile protein)
Pink salmon	Angoon, 1989 (4)	4,400 ± 4,900	4,300 ± 5,100
	Tatitlek, 1989 (4)	44,000 ± 40,000	560 ± 290
	Chenega Bay, 1989 (22)	180,000 ± 170,000	6,000 ± 3,400 *
	Chenega Bay, 1990 (5)	14,000 ± 9,500	490 ± 230
	Port Graham/EB, 1989 (5)	27,000 ± 19,000	1,500 ± 920
	Port Graham/EB, 1990 (5)	7,800 ± 4,200	420 ± 230
	Windy Bay, 1990 (4)	23,000 ± 14,000	1,200 ± 650
	Kodiak, 1989 (10)	100,000 ± 150,000	2,800 ± 1,900 *
	Kodiak, 1990 (5)	28,000 ± 21,000	2,400 ± 2,000
	Chiniak, 1989 (21)	35,000 ± 28,000	770 ± 410
	Chiniak, 1990 (11)	7,200 ± 3,100	480 ± 160
	Old Harbor, 1989 (16)	64,000 ± 25,000	1,800 ± 610 *
	Old Harbor, 1990 (12)	29,000 ± 24,000	1,200 ± 620
	Akhiok, 1989 (1)	8,600	
	Karluk, 1990 (11)	3,600 ± 1,900	260 ± 200
	Larsen Bay, 1989 (16)	56,000 ± 39,000	1,900 ± 2,000
	Larsen Bay, 1990 (4)	3,500 ± 1,200	640 ± 540
	Port Lions, 1989 (16)	23,000 ± 6,600	980 ± 1,300 *
	Port Lions, 1990 (11)	4,400 ± 1,300	1,000 ± 1,700
	Ouzinkie, 1989 (6)	7,800 ± 4,200	760 ± 530
	Ouzinkie, 1990 (1)	8,100	1,400
Coho salmon	Angoon, 1989 (6)	1,700 ± 670	530 ± 280
	Tatitlek, 1989 (12)	19,000 ± 11,000	1,500 ± 1,000
	Chenega Bay, 1990 (4)	6,000 ± 1,400	630 ± 280
	Port Graham/EB, 1989 (2)	3,900 ± 3,300	860 ± 630
	Akhiok, 1989 (3)	11,000 ± 8,100	1,600 ± 240
	Karluk, 1989 (4)	3,200 ± 2,300	1,000 ± 630
	Port Lions, 1989 (11)	5,900 ± 2,900	1,100 ± 470
	Ouzinkie, 1989 (4)	22,000 ± 12,000	2,000 ± 830
Sockeye salmon	Yakutat, 1990 (11)	4,500 ± 2,500	560 ± 180
	Karluk, 1990 (14)	8,900 ± 6,200	410 ± 200
	Larsen Bay, 1989 (7)	2,400 ± 1,300	260 ± 300 *
	Larsen Bay, 1990 (3)	5,600 ± 800	1,100 ± 520
	Port Lions, 1990 (1)	2,800	560
Chum salmon	Port Graham/EB, 1990 (3)	9,300 ± 4,900	750 ± 420
	Chiniak, 1989 (4)	6,300 ± 5,200	310 ± 110
	Old Harbor, 1990 (8)	19,000 ± 5,900	760 ± 240
	Larsen Bay, 1990 (1)	6,800	790
	Ouzinkie, 1990 (12)	25,000 ± 11,000	2,500 ± 940
Chinook salmon	Angoon, 1989 (3)	1,400 ± 440	490 ± 290
	Yakutat, 1990 (4)	2,000 ± 950	540 ± 210
Dolly Varden	Karluk, 1990 (5)	3,200 ± 1,700	1,100 ± 530

* The number of samples used for the mean was smaller because some samples contained insufficient bile to be analyzed for protein.

EB = English Bay.

Table 5. Concentrations (mean ± standard deviation) of fluorescent aromatic compounds measured at phenanthrene wavelengths ($FACs_{PHN}$ (ng phenanthrene equivalents)) in bile of bottomfish collected during the 1989 and 1990 studies. The number of samples analyzed is in parentheses.

Species	Village sampling site, year	FACs (ng PHN eq./g bile)			FACs (ng PHN eq./mg bile protein)		
Halibut	Angoon, 1989 (3)	740	±	270	250	±	35
	Yakutat, 1990 (10)	2,200	±	600	1,600	±	1,100
	Tatitlek, 1989 (3)	4,600	±	1,300	1,300	±	970
	Chenega Bay, 1989 (8)	6,800	±	6,000	4,100	±	3,600
	Port Graham/EB, 1989 (2)	2,800	±	2,400	1,100	±	730
	Kodiak, 1989 (1)	6,000			7,400		
	Chiniak, 1989 (2)	4,300	±	2,700	3,100	±	3,100
	Old Harbor, 1989 (4)	1,100	±	520	740	±	260
	Old Harbor, 1990 (1)	1,900			870		
	Larsen Bay, 1989 (9)	3,800	±	2,600	2,400	±	2,600
	Larsen Bay, 1990 (1)	1,200			590		
	Port Lions, 1989 (8)	3,300	±	1,700	2,700	±	1,700
	Ouzinkie, 1989 (9)	4,900	±	2,300	3,900	±	1,700
Yellowfin sole	Yakutat, 1990 (1)	1,800			2,000		
	Chenega Bay, 1990 (2)	2,000	±	2,600	840	±	1,200
	Chiniak, 1990 (1)	2,300			650		
	Old Harbor, 1990 (1)	730			660		
Rock sole	Port Graham/EB, 1990 (5)	6,000	±	6,100	1,300	±	1,100 *
	Kodiak, 1990 (1)	900			92		
	Akhiok, 1990 (1)	1,900			9,700		
Pacific cod	Angoon, 1989 (1)	1,900			480		
	Yakutat, 1990 (1)	10,000			330		
	Tatitlek, 1990 (5)	22,000	±	21,000	1,600	±	700
	Chenega Bay, 1989 (3)	50,000	±	15,000	5,200	±	2,300
	Chenega Bay, 1990 (9)	10,000	±	6,400	2,000	±	1,600
	Port Graham/EB, 1990 (1)	8,300			1,400		
	Chiniak, 1990 (1)	5,100			160		
	Old Harbor, 1989 (3)	9,800	±	6,800	1,400	±	870
	Old Harbor, 1990 (8)	4,500	±	2,900	560	±	290
	Akhiok, 1990 (4)	5,800	±	1,600	400	±	170
	Larsen Bay, 1989 (2)	1,700	±	410	340	±	32
	Larsen Bay, 1990 (2)	5,600	±	350	800	±	480
	Port Lions, 1990 (7)	6,200	±	2,300	860	±	190
	Ouzinkie, 1990 (4)	5,500	±	1,900	510	±	290
	Chignik Villages, 1990 (4)	5,700	±	2,700	570	±	370

Table 5. Continued.

Species	Village sampling site, year	FACs (ng PHN eq./g bile)	FACs (ng PHN eq./mg bile protein)
Ling cod	Chenega Bay, 1990 (2)	2,700 ± 130	1,400 ± 350
Rockfish	Tatitlek, 1989 (1)	3,700	620
	Tatitlek, 1990 (2)	5,200 ± 70	3,500 ± 1,300
	Chenega Bay, 1989 (1)	24,000	13,000
	Chenega Bay, 1990 (4)	5,900 ± 5,200	1,900 ± 1,200
Irish Lord	Ouzinkie, 1990 (1)	300	5
	Perryville, 1990 (2)	1,500 ± 1,400	660 ± 910
Greenling	Chenega Bay, 1990 (2)	4,400 ± 3,400	1,200 ± 760
	Port Graham/EB, 1990 (5)	5,200 ± 840	1,900 ± 850
	Perryville, 1990 (5)	3,700 ± 2,300	630 ± 640
Starry flounder	Chenega Bay, 1990 (1)	5,900	820
	Akhiok, 1990 (6)	2,500 ± 620	3,400 ± 3,900
Rock flounder	Port Graham, 1990 (2)	8,100 ± 1,700	2,100 ± 2,100
Sablefish	Old Harbor, 1990 (2)	2,200 ± 620	720 ± 200
Sculpin	Ouzinkie, 1990 (1)	1,700	240

* The number of samples used for the mean was smaller because some samples contained insufficient bile to be analyzed for protein.
EB = English Bay.

Table 6. Mean concentrations, ng/g wet weight, of aromatic contaminants in fish (and number of samples analyzed) by site, species, and year collected.

Village (sampling site), year	Salmon							Bottom fish									
	Pink salmon	Coho salmon	Sockeye salmon	Chum salmon	Chinook salmon	Dolly Varden	Smoked salmon	Halibut	Yellowfin sole	Rock sole	Pacific cod	Ling cod	Rockfish	Irish Lord	Herring roe	Greenling	Starry flounder
Angoon, 1989	2 (2)	3 (3)			5 (1)			0.4 (1)			0.6 (1)						
Yakutat, 1990			3 (6)					4 (6)									
Tatitlek, 1989	0.01 (5)	9 (7)					23,000 (1)	nd (2)			nd (1)		0.8 (2)				
Tatitlek, 1990											nd (4)		2 (2)		18 (3)		
Chenega Bay, 1989	2 (20)							0.1 (4)			0.08 (4)		nd (3)				
Chenega Bay, 1990	0.8 (3)							3 (2)	nd (1)		1 (6)	0.8 (2)	0.5 (2)			nd (1)	
Port Graham/EB, 1989	0.1 (8)	0.6 (2)						0.1 (2)						0.5 (2)			
Port Graham/EB, 1990	0.6 (4)			7 (1)						nd (6)	nd (1)					0.2 (4)	
Windy Bay, 1990	0.4 (2)																
Kodiak, 1989	30 (10)		12 (1)			1 (1)		0.4 (3)					nd (1)				
Kodiak, 1990	34 (3)																
Chiniak, 1989	1 (12)		1 (1)	2 (3)				1 (2)					nd (1)				
Old Harbor, 1989	0.6 (18)					1 (1)	8,100 (1)	0.7 (3)			0.4 (2)						
Old Harbor, 1990	1 (7)			2 (1)							1 (1)						
Akhiok, 1989	3 (2)	nd (1)	nd (1)														
Akhiok, 1990										0.6 (1)							2 (2)
Karluk, 1989	nd (1)	0.5 (2)	0.4 (2)			0.6 (1)											
Karluk, 1990			2 (2)			nd (5)											
Larsen Bay, 1989	2 (14)		4 (5)	1 (1)				0.4 (5)			0.4 (2)						
Larsen Bay, 1990	0.5 (2)		nd (1)								0.7 (1)						
Port Lions, 1989	0.7 (10)	1 (6)						0.3 (4)	0.8 (1)								
Port Lions, 1990	8 (2)					nd (1)					1 (2)						
Ouzinkie, 1989	2 (10)	3 (8)						0.3 (5)									
Ouzinkie, 1990	nd (1)	0.5 (2)		2 (6)				1 (2)			3 (1)						
Perryville, 1990		nd (2)												nd (1)		nd (2)	

nd = not detected.
EB = English Bay.

Table 7. Concentrations of total aromatic contaminants (ACs) that exceeded 10 ng/g wet weight in edible flesh of fish listed by decreasing concentrations. The last two entries are for two samples of smoked salmon.

Sample no.	Village sampling site	Species	Year collected	Concentration of ACs
60-166, 60-195	Kodiak	Pink salmon	1989	100 *
60-1814	Kodiak	Pink salmon	1990	82
60-628, 60-637	Kodiak	Pink salmon	1989	60 *
60-187	Kodiak	Pink salmon	1989	59
60-630	Kodiak	Pink salmon	1989	37
60-188	Kodiak	Pink salmon	1989	24
60-364	Tatitlek	Coho salmon	1989	22
60-138	Chenega Bay	Pink salmon	1989	20
60-363	Tatitlek	Coho salmon	1989	16
60-362	Tatitlek	Coho salmon	1989	15
60-1813	Kodiak	Pink salmon	1990	14
60-2442	Port Lions	Pink salmon	1990	14
60-3, 60-29	Larsen Bay	Pink salmon	1989	14 *
60-194	Kodiak	Sockeye salmon	1989	12
60-3063, 60-3070	Yakutat	Sockeye salmon	1990	12 *
60-3064	Yakutat	Halibut	1990	11
60-526, 60-527	Tatitlek	Smoked salmon	1989	23,000 *
60-241, 60-244	Old Harbor	Smoked salmon	1989	8,100 *

* Average of duplicate analyses.

Table 8. Concentrations of fluorescent aromatic compounds measured at phenanthrene ($FACs_{PHN}$ (ng phenanthrene equivalents/g bile)) or naphthalene ($FACs_{NPH}$ (ng naphthalene equivalents/g bile)) wavelengths in bile from harbor seals. * denotes samples collected by the Alaska Department of Fish and Game; other samples were collected by NOAA.

Sample no.	Site	Visibly oiled	FACs NPH	FACs PHN	Protein mg/ml	Date collected
TS-HS-1*	Herring Bay/PWS	Yes	200,000	95,000	23.0	4/89
TS-HS-10*	Herring Bay/PWS	Yes	38,000	17,000	27.3	6/89
TS-HS-11*	Herring Bay/PWS	Yes	30,000	15,000	21.9	6/89
TS-HS-20*	Herring Bay/PWS	No	68,000	14,000	44.0	4/90
TS-HS-24*	Herring Bay/PWS	No	36,000	5,400	32.4	4/90
TS-HS-22*	Herring Bay/PWS	No	28,000	4,200	23.3	4/90
TS-HS-21*	Herring Bay/PWS	No	22,000	4,000	17.0	4/90
TS-HS-9*	Herring Bay/PWS	Yes	4,900	1,300	68.0	6/89
TS-HS-8*	Bay of Isles/PWS	Yes	360,000	210,000	10.4	6/89
TS-HS-7*	Bay of Isles/PWS	Yes	53,000	36,000	10.9	6/89
TS-HS-5*	Bay of Isles/PWS	Yes	52,000	32,000	13.2	6/89
TS-HS-25*	Bay of Isles/PWS	No	67,000	12,000	84.4	4/90
TS-HS-2*	Bay of Isles/PWS	Yes	31,000	8,800	12.6	6/89
TS-HS-4*	Seal Island/PWS	Yes	46,000	25,000	15.4	6/89
TS-HS-3*	Seal Island/PWS	Yes	2,300	2,700	4.0	6/89
TS-HS-6*	Applegate Rocks/PWS	Yes	7,000	3,700	16.9	6/89
TS-HS-19*	Agnes Island/PWS	No	20,000	6,200	21.4	11/89
692-HBSL-001	New Year Island/PWS	No	12,000	1,500	44.0	3/90
692-HBSL-003	Galena Bay/PWS	No	29,000	2,500	40.6	4/90
692-HBSL-002	Galena Bay/PWS	No	17,000	1,100	26.7	4/90
TS-HS-23*	NE Eleanor Island/PWS	No	110,000	44,000	53.2	4/90
TS-HS-23F*	NE Eleanor Island/PWS	No	3,300	1,800	55.8	4/90
TS-HS-17*	Perl Island/Outer Kenai	Yes	7,700	2,200	14.1	7/89
TS-HS-18*	Big Fort Island/GOA	No	1,400	170	14.8	10/89
TS-HS-14*	West Amatuli - Barren Islands/GOA	Yes	14,000	8,000	18.5	6/89
TS-HS-15*	Ushagat Island - Barren Islands/GOA	No	11,000	3,000	31.4	6/89
TS-HS-16*	Ushagat Island - Barren Islands/GOA	No	4,400	800	11.4	6/89
TS-HS-12*	Perenosa Bay - Afognak/GOA	No	5,600	730	16.8	6/89
TS-HS-13*	Between Perenosa and Seal Bay/GOA	No	7,200	2,200	23.8	6/89

PWS = Prince William Sound, GOA = Gulf of Alaska, F= fetus.

Table 9. Concentrations of fluorescent aromatic compounds measured at phenanthrene ($FACs_{PHN}$ (ng phenanthrene equivalents/g bile)) or naphthalene ($FACs_{NPH}$ (ng naphthalene equivalents/g bile)) wavelengths in bile from Steller sea lions. * denotes samples collected by the Alaska Department of Fish and Game; other samples were collected by NOAA.

Sample no.	Site	FACs NPH	FACs PHN	Protein mg/ml	Date collected
SL-586*	The Needle/PWS	37,000	8,500	30.8	7/89
SL-585*	The Needle/PWS	19,000	3,700	9.0	7/89
SL-583*	The Needle/PWS	29,000	3,100	47.5	7/89
SL-584*	The Needle/PWS	31,000	3,000	34.6	7/89
SL-582*	The Needle/PWS	19,000	890	35.9	7/89
SL-587*	Chiswell Island/GOA	4,200	390	7.8	7/89
692-STSL-001	Flat Island/GOA	38,000	4,600	13.3	3/90
SL-580*	Ushagat Island - Barren Islands/GOA	13,000	2,700	39.2	6/89
SL-581*	Ushagat Island - Barren Islands/GOA	45,000	2,100	54.4	6/89
SL-579*	Ushagat Island - Barren Islands/GOA	18,000	1,200	29.9	6/89

PWS = Prince William Sound, GOA = Gulf of Alaska.

Table 10. Mean concentrations of aromatic contaminants (ACs) ng/g wet weight, in tissue samples of marine mammals by site, station, species, year collected, tissue type, and number of samples analyzed (in parentheses). Results of replicate analyses were averaged and the average used in the calculations of the mean concentration. [a]

Village, sampling site	Year sampled	Harbor seal Tissue type Blubber	Liver	Muscle	Steller sea lion Tissue type Blubber	Liver	Muscle
Herring Bay/PWS	1989	280 (4)	0.4 (4)	0.4 (3)	-	-	-
Herring Bay/PWS	1990	26 (4)	4 (4)	0.6 (4)	-	-	-
Bay of Isles/PWS	1989	200 (4)	0.4 (4)	5 (4)	-	-	-
Bay of Isles/PWS	1990	69 (1)	0 (1)	0.8 (1)	-	-	-
Seal Island/PWS	1989	18 (2)	0 (2)	12 (2)	-	-	-
Applegate Rocks/PWS	1989	6 (1)	0 (1)	1 (1)	-	-	-
Agnes Island/PWS	1989	12 (1)	0 (1)	0.4 (1)	-	-	-
New Year Island/PWS	1990	2 (1)	3 (1)	0 (1)	-	-	-
Little Green Island/PWS	1990	4 (2)	6 (4)	-	-	-	-
Galena Bay/PWS	1990	7 (2)	2 (2)	0 (2)	-	-	-
NE Eleanor Island/PWS	1990	15 (2)	0 (2)	4 (2)	-	-	-
The Needle/PWS	1989	-	-	-	0.4 (5)	2 (5)	0.6 (5)
Perl Island/Outer Kenai	1989	2 (1)	6 (1)	0 (1)	-	-	-
Big Fort Island/GOA	1989	9 (1)	0 (1)	0 (1)	-	-	-
Chiswell Island/GOA	1989	-	-	-	0.6 (1)	0 (1)	0.7 (1)
Flat Island/GOA	1990	-	-	-	17 (1) [b]	1 (1)	0.5 (1)
West Amatuli Island - Barren Islands/GOA	1989	0 (1)	0 (1)	0 (1)	-	-	-
Ushagat Island - Barren Islands/GOA	1989	2 (2)	3 (2)	0 (2)	0.7 (3)	3 (3)	0 (3)
Perenosa Bay - Afognak/GOA	1989	4 (1)	4 (1)	0 (1)	-	-	-
Between Perenosa and Seal Bay/GOA	1989	0 (1)	5 (1)	0.4 (1)	-	-	-

[a] Kidney samples were not contaminated with ACs and so are not included here. They are found in Vol. II, Section D.

[b] Average for replicate analyses.

PWS = Prince William Sound, GOA = Gulf of Alaska.

Table 11. Concentrations of total aromatic contaminants (ACs) that exceeded 10 ng/g wet weight, in edible tissues of harbor seals listed by decreasing concentrations. The concentrations of fluorescent aromatic compounds measured at phenanthrene wavelengths ($FACs_{PHN}$ (ng phenanthrene equivalents/g bile)) in the corresponding bile sample and evidence of oiling are included.

Laboratory sample no.	Field sample no.	Sample location	Year collected	Visibly oiled	FACs PHN	Concentration of ACs
60-1325B	TS-HS-1	Herring Bay	1989	Yes	95,000	810
60-1424B 60-1412B	TS-HS-7	Bay of Isles	1989	Yes	36,000	460 [b]
60-1323B	TS-HS-8	Bay of Isles	1989	Yes	210,000	210
60-1414B	TS-HS-10	Herring Bay	1989	Yes	17,000	130
60-1425B	TS-HS-11	Herring Bay	1989	Yes	15,000	94
60-1413B	TS-HS-9	Herring Bay	1989	Yes	4,900	85
60-1410B	TS-HS-5	Bay of Isles	1989	Yes	32,000	71
60-1440B	TS-HS-24	Herring Bay	1990	No	5,400	69
60-1441B	TS-HS-25	Bay of Isles	1990	No	12,000	69
60-1407B	TS-HS-2	Bay of Isles	1989	Yes	8,800	63
60-1408B	TS-HS-3	Seal Island	1989	Yes	2,700	23
60-1430B	TS-HS-22	Herring Bay	1990	No	4,200	20
60-1431B	TS-HS-23	NE Eleanor Island	1990	No	44,000	16
60-1445M [c]	TS-HS-4	Seal Island	1989	Yes	25,000	16
60-1393L	TS-HS-22	Herring Bay	1990	No	4,200	15
60-1432B	TS-HS-23F	NE Eleanor Island	1990	No	1,800	14
60-1427B	TS-HS-19	Agnes Island	1989	No	6,200	12
60-1409B [c]	TS-HS-4	Seal Island	1989	Yes	25,000	12

[a] Tissue type is noted by letter at the end of the laboratory sample number: B for blubber, L for liver, and M for muscle.
[b] Average of duplicate analyses. [c] Sample collected from a harbor seal pup. F=fetus.

Table 12. Number of invertebrate and other tissue samples analyzed.

	1989	1990	1991	Total
Prince William Sound				
Chenega Bay	7	81	106	194
Tatitlek	9	36	-	45
Lower Cook Inlet				
Windy Bay	7	81	99	187
Port Graham/English Bay	16	69	-	85
Other Areas *	4	73	-	77
Kodiak				
Akhiok	7	18	-	25
Chiniak	21	33	-	54
Karluk	7	16	-	23
Kodiak	8	40	-	48
Larsen Bay	17	33	-	50
Old Harbor	18	53	-	71
Ouzinkie	9	52	-	61
Port Lions	20	49	-	69
Alaska Peninsula				
Chignik	-	19	-	19
Ivanof Bay	-	14	-	14
Kashvik Bay	-	4	-	4
Perryville	-	10	-	10
Reference areas				
Angoon	6	-	-	6
Yakutat	-	24	-	24

- Samples not collected.
* Other areas include: Port Dick, Chugach Bay, Port Chatham, Point Bede, Kasitsna Bay, and Sadie Cove.

Table 13. Mean concentrations, ng/g ± standard deviation wet weight, of aromatic contaminants (number of samples analyzed in parentheses) in the four target invertebrate species by area, station, and year collected.

Village Sampling area/station	Year	Species Mussels	Butter clams	Littleneck clams	Chitons	Other biota *
Reference Areas						
Angoon						
AGN1	1989	0.8 ± 0.6 (2)			1 ± 0.02 (2)	
AGN2	1989		0.5 (1)			(1)
Yakutat						
YAK1	1990	3 ± 2 (6)	1 ± 1 (6)	0.8 ± 0.3 (6)		
YAK5	1990				1 ± 0.3 (6)	
Prince William Sound						
Tatitlek						
T1	1990	23 ± 7 (3)	62 ± 46 (6)			
TAT1	1989	nd (1)				
TAT1	1990	6 ± 5 (7)	8 ± 12 (7)	4 ± 2 (4)		
TAT2	1990	9 ± 3 (4)	12 ± 6 (3)	4 ± 2 (2)		
TAT5	1989	2 ± 1 (6)			0.6 ± 0.9 (2)	
Chenega Bay						
CHE1	1989	190 ± 51 (5)	30 ± 16 (2)			
CHE1	1990	24 ± 35 (6)	33 ± 46 (7)	18 ± 18 (4)	4 ± 5 (2)	
CHE1	1991	78 ± 18 (4)	20 ± 7 (4)	16 ± 4 (4)		
CHE7	1990	640 ± 830 (8)	330 ± 340 (9)	120 ± 44 (16)		
CHE7	1991	78 ± 33 (4)	110 ± 27 (4)	61 ± 5 (4)		
CHE9	1990	34 ± 12 (4)			0.4 ± 0.9 (4)	
CHE9	1991	1 ± 1 (4)			0.6 ± 0.2 (4)	
CHE10	1990	1,100 ± 620 (3)	27 ± 10 (8)	18 ± 11 (4)	2 ± 0.3 (2)	
CHE10	1991	23 ± 11 (8)	5 ± 3 (8)	11 ± 18 (8)		
CHE11	1990					(4)
CHE18	1991					(3)
CHE19	1991				2 (1)	
CHE20	1991				nd (1)	
CHE21	1991				1 ± 2 (8)	
CHE22	1991	0.8 ± 0.5 (8)		3 ± 3 (4)		
CHE23	1991	2 ± 3 (8)		0.6 ± 0.09 (4)	0.5 ± 0.2 (3)	
CHE24	1991	37 ± 100 (8)	0.4 (1)	0.4 (1)		
Lower Cook Inlet						
Port Graham/English Bay						
PTG1	1989	2 ± 2 (6)		29 (1)	0.5 ± 0.3 (3)	(1)
PTG1	1990	2 ± 2 (21)		nd (1)	0.2 ± 0.3 (9)	(2)
PTG4	1989	9 ± 7 (4)				(1)
PTG4	1990	5 ± 2 (3)		20 (1)	4 ± 1 (2)	(6)
PTG8	1990				nd (7)	
PTG8/9	1990				0.7 ± 0.6 (3)	
PTG9	1990				nd (4)	
PTG10	1990				2 ± 1 (8)	(2)
Windy Bay						
WNB1	1989	8,400 ± 8,800 (3)			2,900 ± 4,000 (2)	(1)
WNB1	1991	18 ± 12 (8)			0.6 ± 0.5 (4)	

Table 13. Continued.

Village Sampling area/station	Year	Species Mussels	Butter clams	Littleneck clams	Chitons	Other biota *
Lower Cook Inlet (Cont.)						
Windy Bay (Cont.)						
WNB2	1989			960 (1)		
WNB2	1990	51 ± 55 (6)				(18)
WNB2	1991	14 ± 26 (5)				(5)
WNB3	1990	1,600 ± 2,100 (24)			10 ± 25 (12)	(1)
WNB3	1991	110 ± 170 (38)			5 ± 8 (13)	
WNB4	1990	23 ± 11 (8)		50 ± 21 (5)		(7)
WNB4	1991	10 ± 1 (5)		7 ± 2 (3)		(7)
WNB5	1991	20 ± 18 (5)		17 ± 2 (5)		(1)
Port Dick						
PTD1	1990	9 (1)		6 ± 1 (6)		(2)
Chugach Bay						
CHB1	1990				4 ± 3 (7)	
Port Chatham						
PTC1	1990			5 ± 3 (5)		
PTC2	1990	11 ± 10 (2)			3 ± 1 (9)	(2)
Point Bede						
BED1	1990				1 ± 0.6 (7)	(5)
Kasitsna Bay						
KAS1	1989	0.9 ± 0.3 (2)	3 (1)		2 (1)	
KAS1	1990			10 ± 2 (6)		(9)
Sadie Cove						
SAD1	1990	2 ± 0.4 (2)		4 ± 0.8 (5)		(5)
Kodiak Island						
Kodiak						
KOD3	1989	1,700 (1)	460 (1)	250 ± 150 (2)	190 ± 99 (2)	
KOD3	1990	630 ± 200 (4)	1,200 ± 680 (12)	310 ± 83 (4)	43 ± 14 (4)	
KOD4	1989					(1)
KOD5	1989					(1)
KOD7	1990		9 ± 5 (4)	7 ± 2 (4)	1 ± 1 (4)	
K7	1990	89 ± 31 (3)				(1)
Chiniak						
CHI1	1989	nd (1)	0.8 ± 0.6 (3)	2 ± 1 (2)		
CHI1	1990	5 ± 2 (7)	2 ± 2 (2)			
CHI2	1989	nd (1)	0.5 ± 0.3 (4)	1 (1)	0.9 ± 0.5 (5)	(3)
CHI2	1990	4 ± 3 (5)	10 ± 14 (6)	12 ± 6 (4)	1 ± 1 (4)	(1)
CHI3	1989					(1)
CHI7	1990	9 ± 7 (4)				
Old Harbor						
OHA2	1989					(1)
OHA3	1989	nd (1)	2 ± 0.9 (5)	3 (1)	1 ± 1 (3)	(1)
OHA3	1990	5 ± 3 (5)	5 ± 4 (11)	2 ± 2 (4)	0.2 ± 0.5 (7)	(6)
OHA4	1989		150 ± 150 (5)	220 (1)		
OHA4	1990	120 ± 190 (5)	17 ± 9 (9)	24 ± 22 (6)		
Akhiok						
AKH2	1989	0.3 (1)	0.2 ± 0.2 (3)		1 (1)	
AKH3	1989	0.4 (1)		0.5 (1)		
AKH3	1990	10 ± 8 (4)	2 ± 0.3 (3)	2 ± 1 (6)		(1)
AKH6	1990	1 ± 1 (4)				

Table 13. Continued.

Village Sampling area/station	Year	Species Mussels	Butter clams	Littleneck clams	Chitons	Other biota *
Karluk						
KAR1	1989	nd (1)			0.2 (1)	
KAR1	1990	nd (4)				
KAR2	1989	0.3 ± 0.06 (3)	0.3 (1)		nd (1)	
KAR2	1990	5 ± 9 (4)	0.6 ± 0.4 (4)	3 ± 2 (4)		
Larsen Bay						
LAB1	1989	1 (1)	2 ± 2 (3)		1 ± 0.6 (2)	(1)
LAB1	1990		16 ± 9 (6)			
LAB2	1989		3 ± 2 (4)		0.4 (1)	
LAB2	1990	10 ± 4 (4)	2 ± 1 (6)	2 ± 1 (4)		(2)
LAB3	1989					(1)
LAB4	1989					(4)
LAB9	1990					(1)
LAB10	1990		34 ± 4 (2)	17 ± 5 (3)		(4)
LAB11	1990				8 (1)	
Port Lions						
PTL1	1989		2 ± 0.6 (5)	3 ± 0.5 (2)	1 ± 0.6 (3)	(1)
PTL1	1990	29 ± 21 (10)	15 ± 13 (7)	12 ± 5 (10)		
PTL2	1989		3 ± 1 (2)		0.7 ± 0.6 (2)	(1)
PTL2	1990	15 ± 8 (4)	23 ± 5 (4)	20 ± 7 (4)	0.2 ± 0.5 (4)	(4)
PTL4	1989					(3)
PTL5	1989					(1)
PTL9	1990					(2)
Ouzinkie						
OUZ2	1989	0.9 (1)	0.4 ± 0.6 (2)	0.8 ± 0.3 (2)	0.3 ± 0.3 (2)	
OUZ2	1990	3 ± 1 (4)	4 ± 1 (4)	3 ± 1 (4)	5 ± 7 (4)	
OUZ3	1989		8 (1)			
OUZ3	1990	20 (1)	19 ± 22 (8)	3 ± 1 (2)		(1)
OUZ4	1989		3 (1)			
OUZ4	1990	10 ± 8 (4)	13 ± 3 (4)	7 ± 2 (4)	2 ± 0.2 (4)	
OUZ7	1990				nd (1)	
OUZ9	1990		22 ± 20 (6)			(1)
Alaska Peninsula						
Chignik						
CHG1	1990	42 ± 46 (9)				
CHG3	1990	40 ± 54 (10)				
Ivanof Bay						
IVB1	1990					(1)
IVB2	1990					(1)
IVB3	1990	5 ± 7 (9)	1 ± 0.8 (3)			
Perryville						
PER1	1990				8 (1)	
PER3	1990	1 ± 1 (9)				
Kashvik Bay						
KAT1	1990					(4)

nd = not detected.

* Other biota sampled include species such as crab, shrimp, and herring roe on kelp.

Table 14. Number of invertebrate samples by concentration for only those stations where concentrations of aromatic contaminants in at least one sample exceeded 100 ng/g wet weight.

	Number of samples containing ACs			
	Concentration range			
Station no.	Not contaminated (Category 1) (<10 ng/g)	Minimally contaminated (Category 2) (10-99 ng/g)	Moderately contaminated (Category 3) (100-1,000 ng/g)	Highly contaminated (Category 4) (>1,000 ng/g)
Tatitlek				
T1	0	7	2	0
Chenega Bay				
CHE1	8	24	6	0
CHE7	0	14	28	3
CHE10	16	22	2	1
CHE24	9	0	1	0
Windy Bay				
WNB1	6	7	1	4
WNB2	16	17	2	0
WNB3	22	37	21	8
WNB5	2	8	1	0
Kodiak				
K7	1	2	1	0
KOD3	0	4	17	9
Old Harbor				
OHA4	5	17	4	0
Chignik				
CHG1	3	4	2	0
CHG3	4	3	3	0

Table 15. Concentrations, ng/g wet weight, of aromatic contaminants (ACs) >100 ng/g in mussels by decreasing concentration at each individual station of a sampling area.

Village Sampling area/station	Sample no.	Date collected	Total ACs
Prince William Sound			
Chenega Bay			
CHE1	60-44	7/4/89	240
CHE1	60-304	8/30/89	220
CHE1	60-305	8/30/89	210
CHE1	60-114	8/8/89	180
CHE1	60-306	8/30/89	110
CHE7	60-1753	7/21/90	2,200
CHE7	60-1754	7/21/90	1,700
CHE7	60-1530	4/25/90	400
CHE7	60-1538	4/25/90	240
CHE7	60-1756	7/21/90	180
CHE7	60-1755	7/21/90	140
CHE7	60-1537	4/25/90	130
CHE7	60-1536	4/25/90	120
CHE7	60-2839	6/11/91	120
CHE10	60-1514	4/27/90	1,800
CHE10	60-1513	4/27/90	780
CHE10	60-1512	4/27/90	680
CHE24	60-2959	8/12/91	290
Lower Cook Inlet			
Windy Bay			
WNB1	60-242	9/2/89	18,000
WNB1	60-47	7/7/89	3,700
WNB1	60-243	9/2/89	2,900
WNB2	60-889	3/25/90	150
WNB3	60-1735	7/23/90	5,500
WNB3	60-1732	7/23/90	5,400
WNB3	60-885	3/25/90	5,300
WNB3	60-884	3/25/90	4,600
WNB3	60-887	3/25/90	4,200
WNB3	60-886	3/25/90	4,000
WNB3	60-1733	7/23/90	3,300
WNB3	60-1734	7/23/90	3,000
WNB3	60-2997	8/9/91	860
WNB3	60-2993	8/9/91	750
WNB3	60-1539	4/28/90	570

Table 15. Continued.

Village Sampling area/station	Sample no.	Date collected	Total ACs
Lower Cook Inlet (Cont.)			
Windy Bay (Cont.)			
WNB3	60-1541	4/28/90	350
WNB3	60-1542	4/28/90	350
WNB3	60-1540	4/28/90	290
WNB3	60-1737	7/23/90	190
WNB3	60-2728	4/15/91	180
WNB3	60-2975	8/9/91	150
WNB3	60-2715	4/15/91	150
WNB3	60-1009	3/25/90	150
WNB3	60-1543	4/28/90	140
WNB3	60-2731	4/15/91	140
WNB3	60-1544	4/28/90	130
WNB3	60-3001	8/9/91	130
WNB3	60-1738	7/23/90	110
WNB3	60-2716	4/15/91	110
WNB3	60-2729	4/15/91	100
WNB3	60-2725	4/15/91	100
WNB3	60-2732	4/15/91	100
Kodiak Island			
Kodiak			
K7	60-2155	9/7/90	120
KOD3	60-48	7/16/89	1,700
KOD3	60-1846	4/29/90	820
KOD3	60-1844	4/29/90	720
KOD3	60-1853	4/29/90	620
KOD3	60-1845	4/29/90	360
Old Harbor			
OHA4	60-1158	3/8/90	500
Alaska Peninsula			
Chignik Villages			
CHG1	60-1582	4/30/90	120
CHG1	60-1584	4/30/90	120
CHG3	60-2140	9/12/90	150
CHG3	60-2138	9/12/90	110
CHG3	60-2139	9/12/90	100

Table 16. Concentrations, ng/g wet weight, of aromatic contaminants (ACs) >100 ng/g in butter clams by decreasing concentration at each individual station of a sampling area.

Village Sampling area/station	Sample no.	Date collected	Total ACs
Prince William Sound			
Tatitlek			
T1	60-1596	6/6/90	130
T1	60-1598	6/6/90	110
Chenega Bay			
CHE1	60-945	2/22/90	140
CHE7	60-947	2/25/90	1,000
CHE7	60-949	2/25/90	720
CHE7	60-948	2/25/90	540
CHE7	60-1603	6/13/90	220
CHE7	60-1612	6/13/90	160
CHE7	60-1602	6/13/90	150
CHE7	60-2831	6/11/91	140
CHE7	60-2832	6/11/91	120
CHE7	60-2833	6/11/91	100
Kodiak Island			
Kodiak			
KOD3	60-1157	3/28/90	2,100
KOD3	60-1166	3/28/90	2,100
KOD3	60-1650	5/27/90	1,700
KOD3	60-2125	9/6/90	1,700
KOD3	60-1649	5/27/90	1,400
KOD3	60-2124	9/6/90	1,200
KOD3	60-2382	9/6/90	1,200
KOD3	60-1656	5/27/90	1,200
KOD3	60-212	8/14/89	460
KOD3	60-1868	4/29/90	370
KOD3	60-1869	4/29/90	360
KOD3	60-1862	4/29/90	360
KOD3	60-1870	4/29/90	350
Old Harbor			
OHA4	60-419 60-418	9/15/89	300 *
OHA4	60-433	9/15/89	230

* Average of duplicate analyses.

Table 17. Concentrations, ng/g wet weight, of aromatic contaminants (ACs) >100 ng/g in littleneck clams by decreasing concentration at each individual station of a sampling area.

Village Sampling area/station	Sample no.	Date collected	Total ACs
Prince William Sound			
Chenega Bay			
CHE7	60-1780	7/21/90	200
CHE7	60-1777	7/21/90	180
CHE7	60-1006	3/14/90	170
CHE7	60-1779	7/21/90	170
CHE7	60-930	3/14/90	140
CHE7	60-932	3/14/90	140
CHE7	60-1778	7/21/90	130
CHE7	60-1526	4/25/90	120
CHE7	60-1524	4/25/90	120
CHE7	60-933	3/14/90	110
CHE7	60-1007	3/14/90	110
CHE7	60-1529	4/25/90	100
CHE7	60-1525	4/25/90	100
Lower Cook Inlet			
Windy Bay			
WNB2	60-666	7/7/89	960
Kodiak Island			
Kodiak			
KOD3	60-1888	4/29/90	430
KOD3	60-437	9/11/89	360
KOD3	60-1887	4/29/90	320
KOD3	60-1886	4/29/90	290
KOD3	60-1986 60-1889	4/29/90	250 *
KOD3	60-447	9/11/89	140
Old Harbor			
OHA4	60-616	9/15/89	220

* Average of duplicate analyses.

Table 18. Concentrations, ng/g wet weight, of aromatic contaminants (ACs) >100 ng/g in chitons by decreasing concentration at each individual station of a sampling area.

Village Sampling area/station	Sample no.	Date collected	Total ACs
Lower Cook Inlet			
Windy Bay			
WNB1	60-360	9/2/89	5,800
Kodiak Island			
Kodiak			
KOD3	60-208	8/14/89	260
KOD3	60-396	9/11/89	120

FIGURES

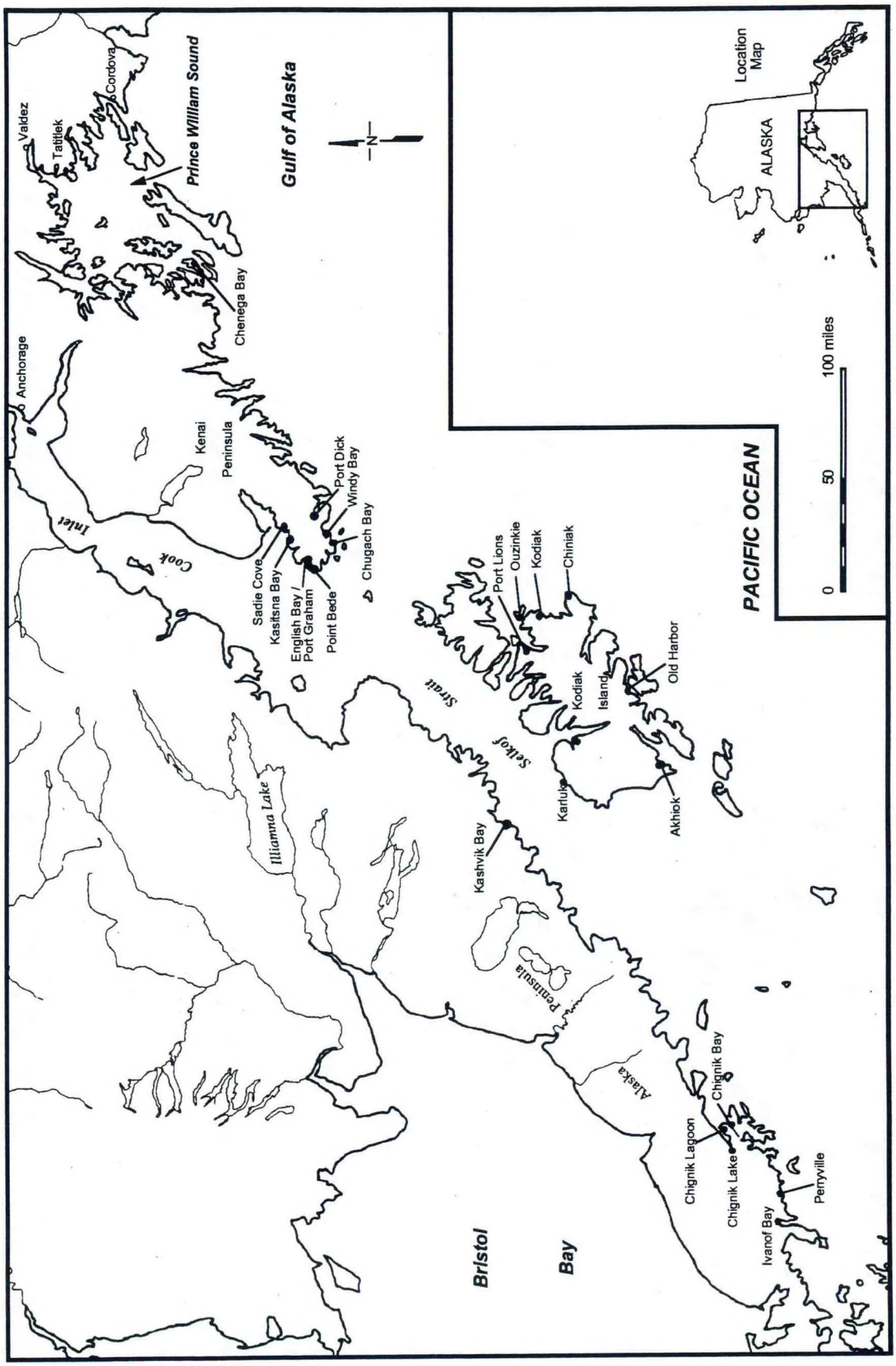

Figure 1. Map of the sampling areas for subsistence seafoods following the Exxon Valdez oil spill.

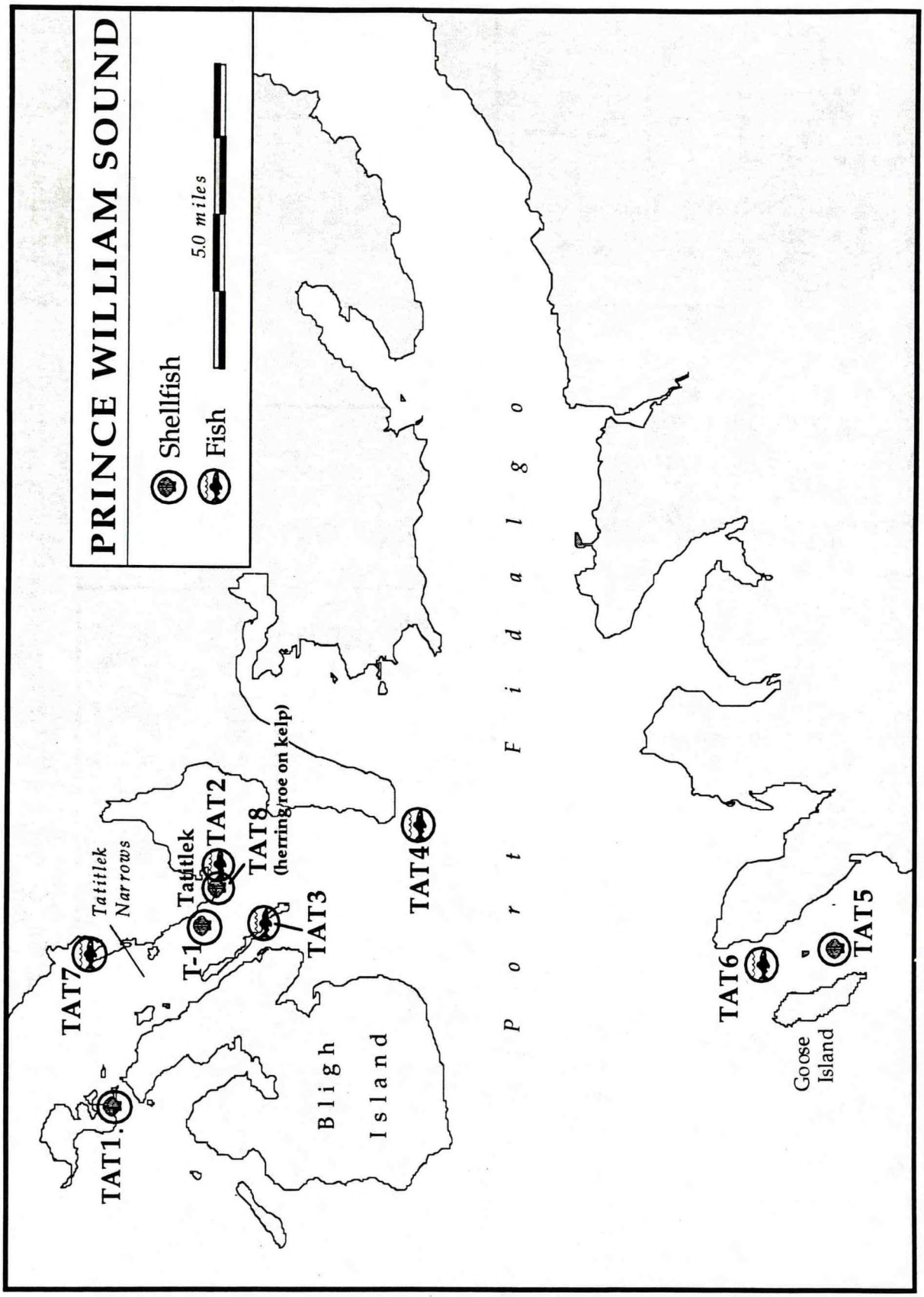

Figure 2. Fish and shellfish sampling stations in the vicinity of Tatitlek.

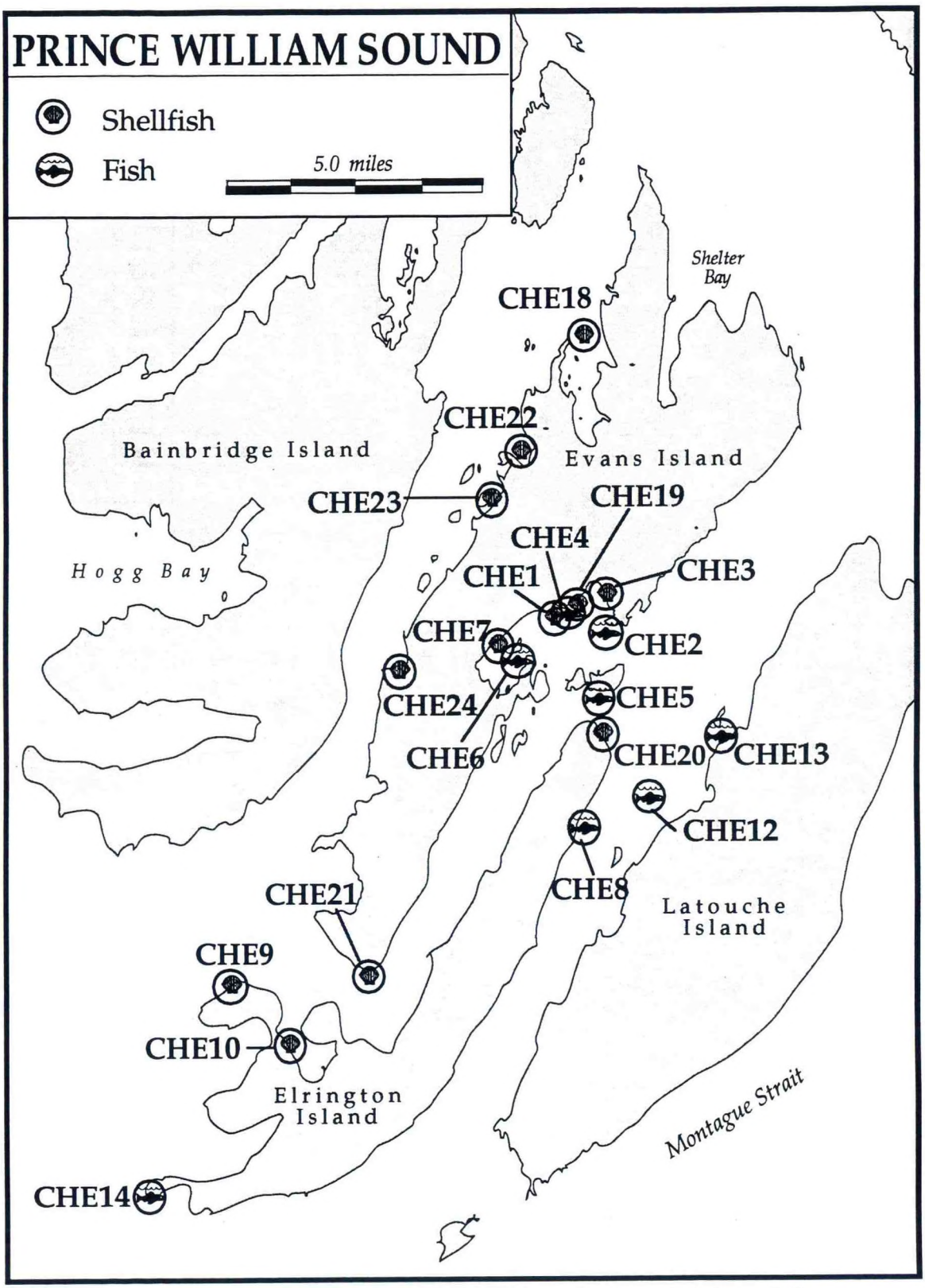

Figure 3. Fish and shellfish sampling stations in the vicinity of Chenega Bay.

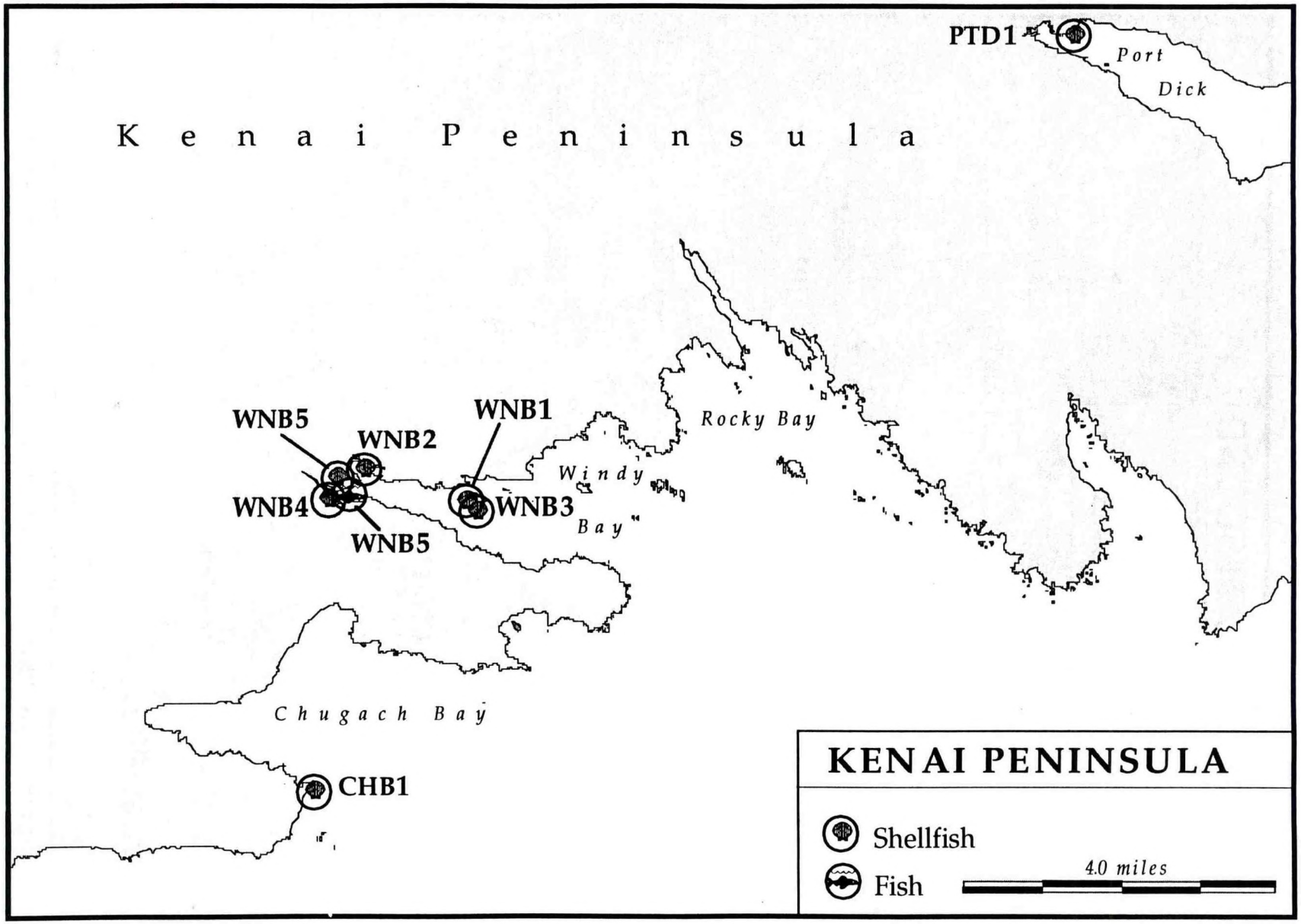

Figure 4. Fish and shellfish sampling stations in Windy Bay, Port Dick, and Chugach Bay.

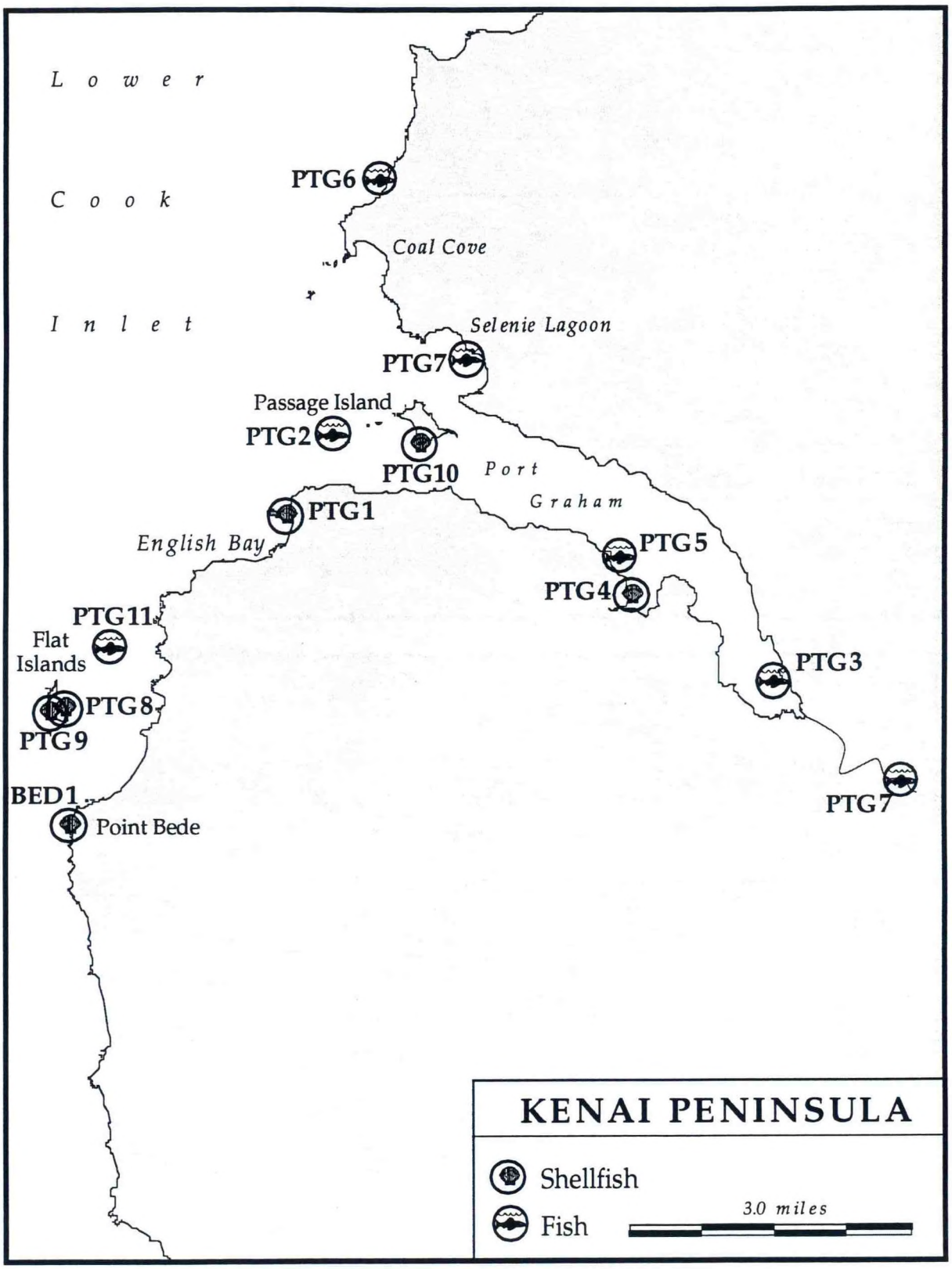

Figure 5. Fish and shellfish sampling stations in the vicinity of Port Graham / English Bay and Point Bede.

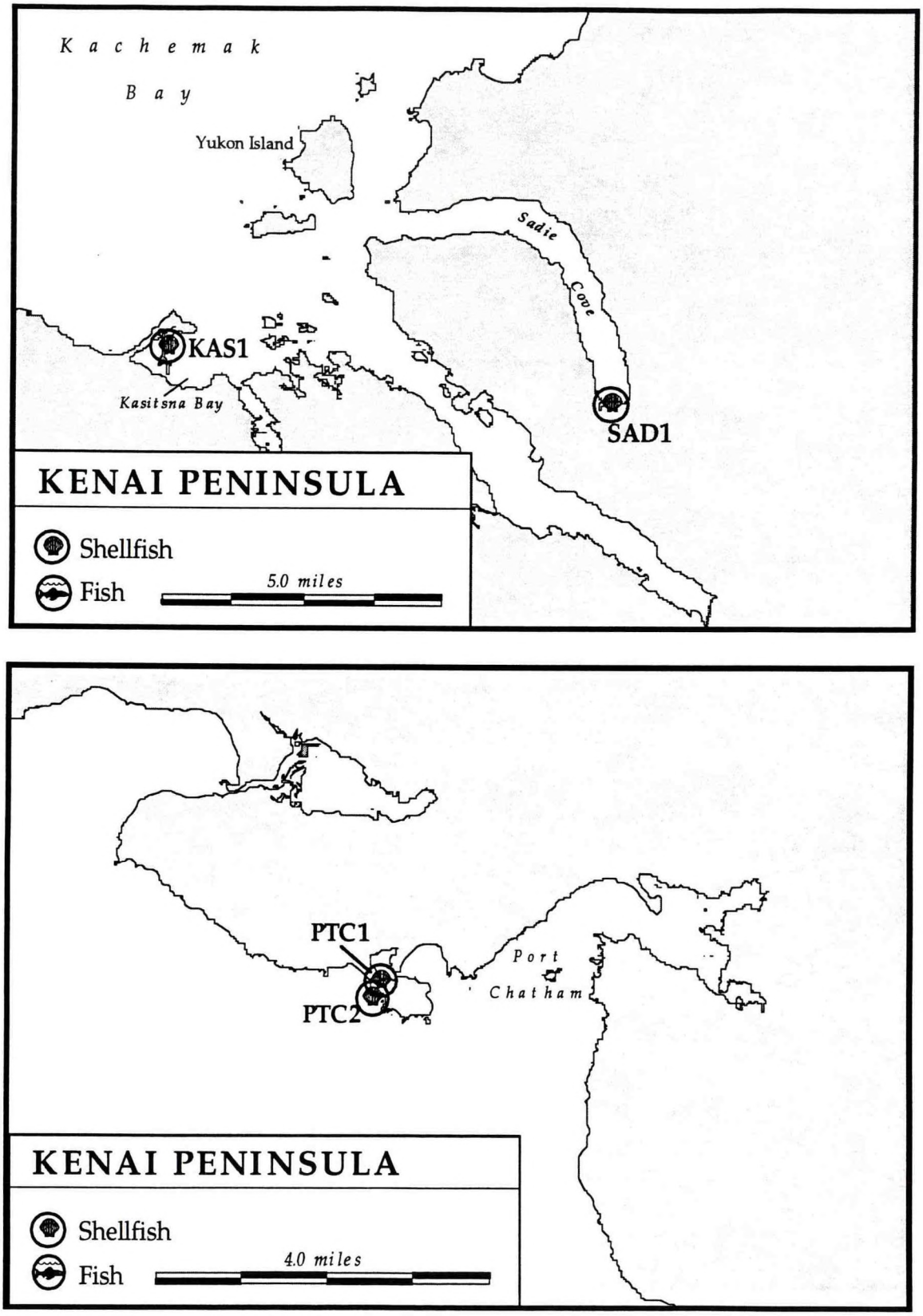

Figure 6. Fish and shellfish sampling stations in the vicinity of Kasitsna Bay, Sadie Cove, and Port Chatham.

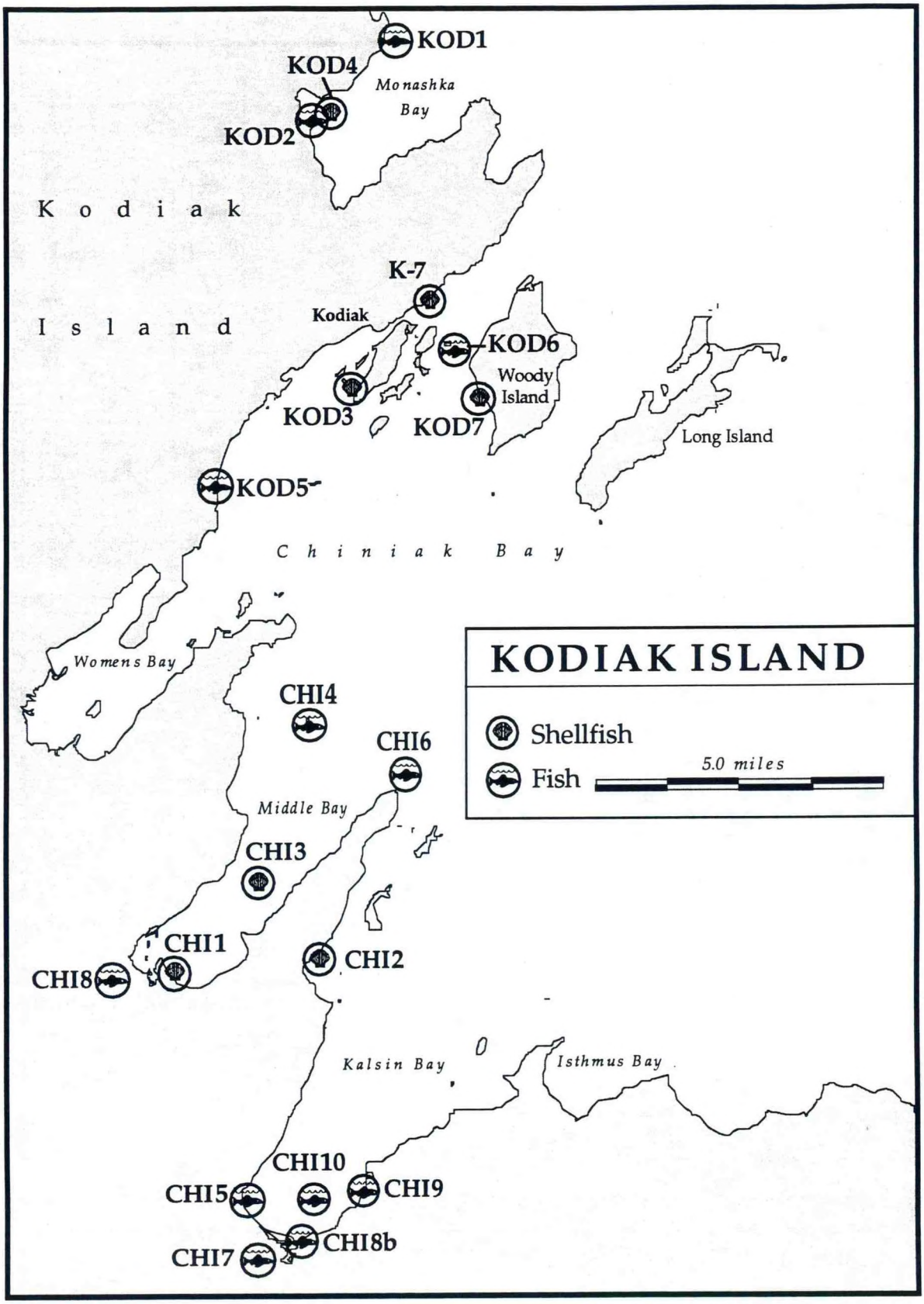

Figure 7. Fish and shellfish sampling stations in Kodiak and Chiniak.

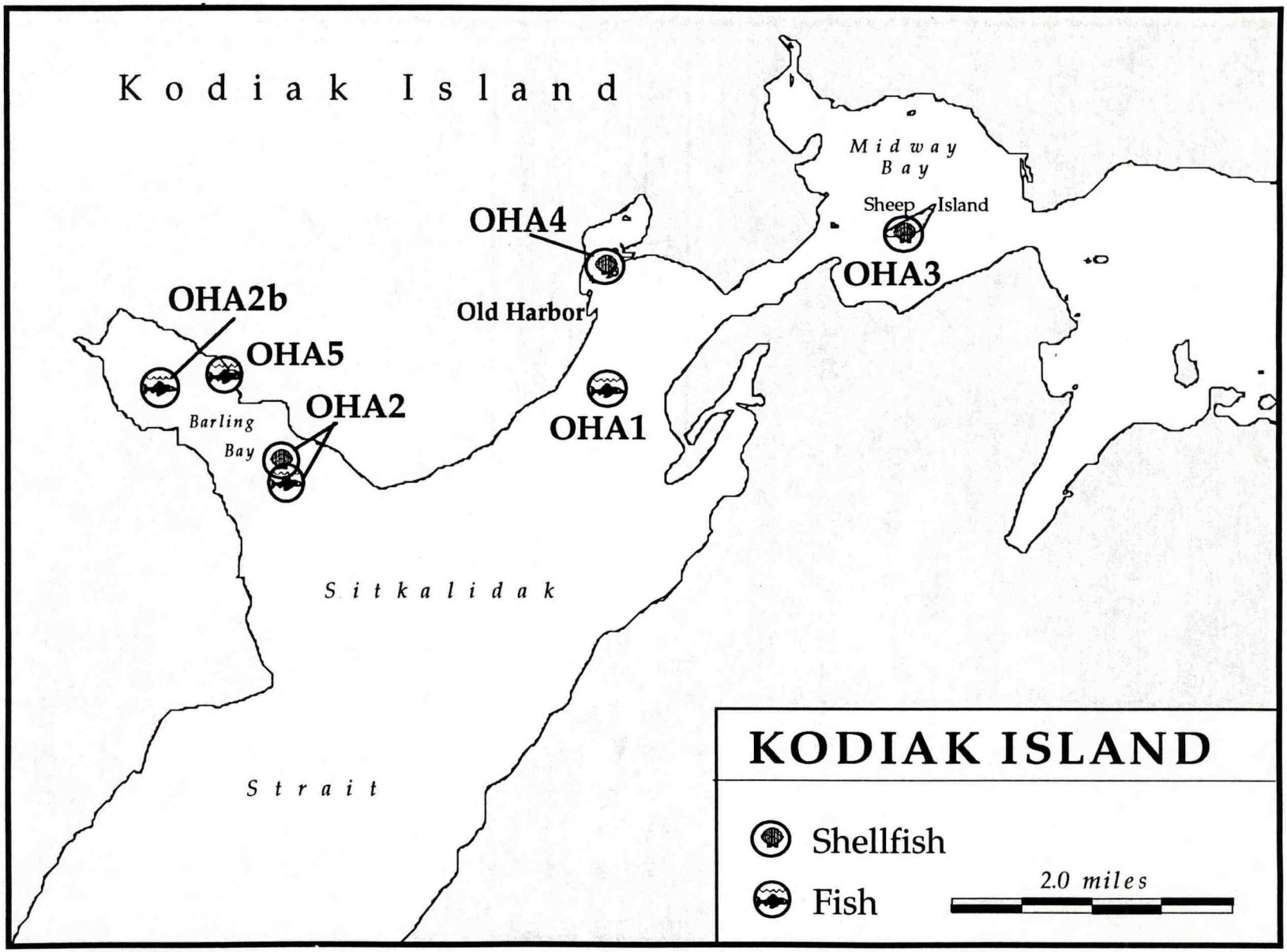

Figure 8. Fish and shellfish sampling stations in the vicinity of Old Harbor.

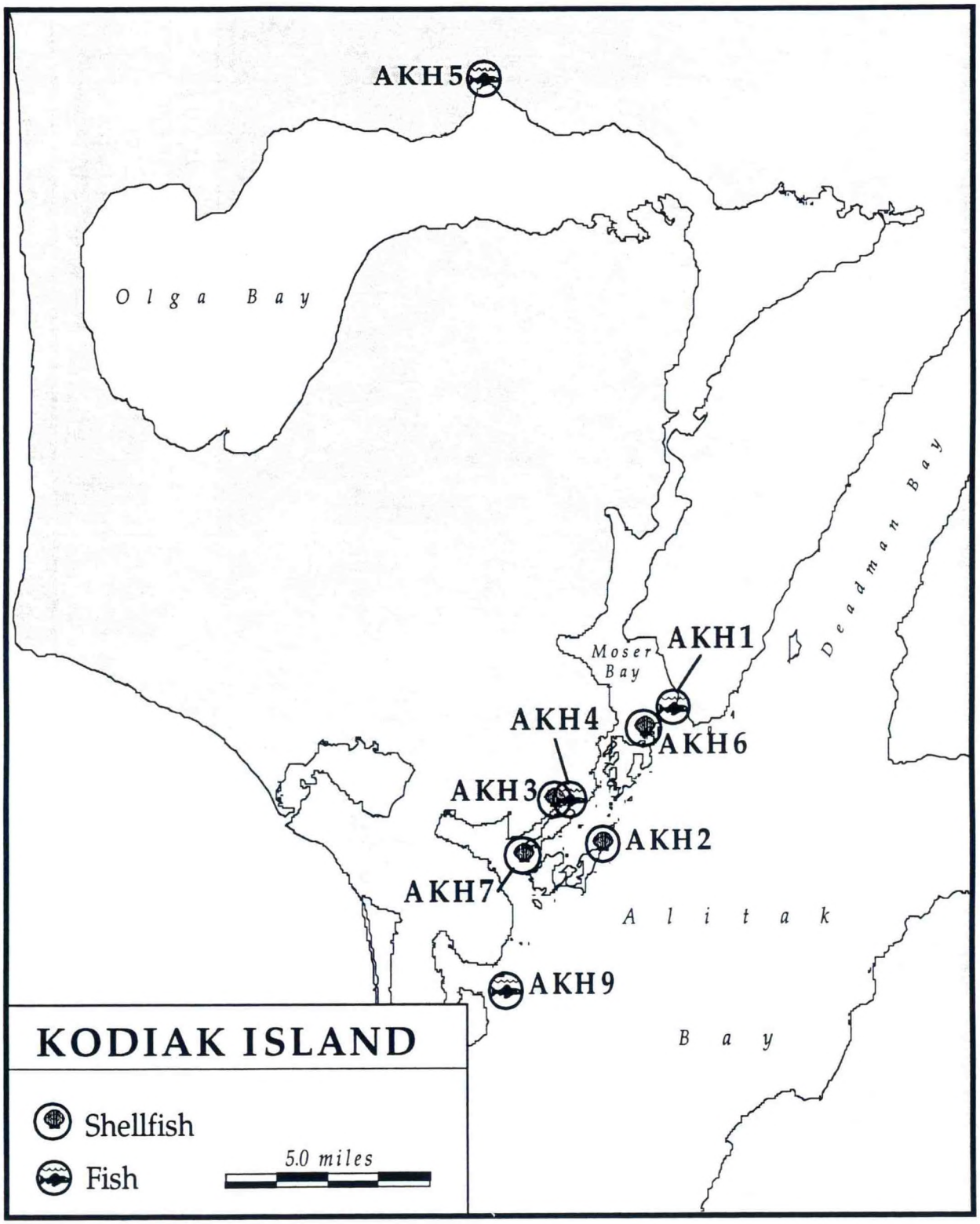

Figure 9. Fish and shellfish sampling stations in the vicinity of Akhiok.

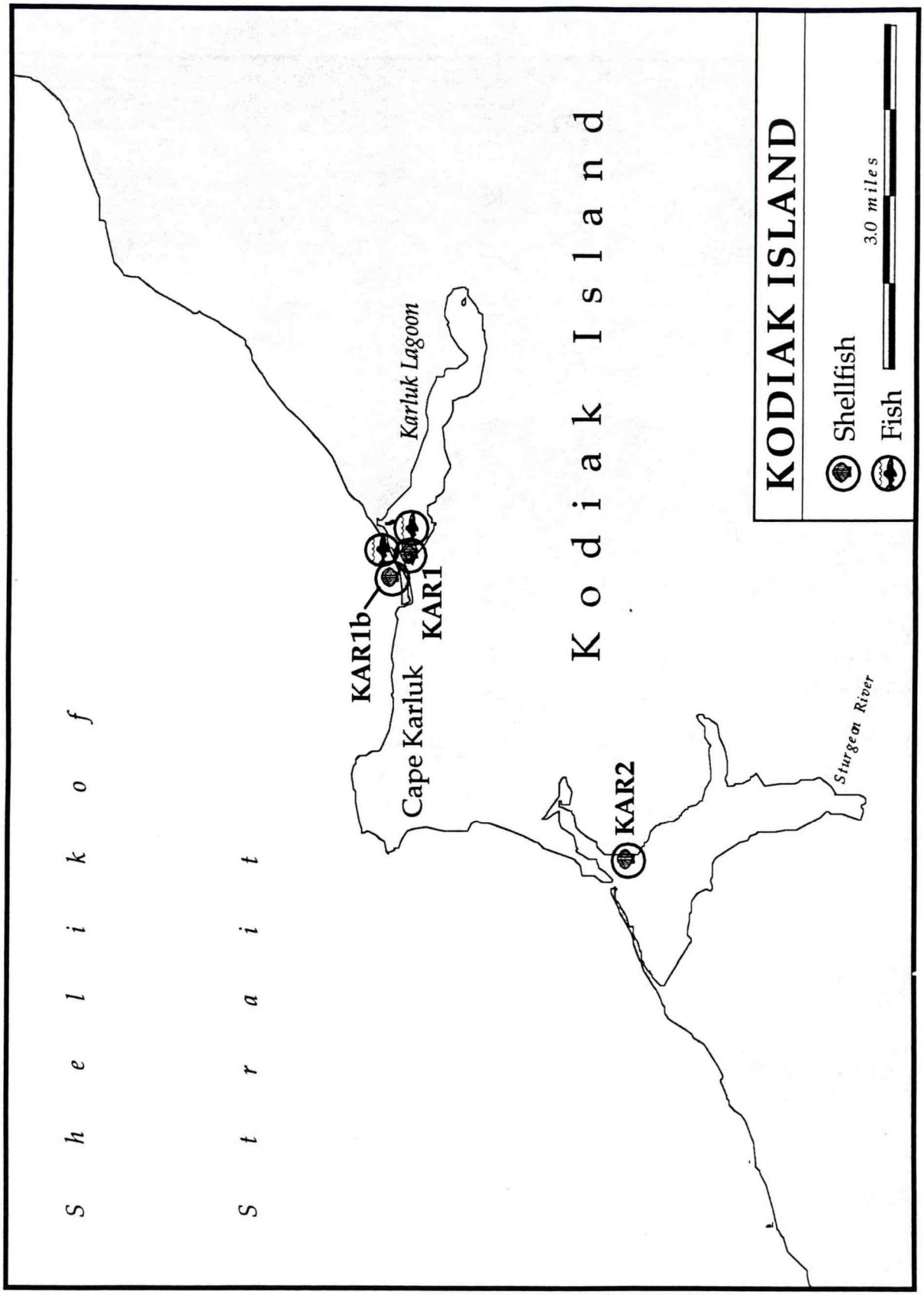

Figure 10. Fish and shellfish sampling stations in the vicinity of Karluk.

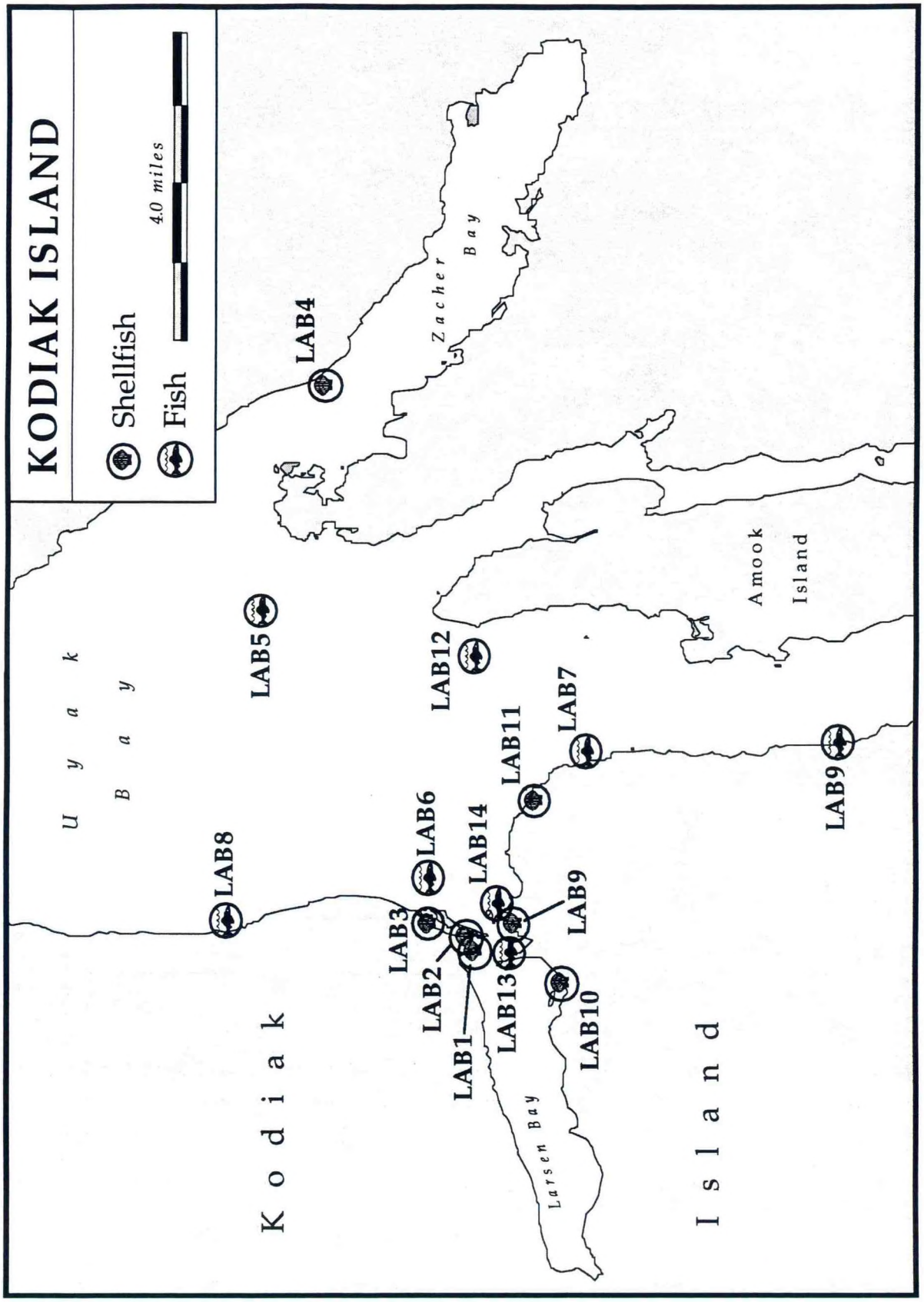

Figure 11. Fish and shellfish sampling stations in the vicinity of Larsen Bay.

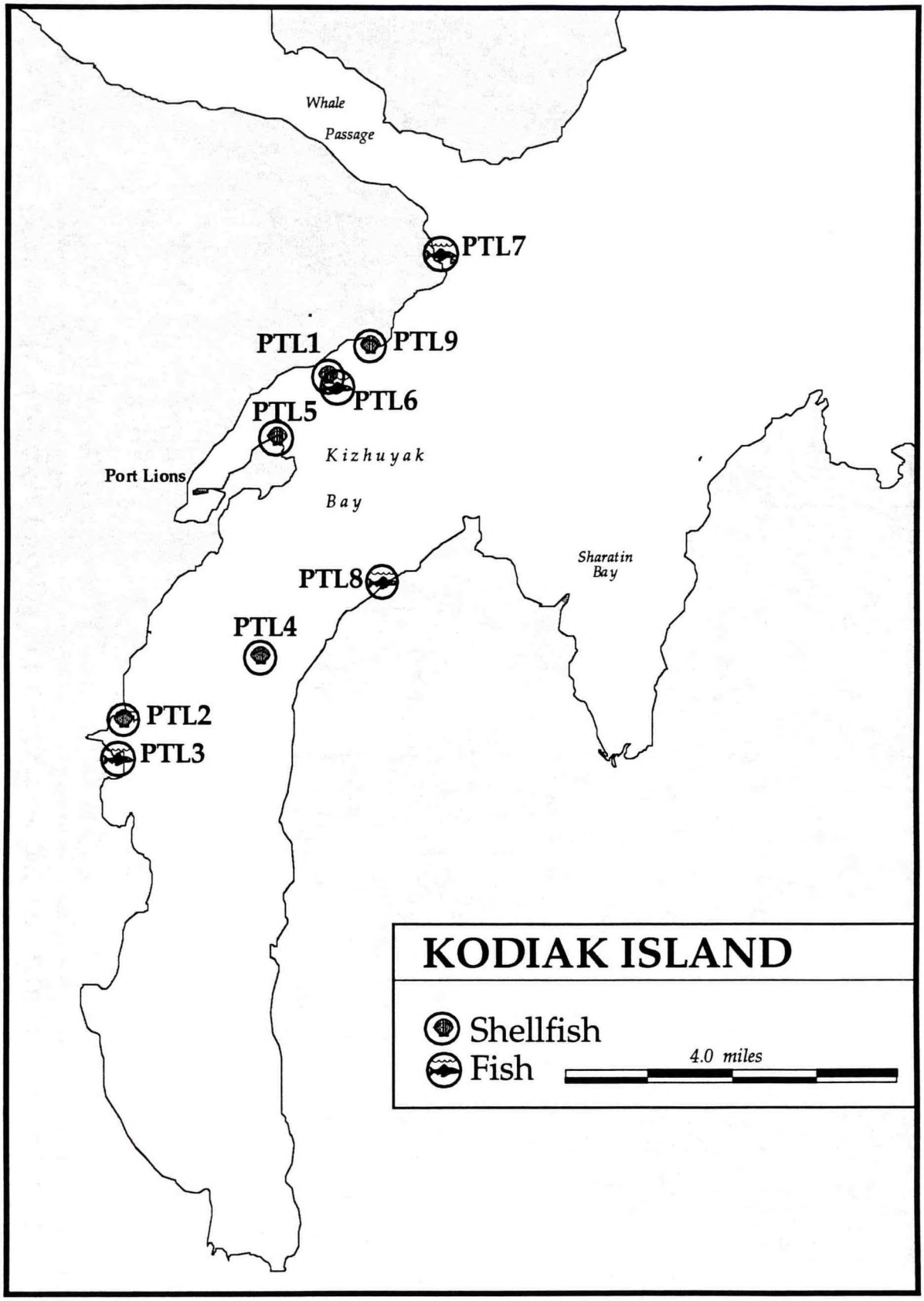

Figure 12. Fish and shellfish sampling stations in the vicinity of Port Lions.

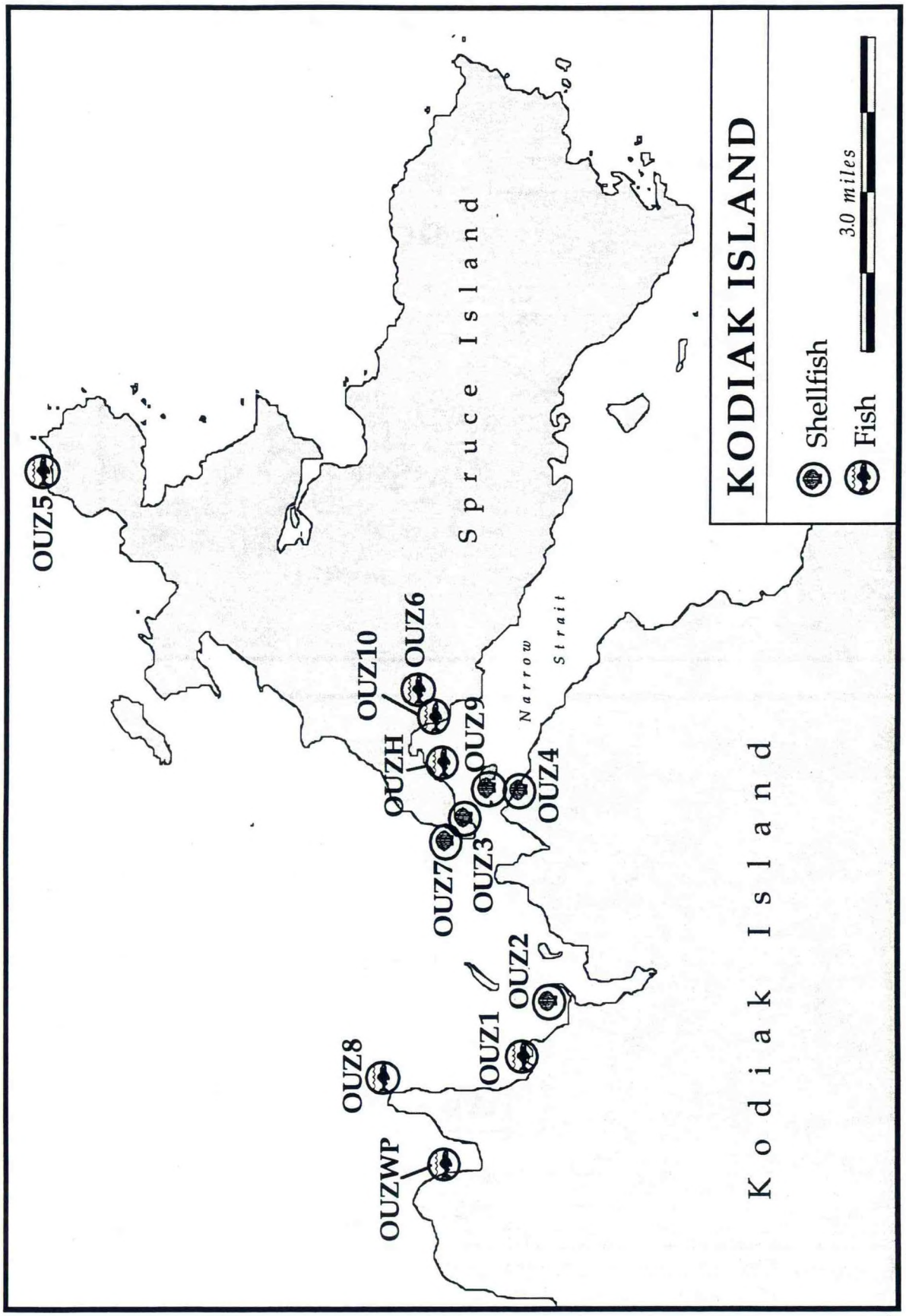

Figure 13. Fish and shellfish sampling stations in the vicinity of Ouzinkie.

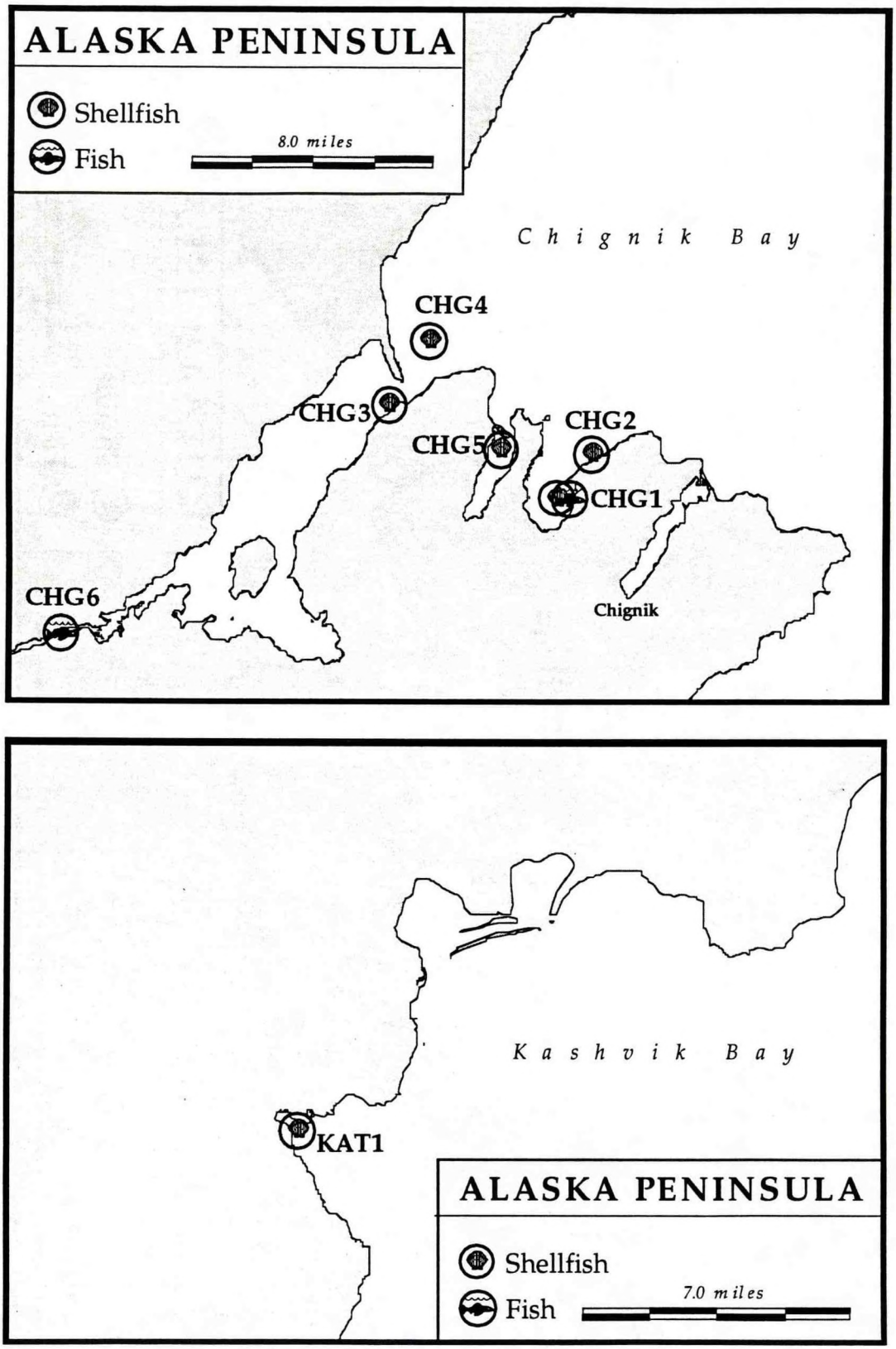

Figure 14. Fish and shellfish sampling stations in the vicinity of Chignik and Kashvik Bay (Katmai area).

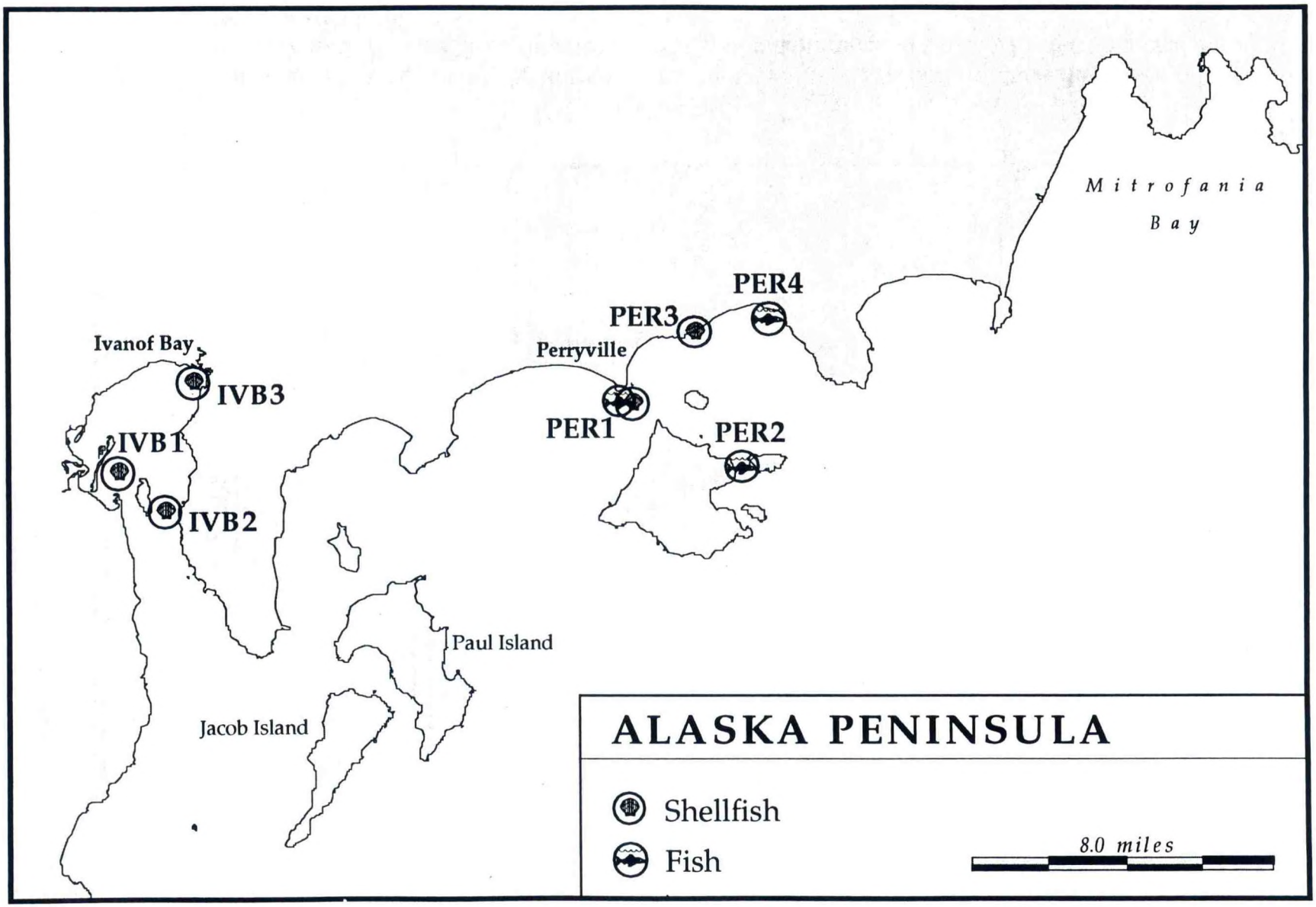

Figure 15. Fish and shellfish sampling stations in the vicinity of Ivanof Bay and Perryville.

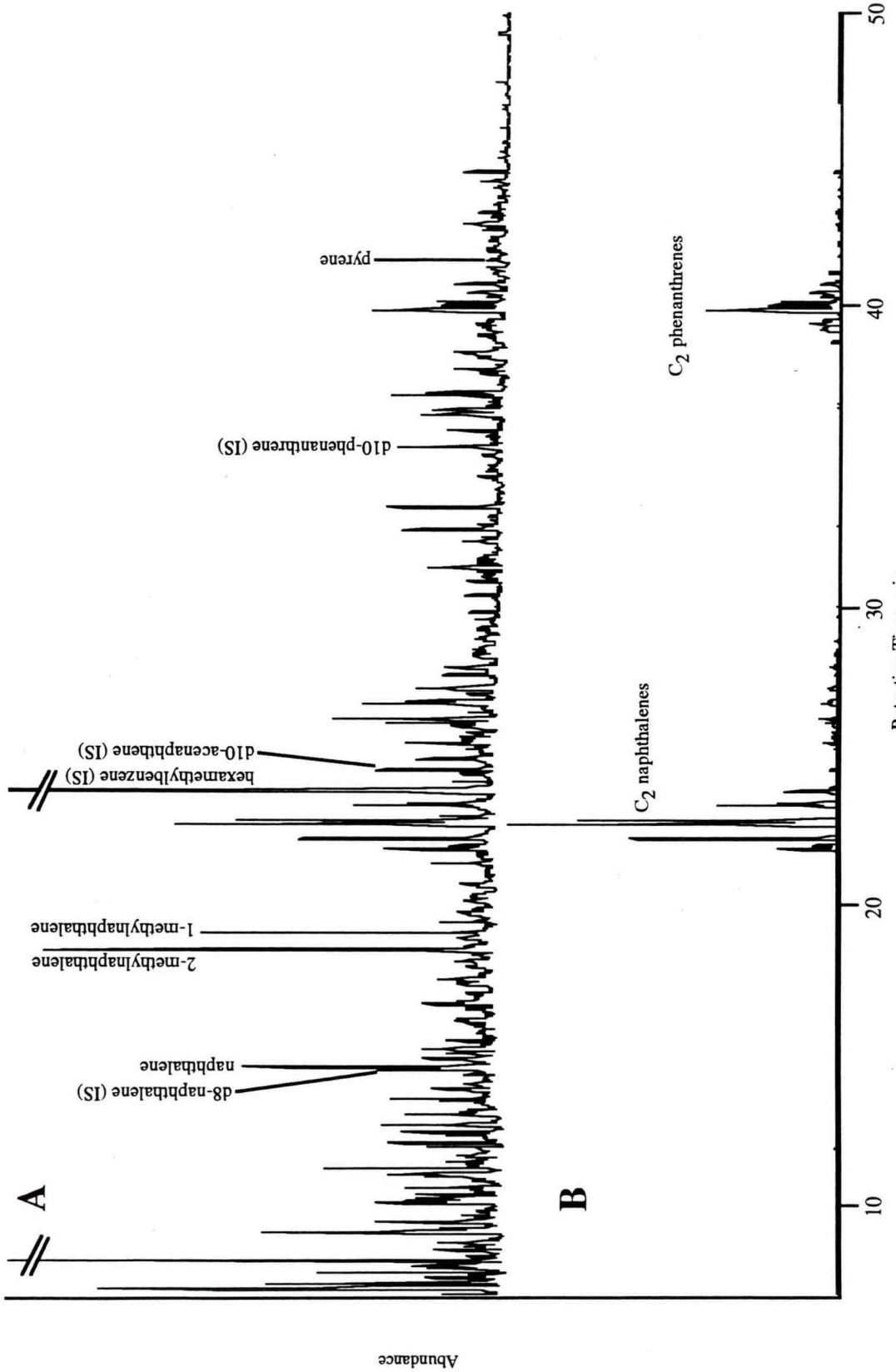

Figure 16. Chromatograms showing the aromatic contaminants in (A) spilled Prudhoe Bay crude oil (PBCO) and (B) the C2-naphthalenes and C2-phenanthrenes in PBCO. IS in ( ) denotes internal standard.

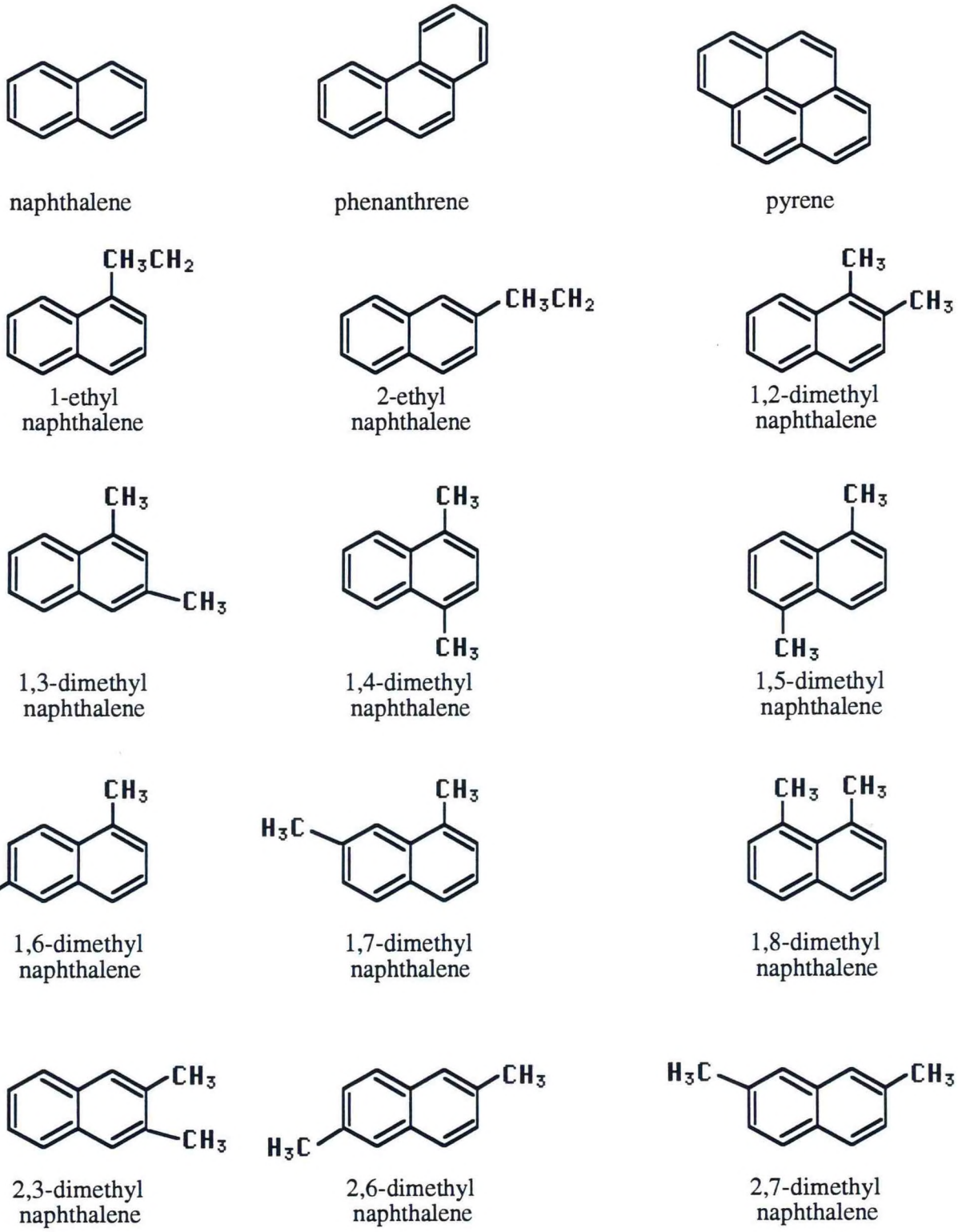

Figure 17. Structures of selected parent and alkyl aromatic compounds, including all of the possible C2-naphthalene isomer structures.

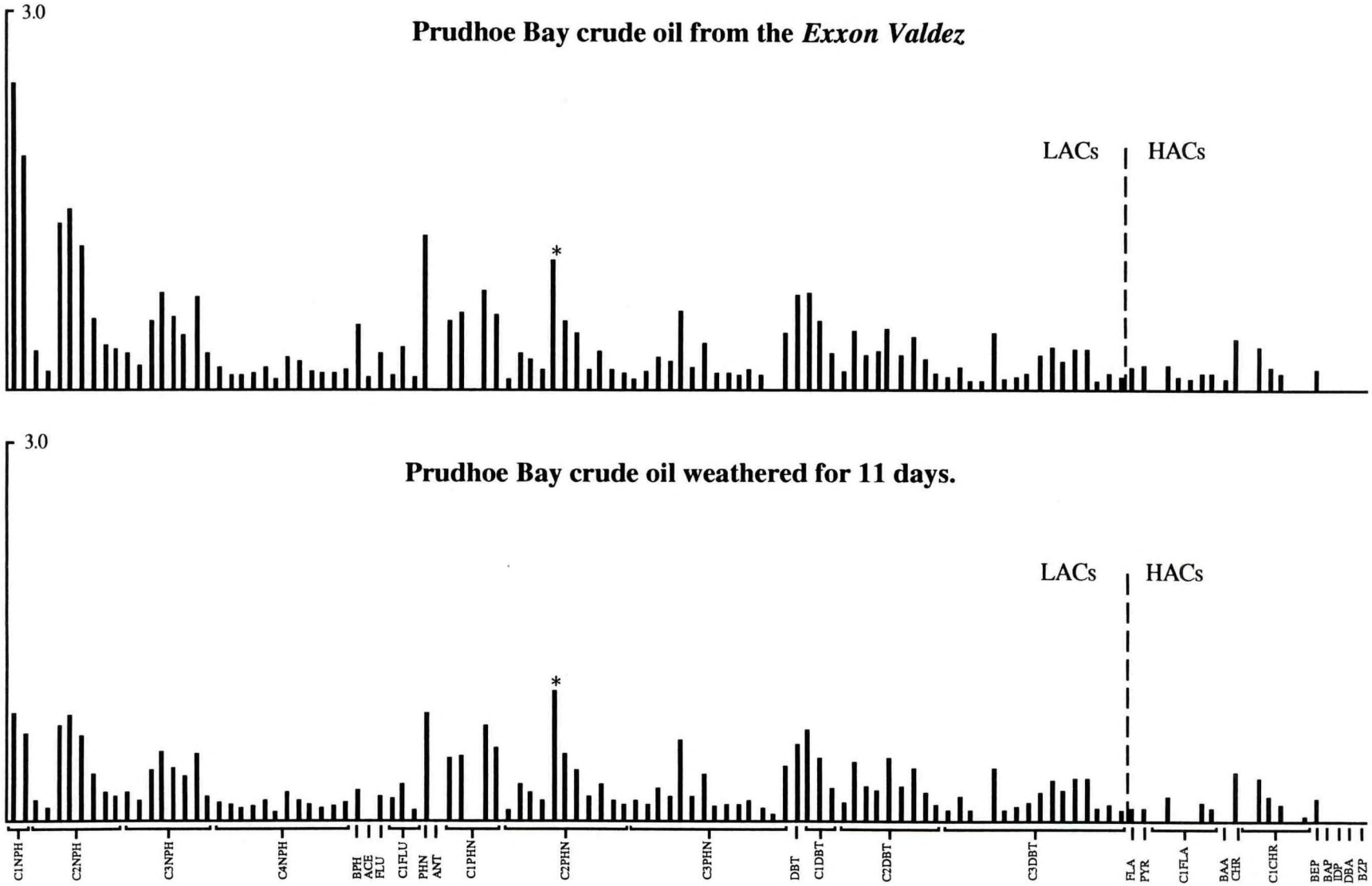

Figure 18. Isomer pattern graphs with peak areas normalized to the peak area of one of the C2-phenanthrene isomers(*) for weathered and unweathered Prudhoe Bay crude oil. Abbreviations are in Table 1, except for biphenyl (BPH), anthracene (ANT), and benzo[e]pyrene (BEP).

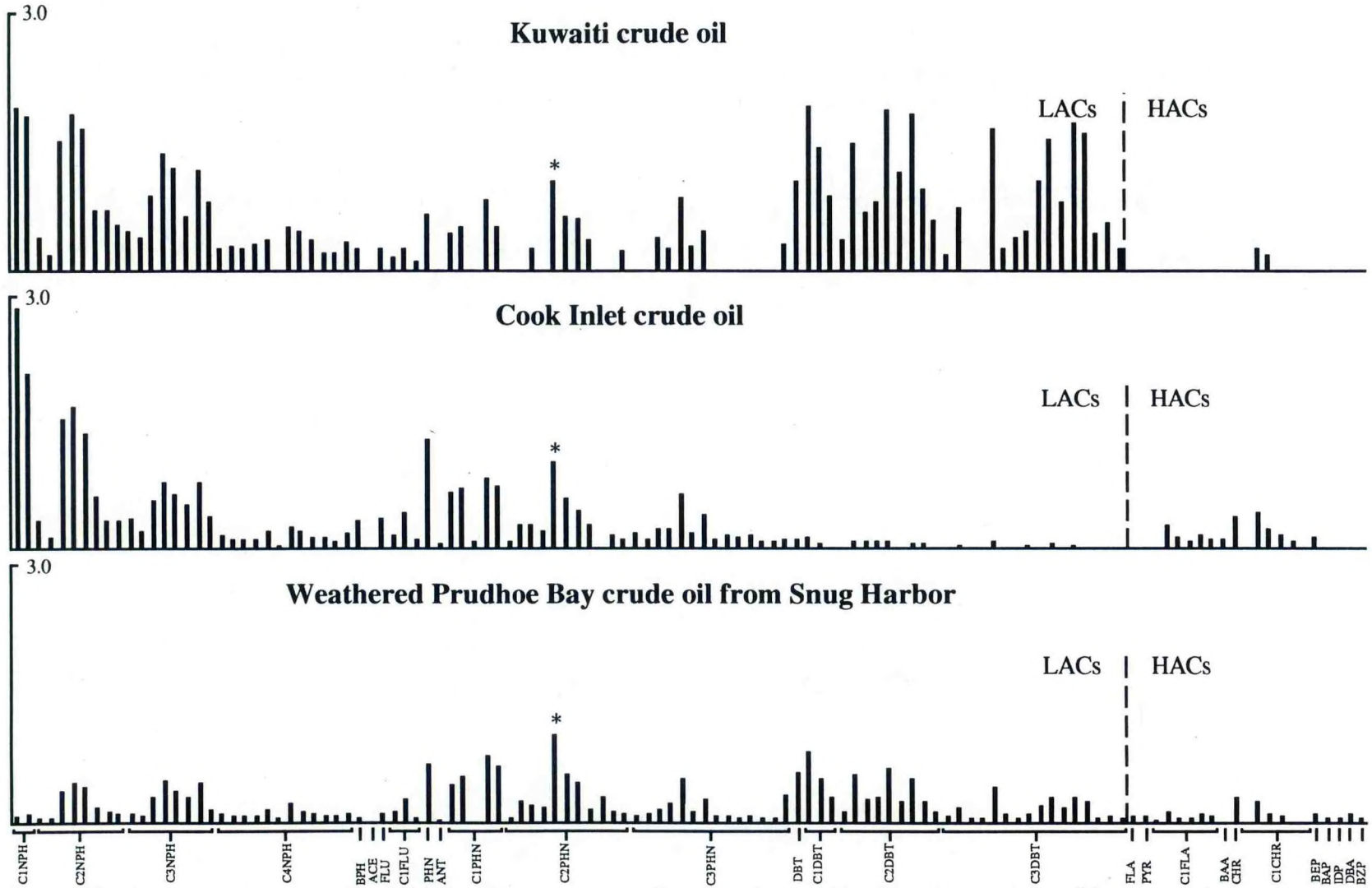

Figure 19. Isomer pattern graphs with peak areas normalized to the peak area of one of the C2-phenanthrene isomers(*) for fresh Kuwaiti crude oil, fresh Cook Inlet crude oil, and 15-month weathered Prudhoe Bay crude oil from Snug Harbor. Abbreviations are in Table 1, except for biphenyl (BPH), anthracene (ANT), and benzo[e]pyrene (BEP).

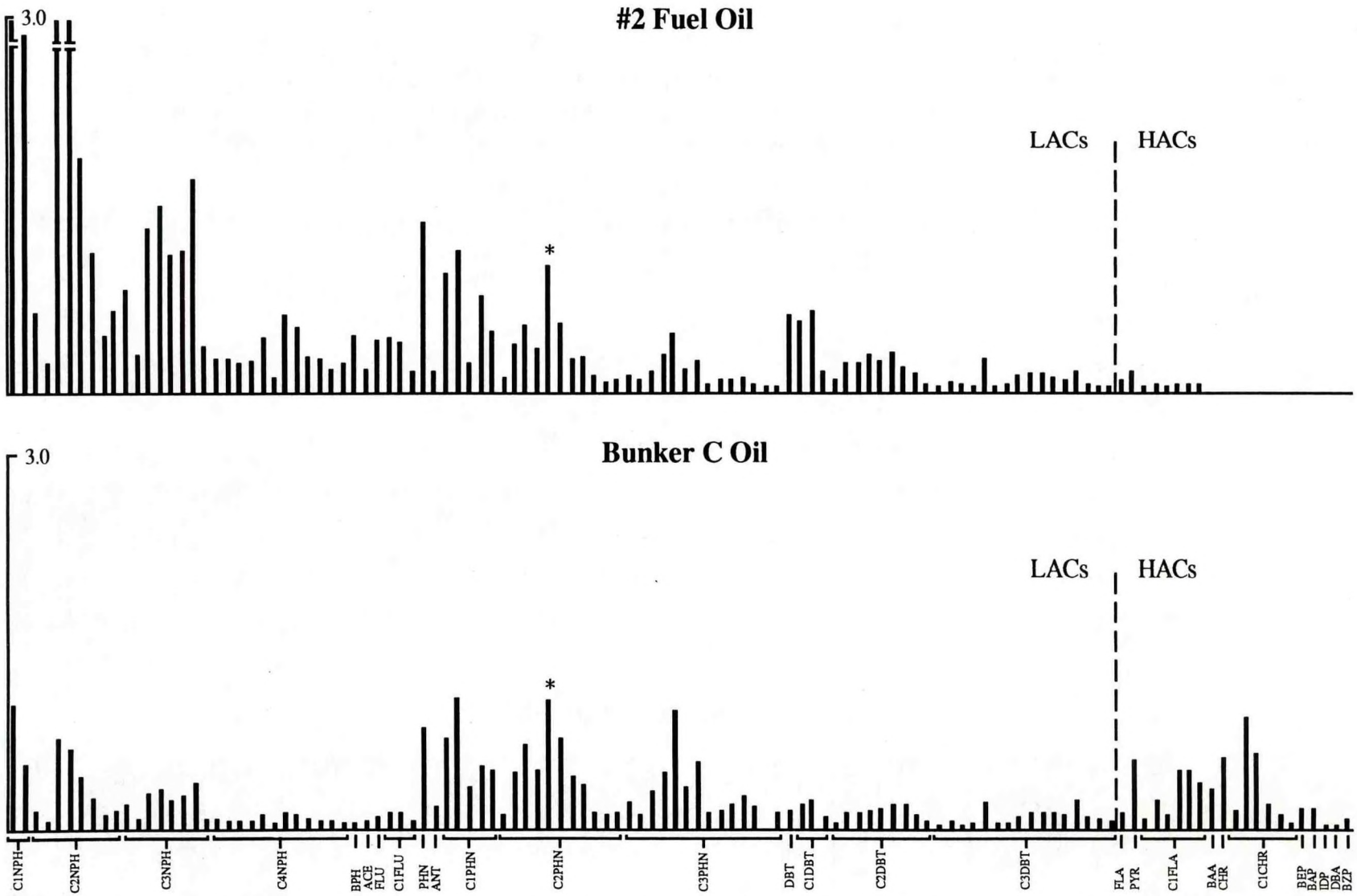

Figure 20. Isomer pattern graphs with peak areas normalized to the peak areas of one of the C2-phenanthrene isomers (*) for #2 fuel oil and Bunker C oil. Abbreviations are in Table 1, except for biphenyl (BPH), anthracene (ANT), and benzo[e]pyrene (BEP).

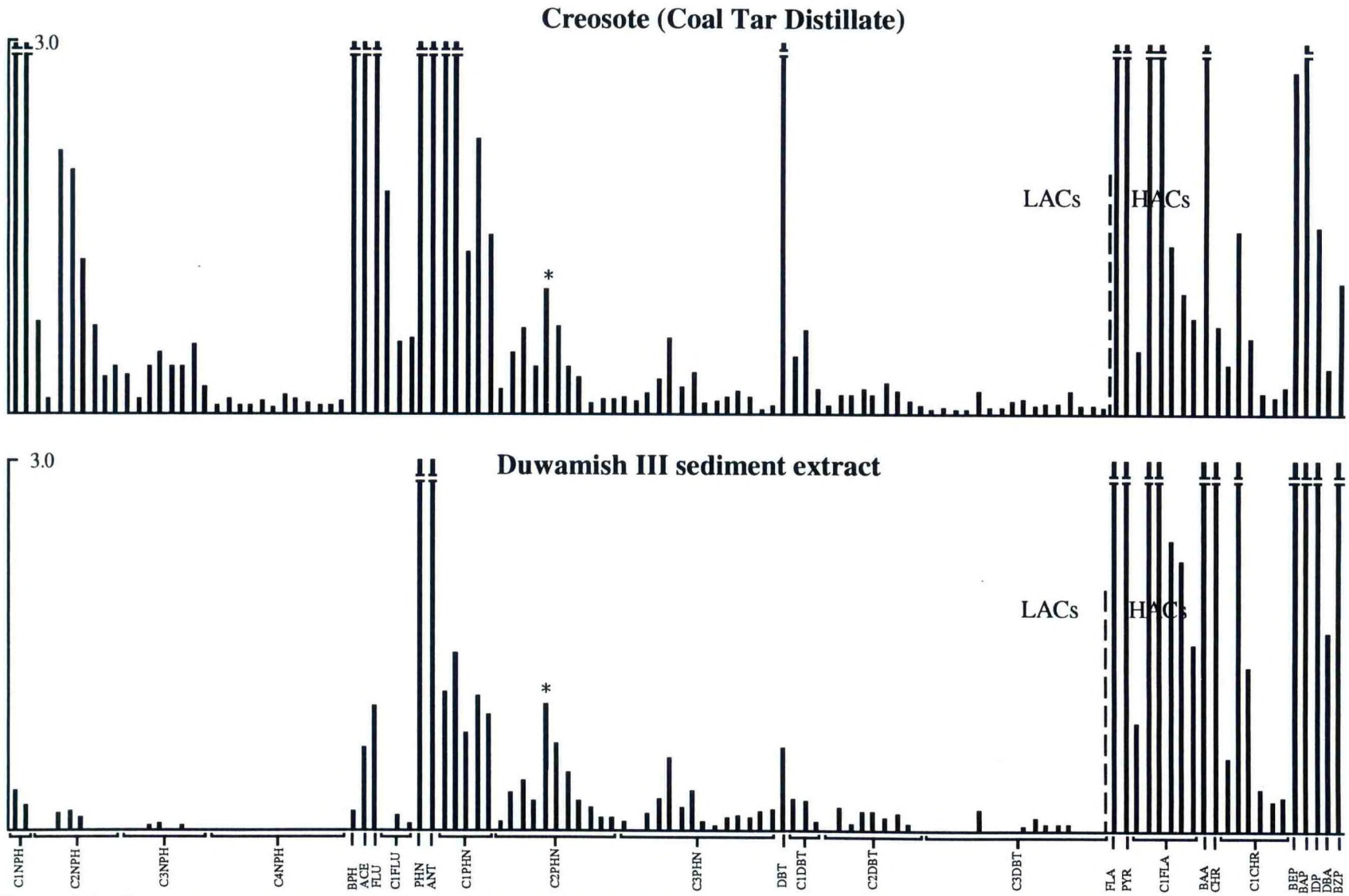

Figure 21. Isomer pattern graphs with peak areas normalized to the peak areas of one of the C2-phenanthrene isomers (*) for creosote and Duwamish III sediment extract. Abbreviations are in Table 1, except for biphenyl (BPH), anthracene (ANT), and benzo[e]pyrene (BEP).

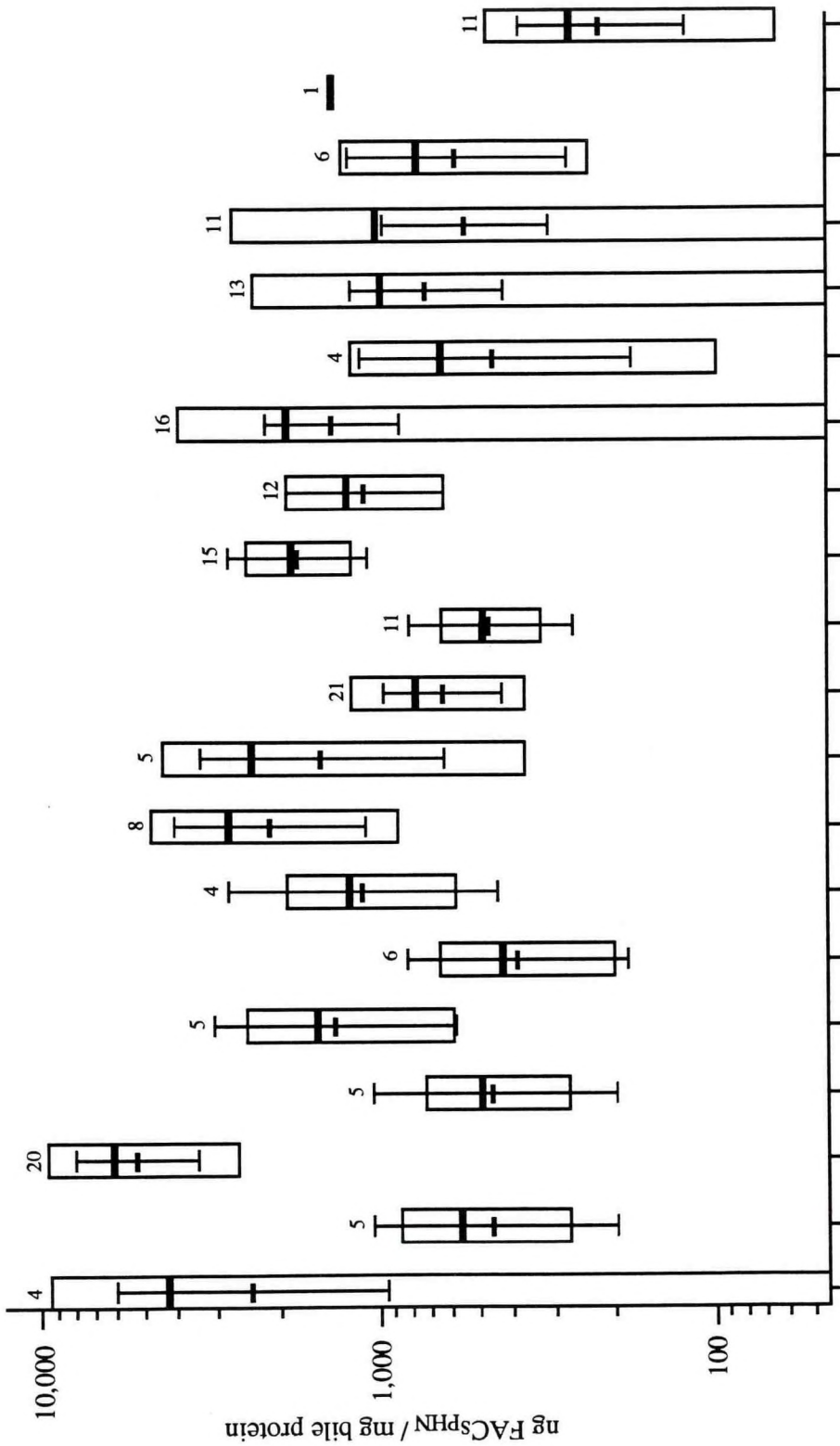

Figure 22. Mean concentrations and GT2 comparison intervals for fluorescent aromatic compounds measured at phenanthrene wavelengths [$FACS_{PHN}$ (ng phenanthrene equivalents / mg bile protein)] in pink salmon bile by station and year. Arithmetic mean [▬] concentrations ± 1 standard deviation [□] and geometric mean [▬] ± comparison interval [⌶], and number of samples written above the standard deviation box. Abbreviations are identified in Table 2.

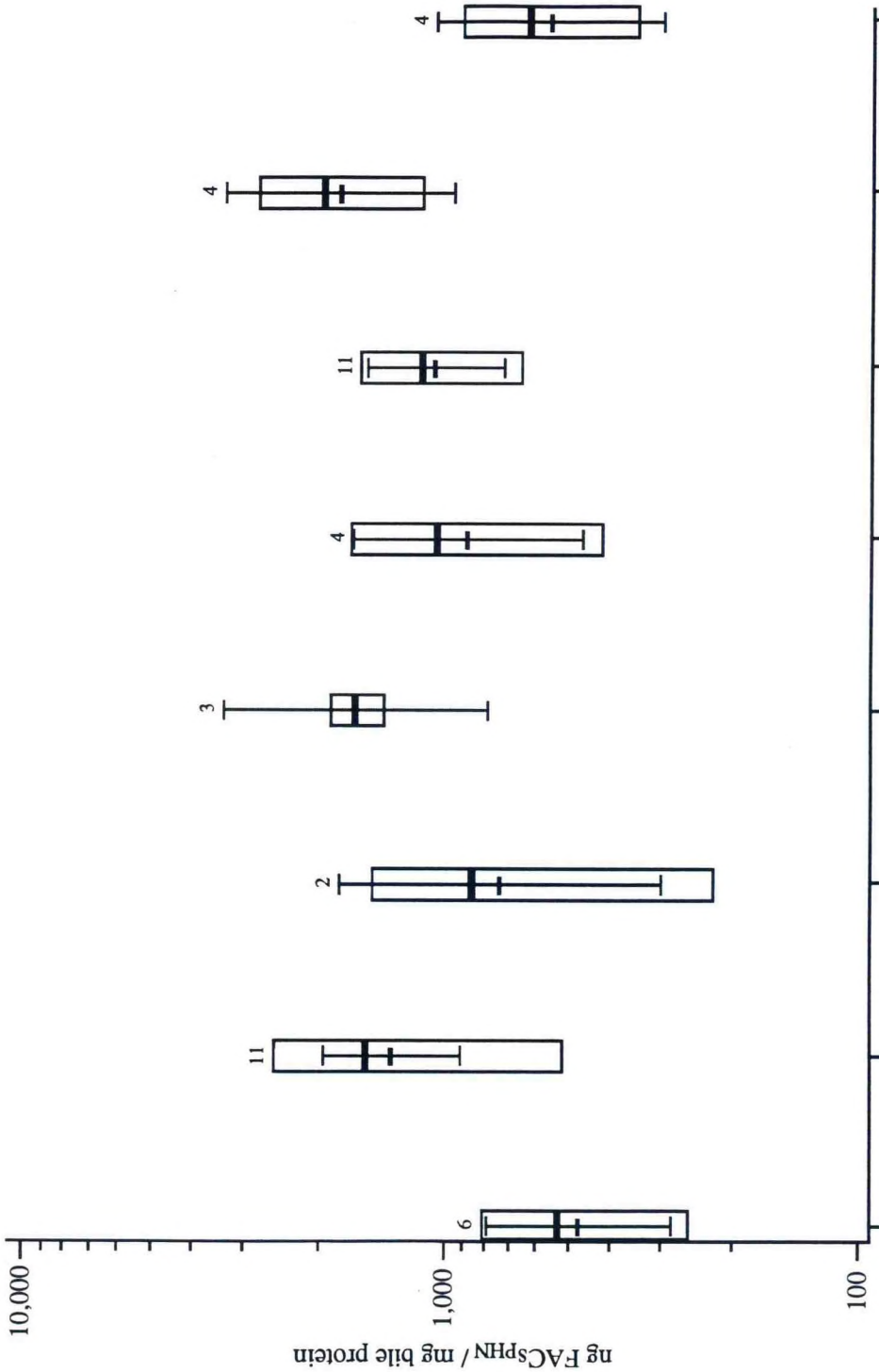

Figure 23. Mean concentrations and GT2 comparison intervals for fluorescent aromatic compounds measured at phenanthrene wavelengths [$FACS_{PHN}$ (ng phenanthrene equivalents / mg bile protein)] in coho salmon bile by station and year. Arithmetic mean [▬] concentrations ± 1 standard deviation box [□] and geometric mean [▬] ± comparison interval [⊥], and number of samples written above the standard deviation box. Abbreviations are identified in Table 2.

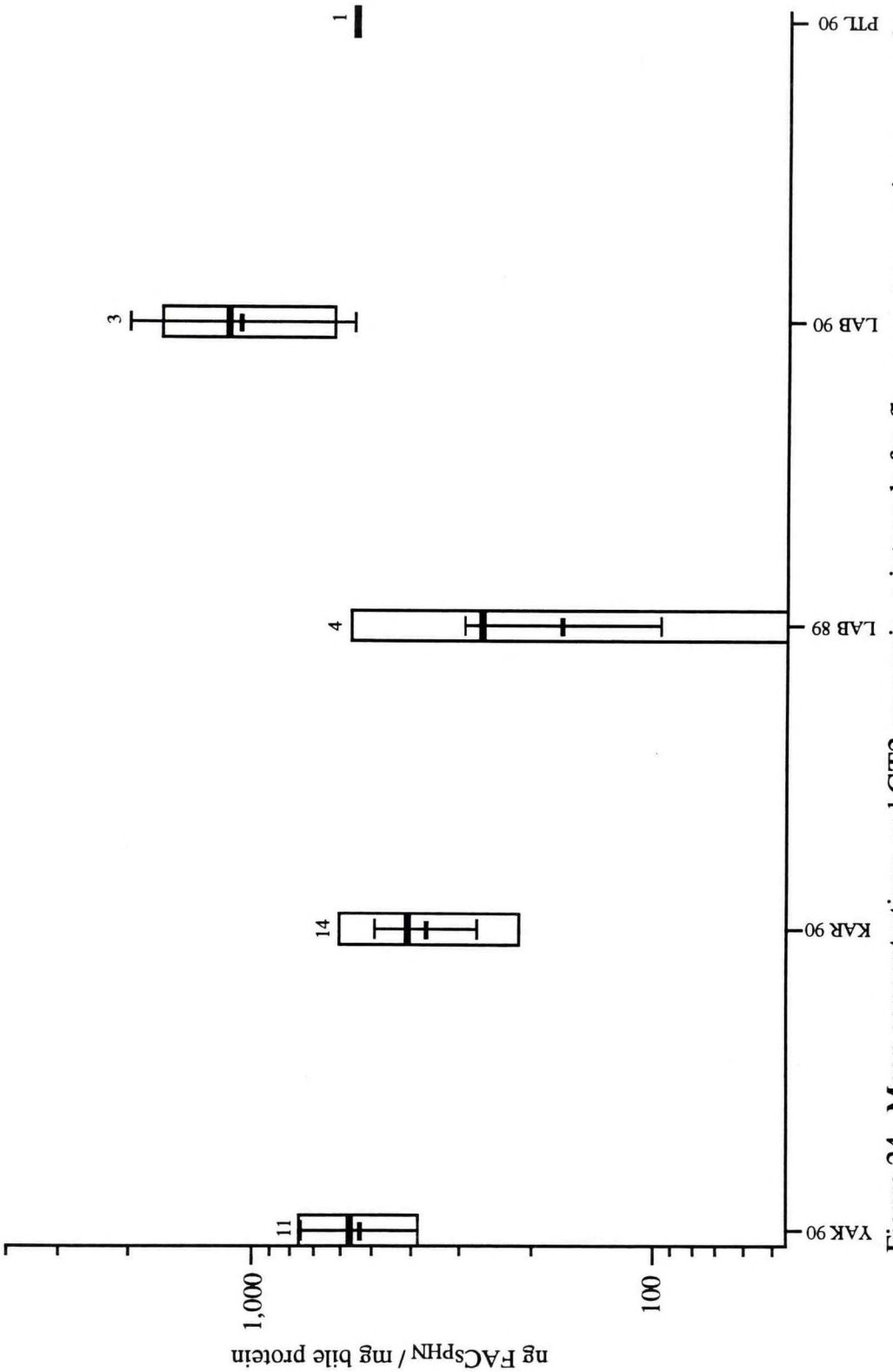

Figure 24. Mean concentrations and GT2 comparison intervals for fluorescent aromatic compounds measured at phenanthrene wavelengths [FAC_{SPHN} (ng phenanthrene equivalents / mg bile protein)] in sockeye salmon bile by station and year. Arithmetic mean [—] concentrations ± 1 standard deviation box [□] and geometric mean [–] ± comparison interval [⊥], and number of samples written above the standard deviation box. Abbreviations are identified in Table 2.

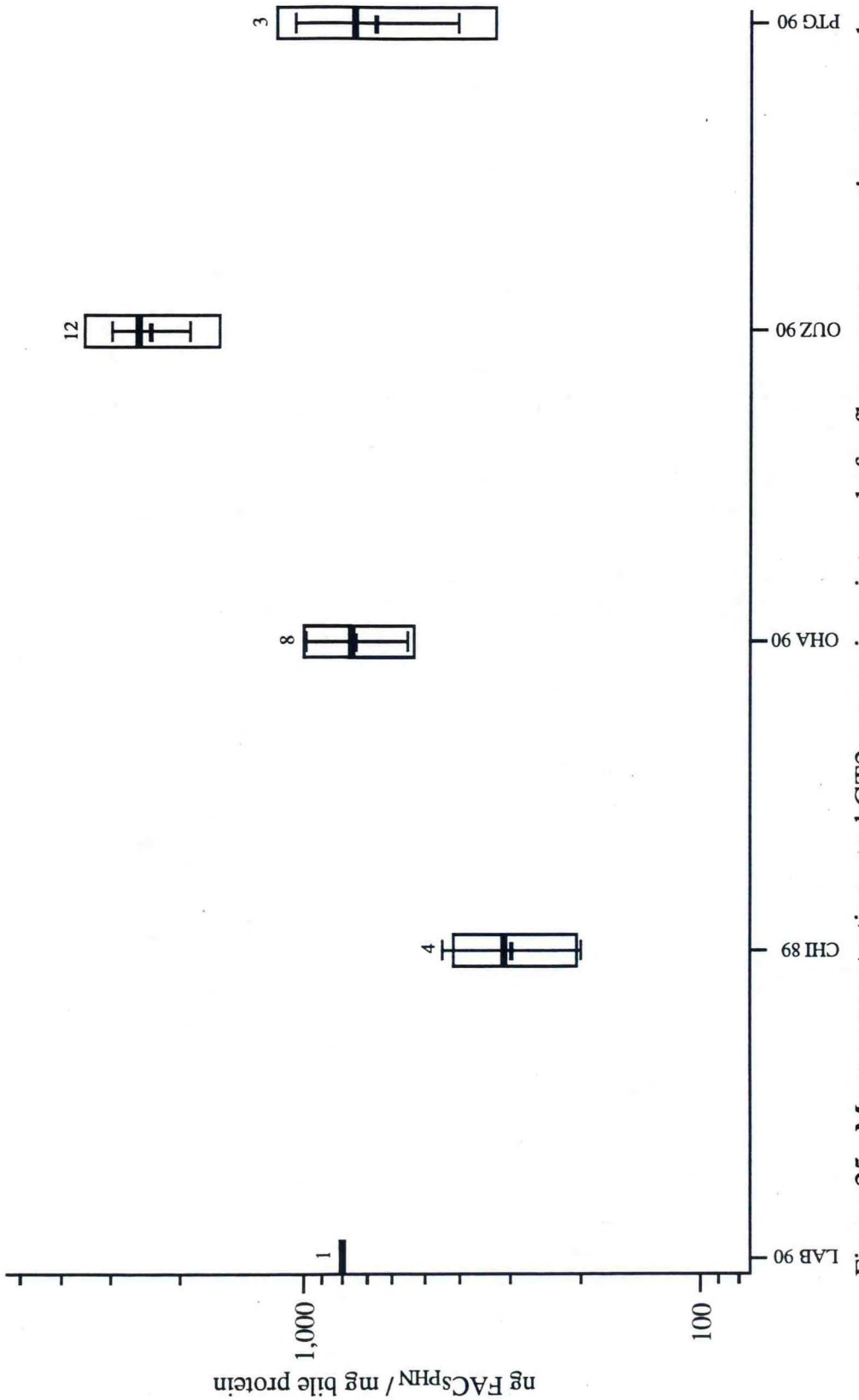

Figure 25. Mean concentrations and GT2 comparison intervals for fluorescent aromatic compounds measured at phenanthrene wavelengths [FAC_{SPHN} (ng phenanthrene equivalents / mg bile protein)] in chum salmon bile by station and year. Arithmetic mean [▬] concentrations ± 1 standard deviation box [□] and geometric mean [▬] ± comparison interval [⌶], and number of samples written above the standard deviation box. Abbreviations are identified in Table 2.

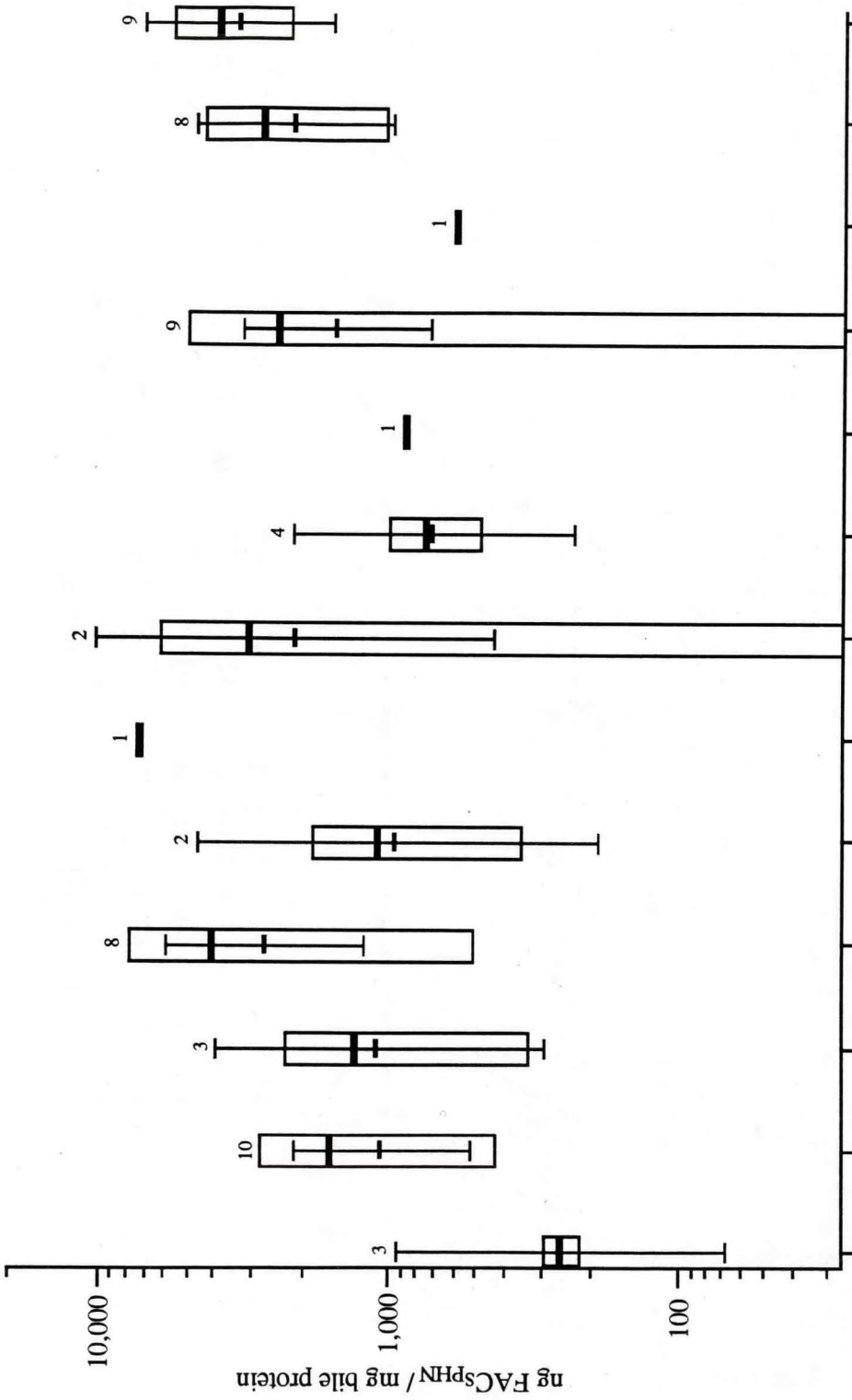

Figure 26. Mean concentrations and GT2 comparison intervals for fluorescent aromatic compounds measured at phenanthrene wavelengths [$FACS_{PHN}$ (ng phenanthrene equivalents / mg bile protein)] in halibut bile by station and year. Arithmetic mean [—] concentrations ± 1 standard deviation box [□] and geometric mean [–] ± comparison interval [∓], and number of samples written above the standard deviation box. Abbreviations are identified in Table 2.

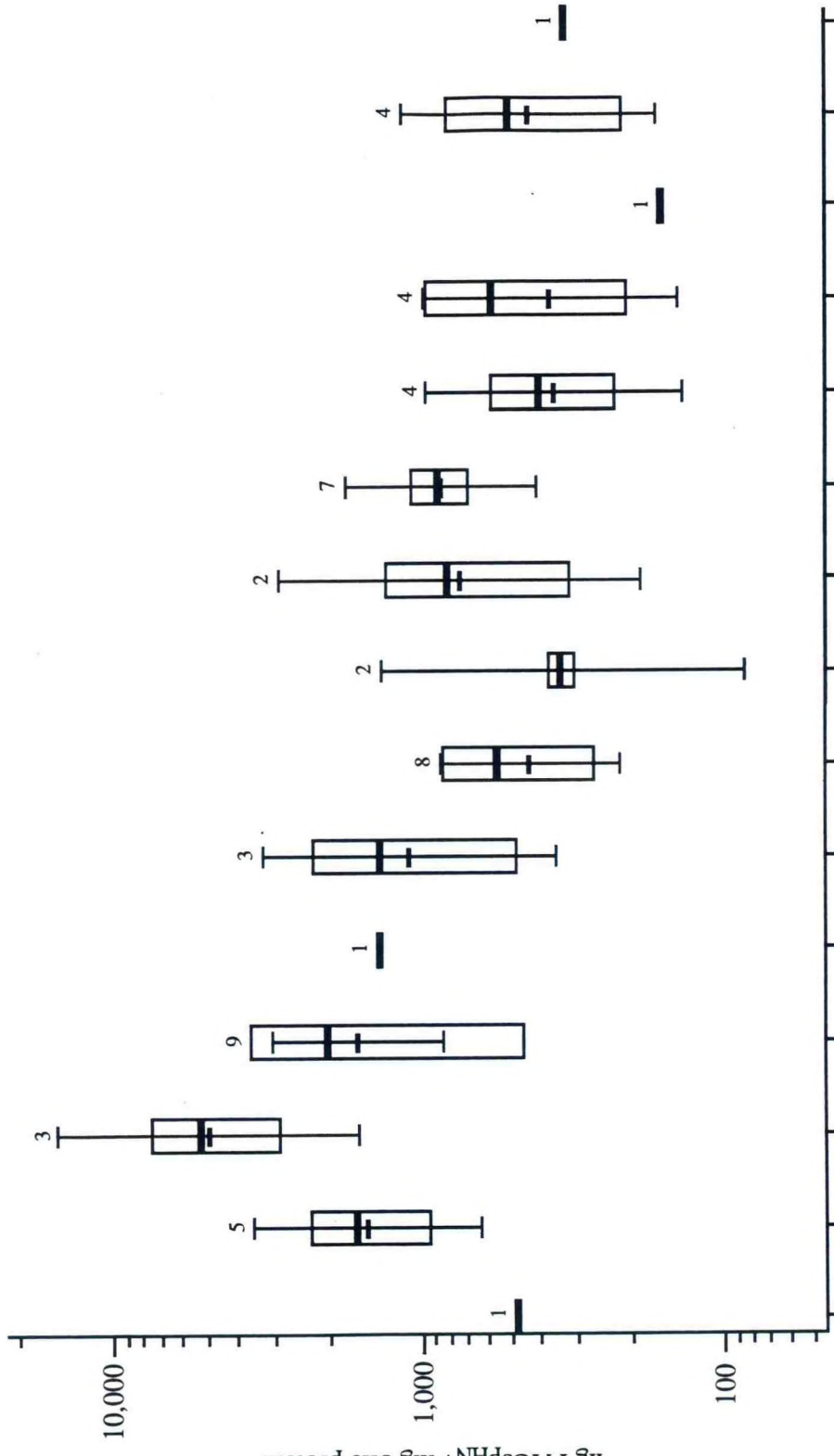

Figure 27. Mean concentrations and GT2 comparison intervals for fluorescent aromatic compounds measured at phenanthrene wavelengths [FAC_{SPHN} (ng phenanthrene equivalents / mg bile protein)] in Pacific cod bile by station and year. Arithmetic mean [—] concentrations ± 1 standard deviation box [□] and geometric mean [–] ± comparison interval [I], and number of samples written above the standard deviation box. Abbreviations are identified in Table 2.

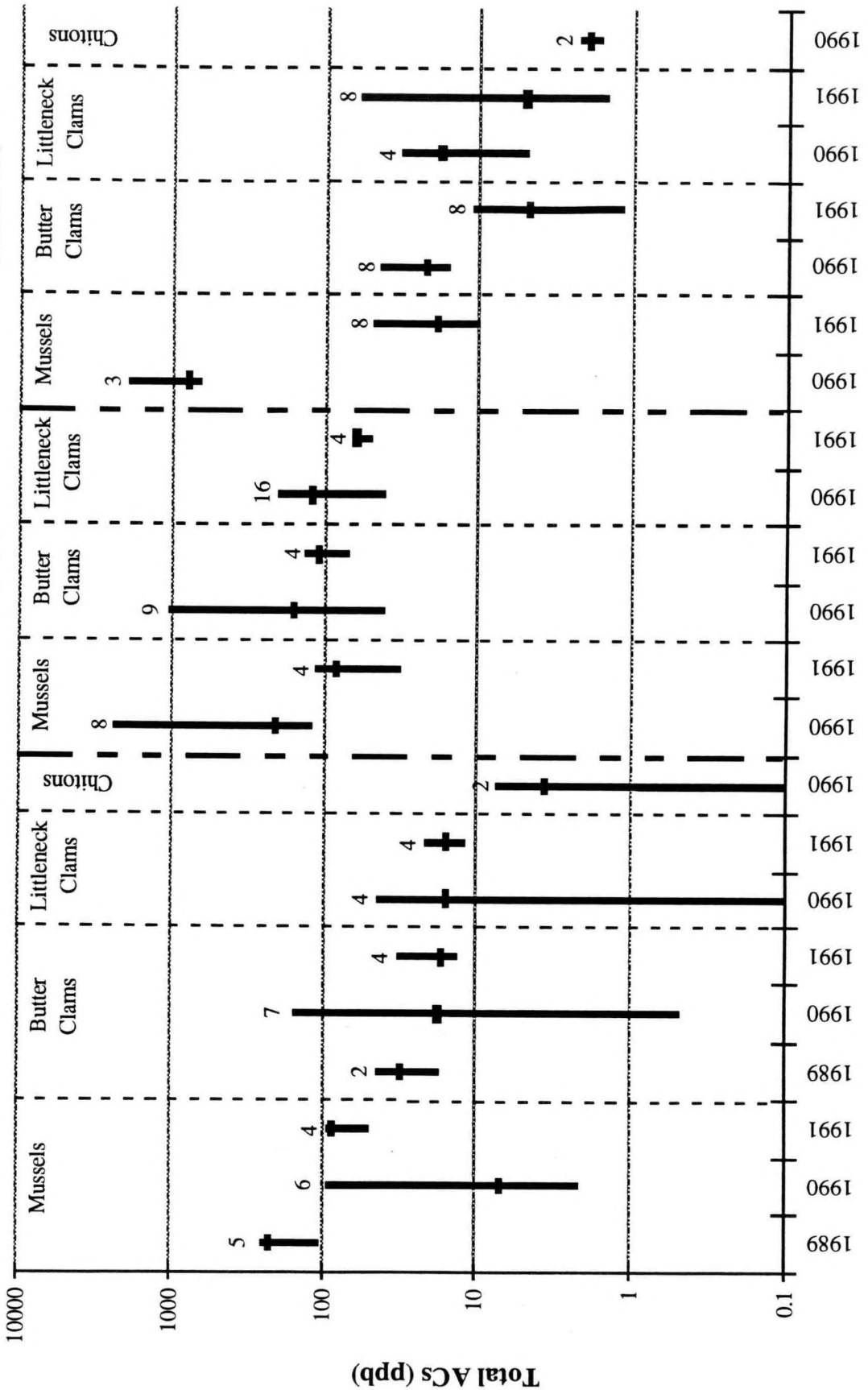

Figure 28. Concentrations (high, low, and median (▬); ng/g wet weight) of aromatic compounds (ACs) in mollusc samples from three Chenega stations.

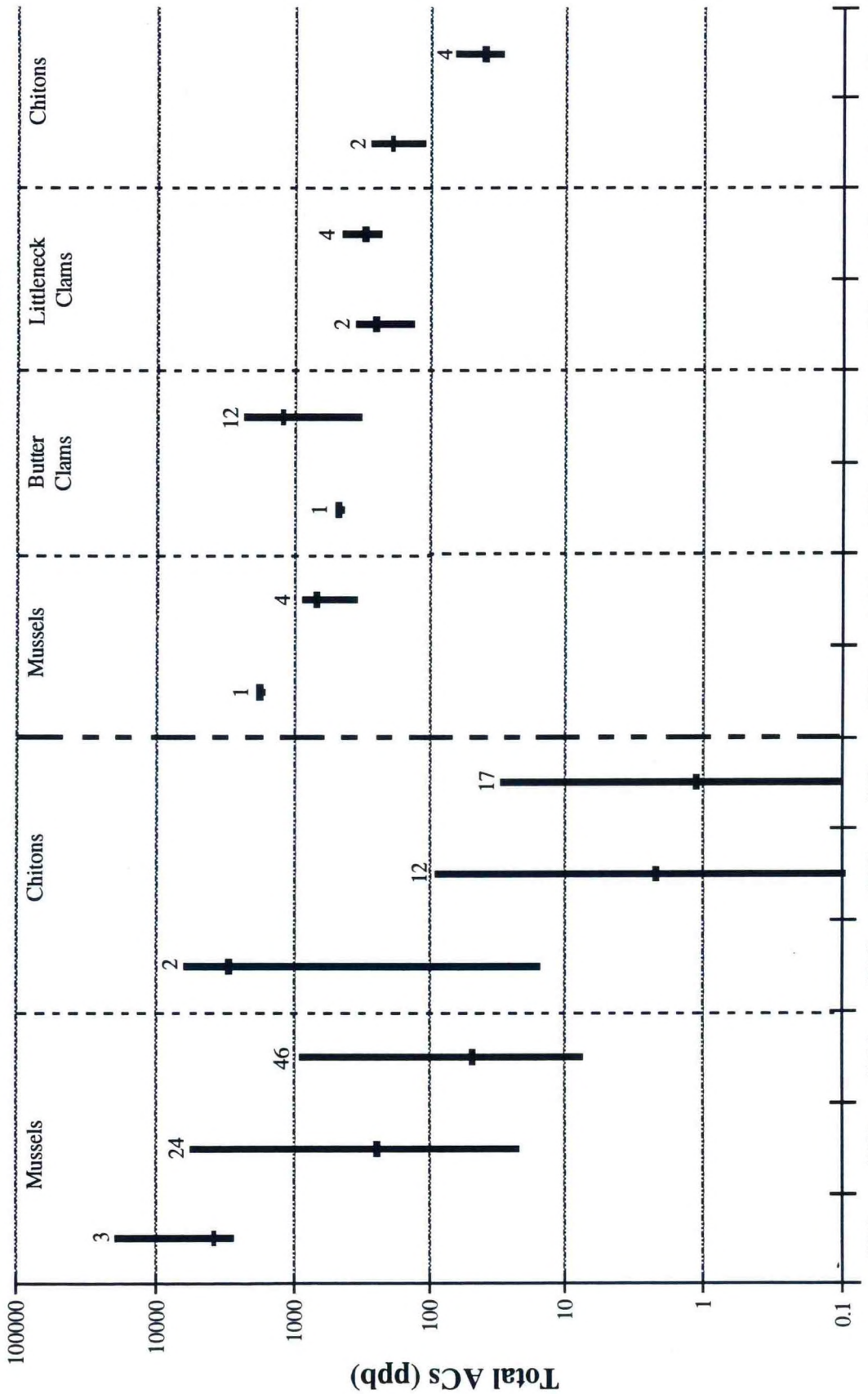

Figure 29. Concentrations (high, low, and median (-); ng/g wet weight) of aromatic compounds (ACs) in mollusc samples from selected Windy Bay and Kodiak stations.

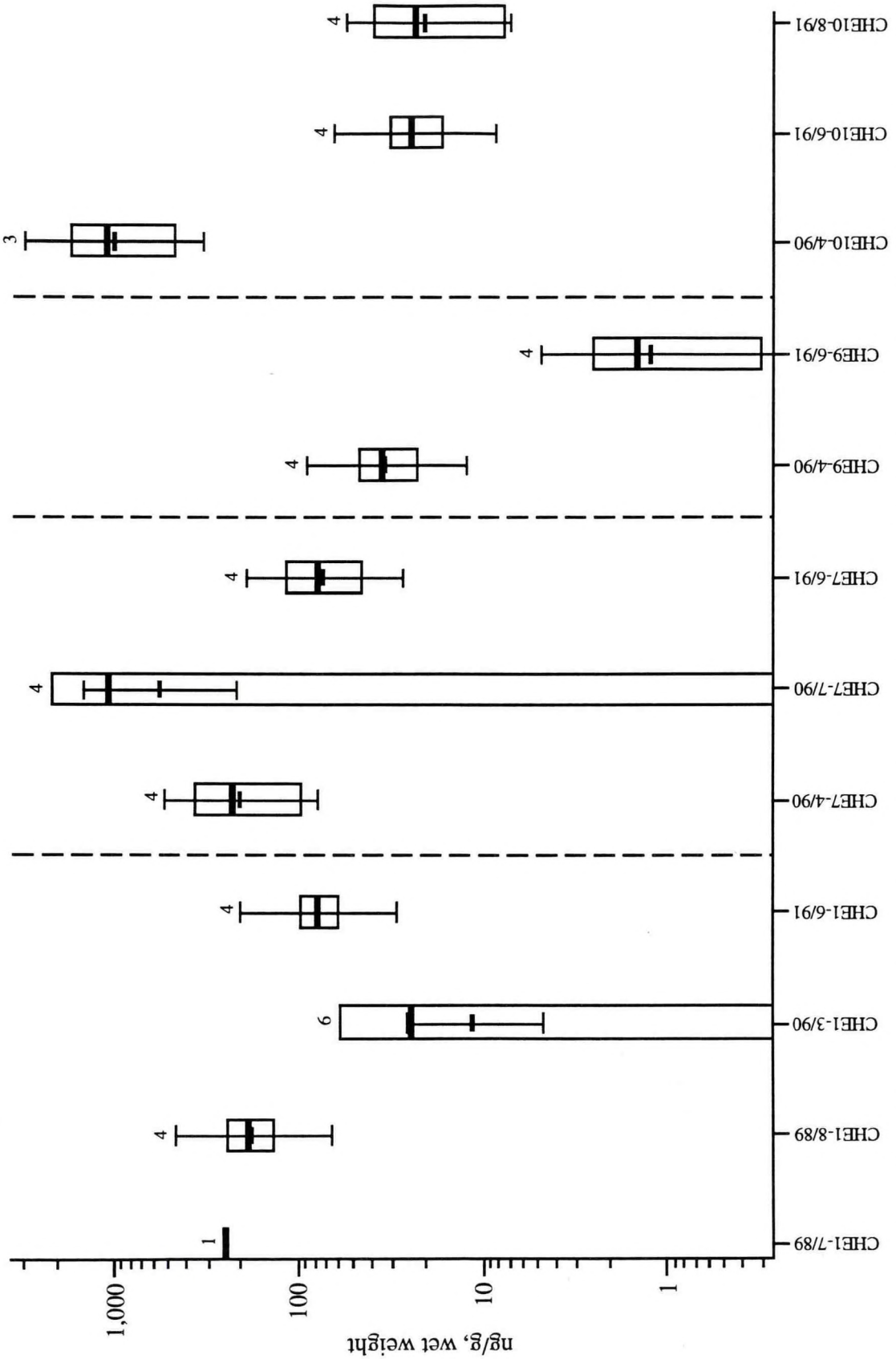

Figure 30. Mean concentrations and GT2 comparison intervals for total aromatic contaminants in Chenega Bay mussels by station and year. Arithmetic mean [—] concentrations (ng/g wet weight) ± 1 standard deviation [□] and geometric mean [–] ± comparison interval [⊥], and number of samples written above the standard deviation box. Abbreviations are identified in Table 2.

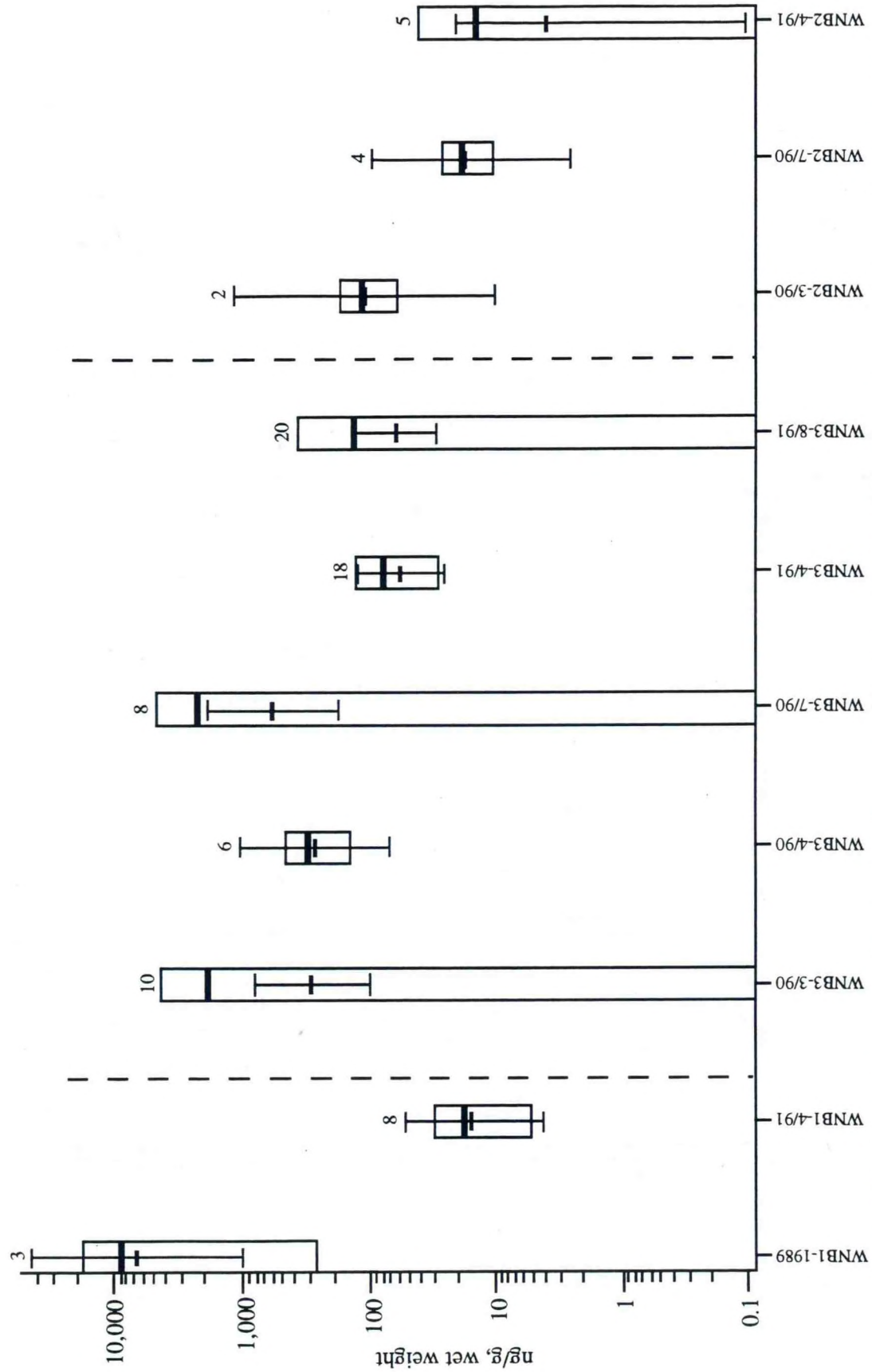

Figure 31. Mean concentrations and GT2 comparison intervals for total aromatic contaminants in Windy Bay mussels by station and year. Arithmetic mean [—] concentrations, (ng/g. wet weight) ± 1 standard deviation [□] and geometric mean [–] ± comparison interval [⊥], and number of samples written above the standard deviation box. Abbreviations are identified in Table 2.

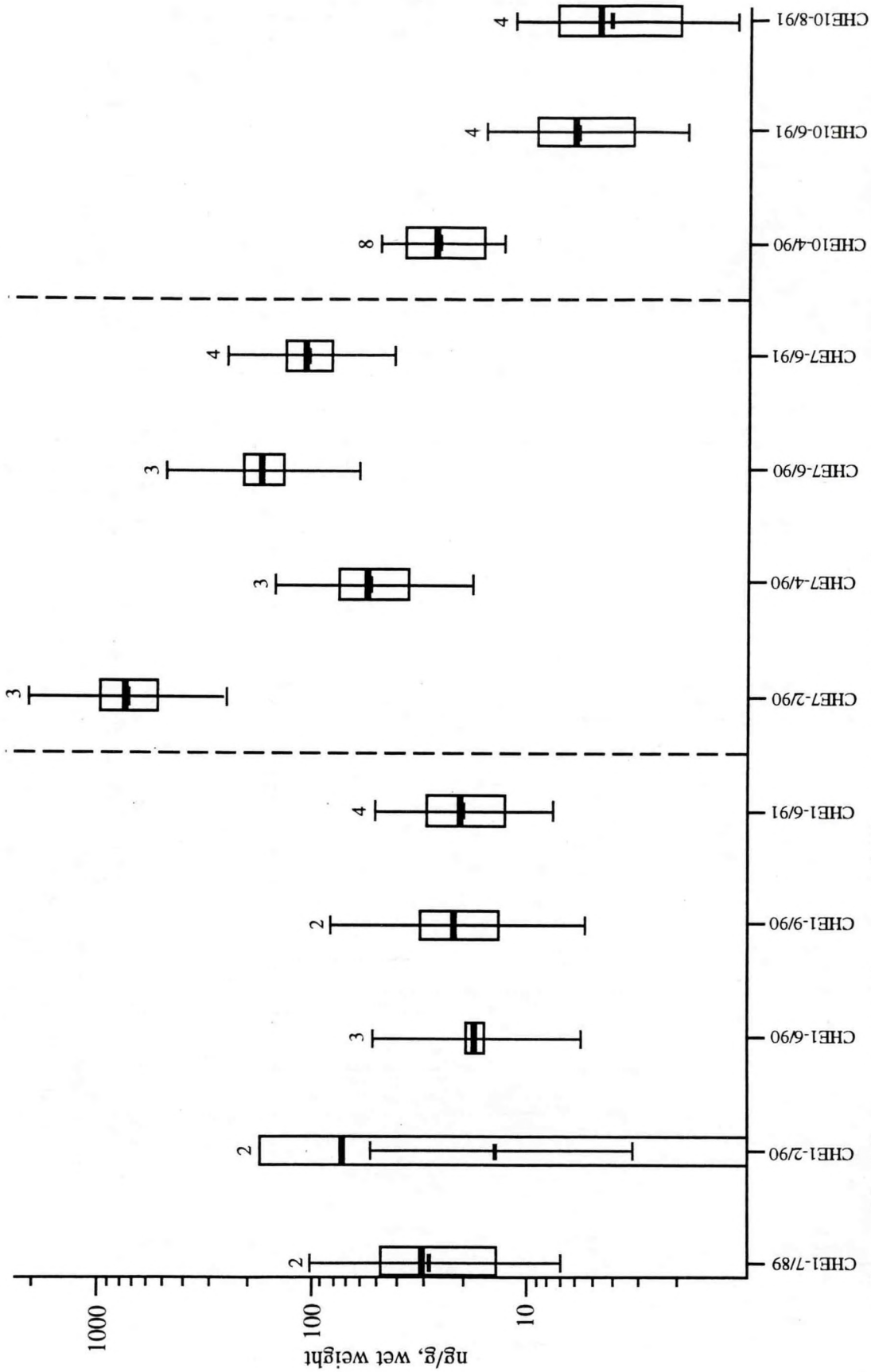

Figure 32. Mean concentrations and GT2 comparison intervals for total aromatic contaminants in Chenega Bay butter clams by station and year. Arithmetic mean [—] concentrations, (ng/g. wet weight) ± 1 standard deviation [□] and geometric mean [-] ± comparison interval [⊥], and number of samples written above the standard deviation box. Abbreviations are identified in Table 2.

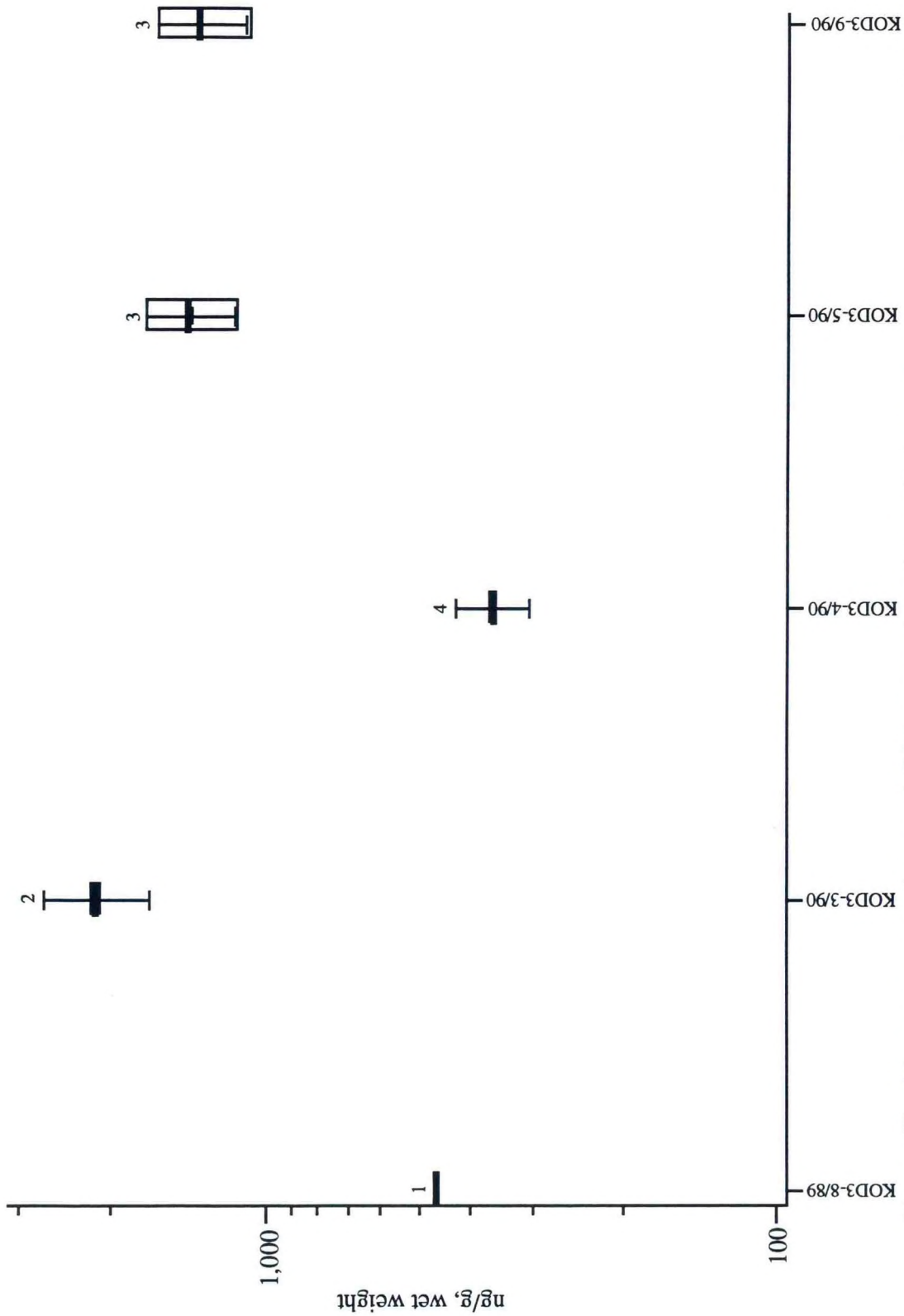

Figure 33. Mean concentrations and GT2 comparison intervals for total aromatic contaminants in Kodiak butter clams by station and year. Arithmetic mean [▬] concentrations, (ng/g. wet weight) ± 1 standard deviation [□] and geometric mean [–] ± comparison interval [⊥], and number of samples written above the standard deviation box. Abbreviations are identified in Table 2.

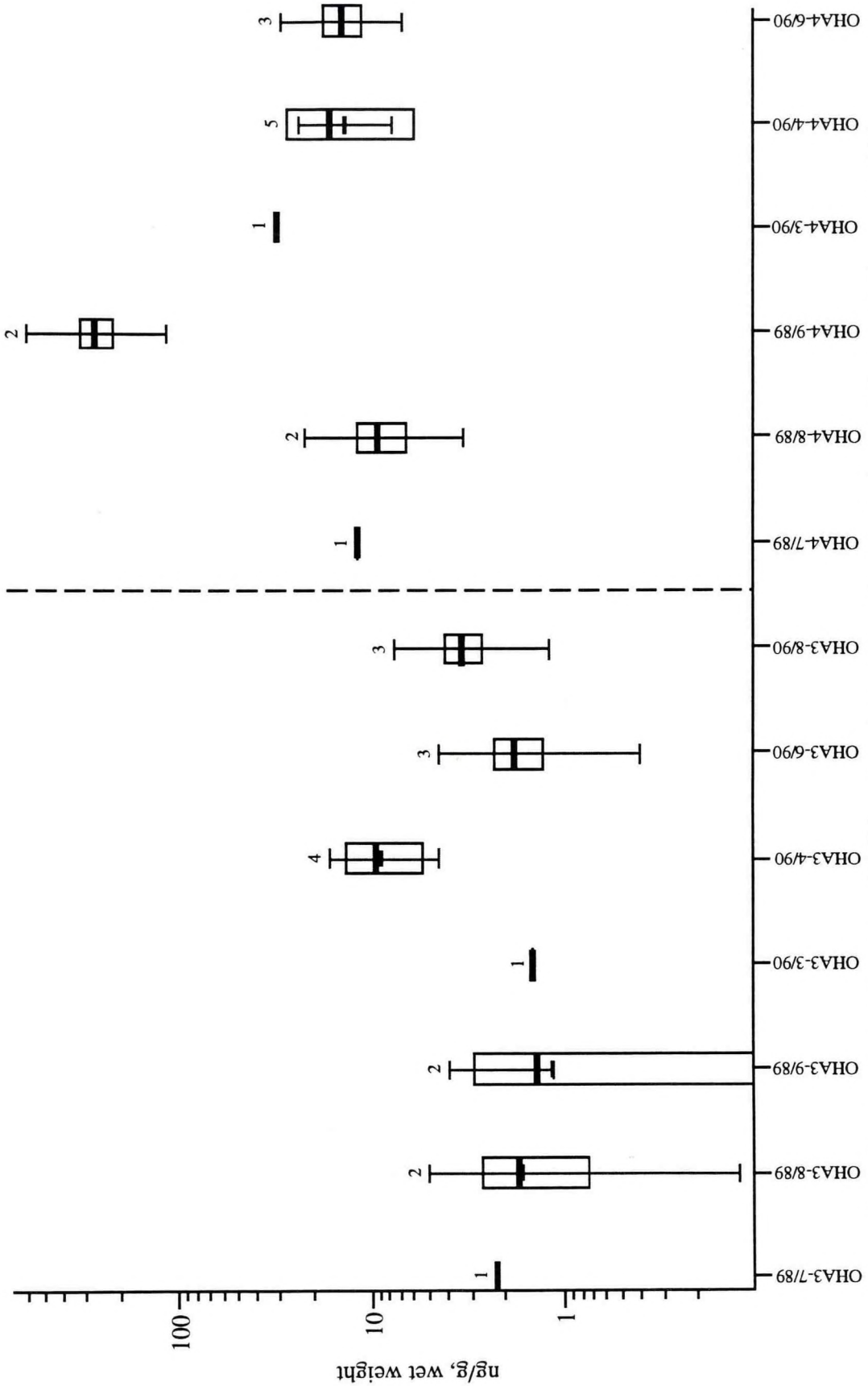

Figure 34. Mean concentrations and GT2 comparison intervals for total aromatic contaminants in Old Harbor butter clams by station and year. Arithmetic mean [—] concentrations, (ng/g. wet weight) ± 1 standard deviation [□] and geometric mean [-] ± comparison interval [⊥], and number of samples written above the standard deviation box. Abbreviations are identified in Table 2.

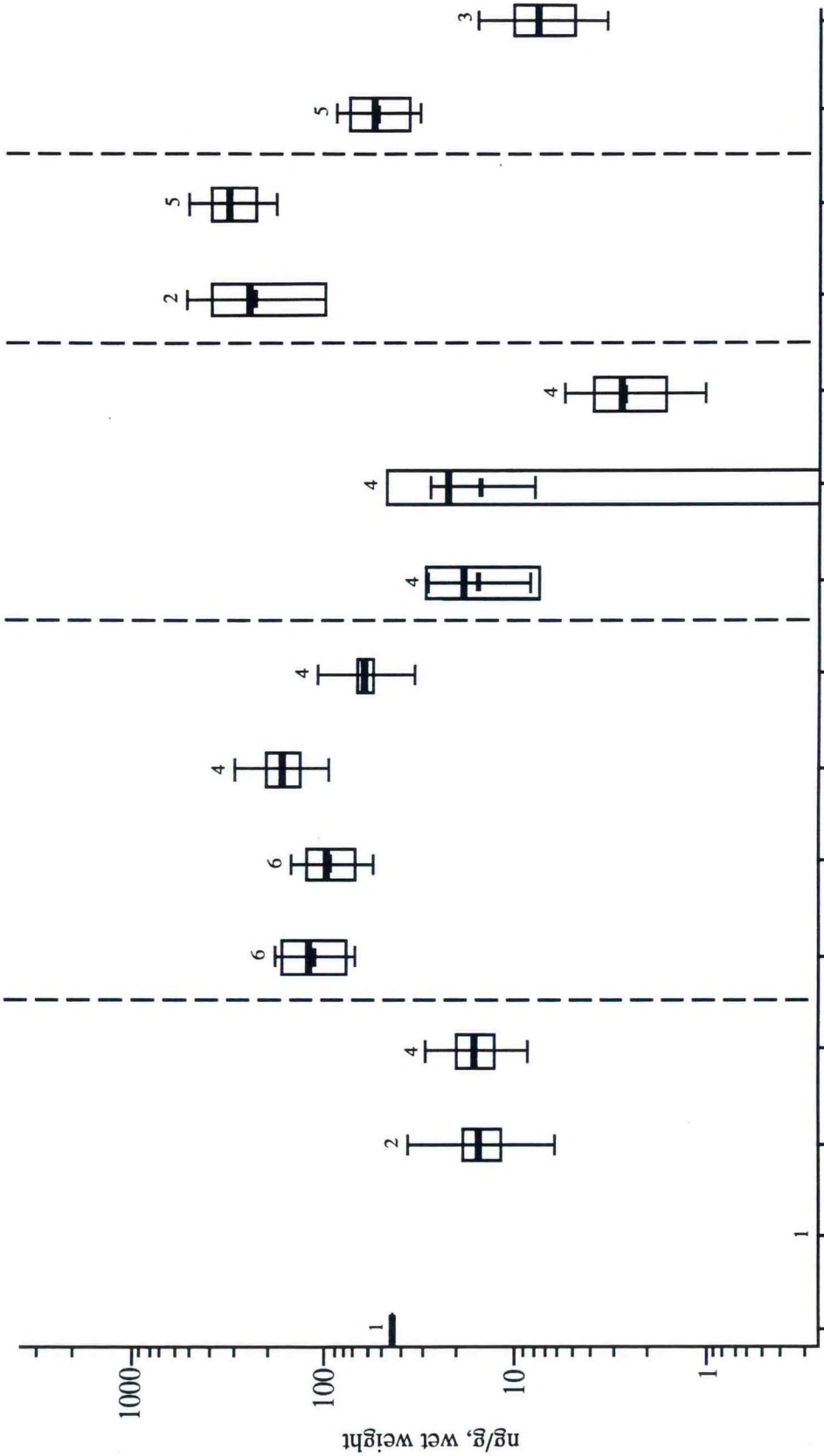

Figure 35. Mean concentrations and GT2 comparison intervals for total aromatic contaminants in littleneck clams by station and year. Arithmetic mean [▬] concentrations, (ng/g. wet weight) ± 1 standard deviation [□] and geometric mean [-] ± comparison interval [⌶], and number of samples written above the standard deviation box. Abbreviations are identified in Table 2.

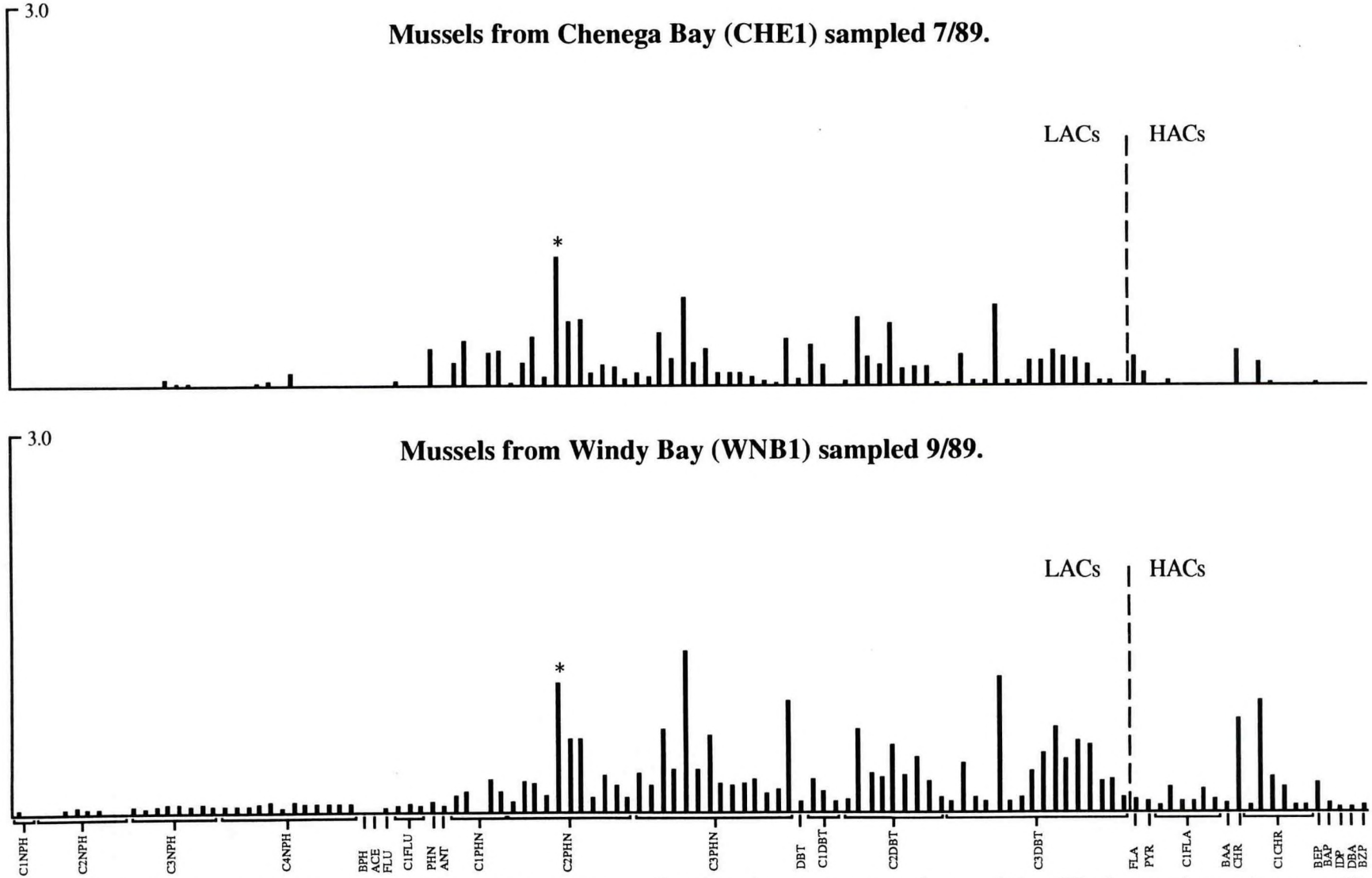

Figure 36. Isomer pattern graphs with peak areas normalized to the peak area of one of the C2-phenanthrene isomers(*) for mussels from CHE1 sampled 7/89 (sample no. 60-44) and WNB1 sampled 9/89 (sample no. 60-243). Abbreviations are in Table 1, except for biphenyl (BPH), anthracene (ANT), and benzo[e]pyrene (BEP).

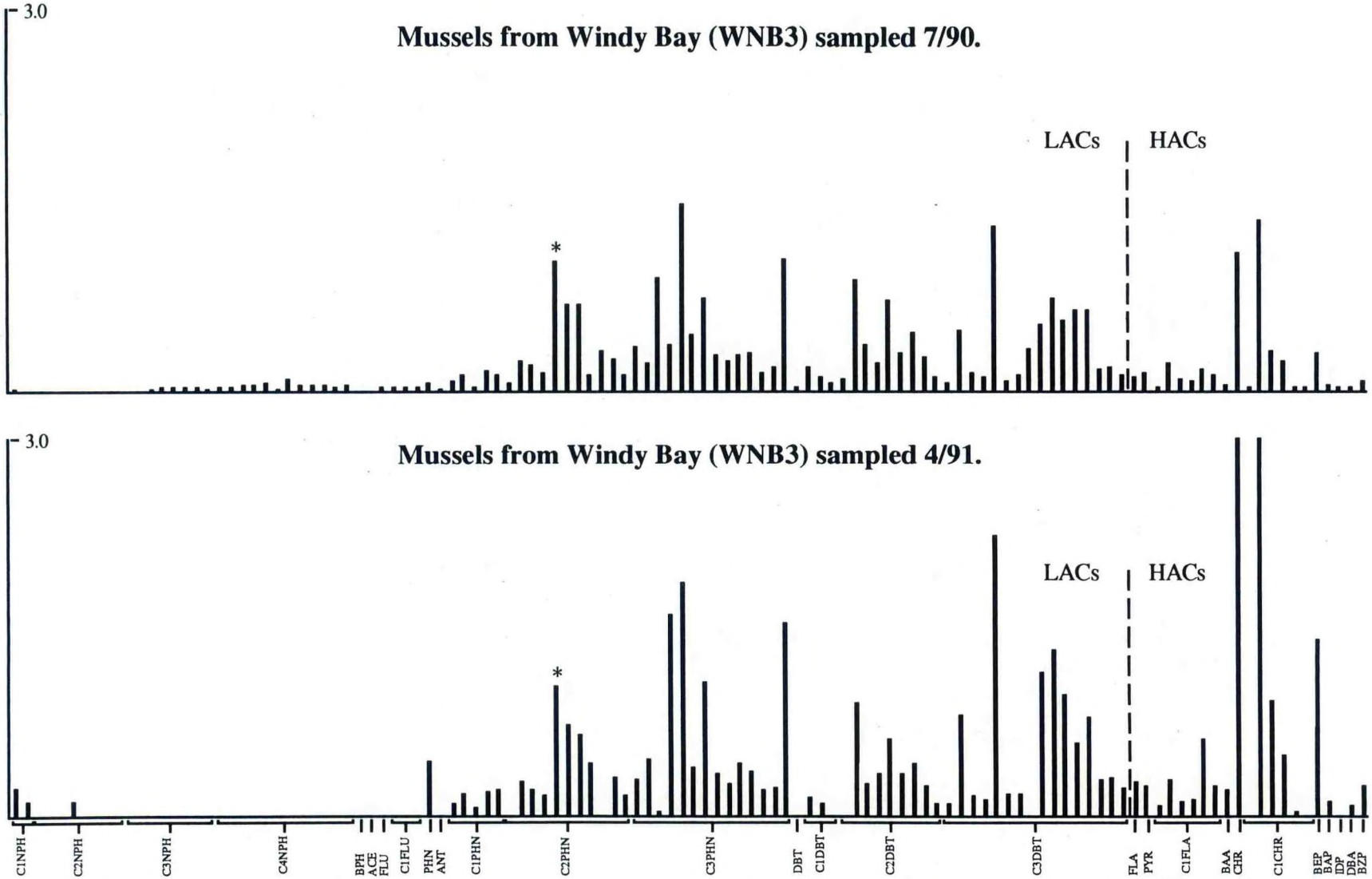

Figure 37. Isomer pattern graphs with peak areas normalized to the peak area of one of the C2-phenanthrene isomers(*) for mussels from WNB3 sampled 7/90 (sample no. 60-1733) and WNB3 sampled 4/91 (sample no. 60-2715). Abbreviations are in Table 1, except for biphenyl (BPH), anthracene (ANT), and benzo[e]pyrene (BEP).

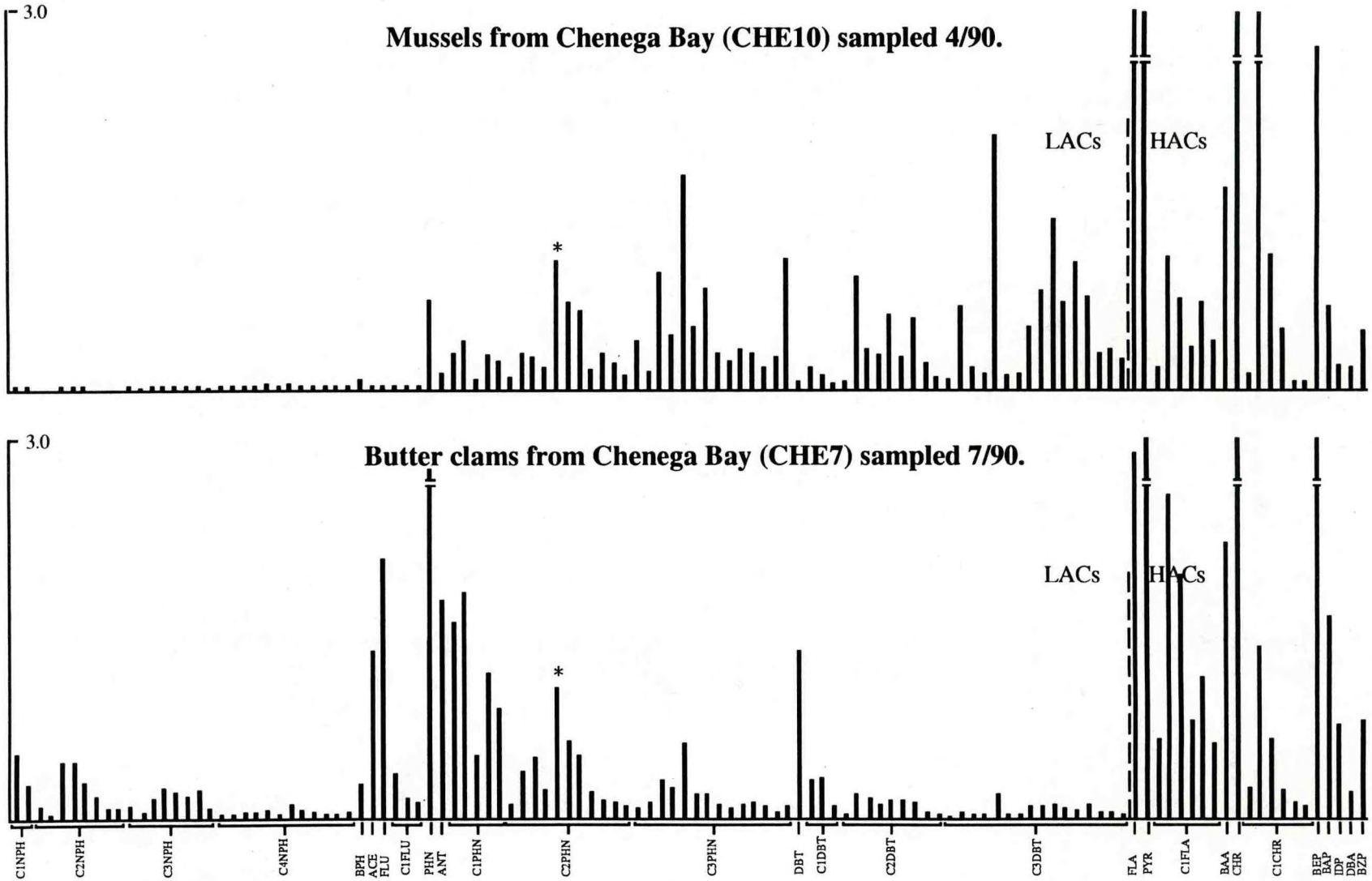

Figure 38. Isomer pattern graphs with peak areas normalized to the peak area of one of the C2-phenanthrene isomers(*) for mussels from CHE10 sampled 4/90 (sample no. 60-1514) and butter clams from CHE7 sampled 7/90 (sample no. 60-1753). Abbreviations are in Table 1, except for biphenyl (BPH), anthracene (ANT), and benzo[e]pyrene (BEP).

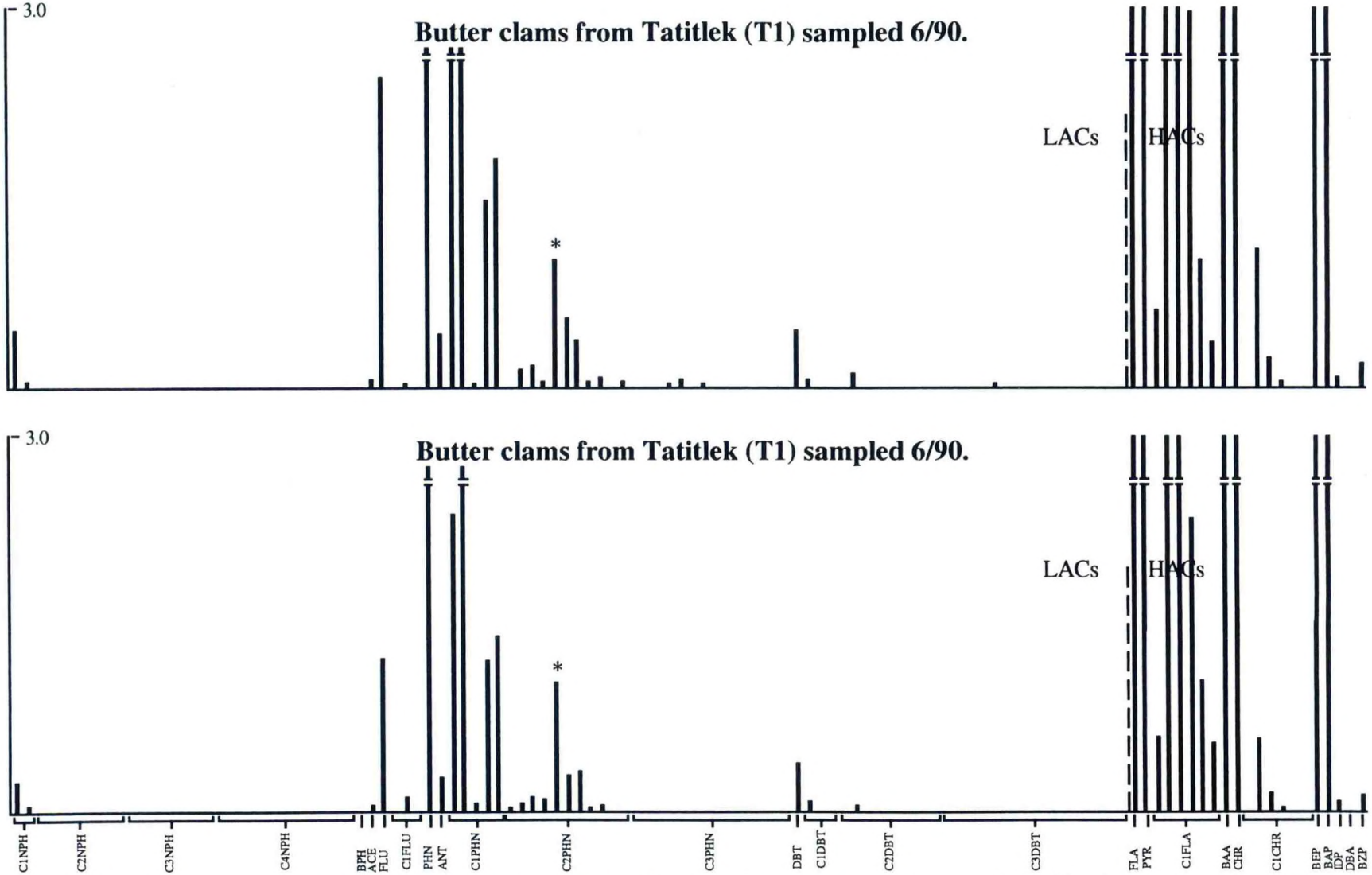

Figure 39. Isomer pattern graphs with peak areas normalized to the peak area of one of the C2-phenanthrene isomers(*) for butter clams from T1 sampled 6/90 (sample nos. 60-1597 and 60-1596). Abbreviations are in Table 1, except for biphenyl (BPH), anthracene (ANT), and benzo[e]pyrene (BEP).

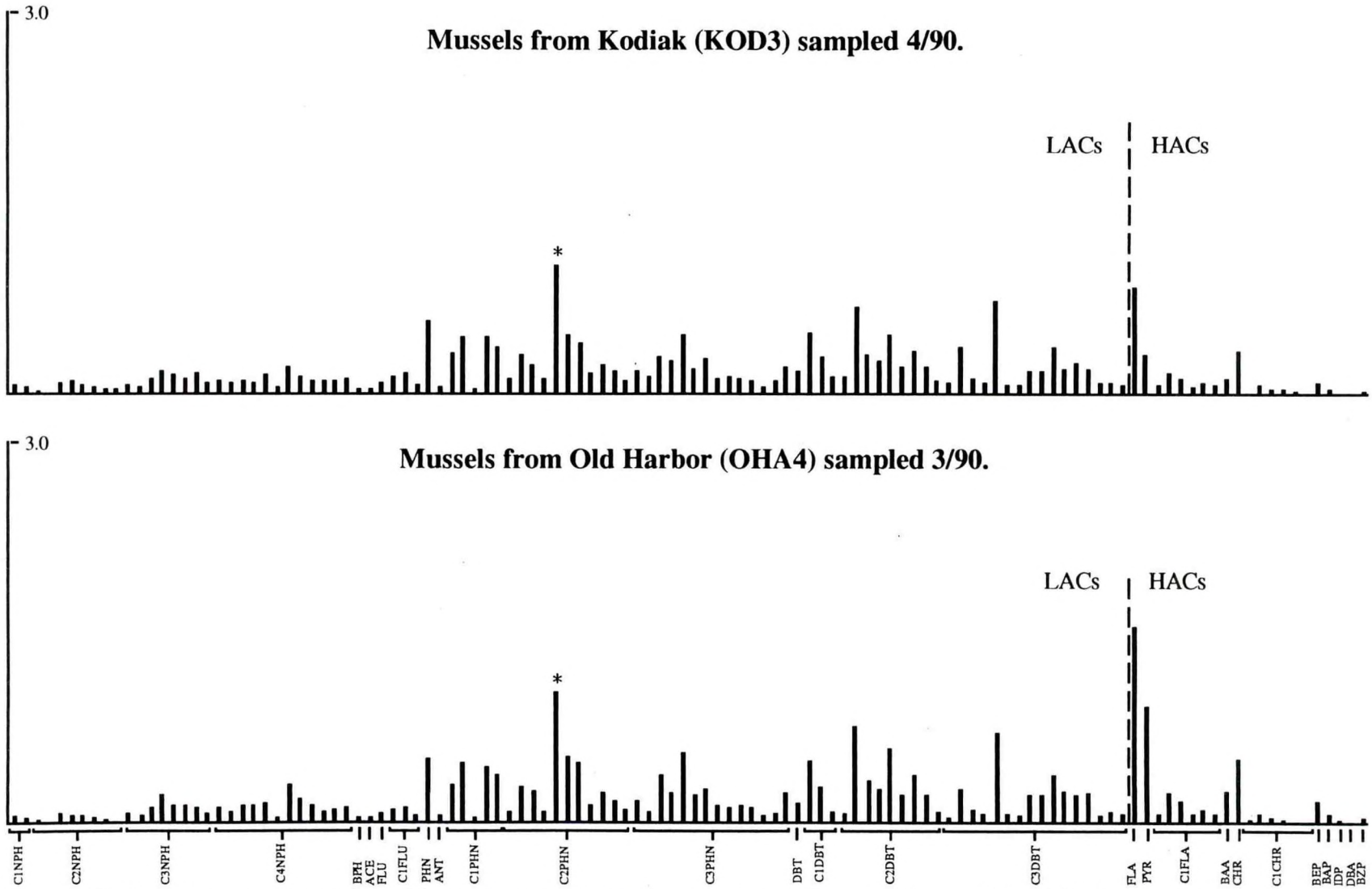

Figure 40. Isomer pattern graphs with peak areas normalized to the peak area of one of the C2-phenanthrene isomers(*) for mussels from KOD3 sampled 4/90 (sample no. 60-1846) and from OHA4 sampled 3/90 (sample no. 60-1158). Abbreviations are in Table 1, except for biphenyl (BPH), anthracene (ANT), and benzo[e]pyrene (BEP).

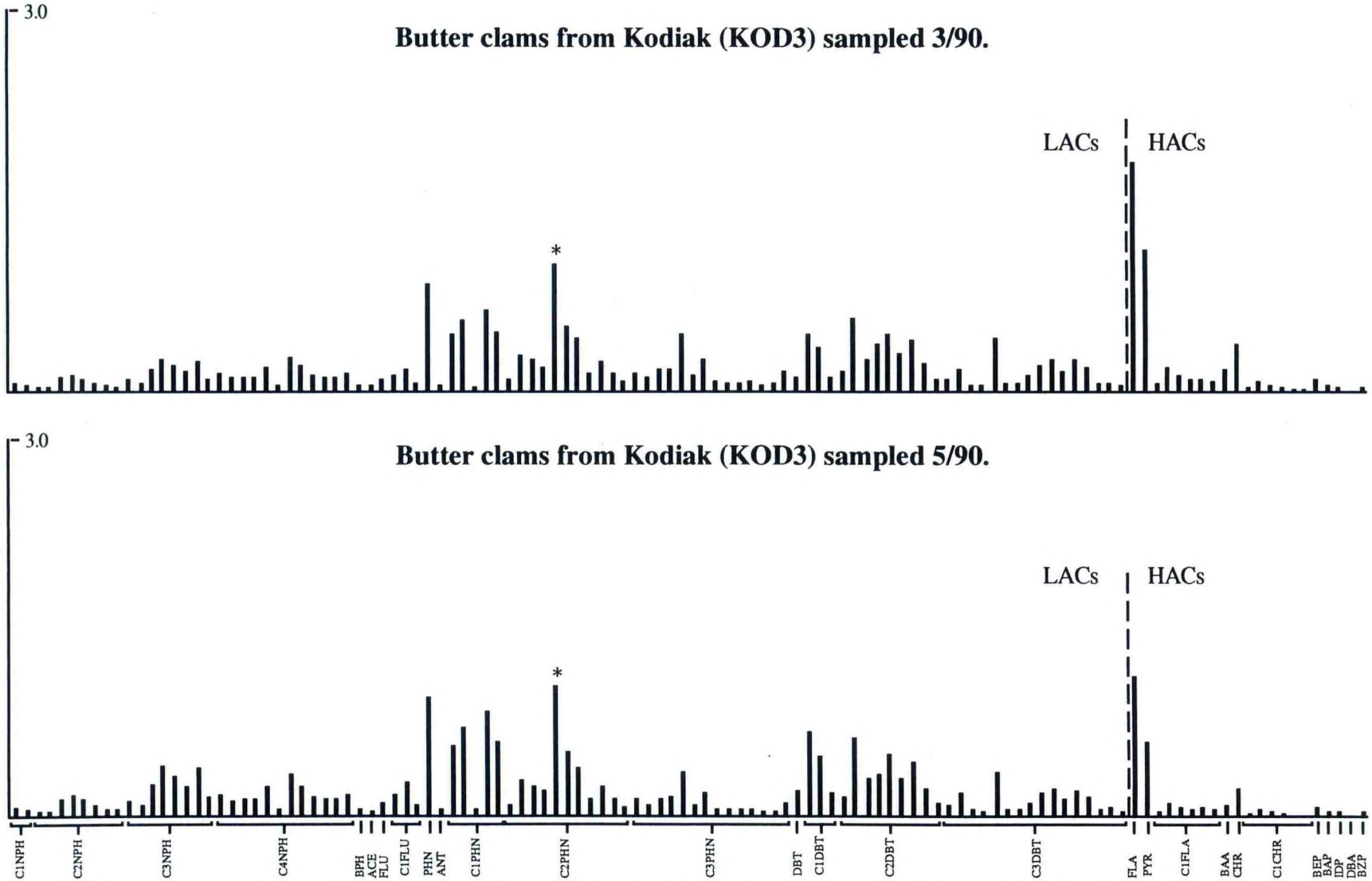

Figure 41. Isomer pattern graphs with peak areas normalized to the peak area of one of the C2-phenanthrene isomers(*) for mussels from KOD3 sampled 3/90 (sample no. 60-1157) and 5/90 (sample no. 60-1649). Abbreviations are in Table 1, except for biphenyl (BPH), anthracene (ANT), and benzo[e]pyrene (BEP).

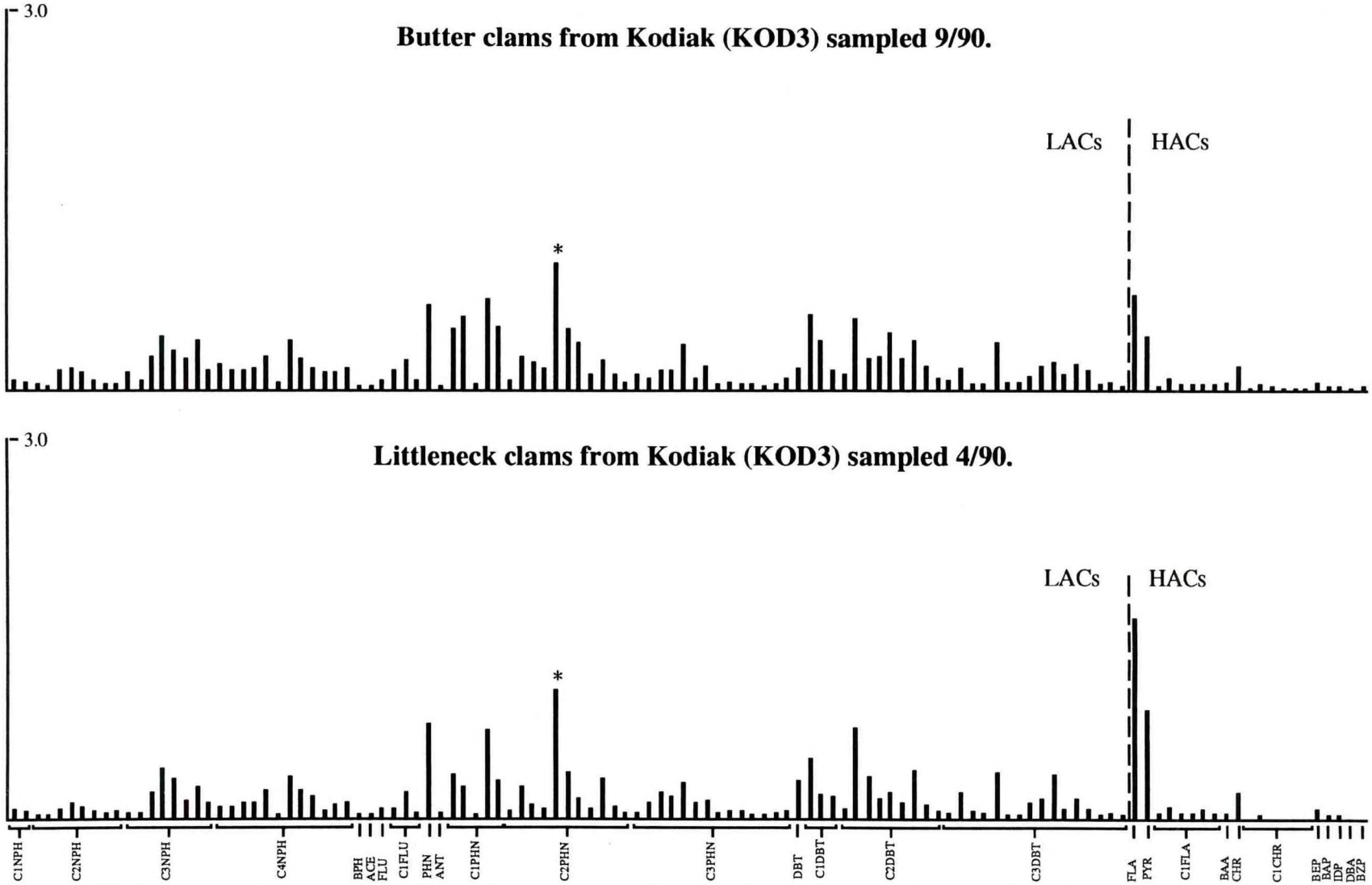

Figure 42. Isomer pattern graphs with peak areas normalized to the peak area of one of the C2-phenanthrene isomers(*) for butter clams from KOD3 sampled 9/90 (sample no. 60-2124) and littleneck clams from KOD3 sampled 5/90 (sample no. 60-1888). Abbreviations are in Table 1, except for biphenyl (BPH), anthracene (ANT), and benzo[e]pyrene (BEP).

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9 LEDGERWOOD, R. D., E. M. DAWLEY, P. J. BENTLEY, L. G. GILBREATH, T. P. POE, and H. L. HANSEN. 1993. Effectiveness of predator removal for protecting juvenile fall chinook salmon released from Bonneville Hatchery, 1991, 63 p. NTIS No. PB93-216315.

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