

# Sediment Quality in Depositional Areas of Shelikof Strait and Outermost Cook Inlet

## Final Report

U.S. Department of the Interior  
Minerals Management Service  
Anchorage, Alaska



**MMS**

Submitted By:  
Arthur D. Little, Inc.  
Cambridge, Massachusetts  
Contract No. 1435-01-97-CT-30830  
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**Arthur D Little**

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**Final Report**

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## List of Acronyms and Abbreviations

ACC	Alaska Coastal Current
ADL	Arthur D. Little, Inc.
AMS	Applied Marine Sciences
ANOVA	Analysis of Variance
APHA	American Public Health Association
ASTM	American Society for Testing and Materials
AVS	Acid-Volatile Sulfide
AWQC	Ambient Water Quality Criteria
B[a]PEq	Benzo[a]pyrene Equivalents
BPTCP	California State Bay Protection and Toxic Cleanup Program
CAB	Cellulose-Acetate-Butyrate
CIRCAC	Cook Inlet Regional Citizens' Advisory Council
CPI	Carbon Preference Index
CTD	Conductivity, Temperature, and Depth
CV	Coefficient of Variation
CVAAS	Cold Vapor Atomic Absorption Spectrometry
DCM	Dichloromethane
DDW	Distilled Deionized Water
DO	Dissolved Oxygen
DQO	Data Quality Objectives
DTT	Dithiothreitol
E&P	Exploration and Production
EDTA	Ethylene Diamine Triacetic Acid
EPA	U. S. Environmental Protection Agency
ERL	Effects Range-Low
ERM	Effects Range-Medium
EVS	EVS Environment Consultants
FAAS	Flame Atomic Absorption Spectrometry
FID	Flame Ionization Detector
FIT	Florida Institute of Technology
GC	Gas Chromatography
GC/MS	Gas Chromatography/Mass Spectrometry
GFAAS	Graphite Furnace Atomic Absorption Spectrometry
GLM	General Linear Model
GPC	Gel Permeation Chromatography
HCl	Hydrochloric Acid
HPLC	High-Performance Liquid Chromatography
ICP/MS	Inductively Coupled Plasma-Mass Spectrometry
ID	Inner Diameter
IHC	Immunohistochemical

IRM	Instrumental Reference Material
LALK	Lower Molecular Weight Alkanes
LCS	Laboratory Control Spike
MDL	Method Detection Limit
MMS	Minerals Management Service
MPN	Most Probable Number
MPS	Mean Percent Survival
MRL	Minimum Reporting Limit
NCS	Nitrogen-Carbon-Sulfur Analyzer
NIST	National Institute of Standards and Technology
NOAA	National Oceanic and Atmospheric Administration
NODC	National Oceanographic Data Center
N/P	Naphthalene/Phenanthrene Ratio
NRC	National Research Council of Canada
NTL	Northern Testing Laboratory
OCS	Outer Continental Shelf
OSI	Organism-Sediment Index
PAH	Polycyclic Aromatic Hydrocarbon
PCB	Polychlorinated Biphenyl
PERL	Pacific Ecorisk Laboratory
%REC	Percent Recovery
PHC	Petroleum Hydrocarbons
ppb	Parts Per Billion
ppm	Parts Per Million
ppt	Parts Per Trillion
‰	Parts Per Thousand
PVC	Polyvinyl Chloride
QA	Quality Assurance
QA/QC	Quality Assurance/Quality Control
QC	Quality Control
R/V	Research Vessel
RF	Response Factor
RGS	Reporter Gene System
RLU	Relative Light Unit
RPD	Relative Percent Difference
rpm	Revolutions Per Minute
RRF	Relative Response Factor
RSD	Relative Standard Deviation
S/T	Steranes/Triterpanes
SAOB	Sulfide Antioxidant Buffer
SD	Standard Deviation
SEM	Simultaneously Extracted Metals

SFBRMP	San Francisco Bay Regional Monitoring Program for Trace Sediments
SHC	Saturated Hydrocarbons
SIM	Selected Ion Monitoring
SKM	Susitna-Knik-Matanuska River System
SL	Standard Length
SNK	Student-Newman Keuls
SOD	Sediment Oxygen Demand
SOP	Standard Operating Procedure
SPI	Sediment Profile Imaging
SRM	Standard Reference Material
TALK	Total Alkanes
TBPF	Trading Bay Production Facility
TCDD	Tetrachlorodibenzo-p-dioxin
TEQ	Toxic Equivalents
TL	Total Length
TOC	Total Organic Carbon
TPHC	Total Petroleum Hydrocarbons
UCM	Unresolved Complex Mixture
USGS	United States Geologic Survey
V/V	Volume to Volume
WQC	Water Quality Criteria
WWTF	Wastewater Treatment Facility
ZGFAAS	Zeeman Graphite Furnace Atomic Absorption Spectrometry

## Executive Summary

### Background

Oil and gas exploration, production, and transportation activities in Cook Inlet, Alaska have the potential for impacting marine resources. Though these operations are well-managed and are regulated so as to minimize the input of pollutants to the marine environment, the longer-term accumulation of pollutants in depositional areas on the sea floor is an area of concern when contemplating future Outer Continental Shelf (OCS) leases.

After discharge, contaminants that are in a particulate form or which are sorbed to particles after discharge are rapidly diluted due to a large combined water flow from tidal, current, and riverine inputs of fresh and seawater. Though at low levels in the water column, a combination of oceanographic and sediment transport processes pointed to the lower Cook Inlet (Kamishak and Kachemak Bays) and Shelikof Strait as potential areas for this longer-term deposition of these sorbed pollutants.

Estimation of current impact and prediction of future environmental risk and impacts were complicated by the existence of multiple sources of similar pollutant assemblages to the region beyond exploration and production (E&P) operations. Natural oil seepages were common in the area and were known to represent an important part of the hydrocarbon assemblage in the sedimentary environments of areas of the Gulf of Alaska. Oil spillages, especially that from the *Exxon Valdez* spill, were potential contributors, though no evidence of the impact of this spill, in particular, was observed in the subtidal sediments of Cook Inlet or Shelikof Strait. Tremendous quantities of suspended material were swept into the region from glacial runoff with associated metals and hydrocarbons. Municipal discharges and other permitted industrial (e.g., seafood processing) discharges contributed important quantities of wastes over time to the immediate coastal areas and presumably to the area's deeper depositional locations.

### Study Rationale

Because of the need to definitively examine the distribution and environmental risk of anthropogenic chemicals (i.e., metals, petroleum hydrocarbons including polynuclear aromatic hydrocarbons [PAHs]) in advance of any future oil and gas E&P activities that could potentially affect the lower Cook Inlet and Shelikof Strait, MMS contracted with Arthur D. Little, Inc. (ADL) to undertake a two-year study in the region.

The objectives of the study were to:

- Evaluate the Shelikof Strait and outermost Cook Inlet as potential depositional areas or "traps" for oil industry contaminants
- Determine whether contaminant concentrations in sediments of these areas pose an environmental risk
- Determine whether contaminants in these areas have accumulated relative to pre-industry concentrations

- Determine whether any increases can be correlated with specific discharge events or activities (e.g., the *Exxon Valdez* oil spill)
- Determine the importance of other hydrocarbon and metal sources to the sediments

The study objectives were recast in a risk assessment-type framework (U.S. EPA; EPA/630/R-95/002, *Draft Proposed Guidelines for Ecological Risk Assessment*). In this framework a formulation of the problem leads to a characterization of exposure and effects, which in turn leads to a characterization of the risk. This program was structured to follow that approach to meeting the goals.

In designing an investigation to meet these goals, ADL and its team members put forth several hypotheses for scientific testing. These hypotheses were:

- Hypothesis 1: The offshore area of outermost Cook Inlet and Shelikof Strait is not a trap for organic and metal pollutants (i.e., there is no indication of deposition)
- Hypothesis 2: Concentrations of organic and metal contaminants in sediment cores do not show increases since before offshore oil exploration and production began in Cook Inlet (circa 1963)
- Hypothesis 3: Compositions of organics and metals in sediment cores do not show changes in composition since before offshore oil exploration and production began in Cook Inlet (circa 1963)
- Hypothesis 4: Concentrations of organic and metal contaminants in outermost Cook Inlet and Shelikof Strait do not pose any environmental risk

The field program was designed to collect data to test these null hypotheses. Hypotheses are stated as the null hypotheses since the null hypotheses were tested during the statistical analyses.

### **Field Program Design**

The design of the data acquisition/field program for the two-year study focused on two facets. The first was the deep subtidal bottom sediments of the region as the focal point of any long-range contaminant deposition. The design was intended to obtain both chemical (i.e., exposure) and biological (i.e., effects) data on surface sediments. It also was directed at looking at historical deposition in the study area through the use of dated sediment cores. The second facet addressed the status of chemical body burdens in bottom-feeding fish and indicators of sublethal effects. These "biomarker" measurements were made to address their exposure to contaminants.

The field sampling design included:

- Separation of the study area into four zones, each assumed to be relatively homogeneous
- The selection of a group of random sediment stations in each zone from a large number of candidate stations, each station representing a replicate of that zone
- The selection of fixed or biased stations at key locations from which we wanted to obtain data
- The selection of a limited number of stations from each zone (including the fixed

- stations) from which to take replicates to examine within-station variability
- The selection of additional sampling stations in the Gulf of Alaska off the Kenai Peninsula to represent "upstream" source material
- The selection of additional stations south of Shelikof Strait to examine longer-range transport
- The field-truthing of the suitability of each station prior to sampling
- The sampling of stations for surface sediments; selected locations for sediment coring; and selected locations for obtaining fish samples
- The selection and sampling of potential contaminant sources -- oil seeps; river runoff; coal seams; and oil and gas operational discharges

## Analytical Design

The analytical design centered on organic (i.e., petroleum-related) and metal parameters as measured in sediment, sediment core, fish tissue, and source samples. The design consisted of the following measurements:

- Petroleum hydrocarbons (PHC), including PAHs of petroleum and other origins, and steranes/triterpanes (S/T) in sediments and PAHs in fish tissue
- The use of detailed alkylated PAHs and S/T to elucidate source characteristics of source samples and source identification in the field samples
- Major and trace metals including silver, aluminum, arsenic, barium, beryllium, calcium, cadmium, chromium, copper, iron, mercury, potassium, manganese, magnesium, nickel, lead, antimony, selenium, tin, thallium, vanadium, and zinc in sediments
- Acid volatile sulfide/simultaneously extracted metals (AVS/SEM) in sediments (Year 1 only)
- All metals except calcium, potassium, magnesium, and nickel in fish tissues
- Amphipod toxicity tests in sediments
- Reporter gene system (RGS) P450 measurements for sediment and fish tissue extracts
- Cytochrome P450 (CYP1A) induction determinations on selected tissues
- Dating of sediment cores by <sup>210</sup>Pb and <sup>137</sup>Cs methods and analysis of core sections for hydrocarbons and metals as in the surface sediments
- Sediment profile imagery (SPI) of surface sediments (Year 1 only)

## Findings

The analysis of the findings was used to perform tests of the study's four hypotheses, using field data from 1997 and 1998. The outcomes of this hypothesis testing are as follows:

- *Potential for contaminant deposition in the study area.* In summary, in the context of the null hypothesis, **the surface sediments of outermost Cook Inlet and the Shelikof Strait are traps for fine-grained sediment and are potential traps for contaminants from oil and gas production activities in upper Cook Inlet.** However, based on evaluations of the organic and inorganic data, no contamination in the surface sediments from oil and gas production activities in upper Cook Inlet was identified. Elevated Hg concentrations were identified in Kachemak Bay. However, the present-day Hg levels are

comparable to values observed throughout the twentieth century, suggesting that the Hg results are typical for the region.

- *Contaminant depositional changes over time.* In summary, in the context of the null hypothesis, **the concentrations of metals and organics (i.e., PAHs) in sediments in outermost Cook Inlet and Shelikof Strait have not increased significantly since offshore oil exploration and production began in Cook Inlet (circa 1963).**
- *Compositional changes over time.* In the context of the null hypothesis, **the composition (source[s]) of metals in the sediments of outermost Cook Inlet and Shelikof Strait do not appear to have changed since offshore oil exploration and production began in Cook Inlet (circa 1963). The composition of hydrocarbons in sediment cores shows subtle changes in outermost Cook Inlet over the past 25 to 50 years, but these changes do not appear to be correlated with petroleum production activities or spills.**

The study of the magnitude of sediment deposition from the major rivers in the region (i.e., Susitna-Knik-Matanuska; Copper River) indicates that the Copper River accounts for 10 to 20 percent of the total sediment deposited in the study area.

- *Assessment of risk.* The two sampling seasons have provided a picture of contaminants and potentially toxic trace substances in the environment at very low concentrations with an attendant low biological risk. Using multiple measures of risk that were built into the study design, we conclude that **the concentrations of organics (i.e., PAHs) and metals do not appear to pose any immediate ecological risk to the marine environment in the study area.**

The concentrations of trace metals are consistently below the risk levels identified by Long and Morgan (1995), except for Ni, which has a crustal abundance higher than the designated effects range-low (ERL) and effects range-medium (ERM) concentrations, and Cu. Concentrations of Cu exceeded the ERL in a number of cases, but source sediment from the Susitna River along with Alaskan rocks, show that natural levels of Cu are all close to or above the ERL value.

The concentrations of PAH detected in sediments are also below the ERL identified by Long and Morgan (1990).

The P450 RGS results also indicated low to negligible biological risk associated with extractable organic compounds, namely PAH, in the sediments. Sediment bioassays with two species of amphipods indicate that sediment chemicals do not exhibit any significant toxicity. Some low survival rates appear to be related to testing sediments with high silt content rather than any trace chemicals in the sediments.

The levels and patterns of induction of CYP1A in cells of bottom-dwelling fish (i.e., Halibut and Pacific Cod) are consistent with some mild induction by contaminants, but with weak induction in the gills they appear not to be waterborne, but rather from the diet.

None of the measured contaminants in the fish tissues correlated with CYP1A induction, but chlorinated hydrocarbons were not measured. Specifically, the results on the hepatocytes and the kidney cells are consistent with some low level of enzyme-inducing compounds in the diet of these fish. There were no significant correlations between the CYP1A scores and the locations (i.e., zones) of the fish.

In summary, using multiparameter measures to assess potential exposure and potential risk, the comprehensive findings of this two-year investigation indicate that **the current concentrations of metals and PAHs in the Shelikof Strait and Outermost Cook Inlet are neither linked to oil and gas development in the upper Cook Inlet, nor to the Exxon Valdez oil spill. The residues that are present, from a combination of natural sources -- river inputs, oil seepages, etc. -- pose no significant risk to the biota and the benthic environment of outermost Cook Inlet and Shelikof Strait.** The degree of current risk is indeed very low and is similar to non-impacted coastal regions in Alaska and elsewhere.

## 1.0 Introduction

The Minerals Management Service (MMS) program "Sediment Quality in Depositional Areas of Shelikof Strait and Outermost Cook Inlet," consisted of a two-year study whose hypotheses and objectives are explored in this report. As part of this study, a scientific crew on board the Research Vessel (R/V) *Alpha Helix*, collected samples for biological, chemical, and toxicological analyses from the program study area during two sampling surveys. The first survey was conducted from July 7 to July 17, 1997 and the second undertaken the following year, from June 27 to July 5, 1998. In this report, the final results including the field sampling and analytical methods are summarized, and the results and interpretation of the chemical, biological, and physical measurements from both the 1997 and 1998 field surveys are presented.

### 1.1 Background

The purpose of this two-year study was to provide and update environmental information to support future MMS oil- and gas-leasing decisions in the outermost Cook Inlet/Shelikof Strait planning area. Such uses of this information include environmental risk assessments, environmental impact statements, and other pre- and post-leasing decision documents. This study was initiated to establish baseline environmental conditions prior to any oil- and gas-leasing activities. The results of the entire two-year field survey data are described in this report.

The literature on the study area has been reviewed and summarized as part of this program (Boehm *et al.*, 1998) and an excerpt appears below.

#### 1.1.1 Physical Setting

Cook Inlet is a large tidal estuary, 350 km long and ranging from 20 to 90 km wide. The average water depth is approximately 60 m, varying from 100 m near the entrance to less than 20 m near the head of the estuary (Arthur D. Little, 1995). It is bordered on the west and northwest by the Alaska Range, on the northeast by the Talkeetna Mountains, and on the southeast by the Kenai-Chugach Mountains. Cook Inlet can be divided into three distinct regions: the head, consisting of Knik and Turnagain Arms; upper Cook Inlet, extending from the Forelands to Point Woronzof; and lower Cook Inlet, from the Forelands to the Gulf of Alaska. Outermost Cook Inlet, as defined by the area encompassing both the Kachemak and Kamishak Bays, from Cape Douglas to the Barren Islands in the Gulf of Alaska, is the potential depositional area on which this study focused.

Shelikof Strait is a marine channel situated between the Kodiak Island archipelago and the Alaska Peninsula. Shelikof Strait is approximately 200 km long and 50 km wide. A central trough extending beyond both ends of Shelikof Strait characterizes the sea floor, which has a gradually southwest-sloping central platform bordered by narrow marginal channels. Currents bring sediment into the northwest end of the strait from Cook Inlet, near Cape Douglas, depositing a covering of well stratified sediment throughout the depositional areas of the strait. The complex oceanography and biology of the outermost Cook Inlet and Shelikof Strait are described in detail in the literature study (Boehm *et al.*, 1998) and summarized briefly below.

### 1.1.2 Oceanography

Interactions of tides and geostrophic, baroclinic, and wind-induced currents with the topography of outermost Cook Inlet and Shelikof Strait provide a complex hydrographic regime that determines the distribution and eventual deposition of particle-associated contaminants released from offshore production platforms in upper Cook Inlet (Hampton *et al.*, 1987). Vigorous, tidal-induced mixing results in strong initial dilution of contaminant inputs at their sources with naturally derived terrigenous materials. The main sources of these natural sediments are several large, glacially influenced rivers emptying into upper Cook Inlet, while, farther south and east in the Inlet and in Shelikof Strait, the Copper River to the east of the study area is the predominant source of suspended sediments. These suspended sediments are transported by the Kenai Current (the Alaska Coastal Current [ACC]) along the Kenai Peninsula into lower Cook Inlet and Kachemak Bay, as well as Shelikof Strait (Hampton, 1985).

The import of inshore flow to Cook Inlet-Shelikof Strait is through the Kennedy and Stevenson Entrances, while offshore flow occurs through these passages as well as the lower end of Shelikof Strait. With the slackening of prevailing winds during the summer months in the Gulf of Alaska, the strong onshore convergence relaxes. As a consequence, cold, nutrient-rich water is upwelled onto the shelf (Strickland and Sibley, 1984) and can be observed in the general area of the passages on either side of the Barren Islands. This upwelled water supports high gross biological productivity in the study area. A large, clockwise gyre develops in eastern Cook Inlet offshore of Kachemak Bay, although net flow is to the southeast through outermost Cook Inlet.

In Shelikof Strait, net flow is also strongly to the southeast; however, mesoscale eddies have also been documented in the surface waters in the northeast portion of Shelikof Strait (Schumacher *et al.*, 1993; Bogard *et al.*, 1994). The main sediment deposition sites in the study areas are the shallows of Kamishak Bay (for sediments transported down the western side of Cook Inlet), Kachemak Bay (with a strong component of Copper River sediments), and some deeper portions of outermost Cook Inlet and Shelikof Strait (Hampton *et al.*, 1987). Other possible sites of sediment deposition of platform materials from upper Cook Inlet include glacier-incised scars in the Kodiak shelf, the shelf slope, and shallow bays on either side of Shelikof Strait. However, local sources become increasingly important with distance from the upper Cook Inlet, and sills limit the depths from which suspended materials may be imported.

### 1.1.3 Biology

The northern shelf of the Gulf of Alaska is extremely productive, and annual primary productivity in outermost Cook Inlet is greater than  $300 \text{ g C m}^{-2}$  (Sambrotto and Lorenzen, 1987). The intrusion of cold, nutrient-rich water brought by the ACC into outermost Cook Inlet in late spring and summer, combined with long days, supports vigorous biological activity in the oceanic regime from phytoplankton growth through baleen whale foraging. The Cook Inlet/Shelikof Strait area contains a great variety of biological habitats. Shallow intertidal and subtidal areas are predominantly unconsolidated sediments containing mainly polychaetes, bivalves, crustaceans, and echinoderms (O'Clair and Zimmerman, 1987; Feder and Jewett, 1987). These habitats also support a rich variety of algae and epibenthic invertebrates, and are frequented by nekton, pelagic fishes, nearshore demersal fishes (Rogers *et al.*, 1986), a variety of seabirds, and several species of marine mammals. Rocky habitat is much less common in Cook

Inlet and Shelikof Strait, although it predominates on Kodiak Island. The rocky intertidal habitats are dominated by barnacles, limpets, mussels, and snails, a rich variety of attached algae, other invertebrates, and associated semidemersal fishes (O'Clair and Zimmerman, 1987). The deeper neritic environments are dominated by typical pelagic and nektonic communities, and overlay important benthic environments in the finer unconsolidated sediments, including those expected to be depositional areas for platform-derived contaminants (Hampton *et al.*, 1987). Here the communities are also dominated by polychaetes, crustaceans, echinoderms, and bivalves with a variety of demersal, semidemersal, and associated pelagic fishes. The peculiarities of sediment transport put the main depositional areas for platform-derived contaminants in both shallow water embayments (e.g., Kamishak Bay) and deeper open waters (deeper portions of outermost Cook Inlet, bottom of Shelikof Strait, and shelf slope).

## 1.2 Objectives

Due to the need to definitively examine the distribution and environmental risk of anthropogenic chemicals (i.e., metals, petroleum hydrocarbons) in advance of any future oil and gas E&P activities that could potentially affect the lower Cook Inlet and Shelikof Strait, MMS established a multi-disciplinary sediment quality evaluation program for the region. The objectives of the overall MMS program were to evaluate:

- The Shelikof Strait and outermost Cook Inlet depositional areas as traps for oil-industry contaminants.
- Whether the contaminant concentrations in sediment of these areas pose an environmental risk.
- Whether contaminants in these areas have accumulated relative to pre-industry concentrations and to determine whether any increases can be correlated to specific discharge events or activities (e.g., the *Exxon Valdez* spill).

### 1.2.1 Null Hypotheses

Based on the objectives of the program, four null hypotheses were developed. These null hypotheses were finalized at technical meetings held in May 1997 between the Arthur D. Little team, MMS, industry and regulatory representatives (e.g., UNOCAL, Alaska Department of Fish and Game, and U.S. Environmental Protection Agency [EPA]), and other interested parties (e.g., Cook Inlet Regional Citizens' Advisory Council [CIRCAC]).

The hypotheses which form the scientific framework for the study are as follows:

- Hypothesis 1: The offshore area of outermost Cook Inlet and Shelikof Strait is not a trap for organic and metals pollutants (i.e., there is no indication of net deposition).
- Hypothesis 2: Concentrations of organic and metal contaminants in sediment cores do not show increases since offshore oil exploration and production began in Cook Inlet (circa 1963).

- Hypothesis 3: Compositions of organics and metals in sediment cores do not show changes in composition (i.e., cannot be correlated with known sources, such as the *Exxon Valdez* oil spill residues) since offshore oil exploration and production began in Cook Inlet (circa 1963).
- Hypothesis 4: Concentrations of organic and metal contaminants in outermost Cook Inlet and Shelikof Strait do not pose an ecological risk to marine organisms as defined by sediment toxicology measurements (i.e., compared to reference sediments), sediment quality criteria, and fish P-450 response.

The study design centered on the testing of these hypotheses. The first year's effort in 1997 focused on sediment quality across the study area. Potential uptake of contaminants by bottom-dwelling fish and resulting indicators of exposure to contaminants were also evaluated by analyzing fish collected from each zone. Based on these results, a number of recommendations were made to enhance the following year's survey in 1998. These included additional source sampling, expansion of the fish species collected, sampling for hydrocarbon degrading microbes, and extending the sampling region to investigate the potential depositional area to the south of Shelikof Strait. In this report, we evaluate the specific objectives and hypotheses based on the entire field survey data.

## **2.0 Methods**

In this section, the methods used in field sampling, field measurements, and laboratory analyses are described.

### **2.1 Field Methods and Study Design**

#### **2.1.1 Study Design**

The program study area was identified as outermost Cook Inlet and Shelikof Strait of Alaska. The term "outermost Cook Inlet" has been used to avoid confusion with the lower Cook Inlet salmon district north of the study area. The study encompassed two separate field surveys, the first undertaken in 1997 and the second in 1998. For purposes of the scientific program, five regions or zones within the study area were defined as indicated in Figure 2-1. The first zone (zone 0) was outermost Cook Inlet, including the region from Anchor Point across to approximately Mt. Chinitna, and from the lower tip of Kenai Peninsula to the Barren Islands and across to Cape Douglas. Zone 1 was defined as North Shelikof Strait, stretching from the Barren Islands and Cape Douglas down to the mid-section of Afognak Island (Cape Paramanof) and across the Alaska Peninsula. Zone 2 was defined as the mid-Shelikof Strait region, from the mid-section of Afognak Island (Cape Paramanof) to Hallo Bay on the Alaska Peninsula, and down to Uganik Bay on Kodiak Island and Katmai Bay on the Alaska Peninsula. Zone 3 was defined as the south Shelikof Strait region, stretching down from zone 2 to the widening area of the strait as indicated in Figure 2-1. Finally, zone 4 was added during the 1998 survey and extended to the south of zone 3, just southeast of Kodiak Island.

Stations for sediment sampling were composed of random and fixed stations. The locations of the sampled random and fixed stations are provided in Table 2-1 and shown in Figure 2-1. In zones 1, 2, and 3 (Shelikof Strait), 15 random and 2 fixed stations were sampled in 1997, while 6 random and 2 fixed stations were sampled in each of these zones in 1998. In zone 0 (outermost Cook Inlet), 8 fixed stations were sampled during each of the 1997 and 1998 surveys. Only fixed stations were selected from outermost Cook Inlet due to the limited area where potential depositional environments could be identified (i.e. mud or silt/clay bottom). Three fixed stations were sampled in zone 4, exclusive to the 1998 survey.

Random stations were selected in zones 1, 2, and 3 by establishing a 5-km grid within the 50 fathom depth contour of each zone. This grid resulted in more than 100 blocks fully contained in each zone. Each block within a zone was sequentially numbered. Random numbers were then generated to identify the random stations within each zone. The first 15 stations randomly identified in each zone that contained silt/clay sediment, based on historical data, were established as the primary random stations. The station location was positioned in the center of the random block selected. An additional 10 alternate stations in each zone were identified in the same manner. The selection criteria for alternate stations were defined so that the next closest alternate station was selected if sampling at any random or fixed station was unsuccessful (did not contain silt/clay sediment). At each location, a grab sample was collected to determine if the station sediment was acceptable for sampling. A sediment sample was considered acceptable if it contained greater than 50 percent silt/clay (i.e., mud). The percent silt/clay was estimated by

visual observation of the sediments. If the sediment sample was not acceptable, repeat grabs were attempted at the station, but no more than three attempts were performed. If after repeated grab attempts the station was deemed unacceptable, the next closest alternate station was selected from the list in the sampling and logistics plan (Arthur D. Little, 1997a).

Several alternate stations were sampled during the course of the survey due to inappropriate bottom substrate. In Table 2-1, the alternate stations sampled and the rationale for requiring an alternate station selection are included. The two fixed stations in zones 1, 2, and 3 were selected in deep "holes" that contained depositional sediment. The three fixed stations in zone 4 were selected in deep areas where fine-grained depositional sediment was likely to occur.

The eight fixed stations in zone 0 were selected to obtain representative spatial coverage within the zone (e.g., Kachemak Bay, Kamishak Bay, and Kennedy Entrance). The eight fixed stations were selected from areas where historical grain-size data indicated depositional sediments occurred. In addition, four alternate fixed stations were identified in case depositional sediment could not be collected from any of the eight primary fixed stations.

### **2.1.2 Field Sampling**

The 1997 field survey was conducted aboard the R/V *Alpha Helix*, based out of the University of Alaska, Seward Marine Center, Alaska. The cruise was conducted from July 7 to July 17, 1997, and coincided with the most favorable tidal and current conditions in the program study area. The field team arrived in Seward, Alaska on July 6. Mobilization of the field team and the R/V *Alpha Helix* took place on July 7, and the R/V *Alpha Helix* departed Seward on July 8, 1997. Sediment and fish sampling was conducted from July 9 through July 16. The *Alpha Helix* returned to Seward on July 17 for demobilization at the Seward Marine Center. Field sampling personnel from Arthur D. Little, Inc. (ADL), the Florida Institute of Technology (FIT), Applied Marine Sciences (AMS), EVS Environment Consultants (EVS), and MMS participated in the survey. The scientific team and ship's crew conducted the work on a 24-hour-a-day shift schedule.

The 1998 field survey was also conducted aboard the R/V *Alpha Helix*, from June 27 to July 5, 1998. After arrival of the field team on June 25, the mobilization of the R/V *Alpha Helix* and the field team occurred on June 26, followed by departure from Seward on June 27, 1998. Sediment and fish sampling was conducted from June 27 through July 5. The *Alpha Helix* returned to Seward on July 5 (one day ahead of schedule) for demobilization at the Seward Marine Center. Field sampling personnel from ADL, FIT, AMS, and MMS participated in the survey, with the scientific team and ship's crew conducting the work on a 24-hour-a-day shift schedule.

The field sampling methods were conducted in accordance with the ADL Team's Standard Operating Procedures (SOPs). The field sampling and logistics plan (Arthur D. Little, 1997a; Arthur D. Little, 1998a), prepared for the 1997 field survey, provides detailed explanation of the field methods used in sample collection, equipment decontamination, subsampling of fish tissues and sediment cores, and sediment profile imaging (SPI) film development. In this section, we summarize the methods for station selection, field sampling, and source sample collection.

Sediment samples were collected from 14 fixed stations and 45 random stations, fish samples were collected from 3 stations, and 12 source samples were collected from the Shelikof Strait and outermost Cook Inlet region in 1997. During the 1998 survey, sediments were collected from 19 fixed stations and 18 random stations, fish samples were collected from 3 locations, and an additional 12 source samples were collected. All samples were analyzed for the appropriate chemical and physical parameters. Figure 2-1 shows the field survey station locations where surface sediment, sediment core, and fish samples were taken. The samples collected are also listed in Table 2-1, which summarizes the station locations and number and type of samples collected at each location and the analyses performed. Additional information is presented in the field survey cruise reports (Arthur D. Little, 1997b; Arthur D. Little, 1998b). The sample analysis results are discussed in Section 3.

The sequence of events at each sampling station followed specific procedures, described in detail in the sampling and logistics plan (Arthur D. Little, 1997a; Arthur D. Little, 1998a), including:

- Identify station (latitude and longitude)
- Navigate to station position within 0.2 nautical mile (nm) radius of the grid location
- Review the acoustic bottom profile for likelihood of depositional sediments
- Deploy seabird conductivity, temperature, and depth (CTD) and collect CTD measurements
- Collect Van-Veen grab samples
- Deploy SPI camera to photograph sediments on the ocean floor (1997 cruise only)
- Deploy box core or gravity core, where appropriate, and collect sediment cores

Equipment decontamination procedures were followed as described in the sampling and logistics plan (Arthur D. Little, 1997a). Decontamination typically included a physical scrub, rinses with seawater and distilled water, and a rinse with ethanol or isopropanol.

Replicate samples were collected as part of the field sampling design. At several locations, sediment samples were taken in triplicate, and at other locations as seven replicates (e.g., seven sample jars for one location). Reproducibility and range of results were demonstrated by analysis of replicate samples.

#### **2.1.2.1 Conductivity, Temperature, and Depth Measurements**

At each station, the seabird CTD was deployed to collect data on CTD. These data were downloaded by a data logger to a computer system where they were analyzed, graphically displayed, and stored electronically. The CTD data were recorded in hard copy and digital format on board the *Alpha Helix*.

For most stations, the CTD was deployed to a depth of 2 m above the ocean floor. However, the depth required for the CTD measurements was redefined due to the extended wire time involved for deployments at deep stations in zones 2, 3, and 4. A maximum CTD depth of 200 m was determined to be acceptable at deep stations. As a result, CTD measurements were collected to a depth of 200 m (or bottom, whichever was shallower) during the R/V *Alpha Helix* cruises.

The CTD data collected will be submitted to the National Oceanographic Data Center (NODC) in electronic format. It was not in the scope of work under this program to analyze the collected CTD data, therefore, no discussions nor interpretation of data are included in this report.

### 2.1.2.2 Sediment Sampling

Sediment sampling included the collection of surface sediments and sediment cores. During the collection and handling of sediment samples from the grab sampler, box core, and gravity core, extreme care was taken throughout the subsampling process to avoid contact with metals and hydrocarbon sources. Samples were taken away from the metal sides of the box core and no metal spatulas were used for the trace metal samples. The grab sampler, box core, and gravity core were protected from stack smoke, grease drips from winches and wire, and other potential airborne contaminants during the sampling process.

*Surface Sediments.* The modified Van-Veen grab sampler (0.1 m<sup>2</sup>), constructed of stainless steel and Kynar coated, was the primary equipment used for surface sediment sample (0 to 2 cm depth) collection at all stations except where sediment cores were collected. For sediment cores, a box core was used in addition to the Van-Veen grab sampler. The grab sampler was designed to be deployed from a vessel equipped with a power winch and A-frame or boom system and to collect undisturbed surface sediment samples to a maximum depth of approximately 15 cm. The operation of the grab sampler for collection of a bulk sediment sample (SOP ADL-1018) and the collection and handling of subtidal sediment chemistry samples from the Van-Veen grab sampler (SOP ADL-1019) are summarized below.

The grab sampler required some modifications (a shock cord dampener and adjustable stainless-steel feet) to successfully collect samples at deep stations in the heavy seas encountered during the survey. In addition, the order of gear deployment was modified at some stations due to limitations in the crane wire length (i.e., the grab sampler and CTD were deployed consecutively from the hydrowire winch at many stations).

When the grab was returned to the deck of the vessel, the sample was visually inspected to ensure the bucket was closed and the scissors extended upright. The doors were opened and the sample was visually inspected for sediment and overlying water in the bucket. Overlying water indicates that the sediment sample is undisturbed and that surface sediments remain intact (i.e., there was no leakage of water and hence fine sediment from the grab). If the grab was successful, samples were collected; if not, the grab's contents were discarded and the grab was redeployed.

Subsamples were removed from the grab sampler through the hinged doors on the top of the bucket. Overlying water was removed from the grab by siphoning through a precleaned Teflon<sup>®</sup> tube using a siphon bulb, or by carefully cracking the grab jaws to allow the water to flow out without disturbing the sediments. If used, the Teflon<sup>®</sup> tube was decontaminated prior to use and stored in precleaned aluminum foil.

Sediment samples were collected from the top 2 cm of the grab, which represents recent accumulation. Unconsolidated sediment 2 cm deep was removed from the grab with an aluminum, Kynar-coated scoop. The 2 cm-deep scoop facilitated accurate depth collection of the sediment. The top 2 cm were collected by several scoops up to the volume needed for subsamples and placed directly in appropriate sample containers for organics, metals, total organic carbon (TOC), and grain-size analyses. At stations where toxicity samples were needed, 3 to 6 grabs were necessary to obtain enough sediment volume for toxicity subsamples. Toxicity sediments from multiple grabs were composited in a Kynar-coated bowl. When the appropriate volume was reached, the sample was homogenized in the bowl and then transferred into

appropriate precleaned containers. All sampling equipment was decontaminated before use as outlined in the field sampling and logistics plan (Arthur D. Little, 1997a). Specific subsamples were collected from each grab into their individual container and stored in the freezer or the refrigerator (toxicity samples), as appropriate.

Trace metal samples were removed from the grab sampler with a Teflon® spatula, placed into labeled 48 mL plastic vials, and refrigerated. Samples to be used for grain-size analysis were doubled-wrapped in labeled Ziploc® storage bags and refrigerated.

Sediments for acid-volatile sulfide and simultaneously extracted metals (AVS/SEM) were collected, exclusively during the 1997 sampling event, from the top 2 to 3 cm of the grab sampler using a 50 mL plastic syringe with the lower end cut off such that the barrel was completely open. The syringe was carefully pushed laterally into the sediment as the plunger was pulled back. When the syringe was full, the outer plastic of the syringe was carefully wiped clean and the open end was covered with Parafilm®. Syringes were placed in labeled plastic bags and frozen.

Sediments were collected for hydrocarbon degrading microorganisms (1998 field survey only). A top 2 cm sediment subsample from the grab was collected in a pre-cleaned plastic jar and stored refrigerated. A total of 40 samples for hydrocarbon degrading organisms were collected in 1998 and shipped on ice to the University of Alaska, Fairbanks for analysis.

After the desired subsamples were removed, an open basin was placed beneath the grab on the grab stand. The grab jaws were then opened by releasing tension on the lifting wire and collapsing the scissor mechanism. Any remaining sediment that fell into the basin was discarded. The grab was rinsed with clean seawater from the deck hose and decontaminated with distilled water and ethanol/isopropanol rinses prior to deployment at a new station.

*Sediment Cores.* After grab samples, CTD measurements, and SPI (1997 cruise only) were collected, an MK III box core was used to collect sediment cores at stations where geochronology cores were specified. In addition, two gravity cores were collected from the 1997 cruise (Table 2-1) and archived frozen for possible future analysis. One gravity core was collected from the 1998 cruise and analyzed to obtain a deep sediment profile.

The box coring device was deployed by a remotely operated winch system to the ocean floor. Prior to deployment, the box coring device was decontaminated according to procedures in the field sampling and logistics plan (Arthur D. Little, 1997a).

After retrieval of the box core, the overlying water was siphoned off as quickly as possible without disturbing the surface sediment layer. The inner box containing the sediment was moved into a covered deck area to further reduce contamination. Sediment cores were collected by carefully pushing four premeasured, 40 cm lengths of cellulose-acetate-butyrate (CAB) tubing down into the box core. Then, one person reached into the sediment and, placing one hand over the lower end of the CAB tubing, pulled the core out from the sampler. Both ends of the core were capped and taped. The cores were labeled and stored upright in a refrigerator until subsectioning was carried out within 24 to 48 hours. The CAB tubing had been precleaned with detergent and water, then rinsed with distilled water.

Sediment cores were subsectioned aboard ship. Cores to be used for analysis of trace metals, organic substances, and grain size were subsectioned into 2 cm intervals over the top 10 cm (5 samples) of the core and at 5 selectively spaced 2 cm intervals over the remainder of the core to obtain 10 samples. Subsections were obtained by placing the core upright in a fixed holder and slowly moving a polyvinyl chloride (PVC) piston up from the bottom of the core to extrude the sediment. Using a ruler, a 2 cm section of sediment was carefully extruded. Then the outer layer of sediment (2 to 3 mm) in contact with the CAB tubing was removed to minimize potential contamination from the core liner or from any smearing during sample collection and/or extrusion. Using a stainless-steel spatula, the extruded sediment was transferred to a clean glass jar and homogenized. After homogenization, about 10 g of sediment (wet weight) for analysis of metals and TOC were transferred to a labeled 48 mL plastic vial and stored in a refrigerator. Sediment in the glass jar was stored frozen to preserve organic substances. Sediment samples obtained from the core were set aside for grain-size analysis by placing them in labeled plastic bags and storing them in a refrigerator. During 1997, whole cores for grain-size analysis were returned to the Marine and Environmental Chemistry Laboratories at FIT and transferred to the Marine Geology Laboratory at FIT. In the Marine Geology Laboratory, the cores were subsectioned following the same sampling criteria outlined for obtaining samples for trace metals and organic substances.

The third core from each site also was subsectioned aboard ship for determination of sediment accumulation rates. For this core, the top 10 cm were subsectioned into 0.5 cm sections and 1 cm intervals were taken throughout the remainder of the core. Using a ruler, a 0.5 cm or 1 cm layer was carefully extruded and the sediment in contact with the CAB tubing was removed to avoid smearing recent sediment with older sediment during sampling and extrusion of the core. Sampling over 0.5 cm sediment intervals over the top 10 cm was carried out to ensure that the  $^{137}\text{Cs}$  record, dating back only to 1950, was observed. For example, if the sediment accumulation rate was 0.2 cm/y, then the complete  $^{137}\text{Cs}$  record would be found within the top 9.5 cm unless extensive in situ mixing had occurred. Sediment from each interval was placed into a labeled 48 mL plastic vial and refrigerated. The fourth core from each site was archived at Arthur D. Little.

Surface sediments and core samples were shipped to the Arthur D. Little and the Marine and Environmental Chemistry Laboratories at FIT in coolers packed with blue ice and custody sheets. Upon receipt, each sample was logged and the samples were transferred to a refrigerator (trace metals, age dating) or a freezer (organics, AVS/SEM). Samples collected for grain-size analysis were transferred to the Marine Geology Laboratory at FIT.

### **2.1.2.3 Sediment Toxicity Sample Collection**

The methods used to obtain sediments for toxicity evaluation are described in this section. Details of the location and composition of samples are reported in their respective cruise reports (Arthur D. Little, 1997b; Arthur D. Little, 1998b).

Sediments were collected with the Van-Veen grab and/or the MK III box core. Multiple grabs were often required to obtain sufficient sample quantities for all measured parameters. When this was the case, aliquots of sediments were held in a Kynar-coated stainless-steel bowl. Between grabs, the bowl was covered with clean aluminum foil and held in the dry laboratory. Once sufficient quantities of sediment were obtained, the sample was well mixed and aliquoted into labeled 2 L, wide-mouth (factory-cleaned) polyethylene jars. The samples were held in a 4°C refrigerator while on board the vessel, then shipped to the analytical laboratory (Pacific Eco-

Risk Laboratory [PERL]). The sediments for toxicity testing were not frozen when stored and shipped. Chain-of-custody forms accompanied the samples.

#### **2.1.2.4 Sediment Profile Imaging**

The purpose of the SPI survey was to delineate sediment type, provide information on patterns of sediment deposition and erosion, and describe biological community characteristics in the region. During the 1997 cruise on the R/V *Alpha Helix*, 57 stations were sampled by SPI. The SPI survey was not repeated on the 1998 cruise. The sediment profile images were taken by the EVS field crew according to the procedures described below. The complete SPI report was issued by Arthur D. Little as a separate stand-alone document in 1998 (Arthur D. Little, 1998c).

At the beginning of the survey, the time on the SPI camera's internal data logger was synchronized with the internal clock on the computerized navigation system to Greenwich Mean Time (plus 8 hours). Three replicate images were taken at each station; each SPI replicate was identified by the time recorded on the film and on disk, along with vessel position. Even though multiple images were taken at each location, each image was assigned a unique frame number by the data logger and cross-checked with the time stamp in the navigational system's computer data file. Redundant sample logs were kept by the field crew.

Test exposures of the Kodak® Color Separation Guide (Publication No. Q-13) were fired on deck at the beginning and end of each survey day to verify that all internal electronic systems were working to design specifications and to provide a color standard against which final film emulsion could be checked for proper color balance. Charged spare batteries were carried in the field at all times to ensure uninterrupted sample acquisition. After deployment of the camera at each station, the frame counter was checked to make sure that the requisite number of replicates had been taken. In addition, a prism penetration depth indicator on the camera frame was checked to verify that the optical prism had actually penetrated the bottom to a sufficient depth to acquire a profile image. If images were missed (frame counter indicator) or the penetration depth was insufficient (penetration indicator), weights were added or removed and additional replicates taken. Changes in prism weight amounts, the presence or absence of mud doors, and chassis stop positions were noted in the log for each replicate image. All film taken was developed in the field at the end of each survey day to verify successful data acquisition; strict controls were maintained for development temperatures, times, and chemicals to ensure consistent density on the film emulsion. The film was then visually inspected under magnification to determine whether any stations needed resampling.

Following completion of field operations, the color slides were scanned and stored in photo-CD format by ProLab®, Inc., Seattle, Washington. One hundred fifty-six digital images were analyzed from this survey using Image Pro® (Media Cybernetics, Inc.). Calibration information was determined by measuring 1 cm gradations from the Kodak Color Separation Guide. This calibration information was applied to all SPI images analyzed. Linear and area measurements were recorded as number of pixels and converted to scientific units using the calibration information.

Measured parameters were recorded on a Microsoft® Excel™ spreadsheet. These data were subsequently checked by an EVS senior scientist (Dr. J. Germano) as an independent quality assurance/quality control (QA/QC) review of the measurements before final interpretation was performed.

### 2.1.2.5 Fish Collection

The methods used to capture fish for analysis are described in this section. Details of time, location, depth, and species of fish caught were reported in their respective cruise reports (Arthur D. Little, 1997b; Arthur D. Little, 1998b).

The primary fish species targeted by this study were Arrowtooth flounder. However, very few were caught in 1997, so Halibut became the primary target species based on the results of the long-line catches, though five Sablefish (black cod) and five Arrowtooth flounder were also caught and analyzed. In 1998, Halibut and Pacific cod were caught in nearly equal numbers in all zones fished, so both species were analyzed. In addition to these two primary species analyzed in 1998, 9 Arrowtooth flounder, 4 Sablefish, 1 Aleutian skate and 1 Longnose skate were also caught and analyzed.

Table F-1 in the appendix lists all of the species caught and analyzed or discarded during both years of the study. The two skates were analyzed in 1998 out of interest stemming from differences in physiology and life history between elasmobranchs and teleosts (cartilaginous vs bony fishes).

Fish were captured by long-line. The gear used for this study had approximately 200 circle hooks with a shaft-to-point distance of 2 cm. The hooks were tied to 30 cm leaders of approximately 200 kg breaking strength, which were attached to the main line every 2 m. The main line was approximately 7 mm in diameter, with a breaking strength of approximately 1,000 kg. Each end of the long-line had an anchor/buoy line attached to it, with the long-line attached near the anchor, allowing the hooks to fish on or near the bottom. The buoys located the long-line at the surface. Each hook was baited with a piece of salted herring, and the gear was deployed for 4 to 6 hours and then retrieved (longer fishing times would have precluded returning all unused Halibut alive, as mortality increases with time).

A large tub was filled with seawater prior to retrieving the fishing gear. As the gear was brought on board, fish were removed from the hooks and either placed in the tub or discarded overboard. Fish were discarded if they were not a species of interest, or if they were dead. The species of all fish captured were documented regardless of whether they were kept for analysis. All unused target fish were returned to the ocean alive, after their total length (TL) was measured.

The methods used for tissue sampling of captured fish are described in this section. Weight and length were reported in the first cruise report as reported to the Alaska Department of Fish and Game (Arthur D. Little, 1997b).

Dissections commenced as soon as the fishing gear was retrieved. Dissections were done on several species of fish, but all were accomplished using the following protocol. Dissections were conducted by four scientists: one to record data, one to prepare the sample containers and assist the dissector, the third to weigh and measure, and a fourth to dissect the fish. The fish were removed from the tub, sacrificed with a fatal blow to the head, weighed on deck using a pesola (hanging balance), and then brought into the wet laboratory and placed on a precleaned nylon cutting board. General observations (e.g., parasites, deformations) were recorded. The fish were then measured (TL) and dissected.

All dissection equipment was cleaned with Alconox® detergent and water, and then rinsed with 1 percent hydrochloric acid (HCl) and methanol prior to each dissection. The dissections were performed “in the fish” to minimize the potential for sample contamination. This was accomplished by placing the fish blind side up (for the flatfishes, i.e., the Halibut, flounder, and skates) and making a cut with a cleaned stainless-steel filet knife along the lateral line from the pelvic girdle to the caudal peduncal. Round fish (i.e., Pacific Cod and Sablefish) were laid on their side, but otherwise dissected with the same methodology. The musculature covering the peritoneal cavity was then cut away, and a small portion of the flesh from the caudal end of the fish (without skin) was removed for metals analysis (FIT ancillary samples). General observations (e.g., parasites, deformities, sex of the fish) of the peritoneal cavity were made and then sections of liver for Reporter Gene System (RGS) P450, metals, and organic contaminant analyses were removed and placed in precleaned glass containers. A section of liver was also removed for immunohistochemical analysis of CYP1A (P4501A) and placed in a polyethylene container. Finally, a section of kidney and gill were removed and placed with the liver CYP1A sample. The liver samples for RGS-P450, metals, and organics were composited if sufficient numbers of target species were obtained, or were collected as individual samples where small numbers of individuals were caught; all samples were frozen after collection (Arthur D. Little, 1997b; Arthur D. Little, 1998b). The samples for CYP1A analysis were fixed with 10 percent-neutral-buffered formalin. The muscle samples for metals analysis were placed in plastic bags and frozen. Chain-of-custody forms accompanied the samples to each analytical laboratory.

### **2.1.3 Source Sample Collection**

Source samples were collected in order to compare concentrations and distributions of contaminants in the sediments to potential contaminant sources. Based on the literature review of historical data on the outermost Cook Inlet and Shelikof Strait (Boehm *et al.*, 1998), a number of potential contamination sources for the depositional sediments were identified. These sources include oil and gas activities, oil seeps, coals, municipal discharges, boat harbors, and riverine and coastal inputs. Samples representative of these separate source types were collected as part of the both the 1997 and 1998 sample cruises and are summarized in Table 2-2.

#### **2.1.3.1 Source Oils**

A source sample of Cook Inlet crude oil was collected from the Unocal Trading Bay Production Facility (TBPF) in August 1997 by Northern Testing Labs (NTL). A second oil source sample consisted of Swanson River Field oil, and was collected by UNOCAL in 1998. Finally, oil seep samples were collected from Well Creek, which drains into Oil Bay on the Iniskin Peninsula (Figure 2-1). The samples of seep oil were collected from the surface water of a pond adjacent to the creek. Each oil sample was collected in a precleaned glass jar for organics and metals, then shipped to Arthur D. Little for analysis.

#### **2.1.3.2 Source Coals**

A coal source sample was collected from the bluff area west of Homer Spit by Cook Inlet Regional Citizens' Advisory Council (CIRCAC), in November 1997. Five chunks of beach-washed coal were collected from the beach approximately one mile west of Bishops Beach, in Homer, Alaska (Figure 2-1), placed in a precleaned glass jar, then shipped to Arthur D. Little for analysis. A second coal source sample was collected from scattered pieces along Coal Bay Beach, Homer in 1998 (Figure 2-1) following the R/V *Alpha Helix* cruise.

Additional coal source samples collected in 1998 included those from coal seams in Ninilchik Bluff (Figure 2-1) and at Matanuska (Figure 2-2), one collected from a coal pocket at Coyote Lake (Figure 2-2) and two separate samples from the Beluga Coal Fields provided by CIRCAC.

### 2.1.3.3 Source Sediment

Several locations were sampled during both surveys to determine the potential influence of resuspended river sediment and coastal bottom sediment to the study area.

The Homer boat harbor sediment source samples were collected during the July 1997 R/V *Alpha Helix* cruise. These sediment source samples were collected just outside the entrance of the boat harbor to the west of the dredged channel in an area where sampling activities did not interfere with boat traffic in the harbor. Two samples were collected from the Van-Veen grab, using a 2 cm-deep, Kynar-coated, stainless-steel scoop, at 0- to 2-cm and 4- to 6-cm intervals.

The Copper River sediment samples were collected in July 1997 by P. Boehm of Arthur D. Little. Figure 2-3 shows the four Copper River sediment sampling locations from Round and Long Islands (CR-2 to CR-4), and upstream near Million Dollar Bridge (CR-1). The samples were collected on the shoreline one meter above water level, from surface sediments (0 to 2 cm) using a stainless-steel spoon and precleaned glass sample jars. Sampling equipment was decontaminated between sample locations by rinsing with distilled water. Additional sediment (CR-5) was collected from the Copper River in 1998 (Figure 2-3). The sediment was placed into glass jars (organics) and plastic vials (metals), and shipped to Arthur D. Little and FIT.

The Susitna River sediment samples were collected in July 1997 by J. Trefry of FIT (Figure 2-3). The two Susitna River samples were taken from the northern bank of the river, 200 yards downstream (west) of the bridge at mile 105 on George Parks Highway (Highway No. 2). Sediment from the Susitna River was collected where there was fine-grained sediment, approximately one meter from the shore. At the time of sampling, the Susitna River was at a relatively high stage and the water was very turbid. The samples were collected using a stainless-steel spoon that was rinsed well with alcohol and Susitna River water. The sediment was placed directly into precleaned glass jars provided by Arthur D. Little. The samples were stored on ice in a cooler and shipped frozen with blue ice to Arthur D. Little.

Other sediment source samples were collected from one location in the influence of the Alaska Coastal Current, up-current of Cook Inlet offshore of the Kenai Peninsula, during the 1998 R/V *Alpha Helix* cruise (Figure 2-1). Additional sediment samples were collected offshore of St. Augustine Island with a Van-Veen grab sampler for grain-size and chemistry analysis (Figure 2-1). A sediment sample was collected near Holgate Glacier (Kenai Peninsula), not for the purpose of source influence, but to be used as a toxicity reference sample representing the fine-grained sediment encountered in the study area (Figure 2-1). This location was selected since it represented fine grained and glacial sediment and was up current from Cook Inlet (would not have Cook Inlet contaminants) and inshore of the influence of the Gulf of Alaska. In May 1998, Matanuska River sediment was collected for both metals and organic analysis (Figure 2-2). Finally, a miscellaneous volcanic ash sample was collected from the beach of St. Augustine Island for metals analysis only (Figure 2-1).

#### **2.1.3.4 Aqueous Sources**

Water samples from the Susitna, Knik, Matanuska, and Copper rivers were collected in 1998 (Figures 2-2 and 2-3) using 1-L, acid-washed polyethylene bottles. Each bottle was submerged, opened, partially filled, and closed. Once closed, the bottle was shaken and the sample discarded as an equipment rinse. Then, the closed bottle was resubmerged, opened, filled, and closed. To minimize sample contamination, all bottles were handled using powder-free polyethylene gloves. The bottles were double-bagged, labeled, placed in a cooler, and shipped cold to FIT for filtration and analysis of the suspended solids.

The municipal discharge produced water source sample was collected by personnel at the Point Woronzof, Anchorage Municipal Wastewater Treatment Facility (WWTF) in August 1997, and shipped to Arthur D. Little for analysis. The sample of final effluent was collected after treatment from the discharge location.

A produced water sample from the Unocal TBPF, representing oil and gas production activities, was sampled by a Unocal contractor. The produced water samples were collected in August 1997 from a final effluent outfall at the facility (TBPF-Outfall). The samples were collected in a precleaned glass jar for organics, and a plastic bottle for metals, and shipped on ice to Arthur D. Little for analysis of the suspended solids.

## **2.2 Analytical Methods**

### **2.2.1 Physical Parameters**

#### **2.2.1.1 Grain Size**

Surface sediment samples (0 to 2 cm) for grain-size analysis were double-wrapped in Ziploc® plastic bags and kept refrigerated while at sea. A separate subcore was collected for grain size at each of the nine coring locations during 1997 and four coring locations during 1998. Water was siphoned from the top of the core and the core was stored in a refrigerator at sea. Surface sediment and core samples were shipped to the Marine Geology Laboratory at FIT in coolers packed with blue ice and a chain-of-custody sheet. Upon receipt, each sample was logged in and prepared for analysis as described below.

Determination of grain-size distribution followed the classic method of Folk (1974). Initially, a dispersant (2 g of sodium hexametaphosphate "Calgon®" per 1 L of distilled water) was added to about 20 g of wet sediment to disaggregate and deflocculate the sediment. The subsample was immersed in this solution for 24 hours, prior to wet-sieving the sample through mesh sizes No. 10 (2 mm) and No. 230 (0.063 mm) to separate the gravel, sand, and mud fractions. The gravel and sand fractions were collected in preweighed beakers, dried in an oven at 60°C and reweighed. The mud fraction was collected in an evaporating bowl and transferred to a 1,000 mL cylinder. This fraction was deflocculated with a mechanical mixer for 5 minutes. Dispersant was added to the cylinders to bring the volume to 1,000 mL. The mud subsample was soaked for another 24 hours. Pipette analysis was performed for each cylinder using a 20 mL pipette. The fractions were withdrawn at a depth of 20 cm after 20 seconds (silt) and at a depth of 10 cm after 2 hours (clay). The samples were placed in preweighed beakers and dried. Weights for all size fractions were recorded in a spreadsheet for later calculations. The 2 g/L of deflocculant was subtracted from the final weights during calculations. The final data are presented as percent

sand (2 mm to 0.062 mm), silt (0.062 to 0.004 mm), and clay (<0.004 mm). No gravel (particle sizes greater than 2 mm) was found in any samples.

#### **2.2.1.2 Total Organic Carbon**

Sediment stored in 48 mL plastic vials was initially freeze-dried to a constant mass (approximately 48 hours) after a 2 g portion of wet sediment had been taken for mercury (Hg) analysis. A 0.5 to 1 g portion of the freeze-dried sediment was placed in a 10 mL Pyrex® beaker and treated with 2 mL of concentrated HCl to remove any inorganic carbon present. The sediment was dried at 60°C and reweighed to determine the increase in weight due to the formation of calcium chloride (CaCl<sub>2</sub>) as a result of adding HCl. Then, approximately 5 to 20 mg of pretreated sediment were weighed into tin cups and combusted at 1,020°C in a Carlo-Erba® NA1500 carbon analyzer following the manufacturer's instructions. The TOC content of the sediment samples was determined using a four-point calibration curve with sulfanilamide as the standard. The TOC concentrations were corrected to account for the increase in sediment mass following the addition of HCl. The calibration curve was checked every 10 samples by analyzing standard reference material (SRM) BCSS-1, a marine sediment issued by the National Research Council of Canada (NRC).

#### **2.2.2 Organic Parameters**

Arthur D. Little provided analytical chemistry services as part of the Sediment Quality in Depositional Areas of the Shelikof Strait and Outermost Cook Inlet study. Arthur D. Little performed selected organic chemical analyses on 302 sediment, 43 tissue, and 27 source samples. This section describes the analytical methods that were used in performing these chemical analyses.

The core target analytes for the sediment and source samples were saturated hydrocarbons (SHC) as reported in Table 2-3, polycyclic aromatic hydrocarbons (PAH) as reported in Table 2-4, and biomarkers (steranes/triterpanes [S/T]) as reported in Table 2-5. Instrumental analysis included gas chromatography/flame ionization detection (GC/FID) for SHC determinations and gas chromatography/mass spectrometry detection (GC/MS) for PAH and biomarker determinations. Samples were grouped together in batches of no more than 20 field samples plus associated quality control (QC) samples. All organic sample analyses were conducted according to Arthur D. Little analytical SOPs.

##### **2.2.2.1 Sample Preparation**

**Sediment Extraction.** The sediment samples were extracted based on EPA Method 3550A, Ultrasonic Extraction, which has been modified to include orbital shaking of the sample in extraction solvent for 1 hour following the final sonication. The following is a summary of the procedure used:

A 50 g weight of the homogenized sediment was placed into a Teflon® jar and dried with sodium sulfate. Another 5 g subsample was placed into an aluminum weighing pan for dry weight determination. The sample was serially extracted 3 times with 100 mL of dichloromethane (DCM) and acetone (1:1, volume to volume [V/V]), each time by sonication. The final sonication was followed by orbital shaking for 1 hour. The surrogates were spiked into the sample after the first addition of solvent and before the first extraction. All sediment samples were spiked with low-level surrogates. The surrogates were: naphthalene-d<sub>8</sub>, acenaphthene-d<sub>10</sub>,

phenanthrene-d<sub>10</sub>, and benzo[a]pyrene-d<sub>12</sub> for PAH analysis, 5 $\alpha$ -androstane and d<sub>50</sub>-tetracosane for SHC analysis, and 5 $\beta$ (H)-cholane and d<sub>66</sub>-dotriacontane for biomarker analysis.

After extraction, samples were concentrated by Kuderna-Danish on a hot water bath and an extract weight was taken, if necessary. Extracts were treated with copper to remove sulfur, and split in half. One-half was archived and the other half processed through a neutral alumina column (optionally, silica gel High-Performance Liquid Chromatography [HPLC] fractionation was performed in addition to the alumina cleanup).

The QC samples processed along with the sediment samples included one procedural blank, one blank spike, and one SRM (sediment SRM 1941a) per batch. The blank spike sample was fortified with PAH matrix spike solution and SHC matrix spike solution.

**Tissue Homogenization.** Each tissue sample was a composite of the livers of up to five individual fish. Samples were homogenized in a blender prior to extraction. A 30 g aliquot was removed from each homogenized sample, frozen, and sent to Columbia Analytical Services for RGS-P450 analysis. A 10 to 15 g aliquot of frozen liver homogenate was sent to the Marine and Environmental Chemistry Laboratories at FIT for trace metals analysis.

**Tissue Extraction.** Twenty-five grams of the homogenized wet tissue sample were placed into a Teflon<sup>®</sup> jar and dried with sodium sulfate. Another 5 g subsample was placed into an aluminum weighing pan for dry weight determination. The sample was then serially extracted 3 times with 100 mL of DCM by maceration using a Tissuemizer<sup>®</sup>. The surrogates were spiked into the sample after the first addition of solvent and before the first extraction. The surrogates were: naphthalene-d<sub>8</sub>, acenaphthene-d<sub>10</sub>, phenanthrene-d<sub>10</sub>, and benzo(a)pyrene-d<sub>12</sub> for PAH analysis and 5 $\beta$ (H)-cholane and d<sub>66</sub>-dotriacontane for biomarker analysis. Surrogate compounds were spiked into all tissue samples at the low level.

After extraction and concentration the gravimetric weight (lipid weight) was recorded. Extracts were then processed through an alumina column and a post-alumina gravimetric weight recorded prior to cleanup on the HPLC. Percent solid determinations for the tissue samples are provided in Appendix C.

The QC samples processed with each batch of tissue samples included one procedural blank, one blank spike, one SRM (1974a), and one duplicate analysis. The blank spike sample was fortified with PAH matrix spike solution.

**Source Samples.** Source samples included crude oils, produced water, sediments, coals, and municipal discharge. These samples were expected to exhibit high concentrations of the targeted analytes. As such, they were segregated from the other samples to avoid the possibility of contaminating low-level samples. Following is a summary of the procedures used for the preparation of source samples.

**Crude Oil:** A dilution was prepared from each crude oil or seep sample in DCM at an approximate concentration of 5 mg/mL. Each dilution was spiked directly with SHC, PAH, and S/T surrogates at the low level. Extracts were then passed through an alumina column and prepared for instrumental analysis.

*Produced Water and Municipal Discharges:* Produced water and municipal discharge samples were extracted serially with DCM by the liquid-liquid method. These samples were spiked with surrogates at the high level. After extraction, the combined extracts were passed through an alumina column.

*Source Sediment Samples:* Source sediment samples from Homer Harbor and the Copper and Susitna rivers were extracted by the sediment extraction procedure described in Section 2.2.2.1.

*Coals:* Coal source samples (approximately 5 g) were first ground to a fine particle size using a mortar and pestle, followed by extraction using the procedure described in section 2.2.2.1. The extracts were then passed through an alumina column and fractionated by silica gel into saturates and aromatics.

### **2.2.2.2 Organic Extract Cleanup**

*Alumina Column.* Sediment extracts were treated with activated copper to remove sulfur and split in half. One-half was archived, and the other half passed through a neutral alumina column. Silica gel fractionation by HPLC was performed in addition to alumina cleanup to remove additional interferences from the S/T extracts.

Tissue extracts were weighed and passed through a 2 percent deactivated F-20 alumina column, and a post-alumina gravimetric weight was recorded.

*High-Performance Liquid Chromatography.* Tissue sample extracts were cleaned up by HPLC using a preparative gel permeation chromatography (GPC) column. The extracts were split according to total extract weight following the criteria in the SOP. The resulting post-HPLC extracts were analyzed by GC/MS for PAH. The pre-HPLC archive was saved for possible biomarker analysis at a later date.

### **2.2.2.3 Internal Standard Addition for Instrumental Analysis**

The post-alumina and post-HPLC extracts were spiked with SHC, PAH, and S/T internal standards as appropriate for each extract/fraction. In general, the extracts were concentrated to approximately 250  $\mu$ L before adding the internal standards. The internal standard compounds were: chrysene- $d_{12}$  and fluorene- $d_{10}$  for PAH; chrysene- $d_{12}$  for S/T; and  $d_{62}$ -triacontane for SHC. The amount of SHC internal standard added to the extracts was adjusted to obtain a target concentration of 50  $\mu$ g/mL. The amount of PAH and S/T internal standard added to the extract was adjusted to obtain a target concentration of 1  $\mu$ g/mL. Aliquots (approximately 100  $\mu$ L) were removed from the spiked extracts for GC and GC/MS analyses. Due to the low extract volume all instrumental aliquots were recombined.

### **2.2.2.4 Instrumental Analysis**

Instrumental analysis included GC/FID and GC/MS analysis of all sediment samples, and GC/MS analysis of tissue samples. A five-point calibration, an Instrumental Reference Material (IRM), a North Slope Crude Reference, and a Cook Inlet Crude Reference were run at the beginning of each instrumental sequence with each batch of samples.

All instruments were calibrated with analytical standards prior to the analysis of sample extracts. Target analyte concentrations were calculated versus the internal standard compound and were

corrected for recovery of the surrogate compounds. The recovery of the surrogate compounds was calculated versus the internal standards added to the extracts prior to instrumental analysis.

**Gas Chromatography/Flame Ionization Detection.** Approximately 100  $\mu\text{L}$  of the internal standard containing sample extract were submitted for GC/FID analysis. Sample extracts were injected onto a 30 m long by 0.25 mm inner-diameter (ID) fused-silica capillary column with DB5 bonded phase. This column provides baseline resolution of n-alkanes from n-C<sub>8</sub> to n-C<sub>40</sub> and n-C<sub>17</sub>/pristane and n-C<sub>18</sub>/phytane pairs. The injection port is designed for splitless injection and includes a silanized wide-bore glass liner containing a plug of silanized glass wool to reduce high-molecular-weight mass discrimination.

**Gas Chromatography/Mass Spectrometry Analysis.** The GC/MS analysis of sample extracts for PAH and biomarkers was performed in accordance with EPA Method 8270 modified to include alkyl PAH and selected ion monitoring (SIM). The PAH and S/T analyses were performed on sediments. PAH analyses only were performed on tissues. Approximately 100  $\mu\text{L}$  of extract were submitted for analysis. The sample extract was injected onto a 30 m long by 0.25 mm ID fused-silica capillary column with DB5 bonded phase.

#### **2.2.2.5 Compound Quantification/Identification**

**Saturated Hydrocarbons.** The C<sub>8</sub> through C<sub>40</sub> normal alkanes, pristane, phytane, and selected isoprenoids were determined in the extract per EPA Method 8015 modified (Table 2-3). Two control oil solutions were analyzed with the samples. Quantification of the analytes was based on the internal standard compound (d<sub>62</sub>-triacontane) which was spiked into the sample just prior to analysis. The target analyte concentrations were corrected for surrogate recovery. The SOP includes the acceptability criteria for the calibration, procedural blank, surrogate compound recoveries, and matrix spike recoveries, as well as the corrective action if the criteria are not met, reporting requirements, and method detection limit (MDL) protocols. The data quality objectives (DQO) for this analysis are summarized in Table 2-8.

**Polycyclic Aromatic Hydrocarbons.** The extracts were analyzed by GC/MS in the SIM mode per modified EPA Method 8270, to determine the concentrations of parent and alkylated PAH in the samples (Table 2-4). Two control oils and a 1:10 dilution of SRM 1491 spiked with 250 ng/mL of surrogates and internal standards were also analyzed with the samples.

The concentrations of the individual PAH were calculated relative to one of the two internal standards that were spiked into the sample just prior to instrumental analysis (Table 2-4). The analyte concentrations were corrected for their respective surrogate recoveries (Table 2-4). The target PAH concentrations were quantified using average response factors (RFs) generated from the five-point calibration curve. To quantify the alkyl PAH, homologues were assigned the RF of their respective parent PAH compound.

**Steranes and Triterpanes.** Only sediment extracts were analyzed for steranes and triterpanes by GC/MS in the SIM mode by modified EPA Method 8270 (Table 2-5). An initial four-point calibration was performed before each batch sequence. A control oil (approximately 5 mg/mL) was analyzed to obtain a good biomarker signal and the identification of target compounds was based on the retention times of this oil. There was no analysis of sediment or instrumental SRM, since there was no recognized SRM for these compounds.

The concentrations of all identified S/T were calculated versus the internal standard chrysene-d<sub>12</sub>. All target triterpane concentrations were quantified using the average RF of 17β(H), 21β(H)-hopane (T23) generated from the initial S/T four-point calibration. All target sterane concentrations were quantified using the average RF of cholestane (S17) in the initial four-point calibration. Analyte concentrations were corrected for surrogate recovery. Surrogate recovery of 5β(H)-cholane was calculated relative to the internal standard. If the determination of 5β(H)-cholane was interfered with, the extract archive was analyzed, using the alternate internal standard triacontane-d<sub>62</sub> and the alternate surrogate dotriacontane-d<sub>66</sub>. Extracted ion chromatograms of m/z 191 for the diterpanes and triterpanes and m/z 217 for the steranes were annotated with peak names and printed out for all samples.

## 2.2.3 Inorganic Parameters

### 2.2.3.1 Trace and Major Metals in Sediments

Initially, each wet sediment sample was homogenized in the original 48 mL plastic vial using a Teflon<sup>®</sup> mixing rod. Then, a portion (approximately 2 g) of each sample was transferred to a preweighed plastic vial to determine water content. Once transferred, the wet sediment and the vial were reweighed. In addition, approximately 2 to 4 g of sample were transferred into a polyallomer centrifuge tube to determine the Hg content of the sediment (element symbols are defined in Table 2-6). Samples intended for water content were frozen, freeze-dried, and reweighed to determine the water content. The dried sediment samples were homogenized again using a Teflon<sup>®</sup> mixing rod.

Approximately 0.45 g of freeze-dried, homogenized sediment and standard reference sediment (BCSS-1) were totally digested in Teflon<sup>®</sup> beakers using concentrated, high-purity HF-HNO<sub>3</sub>-HClO<sub>4</sub>. Total digestion of the sediments is preferred because then no doubt remains about the absolute amount of metal associated with a sample. In the digestion process, 1 mL HClO<sub>4</sub>, 1 mL HNO<sub>3</sub>, and 3 mL HF were added to the sediment in the Teflon<sup>®</sup> beaker and heated at 50°C with a Teflon<sup>®</sup> watch cover in place until a moist paste formed. The mixture was heated for another 3 hours at 80°C with an additional 2 mL HNO<sub>3</sub> and 3 mL HF before bringing the sample to dryness. Finally, 1 mL HNO<sub>3</sub> and about 30 mL distilled, deionized water (DDW) were added to the sample and heated strongly to dissolve perchlorate salts and reduce the volume. The completely dissolved and clear samples were then diluted to 20 mL with DDW. This technique is 100 percent efficient with no loss of the elements studied and has been used successfully in the FIT laboratory for many years with a variety of sediment types.

Sediment for Hg analysis was digested by heating 2 to 4 g of wet sediment in an acid-washed, polyallomer centrifuge tube with 4 mL HNO<sub>3</sub> and 2 mL H<sub>2</sub>SO<sub>4</sub>. Sample tubes were heated for 1 hour in a 90°C water bath and allowed to cool. Each tube was centrifuged at 2,000 revolutions per minute (rpm) and the supernate was decanted into a 25 mL graduated cylinder. The sediment pellet was rinsed twice with 5 mL DDW, centrifuged, and decanted into the graduated cylinder before diluting to a final volume of 20 mL with DDW.

Labware used in the digestion process was acid-washed with hot, 8N HNO<sub>3</sub> and triple-rinsed with DDW. Two procedural blanks, two duplicate samples, and two SRMs were prepared with each set of 40 samples. SRM BCSS-1 (trace metals except Hg) and MESS-2 (Hg), sediment samples issued by the NRC, and 1646a (Hg), issued by the National Institute of Standards and Technology (NIST), respectively, were used.

Samples, SRM, and procedural and reagent blanks were analyzed by either flame atomic absorption spectrometry (FAAS), Zeeman graphite furnace atomic absorption spectrometry (ZGFAAS), cold vapor atomic absorption spectrometry (CVAAS), or inductively coupled plasma/mass spectrometry (ICP/MS). The method used for each element and the corresponding MDLs are presented in Table 2-6. All analytical techniques followed manufacturers' specifications, SOPs on file at FIT, and the details provided in the QA/QC section below. These methods are very similar to the EPA methods described for Series 7000 FAAS and ZGFAAS, Series 7470 CVAAS, and Series 6010A ICP/MS as described in EPA 1992. Matrix interferences were carefully monitored for all elements using the method of standard additions.

### **2.2.3.2 Trace Metals in Tissues**

In preparation for analysis, each tissue sample was homogenized with a Teflon<sup>®</sup> mixing rod (fish liver-composite samples) or stainless-steel instruments (fish flesh). Then, between 0.3 to 1.5 g of tissue were transferred to a preweighed plastic vial and reweighed to determine percent water content (required for Hg analyses). The plastic vial was frozen, freeze-dried, reweighed, and the water content was calculated. In addition, an additional weighed portion of each homogenized wet tissue (approximately 1 g of liver-composite or 2 to 3 g of fish flesh) was transferred to a 50 mL polypropylene centrifuge tube to be digested for total Hg content.

Liver-composite and fish flesh samples for determining concentrations of all metals except Hg were prepared using approximately 4 g of wet sample. The samples were transferred to preweighed, 100 mL glass digestion flasks, reweighed, frozen, freeze-dried, and the percent water content was calculated. These freeze-dried tissues and approximately 0.5 g portions of tissue SRM were totally dissolved by refluxing with concentrated, high-purity HNO<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, and HCl. Once the tissue samples were completely dissolved, the clear solutions were transferred to graduated cylinders, diluted to 20 mL with DDW rinses of the flasks, and then stored for analysis in 30 mL polyethylene bottles.

The wet tissue samples (1 to 3 g) for Hg analysis, along with 0.2 to 0.4 g portions of tissue SRM, were digested using high-purity HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>. Each sample was refluxed for 1 hour in a 90°C water bath and allowed to cool. Once cool, the solution was decanted into a graduated cylinder, diluted to a final volume of 20 mL with DDW rinses of the centrifuge tubes, and stored for analysis in a 30 mL polyethylene bottle.

Metal concentrations in the digested tissue samples, tissue SRM, and procedural blanks were determined by FAAS, ZGFAAS, CVAAS, or ICP/MS in a manner compatible with the EPA Series 200.3 techniques (EPA, 1991). The methods used for each element and the corresponding MDL are listed in Table 2-6. In all cases, the manufacturers' specifications were followed and adherence to QA/QC requirements was maintained.

### **2.2.3.3 Trace Metals in Aqueous and Oil Source Samples**

Initially, the salinity of the aqueous source samples (effluent and produced water) was obtained using a Reichert-Jung<sup>®</sup> Model 10419 refractometer to help determine the appropriate analytical technique or dilution for determining trace metal concentrations. Then, 20 mL of each sample (effluent and produced water) was pipetted into a 30-mL polyethylene bottle. The sample was acidified with 0.2 mL of high-purity HNO<sub>3</sub> and stored for the determination of all metal concentrations. The liquid source samples were not shaken to resuspend particulate matter prior to the transfer.

Subsamples of the crude oils (approximately 1 g) were transferred to glass digestion flasks and digested by refluxing with high-purity HNO<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, and HCl for the determination of all metals except Hg. The digested oil samples were poured into graduated cylinders and diluted to a final volume of 15 mL with DDW rinses of the digestion flask. The Hg concentration of the crude oil was determined using 0.2 g subsamples that were placed in polypropylene copolymer centrifuge tubes and refluxed with high-purity HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> for 1 hour in a 90°C water bath. After the Hg digestion was complete, the sample was transferred into a graduated cylinder, diluted to a final volume of 20 mL with DDW rinses of the centrifuge tube, and stored for analysis in 30 mL polyethylene bottles.

Metal concentrations for the water source samples, crude oil, SRM, and procedural and reagent blanks were determined by FAAS, ZGFAAS, CVAAS, or ICP/MS following methods comparable with EPA Series Method 200 and 200.8 (EPA, 1992). Levels of Ba in produced water and Zn in the crude oil were determined by FAAS using a Perkin-Elmer® Model 4000 instrument. Concentrations of Cd (except produced water), Cr, Cu, Fe, Mn, Ni, and V were determined by ZGFAAS using a Perkin-Elmer® Model 4000 instrument equipped with an HGA-400 graphite furnace, and an AS-40 autosampler. Levels of Ag, As, Be, and Se were determined by ZGFAAS using a Perkin-Elmer® Model 5100 instrument equipped with Zeeman background correction, an HGA-600 graphite furnace, and an AS-60 autosampler. Values for Ba, Pb, Sb, Sn, Tl, and Zn in the low-salinity effluent water and crude oil (except Zn) were determined by ICP/MS using a Perkin-Elmer® ELAN 5000. Dissolved concentrations of Cd, Pb, Sb, Sn, Tl, and Zn in the high-salinity water were determined by ICP/MS using the method of standard additions. All Hg values were determined by CVAAS using a Laboratory Data Control Model 1235 Mercury Monitor. In all cases, the manufacturers' specifications were followed and adherence to QA/QC requirements was maintained.

#### **2.2.3.4 Trace Metals in River Particulate and Coal Source Samples**

River water samples were vacuum filtered through polycarbonate filters (Poretics®, 47-mm diameter, 0.4 µm pore size). Prior to use, the filters had been acid-washed in 5N HNO<sub>3</sub>, triple-rinsed with DDW, dried, and then weighed to the nearest µg using a Sartorius® Model M3P 6-place electronic balance under cleanroom conditions. Vacuum filtration was carried out in a Class-100 laminar-flow hood in the FIT cleanroom facility using acid-washed glassware. The filters were dried and reweighed prior to digestion for trace metals analysis.

Filters with riverine particulates and milligram quantities of SRM No. 2704, a river sediment issued by the NIST, were digested in stoppered, 15 mL Teflon® test tubes using Ultrex II® HNO<sub>3</sub>, HF, and HCl. The sealed test tubes were placed in an 80°C water bath where refluxing of the acids completely dissolved the particles on the filters. After digestion, the resultant solutions were transferred to acid-washed, labeled 15 mL polyethylene bottles, diluted to approximately 6 mL with DDW rinses of the Teflon® test tubes, and stored in a plastic bag until analysis. No separate digestion was required for Hg.

Metal concentrations for the dissolved particulate samples, SRM, and blanks were determined by FAAS, ZGFAAS, CVAAS, or ICP/MS in a manner compatible with EPA Series 7000, 6010A, and 7470 (EPA, 1992), respectively. Particulate Al, Fe, Mn, and Zn concentrations were measured by FAAS using a Perkin-Elmer® Model 4000 AAS. Silver, As, Be, and Se values were determined by ZGFAAS using a Perkin-Elmer® Model 5100PC AAS equipped with Zeeman background correction, an HGA-600 graphite furnace, and an AS-60 autosampler.

Concentrations of Cr, Cu, Ni, and V were quantified by ZGFAAS using a Perkin-Elmer® Model 4000 AAS equipped with an HGA-400 graphite furnace, and an AS-40 autosampler. Values for Ba, Cd, Pb, Sb, Sn, and Tl were measured by ICP/MS using a Perkin-Elmer® ELAN 5000 spectrometer. Particulate Hg levels were determined by CVAAS using a Laboratory Data Control Model 1235 Mercury Monitor. In all cases, the instrument manufacturers' specifications were followed and adherence to QA/QC requirements was maintained.

Coal samples were digested and analyzed following the methods used for sediments as outlined in Section 2.2.3.1

#### **2.2.3.5 Acid-Volatile Sulfide/Simultaneously Extracted Metals**

Approximately 4 to 9 g of wet sediment were homogenized, weighed, and analyzed for AVS using the cold acid purge-and-trap method (Di Toro *et al.*, 1990). The homogenized sample was placed in a flask containing 45 mL of DDW after the system had been purged with 99.999 percent nitrogen. The sulfide in the sediment was then volatilized by injecting 45 mL of deoxygenated 2N HCl through a septum. The flask was continuously stirred and purged with 99.999 percent nitrogen. The nitrogen was passed through an impinger containing 45 mL of a sulfide anti-oxidant buffer (SAOB) which acted to trap and prevent oxidation of the sulfide. The SAOB buffer consisted of 2M NaOH, 0.1M ascorbic acid, and 0.1M ethylene diamine triacetic acid (EDTA). After a reaction time of 1 hour, the SAOB solution was placed into a 100 mL volumetric flask and brought to a final volume of 100 mL by adding the solution obtained from rinsing the impinger flask with a 1:1 solution of SAOB and DDW. The sulfide concentration of the SAOB solution was determined using a sulfide-specific ion probe (Orion® Model No. 9616BN). The probe was calibrated for each analysis using known concentrations of sodium sulfide/SAOB solution with a five-point curve. The sediment/acid slurry that remained at the end of the reaction was filtered into a 100 mL volumetric flask using Whatman® No. 40 ashless paper filter. The reaction flasks were rinsed with DDW and the rinse was used to bring the filtrate volume to 100 mL. This filtrate was then stored in acid-washed polyethylene bottles until analysis for SEM. Concentrations of Cu, Fe, and Zn were determined by FAAS using a Perkin-Elmer® Model 4000 instrument. Cadmium, Ni, and Pb values were obtained by ZGFAAS using a Perkin-Elmer® Model 4000 instrument equipped with an HGA-400 graphite furnace and an AS-40 autosampler.

#### **2.2.4 Geochronology**

Approximately 8 to 10 g of freeze-dried sediment from each layer (0.5 to 1.0 cm thick) of the sediment cores were ground to a fine powder using a Spex® 8000 mixer mill. Then, each sample was tightly packed in a 2 cm diameter, 5 cm long polycarbonate vial to a depth of  $30 \pm 1$  mm. A rubber stopper was cemented in place with two-part epoxy to seal the vials and prevent leakage of  $^{222}\text{Rn}$  and disruption of secular equilibrium between  $^{226}\text{Ra}$  and  $^{210}\text{Pb}$ . The samples were set aside for at least 20 days to establish secular equilibrium. Activities of the various radionuclides were then determined by counting using a well-type intrinsic germanium detector, "WiGe" (Princeton Gamma Tech® Model IGW11023). The samples were counted for a period of 1 to 2 days or until sufficient counts of the pertinent radionuclides were obtained (greater than 1,000 net counts for  $^{210}\text{Pb}$ ).

The peaks monitored for the purposes of this study were as follows:  $^{210}\text{Pb}$  at 46.5 KeV,  $^{214}\text{Pb}$  at 295.2 KeV and 351.9 KeV,  $^{214}\text{Bi}$  at 609.3 KeV, and  $^{137}\text{Cs}$  at 661.6 KeV. The  $^{226}\text{Ra}$  daughter

isotopes  $^{214}\text{Pb}$  (2 peaks) and  $^{214}\text{Bi}$  were used to determine the activity of  $^{226}\text{Ra}$ . Detector efficiency and counting accuracy were standardized using SRM sediment 4350B ( $^{137}\text{Cs}$ ) issued by the NIST and RGU-1 ( $^{210}\text{Pb}$ ) from the International Atomic Energy Agency.

Sedimentation rates (S) in cm/yr were calculated using the following equations with the reasonable assumption for these samples that sediment mixing was minimal:

For  $^{137}\text{Cs}$ :

$$S = \frac{\text{Depth in cm at which Activity } ^{137}\text{Cs} = \text{maximum}}{(\text{Year} - 1963) \text{ in years}}$$

and/or

$$S = \frac{\text{Depth in cm at which Activity } ^{137}\text{Cs} \text{ not detectable}}{(\text{Year} - 1950) \text{ in years}}$$

For  $^{210}\text{Pb}$ :

$$S = \frac{(-) \text{ decay constant for } ^{210}\text{Pb} (0.0311 \text{ y}^{-1})}{\text{Slope for plot of natural logarithm (ln) excess } ^{210}\text{Pb vs. sediment depth}}$$

The activity of excess  $^{210}\text{Pb}$  was calculated by subtracting the mean of  $A_{(\text{Pb-214, Bi-214})}$  from  $A_{\text{Pb-210}}$ .

## 2.2.5 Biological Parameters

### 2.2.5.1 Sediment Toxicity Tests

The toxicity tests followed guidelines established by the EPA (1994) and were performed on surface sediments collected from both the 1997 and 1998 surveys, and a “reference” sample collected from Aialik Bay near Holgate glacier. This fine-grained sediment was tested to evaluate the test organism’s sensitivity to fine-grained sediment.

Sediment samples from 20 locations in 1997, and 7 locations in 1998, were received at the testing laboratory in Martinez, California. Upon receipt, the sediment samples were stored at 4°C until used to set up the test replicates for the sediment toxicity tests. The test organisms for the 1997 sediments, *Eohaustorius estuarius*, were obtained from a commercial supplier (Northwestern Aquatic Sciences, Newport, Oregon). These organisms were acclimated to the test salinity of 34 ppt (parts per thousand). The test organisms for the 1998 sediments, *Ampelisca abdita*, were obtained from a commercial supplier (John Brezina and Associates, Dillon Beach, California).

The sediment toxicity test replicates were established on 1 day at 4 replicates for each site. Each replicate consisted of a 1 L glass beaker to which approximately 175 ml (approximately 2 cm deep) of sediment was added (each sediment sample was homogenized prior to loading of the test replicate containers). Test replicates were similarly established for a “home” control treatment, which consisted of the same sediment from which the test organisms were originally collected; this sediment was a fine-grained sand mixture. An additional “reference” control, consisting of sediment collected from Aialik Bay, was included in the 1998 sediment toxicity test; this sediment was autoclaved for 30 minutes prior to use. The overlying water consisted of 0.45 µm

filtered seawater (collected from the U.C. Bodega Bay Marine Laboratory); approximately 800 ml of this water was carefully poured into each test replicate so as to minimize disturbance of the sediment. These test replicates were then placed in a temperature-controlled water bath at 15°C (20°C for the *Ampelisca*) under continuous illumination from fluorescent lighting. Each test replicate was gently aerated.

The following day, routine water qualities (temperature, pH, dissolved oxygen [DO], and salinity) were determined for each test replicate. Then, the tests were initiated with the random allocation of 20 randomly selected organisms, into each replicate container (aeration was shut off until the amphipods reburied themselves, approximately 1 hour after their introduction). Each day, for the next 10 days, the temperature, pH, DO, and salinity were analyzed. Also on each day, a sample of the overlying water was collected from each replicate for each sediment treatment containing the *Eohaustorius*, composited, and analyzed to determine the total ammonia at that treatment. For the *Ampelisca*, water was collected on days 2 and 8 for ammonia determination.

After 10 days' exposure, routine water qualities (temperature, pH, DO, and salinity) were determined for each replicate. Then the contents of each replicate beaker were sieved and examined, and surviving amphipods were collected and counted. The resulting percent survival data were statistically analyzed using the ToxCalc statistical software (Tide-Pool Scientific, McKinleyville, California). Comparison of the survival data from each of the sites with the control treatment was made using the Homoscedastic t-Test.

#### **2.2.5.2 CYP1A (P4501A) Determinations**

Preserved sections of liver, gill, heart, and kidney were placed in cassettes in 10 percent neutral buffered formalin, embedded in paraffin, and analyzed immunohistochemically for the presence of CYP1A. Tissue sections (5- $\mu$ m) mounted on Superfrost Plus slides (Fisher), were deparaffinated and hydrated as before (Smolowitz *et al.*, 1991). Matching serial sections were incubated with 150  $\mu$ l of 1-12-3p6 monoclonal antibody against scup CYP1A, using modifications of Smolowitz (Smolowitz *et al.*, 1991). Formalin-fixed tissues were embedded in paraffin, and 5- $\mu$ m sections were mounted on Superfrost Plus slides (Fisher) and analyzed immunohistochemically for the presence of CYP1A as before (Smolowitz *et al.*, 1991). Matching serial sections were incubated using the Shandon™ coverslip system for 2 hours with two 150  $\mu$ L aliquots of MAb 1-12-3p6 or with nonspecific purified mouse myeloma protein (UPC-10, IgG2A, Organon Teknika, West Chester, Pennsylvania), each at 1.5 g/ml in 1 percent BSA/TBS added at 0 and 60 minutes. Blocking solutions, secondary antibodies, linker, and color developer were components of the Signet (Medford, Massachusetts) murine immunoperoxidase kit.

Color development was achieved as described before using 2 percent 3-amino-9-ethylcarbazole and 1 percent hydrogen peroxide. Sections were counterstained with Mayer's hematoxylin. Slides were examined with a Zeiss Axioskop microscope and relative staining intensities were determined subjectively by comparing the staining of samples to that of control and highly induced 3,3',4,4' tetrachlorobiphenyl-treated scup liver sections included in each run. Nonspecific staining, if present, was determined by comparison with UPC-10 stained sections. Staining occurrence was scored as 0-no staining (or equal to UPC staining), 1-rare- few cells staining, 2-many cells staining, 3-multifocal and diffuse-all cells staining. The intensity of staining was scored as 0-none (or equal to UPC staining), 1-mild, 2-moderate, 3-medium, 4-

strong, 5-very strong. A scaled product of staining occurrence times the staining intensity was determined for each cell type. Therefore, immunohistochemical (IHC) scores (being the product of 2 numbers, the first from 0 to 3, and the second from 0 to 5) could range from 0 to 15. In this study, scores of 1-5 are considered low, 6-10 are considered moderate, and 11-15 are considered high.

### **2.2.5.3 P450 Reporter Gene System Tests**

The detailed methodology used in this study has been described previously (Anderson et al., 1995; American Public Health Association [APHA], 1996; American Society for Testing and Materials [ASTM], 1997). The P450 Reporter Gene System (RGS) utilizes 101L cells, human hepatoma cells stably transfected with a luciferase reporter gene downstream of human CYP1A1 promoter sequences. So, CYP1A inducers also trigger a bioluminescent response in affected cells.

Two reference toxicant solutions representing two classes of CYP1A inducers, 2,3,7,8-tetrachlorodibenzo-p-dioxin TCDD, (a dioxin) and benzo[a]pyrene, (a PAH) and environmental sample extracts are applied at volumes of 2 to 20 mL to replicate wells in 6-well plates containing 2 mL of culture media. Both sediment and tissue extracts are applied in the same manner. Both reference toxicants are commonly used when the constituent contaminants of an environmental sample are unknown and/or are a complex mixture. Every RGS test includes an application of at least one and normally both reference toxicants, as the performance of the test cells varies from test to test. Use of reference toxicants in every test results in consistently accurate comparisons of toxicity of test matrices to benzo[a]pyrene (B[a]PEq) and dioxin, the most potent of the chlorinated hydrocarbons, (TEQ). Dioxin is an order of magnitude more toxic to the test cells than benzo[A]pyrene. Both 6 and 16hr. exposures were tested in this study. Duplicate plates were dosed such that one plate was incubated for 6h, and the second for 16h. Approximately 80% of the response due to PAH's is typically measurable after 6 hr. of exposure. Response due to chlorinated hydrocarbons (dioxins/furans, coplanar PCB's) is best measured with 16 hr. exposure periods, as it typically requires 16 hours for chlorinated hydrocarbons to fully induce test cells. Due to the unknown nature of contaminants in sediments and fish tissues collected in this study, both exposure periods were tested. RGS response rarely results from a single chemical contaminant, as contaminants most often occur as complex mixtures in environmental matrices (sediment, water, or tissues). The RGS values are expressed as both B[a]PEq and Toxic Equivalents (TEQ), since prior to chemical confirmation it can not be determined if the response was from exposure to PAH's (B[a]PEq) or from chlorinated hydrocarbons (TEQ). The use of (B[a]PEq) and TEQ's also allows comparison of relative toxicity of environmental samples from complex mixtures of contaminants and diverse studies.

After 6h or 16h incubation with the test solutions, the cells were washed with Hank's Balanced Salt Solution (Mediatech, Herndon, Virginia), and lysed with 200 mL of buffer containing 1 percent Triton, 25 mM Tricine, pH 7.8, 15 mM MgSO<sub>4</sub>, 4 mM EDTA, and 1 mM dithiothreitol (DTT). Cell lysates were centrifuged at 6,000 rpm for 10s, and 50 mL of the supernatant was applied to a 96-well plate, followed by 100 mL of 0.1 M potassium phosphate buffer, pH 7.8, containing 5 mM ATP and 10 mM MgCl<sub>2</sub>. Reactions were initiated by injection of 100 mL of luciferin, dissolved in 0.1 M potassium phosphate buffer, pH 7.8. Luminescence in relative light units (RLUs) was measured using a ML2250 Luminometer (Dynatech Laboratories, Chantilly, Virginia). Luciferase assay buffers were purchased from PharMingen (San Diego, California).

With each test run, a solvent blank (using a volume of DCM equal to the sample volume being tested) and a reference toxicant (1 ng/mL tetrachlorodibenzo-p-dioxin [TCDD]) were also applied to two separate replicate wells. Mean fold induction of the solvent blank was set equal to 1, and the fold induction of the reference toxicant and each sample were determined by dividing the mean RLUs produced by these samples by the mean RLUs produced by the solvent blank. The coefficient of variation among replicates was acceptable if less than 20 percent.

**Equivalency Calculations.** RGS Toxic Equivalents (TEQ) are a measure of the RGS response if the sample contained only dioxins and furans, and are calculated using the equation below. According to previous concentration-response studies using a standard mixture of dioxins and furans, the RGS response is equivalent to the mixture TEQ in pg/mL (calculated using Toxic Equivalency Factors established by Safe, 1990). Dividing by 1,000 yields the TEQ in ng/g.

$$\text{RGS TEQ} = (\text{fold induction}/1,000) * ((V_e/V_a)/W_d)$$

Where,

$V_e$  = total extract volume

$V_a$  = volume of extract applied to cells

$W_d$  = dry weight of sample

Similarly, RGS Benzo[a]pyrene Equivalents (B[a]PEq) are a measure of the RGS response if the sample contained only PAH, and are calculated in mg/g using the equation below. Based on RGS concentration-response curves for Benzo[a]pyrene, a fold induction of 60 is produced by 1 mg/mL B[a]P.

$$\text{RGS B[a]PEq} = (\text{fold induction}/60) * ((V_e/V_a)/W_d)$$

Where,

$V_e$  = total extract volume

$V_a$  = volume of extract applied to cells

$W_d$  = dry weight of sample

#### **2.2.5.4 Enumeration of Heterotrophs and Hydrocarbon-Degrading Microorganisms**

Microbial analyses were performed on surface sediments from the 1998 field survey. The analyses were for the enumeration of total heterotrophic microorganisms and hydrocarbon-degrading microorganisms, and was a modification of the most probable number (MPN) technique (Brown and Braddock, 1990; Braddock and McCarthy, 1996). Once the samples arrived in the laboratory they were stored at 4°C and were all processed within a week.

First, each sample was homogenized by mixing the sample in the sample jar with a clean spatula. Then, 10 g ( $\pm$  0.1 g) sediment was diluted into 90 ml of marine Bushnell Heas Broth. These initial dilutions were shaken by hand for one minute before further dilutions for the MPN test. Duplicates (two separate dilution series) were prepared for each sediment. In addition, for heterotrophs, laboratory duplicates were run on each dilution. Finally, approximately 5 to 10 g of sediment was dried overnight at 105°C to determine dry weights for the sediment. Final values reported were all corrected to sediment dry weight.

The cell culture plates for the MPN tests were filled with either Marine Broth (Difco) (96-well plates for heterotrophs) or marine Bushnell Heas Broth (24-well plates for hydrocarbon degraders). Following inoculation, one drop of autoclaved Cook Inlet crude oil was added to

each of the wells of the hydrocarbon-degrader plates. The plates were incubated at room temperature. After three weeks and after five weeks, the marine heterotroph plates were scored for growth. Full growth was obtained in the plates at three weeks, confirmed by rescoreing the plates at five weeks. After six weeks, the hydrocarbon degrader plates were scored for emulsification of crude oil.

## **2.2.6 Measuring, Interpreting, and Mapping Sediment Profile Imaging Parameters**

The SPI camera was used to photograph the surface and subsurface layers of sediment on the ocean floor during the 1997 survey. These images can be used to describe benthic community and benthic structure, physical setting (e.g., grain size), biochemical parameters, and depth of the redox layer.

### **2.2.6.1 Sediment Type**

The sediment grain-size major mode and range were visually estimated from the color slides by overlaying a grain-size comparator that was at the same scale. This comparator was prepared by photographing a series of Udden-Wentworth size classes (equal to or less than coarse silt up to granule and larger sizes) with the SPI camera. Seven grain-size classes were on this comparator:  $>4 \phi$ ,  $4-3 \phi$ ,  $3-2 \phi$ ,  $2-1 \phi$ ,  $1-0 \phi$ ,  $0-(-)1 \phi$ ,  $< -1 \phi$ . The lower limit of optical resolution of the photographic system was about 62 microns, allowing recognition of grain sizes equal to or greater than coarse silt ( $\geq 4 M$ ). The accuracy of this method has been documented by comparing SPI estimates with grain-size statistics determined from laboratory sieve analyses.

The comparison of the SPI images with Udden-Wentworth sediment standards photographed through the SPI optical system was also used to map near-surface stratigraphy such as sand-over-mud and mud-over-sand. When mapped on a local scale, this stratigraphy can provide information on relative transport magnitude and frequency.

### **2.2.6.2 Prism Penetration Depth**

The SPI prism penetration depth was measured from the bottom of the image to the sediment-water interface. The average penetration depth was determined by measuring across the entire cross-sectional image. Linear maximum and minimum depths of penetration were also measured. Maximum, minimum, and average penetration depths were recorded in the data file.

Prism penetration is potentially a noteworthy parameter; if the number of weights used in the camera is held constant throughout a survey, the camera functions as a static-load penetrometer. Comparative penetration values from sites of similar grain size give an indication of the relative water content of the sediment. Highly bioturbated sediments and rapidly accumulating sediments tend to have the highest water contents and greatest prism penetration depths.

The depth of the camera's penetration into the bottom also reflects the bearing capacity and shear strength of local sediments. Over-consolidated or relic sediments and shell-bearing sands resist camera penetration. Highly bioturbated, sulfidic, or methanogenic muds are the least consolidated, and deep penetration is typical. Seasonal changes in camera prism penetration are typically observed at the same station and are related to the control of sediment geotechnical properties by bioturbation (Rhoads and Boyer, 1982). The effect of water temperature on bioturbation rates appears to be important in controlling both biogenic surface relief and prism penetration depth (Rhoads and Germano, 1982).

### **2.2.6.3 Small-Scale Surface Boundary Roughness**

Surface boundary roughness was determined by measuring the vertical distance (parallel to the film border) between the highest and lowest points of the sediment-water interface. The surface boundary roughness (sediment surface relief) measured over a horizontal distance of 15 cm typically ranges from 0.02 to 3.8 cm and may be related to either physical structures (ripples, rip-up structures, mud clasts) or biogenic features (burrow openings, fecal mounds, foraging depressions). Biogenic roughness typically changes seasonally and is related to the interaction of bottom turbulence and bioturbational activities.

The camera must be level to take accurate boundary roughness measurements. In sandy sediments, boundary roughness can be a measure of sand wave height. On silt-clay bottoms, boundary roughness values often reflect biogenic features such as fecal mounds or surface burrows.

### **2.2.6.4 Thickness of Depositional Layers**

Because of the camera's unique design, SPI can be used to detect the thickness of depositional and dredged material layers. SPI is effective in measuring layers ranging in thickness from 20 cm (the height of the SPI optical window) to 1 mm. During image analysis, the thickness of the newly deposited sedimentary layers can be determined by measuring the linear distance between the pre- and post-disposal sediment-water interface. Recently deposited material is usually evident because of its unique optical reflectance and/or color relative to the underlying material representing the predisposal surface. Also, in most cases, the point of contact between the two layers is clearly visible as a textural change in sediment composition, facilitating measurement of the thickness of the newly deposited layer.

### **2.2.6.5 Mud Clasts**

When fine-grained, cohesive sediments are disturbed, either by physical bottom scour or faunal activity (e.g., decapod foraging), intact clumps of sediment are often scattered about the seafloor. These mud clasts can be seen at the sediment-water interface in SPI images. During analysis, the number of clasts was counted, the diameter of a typical clast was measured, and their oxidation state (discussed below) was assessed. The abundance, distribution, oxidation state, and angularity of mud clasts can be used to make inferences about the recent pattern of seafloor disturbance in an area.

Depending on their place of origin and the depth of disturbance of the sediment column, mud clasts can be reduced or oxidized. In SPI images, the oxidation state is apparent from the reflectance (MMS, 1998). Also, once at the sediment-water interface, these mud clasts are subject to bottom-water oxygen concentrations and currents. Based on laboratory microcosm observations of reduced sediments placed within an aerobic environment, oxidation of reduced surface layers by diffusion alone is quite rapid, occurring within 6 to 12 hours (Germano, 1983). Consequently, the detection of reduced mud clasts in an obviously aerobic setting suggests a recent origin. The size and shape of the mud clasts are also revealing. Mud clasts may be moved and broken by bottom currents and animals (macro- or meiofauna; Germano, 1983). Over time, large angular clasts become small and rounded.

### **2.2.6.6 Apparent Redox Potential Discontinuity Depth**

Aerobic near-surface marine sediments typically have higher reflectance relative to underlying

hypoxic or anoxic sediments. Surface sands washed free of mud also have higher optical reflectance than underlying muddy sands. These differences in optical reflectance are readily apparent in SPI images; the oxidized surface sediment contains particles coated with ferric hydroxide (an olive or tan color when associated with particles), while reduced and muddy sediments below this oxygenated layer are darker, generally grey to black. The boundary between the colored ferric hydroxide surface sediment and underlying grey to black sediment is called the apparent redox potential discontinuity (RPD).

The depth of the apparent RPD in the sediment column is an important time-integrator of DO conditions within sediment porewaters. In the absence of bioturbating organisms, this high-reflectance layer (in muds) will typically reach a thickness of 2 mm (Rhoads, 1974). This depth is related to the supply rate of molecular oxygen by diffusion into the bottom and the consumption of that oxygen by the sediment and associated microflora. In sediments that have very high sediment oxygen demand (SOD), the sediment may lack a high reflectance layer even when the overlying water column is aerobic.

In the presence of bioturbating macrofauna, the thickness of the high-reflectance layer may be several centimeters. The relationship between the thickness of this high-reflectance layer and the presence or absence of free molecular oxygen in the associated porewaters must be considered with caution. The actual RPD is the boundary (or horizon) that separates the positive Eh region of the sediment column from the underlying negative Eh region. The exact location of this Eh = 0 potential can be determined accurately only with microelectrodes; hence, the relationship between the change in optical reflectance, as imaged with the SPI camera, and the actual RPD can be determined only by making the appropriate in situ Eh measurements. For this reason, the optical reflectance boundary, as imaged, was described in this study as the "apparent" RPD and it was mapped as a mean value. In general, the depth of the actual Eh = 0 horizon will be either equal to or slightly shallower than the depth of the optical reflectance boundary. This is because bioturbating organisms can mix ferric hydroxide-coated particles downward into the bottom below the Eh = 0 horizon. As a result, the apparent mean RPD depth can be used as an estimate of the depth of porewater exchange, usually through porewater irrigation (bioturbation). Biogenic particle mixing depths can be estimated by measuring the maximum and minimum depths of imaged feeding voids in the sediment column. This parameter represents the particle mixing depths of head-down feeders, mainly polychaetes.

The rate of depression of the apparent RPD within the sediment is relatively slow in organic-rich muds, on the order of 200 to 300 micrometers per day; therefore this parameter has a long time constant (Germano and Rhoads, 1984). The rebound in the apparent RPD is also slow (Germano, 1983). Measurable changes in the apparent RPD depth using the SPI optical technique can be detected over periods of 1 or 2 months. This parameter is used effectively to document changes (or gradients) that develop over a seasonal or yearly cycle, related to water temperature effects on bioturbation rates, seasonal hypoxia, SOD, and infaunal recruitment. Time-series RPD measurements following a disturbance can be a critical diagnostic element in monitoring the degree of recolonization in an area by the ambient benthos (Rhoads and Germano, 1986).

The apparent mean RPD depth also can be affected by local erosion. The peaks of disposal mounds commonly are scoured by divergent flow over the mound. This scouring can wash away

finer and shell or gravel lag deposits, and can result in very thin apparent RPD depths. During storm periods, erosion may completely remove any evidence of the apparent RPD (Fredette *et al.*, 1988).

Another important characteristic of the apparent RPD is the contrast in reflectance at this boundary. This contrast is related to the interactions among the degree of organic loading, the bioturbation activity in the sediment, and the concentrations of bottom-water dissolved oxygen in an area. High inputs of labile organic material increase SOD and, subsequently, sulfate reduction rates and the associated abundance of sulfide end products. This results in more highly reduced, lower-reflectance sediments at depth and higher RPD contrasts. In a region of generally low RPD contrasts, images with high RPD contrasts indicate localized sites of relatively high past inputs of organic-rich material such as phytoplankton or other naturally occurring organic detritus, dredged material, and sewage sludge.

#### **2.2.6.7 Sedimentary Methane**

If organic loading is extremely high, porewater sulfate is depleted and methanogenesis occurs. The process of methanogenesis is indicated by the appearance of methane bubbles in the sediment column, and the number and spatial coverage of all methane pockets is measured. These gas-filled voids are readily discernable in SPI images because of their irregular, generally circular aspect and glassy texture (due to the reflection of the strobe off the gas bubble).

#### **2.2.6.8 Infaunal Successional Stage**

The mapping of infaunal successional stages is readily accomplished with SPI technology. These stages are recognized in SPI images by the presence of dense assemblages of near-surface polychaetes and/or the presence of subsurface feeding voids; both may be present in the same image. Mapping of successional stages is based on the theory that organism-sediment interactions in fine-grained sediments follow a predictable sequence after a major seafloor perturbation. This theory states that primary succession results in "the predictable appearance of macrobenthic invertebrates belonging to specific functional types following a benthic disturbance. These invertebrates interact with sediment in specific ways. Because functional types are the biological units of interest, our definition does not demand a sequential appearance of particular invertebrate species or genera" (Rhoads and Boyer, 1982). This theory is presented in Pearson and Rosenberg (1978) and further developed in Rhoads and Germano (1982) and Rhoads and Boyer (1982).

This continuum of change in animal communities after a disturbance (primary succession) has been divided subjectively into three stages: Stage I is the initial community of tiny, densely populated polychaete assemblages; Stage II is the start of the transition to head-down deposit feeders; and Stage III is the mature, equilibrium community of deep-dwelling, head-down deposit feeders.

After an area of bottom is disturbed by natural or anthropogenic events, the first invertebrate assemblage (Stage I) appears within days after the disturbance. Stage I consists of assemblages of tiny tube-dwelling marine polychaetes that reach population densities of  $10^4$  to  $10^6$  individuals per  $m^2$ . These animals feed at or near the sediment-water interface and physically stabilize or bind the sediment surface by producing a mucous "glue" that they use to build their tubes. Sometimes deposited dredged material layers contain Stage I tubes still attached to mud clasts

from their location of origin; these transported individuals are considered as part of the in situ fauna in our assignment of successional stages.

If there are no repeated disturbances to the newly colonized area, then these initial tube-dwelling suspension or surface-deposit feeding taxa are followed by burrowing, head-down deposit-feeders that rework the sediment deeper and deeper over time and mix oxygen from the overlying water into the sediment. The animals in these later-appearing communities (Stage II or III) are larger, have lower overall population densities (10 to 100 individuals per m<sup>2</sup>), and can rework the sediments to depths of 3 to 20 cm or more. These animals loosen the sedimentary fabric, increase the water content in the sediment, thereby lowering the sediment shear strength, and actively recycle nutrients because of the high exchange rate with the overlying waters resulting from their burrowing and feeding activities.

### **2.2.6.9 Organism-Sediment Index**

The Organism-Sediment Index (OSI) is a summary mapping statistic that is calculated on the basis of four independently measured SPI parameters: 1) apparent mean RPD depth, 2) presence of methane gas, 3) low/no dissolved oxygen at the sediment-water interface, and 4) infaunal successional stage. Table 2-7 shows how these parameters are summed to derive the OSI.

The highest possible OSI is +11, which reflects a mature benthic community in relatively undisturbed conditions (generally a good yardstick for high benthic habitat quality). These conditions are characterized by deeply oxidized sediment with a low inventory of anaerobic metabolites and low SOD, and by the presence of a climax (Stage III) benthic community. The lowest possible OSI is -10, which indicates that the sediment has a high inventory of anaerobic metabolites, has a high oxygen demand, and is azoic. Based on Joe Germano's (EVS Environmental Consultants) mapping experience over the past 15 years, he has found that OSI values of 6 or less indicate that the benthic habitat has experienced physical disturbance, eutrophication, or excessive bioavailable contamination in the recent past.

## **2.3 Statistical Methods**

### **2.3.1 Coefficient of Variation**

The coefficient of variation (CV) was used to describe the variation in several populations of physical and chemical sediment parameters. The CV can be expressed as a percent and is generally defined by:

$$CV = 100 * \sigma / m$$

Where  $\sigma$  is the standard deviation and  $m$  is the population mean (Snedecor and Cochran, 1978). The utility of the measure lies partly in the fact that within many data sets, the mean and standard deviation tend to change in concert. The experimental design associated with the 1997 sediment surface sampling program included three stations possessing seven replicate samples each. Intensive sampling at selected stations was conducted for the purpose of evaluating within station variation.

A modification of the general CV statistic of the equation above was used to describe the within station variation for each of the measured chemical/physical parameters. The following equation

was used to generate within station CVs for each measured parameter at the multi-replicate stations:

$$CV = 100 * \sqrt{(SS_1 + SS_2 \dots + SS_i) / (df_1 + df_2 \dots + df_i) / X}$$

Where,

$SS_1, SS_2, \dots, SS_i$  are the parameter-specific sums of squares at each of the stations with seven field replicates;  $df_1, df_2, \dots, df_i$  are the associated degrees of freedom, and X is the grand mean of the parameter of interest from all seven-replicate stations. All data manipulations were aided by the Statistical Analysis System (SAS, ver. 6.12).

Within-zone variation was also explored using the general CV statistic for each zone and chemical/physical parameter. For this analysis, all stations with greater than one replicate per station were included in calculations. Additionally, a parameter-specific "Grand CV" was calculated incorporating all parameter-specific information gathered at stations with greater than one replicate. A CV ratio was then calculated by dividing the zone parameter-specific CV by the Grand CV. Ratios less than one can be used to highlight parameters where within zone variability is less than overall system variability.

### 2.3.2 Analysis of Variance

The General Linear Model (GLM), an application of an analysis of variance (ANOVA), was used to elucidate significant differences between zones. Under the GLM, a continuous response, or dependent, variable (e.g., zinc) is measured under experimental conditions identified by classification, or independent, variables (*i.e.*, zone and year). The variation in the response is explained as being due to effects in the classification, with random error accounting for the remaining variation (Searle, 1971). Prior to running the GLM analyses, mean values were generated for each of the multireplicates. This was deemed appropriate since the variability within stations was much lower than variability between stations, and thus stations can be considered replicates within a zone. Mean station values were subsequently used in all GLM hypothesis testing.

A significant effect identified by the GLM statistic indicates that the classification variables (e.g., Zones) differ for a specific dependent variable (e.g., zinc), but the model does not tell how this difference is manifested (*i.e.*, which Zones are different). A Student-Newman-Keuls (SNK) multiple range test (Steel and Torrie, 1980) was used to identify significant differences ( $p < 0.05$ ) between classification variables when the associated GLM indicated a significant difference. Simply put, the SNK test was used to separate classification variables into significantly different groupings. These tests were performed on the following sets of data:

- Surface sediments collected from 59 stations within zones 0, 1, 2, and 3 in 1997, measured for 23 organic and 26 inorganic parameters
- Surface sediments collected from 35 stations within zones 0, 1, 2, 3, and 4 in 1998, measured for 23 organic, 23 inorganic, and 5 biological parameters

It is well established that certain chemical/physical parameters tend to predict concentrations of other analytes. Because of this, several GLM analyses were performed on the surface sediment data set before and after the transformation (normalization) of metals (dividing metal concentration by percent iron at the station) and organic compounds (dividing by percent total organic carbon at a station).

A GLM analysis was also performed on surface sediment collected from both the 1997 and 1998 sampling periods in order to determine whether significant variance could be attributed to time of collection/analysis. A Bonferroni multiple range test was used to identify significant differences ( $p < 0.05$ ) between classification variables when the associated GLM indicated a significant difference. The Bonferroni multiple range test is conceptually similar to the SNK, however, it is less sensitive to problems associated with an unbalanced experimental design (unequal number of stations, zones, and/or replicates). This test was performed on a subset of data where station sampling and parameter analysis was repeated during both years and totaled 16 stations (14 stations for the RGS-P450 data).

### **2.3.3 Pearson Product-Moment Correlation**

#### **2.3.3.1 Sediments**

Not all chemical, physical, and biological parameters were measured at all stations. However, subsets of the data were collected to identify significant correlations between measurement parameters and additional differences between zones. These subsets included the following:

- 20 stations in 1997 shared 37 common measurement parameters
- 14 stations where sampling was repeated during both the 1997 and 1998 surveys over 37 measurement parameters

Again, the correlation analyses were performed on both transformed and nontransformed organic/inorganic data. Aquatic toxicity test results were reported as mean percent survival (MPS) and, along with the chemical/physical measurements reported as percents, was transformed by applying an arc sine square root to the fractional data.

Correlative analyses were performed on the separate data sets using the Pearson product-moment which measures the strength of the linear relationship between two variables. If one variable (e.g., length) can be expressed exactly as a linear function of another variable (e.g., weight), then the correlation is 1 if the variables are directly related, or -1 if the variables are inversely related. A correlation of 0 between two variables suggests that each variable has no linear predictive ability for the other. If the values associated with the variables are normally distributed, a correlation of 0 also means the variables are independent of one another. Again, SAS ver. 6.12 was used to perform data manipulations and analysis.

#### **2.3.3.2 Tissues**

Measurements of chemical and biological parameters, similar to those applied to sediments were used in the examination of fish tissues at three stations. Three species of mixed size and sex were acquired. Subsetting of tissues was necessary for microscopic analyses and not all fish were examined for all chemical/biological parameters. Chemical analyses were performed on composite samples of fish tissue (a requirement of chemical analytical methods), while all fish

were measured or evaluated for “non-quantity dependent” variables (e.g., length). Data sets included the following:

- In 1997, P450 measurements (Section 2.5.2) were made on 45 individuals and chemical/biological measurements were made on 13 tissue composites.
- In 1998, P450 measurements were made on 116 individuals and chemical/biological measurements were made on 30 tissue composites.

By collecting data in the form of discrete (e.g., length) and composite (e.g., chemical) measurements it was not possible to correlate measures on a one-to-one basis. To evaluate the degree to which two or more variables were related and changed together (correlated), it was necessary to calculate average individual measurements (e.g., length and P450) using groupings defined by the chemical composite groupings. A Pearson’s correlation was applied to the data, after the averaging process, and significant correlations ( $p \leq 0.05$ ) were retained and reported.

#### **2.3.4 Analysis of Variance/Covariance**

GLM and SNK procedures were applied to both the combined chemical/biological and the P450 data sets. In general, fish length positively correlates with fish age, and fish age has been shown to covary with several chemical and biological (P450) parameters. The tendency of one statistical variable to change in relation to another is commonly termed as covariance. Analysis of covariance combines some of the features of a typical regression model with analysis of variance. Typically, a continuous variable (the covariate length in the example above) is introduced into the analysis of variance model in an attempt to lessen the influence of the covariate. GLM processing used length as a covariant for this reason. Additionally, since sex was recorded for each fish sex and is known to correlate with many of the measured parameters sex was examined as a possible covariate during the analytical process.

#### **2.3.5 Random Effects Analysis of Variance**

The basic data analysis and statistical questions center around whether there is a consistent and statistically significant pattern associated with the oil and gas development and production operations initiated in 1963. Although concentrations of metals and hydrocarbons associated with post-1963 oil and gas development would be expected to differ by zone and distance from the production sites, as detailed in Section 3.4, indicator ratios of metal and hydrocarbon concentrations might be expected to show consistent patterns even as the absolute concentrations decline with distance from the production site.

Since information from the cores is limited, a parsimonious statistical model was developed to explain post-1963 shifts in metal and organic indices. This statistical analysis models the individual cores as randomized blocks, where each core is considered as a random sample, with a mean effect and an oil and gas development and production effect.

The statistical model for the  $i^{\text{th}}$  core and the  $j^{\text{th}}$  slice is

$$y_{ij} = \mu + \alpha_i + \beta_i I_{ij} + \epsilon_{ij}$$

Where  $\alpha_i$  is the core effect and  $I_{ij}$  is the indicator variable, which is one if the core is post-1963 and zero otherwise. Within this type of model, there are two modeling approaches. First, we can think of the oil production effect as fixed and constant between cores, thus  $\beta_i = \beta$ , and test the null hypothesis that the effect is zero. The second, and more realistic approach, is to consider the sampled cores as a random sample of all cores, where the oil production effect is consistent, that is, in the same direction, but variable between cores. For the second random effect model, the null hypothesis is that the mean of the random effect differs from zero. Subsequently, the alternate hypothesis is that there is a consistent but variable effect between cores.

Data were analyzed and plotted using the statistical package S-plus. The linear mixed effects models within S-plus were used for the "random cores analysis." The analysis is based on methods developed in Laird and Ware (1982) using restricted maximum likelihood methods. The distribution theory is approximate for small sample sizes. The P-values reported for the random effects models are only approximated and should be used only to judge the relative strength of the evidence for post-1963 shifts.

## **2.4 Quality Assurance/Quality Control**

As part of our overall QA/QC program, both field and laboratory QA/QC measures were taken. Several types of field QC samples were collected during the survey, including field blanks, equipment blanks, replicate samples, an *Alpha Helix* reference diesel-fuel sample, and a trip blank. These samples were collected to characterize potential influences from equipment (Van-Veen grab, boxcore, core liner, fish dissection tools) and each type of sampling activity (sediment sample collection, fish sampling, and dissection). For the field QA/QC samples, one jar each was collected for metals and organics analyses. Laboratory quality assurance (QA) measures included maintaining detailed laboratory records and comprehensive validation of data packages. In addition, several QC measures were implemented in conjunction with hydrocarbon and metals analyses in order to provide a measure of analytical accuracy, precision, and potential contamination.

### **2.4.1 Field Quality Assurance/Quality Control**

QA/QC samples were collected during the field sampling program to assess overall accuracy and representativeness of the sampling efforts. The number of QC samples collected for this effort is based on the total number of field samples as established in the sampling and logistics plans (Arthur D. Little, 1997a; Arthur D. Little, 1998). Discussion and interpretation of analytical results for these samples are provided in Section 3.6. Quality assurance techniques were used in sampling activities to avoid potential contamination and cross-contamination including use of: precleaned sample containers; clean sampling equipment; decontamination protocol; and good laboratory practices. Standard sampling procedures and protocols were followed. In this section, the field methods used for collecting field QC samples are summarized.

Several types of field QC samples were collected during the field survey, including equipment blanks, field blanks, and trip blanks. For all field QA/QC samples, one jar each was collected for metals and organics analyses.

#### **2.4.1.1 Equipment Blanks**

Three equipment blank samples were collected from rinsate of the grab sampling equipment at locations Z0F1, Z0F8, and Z3R13 in 1997, and three similar rinsates were collected at locations Z1R19, Z2R14A, and Z2R23 in 1998. Both the 1997 and the 1998 surveys included an equipment blank collected from rinsate of fish dissection equipment that was used in the on-board laboratory associated with location Z2R14A. One additional equipment blank sample was collected from rinsate of the box core sampling equipment (and core liner) at location Z0F1. The procedure for collecting the equipment blank samples followed these steps:

- The equipment was decontaminated according to the SOP
- The equipment was rinsed with high-purity, deionized water and the rinsate collected directly into two clean, pre-labeled water sample containers
- A pre-cleaned stainless-steel funnel was used to assist in the collection
- The rinsate equipment blank sample was refrigerated at 4°C

#### **2.4.1.2 Field Blanks**

Field blanks were collected during sampling, representing atmospheric or other contamination that the field samples may have been subject to. Three field blank samples were taken during the collection of sediment samples. One field (deck) blank was collected during sediment sampling in 1997 at location Z1R9 when a forest fire smoke smell was noticed in the air. The other two field blank samples, deck blanks, were collected during sediment sampling at location Z2F1 and location Z2R23, in 1997 and 1998, respectively.

To collect field blank samples, a clean, pre-labeled sample jar of the same batch used for sample collection was carried into the working area, opened during the collection of one sample, and returned to the laboratory with the field samples. For each field blank, two sample containers were collected for metals and organics analysis, respectively. The field blanks were stored under the same conditions as their associated field samples.

#### **2.4.1.3 Trip Blanks**

A trip blank sample was prepared to accompany the samples from location Z0F1 during the 1997 survey. The trip blank was a sample jar that was never opened. The trip blank was treated similar to other field samples during storage and shipment.

#### **2.4.1.4 Field Source Sample**

A source sample of the R/V *Alpha Helix* diesel fuel was taken during the 1997 field survey. The purpose of this sample was to, if necessary, be able to characterize any potential sample contamination believed to originate from the shipboard diesel fuel (e.g., exhaust and surface sheen). The ship's engineer collected a sample of diesel fuel in a pre-cleaned glass jar. The sample was stored separately from the other samples at room temperature, and shipped packaged in two plastic bags to prevent leaking or cross-contamination to other samples.

## 2.4.2 Organics Analysis Quality Assurance/Quality Control

### 2.4.2.1 Quality Assurance

*Laboratory Records.* All laboratory operations were documented and placed in three-ring binders. Documentation included the following:

- Lot number and vendors for reagents and standards
- Preparation of stock solutions, standards, and spiking solutions
- Sample preparation
- Analytical procedures
- Analytical instrument and conditions
- Dates of analysis of standards
- Dates of analysis of samples
- Problems encountered
- Corrective actions

All entries were initialed and dated by the analyst at the time of entry. Any deviations from SOP were explained, initialed, and dated. All the raw data and chromatograms acquired on the data systems linked with GC/FID and GC/MS instruments were archived in both hardcopy and electronic form.

*Data Validation.* All chemistry data generated by Arthur D. Little's laboratories were assembled in data packages and validated by the designated team member in charge of each analysis to ensure that the data quality objectives (DQOs) for accuracy and precision were met, that the data were generated in accordance with the Laboratory Quality Assurance (QA) Plan, and that data are both traceable and defensible. Data packages were also reviewed by the Project Manager to ensure compliance with procedures and (DQOs) specified in the QA Plan. Data were also reviewed for their consistency with expected petroleum hydrocarbon, PAH, or saturated hydrocarbon distributions.

When data validation was successfully completed by each facility, all data sets were submitted to the QA Officer for a formal audit. This formal audit included a 100 percent review on all hand-entered and calculated data, i.e., preparation documentation, standard amounts, weights, etc. Approximately 20 percent of each data set that was generated by an automated system was checked for accuracy. This involved tracking the final reported concentrations back to the raw data. After any necessary corrections were made, the data were approved by the auditor and forwarded to the Case Leader for review. A formal report documenting the audit findings was generated and maintained in the QA Unit files.

### 2.4.2.2 Quality Control

*Data Quality Requirements.* DQOs are established to ensure that analytical data are of the quality necessary to achieve project objectives. Our DQOs are designed to enhance our ability to identify and accurately quantify source-specific oils. The DQO limits are listed in the specific laboratory and analytical SOP. PAH and SHC DQOs and criteria are summarized in Table 2-8. DQOs for biomarker analysis are summarized in Table 2-9.

Target analyte concentrations, surrogate recoveries, and QC sample results were determined at the respective GC/FID and GC/MS facilities. After careful checking and review by the facility's

manager, these data were arranged in Excel spreadsheet format. Diagnostic graphics were also generated and submitted to the program manager for review. Any subsequent changes to or updates of the data in the spreadsheet were performed by the respective facility. The data packages containing all the information (e.g., chain-of-custody sheets, sample preparation data) required for QA audits were submitted to the QA data auditor.

The auditor prepared a concise audit report for each type of analysis. Comments and action items in the audit report were addressed by the Arthur D. Little laboratory manager and instrument facility supervisors.

### **2.4.3 Metals and Total Organic Carbon Analysis Quality Assurance/Quality Control**

#### **2.4.3.1 Quality Assurance**

*Sample Tracking Procedure.* Upon receipt, each sediment, tissue, and source sample received by the Marine and Environmental Chemistry Laboratories at FIT was carefully inspected to ensure that it was intact and that the identification number on the sample container matched that found on the custody sheet. All sediment and source samples were kept refrigerated ( $\sim 1^{\circ}\text{C}$ ) and all tissue samples were kept frozen ( $\sim 18^{\circ}\text{C}$ ) until processed for analysis.

#### **2.4.3.2 Quality Control**

For this project, QC measures included balance calibration, instrument calibration (FAAS, ZGFAAS, CVAAS, ICP/MS, and NCS analyzer), matrix spike analysis for each metal, duplicate sample analysis, SRM analysis, procedural blank analysis and standard checks. With each batch of up to 40 samples, 2 procedural blanks, 2 SRM, 2 duplicate samples, and 2 matrix spiked samples also were analyzed. DQOs for these QC measurements are provided in Table 2-10.

*Instrument Calibration.* Electronic balances used for weighing samples and reagents were calibrated prior to each use with certified (NIST traceable) standard weights. All pipets (electronic or manual) were calibrated prior to use. Each of the spectrometers used for metal analysis was initially standardized using a three- to five-point calibration curve with a linear correlation coefficient of  $r \geq 0.999$  required before experimental samples could be analyzed. Analysis of complete three- to five-point calibrations and/or single standard checks alternated every 5 to 10 samples until all the analyses were complete. The relative standard deviation (RSD) between complete calibration and standard check was required to be less than 15 percent or recalibration and reanalysis of the affected samples was performed.

*Matrix Spike Analysis.* Matrix spikes were prepared for a minimum of 5 percent of the samples analyzed and included each metal to be determined. Results from matrix spike analysis using the method of standard additions provided information on the extent of any signal suppression or enhancement due to the sample matrix. If necessary (i.e., spike results outside an 80 to 120 percent limit), all samples were analyzed by the method of standard additions.

*Duplicate Sample Analysis.* Duplicate samples from homogenized field samples (as distinct from field replicates) were prepared in the laboratory for a minimum of 5 percent of the total samples. These laboratory duplicates were included as part of each set of sample digestions and analyses to provide a measure of analytical precision.

**Procedural Blank Analysis.** Two procedural blanks were prepared with each set of 40 samples to monitor potential contamination resulting from laboratory reagents, glassware, and processing procedures. These blanks were processed using the same analytical scheme, reagents, and handling techniques as used for the experimental samples.

**Standard Reference Material Analysis.** A common method used to evaluate the accuracy of environmental data is to analyze SRM, samples for which consensus or "accepted" analyte concentrations exist. The following SRM were used: Marine Sediments, BCSS-1 and MESS-2 (NRC); Estuarine Sediment 1646a (NIST); Buffalo River Sediment 2704 (NRC); Oyster Tissue 1566a (NIST); Dogfish Muscle DORM-2 (NRC); Lobster Hepatopancreas TORT-2 (NIST), River Water SLRS-3 (NRC) and Trace Elements in Water 1643d (NIST). Metal concentrations obtained for the SRM were required to be within  $\pm 20$  percent of accepted values for greater than 85 percent of other certified analyses. When no certified values exist for a metal, matrix spikes were used to evaluate analytical accuracy.

**Filter Weighing.** All weighing-related manipulation of the filters used for suspended particulate quantification took place under cleanroom conditions, including controlled temperature and relative humidity. Each filter was weighed twice in random order, with a minimum of 5 percent of the filters being weighed in triplicate. Static effects during filter weighing were controlled by placement of two  $^{210}\text{Po}$  antistatic devices near the weighing pan within the balance. The standard deviation for the mass of each filter was required to be less than 2  $\mu\text{g}$  for the value to be accepted.

#### **2.4.4 Biology Quality Assurance/Quality Control**

##### **2.4.4.1 Sediment Toxicity Tests**

The methods used in conducting these tests followed the guidelines established by the EPA manual *Methods for measuring the toxicity of sediment-associated contaminants with estuarine and marine amphipods* (EPA, 1994). The following methodological QA/QC criteria were met at test initiation and validate the results obtained:

- Adult organisms, 3 to 5 mm and in good condition, were used at test initiation; all organisms were from the same source
- Tests were started within 2 days of sediment sample receipt, well within acceptable holding time limits
- Test chambers were identical and contained the same amount of sediment and overlying water
- All instruments used for routine measurements of chemical and physical characteristics were calibrated each day according to the instrument manufacturer's instructions

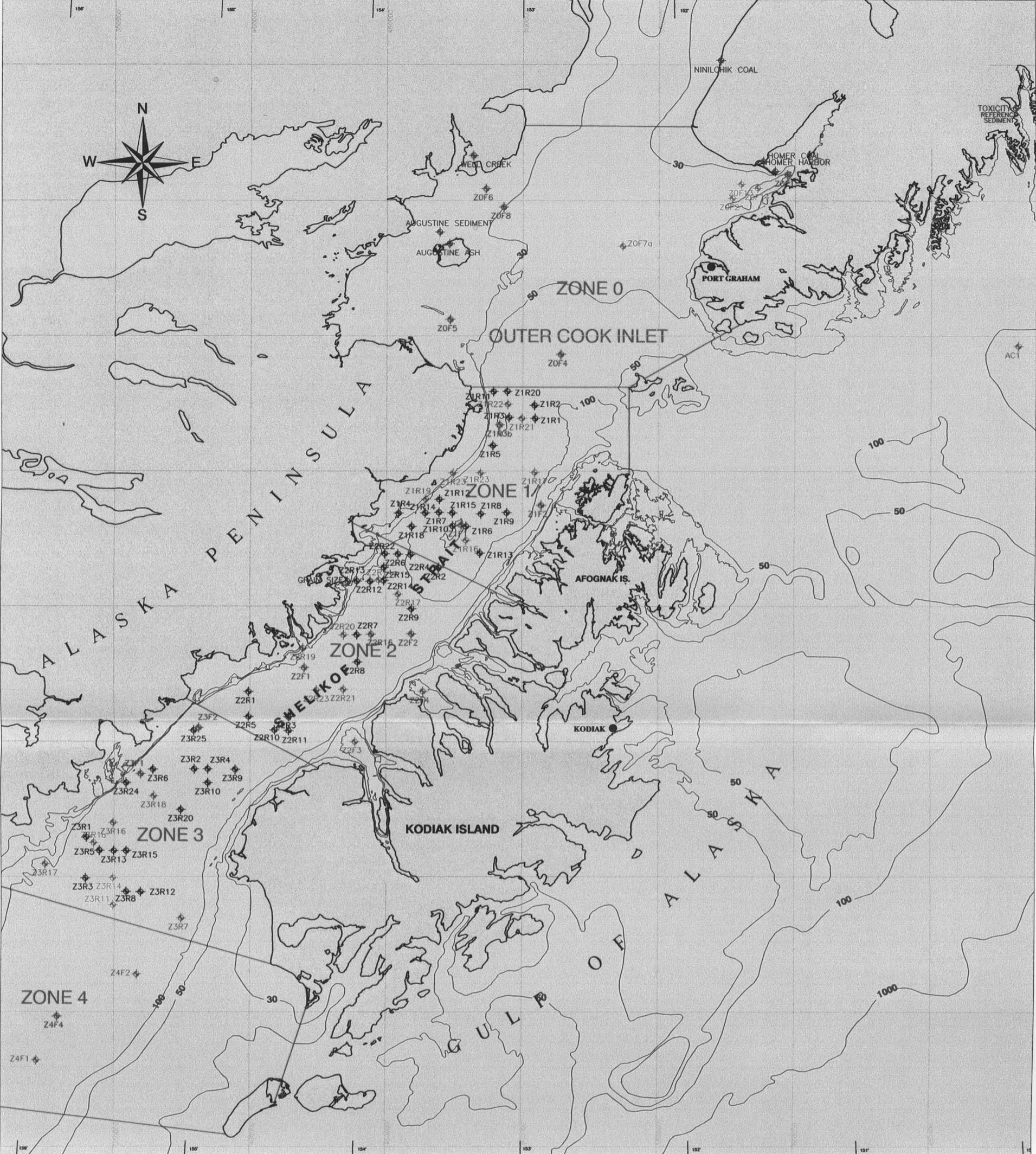
##### **2.4.4.2 CYP1A (P4501A) Determinations**

- Internal standards were included in each staining run to ensure the consistency and quality of a run, and to determine maximum (occurrence 3 times intensity 5=15) and minimum (0) staining
- All tissues were stained with UPC 10 to determine if nonspecific staining was present
- As part of the standard Signet protocol, slides were presoaked in 3 percent  $\text{H}_2\text{O}_2$  to eliminate endogenous peroxidase activity
- Any slides with questionable staining were rerun

#### **2.4.4.3 P450 Reporter Gene System Determinations**

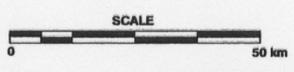
Measures of QA/QC were taken during testing of each batch of environmental samples. The reference inducer (TCDD) at a concentration of 1 ng/mL, and a solvent blank, typically DCM, are each applied to replicate wells. The fold induction response, that is, the mean RLU of the TCDD divided by the mean RLU of the DCM blank, is compared to a long-term QC chart. The response to 1 ng/mL TCDD must be within 2 standard deviations of the running mean (approximately  $100 \pm 30$ ). Calibration of the luminometer is performed monthly, using a luciferase control kit purchased from Pharmingen.

Environmental extracts are applied to 2 (for both 6h and 16h time periods) or 3 (for only the 16h time period) replicate exposure wells, and the CV is evaluated for each sample. A CV that is in excess of 20 percent is unacceptable, and that extract must be re-tested. In addition, any extract that produces a fold induction response greater than 100 percent must be diluted and retested. Typically, an extract is diluted 1:10 in DCM, and applied to 3 replicate wells.

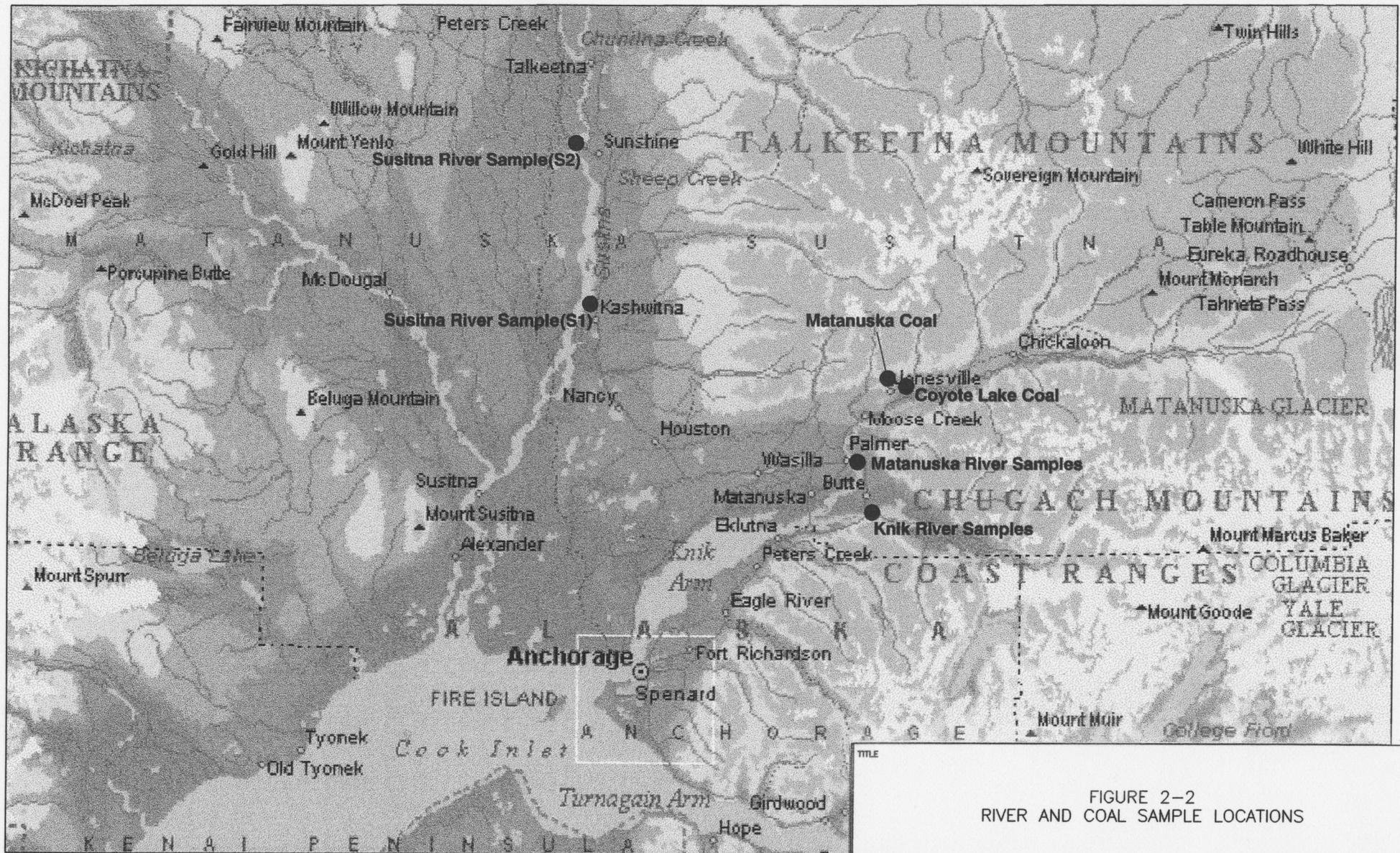


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LEGEND		ZONE DESCRIPTIONS	
Z3R7	1997 STATION LOCATION	ZONE 1	NORTH SHELIKOF STRAIT
ZOF1	1998 STATION LOCATION	ZONE 2	MID-SHELIKOF STRAIT
ZOF1	1997 and 1998 STATION LOCATION	ZONE 3	SOUTH SHELIKOF STRAIT
Z4F4	CORE STATION LOCATION (1997 and/or 1998)	ZONE 4	OUTER SHELIKOF STRAIT
Z1R23	FISH STATION LOCATION (1997 and/or 1998)		
WELL CREEK	1997/1998 SOURCE/REFERENCE STATION		
— 50.0 —	BATHYMETRY IN FATHOMS		

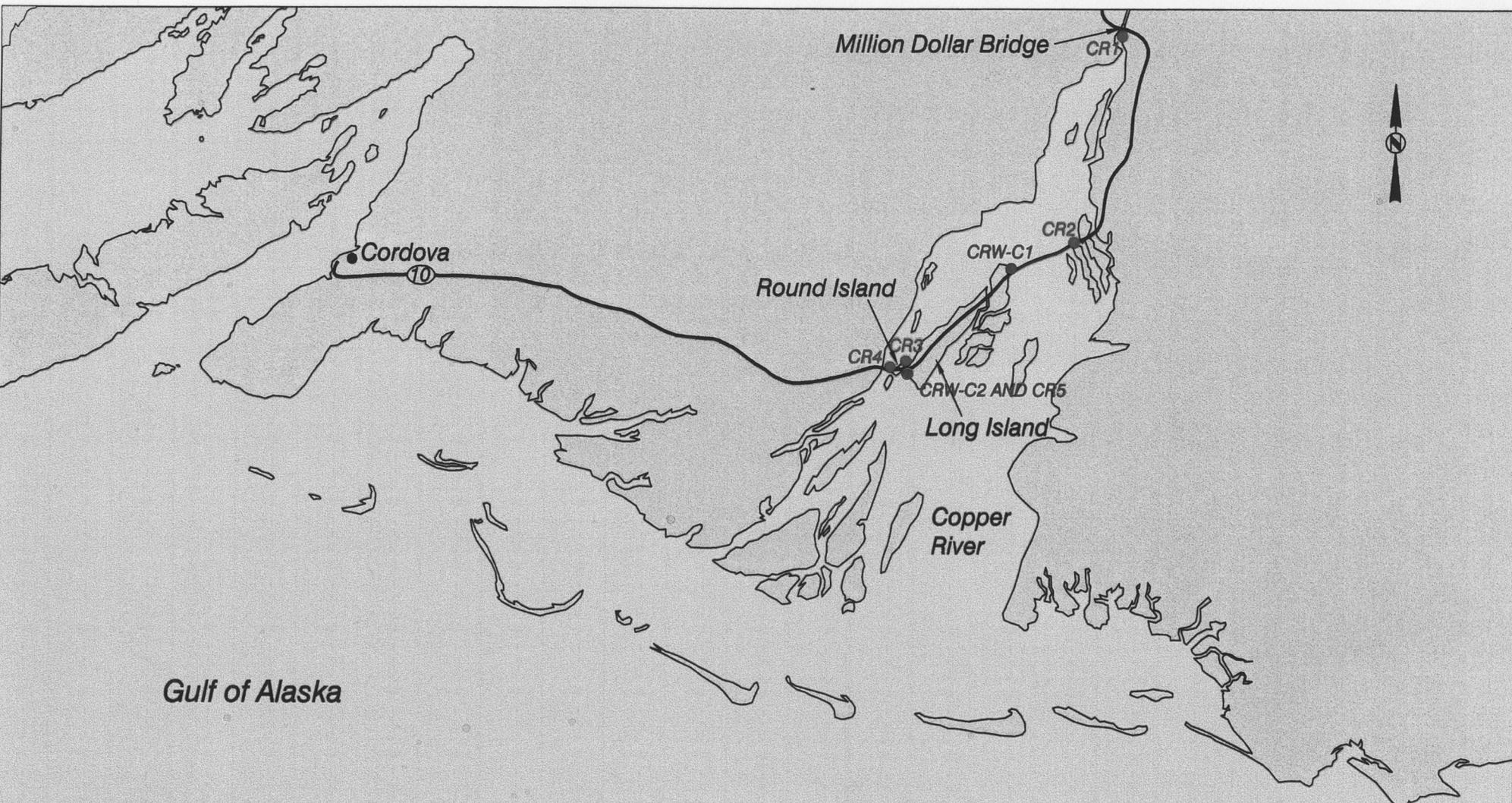


**FIGURE 2-1**  
**COOK INLET AND THE SHELIKOF STRAIT**  
**1997 AND 1998 FIELD SURVEY**  
**STATION LOCATIONS**



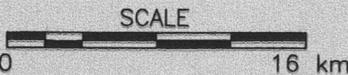
● RIVER AND COAL SAMPLE LOCATIONS

TITLE		FIGURE 2-2 RIVER AND COAL SAMPLE LOCATIONS	
PREPARED FOR	MINERALS MANAGEMENT SERVICE	SCALE	NOT TO SCALE
DATE	OCT. 1999	DWG. NO.	32319-010
SOURCE	EXPEDIA MAPS	SHEET	1 OF 1



Gulf of Alaska

LEGEND	
●	1997 SAMPLING POINT
●	1998 SAMPLING POINT



<p style="text-align: center;"><b>Arthur D Little</b></p>		TITLE	
		FIGURE 2-3 COPPER RIVER SOURCE SAMPLING LOCATIONS JULY 1997/MAY 1998	
APPROVALS	DATE	PREPARED FOR	SCALE
DRAWN		MINERALS MANAGEMENT SERVICE	1 cm = 4 km
CHECKED		DATE	DWG. NO.
QA/CONTROL		SEPT. 1999	32319-006
TECH REVIEW		SOURCE	SHEET <u>1</u> OF <u>1</u>
PROJ MNGR		ARTHUR D. LITTLE, INC.	

**Table 2-1: 1997 and 1998 MMS Shelikof Strait and Outermost Cook Inlet Stations**

1997 Station ID	Station Type	Latitude	Longitude	Depth (m)	Date	Time	Samples Collected											Comments	
							Organics	Metals	Grain Size	TOC	RGS-P450	Toxicity	AVS/SEM	Core	SPI	Fish/P450	CTD		QC
Z0-F1	Fixed	59°36.30	151°20.12	75	7/17/97	0429-0526	3	3	3	3	1	1	1	4	1	NS	1	3	1 Archive Core & 1 Gravity Core
Z0-F2	Fixed	59°31.55	151°41.88	101	7/16/97	2352-0055	3	3	3	3	1	1	1	NS	NS	NS	1	NS	
Z0-F3	Fixed	59°10.00	152°13.83	126	7/16/97	1759	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	Abandoned due to coarse substrate
Z0-F4	Fixed	59°01.79	152°45.59	162	7/16/97	0112-0336	3	3	3	3	1	1	1	1	1	NA	1	NS	1 Archive Core
Z0-F5	Fixed	58°08.66	153°28.11	42	7/16/97	0506-0622	3	3	3	3	1	1	1	3	1	NS	1	NS	1 Archive Core & 1 Chem Core
Z0-F6	Fixed	59°34.8	153°14.41	28	7/16/97	1125-1245	3	3	3	3	1	1	1	3	1	NS	1	NS	CTD from station Z0-F6a; 1 Archive Core & 1 Chem Core
Z0-F6a	Fixed	59°36.69	153°15.22	21	7/16/97	1100	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	Station abandoned due to coarse sand and some silt.
Z0-F7	Fixed	59°25.72	152°19.06	72	7/16/97	1554	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	Station abandoned due to coarse sand and shell substrate.
Z0-F7a	Fixed-long line	59°23.72	152°21.41	75	7/16/97	1527-2100	6	6	NS	NS	6	NS	NS	NS	NS	NS	NS	NS	29 halibut for P450
Z0-F8	Fixed	59°31.23	153°07.70	37	7/16/97	0925-1017	3	3	3	3	1	1	1	NS	1	NS	1	1	No box core due to coarser grained sediment below surface. Equipment blank DI water rinse of the grab sampler.
Z0-F9	Fixed Alternate	59°22.03	152°22.05	78	7/16/97	1632	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	Station abandoned due to coarse sediment.
Z0-F10	Fixed Alternate	59°09.94	152°24.04	108	7/16/97	2010	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	Station abandoned due to coarse substrate.
Z0-F12	Fixed Alternate	59°33.00	152°01.94	44	7/16/97	2244	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	Station abandoned due to shell hash. Two new stations selected: Z0-F13 and Z0-F14.
Z0-F13	Fixed Alternate	59°34.34	151°38.06	76	7/17/97	0125-0212	3	3	3	3	1	1	1	NS	1	NS	1	NS	
Z0-F14	Fixed Alternate	59°33.63	151°31.94	125	7/17/97	0241-0332	3	3	3	3	1	1	1	NS	1	NS	1	NS	
Z1-F1	Fixed	58°27.72	153°23.21	195	7/14/97	1751 - 2108	3	3	3	3	1	1	1	4	1	NS	1	NS	AVS/SEM from Rep. 1; Tox. and RGS from composite of all 3 reps; 1 Chem, 1 Archive, and 1 Gravity Core.
Z1-F2	Fixed	58°32.66	152°52.19	215	7/10/97	121	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	Station abandoned due to washouts, sand, shell fragments, and/or mud for both grab attempts. Transit to Zone 2, F2.
Z1-F2	Fixed Alternate	58°31.67	152°53.16	215	7/15/97	0953-1130	3	3	3	3	1	1	1	3	1	NS	1	NS	Second attempt at station, position moved to obtain more favorable bottom substrate.
Z1-R1	Random	58°49.12	152°55.29	152	7/15/97	1447-1522	1	1	1	1	NS	NS	NS	NS	1	NS	1	NS	
Z1-R2	Random	58°51.68	152°55.55	162	7/15/97	1543-1622	1	1	1	1	NS	NS	NS	NS	1	NS	1	NS	
Z1-R3	Random	58°48.98	153°05.46	172	7/15/97	1802-1845	1	1	1	1	NS	NS	NS	NS	1	NS	1	NS	
Z1-R3a	Random-long-line	58°48.41	153°09.16	197	7/15/97	1721-2154	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	
Z1-R4	Random	58°29.98	153°46.99	51	7/15/97	0408-0435	1	1	1	1	1	NS	1	NS	1	NS	1	NS	No fish samples collected from catch. Not enough replicates for composites. Arrowtooth flounder heavily "eaten" by amphipods.
Z1-R5	Random	58°43.59	153°11.42	172	7/15/97	1256-1340	1	1	1	1	NS	NS	NS	NS	1	NS	1	NS	
Z1-R6	Random	58°27.53	153°21.29	180	7/14/97	1655-1726	1	1	1	1	NS	NS	NS	NS	1	NS	1	NS	
Z1-R7	Random	58°30.24	153°31.56	141	7/15/97	0032-0124	1	1	1	1	1	1	1	NS	1	NS	1	NS	
Z1-R8	Random	58°30.13	153°15.72	175	7/15/97	0710-0745	1	1	1	1	1	NS	1	NS	1	NS	1	NS	
Z1-R9	Random	58°30.31	153°05.75	171	7/15/97	0824-0858	1	1	1	1	NS	NS	NS	NS	1	NS	1	1	Deck exposure blank collected due to "forest fire smoke smell" in air
Z1-R10	Random	58°27.55	153°26.39	115	7/14/97	2121	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	Station abandoned due to bottom type, sand/shell/cobble with some silt.
Z1-R11	Random	58°54.35	153°11.15	162	7/15/97	1948	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	Station abandoned due to sand content. Transit to Z1-R20.
Z1-R12	Random	58°32.87	153°31.69	122	7/15/97	0548-0559	1	1	1	1	NS	NS	NS	NS	1	NS	1	NS	
Z1-R13	Random	58°22.20	153°15.84	178	7/14/97	1516-1620	1	1	1	1	1	1	1	NS	1	NS	1	NS	
Z1-R14	Random	58°30.02	153°36.81	130	7/15/97	0155-0240	1	1	1	1	NS	NS	NS	NS	1	NS	1	NS	
Z1-R15	Random	58°30.20	153°26.64	156	7/14/97	2345-2359	7	7	7	7	NS	NS	NS	NS	1	NS	1	NS	
Z1-R18	Random; Alternate for Z1-R10	58°27.35	153°41.84	144	7/15/97	0259-0340	1	1	1	1	NS	NS	NS	NS	1	NS	1	NS	
Z1-R20	Random; Alternate for Z1-R11	58°54.47	153°05.79	171	7/15/97	2018-2058	1	1	1	1	NS	NS	NS	NS	1	NS	1	NS	Replaces Z1-R11
Z2-F1	Fixed	57°58.96	154°21.43	287	7/13/97	1832-2030	3	3	3	3	1	1	1	3	1	NS	1	NS	1 Archive & 1 Chem. Core; Grab 1 = Rep 1, Grab 2 = Rep 2, and Box Core = Rep 3

Table 2-1: 1997 and 1998 MMS Shelikof Strait and Outermost Cook Inlet Stations (continued)

1997 Station ID	Station Type	Latitude	Longitude	Depth (m)	Date	Time	Samples Collected											Comments	
							Organics	Metals	Grain Size	TOC	RGS-P450	Toxicity	AVS/SEM	Core	SPI	Fish/P450	CTD		QC
Z2-F2	Fixed Alternate	58°06.05	153°41.16	206	7/10/97	1036-1340	3	3	3	3	1	1	1	3	1	NS	1	NS	Station Z2-R18 was chosen as the alternate position for Z2-F2. 1 Archive & 1 Chem. Core; Reps 1 and 2 from grab; rep 3 from box core
Z2-F2	Fixed	58°06.03	153°34.77	255	7/10/97	655	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	Station abandoned due to coarse "shell" sand, washout. Move to Z2-R18 as alternate location for Z2-F2.
Z2-R1	Random	57°54.21	154°42.00	269	7/13/97	1546-1706	3	3	3	3	1	1	1	NS	1	NS	1	NS	
Z2-R2	Random	58°19.29	153°31.32	170	7/14/97	1148-1347	7	7	7	7	NS	NS	NS	NS	1	NS	1	NS	
Z2-R3	Random	57°49.07	154°26.81	222	7/10/97	2024-2045	1	1	1	1	NS	NS	NS	NS	3	NS	1	NS	
Z2-R4	Random	58°21.72	153°42.10	181	7/14/97	1041-1100	1	1	1	1	NS	NS	NS	NS	1	NS	1	NS	
Z2-R05	Random	57°49.15	154°41.52	240	7/11/97	1204	1	1	1	1	NS	NS	NS	NS	1	NS	1	NS	
Z2-R6	Random	58°21.75	153°46.87	200	7/14/97	0920-1000	1	1	1	1	NS	NS	NS	NS	1	NS	1	NS	
Z2-R7	Random	58°05.76	154°01.67	216	7/10/97	1510	1	1	1	1	NS	NS	NS	NS	1	NS	1	NS	
Z2-R8	Random	58°00.40	154°01.32	203	7/10/97	1644-1720	1	1	1	1	NS	NS	NS	NS	3	NS	1	NS	
Z2-R9	Random	58°10.88	153°41.41	198	7/13/97	2316-2332	1	1	1	1	NS	NS	NS	NS	NS	NS	1	NS	
Z2-R10	Random	57°46.43	154°31.86	210	7/10/97	2244-2314	1	1	1	1	NS	NS	NS	NS	3	NS	1	NS	
Z2-R11	Random	57°46.41	154°26.59	214	7/10/97	2125-2158	1	1	1	1	NS	NS	NS	NS	3	NS	1	NS	
Z2-R12	Random	58°16.23	153°57.26	237	7/14/97	0056-0128	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	No samples; over 50% gravel and sand
Z2-R13	Random	58°16.33	154°02.14	156	7/13/97	0150-0254	3	3	3	3	1	1	NS	NS	1	NS	1	NS	
Z2-R14	Random	58°16.55	153°52.10	217	7/14/97	0331-0418	1	1	1	1	1	NS	1	NS	1	NS	1	NS	
Z2-R14a	Random, long-line	58°16.72	153°54.40	256-265	7/14/97	0033-0555	5	5	NA	NA	5	NA	NA	NA	NA	20	NA	1	16 halibut and 4 Arrowtooth for P450
Z2-R15	Random	58°18.87	153°52.24	240	7/14/97	0644-0734	1	1	1	1	NS	NS	NS	NS	1	NS	1	NS	
Z2-R22	Random; Alternate for Z2-R12	58°21.71	153°51.90	237	7/14/97	0824-0852	1	1	1	1	1	NS	1	NS	1	NS	1	NS	
Z3-F1	Fixed	57°36.72	155°21.03	336	7/11/97	0707-0942	3	3	3	3	1	1	1	3	3	NS	1	NS	1 Archive and 1 Chem. Core
Z3-F2	Fixed	57°46.56	154°59.82	320	7/11/97	0244-0443	3	3	3	3	1	1	1	3	1	NS	1	NS	1 Archive and 1 Organics Core
Z3-R1	Random	57°23.86	155°40.47	284	7/11/97	1335-1518	1	1	1	1	NS	NS	NS	NS	1	NS	1	NS	
Z3-R1a	Random	57°22.75	155°37.11	280	7/11/97	1311-1740	NS	NS	NS	NS	NS	NS	NS	NS	NS	13	NS	NS	Composite liver samples for sablefish & halibut for chemistry.
Z3-R2	Random	57°38.19	155°01.27	244	7/12/97	1554-1628	1	1	1	1	NS	NS	NS	NS	1	NS	1	NS	
Z3-R3	Random	57°15.77	155°39.97	280	7/13/97	0600-0655	1	1	1	1	NS	NS	NS	NS	1	NS	1	NS	
Z3-R4	Random	57°38.14	154°56.49	232	7/12/97	1431-1512	1	1	1	1	NS	NS	NS	NS	1	NS	1	NS	
Z3-R5	Random	57°21.18	155°35.39	297	7/11/97	1855-1941	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	Station abandoned due to weather. Returned 07/12/97.
Z3-R5	Random	57°21.27	155°35.05	292	7/13/97	0751-0840	1	1	1	1	NS	NS	NS	NS	1	NS	1	NS	Resampling of Z3-R5 after abandoning station 7/10/97 due to weather conditions.
Z3-R6	Random	57°37.76	155°16.67	309	7/11/97	1025-1105	1	1	1	1	NS	NS	NS	NS	3	NS	1	NS	
Z3-R8	Random	57°13.24	155°24.91	257	7/13/97	0056-0130	1	1	1	1	1	NS	1	NS	1	NS	1	NS	
Z3-R9	Random	57°38.20	154°45.97	229	7/12/97	1921-1937	1	1	1	1	NS	NS	NS	NS	1	NS	1	NS	
Z3-R10	Random	57°35.50	154°56.12	232	7/12/97	1718-1756	1	1	1	1	1	NS	1	NS	3	NS	1	NS	
Z3-R11	Random	57°10.58	155°29.54	263	7/13/97	0213-0315	1	1	1	1	1	1	1	NS	1	NS	1	NS	
Z3-R12	Random	57°13.39	155°19.68	250	7/12/97	2337-0016	1	1	1	1	NS	NS	NS	NS	1	NS	1	NS	
Z3-R13	Random	57°21.32	155°29.78	282	7/13/97	0924-1035	7	7	7	7	NS	NS	NS	NS	1	NS	1	1	Reps 1 & 2 from Grab 1; Reps 3 & 4 from Grab 2; Reps 5, 6, & 7 from Grab 3. Equipment blank was DI water rinse of deconed grab sampler.
Z3-R14	Random	57°16.03	155°29.94	268	7/13/97	0412-0505	3	3	3	3	1	1	1	NS	1	NS	1	NS	
Z3-R15	Random	57°21.38	155°25.20	269	7/13/97	1100-1145	1	1	1	1	NS	NS	NS	NS	1	NS	1	NS	
Z3-R20	Random; Alternate for Z3-R7	57°29.91	155°05.77	242	7/12/97	2127	3	3	3	3	1	NS	1	NS	NS	NS	1	NS	Z3-R20 designated random alternate for Z3-R7 due to transit time and expected weather.

**Table 2-1: 1997 and 1998 MMS Shelikof Strait and Outermost Cook Inlet Stations (continued)**

1998		Analysis/Replicates															Comments	
Station ID	Station Type(1)	Sample Type	Latitude	Longitude	Depth (m)	Date	Time	Organics	Metals	GS/TOC	RGS-P450	Fish/P450	TOX	Oil Degraders	Geo. Core (2)	CTD		QC
Z0-F1	Fixed	Sed. Grabs/Core	59°36.32	151°20.15	78	7/4/98	0758-0846	3	3	3	1	NA	1	1	1 Core	1	NA	1 Gravity core (230 cm) for Geo. and Chem., 1 Archive core
Z0-F2	Fixed	Sed. Grabs	59°31.57	151°48.88	96	7/4/98	0514-0538	1	1	1	1	NA	NA	1	NA	1	NA	
Z0-F4	Fixed	Sed. Grabs	59°01.86	152°45.55	161	7/3/98	1457-1514	1	1	1	1	NA	NA	1	NA	1	NA	
Z0-F5	Fixed	Sed. Grabs	59°08.70	153°27.22	43	7/3/98	1742-1754	1	1	1	1	NA	NA	1	NA	1	NA	
Z0-F6	Fixed	Sed. Grabs	59°34.94	153°14.36	25	7/3/98	2111-2136	1	1	1	1	NA	1	1	NA	1	NA	
Z0-F8	Fixed	Sed. Grabs/Core	59°31.24	153°07.66	35	7/3/98	2218-2345	1	1	1	1	NA	NA	1	6 Cores	1	NA	Sediment Cores (2)
Z0-F13	Fixed	Sed. Grabs	59°34.30	151°38.25	74	7/4/98	0614-0624	1	1	1	1	NA	NA	1	NA	1	NA	
Z0-F14	Fixed	Sed. Grabs	59°33.67	151°31.97	119	7/4/98	0654-0709	1	1	1	1	NA	NA	1	NA	1	NA	
Z0-F7a	Fixed, Long-line	Fish	NS	NS	NS	NS	NS	NS	NS	NA	NS	NS	NS	NS	NS	NS	NS	Fish sampling not conducted because fish catch limit nearly met after first three sets.
Z1-R16	Random	Sed. Grabs	58°24.66	153°21.37	174	7/3/98	0015-0036	1	1	1	1	NA	NA	1	NA	1	NA	
Z1-R17	Random	Sed. Grabs	58°38.33	152°55.47	156	7/3/98	0758-0812	1	1	1	NA	NA	NA	1	NA	1	NA	
Z1-R19	Random	Sed. Grabs	58°32.91	153°36.61	72	7/3/98	0326-0342	1	1	1	NA	NA	NA	1	NA	1	1	QC: 1 Van-Veen grab equipment blank
Z1-R21	Random	Sed. Grabs	58°49.01	153°00.40	146	7/3/98	1145-1210	1	1	1	1	NA	NA	1	NA	1	NA	
Z1-R22	Random	Sed. Grabs	58°51.80	153°05.83	160	7/3/98	1254-1315	1	1	1	NA	NA	NA	1	NA	1	NA	
Z1-R23	Random	Sed. Grabs	58°38.16	153°26.41	46	7/3/98	0550-0602	1	1	1	NA	NA	NA	1	NA	1	NA	
Z1-F1	Fixed	Sed. Grabs	58°27.82	153°23.29	186	7/3/98	0111-0223	3	3	3	1	NA	NA	1	NA	1	NA	
Z1-F2	Fixed	Sed. Grabs	58°31.68	152°53.07	212	6/29/98	0350-0412	1	1	1	1	NA	NA	1	NA	1	NA	Station sampled in transit to Zone 4
Z1-R3b	Fixed-Optional	Sed. Grabs/Core	58°48.11	153°08.15	191	7/5/98	0128-0147	NA	NA	NA	NA	NA	NA	NA	6 Cores	NA	NA	Cores collected (archived) as substitute for unsuccessful gravity core at Z2-R16 (2)
Z1-R23a	Fixed, Long-line	Fish	58°38.11	153°15.90	152-158	7/3/98	0505-0922	9*	9*	NA	9*	30	NA	NA	NA	NS	NA	Fish composites: 4 Pacific cod, 3 halibut; Individual fish samples: 1 halibut, 1 skate
Z2-R16	Random	Sed. Grabs/Core	58°05.81	153°56.62	200	7/2/98	1145-1406	1	1	1	1	NA	NA	1	6 Cores	1	NA	Sediment Cores (2). Gravity core poor penetration. Did not retain core.
Z2-R17	Random	Sed. Grabs	58°13.61	153°46.54	195	7/2/98	1828-1851	1	1	1	1	NA	NA	1	NA	1	NA	
Z2-R19	Random	Sed. Grabs	58°02.80	154°22.07	166	7/2/98	0920-0942	1	1	1	NA	NA	NA	1	NA	1	NA	
Z2-R20	Random	Sed. Grabs	58°05.65	154°06.63	253	7/2/98	1050-1109	1	1	1	1	NA	NA	1	NA	1	NA	
Z2-R21	Random	Sed. Grabs	57°54.89	154°06.41	200	7/2/98	0550-0620	1	1	1	NA	NA	NA	1	NA	1	NA	
Z2-R23	Random	Sed. Grabs	57°54.56	154°16.67	212	7/2/98	0650-0723	1	1	1	NA	NA	NA	1	NA	1	2	QC: 1 field blank and 1 Van-Veen grab equipment blank
Z2-F1	Fixed	Sed. Grabs	57°59.02	154°21.34	283	7/2/98	0756-0846	1	1	1	1	NA	1	1	NA	1	NA	Samples collected from homogenized composite of 2 grabs
Z2-F2	Fixed	Sed. Grabs	58°06.11	153°41.24	197	7/2/98	1513-1604	3	3	3	1	NA	NA	3	NA	1	NA	
Z2-F3	Fixed	Sed. Grabs	57°44.26	154°02.13	241	7/1/98	2333-2359	3	3	3	1	NA	NA	1	NA	1	NA	Soft mud - extended grab feet
Z2-F4	Fixed	Sed. Grabs	57°54.52	153°36.87	252	7/2/98	0303-0400	3	3	3	1	NA	NA	1	NA	1	NA	
Z2-R14a	Fixed, Long-line	Fish	58°16.79	153°54.39	256	7/2/98	1735-2218	12*	12*	NA	12*	51	NA	NA	NA	NS	2	Fish composites: 4 Halibut , 6 Pacific cod, 1 Arrowtooth flounder; Individual fish sample: 1 halibut; QC: 1 fish dissection tools equipment blank; 1 dissection deck blank

**Table 2-1: 1997 and 1998 MMS Shelikof Strait and Outermost Cook Inlet Stations (continued)**

1998								Analysis/Replicates										Comments
Station ID	Station Type(1)	Sample Type	Latitude	Longitude	Depth (m)	Date	Time	Organics	Metals	GS/TOC	RGS-P450	Fish/P450	TOX	Oil Degraders	Geo. Core (2)	CTD	QC	
Z3-R7	Random	Sed. Grabs/Core	57°08.42	155°04.47	217	6/29/98	1416-1619	1	1	1	1	NA	NA	1	NS	1	NA	Seas too high for box core
Z3-R11	Random	Sed. Grabs	57°10.44	155°29.76	265	6/30/98	0504-0702	1	1	1	NA	NA	1	1	NA	1	NA	TOX composite from 3 grabs, others taken from grab 1
Z3-R14	Random	Sed. Grabs	57°16.09	155°29.99	272	6/30/98	0830-1140	1	1	1	NA	NA	1	1	NA	1	NA	All samples collected from homogenized 2 grabs (other 5 grab attempts pre-trips)
Z3-R16	Random	Sed. Grabs	57°26.85	155°30.64	296	6/30/98	1317-1340	1	1	1	1	NA	NA	1	NA	1	NA	
Z3-R17	Random	Sed. Grabs	57°18.20	155°54.82	240	6/30/98	1638-1701	1	1	1	NA	NA	NA	1	NA	1	NA	
Z3-R18	Random	Sed. Grabs	57°32.47	155°16.09	270	7/1/98	1314-1331	1	1	1	1	NA	NA	1	NA	1	NA	
Z3-F1	Fixed	Sed. Grabs	57°36.69	155°21.26	327	7/1/98	1420-1610	1	1	1	1	NA	1	1	NA	1	NA	All samples collected from composite of 3 grabs
Z3-F2	Fixed	Sed. Grabs	57°46.81	155°00.23	320	7/1/98	1805-1956	3	3	3	1	NA	1	1	NA	1	NA	TOX was composite of 3 grabs, all others from individual grabs
Z3-R1a	Fixed, Long-line	Fish	57°22.76	155°37.28	290	6/30/98	1520-1910	9*	9*	NA	9*	36	NA	NA	NA	NS	NA	Fish composites: 1 Arrowtooth flounder, 1 Black cod, 3 Pacific cod, 3 halibut; Individual fish sample: 1 Aleutian skate
Z4-F1	Fixed	Sed. Grabs	56°38.96	155°54.58	281	7/1/98	0520-0652	3	3	3	1	NA	NA	1	NS	1	NA	Cores collected at Z4F4 instead due to weather.
Z4-F2	Fixed	Sed. Grabs	56°57.01	155°19.77	253	6/29/98	1817-2137	3	3	3	1	NA	NA	1	NA	1	NA	
Z4-F3	Fixed	Sed. Grabs	57°01.04	155°53.25	300	6/28-29/98	2350-0230	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	No samples collected due to unacceptable substrate
Z4-F4	Fixed, Alternate	Sed. Grabs/Core	56°48.06	155°47.96	290	7/1/98	0059-0347	3	3	3	1	NA	NA	1	5 Cores	1	NA	Alternate for Z4F3; Cores collected here instead of at Z4F1 due to weather (2)

Notes:

NA = Not applicable

NS = Not sampled

TBD = To be determined (i.e., optional analyses)

(1) An alternate station was substituted for a fixed or random station when necessary (i.e., not acceptable % of silt/clay)

The fourth fish station in Zone 0 was not sampled because it was unnecessary as dictated by catch results.

(2) Cores were collected from each station: 1 - chemistry, 1 - grain size/TOC, 1 - geochronology, 1 - archive, 1 - fish scale, 1 - x-ray

One gravity core was collected from Z0-F1. Additional geochronology cores were sampled for archive.

\* Each sample is a composite of 3 - 5 fish livers.

**Table 2-2: 1997-1998 Source Samples from the Outermost Cook Inlet/Shellikof Strait Region**

Station ID (plot ID)	Station Location	Matrix	Date	Time	Comments
Copper River-1 (CR-1)	Million Dollar Bridge	Sediment	07/15/97	13:38	30 m upstream of Sonar facility @ 1 m above water level.
Copper River-2 (CR-2)	Northwest end of bridge, Long Island (N)	Sediment	07/15/97	14:22	In "catch basin" west side of hwy (milepost 35-36).
Copper River-3 (CR-3)	South end of Long Island	Sediment	07/15/97	14:53	NW end of bridge separating Round and Long Islands.
Copper River-4 (CR-4)	South end of Round Island	Sediment	07/15/97	15:08	Mainland and Round Island.
Homer 0-2 cm (H-2) and 4-6 cm (H-4)	Homer Harbor	Sediment	07/16/97	06:56	Just outside boat harbor entrance, west of dredged channel (59° 36.37, 151° 19.94) (39 m depth).
Susitna-01 (SR-1)	Susitna River	Sediment	07/20/97	13:30	Northern bank, west of bridge at mile 105 on George Parks Hwy.
Susitna-02 (SR-2)	Susitna River	Sediment	07/20/97	16:30	Northern bank, west of bridge at mile 105 on George Parks Hwy.
Crude TBPf	Cook Inlet crude	Crude Oil	08/14/97	02:55	UNOCAL TBPf/NTL.
Swanson River Field Oil (SW-O)	Swanson River crude	Oil	1998	NA	None.
TBPf-Outfall (TB-W)	UNOCAL TBPf	Produced Water	08/26/97	03:00	UNOCAL TBPf/NTL.
Coal-1 (H-C1)	Homer Spit, Homer, AK	Coal	11/09/97	15:30	Beach-washed coal (5 chunks), approximately 1 mile W. of Bishops Beach/ CIRCAC.
WWTF Final Effluent	Point Woronzof, Anchorage	Water	08/12/97	11:00	Municipal WWTF Final Effluent.
AC1 (AK-C-S)	Offshore Kenai Peninsula	Sediment	06/27/98	15:59-17:21	Offshore Alaska Coastal Current station. Shake-down gear, sampling with 2 shifts.
St. Augustine Ash	St. Augustine Island	Ash	07/04/98	07:51-08:48	Beach sample collected onshore St. Augustine Island for volcanic ash.
St. Augustine Sediment (AI-S)	Offshore St. Augustine Island	Sediment	07/04/98	09:20	Offshore Island sediment grab for evidence of ash layer.
Toxicity Reference	Holgate Glacier	Sediment	07/05/98	15:42	Sediment Collected as a toxicity reference sediment sample, near the Holgate Glacier
Homer Coal (H-C2)	Coal Bay Beach, Homer	Coal	07/07/98	15:00	Coal source sample collected from Coal Bay Beach, Homer.
Ninilchik Coal (N-C)	Ninilchik Bluff	Coal	07/07/98	13:00	Coal source sample collected from coal seam in Ninilchik bluff.
Well Creek Oil (WC-O)	Well Creek "beaver ponds"	Oil Seep	07/07/98	12:55-14:09	Oil seep sample collected at Well Creek "beaver ponds". Transported by helicopter.
Matanuska Coal (M-C)	Northwest of Sutton, AK	Coal	05/16/98	PM	Coal collected from exposed coal seam.
CLC (CL-C)	Coyote Lake Sutton, AK	Coal	05/16/98	PM	Coal collected from coal pocket.
Susitna-03 (SR-W1)	Deshka Landing, Susitna River	Surface Water	05/13/98	AM	Approximately mile 82.5 on George Parks Hwy
Matanuska-01 (MR-W1)	Matanuska River	Surface Water	05/13/98	AM	Collected at intersection of Old Glenn Hwy and Matanuska River
Matanuska-02 (MR-S)	Matanuska River	Sediment	05/13/98	AM	Collected at intersection of Old Glenn Hwy and Matanuska River.

**Table 2-2: 1997-1998 Source Samples from the Outermost Cook Inlet/Shelikof Strait Region**

Station ID (plot ID)	Station Location	Matrix	Date	Time	Comments
Knik-01 (KR-W1)	Knik River	Surface Water	05/13/98	AM	Collected at intersection of Old Glenn Hwy and Knik River.
Copper River- W	Copper River	Surface Water	05/16/98	06:30- 07:30	Sample "C1" from Copper River Hwy mile 25, and "C2" from mile 28.
Copper River-5 (CR-5)	Copper River	Sediment	05/16/98	07:30	Copper River Highway, mile 25.
Susitna-04	Susitna River	Surface Water	06/25/98	PM	Collected at intersection of Susitna River and Parks Hwy, @ approximately mile 101.
Matanuska- 03	Matanuska River	Surface Water	06/25/98	AM	Collected at intersection of Old Glenn Hwy and Matanuska River.
Knik-02	Knik River	Surface Water	06/25/98	AM	Collected at intersection of Old Glenn Hwy and Knik River.
SSCoal 4 (SS-C4)	Beluga Coal Fields	Coal	06/22/98 06/23/98	NA	None.
SSCoal 5 (SS-C5)	Beluga Coal Fields	Coal	06/22/98 06/23/98	NA	None.

**Table 2-3: Saturated Hydrocarbons Target Analyte List**

<b>Compound</b>	<b>Internal Standard/ Surrogate Reference</b>	<b>Compound</b>	<b>Internal Standard/ Surrogate Reference</b>
nC8	A/1	nC28	A/1
nC9	A/1	nC29	A/1
nC10	A/1	nC30	A/1
nC11	A/1	nC31	A/1
nC12	A/1	nC32	A/1
nC13	A/1	nC33	A/1
1380	A/1	nC34	A/1
nC14	A/1	nC35	A/1
1450	A/1	nC36	A/1
nC15	A/1	nC37	A/1
1650	A/1	nC38	A/1
nC16	A/1	nC39	A/1
nC17	A/1	nC40	A/1
Pristane	A/1		
nC18	A/1		
Phytane	A/1		
nC19	A/1		
nC20	A/1		
nC21	A/1	<b>Internal Standard</b>	
nC22	A/1	Triacontane-d <sub>62</sub>	A
nC23	A/1		
nC24	A/1	<b>Surrogate</b>	
nC25	A/1	Tetracosane-d <sub>50</sub>	1/A
nC26	A/1	5-a-Androstane	2/A
nC27	A/1		

Table 2-4: Polycyclic Aromatic Hydrocarbons Target Analyte List

Compound	Surrogate/ Internal Standard Reference	Compound	Surrogate/ Internal Standard Reference
Naphthalene (C0N)	2, A	Benzo[a]anthracene	3, B
C1-Naphthalenes (C1N)	2, A		
C2-Naphthalenes (C2N)	2, A	Chrysene (C0C)	3, B
C3-Naphthalenes (C3N)	2, A	C1-Chrysenes (C1C)	3, B
C4-Naphthalenes (C4N)	2, A	C2-Chrysenes (C2C)	3, B
		C3-Chrysenes (C3C)	3, B
Acenaphthene (ACE)	2, A	C4-Chrysenes (C4C)	3, B
Acenaphthylene (ACEY)	2, A		
Biphenyl (BIP)	2, A	Benzo[b]fluoranthene	3, B
		Benzo[k]fluoranthene	3, B
Fluorene (C0F)	2, A	Benzo[a]pyrene (BAP)	4, B
C1-Fluorenes (C1F)	2, A	Benzo[e]pyrene (BEP)	4, B
C2-Fluorenes (C2F)	2, A	Perylene (PER)	4, B
C3-Fluorenes (C3F)	2, A	Indeno[1,2,3-c,d]pyrene	4, B
		Dibenzo[a,h]anthracene	4, B
Dibenzothiophene (C0D)	3, A	Benzo[g,h,i]perylene	4, B
C1-Dibenzothiophenes (C1D)	3, A		
C2-Dibenzothiophenes (C2D)	3, A		
C3-Dibenzothiophenes (C3D)	3, A		
Phenanthrene (C0P)	3, A	<b>Surrogate Compounds</b>	
Anthracene (C0A)	3, A	Naphthalene-d8 (D8N)	1, A
C1-Phenanthrenes/Anthracenes	3, A	Acenaphthene-d10	2, A
C2-Phenanthrenes/Anthracenes	3, A	Phenanthrene-d10	3, A
C3-Phenanthrenes/Anthracenes	3, A	Benzo[a]pyrene-d12	4, B
C4-Phenanthrenes/Anthracenes	3, A		
Fluoranthene (FLANT)	3, A		
Pyrene (PYR)	3, A	<b>Recovery Standards</b>	
C1-Fluoranthenes/Pyrenes (C1F/P)	3, A	Fluorene-d10 (D10FL)	A
C2-Fluoranthenes/Pyrenes (C2F/P)	3, A	Chrysene-d12 (D12C)	B
C3-Fluoranthenes/Pyrenes (C3F/P)	3, A		

**Table 2-5: Steranes/Triterpanes Target Analyte List**

Steranes/Triterpanes	Peak Number
Diacholestane	S4
Diacholestane	S5
Methylcholestane	S24
Ethylcholestane	S25
Ethylcholestane	S28
Diterpane	T4
Tricyclitriterpane	T9
Tricyclitriterpane	T10
Trisnorhopane (TS)	T11
Trisnorhopane (TM)	T12
Norhopane	T15
Oleanane	T18
Hopane	T19
Homohopane	T21
Homohopane	T22
<b>Internal Standards</b>	
Chrysene-d12	
Triacontane-d62 (Alternate)	
<b>Surrogates</b>	
5B(H)-Cholane	
Dotriacontane-d66 (Alternate)	

**Table 2-6: Summary of Instrumental Methods and Method Detection Limits (MDL) for Metal Analysis of Sediment and Fish**

Metal	Sediments		Fish	
	Method	MDL (µg metal/g dry sediment)	Method	MDL (µg metal/g tissue-dry wt.)
Ag - Silver	ZGFAAS	0.01	ZGFAAS	0.004
Al - Aluminum	FAAS	6	FAAS	2.3
As - Arsenic	ZGFAAS	0.1	ZGFAAS	0.03
Ba - Barium	ICP/MS	0.1	ICP/MS	0.006
Be - Beryllium	ICP/MS	0.1	ZGFAAS	0.002
Ca - Calcium	FAAS	5	Not analyzed	--
Cd - Cadmium	ICP/MS	0.02	FAAS	0.3
Cr - Chromium	FAAS	1	GFAAS	0.003
Cu - Copper	FAAS	2	FAAS	0.7
Fe - Iron	FAAS	5	FAAS	2.5
Hg - Mercury	CVAAS	0.001	CVAAS	0.001
K - Potassium	FAAS	5	Not analyzed	--
Mg - Mannesium	FAAS	1	Not analyzed	--
Mn - Manganese	FAAS	2	FAAS	1.1
Ni - Nickel	ICP/MS	0.2	Not analyzed (Year 1)	—
Pb - Lead	ICP/MS	0.1	ICP/MS	0.001
Sb - Antimony	ICP/MS	0.2	ICP/MS	0.001
Se - Selenium	ZGFAAS	0.05	ZGFAAS	0.03
Sn - Tin	ICP/MS	0.1	ICP/MS	0.001
Tl - Thallium	ICP/MS	0.1	ICP/MS	0.0001
V - Vanadium	FAAS	10	GFAAS	0.007
Zn - Zinc	FAAS	1	FAAS	0.4
Other Parameters				
Grain-Size	Sieve and Pipet	--		
TOC	Carlo Erba NCS System	0.1		

Notes:

FAAS = Flame Atomic Absorption Spectrometry

GFAAS = Graphite Furnace Atomic Absorption Spectrometry

ZGFAAS = Zeeman Graphite Furnace Atomic Absorption Spectrometry

CVAAS = Cold Vapor Atomic Absorption Spectrometry

ICP/MS = Inductively Coupled Plasma-Mass Spectrometry

NCS = Nitrogen - Carbon - Sulfur Analyzer

TOC = Total Organic Carbon

**Table 2-7: Calculation of the Sediment Profile Imaging Organism-Sediment Index**

Parameter	Range/Type	Index Value
<b>A. Mean RPD Depth</b> (choose one)		
	0.00 cm	0
	> 0 - 0.75 cm	1
	0.76 - 1.50 cm	2
	1.51 - 2.25 cm	3
	2.26 - 3.00 cm	4
	3.01 - 3.75 cm	5
	> 3.75 cm	6
<b>B. Successional Stage</b> (choose one)		
	Azoic	-4
	Stage I	1
	Stage I II	2
	Stage II	3
	Stage II III	4
	Stage III	5
	Stage I on III	5
	Stage II on III	5
<b>C. Chemical Parameters</b> (choose one or both if appropriate)		
	Methane Present	-2
	No/Low Dissolved Oxygen <sup>a</sup>	-4

**Notes:**

Organism-sediment Index = Total of above subset indices (A+B+C); Range: -10 to +11.

<sup>a</sup>This is not based on a Winkler or polarographic electrode measurement, but on the imaged evidence of reduced, low reflectance (i.e., high-oxygen-demand) sediment at the sediment-water interface.

**Table 2-8: Data Quality Objectives for Saturated Hydrocarbons and Polycyclic Aromatic Hydrocarbons Analyses**

<b>Element or Sample Type</b>	<b>Minimum Frequency</b>	<b>Data Quality Objective/Acceptance Criteria</b>
Initial Calibration	Prior to every instrument sequence for GC/MS analysis and as needed for GC/FID analysis	5-point curve, percent RSD < 35 percent for all CC target analytes, 90 percent must be < 25 percent
Continuing Calibration (CC)	After every 12 samples or 16 hours, whichever is more frequent, and at end of instrument sequence	Percent RSD < 35 percent for all CC target analytes; 90 percent must be < 25 percent
Oil Reference Standard	Two with each instrument sequence (One North slope Crude and one Cook Inlet Crude)	North Slope Crude < 35 percent D from laboratory mean for target compounds (use surrogate corrected values) except for compounds below the reporting limit
Procedural Blank	One per batch	No analyte to exceed 5X the MDL unless sample amount is > 10X blank amount
Blank Spike	One per batch	Recovery between 35 and 125 percent
Instrument SRM (1491)	One per instrument sequence Not applicable to SHC analysis	Values must be <15 percent difference of true value for all certified analytes
Sediment SRM (1941a) Tissue SRM (1974a)	One per batch as appropriate	Values must be within 30 percent of the true value on average for all analytes, not to exceed 35 percent of true value for more than 2 analytes
Duplicate Analysis	One per 40 field samples	RPD < 30 percent for all analytes >10 times the MDL; Mean RPD < 30 percent
Surrogate Standards	Every sample	Recovery between 45 and 125 percent

**Table 2-9: Quality Control Summary for Sterane and Triterpane Analyses**

Element or Sample Type	Minimum Frequency	Data Quality Objective/Acceptance Criteria
Initial Calibration	Prior to every instrument sequence	4-point curve, percent RSD < 25 percent for all target analytes
Continuing Calibration	After every 12 samples or 16 hours, whichever is more frequent, and at end of each sequence	Percent RSD < 25 percent for all analytes
Oil Reference Standard (North Slope Crude)	One with each instrument sequence	< 35 percent Dif. from laboratory mean for target compounds (use surrogate corrected values) except for compounds below the reporting limit
Procedural Blank	One per batch	No analyte to exceed 5X the MDL unless sample amount is > 10X blank amount
Surrogate Standards	Every sample	Recovery between 45 and 125 percent

**Table 2-10: Data Quality Objectives and Criteria for Metals and Total Organic Carbon**

Element or Sample Type	Minimum Frequency	Data Quality Objective/Acceptance Criteria
Initial Calibration	Prior to every batch of samples	3- to 5-point curve depending on the element and a blank. Standard curve correlation coefficient $r \geq 0.999$ for all analytes
Continuing Calibration	Must end every analytical sequence; for flame, repeat all standards every five samples; for graphite furnace and ICP/MS, recheck standard after every 8 to 10 samples	Percent RSD < 15 percent for all analytes
Standard Reference Materials	One per batch of 20 samples	Values must be within $\pm 20$ percent of accepted values for > 85 percent of the certified analytes and within $\pm 25$ percent for Hg
Method Blank	One per batch of 20 samples	No more than 2 analytes to exceed 5X MDL unless analyte not detected in associated sample
Matrix Spike and Spike Method Blank	One per batch of 20 samples	Analyte recoveries between 80 to 120 percent
Laboratory Duplicate	One per batch of 20 samples	RSD < 25 percent for 65 percent of the analytes

## 3.0 Results

### 3.1 Contaminant Sources

Source samples were collected throughout the study area at several locations representing potential contaminant input sources such as oil and gas activities (crude oil and produced water), coals, municipal discharges, boat harbors, riverine and coastal inputs (Section 2.1.3). The results were used to compare concentrations and distributions of contaminants found in the sediment samples from zones 0, 1, 2, 3, and 4 to potential known contaminant sources. The source samples from surface sediment, oil, coal, and water matrices were analyzed for organics and metals. In addition, the source sample sediments were analyzed for grain size and TOC.

#### 3.1.1 Physical Measurements

The TOC content for bottom sediments from the Susitna and Copper Rivers, two primary sediment sources to outermost Cook Inlet and the Shelikof Strait, average  $0.20 \pm 0.01$  percent and  $0.14 \pm 0.02$  percent, respectively (Table 3-1). Low TOC values in sediments from these two rivers reflect the high sand content. For example, bottom sediment from the Susitna River has 56.2 percent sand, 37.9 percent silt and only 5.9 percent clay. The Copper River contains 35.8 percent sand, 48.7 silt and 15.5 percent clay. In contrast, bottom sediment recovered from Homer Harbor, also a potential source of sediment to the study area, contains 1.6 percent TOC, 5.6 percent sand, 43.6 percent silt and 50.7 percent clay. The TOC content of a coal sample from Homer, Alaska is 67.1 percent (Table 3-1).

#### 3.1.2 Organics

Analyses for SHC, PAH, and S/T target analytes were conducted on the various source samples, and included the following: crude oil from Cook Inlet; Swanson River Field oil; seep oil from Well Creek; coals from Cook Inlet, Homer coals, Ninilchik, Matanuska, Coyote Lake, and Beluga; sediments from the Susitna River, Copper River, Homer Harbor, Matanuska River, Alaska Coastal Current, and Augustine Island; Trading Bay produced water; and Point Woronzof municipal effluent. Inputs from crude oil (e.g., seeps), produced water, municipal effluent, and coal were all considered to be the potential source(s) of organic hydrocarbons to outermost Cook Inlet and the Shelikof Strait (Boehm *et al.*, 1998).

Results for each source sample are summarized in Table 3-2 as total PAH, total petroleum hydrocarbons (PHC), and total S/T concentrations. Where more than one sample was analyzed for a source (e.g., Copper River, Susitna River, and Homer Harbor), an average is presented. For the Cook Inlet crude oil, the source sample as well as all Cook Inlet crude "check" oils that were analyzed with respective PAH, SHC, and S/T field sample analyses were averaged together. The complete organics results data tables are presented in Appendix B. Figures 3-1 through 3-18 provide a representative GC/FID chromatogram (top), PAH distribution histogram (middle), and S/T extracted ion chromatogram (bottom) for each source sample type. The GC/FID chromatograms represent the total signal detected by the instrument (GC/FID) during the sample analysis. The extracted ion chromatogram is similar, but represents the signal of only one ion or

mass (in this case mass 191 which is characteristic of triterpanes) from the total signal detected by the mass spectrometer (GC/MS) during the sample analysis.

### 3.1.2.1 Source Oils

**Cook Inlet Crude.** Results for the Cook Inlet crude oil show an average total PHC concentration of  $700,000 \pm 34,000 \mu\text{g/g}$  ( $n=24$ ). The Cook Inlet crude oil sample chromatogram (Figure 3-1) reveals a predominance of resolved n-alkanes in the C8 through C34 carbon range, typical for a fresh crude oil. An unresolved complex mixture (UCM - seen as a baseline rise) extends across the entire n-alkane range. The distribution of alkanes gradually tapers from highest concentrations of lower molecular weight carbon alkanes (C12) down to the higher molecular weight carbon compounds (C34). The crude oil source results may be used to typify possible hydrocarbon contributions from fresh crude oil and/or seep areas in the Shelikof Strait and Cook Inlet in the sediment samples.

The results of GC/MS analyses of Cook Inlet crude oil show an average total PAH concentration of  $13,000 \pm 1,000 \mu\text{g/g}$  ( $n=29$ ), or 1.3 percent PAH. The distribution of the PAH analytes (Figure 3-1) shows a typical petrogenic PAH signature, with an abundance of 2- and 3-ring PAH (naphthalenes through phenanthrenes), substantially lower levels of 4-ring PAH (fluoranthenes/pyrenes and chrysenes) and only traces of 5- and 6-ring PAH. The Cook Inlet crude oil has a low sulfur content as indicated by the low levels of the 3-ring, sulfur-containing dibenzothiophenes. The observed PAH distribution with the C-2 or C-3 alkyl homologues greater than the parent PAH is also characteristic of petroleum PAH.

The steranes and triterpanes in the Cook Inlet crude averaged  $510 \pm 81 \mu\text{g/g}$  ( $n=21$ ) and exhibit a characteristic petroleum pattern dominated by the C30-triterpane,  $17\alpha(\text{H})$ -hopane (Figure 3-1). In addition, the triterpane  $18\alpha(\text{H})$ -oleanane, an indicator of higher plant (e.g., angiosperm) input to crude oils from the upper Cretaceous period and later (Peters and Moldowan, 1993), is absent. Thus the presence of oleanane can be used as an indicator of non-Cook Inlet crude oil inputs.

**Swanson River Field Oil.** The total petroleum hydrocarbons determined for the Swanson River Field oil sample was comparable to the Cook Inlet crude oil, at  $630,000 \mu\text{g/g}$  (Table 3-2). The GC/FID chromatogram also portrays a virtually identical pattern of the resolved n-alkanes.

The total PAH concentration of  $12,000 \mu\text{g/g}$  (Table 3-2) and overall PAH distribution (Figure 3-2) are also similar to that determined for the Cook Inlet crude oil, i.e., an increased abundance of alkyl homologues relative to both the parent PAH and higher molecular weight PAH.

Comparable concentrations and S/T distribution of the Swanson River Field oil with the Cook Inlet crude oil sample (Figures 3-2 and 3-1, respectively), lend further support to the consistencies found within each of the hydrocarbon subclasses.

**Well Creek Seep Oil.** On average, the Well Creek oil samples contained  $660,000 \pm 130,000 \mu\text{g/g}$  ( $n=2$ ) of total PHC. The sample chromatogram (Figure 3-3) exhibits a deficiency of resolved n-alkanes, likely due to the fair amount of weathering expected for a sample of this type. The UCM predominates the chromatogram and extends across the entire range of the GC/FID analysis.

The average total PAH for the Well Creek seep oil was  $4,400 \pm 2,000 \mu\text{g/g}$  ( $n=2$ ). As seen with the SHC chromatogram, the PAH distribution (Figure 3-3) also shows some degree of weathering. Losses of the low molecular weight PAH such as naphthalene, fluorene, and their alkyl homologues are common due to their heightened solubility/volatility when compared with the higher molecular weight compounds such as the alkylated phenanthrenes and fluoranthenes.

Steranes and triterpanes averaged  $250 \pm 5.6 \mu\text{g/g}$  ( $n=2$ ) in the Well Creek seep oil and, similar to observations in the Cook Inlet crude oil S/T extracted ion chromatogram, is also dominated by the C30-triterpane,  $17\alpha(\text{H})$ -hopane and lacks the triterpane  $18\alpha(\text{H})$ -oleanane (Figure 3-3).

### 3.1.2.2 Source Coals

**Homer Spit Coal.** This coal source sample was collected from a beach in the Kachemak Bay area and contained low concentrations of total PHC ( $1,200 \mu\text{g/g}$ ) relative to the Cook Inlet crude oil. The GC/FID chromatogram of the coal reveals a complex mixture of hydrocarbons in the C26 to C34 carbon range; however, there is no homologous pattern of normal alkanes observed (Figure 3-4). Although the concentrations of PHC are low, the coal represents a potentially significant source of hydrocarbon input to the marine sediments of the region.

The PAH analysis of the coal sample reveals a substantially lower total PAH concentration ( $5.3 \mu\text{g/g}$ ) than the Cook Inlet crude oil. The PAH distribution of the coal is comprised of 2- and 3-ring PAH, with a predominance of alkyl naphthalenes. Perylene, a biogenic PAH, which occurs naturally as a product of diagenesis of terrigenous organic matter in sediments, is one of the most abundant PAH compounds. The sulfur-containing dibenzothiophenes are low relative to the phenanthrenes, but appear to be slightly more abundant than in the Cook Inlet crude oil.

The S/T in the coal are distinctive and very different from Cook Inlet crude oil. The triterpanes are dominated by moretane (the largest peak in Figure 3-4), which is an indicator of recent biogenic material. In comparison, C30-hopane, the primary triterpane in Cook Inlet crude oil, is a relatively minor component in the coal. The large relative abundance of the C31-homohopane 22R isomer over the 22S isomer (peaks T22 and T21 in Figure 3-4, respectively) is further evidence of the immature/recent biogenic nature of the coal.

**Homer Coal.** This coal sample was very similar to that described above for the Homer Spit coal in that it contained low concentrations of total PHC ( $660 \mu\text{g/g}$ ). In addition, the GC/FID chromatogram of the coal reveals a complex mixture of saturated hydrocarbons in the C26 to C34 carbon range (Figure 3-5).

The total concentration of PAH is fairly low, at  $2.4 \mu\text{g/g}$ , and is comprised mainly of the parent and alkylated naphthalenes and phenanthrenes (Figure 3-5). However, the biogenic component (perylene) is fairly large in this coal, at a concentration of  $0.25 \mu\text{g/g}$  or just above 10 percent of the total PAH.

The amount of S/T is also comparable to the Homer Spit coal, with a total S/T of  $2.1 \mu\text{g/g}$ . Additionally, the C30-hopane is present, although not dominant as was seen with the Cook Inlet crude. The relative abundance of the C31-homohopane 22R isomer over the 22S isomer (peaks T22 and T21 in Figure 3-5, respectively), is the reverse of that seen in the Homer Spit coal, perhaps evidence of a more mature nature of this coal sample.

**Ninilchik Coal.** Total PHC for this coal source (4.7 µg/g) is comparable to that of the Homer coals (Table 3-2). The GC/FID chromatogram (Figure 3-6) also illustrates the similar heightened distribution of saturated hydrocarbons in the C26 to C34 carbon range.

The concentration of total PAH in the Ninilchik coal was also similar to the other coal source samples, but was clearly dominated by the biogenic PAH, perylene (Figure 3-6), comprising nearly 80 percent of the total PAH distributions.

Results for Ninilchik coal total S/T were 0.95 µg/g, within the range spanned by the other coal source samples (Table 3-2). The extracted ion chromatogram shows the presence of the C30-hopane (peak T19, Figure 3-6), in addition to a minor triterpane 18α(H)-oleanane component.

**Matanuska Coal.** The TPH results for the Matanuska coal are comparable to the other coals (1,200 µg/g). The GC/FID chromatogram (Figure 3-7) reveals the presence of a wider range of the resolved n-alkanes, generally extending across the domain of the analysis (from C9 through C36), compared with the other coal samples.

The total PAH for the Matanuska coal was the highest compared to all other coals, at 62 µg/g (Table 3-2). The overall PAH distribution is similar to a petrogenic source, with a predominance of the low molecular weight naphthalenes and phenanthrenes; however a clear absence of fluorenes and dibenzothiophenes render it quite unique. There are also only trace amounts of the 4- and 5-ring PAH, in addition to a minimal biogenic PAH component (Figure 3-7).

Results for the S/T concentrations are comparable to the Homer coals, with a total S/T of 2.1 µg/g. The distribution of analytes, however, is not similar and is noted by maximums at the C-31-homohopanes, with the 22S isomer dominant over the 22R isomer (Figure 3-7).

**Coyote Lake Coal.** The total concentration of petroleum hydrocarbons was the lowest of the coal samples measured in this study (400 µg/g). The GC/FID chromatogram is very similar to that of the Matanuska coal, although there appears to be a degree of weathering associated with the loss of some of the resolved n-alkanes (Figure 3-8).

Total PAH for the Coyote Lake coal source sample was about one-third that of the Matanuska coal (23 µg/g), but still substantially higher than the other coals (Table 3-2). The coal sample from Coyote Lake (Figure 3-8) also exhibits similarity to the Matanuska coal (Figure 3-7) regarding the high abundance of the alkylated naphthalenes and phenanthrenes and lack of most other PAH measured here.

Comparable distributions of S/T, e.g., the dominance of the C-31 homohopanes, the lack of oleanane and similarities among the other hydrocarbon analytes, lead to the conclusion that these two source coals (Coyote Lake and Matanuska) are from the same coal-bearing formation.

**Beluga Coal.** Results for the TPH concentration are within the range of the other coals measured in this study (750 ± 180 µg/g). The GC/FID chromatogram contains a complex mixture of saturated hydrocarbons in the C26 to C34 range, much like that of the Homer and Ninilchik coals, but the concentrations of the resolved n-alkanes are much lower (Figure 3-9).

The Beluga coal sample contained a low concentration of total PAH ( $4.4 \pm 0.44 \mu\text{g/g}$ ) and, just as observed with the Ninilchik coal, was dominated by the biogenic PAH perylene (Figure 3-9). The similarities between these two coals also extend to the S/T distribution, with a dominance of the 22S isomer of C31-homohopane and the presence of oleanane (Figures 3-6 and 3-9).

### 3.1.2.3 Source Sediments

**Homer Harbor Sediment.** Results of SHC analyses for the two Homer boat harbor sediment source samples were very similar at the surface (0- to 2-cm) and subsurface (4- to 6-cm) depth intervals. This sediment was a black, anoxic, silt-clay, and as expected, the SHC and other organic hydrocarbon concentrations were approximately 3 to 10 times greater than the riverine and surficial sediments collected throughout the study region. The average total PHC concentration was  $120 \pm 7.1 \mu\text{g/g}$  (Table 3-2). The SHC chromatogram (Figure 3-10) shows a predominance of higher molecular weight alkanes in the C27 to C31 range and a corresponding UCM. The assemblage of saturated hydrocarbons in these samples is predominated by the plant wax alkanes; however, there are also indicators of weathered petroleum as well.

The mean total PAH concentration in the Homer Harbor sediments is  $0.78 \mu\text{g/g}$ . The PAH distribution is comprised primarily of petroleum PAH and perylene, with a minor combustion PAH contribution (Figure 3-10). The relative distribution within the series of alkyl naphthalenes indicates that the petroleum PAH are moderately weathered (e.g., the C4-naphthalenes > C3-naphthalenes > C2-naphthalenes). The predominance of perylene is indicative of recent diagenesis of terrestrial hydrocarbons in the sediments, or alternatively may be linked to a coal source (i.e., Homer coals, Figures 3-4 and 3-5). The abundance of the C4-phenanthrenes, which are the dominant PAH analyte in the distribution, is likely due to an interferent which may be related to combustion sources.

The S/T distributions of the Homer Harbor sediments are clearly different from the other source samples. An unidentified triterpane, perhaps normoretane, is the most abundant compound, followed by the C31-homohopane 22R isomer (Figure 3-10). C30-hopane and oleanane are only minor components. Some similarities in the triterpane distributions between the Homer Harbor sediments and the Homer coals (e.g., the large relative abundance of the C31-homohopane 22R isomer versus the 22S isomer) indicate that Homer Spit coal (Figure 3-4) may be a major component of the observed hydrocarbon assemblage.

**Copper River Sediment.** The total PHC concentrations in the Copper River sediment samples were very low in 4 of the 5 samples and ranged from 2.6 to  $68 \mu\text{g/g}$ , with an average total PHC concentration of  $18 \pm 28 \mu\text{g/g}$ . The SHC distributions in all the samples were dominated by terrigenous alkanes in the C25 to C33 range (Figures 3-11 and 3-12). None of the samples exhibited evidence of a petroleum hydrocarbon signature based on the GC/FID chromatograms. In comparison to the total PHC concentrations in the oil, coal, and Homer Harbor sediment source samples, the PHC levels in these riverine sediments were quite low. The one exception is the CR-1 sample collected near the Million Dollar Bridge. This sample had a total PHC concentration approximately 15 times higher than the other 4 samples (CR-2 to -5), and is likely the result of incorporation of terrigenous/plant material in this sample.

The total PAH concentrations from the Copper River sediments were very low, with many target compounds below the detection limit of the method (i.e., not detected). The mean total PAH concentrations of the Copper River sediments were  $0.041 \mu\text{g/g}$  (Table 3-2). The PAH

distribution of the Copper River sediments (Figure 3-11) contains trace levels of petrogenic 2- and 3-ring PAH, as well as combustion-related 4-, 5-, and 6-ring PAH. Furthermore, the Copper River sediment also contains a significant biogenic PAH component, i.e., perylene (Figure 3-12).

S/T are present at only trace levels in the Copper River sediments and many compounds were not detected (Figures 3-11 and 3-12). This further supports the observation that petroleum is not a significant component of the total hydrocarbons in the samples. Overall, the trace levels of SHC and PAH in these riverine samples indicate that they are not likely to be a significant source of petroleum hydrocarbon input to the Cook Inlet and Shelikof Strait region.

**Susitna River Sediment.** The Susitna River sediment samples have low total PHC concentrations ( $3.4 \pm 1.3 \mu\text{g/g}$ ). The Susitna River sediment SHC distributions are similar to the Copper River samples and are characterized by a predominance of terrigenous alkanes in the C27 to C31 carbon range (Figure 3-13). There is no evidence of petroleum hydrocarbons in these sediments based on the GC/FID chromatograms.

In contrast to the Copper River sediment, the PAH distribution of the Susitna River sediment shows only trace levels of total PAH ( $0.0074 \pm 0.00094 \mu\text{g/g}$ ), composed primarily of the combustion-related PAH (phenanthrene, fluoranthene, and pyrene) and the biogenic PAH, perylene.

S/T are present at only trace levels in the Susitna River sediments and many compounds were not detected (Figures 3-13). This further supports the observation that petroleum is not a significant component of the total hydrocarbons in the samples. Overall, the trace levels of SHC and PAH in these riverine samples indicate that they are not likely to be a significant source of petroleum hydrocarbon input to the Cook Inlet and Shelikof Strait region.

**Matanuska River Sediment.** Sediment collected from the Matanuska River contained low concentrations of total PHC ( $6.3 \mu\text{g/g}$ ). The SHC distributions are similar to the Copper and Susitna River samples and are characterized by a predominance of terrigenous alkanes in the C24 to C31 carbon range (Figure 3-14). There is no evidence of petroleum influence in these sediments based on the GC/FID results.

The PAH concentrations in these sediments were higher than the other two rivers but still less than that of the Homer Harbor sediment (Table 3-2). The PAH distribution of the Matanuska River sediment (Figure 3-14) contains trace levels of petrogenic 2- and 3-ring PAH, as well as combustion-related 4-, 5-, and 6-ring PAH.

S/T are present at only trace levels in the Matanuska River sediments and many compounds were not detected (Figures 3-14). This further supports the observation that petroleum is not a significant component of the total hydrocarbons in the samples and indicates that they are not likely to be a significant source of petroleum hydrocarbon input to the Cook Inlet and Shelikof Strait region.

**Alaska Coastal Current Sediment.** Results for the ACC sediment revealed a total PHC concentration of  $47 \pm 3.0 \mu\text{g/g}$  (Table 3-2). The pattern of saturated hydrocarbons extends across the range of GC/FID analysis (Figure 3-15), with a similar distribution of the lower n-alkanes and terrigenous C27 to C31 alkanes, as seen in Cook Inlet and Shelikof Strait sediments.

GC/MS results showed the highest PAH concentrations ( $1.7 \pm 0.06 \mu\text{g/g}$ ) compared with each of the other source sediments analyzed (Table 3-2). The distribution of PAH analytes represents a mixture of both petrogenic (i.e., 2- and 3-ringed alkylated PAH) and typical pyrogenic (5- and 6-ringed PAH) signatures (Figure 3-15).

The concentrations of S/T in the ACC sediments were moderately low, at  $0.049 \pm 0.0021 \mu\text{g/g}$ . The extracted ion chromatogram exhibits a biomarker distribution similar to that of the oils, with a dominance of the C30-triterpane,  $17\alpha(\text{H})$ -hopane (Figure 3-15), although the sediments did contain a significant amount of oleanane. These results indicate that these sediments are likely influenced by both "background" petroleum and pyrogenic sources of hydrocarbons.

**Augustine Island Sediment.** Total petroleum hydrocarbons in the Augustine Island sediments were  $12 \mu\text{g/g}$  (Table 3-2). The overall SHC (Figure 3-16) distribution reflects the influence of terrigenous plants (C23 through C30) just as observed with each of the river sediments.

PAH concentrations for these sediments were moderate ( $0.17 \mu\text{g/g}$ ), with a distribution reflecting the influence of petrogenic, pyrogenic, and biogenic (perylene) PAH (Figure 3-16).

The concentration of S/T for the Augustine Island sediments was  $0.019 \mu\text{g/g}$ , with a profile containing similar dominance of the 22R isomer of C31-homohopane (Figure 3-16), as was observed with the Homer Spit coal and Homer Harbor sediments (Figures 3-4 and 3-10, respectively).

#### 3.1.2.4 Aqueous Sources

**Point Woronzof Municipal Effluent.** The total PHC concentration for the Point Woronzof (Anchorage) municipal effluent was  $2,300 \mu\text{g/L}$  (Table 3-2). The chromatogram of the municipal effluent sample reveals a predominance of higher molecular weight alkanes (C27 to C34) which are typical of terrigenous hydrocarbon sources (i.e., plant wax alkanes), and only a trace PHC signature.

The Anchorage municipal effluent has a total PAH concentration of  $6.7 \mu\text{g/L}$ , with a PAH distribution characterized by a full suite of 2-, 3-, and 4-ring PAH, with considerably lower levels of 5- and 6-ring PAH (Figure 3-17). Three of the most abundant compounds in the PAH distribution are phenanthrene, fluoranthene, and pyrene, which are indicative of pyrogenic or combustion-related sources (e.g., urban runoff). The effluent also contains a complete series of C1- through C4-alkyl naphthalenes, phenanthrenes, and dibenzothiophenes, which is characteristic of petroleum sources.

The full suite of triterpanes, dominated by hopane (Figure 3-17), is also characteristic of PHC material. Based on the SHC, PAH, and S/T data, the Anchorage effluent contains a mixture of petroleum and combustion-related hydrocarbons.

**Trading Bay Produced Water.** Total SHC in the produced water sample from the Trading Bay Production Facility had a concentration of  $6,200 \mu\text{g/L}$  (Table 3-2). The chromatogram for the produced water (Figure 3-18) displays a homologous series of alkanes and a UCM similar to the Cook Inlet crude oil (Figure 3-1), although the produced water is depleted in the low molecular weight alkanes (C9 to C14).

The total PAH concentration of 380  $\mu\text{L}$  in the TBPF produced water sample is substantially higher than the municipal effluent, but within the range for other produced water samples from Cook Inlet (Hyland, *et al.*, 1995). The PAH distribution (Figure 3-18) is characterized by an abundance (>90 percent) of naphthalene and alkyl naphthalene relative to the 3- and 4-ring PAH (phenanthrenes and chrysenes). The observed enrichment of the naphthalenes is due to the higher solubility of these 2-ring PAH relative to the 3-, 4-, 5-, and 6-ring PAH. The distribution of the 3-, 4-, and 5-ring PAH and the S/T (Figure 3-18) in the produced water are comparable to the Cook Inlet crude (Figure 3-1).

### 3.1.3 Metals

Twenty-three source samples were analyzed for trace metals and major elements including the following: Susitna River bottom sediment (2), Copper River bottom sediment (4), Homer Harbor bottom sediment (1), Susitna River suspended solids (2), Knik River suspended solids (2), Matanuska River suspended solids (2), Copper River suspended solids (2), coal (5), Cook Inlet crude oil (1), Cook Inlet produced water (1), and Point Woronzof municipal effluent (1). Samples of sediment, water, and oil were collected during 1997 and samples of suspended solids and coal were collected during 1997 and 1998. At the beginning of this study, riverine inputs were hypothesized to be the dominant source of sediment and sediment metals to outermost Cook Inlet and the Shelikof Strait (Boehm *et al.*, 1998). Thus, the Susitna and Copper Rivers, two primary sources of metals to the study area, were sampled for bottom sediment and suspended solids.

#### 3.1.3.1 Source Sediments and Suspended Solids

Results for bottom sediment from the Susitna and Copper Rivers (Table 3-1) show that concentrations of nine metals (Al, Be, Cr, Fe, Hg, Ni, Pb, Sn, Tl, and Zn) are comparable to or less than values for average continental crust (Table 3-3). In contrast, and again relative to average continental crust, concentrations of As, Ba, Cd, Cu, Sb, and Zn are higher in bottom sediment from both rivers, Ag and Se are greater in Susitna River sediments, and Mn and V are higher in Copper River sediments (Table 3-1). However, when these metals in river sediment are compared with native sedimentary, volcanic, and plutonic rocks from Alaska (Table 3-3), the river sediments contain comparable or lower levels of all metals.

During 1998, suspended solids were collected from the Susitna, Knik, Matanuska, and Copper Rivers. All concentrations of As, Cd, Cu, Fe, Hg, Mn, Sb, V, and Zn in river suspended solids are higher than levels reported for average continental crust (Table 3-3). However, relative to Alaskan rocks, only concentrations of Al, Cr, and Ni are higher in most samples of river suspended solids (Tables 3-1 and 3-3). This enrichment is most likely due to higher natural levels of these three metals in the fine-grained aluminosilicate clays carried in suspension. Maximum concentrations of Ba and Pb in suspended solids are about 30 percent higher than Alaskan rocks for just one or two isolated instances that may be tied to natural or anthropogenic processes. Collectively, metal values for bottom sediments and suspended solids from the important source rivers provide one valuable frame of reference that will be used to help identify inputs of contaminants to sediments as they are carried through Cook Inlet and on to the Shelikof Strait.

Bottom sediment from Homer Harbor also was chosen as a potential source material to outermost Cook Inlet and the Shelikof Strait. This sediment is fine-grained, black mud (94.3 percent silt

plus clay) with 1.6 percent organic C. Despite the nature of this material, concentrations of all metals in river suspended solids are greater than levels found in sediments from Homer Harbor. When Homer Harbor sediments are compared with river sediments, concentrations of Hg, V, and Zn are elevated in Homer Harbor (Table 3-1). However, bottom sediment from the Susitna River contains 56 percent sand and may not be representative of the material carried seaward from the river system. At this point, Homer Harbor sediment will be considered an additional potential source of Hg, V, and Zn to the study area. The degree of anthropogenic additions of Hg, V, and Zn to Homer Harbor will be discussed in Section 4.1.

### 3.1.3.2 Source Coals

Coal is an important deposit in the drainage basin of the study area (MMS, 1996). Concentrations of metals in five samples of coal are generally lower than in bottom sediment from the Susitna or Copper Rivers (Table 3-1). Notable exceptions to this observation are higher levels of Cd, Cu, and Hg in the Ninilchik coal and elevated concentrations of Sb in the Matanuska coal relative to river bottom sediment and suspended solids. When source coals for this study are compared with the USGS (1998) database for coal in Alaska (Table 3-1), the following metals (samples) are above the range of observed concentrations: Al (Homer), Cd (Ninilchik), Cr (Beluga), Cu (Matanuska and Ninilchik), Fe (Homer), Hg (Ninilchik), Mn (Homer), Pb (Beluga and Ninilchik), and Sb (Matanuska). However, coal is unlikely to be an important source of metals to any of the sediments in outermost Cook Inlet and the Shelikof Strait because the highest TOC values in sediment (TOC  $\approx$  2 percent) are more than 30 times lower than in coal (TOC > 60 percent). Even if all the TOC in the sediment was from coal, metals in the coal would be diluted by a factor of 30 or more. Thus, concentrations of Sb, with a 3-fold enrichment in coal, would not be enhanced in sediment due to the presence of a small fraction (< 3 percent) of coal.

### 3.1.3.3 Aqueous and Oil Sources

Metal concentrations in the source sample of TBPF produced water (salinity = 25 g/L), Cook Inlet crude oil, and final effluent from Point Woronzof WWTF (Table 3-4) are low, with concentrations > 1 mg/L only for Ba and Mn in the produced water, Fe and Ni in the crude oil, and Fe in the final effluent. At these low concentrations and discharge rates, the aqueous and oil samples are unlikely to serve as a detectable source of metals to sediments in the study area. Trefry *et al.* (1996) found no statistical differences ( $\alpha = 0.05$ ) in concentrations of Ba, Cd, Cu, Fe, Mn, Ni, Pb, V, or Zn in fish collected from oil production platforms in the Gulf of Mexico where there were discharges of produced water versus non-discharging sites. Furthermore, metal levels of produced water from the Gulf of Mexico were considerably higher than those found in the sample from TBPF.

## 3.2 Surface Sediments

### 3.2.1 Physical Measurements

A total of 170 surficial sediments were analyzed for TOC and percent sand, silt, and clay. The TOC values in surficial sediments range from 0.26 percent to 1.49 percent (Table 3-5). Relative to TOC concentrations in bottom sediment from the Susitna ( $0.20 \pm 0.01$  percent) and Copper ( $0.14 \pm 0.02$  percent) Rivers, TOC levels in sediment from outermost Cook Inlet and the Shelikof Strait are significantly higher. Average TOC values are similar in zones 0 and 1, increasing by about 40 percent in zones 2 and 3 (Table 3-5). Highest TOC levels (> 1 percent TOC) are

observed at Z0F1 and Z0F14 (Homer Harbor), at selected sites in zones 2 and 3, and throughout zone 4 (Appendix A).

Sand values in surficial sediments average about 42 percent in zone 0 and 41 percent in zone 1 (Table 3-5). However, the sand content decreases dramatically in the remaining three zones. For example, sediment from zone 2 averages about 7 percent sand, zone 3 contains only 2 percent sand, and zone 4 has about 1 percent sand. In contrast, the silt+ clay levels in surficial sediments from outermost Cook Inlet and the Shelikof Strait increase from 57.9 percent in zone 0 to >97 percent in zones 3 and 4 (Table 3-5).

### 3.2.2 Organics

In this section, the surface sediment grab sample results and general trends in the data will be discussed for the outermost Cook Inlet and Shelikof Strait study area as a whole, as well as within each of the five zones.

Average concentrations of total PAH, total PHC, and total S/T were calculated for each zone by first averaging replicates, where appropriate, to obtain a value for each station location, and then averaging the station location values within each zone to obtain an average total concentration for each zone. The data presented reflect concentrations on a dry sediment weight basis. The concentrations presented for the combined years (1997 and 1998) are simply the average of the zone for each sample period (n=2). The study area-wide grand average concentrations were obtained by averaging the average total concentration for each zone (i.e., n=4 for 1997, n=5 for 1998, n=5 for 1997 and 1998). The range of values presented for each grand average includes the minimum and maximum concentration values for all station locations. These calculated means and ranges for the summary organic parameters in all zones are presented in Table 3-6. The complete organics data for all surface sediments are included as data tables in Appendix B. In addition, the key diagnostic parameters for the organics data, as defined in Table 3-7, which were used in the statistical analysis of the surface sediment data for both years, are summarized in Table 3-8.

To facilitate the presentation and discussion of the organics data, GC/FID chromatograms, PAH distribution plots, and triterpane extracted ion chromatograms that are representative of surface sediments in zones 0, 1, 2, 3, and 4 were selected, and are presented in Figures 3-19 through 3-27. The stations selected for presentation are as follows:

- **Zone 0** - Fixed station locations F1 - Kachemak Bay (sample 97-0-F1-01-00-PHC-S, Figure 3-19), station F4 - center of outermost Cook Inlet (samples 97-0-F4-02-00-PHC-S, Figure 3-20 and 98-0-F4-01-00-PHC-S, Figure 3-21), and F5 - Kamishak Bay (samples 97-0-F5-02-00-PHC-S, Figure 3-22 and 98-0-F5-01-00-PHC-S, Figure 3-23)
- **Zone 1** - Random station 09 - North Shelikof Strait (sample 97-1-08-01-00-PHC-S, Figure 3-24)
- **Zone 2** - Random station 08 - Middle Shelikof Strait (sample 97-2-08-01-00-PHC-S, Figure 3-25)
- **Zone 3** - Random station 10 - South Shelikof Strait (sample 97-3-10-01-00-PHC-S, Figure 3-26)
- **Zone 4** - Fixed station location F2 - Outside Shelikof Strait (sample 98-4-F2-01-00-PHC-S, Figure 3-27)

Surface sediments were also collected in triplicate at two embayment stations located within Kodiak Island (Figure 2-1). Due to their close proximity to the shore and the presence of a sill between them and the open strait (as indicated by the water depths of the two embayment stations), these stations were not included in the statistical zone analysis, but are discussed separately.

### 3.2.2.1 Saturated Hydrocarbons

Concentrations of total PHC in surficial sediments from outermost Cook Inlet and Shelikof Strait ranged from 6.8 to 71.0 µg/g throughout the study area. The total PHC concentrations were generally at low to moderate levels with average total PHC concentration across the four zones of 28.5 µg/g in the sediments collected in 1997, with a coefficient of variation (CV) of 18 percent (Table 3-6). The total PHC concentrations for surface sediment averaged across the five zones collected in 1998 was 28.8 µg/g, with a CV of 19 percent (Table 3-6). The grand average total PHC for the study area over the entire sampling period was  $29.4 \pm 5.41$  (Table 3-6). Comparison of both sample periods reveals little variation across both years, with the CV for zones ranging from 0.2 percent to 7.4 percent. A more detailed comparison of the analysis of variance among measured and calculated parameters between years is presented in Section 3.5. Among samples in each zone, the average total PHC concentration was highest in zones 3 and 4 (34.8 µg/g and 35.8 µg/g, respectively), with somewhat lower average concentrations in zones 0, 1, and 2 (25.5 µg/g, 24.9 µg/g, and 26.0 µg/g, respectively).

In general, the surficial sediments collected in zones 1, 2, 3, and 4 (GC/FID chromatograms in Figures 3-24 through 3-27) exhibit a mixture of terrestrial and marine hydrocarbons dominated by an assemblage of plant wax alkanes in the C27 through C33 carbon range. This is further demonstrated by Carbon Preference Index (CPI - calculated as:

$$\frac{C26 + C28 + C30}{C27 + C29 + C31}$$

values, on average, ranging from 2.3 to 3.6, and is characteristic of sediments influenced by terrigenous plant inputs (Wakeham and Carpenter, 1976; Boehm, 1984). Traces of lower molecular weight alkanes (LALK), indicative of petroleum, are visible in the chromatograms only as a minor component relative to the plant wax alkanes. The GC/FID chromatograms from three stations in zone 0 (Figures 3-19 through 3-23) show a similar distribution of terrestrial hydrocarbons (an average CPI of 3.2 and 5.4 for 1997 and 1998, respectively), but show even less evidence of lower molecular weight petroleum hydrocarbons.

The sediment for the two embayment stations adjoining zone 2, but within Kodiak Island sills, contained substantially higher total PHC concentrations of SHC's, with a mean total PHC of  $71.3 \pm 17.5$  µg/g and  $47.7 \pm 10.7$  µg/g for stations Z2F3 and Z2F4, respectively. The composition of SHCs however, was similar to the other zone 2 sediments although primarily influenced by terrigenous plants. Each chromatogram (not shown) was dominated by the plant wax alkanes along with a large corresponding UCM, and revealed low abundances of the nC9 through nC20 alkanes (LALK) relative to the entire suite of alkanes (between 18 and 23 percent), compared with a mean abundance of 42 percent for the LALK in the zone 2 sediments.

### 3.2.2.2 Polycyclic Aromatic Hydrocarbons

In general, low to moderate levels of PAH were found across the study area. The average total PAH concentration in sediment for all four zones collected in 1997 was  $0.457 \mu\text{g/g}$  (CV of 32 percent) and  $0.432 \mu\text{g/g}$  (CV of 38 percent) for the five zones collected in 1998. The grand average for total PAH in the entire study region across both years was  $0.459 \pm 0.151 \mu\text{g/g}$ , with minimal variation between the sampling period within zones (CV of 2.2 to 21 percent). In outermost Cook Inlet (zone 0), the average total PAH concentration was  $0.235 \mu\text{g/g}$ , while the average total PAH concentrations in Shelikof Strait (zones 1, 2, 3, and 4) gradually increased with distance from Cook Inlet ( $0.376 \mu\text{g/g}$ ,  $0.534 \mu\text{g/g}$ ,  $0.548 \mu\text{g/g}$ , and  $0.604 \mu\text{g/g}$ , respectively). These levels of PAH are consistent with previously reported values for the Cook Inlet/Shelikof Strait region, as well as other Alaskan coastal sediments (e.g., Prince William Sound and the Beaufort Sea - Table 3-9).

The PAH distributions for most surficial sediments show that the PAH are primarily of a combined fossil fuel origin (i.e., petroleum and coal), with a somewhat variable biogenic component (perylene) and lesser contribution of pyrogenic or combustion-related compounds (4-, 5-, and 6-ring PAH). Perylene concentrations were relatively high in most surficial sediments, but varied widely from zone to zone and among samples within a zone. Perylene is a naturally occurring PAH formed during early diagenesis in sediments from biological source precursors (Wakeham and Farrington, 1980; Wakeham, *et al.*, 1980). It may also be found in crude oil at very trace concentrations. In past studies, perylene was found at comparable concentrations in the sediments of Cook Inlet and Alaska nearshore sediments (Boehm *et al.*, 1998).

The variations in PAH composition in the surface sediments of zone 0 are shown in PAH distribution plots in Figures 3-19 through 3-23. In Kachemak Bay (Station ZOF1, Figure 3-19) the PAH assemblage is dominated by perylene, with a full suite of 2-, 3-, and 4-ring petroleum PAH, and lower levels of combustion PAH. In contrast, in the center of Cook Inlet (Station ZOF4, Figures 3-20 and 3-21) only traces of perylene are found, and the PAH distribution is primarily comprised of moderately weathered petroleum PAH (i.e., naphthalenes generally < phenanthrenes), with trace combustion PAH. In Kamishak Bay (Station ZOF5, Figures 3-22 and 3-23), the PAH concentration is somewhat lower and is characterized by a full suite of petrogenic PAH, a significant perylene component, and only trace combustion PAH.

The PAH distributions in zones 1, 2, 3, and 4 are generally similar throughout, and are characterized by the presence of a full suite of relatively "unweathered" petroleum PAH (i.e., naphthalenes  $\geq$  phenanthrenes). Perylene is present at somewhat variable concentrations, and does not appear to correlate with the total PAH concentrations. Trace levels of 4-, 5-, and 6-ring combustion PAH are present, but are generally only a minor component of the overall PAH composition.

The total PAH concentrations for sediments located within the Kodiak Island embayment area were consistent and within the range of all zones (Table 3-8), with a mean of  $0.530 \pm 0.043 \mu\text{g/g}$  and  $0.415 \pm 0.033 \mu\text{g/g}$  for the stations Z2F3 and Z2F4, respectively. The composition of PAH were similar to the other Shelikof Strait sediments, containing a mixture of the relatively "unweathered" petroleum PAH combined with a minor combustion PAH component similar to that observed for the adjacent zone 2 sediments, as well as, sediments from zones 1, 3, and 4 (Figures 3-24 through 3-27).

### 3.2.2.3 Steranes and Triterpanes

In general, the S/T appear somewhat different in zone 0 than in zones 1, 2, 3, and 4, where the S/T results were generally similar. Figures 3-19 through 3-27 show the distribution of triterpanes for surficial sediments in all 5 zones of the study area. The average total S/T concentrations for zones 1, 2, 3, and 4 range from 0.016 to 0.029  $\mu\text{g/g}$  (CV of 31 to 71 percent) for surface sediment collected in 1997, while the range of average S/T concentrations for the sediment collected in 1998 was 0.016 to 0.030  $\mu\text{g/g}$  (CV of 4 to 81 percent). The grand average for total S/T for all zones across both years was  $0.024 \pm 0.005 \mu\text{g/g}$ , with minimal year-to-year variation within zones (CV of 0 to 23 percent).

Generally, there were low levels of S/T characteristic of petroleum found at all stations in zones 1, 2, 3, and 4 with C30-hopane (T19) present and often the most abundant compound in the overall triterpane distribution. Oleanane (T18) was detected in all samples in zones 1, 2, 3, and 4, indicating the presence of a non-Cook Inlet post-Cretaceous/Tertiary petroleum source (i.e., T18 is absent in Cook Inlet crude). In addition, the relative abundance of T22 > T21 and the presence of the moretananes are indicators of recent organic matter inputs to the surficial sediments.

The S/T concentrations at station Z2R22 (1997) and Z3R11 (1998) were substantially higher than all other stations, thus contributing to relatively heightened CVs for these zones (Table 3-6). A closer evaluation of the triterpane distribution in these samples indicates the presence of a different petroleum source (or a mixture) than in the other samples and currently suggests that these stations may be an outlier in the data set for triterpanes (all other organic parameters were within the range of other samples from the study area).

The S/T analyses from zone 0 (outermost Cook Inlet) stations reveal a slightly different pattern of triterpanes, particularly in Kachemak Bay (Figure 3-19). The triterpanes from this station show an abundance of recent biogenic triterpanes and the greater abundance of T22 versus T21 is similar to that observed for the Homer Spit coal source sample (Figure 3-4). While a characteristic petroleum triterpane distribution is present, it is only a minor component, indicating that coal may be the primary source of the S/T. Three other samples taken from the Kachemak Bay area (Z0F2, Z0F13, and Z0F14) also have similar triterpane distributions, indicating the influence of a coal source. In general, the remaining stations in zone 0 (Figures 3-21 through 3-23) have triterpane patterns more similar to those observed in zones 1, 2, 3, and 4 (Figures 3-24 through 3-27). However, there appears to be a greater component of coal influence as indicated by the T22 > T21 abundance. Oleanane was also present in all of the zone 0 samples, indicating a non-Cook Inlet petroleum contribution. At station Z0F6 only trace oleanane was detected, indicating a different petroleum source (discussed below).

The total S/T concentrations for sediments located within the Kodiak Island embayment area were similar to those measured in all zones (Table 3-8), with a mean of  $0.023 \pm 0.003 \mu\text{g/g}$  and  $0.020 \pm 0.005 \mu\text{g/g}$  for the stations Z2F3 and Z2F4, respectively. The composition of S/T were similar to the other Shelikof Strait sediments, i.e., dominated by the C30-hopane and containing a minor presence of oleanane, in addition to having a relative abundance of T22 > T21.

### 3.2.2.4 Hydrocarbon Sources in Surface Sediments

As mentioned previously, selected diagnostic ratios and parameters were used in the statistical evaluation and to support the interpretation of the organics data (SHC, PAH, and S/T). The data

sets were analyzed separately by year due to the additional zone (zone 4) included in the 1998 sampling survey. The initial statistical analysis of the hydrocarbon data focused on identifying differences between zones for the selected diagnostic parameters, in order to evaluate potential source trends i.e., higher concentrations of hydrocarbons closer to Cook Inlet oil and gas production activities.

The statistical results (Student Newman-Keuls test on non-normalized data) of the organics diagnostic parameters for the surface sediments collected in 1997 are shown in Table 3-8 (complete details of the statistical results are included in Appendix I Table H-I). Zones were not significantly different for 8 of the 23 parameters measured. For 11 of the remaining 16 parameters, zone 0 was significantly different from zones 1, 2, and 3. The remaining parameters resulted in some overlap in significant differences between zones. Results for the 1997 surface sediment data normalized by TOC were not substantially different, with zone 0 again statistically separate from the other zones, which were overlapped among each other.

The statistical results (Student Newman-Keuls test on non-normalized data) of the organics diagnostic parameters for the surface sediments collected in 1998 are also shown in Table 3-8. Two additional parameters were introduced during this sample period, i.e., the presence of oil degrading bacteria and mean heterotrophic bacterial population (Section 2.2.5.4). All zones were not significantly different for 18 of the 25 parameters measured. For 2 of the remaining 7 parameters, zone 0 was significantly different from zones 1, 2, 3 and 4. The remaining parameters resulted in some overlap in significant differences between zones. Results for the 1998 data normalized by TOC were, once again, not substantially different with zone 0 statistically separate from the other zones, which were themselves overlapped among each other.

Generally, these results show that zone 0 was different from the other zones due to lower concentrations of the total or summed hydrocarbon parameters (e.g., Total PAH, petrogenic PAH, isoprenoids, LALK). Zone 0 had significantly higher concentrations of perylene and a higher pyrogenic/petrogenic ratio (for the 1997 and 1998 sediments), showing that zone 0 is more subject to biogenic and combustion inputs than zones 1, 2, 3, and 4. The naphthalene/phenanthrene (N/P) ratio in zone 0 was lower in the 1997 sediment analysis, supporting earlier observations that the PAH in zone 0 appeared more weathered than zones 1, 2, 3, and 4. The Carbon Preference Index (CPI) was not significantly different between zones in the sediment collected in 1997, while in 1998 the zone 0 sediment had a significantly higher CPI, confirming a consistent influence of terrigenous hydrocarbon input throughout the area, particularly in zone 0. The key petroleum source parameters (e.g., C2D/C2P, C3D/C3P, oleanane/hopane, and Ts/Ts+TM, ) were either not different or resulted in overlap between zones, indicating a common source of petroleum hydrocarbons to the study area. Overall, these statistical results indicate that zone 0 was generally different from the other zones due to lower concentrations of organic parameters, and there is no reproducible trend showing higher levels of organics closer to Cook Inlet oil and gas production activities.

Based on a review of the key diagnostic parameters for organics, an evaluation of the petroleum hydrocarbon sources in the surface sediments is best described by the double-ratio plot of the alkyl dibenzothiophenes and alkyl phenanthrenes (C2D/C2P versus C3D/C3P). This double ratio has been well documented as an accurate source indicator in other studies investigating the sources of petroleum hydrocarbons in the environment (Brown and Boehm, 1993; Page *et al.*, 1996; Bence *et al.*, 1997).

A double-ratio plot of the source samples and all the surface sediment samples collected during both surveys is shown in Figure 3-28. The plot reveals that North Slope crude oil (i.e., *Exxon Valdez* crude) and Point Woronzof effluent have significantly higher ratios than any of the study samples, effectively eliminating either of these sources as significant contributors to the surface sediments. Four of the Copper River and both of the Susitna River source samples contained only trace concentrations of most individual PAH, while the alkyl dibenzothiophenes and phenanthrenes were not detected. As a result, both of these sources plot at the origin and are likewise eliminated as a source of petroleum hydrocarbons. One of the Copper River samples, however, did contain detectable alkyl PAH, and the subsequently calculated ratio did fall near many of the sediment samples. As stated earlier though, the PAH levels present in this source are insufficient to be considered as an influential contributor of PAH. Furthermore, the Well Creek seep oil and the Matanuska and Coyote Lake coals can also be discounted as primary sources of hydrocarbons based on their positioning within the double-ratio plot (Figure 3-28).

Several of the other source samples, the Homer Harbor sediment, St. Augustine Island sediment, Alaska Coastal Current sediment, Homer Spit coal, Ninilchik coal, TBPF produced water, Cook Inlet crude oil, and Swanson River Field oil, all have source ratios within the range observed for all the surface sediments. The TBPF produced water sample has a similar ratio to the Cook Inlet crude oil and falls within the ellipse representing 1 standard deviation (SD) around the mean of the 29 replicate Cook Inlet crude oil analyses. In contrast, nearly all the samples appear in a cluster above and to the right of the Cook Inlet crude (Figure 3-28), and only 4 of the surface samples plot within the Cook Inlet crude oil ellipse.

An evaluation of the same source ratios from other studies of offshore sediments and oil seeps to the east of the study area revealed that the sediments associated with the Katalla and Yakataga seeps and petroleum-bearing formations have C2D/C2P and C3D/C3P ratios that are similar to the major cluster of samples from this study (Page, *et al.* 1995; Page *et al.*, 1996; Bence *et al.*, 1997). The Katalla production oil has C2D/C2P and C3D/C3P ratio values which are central to the main cluster of samples, and the same ratio was determined for the deep subtidal "background" sediments in Prince William Sound (Bence *et al.*, 1997). Results from "background" subtidal sediments off the Alaska Peninsula to the south of the study area have also yielded similar C2D/C2P and C3D/C3P ratios (Manen *et al.*, 1993). The Alaska Coastal Current sediment sample collected east of Cook Inlet in 1998 as part of this study also has C2D/C2P and C3D/C3P ratios which plot centrally to the main cluster of sediment samples. These results, coupled with the known sediment transport to the area by the Alaska Coastal Current (Boehm *et al.*, 1998), demonstrate that petroleum hydrocarbons, likely from the Katalla and Yakataga region formations, are the primary source of petroleum hydrocarbons in the outermost Cook Inlet and Shelikof Strait sediments. Others have suggested that coal particles may also represent a source of hydrocarbons to the Alaska Coastal Current sediments (Short, *et al.*, 1999, Hostettler, *et al.*, 1999). However, a recent comprehensive study of Alaska Coastal Current and Prince William Sound sediment sources, concluded that erosional sediments and glacial flour from tertiary shales, and seep oils to the east (e.g., Katalla and Yakataga region, Malspina Glacier), are the primary source of hydrocarbons to the sediment loading of the Alaska Coastal Current (Boehm, *et al.*, 2001).

When the double-ratio plots of the surface sediments are examined by zone, a pattern of hydrocarbon sources becomes apparent. In zone 0 the double-ratio plot reveals a greater scatter of samples. This scatter is likely due to the influence of coal and Homer Harbor source(s)

mixing with the influx of “background” sediment and seep oil hydrocarbons (Figure 3-29). The sediments plotting most distant from the Cook Inlet ellipse and proximal to the Homer Harbor source samples were consistently collected from locations in or near Kamechak Bay (ZOF14, ZOF1).

In zone 1 there is substantially less scatter of the ratio as it approaches the “background” sediment value of seep-associated petroleum hydrocarbons with minimal coal source influence (Figure 3-30). Four of the surface sediment samples from zone 1 occur within the Cook Inlet crude source ellipse, indicating a possible contribution or mixing from Cook Inlet crude or related seep oil(s) from Cook Inlet (Iniskin Peninsula). In zones 2 and 3 the sediment samples generally cluster in the area of the “background” sediments and seep-associated hydrocarbons oil formation (Figures 3-31 and 3-32). Many of the sediments collected from zone 4 also mirror the calculated “background” sources, although several samples did fall outside the range of sources measured as a part of this study (Figure 3-33).

### **3.2.3 Metals**

#### **3.2.3.1 Trace and Major Elements**

All surficial sediments were analyzed for total concentrations of Ag, Al, As, Ba, Be, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Sb, Se, Sn, Tl, V, and Zn (Table 3-10 and Appendix C). The 1997 samples also were analyzed for the major elements Ca, K, and Mg for use as possible indicators of differences in composition of material from the Susitna River versus the Copper River. The resulting data show that concentrations of Ag, Al, Be, Cd, Cr, Fe, Mn, Ni, Pb, Sn, Tl, and V in surficial sediments from outermost Cook Inlet and the Shelikof Strait are similar to or less than average continental crust, whereas concentrations of As, Ba, Cd, Hg, Sb, Se, V, and Zn are enriched by a factor of 1.4 to 5 (Table 3-11). When average metal values for these Alaskan sediments are compared with data for sediment from the Susitna and Copper Rivers (Table 3-11), only levels of Fe, Hg, Mn, Pb, Tl, V, and Zn are 16 to 50 percent higher (Table 3-11). Further comparison of average metal concentrations for the surficial sediments from this study (Table 3-11) with available values for sedimentary, volcanic, and plutonic rocks from Alaska (Table 3-3) and river suspended solids (Table 3-1), show that average levels for all metals in these sediments are within the range of values in potential source rocks and river suspended solids.

Average metal concentrations for surficial sediments from zones 0, 1, 2, 3, and 4 (Table 3-10) are relatively uniform throughout this region which extends over approximately 350 km. For example, the CV [CV = (standard deviation/mean) x 100 percent] for all metals in all surficial sediments (except zone AC) range from about 9 to 35 percent. As shown in Table 3-12, 14 of the 22 metals have a CV  $\leq$  20 percent. Only Ag, Hg, and Se have a CV of  $>$ 30 percent. The high CV for Hg results from high concentrations ( $>$ 0.1  $\mu$ g Hg/g) in sediments from Homer Harbor.

To make inter-comparisons among sediment samples, it is often necessary to normalize metal values to either Al or Fe, thereby removing variations in metal concentrations that result from changes in grain size and/or mineralogy. Aluminum and Fe exhibit a strong linear relationship when they are introduced by a common suite of aluminosilicate and/or Fe-bearing minerals to a sedimentary basin. This trend results from progressive dilution of Al- and Fe-rich minerals with quartz sand and/or shell carbonates that are depleted in these two elements. In addition, trace metals tend to be enriched in aluminosilicate minerals and depleted in quartz sand and shell carbonates, thereby showing a positive relationship with Al and/or Fe.

In contrast with typical marine sediments, no distinct relationship between Fe and Al (Figure 3-34) is observed for surficial sediments from zones 0, 1, 2, 3, and 4. This lack of a simple trend between Fe and Al suggests that more than one source (or suite) of Al- and Fe-bearing minerals is responsible for observed concentrations of these elements. For example, abundant magnetite (Fe-rich, Al-poor) was observed in some sediment samples. Furthermore, no strong positive linear trends between trace metals and Al were obtained for these surficial sediments, suggesting that Al is not a dependent variable for most trace metals. Metal/Fe plots for the surficial sediments from zones 0, 1, 2, 3, and 4 showed good linear relationships ( $r > 0.70$ ) for Cr, Cu, Ni, Pb, Sb, V, and Zn (Figures 3-34, 3-35, and 3-36), suggesting that Fe-bearing phase(s) are the more important carriers of these trace metals to the sediments. Less significant trends ( $r < 0.70$ ) between Fe and the trace metals Ag, As, Ba, Be, Cd, Hg, Mn, Se, Sn, and Tl (Figures 3-34 and 3-35) were observed, indicating that a more complex or varied suite of mineral phases carry these metals to the study area.

Twenty-five samples of surficial sediment collected during 1997 were resampled in 1998 to assess interannual variability. Metal concentrations in the 1997 samples agreed within  $\pm 10$  percent with results from 1998 for Al, Ba, Be, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Sb, Tl, and Zn. For As, Sn, and TOC, agreement between years was within  $\pm 20\%$ . Only concentrations of Ag and Se varied by  $>20$  percent, at 39 percent and 23 percent, respectively.

Statistical analysis (1997 Student Newman-Keuls test) of the metal/Fe ratios by zone for the surficial sediments showed that the metals divided into three separate groups (Table 3-13). In the first group, values for Ag/Fe, Mn/Fe, Ni/Fe, and Tl/Fe show no significant differences at  $\alpha = 0.05$  among the four zones in outermost Cook Inlet and the Shelikof Strait. Within the second group, comprising As, Ba, Cr, Cu, Hg, Pb, Sb, Sn, V, and Zn normalized to Fe, two different subgroupings (A and B) could be identified. For example, Pb/Fe and Sn/Fe ratios in zone 0 are statistically different from zones 1, 2, and 3, whereas Cr/Fe and Cu/Fe ratios in zone 2 differ from zone 1, but are similar to zones 0 and 3 (Table 3-13). Beryllium, Cd, and Se normalized to Fe make up the third group with three different groupings (A, B, and C). In this group, the metal/Fe ratio in one zone is statistically different from two other zones (Table 3-13). For example, the Be/Fe ratio in zone 0 is statistically different at  $\alpha = 0.05$  from zone 2 and 3 and zone 2 differs from zone 3. The statistical results by zone show that the metal/Fe ratios in zones 0, 1, 2, and 3 are all similar with the exception of Cd and Se in zone 0 and Be in zone 2.

Statistical analysis (1997 and 1998 Combined Student Newman-Keuls test) of the metal/Fe ratios by zone for the surficial sediment data for 13 of the 17 metals (Ag, As, Ba, Be, Cr, Cu, Hg, Pb, Ni, Sb, Se, Tl, and V) showed no significant differences at  $\alpha = 0.05$  among the four zones in outermost Cook Inlet and the Shelikof Strait (Table 3-13). For Cd, Mn, Sn, and Zn ratioed to Fe, two different sub-groupings (A and B) could be identified. In each case, higher metals values are observed for zone 3 relative to zone 1, possibly the result of sediment with a greater surface area in zone 3. However, in the cases of Cd, Sn, and Zn, standard deviations (SD) for average metal concentrations in a given zone are often quite low ( $CV < 2\%$  or absolute value of  $SD < 0.05$  ug/g). Thus, relatively small absolute differences between metal values from zone to zone test as being statistically significant. For Mn, variation may be related to differences in the degree of Mn remobilization, as previously discussed.

Statistical results for metal/Fe ratios for 1997 versus 1998 show no annual differences (at  $\alpha = 0.05$ ) for 15 of the 17 metals (Appendix I Table I-29). In the case of Sn, the absolute difference

in mean concentrations for 1997 ( $1.67 \pm 0.07 \mu\text{g/g}$ ) versus 1998 ( $1.46 \pm 0.07 \mu\text{g/g}$ ) was small and is not considered to be related to any defensible shifts during the sampling periods. A similar, small absolute difference was observed in Ag levels for 1997 ( $0.08 \pm 0.01 \mu\text{g/g}$ ) versus 1998 ( $0.05 \pm 0.01 \mu\text{g/g}$ ). Much of this statistical result for Ag results from an interannual difference of  $0.03 \mu\text{g/g}$  for zones 0 and 3. The overall mean ( $\pm$  standard deviation) for Ag in all surface samples of  $0.07 \pm 0.02$  supports no easily detectable differences in Ag levels.

### 3.2.3.2 Acid-Volatile Sulfide/Simultaneously Extracted Metals

Concentrations of AVS and SEM were determined for 29 samples of surficial sediment (0 to 2cm) collected during 1997. Results for AVS range from  $<0.005 \mu\text{moles/g}$  (the detection limit) at four stations (Z0F6, Z0F8 [1 of 3 field replicates], Z1F1, and Z1R8) to  $18.6 \mu\text{moles/g}$  at station Z0F14 (Figure 3-37). This maximum value is much higher than the next closest value of  $3.1 \mu\text{moles/g}$  (at both Z0F1 and Z3R20). Only six values in the data set are  $>1 \mu\text{mole/g}$ , the level considered to be the threshold of applicability for the SEM-AVS technique (DiToro *et al.*, 1990). The overall mean value of  $1.2 \pm 3.6 \mu\text{moles/g}$  decreases to  $0.6 \pm 0.8 \mu\text{mole/g}$  when the maximum value is excluded. The six samples with  $>1 \mu\text{mole AVS/g}$  are scattered across all these zones with no simple trend except that the two highest values are for zone 0.

Analyses for SEM included the following metals: Cd, Cu, Ni, Pb, and Zn. Of the 5 SEM metals, Zn is the most abundant in all cases, comprising 50 percent or more of the total SEM (Figure 3-38 and Appendix D). Copper and Ni are the second and third most abundant metals in the SEM summation, with typical contributions of about 10 to 35 percent of the total SEM. In contrast, Pb and Cd account for  $<7$  percent and  $<1$  percent, respectively, of the total SEM in all samples.

The underlying principle for this technique is to use the value for SEM minus AVS as an interpretative tool. For these samples, values of (SEM-AVS) range from  $-17.5$  to  $+2.3 \mu\text{moles/g}$  (Figure 3-37 and Appendix D). In the total data set, six values are negative and the remainder are positive. In those instances where the value for (SEM-AVS) is negative, the amount of sulfide exceeds the total amount of metal and thus these metals should all be bound in the sediments as a sulfide phase. When the (SEM-AVS) value is positive, acid-leachable metals are present in the sediment in other than a sulfide phase. The implications of these results are discussed in Section 4.4.

The data for SEM was used to determine the percent of total metal that is released into 2N HCl with the following overall mean values: Cd, 88%; Cu, 40%; Ni, 20%; Pb, 44%; and Zn, 41% (Table 3b). Cadmium is clearly the most labile of the five metals and Ni is the least labile. The variability in the percent of total metal leached was  $<40\%$  (as a coefficient of variance) for each metal except Zn (Table 3b). A complementary study by Gray (1999) showed that  $<3\%$  of the total metal was leached at pH levels of 4 (*i.e.*, 0.0001N HCl).

### 3.2.4 P450 Reporter Gene System Response in Extracts of Sediment

Twenty-seven sediment samples were analyzed by the RGS assay in 1997 and another twenty-seven were analyzed in 1998. The RGS B[a]PEq ranged from 0.8 to  $6.3 \mu\text{g/g}$  dry weight (a mean of 3.2 with a CV of 54 percent) in 1997. The RGS B[a]PEq ranged from 0.6 to  $3.8 \mu\text{g/g}$  dry weight (a mean of 2.2 with a CV of 38 percent) for 1998 samples.

Values in the range of 1 to 10 µg/g dry weight are generally considered to be at background levels in embayment areas and 1 to 5 µg/g dry weight are considered to be at background levels in coastal marine sediments. Only two samples collected in 1997, Z1R13 and Z3R14, were slightly above the coastal marine background with concentrations of 6.3 and 6.2 µg/g dry weight B[a]PEq, respectively. These results are consistent with the concentrations of the PAH measured in the surface sediment, i.e., generally low concentrations of PAH, as well as the results from the 6hr. vs. 16hr which indicate that the RGS response was due to PAH's rather than chlorinated hydrocarbons (dioxins/furans, coplanar PCB's).

Examination of the trends in the mean values for the zones, including the standard deviations for each set of data indicated that sediments from zone 0 had the lowest level of inducing compounds in comparison to the other zones. Also, the mean values for all zones were somewhat lower in 1998 than in 1997. The complete results of the P450 RGS sediment tests are included in Appendix E.

### 3.2.5 Sediment Toxicity Tests

Amphipod toxicity tests were conducted using marine amphipods and surface sediments collected during both sample cruises. The test organism for the 1997 sediments was *Eohaustorius estuarius*, while the test organism for the 1998 sediments was *Ampelisca abdita*. The percent survival of the amphipods exposed to sediment collected during the 1997 cruise is presented in Table 3-14. Statistical analysis (using ToxCalc v5.0 software) of the results from the 1997 sediment bioassay conducted by PERL demonstrated that 15 of the 20 sediment samples resulted in survival less than the control at  $p < 0.05$ . However, most laboratories conducting sediment bioassays only indicate toxicity if the following criteria are met:

- There is a significant difference between the laboratory control and the test using a *t*-test, as was done here.
- Mean organism response in the bioassay test was less than 80 percent of the laboratory control value.

Application of the second criterion eliminates the problem of designation of toxicity based only on comparison to controls with low replicate variance.

The 80 percent of control criterion was established by statistical analysis of many amphipod data sets by other investigators (e.g., Thursby and Schlekat, 1993). The two criterion approach is currently being used by the EPA's EMAP (Schlimmel *et al.*, 1994), by California's State Bay Protection and Toxic Cleanup Program (BPTCP, 1993) and by the Regional Monitoring Program for Trace Substances in the San Francisco Estuary (SFBRMP, 1995).

Applying these criteria to the bioassay results demonstrates that only 7 of the 20 sample sites had sediments with significantly lower survival than the controls: 2 of 8 from zone 0; 1 of 4 from zone 2; and 4 of 4 from zone 3. None of the 4 sites in zone 1 demonstrated significantly lower survival than the controls. A detailed analysis of the data for these toxicity tests (discussed in Sections 3.6 and 4.4) indicates that the significantly lower survival observed in these sediments was correlated with sediment grain size and therefore probably not due to the measured concentrations of metals or organics.

Results for the toxicity tests conducted on the 7 sediment sites collected in 1998 are presented in Table 3-15. Statistical analysis of these results from sediment bioassay demonstrated that 5 of the 7 sediment samples resulted in survival less than the 'home' control at  $p < 0.05$ . However, not one of the amphipod test exposures to surface sediment had less than 90 percent survival. In addition, none of the exposure groups were significantly less than the Holgate Glacier "reference" sediment, which averaged 91 percent survival. (This reference location was selected since it represented fine grained and glacial sediment and was up current from Cook Inlet and inshore of the influence of the Gulf of Alaska). These results support the theory that the toxicity observed in the 1997 and 1998 sediments was not due to the measured concentrations of metals or organics, but likely the result of grain size effects.

### **3.2.6 Enumeration of Heterotrophs and Hydrocarbon Degrading Microorganisms**

Heterotrophic bacteria ranged from approximately  $8 \times 10^3$  to  $8 \times 10^6$  organisms per gram of dry weight sediment. Most samples contained about  $10^4$  to  $10^5$  organisms per gram of dry weight sediment. Hydrocarbon degrader populations were very low for all samples - 30 sample results were zero and the 10 remaining results ranged from 26-300 organisms per gram of dry weight sediment. These results indicate that the petroleum hydrocarbons present in the sediment are not readily bioavailable.

Complete information on the sample handling and the mean MPN populations are found in Appendix H Table H-1.

### **3.2.7 Sediment Profile Imaging Camera**

In this section, a summary of the SPI camera analyses is presented. A complete set of all the summary data measured from each image is included in the SPI report, which was issued by MMS as a separate stand-alone document in 1998 (MMS, 1998).

Parameters such as boundary roughness and mud clast data (number, size) provide supplemental information pertaining to the physical regime and bottom sediment transport activity at a site. Even though mud clasts are definitive characteristics whose presence can indicate physical disturbance of some form, the mud clasts noted in the images from this survey were either biogenic in origin or artifacts due to sampling (mud clumps clinging to the frame base) and not indicative of physical disturbance or sediment transport activities. Therefore, mud clast data were not used as individual parameters for interpretation. Rather, they were used to enhance the overall comprehension of characteristics at the various areas sampled in conjunction with other SPI parameters such as RPD and OSI.

#### **3.2.7.1 Grain Size**

The sediments throughout the entire area surveyed were primarily fine-grained, with very few occurrences of any substantial amount of sand-sized particles except at 5 of the 57 stations sampled (see Appendix Figure A1). For the majority of stations, the sediment grain-size major mode was  $\geq 4 \phi$  ( $4 \phi$  is an upper particle size limit of 0.0625 mm, or coarse silt). Appendix Figure A1 shows the spatial distribution of sediment grain-size major mode and bottom kinetic regimes at all stations sampled. Most of the images from zone 1 and all the images from zones 2 and 3 in the Shelikof Strait displayed a grain-size major mode of silt-clay with little to no fine sand as part of the grain-size range; Appendix Figure A2 shows a typical profile image from the

area. These well-sorted sediments are most likely derived from glacial till and are indicative of low-energy, depositional environments.

At the northern end of the Shelikof Strait and moving into outermost Cook Inlet, evidence of fine- to medium-sand surface layers appeared at 5 of the stations (Stations 1, 3, 5, and 20 in zone 1; Station F4 in zone 0); medium sand was also the grain-size major mode at 1 station in Kachemak Bay (Station 2, zone 0; Appendix Figure A3). The cluster of these 5 stations in zones 0 and 1 represented a localized area at depths ranging from approximately 150 to 175 m that was influenced by strong bottom transport and displayed coarser-grained sediment. Station 2 (zone 0) presented a transitional facies of a silt-clay bottom with a 2- to 3-cm layer of fine sand at the surface and a hint of bedforms occurring as the result of bottom currents (Appendix Figure A4). The stations surrounding Station 2 with sandy bottoms (Appendix Figure A1) ranged from those with a level sediment-water interface and a grain-size major mode of medium sand (Appendix Figure A5) to stations with allochthonous surface fine-sand layers that showed evidence of active transport (Appendix Figure A6).

Set against a background that is predominantly fine-grained glacial till, the source of sand in this localized region was not readily apparent; however, the presence of these coarser sediments did not appear to be related to water depths (Appendix Figure A7).

#### **3.2.7.2 Surface Boundary Roughness**

Surface boundary roughness ranged from 0.26 to 4.81 cm, principally due to fecal mounds or burrow openings caused by infaunal activities. The large roughness features at the high end of the range were all macro- or megafaunal burrow structures (Appendix Figure A8). Because most of the area sampled was represented by a low-energy, depositional environment, the surface boundary roughness elements were primarily of biogenic origin and not indicative of active transport regimes. The locations that appeared to have active transport had surface boundary roughness values ranging between 0.26 and 2.12 cm.

#### **3.2.7.3 Prism Penetration Depth**

With sediment grain-size fairly uniform across the entire study area, the variation in prism penetration was a good indicator of relative sediment shear strength as a function of biological mixing depth. The average prism penetration depth at the fine-grained stations (sediment grain-size major mode  $\geq 4 \phi$ ) in the study area ranged from 3.75 to 20.69 cm; the spatial distribution of mean penetration depth at all stations sampled is shown in Appendix Figure A9. Sediments appeared to be more consolidated (lower penetration) at those stations in outermost Cook Inlet and the northern end of the Shelikof Strait; while this was due primarily to a shift in sediment grain-size major mode to a coarser fraction (very fine to medium sand), there were 5 stations (Stations 7, 8, 15, and F2, zone 1; Station F5, zone 0) in this elliptical region outlined in Appendix Figure A9 that were fine-grained.

The typical variation in sediment water content and shear strength caused by differences in bioturbation intensity at stations with similar grain-size distributions is dramatically illustrated by the two example images in Appendix Figure A10. Fine-grained sediments can be substantially dilated through the activity of deep bioturbating infauna; for example, Station 15 in zone 3 (Appendix Figure A11) shows a dramatic difference in geotechnical properties compared to the sediments shown in Appendix Figures 6 and 8, because of the burrowing activity of head-down, deposit-feeding infauna. Low-shear-strength sediments are susceptible to erosion, and the high

frequency of stations with penetration depths in excess of 14 to 15 cm is further evidence of the low-energy, depositional nature of most of this site.

#### **3.2.7.4 Apparent Redox Potential Discontinuity Depth**

The distribution of mean apparent Redox Potential Discontinuity depths is shown in Appendix Figure A12; depths from individual image measurements ranged from 0.57 to 8.32 cm. The greatest depths were found in the southern end of the Shelikof Strait. The variation in Redox Potential Discontinuity depth was largely a function of the number, size, and type of infauna present at a particular location; apparent Redox Potential Discontinuity depths were not related to water depth ( $r^2 = 0.48$ ). The lowest apparent Redox Potential Discontinuity depths were found at those stations in the northern end of the Shelikof Strait and in outermost Cook Inlet where the more consolidated sediments, with lower prism penetration due to lower bioturbation rates, were found.

There was no evidence of low-oxygen stress in the overlying water or high SOD caused by excess organic loading at any of the locations sampled. The range of apparent Redox Potential Discontinuity depths encountered did not display any anomalous patterns or unusual variations given the sediment type and amount of biological activity in the surveyed areas, indicating normal sediment with appropriate natural Redox development.

#### **3.2.7.5 Infaunal Successional Stage**

The mapped distribution of infaunal successional stages is shown in Appendix Figure A13. There was evidence of head-down, deposit-feeding infaunal taxa (mature Stage III communities) at all locations sampled except for Station F8, zone 0. Only one successful image was obtained from this station, and while it is possible that deposit-feeding taxa were present at this location in low densities, the shallow penetration depth (2.2 cm) prevented the detection of any subsurface feeding voids. This same phenomenon of shallow penetration obscuring the detection of Stage III communities was observed at the adjacent Station F6, zone 0 (Appendix Figure A14).

Because of their location at the sediment-water interface, Stage I taxa are ideal prey items for demersal fish and epifaunal macroinvertebrates. Appendix Figure A15 shows a crab at Station 1 (zone 1) that is most likely foraging on the tubicolous fauna evident at the sediment-water interface. However, the dominant infaunal community at all of the fine-grained stations were head-down, deposit-feeding taxa that were reworking the sediment to depths of 10 to 15 cm or more which is generally consistent with the results of sediment core age dating (Appendix Figure A16). Almost half the images collected (69 out of 156) showed evidence of secondary succession (Stage I fauna recolonizing the sediment surface after Stage III communities are established); Appendix Figure A17 shows an example of Stage I and III taxa present at the same location.

One unique faunal component recorded in this survey was at Station 3 in zone 3 at a depth of 279 m. Appendix Figure A18 shows a rare, in situ photograph of an obscure family of sea cucumbers, the Chirodotidae; the oral ends of the individuals bear a striking resemblance to coelenterates. Very little is known about the life-history of these elongate, worm-like holothurians, but the oral ends of individuals can be seen both above the sediment-water interface and 1 to 5 cm below the sediment surface.

### **3.2.7.6 Organism-Sediment Index**

The spatial distribution of OSI values throughout the study area can be seen in Appendix Figure A19. An OSI of 6 or less typically indicates that a benthic habitat has experienced physical disturbances, eutrophication, or excessive bioavailable contamination in the recent past. The four stations that had median OSI values  $\leq 6$  were quiescent locations with limited profile information due to shallow camera prism penetration caused by coarser sediments or limited biological reworking. The low OSI at these four locations were attributed more to physical factors such as coarse or overconsolidated sediments than to anthropogenic sources of disturbance. Most OSI throughout the site were very high, reflecting a largely undisturbed environment with a mature biological community.

### **3.2.7.7 Interpretation of Sediment Profile Imaging Results**

All the results from the SPI technology survey supported the conclusion that there was a largely undisturbed, low-energy depositional basin throughout the sampled area of the Shelikof Strait. Water depths throughout most of zones 1 through 3 ranged between 100 and 350 m, well below the depth at which storm energy would typically be able to impact the bottom. Only nine stations sampled at the northern end of the Shelikof Strait (Stations 1, 3, 5, and 20 in zone 1) and in outermost Cook Inlet (Stations F2, F4, F6, F8, and F13) were clearly unrepresentative of a quiescent environment. Station 2 in zone 1 was a transitional zone between the quiescent silt-clay facies found at the majority of stations and the few stations that had a surface sand layer present. Because the sand appeared primarily as a discrete stratum at the sediment surface (Appendix Figure A20), it most likely represented a quantum input of sand-sized particles at some point in the recent past; over time, this surface sand layer should get thoroughly mixed in with the underlying mud by the burrowing and feeding activities of the resident infauna.

Based on the reflectance contrast of the sediment profile, there were no areas obviously suffering from excess organic carbon loading, and no areas that appeared to have their biological communities compromised by any form of excess chemical contamination. One of the images at Station F2 in zone 2 (Appendix Figure A21) shows a localized patch of highly reduced sediment at depth, but this was more likely due to some form of biogenic decomposition rather than anthropogenic contamination. The uniform silt-clay sediment grain size, the prism penetration depths in excess of 12 cm reflecting low-shear strength, dilated sediments, the high OSI, and the high frequency of mature, Stage III infaunal assemblages at most of the stations sampled are all attributes that would be found in a low-disturbance, depositional regime. From the characteristics seen in the profile images, we would predict sediment organic carbon concentrations ranging between 0.5 and 2 percent at the majority of the stations, and annual depositional rates in the Shelikof Strait basin of between 0.2 and 1.5 cm/year.

All the data from the profile images point to both high sediment quality and benthic habitat values at most of the area surveyed throughout the site. From the data available from SPI technology, there appeared to be no detectable adverse impacts to this area from any of the oil and gas development activities in the region.

### 3.3 Sediment Cores

#### 3.3.1 Geochronology

Sedimentation rates were calculated for 13 cores for which concentrations of organics and/or metals were determined. Sediment ages were determined using the fission-produced radionuclide  $^{137}\text{Cs}$  (first introduced to Earth by bomb testing during the early 1950s) in tandem with excess  $^{210}\text{Pb}$  (a naturally occurring decay product of  $^{238}\text{U}$ ; half-life  $^{210}\text{Pb} = 22.3$  y). By using two different independent radioisotopes, sedimentation rates could be verified by separate methods. Results for 9 of the 13 cores that could be dated showed good agreement between the two methods (Table 3-16). The sedimentation rate in the core collected from ZOF1 (Homer Harbor) in 1997 was too fast to obtain a reliable rate over the 34 cm core length and thus a longer, 2-m gravity core was collected during 1998 with successful dating results. The cores from ZOF8, Z1F2, and Z2F1 had discordant ages between the two methods; however, a range of likely sedimentation rates was established using one of the two isotopes.

Results for core Z3F2 (Figure 3-39) show an ideal decay curve (natural logarithm scale) for excess  $^{210}\text{Pb}$ . The sedimentation rate calculated using the activities of excess  $^{210}\text{Pb}$  is 0.44 cm/yr. A sedimentation rate of 0.45 cm/y calculated from the  $^{137}\text{Cs}$  profile is in excellent agreement with the rate determined from the excess  $^{210}\text{Pb}$  profile. When the  $^{137}\text{Cs}$  activities for the core from Z3F2 are compared with the year determined from excess  $^{210}\text{Pb}$  (Figure 3-39), the highest peak for  $^{137}\text{Cs}$  corresponds well with the 1963 date of maximum  $^{137}\text{Cs}$  input to the atmosphere. Thus, the geochronology results for the core from Z3F2 are considered reliable. Results from the other cores will be evaluated on a zone-by-zone basis below using the same perspective described here.

Sedimentation rates of about 1.3 to 1.5 cm/y are obtained for the 1998 core from Homer Harbor (ZOF1) (Figure 3-40). Thus, a record of contaminant inputs can be traced back to at least 1900 in this 2-m core. Sedimentation rates for all three cores from Kamishak Bay (ZOF5, ZOF6, and ZOF8) are about 0.1 to 0.3 cm/y (Table 3-16 and Figures 3-41, 3-42, and 3-43). Two minor discontinuities (lower activities of  $^{210}\text{Pb}$  than predicted by the overall trend) in the activity profile for core ZOF5 occur at 2 to 4 cm and 8 to 10 cm; however, they have been included in the overall calculation of sedimentation rate using excess  $^{210}\text{Pb}$  because we did not identify any reason to exclude them. The resultant sedimentation rate for the core from ZOF5 has a lower correlation coefficient than the other sites and an associated error as large as  $\pm 25\%$ . Results for cores from sites ZOF6 and ZOF8 are much better (Figures 3-42 and 3-43). The activity of  $^{137}\text{Cs}$  decreases to zero about 1950 in each of the cores from Kamishak Bay based on the excess  $^{210}\text{Pb}$  age. Such concordance verifies the overall reliability of the sedimentation rate for these sites.

Calculated sedimentation rates for cores from zone 1 (Z1F1, Z1F2, and Z1R3B) are all similar at about 0.2 to 0.3 cm/y (Table 3-16 and Figures 3-44, 3-45, and 3-46). The profile for  $^{137}\text{Cs}$  in the core from site Z1F1 contains some discontinuities in the upper 5 cm that may be due to post-depositional disturbances and the excess  $^{210}\text{Pb}$  profiles support some mixing in the upper 2.5 cm of the core. Using data from below the mixed zone, the sedimentation rates are concordant (Table 3-16). The excess  $^{210}\text{Pb}$  profile for the second core from zone 1 (Z1F2, Figure 3-45) exhibits a large discontinuity at a depth of 10 cm where the activity of the  $^{210}\text{Pb}$  decreases from approximately 7.5 dpm/g ( $\ln = 2.0$  dpm/g on Figure 3-45) to 1 dpm/g ( $\ln = 0.0$  dpm/g on Figure 3-45). This large change in activity complicates calculation of a sedimentation rate. If we use the point at which the activity of  $^{137}\text{Cs}$  goes to zero ( $12.5 \pm 2.5$  cm), then the sedimentation rate is

about 0.27 cm/y. Thus, a general estimate of sedimentation rate can be made at this site. The third core from zone 1 also contains some minor anomalies at ~4 and 14 cm (Figure 3-46).

Sedimentation rates calculated using excess  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  for core Z2F2 (Figure 3-47) agree well at 0.62 and 0.65 cm/y, respectively, despite evidence for some mixing at the top of the core. The vertical profile for excess  $^{210}\text{Pb}$  in the core from site Z2R16 shows clear indications of mixing over the top 10 cm of the sediment column (Figure 3-48). Excluding the 0 to 10 cm section, the calculated sedimentation rate is 0.53 cm/y relative to 0.72 cm/y using the full data set. The  $^{137}\text{Cs}$  profile also does not fit simple interpretation and the sedimentation rate is 0.76 cm/y based on the assumed peak activity at 24.5 cm. Thus, a sedimentation rate of 0.5 to 0.7 cm/y was similar to that found for site Z2F2 and at least 3 times greater than found in zone 1. In contrast with results for Z2F2 and Z2R16, the calculated sedimentation rate for the core from site Z2F1 is 2 times higher at 1.3 cm/y (Table 3-16 and Figure 3-49). The slope of the excess  $^{210}\text{Pb}$  profile, along with an incomplete  $^{137}\text{Cs}$  profile, supports a high sedimentation rate at site Z2F1. Site Z2F1 was located in a depositional basin in zone 2 that may serve as an effective trap for fine-grained sediments.

Both cores from zone 3 (Z3F1 and Z3F2) had sedimentation rates of 0.60 and 0.44 cm/y, respectively (Table 3-16 and Figures 3-49 and 3-50). These rates are comparable with two sites from zone 2, but 2 to 3 times higher than found in zone 1.

The excess  $^{210}\text{Pb}$  profile for one core collected from zone 4 during 1998 (Figure 3-51) may be interpreted as having 2 different sedimentation rates. Using data from the top 20 cm, the calculated sedimentation rate is 1.0 cm/y relative to a rate of 0.52 cm/y for the 20 to 43-cm interval in the core. The  $^{137}\text{Cs}$  profile corroborates this perspective. The peak activity for  $^{137}\text{Cs}$  at 29.5 cm (1963 or 35 y BP) is consistent with 20 years of sedimentation at 1.0 cm/y and 9 cm of sedimentation at 0.5 cm/y to yield about 38 years.

### 3.3.2 Physical Measurements

Concentrations of TOC in 14 sediment cores from outermost Cook Inlet (zone 0) and the Shelikof Strait (zones 1, 2, 3, and 4) range from 0.21 percent to 1.24 percent (Table 3-17). The highest TOC values are for cores from sites Z0F1 (Homer Harbor-1997, 1998) and Z4F4 (southernmost Shelikof Strait), whereas the lowest values for TOC are for cores from sites Z1R3B, Z0F6, and Z0F8 (Table 3-17 and Appendix A).

In zone 0, levels of TOC in all four cores (Z0F1, Z0F5, Z0F6, and Z0F8) have remained relatively uniform since the 1940s (Figures 3-52 through 3-56). Data for core Z1F1, with an average of  $0.62 \pm 0.08$  percent TOC, show that inputs of TOC to the sediment column have been fairly constant since the turn of the century (Figure 3-57). In contrast, TOC values for core Z1F2 are more variable (Figure 3-58) since the 1950s. Prior to the 1950s, TOC concentrations increased from 0.60 percent at about 13 cm (~1950s) to 1.01 percent at 29 cm.

Sediment cores from zone 2 average  $0.87 \pm 0.11$  percent TOC, (Z2F1, Z2F2, and Z2R16, Figures 3-60, 3-61 and 3-62). Values of TOC are relatively uniform in cores Z2F1 and Z2R16 (Figures 3-60 and 3-62), whereas in core Z2F2, TOC levels decrease gradually from 1.14 percent in the surficial layer to 0.84 percent at 32 cm (Figure 3-61). Average values for TOC in cores Z3F1 and Z3F2 are comparable at 0.83 percent and 0.81 percent, respectively. However, only values in

core Z3F1 are uniform throughout the entire sediment column (Figure 3-63). Values for TOC in core Z3F2 decrease from 0.89 percent between 0 to 2 cm to 0.70 percent at 32 cm (Figure 3-64). In zone 4, TOC values of  $1.08 \pm 0.06$  percent for core Z4F4 (Figure 3-65), are comparable with those obtained for Homer Harbor (Z0F1) (Table 3-17).

Sand levels in sediment cores from Homer Harbor (1997-total length 35 cm) and zones 2, 3, and 4 average  $\leq 6$  percent. For these sediment cores, the silt+clay content is  $>90$  percent and values are uniform throughout the length of the core (Figure 3-52 and Figures 3-60 through 3-65). However, the sand content in the sediment core recovered from Homer Harbor during 1998 averages  $13.0 \pm 9.6$  percent from 20 to 235 cm (Table 3-17 and Figure 3-53). The grain-size distribution for the upper 20 cm was not determined. In the remainder of the sediment cores from zone 0 (Z0F5, Z0F6, and Z0F8) and those from zone 1 (Z1F1, Z1F2, and Z1R3B), the sand content averages between 17.8 percent and 59.6 percent (Table 3-17). The silt+clay levels in cores Z0F5, Z0F6, and Z0F8 are fairly uniform, averaging  $69.4 \pm 5.7$  percent,  $49.5 \pm 6.9$  percent and  $46.6 \pm 4.2$  percent, respectively (Figures 3-54, 3-55, and 3-56). Values for silt+clay in core Z1F1 vary between 50 percent and 81 percent in the upper 14 cm, but are relatively uniform over the remaining 10 cm of the core, ranging between 67.1 percent and 71.9 percent (Figure 3-57). Silt+clay concentrations in the sediment core recovered from Z1F2 are fairly uniform throughout the core, with values ranging between 71 percent and 91 percent (Figure 3-58).

### 3.3.3 Organics

Sediment cores for organics analysis were collected from 11 of the fixed (non-random) stations and from 1 of the random stations in the study region (5 cores from zone 0, 2 cores each from zones 1 and 3, 3 from zone 2, and 1 from zone 4). The sediment cores ranged from 18 to 235 cm in length (depth of the core). Approximately 9 to 12 separate 2-cm sediment intervals were subsampled within a core section and analyzed for the same suite of organic target analytes as the surface sediments (Section 2.2.2). Finer resolution of the core at station Z2R16 was desired, therefore this core was subsectioned at separate 1-cm intervals over the first 15 cm of the core. Approximate sedimentation rates from an earlier core collected at station Z0F1 indicated that subsamples needed to be much larger than 2-cm intervals. A 230 cm core from Z0F1 was obtained during the 1998 sampling survey and was subsectioned between intervals of 5 cm and 35 cm.

The results of the sediment core analyses are summarized in Table 3-18 and detailed results including individual analyte measurements are included in Appendix B. The average concentrations of the three key total organic parameters measured (TPHC, total PAH, and total S/T) are comparable to the values observed in the surface sediments from the 5 zones in the study region (Tables 3-6 and 3-18). Core profiles for selected organic diagnostic parameters (Section 3.2.2) and TOC are shown for all 13 of the sediment cores in Figures 3-66 through 3-78. The selected diagnostic parameters were chosen based on their capacity to show the overall trends in total concentration, composition, and source of hydrocarbons.

In general, the core profiles do not show any clear trends that would indicate increases in the overall petroleum hydrocarbon concentrations over time. Geochronology of the cores has resulted in seven cores of sufficient depth to be dated to 1920 or earlier and four additional cores that can be dated to 1950 or earlier. The established dates for these cores provide sufficient data

to evaluate the potential impact of Cook Inlet petroleum exploration and production activities, and is evaluated statistically in Section 3.3.5.

The core profiles of organics from zone 0 (Figures 3-66 through 3-70) do not reveal any patterns of analytes that are consistent between parameters. However, there are several slight patterns or anomalies which merit discussion. In the ZOF1 core (Kachemak Bay) collected in 1997 the CPI increases by a factor of 4 at the 2 to 4 cm depth interval (Figure 3-66). This anomalous increase in CPI is likely associated with particles of plant material (possibly from the wood chip processing operation on Homer Spit) entrained in the sediment. The deeper core from station ZOF1 (1998) does contain a trend of increasing total hydrocarbons over the past decade; however, the CPI is within the range of terrestrial plant influence and the corresponding PAH profile during that time frame is decreasing (Figure 3-67). The core profiles of ZOF5 (Kamishak Bay), ZOF6 (near Oil Bay), and ZOF8 show a recent decrease in the combustion/petroleum PAH ratio (0 to 5 cm depth - ~1970 to present), suggesting a possible shift in PAH composition (Figures 3-68 and 3-70). However, the total PAH decreases slightly in each core at the same depth interval, indicating that the decrease in the combustion/petroleum ratio is due to lower combustion PAH input.

A slight increase in the C2D/C2P source ratio is also apparent in the ZOF6 core at the 0 to 6 cm depth (Figure 3-69). The C2D/C2P ratio for the remainder of the core is considerably lower than other sediments from the study. The Well Creek seep oil sample analyzed as part of this study had a C2D/C2P value of 0.046, which is substantially lower than the value at depth in the ZOF6 core (0.082). This could indicate a mixture of "background" and Well Creek sources, with a greater Well Creek component in the past. In a study of Southern Alaska seeps, Page *et al.* (in press) reported a C2D/C2P ratio for an Oil Bay seep oil of 0.071. This value is close to the ratio at depth in the ZOF6 core (0.082), further indicating that the inputs of Oil Bay seep oil are an important local source of petroleum hydrocarbons in this area. There is also an apparent rise in the C2D/C2P ratio in the ZOF8 core (Figure 3-70) and the ZOF5 core (Figure 3-68), although at depth the ratios are higher than ZOF6 (~0.10) and increase to a value of ~0.20. The rise in the C2D/C2P ratio at the surface of these cores may indicate a greater contribution from "background" petroleum sources more recently.

The core profiles for the six stations in zones 1, 2, 3, and 4 are remarkably similar (Figures 3-71 through 3-78) with some variability in parameters. The total PAH values exhibit minimal variation, with some cores showing a slight decrease in total PAH over time to the present-day sediment (e.g., total PAH at Z1F1 increases as the core date approaches ~1920). The source parameter C2D/C2P ratio is very consistent with depth in all six cores, indicating a continuing and unchanging source of petroleum hydrocarbons from the early 1900s to the present. This is further supported by the Ts/Ts+Tm maturity ratio which is similarly constant throughout the core profiles. Overall, evaluation of the core profiles does not reveal any substantial petroleum hydrocarbon trend (either increase or decrease) which can be attributed to the onset of petroleum exploration and production activities (circa 1963) in Cook Inlet.

### 3.3.4 Trace and Major Metals

Sediment cores, ranging in length from 15 to 235 cm, were collected for metal analysis from 14 sites in the study area. Two sediment cores were obtained from Homer Harbor in zone 0 (F1), a 35-cm core in 1997 and a 235-cm core in 1998. Three additional cores were collected from zone

0 at sites F5, F6, and F8. In the Shelikof Strait, the following samples were collected: 3 cores from zone 1 (F1, F2, and R3B) and zone 2 (F1, F2, and R16), 2 cores from zone 3 (F1 and F2), and 1 core from zone 4 (F4). Approximately 5 to 12 separate 1- or 2-cm sediment intervals were subsampled from each core and analyzed for the same suite of metals as the surface samples (Table 3-19, Appendix C).

Average metal concentrations for Al, Ag, As, Ba, Be, Cd, Mn, Pb, Sb, Sn, and Tl from each core site (Table 3-19) are comparable with levels obtained for bottom sediments from the Susitna and Copper Rivers (Table 3-1). For Cr, Cu, Hg, Ni, Se and V, average concentrations for all sediment cores, except Homer Harbor (Z0F1) and Z0F4 (Hg only), also are consistent with results obtained for bottom sediments from the Susitna and Copper Rivers. However, sediments from Homer Harbor are about 14 to 225 percent higher for these 6 metals relative to values for bottom sediments from the Susitna and Copper Rivers. Average Zn concentrations for all 14 cores range from 81.2 to 125  $\mu\text{g/g}$  (Table 3-19). These Zn values are consistently higher than the average Zn level of  $75 \pm 4 \mu\text{g/g}$  in bottom sediments from the Susitna and Copper Rivers (Table 3-1). However, as previously discussed (Section 3.2.3 and Table 3-3), concentrations of all metals in suspended solids from the Susitna and Copper Rivers are higher than found in sediment cores. Further consideration of the relative contributions of river-borne sediment from the Susitna River versus the Copper River is presented in Section 4.1.

Sediment in cores from Homer Harbor (Z0F1) are fine-grained (>85 percent silt + clay) and organic-rich (~1.1 percent organic C). Besides having the highest sedimentation rate (~1.4 cm/y), sediments from Homer Harbor also contain the highest levels of Fe, Ag, As, Cr, Cu, Hg, Ni, Sb, and V (Table 3-19). With such a high sedimentation rate, the 235-cm long core from site Z0F1 collected during 1998 (Figure 3-53) records the turn of the twentieth century at ~140 cm. During this past century, concentrations of trace metals have varied only slightly, with most metals having a CV for the entire core of <5 percent, except for Ag and As (~12 percent) and Se (21 percent).

The other 3 cores collected from zone 0 (F5, F6, and F8) were all from the outer portions of Kamishak Bay. The average silt+clay content at these 3 sites (69 percent for Z0F5, 49 percent for Z0F6, and 46 percent for Z0F8) is considerably lower than observed for Homer Harbor (87 percent). Likewise, TOC values are lower at 0.44, 0.34, and 0.36 percent, respectively. Concentrations of trace metals for these 3 cores from zone 0 also are lower than in Homer Harbor (Table 3-19 and Figures 3-54, 3-55 and 3-56); however, they are comparable to metal values for bottom sediments or suspended solids from the Susitna and Copper Rivers. Despite sizeable differences in grain size among these cores from zone 0 (Table 3-19), metal concentrations generally varied by <10 percent. Overall, metal concentrations in sediment from this study do not show a strong positive relationship with levels of silt+clay as commonly observed in many other shelf and slope locations. This trend suggests that the mineralogy is similar among sediments with different grain-size distributions, and thus, only the size of the particles most likely varies as a function of the degree of powdering by glacial activity.

The sedimentation rate of 0.10 to 0.27 cm/y for cores from zone 0 (F5, F6, and F8) facilitates tracing the record of metal inputs back to the 1920s (Figure 3-54). Relatively minor shifts (CV<10 percent) in metal concentrations occur over this ~ 70-y time interval. However, As and Hg levels in the top 2 cm (the 1990s) of the core (from Z0F5), are about 20 and 30 percent higher, respectively, relative to subsurface sediment, with no significant shifts in levels of Fe, Al,

and most other metals. In core Z0F8 concentrations of TOC, Ba, Be, Cd, Hg, Sb, and Zn have decreased by 20 to 30 percent over the past 20 years (top 5cm), yet no changes in the Fe and Al content of these sediments was observed (Figure 3-56). Similar to core Z0F5, As levels are about 20 percent higher in the top 2 to 5 cm of core Z0F8 and Z0F6. Concentrations of Fe, Ca, Cd, Cu, Cr, Mg, Mn, Ni, Sb, V, and Zn (Figure 3-55 and Table 3-19) are ~ 30 percent lower at 4 to 6 cm in the core from Z0F6 relative to other samples from Kamishak Bay. In sharp contrast, concentrations of Be, Sn, and Tl are 20 to 25 percent higher in the same layer. These transitions may be related to input of volcanic material deposited during the rather large time interval of  $1947 \pm 10$  years.

Two of the three cores recovered from zone 1 (F1 and F2) have similar metal concentrations throughout the cores ( $CV \leq 10$  percent) (Table 3-19) with the exceptions of about 25 percent higher As and Cd and about 15 percent lower Al in core Z1F2 relative to core Z1F1 (Figures 3-57 and 3-58). These three exceptions match higher TOC levels in core Z1F2 and may be related to deposition of more As- and Cd-rich (Al-poor) organic matter in these sediments. Core Z1F1 (Figure 3-57) records about 100 years of sediment input with little change in metal levels, except for slightly higher Cr levels (10 to 20 percent) prior to the 1920s. Higher concentrations of Fe, Ni, Cr, V, and Zn are observed in core Z1F2 below a depth of about 15 cm, which corresponds to the 1940s (Figure 3-58). The third core from zone 1 (R3B), has the lowest values of As, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Sb, Sn, Tl, V, Zn, and TOC observed throughout the study area (Figure 3-59 and Table 3-19). These low levels of trace metals most likely result because sediment from this core averages 60 percent sand-size particles that include extensive amounts of volcanic ash.

Sediment cores from zone 2 (Figure 2-1) were collected near the western (Z2F1) and eastern (Z2F2) sides of the Shelikof Strait, respectively, whereas core Z2R16 was from a central basin. The silt+clay content for these cores is uniform at 95 to 99 percent. No differences greater than  $\pm 5$  percent occur for concentrations of Fe and Al (Table 3-19). Trace metal levels also vary by  $< 10$  percent (CV) among these three sites with the exception of Cd (Table 3-19 and Figures 3-60, 3-61, and 3-62). Cadmium concentrations at Z2F2 vary downcore from 0.14  $\mu\text{g/g}$  in the surficial 2 cm interval to 0.27  $\mu\text{g/g}$  at 19 cm (Figure 3-61). A similar increase downcore also is observed in core Z2R16, with Cd values increasing from 0.10  $\mu\text{g/g}$  in the top 1 cm to 0.15  $\mu\text{g/g}$  at 5 cm (Figure 3-62). In contrast, levels of Cd were relatively uniform in core Z2F1 at  $0.13 \pm 0.01$   $\mu\text{g/g}$  over the entire 33 cm length of the core (Figure 3-60). Overall, in zone 2, no changes in concentrations of trace metals, with the exception of Cd in Z2F2 and Z2R16, have occurred over the past 50 years (Figures 3-60, 3-61, and 3-62).

Two cores were recovered along a track extending north (Z3F2) to south (Z3F1) in zone 3 (Figure 2-1). The grain-size distribution (Table 3-19, Figures 3-63 and 3-64), indicates that the sediments in this region are very fine-grained, containing  $> 98$  percent silt+clay. Average Al and Fe for all samples from the two cores vary by  $< 6$  percent, averaging  $7.15 \pm 0.42$  percent and  $4.39 \pm 0.08$  percent, respectively. In addition, average concentrations of Ba, Cd, Cr, Cu, Hg, Ni, Pb, Sb, Sn, Tl, V, and Zn differ by  $\leq 10$  percent for these sediment cores and about 10 to 20 percent for Ag, As, Be, Mn, and Se. Relative to the other three zones, maximum concentrations of Ba, Mn, Sn, Tl, and Zn were found in sediments from zone 3 (Appendix C).

Sedimentation rates in cores from zone 3 were 0.60 cm/y and 0.44 cm/y. These rates indicate that the history of metal inputs at these sites can be traced to the 1950s in core Z3F1 and the

1920s in core Z3F2 (Figures 3-63 and 3-64). Thus, metal trends throughout these two cores, except for Cd, show that inputs to this region have been uniform over the past 70 to 80 years (Figures 3-63 and 3-64). Cadmium values in Z3F2 increase from 0.14  $\mu\text{g/g}$  in the surficial 2 cm to 0.25  $\mu\text{g/g}$  at 24 cm (Figure 3-64). The depth of peak Cd values is about the 1940s; however, such peaks may sometimes be explained by biogeochemical processes and may not be time-dependent. For example, in core Z3F1, a 50 percent increase in Mn (and As) values occurs in the top 2 cm of sediment, most likely the result of remobilization as previously shown for Mn in the Shelikof Strait (Massoth et al., 1979) and other depositional environments (e.g., the Gulf of Mexico, Trefry and Presley, 1982).

Sediment recovered from zone 4 (Z4F4), has >98 percent silt+clay and an organic carbon content of 1.08 percent (Figure 3-65), similar to that obtained for sediments collected in Homer Harbor (Table 3-19). Sediments in core Z4F4 have the highest concentrations of Al, Mn and Pb. Average concentrations of Al, Ba, Be, Cr, Cu, Fe, Hg, Ni, Pb, Sb, Tl, V and Zn differ by  $\leq 5$  percent and about 10 to 20 percent for Ag, As, Mn, Se, and Sn. Cadmium values vary downcore and range from 0.12  $\mu\text{g/g}$  to 0.20  $\mu\text{g/g}$  (Figure 3-65). The upper 2 to 5 cm of sediment show a 40-percent increase in Mn (and As) values, most likely indicative of remobilization, as previously discussed.

### 3.3.5 Statistical Results of Core Data

***Indices Shifts Associated with the Post-1963 Development Time Period.*** Trends in metals and organic indices were analyzed to investigate the hypothesis that there was a shift in these indices associated with post-1963 oil development. In this analysis, post-1963 core sections were compared to pre-1963 sections for the 12 cores where appropriate dating and thus sedimentation rates were available. These cores were taken at the fixed stations Z0F1, Z0F5, Z0F6, Z0F8, Z1F1, Z1F2, Z2F1, Z2F2, Z3F1, Z3F2, Z4F4, and the random station Z2R16.

Small changes in the selected indices can also result from geochemical and biochemical processes in the sediments as detailed in Sections 3.2 and 3.3. The major finding here is that there are relatively small variations in the important indices with time or depth within a core and that the empirical association with the post-1963 oil development accounts for a small percentage of the total variation within a core. All 23 organic indices that were used to describe the spatial patterns in the surface sediments were analyzed using a standard randomized block analysis of variance. The results of this analysis are detailed below.

In Table 3-20, the first column gives the organic index analyzed. The second column gives the percent of the variation within a core (after the between-core variability has been removed) that can be attributed to the post-1963 intervention. The third and fifth columns give the mean shift in the index that is associated with the post-1963 intervention. A negative value indicates the index is decreasing historically to current time, a positive value indicates the index is increasing historically to current time. Associated with each of the mean shift columns are their respective results of the two analysis of variance tests, i.e., for the null hypothesis that the mean shift associated with the post-1963 development is zero.

In the first analysis (columns three and four in Table 3-20), the cores are considered fixed (i.e., non-random samples), and the statistical test is for a mean shift associated with the 1963 intervention within these twelve fixed cores. In the second, and more realistic analysis (columns

five and six in Table 3-20), the twelve cores are considered as random samples, and the statistical test is for a mean shift associated with the 1963 intervention for the population of all possible sediment profiles from the study area. In this second analysis, the variation in the intervention effect from core to core is modeled as a random effect, contributing to the statistical uncertainty in estimating the mean intervention effect and thus increasing the P-value. P-value here is defined as the probability (assuming no 1963 intervention effect) of obtaining a mean shift as large or larger than the observed mean shift.

The major statistically significant feature in this table is the increase in perylene with depth in the cores, which is clearly detected in this analysis. For perylene, the higher mean value in pre-1963 core sections is scored as a negative intervention effect. The increase in perylene concentration with depth in all cores is due to well known biogenic processes of early diagenesis in marine sediments (Wakeham *et al.*, 1980).

A few of the other organic indices had statistically significant associations with the post-1963 period. The diagnostic PAH source parameters, C2D/C2P and C3D/C3P exhibited a positive intervention effect and could suggest a slight shift in petroleum source with depth. A decrease in the Ts/Ts+Tm ratio with depth could also be indicative of a shift in petroleum source over time, with the lower Ts/Ts+Tm ratios at depth indicating a greater contribution from a less-mature petroleum source. Several other hydrocarbon parameters also showed significant increases after 1963 (pristane, TPHC, nC27+nC29+nC31, and TOC). However, increases in all of these parameters can be associated with increases in plant wax or terrigenous hydrocarbon inputs. This is supported by the result that there are no corresponding post-1963 significant increases in any of the key petroleum hydrocarbon parameters (e.g., TPAH, petrogenic and pyrogenic PAH, N/P, etc.). This suggests that the observed post-1963 increases in these parameters may be due to increased terrigenous hydrocarbon inputs associated with terrestrial development activities (i.e., logging). Overall, based on this analysis, no increases in the key petroleum hydrocarbon indices were observed that are associated with the onset of petroleum exploration and production activities in 1963.

For post-1963 shifts in metal concentrations, the data were first normalized for iron concentration, generally removing differences between cores due to sediment properties. Table 3-21 presents the same kind of analysis as was done for the organic indices.

Higher concentrations of Mn (normalized to Fe) in surficial sediment (top 5cm) layers are commonly observed in marine sediments at outer continental shelf and slope environments (Trefry and Presley, 1982). Under reducing conditions at depth in the sediment, manganese oxides dissolve and dissolved Mn<sup>2+</sup> ions diffuse upward until they are reoxidized near the sediment surface. This natural process leads to the surface sediment enrichment of Mn as seen most clearly at the following sites from this study: Z0F6, Z1F2, Z2F2, Z2R16, Z3F1, and Z4F4.

Concentrations of Ba (and the Ba/Fe ratio) in sediment cores show relatively uniform values (<10 percent deviation) from 1963 to the present at most sites. At two sites, Z0F8 and Z4F4, Ba levels were distinctly lower in the surficial layers of the sediment column. No systematic reason can be given for this trend in this study. However, barium sulfate is produced naturally in the tests of some decaying organisms (Bishop, 1988), a portion of which is likely to dissolve at the seafloor. In any case, the observed lower Ba/Fe ratios in surficial sediments at 2 to 3 sites is not likely to be related to any anthropogenic inputs. Cadmium (and the Cd/Fe ratio) shows a similar and more

widespread (about 8 cores) trend of lower levels in more recent, surface layers. Cadmium is known to be released from sediment organic matter during early chemical diagenesis (Nriagu and Sprague, 1987). However, no simple reason explains why this process may be more exaggerated in recent times (e.g., why more Cd may be released from sediments now than in the past). A general decrease in the input of Cd to the sediments of the Shelikof Strait is possible; however, there are no other data to support this explanation.

In addition to more obvious lower levels of Ba and Cd in surficial sediment, decreased concentrations of Sb, Cu and Tl were observed in surface layers from 1 or more cores, thereby yielding a statistical trend of lower metal/Fe ratios since 1963. In the case of Sb and Tl, the actual change in concentrations is small (<0.05 to 0.2 µg/g) and the generally high analytical precision for these elements ( $\pm 0.01$  to 0.04 µg/g) leads to the observation of statistically significant changes. Overall, no increases in metal concentrations have been observed since 1963 that can be related to the anthropogenic activities.

### **3.4 Fish Tissue**

This section documents the collection and analytical results for the fish sampled during the 1997 and 1998 R/V *Alpha Helix* cruises. Time, location, depth, and fish species caught are reported in their respective cruise reports (Arthur D. Little, 1997a; Arthur D. Little 1998a). Details of the number collected, physical measurements (sex, length, and weight), composite information, and the biological results for individual fish are given in Appendix F Tables F-1 through F-3.

#### **3.4.1 Organics (PAH)**

During the 1997 cruise, fish samples were collected from 3 different stations across 3 zones (zones 0, 2, and 3), and 3 species of fish were collected (Halibut, Arrowtooth Flounder, and Black Cod). Three stations across 3 different zones were also sampled in 1998 (zones 1, 2, and 3), with 6 species collected (Halibut, Arrowtooth Flounder, Black Cod, Aleutian Skate, Longnose Skate, and Pacific Cod). The catch distribution across the zones, in addition to the total samples for each year, are presented in Table 3-22. Fish liver samples were prepared from collected specimens and analyzed for PAH. Livers were analyzed because the highest concentrations of PAH would accumulate and be detected in this fatty organ if the fish were exposed to petroleum contamination.

Distributions of PAH in most fish tissue samples indicated a combination of petrogenic (e.g., C2-alkylated naphthalenes), pyrogenic (e.g., fluoranthene), and biogenic (perylene, detected at less than 2 µg/kg in 2 samples in 1997) hydrocarbons, all at very low concentrations. The individual PAH concentrations in fish tissue samples are included in Appendix B. Method detection limits (MDL), based on laboratory MDL tissue studies, range from approximately 1 to 5 µg/g (parts per billion [ppb]) dry weight. Minimum reporting limits (MRL), based on the lowest calibration standard, sample size, and pre-injection extract volume, ranged from approximately 2.8 ppb to 35 ppb dry weight. Values below the MRL are considered estimates and should be treated accordingly.

The concentrations of individual PAH rarely exceeded 20 µg/kg (ppb) and values of most individual PAH were near or below the MRL of the method (74 percent in 1997, 78 percent in

1998). Most of the PAH that were detected above the MRL were associated with low ppb blank contamination (66 percent of PAH above the MRL in 1997 tissues and 51 percent in 1998).

Naphthalene and phenanthrene concentrations were high for several fish liver samples. However, analysis of laboratory procedural blanks revealed low concentrations of naphthalene, C1-naphthalenes, phenanthrene, and benzo[g,h,i]perylene (see Section 3.6.2 for complete laboratory QA/QC results). Table 3-23 compares the PAH detected in procedural blanks to the average PAH concentrations in fish tissue samples in zones 0, 1, 2, and 3.

In most instances, the concentrations of these PAH compounds in fish tissue samples were similar to or less than the concentrations of these compounds found in the procedural blanks. The average phenanthrene concentrations were elevated in Halibut tissue samples from all 3 zones in 1997, with concentrations ranging from 0.027 mg/kg to 0.052 mg/kg which were greater than the phenanthrene concentrations found in the two associated procedural blanks (0.016 and 0.006 mg/Kg). For the 13 tissue samples collected in 1997, the mean percent increase of the detected phenanthrene concentrations relative to the mean of the two procedural blanks (for each sample), is 55 percent. The Halibut tissues again contained the highest concentrations compared to the other species collected in 1998, but there was a smaller difference between the lowest blank and the tissue concentrations, in particular phenanthrene, ranging from 0.006 mg/kg to 0.009 mg/kg (Table 3-23).

The trace concentrations and distribution of PAH detected in the liver samples (Figure 3-79 and Table 3-24) are characteristic of pyrogenic sources (e.g., primarily non-alkylated PAH), most likely derived from atmospheric deposition, land runoff, and creosote pilings (Page *et al.*, 1995). The characteristic petroleum-alkylated homologue distribution (NRC, 1985) was not observed in any of the samples and represents clear evidence that these samples do not contain petroleum-derived hydrocarbons. Due to trace concentrations of PAH in these samples (e.g., most of the data were below the MRL) and the low-level blank contaminants, there are no apparent differences between the background levels of hydrocarbons detected in the fish and the zone from which they were collected.

### 3.4.2 Metals

Concentrations of trace metals were determined for 36 composite samples of liver from Halibut and Pacific Cod from single sites in zones 0, 1, 2 and 3 (Table 3-25 and Figures 3-80 to 3-83). Overall, metal values for these fish livers are quite variable (Table 3-25). In general, fish length and weight did not correlate well with liver metal concentrations in the Halibut, except for Hg (Figure 3-84). Mercury concentrations in Halibut liver correlated positively with both length and weight ( $r = 0.80$  and  $r = 0.82$ , respectively). Concentrations of Be in all liver samples were below the MDL (0.002  $\mu\text{g/g}$ , dry weight).

Metal concentrations in liver samples from the Arrowtooth Flounder (3), Black Cod (2), and skates (2) are within the range of values obtained for the Halibut livers (Table 3-25). However, lower concentrations of Ag, As, Cd, Cu, Se, V, and Zn in Black Cod livers, Ag, Hg, Mn, Ni, and Pb in Flounder livers, and Al, Cd, Hg, Mn, Ni, Pb, Se, Sn, V, and Zn in skate livers are observed relative to the Halibut livers collected in the same zone. In contrast, values of Ag in skate livers and Ag, As, and Sb in Pacific Cod livers are higher than the Halibut livers (Table 3-25).

Fifty-three samples of fish flesh (muscle) from halibut collected in zones 0, 2, and 3 were analyzed separately for total Hg content (Table 3-26). Concentrations ranged from 0.128 to 2.43 µg/g (dry weight) or 0.022 to 0.486 ug/g (wet weight). The highest levels were found in zone 2. In general, the highest Hg levels in halibut flesh are found in longer (older) specimens (Figure 3-85). Concern for adverse effects from Hg during human consumption of fish is based on a daily Hg intake of 0.1 ug/Kg mass of human (EPA, 1999). At typical Hg levels of 0.10-0.15 ug/g, as discussed by EPA (1999), a 70-Kg human could consume 50-70 g (2-2.5 ounces) of fish per day or 350 to about 500 g (about 2-18 ounces) per week. All mean values for Hg in halibut flesh from all zones in the Shelikof Strait are between 0.10 and 0.15 ug/g (wet weight). These are all considered within the range of natural levels. One of the lowest Hg levels of concern noted by EPA (1999) is 0.4 ug/g (wet weight); a point whereat consumption should be adjusted accordingly. Only one sample from this study has a Hg level >0.4 ug/g (wet weight) at 0.486 ug/g (wet weight).

### **3.4.3 P450 RGS Response in Extracts of Fish Liver**

Three replicates of 13 fish liver extracts (10 µl) were analyzed after 16h of exposure using P450 RGS on September 29 and October 17, 1997. Of the 13 samples analyzed, only 3 samples produced a detectable RGS response (i.e., the fold induction > 1.0). These responses were just above background, yielding B[a]PEq of 0.9, 1.0, and 1.6 µg B[a]PEq /g lipid, which is consistent with results from an uncontaminated environment.

Extracts of 12 fish liver samples were analyzed by P450 RGS on January 7-8 and January 11-12, 1999, with the addition of 10 µL of each extract to two replicate exposure wells for both 6h and 16h. Extracts were notably oily, and in some instances, the fold induction responses were very low, indicating possible toxicity to the cells. Additional extract was obtained from the CAS/Kelso laboratory, and the RGS assay was again conducted on January 18-19, 1999, with the addition of 5 µL of each extract. No evidence of toxicity occurred with this test. The wide variation in percent lipids (2.5 to 79 percent) and percent solids (28 to 92 percent) of these samples produced high variability in the calculated equivalency values. Most samples produced very low responses, with 4 samples producing responses that were greater than the solvent blank (fold induction > 1.0). The 6h/16h response patterns were indicative of PAH (6h greater than 16 h). Based on the 16 h responses, these 4 samples yielded B[a]PEq from 0.3 to 6.5 µg/g lipid.

These results indicate that the livers of the fish contain little or no contamination by PAH or chlorinated compounds, which is supported by the very low PAH levels measured in the livers (Section 3.4.1). The complete results of the P450 RGS analyses are included in Appendix E.

### **3.4.4 CYP1A (P4501A) Response in Different Species and Different Tissues**

*1997.* This section will first address all three species of fish analyzed in 1997 and then discuss the results for Pacific Halibut (*Hippoglossus stenolepis*) in more detail, as this was the species with the greatest number of specimens and geographic coverage and therefore provides the best opportunity (therefore, the most power) to contrast conditions in the three zones as they affect CYP1A response in fish.

*All fish species--*Fish were captured at 1 station each in zones 0, 2, and 3 (Figure 2-1). The majority of fish analyzed (35) were Pacific Halibut, and these were caught in each of the 3 zones.

There were 4 Arrowtooth Flounder (*Atherestes stomias*) captured in zone 2 and 1 captured in zone 3. There were 5 Black Cod, or Sablefish (*Anoplopoma fimbria*), all caught in zone 3.

With few exceptions, CYP1A was detected in 2 organs (liver and kidney) which included responses in 3 cell types--hepatocytes in liver, and tubules and vascular endothelium in the kidney (Table 3-27). A few responses (1/44) were also observed in the liver vascular endothelium and liver bile duct cells (1/44). Likewise, in the gills a few responses were seen: pillar cells (4/44), epithelial cells (2/44), and vascular endothelium (2/44). In general, however, the gills showed little or no induced CYP1A protein; only hepatocytes in the liver and both kidney cell types were responsive.

In the hepatocytes, responses ranged from 0 to 10.5 out of a possible maximum score of 15. Likewise, in the kidney tubules scores ranged from 0 to 10.5 out of a possible maximum score of 15. In the kidney vascular epithelium scores ranged from 0 to 12, with the same maximal score possible.

*Pacific Halibut*-- Halibut were collected in zones 0, 2, and 3. The specimens ranged in length from 72 to 145 cm (standard length [SL]). Both males and females were retained. The mean Pacific Halibut IHC scores are provided by zone in Table 3-28. Although for each of the 3 cell types in Table 3-27, there was a trend of highest mean scores in zone 0, intermediate scores in zone 3, and lowest scores in zone 2, in only one cell type, kidney tubules, were these differences significant across all zones ( $p=0.007$ ). The results of the Student Newman-Keuls test indicated that for the kidney tubule, CYP1A response for zones 0 and 3 fell within the same group while zone 2 was lower and significantly different. Sex and length did not explain a significant amount of the variance of CYP1A response in Pacific Halibut cell types.

**1998.** This section will first address all 6 species of fish analyzed in 1998, and then discuss the results for Pacific Halibut (*Hippoglossus stenolepis*) and Pacific Cod (also called True Cod or Grey Cod) (*Gadus macrocephalus*) in more detail. Both of these latter species were collected in larger numbers than the other species, and from all 3 sites. In 1998, heart was added to the gill, liver, and kidney tissues analyzed for CYP1A response and histopathologies.

*All fish species*--Fish were collected at 1 station each in zones 1, 2, and 3 (Figure 2-1). The majority of fish analyzed were Pacific Cod (60) and Pacific Halibut (41) which were collected in each of the 3 zones. The sites in zone 2 (Z2 R14A) and zone 3 (Z3 R1A) were the same sites at which Halibut were collected in 1997. There were also 4 Arrowtooth Flounder (*Atherestes stomias*) collected in zone 3 and 5 collected in zone 2; 4 Black Cod (or Sablefish) (*Anoplopoma fimbria*) collected in zone 3; 1 Aleutian Skate (*Bathyraja aleutica*) collected in zone 3; and 1 Longnose Skate (*Raja rhina*) collected in zone 1.

CYP1A was detected in all 4 organs analyzed (Table 3-27). The majority of the responses (scores other than zero) were in 4 cell types--hepatocytes in liver (45/116), tubules in the kidney (37/116), epithelial cells in the gill (30/116), and endothelial cells in the heart (30/116). Additionally, a few responses were observed in gill pillar cells (3/116).

The possible range of scores for the CYP1A response in each of the cell types analyzed was from 0 to 15. Liver hepatocyte scores ranged from 0 to 4.5; kidney tubule scores ranged from 0 to 9;

gill epithelial cell scores ranged from 0 to 4.5; heart endothelial cell scores ranged from 0 to 8; and gill pillar cell scores ranged from 0 to 4.

*Aleutian Skate*--One Aleutian Skate was collected in zone 3. It was female, weighed 6.6 kg, and was 145 cm long (SL). This skate received a liver hepatocyte score of 1.5, a gill pillar cell score of 4, a gill epithelium score of 3, and a kidney tubule score of 9. The gill pillar cell and kidney tubule scores were the highest scores for those cell types among all fishes collected in 1998.

*Longnose Skate*--One Longnose Skate was collected in zone 1. It was male, weighed 8.25 kg, and was 110 cm long (SL). This skate received a liver hepatocyte score of 1.5 and a kidney tubule score of 6.

*Black Cod*--Four male Black Cod were collected in zone 3. They ranged from 58 to 70 cm (SL) and from 1.8 to 3.8 kg in weight. Black Cod received CYP1A scores ranging from 1.5 to 3 for liver hepatocytes, 3 for gill epithelium, 1 to 2 for kidney tubules, and 4.5 to 8 for heart endothelium. Each fish had a measurable response (above zero) for each of these cell types. The heart endothelium scores were the highest among all the analyzed species.

*Arrowtooth Flounder*--Four Arrowtooth Flounder were collected in zone 3 and 5 were collected in zone 2. The fish from zone 3 ranged from 55 to 76 cm (SL) in size and from 1.5 to 4.4 kg in weight. The largest fish was female and the other 3 were male. Two of the fish (both males) received CYP1A scores for kidney tubules of 5. There were no other CYP1A responses (above zero) in these fish. Arrowtooth Flounder from zone 2 ranged from 49 to 80 cm (SL) in size and from 0.8 to 4.4 kg in weight. One of these fish was female (61 cm/2.2 kg) and the rest were male. As found in Arrowtooth Flounder from zone 3, those from zone 2 received CYP1A scores only for kidney tubules. The scores ranged from 1.5 to 4.

*Pacific Halibut, zone 1*--Twelve Halibut were collected in zone 1. They ranged from 73 to 122 cm (SL) in size and from 3.2 to 20 kg in weight. There were 4 females and 8 males, and the 2 largest fish were both female. These fish received CYP1A scores only for liver hepatocytes, ranging from 0.75 to 1.5. Only 3 of the 12 fish from zone 1 had scores other than zero.

*Pacific Halibut, zone 2*--Seventeen Halibut were collected in zone 2. They ranged from 77 to 110 cm (SL) in size and from 5 to 18 kg in weight. Five of the fish were female and 12 were male. As in zone 1, the 2 largest fish were both female. These fish received CYP1A scores for both liver hepatocytes and kidney tubules, though only 1 fish had a score other than zero (1.5) for liver hepatocytes, and only 3 fish had scores other than zero (1.25 to 8) for kidney tubules. The score of 8 for kidney tubules was the second highest kidney tubule score in 1998.

*Pacific Halibut, zone 3*--Twelve Halibut were collected in zone 3. They ranged from 72 to 115 cm (SL) in size and from 4 to 13.6 kg in weight. Four of the fish were female and 8 were male. The largest fish was female. These fish received CYP1A scores only for kidney tubules, and only 1 fish had a score other than zero (3).

*Pacific Cod, zone 1*--Sixteen Pacific Cod were collected in zone 1. They ranged from 55 to 81 cm (SL) in size and from 1.8 to 5.2 kg in weight. Ten of the fish were female and 6 were male. The 3 largest fish were female. Thirteen of the 16 fish received CYP1A scores for liver hepatocytes that ranged from 1.5 to 3; 4 fish received scores for gill epithelium that ranged from

2 to 3; 10 fish received scores for kidney tubules that ranged from 1 to 4; and 7 fish received scores for heart endothelium that ranged from 0.5 to 5.

*Pacific Cod, zone 2*--Twenty-nine Pacific Cod were collected in zone 2. They ranged from 55 to 81 cm (SL) in size and from 1.9 to 7.8 kg in weight. Twenty-one of the fish were female and 8 were male. The 7 largest fish were female. These fish received scores for the same cell types as Pacific Cod from zone 1, and for gill pillar cells as well (2 fish had scores other than zero, both scoring 3). Seventeen of the 29 fish received scores for liver hepatocytes, ranging from 1 to 4.5; 15 fish had scores for gill epithelium ranging from 0.5 to 4.5; 5 fish had scores for kidney tubules ranging from 0.5 to 5; and 15 fish had scores for heart endothelium that ranged from 0.5 to 5.

*Pacific Cod, zone 3*--Fifteen Pacific Cod were collected in zone 3. They ranged from 55 to 79 cm in size and from 1.9 to 5.5 kg in weight. Eight of the fish were male and 7 were female. Five of the 15 fish received CYP1A scores for liver hepatocytes that ranged from 1.5 to 3; 6 fish received scores for gill epithelium that ranged from 1 to 3; 5 fish received scores for kidney tubules that ranged from 1 to 4; and 4 fish received scores for heart endothelium that ranged from 2 to 6.

*CYP1A Response by Organ*--The number of responses (greater than zero) per organ (inclusive of all species) was similar among organs; the highest was liver (0.39), followed by kidney (0.32), gill (0.28), and heart (0.26).

*CYP1A Response by Species*--Considered by species, Halibut had the lowest number of responses (greater than zero) per individual (0.2), followed by Arrowtooth flounder (0.78), Pacific Cod (1.87), Longnose Skate (2), and Black Cod and Aleutian Skate (4).

*CYP1A Response by Zone*--Without consideration of species caught, zone 1 had the highest number of responses (greater than zero) per fish (1.36 responses/fish), followed by zone 2 (1.24 responses/fish), and zone 3 (1.19 responses/fish). When Halibut collected in 1998 are considered in a statistical analysis as was performed previously for fish collected in 1997 (see above), no significant differences between zones were noted in any of the CYP1A responses (Appendix Table I-40). The same followed for the Student Newman-Keuls test results for the Pacific Cod, i.e., no differences in the CYP1A response between zones. The significance of the low to moderate IHC (CYP1A) scores measured in the fish tissues analyzed in this study is discussed in Section 4 of this report.

### **3.5 Statistical Results**

This section summarizes and provides highlights of the statistical analyses. Full results of statistical analyses are provided in Appendix I. The majority of corresponding figures and tables are also provided in Appendix I of this report.

Surface sediments were collected from 59 locations and examined for 121 chemical and physical parameters as part of the 1997 *Alpha Helix* survey. Sediments from 35 locations, analyzed for 118 chemical and physical parameters, comprised the 1998 statistical analysis data set (Ca, Mn, K, and AVS/SEM were not measured in these sediments, but oil-degrading bacteria were added). Ninety-five organic compounds in each sediment sample were analyzed. Appendix I Table I-1 is a presentation of analyte number and name. While the entire list is necessary for the

fingerprinting of specific petroleum sources, combinations and/or ratios of individual analytes can best describe spatial differences. For this reason, and to reduce errors associated with multiple testing, the large organic list was reduced to 23 chemically and biologically important groupings (Appendix I Table I-2). The statistical comparisons presented below were performed using these critical organic compounds plus an additional 26 inorganic sediment measurements (49 analytical values per sediment sample) for the 1997 surface sediments. Twenty-three inorganic and five biological parameters were determined in the 1998 surface sediment, resulting in a total of 51 analytical parameters per sediment sample.

As part of the 1997 survey, replication was varied within and between zones for the purpose of establishing estimates of within station and within zone. Between-zone variability of parameters of interest was modeled using sediments from both the 1997 and 1998 sampling periods in addition to monitoring the variance associated with the years of sampling.

### **3.5.1 Coefficient of Variation**

#### **3.5.1.1 Variability Within Surface Stations**

Three stations (Z1R15, Z2R2, and Z3R13) containing 7 field replicate surface grabs collected in 1997 each were used to assess within-station variability. The CV was used to describe the amount of variation of each analyte measured in the 3 zones. The objective of the analysis was to establish a means of comparison between the small-scale distribution of individual analytes at a station with the overall variance of individual analytes in all zones. Appendix I Table I-3 presents the CVs for each of the 49 parameters of interest. Overall the variation was quite low, ranging from 0.22 percent for Fe to a maximum of 8.07 percent for total S/T, suggesting that overall small-scale spatial variance (e.g., within an individual station) is minimal.

#### **3.5.1.2 Variability Within Zones (Surface Stations)**

As described in Section 2.1.2, 59 station locations were established and sampled over 4 zones in 1997 (Zones 0, 1, 2, and 3). "Randomness" of location and the number of replicate samples varied within each zone. Zone 0 was dominated by "fixed" stations (8 stations of 3 replicates each), a consequence of bottom sediment type. Zones 1, 2, and 3 contained 14 stations each; 11 possessing 1 replicate, 2 with 3 replicates, and 1 with 7 replicate surface samples. A fourth analysis was conducted on a subcore taken from one sample at each of the "3 replicate stations" (those stations where 3 distinct field replicate samples were taken). This fourth chemical analysis was not considered to be a station replicate due to lack of independence. At best, it could be considered a duplicate, or pseudo-replicate (Hurlbert, 1979). The information contained in these samples is nonetheless important and has been averaged into the values of the source replicate. Coefficient of variation was again used to address variability; however, this analysis included all samples taken within each of the 4 sampling zones in 1997. Appendix I Table I-3 provides the CV on all parameters for each of the 4 zones and a single CV which describes the system variability represented by all zones, stations, and replicates (105 total samples). As expected, variability within zones was greater than within stations.

Coefficient of variation was greatest in zone 0, ranging from 8.52 (Al) to 101.51 (Perylene) percent with only 16 of the 49 analytes having a CV of less than 25 percent. Following in descending order of variability and ascending distance from outermost Cook Inlet: zone 1 had 28 analytes with a CV less than 25 percent (range 4.32 percent Al - 82.36 percent TALK); zone 2 had 31 analytes with a CV lower than 25 percent (range 4.24 percent Al - 107.05 percent sand);

and zone 3 had 34 analytes with a CV less than 25 percent (1.88 percent Fe – 114.67 percent sand). The range of CV calculated for all stations ranged from 6.2 percent (Al) to 114.67 percent (sand) and had only 18 analytes with a CV lower than 25 percent.

Figure 3-86 plots in descending order the analyte CV for each of the zones normalized to the overall analyte CV. It is obvious that zone 0 is the most variable and that zones 1, 2, and 3 are quite similar, with zone 3 exhibiting a slightly lower level of variability. The CV ratio depicted in Figure 3-86 is also of interest in that ratios less than 1 indicate that the variability within a zone is less than overall variability for a specific analyte. Variability appears to decrease with increasing distance from outermost Cook Inlet with 69, 20, 12, and 4 percent of the analytes displaying a CV ratio of greater than 1 in zones 0, 1, 2, and 3 respectively.

### 3.5.2 Analysis of Variance

#### 3.5.2.1 Between-Zone Comparisons

A General Linear Models (GLM, see Section 2.3.2) analysis was conducted to identify significant between-zone analyte differences ( $p \leq 0.05$ ). Additionally, if the GLM indicated a statistically significant difference between zones, a Student Newman-Keuls multiple range test (SNK, see Section 2.3.2) was run to separate zones at the 0.05 level of significance. Results of the SNK comparisons are generally arranged in descending order of the dependent variable (e.g., zinc), with significant differences between categorical variables (e.g., Zone) identified by a unique letter code (e.g., A,B,C). Categorical variables sharing the same code are not significantly different and can be considered as a group. Categorical variables that share more than one code (e.g., AB) indicate an overlap between groups and/or individual categorical variable. When overlap is noted, only categorical variables with unique codes differ significantly. Table 3-8 provides a summary of the 1997 and 1998 results. Appendix I Tables I-4 through I-8 summarize the GLM/SNK results performed on the surface sediments collected in 1997. Appendix I Tables I-16 through I-23 summarize the GLM/SNK results performed on the surface sediments collected in 1998.

**Surface Sediments - 1997.** Seventeen metals were examined for significant zone differences. Untransformed data produced significant results for all metals, with the exception of Mn, Ni, Ag, and Tl. In general, zones 0 and 3 are most often different and that zones 1 and 2 regularly overlap with each other and/or with zones 0 and 3. The results of this test are given in Appendix I, Table I-4. When metals data are transformed by dividing by the percent Fe within a sample, all metals are different between zones except As, Mn, Hg, and Ag. Again, zones 0 and 3 are most often identified as unique by the SNK.

Nine chemical/physical sediment parameters measured as percentages of sediment (Al, Ca, clay, Fe, Mg, K, sand, silt, and TOC) were examined and are presented in Appendix I Table I-6. Only Al shows no significant difference between zones. The trend in zone differences differs somewhat from that in the trace metals analyses presented in Appendix I Table I-5. These higher represented analytes tended to group together in pairs, with four of them combining zone 0 with zone 1, and zone 2 with zone 3.

Organic compounds of interest (Appendix I Table I-2) were treated in a manner similar to sediment metals. Two sets of GLM analyses were performed on the 23 organic groupings. The first set of statistical analyses examined untransformed data and the second examined TOC

transformed data. Appendix I Tables I-7 and I-8 summarize the statistical results. Fifteen organic groups showed significant difference between zones in the untransformed data set (Table 3-8), while after TOC transformation 18 groupings were indicated as having significant zone differences. Zone 0 was most often unique; however, trends of increasing, or decreasing, concentration with distance from outermost Cook Inlet were less frequent for this group of chemicals than for either the trace metals or the physical sediment parameters.

*Surface Sediments - 1998.* The GLM/SNK zone analysis was repeated for the 1998 data set on surface sediments measured for 17 metals. Two data sets were evaluated for differences among the defined zones, 1 transformed by dividing each analyte by the percent Fe and 1 non-transformed. Nine of the 17 metals analyzed showed significant differences between zones using the non-transformed data. In general, zones 0 and 1 were not different from one another on most of the parameters, but different from the other zones (2, 3, and 4) that were grouped together. Following transformation, 6 of 19 metals were shown to have statistical difference between the zones. The differences were less distinct among the zones, but in general, zones 0 and 1 were unique compared with the other zones. The complete analysis results are reported in Appendix I Tables I-16 and I-17.

Six chemical/physical sediment parameters measured as percentages of sediment (Al, clay, Fe, sand, silt, and TOC) were examined and are presented in Appendix I Table I-18. Only Al and Fe showed no significant difference between zones. The groupings were similar to that observed with the trace metals, with the zone 0 and zone 1 sediments paired together and significantly different from the other three zones which were not different from one another. Transformation of the data by the percent iron yielded identical results (Appendix I Table I-19).

The GLM/SNK zone analysis was performed on the same 23 organic groupings measured in 1997, both transformed by TOC and non-transformed. The results are summarized in Table 3-8 (non-transformed data only) and Appendix I Tables I-20 and I-21. Only seven organic groups showed significant difference between zones in the non-transformed data set (Table 3-8 and Appendix Table I-20), while after TOC transformation eight groupings were indicated as having significant zone differences. In general, zone 0 tended to be the most unique, particularly after transformation, with differences attributed mostly due to the concentrations parameters such as the Total PAH and Petrogenic PAH.

As part of the biological analyses, surface sediments were collected to evaluate the RGS-P450 response to corresponding extracts. Significant zone differences for both parameters (TEQ and B[a]PEq) were detected in both the data transformed by TOC and data non-transformed. For each analysis, the response at zone 0 was generally significantly lower than all other zones (1, 2, 3, and 4). The results of this test are given in Appendix I Tables I-22 and I-23. Two new variables were introduced in the 1998 sampling survey, i.e., heterotrophic and crude oil emulsifying bacteria. These were also analyzed for between-zone differences and resulted in no differences, using either transformed or non-transformed data (Table 3-8, Appendix I Tables I-22 and I-23). The mean percent survival for the sediment toxicity tests was also assessed and the results revealed that no significant difference in toxicity exists between zones where sediments were collected (zones 0, 2, and 3). The results for both transformed and non-transformed data are given in Appendix I Tables I-22 and I-23.

**Surface Sediments - 1997 and 1998 Combined.** A data set consisting of 16 stations, evaluated for 19 metals and 4 physical parameters and sampled during both the 1997 and 1998 surveys (including zones 0, 1, 2, and 3), was constructed to examine the zone differences over the entire sample survey. A GLM model paired with a Bonferroni multiple comparison test was used to establish significant differences ( $p < 0.05$ ) between the zones. Seven metals contained significant differences among zones using the non-transformed data. Many of the zones were grouped together (i.e., two groupings that overlapped one another) and followed the patterns observed with the individual sampling year analyses. Three physical parameters were determined to be significantly different across zones, essentially separating zone 0 from the other zones (1, 2, and 3) or from zone 3. Data transformed by the percent Fe yielded 4 of the metals and 3 physical parameters significantly different across zones, generally isolating zone 0 from the other zones or zone 3. The complete summary for these analyses is given in Appendix I Tables I-24 and I-25. Only where the GLM determined a significant difference were the data then subjected to the Bonferroni analysis and included in the summary tables.

The GLM/Bonferroni model was also used to establish significant differences among the zones using a data set comprised of the 23 organic groupings measured at the 16 stations. For the non-transformed data set, only 6 of the organic groupings were found to contain significant differences among the zones. As was observed with the results for the surface sediment zone analyses performed separately above, zone 0 was distinct from the other zones mainly due to the lower concentration of parameters such as total and petrogenic PAH, and the sum of the LALK. The same six parameters were determined to be significantly different in the analysis of the transformed data. The results for these data are summarized in Appendix I Tables I-26 and I-27.

The two RGS-P450 biological indicators (TEQ and B[a]PEq) were statistically analyzed for differences across zones using data normalized to TOC and non-transformed data collected at 14 common stations where measurements were performed during each sampling year. Zone 0 was distinctly lower than zone 2 on both biological parameters, with the other zones (1 and 3) no different from either of these two zones using the non-transformed data. After normalization to TOC, the B[a]PEq showed similar differences to the non-transformed data (i.e., zone 0 distinct from zone 2) while the TEQ was not statistically different across the zones. The results for these data are summarized in Appendix I Tables I-26 and I-27.

#### **3.5.2.2 Between-Year Comparison (1997 vs. 1998)**

A data set consisting of repeated station sampling for both the 1997 and 1998 surveys was analyzed for differences across the sampling period. The 16 stations were analyzed first using GLM followed by a Bonferroni multiple comparison test to establish whether there were significant differences between the sampling periods. Only where the GLM determined a significant difference were the data then subjected to the Bonferroni analysis and included in the summary tables.

Out of the 19 trace metals analyzed, 3 (Al, Ag, and Sn) exhibited statistical differences during the 2 sampling periods using the non-transformed data and 2 (silt and clay) of the physical parameters showed significant differences. Following transformation, only 2 (Ag and Sn) of the 19 metals and the same 2 physical parameters were found statistically different between the years of sampling. Results for this analysis are summarized in Appendix I Tables I-28 and I-29.

The 23 organic parameters were compiled from the 16 common stations and evaluated using the GLM/Bonferroni model to test for yearly differences. Only 1 of the 23 organic groupings was found to be significantly different between the years of collection (Oleanane/Hopane) using either the transformed or non-transformed data set. A summary of this analysis is given in Appendix I Tables I-30 and I-31.

Differences between years for the two RGS-P450 biological indicators (TEQ and B[a]PEq) were evaluated using data normalized to TOC and non-transformed data that was collected from 14 common stations. There were significant differences between the sampling years for both the transformed and non-transformed data (Appendix I Tables I-30 and I-31).

### **3.5.3 Pearson's Product-Moment Correlations**

#### **3.5.3.1 Sediments**

*Twenty-Station Sediment Data Analysis.* Concurrent measurements for 35 physical/chemical parameters and 2 biological indicators (Appendix I Table I-9) were made at 20 stations during the 1997 sampling survey; 8 in zone 0 and 4 in each of zones 1, 2, and 3. Six stations (zone 1, 7 and 13; zone 2, 1 and 13; zone 3, 11 and 14) had a single field replicate. Three field replicates were taken at the remaining 14 stations. To explore possible correlations between sediment parameters of special interest (amphipod MPS, RGS-P450 toxicity equivalent, AVS concentration, total SEM minus AVS concentration) a Pearson's correlation was performed. Appendix I Table I-10 presents a summary of the results of the processing of untransformed data.

The mean amphipod survival had significant ( $z \leq 0.05$ ) negative correlations with 15 metals, depth, silt, and TOC, but no significant correlation was observed with SEM-AVS. RGS-P450 expressed as TEQ positively correlated with depth, silt, TOC, two metals, and three organic compounds. SEM-AVS correlated negatively with two metals and two organics and had no positive associations. Conversely, AVS positively correlated with three metals and two organic compounds. However, after the percent silt effect was removed, there were few significant differences due to metals or organic contaminants (Table 3-29).

An arc sine square root transformation was applied on all data reported as percents (e.g., amphipod toxicity, clay, and Fe) and the Pearson's correlation was again performed. Appendix I Table I-11 is a summary of this analysis. Amphipod toxicity negatively correlated with the same analytes as with the untransformed data. RGS-P450 positively associated with eight analytes. SEM-AVS and AVS remained unchanged.

*Fourteen-Station Sediment Data Analysis.* Concurrent measurements for 30 physical/chemical parameters and two biological indicators (Appendix I Table I-32) were made at 14 stations during the 1997 and 1998 sampling surveys; 8 in zone 0 and 2 in each of zones 1, 2, and 3. To explore possible correlations between sediment parameters of special interest (i.e., RGS-P450 toxicity equivalent) a Pearson's correlation was performed. Appendix I Tables I-33 presents a summary of the results for the untransformed data.

The B[a]PEq biological parameter contained significant ( $p < 0.05$ ) positive correlations with 6 metals, 4 organic indices and 2 physical parameters and exhibited a significant negative correlation with the percent sand. The TEQ had significant positive correlations with 4 metals, 2 physical parameters, and 4 organic indices in addition to containing a significant negative

correlation with the sand parameter. The complete results for this analysis are given in Appendix I Table I-33. Following normalization, the B[a]PEq was determined to be positively correlated to 2 metals, 1 physical parameter, and 2 organic indices, while containing significant negative correlations with 2 metals and 1 of the organic indices. After normalization, the TEQ data set contained significant positive correlations with 2 organic indices (total PAH and petrogenic PAH) and significant negative correlations with 2 metals (Ni and Cr). The complete results for this analysis are given in Appendix I Table I-34.

Sediment toxicity tests were only performed on seven sediment stations collected in 1998, five of which were repeats of stations that were collected in 1997 (therefore, ten samples are common to both years, with the remaining sediment toxicity test results from nine stations collected in 1997). However the organism used for each year of sampling was different, therefore effectively eliminating any meaningful correlations between this parameter and the physical/chemical measurements on a set consisting of both years' data.

The seven 1998 stations where sediment toxicity to the amphipod *Ampelisca* was determined were analyzed separately for correlation to the physical/chemical parameters, even though amphipod toxicity can be considered marginal if at all (see Section 3.25). No significant/meaningful correlations were observed between the metals and organic parameters and the mean percent amphipod survival. For example, the only significant correlations, the total PAH ( $r=0.81$ ,  $p=0.026$ ), petrogenic PAH ( $r=0.77$ ,  $p=0.041$ ), percent clay ( $r=0.74$ ,  $p=0.036$ ), and TOC ( $r=0.85$ ,  $p=0.016$ ) were all *positively* correlated with the amphipod survival indicating that mean percent amphipod survival increased with increasing PAH concentrations.

### 3.5.3.2 Fish Tissue

**Tissues - 1997.** Sixty-one fish of three species (Black Cod, Arrowtooth Flounder, and Halibut) were collected from zones 0, 2, and 3, at stations F7, 14, and 01, respectively. Tissues from multiple fish within a station and species were composited to generate 13 tissue samples which were processed for 41 organic chemicals, 18 metals, and 2 biological indices (Appendix I Table I-12). A subset of 45 fish was measured for standard length, sexed, and sampled for P450 indicators. Two distinct data sets containing analytical results were generated, one populated with chemical tissue concentrations and the other with length, sex, and P450 indicators. For the purpose of correlative statistics, mean lengths and P450 indicators for unique species and their associated composite were merged into the analytical data set containing analytical chemical results.

The results presented in Appendix I Table I-13 show that very few meaningful, significant correlations between the biological parameters and tissue chemical parameters were obtained.

**Tissues - 1998.** In 1998, one hundred sixteen individuals from six species (Black Cod, Arrowtooth Flounder, Halibut, Aleutian Skate, Longnose Skate, and Pacific Cod) were collected from zones 1, 2, and 3. Thirty tissue composites were generated and analyzed for 41 organic chemicals, 19 metals, and 2 biological indices. Again, individual tissue responses were averaged in order to correspond to the appropriate chemical/physical measurement performed on the tissue composite. The data sets compiled for Pearson's correlation analysis included all fish regardless of species, a Halibut subset, and a Pacific Cod subset. A summary of the analytes within each data set is given in Appendix I Table I-35.

The review of all significant correlates, both positive and negative, is given in Appendix I Tables I-36 and I-37. Consideration as to the detection limits of both the biological and PAH parameters precludes conclusions regarding the validity of the statistically significant correlations. The response of the biological variables "hepatocyte" and "kidney tubules" contain the most detections across all species (see Table 3-27) and can potentially contain the most reasonable correlations. However, when observing these two variables' significant correlates in the "all fish" data set (Appendix I Table I-36), there are only 3 metals and 2 organic compounds with positive correlations to these response variables. The significant correlations for the two organic compounds (benzo[ghi]perylene and Total PAH) are primarily driven by the same measurement, an exceptionally high value for the benzo[ghi]perylene in one fish composite sample (see Zone 3, Aleutian Skate, in Table 3-24).

*Tissues - 1997 and 1998 Combined.* Data from both years were combined to determine correlations among the biological parameters with the chemical/physical measurements. Data sets included all fish regardless of species, a Halibut subset and a Pacific Cod subset. The review of all significant correlates, both positive and negative, is given in Appendix I Tables I-38 and I-39. Results are no different than from those discussed for the individual years' data sets, that is, there are very few meaningful correlations between the biological and tissue chemical parameters.

#### **3.5.4 Analysis of Variance/Covariance**

*Tissues - 1997.* Hypothesis tests using the GLM/SNK procedures were applied to both the combined P450/chemical data set and the P450 exclusive data set. The combined data set was examined in a series of three GLM tests; 1) all fish, 2) Halibut only, and 3) Halibut only with length as a covariant. Appendix I Table I-14 summarized the significant results of these analyses. Zones that can be described by the SNK multiple range test possess unique letters (A or B). It is apparent that few of the 68 chemical/biological parameters examined differ significantly with zone.

Appendix I Table I-15 summarizes four GLM processes using only the Halibut tissue measurements, with the P450 indicators as dependent variables, zone as the independent variable and various combinations of sex and length as covariants. The addition of both sex and length appears to refine the analysis and bring into closer focus differences between zones.

*Tissues - 1998.* Hypothesis tests using the GLM/SNK procedures were applied to the P450 data set, and consisted of fish species that were collected in more than one zone, that is, the Halibut, Pacific Cod, and Arrowtooth Flounder. Each species was investigated separately with 1) no covariate, 2) with sex as a covariate, and 3) with length as a covariate. The results for each species analyzed with no covariate is given in Appendix I Table I-40. Of the significant GLMs, not one resulted in statistical separation using the SNK test. The analysis of covariance yielded identical results, with no difference across the zones for any species.

*Tissues - 1997 and 1998.* Hypothesis tests using the GLM/SNK procedures were applied to both to a chemical data set and a P450 data set, each consisting of zones where Halibut sampling was repeated during both years, that is zone 2 and zone 3. Analytes for the chemical data set included the individual and total PAH, the individual metals, and the P450-RGS response variables (see Appendix I Table I-35 for complete listing). Analytes for the P450 data set included the cellular

biological measures (Appendix I Table I-35). Classification variables in both data sets included year, zone, and the year-zone interaction. Both sex and length were also analyzed as covariates in the biological data GLM. The results for the GLM/SNK analysis for chemical/biological parameters (with no analysis of covariance) are given in Appendix I Tables I-41 and I-42. Very few of the analytical parameters exhibited significant differences across any of the classification variables. Furthermore, any relationships observed among the biologic measures were identical after an analysis of covariance was performed using sex and length as separate covariates (length was noted as an insignificant covariate).

### **3.6 Quality Control Results**

This discussion is intended to provide an evaluation of data quality and usability based on the field and laboratory QC samples collected and analyzed during the first year of this study.

#### **3.6.1 Quality Control in the Field**

QC samples were collected in the field to assess overall precision, accuracy, and representativeness of the sampling and analytical efforts. The number of QC samples collected for this effort is based on the total number of field samples as established in the Field Logistics Plans (Arthur D. Little, 1997a; Arthur D. Little, 1998). All results for these samples are presented in Appendix B. Discussion and interpretation of the results are provided in the following sections.

The quality of the sample collection process is evaluated by means of equipment, field, and trip blanks. These sample blanks provide valuable data by monitoring the sampling process for field contaminants and cross-contamination. The trip blank was transported along with the empty sample containers being taken by the sampling team into the field. Equipment and field blanks are used to assess contamination introduced in the field environment and by sampling equipment. When sampling is complete, the blanks are submitted along with the field samples for laboratory analysis. In addition, replicate samples were collected to demonstrate reproducibility and to assess precision.

##### **3.6.1.1 Trip Blank**

One trip blank was prepared and shipped along with the station ZOF1 samples in 1997, but its results can be interpreted to assess the potential cross-contamination during transportation of all samples collected for this study. The trip blank was analyzed for PAH, SHC, and S/T. Only one sample shipment was required. Overall, no significant concentrations of relevant analytes were detected in this sample.

For PAH analysis, low molecular weight PAH compounds (i.e., naphthalenes and phenanthrene) were detected at very low concentrations. These were flagged with J and B codes. This demonstrates that values detected were below the detection limits and present on the procedural blanks associated with this sample, and that no cross-contamination occurred during transportation. For SHC analysis, several n-alkanes were detected between 0.026 and 0.14  $\mu\text{g/g}$ . These low concentrations are probably due to the presence of non-SHC compounds at the same elution time or trace laboratory contamination from solvents and/or septa. No analytes were detected for S/T analysis.

### **3.6.1.2 Equipment Blanks**

A total of nine equipment blanks were prepared and submitted for analysis over the entire study period. Three were collected from rinsate of the grab sampling equipment at stations ZOF1, ZOF8, and Z3R13 in 1997, and three similar rinsates were collected at locations Z1R19, Z2R14A, and Z2R23 in 1998. Both the 1997 and the 1998 surveys included an equipment blank collected from rinsate of fish dissection equipment that was used in the on-board laboratory associated with location Z2R14A. One additional equipment blank sample was collected from rinsate of the box core sampling equipment (and core liner) at location ZOF1.

Low molecular weight PAH compounds (i.e., naphthalenes, phenanthrene, and dibenzothiophene) were detected at very low concentrations in the fish dissection and rinsate equipment blanks. These analytes were flagged with J and B codes. This indicates that the values detected were below the detection limits, detected in the procedural blanks associated with these samples, and that no cross-contamination occurred while using the sampling and dissection tools. Low concentrations of midrange n-alkanes were detected (i.e., nC22 through nC31) in the equipment blanks. In the case of samples ZOF1 and ZOR13, concentrations of high-end n-alkanes were also detected. When taking into account the differing volume levels and collection techniques in comparing results from the equipment blanks and field samples, it can be concluded that the potential for cross-contamination from the equipment used to the field samples is negligible. These results are consistent with what is expected in equipment blanks and no further data qualification is required. In addition, these analytes were also observed in procedural blanks at comparable concentration levels. No S/T compounds were detected in the equipment blanks.

### **3.6.1.3 Field Blanks**

Three field blank samples were taken during the collection of sediment samples. One field (deck) blank was collected during sediment sampling in 1997 at location Z1R9 when a forest fire smoke smell was noticed in the air. The other two field blank samples, deck blanks, were collected during sediment sampling at location Z2F1 and location Z2R23, in 1997 and 1998, respectively.

Low molecular weight PAH compounds (i.e., naphthalenes, phenanthrene, and dibenzothiophene) were detected at very low concentrations. These were flagged with J and B codes. This indicates that the values detected were below the detection limits and present in the procedural blanks associated with these samples, and that no contamination can be attributed to ambient sources. Low concentrations of midrange n-alkanes were detected (i.e., nC22 through nC31), probably due to laboratory contamination from solvents and/or septa. The analytes were also observed in the procedural blanks at the same concentration levels. No S/T compounds were detected in the field blanks.

## **3.6.2 Organics Quality Control**

For this program QC measures for organics analysis included evaluation of surrogate compound recoveries and analysis of procedural blank samples, laboratory control spike samples, SRM samples, and control samples.

In addition, ADL participated in the NOAA/NIST intercalibration exercises for organics in 1998, 1999 and 2000. Triplicate analyses of marine and mussel tissue were analyzed for organics

(including PAH) as part of these exercises. The results of the ADL analyses were within the top 10% of the more than 30 laboratories participating in the exercises.

### **3.6.2.1 Surrogate Results**

Surrogate compounds were added to all samples including the tissue, sediment, and QC samples. These compounds were added at different concentrations, depending on the matrix, to determine the recovery efficiency during sample extraction, processing, and analysis. Recoveries of the analytes of interest are inferred from the recoveries of the surrogates. The recovery efficiency of all samples collected and analyzed for this study are presented in Table 3-30. In order to simplify the presentation of the surrogate data, only the mean percent recovery, standard deviation, and relative standard deviation were included in the table (percent recovery data for each sample are included in Appendix B). Overall, the surrogate recovery results met the DQO for the project.

### **3.6.2.2 Laboratory Control Spike Summary**

Laboratory control spike (LCS) samples measure the normal concentration bias due to such issues as matrix effects and analytical method errors. For this project, LCS were analyzed on each of the matrices (i.e., sediments, water, oil, and coal), except tissue, as shown in Table 3-31. Fifteen sediment LCS were analyzed for PAH and 17 for SHC. Water LCS were also analyzed, 5 for PAH determination and 5 for SHC. As for the oil and "coal" matrices, only 1 LCS sample was analyzed for both PAH and SHC. Overall, the results are acceptable and demonstrate that the system was in control. Average recoveries were within the range specified in the Work Plan (35 percent to 125 percent). The SD and RSD are all at acceptable levels; the only exceptions are n-Decane for the water SHC LCS analysis with an RSD of 37 and acenaphthylene for the sediment PAH LCS analysis with an RSD of 36 (30 is the limit). The oil and coal matrices LCS recoveries are acceptable for both PAH and SHC analyses.

### **3.6.2.3 Procedural Blanks**

Twenty-nine procedural blanks were analyzed in conjunction with the organics samples. Traces of some PAH target analytes were detected in the blanks at the low ppb concentration and were generally below the reporting limit for the method. Naphthalene and C1-naphthalene were identified in all the blanks, occasionally at concentrations above the reporting limit; however, these compounds are common contaminants associated with the solvents used during extraction and processing. Traces of some SHC target analytes were also detected in the procedural blanks (low ppb). Only in a few cases did the concentrations of any target SHC analyte exceed the reporting limit of the method. S/T target analytes were detected in the low ppb in only one of the procedural blanks analyzed. Overall, the procedural blanks met the DQO in the laboratory QA plan for the program, and do not indicate concentrations of laboratory contamination that will affect the quality or usability of the organics data.

### **3.6.2.4 Standard Reference Materials**

**Calibration Solution.** SRM 1491 (a solution of certified PAH) was analyzed prior to each GC/MS sequence of samples for PAH analysis. The results of the SRM 1491 analyses are presented in Table 3-32. The difference of the measured values from the certified values is less than the  $\pm 15$  percent required in the QA plan, for all samples analyzed.

**Sediment.** One sediment SRM (SRM 1941a - certified for PAH) was analyzed with each batch of sediment samples. The results of the SRM 1941a analyses are summarized in Table 3-32. The percent difference of the measured values versus the certified values for PAH compounds was within the acceptance criteria ( $\pm 35$  percent) for all target analytes with a few exceptions.

Naphthalene had a mean percent difference of minus 43 percent and minus 51 percent in the 1997 and 1998 analyses, respectively. Fluorene was also below the acceptance criteria at minus 43 percent in 1998 only. These results indicate that the measurement of naphthalene and perhaps fluorene in the sediments could be biased low due to loss of these more volatile PAH during sample processing. Average recovery of dibenzo[a,h]anthracene exceeded the certified value by 41 percent in 1998, and could indicate a high bias for measurement of this compound in sediments.

*Tissue.* Four tissue SRM (SRM 1974a - certified for PAH) were analyzed along with the tissue samples. The results of the SRM 1974a analysis are included in Table 3-32. Several analytes (naphthalene, anthracene, and phenanthrene) are outside the acceptance criteria (less than 35 percent difference from the certified value). The high recoveries of naphthalene and phenanthrene are likely the result of laboratory contamination as these analytes were detected in the associated procedural blank. The results for these compounds were qualified in the corresponding tissue samples. The high recovery of anthracene is consistent with the results obtained for this compound in multiple (more than 20 samples) analyses of SRM 1974a over the last three years, and is likely due to the light-sensitive nature of this analyte.

#### **3.6.2.5 Analysis of Control Oils**

Cook Inlet crude oil and North Slope crude oil samples were analyzed prior to each batch sequence for PAH, SHC, and S/T analysis. The results of the control oil analyses are compared to the laboratory mean values generated from multiple analyses of the oils. The results of the control oil analyses (Tables 3-33 and 3-34) indicate that accuracy and precision of the analytical methods for PAH, SHC, and S/T analyses are within the acceptance criteria required in the Laboratory QA Plan for the program.

#### **3.6.3 Metals and Total Organic Carbon Quality Control**

For this project, QC measures included instrument calibration, standard checks, analysis of standard reference materials (SRM), duplicate sample analysis, method and field blank analysis, and matrix spike analysis for each analyte.

##### **3.6.3.1 Instrument Calibration and Standard Checks**

Before instrumental analysis by FAAS, ZGFAAS, CVAAS, ICP/MS or nitrogen-carbon-sulfur analyzer, a three- to five-point calibration was carried out and the linearity of the individual analyte response factors checked. In all instances, the calibration curve for the standards met with the DQO of  $r \geq 0.999$ . The RSDs between the initial calibration and subsequent calibration checks were <15 percent in all instances.

##### **3.6.3.2 Standard Reference Material Analysis and Intercalibration Exercise**

For sediment and coal samples, the accuracy of the digestion and analytical techniques was determined by analyzing SRM BCSS-1, a marine sediment sample issued by the NRC in duplicate with each batch of 40 field samples. A total of 18 SRM BCSS-1 samples were analyzed. Metal concentrations obtained for the SRM BCSS-1 were within the limits specified by the NRC, except for Sb, Sn (1997) and TOC (1998) (Table 3-35). However, Sb, Sn and TOC values obtained for the SRM samples were within 15 percent of the concentrations reported by the NRC (Table 3-35), well within 20 percent of the certified value required by the DQO (Table 2-10). Because SRM BCSS-1 is not certified for Hg, SRM MESS-2, a marine sediment sample issued by the NRC, and SRM 1646a, an estuarine sediment certified by the NIST, were analyzed

in duplicate with each batch of 40 field samples. Values obtained for these standards were within the limits certified by the NRC and NIST, respectively (Table 3-35).

To determine the accuracy for the liver and muscle tissue, SRM 1566a, an oyster tissue certified by the NIST, SRM DORM-2, a dogfish muscle, and SRM TORT-2, a lobster hepatopancreas standard, both issued by the NRC, were analyzed in duplicate for every 20 samples. Metal concentrations obtained for SRM 1566a, SRM DORM-2, and SRM TORT-2 are within the limits specified by the NIST (Table 3-36). Because no certified or reference data are available for Ba and Be in SRM 1566a, SRM DORM-2, and SRM TORT-2, a water sample certified by the NIST, SRM 1643d, was used to check the analytical accuracy for these elements and provide additional quality assurance for Sb, Se, and Tl. The metal values obtained for SRM 1643d are within the range of values certified by NIST (Table 3-36) and met the specified DQO (Table 2-10).

Accuracy for suspended solids from the Susitna, Knik, Matanuska and Copper Rivers was determined by the analysis of SRM 2704 (1998), a river sediment, and SRM 1643d (1998), a water sample, both issued by the NIST. Metal values for both SRM are within the certified limits specified by the NIST (Table 3-37). However, no certified reference values are available for Tl, V, and Zn. For the remaining source samples (Cook Inlet crude oil, Cook Inlet produced water, and the Point Woronzof municipal effluent), SRM 1643d (1997), a water sample certified by the NIST, and SRM SLRS-3 (1997), a riverine water sample certified by NRC, were analyzed. Results for these standards are within the limits specified by NIST and NRC, except for As, Ba, Sb, and Se (Table 3-37). Values obtained for these SRM samples are within 12 percent of the concentrations reported by the NIST and NRC (Table 3-37), well within specifications required by the DQO (Table 2-10). Because SRM 1643d and SRM SLRS-3 are not certified for Hg, SRM MESS-2 was digested and analyzed along with the Cook Inlet crude oil sample. Mercury concentrations for this standard are within the limits certified by the NRC (Table 3-37).

Florida Institute of Technology also participated in the 1998 NRC and NOAA intercalibration exercise for trace metals in marine sediments and biological tissues. Two samples of sediment and two samples of tissue were analyzed in quintuplicate for 17 and 13 different metals, respectively. The FIT laboratory was among 13 of 41 laboratories in the intercalibration effort to be rated superior and the only laboratory to report results for 60 sets of data with no values outside the accepted limits (Willie, 1998).

### **3.6.3.3 Duplicate Sample Analysis**

Average analytical precision for the sediment portion of this study (including source material from the Susitna River, Copper River, Homer Harbor, and the coal sample) was determined from analysis of 10 duplicate samples and expressed as average of [(std. deviation/mean) x 100 percent]. The results are as follows: Ag (12 percent), Al (2 percent), As (6 percent), Ba (2 percent), Be (3 percent), Ca (4 percent), Cd (4 percent), Cr (5 percent), Cu (2 percent), Fe (2 percent), Hg (3 percent); K (0.5 percent), Mg (3 percent), Mn (2 percent), Ni (3 percent), Pb (2 percent), Sb (4 percent), Se (9 percent), Sn (5 percent), Tl (1 percent), V (5 percent), and Zn (5 percent). Results of the duplicates indicate precision is in all cases below the 25 percent required by the DQO (Table 2-10). Analytical precision for fish liver and muscle tissue analyzed in duplicate range from 0 to 18 percent. For the source samples, Cook Inlet crude oil, produced water and Point Woronzof municipal effluent, analytical precision ranges from 0 to 18 percent, except for Pb which, at low levels, averages 28 percent. Analytical precision for the river

suspended solids ranges from 0.4 to 14 percent. Thus, results for these samples are well within the DQO (Table 2-10).

#### **3.6.3.4 Method Blank Analysis**

Two method blanks were processed and analyzed with each batch of samples to monitor potential contamination resulting from laboratory reagents, glassware, and processing procedures. No contamination from any of these sources was noted and concentrations of analytes in the blanks do not exceed 5 times the MDL.

#### **3.6.3.5 Field Blank Analysis**

Six field blanks (2 Van-Veen grab rinses, 1 trip blank, 1 deck blank, 1 fish lab blank, and 1 fish tool rinse) were analyzed for trace metals to monitor potential contamination from field operations. No contamination from any of these possible sources was noted. Concentration of all metal analytes in the blanks was <5 times the MDL.

#### **3.6.3.6 Matrix Spike Analysis**

Two matrix spike samples were analyzed with each batch of 40 sediments and/or source materials using the method of standard additions. Results from these analyses provide information on the extent of any signal suppression or enhancement due to the matrix. Spike results for the sediment, and source samples from Susitna River and Copper River, Homer Harbor and the coal samples (Tables 3-35 through 3-37), are within the 80 to 120 percent range specified in the DQO (Table 2-10), except for Ag, Hg (1998), Se, Sn (1998), and V. Even though the recoveries for these metals were <80 percent, no spike corrections were made to the results for these metals.

The percent recovery for the matrix spike samples for the fish liver and muscle samples (Table 3-36) were within the 80 to 120 percent range specified by the DQO for all metals, except Hg and Ni. Spike recovery for Hg averaged 60 percent for the liver-composite samples and 75 percent for the fish flesh samples. This low recovery is commonly observed when organic-rich samples are analyzed by CVAAS. All tissue Hg concentrations reported in Table 3-25, Table 3-26 and Table 3-36 were corrected for their spike recoveries. The Ni values for the liver composite samples were also spike corrected. Recovery of matrix spikes (Table 3-37) in the aqueous and oil source samples also were within the 80 to 120 percent range except for Ag, As (oil), Ba (water), Fe (oil), Ni (water), Se, and V. Nickel values (1998) and all V concentrations were spike corrected. Spike recovery for the river suspended solids (Table 3-37) averaged  $97 \pm 8$  percent, well within the range required by the DQO (Table 2-10).

#### **3.6.4 Toxicity Test Quality Control**

During the conduct of the sediment toxicity tests, the established QA/QC measures were performed and monitored to evaluate the validity of the results. The following required QA/QC criteria were met during the performance of these tests and validate the results obtained:

- A 96.5 and 100 percent survival of amphipods in the 'home' control sediment for the *Eohaustorius* and *Ampelisca*, respectively, was greater than the acceptability criteria of 90 percent at the end of the test
- A 91.25 percent survival of amphipods in the 'reference' control sediment was greater than the acceptability criteria of 90 percent at the end of the test

- Salinity, pH, and ammonia in the overlying water were all within the tolerance limits of the test species
- The time-weighted average of daily temperature readings was within  $\pm 1^\circ\text{C}$  of the desired temperature and the instantaneous temperature was always within  $\pm 3^\circ\text{C}$  of the desired temperature
- Data used in statistical analyses and reported in Tables 3-14 and 3-15 were independently reviewed for accuracy by a second biologist

### 3.6.5 CYP1A (P4501A) Quality Control

The QC measures for the CYP1A determination included:

- Scoring of samples was performed blind (identities of samples were unknown to scorer)
- The correlation of subjectively determined CYP1A immunohistochemical staining scores with protein immunoblotting of hepatic microsomes, an independent and nonsubjective measurement of CYP1A, has been established at the laboratory in Woods Hole, Massachusetts (Woodin, *et al.*, 1997)

### 3.6.6 P450 Reporter Gene System Quality Control

*1997.* From the long-term QC chart, the mean RGS fold induction response to 1 ng/mL TCDD was  $100 \pm 30$  (Figure 3-87). The RGS fold induction responses to TCDD on all assay dates in this study are shown in Table 3-38. These values are within two standard deviations of the running mean, indicating that the tests were acceptable. In addition, the CV of all samples tested, including both sediments ( $n = 27$ ) and tissues ( $n = 13$ ), were  $< 20$  percent, indicating low between-replicate variability. The luminometer was calibrated on August 22, September 22, and October 21, 1997 and yielded linear response curves with an  $r^2 = 0.9$ , and a detection of 2 pg of luciferase.

*1998.* The RGS fold induction responses to TCDD on all assay dates in this study are shown in Table 3-38. These values are within two standard deviations of the running mean, indicating that the tests were acceptable. In addition, the percent CV of all samples tested, including both sediments ( $n = 27$ ) and tissues ( $n = 12$ ), were  $< 20$  percent, indicating low between-replicate variability. The luminometer was calibrated on September 17, 1998 as well as January 29, 1999 and yielded linear response curves with an  $r^2 = 0.9$ , and a detection of 2 pg of luciferase.

### 3.6.7 Marine Heterotrophs and Crude Oil Emulsifier Quality Control

The QC measures for the enumeration of marine heterotrophs and crude oil emulsifiers included dilution duplicates of each sediment sample. Agreement between the duplicates for the marine heterotrophs was very good, indicating fairly homogeneous samples. The mean relative percent difference (RPD) for the marine heterotrophs counts within a plate (an individual plate was counted at three and five weeks) was 31 percent, while the mean RPD for the duplicate plate analysis per sample was 34 percent. The counts for the hydrocarbon degrader populations were low or barely detected among all samples. Where populations were detected on duplicate plates, the RPD was 51 percent.

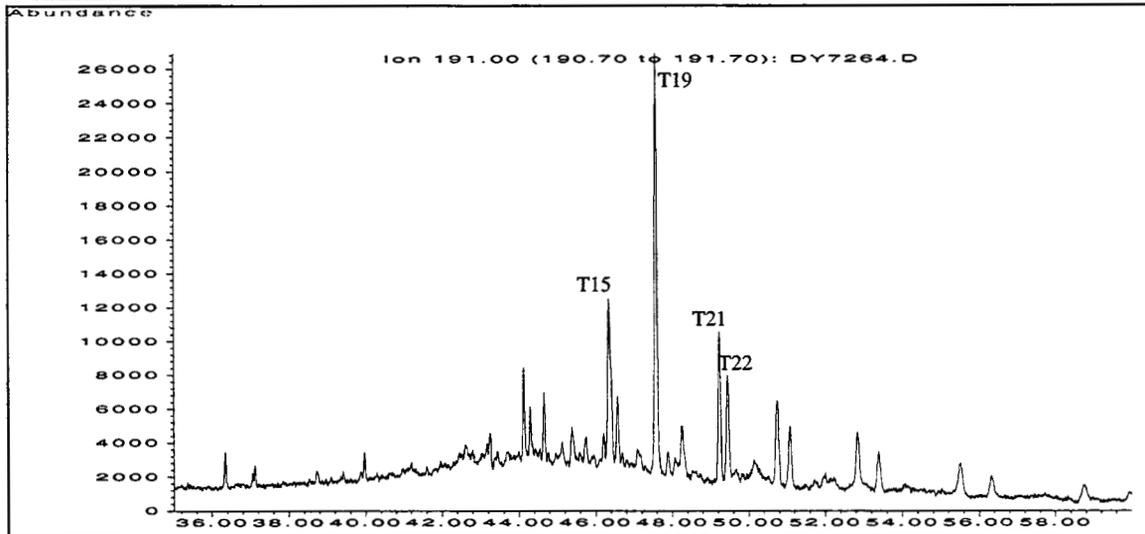
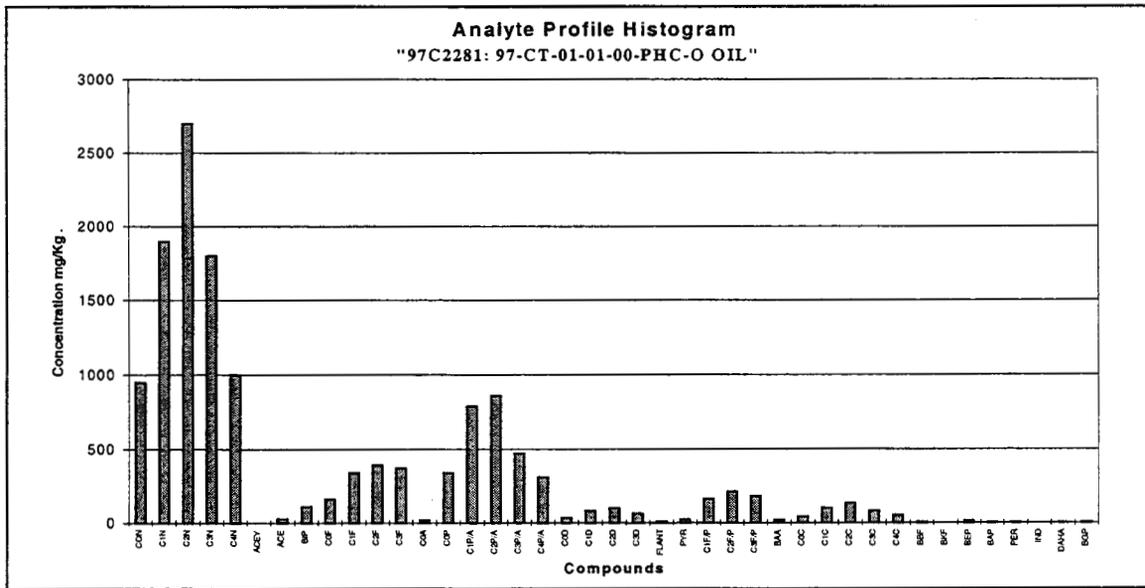
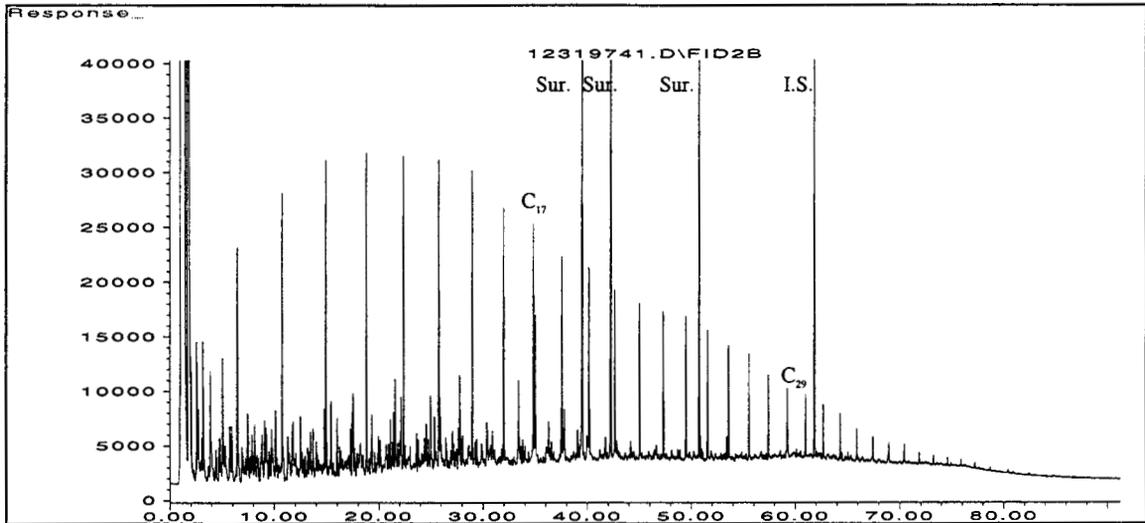
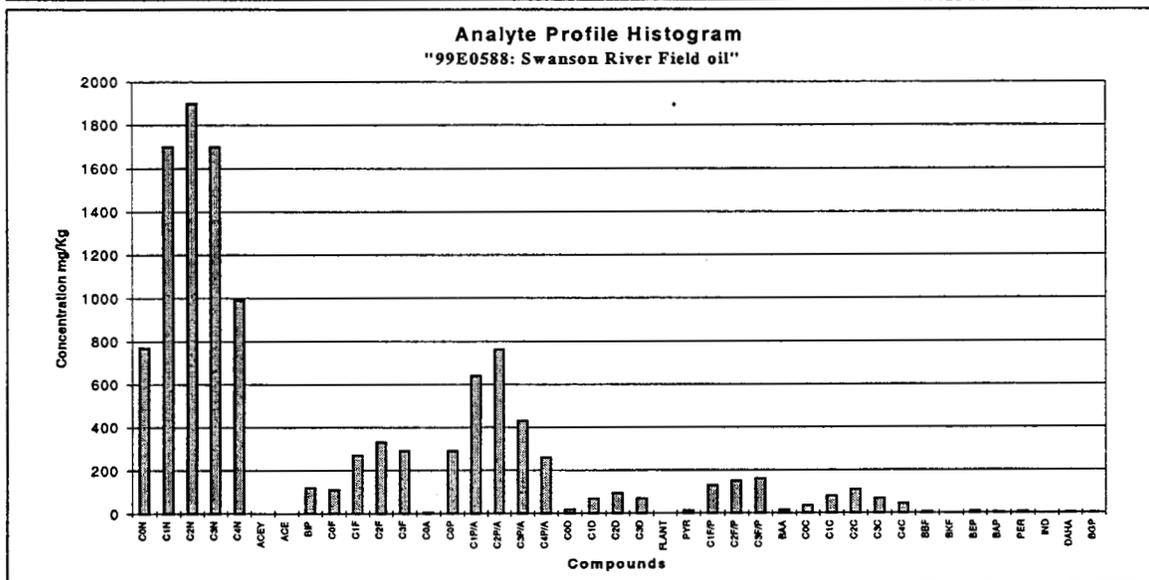
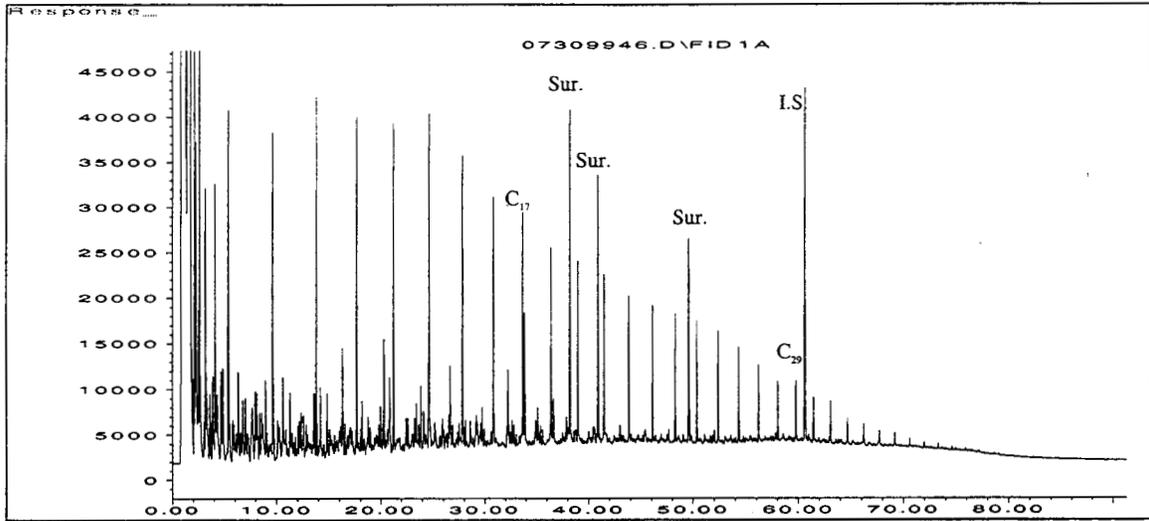


Figure 3-1: Cook Inlet Crude Oil Source Sample Results: GC/FID chromatogram (top), PAH distribution plot (middle), Triterpane extracted ion chromatogram (bottom).



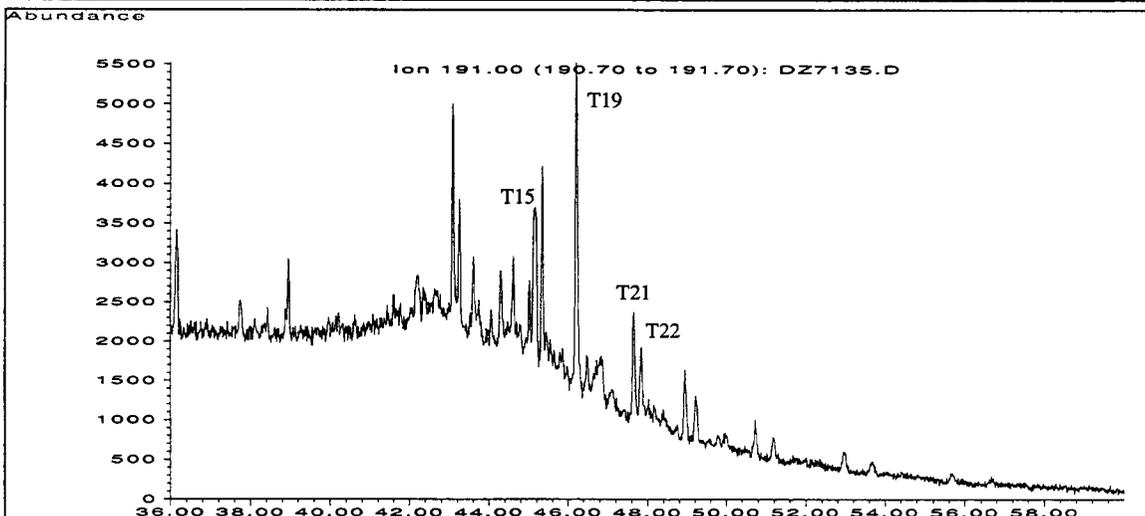
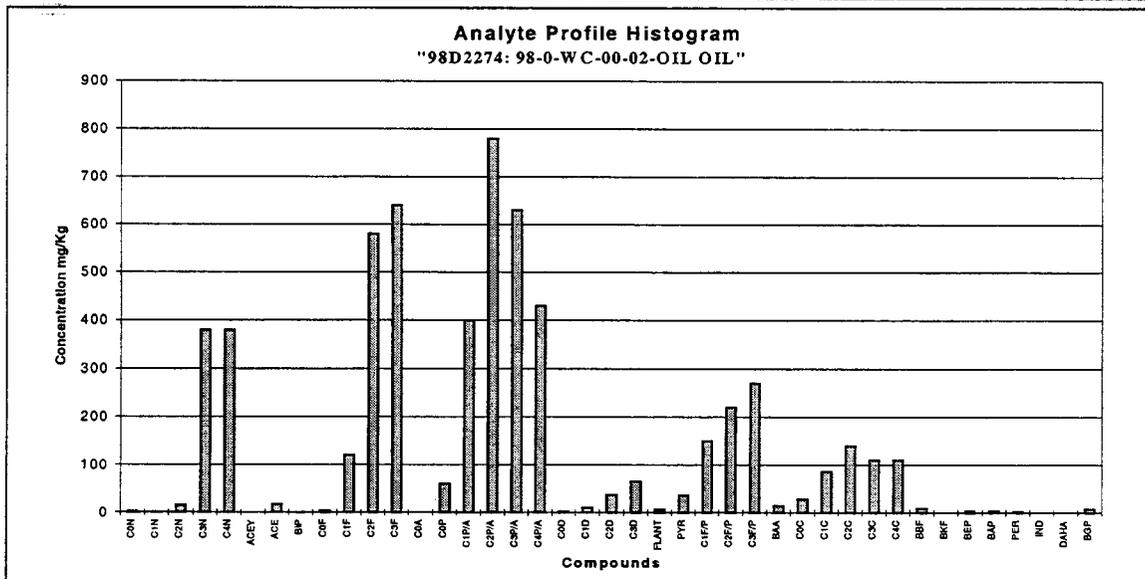
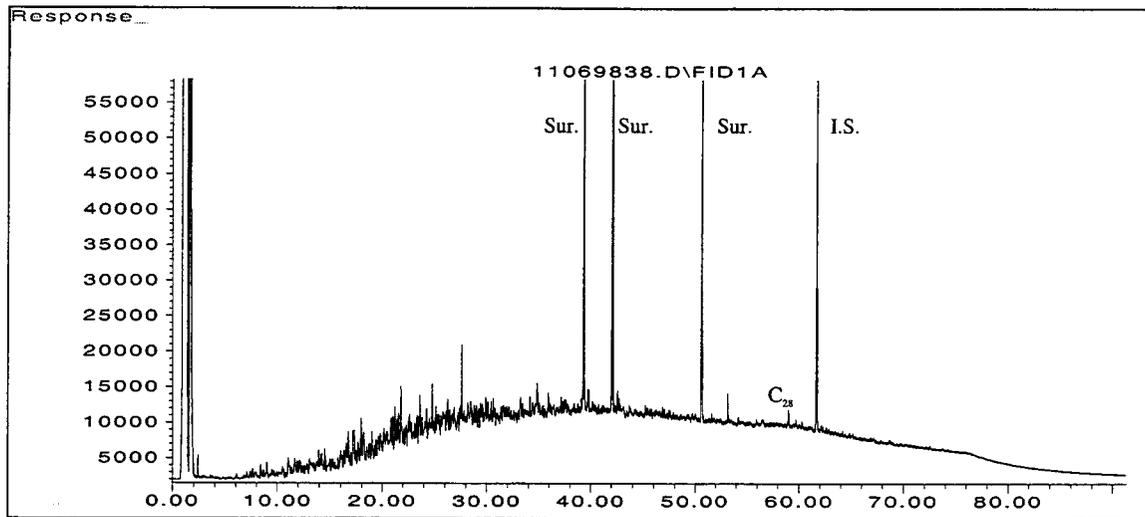
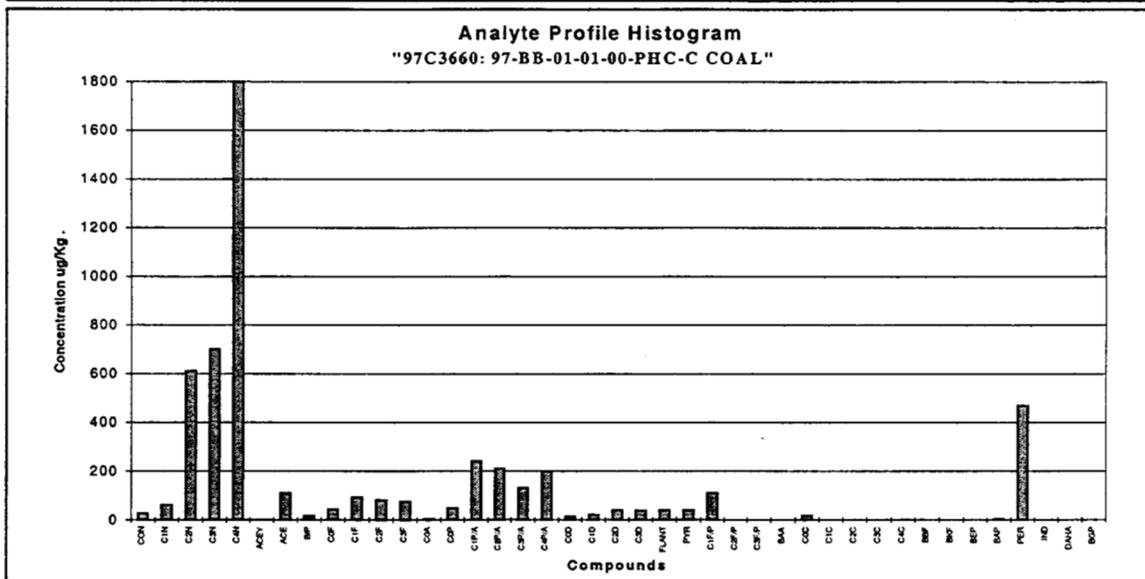
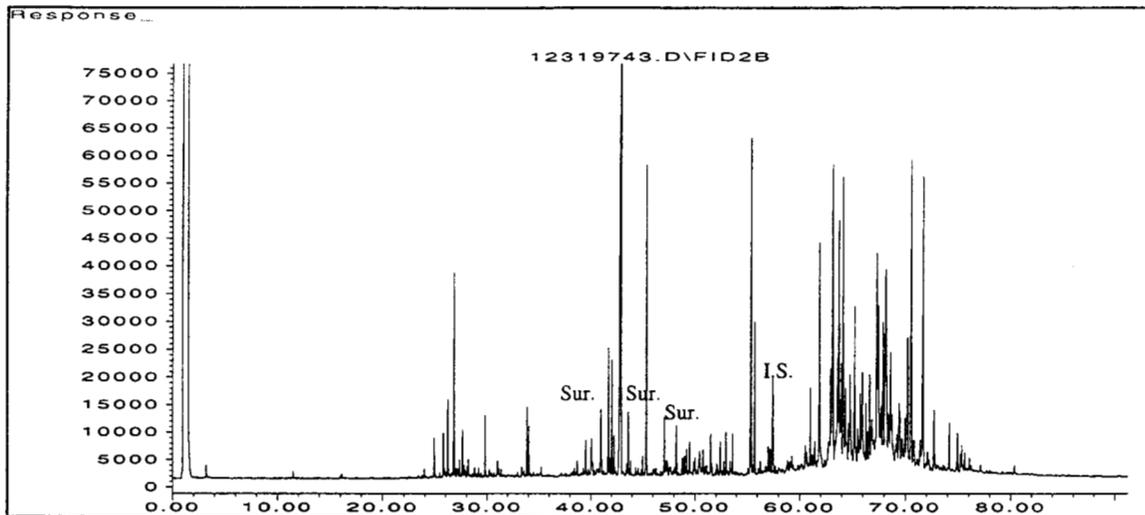


Figure 3-3: Well Creek Oil Seep Source Sample Results: GC/FID chromatogram (top), PAH distribution plot (middle), Triterpane extracted ion chromatogram (bottom).



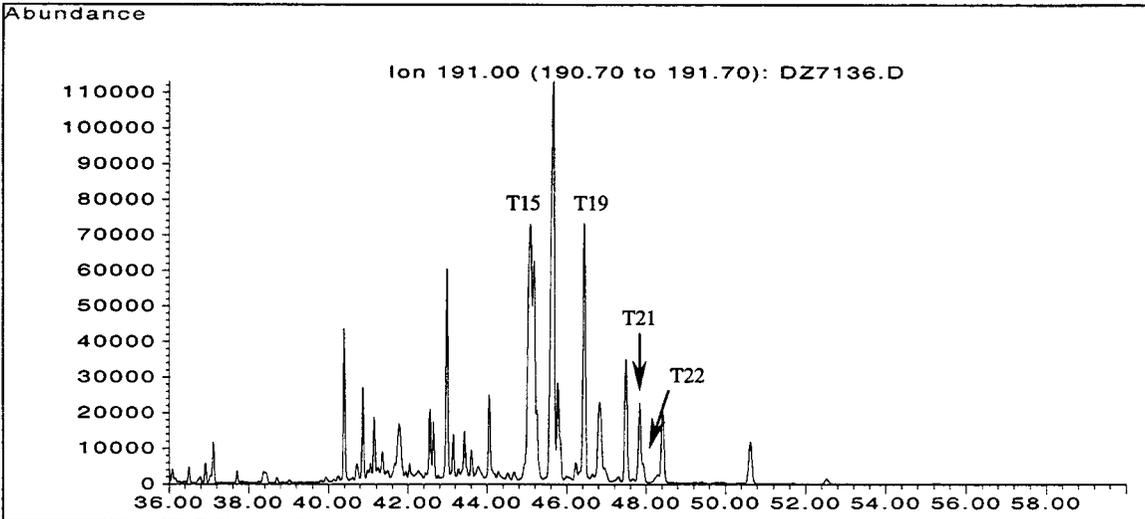
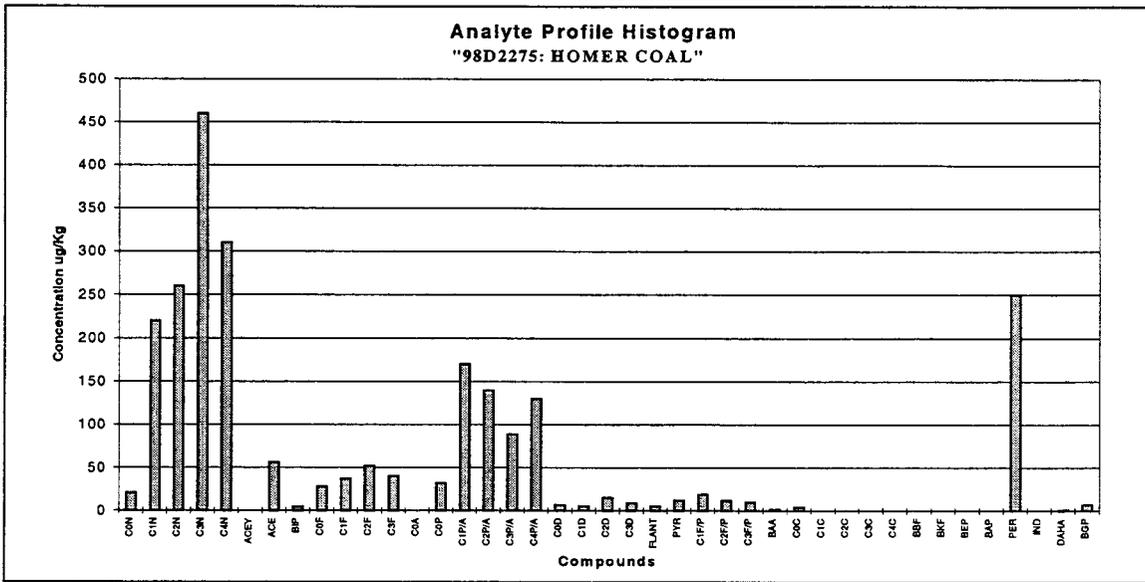
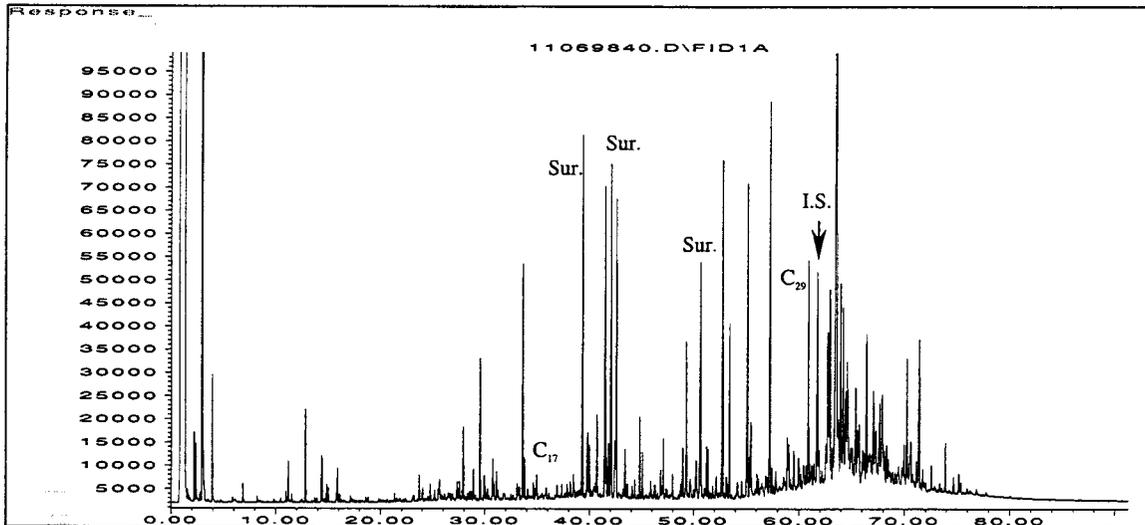


Figure 3-5: Homer Coal Bay Source Sample Results: GC/FID chromatogram (top), PAH distribution plot (middle), Triterpane extracted ion chromatogram (bottom).



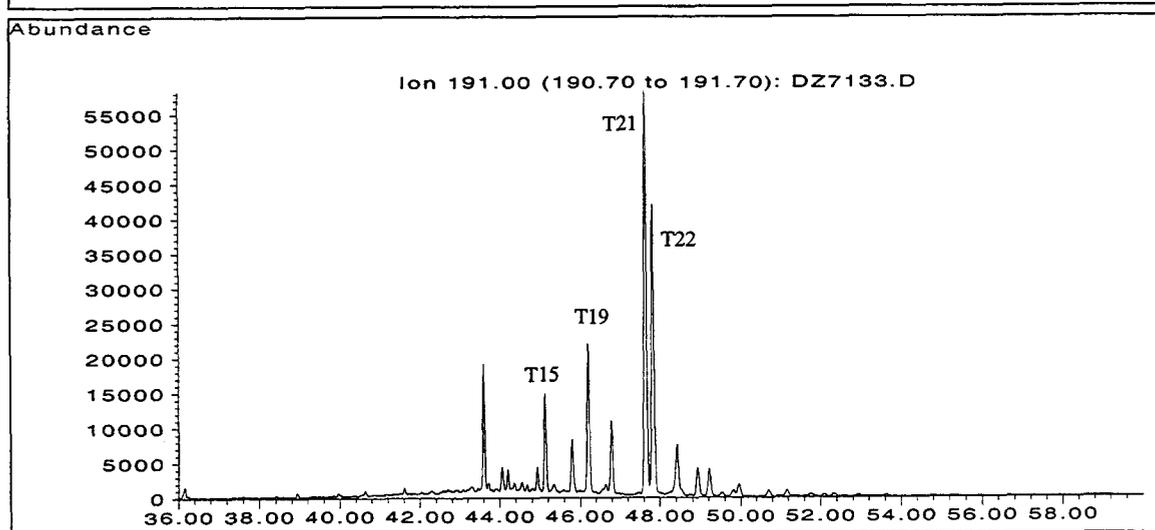
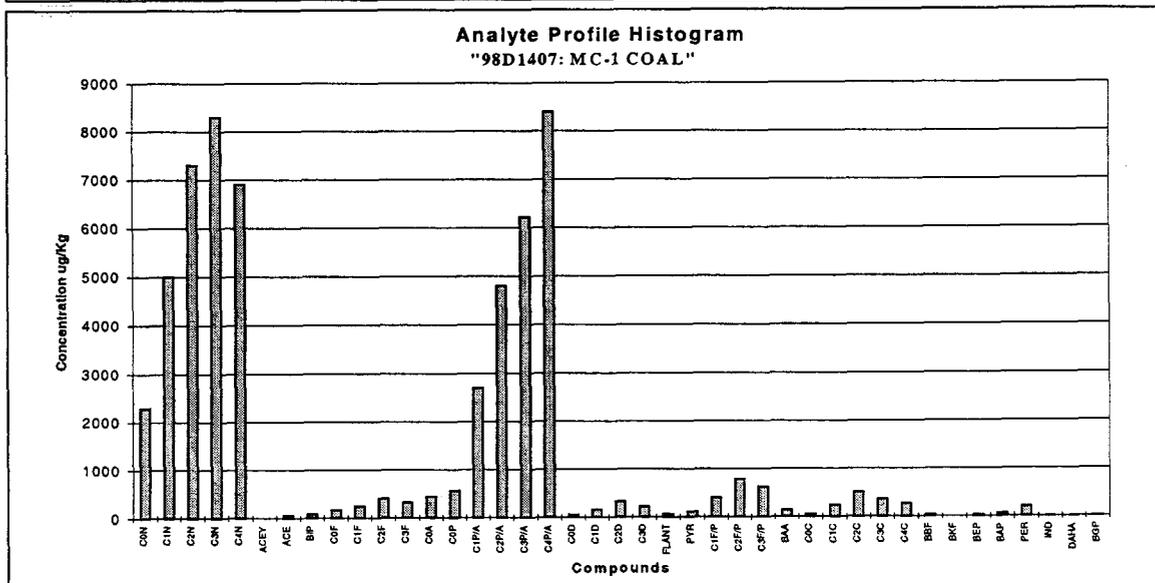
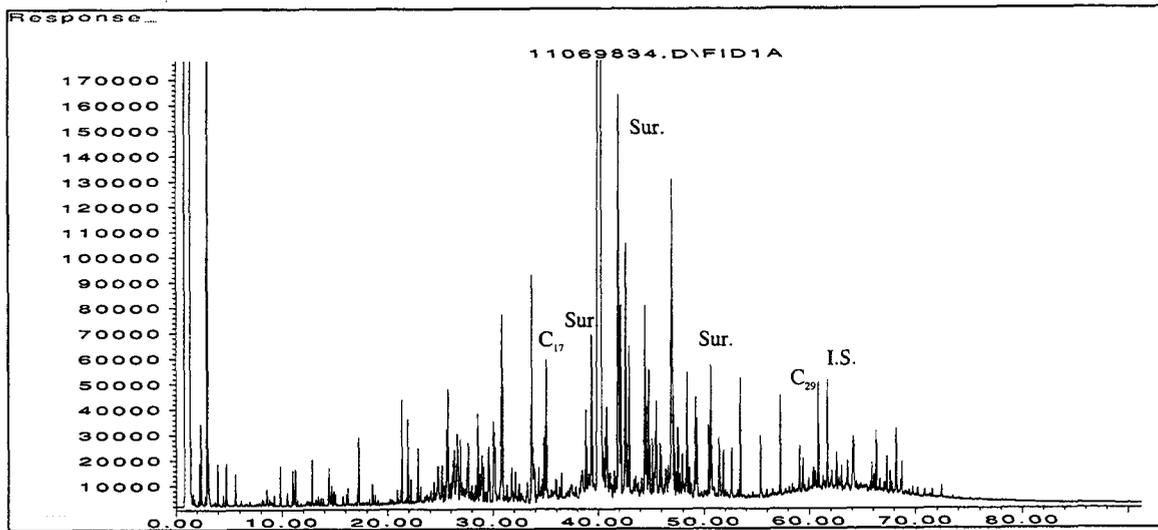


Figure 3-7: Matanuska Coal Source Sample Results: GC/FID chromatogram (top), PAH distribution plot (middle), Triterpane extracted ion chromatogram (bottom).

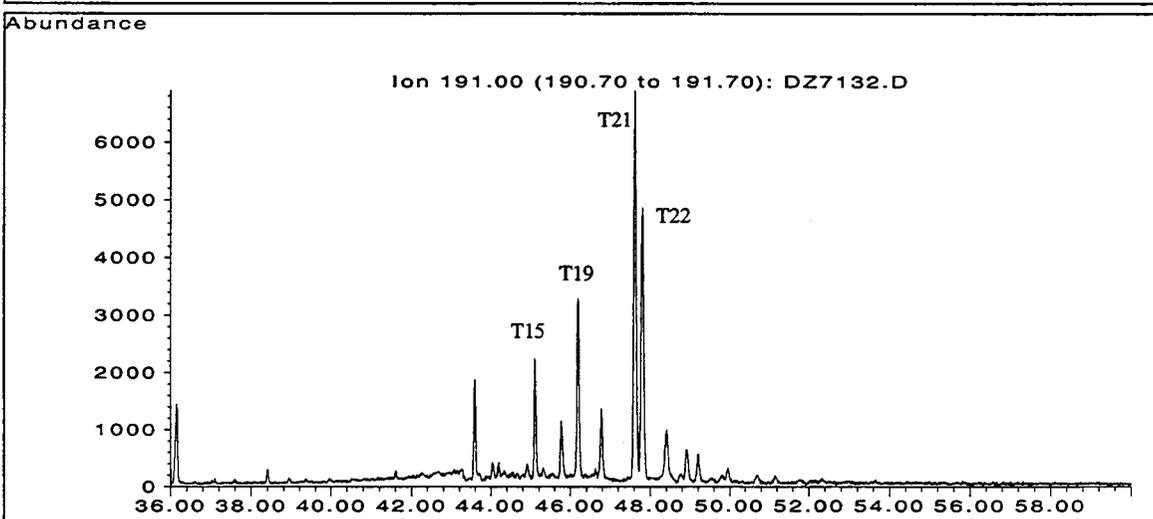
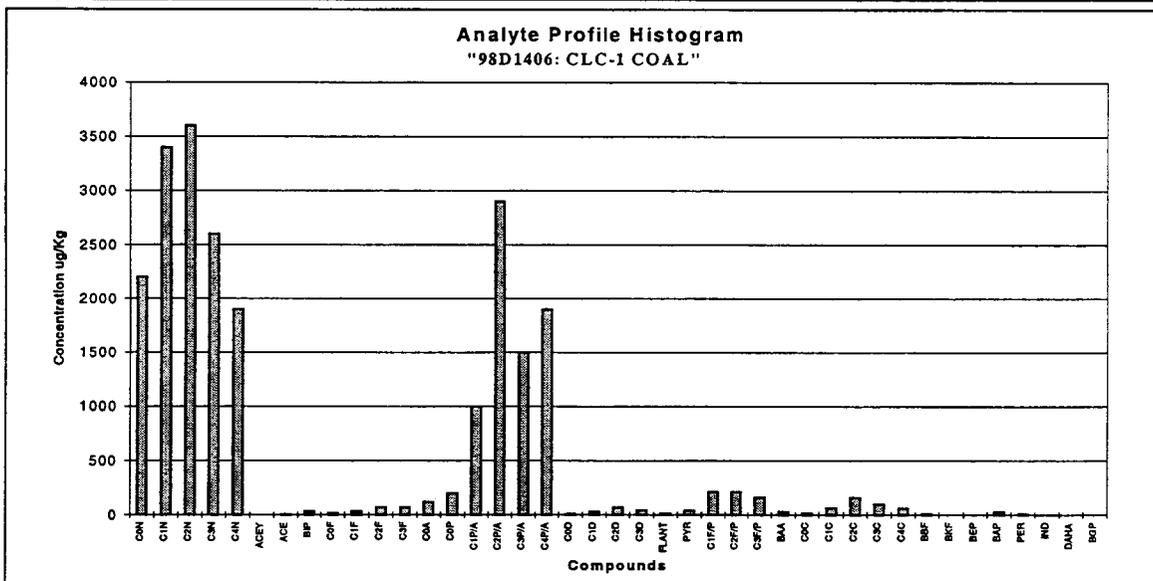
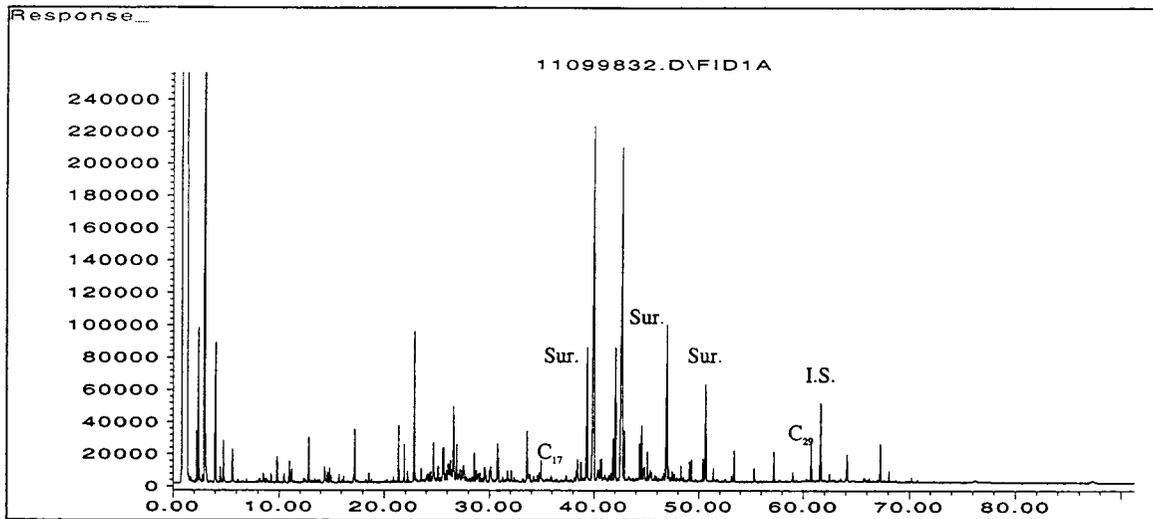


Figure 3-8: Coyote Lake Coal Source Sample Results: GC/FID chromatogram (top), PAH distribution plot (middle), Triterpane extracted ion chromatogram (bottom).

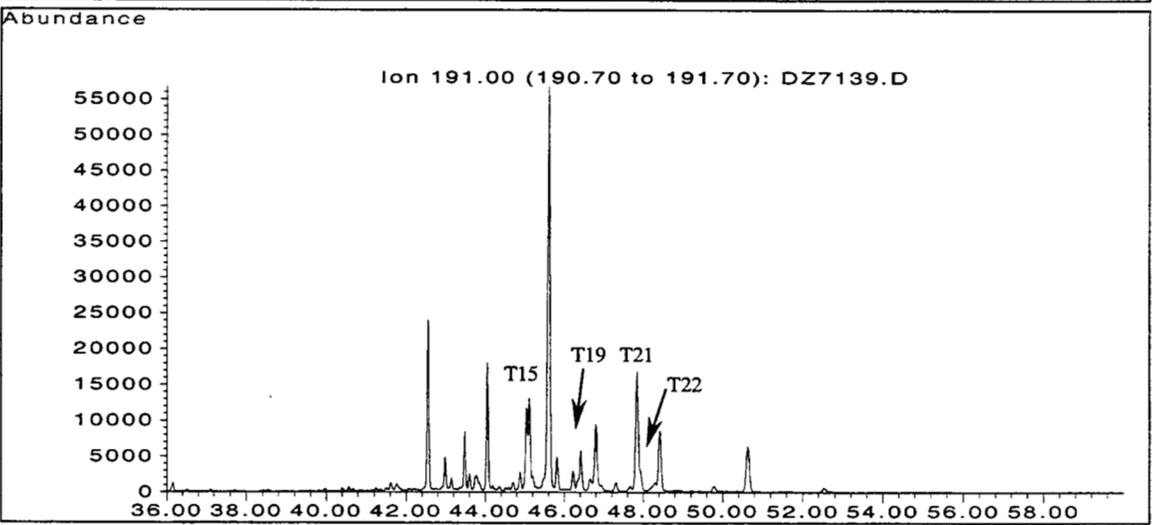
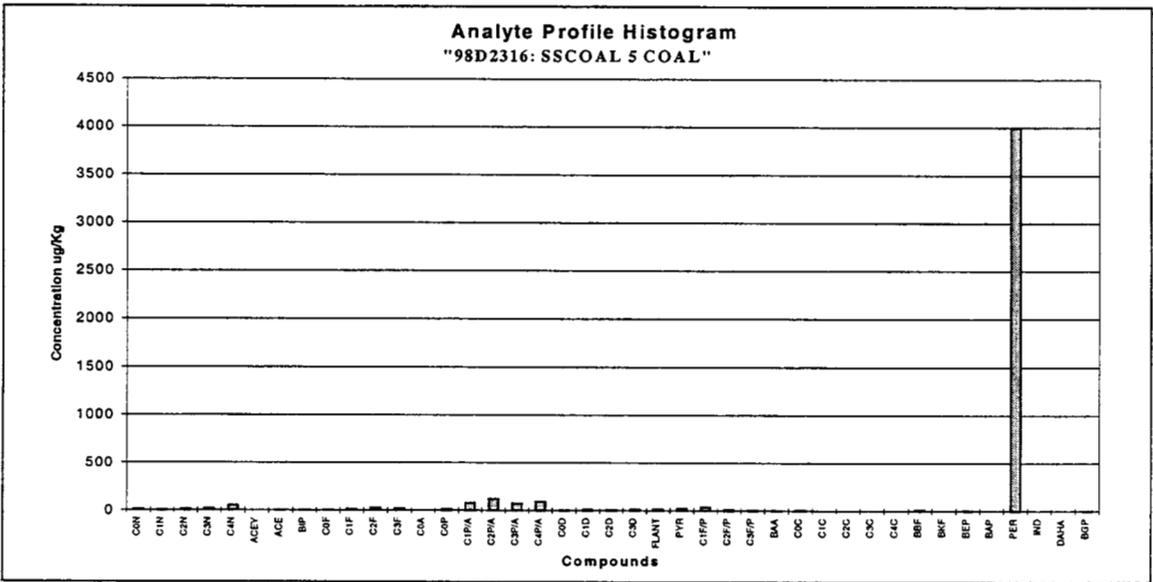
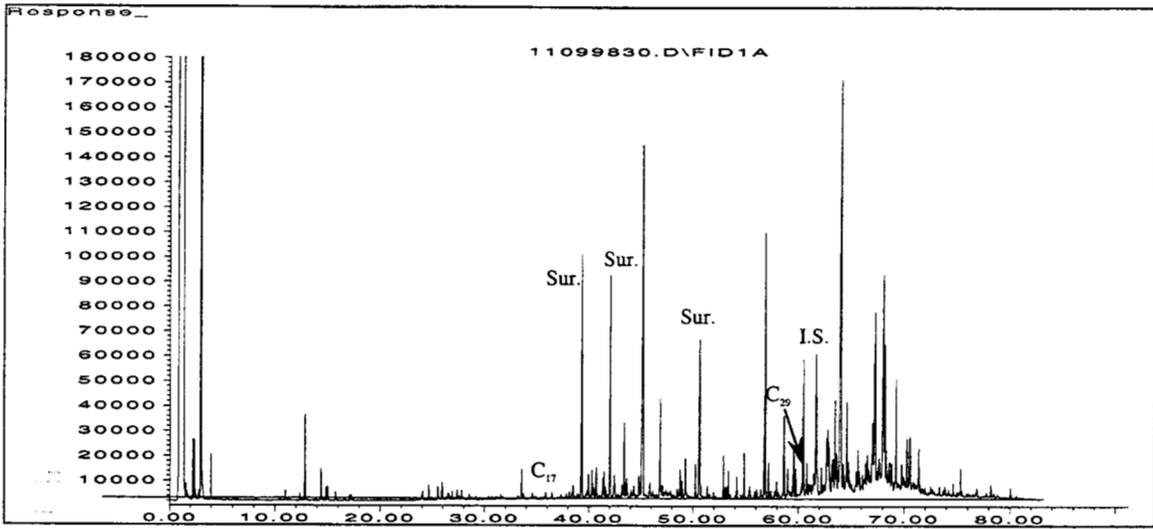


Figure 3-9: Beluga Coal Source Sample Results: GC/FID chromatogram (top), PAH distribution plot (middle), Triterpane extracted ion chromatogram (bottom).

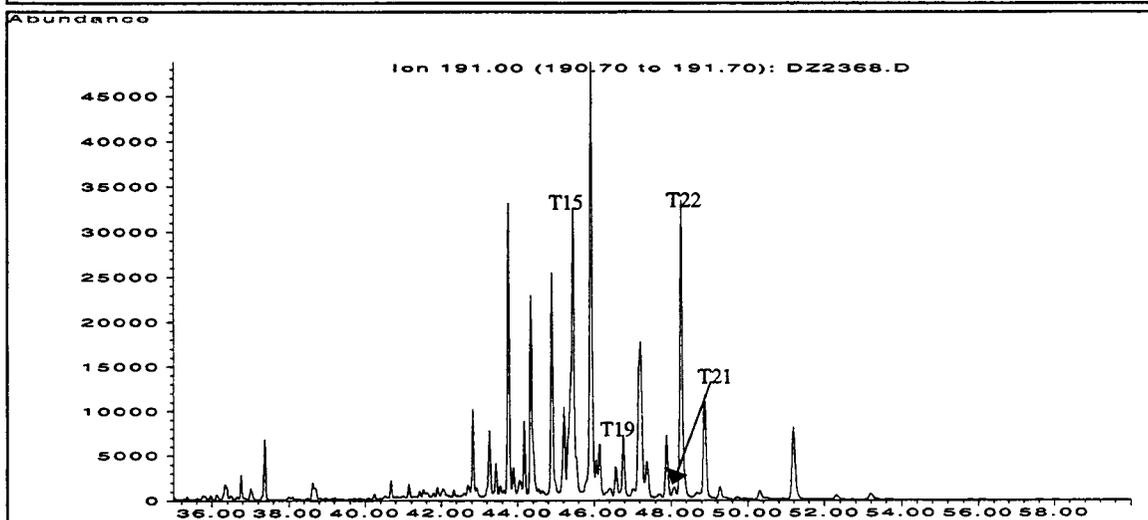
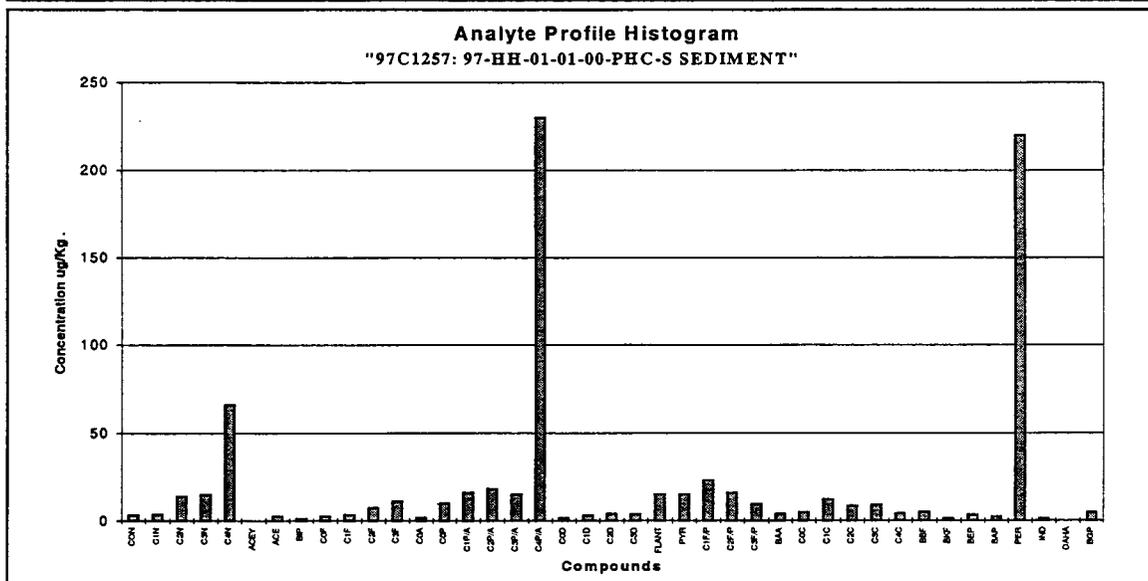
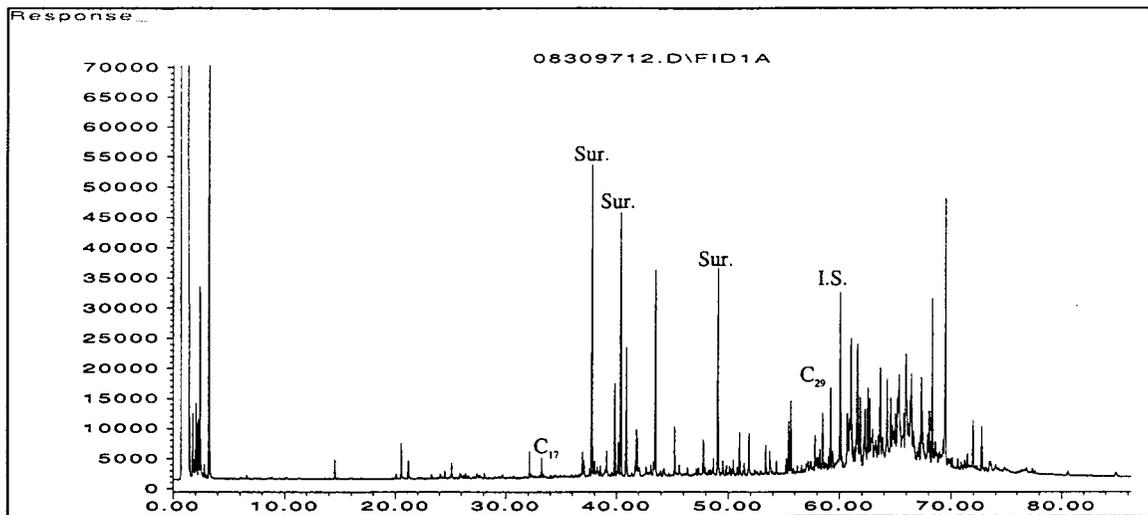


Figure 3-10: Homer Harbor Sediments 0-2 cm Depth Source Sample Results: GC/FID chromatogram (top), PAH distribution plot (middle), Triterpane ion chromatogram (bottom).



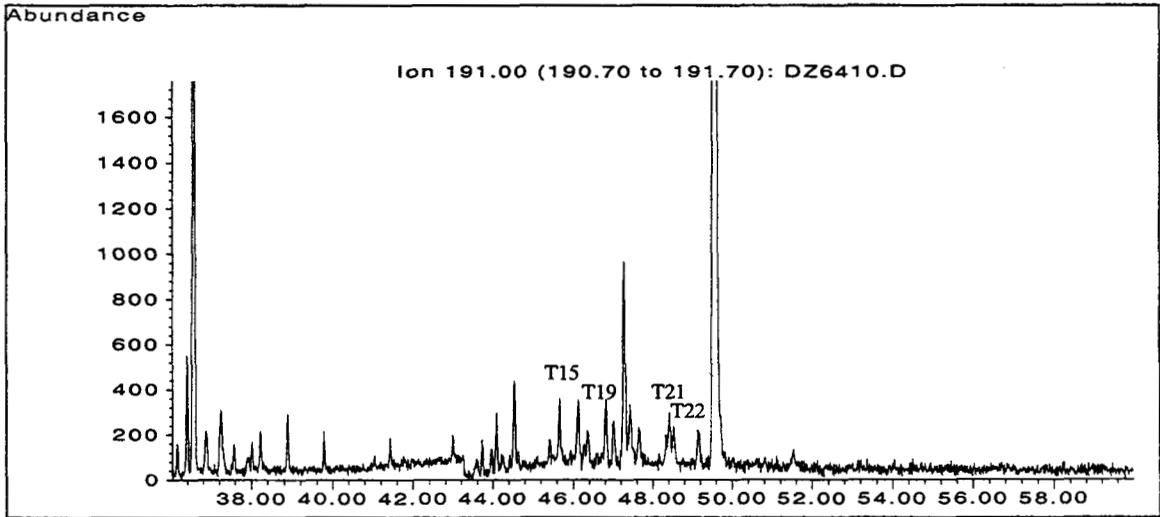
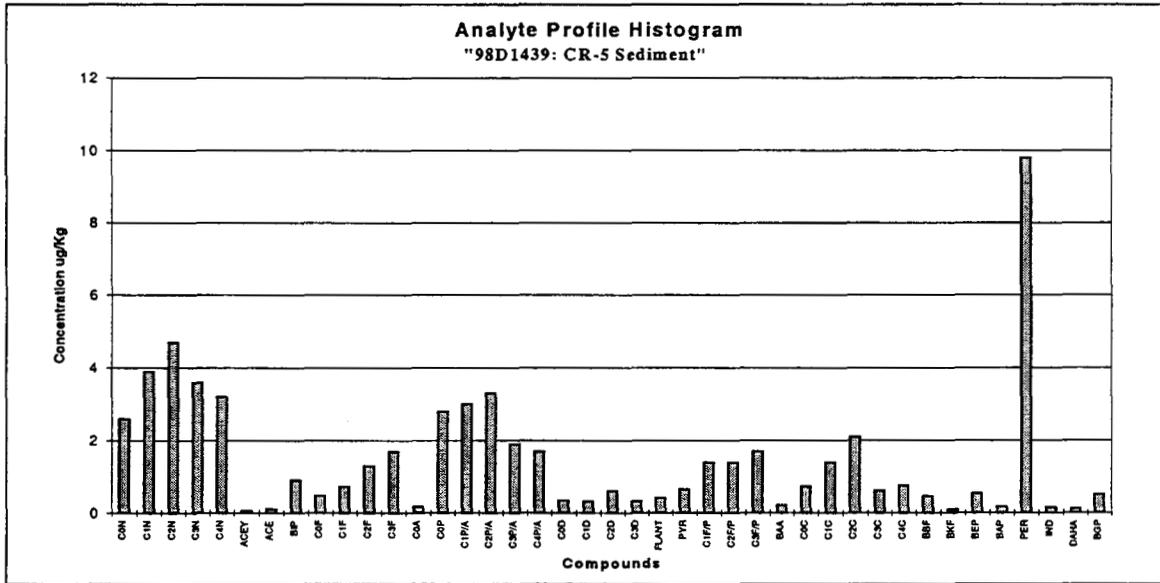
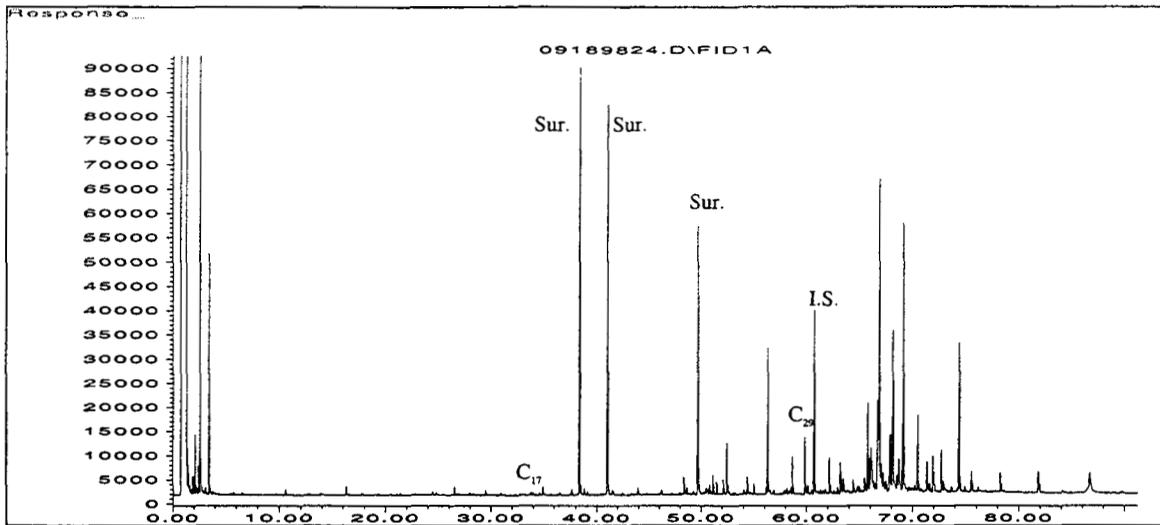


Figure 3-12: 1998 Copper River Sediment Source Sample Results: GC/FID chromatogram (top), PAH distribution plot (middle), Triterpane extracted ion chromatogram (bottom).

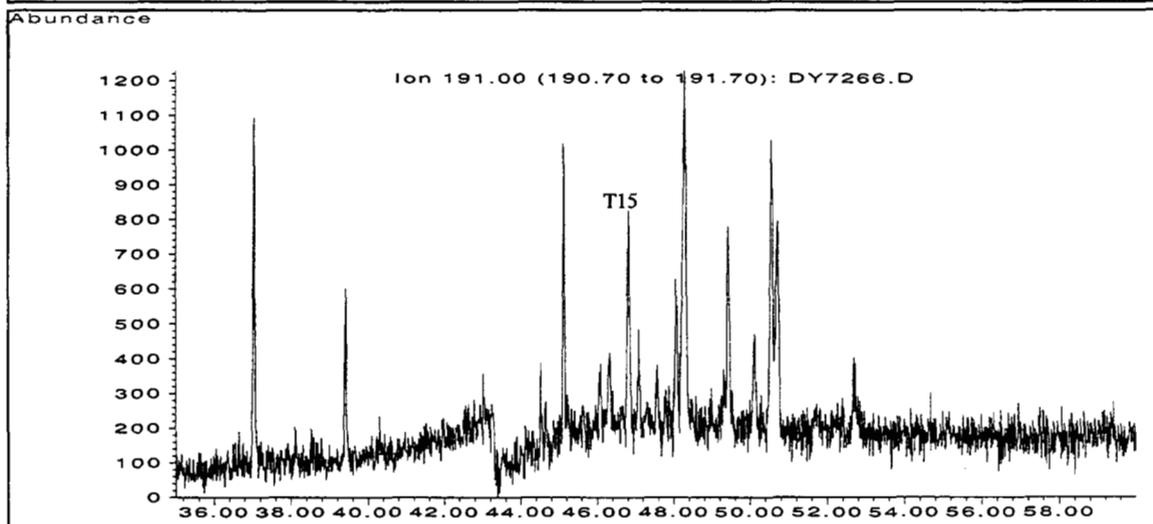
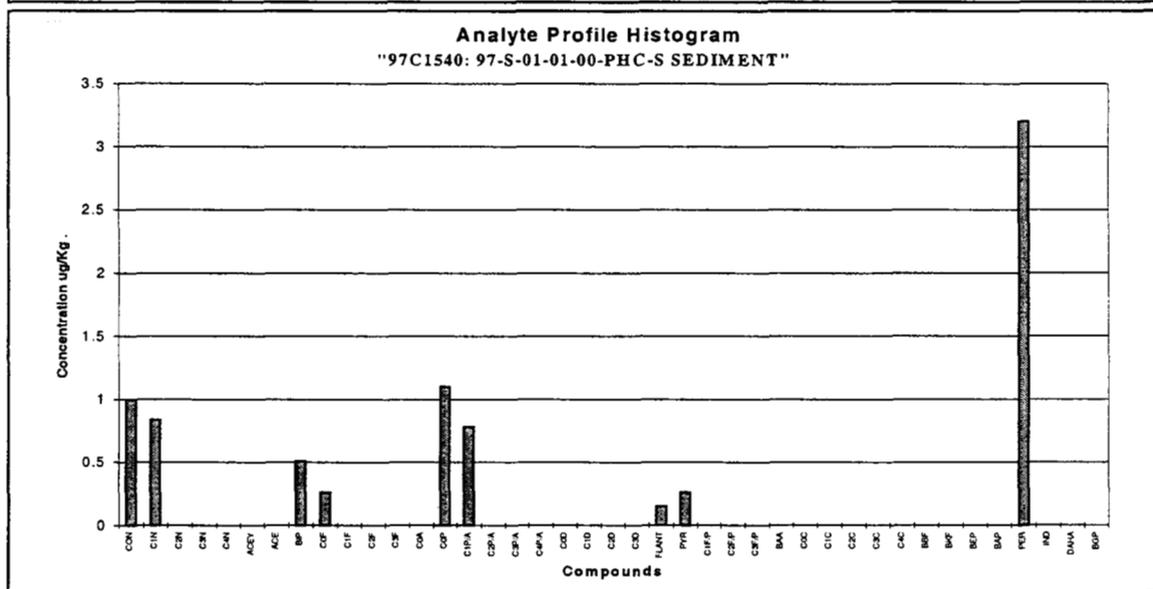
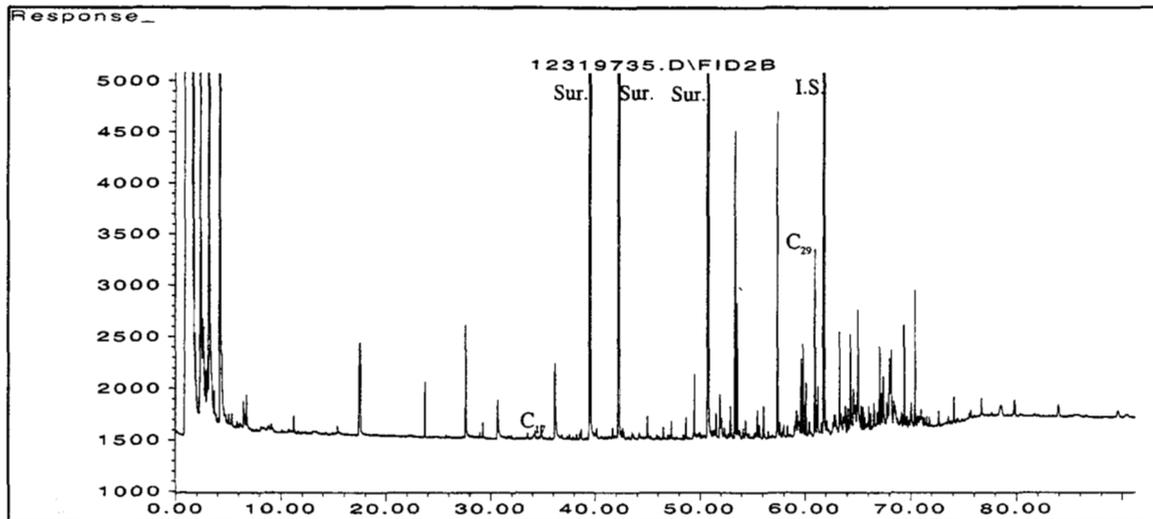


Figure 3-13: Susitna River Sediments 0-2 cm Depth Source Sample Results: GC/FID chromatogram (top), PAH distribution plot (middle), Triterpane extracted ion chromatogram (bottom).

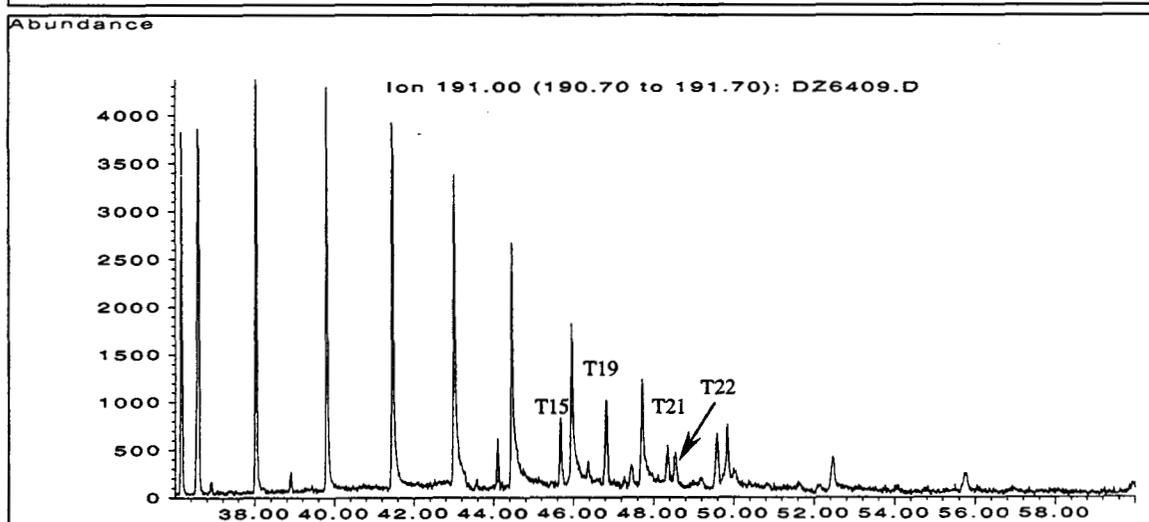
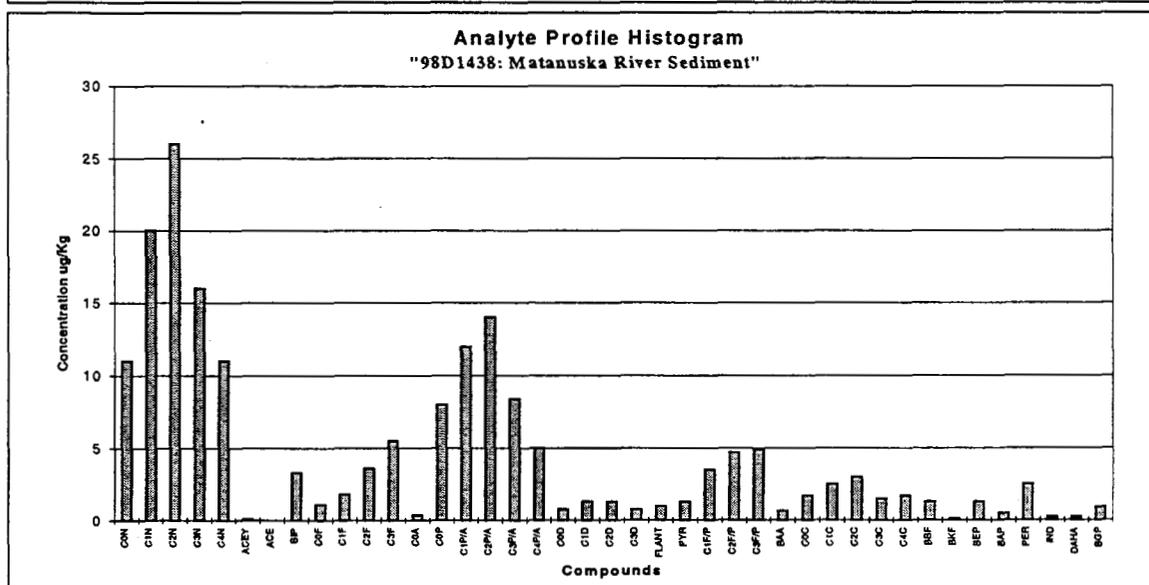
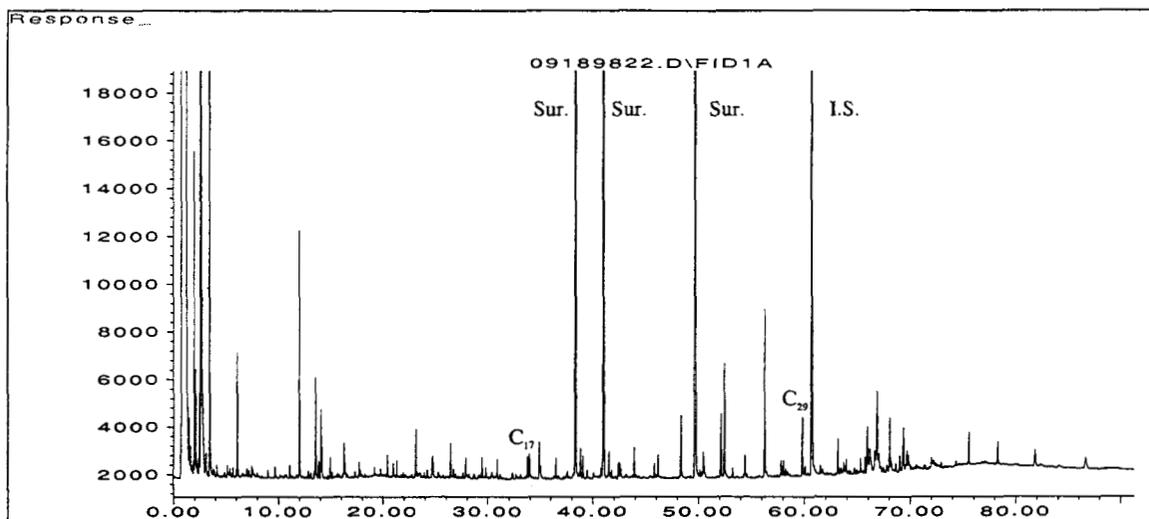


Figure 3-14: Matanuska River Sediment Source Sample Results: GC/FID chromatogram (top), PAH distribution plot (middle), Triterpane extracted ion chromatogram (bottom).



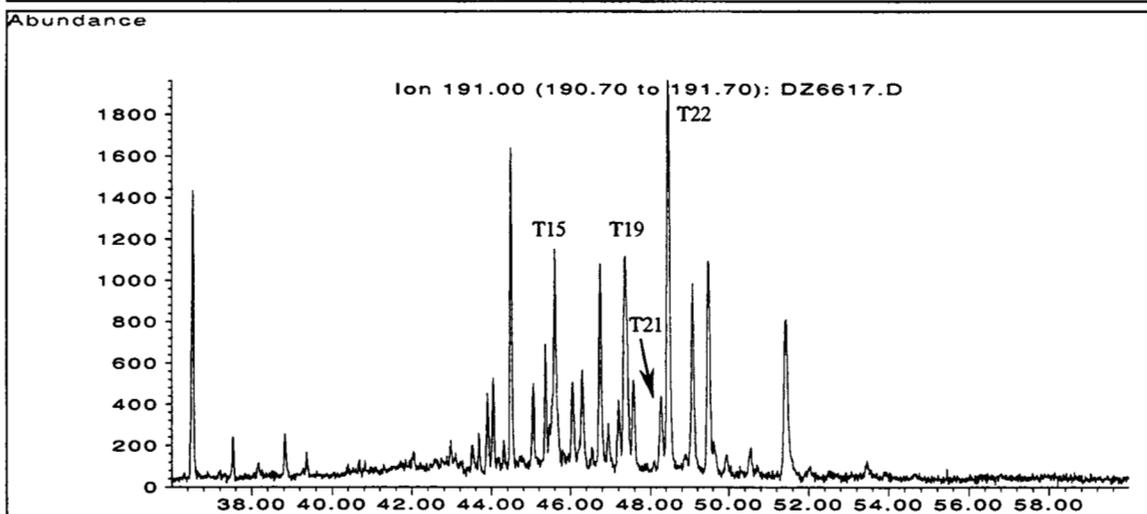
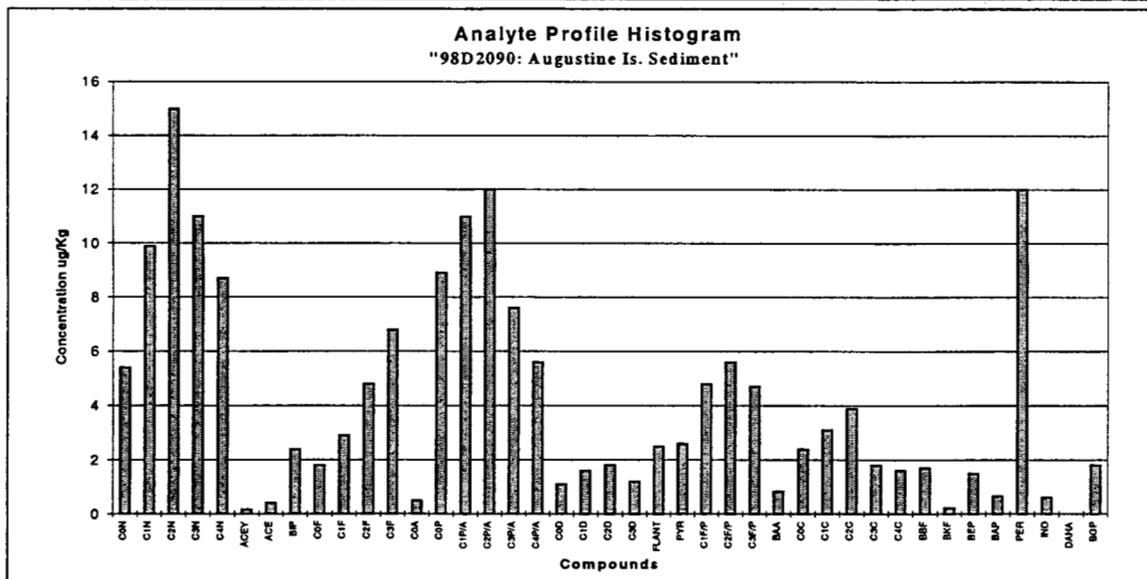
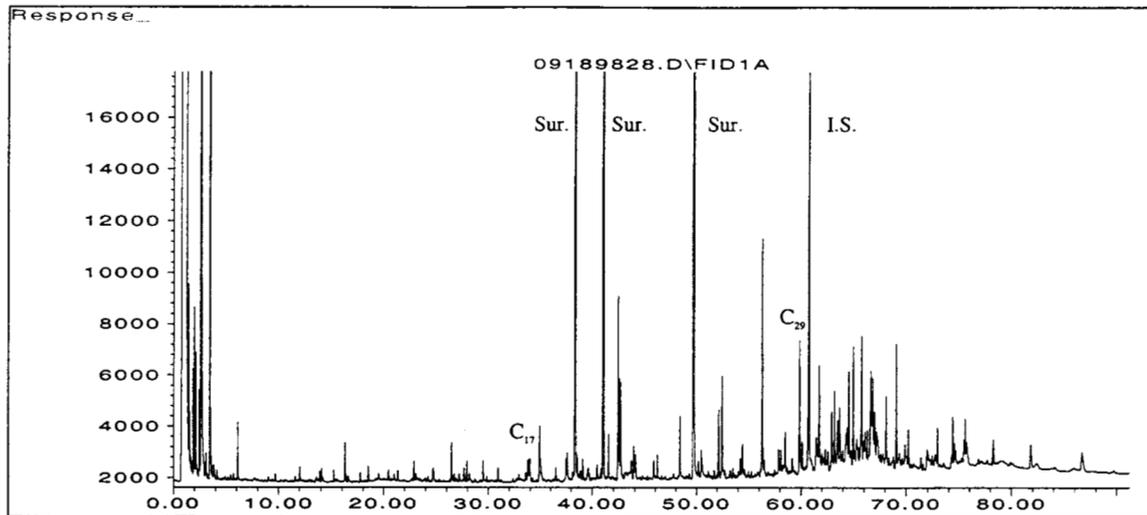


Figure 3-16: St. Augustine Island Sediment Source Sample Results: GC/FID chromatogram (top), PAH distribution plot (middle), Triterpane extracted ion chromatogram (bottom).



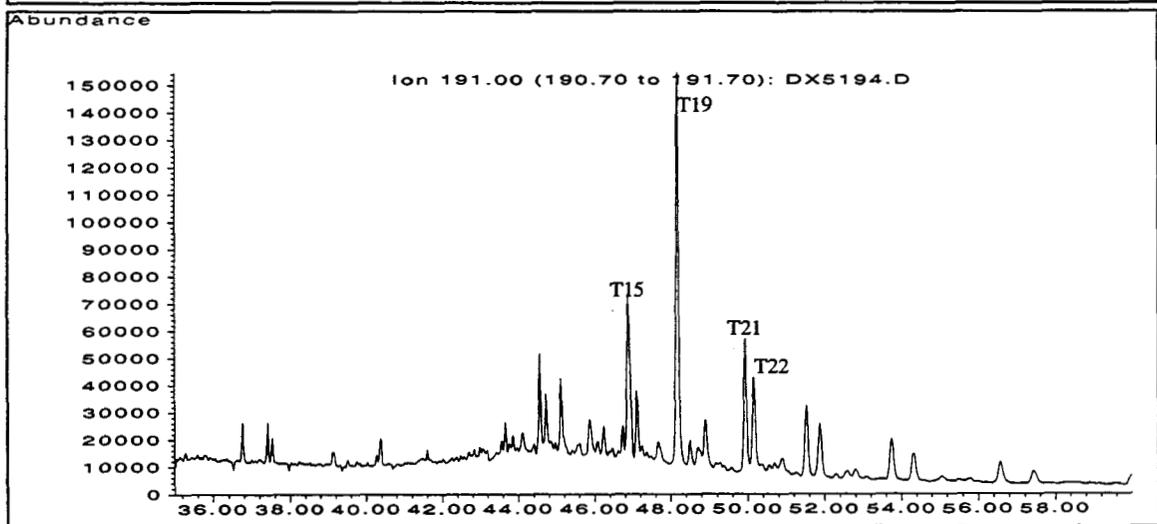
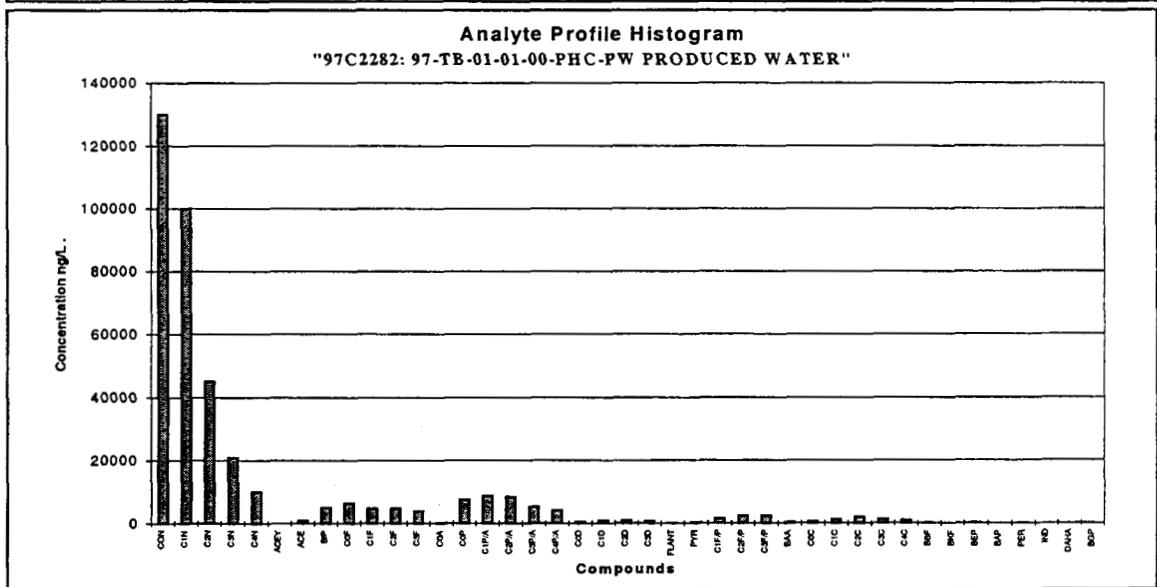
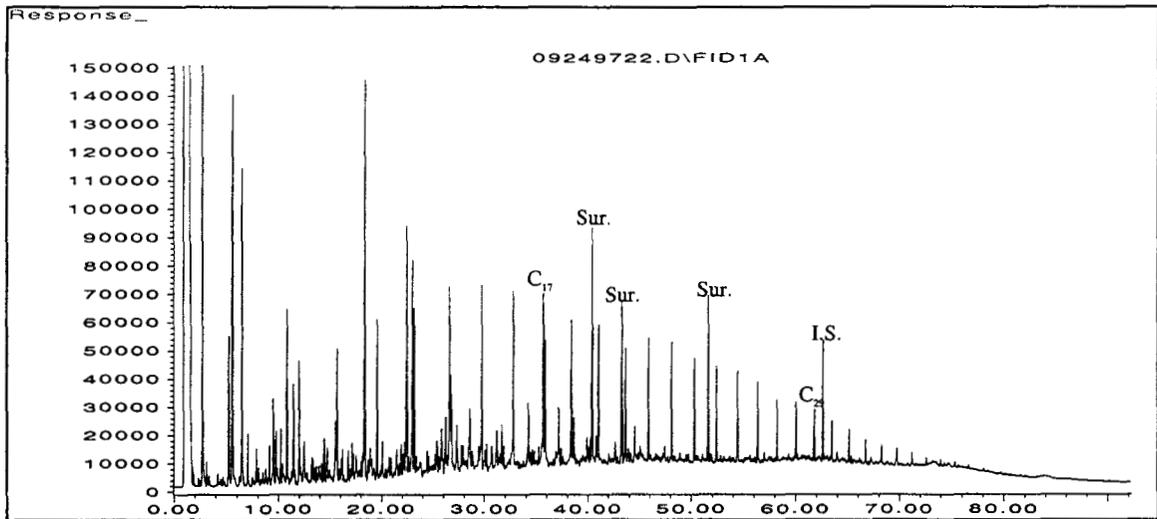


Figure 3-18: Produced Water TBPf Outfall Source Sample Results: GC/FID chromatogram (top), PAH distribution plot (middle), Triterpane extracted ion chromatogram (bottom).

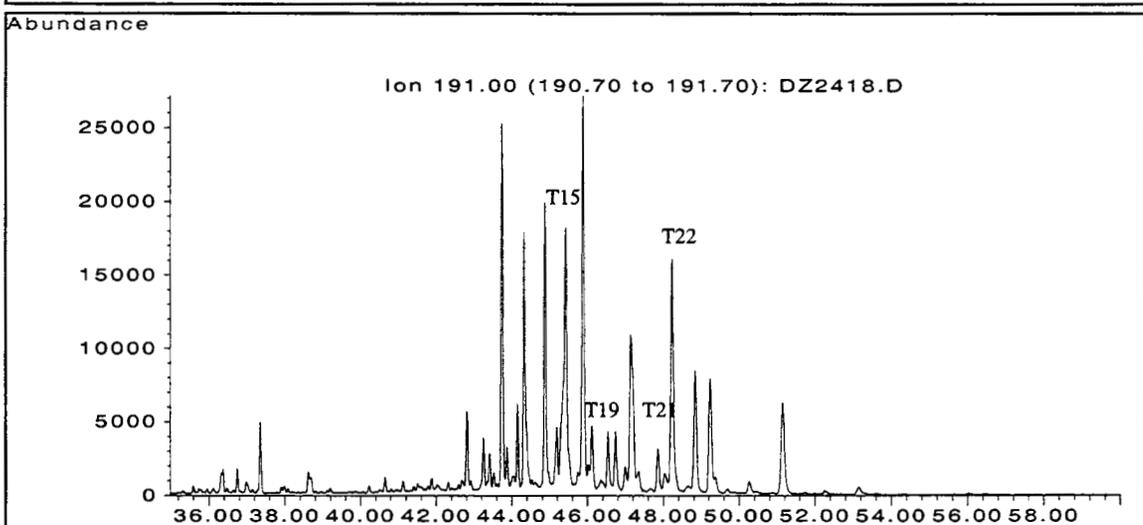
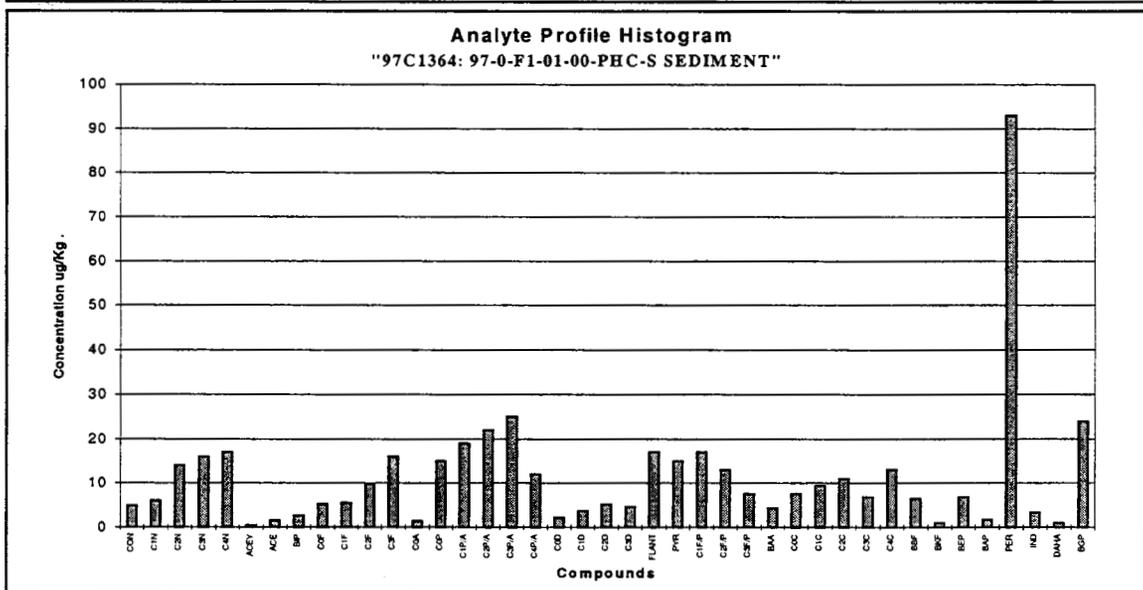
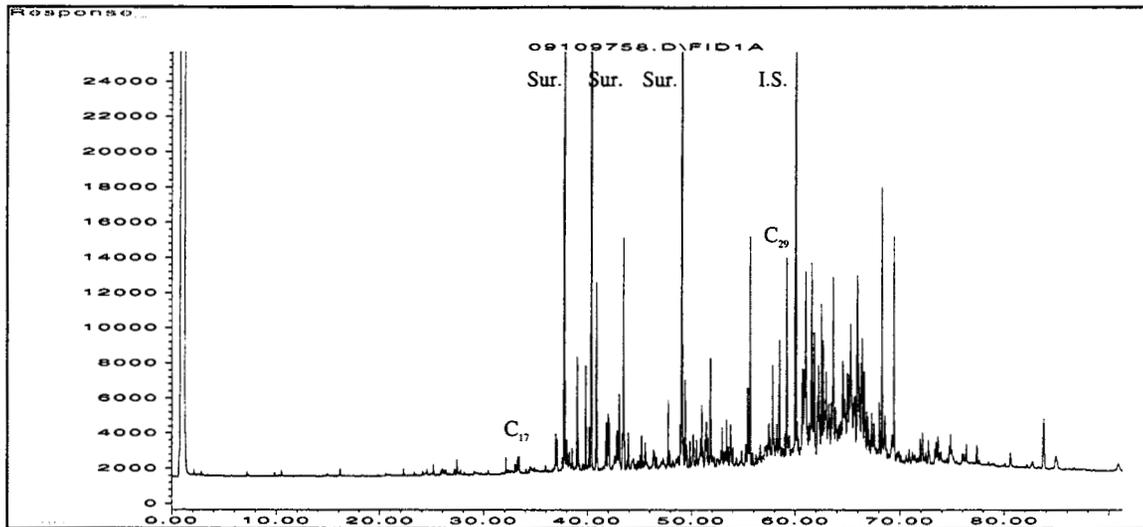


Figure 3-19: Zone 0, Station F1, Surface Sediment Sample 97-0-F1-01-00-PHC-S (rep 01) Results: GC/FID chromatogram (top), PAH distribution plot (middle), Triterpane extracted ion chromatogram (bottom).

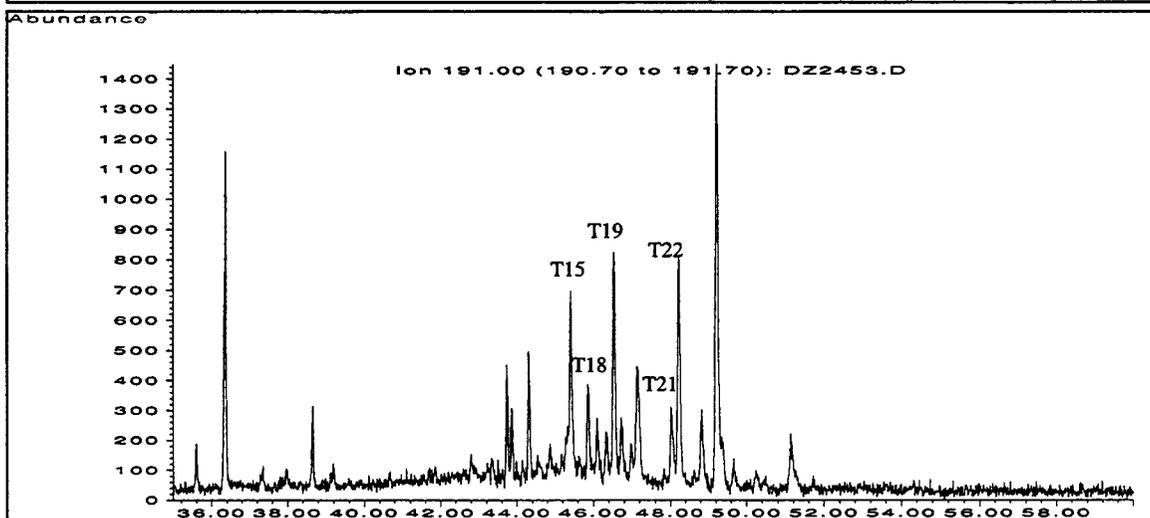
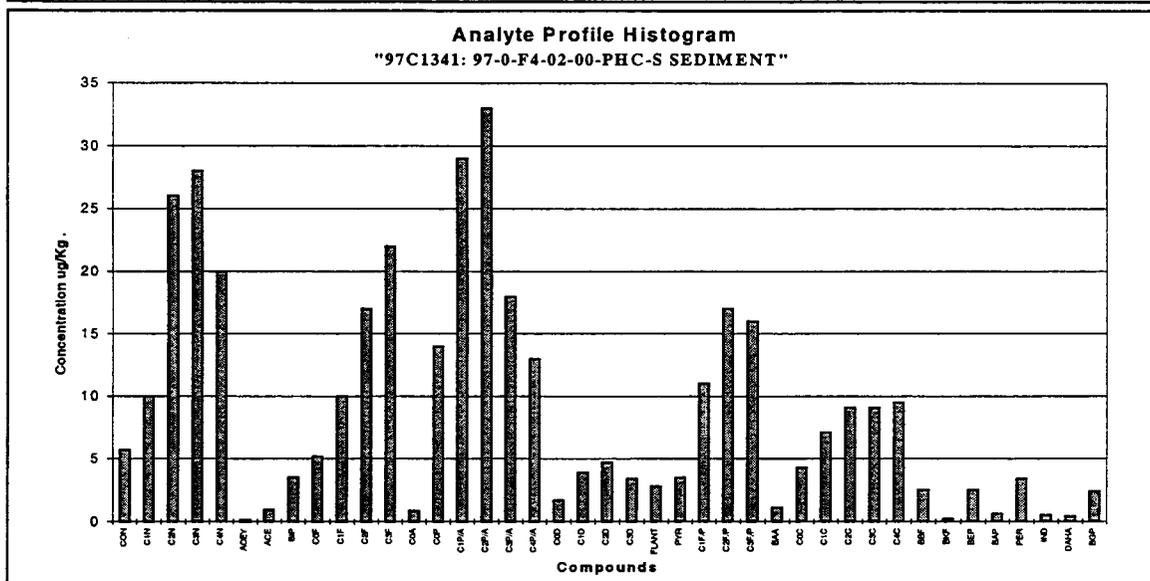
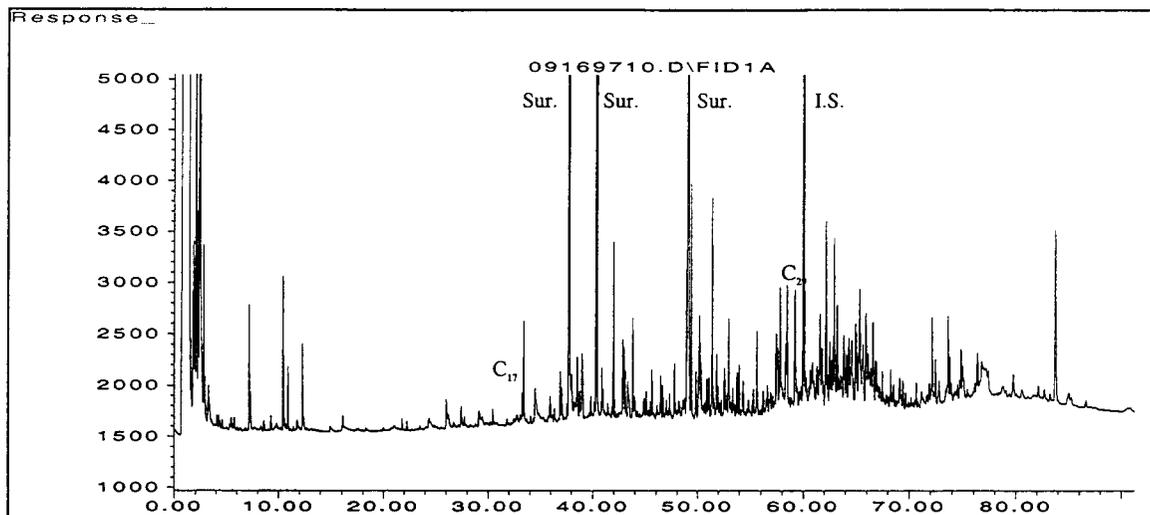


Figure 3-20: Zone 0, Station F4, Surface Sediment Sample 97-0-F4-02-00-PHC-S (rep 02) Results: GC/FID chromatogram (top), PAH distribution plot (middle), Triterpane extracted ion chromatogram (bottom).

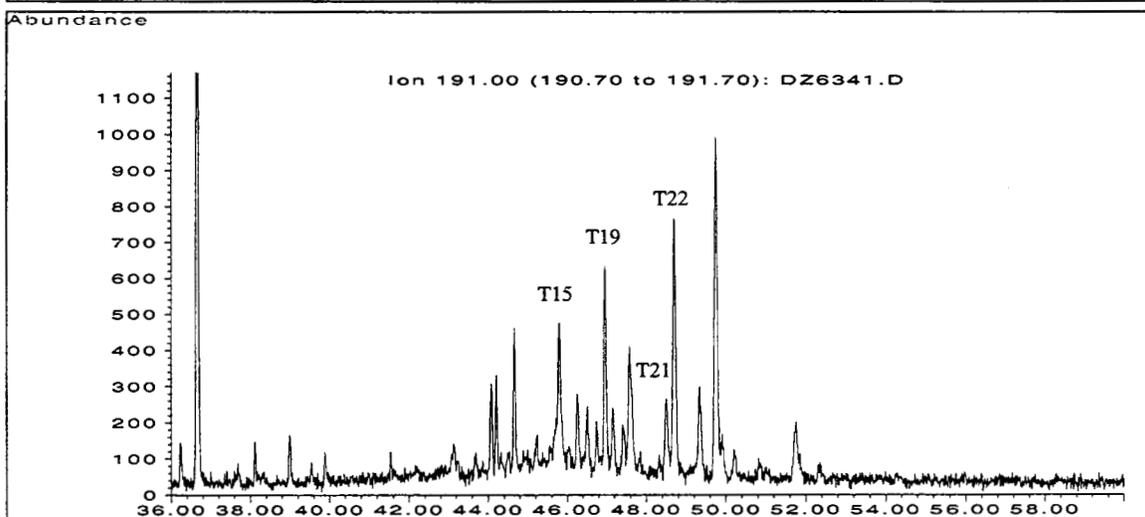
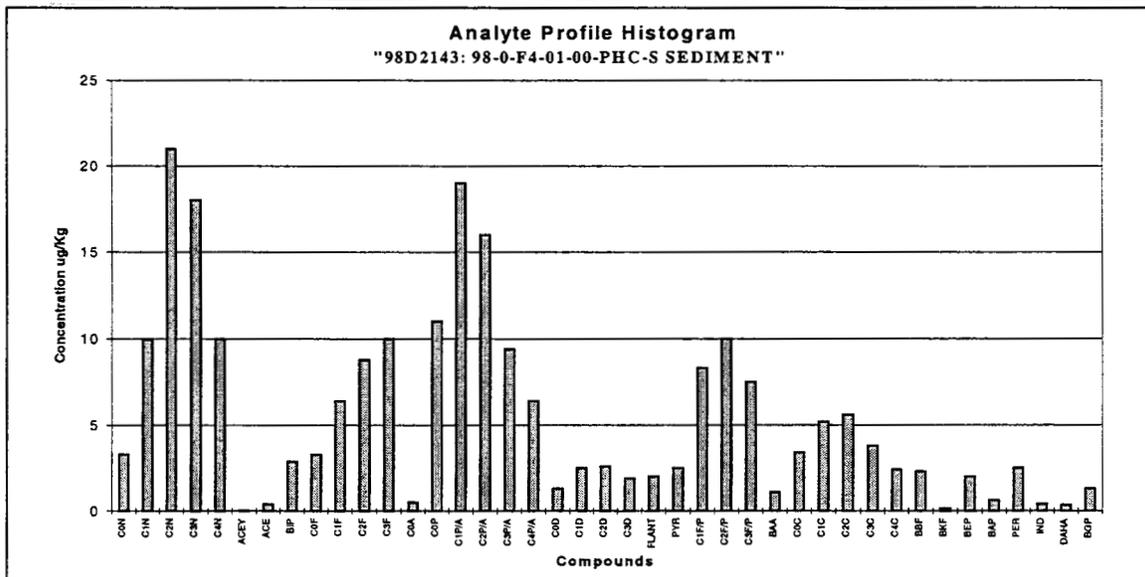
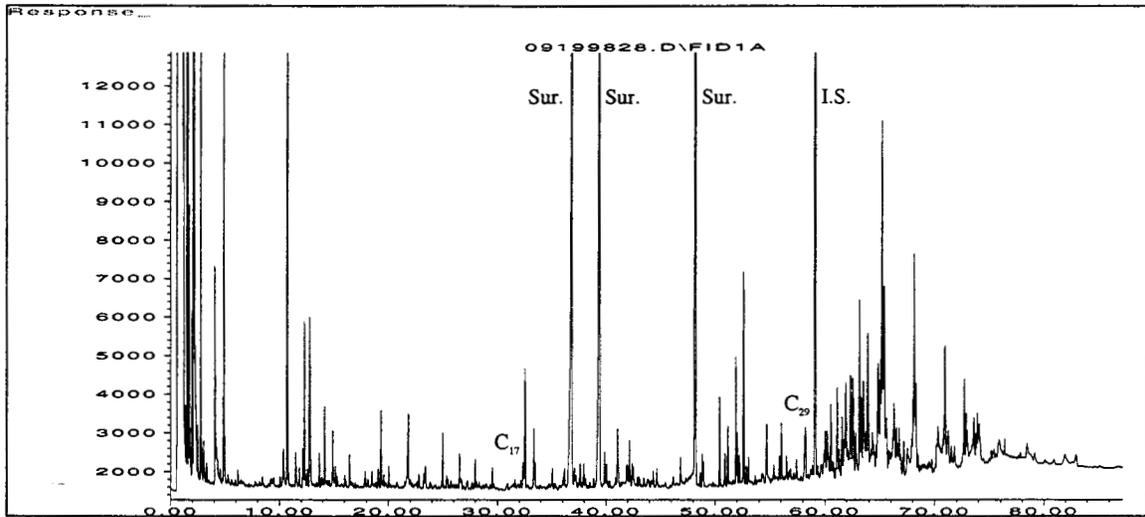


Figure 3-21: Zone 0, Station F4, Surface Sediment 98-0-F4-01-00-PHC-S: GC/FID chromatogram (top), PAH distribution plot (middle), Triterpane extracted ion chromatogram (bottom).

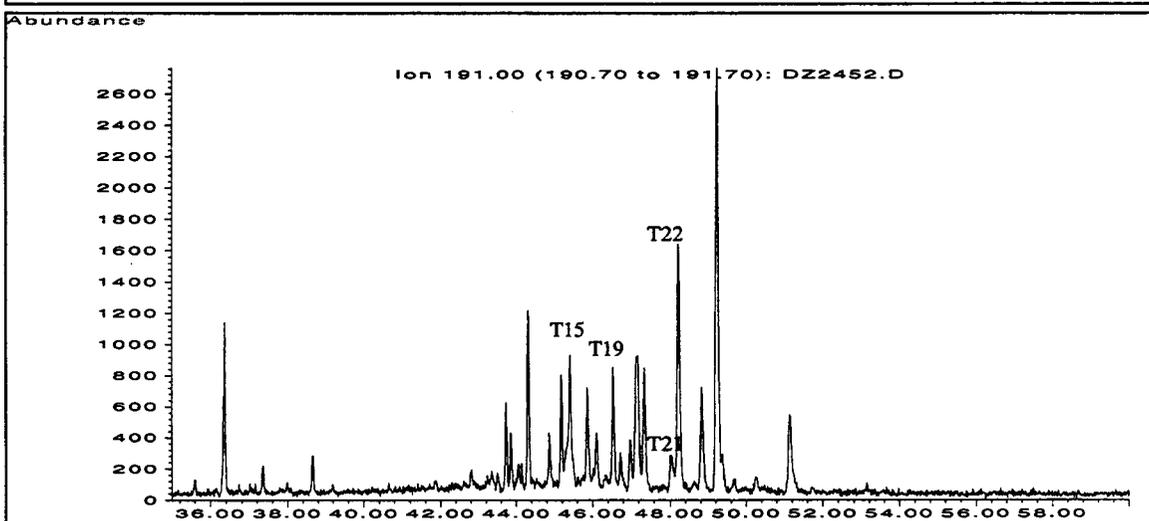
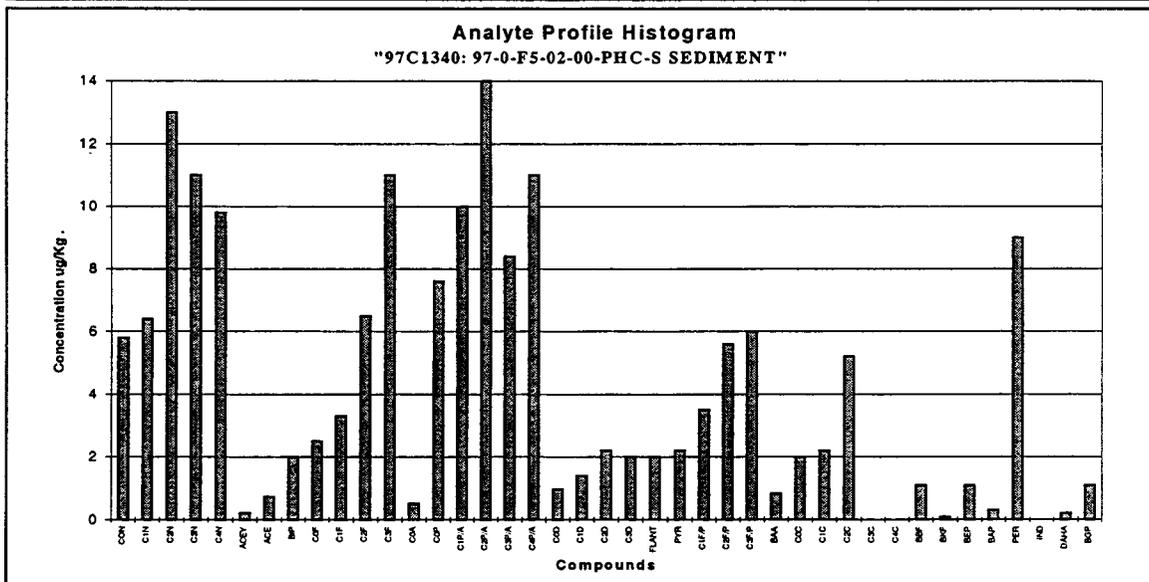
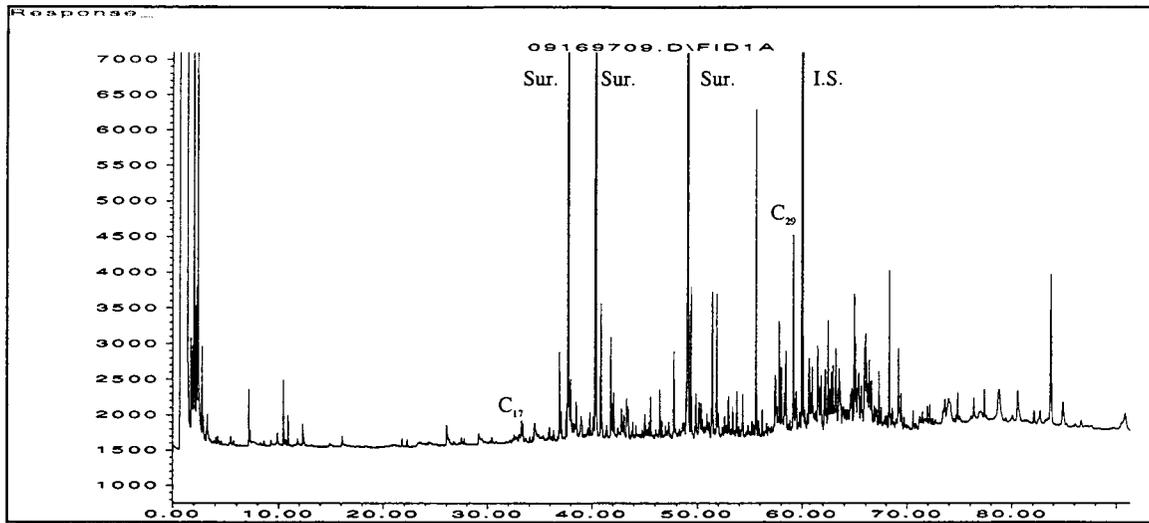


Figure 3-22: Zone 0, Station F5, Surface Sediment Sample 97-0-F5-02-00-PHC-S (rep 02) Results: GC/FID chromatogram (top), PAH distribution plot (middle), Triterpane extracted ion chromatogram (bottom).

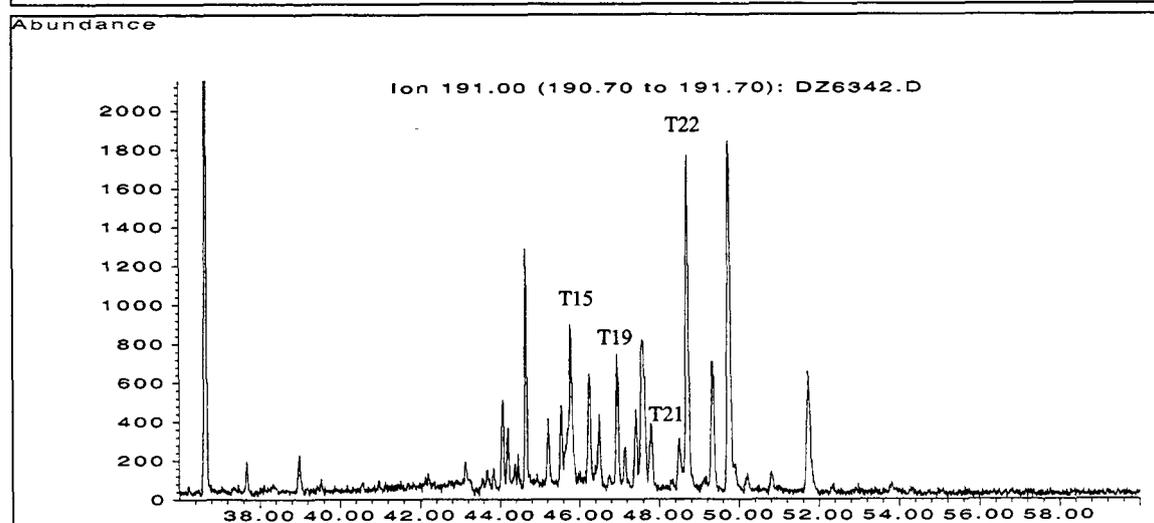
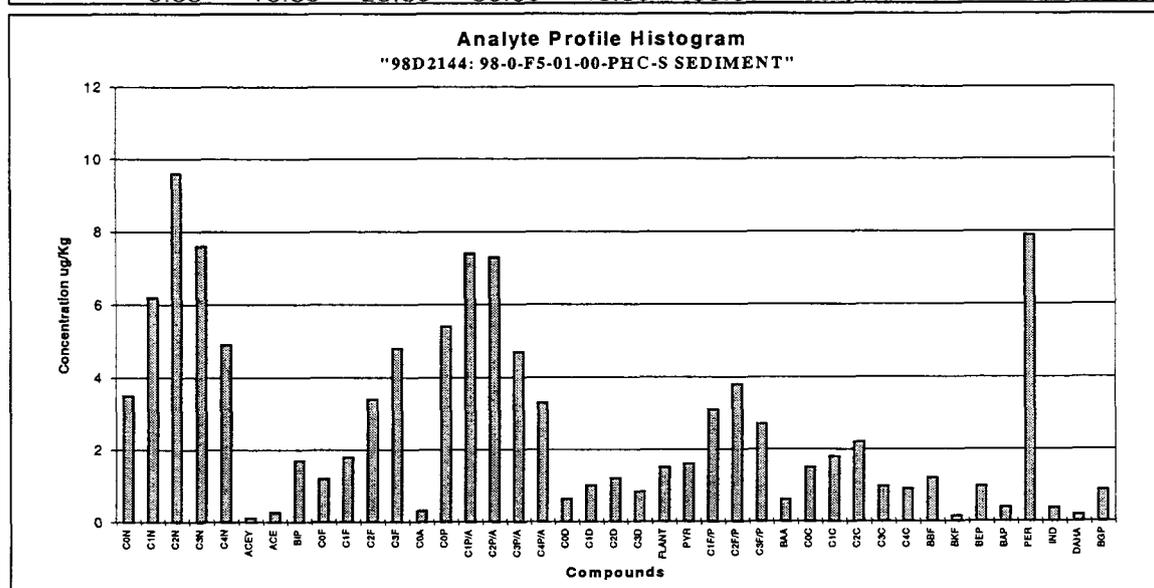
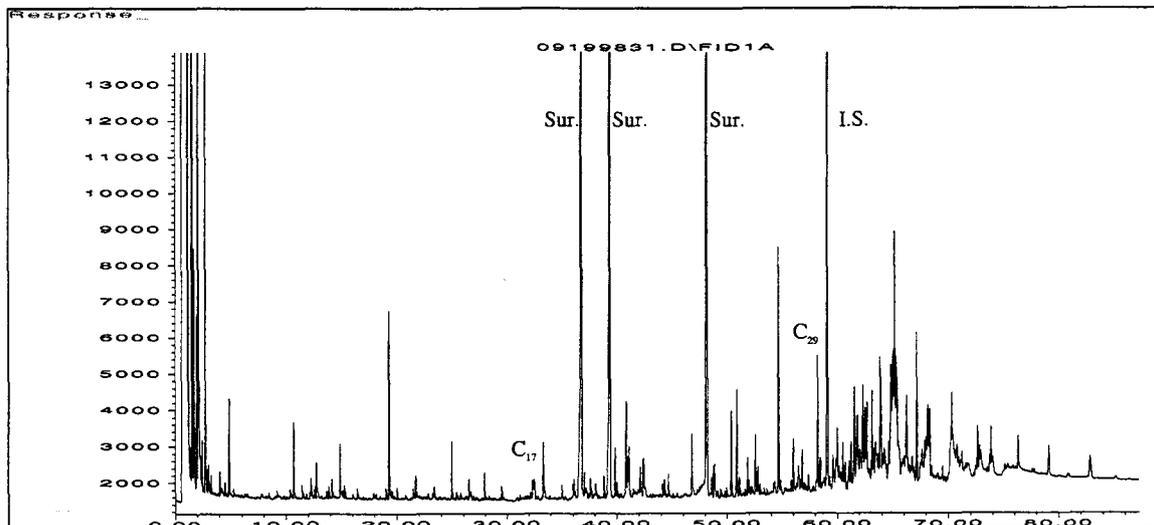


Figure 3-23: Zone 0, Station F5, Surface Sediment 98-0-F5-01-00-PHC-S: GC/FID chromatogram (top), PAH distribution plot (middle), Triterpane extracted ion chromatogram (bottom).

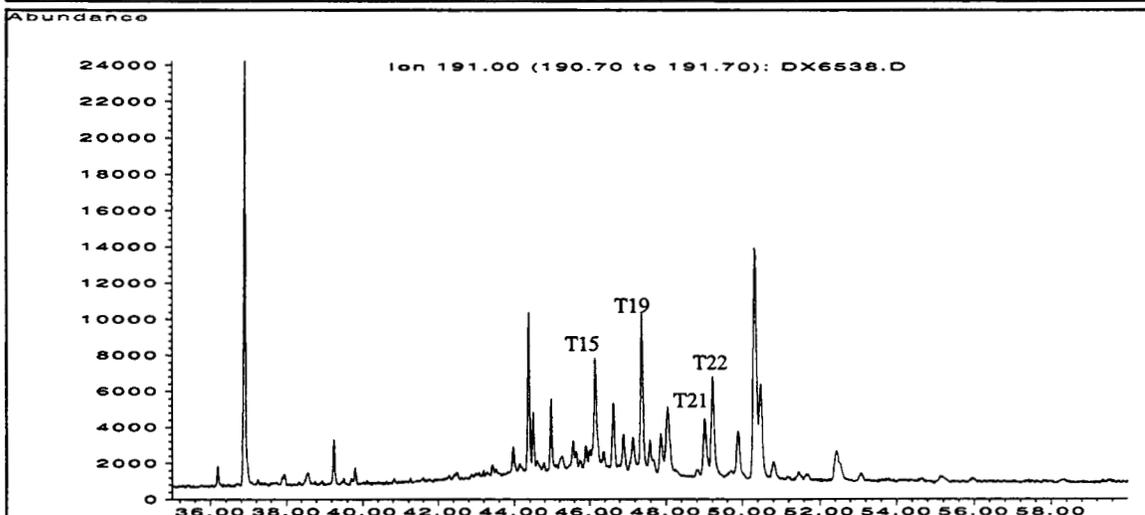
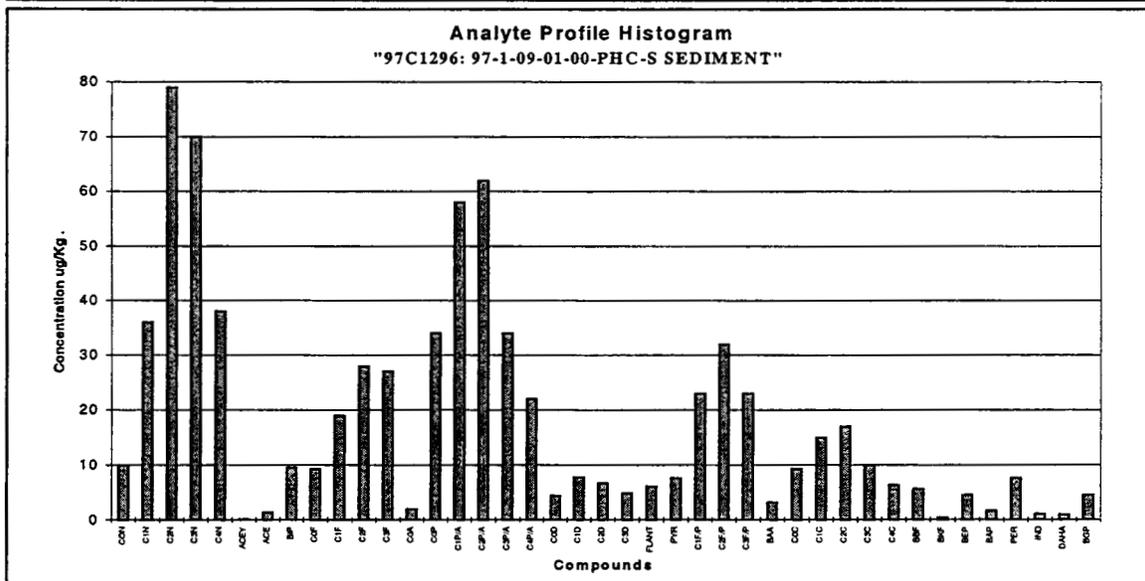
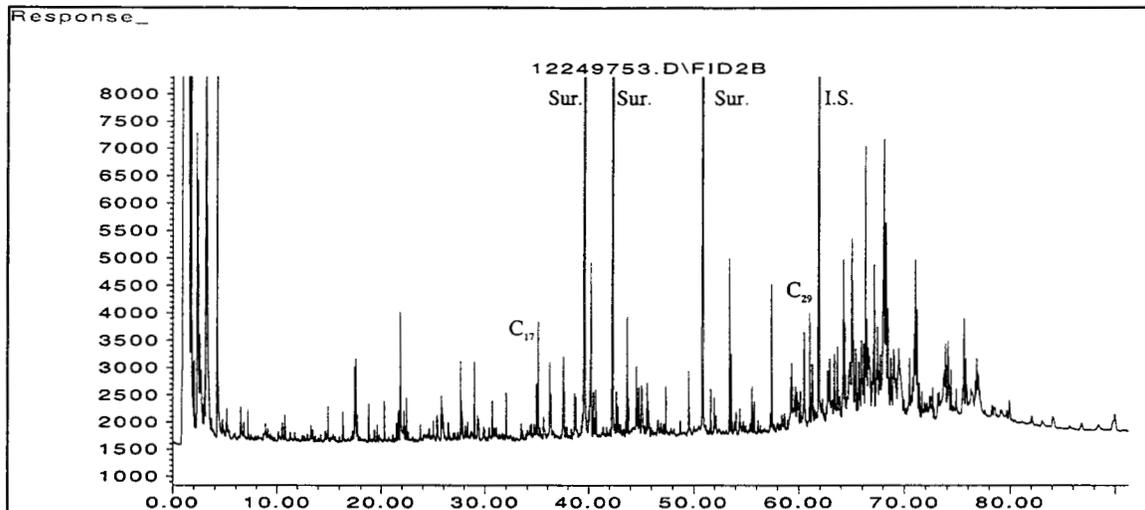


Figure 3-24: Zone 1, Station R9, Surface Sediment Sample 97-1-09-01-00-PHC-S Results: GC/FID chromatogram (top), PAH distribution plot (middle), Triterpane extracted ion chromatogram (bottom).

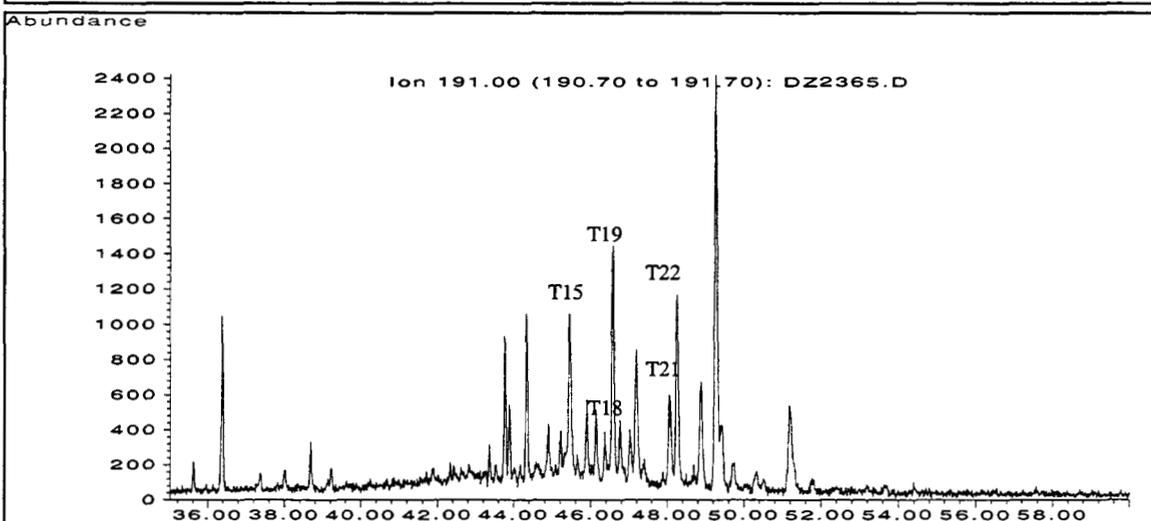
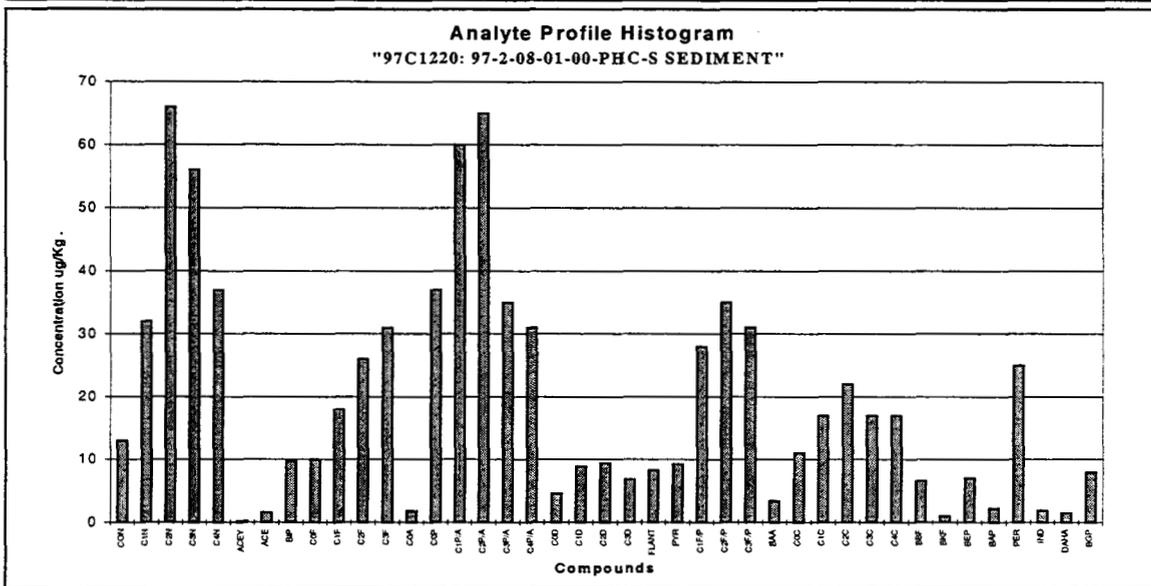
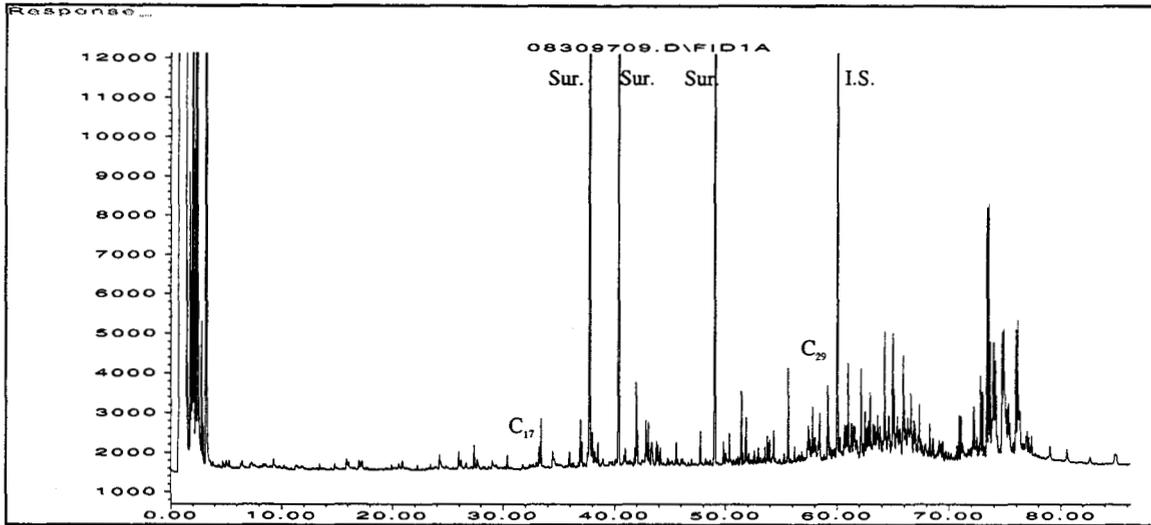


Figure 3-25: Zone 2, Station R8, Surface Sediment Sample 97-2-08-01-00-PHC-S Results: GC/FID chromatogram (top), PAH distribution plot (middle), Triterpane extracted ion chromatogram (bottom).

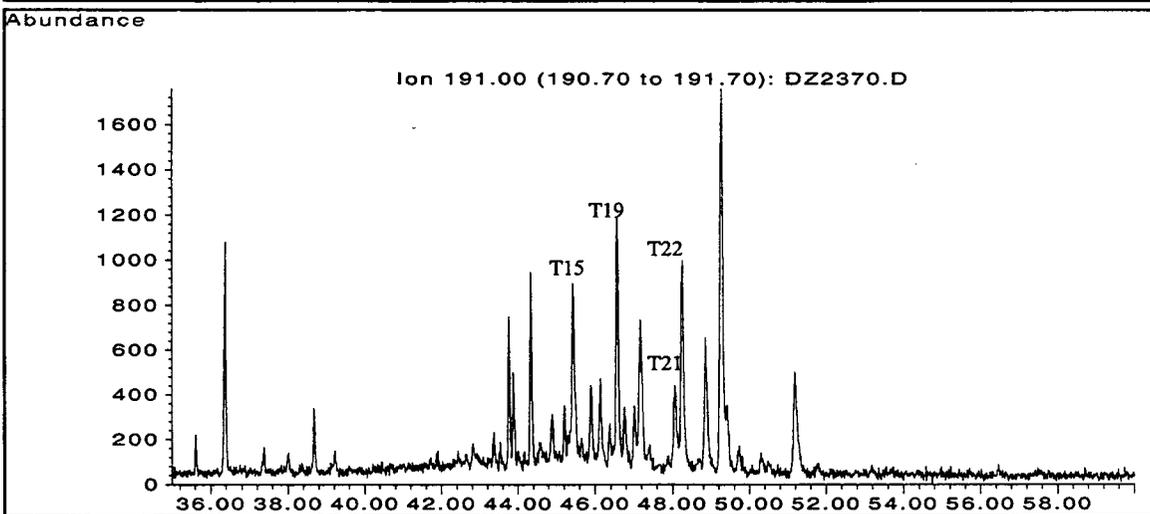
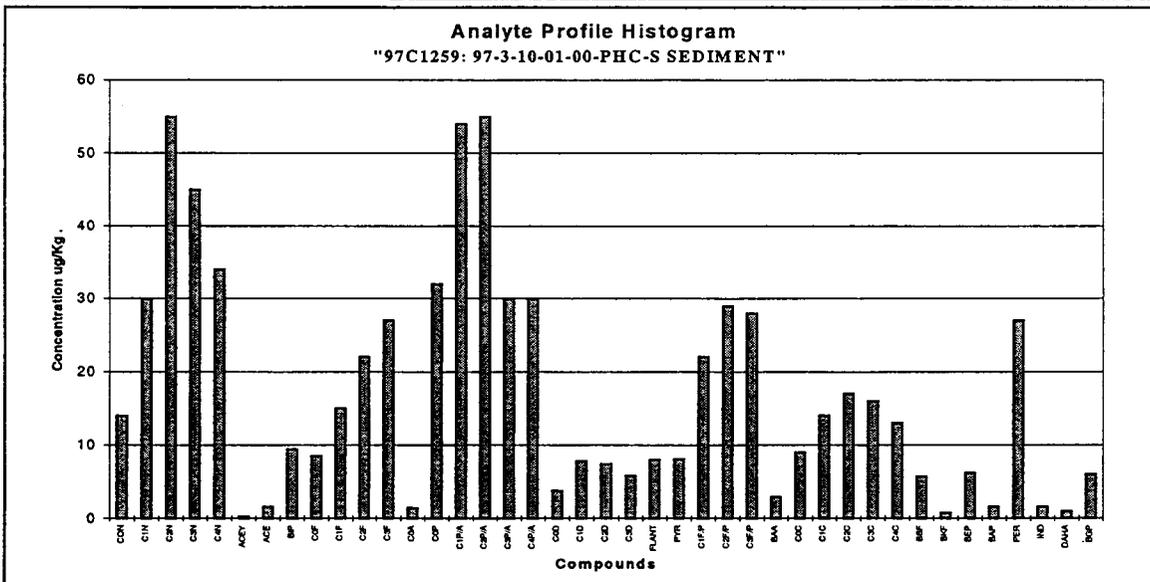
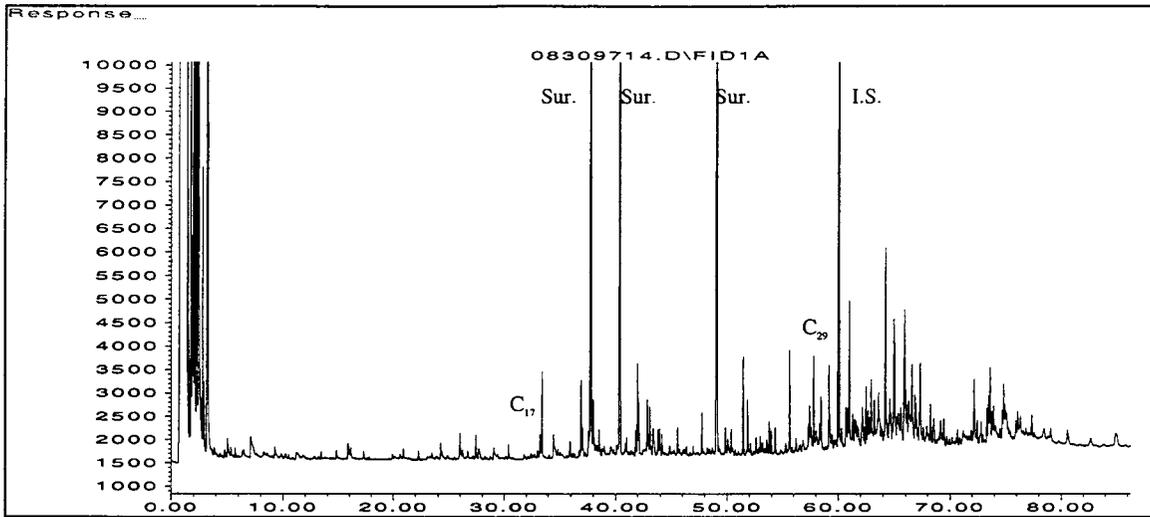


Figure 3-26: Zone 3, Station R10, Surface Sediment Sample 97-3-10-01-00-PHC-S Results: GC/FID chromatogram (top), PAH distribution plot (middle), Triterpane extracted ion chromatogram (bottom).

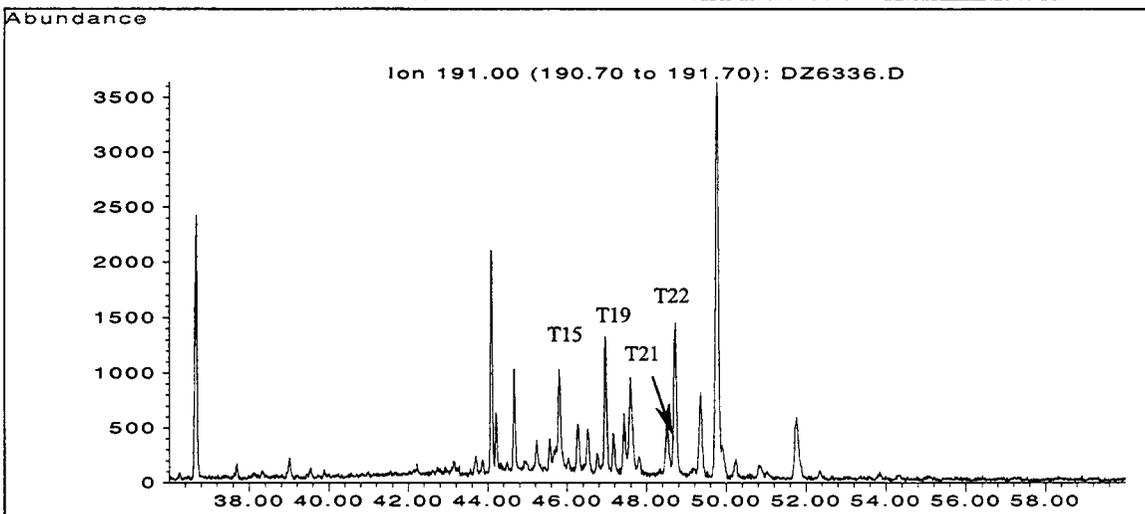
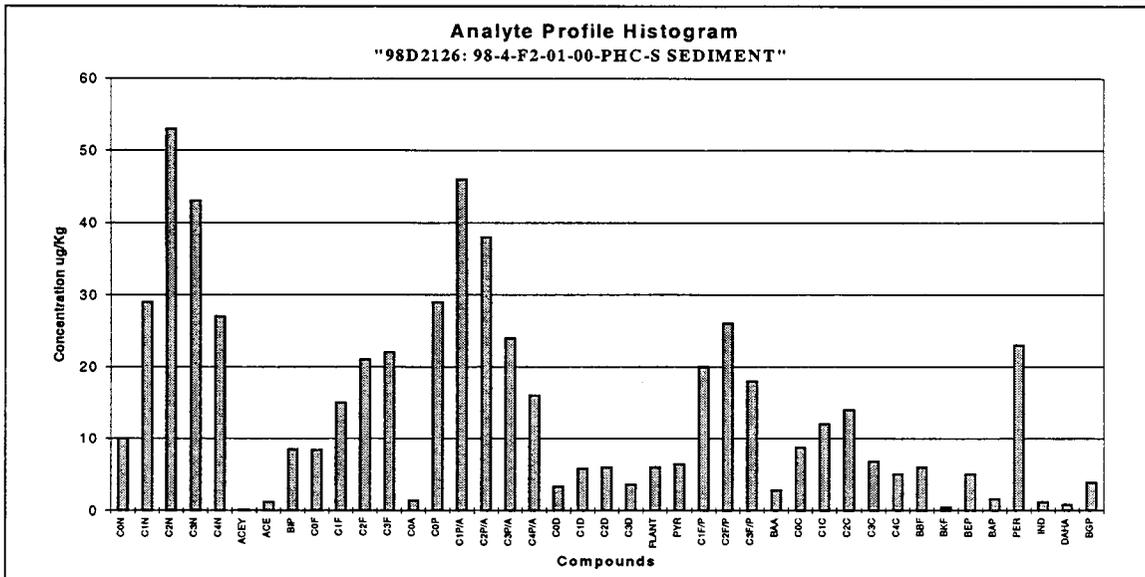
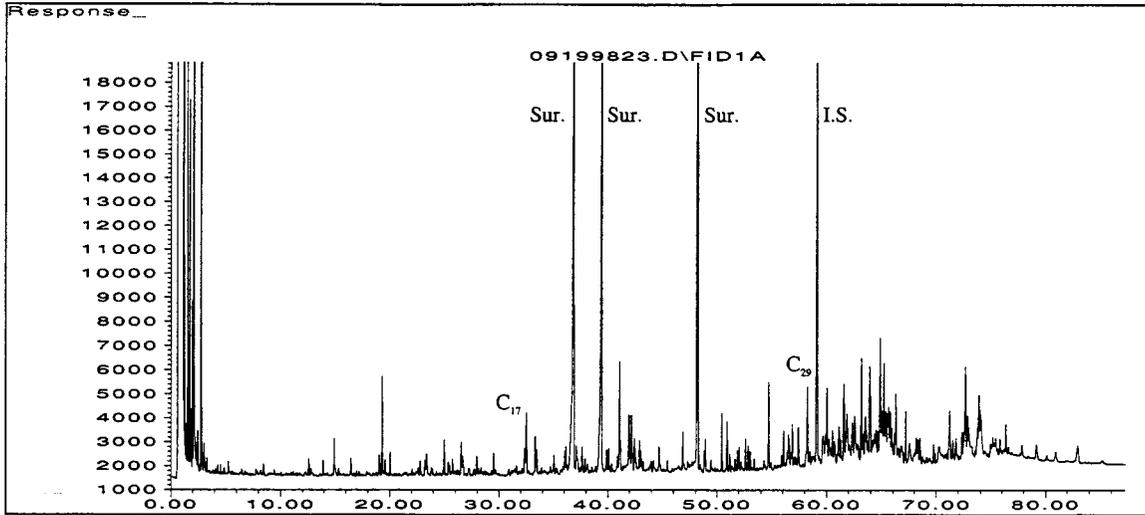


Figure 3-27: Zone 4, Station 2, Surface Sediment Sample 98-4-F2-01-00-PHC-S: GC/FID chromatogram (top), PAH distribution plot (middle), Triterpane extracted ion chromatogram (bottom).

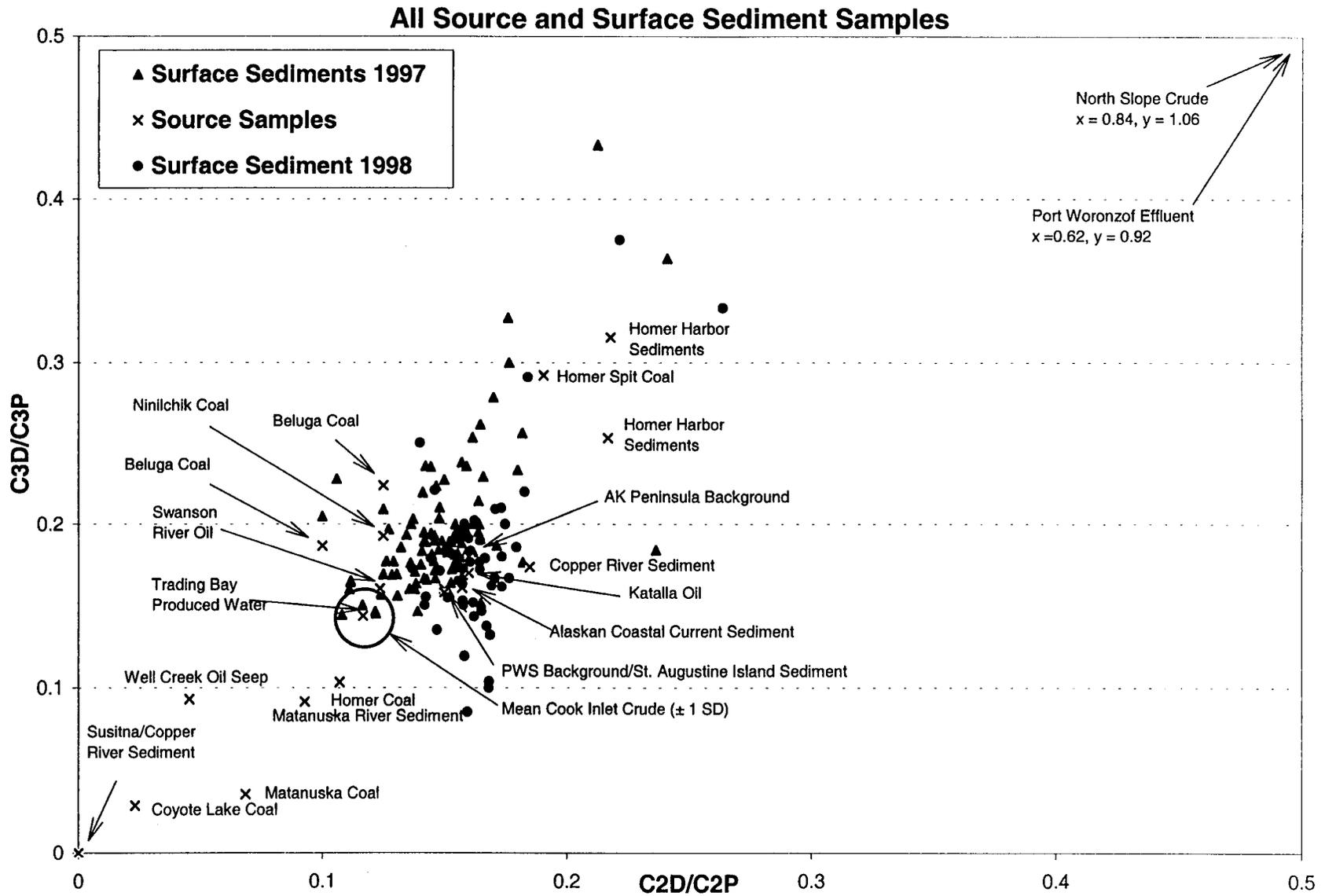


Figure 3-28: Double Ratio Plot of  $C2D/C2P$  and  $C3D/C3P$  for all Source and Surficial Sediments (Zones 0, 1, 2, 3 and 4).

### All Source and All Zone 0 (1997 & 1998) Surface Sediment

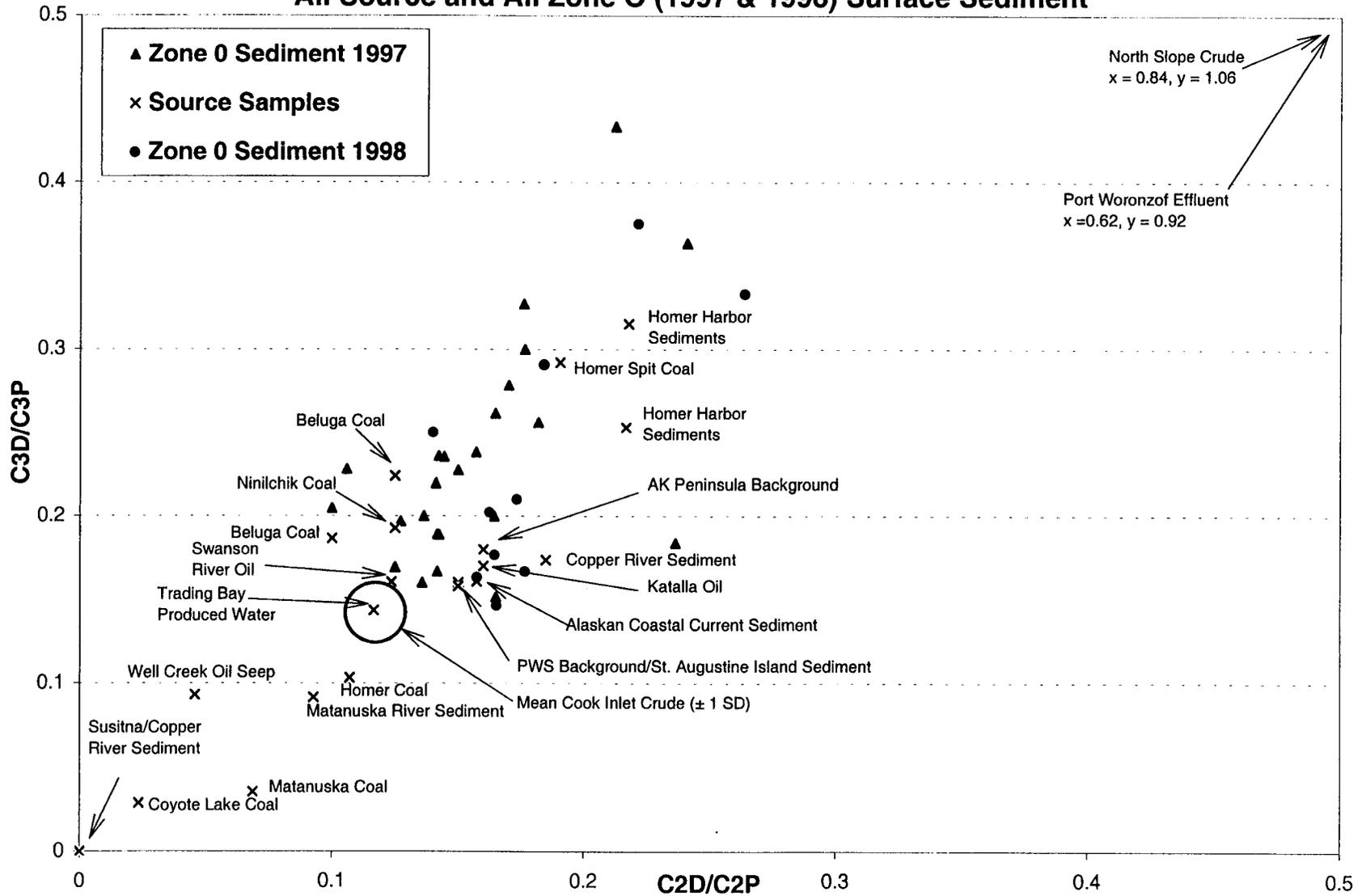


Figure 3-29: Double Ratio Plot of C2D/C2P and C3D/C3P for all Source and Zone 0 Surficial Sediments.

### All Source and Zone 1 1997 & 1998 Surface Sediment

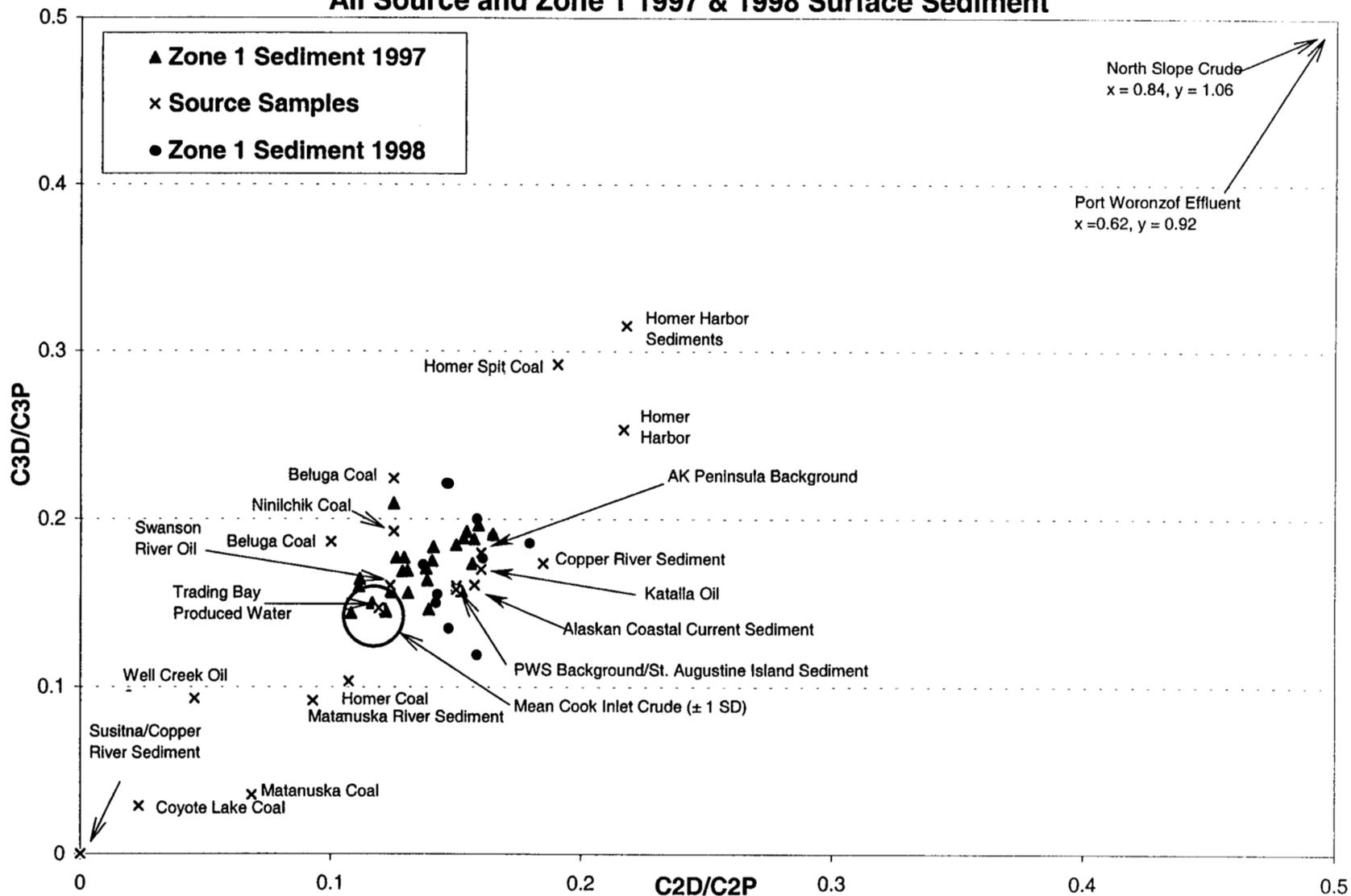


Figure 3-30: Double Ratio Plot of C2D/C2P and C3D/C3P for all Source and Zone 1 Surficial Sediments.

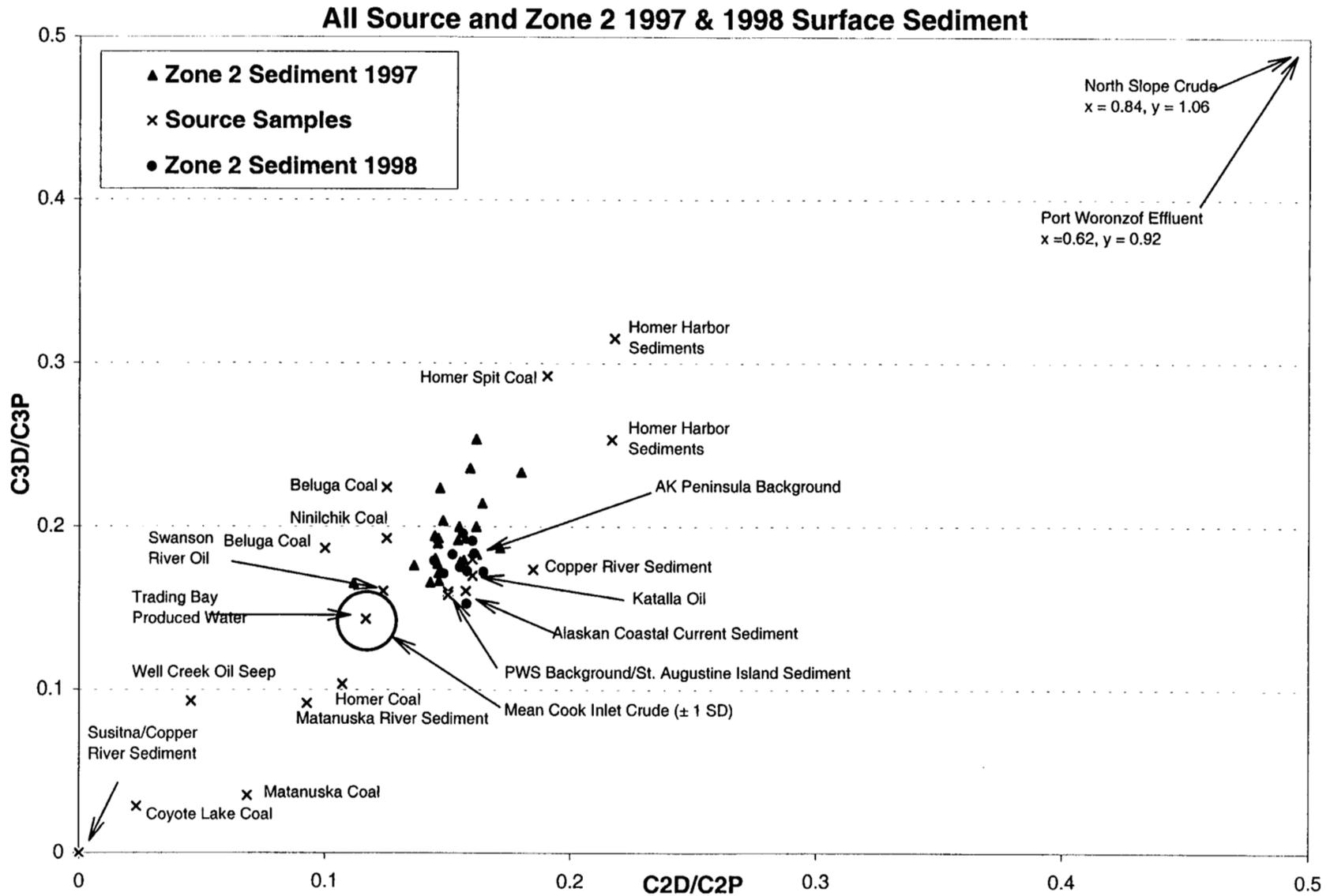


Figure 3-31: Double Ratio Plot of C2D/C2P and C3D/C3P for all Source and Zone 2 Surficial Sediments.

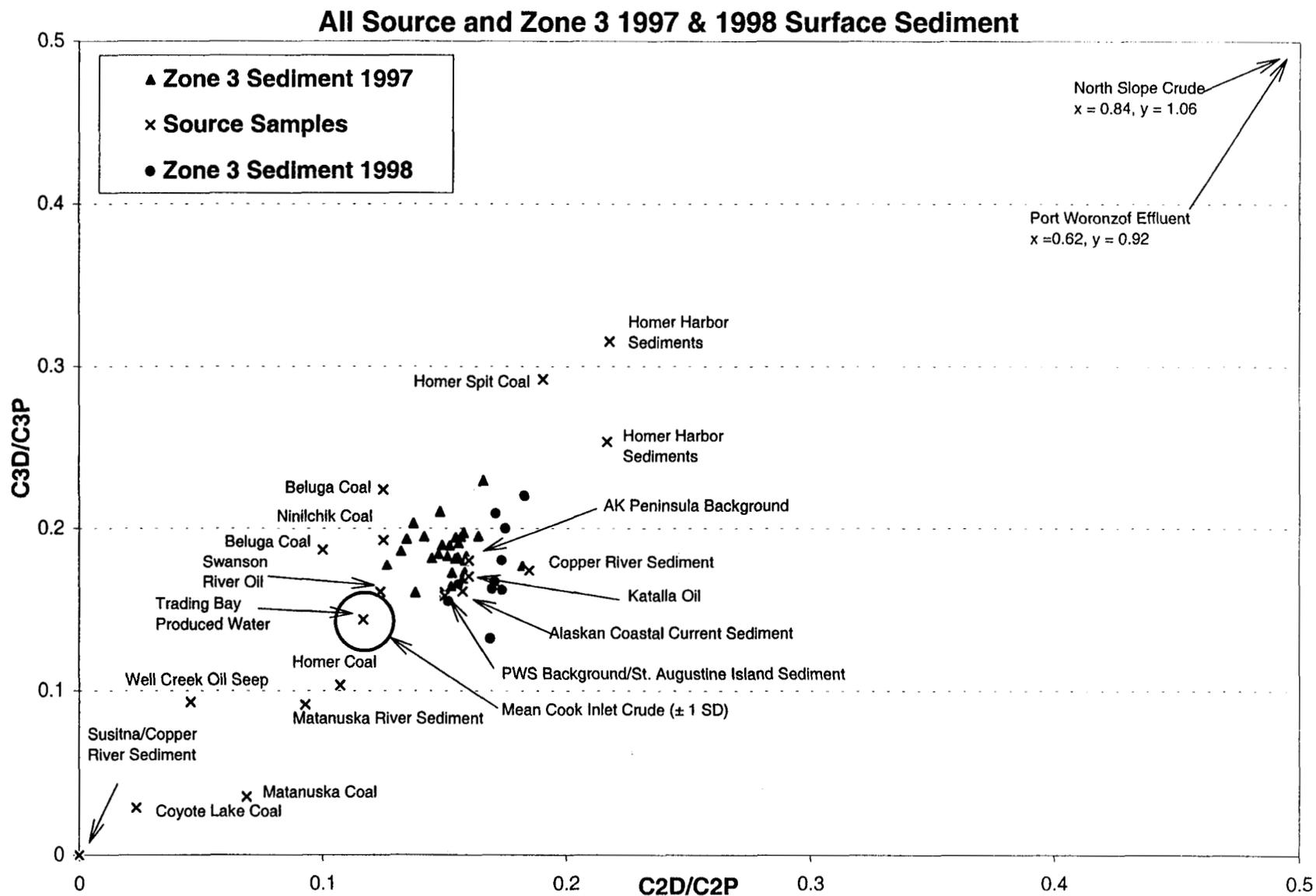


Figure 3-32: Double Ratio Plot of C2D/C2P and C3D/C3P for all Source and Zone 3 Surficial Sediments.

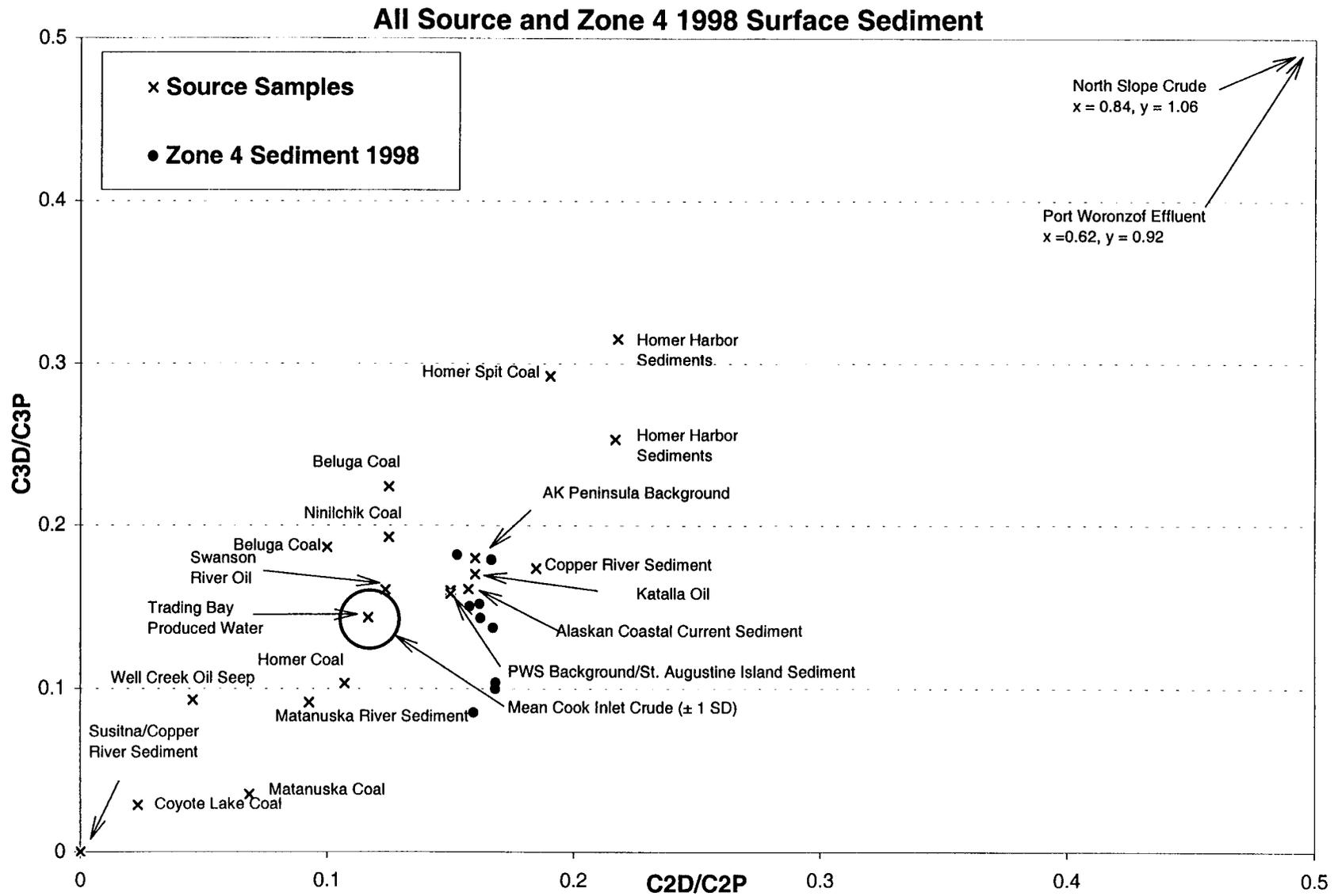
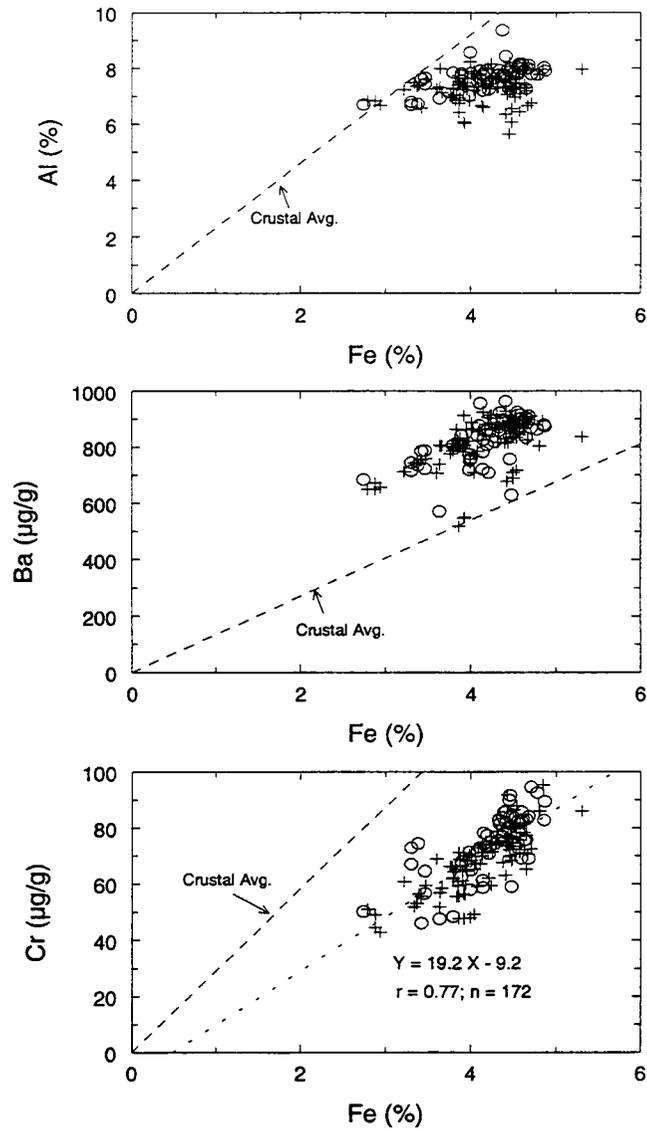
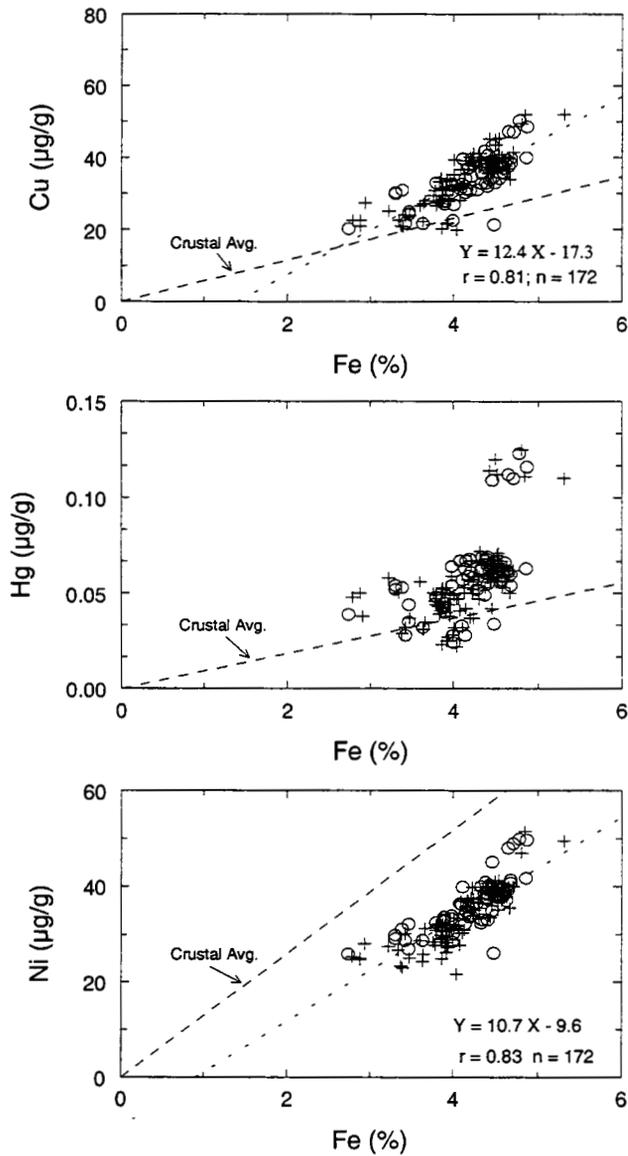


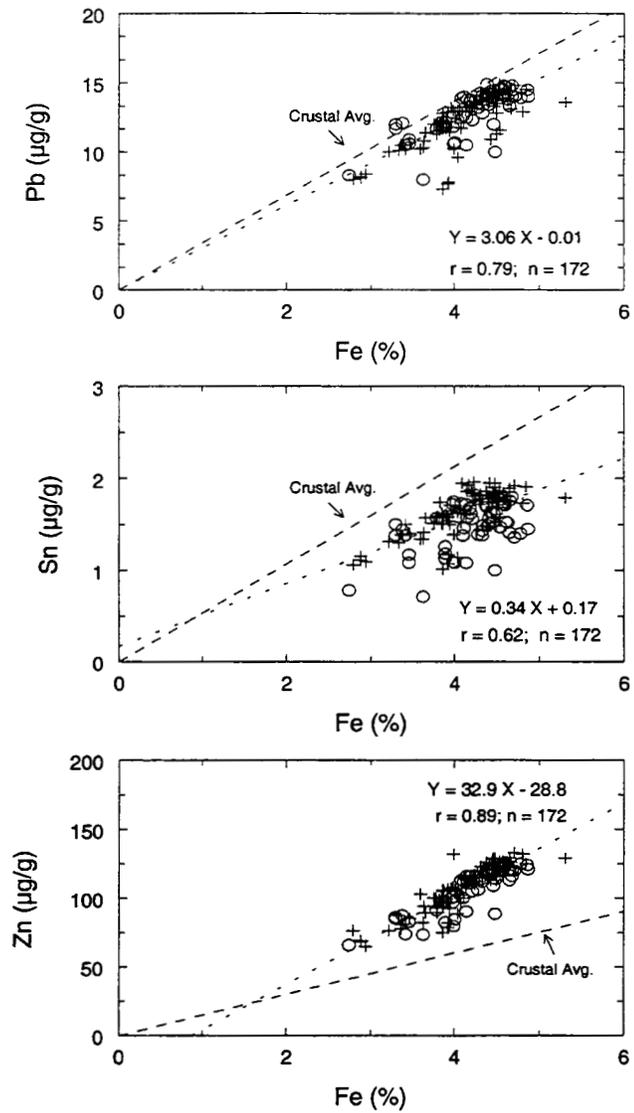
Figure 3-33: Double Ratio Plot of C2D/C2P and C3D/C3P for all Source and Zone 4 Surficial Sediments.



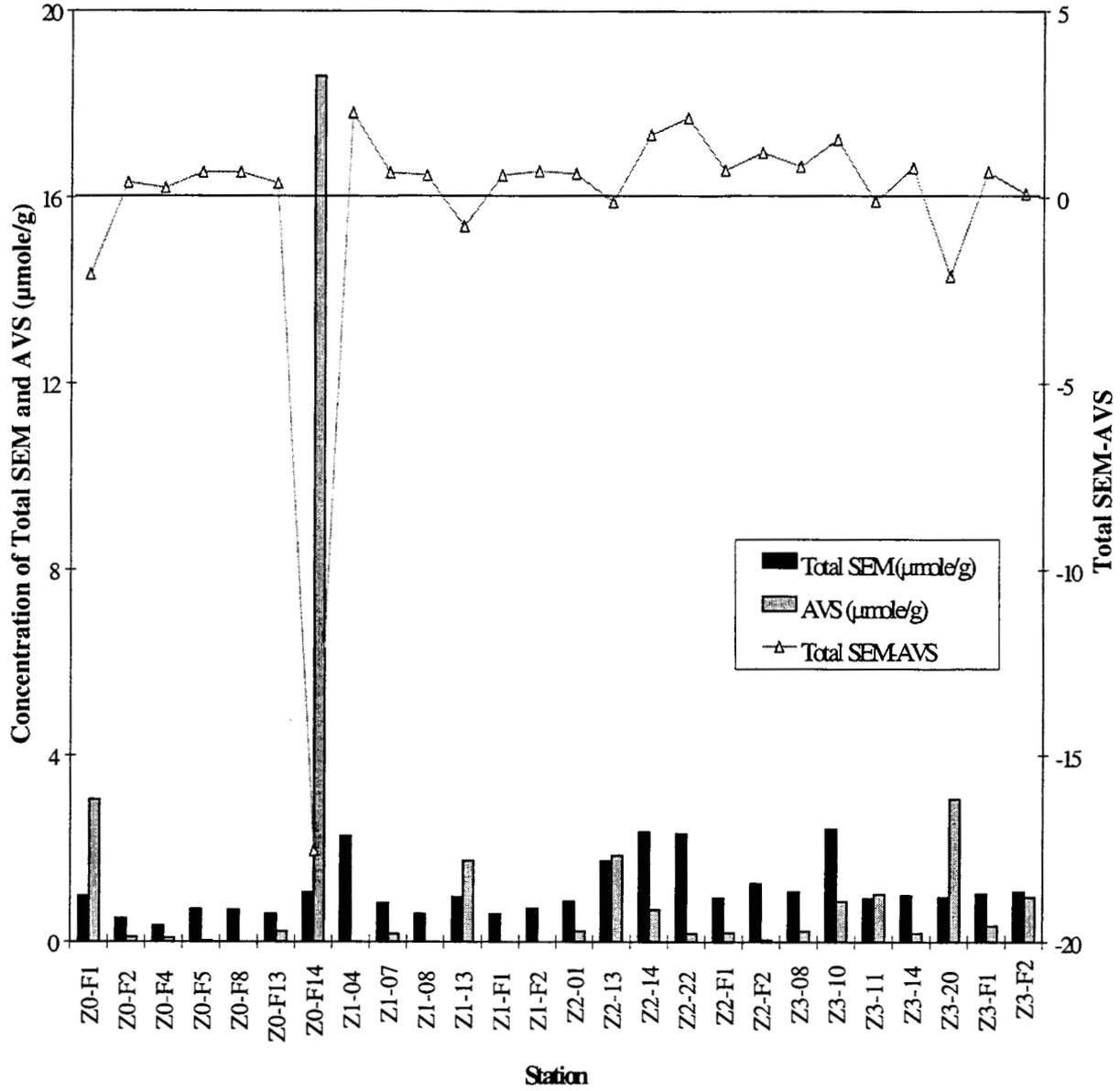
**Figure 3-34: Plots Showing Fe Versus Al, Ba, and Cr for Surficial Sediments from Outermost Cook Inlet (Zone 0) and the Shelikof Strait (Zones 0, 1, 2, 3 and 4). Dashed Lines Show Metals/Fe Ratios for Average Continental Crust from Wedephol (1995). Dotted Line and Equation for Cr are from the Linear Regression for the Surficial Sediments. Symbols are (+) for 1997 and (o) for 1998.**



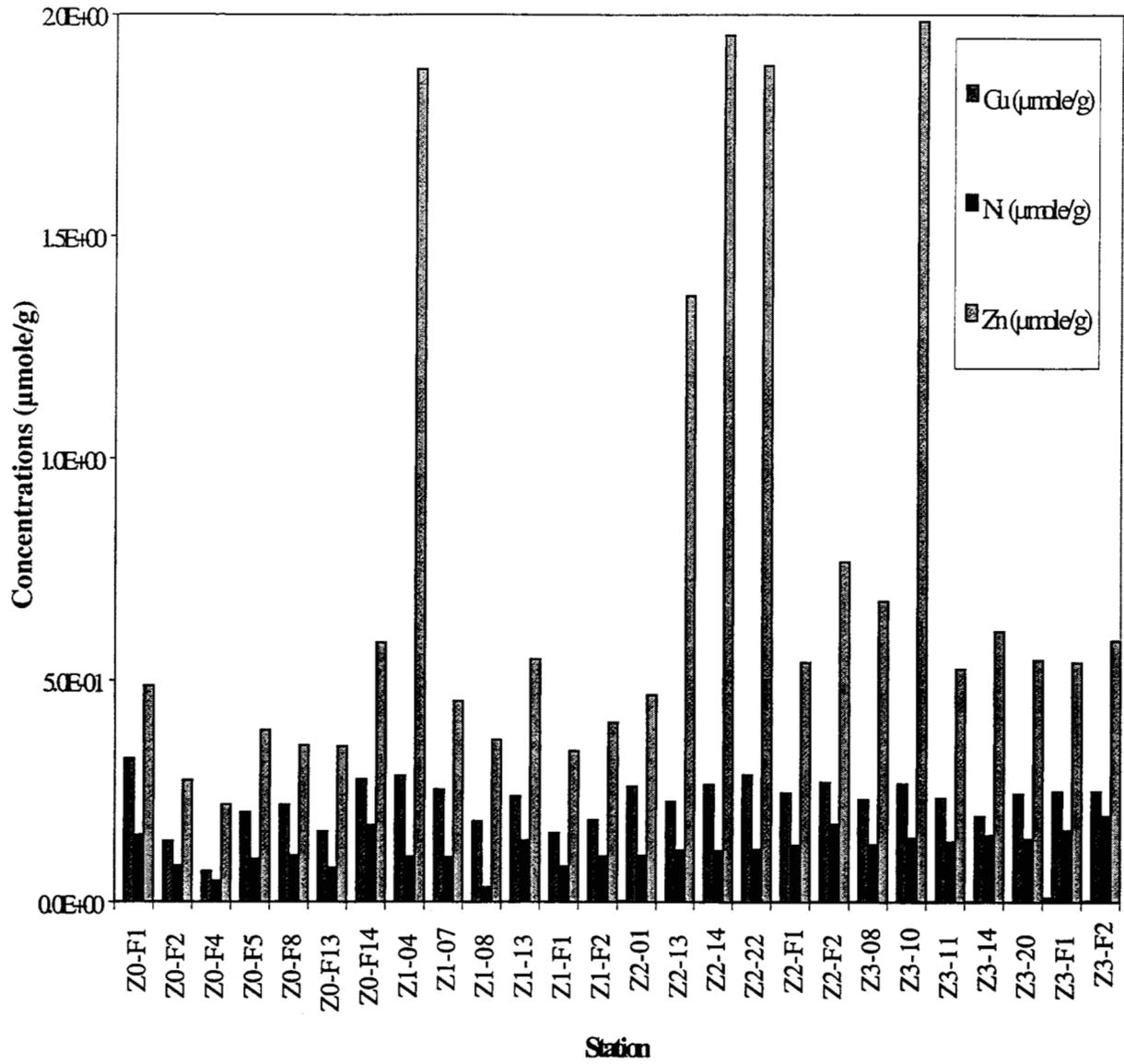
**Figure 3-35: Plots Showing Fe Versus Cu, Hg, and Ni for Surficial Sediments from Outermost Cook Inlet (Zone 0) and the Shelikof Strait (Zones 0, 1, 2, 3 and 4). Dashed Lines Show Metal/Fe Ratios for Average Continental Crust from Wedepohl (1995). Dotted Lines and Equations for Cu and Ni are from the Linear Regression for the Surficial Sediments. Symbols are (+) for 1997 and (o) for 1998.**



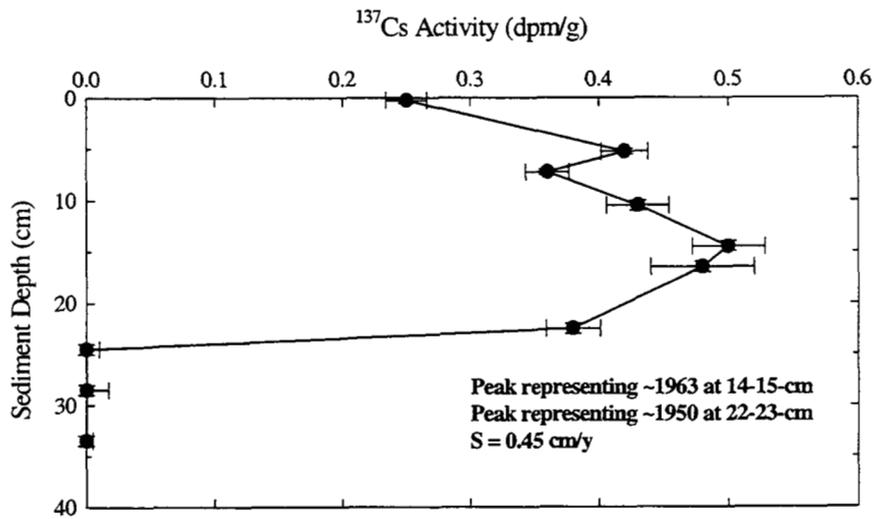
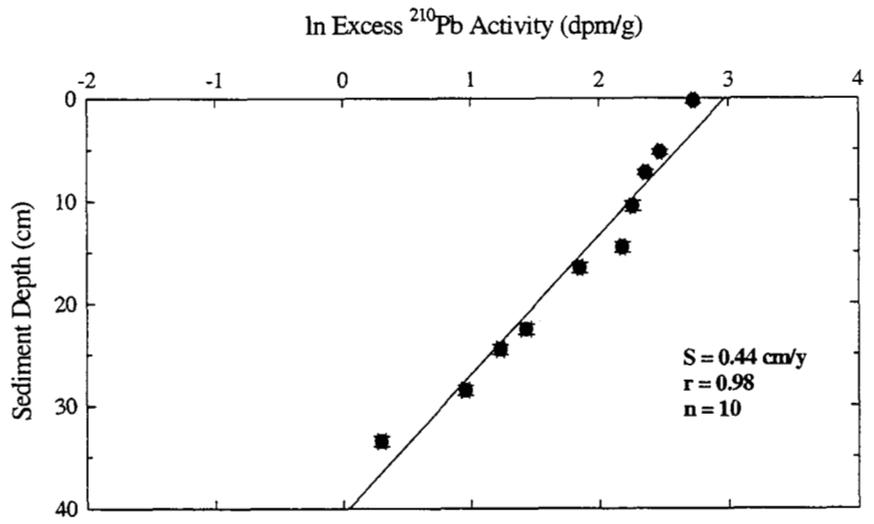
**Figure 3-36: Plots Showing Fe Versus Pb, Sn, and Zn for Surficial Sediments from Outermost Cook Inlet (Zone 0) and the Shelikof Strait (Zones 0, 1, 2, 3 and 4). Dashed Lines Show Metal/Fe Ratios for Average Continental Crust from Wedepohl (1995). Dotted Lines and Equations are from the Linear Regression for the Surficial Sediments. Symbols are (+) for 1997 and (o) for 1998.**



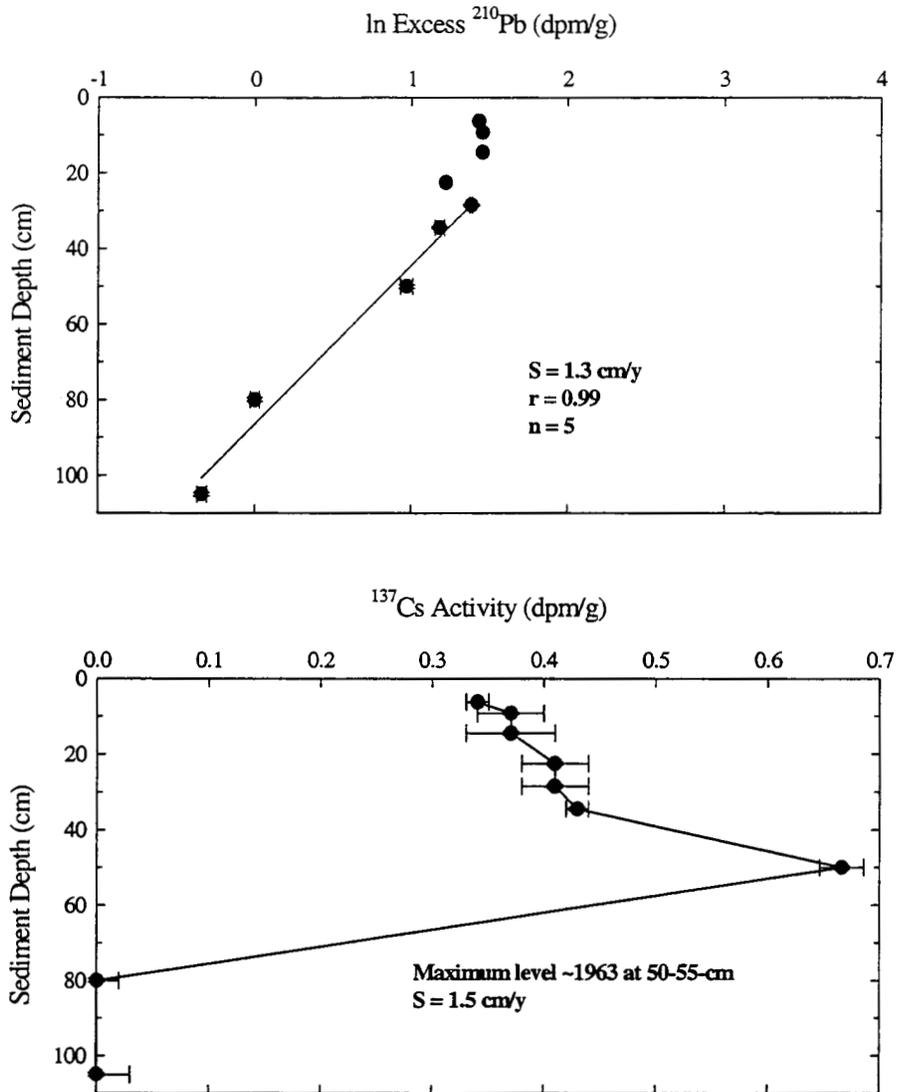
**Figure 3-37: Bar Graph Showing Concentrations of Simultaneously Extracted Metals (SEM) and Acid Volatile Sulfide (AVS) for each Station. Line Graph Shows (SEM-AVS) Levels for each Station.**



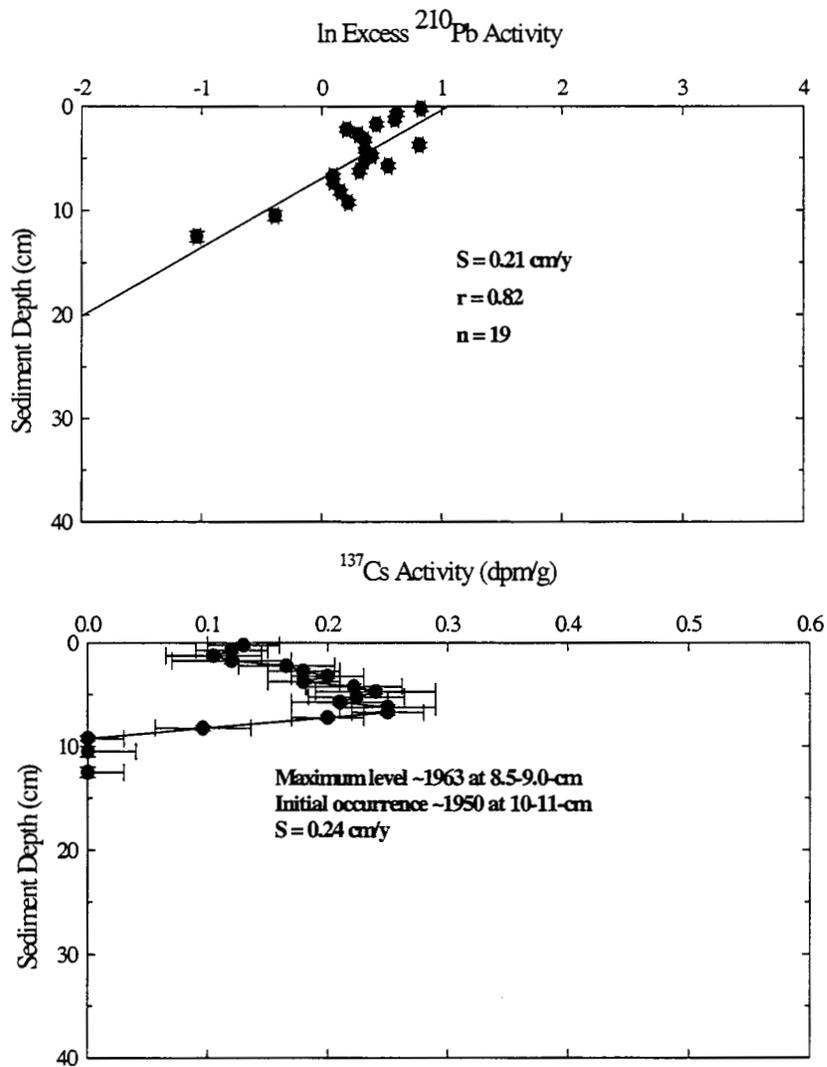
**Figure 3-38: Bar Graph Showing Concentrations of Simultaneously Extracted Metals for Cu, Ni, and Zn.**



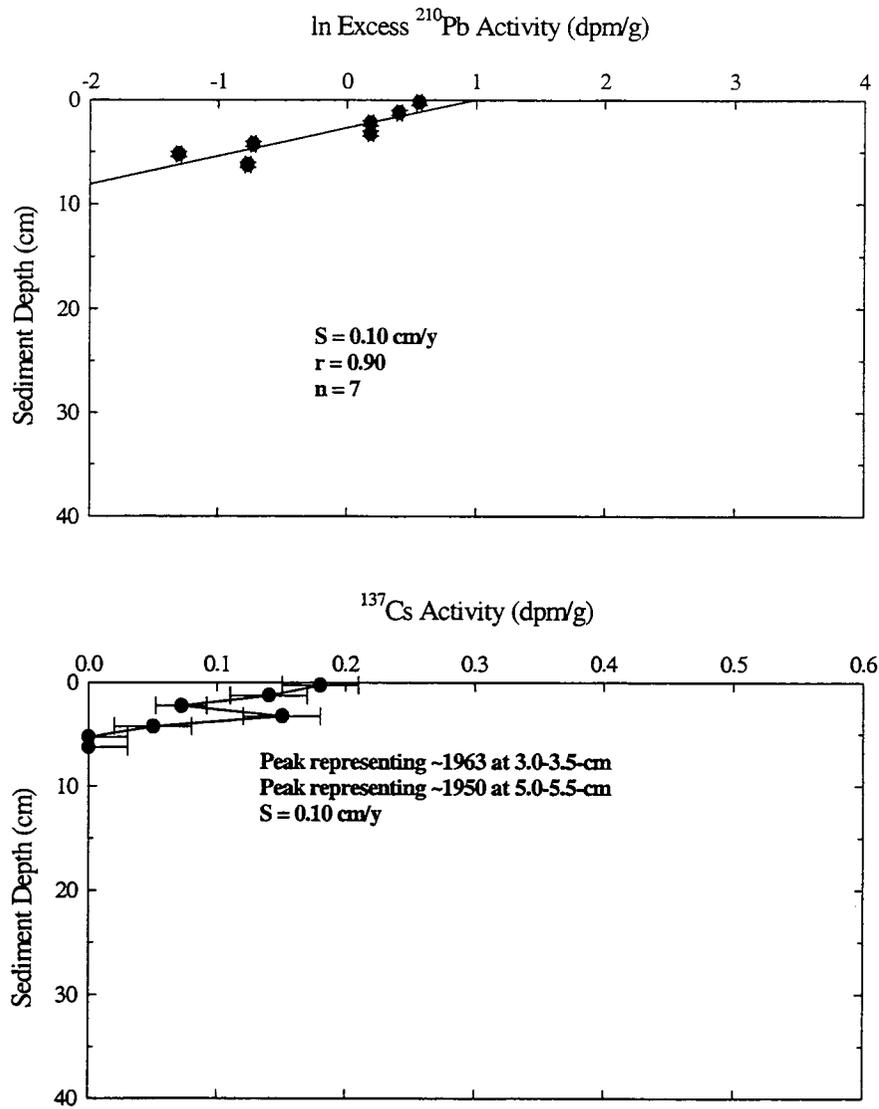
**Figure 3-39: Vertical Profiles Showing Activities of Excess  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  for Sediment Core 97-Z3F2 versus Sediment Depth. Calculated Sedimentation Rates (S) are Shown for each Isotope Technique.**



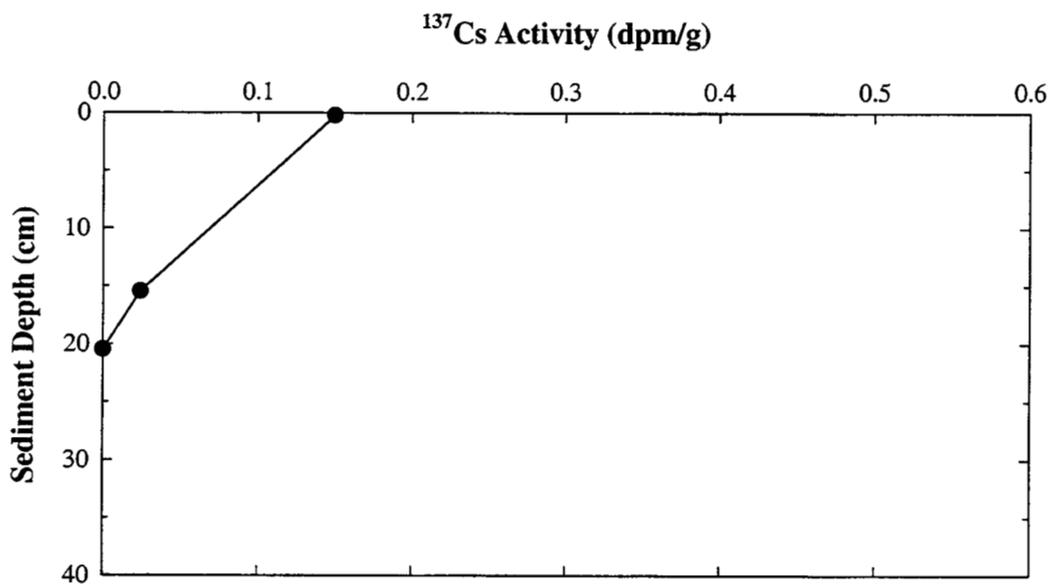
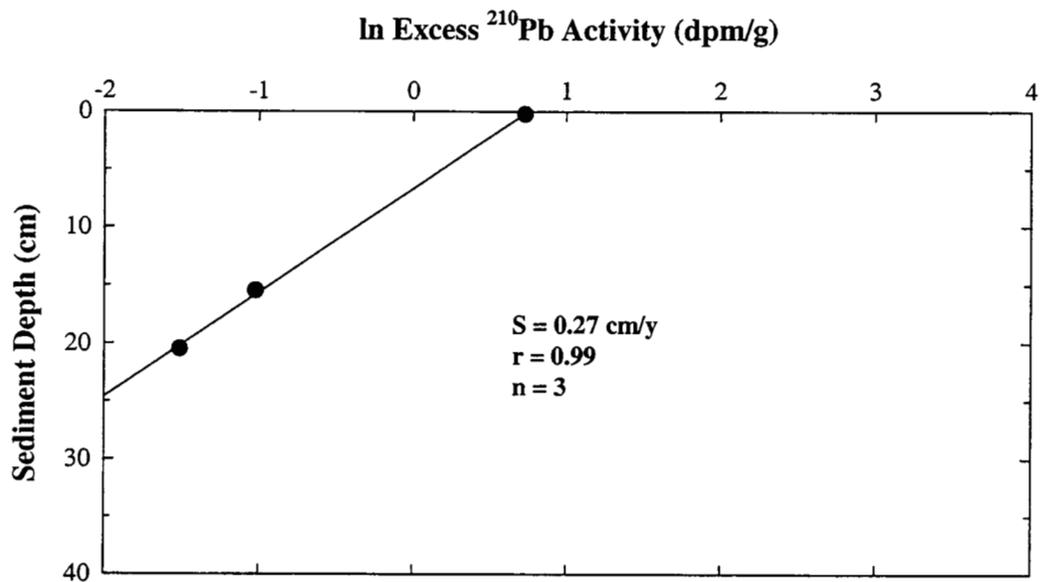
**Figure 3-40: Vertical Profiles Showing Activities of Excess  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  for Sediment Core 98-Z0F1 versus Sediment Depth. Calculated Sedimentation Rates (S) are Shown for each Isotope Technique.**



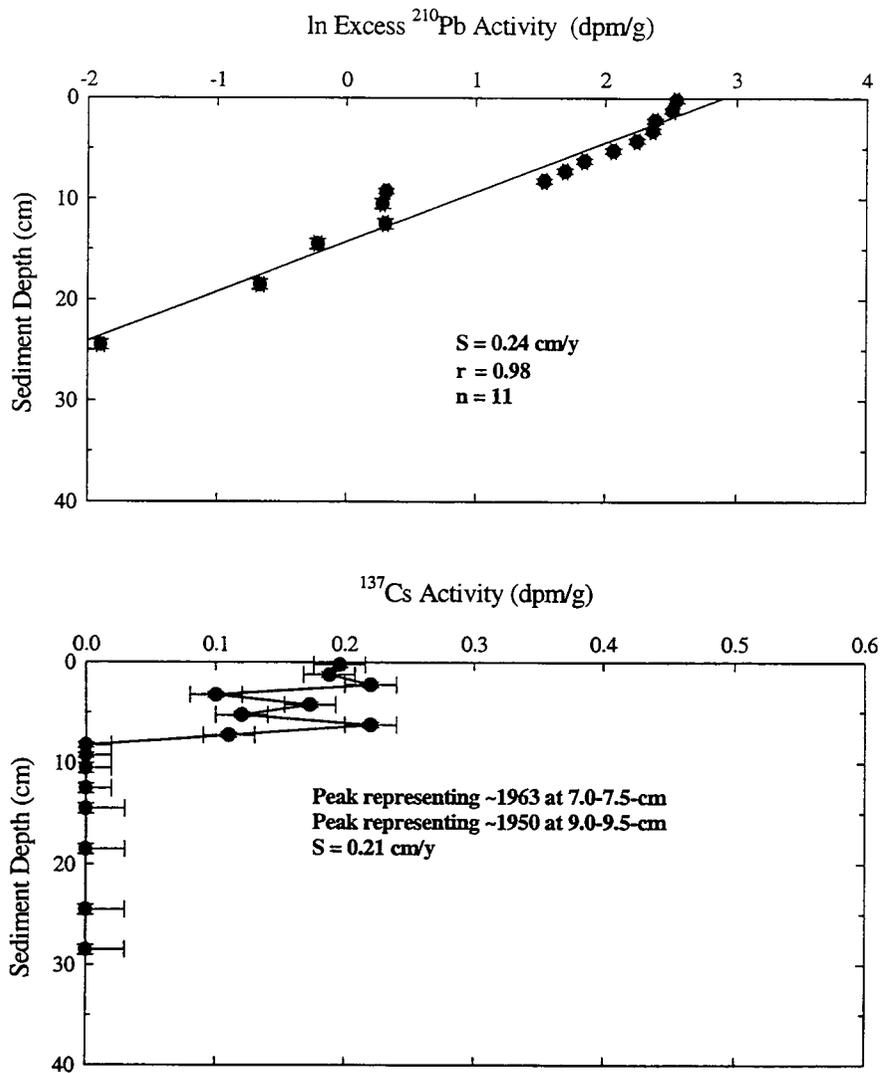
**Figure 3-41: Vertical Profiles Showing Activities of Excess  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  for Sediment Core 97-Z0F5 versus Sediment Depth. Calculated Sedimentation Rates (S) are Shown for each Isotope Technique.**



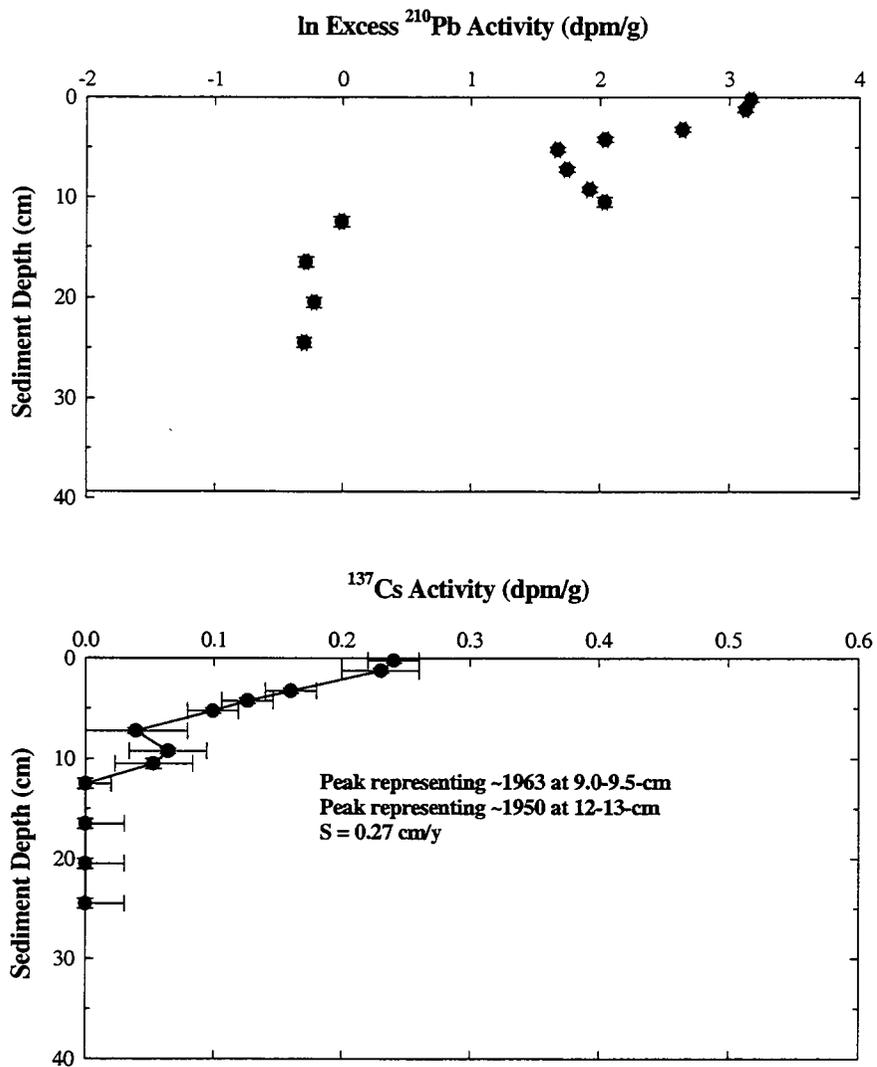
**Figure 3-42: Vertical Profiles Showing Activities of Excess  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  for Sediment Core 97-Z0F6 versus Sediment Depth. Calculated Sedimentation Rates (S) are Shown for each Isotope Technique.**



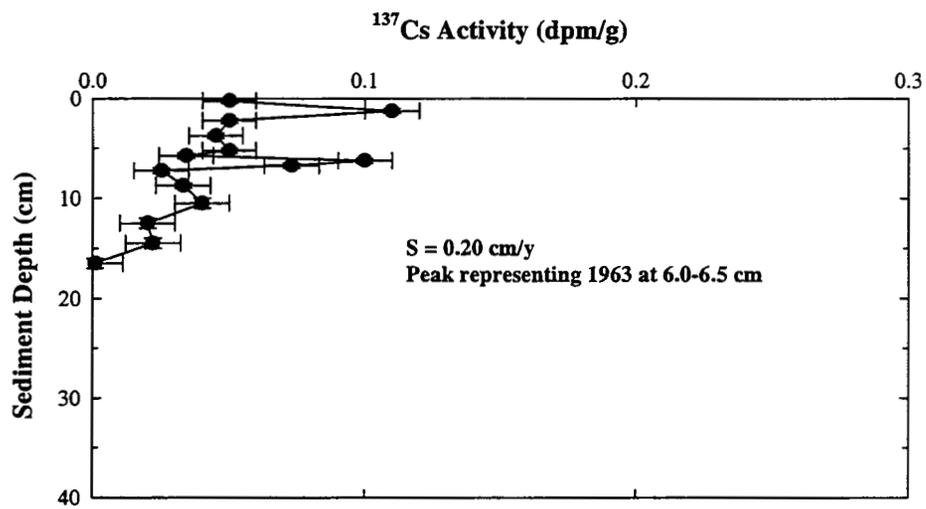
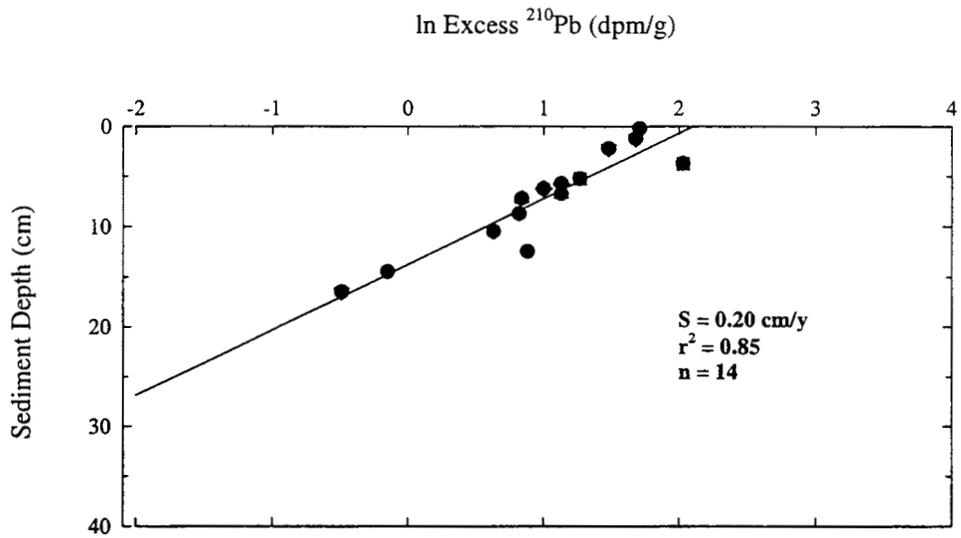
**Figure 3-43: Vertical Profiles Showing Activities of Excess  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  for Sediment Core 97-Z0F8 versus Sediment Depth. Calculated Sedimentation Rate (S) is Shown for Excess  $^{210}\text{Pb}$ .**



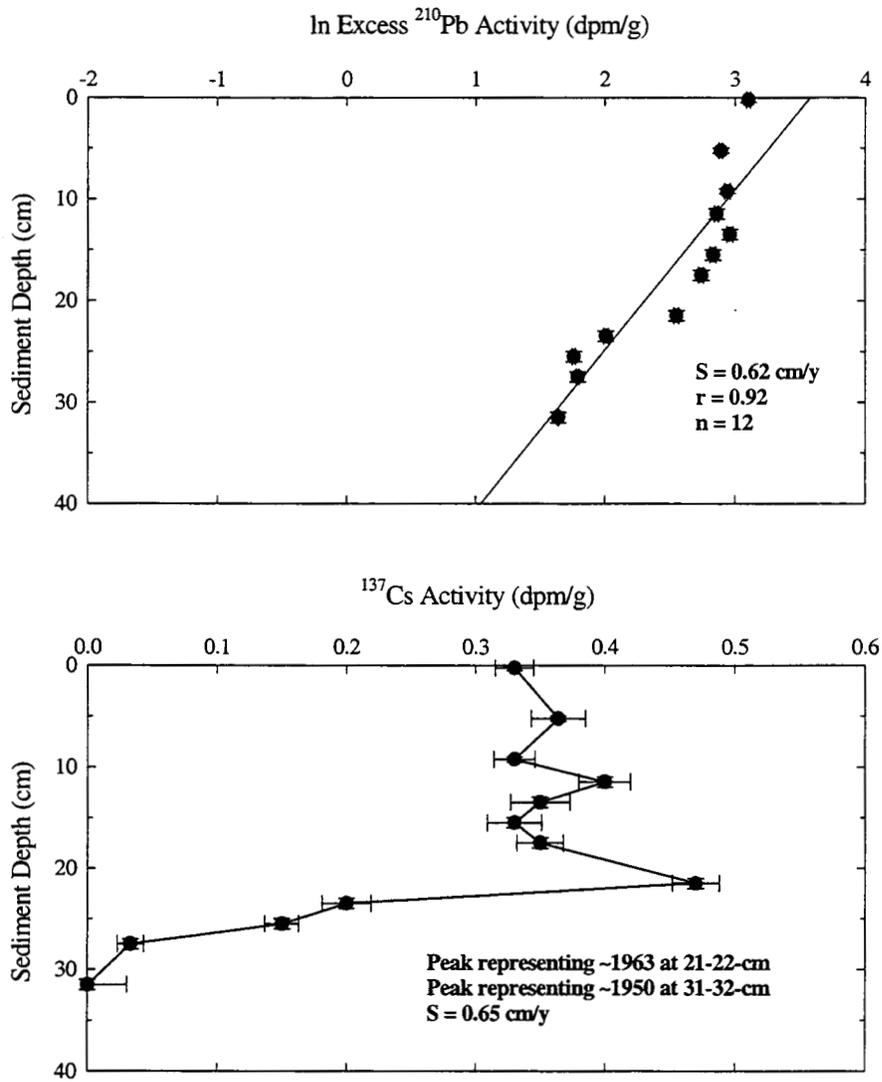
**Figure 3-44: Vertical Profiles Showing Activities of Excess  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  for Sediment Core 97-Z1F1 versus Sediment Depth. Calculated Sedimentation Rates (S) are Shown for each Isotope Technique.**



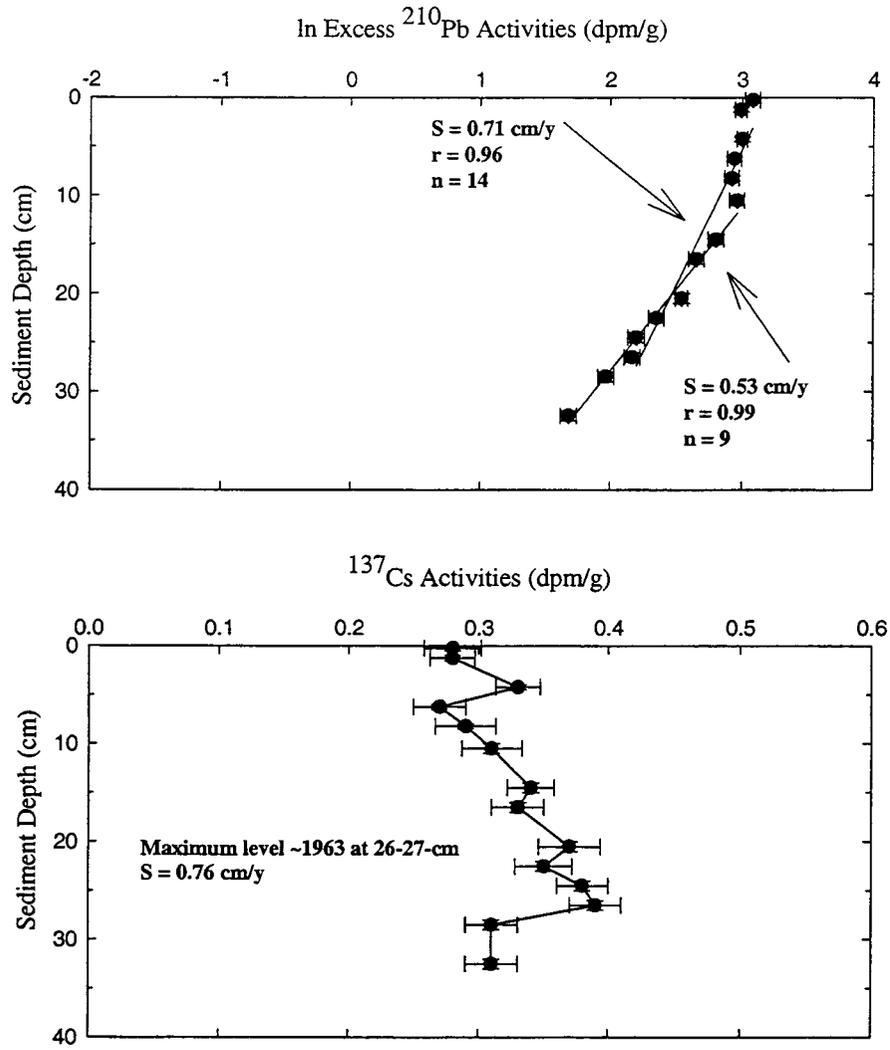
**Figure 3-45: Vertical Profiles Showing Activities of Excess  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  for Sediment Core 97-Z1F2 versus Sediment Depth. Calculated Sedimentation Rate (S) is Shown for  $^{137}\text{Cs}$ .**



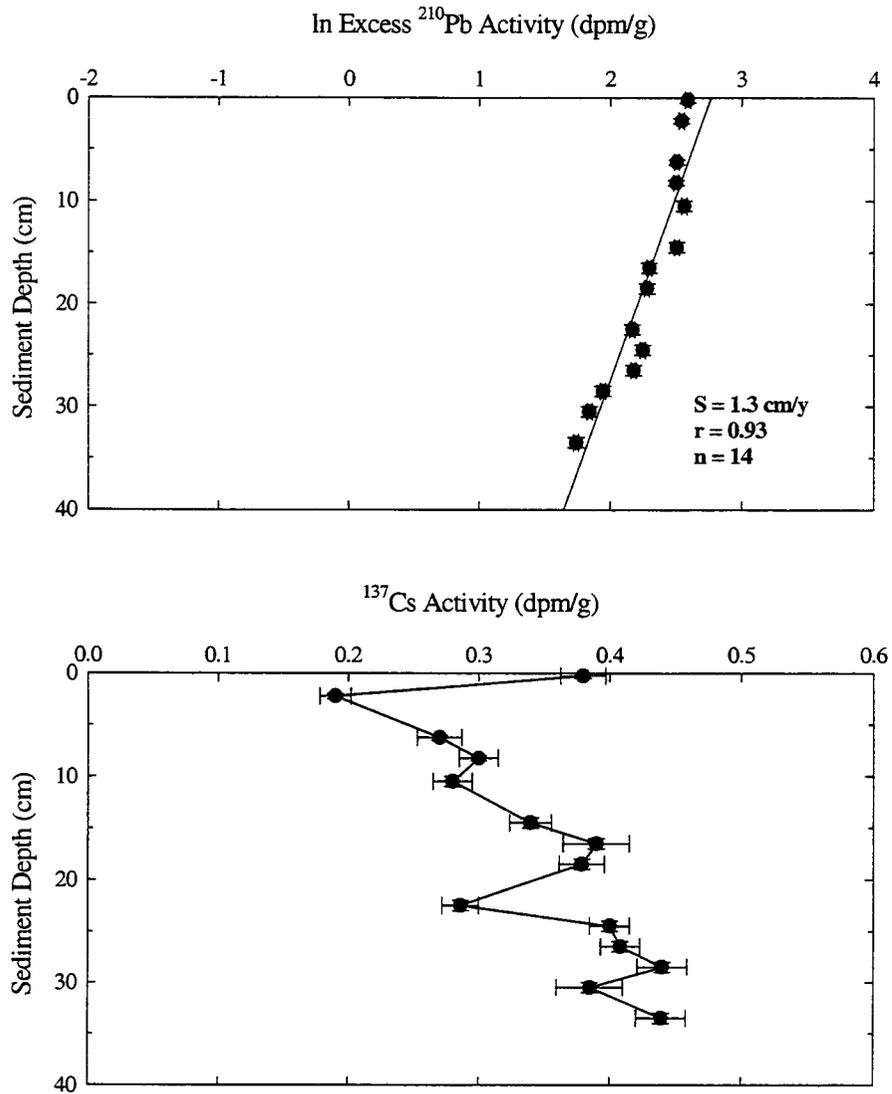
**Figure 3-46: Vertical Profiles Showing Activities of Excess  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  for Sediment Core 98-Z1R3B versus Sediment Depth. Calculated Sedimentation Rates (S) are Shown for each Isotope Technique.**



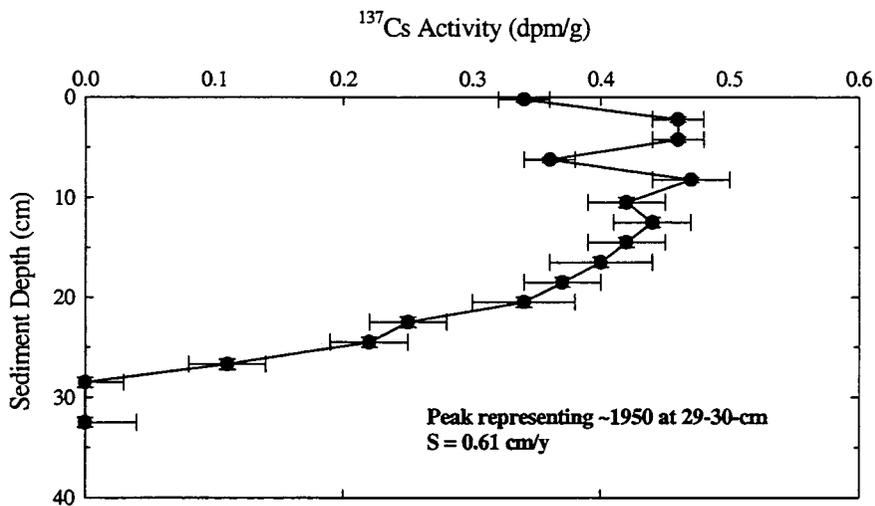
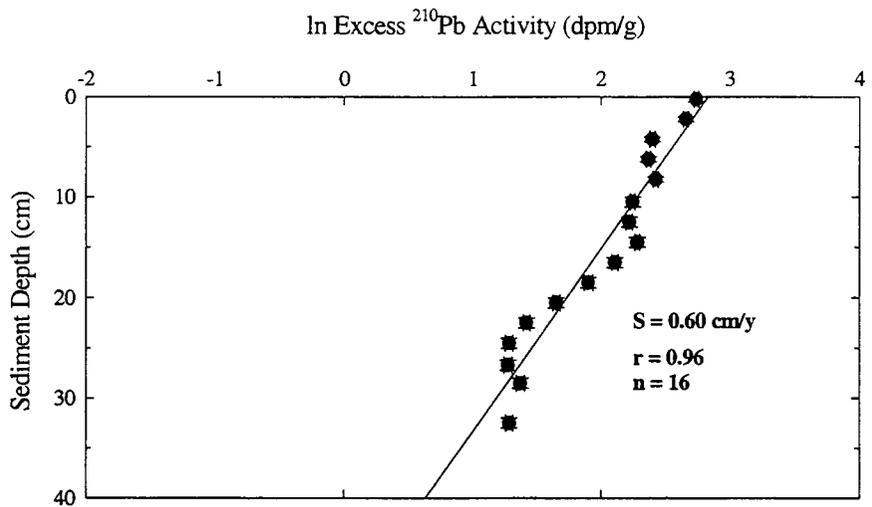
**Figure 3-47: Vertical Profiles Showing Activities of Excess  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  for Sediment Core 98-Z2F2 versus Sediment Depth. Calculated Sedimentation Rate (S) is Shown for each Isotope Technique.**



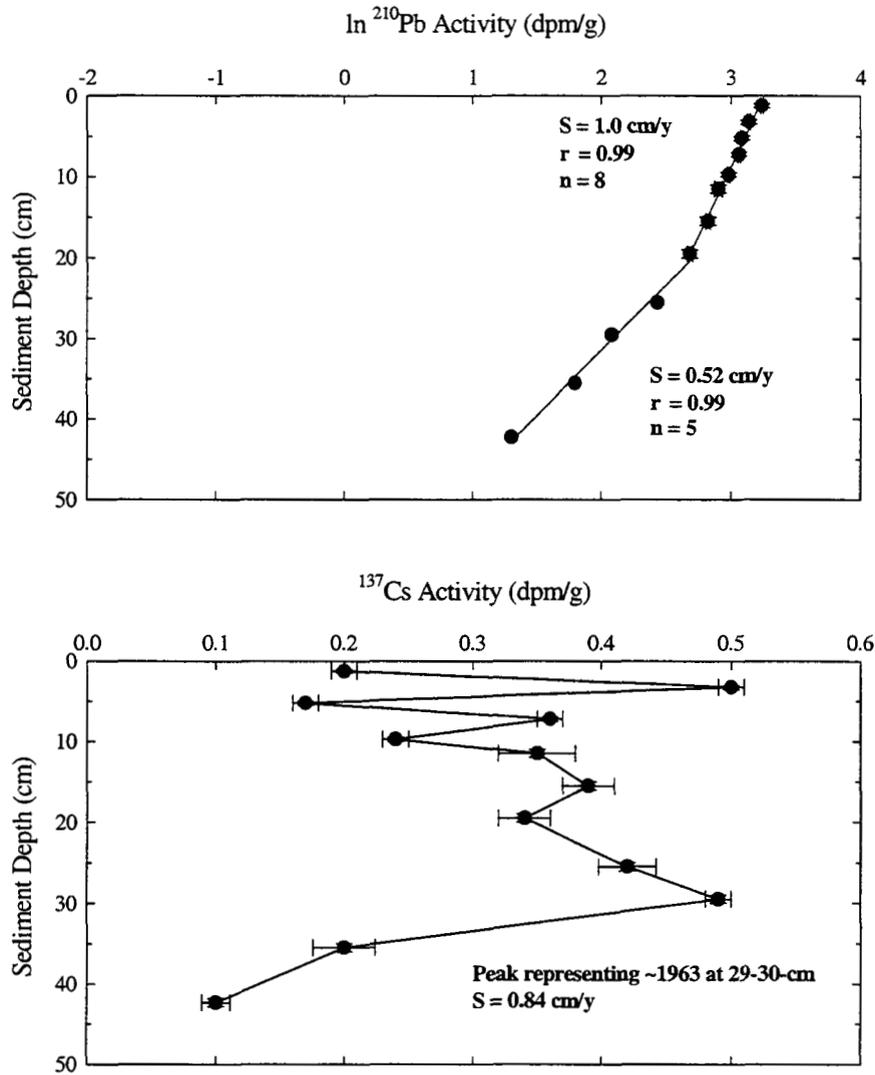
**Figure 3-48: Vertical Profiles Showing Activities of Excess  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  for Sediment Core 97-Z2R16 versus Sediment Depth. Calculated Sedimentation Rate (S) is Shown for each Isotope Technique.**



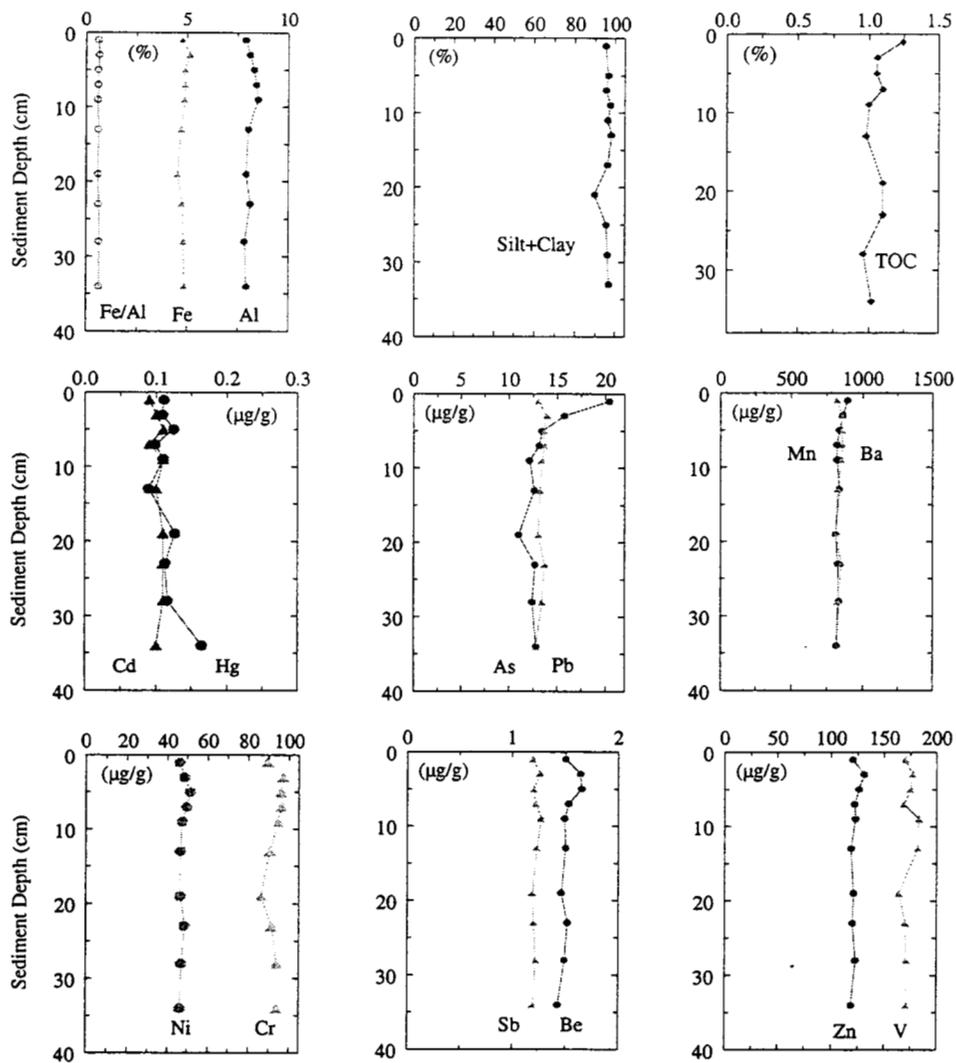
**Figure 3-49: Vertical Profiles Showing Activities of Excess  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  for Sediment Core 97-Z2F1 versus Sediment Depth. Calculated Sedimentation Rate (S) is Shown for excess  $^{210}\text{Pb}$ .**



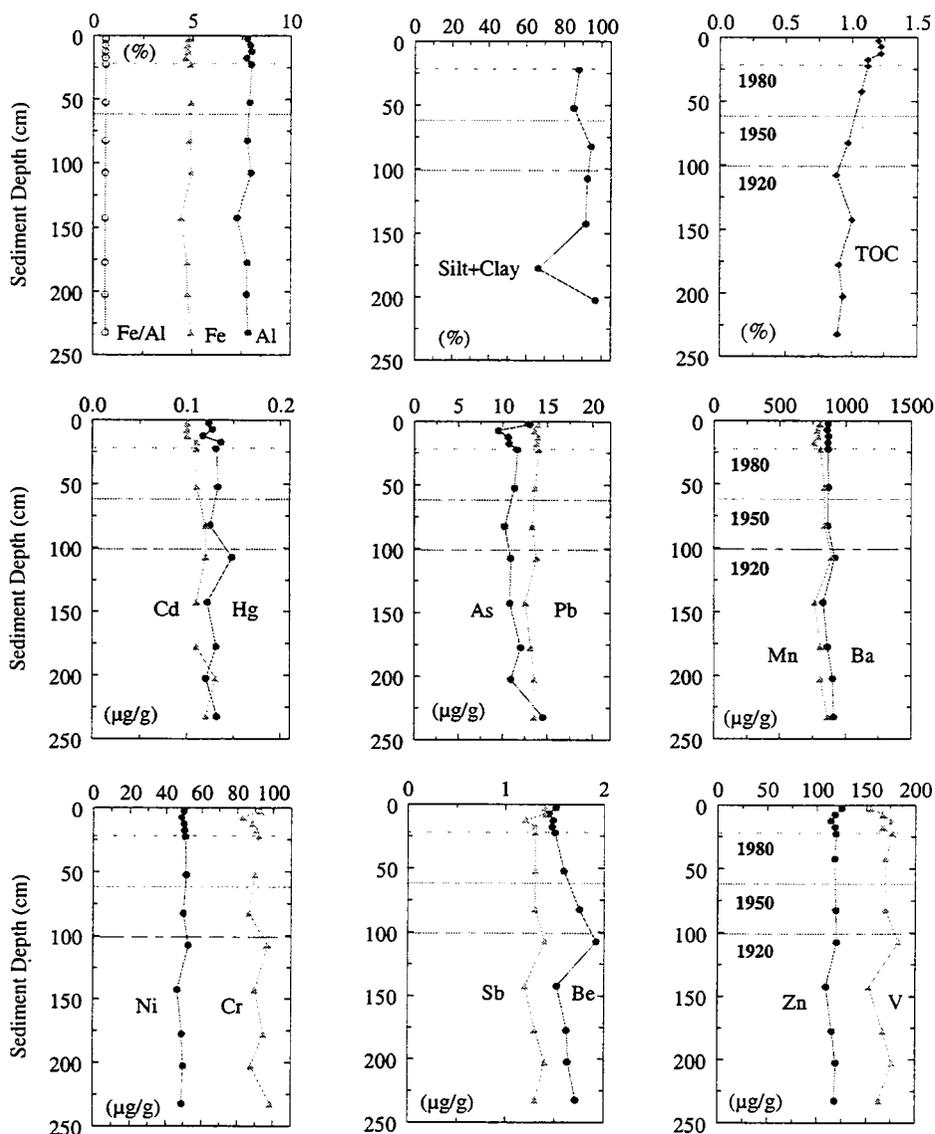
**Figure 3-50: Vertical Profiles Showing Activities of Excess  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  for Sediment Core 97-Z3F1 versus Sediment Depth. Calculated Sedimentation Rates (S) are Shown for each Isotope Technique.**



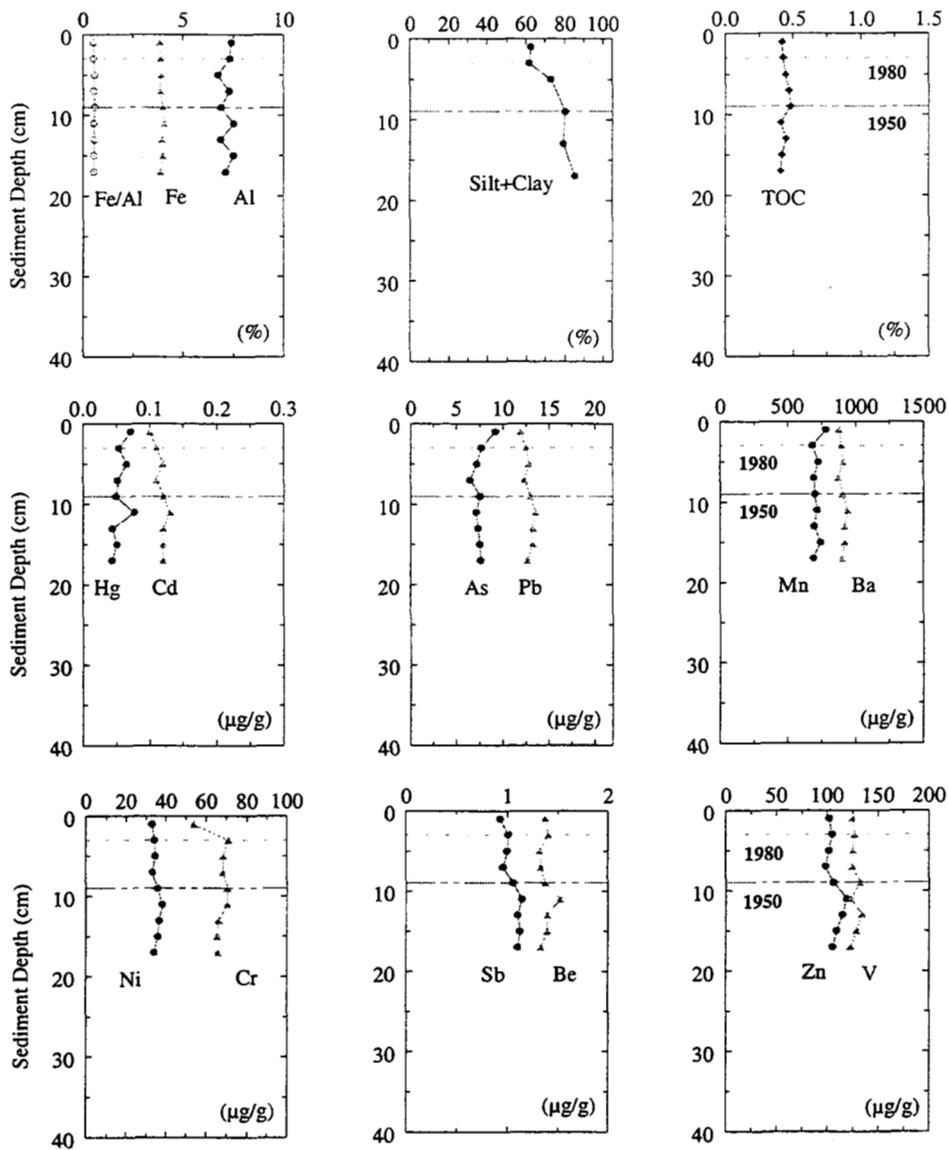
**Figure 3-51: Vertical Profiles Showing Activities of Excess <sup>210</sup>Pb and <sup>137</sup>Cs for Sediment Core 98-Z4F4 versus Sediment Depth. Calculated Sedimentation Rates (S) are Shown for each Isotope Technique.**



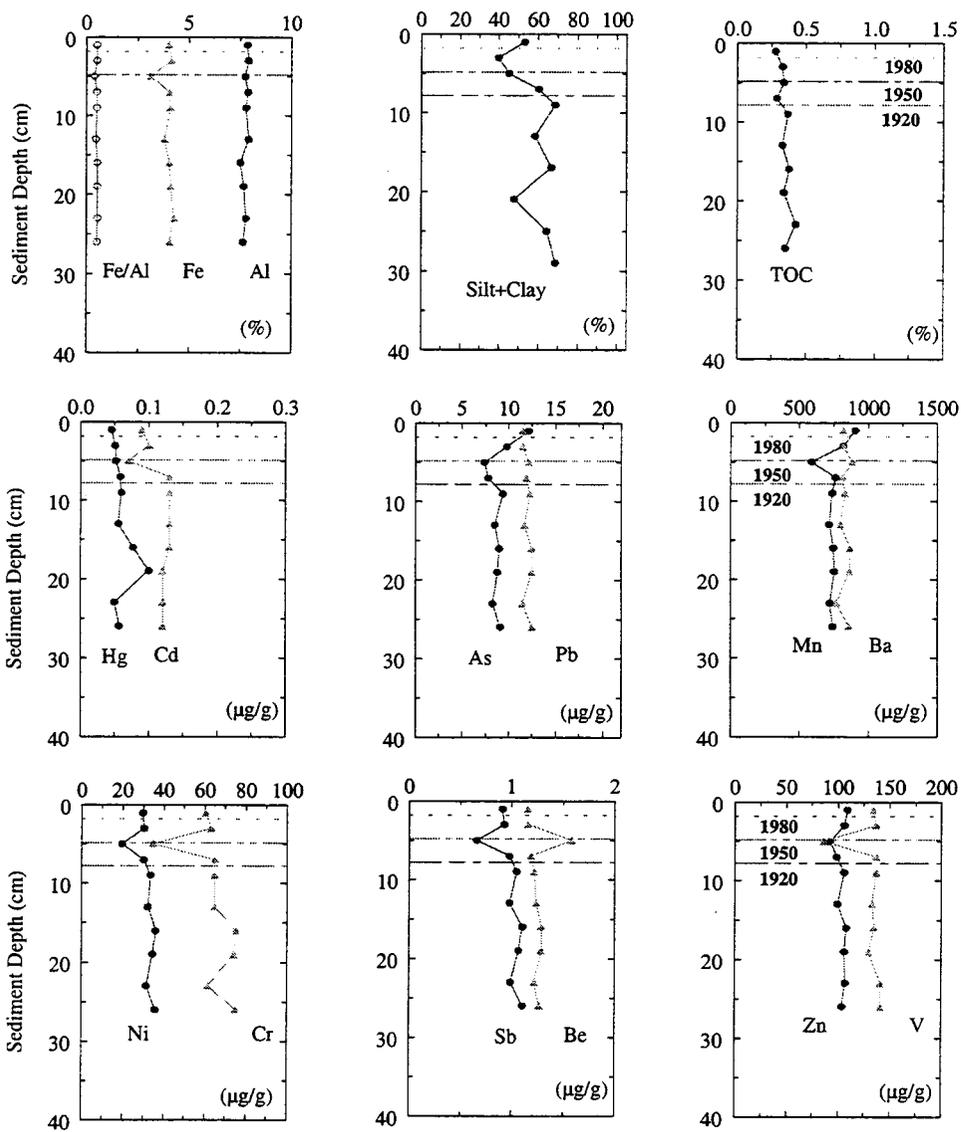
**Figure 3-52: Vertical Profiles from Sediment Core 97-Z0F1 (Homer Harbor) for Al, Fe, Silt Plus Clay, TOC, and Selected Trace Metals. Sedimentation Rate was not Valid for this Core (See Figure 3-53 for Age Record at Site Z0F1).**



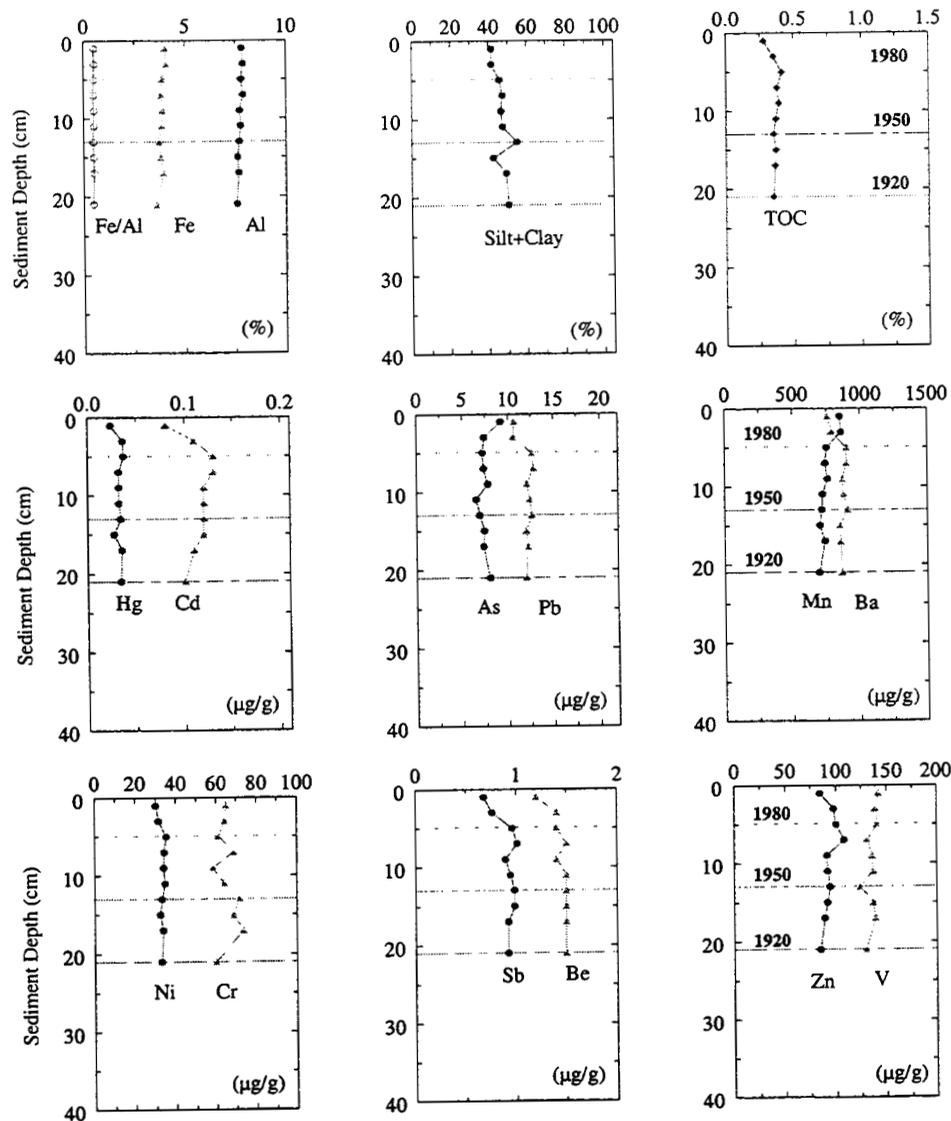
**Figure 3-53: Vertical Profiles from Sediment Core 98-Z0F1 (Homer Harbor) for Al, Fe, Silt Plus Clay, TOC, and Selected Trace Metals. Dotted Line Indicates Approximate Sediment Depth for 1980 and Dashed Lines Correspond to 1950 and 1920.**



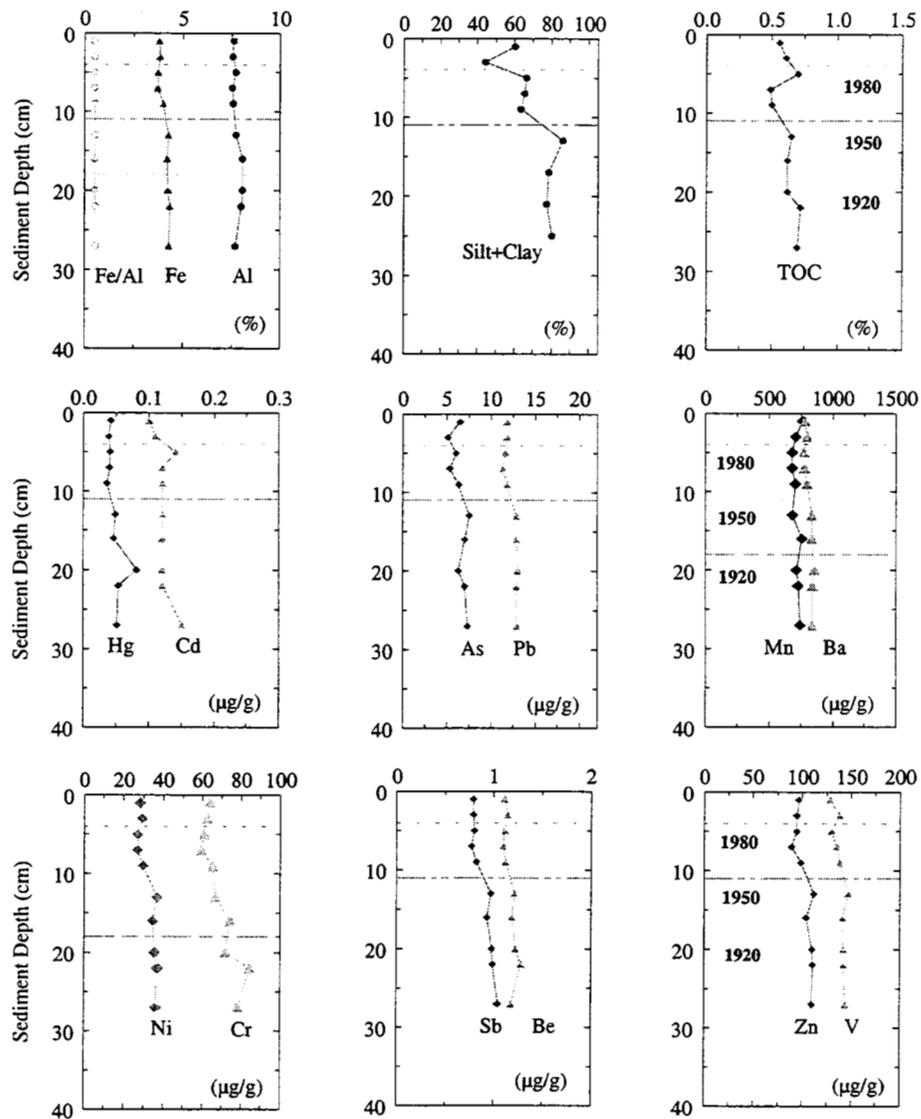
**Figure 3-54: Vertical Profiles from Sediment Core 97-Z0F5 for Al, Fe, Silt Plus Clay, TOC, and Selected Trace Metals. Dotted Line Indicates Sediment Depth for 1980 and Dashed Line Corresponds to 1950.**



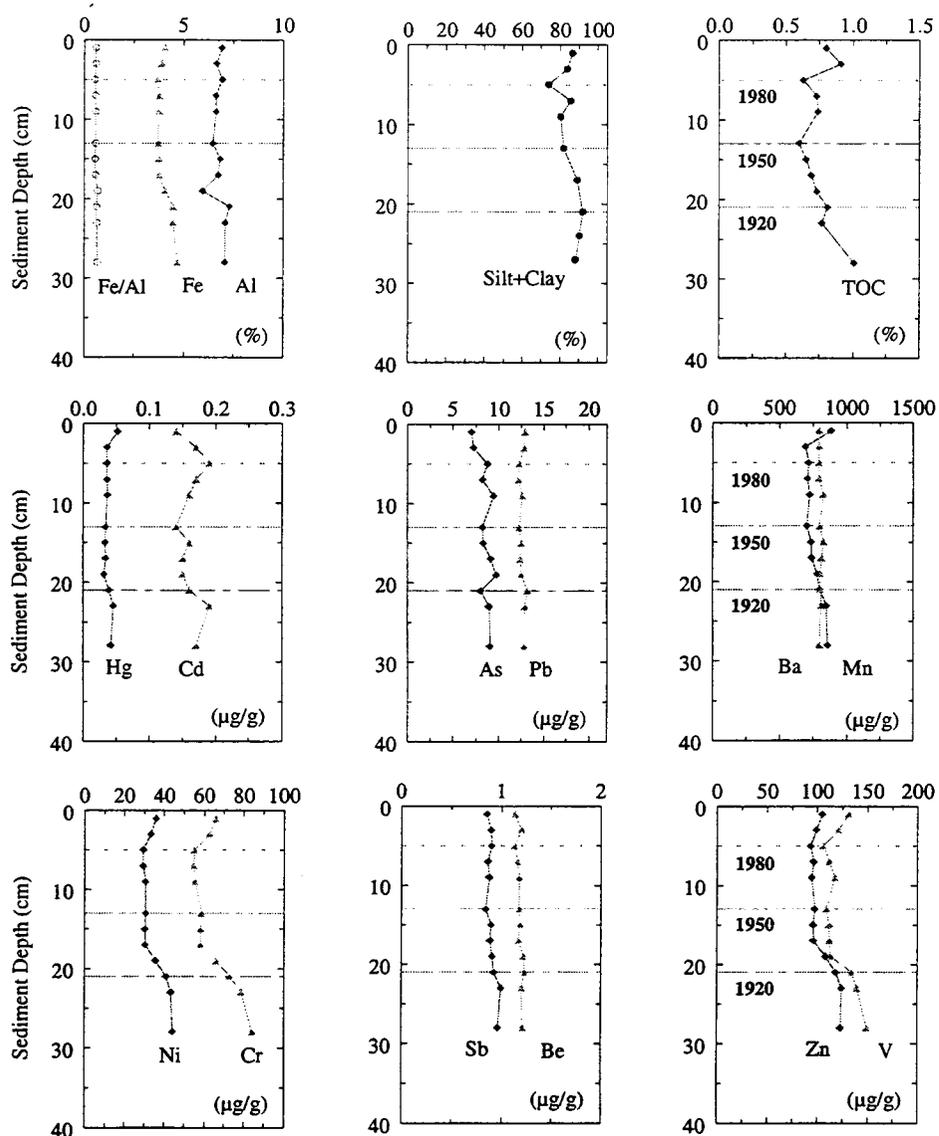
**Figure 3-55: Vertical Profiles from Sediment Core 97-Z0F6 for Al, Fe, Silt Plus Clay, TOC, and Selected Trace Metals. Dotted Line Indicates Sediment Depth for 1980 and Dashed Lines Correspond to 1950 and 1920.**



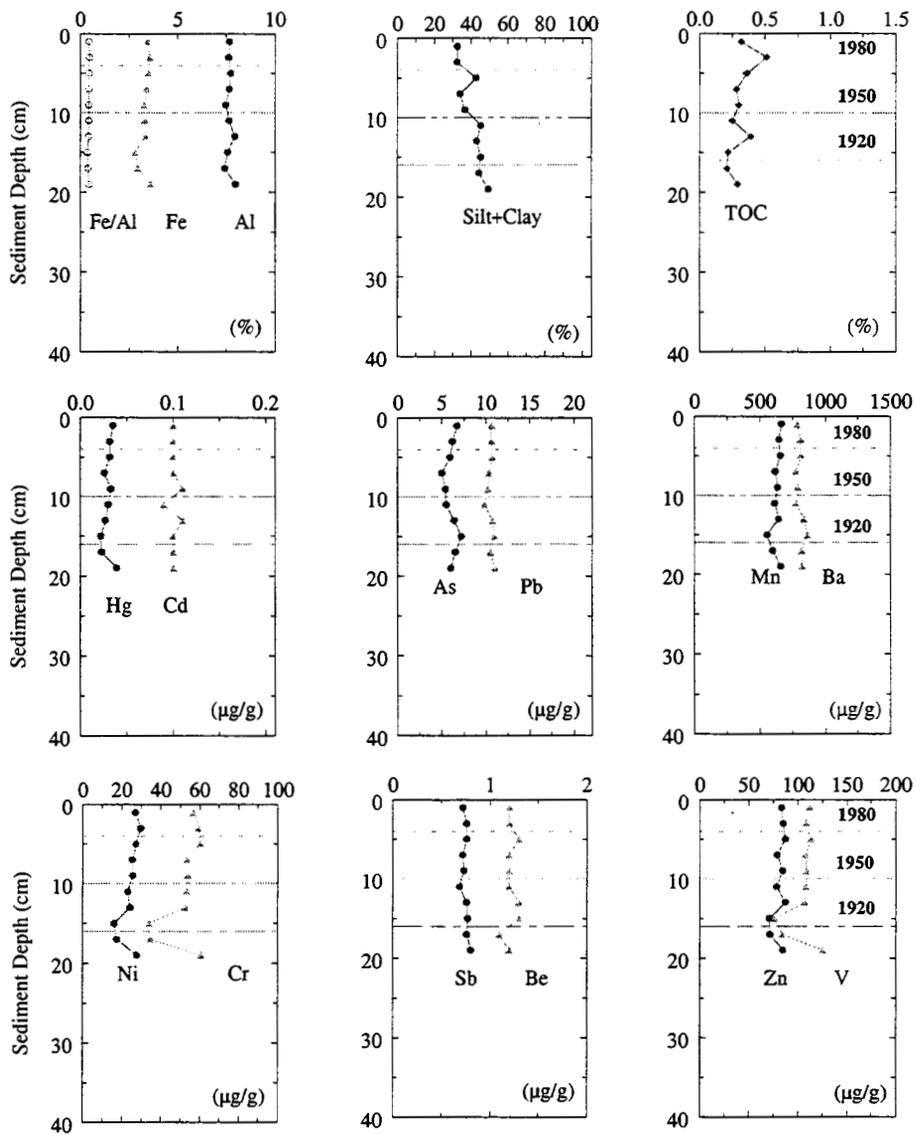
**Figure 3-56: Vertical Profiles from Sediment Core 98-Z0F8 for Al, Fe, Silt Plus Clay, TOC, and Selected Trace Metals. Dotted Line Indicates Sediment Depth for 1980 and Dashed Lines Correspond to 1950 and 1920.**



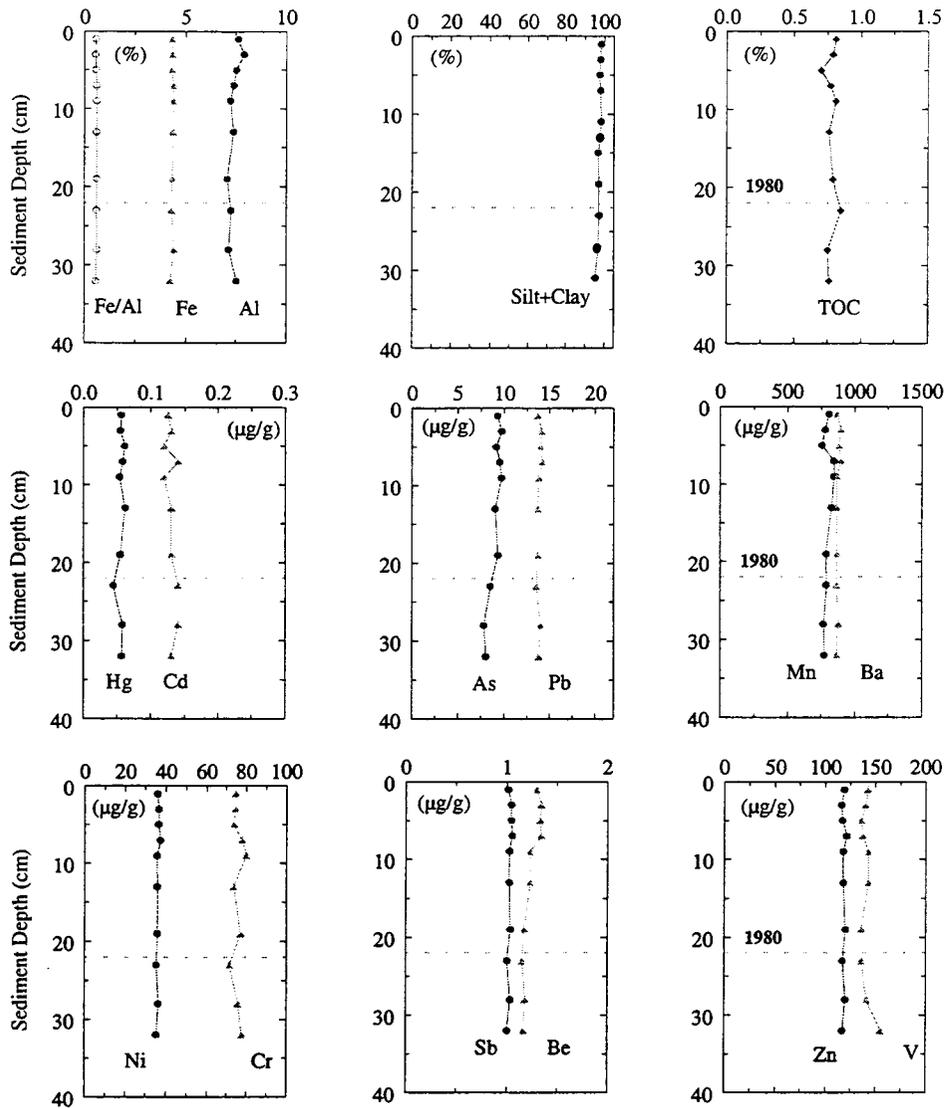
**Figure 3-57: Vertical Profiles from Sediment Core 97-Z1F1 for Al, Fe, Silt Plus Clay, TOC, and Selected Trace Metals. Dotted Line Indicates Sediment Depth for 1980 and Dashed Lines Correspond to 1950 and 1920.**



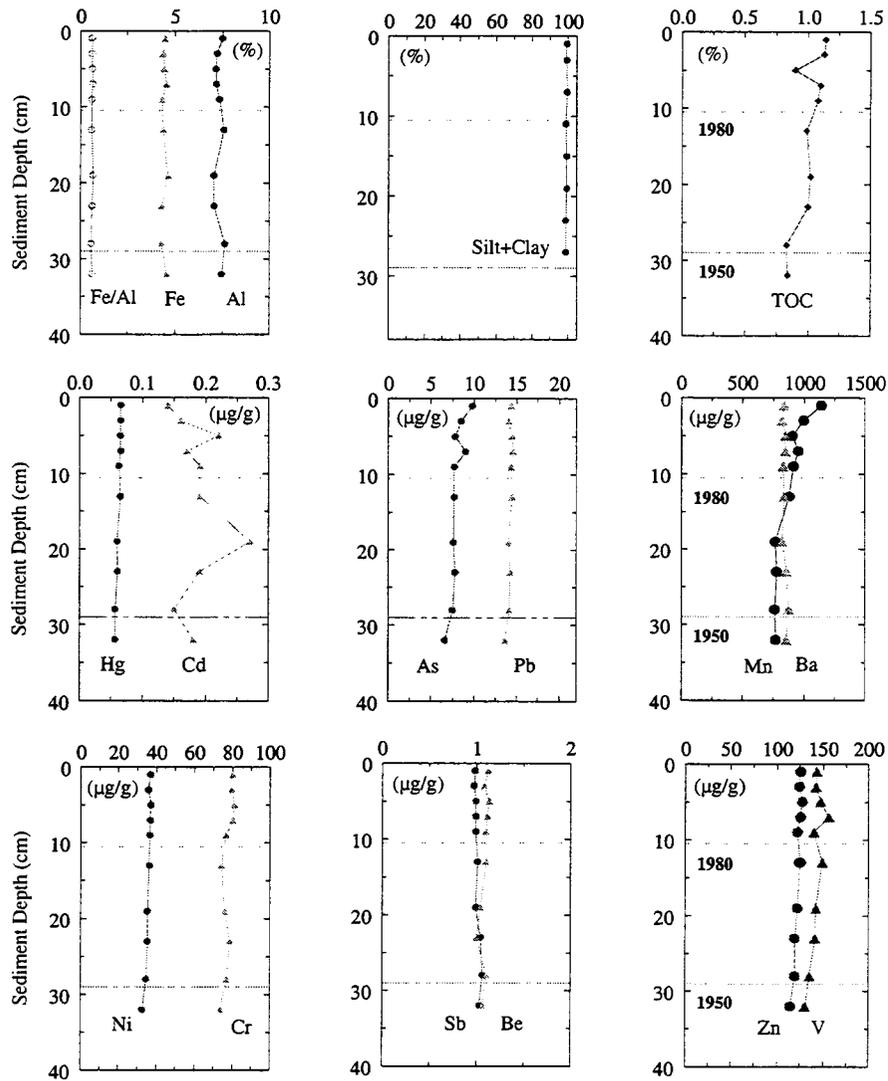
**Figure 3-58: Vertical Profiles from Sediment Core 97-Z1F2 for Al, Fe, Silt Plus Clay, TOC, and Selected Trace Metals. Dotted Line Indicates Sediment Depth for 1980 and Dashed Lines Correspond to 1950 and 1920.**



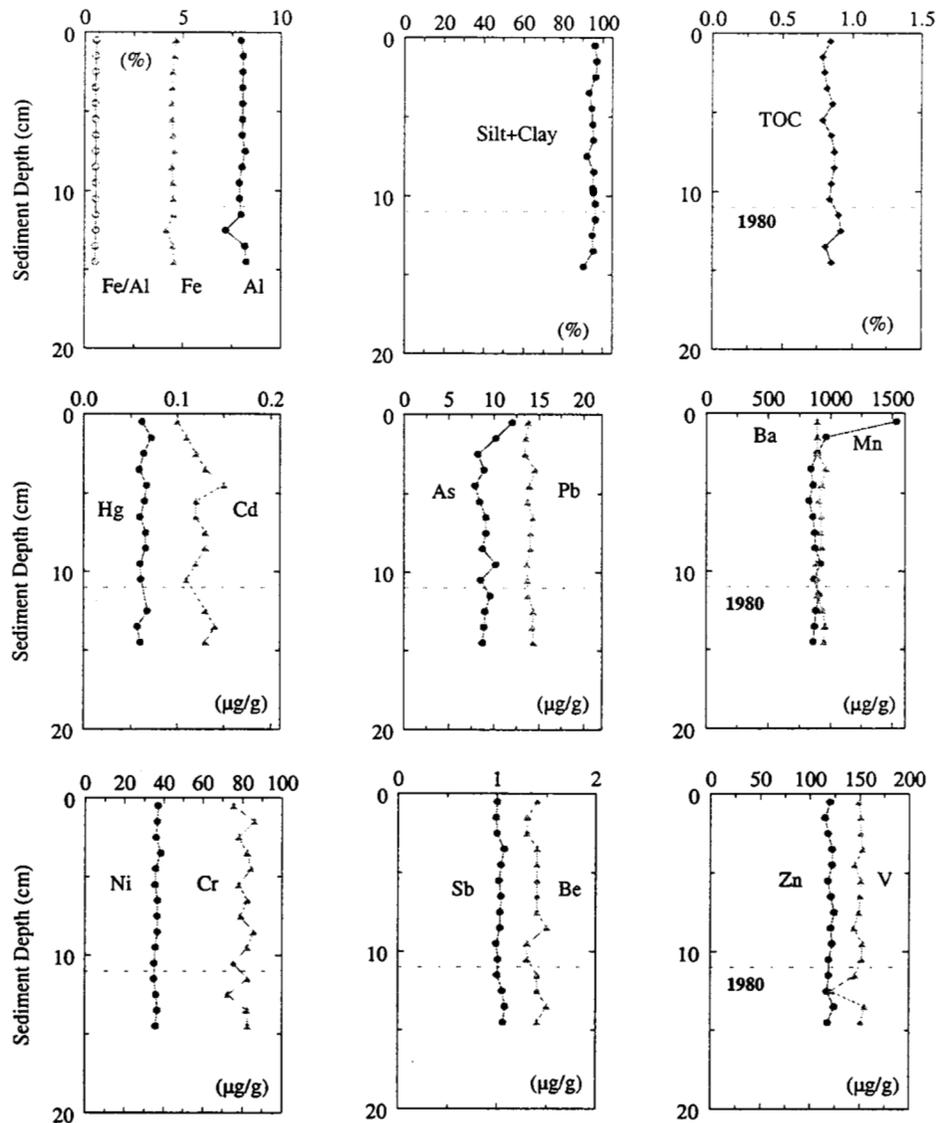
**Figure 3-59: Vertical Profiles from Sediment Core 98-Z1R3B for Al, Fe, Silt Plus Clay, TOC, and Selected Trace Metals. Dotted Line Indicates Sediment Depth for 1980 and Dashed Lines Correspond to 1950 and 1920.**



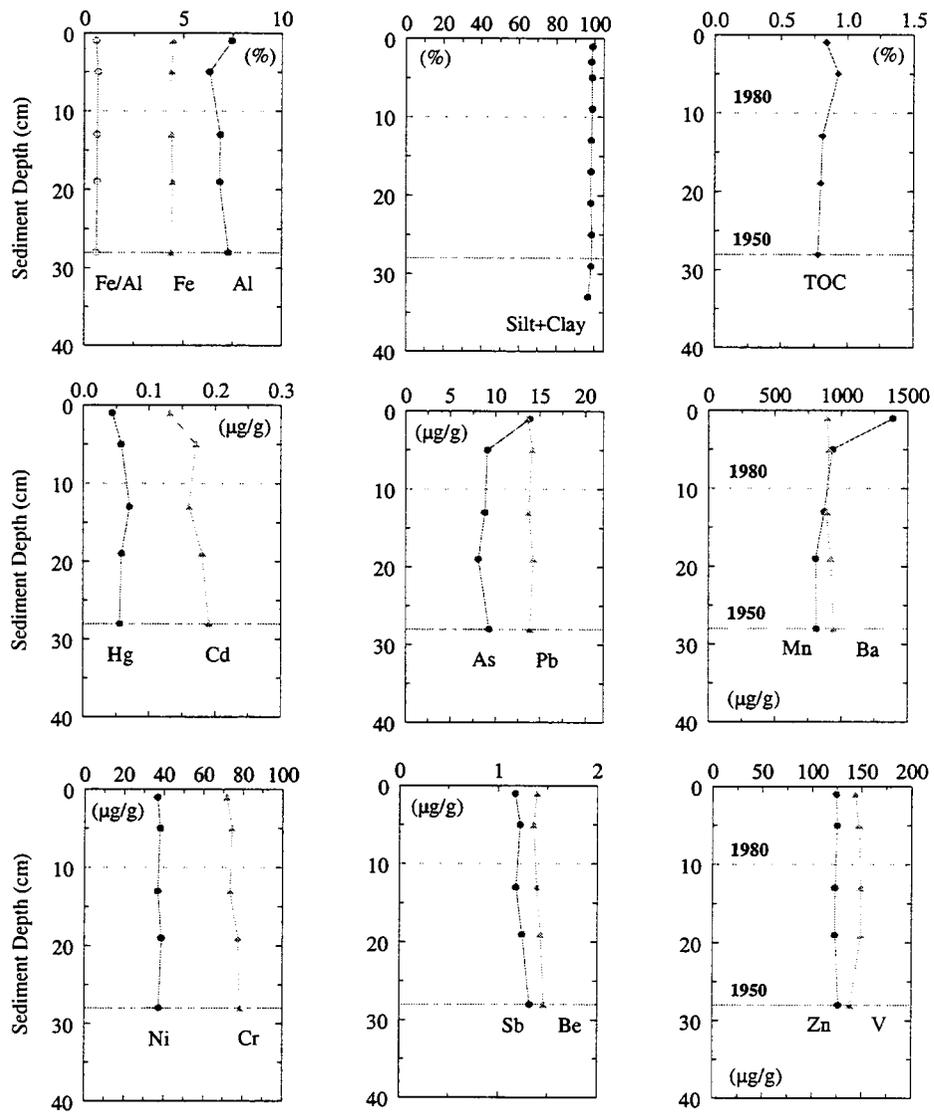
**Figure 3-60: Vertical Profiles from Sediment Core 97-Z2F1 for Al, Fe, Silt Plus Clay, TOC, and Selected Trace Metals. Dotted Line Indicates Sediment Depth for 1980.**



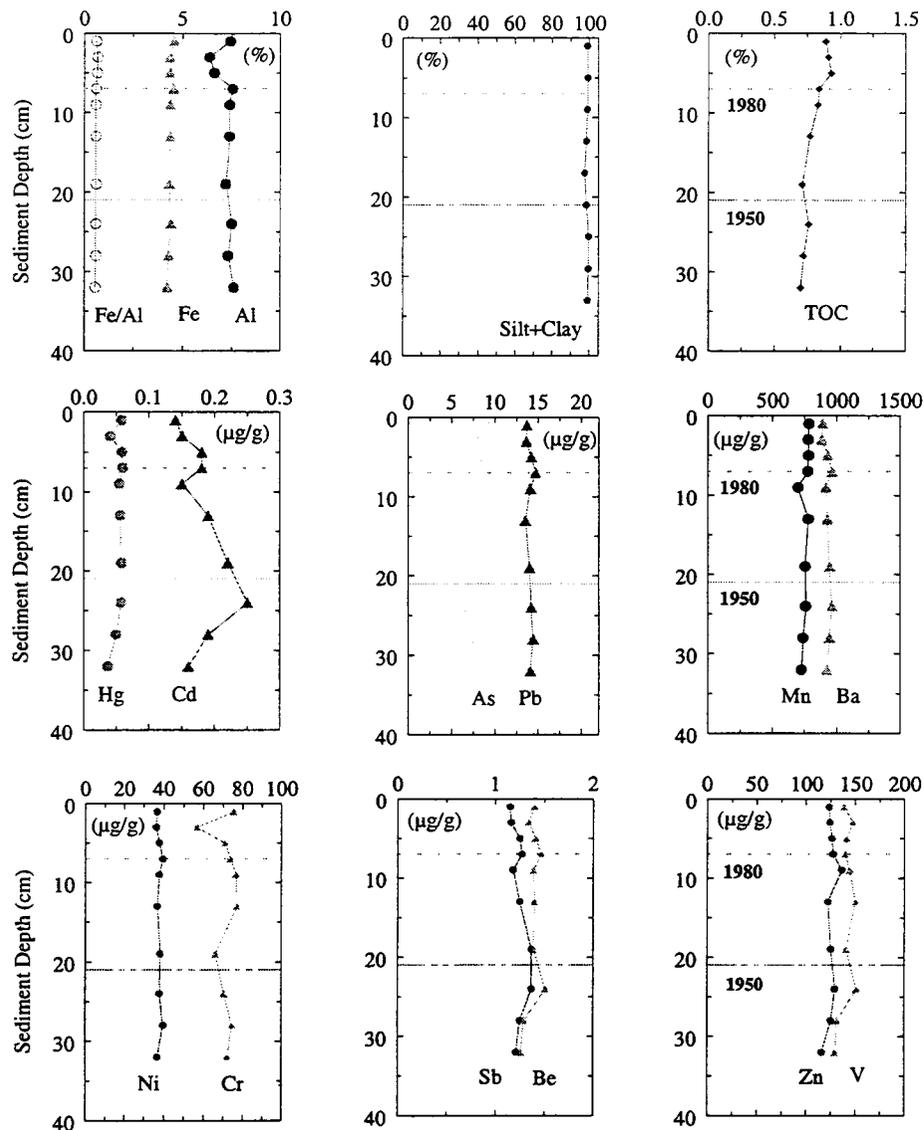
**Figure 3-61: Vertical Profiles from Sediment Core 97-Z2F2 for Al, Fe, Silt Plus Clay, TOC, and Selected Trace Metals. Dotted Line Indicates Sediment Depth for 1980 and Dashed Line Corresponds to 1950.**



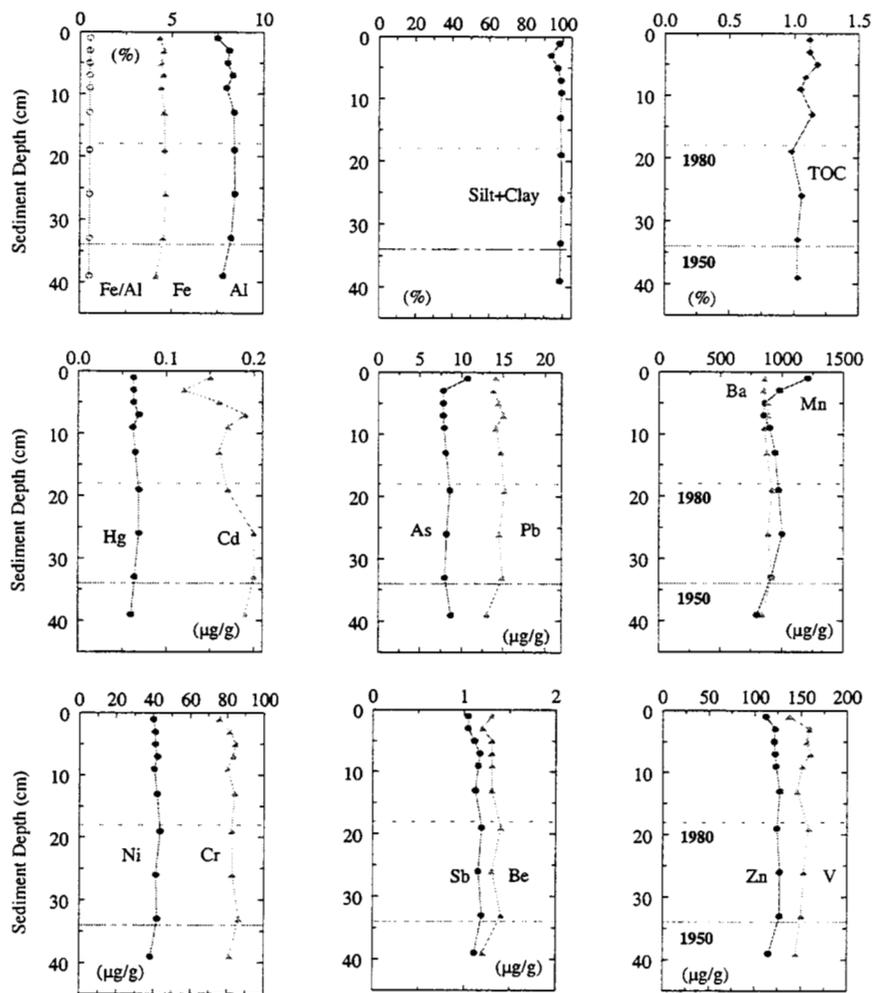
**Figure 3-62: Vertical Profiles from Sediment Core 98-Z2R16 for Al, Fe, Silt Plus Clay, TOC, and Selected Trace Metals. Dotted Line Indicates Sediment Depth for 1980.**



**Figure 3-63: Vertical Profiles from Sediment Core 97-Z3F1 for Al, Fe, Silt Plus Clay, TOC, and Selected Trace Metals. Dotted Line Indicates Sediment Depth for 1980 and Dashed Line Corresponds to 1950.**

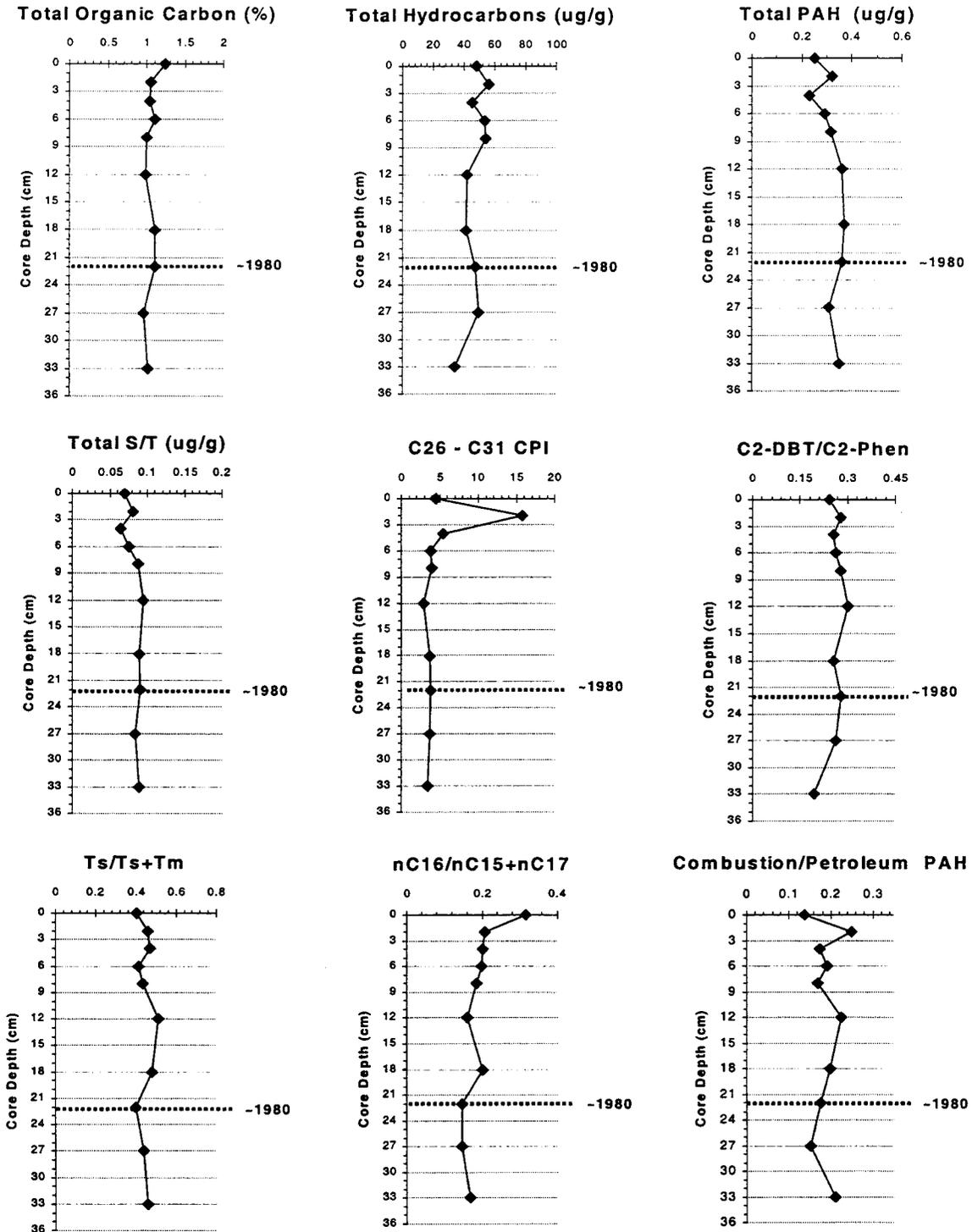


**Figure 3-64: Vertical Profiles from Sediment Core 97-Z3F2 for Al, Fe, Silt Plus Clay, TOC, and Selected Trace Metals. Dotted Line Indicates Sediment Depth for 1980 and Dashed Line Corresponds to 1950.**



**Figure 3-65: Vertical Profiles from Sediment Core 98-Z4F4 for Al, Fe, Silt Plus Clay, TOC, and Selected Trace Metals. Dotted Line Indicates Sediment Depth for 1980 and Dashed Line Corresponds to 1950.**

# Z0F1



**Figure 3-66: Vertical Core Profiles of Selected Diagnostic Organic Parameters for Station Z0F1 versus Sediment Depth (1997).**

# Z0F1

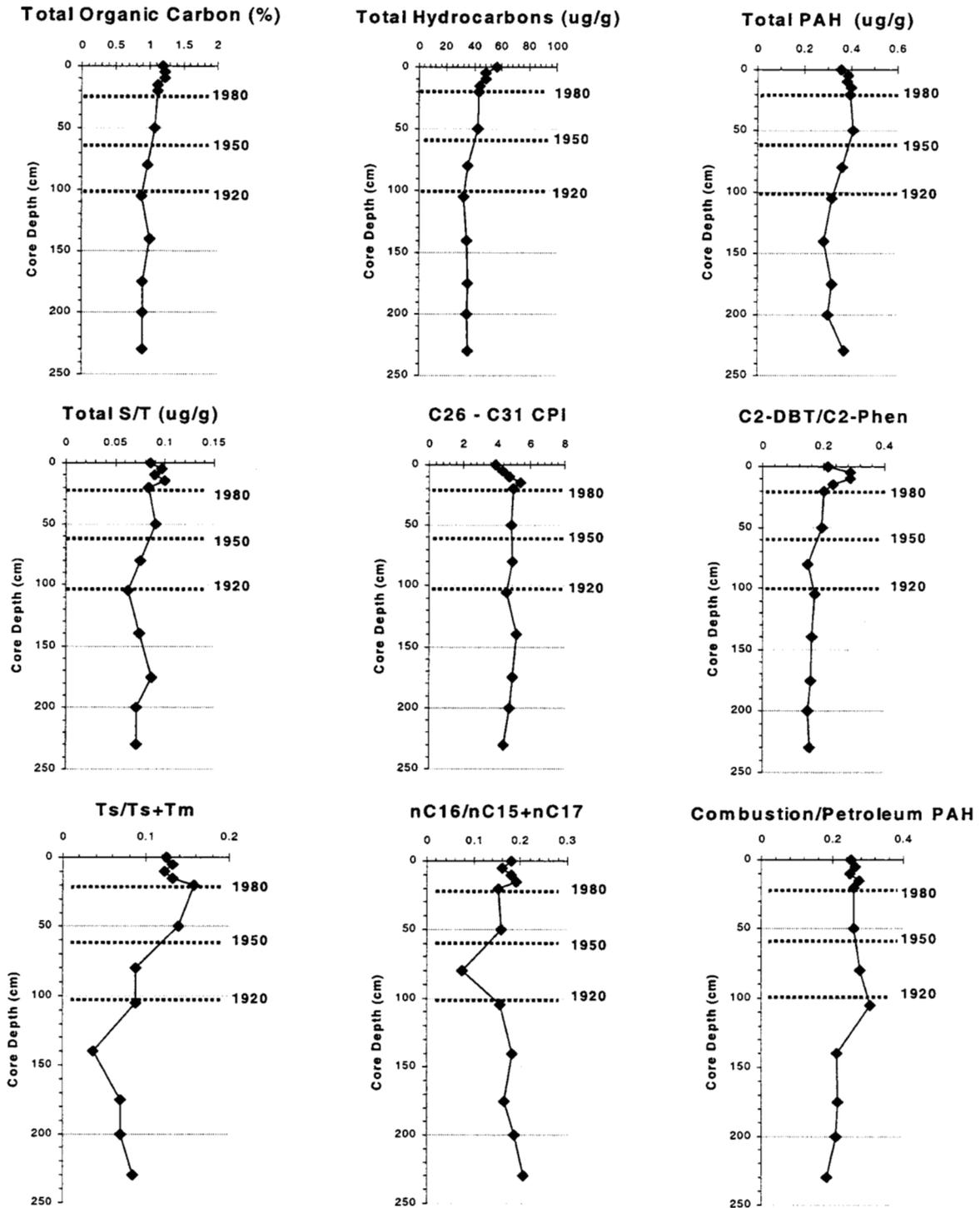
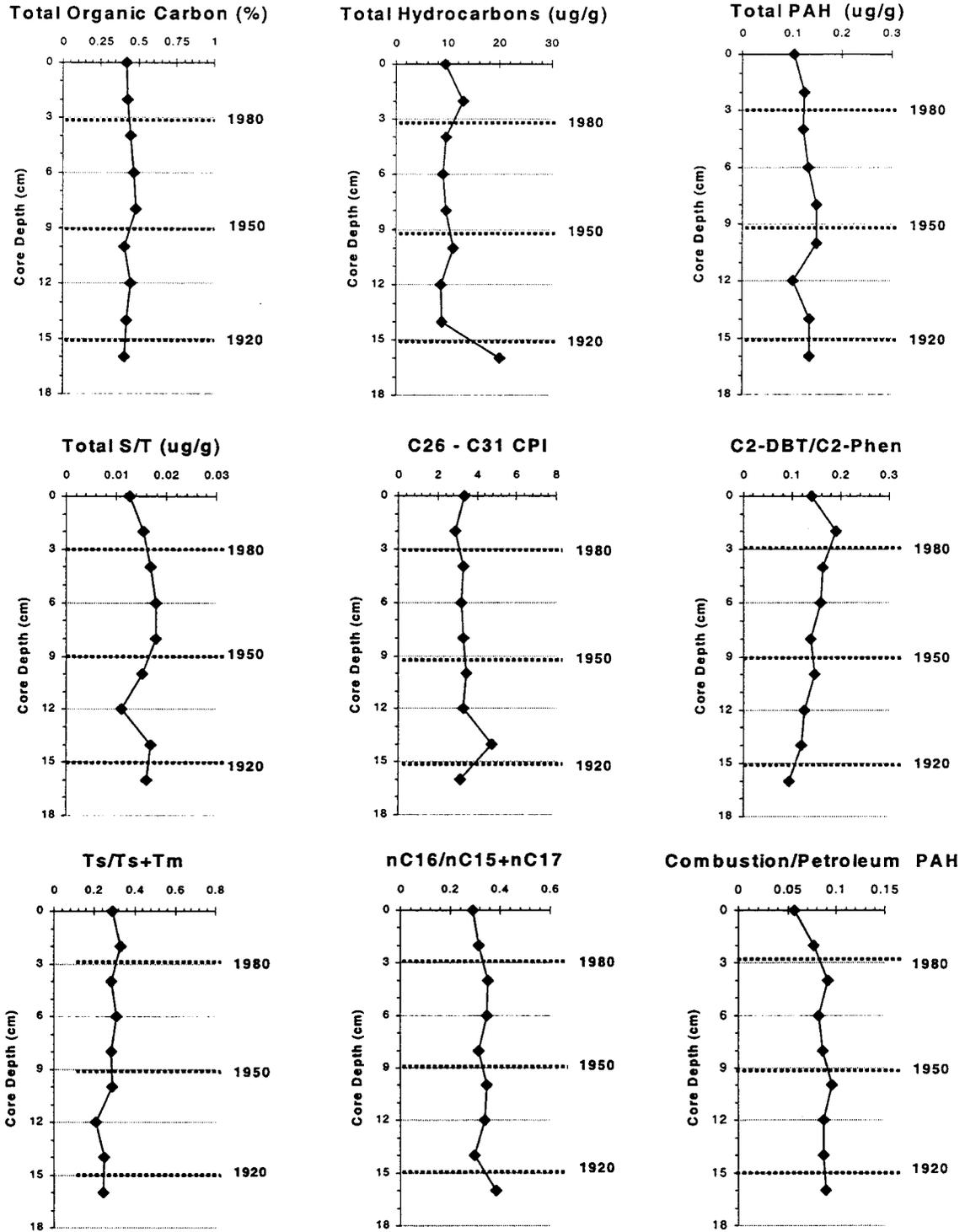


Figure 3-67: Vertical Core Profiles of Selected Diagnostic Organic Parameters for Station Z0F1 versus Sediment Depth (1998).

## Z0F5



**Figure 3-68: Vertical Core Profiles of Selected Diagnostic Organic Parameters for Station Z0F5 versus Sediment Depth (1997).**

# Z0F6

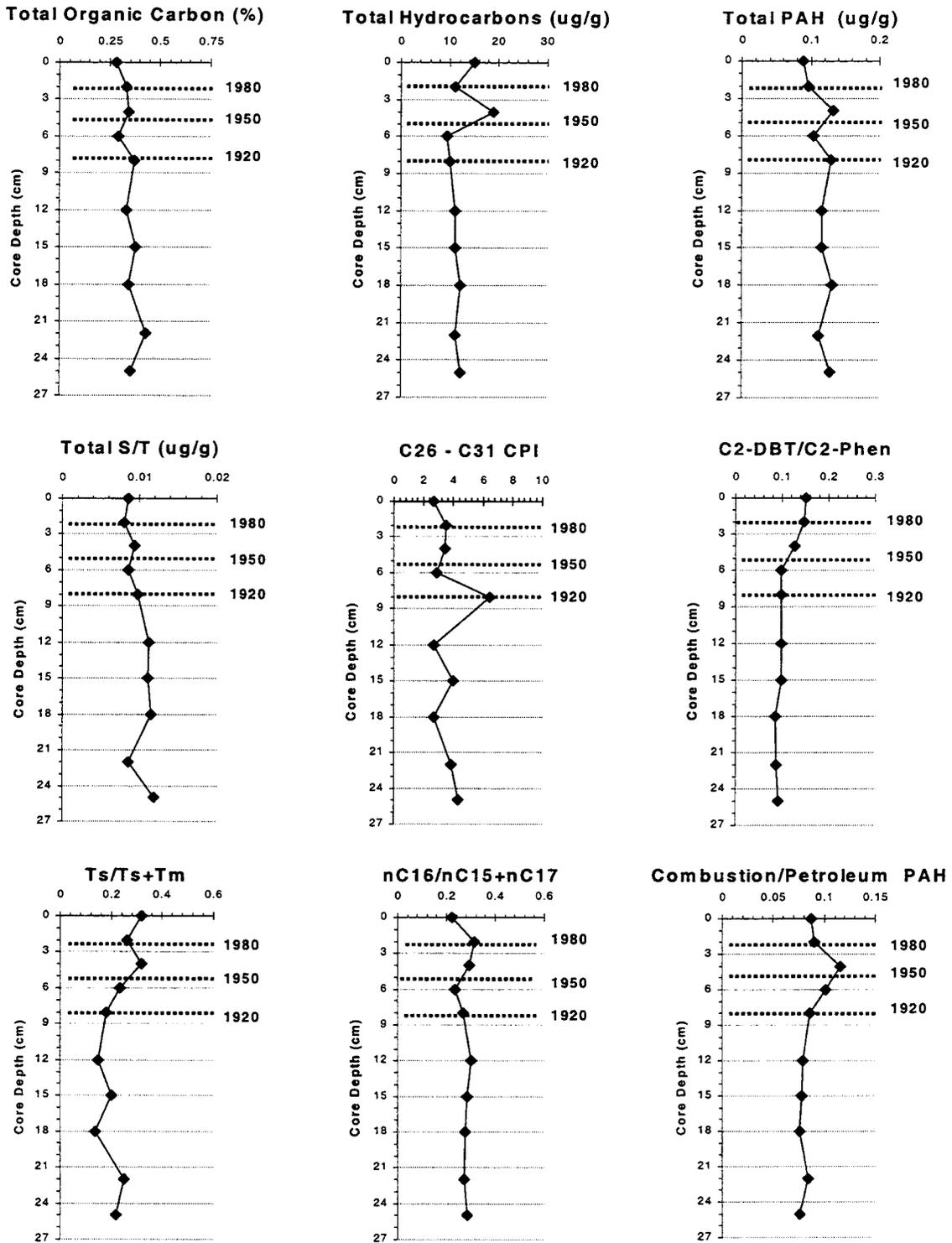
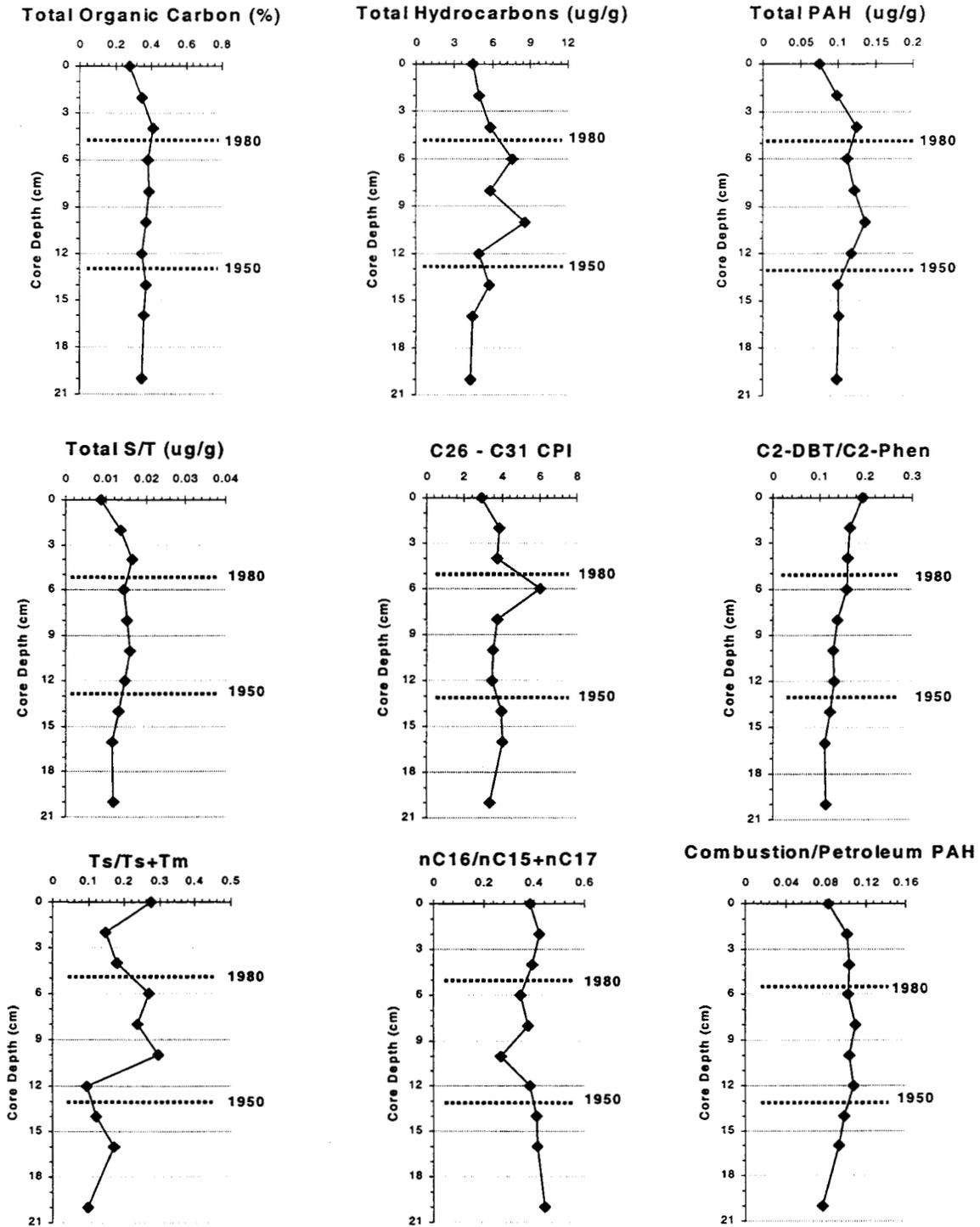


Figure 3-69: Vertical Core Profiles of Selected Diagnostic Organic Parameters for Station Z0F6 versus Sediment Depth (1997).

# Z0F8



**Figure 3-70: Vertical Core Profiles of Selected Diagnostic Organic Parameters for Station Z0F8 versus Sediment Depth (1998).**

# Z1F1

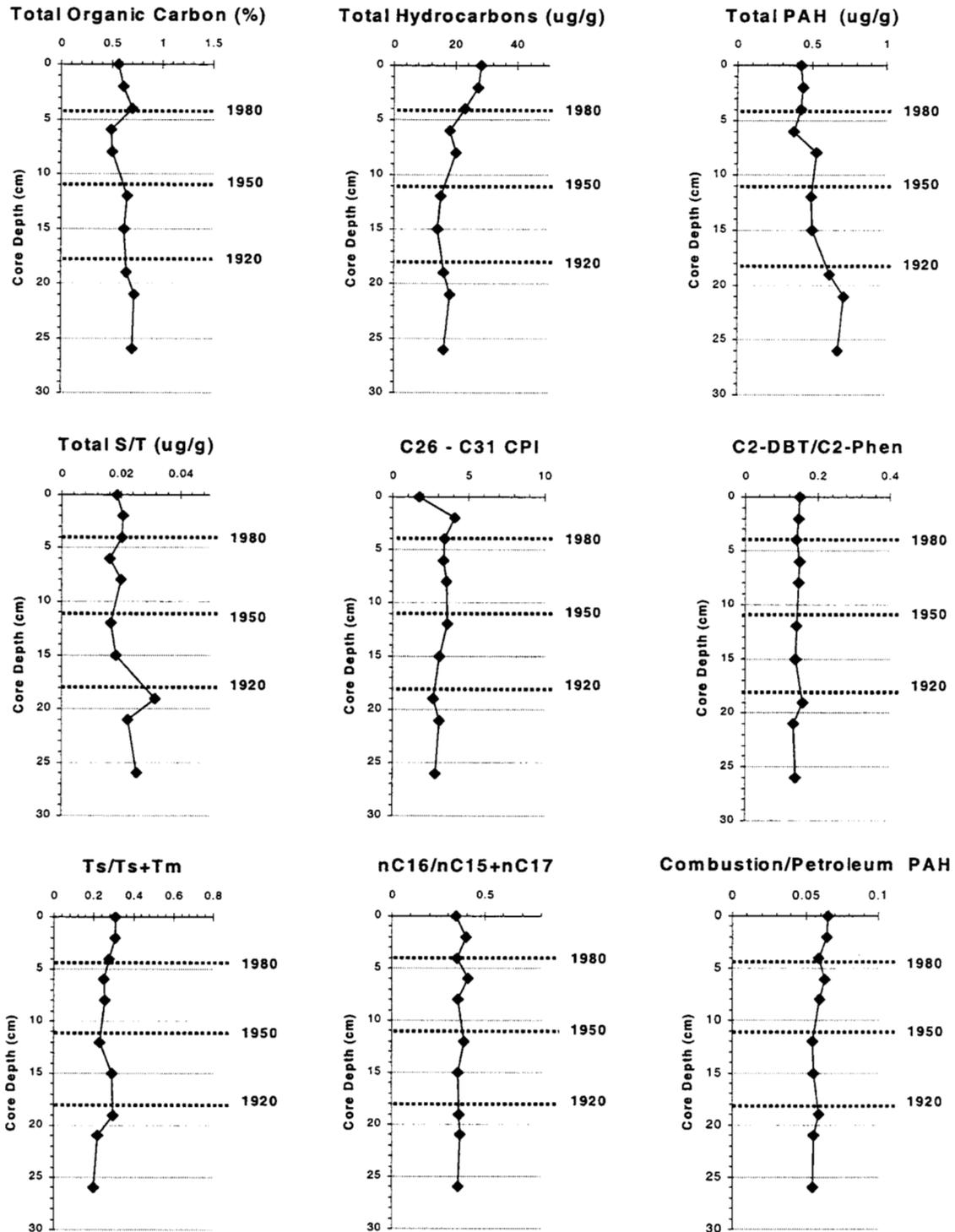
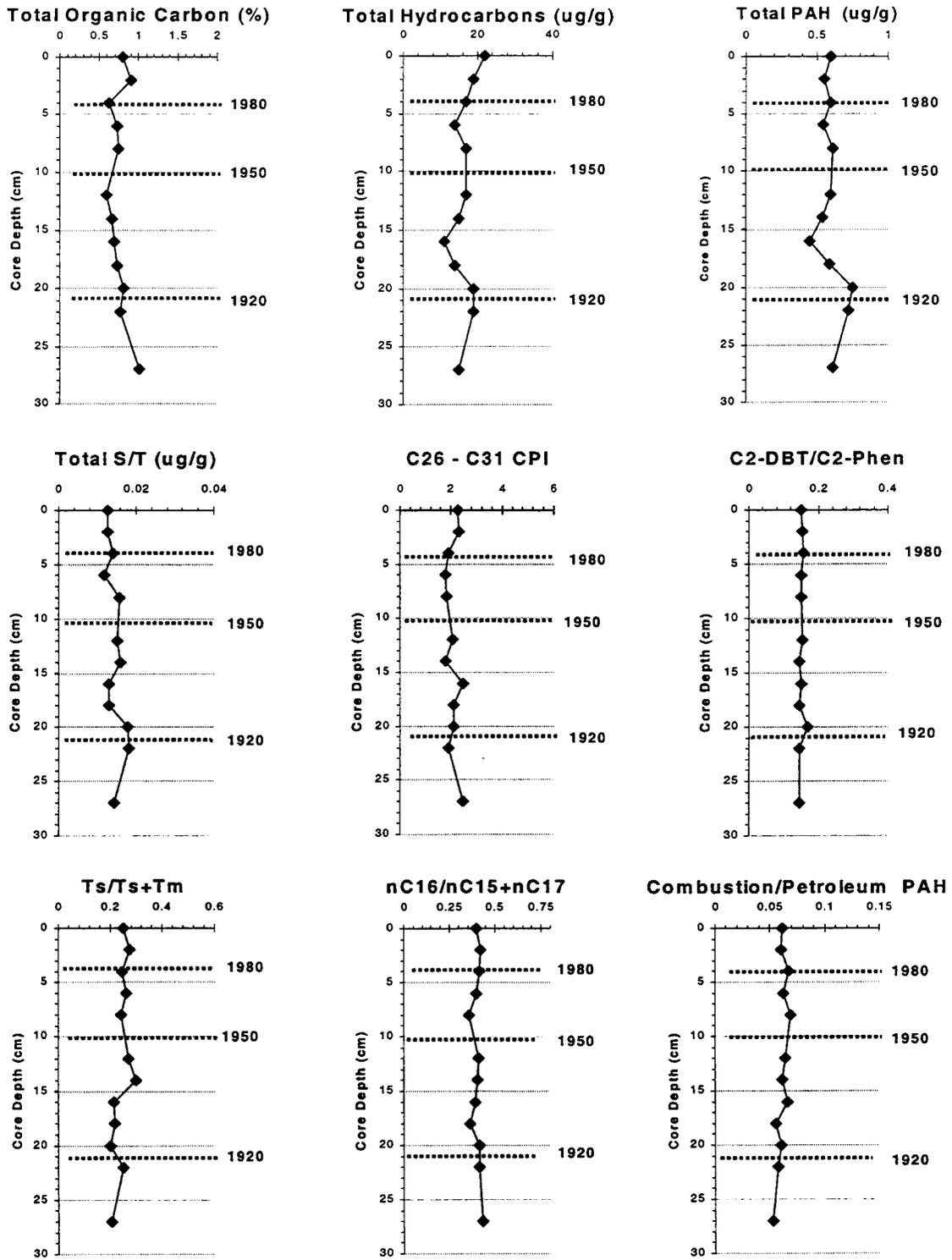


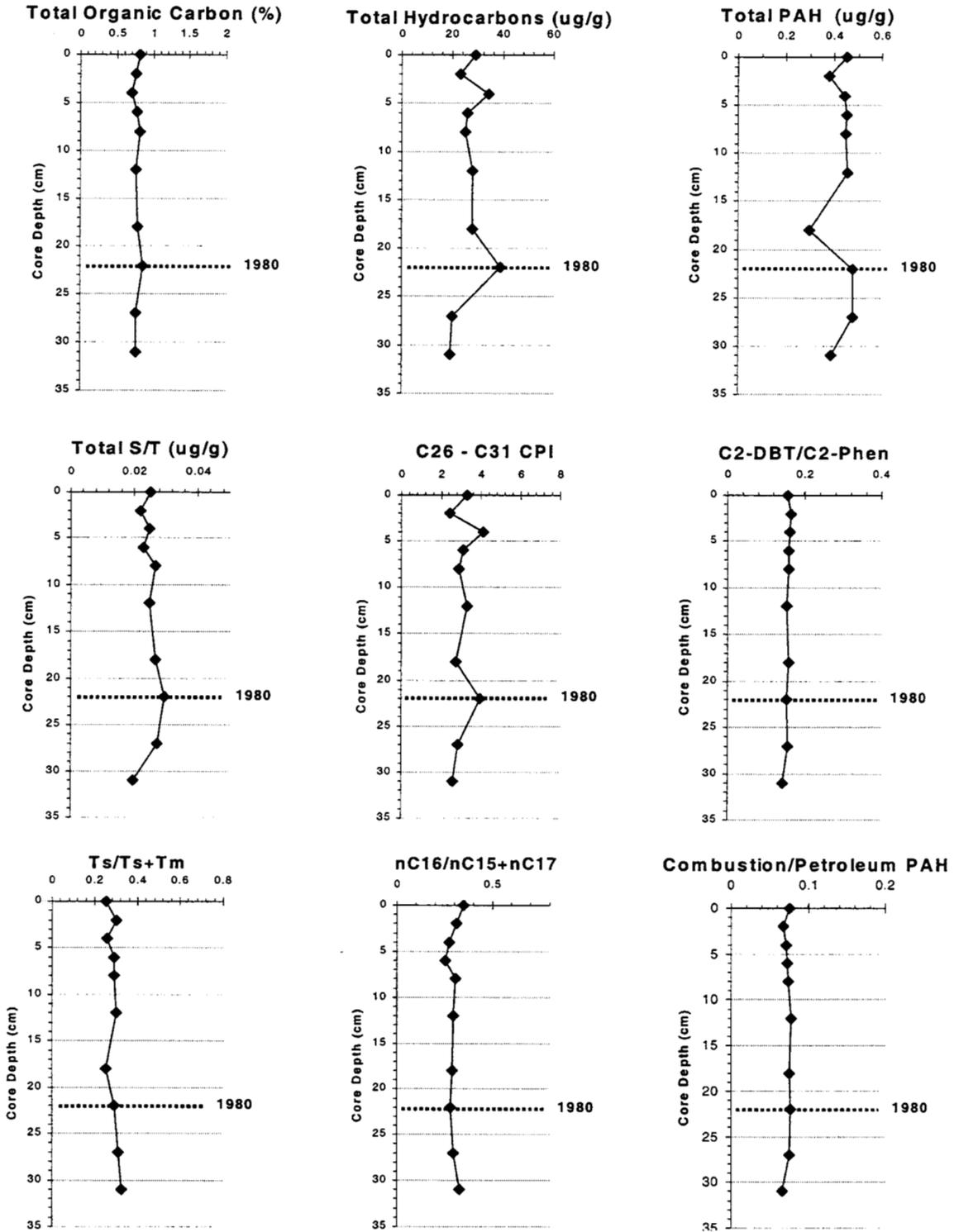
Figure 3-71: Vertical Core Profiles of Selected Diagnostic Organic Parameters for Station Z1F1 versus Sediment Depth (1997).

## Z1F2



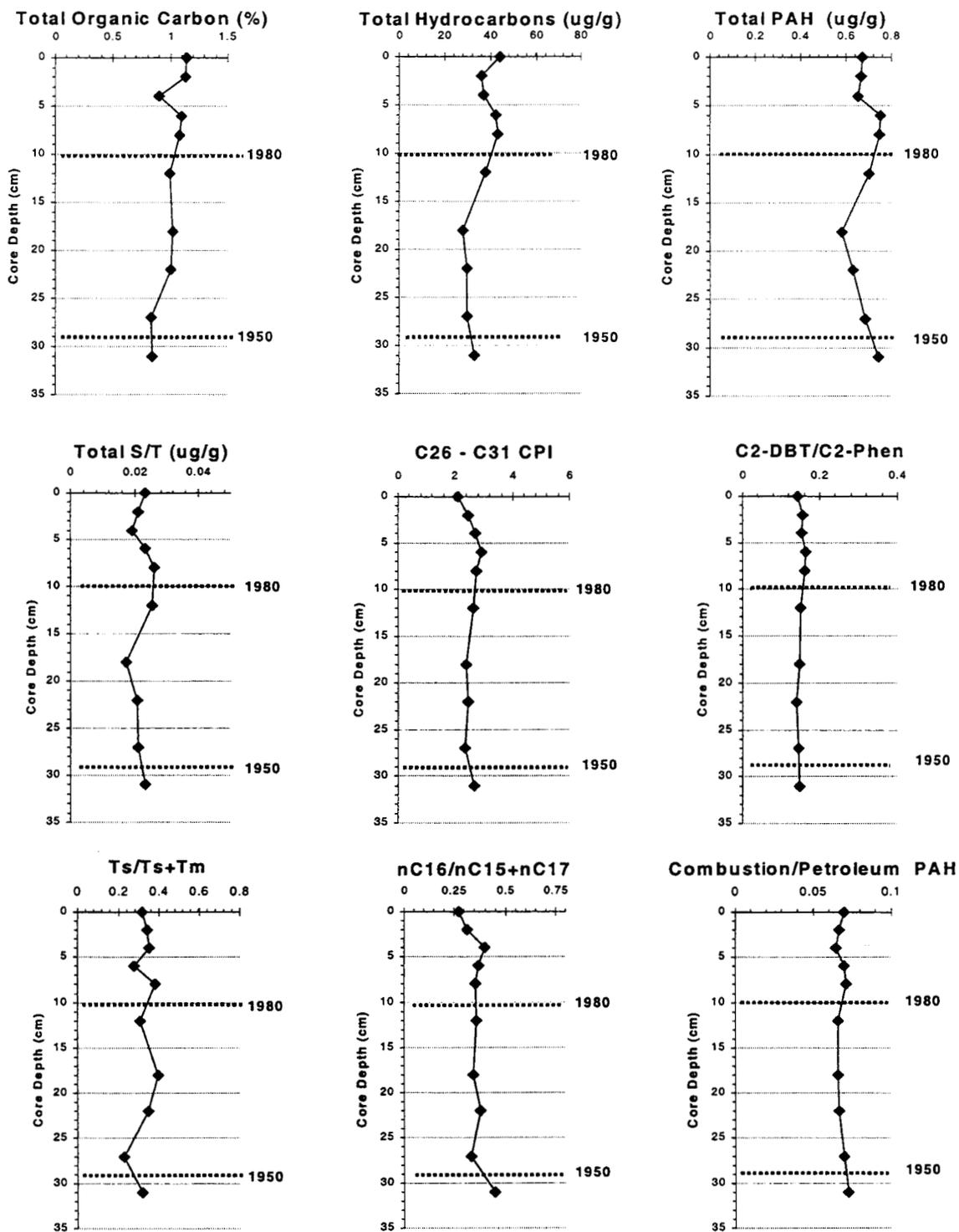
**Figure 3-72: Vertical Core Profiles of Selected Diagnostic Organic Parameters for Station Z1F2 versus Sediment Depth (1997).**

## Z2F1



**Figure 3-73: Vertical Core Profiles of Selected Diagnostic Organic Parameters for Station Z2F1 versus Sediment Depth (1997).**

## Z2F2



**Figure 3-74: Vertical Core Profiles of Selected Diagnostic Organic Parameters for Station Z2F2 versus Sediment Depth (1997).**

## Z2R16

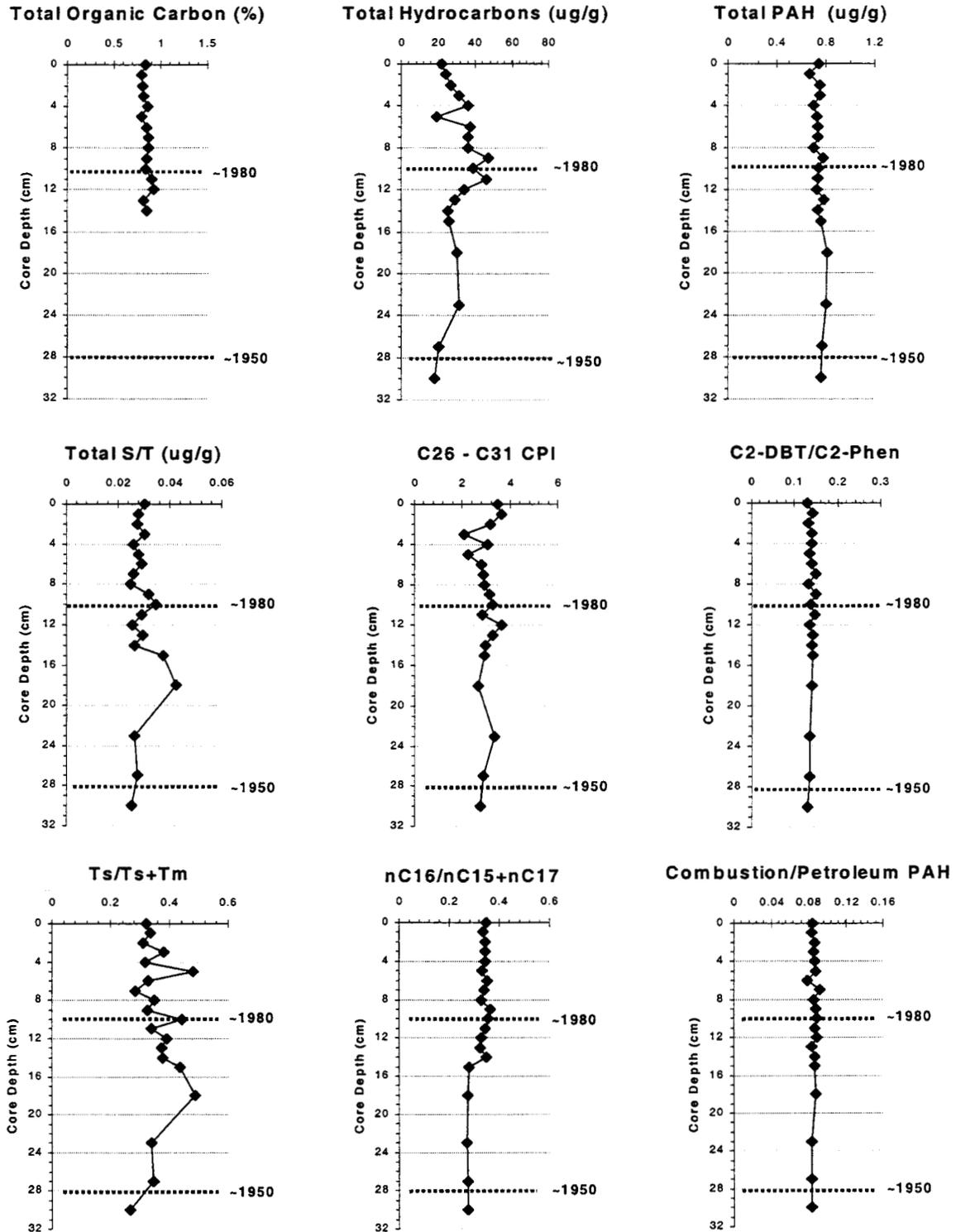
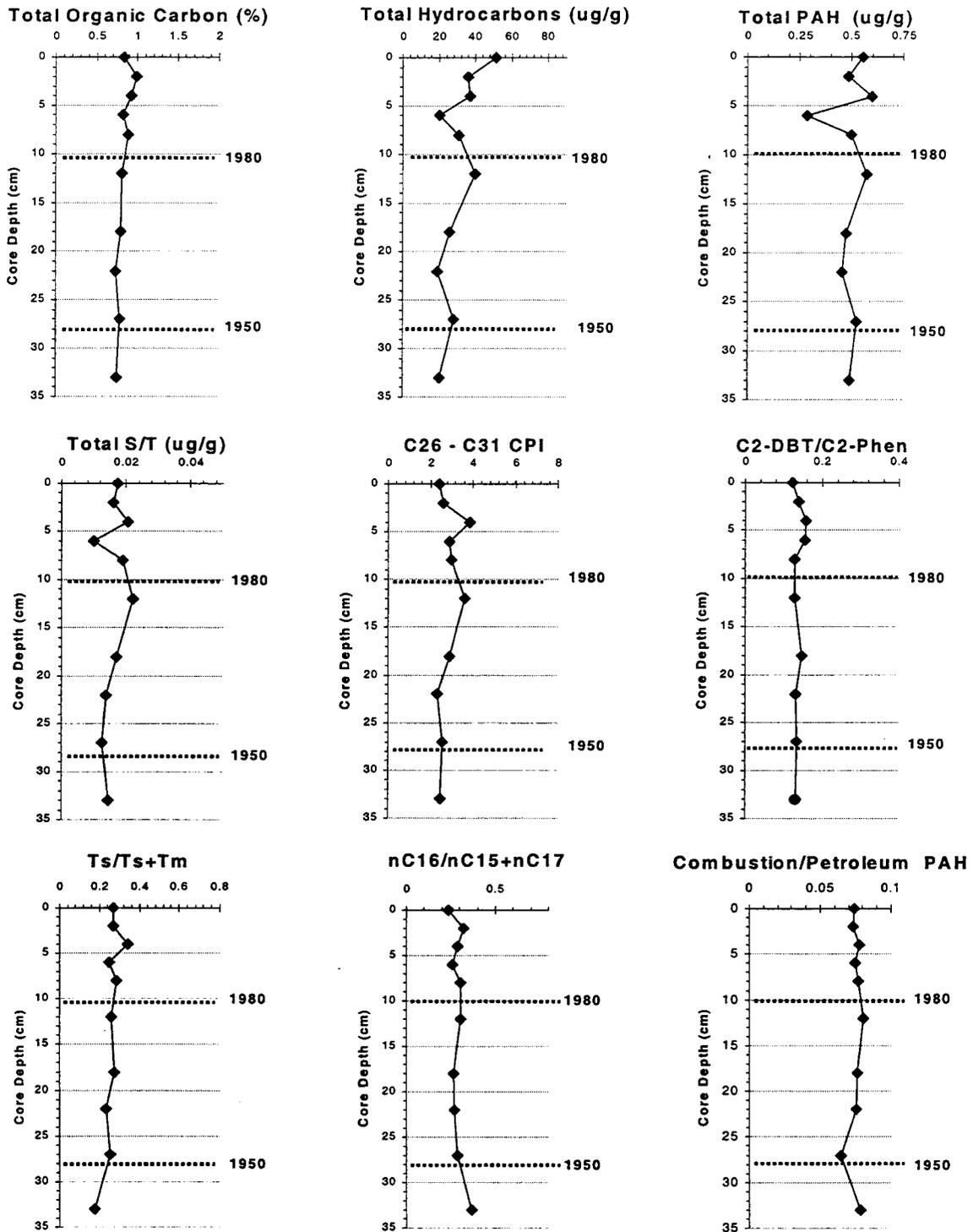


Figure 3-75: Vertical Core Profiles of Selected Diagnostic Organic Parameters for Station Z2R16 versus Sediment Depth (1998).

# Z3F1



**Figure 3-76: Vertical Core Profiles of Selected Diagnostic Organic Parameters for Station Z3F1 versus Sediment Depth (1997).**

## Z3F2

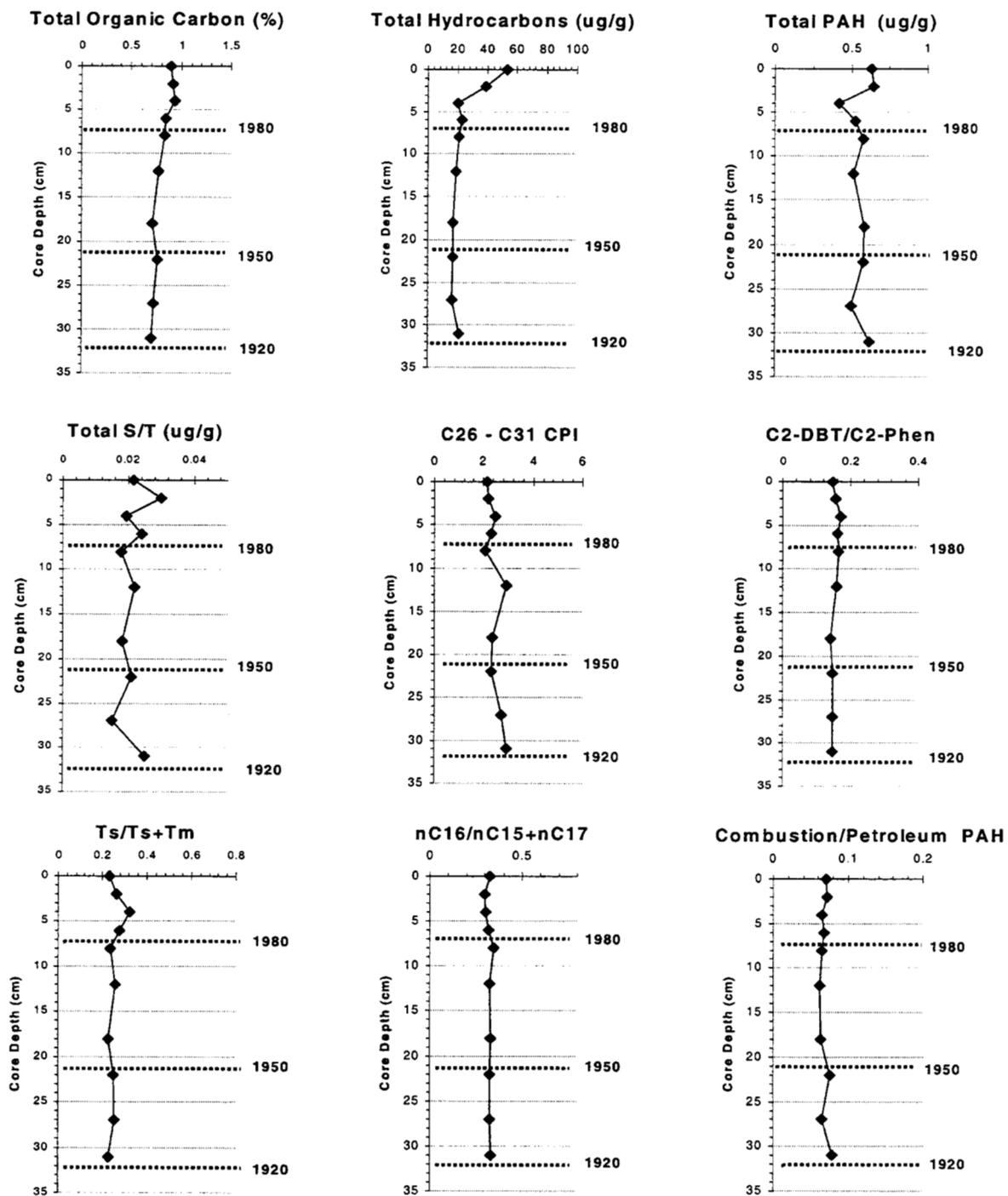
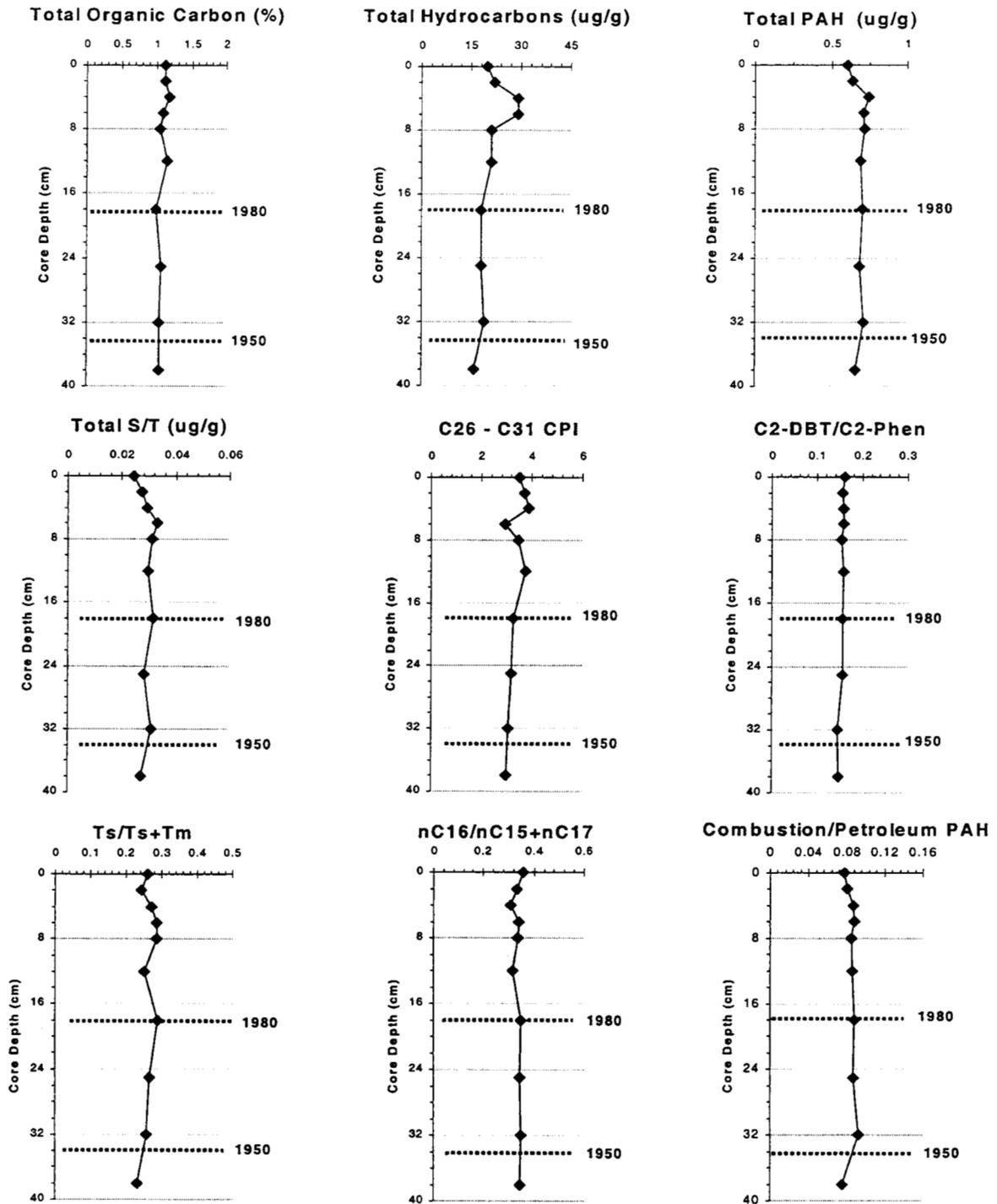


Figure 3-77: Vertical Core Profiles of Selected Diagnostic Organic Parameters for Station Z3F2 versus Sediment Depth (1997).

# Z4F4



**Figure 3-78: Vertical Core Profiles of Selected Diagnostic Organic Parameters for Station Z4F4 versus Sediment Depth (1998).**

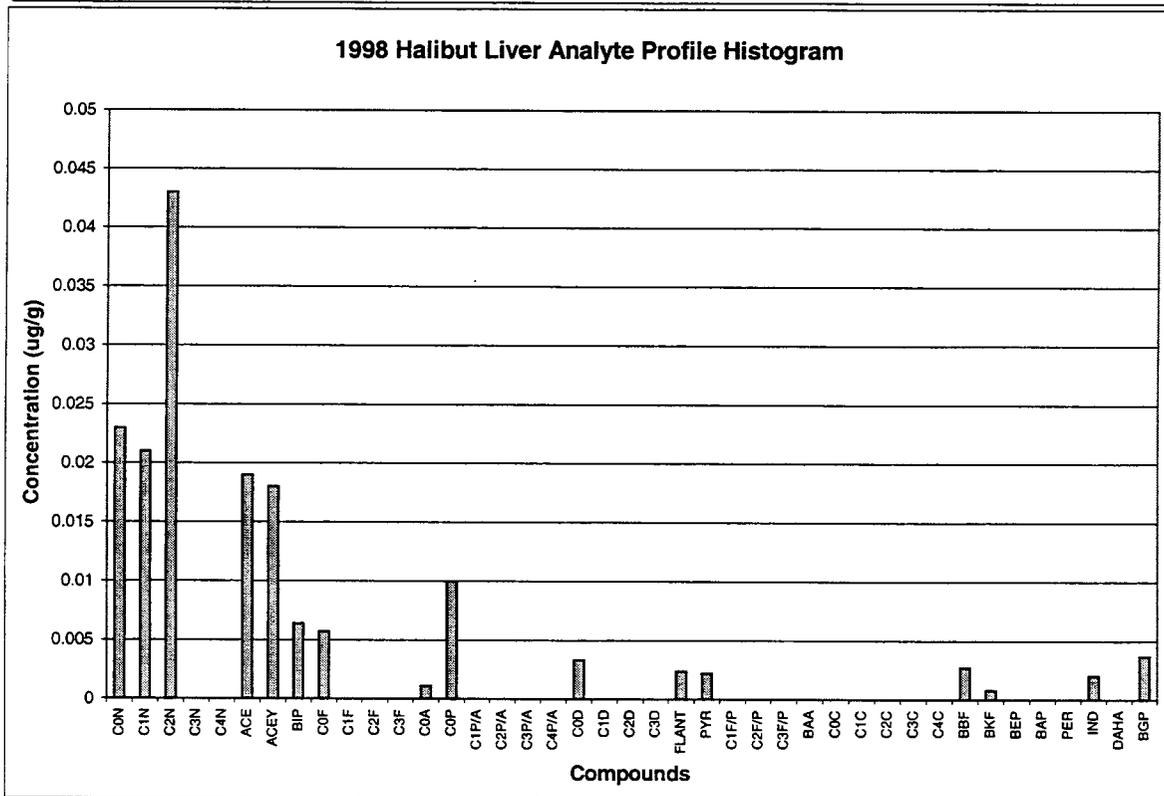
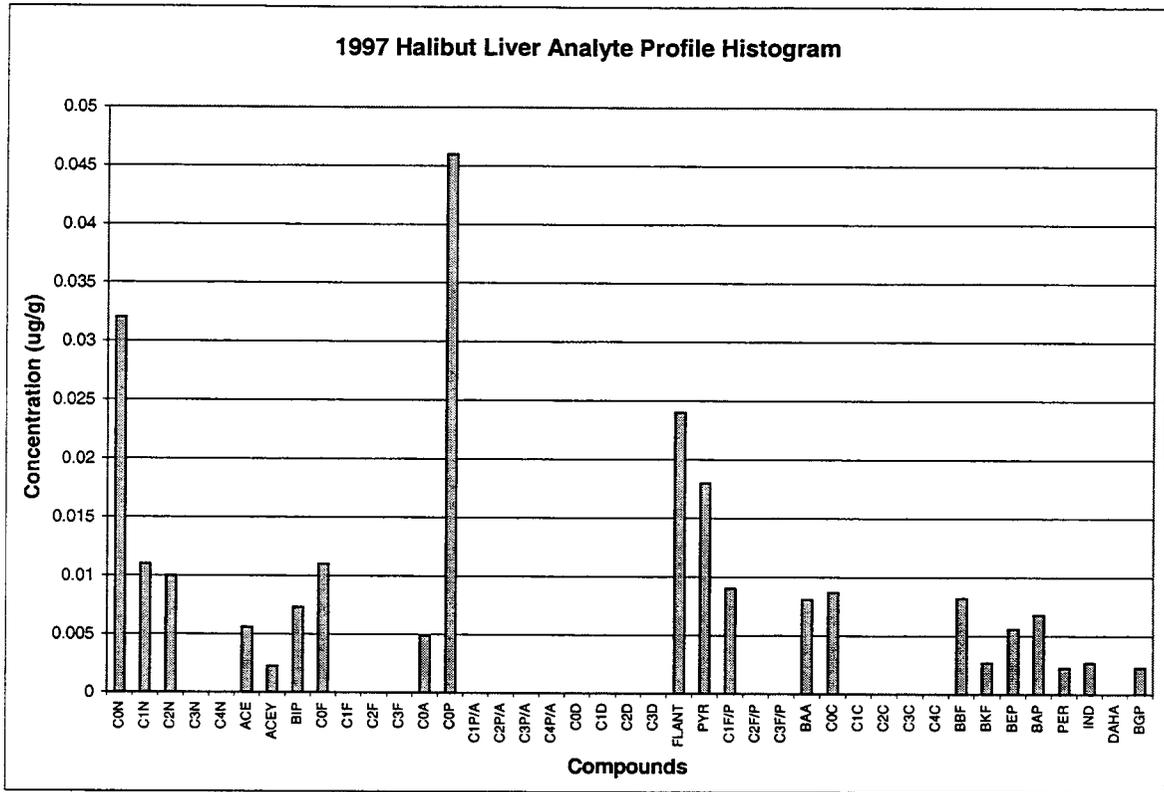
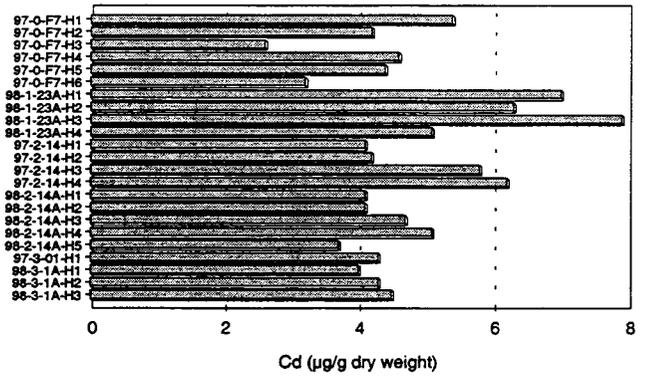
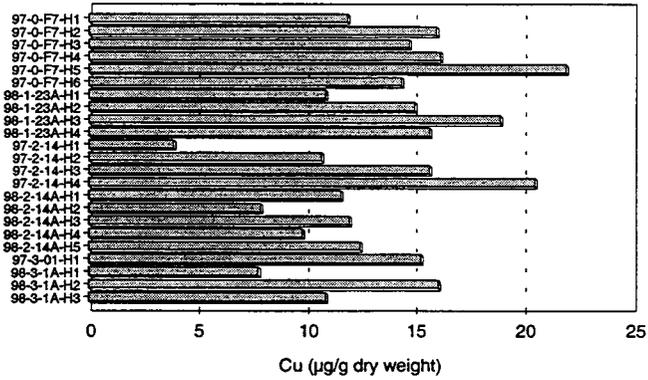
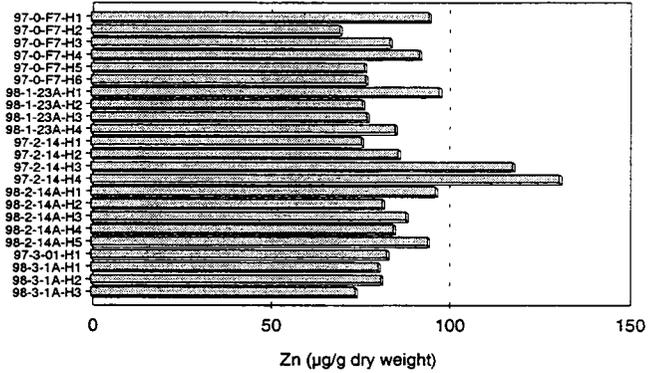
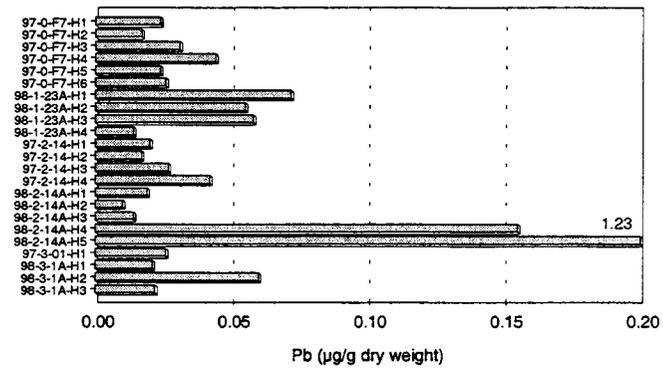
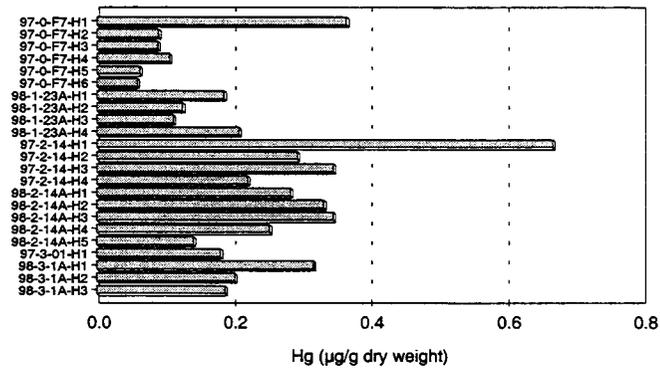
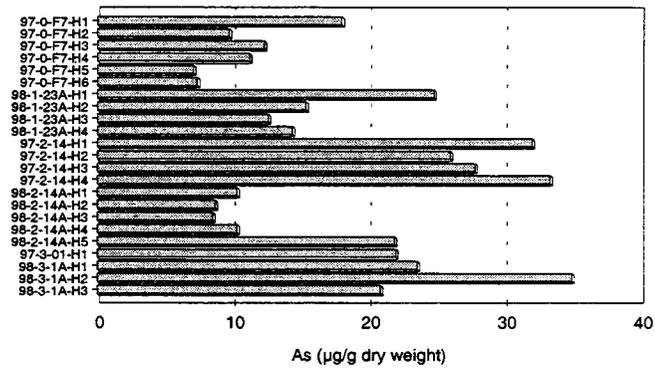


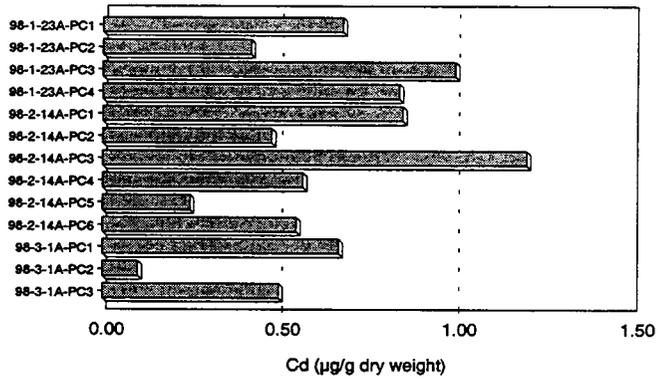
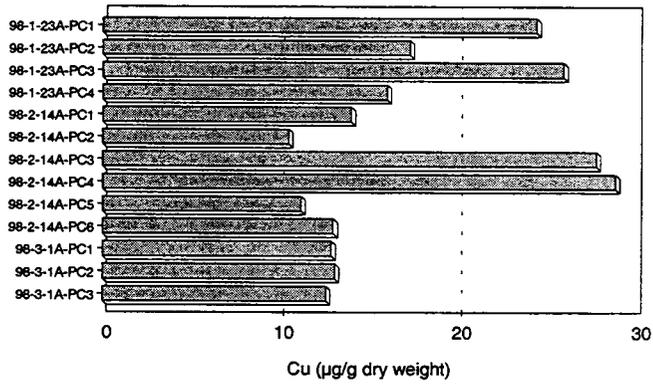
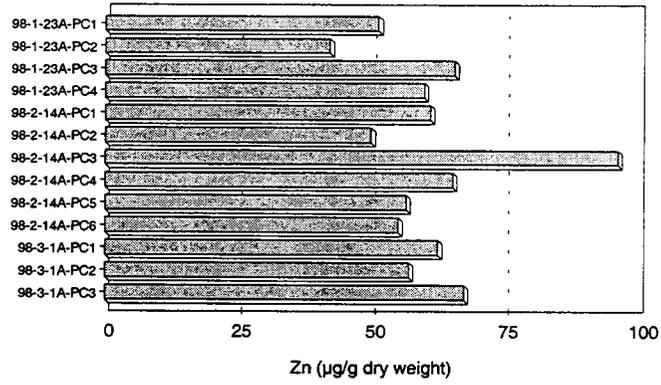
Figure 3-79: PAH distribution for Halibut Livers (ug/g dry weight). Zone 2, Station R14a-H2 (top) and Zone 2, Station R14a-H1 (bottom).



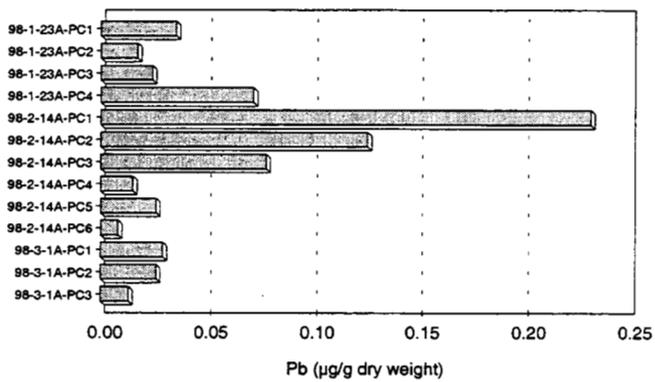
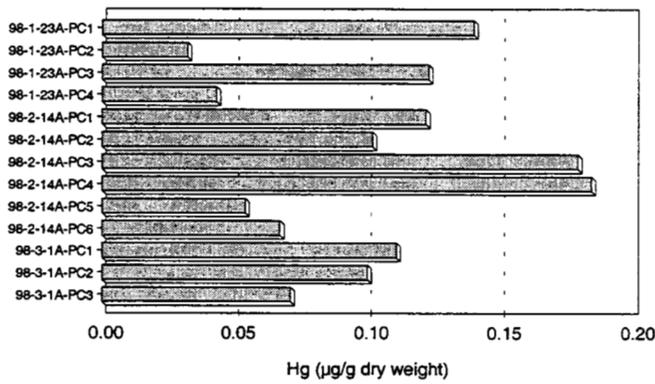
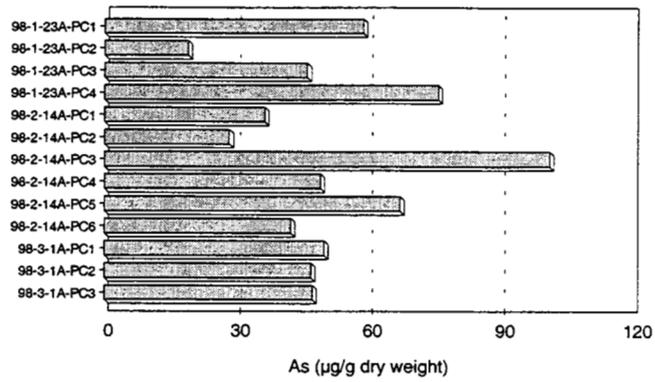
**Figure 3-80: Concentrations of Zn, Cu and Cd in Liver Composite Samples from Halibut.**



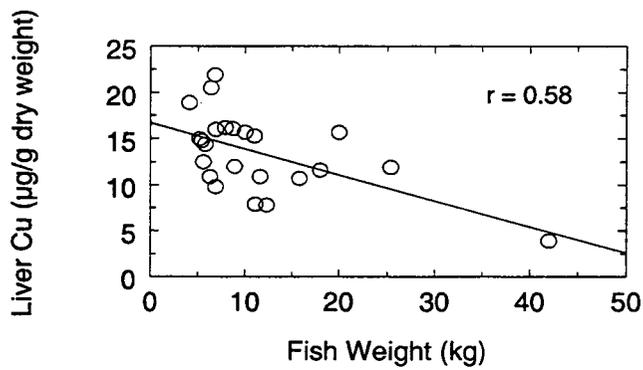
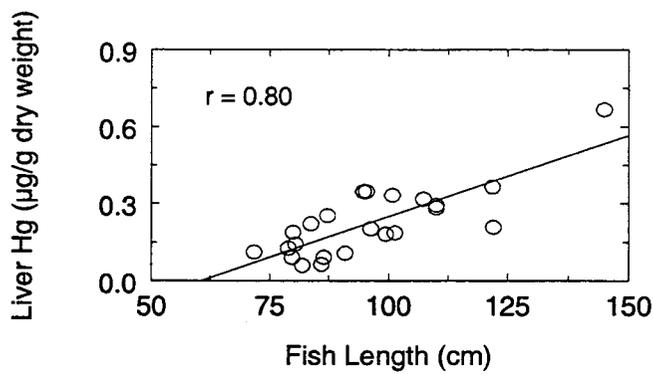
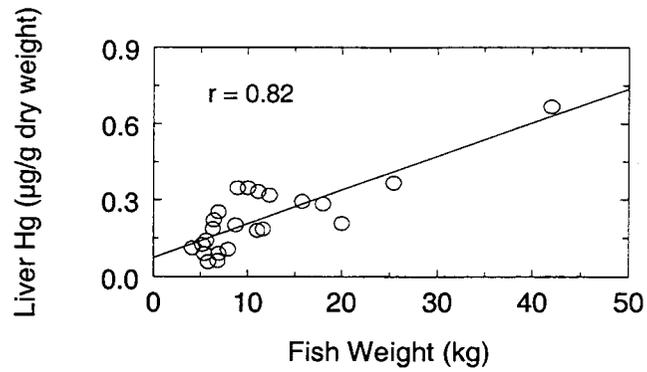
**Figure 3-81: Concentrations of As, Hg, and Pb in Liver Composite Samples from Halibut.**



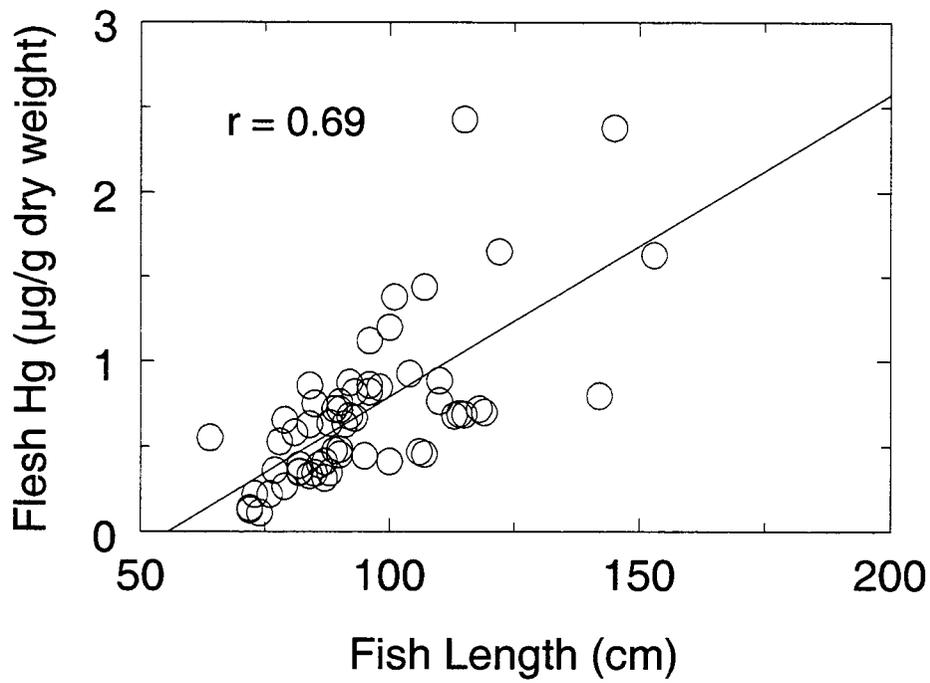
**Figure 3-82: Concentrations of Zn, Cu and Cd in Liver Composite Samples from Pacific Cod.**



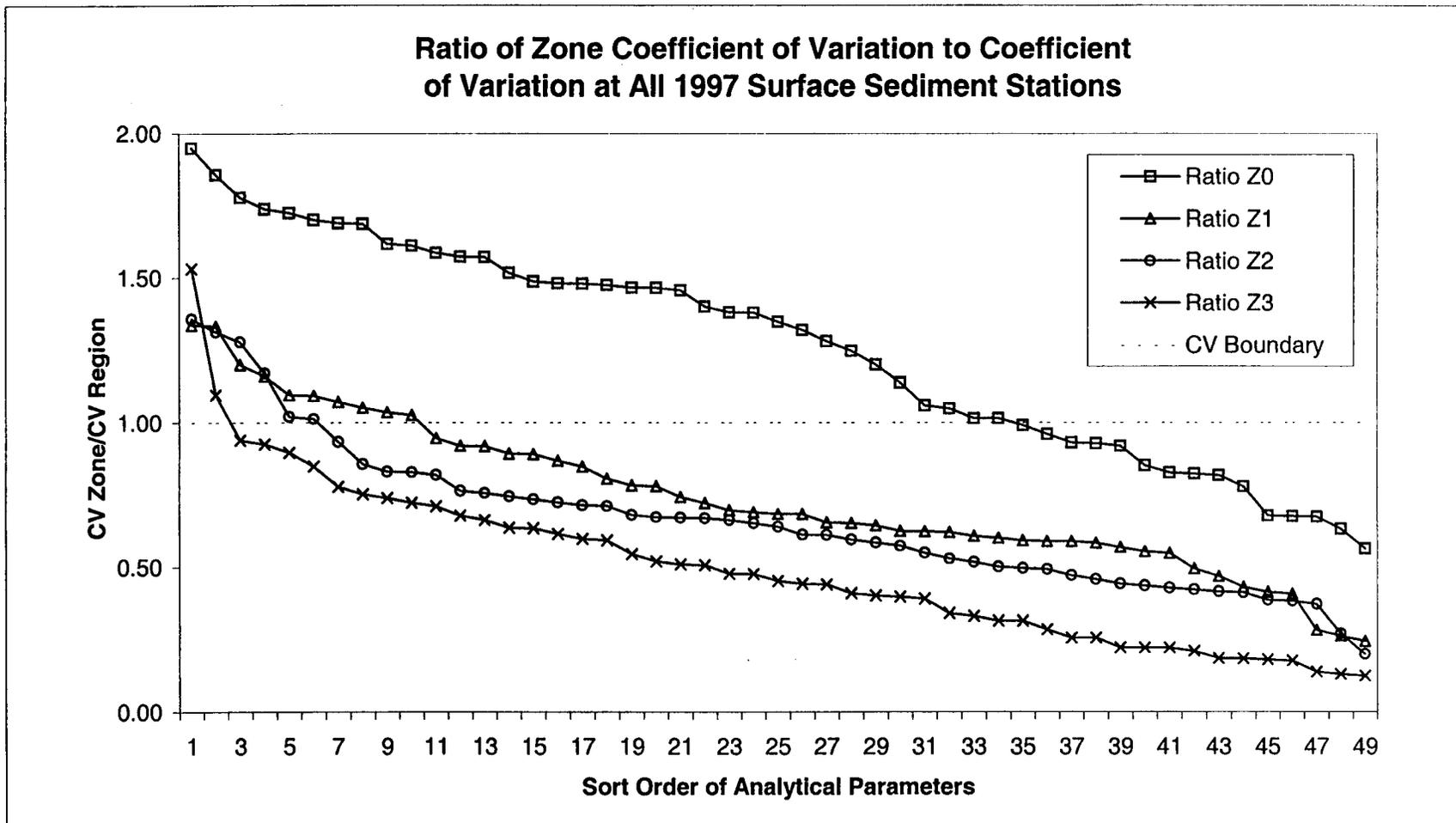
**Figure 3-83: Concentrations of As, Hg and Pb in Liver Composite Samples from Pacific Cod.**



**Figure 3-84: Zinc Concentrations in Liver Composite Samples from Halibut as a Function of Fish Length and Fish Weight, as well as Cu Values in Liver Composite Samples from Halibut versus Fish Weight.**



**Figure 3-85: Concentrations of Hg in Flesh (Muscle) Samples from Halibut versus Fish Length.**



**Figure 3-86: Ratio of Zone Coefficient of Variation to Coefficient of Variation at all Stations for Surface Sediments Collected in 1997.**

### Quality Control Chart

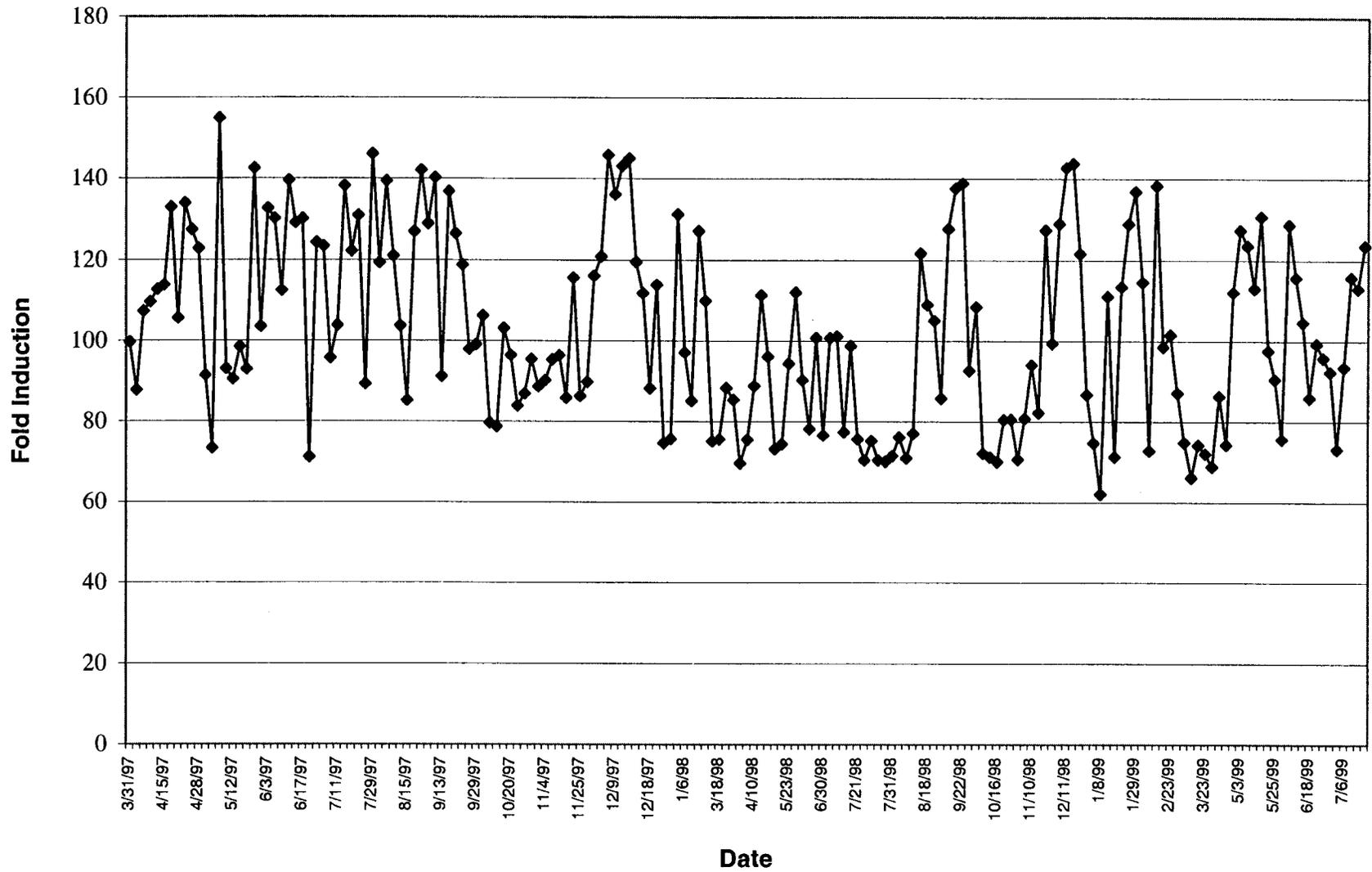


Figure 3-87: P450 Reporter Gene System Response to 1 ng Tetrachlorodibenzo-p-dioxin/mL.

**Table 3-1: Concentrations of Trace Metals, Total Organic Carbon (TOC), and Grain Size in Source Samples (Dry Weight)**

Sample Type	Matrix Type	Al (%)	Ca (%)	Fe (%)	K (%)	Mg (%)	TOC (%)	Sand (%)	Silt (%)	Clay (%)
Homer Harbor	Sediment	6.94	1.51	3.84	1.53	1.13	1.6	5.6	43.6	50.7
Susitna River #1 (5/97)	Sediment	6.08	1.99	2.67	1.86	1.03	0.21	--	--	--
Susitna River #2 (5/97)	Sediment	6.08	2.05	2.54	1.86	1.00	0.20	56.2	37.9	5.9
Copper River #1 (7/97)	Sediment	7.38	5.97	3.84	1.25	1.82	0.17	--	--	--
Copper River #2 (7/97)	Sediment	7.45	5.83	3.85	1.27	1.79	0.13	--	--	--
Copper River #3 (7/97)	Sediment	7.21	6.50	4.02	1.25	1.95	0.13	--	--	--
Copper River #4 (7/97)	Sediment	7.46	5.65	3.88	1.34	1.84	--	35.8	48.7	15.5
Susitna River #1 (5/98)	Suspended Solids	6.61	--	5.15	--	--	--	--	--	--
Knik River #1 (5/98)	Suspended Solids	10.13	--	7.01	--	--	--	--	--	--
Matanuska River #1 (5/98)	Suspended Solids	9.00	--	6.19	--	--	--	--	--	--
Copper River #1 (5/98)	Suspended Solids	8.14	--	5.43	--	--	--	--	--	--
Copper River #2 (5/98)	Suspended Solids	7.61	--	4.40	--	--	--	--	--	--
Susitna River #2 (6/98)	Suspended Solids	8.34	--	6.06	--	--	--	--	--	--
Knik River #2 (6/98)	Suspended Solids	9.85	--	6.23	--	--	--	--	--	--
Matanuska River #2 (6/98)	Suspended Solids	9.70	--	6.06	--	--	--	--	--	--
Homer Coal (1997)	Solid	0.42	1.14	1.49	0.06	0.11	67.1	--	--	--
Beluga Coal	Solid	4.76	--	1.03	--	--	--	--	--	--
Homer Coal (1998)	Solid	1.37	--	0.33	--	--	--	--	--	--
Matanuska Coal	Solid	0.18	--	0.14	--	--	--	--	--	--
Ninilchik Coal	Solid	3.04	--	0.96	--	--	--	--	--	--
Coal (USGS,1998)	Solid	0.3-4.0	0.3-1.5	0.2-1	0.02-0.60	0.06-0.55	--	--	--	--

**Table 3-1: Concentrations of Trace Metals, Total Organic Carbon (TOC), and Grain Size in Source Samples (Dry Weight) (continued)**

Sample Type	Matrix Type	Ag ( $\mu\text{g/g}$ )	As ( $\mu\text{g/g}$ )	Ba ( $\mu\text{g/g}$ )	Be ( $\mu\text{g/g}$ )	Cd ( $\mu\text{g/g}$ )	Cr ( $\mu\text{g/g}$ )	Cu ( $\mu\text{g/g}$ )	Hg ( $\mu\text{g/g}$ )	Mn ( $\mu\text{g/g}$ )
Homer Harbor	Sediment	0.10	9.3	800	1.34	0.13	72.3	32.2	0.075	626
Susitna River #1 (5/97)	Sediment	0.20	13.7	1092	1.56	0.30	76.9	31.8	0.023	602
Susitna River #2 (5/97)	Sediment	0.18	12.3	1092	1.60	0.29	73.5	29.4	0.019	619
Copper River #1 (7/97)	Sediment	0.07	5.5	619	1.03	0.14	60.5	41.1	0.043	810
Copper River #2 (7/97)	Sediment	0.09	6.3	650	1.08	0.17	58.3	43.4	0.057	829
Copper River #3 (7/97)	Sediment	0.08	5.3	611	1.04	0.16	62.8	44.4	0.042	876
Copper River #4 (7/97)	Sediment	0.09	6.0	673	1.09	0.16	67.7	43.1	0.047	821
Susitna River #1 (5/98)	Suspended Solids	0.20	37.2	1050	3.44	0.49	103	46.4	0.304	995
Knik River #1 (5/98)	Suspended Solids	0.10	38.5	1250	2.33	0.40	163	77.9	0.428	1140
Matanuska River #1 (5/98)	Suspended Solids	0.66	23.8	897	0.60	0.19	119	65.5	0.267	1240
Copper River #1 (5/98)	Suspended Solids	0.10	18.0	636	1.14	0.24	98	63.5	0.206	1000
Copper River #2 (5/98)	Suspended Solids	0.07	11.9	514	0.97	0.19	80	53.3	0.183	961
Susitna River #2 (6/98)	Suspended Solids	0.36	34.8	1540	1.99	0.58	159	68.5	0.133	1180
Knik River #1 (6/98)	Suspended Solids	0.20	26.1	1170	2.18	0.21	162	64.9	0.186	1050
Matanuska River #1 (6/98)	Suspended Solids	0.38	23.1	1110	0.82	0.35	114	55.2	0.111	1050
Homer Coal (1997)	Solid	0.09	4.7	348	0.22	0.05	5.0	19.7	0.049	423
Beluga Coal	Solid	0.11	6.1	400	1.10	0.17	75	1.5	0.112	103
Homer Coal (1998)	Solid	0.02	3.8	384	0.74	<0.01	8.3	7.2	0.039	25
Matanuska Coal	Solid	0.02	0.1	63	0.29	<0.01	7.3	51.8	0.021	6
Ninilchik Coal	Solid	0.15	5.9	195	0.58	0.44	24.0	89.4	0.419	204
Coal (USGS, 1998)	Solid	0.01-11	2-20	120-	0.2-3.2	0.02-0.23	2.4-39	7-35	0.02-0.12	18-290

**Table 3-1: Concentrations of Trace Metals, Total Organic Carbon (TOC), and Grain Size in Source Samples (Dry Weight)  
(continued)**

Sample Type	Matrix Type	Ni ( $\mu\text{g/g}$ )	Pb ( $\mu\text{g/g}$ )	Sb ( $\mu\text{g/g}$ )	Se ( $\mu\text{g/g}$ )	Sn ( $\mu\text{g/g}$ )	Tl ( $\mu\text{g/g}$ )	V ( $\mu\text{g/g}$ )	Zn ( $\mu\text{g/g}$ )
Homer Harbor	Sediment	33.9	11.5	1.12	0.29	1.56	0.41	114	94.3
Susitna River #1 (5/97)	Sediment	41.3	13.8	1.44	0.42	1.91	0.57	83.2	80.0
Susitna River #2 (5/97)	Sediment	38.6	13.7	1.41	0.31	1.86	0.54	90.5	73.3
Copper River #1 (7/97)	Sediment	35.3	9.0	0.63	<0.1	1.36	0.24	132	70.0
Copper River #2 (7/97)	Sediment	36.7	9.7	0.71	<0.1	1.50	0.27	145	76.8
Copper River #3 (7/97)	Sediment	37.5	9.2	0.75	<0.1	1.48	0.26	141	76.1
Copper River #4 (7/97)	Sediment	36.4	9.6	0.69	<0.1	1.91	0.29	119	79.2
Susitna River #1 (5/98)	Suspended Solids	48.5	16.2	1.92	N.D.	2.82	0.62	170	118
Knik River #1 (5/98)	Suspended Solids	57.8	32.5	2.88	N.D.	3.27	0.75	209	84.3
Matanuska River #1 (5/98)	Suspended Solids	55.0	18.9	1.31	N.D.	2.88	0.53	202	119
Copper River #1 (5/98)	Suspended Solids	41.4	15.0	1.13	N.D.	2.74	0.43	176	109
Copper River #2 (5/98)	Suspended Solids	38.5	12.9	0.86	N.D.	2.00	0.29	145	81.9
Susitna River #2 (6/98)	Suspended Solids	76.7	21.8	2.88	N.D.	3.59	0.98	197	184
Knik River #1 (6/98)	Suspended Solids	70.9	20.8	2.55	N.D.	2.04	0.65	203	143
Matanuska River #1 (6/98)	Suspended Solids	47.2	21.8	0.93	N.D.	1.22	0.57	208	267
Homer Coal (1997)	Solid	8.2	2.7	1.65	0.37	0.39	0.07	12.9	3.7
Beluga Coal	Solid	14.3	8.4	2.66	0.30	0.89	0.31	--	46.3
Homer Coal (1998)	Solid	8.9	1.8	0.26	<0.10	0.23	0.11	--	7.7
Matanuska Coal	Solid	4.9	3.2	10.4	0.11	0.09	0.21	--	5.1
Nimilchik Coal	Solid	14.0	7.9	0.96	<0.10	0.53	0.54	--	15.8
Coal (USGS,1998)	Solid	5-27	1-7	0.2-5	0.07-3.2	0.4-1.7	0.7-2	9-120	3-46

**Table 3-2: Mean and Standard Deviation Values for Total PAH, Total PHC, and Total S/T for Source Samples in Outermost Cook Inlet and Shelikof Strait**

Sample Type	Matrix Type	Total PAH ( $\mu\text{g/g}$ ) <sup>1</sup> Mean $\pm$ SD	Total PHC ( $\mu\text{g/g}$ ) <sup>1</sup> Mean $\pm$ SD	Total S/T ( $\mu\text{g/g}$ ) <sup>1</sup> Mean $\pm$ SD
Cook Inlet Crude	Oil	13,000 $\pm$ 1000 (n=29)	700,000 $\pm$ 34,000 (n=24)	510 $\pm$ 81 (n=21)
Well Creek Seep	Oil	4,400 $\pm$ 2,000 (n=2)	660,000 $\pm$ 130,000 (n=2)	250 $\pm$ 5.6 (n=2)
Swanson River Field	Oil	12,000	630,000	660
Homer Spit Coal	Solid	5.3	1,200	1.4
Homer Coal Bay	Solid	2.4	660	2.1
Ninilchik Coal	Solid	4.7	1400	0.95
Matanuska Coal	Solid	62	1200	1.9
Coyote Lake Coal	Solid	23	400	0.33
Beluga Coal	Solid	4.4 $\pm$ 0.44 (n=2)	750 $\pm$ 180 (n=2)	1.5 $\pm$ 0.46 (n=2)
Homer Harbor	Sediment	0.78 $\pm$ 0.021 (n=2)	120 $\pm$ 7.1 (n=2)	0.26 $\pm$ 0.010 (n=2)
Copper River	Sediment	0.041 $\pm$ 0.013 (n=5)	18 $\pm$ 28 (n=5)	0.0016 $\pm$ 0.00063 (n=5)
Susitna River	Sediment	0.0074 $\pm$ 0.00094 (n=2)	3.4 $\pm$ 1.3 (n=2)	0.0006 $\pm$ 0.00086 (n=2)
Matanuska River	Sediment	0.19	6.3	0.0064
Alaska Coastal Current	Sediment	1.7 $\pm$ 0.06 (n=3)	47 $\pm$ 3.0 (n=3)	0.049 $\pm$ 0.0021 (n=3)
Augustine Island	Sediment	0.17	12	0.019
		<b>Total PAH (<math>\mu\text{g/L}</math>)<sup>1</sup></b>	<b>Total PHC (<math>\mu\text{g/L}</math>)<sup>1</sup></b>	<b>Total S/T (<math>\mu\text{g/L}</math>)<sup>1</sup></b>
Final Effluent Point Woronzof	Water	6.7	2,300	1.3
TBPF Outfall	Water	380	6,200	6.2

Notes:

<sup>1</sup> dry weight for solid and sediments, wet weight for oil and waters

PAH – Polycyclic Aromatic Hydrocarbons

SHC – Saturated Hydrocarbons

S/T – Steranes and Triterpanes

SD – Standard Deviation

n – Number of Samples

**Table 3-3: Ranges of Metal Concentrations in Susitna and Copper River Bottom Sediment and Suspended Solids (This Study), Sedimentary, Volcanic and Plutonic Rocks from Alaska (Los Alamos National Laboratory, 1983), and Average Continental Crust (Wedepohl, 1995)**

<b>Metal*</b>	<b>Bottom Sediments: Susitna and Copper River Bottom Sediments (<math>\mu\text{g/g}</math>)*</b>	<b>Suspended Solids: S-K-M** and Copper Rivers (<math>\mu\text{g/g}</math>)*</b>	<b>Alaskan Rock (<math>\mu\text{g/g}</math>)*</b>	<b>Average Continental Crust (<math>\mu\text{g/g}</math>)*</b>
Ag	0.07-0.20	0.07-0.66	--	0.07
Al	6.08-7.46%	6.61-10.13%	2.67-7.81%	7.96%
As	5.3 -13.7	11.9-38.5	8-39	1.7
Ba	611-1090	514-1540	383-1160	584
Be	1.0-1.6	0.6-3.4	--	2.4
Cd	0.14-0.30	0.19-0.58	--	0.10
Cr	58-77	80-163	47-84	126
Cu	29-44	46-78	16-75	25
Fe	2.54-4.02%	4.40-7.01%	1.59-6.66%	4.32%
Hg	0.019-0.057	0.111-0.428	--	0.040
Mn	602-876	961-1240	351-1710	716
Ni	35-41	38-77	19-47	56
Pb	9-14	13-32	6-25	14.8
Sb	0.6-1.4	0.9-2.9	--	0.30
Se	<0.1-0.4	<0.1	--	0.12
Sn	1.4-1.9	1.2-3.6	--	2.3
Tl	0.24-0.57	0.29-0.98	--	0.52
V	83-145	145-209	55-278	98
Zn	70-80	82-267	96-288	65

Notes:

\*Concentrations in  $\mu\text{g/g}$ , except where noted.

\*\* S-K-M = Susitna - Knik - Matanuska.

**Table 3-4: Concentrations of Trace Metal in Source Solutions (Wet Weight)**

Sample Type	Matrix Type	Ag (mg/L)	As (mg/L)	Ba (mg/L)	Be (mg/L)	Cd (mg/L)	Cr (mg/L)	Cu (mg/L)	Fe (mg/L)	Hg (mg/L)
TBPF Special Outfall, Unocal	Water	<0.0001	0.0024	20.7	<0.0001	0.0001	0.0032	0.0060	0.76	<0.0005.
Final Effluent Water Pt. Woronzof Water	Water	<0.0001	0.0002	0.010	<0.0001	0.00001	0.0005	0.0020	1.11	<0.0005
Crude Oil TBPF	Oil	<0.0001	<0.0001	0.68	<0.0001	0.0048	0.17	0.0087	1.47	<0.0005

Sample Type	Matrix Type	Mn (mg/L)	Ni (mg/L)	Pb (mg/L)	Sb (mg/L)	Se (mg/L)	Sn (mg/L)	Tl (mg/L)	V (mg/L)	Zn (mg/L)
TBPF Special Outfall, Unocal	Water	1.71	0.0075	0.0001	0.0001	<0.0002	0.008	0.00025	0.067	0.0030.
Final Effluent Water Pt. Woronzof Water	Water	0.23	0.0017	0.0003.	0.0002	0.0004	0.004	0.00002	0.001	0.0065
Crude Oil TBPF	Oil	0.03	1.50	0.15	0.005	<0.0002.	<0.0001	0.0023	0.34	0.21

Notes:  
TBPF = Trading Bay Production Facility

**Table 3-5: Means, Standard Deviations and Ranges of Values for Total Organic Carbon (TOC), Sand, Silt and Clay for Surficial (0-2 cm) Sediments from the Alaska Coastal Current (AC) and Zones 0, 1, 2, 3 and 4 in the Shelikof Strait**

	<b>Zone (Year)</b>	<b>TOC (%)</b>	<b>Sand (%)</b>	<b>Mud (Silt and Clay) (%)</b>
<b>Mean Std. Dev.</b>	AC (1998)	1.13 ±0.04	1.4 ±0.4	98.6 ±0.4
<b>Range</b>		1.09-1.16	0.95-1.62	98.4-99.4
<b>Mean Std. Dev.</b>	0 (1997)	0.62 ±0.32	42.1 ±26.9	57.9 ±26.9
<b>Range</b>		0.31-1.22	3.8-84.9	15.1-96.2
<b>Mean Std. Dev.</b>	0 (1998)	0.82 ±0.36	48.2 ±28.7	58.3 ±30.6
<b>Range</b>		0.28-1.37	7.0-78.6	21.5-93.0
<b>Mean Std. Dev.</b>	1 (1997)	0.57 ±0.18	37.1 ±20.9	62.9 ±20.9
<b>Range</b>		0.26-0.94	2.6-70.3	29.7-97.4
<b>Mean Std. Dev.</b>	1 (1998)	0.60 ±0.20	40.8 ±24.5	55.6 ±22.2
<b>Range</b>		0.32-0.92	12.2-68.0	32.0-87.8
<b>Mean Std. Dev.</b>	2 (1997)	0.83 ±0.13	6.7 ±6.9	93.3 ±6.9
<b>Range</b>		0.48-1.05	0.1-27.2	72.8-99.9
<b>Mean Std. Dev.</b>	2 (1998)	0.83 ±0.13	5.0 ±3.4	91.8 ±7.2
<b>Range</b>		0.59-1.49	1.0-23.8	76.2-99.0
<b>Mean Std. Dev.</b>	3 (1997)	0.94 ±0.08	2.1 ±3.7	97.9 ±3.7
<b>Range</b>		0.79-1.16	0.19-17.7	91.5-99.8
<b>Mean Std. Dev.</b>	3 (1998)	0.98 ±0.10	1.9 ±1.8	97.4 ±3.5
<b>Range</b>		0.80-1.15	0.4-12.2	87.8-99.6
<b>Mean Std. Dev.</b>	4 (1998)	1.13 ±0.04	1.1 ±0.7	98.9 ±0.9
<b>Range</b>		1.08-1.18	0.3-2.9	97.1-99.7
<b>Mean Std. Dev.</b>	All Zones excluding AC	0.81 ±0.28	20.5 ±24.4	81.7 ±19.1
<b>Range</b>	(1997-1998)	0.26-1.49	0.1-84.9	15.1-99.9

**Table 3-6: Non-Transformed Mean, Standard Deviation and Range of Total PAH, Total PHC, and Total S/T for Surficial Sediment (0-2cm) from Zones 0, 1, 2, 3 and 4**

	<b>Zone</b>	<b>Total PAH (<math>\mu\text{g/g}</math>)</b>	<b>Total PHC (<math>\mu\text{g/g}</math>)</b>	<b>Total S/T (<math>\mu\text{g/g}</math>)</b>
<b>1997 Results</b>				
<b>Mean <math>\pm</math>SD</b> <b>Range</b>	0	0.269 $\pm$ 0.134 0.120 – 0.490	25.4 $\pm$ 16.2 9.77 – 50.0	0.029 $\pm$ 0.020 0.009 – 0.069
<b>Mean <math>\pm</math>SD</b> <b>Range</b>	1	0.422 $\pm$ 0.250 0.173 – 1.080	26.2 $\pm$ 10.6 12.0 – 48.0	0.016 $\pm$ 0.005 0.011 – 0.030
<b>Mean <math>\pm</math>SD</b> <b>Range</b>	2	0.542 $\pm$ 0.221 0.221 – 0.957	26.1 $\pm$ 10.1 14.0 – 51.0	0.024 $\pm$ 0.017 0.012 – 0.087
<b>Mean <math>\pm</math>SD</b> <b>Range</b>	3	0.595 $\pm$ 0.152 0.314 – 0.857	36.3 $\pm$ 16.1 15.0 – 71.0	0.022 $\pm$ 0.009 0.011 – 0.037
<b>Mean <math>\pm</math>SD</b> <b>Range</b>	Grand Mean: 0, 1, 2 and 3	0.457 $\pm$ 0.145 0.120 - 1.080	28.5 $\pm$ 5.21 9.77 - 71.0	0.023 $\pm$ 0.005 0.009 - 0.087
<b>1998 Results</b>				
<b>Mean <math>\pm</math>SD</b> <b>Range</b>	0	0.200 $\pm$ 0.119 0.066 – 0.420	25.5 $\pm$ 18.1 6.80 – 54.3	0.027 $\pm$ 0.022 0.009 – 0.069
<b>Mean <math>\pm</math>SD</b> <b>Range</b>	1	0.330 $\pm$ 0.198 0.120 – 0.730	23.6 $\pm$ 8.18 14.0 – 39.0	0.016 $\pm$ 0.004 0.011 – 0.021
<b>Mean <math>\pm</math>SD</b> <b>Range</b>	2	0.525 $\pm$ 0.133 0.290 – 0.687	25.8 $\pm$ 3.58 21.0 – 31.0	0.021 $\pm$ 0.004 0.017 – 0.026
<b>Mean <math>\pm</math>SD</b> <b>Range</b>	3	0.501 $\pm$ 0.060 0.360 – 0.550	33.2 $\pm$ 6.59 24.0 – 42.0	0.030 $\pm$ 0.017 0.021 – 0.072
<b>Mean <math>\pm</math>SD</b> <b>Range</b>	4	0.604 $\pm$ 0.060 0.537 – 0.650	35.8 $\pm$ 6.68 30.7 – 43.3	0.025 $\pm$ 0.001 0.024 – 0.027
<b>Mean <math>\pm</math>SD</b> <b>Range</b>	Grand Mean: 0, 1, 2, 3, 4	0.432 $\pm$ 0.164 0.066 – 0.730	28.8 $\pm$ 5.37 6.80 – 54.3	0.024 $\pm$ 0.005 0.009 – 0.072
<b>1997 &amp; 1998</b>				
<b>Mean <math>\pm</math>SD</b>	0	0.235 $\pm$ 0.049	25.5 $\pm$ 0.071	0.028 $\pm$ 0.001
<b>Mean <math>\pm</math>SD</b>	1	0.376 $\pm$ 0.065	24.9 $\pm$ 1.84	0.016
<b>Mean <math>\pm</math>SD</b>	2	0.534 $\pm$ 0.012	26.0 $\pm$ 0.212	0.023 $\pm$ 0.002
<b>Mean <math>\pm</math>SD</b>	3	0.548 $\pm$ 0.066	34.8 $\pm$ 2.19	0.026 $\pm$ 0.006
<b>Mean <math>\pm</math>SD</b>	4	0.604 $\pm$ 0.060	35.8 $\pm$ 6.68	0.025 $\pm$ 0.001
<b>Mean <math>\pm</math>SD</b>	Grand Mean:	0.459 $\pm$ 0.151	29.4 $\pm$ 5.41	0.024 $\pm$ 0.005

**Table 3-7: Diagnostic Ratios and Parameters of Saturated Hydrocarbons, Polycyclic Aromatic Hydrocarbons, and Steranes and Triterpanes**

Parameter	Relevance in Environmental Samples
<b>Saturated Hydrocarbons (SHC)</b>	
Isoprenoids	The sum of selected branched isoprenoid alkanes including: phytane, pristane, farnesane [1470], and unidentified isoprenoids at relative retention index 1380 and 1650. Isoprenoids are abundant in petroleum and are resistant to degradation relative to the corresponding n-alkanes.
LALK	The sum of lower molecular weight n-alkanes (nC <sub>9</sub> to nC <sub>20</sub> ) generally associated with "fresh" petroleum inputs.
TALK	The sum of total alkanes which includes those of biogenic and petrogenic origin (nC <sub>9</sub> to nC <sub>44</sub> ).
PHY/PRIS	Source of phytane (PHY) is mainly petroleum, whereas pristane (PRIS) is derived from both biological matter and oil. In "clean" environmental samples, this ratio is very low and increases as oil is added.
nC <sub>16</sub> /(nC <sub>15</sub> + nC <sub>17</sub> )	The ratio of n-alkane hexadecane (nC <sub>16</sub> ) over pentadecane (nC <sub>15</sub> ) and heptadecane (nC <sub>17</sub> ). At "background" levels of total hydrocarbons nC <sub>15</sub> and nC <sub>17</sub> can be used as indicators of plankton (algal) hydrocarbon inputs. As plankton productivity increases the ratio decreases.
CPI	Carbon preference index. Describes the relative amounts of odd-and-even-chain alkanes within a specific alkane boiling range. CPI of 2 - 4 indicate terrestrial plants, as oil additions increase the CPI is lowered to near 1.0. The equation for CPI is $(n-C_{27} + n-C_{29} + n-C_{31}) / (n-C_{26} + n-C_{28} + n-C_{30})$ .
TPHC	Total hydrocarbons, the sum of the resolved plus unresolved saturated and aromatic hydrocarbons.
<b>Polycyclic Aromatic Hydrocarbons (PAH)</b>	
N/P	The naphthalenes (N) to phenanthrenes/anthracenes (P) ratio is diagnostic for inputs of fresh petroleum, and as a weathering indicator. Naphthalenes are characteristic of fresh crude oil, the ratio decreases with increased weathering. (N= Naphthalene series [C0N + C1N + C2N + C3N + C4N]; P= Phenanthrene/Anthracene Series [C0P/A + C1P/A + C2P/A + C3P/A + C4P/A]).
C2D/C2P	Ratio of C2 alkyl dibenzothiophenes (D) and C2 alkyl phenanthrenes (P) is a useful diagnostic source ratio for petroleum.
C3D/C3P	Ratio of C3-alkyl dibenzothiophenes (D) and C3-alkyl phenanthrenes (P) is a useful diagnostic source ratio for petroleum.
Perylene	A biogenic PAH formed during the early diagenesis in marine and lacustrine sediments, may be associated with terrestrial plant source precursors.
Total PAH	The sum of all PAH target analytes includes 2- through 6-ring parent PAH and C1 - C4 alkyl substituted PAH.
Pyrogenic PAH	The sum of combustion PAH compounds (4-, 5-, and 6-ring PAH: Fluoranthene, pyrene, chrysene, benzo[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenz[a,h]anthracene, benzo[g,h,i]perylene, and indeno[1,2,3-c,d]pyrene.
Petrogenic PAH	The sum of petrogenic PAH compounds (2-, 3-, and 4 -ring PAH: naphthalenes [C0 - C4], acenaphthene, acenaphthylene, fluorene [C0 - C3], phenanthrenes [C0 - C4], dibenzothiophenes [C0 - C3], chrysenes [C1 - C4], and fluoranthenes/pyrenes [C1 - C3]).
Pyrogenic/Petrogenic	The ratio of pyrogenic PAH compounds to petrogenic PAH compounds is useful for determining the relative contribution of pyrogenic and petrogenic hydrocarbons and in differentiating hydrocarbon sources.

**Table 3-7: Diagnostic Ratios and Parameters of Saturated Hydrocarbons, Polycyclic Aromatic Hydrocarbons, and Steranes and Triterpanes**

Parameter	Relevance in Environmental Samples
<b>Steranes/Triterpanes (S/T)</b>	
Total S/T	The sum of all sterane and triterpane biomarker target analytes.
T21/T22	The ratio of C31-homohopane (22S) (T21) to C31-homohopane (22R) (T22), useful for determining the contribution of recent biogenic material.
Hopane	C30-Hopane (T19), commonly one of the most abundant triterpanes in petroleum.
Ts/(Ts +Tm)	Ratio of C27-trisnorhopane(Ts) to C27-trisnorhopane (Tm); used as a maturity indicator for petroleum, also as a source ratio for different crude oils.
Oleanane/Hopane	The ratio of C30-oleanane (T18) to C30-hopane (T19) indicates the relative amounts of oleanane, which is a marker of angiosperm (post-Cretaceous) contribution to petroleum diagenesis.

**Table 3-8a: Mean, Maximum, Minimum, and Student Newman-Keuls Analysis Results for Key Organic Parameters (Non-Transformed) in 1997 Surface Sediments**

Analyte	Zone	n	Significantly Different	Mean	Min	Max	SD	CV
Total PAH	3	17	A	0.403	0.262	0.531	0.080	19.901
( $\mu\text{g/g}$ )	2	17	A	0.376	0.160	0.583	0.120	31.967
	1	17	A	0.315	0.132	0.624	0.162	51.404
	0	8	B	0.179	0.080	0.329	0.087	48.849
Perylene	0	8	A	0.017	0.003	0.040	0.015	86.744
( $\mu\text{g/g}$ )	3	17	AB	0.013	0.006	0.022	0.005	38.815
	2	17	BC	0.009	0.005	0.016	0.003	32.031
	1	17	C	0.006	0.004	0.010	0.002	25.924
Petrogenic PAH	3	17	A	0.364	0.241	0.475	0.069	19.014
( $\mu\text{g/g}$ )	2	17	A	0.343	0.141	0.533	0.110	32.026
	1	17	A	0.289	0.117	0.573	0.151	52.436
	0	8	B	0.143	0.069	0.247	0.063	44.422
Pyrogenic PAH	3	17	A	0.039	0.021	0.058	0.012	30.177
( $\mu\text{g/g}$ )	0	8	A	0.036	0.011	0.082	0.030	82.134
	2	17	A	0.033	0.019	0.057	0.011	33.549
	1	17	A	0.026	0.014	0.051	0.011	40.914
C2D/C2P	0	8	A	0.159	0.131	0.235	0.034	21.549
	2	17	AB	0.151	0.111	0.164	0.012	8.260
	3	17	AB	0.151	0.126	0.177	0.012	8.132
	1	17	B	0.137	0.108	0.164	0.016	11.992
C3D/C3P	0	8	A	0.215	0.127	0.289	0.048	22.293
	2	17	AB	0.197	0.163	0.250	0.024	11.990
	3	17	BC	0.189	0.173	0.225	0.013	7.068
	1	17	C	0.171	0.143	0.200	0.018	10.662
N/P	2	17	A	0.980	0.652	1.568	0.346	35.265
	3	17	A	0.972	0.743	1.492	0.197	20.237
	1	17	A	0.972	0.713	1.144	0.132	13.557
	0	8	B	0.643	0.523	0.792	0.098	15.196
PYRO/PETRO	0	8	A	0.234	0.087	0.471	0.123	52.391
	3	17	B	0.106	0.084	0.139	0.016	15.018
	2	17	B	0.097	0.071	0.134	0.014	14.163
	1	17	B	0.096	0.076	0.124	0.016	16.283
nC16/(nC15+nC17)	1	17	A	0.162	0.087	0.233	0.033	20.615
	3	17	A	0.155	0.128	0.176	0.013	8.470
	2	17	A	0.153	0.114	0.194	0.025	16.642
	0	8	B	0.092	0.027	0.146	0.043	46.531
Pristane	3	17	A	0.078	0.036	0.140	0.029	37.606
( $\mu\text{g/g}$ )	2	17	A	0.066	0.030	0.100	0.021	32.206
	1	17	A	0.062	0.020	0.143	0.033	53.490
	0	8	B	0.024	0.010	0.041	0.012	49.369

**Table 3-8a: Mean, Maximum, Minimum, and Student Newman-Keuls Analysis Results for Key Organic Parameters (Non-Transformed) in 1997 Surface Sediments**

Analyte	Zone	n	Significantly Different	Mean	Min	Max	SD	CV
<b>Total PHC</b>	3	17	A	23.620	12.000	44.000	8.773	37.143
( $\mu\text{g/g}$ )	1	17	A	21.188	9.100	41.000	8.937	42.181
	2	17	A	18.994	10.000	35.000	6.610	34.802
	0	8	A	17.367	6.500	32.667	11.267	64.879
<b>nC15+nC17</b>	3	17	A	0.058	0.033	0.076	0.014	23.315
( $\mu\text{g/g}$ )	2	17	A	0.056	0.030	0.094	0.017	30.651
	1	17	A	0.048	0.025	0.085	0.020	40.499
	0	8	B	0.032	0.013	0.069	0.020	63.567
<b>nC27+nC29+nC31</b>	0	8	A	0.350	0.116	0.845	0.240	68.463
( $\mu\text{g/g}$ )	2	17	A	0.302	0.171	0.490	0.073	24.228
	3	17	A	0.253	0.080	0.385	0.100	39.429
	1	17	A	0.247	0.037	0.400	0.100	40.467
<b>TALK</b>	1	17	A	1.514	0.526	5.929	1.197	79.099
( $\mu\text{g/g}$ )	2	17	A	1.456	0.696	7.248	1.509	103.580
	3	17	A	1.129	0.584	1.707	0.334	29.552
	0	8	A	0.980	0.427	2.045	0.534	54.474
<b>Isoprenoids</b>	3	17	A	0.127	0.063	0.207	0.039	31.017
( $\mu\text{g/g}$ )	1	17	A	0.111	0.056	0.209	0.046	41.086
	2	17	A	0.110	0.048	0.158	0.032	28.893
	0	8	B	0.044	0.019	0.072	0.019	42.955
<b>LALK</b>	1	17	A	0.460	0.194	0.711	0.189	41.097
( $\mu\text{g/g}$ )	3	17	A	0.403	0.272	0.603	0.094	23.232
	2	17	A	0.345	0.151	0.518	0.106	30.763
	0	8	B	0.161	0.066	0.288	0.077	48.010
<b>Phytane/pristane</b>	0	8	A	0.170	0.097	0.262	0.053	31.300
	1	17	B	0.110	0.052	0.205	0.045	41.042
	2	17	B	0.101	0.073	0.136	0.017	16.536
	3	17	B	0.097	0.052	0.229	0.042	42.744
<b>CPI</b>	1	17	A	3.308	1.356	5.425	1.333	40.305
	0	8	A	3.209	1.859	7.000	1.618	50.418
	2	17	A	2.626	1.618	4.579	0.698	26.566
	3	17	A	2.304	1.136	4.811	0.854	37.042
<b>Total S/T</b>	0	8	A	0.020	0.006	0.057	0.017	81.723
( $\mu\text{g/g}$ )	2	17	A	0.016	0.007	0.055	0.011	68.305
	3	17	A	0.013	0.007	0.019	0.004	32.583
	1	17	A	0.012	0.007	0.019	0.003	26.654
<b>Hopane</b>	2	17	A	0.003	0.001	0.013	0.003	88.482
( $\mu\text{g/g}$ )	3	17	A	0.002	0.001	0.004	0.001	34.689
	1	17	A	0.002	0.001	0.004	0.001	37.450
	0	8	A	0.002	0.001	0.004	0.001	56.307

**Table 3-8a: Mean, Maximum, Minimum, and Student Newman-Keuls Analysis Results for Key Organic Parameters (Non-Transformed) in 1997 Surface Sediments**

Analyte	Zone	n	Significantly Different	Mean	Min	Max	SD	CV
<b>Ts/(Ts+Tm)</b>	1	17	A	0.336	0.229	0.393	0.052	15.519
	2	17	AB	0.313	0.228	0.393	0.044	14.196
	0	8	B	0.279	0.180	0.499	0.102	36.573
	3	17	B	0.274	0.244	0.330	0.028	10.094
<b>Oleanane/Hopane</b>	0	8	A	0.184	0.111	0.250	0.043	23.143
	2	17	A	0.169	0.093	0.231	0.039	22.781
	1	17	A	0.167	0.084	0.278	0.063	37.711
	3	17	A	0.160	0.103	0.246	0.033	20.700
<b>T21/T22</b>	3	17	A	0.452	0.400	0.559	0.035	7.750
	2	17	A	0.437	0.250	0.757	0.127	29.064
	1	17	A	0.333	0.146	0.758	0.189	56.697
	0	8	B	0.160	0.057	0.422	0.115	71.931

**Table 3-8b: Mean, Maximum, Minimum, and Student Newman-Keuls Analysis Results for Key Organic Parameters (Non-Transformed) in 1998 Surface Sediments**

Analyte	Zone	n	Significantly Different	Mean	Min	Max	SD	CV
<b>Total PAH</b>	4	3	A	0.604	0.537	0.650	0.060	9.901
( $\mu\text{g/g}$ )	2	8	A	0.525	0.290	0.687	0.133	25.444
	3	8	A	0.501	0.360	0.550	0.060	11.991
	1	8	B	0.330	0.120	0.730	0.198	60.096
	0	8	B	0.200	0.066	0.420	0.119	59.560
<b>Perylene</b>	4	3	A	0.022	0.020	0.025	0.003	12.031
( $\mu\text{g/g}$ )	0	8	A	0.022	0.002	0.065	0.024	109.603
	3	8	A	0.019	0.015	0.022	0.003	14.093
	2	8	A	0.013	0.010	0.018	0.003	21.050
	1	8	A	0.008	0.004	0.013	0.003	39.217
<b>Petrogenic PAH</b>	4	3	A	0.541	0.478	0.581	0.055	10.155
( $\mu\text{g/g}$ )	2	8	A	0.473	0.254	0.625	0.124	26.267
	3	8	A	0.447	0.313	0.492	0.057	12.719
	1	8	B	0.297	0.101	0.668	0.184	61.940
	0	8	C	0.156	0.056	0.316	0.085	54.644
<b>Pyrogenic PAH</b>	4	3	A	0.042	0.040	0.045	0.002	5.824
( $\mu\text{g/g}$ )	2	8	A	0.038	0.022	0.048	0.009	23.662
	3	8	A	0.036	0.029	0.041	0.005	13.010
	1	8	A	0.025	0.011	0.056	0.015	60.955
	0	8	A	0.022	0.005	0.053	0.019	84.783
<b>C2D/C2P</b>	0	8	A	0.170	0.140	0.214	0.022	12.835
	3	8	A	0.168	0.151	0.175	0.009	5.430
	4	3	A	0.163	0.159	0.166	0.004	2.176
	1	8	A	0.156	0.137	0.179	0.013	8.636
	2	8	A	0.156	0.144	0.165	0.006	3.813
<b>C3D/C3P</b>	0	8	A	0.212	0.146	0.291	0.050	23.655
	1	8	AB	0.176	0.119	0.221	0.032	17.976
	2	8	AB	0.176	0.153	0.191	0.011	6.438
	3	8	AB	0.172	0.155	0.200	0.015	8.851
	4	3	B	0.137	0.113	0.169	0.029	20.902
<b>N/P</b>	4	3	A	1.183	1.063	1.260	0.105	8.862
	0	8	A	1.163	0.915	1.422	0.176	15.158
	3	8	A	1.158	1.051	1.340	0.116	10.000
	2	8	A	1.153	1.069	1.217	0.056	4.858
	1	8	A	1.086	0.896	1.271	0.119	10.957
<b>PYRO/PETRO</b>	0	8	A	0.128	0.078	0.267	0.063	49.190
	1	8	A	0.085	0.070	0.105	0.012	13.820
	3	8	A	0.081	0.069	0.092	0.008	10.430
	2	8	A	0.080	0.075	0.088	0.004	5.123
	4	3	A	0.078	0.074	0.084	0.005	6.391
<b>Total PHC</b>	4	3	A	35.778	30.667	43.333	6.678	18.665
( $\mu\text{g/g}$ )	3	8	A	33.250	24.000	42.000	6.585	19.803
	2	8	A	25.750	21.000	31.000	3.576	13.886
	0	8	A	25.504	6.800	54.333	18.095	70.950
	1	8	A	23.583	14.000	39.000	8.180	34.686

**Table 3-8b: Mean, Maximum, Minimum, and Student Newman-Keuls Analysis Results for Key Organic Parameters (Non-Transformed) in 1998 Surface Sediments (continued)**

Analyte	Zone	n	Significantly Different	Mean	Min	Max	SD	CV
<b>nC16/(nC15+nC17)</b>	4	3	A	0.366	0.324	0.396	0.037	10.147
	2	8	A	0.366	0.340	0.394	0.021	5.722
	3	8	A	0.349	0.301	0.429	0.053	15.221
	0	8	A	0.343	0.222	0.447	0.067	19.608
	1	8	A	0.331	0.300	0.395	0.030	9.087
<b>Pristane (<math>\mu\text{g/g}</math>)</b>	4	3	A	0.142	0.123	0.173	0.027	19.089
	2	8	A	0.126	0.070	0.167	0.032	25.319
	3	8	A	0.110	0.081	0.140	0.017	15.880
	0	8	A	0.106	0.011	0.400	0.127	120.188
	1	8	A	0.102	0.041	0.210	0.058	56.296
<b>nC15+nC17</b>	4	3	A	0.099	0.092	0.112	0.011	11.604
	3	8	A	0.097	0.077	0.121	0.017	17.783
	2	8	A	0.090	0.057	0.108	0.019	21.423
	1	8	AB	0.072	0.038	0.172	0.046	63.568
	0	8	B	0.041	0.016	0.087	0.025	61.476
<b>nC27+nC29+nC31</b>	0	8	A	0.507	0.139	1.550	0.483	95.101
	3	8	A	0.506	0.390	0.580	0.066	13.100
	4	3	A	0.487	0.447	0.523	0.038	7.902
	2	8	A	0.367	0.314	0.439	0.043	11.663
	1	8	A	0.339	0.169	0.540	0.132	38.972
<b>TALK (<math>\mu\text{g/g}</math>)</b>	4	3	A	2.040	1.838	2.253	0.208	10.185
	3	8	A	1.914	1.612	2.070	0.139	7.240
	2	8	A	1.522	1.215	1.810	0.216	14.220
	1	8	A	1.484	0.896	2.260	0.443	29.881
	0	8	A	1.391	0.523	3.268	0.930	66.847
<b>Isoprenoids (<math>\mu\text{g/g}</math>)</b>	4	3	A	0.229	0.210	0.258	0.025	10.874
	2	8	A	0.203	0.114	0.264	0.050	24.736
	3	8	A	0.189	0.145	0.223	0.023	12.026
	1	8	A	0.155	0.069	0.333	0.088	56.986
	0	8	A	0.135	0.024	0.422	0.129	95.463
<b>LALK (<math>\mu\text{g/g}</math>)</b>	4	3	A	0.658	0.651	0.669	0.009	1.407
	2	8	A	0.632	0.424	0.792	0.126	19.956
	3	8	A	0.572	0.505	0.637	0.054	9.463
	1	8	A	0.434	0.195	0.958	0.242	55.912
	0	8	A	0.402	0.094	0.866	0.277	68.963
<b>Phytane/Pristane</b>	3	8	A	0.113	0.076	0.136	0.021	18.390
	2	8	A	0.102	0.089	0.125	0.012	11.650
	4	3	A	0.097	0.087	0.103	0.009	9.554
	0	8	A	0.093	0.000	0.205	0.072	77.634
	1	8	A	0.087	0.056	0.109	0.018	20.239
<b>CPI</b>	0	8	A	5.410	2.682	8.208	2.123	39.237
	3	8	B	3.598	2.890	4.352	0.430	11.953
	2	8	B	3.433	2.856	5.000	0.703	20.487
	1	8	B	3.103	1.690	4.788	0.973	31.346
	4	3	B	3.076	2.865	3.252	0.196	6.376

**Table 3-8b: Mean, Maximum, Minimum, and Student Newman-Keuls Analysis Results for Key Organic Parameters (Non-Transformed) in 1998 Surface Sediments (continued)**

Analyte	Zone	n	Significantly Different	Mean	Min	Max	SD	CV
<b>Total S/T</b> ( $\mu\text{g/g}$ )	3	8	A	0.030	0.021	0.072	0.017	57.514
	0	8	A	0.027	0.009	0.069	0.022	79.961
	4	3	A	0.025	0.024	0.027	0.001	4.601
	2	8	A	0.021	0.017	0.026	0.004	16.911
	1	8	A	0.016	0.011	0.021	0.004	24.246
<b>T19-Hopane</b> ( $\mu\text{g/g}$ )	3	8	A	0.006	0.004	0.016	0.004	74.763
	4	3	A	0.004	0.004	0.004	0.000	1.312
	2	8	A	0.004	0.002	0.005	0.001	22.640
	1	8	A	0.003	0.002	0.004	0.001	37.821
	0	8	A	0.002	0.001	0.004	0.001	61.322
<b>Ts/(Ts+Tm)</b>	1	8	A	0.330	0.293	0.363	0.021	6.442
	2	8	A	0.318	0.259	0.353	0.034	10.686
	3	8	A	0.293	0.167	0.423	0.083	28.389
	0	8	A	0.282	0.191	0.456	0.079	27.922
	4	3	A	0.270	0.240	0.288	0.026	9.733
<b>Oleanane/Hopane</b>	2	8	A	0.178	0.121	0.204	0.026	14.866
	1	8	AB	0.172	0.075	0.218	0.049	28.537
	4	3	AB	0.168	0.159	0.174	0.008	4.494
	3	8	AB	0.144	0.106	0.177	0.022	15.044
	0	8	B	0.119	0.094	0.206	0.037	30.835
<b>T21/T22</b>	2	8	A	0.511	0.342	0.650	0.105	20.593
	3	8	A	0.479	0.339	0.736	0.116	24.254
	4	3	A	0.413	0.379	0.450	0.036	8.650
	1	8	A	0.384	0.161	0.741	0.221	57.593
	0	8	B	0.154	0.059	0.378	0.100	64.850
<b>Crude Oil</b>	2	8	A	47.375	0.000	302.000	104.672	220.944
<b>Emulsifiers</b> (cells per gram)	0	8	A	12.625	0.000	56.000	23.561	186.623
	3	8	A	10.500	0.000	84.000	29.698	282.843
	1	8	A	0.000	0.000	0.000	0.000	
	4	3	A	0.000	0.000	0.000	0.000	
<b>Marine</b>	0	8	A	1183609	8444	7870544	2705535	229
<b>Heterotrophs</b> (cells per gram)	2	8	A	158306	93398	437014	114225	72
	4	3	A	141362	63499	250187	97119	69
	1	8	A	98442	9406	305966	92817	94
	3	8	A	74180	54054	113273	18601	25

**Table 3-9: Average Total Organics Concentrations in Surficial Sediments from Zones 0, 1, 2, 3 and 4 in Outermost Cook Inlet and the Shelikof Strait, Concentrations of Alaska Marine Sediments, and Concentrations in Cook Inlet and the Shelikof Strait from Previous Studies**

<b>Organic Parameter</b>	<b>Study Average Concentrations for Surficial Sediment (µg/g)</b>	<b>Concentrations in Alaska Marine Sediments (µg/g)<sup>a</sup></b>	<b>Concentrations in Cook Inlet and Shelikof Strait (µg/g)<sup>b</sup></b>
<b>Total PAH</b>	0.459	0.016 - 2.4	0.001 - 0.958
<b>Total PHC</b>	29.4	0.47 - 38	0.9 - 69.0
<b>Total S/T</b>	0.024	NA	NA

<sup>a</sup> Prince William sound subtidal and Beaufort Sea (Bence, *et al.*, 1996, Boehm *et al.*, 1991).

<sup>b</sup> ENRI - UAA, 1995, Hyland, *et al.*, 1995, ADL, 1996, KLI, 1996, KLI, 1997.

**Table 3-10: Means, Standard Deviations, and Ranges of Values for Metals, Total Organic Carbon (TOC), Sand, Silt and Clay for Surficial (0-2 cm) Sediments from Zones AC, 0, 1, 2, 3 and 4 in Outermost Cook Inlet and the Shellkof Strait (dry weight)**

	Zone (Year)	Al (%)	Ca (%)	Fe (%)	K (%)	Mg (%)	TOC (%)	Sand (%)	Silt+Clay (%)
Mean Std. Dev.	AC (1998)	8.33 ±0.23	--	5.73 ±0.10	--	--	1.13 ±0.04	1.4 ±0.4	98.6 ±0.4
Range		8.11-8.57		5.64-5.83			1.09-1.16	0.9-1.6	98.4-99.4
Mean Std. Dev.	0 (1997)	7.29 ±0.64	2.68 ±0.92	3.98 ±0.64	1.68 ±0.17	1.51 ±0.17	0.64 ±0.33	42.2 ±26.8	57.9 ±26.9
Range		6.02-8.23	1.26-4.57	2.79-5.31	1.38-2.03	1.12-1.89	0.31-1.22	3.8-84.9	15.1-96.2
Mean Std. Dev.	0 (1998)	7.44 ±0.45	--	3.92 ±0.63	--	--	0.84 ±0.41	41.7 ±29.6	58.3 ±30.6
Range		6.70-7.92		2.74-4.87			0.28-1.37	7.0-78.5	21.5-93.0
Mean Std. Dev.	1 (1997)	7.46 ±0.36	2.21 ±0.17	3.90 ±0.31	1.62 ±0.20	1.45 ±0.17	0.57 ±0.17	32.4 ±22.4	62.9 ±20.9
Range		6.57-8.16	1.87-2.91	3.37-4.40	1.39-2.03	1.21-1.82	0.26-0.94	2.6-70.3	29.7-97.4
Mean Std. Dev.	1 (1998)	8.02 ±0.64	--	4.03 ±0.35	--	--	0.59 ±0.19	44.4 ±22.4	55.6 ±22.2
Range		7.53-9.37		3.42-4.48			0.32-0.92	12.2-68.0	32.0-87.8
Mean Std. Dev.	2 (1997)	7.48 ±0.23	1.86 ±0.19	4.28 ±0.24	1.68 ±0.07	1.71 ±0.08	0.84 ±0.14	6.3 ±7.5	93.3 ±6.9
Range		6.66-7.74	1.49-2.18	3.76-4.57	1.42-1.88	1.55-1.84	0.48-1.05	0.10-27.18	72.8-99.9
Mean Std. Dev.	2 (1998)	7.96 ±0.25	--	4.52 ±0.18	--	--	1.02 ±0.27	8.2 ±7.1	91.8 ±7.2
Range		6.69-8.44		3.30-4.86			0.59-1.49	1.0-23.8	76.2-99.0
Mean Std. Dev.	3 (1997)	7.17 ±0.48	1.75 ±0.13	4.51 ±0.08	1.82 ±0.09	1.85 ±0.07	0.95 ±0.08	2.5 ±4.4	97.9 ±3.7
Range		5.64-7.64	1.51-1.97	4.38-4.71	1.50-2.02	1.64-2.01	0.79-1.16	0.2-17.69	91.5-99.8
Mean Std. Dev.	3 (1998)	7.99 ±0.11	--	4.53 ±0.15	--	--	0.95 ±0.11	2.6 ±3.5	97.4 ±3.5
Range		7.82-8.17		4.18-4.65			0.80-1.15	0.4-12.2	87.8-99.6
Mean Std. Dev.	4 (1998)	7.71 ±0.12	--	4.33 ±0.16	--	--	1.13 ±0.04	1.1 ±0.8	98.9 ±0.9
Range		7.46-7.94		4.08-4.54			1.08-1.18	0.3-2.9	97.1-99.7
Mean Std. Dev.	Avg. of 0,1, 2, 3, and 4 (excluding AC)	7.45 ±0.51	2.14 ±0.61	4.18 ±0.43	1.70 ±0.17	1.63 ±0.20	0.81 ±0.28	20.5 ±24.4	81.7 ±19.1
Range		5.64-9.37	1.26-4.57	2.74-5.31	1.38-2.03	1.12-2.01	0.26-1.49	0.1-84.9	15.1-99.9

**Table 3-10: Means, Standard Deviations and Ranges of Values for Metals, Total Organic Carbon (TOC), Sand, Silt and Clay for Surficial (0-2 cm) Sediments from Zones AC, 0, 1, 2, 3 and 4 in Outermost Cook Inlet and the Shelikof Strait (continued)**

	Zone (Year)	Ag ( $\mu\text{g/g}$ )	As ( $\mu\text{g/g}$ )	Ba ( $\mu\text{g/g}$ )	Be ( $\mu\text{g/g}$ )	Cd ( $\mu\text{g/g}$ )	Cr ( $\mu\text{g/g}$ )	Cu ( $\mu\text{g/g}$ )	Hg ( $\mu\text{g/g}$ )	Mn ( $\mu\text{g/g}$ )
Mean	AC	0.03	4.2	695	1.1	0.10	94.4	31.7	0.064	790
Std. Dev.	(1998)	$\pm 0.01$	$\pm 0.4$	$\pm 13$	$\pm 0.1$	$\pm 0.01$	$\pm 10.9$	$\pm 0.5$	$\pm 0.003$	$\pm 19$
Range		0.3-0.4	4.0-4.7	682-707	1.0-1.1	0.10-0.11	86.9-107	31.3-32.3	0.062-0.068	771-808
Mean	0	0.07	10.0	758	1.1	0.09	66.3	34.1	0.057	819
Std. Dev.	(1997)	$\pm 0.03$	$\pm 4.2$	$\pm 126$	$\pm 0.1$	$\pm 0.01$	$\pm 15.8$	$\pm 10.5$	$\pm 0.035$	$\pm 126$
Range		0.04-0.13	3.8-16.0	518-924	0.89-1.40	0.04-0.11	42.8-95.3	20.3-52.0	0.023-0.125	615-1000
Mean	0	0.04	8.2	775	1.2	0.09	69.0	32.5	0.057	830
Std. Dev.	(1998)	$\pm 0.02$	$\pm 4.3$	$\pm 123$	$\pm 0.0$	$\pm 0.01$	$\pm 15.8$	$\pm 10.2$	$\pm 0.035$	$\pm 122$
Range		0.01-0.08	2.5-14.6	571-957	1.0-1.4	0.07-0.11	47.5-94.6	20.3-50.3	0.024-0.123	610-999
Mean	1	0.07	8.0	814	1.1	0.10	62.4	30.6	0.043	846
Std. Dev.	(1997)	$\pm 0.01$	$\pm 2.1$	$\pm 57$	$\pm 0.1$	$\pm 0.01$	$\pm 7.1$	$\pm 6.4$	$\pm 0.009$	$\pm 109$
Range		0.05-0.09	4.8-11.8	708-914	1.01-1.36	0.08-0.14	49.1-76.4	19.9-41.1	0.022-0.067	720-1220
Mean	1	0.05	8.2	783	1.2	0.10	63.1	28.8	0.042	895
Std. Dev.	(1998)	$\pm 0.02$	$\pm 2.8$	$\pm 73$	$\pm 0.2$	$\pm 0.04$	$\pm 12.1$	$\pm 7.0$	$\pm 0.010$	$\pm 122$
Range		0.01-0.08	5.3-13.1	630-888	1.0-1.4	0.08-0.16	46.0-77.1	21.4-41.9	0.028-0.054	664-1049
Mean	2	0.07	9.5	854	1.1	0.12	73.4	37.7	0.058	936
Std. Dev.	(1997)	$\pm 0.02$	$\pm 1.6$	$\pm 32$	$\pm 0.1$	$\pm 0.02$	$\pm 5.3$	$\pm 2.9$	$\pm 0.007$	$\pm 328$
Range		0.05-0.10	5.7-13.7	775-916	0.96-1.32	0.09-0.20	59.2-80.9	29.4-41.2	0.047-0.072	688-2140
Mean	2	0.06	12.0	904	1.3	0.11	82.1	38.8	0.062	1122
Std. Dev.	(1998)	$\pm 0.01$	$\pm 1.7$	$\pm 29$	$\pm 0.1$	$\pm 0.01$	$\pm 5.5$	$\pm 1.5$	$\pm 0.006$	$\pm 174$
Range		0.03-0.10	7.4-14.0	709-964	1.0-1.4	0.10-0.18	58.7-90.0	30.0-40.8	0.052-0.069	564-1565
Mean	3	0.09	9.0	878	1.4	0.16	75.2	37.4	0.060	1007
Std. Dev.	(1997)	$\pm 0.01$	$\pm 1.3$	$\pm 17$	$\pm 0.0$	$\pm 0.02$	$\pm 3.6$	$\pm 1.5$	$\pm 0.004$	$\pm 206$
Range		0.08-0.11	7.0-13.4	826-928	1.34-1.48	0.12-0.23	65.1-80.7	33.9-41.5	0.050-0.067	72-1570
Mean	3	0.06	8.9	888	1.3	0.15	79.9	36.5	0.060	904
Std. Dev.	(1998)	$\pm 0.00$	$\pm 0.9$	$\pm 26$	$\pm 0.0$	$\pm 0.02$	$\pm 4.7$	$\pm 1.6$	$\pm 0.003$	$\pm 92$
Range		0.05-0.07	7.4-11.2	846-925	1.2-1.4	0.12-0.18	69.0-85.7	33.0-38.0	0.056-0.066	687-981
Mean	4	0.06	8.4	850	1.3	0.15	78.9	32.7	0.065	908
Std. Dev.	(1998)	$\pm 0.01$	$\pm 1.6$	$\pm 22$	$\pm 0.0$	$\pm 0.01$	$\pm 3.0$	$\pm 1.4$	$\pm 0.003$	$\pm 169$
Range		0.05-0.07	6.0-11.1	808-900	1.2-1.4	0.13-0.17	71.8-84.0	30.9-34.4	0.062-0.068	689-1209
Mean	Avg. of 0,1, 2, 3 and 4 (excluding AC)	0.07	9.1	826	1.2	0.14	71.0	34.5	0.056	907
Std. Dev.		$\pm 0.02$	$\pm 2.6$	$\pm 81$	$\pm 0.1$	$\pm 0.00$	$\pm 11.0$	$\pm 6.8$	$\pm 0.020$	$\pm 208$
Range		0.01-0.13	2.5-16.0	518-964	0.9-1.5	0.04-0.23	44.5-95.3	19.9-52.0	0.022-0.125	564-2140

**Table 3-10: Means, Standard Deviations and Ranges of Values for Metals, Total Organic Carbon (TOC), Sand, Silt and Clay for Surficial (0-2 cm) Sediments from Zones AC, 0, 1, 2, 3 and 4 in Outermost Cook Inlet and the Shelikof Strait (continued)**

	Zone (Year)	Ni ( $\mu\text{g/g}$ )	Pb ( $\mu\text{g/g}$ )	Sb ( $\mu\text{g/g}$ )	Se ( $\mu\text{g/g}$ )	Sn ( $\mu\text{g/g}$ )	Tl ( $\mu\text{g/g}$ )	V ( $\mu\text{g/g}$ )	Zn ( $\mu\text{g/g}$ )
Mean	AC	51.9	14.6	0.59	0.36	1.40	0.37	176	121
Std. Dev.	(1998)	$\pm 0.9$	$\pm 0.4$	$\pm 0.02$	$\pm 0.03$	$\pm 0.06$	$\pm 0.01$	$\pm 4$	$\pm 5$
Range		51.1-52.9	14.2-15.0	0.57-0.61	0.33-0.38	1.33-1.44	0.36-0.37	171-179	116-126
Mean	0	33.5	11.0	0.90	0.20	1.50	0.41	126	100
Std. Dev.	(1997)	7.9	$\pm 2.2$	$\pm 0.36$	$\pm 0.10$	$\pm 0.30$	$\pm 0.04$	$\pm 26$	$\pm 20$
Range		24.7-51.4	7.3-14.5	0.46-1.74	0.05-0.35	1.01-1.91	0.32-0.49	87.0-180	64.8-132
Mean	0	36.1	11.2	0.87	0.26	1.18	0.42	132	93.8
Std. Dev.	(1998)	8.0	$\pm 2.3$	$\pm 0.34$	$\pm 0.12$	$\pm 0.31$	$\pm 0.05$	$\pm 23$	$\pm 19.2$
Range		25.9-49.9	8.0-14.0	0.48-1.53	0.14-0.55	0.71-1.53	0.34-0.51	89.3-173	66.0-125
Mean	1	30.8	12.0	0.84	0.25	1.62	0.42	126	98.4
Std. Dev.	(1997)	$\pm 5.3$	$\pm 1.2$	$\pm 0.14$	$\pm 0.11$	$\pm 0.20$	$\pm 0.03$	$\pm 11$	$\pm 12.4$
Range		22.9-39.9	9.6-13.7	0.63-1.08	0.10-0.53	1.14-1.96	0.34-0.48	106-141	77.7-117
Mean	1	32.1	11.7	0.81	0.24	1.38	0.41	127	93.3
Std. Dev.	(1998)	$\pm 4.2$	$\pm 1.3$	$\pm 0.14$	$\pm 0.07$	$\pm 0.28$	$\pm 0.05$	$\pm 10$	$\pm 14.5$
Range		26.1-38.6	10.0-13.8	0.64-1.11	0.13-0.33	1.00-1.75	0.33-0.50	111-145	73.8-118
Mean	2	35.1	13.7	0.98	0.38	1.73	0.47	143	115
Std. Dev.	(1997)	$\pm 3.8$	$\pm 0.7$	$\pm 0.07$	$\pm 0.08$	$\pm 0.08$	$\pm 0.03$	$\pm 10$	$\pm 7$
Range		27.7-40.7	12.0-14.9	0.80-1.11	0.22-0.56	1.51-1.87	0.40-0.50	119-159	100-127
Mean	2	37.3	13.8	1.02	0.24	1.60	0.46	151	119
Std. Dev.	(1998)	$\pm 4.0$	$\pm 0.7$	$\pm 0.05$	$\pm 0.11$	$\pm 0.15$	$\pm 0.02$	$\pm 8$	$\pm 3.1$
Range		29.1-41.7	11.7-14.8	0.82-1.08	0.10-0.42	1.38-1.80	0.39-0.50	94.3-167	85.1-124
Mean	3	38.5	14.0	1.16	0.33	1.83	0.47	144	126
Std. Dev.	(1997)	$\pm 1.1$	$\pm 0.3$	$\pm 0.03$	$\pm 0.05$	$\pm 0.06$	$\pm 0.02$	$\pm 7$	$\pm 2$
Range		35.4-39.9	13.1-14.8	1.06-1.22	0.25-0.42	1.75-1.95	0.44-0.52	129-154	122-133
Mean	3	38.6	14.4	1.08	0.24	1.73	0.50	153	121
Std. Dev.	(1998)	$\pm 1.4$	$\pm 0.4$	$\pm 0.06$	$\pm 0.03$	$\pm 0.05$	$\pm 0.02$	$\pm 5$	$\pm 4$
Range		35.6-40.1	13.6-14.8	0.95-1.14	0.20-0.30	1.64-1.80	0.47-0.52	144-160	114-126
Mean	4	37.4	14.2	1.03	0.24	1.59	0.46	144	117
Std. Dev.	(1998)	$\pm 2.4$	$\pm 0.3$	$\pm 0.07$	$\pm 0.05$	$\pm 0.04$	$\pm 0.01$	$\pm 3$	$\pm 4$
Range		33.6-40.9	13.8-14.9	0.90-1.15	0.16-0.30	1.38-1.73	0.44-0.47	137-153	111-123
Mean	Avg. of 0,1, 2, 3 and 4 (excluding AC)	35.1	12.8	0.97	0.29	1.60	0.44	137	109
Std. Dev.		$\pm 5.7$	$\pm 1.7$	$\pm 0.22$	$\pm 0.10$	$\pm 0.24$	$\pm 0.04$	$\pm 18$	$\pm 16$
Range		21.6-51.4	7.3-14.9	0.47-1.74	0.05-0.56	0.71-1.96	0.32-0.52	87.0-180	66.0-133

**Table 3-11: Average Metal Concentrations in Surficial Sediments from Zones AC, 0, 1, 2, 3, and 4 in Outermost Cook Inlet and the Shelikof Strait, Average Continental Crust (Wedepohl, 1995) and Average Concentrations for Bottom Sediment from the Susitna and Copper Rivers**

Metal ( $\mu\text{g/g}$ )*	All Zones in Study Area			Continental Crust	Susitna and Copper Rivers
	1997	1998	1997-1998		
Ag	0.08	0.05	0.07	0.07	0.12
Al	7.29%	7.75%	7.45%	7.96%	6.94%
As	9.1	8.8	9.1	1.7	8.2
Ba	823	819	826	584	789
Be	1.2	1.2	1.2	2.4	1.23
Cd	0.12	0.12	0.12	0.10	0.20
Cr	69.1	74.8	71.0	126	66.6
Cu	34.5	33.6	34.5	25	38.9
Fe	4.15%	4.30%	4.18%	4.32%	3.47%
Hg	0.054	0.060	0.056	0.040	0.038
Mn	905	893	907	716	759
Ni	34.3	37.0	35.1	56	37.6
Pb	12.6	13.0	12.8	14.8	0.8
Sb	0.96	0.94	0.97	0.30	0.94
Se	0.29	0.28	0.29	0.12	0.2
Sn	1.66	1.46	1.60	2.3	1.67
Tl	0.44	0.44	0.44	0.52	0.36
V	134	141	137	98	119
Zn	109	108	109	65	73.7

Notes:

\*Concentrations in  $\mu\text{g/g}$ , except where noted.

**Table 3-12: Groupings of Metals in Surficial Sediments from Zones 0, 1, 2, 3 and 4 in Outermost Cook Inlet and the Shelikof Strait Based on Coefficient of Variation**

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<b>Coefficient of Variation</b>	<b>Metal</b>
≤10%	Al, Ba, K, Tl
>10-20%	Be, Cr, Cu, Fe, Mg, Ni, Pb, Sn, V, Zn
>20-30%	As, Ca, Cd, Mn, Sb
>30%	Ag, Hg, Se

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**Table 3-13: Results of the Student Newman Keuls Statistical Test Performed on Metal/Fe Ratios from Surficial Sediments in Zones 0, 1, 2 and 3**

1997 SNK Grouping					
Metal	Zone 0	Zone 1	Zone 2	Zone 3	# of Groups
Ag	A	A	A	A	1
As	A	B	A/B	B	2
Ba	B	A	A/B	B	2
Be	B	A/B	C	A	3
Cd	C	B/C	A/B	A	3
Cr	A/B	B	A	A/B	2
Cu	A/B	B	A	A/B	2
Hg	A	B	A/B	A/B	2
Pb	B	A	A	A	2
Mn	A	A	A	A	1
Ni	A	A	A	A	1
Sb	B	B	B	A	2
Se	C	B/C	A	B	3
Sn	B	A	A	A	2
Tl	A	A	A	A	1
V	B	B	A	B	2
Zn	B	B	A	A	2
1997 and 1998 Combined Data SNK Grouping					
Metal	Zone 0	Zone 1	Zone 2	Zone 3	# of Groups
Ag	A	A	A	A	1
As	A	A	A	A	1
Ba	A	A	A	A	1
Be	A	A	A	A	1
Cd	B	A/B	A/B	A	2
Cr	A	A	A	A	1
Cu	A	A	A	A	1
Hg	A	A	A	A	1
Pb	A	A	A	A	1
Mn	A/B	A	A/B	B	2
Ni	A	A	A	A	1
Sb	A	A	A	A	1
Se	A	A	A	A	1
Sn	B	A/B	A/B	A	2
Tl	A	A	A	A	1
V	A	A	A	A	1
Zn	B	A/B	A/B	A	2

**Table 3-14: Percent Survival of *Eohaustorius estuarius* in the Sediment for Toxicity Tests**

1997 Sediment Site	Percent Survival in Test Replicates				Mean Percent Survival
	Rep A	Rep B	Rep C	Rep D	
Home Control	95	100	90	100	96.25
Z0F1	65	75	65	75	70 <sup>†*</sup>
Z0F2	95	90	100	90	93.75
Z0F4	95	85	100	85	91.25
Z0F5	100	90	85	85	90
Z0F6	90	70	70	70	75 <sup>†*</sup>
Z0F8	85	85	80	75	81.25 <sup>†</sup>
Z0F13	95	85	100	90	92.5
Z0F14	85	95	90	85	88.75 <sup>†</sup>
Z1F1	100	90	90	95	93.75
Z1F2	75	75	85	85	80 <sup>†</sup>
Z1R07	80	90	90	90	87.5 <sup>†</sup>
Z1R13	90	75	85	80	82.5 <sup>†</sup>
Z2F1	75	70	80	85	77.5 <sup>†*</sup>
Z2F2	60	70	50	75	63.75 <sup>†*</sup>
Z2R01	75	85	80	75	78.75 <sup>†*</sup>
Z2R13	80	80	70	90	80 <sup>†</sup>
Z3F1	80	70	70	75	73.75 <sup>†*</sup>
Z3F2	65	70	80	70	71.25 <sup>†*</sup>
Z3R11	70	40	60	55	56.25 <sup>†*</sup>
Z3R14	55	60	70	55	60 <sup>†*</sup>

<sup>†</sup> Statistical analysis indicates that amphipod survival at this site was significantly less than the 'home' control at  $p < 0.05$ .

\* Sites at which mean survival was less than 80% of mean Control survival.

See Appendix A for results of grain size analyses.

**Table 3-15: Percent Survival of *Ampelisca abdita* in the Sediment for Toxicity Tests**

1998 Sediment Site	Percent Survival in Test Replicates				Mean Percent Survival
	Rep A	Rep B	Rep C	Rep D	
Home Control	100	100	100	100	100
Reference Control	90	90	90	95	91.25
Z0F1	100	95	85	90	92.5 <sup>†</sup>
Z0F6	90	85	95	90	90 <sup>†</sup>
Z2F1	95	85	95	100	93.75
Z3F1	95	90	100	95	95 <sup>†</sup>
Z3F2	95	85	90	95	91.25 <sup>†</sup>
Z3R11	100	90	90	100	95
Z3R14	95	100	90	95	95 <sup>†</sup>

<sup>†</sup> Statistical analysis indicates that amphipod survival at this site was significantly less than the 'home' control at  $p < 0.05$ , but not significantly different than the 'reference' sediment at  $p < 0.05$ .  
See Appendix A for results of grain size analyses.

**Table 3-16: Sedimentation Rates (cm/y) Determined Using Excess <sup>210</sup>Pb and <sup>137</sup>Cs. Age-Depth Relationship Based on <sup>210</sup>Pb Sedimentation Rate**

Station ID	Sedimentation Rate (cm/y)		Depth 1980 (cm)	Depth 1950 (cm)	Depth 1920 (cm)
	<sup>210</sup> Pb	<sup>137</sup> Cs			
97-Z0-F1	ND	--	NA	NA	NA
98-Z0-F1	1.3	1.5	22	62	101
97-Z0-F5	0.21	0.24	3	9	15
97-Z0-F6	0.10	0.10	2	5	8
97-Z0-F8	0.27	--	5	13	21
97-Z1-F1	0.24	0.21	4	11	18
97-Z1-F2*	--	0.27	4	10	21
98-Z1-R3B	0.20	0.20	4	10	16
97-Z2-F1	1.3	--	22	[61]	[100]
97-Z2-F2	0.62	0.65	10	29	[48]
98-Z2-R16	0.5-0.7	0.7-0.8	--	--	--
97-Z3-F1	0.60	0.61	10	28	[37]
97-Z3-F2	0.44	0.45	7	21	[32]
98-Z4-F4	1.0 (0-20 cm)	0.84	18	34	[49]
	0.52 (20-43 cm)				

Notes:

[ ] = depth exceeded core length

ND = not determined, sedimentation rate too fast

NA = not applicable

\*Age-depth relationship based on <sup>137</sup>Cs sedimentation rate

**Table 3-17: Means and Standard Deviations for Total Organic Carbon (TOC), Sand, Silt and Clay Values for Sediment Cores from Zone 0, 1, 2, 3 and 4 in Outermost Cook Inlet and the Shelikof Strait**

<b>Station ID</b>	<b>TOC (%)</b>	<b>Sand (%)</b>	<b>Silt (%)</b>	<b>Clay (%)</b>
97-Z0-F1	1.06 ±0.08	6.0 ±3.3	43.4 ±12.5	50.6 ±11.9
98-Z0-F1	1.04 ±0.13	13.0 ±9.6	64.7 ±7.8	22.4 ±7.6
97-Z0-F5	0.44 ±0.03	30.6 ±5.7	25.6 ±15.0	43.9 ±15.9
97-Z0-F6	0.34 ±0.04	50.5 ±6.9	17.1 ±12.5	32.4 ±11.2
98-Z0-F8	0.36 ±0.03	53.5 ±4.2	30.2 ±4.7	16.3 ±5.7
97-Z1-F1	0.62 ±0.08	35.8 ±11.0	28.0 ±16.0	36.2 ±15.0
97-Z1-F2	0.75 ±0.12	17.8 ±5.6	34.7 ±16.1	47.6 ±12.0
98-Z1-R3B	0.31 ±0.09	59.6 ±6.1	29.5 ±6.6	10.9 ±4.1
97-Z2-F1	0.78 ±0.04	3.3 ±1.3	34.8 ±10.8	61.9 ±10.8
97-Z2-F2	1.00 ±0.11	1.0 ±0.5	39.0 ±19.5	60.0 ±19.7
98-Z2-R16	0.84 ±0.04	5.1 ±1.8	66.6 ±4.4	28.3 ±5.2
97-Z3-F1	0.83 ±0.06	2.3 ±0.9	44.3 ±15.3	53.5 ±15.1
97-Z3-F2	0.81 ±0.09	1.5 ±0.8	39.3 ±10.4	59.2 ±10.6
98-Z4-F4	1.08 ±0.06	1.7 ±1.7	61.2 ±6.4	37.1 ±6.9
All Samples	0.74 ±0.27	19.5 ±21.7	40.8 ±18.6	39.7 ±19.2
Range 1997-1998	0.21-1.24	0.2-67.8	3.1-79.4	4.7-83.2

**Table 3-18: Mean and Standard Deviation of Total Organic Parameters for Sediment Cores from Zones 0, 1, 2, 3 and 4**

Year	Zone	Station	Total Hydrocarbons (ug/g)	Total PAH (ug/g)	Total S&T (ug/g)	TOC (%)
1997	0	F1	46.9 ± 6.71	0.316 ± 0.047	0.082 ± 0.010	1.06 ± 0.081
1998	0	F1	40.5 ± 7.51	0.357 ± 0.042	0.082 ± 0.011	1.04 ± 0.135
1997	0	F5	11.0 ± 3.63	0.127 ± 0.017	0.016 ± 0.002	0.438 ± 0.026
1997	0	F6	12.1 ± 2.84	0.115 ± 0.015	0.010 ± 0.001	0.344 ± 0.043
1998	0	F8	5.71 ± 1.41	0.109 ± 0.018	0.014 ± 0.002	0.361 ± 0.035
1997	1	F1	19.5 ± 4.95	0.518 ± 0.114	0.021 ± 0.005	0.619 ± 0.081
1997	1	F2	16.6 ± 2.97	0.595 ± 0.079	0.015 ± 0.002	0.757 ± 0.116
1997	2	F1	27.1 ± 6.08	0.427 ± 0.055	0.025 ± 0.003	0.776 ± 0.041
1997	2	F2	36.1 ± 5.76	0.684 ± 0.055	0.022 ± 0.003	1.003 ± 0.114
1998	2	R16	30.6 ± 8.30	0.743 ± 0.034	0.029 ± 0.004	0.844 ± 0.038
1997	3	F1	30.8 ± 10.3	0.493 ± 0.086	0.016 ± 0.004	0.834 ± 0.081
1997	3	F2	24.6 ± 11.9	0.558 ± 0.069	0.021 ± 0.004	0.806 ± 0.086
1998	4	F4	21.3 ± 4.42	0.687 ± 0.041	0.029 ± 0.002	1.08 ± 0.061
	<b>Range</b>		4.3 - 56	0.074 - 0.805	0.008 - 0.100	0.28 - 1.24

**Table 3-19: Means and Standard Deviations for Trace Metals, Total Organic Carbon (TOC), Sand, Silt and Clay Values for Sediment Cores from Zone 0, 1, 2, 3 and 4 in Outermost Cook Inlet and the Shelikof Strait (dry weight)**

Station ID	Al (%)	Ca (%)	Fe (%)	K (%)	Mg (%)	TOC (%)	Sand (%)	Silt (%)	Clay (%)
97-Z0-F1	8.09	1.51	4.82	1.78	1.67	1.06	6.0	43.4	50.6
98-Z0-F1	7.81	--	4.77	--	--	1.04	13.0	64.7	22.4
97-Z0-F5	7.16	2.28	3.92	1.75	1.47	0.44	30.6	25.6	43.9
97-Z0-F6	7.76	2.38	3.96	1.83	1.53	0.34	50.5	17.1	32.4
98-Z0-F8	7.74	--	3.84	--	--	0.36	53.5	30.2	16.3
97-Z1-F1	7.74	2.17	4.02	1.58	1.47	0.62	35.8	28.0	36.2
97-Z1-F2	6.77	2.31	4.01	1.98	1.56	0.75	17.8	34.7	47.6
98-Z1-R3B	7.67	--	3.32	--	--	0.31	59.6	29.5	10.9
97-Z2-F1	7.43	1.97	4.34	1.63	1.74	0.78	3.3	34.8	61.9
97-Z2-F2	7.30	1.65	4.42	1.68	1.79	1.00	1.0	39.0	60.0
98-Z2-R16	7.98	--	4.48	--	--	0.84	5.1	66.6	28.3
97-Z3-F1	7.00	1.82	4.41	1.76	1.77	0.83	2.3	44.3	53.5
97-Z3-F2	7.24	1.83	4.39	1.78	1.78	0.81	1.5	39.3	59.2
98-Z4-F4	8.13	--	4.48	--	--	1.08	1.7	61.2	37.1
Mean and	7.58	1.99	4.24	1.76	1.64	0.74	19.5	40.8	39.7
Range All	5.94 - 8.50	1.19 - 2.89	2.80 - 5.14	1.35 - 2.14	1.01 - 2.01	0.21 - 1.24	0.2 - 67.8	3.1 - 79.4	4.7 - 83.2

**Table 3-19: Means and Standard Deviations for Trace Metals, Total Organic Carbon (TOC), Sand, Silt and Clay Values for Sediment Cores from Zone 0, 1, 2, 3 and 4 in Outermost Cook Inlet and the Shellkof Strait**

Station ID	Ag ( $\mu\text{g/g}$ )	As ( $\mu\text{g/g}$ )	Ba ( $\mu\text{g/g}$ )	Be ( $\mu\text{g/g}$ )	Cd ( $\mu\text{g/g}$ )	Cr ( $\mu\text{g/g}$ )	Cu ( $\mu\text{g/g}$ )	Hg ( $\mu\text{g/g}$ )	Mn ( $\mu\text{g/g}$ )
97-Z0-F1	0.13	13.6	837	1.2	0.10	92.9	51.1	0.117	836
98-Z0-F1	0.08	11.3	871	1.3	0.11	90.8	51.6	0.128	812
97-Z0-F5	0.10	7.5	904	1.4	0.12	66.5	36.6	0.057	711
97-Z0-F6	0.06	9.0	832	1.3	0.11	63.8	35.7	0.060	749
98-Z0-F8	0.04	7.5	857	1.4	0.11	65.5	31.4	0.032	753
97-Z1-F1	0.08	6.4	812	1.2	0.12	68.6	32.9	0.048	715
97-Z1-F2	0.08	8.5	806	1.1	0.16	64.2	32.4	0.038	766
98-Z1-R3B	0.06	6.1	808	1.2	0.10	51.9	22.7	0.030	627
97-Z2-F1	0.07	9.0	873	1.2	0.13	75.7	39.1	0.056	797
97-Z2-F2	0.06	8.0	841	1.1	0.19	77.6	38.2	0.063	885
98-Z2-R16	0.05	9.2	917	1.4	0.12	80.6	38.6	0.063	922
97-Z3-F1	0.09	9.7	915	1.4	0.17	75.7	38.6	0.057	938
97-Z3-F2	0.08	8.1	931	1.4	0.18	71.2	39.3	0.053	760
98-Z4-F4	0.06	8.4	880	1.3	0.17	82.2	35.0	0.065	945
Mean and	0.07	8.8	864	1.3	0.14	73.7	37.5	0.063	803
Range All	0.02 - 0.14	5.0 - 20.4	759 - 965	1.0 - 1.6	0.07 - 0.27	34.2 - 98.5	19.1 - 58.3	0.022 - 0.165	554 - 1530

**Table 3-19: Means and Standard Deviations for Trace Metals, Total Organic Carbon (TOC), Sand, Silt and Clay Values for Sediment Cores from Zone 0, 1, 2, 3 and 4 in Outermost Cook Inlet and the Shelikof Strait**

Station ID	Ni ( $\mu\text{g/g}$ )	Pb ( $\mu\text{g/g}$ )	Sb ( $\mu\text{g/g}$ )	Se ( $\mu\text{g/g}$ )	Sn ( $\mu\text{g/g}$ )	Tl ( $\mu\text{g/g}$ )	V ( $\mu\text{g/g}$ )	Zn ( $\mu\text{g/g}$ )
97-Z0-F1	47.7	13.4	1.52	0.34	1.78	0.43	173	122
98-Z0-F1	49.8	13.5	1.60	0.48	1.37	0.45	169	118
97-Z0-F5	34.8	12.8	1.05	0.30	1.82	0.46	127	107
97-Z0-F6	31.2	12.0	0.98	0.14	1.72	0.44	131	104
98-Z0-F8	33.1	12.0	0.90	0.21	1.54	0.44	136	93.2
97-Z1-F1	32.0	12.3	0.89	0.44	1.59	0.45	138	102
97-Z1-F2	34.5	12.6	0.90	0.56	1.73	0.42	121	104
98-Z1-R3B	24.3	10.5	0.75	0.24	1.18	0.39	105	81.2
97-Z2-F1	36.0	13.8	1.02	0.28	1.74	0.48	141	118
97-Z2-F2	35.7	14.2	1.00	0.34	1.73	0.46	142	122
98-Z2-R16	36.2	13.9	1.03	0.25	1.66	0.46	148	120
97-Z3-F1	37.6	13.9	1.24	0.24	2.00	0.49	144	125
97-Z3-F2	37.6	14.0	1.25	0.25	1.88	0.49	141	125
98-Z4-F4	41.2	14.4	1.13	0.25	1.54	0.47	151	122
Mean and	36.7	13.1	1.09	0.31	1.65	0.45	141	112
Range All	16.1 - 52.6	9.8 - 15.2	0.66 - 1.92	0.08 - 0.69	1.08 - 3.88	0.37 - 0.53	75.9 - 183	70.9 - 136

**Table 3-20: Analysis of Post-1963 Shifts in Organic Indices**

Parameter	R-square Associated with 1963 Intervention	Mean Shift for 1963 Fixed Effect <sup>1</sup>	P-value for Fixed Cores Model <sup>2</sup>	Mean Shift for 1963 Random Effect <sup>1</sup>	P-value for Random Cores Model <sup>2</sup>
Perylene	0.1035	-0.0026	0.0003	-0.0024	0.0027
Pristane	0.1161	0.0064	0.0001	0.0069	0.0058
Phytane	0.0403	-0.0005	0.0266	-0.0004	0.1537
TPHC	0.1303	2.7406	0	2.6731	0.0003
T19-Hopane	0.0049	0.0001	0.4445	0.0001	0.3604
Total PAH	0.057	-0.0157	0.0081	-0.0174	0.1631
Petrogenic PAH	0.0454	-0.0125	0.0184	-0.0154	0.1606
Pyrogenic PAH	0.0079	-0.0006	0.3295	-0.0008	0.3093
C2D/C2P	0.1021	0.0073	0.0003	0.0067	0.0011
C3D/C3P	0.082	0.0104	0.0014	0.01	0.0062
N/P	0.0019	0.0046	0.6379	0.0077	0.515
nC15+nC17	0.0141	-0.0019	0.1927	-0.0015	0.4144
nC27+nC29+nC31	0.0256	0.0148	0.0781	0.0179	0.0411
TALK	0.018	0.0377	0.1409	0.0501	0.0613
Isoprenoids	0.0457	0.0053	0.018	0.0059	0.0509
LALK	0.003	0.0066	0.552	0.015	0.4983
Phytane/Pristane	0.0266	-0.0105	0.0729	-0.0124	0.2812
Total S/T	0.0033	-0.0003	0.5312	-0.0001	0.8797
Ts/(Ts+Tm)	0.0473	0.0132	0.0161	0.0129	0.0399
Oleanane/Hopane	0.0165	-0.0244	0.1583	-0.0122	0.6038
T21/T22	0.0625	0.0144	0.0055	0.0115	0.318
nC16/(nC15+nC17)	0.0002	0.0005	0.8801	-0.0008	0.8846
CPI	0.0006	0.0155	0.7848	0.0515	0.4918
Pyro/Petro	0.0003	0.0002	0.8573	0.0002	0.8859
TOC	0.0551	0.0224	0.0109	0.0277	0.0106

Notes:

<sup>1</sup> Negative sign indicates parameter increases with increased depth, positive sign indicates parameter decreases with increased depth.

<sup>2</sup> Significance is established at  $p < 0.05$ .

**Table 3-21: Analysis of Post-1963 Shifts in Iron Normalized Metals**

Parameter	R-square Associated with 1963 Intervention	Mean Shift for 1963 Fixed Effect <sup>1</sup>	P-value for Fixed Cores Model <sup>2</sup>	Mean Shift for 1963 Random Effect <sup>1</sup>	P-value for Random Cores Model <sup>2</sup>
Aluminum	0.0204	-0.0468	0.1249	-0.0524	0.1397
Antimony	0.1875	-0.0422	0.0000	-0.0361	0.0004
Arsenic	0.0195	0.1706	0.1334	0.2325	0.1236
Barium	0.1453	-12.0139	0.0000	-10.6451	0.0032
Beryllium	0.0547	-0.0203	0.0112	-0.0085	0.4206
Cadmium	0.0677	-0.0073	0.0046	-0.0084	0.0063
Chromium	0.07	-1.9489	0.004	-1.5389	0.1461
Copper	0.1721	-1.4098	0.0000	-1.054	0.0042
Lead	0.0602	-0.1334	0.0077	-0.0695	0.3206
Manganese	0.0652	30.1483	0.0055	32.6109	0.0264
Mercury	0.0004	0.0002	0.83	-0.0004	0.8334
Nickel	0.0699	-0.8417	0.004	-0.255	0.6629
Selenium	0.0206	-0.0125	0.1225	-0.0143	0.1873
Silver	0.003	-0.0006	0.5557	0.0001	0.9367
Thallium	0.2422	-0.0118	0.0000	-0.0098	0.0018
Tin	0.0001	-0.0041	0.8999	-0.0179	0.6987
Vanadium	0.0027	0.5536	0.5752	1.1589	0.2994
Zinc	0.0249	-1.1095	0.0891	-1.031	0.3864

Notes:

<sup>1</sup> Negative sign indicates parameter increases with increased depth, positive sign indicates parameter decreases with increased depth.

<sup>2</sup> Significance is established at  $p < 0.05$ .

**Table 3-22: MMS Stations Where Fish Liver Tissue Samples were Collected for Chemical Analysis**

Zone	Station	No. Halibut Samples	No. Arrowtooth Flounder Samples	No. Black Cod Samples	No. Pacific Cod Samples	No. Skate Samples
<b>1997 Cruise</b>						
0	F7a	6	ns	ns	ns	ns
2	R14a	4	1	ns	ns	ns
3	R1a	1	ns	1	ns	ns
<b>1997 Totals</b>		<b>11</b>	<b>1</b>	<b>1</b>	<b>ns</b>	<b>ns</b>
<b>1998 Cruise</b>						
1	R23a	4	ns	ns	4	1
2	R14a	5	1	ns	6	ns
3	R1a	3	1	1	3	1
<b>1998 Totals</b>		<b>12</b>	<b>2</b>	<b>1</b>	<b>13</b>	<b>2</b>

Notes:

ns - none sampled

The numbers indicate number of fish samples collected for analysis. In most cases these samples represented liver composites, however, individual fish samples (i.e., non-composites) were collected under circumstances where multiple individuals were not caught.

**Table 3-23: Average PAH Concentrations (in µg/g dry weight) Detected in Fish Tissue Samples and Comparison to PAH Concentrations in Procedural Blanks**

	Naphthalene	C1-Naphthalene	Phenanthrene	Benzo[g,h,i]perylene
<b>1997 Cruise</b>				
Blank 1	0.024	0.009	0.016	0.013
Blank 2	0.033	0.005	0.006	0.020
<b>Halibut</b>				
Zone 0	0.018	0.007	0.027	0.003
Zone 2	0.032	0.012	0.032	0.002
Zone 3	0.025	0.012	0.052	0.001
<b>Arrowtooth Flounder</b>				
Zone 2	0.028	ND	0.012	ND
<b>Black Cod</b>				
Zone 3	0.020	0.009	0.014	ND
<b>1998 Cruise</b>				
Blank 1	0.003	ND	0.002	0.013
Blank 2	0.007	0.005	0.005	0.015
Blank 3	0.010	0.005	0.002	0.014
<b>Halibut</b>				
Zone 1	0.018	0.008	0.008	0.004
Zone 2	0.018	0.009	0.011	0.007
Zone 3	0.031	0.005	0.011	0.002
<b>Pacific Cod</b>				
Zone 1	0.008	0.008	0.005	0.002
Zone 2	0.014	0.010	0.006	0.002
Zone 3	0.007	0.004	0.004	0.002
<b>Arrowtooth Flounder</b>				
Zone 2	0.012	ND	0.005	ND
Zone 3	0.014	ND	0.005	ND
<b>Skates</b>				
Zone 1	0.009	0.005	0.004	0.001
Zone 3	0.012	0.003	0.004	2.7
<b>Black Cod</b>				
Zone 3	0.014	0.006	0.007	0.001

Notes:

ND=Not Detected

**Table 3-24: Mean Total PAH Concentrations (in  $\mu\text{g/g}$  dry weight) Detected in Fish Tissue**

	n	Total PAH		
		Mean ( $\mu\text{g/g}$ dry weight)	SD	Range
<b>1997 Cruise</b>				
Blanks	2	0.063	0.002	0.062 - 0.064
<b>Halibut</b>				
Zone 0	6	0.093	0.033	0.057 - 0.136
Zone 2	4	0.149	0.073	0.059 - 0.235
Zone 3	1	0.143	NA	NA
<b>Arrowtooth Flounder</b>				
Zone 2	1	0.052	NA	NA
<b>Black Cod</b>				
Zone 3	1	0.070	NA	NA
<b>1998 Cruise</b>				
Blanks	3	0.031	0.007	0.023 - 0.036
<b>Halibut</b>				
Zone 1	4	0.079	0.022	0.056 - 0.110
Zone 2	5	0.106	0.042	0.060 - 0.160
Zone 3	3	0.107	0.098	0.048 - 0.220
<b>Pacific Cod</b>				
Zone 1	4	0.065	0.021	0.036 - 0.085
Zone 2	6	0.073	0.058	0.34 - 0.180
Zone 3	3	0.030	0.011	0.022 - 0.042
<b>Arrowtooth Flounder</b>				
Zone 2	1	0.028	NA	NA
Zone 3	1	0.032	NA	NA
<b>Skates</b>				
Zone 1	1	0.047	NA	NA
Zone 3	1	2.7	NA	NA
<b>Black Cod</b>				
Zone 3	1	0.048	NA	NA

Notes:

NA = not applicable since only one sample is considered

**Table 3-25: Trace Metal Concentrations In Liver Composite Samples for Halibut, Arrow Flounder, Black Cod, Pacific Cod and Skate (dry weight)**

	Zone	Ag (µg/g)	Al (µg/g)	As (µg/g)	Ba (µg/g)	Be (µg/g)	Cd (µg/g)	Cr (µg/g)	Cu (µg/g)	Fe (µg/g)
<b>Halibut</b>										
Mean Std. Dev.	0 1997 (n* = 6)	0.074 ±0.029	10.5 ±5.1	11.0 ±4.0	0.055 ±0.020	N.D.	4.1 ±1.0	0.072 ±0.036	15.9 ±3.3	169 ±71
Mean Std. Dev.	1 1998 (n* = 4)	0.073 ±0.018	6.9 ±0.6	16.8 ±5.5	0.050 ±0.026	N.D.	6.6 ±1.2	0.024 ±0.006	15.1 ±3.3	303 ±15
Mean Std. Dev.	2 1997 (n* = 4)	0.104 ±0.041	6.4 ±2.6	29.8 ±3.4	0.092 ±0.039	N.D.	5.0 ±1.1	0.045 ±0.013	12.7 ±7.1	263 ±258
Mean Std. Dev.	2 1998 (n* = 5)	0.064 ±0.017	8.2 ±2.8	15.3 ±4.8	0.084 ±0.014	N.D.	4.3 ±0.6	0.084 ±0.043	10.8 ±1.9	194 ±105
Mean	3 1997 (n* = 1)	0.100	6.2	22.0	0.082	N.D.	4.3	0.051	15.3	197
Mean Std. Dev.	3 1998 (n* = 3)	0.084 ±0.034	4.7 ±0.6	26.5 ±7.4	0.010 ±0.001	N.D.	4.3 ±0.3	0.019 ±0.006	11.6 ±4.2	163 ±52
<b>Arrowtooth Flounder</b>										
Mean	2 1997 (n* = 1)	0.044	5.9	21.4	0.078	N.D.	4.7	0.075	11.1	688
Mean	2 1998 (n* = 1)	0.023	2.8	32.8	0.024	N.D.	2.2	0.041	9.5	195
Mean	3 1998 (n* = 1)	0.024	1.5	22.6	0.011	N.D.	1.7	0.022	9.9	138

**Table 3-25: Trace Metal Concentrations in Liver Composite Samples for Halibut, Arrow Flounder, Black Cod, Pacific Cod and Skate (dry weight) (cont.)**

	Zone	Ag ( $\mu\text{g/g}$ )	Al ( $\mu\text{g/g}$ )	As ( $\mu\text{g/g}$ )	Ba ( $\mu\text{g/g}$ )	Be ( $\mu\text{g/g}$ )	Cd ( $\mu\text{g/g}$ )	Cr ( $\mu\text{g/g}$ )	Cu ( $\mu\text{g/g}$ )	Fe ( $\mu\text{g/g}$ )
<b>Black Cod</b>										
Mean	3 1997 (n* = 1)	0.029	6.1	1.7	0.080	N.D.	1.4	0.032	6.2	433
	3 1998 (n* = 1)	0.17	1.1	3.4	0.033	N.D.	0.99	0.027	4.2	337
<b>Pacific Cod</b>										
Mean Std. Dev.	1 1998 (n* = 4)	0.621 $\pm 0.230$	8.6 $\pm 2.6$	49.9 $\pm 24.0$	0.047 $\pm 0.007$	N.D.	0.7 $\pm 0.2$	0.107 $\pm 0.099$	20.9 $\pm 5.0$	148 $\pm 35$
Mean Std. Dev.	2 1998 (n* = 6)	0.383 $\pm 0.238$	4.1 $\pm 1.8$	54.1 $\pm 26.5$	0.085 $\pm 0.020$	N.D.	0.7 $\pm 0.3$	0.077 $\pm 0.023$	17.5 $\pm 8.4$	143 $\pm 45$
Mean Std. Dev.	3 1998 (n* = 3)	0.472 $\pm 0.156$	2.4 $\pm 0.4$	48.0 $\pm 1.7$	0.023 $\pm 0.012$	N.D.	0.4 $\pm 0.3$	0.048 $\pm 0.015$	12.9 $\pm 0.3$	136 $\pm 22$
<b>Aleutian Skate</b>										
Mean	1 1998 (n* = 1)	0.327	2.3	24.4	0.036	N.D.	0.8	0.019	10.3	130
Mean	3 1998 (n* = 1)	0.474	2.2	60.1	0.018	N.D.	0.6	0.025	41.3	107
<b>Flounder+</b>										
Mean	Atlantic (n* = 44)	0.89	N.D.	17	N.D.	N.D.	0.57	N.D.	30	660

Notes:

\* n = number of samples

+ P.J. Hanson, 1997

**Table 3-25: Trace Metal Concentrations in Liver Composite Samples for Halibut, Arrow Flounder, Black Cod Pacific Cod and Skate (dry weight) (cont.)**

	Zone	Hg ( $\mu\text{g/g}$ )	Mn ( $\mu\text{g/g}$ )	Ni ( $\mu\text{g/g}$ )	Pb ( $\mu\text{g/g}$ )	Sb ( $\mu\text{g/g}$ )	Se ( $\mu\text{g/g}$ )	Sn ( $\mu\text{g/g}$ )	Tl ( $\mu\text{g/g}$ )	V ( $\mu\text{g/g}$ )	Zn ( $\mu\text{g/g}$ )
<b>Halibut</b>											
Mean Std. Dev.	0 1997 (n* = 6)	0.129 $\pm 0.117$	3.3 $\pm 0.2$	-	0.028 $\pm 0.009$	0.007 $\pm 0.010$	6.7 $\pm 0.3$	0.20 $\pm 0.09$	0.003 $\pm 0.001$	0.134 $\pm 0.044$	82.4 $\pm 9.7$
Mean Std. Dev.	1 1998 (n* = 4)	0.158 $\pm 0.046$	3.3 $\pm 0.6$	1.18 $\pm 0.27$	0.050 $\pm 0.025$	0.004 $\pm 0.002$	5.0 $\pm 1.9$	0.14 $\pm 0.05$	0.002 $\pm 0.000$	0.180 $\pm 0.046$	84.2 $\pm 9.9$
Mean Std. Dev.	2 1997 (n* = 4)	0.382 $\pm 0.197$	4.5 $\pm 0.9$	-	0.027 $\pm 0.011$	0.004 $\pm 0.001$	7.3 $\pm 2.9$	0.19 $\pm 0.05$	0.004 $\pm 0.001$	0.283 $\pm 0.142$	102.7 $\pm 25.9$
Mean Std. Dev.	2 1998 (n* = 5)	0.272 $\pm 0.082$	4.6 $\pm 0.6$	2.0 $\pm 0.0$	0.286 $\pm 0.531$	0.003 $\pm 0.002$	6.6 $\pm 0.8$	0.122 $\pm 0.052$	0.002 $\pm 0.000$	0.245 $\pm 0.044$	89.3 $\pm 6.3$
Mean	3 1997 (n* = 1)	0.181	3.7	-	0.026	0.003	6.7	0.22	0.003	0.224	83.1
Mean Std. Dev.	3 1998 (n* = 3)	0.236 $\pm 0.071$	2.9 $\pm 0.3$	1.5 $\pm 0.2$	0.034 $\pm 0.022$	0.003 $\pm 0.001$	4.5 $\pm 0.7$	0.090 $\pm 0.057$	0.001 $\pm 0.000$	0.230 $\pm 0.024$	78.7 $\pm 4.0$
<b>Arrowtooth Flounder</b>											
Mean	2 1997 (n* = 1)	0.096	2.9		0.012	0.003	8.1	0.31	0.002	0.169	72.6
Mean	2 1998 (n* = 1)	0.054	2.4	0.83	0.026	0.002	2.5	0.036	0.001	0.111	53.8
Mean	3 1998 (n* = 1)	0.049	1.9	1.0	0.015	0.002	1.7	0.094	0.001	0.089	51.9

**Table 3-25: Trace Metal Concentrations in Liver Composite Samples for Halibut, Arrow Flounder, Black Cod Pacific Cod and Skate (dry weight) (cont.)**

	Zone	Hg ( $\mu\text{g/g}$ )	Mn ( $\mu\text{g/g}$ )	Ni ( $\mu\text{g/g}$ )	Pb ( $\mu\text{g/g}$ )	Sb ( $\mu\text{g/g}$ )	Se ( $\mu\text{g/g}$ )	Sn ( $\mu\text{g/g}$ )	Tl ( $\mu\text{g/g}$ )	V ( $\mu\text{g/g}$ )	Zn ( $\mu\text{g/g}$ )
<b>Black Cod</b>											
Mean	3 1997 (n* = 1)	0.176	2.2	-	0.112	0.003	3.5	0.12	0.006	0.101	52.5
Mean	3 1998 (n* = 1)	0.099	2.4	1.0	0.040	0.004	2.5	0.021	0.004	0.093	46.6
<b>Pacific Cod</b>											
Mean Std. Dev.	1 1998 (n* = 4)	0.085 $\pm 0.055$	4.3 $\pm 1.2$	0.88 $\pm 0.27$	0.037 $\pm 0.024$	0.016 $\pm 0.004$	3.1 $\pm 1.1$	0.057 $\pm 0.035$	0.002 $\pm 0.001$	0.125 $\pm 0.033$	54.8 $\pm 10.3$
Mean Std. Dev.	2 1998 (n* = 6)	0.118 $\pm 0.055$	3.2 $\pm 0.9$	1.3 $\pm 0.3$	0.081 $\pm 0.086$	0.020 $\pm 0.007$	3.8 $\pm 1.4$	0.083 $\pm 0.051$	0.003 $\pm 0.001$	0.211 $\pm 0.076$	64.0 $\pm 16.6$
Mean Std. Dev.	3 1998 (n* = 3)	0.094 $\pm 0.021$	4.4 $\pm 0.9$	1.2 $\pm 0.2$	0.023 $\pm 0.009$	0.015 $\pm 0.002$	4.3 $\pm 0.6$	0.072 $\pm 0.040$	0.003 $\pm 0.000$	0.178 $\pm 0.046$	62.3 $\pm 5.2$
<b>Skate</b>											
Mean	1 1998 (n* = 1)	0.012	0.9	0.42	0.009	0.002	0.48	0.036	0.001	0.054	17.3
Mean	3 1998 (n* = 3)	0.079	1.4	0.73	0.009	0.002	0.59	0.023	0.001	0.083	24.4
<b>Flounder+</b>											
Mean	Atlantic (n* = 44)	0.31	4.8	0.33	1.4	N.D.	6.2	0.33	N.D.	N.D.	116

Notes:

\* number of samples

+ P.J. Hanson, 1997

**Table 3-26: Mercury Concentrations in Flesh (Muscle) Samples for Halibut**

	Zone	Hg ( $\mu\text{g/g}$ , dry weight)	Hg ( $\mu\text{g/g}$ , wet weight)
<b>Halibut</b>			
Mean Std. Dev. (n* = 4)	0 1997	0.721 $\pm 0.667$	0.149 $\pm 0.133$
Range		0.128-1.63	0.028-0.326
Mean Std. Dev. (n* = 12)	1 1998	0.561 $\pm 0.405$	0.113 $\pm 0.089$
Range		0.111-1.65	0.022-0.363
Mean Std. Dev. (n* = 4)	2 1997	1.494 $\pm 1.070$	0.299 $\pm 0.214$
Range		0.345-2.43	0.069-0.486
Mean Std. Dev. (n* = 17)	2 1998	0.712 $\pm 0.307$	0.133 $\pm 0.055$
Range		0.266-1.38	0.056-0.248
Mean Std. Dev. (n* = 4)	3 1997	0.659 $\pm 0.142$	0.135 $\pm 0.031$
Range		0.478-0.927	0.096-0.164
Mean Std. Dev. (n* = 12)	3 1998	0.629 $\pm 0.353$	0.121 $\pm 0.061$
Range		0.139-1.44	0.029-0.245

Notes:

\*n = number of samples

**Table 3-27: CYP1A Scores in all Fish and Cell Types**

1997 Cruise	ID#	Sex	Gill			Liver			Kidney	
			epithelium	pillar cells	vascular endothelium	hepatocyte	vascular endothelium	bile duct	tubules	vascular endothelium
<b>Zone 0</b>										
Halibut	1	F	0	0	0	9	0	0	7.5	12
	2	?	0	0	0	7.5	0	0	9	9
	3	F	0	0	0	0	0	0	1	12
	4	M	0	0	0	3	0	0	3	9
	5	F	0	0	0	1.5	0	0	6	12
	6	M	0	0	0	3	0	0	4	6
	7	M	0	0	0	1.5	0	0	4.5	12
	8	?	0	0	0	3.75	0	0	5.25	10.5
	9	F	0	0	0	3	0	0	6	12
	10	M	0	0	0	3	0	0	4	9
	11	M	0	0	0	1.5	0	0	4	6
	12	?	0	0	0	0	0	0	2	9
	13	?	0	0	0	0	0	0	4.5	6
<b>Zone 2</b>										
Halibut	1	F	0	0	0	0	0	0	1.5	12
	2	M	0	0	0	4.5	0	0	2	12
	3	F	0	0	0	0	0	0	4.5	6.5
	4	F	0	0	0	0.75	0	0	0.5	6
	5	M	0	0	0	0	0	0	1.5	7.5
	6	F	0	0	0	1.5	0	0	1	2
	7	F	0	0	0	0	0	0	0	2
	8	F	0	0	0	3	0	0	4	12
	9	M	0	0	0	1.5	0	0	1.5	9
	10	F	0	0	0	0	0	0	0	2
	11	M	0	0	0	0	0	0	1	6
	12	M	0	0	0	0	0	0	3	9
	13	F	0	0	0	3	0	0	1.5	9
	14	F	0	0	0	1.5	0	0	2	0
	15	M	0	0	0	3	0	0	4.5	6
Arrowtooth Flounder	1	F	0	0	0	1	0	0	7.5	0
	2	F	2	6	0	3	0	0	4	0
	3	M	0	0	0	1.5	0	0	7.5	0
	4	M	0	0	0	3	0	0	6	0
<b>Zone 3</b>										
Halibut	1	?	0	0	0	0.75	0	0	1	0
	2	M	0	0	0	3	0	0	6	4
	3	F	0	0	0	0	0	0	4	4
	4	M	0	2	0	3	0	0	0	3
	5	F	0	0	0	0	0	0	4.5	6
	6	M	0	0	0	4.5	0	0	9	12
	7	M	0	0	0	0.75	0	0	3	9
Arrowtooth Flounder	1	F	0	0	0	3	0	0	0	0
Black Cod	1	?	0	0	4	7.5	0	0	6	4
	2	?	0	0	0	0	0	0	0	0
	3	?	2	2	2	1.5	0	0	1	0
	4	?	0	2	0	10.5	6	2	10.5	2
	5	?	0	1	0	0.75	0	0	1	0

**Table 3-27: CYP1A Scores in all Fish and Cell Types**

1998 Cruise	ID #	Gill			Liver			Kidney		Heart	
		epithelium	pillar cells	vascular endothelium	hepatocyte	vascular endothelium	bile duct	tubules	vascular endothelium	endothelium	
<b>Zone 1</b>											
Halibut	1	0	0	0	0.75	0	0	0	0	0	
	2	0	0	0	0	0	0	0	0	0	
	3	0	0	0	0	0	0	0	0	0	
	4	0	0	0	0	0	0	0	0	0	
	5	0	0	0	0	0	0	0	0	0	
	6	0	0	0	0.75	0	0	0	0	0	
	7	0	0	0	0	0	0	0	0	0	
	8	0	0	0	1.5	0	0	0	0	0	
	9	0	0	0	0	0	0	0	0	0	
	10	0	0	0	0	0	0	0	0	0	
	11	0	0	0	0	0	0	0	0	0	
	12	0	0	0	0	0	0	0	0	0	
Long-Nose Skate	1	0	0	0	1.5	0	0	6	0	0	
Pacific Cod	1	3	0	0	1.5	0	0	0	0	5	
	2	0	0	0	0	0	0	2	0	0	
	3	0	0	0	3	0	0	3	0	1	
	4	0	0	0	1.5	0	0	0	0	0.5	
	5	0	0	0	1.5	0	0	1.5	0	0	
	6	0	0	0	1.5	0	0	0	0	0	
	7	0	0	0	1.5	0	0	0	0	0	
	8	0	0	0	1.5	0	0	1	0	0	
	9	NIS	NIS	NIS	1.5	0	0	0	0	0	1
	10	2	0	0	1.5	0	0	4	0	0	
	11	3	0	0	1.5	0	0	2	0	0	
	12	3	0	0	1.5	0	0	1	0	2	
	13	0	0	0	1.5	0	0	2	0	0.5	
	14	0	0	0	0	0	0	2	0	0	
	15	0	0	0	1.5	0	0	NIS	0	1	
	16	0	0	0	0	0	0	2	0	0	
<b>Zone 2</b>											
Arrow Tooth Flounder	1	0	0	0	0	0	0	4	0	0	
	2	0	0	0	0	0	0	2	0	0	
	3	0	0	0	0	0	0	2	0	0	
	4	0	0	0	0	0	0	1.5	0	0	
	5	0	0	0	0	0	0	1.5	0	0	
Halibut	1	0	0	0	0	0	0	0	0	0	
	2	0	0	0	0	0	0	0	0	0	
	3	0	0	0	0	0	0	0	0	0	
	4	0	0	0	0	0	0	0	0	0	
	5	0	0	0	0	0	0	0	0	0	
	6	0	0	0	0	0	0	0	0	0	
	7	0	0	0	0	0	0	0	0	0	
	8	0	0	0	0	0	0	1.25	0	0	
	9	0	0	0	0	0	0	0	0	0	
	10	0	0	0	0	0	0	0	0	0	
	11	0	0	0	0	0	0	0	0	0	
	12		NIS	0	0	0	0	2	0	0	



**Table 3-27: CYP1A Scores in all Fish and Cell Types**

1998 Cruise	ID #	Gill			Liver			Kidney		Heart
		epithelium	pillar cells	vascular endothelium	hepatocyte	vascular endothelium	bile duct	tubules	vascular endothelium	endothelium
	6	0	0	0	0	0	0	0	0	0
	7	0	0	0	0	0	0	0	0	0
	8	0	0	0	0	0	0	0	0	0
	9	0	0	0	0	0	0	3	0	0
	10	0	0	0	0	0	0	0	0	0
	11	0	0	0	0	0	0	0	0	0
	12	0	0	0	0	0	0	0	0	0
Pacific Cod	1	0	0	0	0	0	0	1	0	0
	2	0	0	0	1.5	0	0	4	0	3
	3	3	0	0	3	0	0	4	0	4.5
	4	3	0	0	0	0	0	NIS	0	0
	5	0	0	0	0	0	0	NIS	0	0
	6	0	0	0	0	0	0	0	0	0
	7	1	0	0	0	0	0	NIS	0	0
	8	0	0	0	0	0	0	0	0	0
	9	1.5	0	0	1.5	0	0	0	0	0
	10	0	0	0	0	0	0	0	0	0
	11	0	0	0	1.5	0	0	3	0	2
	12	0	0	0	0	0	0	0	0	0
	13	2	0	0	0	0	0	0	0	0
	14	3	0	0	3	0	0	3	0	6
	15	0	0	0	0	0	0	0	0	0

Notes:  
NIS - Not in Section

**Table 3-28: Mean CYP1A Fish Scores in all Cell Types by Zone**

1997 Cruise	Gill			Liver			Kidney	
	epithelium	pillar cells	vascular endothelium	hepatocyte	vascular endothelium	bile duct	tubules	vascular endothelium
<b>Zone 0</b>								
Halibut	0	0	0	2.83	0	0	4.67	9.58
<b>Zone 2</b>								
Halibut	0	0	0	1.25	0	0	1.9	6.73
Arrowtooth Flounder	.5	1.5	0	2.13	0	0	6.25	0
<b>Zone 3</b>								
Halibut	0	.29	0	1.7	0	0	3.93	5.43
Arrowtooth Flounder	0	0	0	3	0	0	0	0
Black Cod	.4	1	1.2	4.05	1.2	.4	3.7	1.2

1998 Cruise	Gill			Liver			Kidney		Heart
	epithelium	pillar cells	vascular endothelium	hepatocyte	vascular endothelium	bile duct	tubules	vascular endothelium	endothelium
<b>Zone 1</b>									
Halibut	0	0	0	.25	0	0	0	0	0
Long-nose Skate	0		0	1.5	0	0	6	0	0
Pacific Cod	.73	0	0	1.31	0	0	1.37	0	.69
<b>Zone 2</b>									
Halibut	0	0	0	.09	0	0	.66	0	0
Arrowtooth Flounder	0	0	0	0	0	0	.22	0	0
Pacific cod	1.24	.22	0	1.07	0	0	.83	0	.90
<b>Zone 3</b>									
Halibut	0	0	0	0	0	0	.25	0	0
Arrowtooth Flounder	0	0	0	0	0	0	2.5	0	0
Black Cod	3	0	0	1.89	0	0	1.75	0	6.63
Aleutian Skate	3	4	0	1.5	0	0	9	0	0
Pacific Cod	1.1	0	0	.7	0	0	1.25	0	1.03

Table 3-28: Mean CYP1A Scores in Pacific Halibut Cell Types by Zone

	(n)	Hepatocytes	Kidney Tubules	Kidney Vascular Endothelium
<b>1997 Cruise</b>				
Zone 0	9	2.44	4.31	9.63
Zone 2	15	1.25	1.9	6.73
Zone 3	7	1.71	3.93	5.43
Probability		NS	0.007	NS

Notes:

NS - not significant

**Table 3-29: Transformed Percent Survival (transformed by silt) and Each Target Metal and AVS for 1997 Twenty-Station Sediment Data Analysis**

<b>Independent Variable</b>	<b>R-squared</b>	<b>P-value for Significant Increase in R-squared Due to Metal</b>
Silt + Clay	0.588	0.000
AVS	0.659	0.078
Ag	0.618	0.262
Al	0.603	0.440
As	0.603	0.428
Ba	0.600	0.486
Be	0.646	0.113
Ca	0.588	0.968
Cd	0.641	0.133
Cr	0.589	0.861
Cu	0.588	0.908
Fe	0.618	0.266
Hg	0.614	0.302
K	0.589	0.828
Mg	0.608	0.365
Mn	0.642	0.127
Ni	0.596	0.561
Pb	0.601	0.463
Sb	0.629	0.187
Se	0.606	0.387
Sn	0.603	0.439
V	0.623	0.229
Zn	0.681	0.040

**Table 3-30: Summary of Surrogate Percent Recoveries**

1997 Results	Tissues (n=13)			Sediment (n=197)			QC (n=8)		
	Mean	SD	RSD	Mean	SD	RSD	Mean	SD	RSD
<b>PAH</b>									
d8-Naphthalene	74	17	22	66	19	28	61	4.6	7.5
d10-Acenaphthene	82	14	18	73	14	19	68	3.3	4.9
d10-Phenanthrene	90	15	16	80	13	16	75	2.7	3.5
d12-Benzo[a]pyrene	61	28	46&	76	14	18	70	5.4	7.7
<b>SHC</b>									
OTP	na	na	na	80	14	18	77	2.8	3.7
5AA	na	na	na	76	13	17	64	3.3	5.1
D50T	na	na	na	79	13	16	69	3.1	4.4
<b>S/T</b>									
5B(H)-Cholane	na	na	na	65	12	18	89	3.5	4.0
D66-Dotriacontane	na	na	na	66	13	19	98	5.0	5.1
1998 Results	Tissues (n=32)			Sediment (n=115)			QC (n=5)		
	Mean	SD	RSD	Mean	SD	RSD	Mean	SD	RSD
<b>PAH</b>									
d8-Naphthalene	70	16	23	74	9.6	13	84	18	22
d10-Acenaphthene	76	15	20	77	9.1	12	82	17	21
d10-Phenanthrene	76	13	17	81	10	12	92	17	18
d12-Benzo[a]pyrene	38&	14	37&	76	11	14	87	27	31
<b>SHC</b>									
OTP	na	na	na	68	9.0	13	81	14	17
5AA	na	na	na	70	8.5	12	80	14	18
D50T	na	na	na	72	7.5	10	82	14	17
<b>S/T</b>									
5B(H)-Cholane	na	na	na	76	9.9	13	98	17	17
D66-Dotriacontane	na	na	na	na	na	na	na	na	na

**Notes:**

%Rec = Percent Recovery

QC = Quality Control

n = Number of Samples

SD = Standard Deviation

RSD = Relative Standard Deviation

PAH = Polycyclic Aromatic Hydrocarbons

SHC = Saturated Hydrocarbons

S/T = Steranes and Triterpanes

na = Not Applicable

& = Qualifier is outside acceptable range

**Table 3-31: Summary of Laboratory Control Spike Recoveries**

1997 Results	Sediment (n=9) <sup>1</sup>			Water (n=4)			Oil (n=1)		
	Mean	SD	RSD	Mean	SD	RSD	Target	Result	%Rec
<b>PAH</b>									
Naphthalene	97	10	10	94	4.9	5.2	50	56	110
Acenaphthylene	88	19	21	95	5.0	5.2	50	63	130
Acenaphthene	96	9.7	10	96	3.8	3.9	50	58	120
Fluorene	98	11	11	96	3.7	3.9	50	60	120
Anthracene	85	16	18	94	6.4	6.8	50	35	70
Phenanthrene	100	8.9	8.9	98	2.9	2.9	50	59	120
Fluoranthene	110	11	10	100	5.8	5.8	50	63	130
Pyrene	100	10	10	100	7.4	7.4	50	62	120
Benzo[a]anthracene	95	14	15	99	7.5	7.6	50	62	120
Chrysene	98	17	18	96	4.5	4.7	50	64	130
Benzo[b]fluoranthene	120	12	9.7	100	6.6	6.5	50	64	130
Benzo[k]fluoranthene	120	15	12	98	3.9	3.9	50	65	130
Benzo[a]pyrene	98	12	12	97	4.6	4.7	50	62	120
Indeno[1,2,3,-c,d]pyrene	120	16	13	99	8.6	8.7	50	61	120
Dibenzo[a,h]anthracene	120	16	13	99	9.0	9.1	50	57	110
Benzo[g,h,i]perylene	110	14	13	94	8.5	9.1	50	57	110
<b>SHC</b>									
n-Decane	61	8.3	14	49	18	37&	5	3.9	78
n-Pentadecane	85	6.1	7.1	86	12	14	5	4.5	90
Pristane	89	5.3	5.9	90	12	14	5	4.7	94
n-Eicosane	96	3.8	4.0	94	9.5	10	5	4.7	94
n-Pentacosane	93	5.2	5.5	92	13	14	5	4.6	92
n-Triacontane	90	5.0	5.6	90	12	13	5	4.6	92
n-Tetratriacontane	91	11	12	92	8.4	9.1	5	4.5	90
n-Hexatriacontane	85	14	16	92	8.0	8.7	5	4.4	88

**Notes:**

<sup>1</sup> n = 11 for SHC

n = Number of Samples

SD = Standard Deviation

RSD = Relative Standard Deviation

%Rec = Percent Recovery

PAH = Polycyclic Aromatic Hydrocarbons

SHC = Saturated Hydrocarbons

& = Qualifier is outside acceptable range

**Table 3-31: Summary of Laboratory Control Spike Recoveries (continued)**

1998 Results	Sediment (n=6)			Water (n=1)			Coal (n=1)		
	Mean	SD	RSD	Result	Target	%Rec	Result	Target	%Rec
<b>PAH</b>									
Naphthalene	96	7.7	8	1700	2000	85	160	200	77
Acenaphthylene	72	26	36&	1800	2000	90	71	200	36
Acenaphthene	100	10	10	1800	2000	90	170	200	85
Fluorene	100	12	12	1900	2000	95	200	200	100
Anthracene	57	16	28	1400	2000	70	78	200	39
Phenanthrene	110	17	15	1800	2000	90	180	200	89
Fluoranthene	110	16	14	1900	2000	95	210	200	105
Pyrene	110	16	14	1800	2000	90	210	200	105
Benzo[a]anthracene	100	14	14	1800	2000	90	170	200	85
Chrysene	100	11	11	1700	2000	85	190	200	95
Benzo[b]fluoranthene	120	12	10	2600	2000	130	206	200	103
Benzo[k]fluoranthene	110	13	12	2600	2000	130	177	200	89
Benzo[a]pyrene	70	23	33	2000	2000	100	90	200	45
Indeno[1,2,3,-c,d]pyrene	110	12	11	2400	2000	120	154	200	77
Dibenzo[a,h]anthracene	110	10	9.1	2500	2000	125	154	200	77
Benzo[g,h,i]perylene	100	12	12	2400	2000	120	166	200	82
<b>SHC</b>									
n-Decane	47	6.4	14	23	50	46	2.3	5	44
n-Pentadecane	84	6.1	7.3	46	50	92	4.2	5	84
Pristane	92	7.5	8.2	48	50	96	4.4	5	88
n-Eicosane	89	6.9	7.8	46	50	92	4.4	5	88
n-Pentacosane	91	6.9	7.6	48	50	96	4.6	5	92
n-Triacontane	87	6.0	6.9	46	50	92	4.4	5	88
n-Tetratriacontane	83	7.6	9.2	46	50	92	4.5	5	90
n-Hexatriacontane	77	8.1	10	43	50	86	4.3	5	86

Notes:

n = Number of Samples

SD = Standard Deviation

RSD = Relative Standard Deviation

%Rec = Percent Recovery

PAH = Polycyclic Aromatic Hydrocarbons

SHC = Saturated Hydrocarbons

& = Qualifier is outside acceptable range

**Table 3-32: Standard Reference Material (SRM) Summary**

1997 Results Compound	SRM 1491 (n=20) Solution			SRM 1941a (n=10) <sup>1</sup> Sediment			SRM 1974a (n=1) Tissue		
	Mean µg/L	Certified µg/L	% DIF	Mean µg/kg	Certified µg/kg	% DIF	Mean µg/kg	Certified µg/kg	% DIF
<b>PAH</b>									
Naphthalene	6620	6890	-3.6	571	1010	-43&	75	23.5	220&
Acenaphthylene	6810	6960	-2.1	na	na	na	na	na	na
Acenaphthene	6940	7280	-4.7	na	na	na	na	na	na
Biphenyl	7180	7000	2.6	na	na	na	na	na	na
Fluorene	6970	7270	-4.1	66	97.3	-32	na	na	na
Anthracene	8380	7820	7.2	166	184	-10	14	6.1	130&
Phenanthrene	7320	7010	4.4	388	489	-21	55	22.2	150&
Fluoranthene	6040	5910	2.2	809	981	-18	170	163.7	4
Pyrene	6160	5890	4.6	676	811	-17	160	151.6	6
Benzo[a]anthracene	3650	3590	1.7	394	427	-8	33	32.5	2
Chrysene	7510	7030	6.8	492	592	-17	89	94.9	-6
Benzo[b]fluoranthene	5140	5250	-2.1	1020	979	4	63	46.4	36&
Benzo[k]fluoranthene	5750	5570	3.2	291	361	-19	22	20.18	9
Benzo[e]pyrene	5900	5620	5.0	518	553	-6	100	84	19
Benzo[a]pyrene	7100	6790	4.6	473	628	-25	18	15.63	15
Perylene	7610	7120	6.9	329	452	-27	7.5	7.68	-2
Indeno[1,2,3,-c,d]pyrene	5890	6290	-6.3	514	501	3	9.2	14.2	-35&
Dibenzo[a,h]anthracene	5070	5180	-2.1	96	73.9	30	na	na	na
Benzo[g,h,i]perylene	5160	5290	-2.5	410	525	-22	17	22	-23

**Notes:**

n = Number of Samples

<sup>1</sup> n = 5 for indeno[1,2,3,-c,d]pyrene, dibenzo[a,h]anthracene, benzo[g,h,i]perylene

PAH = Polycyclic Aromatic Hydrocarbons

%DIF = Percent Difference

na = Not Applicable

& = Qualifier is outside acceptable range

**Table 3-32: Standard Reference Material (SRM) Summary (continued)**

1998 Results Compound	SRM 1491 (n=14) Solution			SRM 1941a (n=7) <sup>1</sup> Sediment			SRM 1974a (n=3) Tissue		
	Mean µg/L	Certified µg/L	% DIF	Mean µg/kg	Certified µg/kg	% DIF	Mean µg/kg	Certified µg/kg	% DIF
PAH									
Naphthalene	6280	6890	-8.8	491	1010	-51&	18	23.5	-23
Acenaphthylene	6550	6890	-4.9	na	na	na	na	na	na
Acenaphthene	6640	6890	-3.6	na	na	na	na	na	na
Biphenyl	6720	6890	-2.5	na	na	na	na	na	na
Fluorene	6580	6890	-4.5	55.6	97.3	-43&	na	na	na
Anthracene	8140	6890	18	160	184	-13	20	6.1	230&
Phenanthrene	6880	6890	-0.14	351	489	-28	22	22.2	-0.9
Fluoranthene	5760	6890	-16	803	981	-18	190	163.7	16
Pyrene	5860	6890	-15	643	811	-21	170	151.6	12
Benzo[a]anthracene	3460	6890	-50	338	427	-21	33	32.5	1.5
Chrysene	6540	6890	-5.1	494	592	-16	83	94.9	-12
Benzo[b]fluoranthene	4930	6890	-28	836	979	-15	94	46.4	100&
Benzo[k]fluoranthene	5600	6890	-19	364	361	0.83	29	20.18	44&
Benzo[e]pyrene	5560	6890	-19	501	553	-9.4	140	84	67&
Benzo[a]pyrene	7170	6890	4.1	508	628	-19	19	15.63	22
Perylene	7240	6890	5.1	338	452	-25	7.5	7.68	-2.3
Indeno[1,2,3,-c,d]pyrene	5630	6890	-18	505	501	0.8	22	14.2	55&
Dibenzo[a,h]anthracene	4740	6890	-31	104	73.9	41&	na	na	na
Benzo[g,h,i]perylene	4860	6890	-29	435	525	-17	36	22	64&

Notes:

n = Number of Samples

<sup>1</sup> n = 6 for indeno[1,2,3,-c,d]pyrene, dibenzo[a,h]anthracene, benzo[g,h,i]perylene

PAH = Polycyclic Aromatic Hydrocarbons

%DIF = Percent Difference

na = Not Applicable

& = Qualifier is outside acceptable range

**Table 3-33: Control Oil Summary for North Slope Crude**

PAH	1997 Data (n=20)			1998 Data (n=14)			Laboratory Data		
	Mean μg/g	SD	RSD	Mean μg/g	SD	RSD	Mean μg/g	1997 %DIF	1998 %DIF
Naphthalene	756	18.4	2.4	742	35.6	4.8	750	0.80	-1.1
C1-Naphthalenes	1700	147	8.6	1800	130	7.2	1700	0.59	5.9
C2-Naphthalenes	2320	278	12	2450	268	11	2400	-3.3	2.1
C3-Naphthalenes	1900	292	15	1920	249	13	2000	-5.0	-4.0
C4-Naphthalenes	1200	207	17	1130	180	16	1200	0.0	-5.8
Biphenyl	222	9.33	4.2	218	12.5	5.7	220	0.91	-0.91
Fluorene	96.8	3.87	4	96.6	2.56	2.6	94	3.0	2.8
C1-Fluorenes	245	16	6.5	243	17.7	7.3	240	2.1	1.2
C2-Fluorenes	370	35	9.4	352	14.2	4	350	5.7	0.57
C3-Fluorenes	430	55.9	13	401	24.8	6.2	400	7.5	0.25
Phenanthrene	278	8.94	3.2	283	6.11	2.2	260	6.9	8.8
C1-Phenanthrenes/anthracenes	639	35.5	5.6	631	33.5	5.3	600	6.5	5.2
C2-Phenanthrenes/anthracenes	791	86.6	11	731	61.5	8.4	740	6.9	-1.2
C3-Phenanthrenes/anthracenes	590	69	12	546	37.7	6.9	540	9.2	1.1
C4-Phenanthrenes/anthracenes	361	53.6	15	351	45.3	13	330	9.4	6.4
Dibenzothiophene	233	9.79	4.2	230	12.4	5.4	240	-2.9	-4.2
C1-Dibenzothiophenes	500	40	8	487	29.7	6.1	500	0.0	-2.6
C2-Dibenzothiophenes	705	88.2	12	654	46.2	7.1	740	-4.7	-12
C3-Dibenzothiophenes	668	92.2	14	596	37.6	6.3	660	1.2	-9.7
Pyrene	13.6	1.05	7.7	12.9	1.33	10	14	-2.9	-7.8
C1-Fluoranthenes/pyrenes	85.8	5.56	6.5	88.8	5.63	6.3	83	3.4	7.0
C2-Fluoranthenes/pyrenes	152	15.2	10	143	9.94	7	150	1.3	-4.7
C3-Fluoranthenes/pyrenes	180	20.6	11	161	14.1	8.8	170	5.9	-5.3
Chrysene	49.6	2.62	5.3	45.7	4.76	10	49	1.2	-6.7
C1-Chrysenes	88.1	6.81	7.7	76.6	5.14	6.7	84	4.9	-8.8
C2-Chrysenes	115	13.5	12	94.5	13.7	14	110	4.5	-14
C3-Chrysenes	98.9	15.1	15	82.8	9.27	11	92	7.5	-10
C4-Chrysenes	80.3	11.9	15	63.8	7.42	12	75	7.1	-15
Benzo[b]fluoranthene	6.18	0.871	14	6.15	0.898	15	7	-6.4	-6.8
Benzo[e]pyrene	11.9	1.13	9.5	12.0	1.29	11	12	-0.83	0.0

**Notes:**

PAH = Polycyclic Aromatic Hydrocarbons

n = Number of Samples

SD = Standard Deviation

RSD = Relative Standard Deviation

%DIF = Percent Difference

& = Qualifier is outside acceptable range

**Table 3-33: Control Oil Summary for North Slope Crude (continued)**

SHC	1997 Data (n=15)			1998 Data (n=12)			Laboratory Data		
	Mean μg/g	SD	RSD	Mean μg/g	SD	RSD	Mean μg/g	1997 %DIF	1998 %DIF
n-Nonane	4700	165	3.5	5080	176	3.5	4800	-2.1	5.8
n-Decane	4110	133	3.2	4160	131	3.1	4200	-2.1	-0.95
n-Undecane	4150	168	4	4230	206	4.9	4300	-3.5	-1.6
n-Dodecane	3880	197	5.1	3950	144	3.6	4000	-3	-1.2
n-Tridecane	3700	220	5.9	3780	166	4.4	4000	-7.5	-5.5
Isoprenoid RRT 1380	1050	74.5	7.1	1050	179	17	1000	5	5.0
n-Tetradecane	4030	388	9.6	4230	456	11	4200	-4	0.71
Isoprenoid RRT 1470	1370	72.4	5.3	1410	144	10	1400	-2.1	0.71
n-Pentadecane	3540	210	5.9	3680	225	6.1	3700	-4.3	-0.54
n-Hexadecane	3210	139	4.3	3250	207	6.4	3200	0.31	1.6
Isoprenoid RRT 1650	1510	96.1	6.4	1520	204	13	1500	0.67	1.3
n-Heptadecane	3020	174	5.8	3150	168	5.3	3200	-5.6	-1.6
Pristane	2030	154	7.6	2120	106	5.0	2200	-7.7	-3.6
n-Octadecane	2790	141	5	2690	239	8.9	2900	-3.8	-7.2
Phytane	1480	101	6.8	1490	131	8.8	1600	-7.5	-6.9
n-Nonadecane	2550	160	6.3	2530	187	7.4	2600	-1.9	-2.7
n-Eicosane	2560	199	7.8	2320	185	8.0	2700	-5.2	-14
n-Heneicosane	2260	145	6.4	2340	99.6	4.2	2400	-5.8	-2.5
nDocosane	2120	115	5.4	2130	77.8	3.6	2200	-3.6	-3.2
n-Tricosane	1950	74.3	3.8	2040	90	4.4	2000	-2.5	2.0
n-Tetracosane	1790	70.4	3.9	1850	67.4	3.6	2000	-10	-7.5
n-Pentacosane	1690	74.3	4.4	1720	62.2	3.6	1700	-0.59	1.2
n-Hexacosane	1450	64	4.4	1440	51.5	3.6	1500	-3.3	-4.0
n-Heptacosane	1080	67.6	6.2	1120	38.9	3.5	1200	-10	-6.7
n-Octacosane	859	38.3	4.4	841	36.5	4.3	880	-2.4	-4.4
n-Nonacosane	761	40.5	5.3	788	72	9.1	810	-6	-2.7
n-Triacontane	636	38.5	6	651	61.4	9.4	650	-2.2	0.15
n-Hentriacontane	555	36.4	6.6	580	41.3	7.1	580	-4.3	0.0
n-Dotriacontane	451	25.6	5.7	424	56	13	440	2.5	-3.6
n-Tritriacontane	390	20.4	5.2	357	38.4	11	400	-2.5	-11
n-Tetratriacontane	348	31	8.9	328	37.9	12	350	-0.57	-6.3
n-Pentatriacontane	353	20.2	5.7	372	53.3	14	350	0.86	6.3
n-Hexatriacontane	223	17.5	7.8	235	14.4	6.1	230	-3	2.2
n-Heptatriacontane	222	13.7	6.2	219	32.3	15	230	-3.5	-4.8
n-Octatriacontane	207	16.3	7.9	216	22.7	10	220	-5.9	-1.8
n-Nonatriacontane	167	16.7	10	164	19.8	12	180	-7.2	-8.9
n-Tetracontane	173	17.2	9.9	165	19.8	12	190	-8.9	-13
Total Resolved Hydrocarbons	205000	16000	7.8	204000	11600	5.7	220000	-6.8	-7.3
Total Petroleum Hydrocarbons	613000	40100	6.5	616000	18800	3.0	660000	-7.1	-6.7

**Table 3-33: Control Oil Summary for North Slope Crude (continued)**

S/T	1997 Data (n=12)			1998 Data (n=10)			Laboratory Data		
	Mean μg/g	SD	RSD	Mean μg/g	SD	RSD	Mean μg/g	%DIF 1997	%DIF 1998
T4-C23 Diterpane	38	8.6	23	36	4.2	12	46	-17	-22
S4-Diacholestane	41	1.8	4.4	45	4.8	11	50	-18	-10
S5-Diacholestane	27	2.4	8.9	28	3.2	11	29	-6.9	-3.4
T9-C29 Tricyclic	15	1.5	10	16	0.97	6.1	16	-6.2	0
T10-C29 Tricyclic	16	1.3	8.1	16	1.8	11	18	-11	-11
T11-Trisnorhopane (TS)	22	3.2	14	23	1.8	7.8	26	-15	-12
T12-Trisnorhopane (TM)	26	2.2	8.5	26	1.4	5.4	32	-19	-19
S25-Ethylcholestane	48	4.4	9.2	56	7.2	13	53	-9.4	5.7
S28-Ethylcholestane	37	2.6	7	41	3.2	7.8	40	-7.5	2.5
T15-Norhopane	87	6.4	7.4	87	4.1	4.7	96	-9.4	-9.4
T19-Hopane	120	9.5	7.9	120	7	5.8	128	-6.2	-6.2
T21-Homohopane	50	3.3	6.6	52	3.5	6.7	53	-5.7	-1.9
T22-Homohopane	34	3	8.8	37	2	5.4	38	-10	-2.6

**Notes:**

S/T= Steranes and Triterpanes

n = Number of Samples

SD = Standard Deviation

RSD = Relative Standard Deviation

%DIF = Percent Difference

& = Qualifier is outside acceptable range

**Table 3-34: Control Oil Summary for Cook Inlet Crude**

PAH	1997 Data (n=15)			1998 Data (n=13)			Laboratory Data		
	Mean µg/g	SD	RSD	Mean µg/g	SD	RSD	Mean µg/g	%DIF 1997	%DIF 1998
Naphthalene	585	27	4.6	595	31	5.2	607	-3.6	-2.0
C1-Naphthalenes	1430	140	9.7	1550	100	6.4	1500	-4.7	3.3
C2-Naphthalenes	2190	270	12	2410	280	12	2270	-3.5	6.2
C3-Naphthalenes	1730	280	16	1850	200	11	1930	-10	-4.1
C4-Naphthalenes	965	190	20	1000	110	11	987	-2.2	1.3
Acenaphthylene	1.93	0.33	17	2.05	2.0	98	1.8	7.2	14
Acenaphthene	52	1.8	3.5	58.3	2.0	3.4	52	0	12
Biphenyl	96.9	3.9	4.1	98.8	4.1	4.1	98	-1.1	0.82
Fluorene	136	8.3	6.1	147	7.5	5.1	133	2.2	10
C1-Fluorenes	297	15	5	319	30	9.4	280	6.1	14
C2-Fluorenes	371	27	7.3	395	20	5.1	363	2.2	8.8
C3-Fluorenes	365	46	13	374	23	6.1	370	-1.4	1.1
Anthracene	14.7	3.4	23	18.3	7.1	39	11	34	66&
Phenanthrene	311	13	4.2	349	8.6	2.5	303	2.6	15
C1-	719	41	5.7	774	37	4.8	690	4.2	12
C2-	831	74	8.9	849	60	7.1	743	12	14
C3-	529	74	14	541	30	5.5	483	9.5	12
C4-	294	32	11	304	56	18	263	12	16
Dibenzothiophene	21	1.4	6.7	22.4	1.7	7.6	19	10	18
C1-Dibenzothiophenes	66.9	5.2	7.8	64.7	6.9	11	61	9.7	6.1
C2-Dibenzothiophenes	99.5	14	14	96.8	6.7	6.9	89	12	8.8
C3-Dibenzothiophenes	75.3	8.4	11	76.5	5.6	7.3	70	7.6	9.3
Fluoranthene	7.57	0.66	8.7	7.83	1.3	17	7.3	3.7	7.3
Pyrene	19.9	1.3	6.4	19.4	2.5	13	19	4.7	2.1
C1-Fluoranthenes/pyrenes	130	10	7.8	143	12	8.4	120	8.3	19
C2-Fluoranthenes/pyrenes	193	18	9.1	196	13	6.6	173	12	13
C3-Fluoranthenes/pyrenes	207	25	12	198	23	12	190	8.9	4.2
Benz[a]anthracene	20.2	2.3	12	23.4	1.7	7.3	20	1	17
Chrysene	43.3	3.8	8.8	47.1	3.2	6.8	43	0.7	9.5
C1-Chrysenes	113	12	10	109	11	10	107	5.6	1.9
C2-Chrysenes	151	16	10	135	18	13	137	10	-1.4
C3-Chrysenes	110	15	14	99.5	12	12	100	10	-0.5
C4-Chrysenes	86	13	15	76.1	14	18	86	0	-12
Benzo[b]fluoranthene	6.99	1.0	14	7.85	0.75	9.6	7.3	-4.2	7.5
Benzo[e]pyrene	11.9	1.6	13	13.7	0.63	4.6	12	-0.83	14
Benzo[a]pyrene	2.83	0.61	22	3.79	0.69	18	3	-5.7	26
Perylene	4.59	0.96	21	4.86	0.75	15	5.3	-13	-8.3
Dibenzo[a,h]anthracene	3.17	0.32	10	3.38	0.18	5.3	3.2	-0.94	5.6
Benzo[g,h,i]perylene	4.51	0.49	11	4.73	0.53	11	4.4	2.5	7.5

**Table 3-34: Control Oil Summary for Cook Inlet Crude (continued)**

SHC	1997 Data (n=12)			1998 Data (n=12)			Laboratory Data		
	Mean μg/g	SD	RSD	Mean μg/g	SD	RSD	Mean μg/g	%DIF 1997	%DIF 1998
n-Nonane	6360	400	6.3	5870	260	4.4	6400	-0.62	-8.3
n-Decane	6020	250	4.2	4970	240	4.8	6100	-1.3	-18
n-Undecane	6660	210	3.2	5580	190	3.4	6700	-0.6	-17
n-Dodecane	6490	280	4.3	5770	280	4.8	6500	-0.15	-11
n-Tridecane	6860	150	2.2	6230	230	3.7	6900	-0.58	-9.7
Isoprenoid RRT 1380	1730	98	5.7	1460	210	14	1800	-3.9	-19
n-Tetradecane	7360	510	6.9	6660	360	5.4	7300	0.82	-8.8
Isoprenoid RRT 1470	2730	150	5.5	2590	230	8.9	2800	-2.5	-7.5
n-Pentadecane	6720	130	1.9	6230	300	4.8	6800	-1.2	-8.4
n-Hexadecane	5830	260	4.4	5550	230	4.1	5900	-1.2	-5.9
Isoprenoid RRT 1650	2830	170	6	2520	270	11	2800	1.1	-10
n-Heptadecane	5450	220	4	5580	350	6.3	5500	-0.91	1.4
Pristane	4610	170	3.7	4540	160	3.5	4600	0.22	-1.3
n-Octadecane	4820	140	2.9	4370	240	5.5	4900	-1.6	-11
Phytane	1760	110	6.2	1680	190	11	1800	-2.2	-6.7
n-Nonadecane	4520	260	5.8	3920	180	4.6	4500	0.44	-13
n-Eicosane	4190	140	3.3	3590	160	4.4	4200	-0.24	-14
n-Heneicosane	3470	110	3.2	3360	90	2.7	3500	-0.86	-4
nDocosane	3110	120	3.8	2880	83	2.9	3200	-2.8	-10
n-Tricosane	2960	79	2.7	2840	79	2.8	3000	-1.3	-5.3
n-Tetracosane	2610	110	4.2	2520	72	2.8	2600	0.38	-3.1
n-Pentacosane	2430	120	4.9	2390	67	2.8	2500	-2.8	-4.4
n-Hexacosane	2060	100	4.8	1950	52	2.7	2100	-1.9	-7.1
n-Heptacosane	1720	75	4.4	1630	49	3	1800	-4.4	-9.4
n-Octacosane	1470	65	4.4	1280	58	4.5	1500	-2	-15
n-Nonacosane	1370	65	4.7	1320	100	7.6	1400	-2.1	-5.7
n-Triacontane	1100	74	6.7	1060	79	7.4	1100	0	-3.6
n-Hentriacontane	1020	55	5.4	1020	110	11	1000	2	2
n-Dotriacontane	798	47	5.9	648	44	6.8	820	-2.7	-21
n-Tritriacontane	552	62	11	532	54	10	560	-1.4	-5
n-Tetratriacontane	496	68	14	441	38	8.6	510	-2.7	-14
n-Pentatriacontane	462	52	11	428	50	12	470	-1.7	-8.9
n-Hexatriacontane	258	18	7	239	23	9.6	260	-0.77	-8.1
n-Heptatriacontane	201	14	7	174	26	15	200	0.5	-13
n-Octatriacontane	184	16	8.7	162	24	15	190	-3.2	-15
n-Nonatriacontane	130	8.5	6.5	125	17	14	130	0	-3.8
n-Tetracontane	129	7.9	6.1	113	12	11	130	-0.77	-13
Total Resolved Hydrocarbons	298000	9400	3.2	262000	17000	6.5	300000	-0.67	-13
Total Petroleum Hydrocarbons	731000	25000	3.4	679000	19000	2.8	730000	0.14	-7

**Table 3-34: Control Oil Summary for Cook Inlet Crude (continued)**

S/T	1997 Data (n=11)			1998 Data (n=10)			Laboratory Data		
	Mean µg/g	SD	RSD	Mean µg/g	SD	RSD	Mean µg/g	%DIF 1997	%DIF 1998
T4-C23 Diterpane	6.3	1.4	22	6.9	0.44	6.4	6	5	15
S4-Diacholestane	48	9.3	19	57	3	5.3	50	-4	14
S5-Diacholestane	32	8.1	25	39	3.8	9.7	36	-11	8.3
T11-Trisnorhopane (TS)	20	4.8	24	20	2.1	10	19	5.3	5.3
T12-Trisnorhopane (TM)	15	2.5	17	18	0.92	5.1	16	-6.2	12
S24-Methylcholestane	22	4.7	21	29	2.2	7.6	26	-15	12
S25-Ethylcholestane	44	11	25	51	6.9	14	46	-4.3	11
S28-Ethylcholestane	42	8.3	20	53	3.5	6.6	47	-11	13
T15-Norhopane	57	11	19	64	6.3	9.8	63	-9.5	1.6
T19-Hopane	120	23	19	130	5.7	4.4	120	0	8.3
T21-Homohopane	43	7.8	18	51	4.6	9	48	-10	6.2
T22-Homohopane	29	5.5	19	36	1.7	4.7	34	-15	5.9

**Notes:**

PAH – Polycyclic Aromatic Hydrocarbons

SHC – Saturated Hydrocarbons

S/T - Steranes and Triterpanes

n – Number of Samples

SD – Standard Deviation

RSD – Relative Standard Deviation

%DIF – Percent Difference

& - Qualifier is outside acceptable range

na – Not Applicable

**Table 3-35: Results for Standard Reference Material (SRM) BCSS-1 and MESS-2, Marine Sediment Samples issued by the National Research Council of Canada (NRC)**

Sample ID	Ag ( $\mu\text{g/g}$ )	Al (%)	As ( $\mu\text{g/g}$ )	Ba ( $\mu\text{g/g}$ )	Be ( $\mu\text{g/g}$ )	Ca (%)	Cd ( $\mu\text{g/g}$ )	Cr ( $\mu\text{g/g}$ )	Cu ( $\mu\text{g/g}$ )	Fe (%)	Hg ( $\mu\text{g/g}$ )
SRM-BCSS-1 This Study (n = 12) 1997	0.12 $\pm 0.02$	6.17 $\pm 0.08$	10.8 $\pm 0.8$	336 $\pm 7$	1.3 $\pm 0.06$	0.55 $\pm 0.02$	0.27 $\pm 0.01$	113 $\pm 3$	18.8 $\pm 0.4$	3.31 $\pm 0.08$	0.035* $\pm 0.001$
SRM-BCSS-1 This Study (n = 6) 1998	0.11 $\pm 0.02$	6.30 $\pm 0.17$	10.5 $\pm 0.3$	333 $\pm 5$	1.3 $\pm 0.1$	--	0.25 $\pm 0.01$	117 $\pm 7$	18.7 $\pm 0.5$	3.33 $\pm 0.08$	--
SRM BCSS-1 NRC Certified	0.11 $\pm 0.03$	6.26 $\pm 0.22$	11.1 $\pm 1.4$	(330)	1.3 $\pm 0.3$	0.54 $\pm 0.05$	0.25 $\pm 0.04$	123 $\pm 14$	18.5 $\pm 2.7$	3.29 $\pm 0.10$	(0.04)*
SRM MESS-2 This Study 1997	--	--	--	--	--	--	--	--	--	--	0.088 $\pm 0.003$
SRM MESS-2 This Study 1998	--	--	--	--	--	--	--	--	--	--	0.090 $\pm 0.004$
SRM MESS-2 NRC Certified	--	--	--	--	--	--	--	--	--	--	0.092 $\pm 0.009$
Spike Recovery (%) 1997	81.3 $\pm 3.3$	96.9 $\pm 3.9$	98.7 $\pm 9.2$	102 $\pm 5$	80.5 $\pm 6.7$	98.9 $\pm 1.5$	93.2 $\pm 4.0$	100 $\pm 7$	98.5 $\pm 1.9$	97.3 $\pm 1.8$	95.0 $\pm 6.3$
Spike Recovery (%) 1998	60.8 $\pm 19.2$	102 $\pm 4$	94.4 $\pm 11.8$	102 $\pm 2$	81.5 $\pm 5.2$	--	97.5 $\pm 3.6$	102 $\pm 6$	95.7 $\pm 1.6$	98.0 $\pm 4.6$	83.4 $\pm 8.9$

Notes:

Values in parenthesis are for reference only; SRM not certified by the NRC or NIST.

\*SRM 1646a, issued by the National Institute of Standards and Technology (NIST) was used for Hg, 1997 (Digest 1 and 2).

N.A. = Not Available.

**Table 3-35: Results for Standard Reference Material (SRM) BCSS-1 and MESS-2 Marine Sediment Sample, Issued by the National Research Council of Canada (NRC) (continued)**

Sample ID	K (%)	Mg (%)	Mn (µg/g)	Ni (µg/g)	Pb (µg/g)	Sb (µg/g)	Se (µg/g)	Sn (µg/g)	Tl (µg/g)	V (µg/g)	Zn (µg/g)	TOC (%)
SRM-BCSS-1 This Study (n = 12) 1997	1.82 ±0.01	1.39 ±0.04	233 ±8	55.0 ±1.9	23.7 ±0.4	0.66 ±0.04	0.42 ±0.03	2.11 ±0.09	0.56 ±0.01	94.1 ±6.9	114 ±6	2.12 ±0.05
SRM-BCSS-1 This Study (n = 6) 1998	--	--	230 ±3	53.9 ±2.0	23.6 ±1.1	0.67 ±0.05	0.45 ±0.04	2.03 ±0.22	0.55 ±0.02	91.6 ±2.2	111 ±2	--
SRM BCSS-1 NRC Certified	1.80 ±0.03	1.47 ±0.14	229 ±15	55.3 ±3.6	22.7 ±3.4	0.59 ±0.06	0.43 ±0.06	1.85 ±0.20	(0.6)	93.4 ±4.9	119 ±12	2.19 ±0.09
SRM MESS-2 This Study 1997	--	--	--	--	--	--	--	--	--	--	--	--
SRM MESS-2 This Study 1998	--	--	--	--	--	--	--	--	--	--	--	2.07 ±0.05
SRM MESS-2 NRC Certified	--	--	--	--	--	--	--	--	--	--	--	2.14 ±0.03
Spike Recovery (%) 1997	96.9 ±3.4	94.4 ±3.3	97.1 ±2.5	96.9 ±4.0	100 ±4	99.0 ±3.9	64.0 ±14.0	108 ±5	102 ±5	123 ±5	99.4 ±3.0	N.A.
Spike Recovery (%) 1998	--	--	102 ±2	102 ±10	105 ±3	103 ±5	35.4 ±6.8	122 ±4	103 ±3	134 ±1	96.1 ±2.9	N.A.

Notes:

Values in parenthesis are for reference only; SRM not certified by the NRC or NIST.

\*SRM 1646a, issued by the National Institute of Standards and Technology was used for Hg, 1997 (Digest 1 and 2).

N.A. = Not Available.

**Table 3-36: Results for Standard Reference Material (SRM) 1566a, an Oyster Tissue Issued by the National Institute of Standards & Technology (NIST), SRM DORM-2, a Dogfish Muscle Certified by the National Research Council of Canada (NRC) and SRM TORT-2, a Lobster Hepatopancreas Standard from the NIST**

Standard Reference Material	Ag ( $\mu\text{g/g}$ )	Al ( $\mu\text{g/g}$ )	As ( $\mu\text{g/g}$ )	Ba ( $\mu\text{g/g}$ )	Be ( $\mu\text{g/g}$ )	Cd ( $\mu\text{g/g}$ )	Cr ( $\mu\text{g/g}$ )	Cu ( $\mu\text{g/g}$ )	Fe ( $\mu\text{g/g}$ )
SRM 1566a (n = 1) (This Study, 1997)	1.74	210	13.8	--	--	4.51	1.48	63.5	544
SRM 1566a (n = 1) (This Study, 1998)	1.74	211	13.7	2.05	0.01	4.08	1.10	66.2	534
SRM 1566a (NIST Certified)	1.68 $\pm 0.15$	203 $\pm 12.5$	14.0 $\pm 1.2$	--	--	4.15 $\pm 0.38$	1.43 $\pm 0.46$	66.3 $\pm 4.3$	539 $\pm 15$
SRM 1643d* (n = 1) (This Study, 1997)	--	--	--	513.4 $\mu\text{g/L}$	12.44 $\mu\text{g/L}$	--	--	--	--
SRM 1643d* (n = 1) (This Study, 1998)				513.4	12.44				
SRM 1643d* (NIST Certified)	--	--	--	506.5 $\mu\text{g/L}$ $\pm 8.9$	12.53 $\mu\text{g/L}$ $\pm 0.28$	--	--	--	--
SRM DORM-2 (n = 1) (This Study, 1997)	0.053	10.3	17.2	2.35	N.D.	N.D.	32.7	2.49	148
SRM DORM-2 (NRC Certified)	0.041 $\pm 0.013$	10.9 $\pm 1.7$	18.0 $\pm 1.1$	--	--	0.043 $\pm 0.008$	34.7 $\pm 5.5$	2.34 $\pm 0.16$	142 $\pm 10$
SRM TORT-2 (n = 1) (This Study, 1998)	3.51	23.0	20.6	1.90	0.01	26.8	0.66	100	100
SRM TORT-2 (NRC Certified)	--	--	21.6 $\pm 1.8$	--	--	26.7 $\pm 0.6$	0.77 $\pm 0.15$	106 $\pm 10$	105 $\pm 13$
Spike Recovery (%) Liver (1997)	94.5 $\pm 1.8$	96.2 $\pm 1.4$	100 $\pm 10$	97.0 $\pm 2.9$	105 $\pm 4$	94.9 $\pm 5.6$	108 $\pm 1$	91.4 $\pm 0.6$	99.1 $\pm 1.8$
Spike Recovery (%) Liver (1998)	92.9 $\pm 2.2$	94.2 $\pm 2.7$	101 $\pm 6$	97.7 $\pm 3.6$	99.6 $\pm 7.0$	93.8 $\pm 3.6$	99.6 $\pm 9.2$	93.0 $\pm 2.1$	101 $\pm 3$

Notes:

Values in parenthesis are for reference only; SRM not certified by the NRC or NIST.

\* SRM 1643d, a water sample certified by NIST.

N.D. = Not Detected.

**Table 3-36: Results for Standard Reference Material (SRM) 1566a, an Oyster Tissue lissued by the National Institute of Standards & Technology (NIST), SRM DORM-2, a Dogfish Muscle Certified by the National Research Council of Canada (NRC) and SRM TORT-2, a Lobster Hepatopancreas Standard from the NIST (continued)**

Standard Reference Material	Hg ( $\mu\text{g/g}$ )	Mn ( $\mu\text{g/g}$ )	Ni ( $\mu\text{g/g}$ )	Pb ( $\mu\text{g/g}$ )	Sb ( $\mu\text{g/g}$ )	Se ( $\mu\text{g/g}$ )	Sn ( $\mu\text{g/g}$ )	Tl ( $\mu\text{g/g}$ )	V ( $\mu\text{g/g}$ )	Zn ( $\mu\text{g/g}$ )
SRM 1566a (n = 1) (This Study, 1997)	0.069	11.5	--	0.362	0.012	2.15	2.73	0.009	4.77	837
SRM 1566a (n = 1) (This Study, 1998)	0.068	11.1	2.33	0.382	0.008	2.20	2.62	0.005	4.70	820
SRM 1566a (NIST Certified)	0.0642 $\pm 0.0067$	12.3 $\pm 1.5$	2.25 $\pm 0.44$	0.371 $\pm 0.014$	(0.01)	2.21 $\pm 0.24$	(3)	--	4.68 $\pm 0.15$	830 $\pm 57$
SRM 1643d* (n = 1) (This Study, 1997)	--	--	--	--	54.6 $\mu\text{g/L}$	--	--	7.45 $\mu\text{g/L}$	--	--
SRM 1643d* (n = 1) (This Study, 1998)	--	--	--	--	55.0	--	--	7.36	--	--
SRM 1643d* (NIST Certified)	--	--	--	--	54.1 $\mu\text{g/L}$ $\pm 1.1$	--	--	7.28 $\mu\text{g/L}$ $\pm 0.25$	--	--
SRM DORM-2 (n = 1) (This Study, 1997)	4.70	3.41	--	0.068	0.026	1.49	0.025	0.005	0.220	24.8
SRM DORM-2 (NRC Certified)	4.64 $\pm 0.26$	3.66 $\pm 0.34$	--	0.065 $\pm 0.007$	--	1.40 $\pm 0.09$	(0.023)	(0.004)	--	25.6 $\pm 2.3$
SRM TORT-2 (n = 1) (This Study, 1998)	0.28	12.8	2.33	0.338	0.024	5.37	0.051	0.011	1.57	181
SRM TORT-2 (NRC Certified)	0.27 $\pm 0.06$	13.6 $\pm 1.2$	2.50 $\pm 0.19$	0.35 $\pm 0.13$	--	5.63 $\pm 0.67$	(0.04)	--	1.64 $\pm 0.19$	180 $\pm 6$
Spike Recovery (%) Liver(1997)	61.0 $\pm 5.3$	95.4 $\pm 3.4$	--	92.7 $\pm 2.2$	92.2 $\pm 1.5$	94.6 $\pm 3.0$	94.6 $\pm 5.9$	90.0 $\pm 1.0$	91.6 $\pm 2.0$	93.7 $\pm 2.6$
Spike Recovery (%) Liver (1998)	58.4 $\pm 5.2$	94.5 $\pm 2.6$	70.5 $\pm 1.3$	94.7 $\pm 5.4$	97.4 $\pm 8.0$	92.8 $\pm 2.8$	100 $\pm 7$	93.5 $\pm 5.3$	95.0 $\pm 4.4$	95.9 $\pm 4.0$

## Notes:

Values in parenthesis are for reference only; SRM not certified by the NRC or NIST.

\* SRM 1643d, a water sample certified by NIST.

N.D = Not Detected.

**Table 3-37: Results for Standard Reference Material (SRM) 1643d, a Water Sample Issued by the National Institute of Standards & Technology (NIST), SRM 2704, a River Sediment from the NIST, SRM SLRS-3, a Riverine Water Sample Certified by the National Research Council of Canada (NRC) and SRM MESS-2 from the NRC**

Standard Reference Material	Ag (mg/L)	Al (mg/L)	As (mg/L)	Ba (mg/L)	Be (mg/L)	Cd (mg/L)	Cr (mg/L)	Cu (mg/L)	Fe (mg/L)	Hg (mg/L)
SRM 1643d (n = 1) (This Study, 1997)	0.0013	--	0.0572	0.527	0.0125	0.0065	0.0184	0.0199	0.0904	--
SRM 1643d (n = 1) (This Study, 1998)	0.0013	--	--	--	0.0127	--	--	--	--	--
SRM 1643d (NIST Certified)	0.001270 ±0.000057	--	0.05602 ±0.00073	0.5065 ±0.0089	0.01253 ±0.00028	0.00647 ±0.00037	0.01853 ±0.00020	0.0205 ±0.0038	0.0912 ±0.0039	--
SRM 2704* (n = 2) (This Study, 1998)	0.42 ±0.03	6.05 ±0.04	24.2 ±0.2	409 ±6	3.08 ±0.05	3.58 ±0.13	131 ±0	97.3 ±3.3	4.17 ±0.03	1.50 ±0.03
SRM 2704* (NIST Certified)	--	6.11 ±0.16	23.4 ±0.8	414 ±12	--	3.45 ±0.22	135 ±5	98.6 ±5.0	4.11 ±0.10	1.47 ±0.07
SRM SLRS-3 (n = 1) (This Study, 1997)	--	--	--	0.0131	--	--	--	--	--	--
SRM SLRS-3 (NRC Certified)	--	--	--	0.0134 ±0.0006	--	--	--	--	--	--
SRM MESS-2* (n = 1) (This Study, 1997)	--	--	--	--	--	--	--	--	--	0.086 ±0.001
SRM MESS-2* (NRC Certified)	--	--	--	--	--	--	--	--	--	0.092 ±0.009
Spike Recovery (%)										
Oil	53.8	--	56.0	94.7	102	90.8	80.6	95.6	73.7	--
Water	52.6	--	87.0	144	102	M.O.A.	93.0	102	91.6	--
Particulates	95.5	104.4	99.2	98.7	76.1	95.2	96.2	94.9	101.6	94.1

Notes:

Values in parenthesis are for reference only; SRM not certified by the NIST.

\* Values in µg/g.

\*\* Final concentrations are corrected for percent spike recovery.

M.O.A. = Method of Standard Addition analysis.

**Table 3-37: Results for Standard Reference Material (SRM) 1643d, a Water Sample Issued by the National Institute of Standards & Technology (NIST), SRM 2704, a River Sediment from the NIST, SRM SLRS-3, a Riverine Water Sample Certified by the National Research Council of Canada (NRC) and SRM MESS-2 from the NRC (continued)**

Standard Reference Material	Mn (mg/L)	Ni (mg/L)	Pb (mg/L)	Sb (mg/L)	Se (mg/L)	Sn (mg/L)	Tl (mg/L)	V (mg/L)	Zn (mg/L)
SRM 1643d (n = 1) (This Study, 1997)	0.0374	0.0564	0.0179	0.0528	0.0128	0.0237	0.0072	0.0364	0.073
SRM 1643d (n = 1) (This Study, 1998)	--	--	--	--	--	--	--	--	--
SRM 1643d (NIST Certified)	0.03766 ±0.00083	0.0581 ±0.0027	0.01815 ±0.00064	0.0541 ±0.0011	0.01143 ±0.00017	--	0.00728 ±0.00025	0.0351 ±0.0014	0.07248 ±0.00065
SRM 2704* (n = 2) (This Study, 1998)	562 ±6	41.6 ±0.3	171 ±8	3.79 ±0.11	1.07 ±0.00	9.52 ±0.42	1.08 ±0.06	93.5 ±3.5	429 ±7
SRM 2704* (NIST Certified)	555 ±19	44.1 ±3.0	161 ±17	3.79 ±0.15	1.12 ±0.05	(9.5)	1.06 ±0.07	95 ±4	438 ±12
SRM SLRS-3 (n = 1) (This Study)	--	--	--	--	--	--	--	--	0.0011
SRM SLRS-3 (NRC Certified)	--	--	--	--	--	--	--	--	0.00104 ±0.00009
SRM MESS-2* (n = 2) (This Study)	--	--	--	--	--	--	--	--	--
SRM MESS-2* (NRC Certified)	--	--	--	--	--	--	--	--	--
Spike Recovery (%)									
Oil	91.6	98.4	97.0	95.8	54.5	86.3	95.0	51.1**	97.1
Water	92.5	79.6**	M.O.A.	M.O.A.	68.9	M.O.A.	M.O.A.	78.7**	M.O.A.
Particulates	107.3	106.7	97.8	103.4	81.7	97.0	101.5	99.8	96.6

Notes:

Values in parenthesis are for reference only; SRM not certified by the NIST.

\* Values in µg/g.

\*\* Final concentrations are corrected for percent spike recovery.

M.O.A. = Method of Standard Addition analysis.

**Table 3-38: RGS Fold Induction of TCDD Control**

<b>Test Date</b>	<b>Fold Induction (1 ng/mL TCDD)</b>	<b>Test Date</b>	<b>Fold Induction (1 ng/mL TCDD)</b>
8/4/97	112.1	8/4/98	71.6
8/5/97	115.0	8/4/98	75.9
8/15/97	85.2	1/8/99	62.1
8/18/97	127.0	1/11/99	110.1
9/29/97	99.1	1/19/99	71.3
10/17/97	103.1		
<b>1997 Mean SD</b>	<b>106.9 ±14.4</b>	<b>1998 Mean SD</b>	<b>78.1 ±18.6</b>

## 4.0 Discussion

In this section the results and interpretation of the chemical and biological tests performed on the sediments and tissues from the study are further evaluated in the framework of the null hypotheses presented in Section 1.2. The title and subject of each of the following subsections correspond to a particular null hypothesis, and include an assessment on the validity of the null hypothesis.

### 4.1 Surface Sediments as Contaminant Sinks

Fine-grained, organic-rich sediments are the most common sink in the coastal ocean for organic and trace metal contaminants because of the large, active surface area available for adsorption. Contaminants introduced by municipal discharges to areas surrounding Anchorage and by oil and gas activities to uppermost Cook Inlet will most likely be deposited with such fine-grained sediments. The upper areas of Cook Inlet have been previously shown to contain only minor deposits of fine-grained sediment because the shallow water, large tidal ranges and active hydrography move sediments southward to outermost Cook Inlet and the Shelikof Strait (Sharma and Burrell, 1970; Carlson *et al.*, 1977; Hampton, 1982). Thus, a primary goal of this study was to identify and sample these potential sinks for fine-grained sediments and determine whether they contain contaminants.

Surface sediments collected during this study help identify patterns of deposition for fine-grained silts and clays in outermost Cook Inlet and the Shelikof Strait. A contour map of silt+clay (Figure 4-1) shows a sharp increase in silt+clay from 30 to 40 percent in outermost Cook Inlet to greater than 95 percent in the middle (zone 2) through the lower (zones 3 and 4) portions of the Shelikof Strait (summary data in Table 3-10). Clearly, the trends shown on Figure 4-1 support the initial assumption of the study and identify most of the Shelikof Strait as an important sink for fine-grained sediment. Furthermore, the observed trend supports deposition of more fine-grained sediment toward the southern areas of Shelikof Strait.

The TOC content of the sediment averages about 0.75 percent for the entire study area with a relatively limited number of sites (Homer Harbor and zone 4) containing greater than 1 percent TOC. These concentrations of TOC compare well with values previously reported by Hampton (1983). Concentrations of TOC tend to be highest in samples with greater than 80 percent silt+clay (Figure 4-2), suggesting that organic matter is associated with fine-grained sediments.

A first approximation of the magnitude of sediment deposition in outermost Cook Inlet and the Shelikof Strait is estimated here based on data for riverine discharge of sediment, as well as sediment accumulation rates. Riverine input of sediment from the Susitna-Knik-Matanuska (S-K-M) River system was reported as  $40 \times 10^6$  tons/year (Feely *et al.*, 1982; USGS, 1998). This value is most likely a lower limit for total sediment input from the S-K-M system because the three rivers are estimated to contribute 75 to 90 percent of the total sediment input to upper Cook Inlet. Thus, estimates of total transport of sediment from the S-K-M system range from 44 to  $53 \times 10^6$  tons/year. Added to inputs from the S-K-M system is some fraction of the sediment transport of  $107 \times 10^6$  tons/year from the Copper River (Reimnitz, 1966). Based on a sediment composition model described in Section 4.3, sediment derived from the Copper River accounts

for 10 to 20 percent of the total sediment deposited in the study area. Total sediment deposition was determined for each zone (Table 4-1). The average sediment accumulation rate was multiplied by the area of fine-grained sediment in each zone to determine total deposition (Table 4-1). Total sediment deposition based on sediment accumulation is ~ 60 to 70 x 10<sup>6</sup> tons/year for zone 0 to zone 4. Using data for river inputs, the 44 to 53 x 10<sup>6</sup> tons/year from the S-K-M system is combined with a 10 to 20 percent contribution from the Copper River (i.e., 6 to 14 x 10<sup>6</sup> tons/year) for a total of 50 to 67 x 10<sup>6</sup> tons/year. Thus, the two approaches to determining total sediment deposition in the study area agree relatively well.

Are fine-grained sediments from outermost Cook Inlet and the Shelikof Strait contaminated with trace metals? Identification of metal contamination in sediments requires knowledge of natural levels of metals. All trace metals are present in marine sediments at some natural level that varies as a function of the mineralogy, grain size, and organic matter content of the sample. As previously described, concentrations of trace metals were normalized to Fe to help account for natural variability in sediment composition and concomitant trends in concentrations of trace metals. Metal/Fe ratios can be compared with source sediments from the Susitna and Copper Rivers, surface sediments from pristine sites, or with older, deeper (pre-industrial) sediments from the same site to help identify anthropogenic additions of metals over space and time. If a particular metal/Fe ratio is significantly increased relative to clean, reference material from the area, then that metal can be identified as having some fraction of the total concentration introduced by anthropogenic sources. For example, Figure 4-3 shows a Cr/Fe plot for all surface sediments, along with source material from the Susitna and Copper Rivers. The Cr/Fe plot (Figure 4-3) shows that most points follow a relatively good linear trend that includes source sediment from the Copper River. The Cr/Fe ratios for average continental crust and sediment from the Susitna River (Figure 4-3) are comparable, yet higher than observed for the samples. Thus, with the available data, no samples show a clear deviation from what are believed to be natural concentrations for Cr.

In contrast with the Cr/Fe relationship described above, the Zn/Fe relationship for source material and surface sediment from the study area fit a linear trend with a slope that is about 2 times higher than shown for average continental crust (Figure 4-3). However, this trend of higher Zn levels in Alaskan sediments, relative to Fe, is consistent with data for Alaskan rocks (Table 3-3). Furthermore, Zn concentrations and the Zn/Fe ratio have been constant in sediments deposited in the study area during the past 100 years (e.g., Figures 3-52 through 3-65). Thus, the higher Zn/Fe ratio for Alaskan sediments is a natural reflection of somewhat higher levels of Zn in sediments from the study area relative to average continental crust. Like Cr, concentrations of Be, Ni, Pb, Se, Sn, and Tl (Figures 4-4 and 4-6) follow linear trends versus Fe with a slope less than shown for average continental crust and with no indications of anthropogenic loading. In contrast, concentrations of Ag, As, Ba, Cd, Cu, Hg, Mn, Sb, and V versus Fe are similar to trends described for Zn versus Fe (Figures 4-4 through 4-7). Six points on the Hg/Fe graph (Figure 4-7) show positive deviations from the basic relationship shown for the source samples and other surface sediments. These samples were collected from ZOF1 and ZOF14, both in Kachemak Bay. However, present-day Hg levels in Kachemak Bay (core 98-ZOF1) are comparable with values observed throughout the twentieth century, suggesting that these concentrations are typical for the Kachemak Bay area. Thus, within the present data set, no clearly identifiable anthropogenic inputs of sediment metals are observed between the source rivers and the sediments of outermost Cook Inlet and the Shelikof Strait.

The levels and extent of PAH, from petroleum and other sources, in outermost Cook Inlet and Shelikof Strait are shown in a contour map of the total PAH concentrations (Figure 4-8). The total PAH concentrations generally follow the pattern observed for silt+clay (Figure 4-1), with an increase in total PAH from approximately 0.20 to approximately 0.40 ppm in zone 0 (outermost Cook Inlet) to approximately 0.50 to 1.0 ppm in zones 1, 2, 3, and 4 (Shelikof Strait). Exceptions to this pattern were observed at stations Z0F1 and Z0F14 (Kachemak Bay), which showed elevated concentrations of PAH relative to other zone 0 surface sediments. The relative elevation of PAH at these two stations was likely due to enrichment from local coal and petroleum hydrocarbon inputs. Coal outcrops are a well documented feature of the nearby Kachemak Bay shoreline, and anthropogenic petroleum hydrocarbon influences were identified from the adjacent Homer Harbor source samples.

However, the total PAH concentrations in all zones are comparable to values reported for background hydrocarbons in other studies from offshore coastal waters of Alaska (Boehm, *et al.*, 1991; Bence *et al.*, 1996; Page, *et al.* 1996; Boehm, *et al.*, 1998). Therefore there does not appear to be any identifiable enrichment of petroleum contaminants (as represented by PAH) from anthropogenic activities, including oil and gas production in upper Cook Inlet.

In summary, in the context of the null hypothesis, **the surface sediments of outermost Cook Inlet and the Shelikof Strait are potential traps for contaminants from oil and gas production activities in upper Cook Inlet**, by virtue of the fact that Shelikof Strait is a depositional area. Based on evaluations of the organic and inorganic data, no contamination of the study area's surface sediments was detected that may have originated from oil and gas production activities in upper Cook Inlet.

## 4.2 Concentration of Pollutants Over Time

### 4.2.1 Geochronology of Metals

A 50- to 100-year chronology of metal levels in sediments from outermost Cook Inlet and the Shelikof Strait was obtained for each zone. Concentrations of Fe, Al (Table 3-19) and/or the Fe/Al ratio were uniform in each core (Figures 3-52 through 3-65) and thus, for convenience, metal concentrations, rather than ratios to Fe, are used in this section.

Profiles for Pb versus time show that concentrations of Pb varied by less than 10 percent (CV) within each core over time periods extending back as far as the late 1800s. For example, at station Z1F1, Pb levels vary by  $\pm 0.7$   $\mu\text{g/g}$  for a mean of 12.3  $\mu\text{g/g}$  (Figure 4-9). A similar trend was observed for station Z3F2 (Figure 4-9) and each of the other sites. The overall constant and low levels of Pb, with a maximum of 15.2  $\mu\text{g/g}$  relative to 14.8  $\mu\text{g/g}$  for average continental crust, show that no detectable anthropogenic Pb has been deposited at the 14 core sites during the past century.

Based on a total of  $\sim 60 \times 10^6$  tons of sediment deposited in the study area per year, about 60 tons of Pb would need to be introduced to the region to observe a 1  $\mu\text{g/g}$  increase in sediment Pb levels. Previous estimates of anthropogenic Pb inputs to the area were about 2 tons of Pb (Boehm *et al.*, 1998) and are consistent with the sedimentary record. Local instances of Pb contamination are still possible; however, none were detected.

In a manner similar to that described for Pb, concentrations of Ag, Ba, Be, Cu, Hg, Ni, Sb, Tl, V and Zn, or their ratios to Fe, generally show less than 10 to 20 percent variation within a core at all sites. Furthermore, many of the observed higher levels (or ratios to Fe) are observed deeper in the cores (i.e., older sediments). Thus, none of these elements show discernible anthropogenic inputs or changes in metal levels during the past 40 to 50 years of industrial activity in the area.

Concentrations of Cr in cores from sites Z1F1 and Z1F2 are 20 to 30 percent higher during the early 1900s relative to the 1940s (Figure 4-10). Uniform profiles of Cr over time are observed for most other sites with the exception of one or two lower values each in cores from Z0F5, Z0F6, Z1R3B, and Z3F2. Chromium was mined on the Kenai Peninsula near Seldovia at varying times from World War I through the late 1950s. The slightly elevated Cr levels in nearby sites Z1F1 and Z1F2 may reflect inputs of small amounts of Cr tailings from this activity. No such evidence of enrichment was found at the other sites.

Concentrations of Cd in the various cores have the greatest variability (Figure 4-10), with an overall range of 0.07 to 0.27  $\mu\text{g/g}$ . At these levels, Cd concentrations are within the bounds of bottom sediments from the Susitna (0.30  $\mu\text{g/g}$ ) and Copper (0.16  $\mu\text{g/g}$ ) Rivers. The variations over time are believed to be a complex function of biological inputs of Cd-rich organic matter, diagenesis in the sediments, and variable inputs of source sediment.

Surface layers (from 1 to 6 cm thick) at stations Z2R16, Z2R2, and Z3F1 have Mn concentrations greater than 1,000  $\mu\text{g/g}$  in what otherwise are generally uniform Mn profiles at the various sites. This surficial enrichment of Mn is most likely related to dissolution of Mn oxides in reducing layers below 6 cm with diffusion of  $\text{Mn}^{2+}$  up to oxic surface sediments where it precipitated as  $\text{MnO}_2$ . Massoth et al. (1979) previously observed such remobilization of Mn in Shelikof Strait. Arsenic follows a similar trend to that observed for Mn, suggesting that As also may follow Mn in this diagenetic process.

#### **4.2.2 Geochronology of Organics**

The geochronology of petroleum hydrocarbons was established in 12 sediment cores from the outermost Cook Inlet and Shelikof Strait. A chronology of 20 to 100 years was established, based on the individual core at each station with at least one core with a 50+ year record in each zone. In general, profiles of the concentrations of the totals for the 3 categories of organic compounds (total PAH, TPHC, and total S/T) did not reveal any significant increases over the oil and gas development time period. This finding was consistent between cores over time. Some variation was noted, as the CV for total PAH and total S/T ranged between 8 and 23 percent within each core. The CVs for TPHC were somewhat higher: 14 to 49 percent, showing greater variability for this parameter, but no consistent trend within cores. The one exception was the core from Z3F2, which exhibited a nearly three-fold increase (from 20  $\mu\text{g/g}$  to 53  $\mu\text{g/g}$ ) in the non-specific TPHC parameter between approximately 1987 and present (Figure 3-77). However, no corresponding increase in either total PAH or total S/T was observed during the same time interval, indicating that the TPHC increase was not related to anthropogenic or petroleum hydrocarbon inputs over the last 10 years.

In all cores, the concentrations of PAH analytes are within the same range as the PAH levels in the surface sediments of the corresponding zone. Perylene is an exception. Perylene concentrations generally increased with core depth at each zone, as shown in Figure 4-11. The

increasing concentration of perylene with depth may be related to the well-known process associated with perylene formation during early sediment diagenesis, or may be related to perylene input associated with coal.

#### **4.2.3 Statistical Analysis of Concentrations in Cores**

As discussed in Section 3.3.5, the dated sediment cores were evaluated statistically to determine if there were any significant trends in the cores that could be associated with the onset of petroleum exploration and production activities in upper Cook Inlet. The results of the statistical analysis revealed that there were no significant increases in the concentration of organics and metals in the sediments which could be correlated with the onset of petroleum activities (circa 1963). Several of the trends in specific parameters which were discussed previously (e.g., increasing perylene with core depth, increases in terrigenous hydrocarbon parameters near the surface, and subtle shifts in several petroleum source ratios) were also validated by the statistical analysis.

In summary, in the context of the null hypothesis, **the concentrations of metals and organics in sediments in outermost Cook Inlet and Shelikof Strait have not increased significantly since offshore oil exploration and production began in Cook Inlet (circa 1963).**

### **4.3 Composition of Pollutants Over Time**

#### **4.3.1 Metals**

Average metal values for Ag, As, Ba, Be, Cd, Cr, Cu, Hg, Mn, Ni, Pb, Sb, Se, Sn, Tl, V, and Zn or their ratios to Fe, from each core site are comparable with levels obtained for source sediments from the Susitna and Copper Rivers. This observation is consistent with the concept that no identifiable additions of these metals occur as sediment is being transported from the source rivers to depositional sites in outermost Cook Inlet and the Shelikof Strait. In other words, oil and gas operations and the Point Woronzof outfall have not had a discernible impact on concentrations of these metals at the study sites.

Knowledge of the relative amounts of sediment in the Shelikof Strait that are derived from the S-K-M system versus the Copper River has valuable scientific and management application. Previous work by Hein *et al.* (1979) qualitatively identified the presence of sediments from the Copper River in Shelikof Strait using clay mineralogy. A first approximation of the quantitative proportions of sediment in each zone that are derived from the S-K-M system was calculated during our study using trace metal data.

Five different metal/metal ratios were selected for this calculation. Metal ratios were used to normalize differences in absolute concentrations of metals from various source and sediment samples. For each ratio used, the following conditions were established: (1) the ratio for river bottom sediment was within  $\pm 10$  percent of the value for river suspended solids, (2) the ratio for the combined S-K-M system differed from that for the Copper River by greater than 30 percent. The average values used for the S-K-M system are based on the following fractions of total sediment transport: Susitna (83 percent), Knik (11 percent), and Matanuska (6 percent), using sediment discharge data from the USGS (1999). Based on these criteria, the five ratios used for the model are Ni/Be, Fe/Zn, Sn/Sb, Pb/Tl, and V/Zn (Table 4-2).

For each surface sample and each ratio, the fraction of sediment derived from the S-K-M system was calculated using a simple 2-member mixing model with average ratios from Table 4-2. Results for all 5 ratios were averaged for each site and the grand average for each sample is presented as a mean  $\pm 2$  standard deviation (95 percent confidence interval) in Table 4-3. In zones 0, 1, and 2, the error of the estimate (95 percent confidence interval) is 24 to 30 percent relative to 8 percent for zones 3 and 4. Alaska Coastal Current sediment collected outside the Shelikof Strait has no discernible input from the S-K-M system. Surficial sediment from outermost Cook Inlet and the Shelikof Strait contains an average of  $81 \pm 22$  percent sediment from the S-K-M system. Thus, the dominant source of sediment to the study area at present is from the S-K-M system.

### 4.3.2 Organics

The sediment core profiles showed that concentrations of the primary hydrocarbon parameters were relatively constant with depth within each core. An evaluation of diagnostic source parameters within the cores revealed that in most cases the source(s) of these hydrocarbons was constant over the time period studied.

As was seen in the surface sediments, double-ratio source plots of C2D/C2P versus C3D/C3P provide a representative fine-tuned summary of the PAH sources in the core samples. Double-ratio source plots for each of the sediment cores are presented in Figures 4-12 through 4-19. Based on an evaluation of the source ratio plots of the cores, several important trends are observed. In the cores from ZOF1 (Kachemak Bay, Figure 4-12) there is greater scatter throughout the cores, likely related to variable local hydrocarbon source inputs (e.g., coal, Homer Harbor sediment, runoff).

The source ratio plot of the sediment core from ZOF5 (Figure 4-13) shows some scatter of the different core sections, with the shallower depth intervals (~1940 to present) clustering between values for "background" sediment and coal. The deeper sections of the core show a trend towards source values corresponding to the Well Creek seep oil value and the Oil Bay seep oil (~1940 and earlier). This result could indicate a possible shift in the source of petroleum hydrocarbons over time. This shift would indicate a greater influence of the Well Creek/Oil Bay seep oil sources to the outermost Cook Inlet sediments in the past (prior to 1940), and an increase in the contribution of the particle-bound "background" hydrocarbons from other petroleum hydrocarbon source(s) to the east (e.g., Katalla, Yakutaga area formations) more recently (post-1940). A mixture of these two "end members" is suggested by the double-ratio plot.

A similar trend is observed in the source ratio plot of the core sample from station ZOF6 (Figure 4-13), where the deeper sections of the core (6 to 25 cm) are more closely associated with the Well Creek seep oil and Oil Bay seep oil sources, and the shallower surface sections (0 to 6 cm) are intermediate to "background" sediment and coal sources. The same follows for the core sample from ZOF8, i.e., the deeper sediments (16 to 20 cm, Figure 4-14) are separated from the cluster of upper sediments and exhibit Well Creek seep oil and Oil Bay seep oil influence. Geochronology for the ZOF6 and ZOF8 cores confirms that each of the deeper sediments within each core is from the 1940s and earlier, establishing a source correlation between the trends observed in these 3 zone 0 core profiles.

The source ratio plots of these three zone 0 cores (Z0F5, Z0F6, and Z0F8) all suggest a shift in the contribution of petroleum hydrocarbon sources in the western portion of outermost Cook Inlet around 1940, with an apparent decrease in the influence of Iniskin Peninsula petroleum sources after 1940. A preliminary statistical evaluation of the source ratios from these three cores was performed to test this trend in the same manner as described previously for the post-1963 intervention effect, except in this analysis a 1940 intervention effect was tested. The results of this analysis (Woolcott Smith - personal communication) show a significant increase ( $P < 0.05$ ) in the C2D/C2P and C3D/C3P source ratios after 1940 in all three cores. Several causes for this observed shift in petroleum hydrocarbon sources could be suggested, including earthquake activity around 1940, which may have diminished the flow of the local Iniskin Peninsula seeps, or a shift in the sedimentary or circulatory regime of the area. Further study would be required to refine these theories; however, with respect to the objectives of this monitoring program it is important to note that the observed trend is only found in the western area of outermost Cook Inlet, and occurred prior to any offshore oil exploration and production activities in Cook Inlet.

The source ratio plots for the zone 1, 2, 3, and 4 cores (Figures 4-15 through 4-19) generally show a consistent cluster of source ratio values throughout the depth intervals sampled. This indicates that the source of hydrocarbons to these sediments has not changed since the early 1900s, based on the geochronologies established to date. The source ratios generally plot in the same area as the "background" sediment, indicating that particle-bound petroleum hydrocarbons associated with seeps and petroleum formation source(s) to the east of the study area (e.g., Katalla, Yakutaga, east of Prince William Sound) are likely the primary source of hydrocarbons over this period.

Thus, in the context of the null hypothesis, **the composition (source[s]) of metals in the sediments of outermost Cook Inlet and Shelikof Strait do not appear to have changed since offshore oil exploration and production began in Cook Inlet (circa 1963). The composition of hydrocarbons in sediment cores does show subtle changes over the past 25 to 50 years, but these changes do not appear to be correlated with petroleum production activities or spills.**

#### **4.4 Risk Associated with Pollutant Concentrations: Exposure Assessment**

In the context of this study multiple parameters were used to evaluate biological and ecological risk. The following sections provide a discussion on both sediment quality and biological and ecological effects (sediment quality criteria, sediment toxicity, CYP1A [P450] induction in fish tissues, and RGS analyses of sediment and fish tissue).

##### **4.4.1 Comparison to Sediment Quality Criteria: Metals**

Sediment quality criteria have been used extensively worldwide to assess possible adverse biological effects from metals and PAH. The most utilized criteria are the ERL (Effects Range-Low) and ERM (Effects Range-Medium) presented by Long *et al.* (1995). These guidelines are based on field, laboratory, and modeling studies conducted in the United States that coupled concentrations of contaminants in sediments with biological effects (e.g., Long and Morgan, 1990). The ERM is defined as the concentration of a substance in the sediment that results in an adverse biological effect in about 50 percent of the test organisms and the ERL is defined as the

concentration of a substance that affects 10 percent of the test organisms. Thus, the general application of the criteria has been to state that adverse biological effects are “rarely” observed when metal or PAH levels are less than the ERL, “occasionally” observed when contaminants are present at levels between the ERL and ERM, and “frequently” observed when concentrations exceed the ERM.

Nine of the 17 metals investigated during this study have been assigned ERL and ERM concentrations by Long *et al.* (1995) at this time. None of these 9 metals are found at levels above the ERM in any sediment samples from this study (Figures 4-20, 4-21, and 4-22). Furthermore, 5 of the metals (Ag, Cd, Hg, Pb, and Zn) are present in sediments at levels below the ERL at all sites (Figures 4-20, 4-21, and 4-22). Concentrations of Cr exceed the ERL by less than 20 percent at 2 sites in Kachemak Bay (ZOF1 and ZOF14). In contrast, concentrations of As exceed the ERL of 8.2 µg/g at 38 of 56 sites by less than 1 to as much as 8 µg/g (Figure 4-20). However, the highest As concentration of 16 µg/g in sediment from ZOF1 is still well below the ERM value of 70 µg/g. Suspended solids from the Susitna River carry As levels of approximately 36 µg/g, with no 2 sites from zone 0 having higher As concentrations than this source material.

Concentrations of Cu exceeded the ERL of 34 µg/g at 53 of 56 sites by as much as 18 µg/g (52 µg Cu/g at ZOF1); however, the maximum Cu level in sediments from this study is well below the ERM for Cu of 270 µg/g. Once again, source sediment from the Susitna River (31 µg Cu/g) and the Copper River (43 µg Cu/g) along with Alaskan rock data (Table 3-3), show that natural levels of Cu in the area are close to or above the ERL value chosen by Long *et al.* (1995). Finally, all samples from this study had Ni levels that exceed the ERL of 20.9 µg/g. The average crustal abundance of Ni is 56 µg/g (Wedepohl, 1995), a value that exceeds that ERM level of 51.6 µg/g. Similarly, the Ni content of sediment from both source rivers exceeds the ERL. Even for Ni values greater than the ERM, only 16.9 percent mortality was recorded by Long *et al.* (1995) for their database, and thus the ERL and ERM values for Ni may need to be revised in the second iteration of these sediment quality criteria. Overall, As and Cr in 2 or 3 sites in zone 0 (mainly Kachemak Bay) are present at levels that exceed the ERL; however, these values are comparable with results for river suspended solids and Alaskan rocks.

#### **4.4.2 Comparison to Sediment Quality Criteria: Polycyclic Aromatic Hydrocarbons**

The PAH analytes in the sampled sediments were compared to the ERL and ERM values for organic parameters in a manner similar to the metals. The results of this comparison for the organics were slightly different from the metals results in that the ERL for both individual and total PAH parameters were not exceeded in any zone or any site. This comparison for organics data is illustrated in Figure 4-23 and indicates that overall, the PAH concentrations in the study sediments are at levels that would not be expected to result in adverse biological effects.

#### **4.4.3 Sediment Toxicity Tests**

Sediment bioassays (using amphipods) were conducted in this study to determine if sediments from selected areas of lower Cook Inlet and Shelikof Strait had the potential to cause biological effects. Reduced survival to amphipods may indicate the potential for biological effects to

benthic organisms. However, as the sediments have a large mixture of trace substances, it may be difficult to determine which substance(s), if any, are responsible for the observed reduced survival of amphipods. This portion of the report will attempt to identify possible sources of the observed reduced survival in some of the bioassays conducted during this study.

Statistical analysis (using ToxCalc v5.0 software) of the results from the 1997 sediment bioassays conducted by PERL demonstrate that 15 of the 20 sediment samples resulted in survival significantly less than the Control at  $p < 0.05$ . However, most laboratories conducting sediment bioassays only indicate toxicity if the following two criteria are met:

1. There is a significant difference between the laboratory control and the test using a t- test, as was done here.
2. Mean organism response in the bioassay test was less than 80 percent of the laboratory control value.

Application of the second criterion eliminates the problem of designation of toxicity based only on comparison to controls with low replicate variance.

The 80 percent of control criterion was established by statistical analysis of many amphipod data sets by other investigators (e.g., Thursby and Schlekot, 1993). The two criterion approach is currently being used by the EPA's EMAP Program (Schlommel *et al.*, 1994), by California's State Bay Protection and Toxic Cleanup Program (BPTCP, 1993) and by the Regional Monitoring Program for Trace Substances in the San Francisco Estuary (SFBRMP, 1995).

Applying these criteria to the bioassay results demonstrates that at 7 of the 20 sites sampled in 1997, amphipod survival was significantly lower than the controls: 2 of 8 from zone 0; 1 of 4 from zone 2; and 4 of 4 from zone 3. None of the 4 sites in zone 1 demonstrated significantly lower survival than controls.

Correlating amphipod survival with the trace contaminants measured in this study is problematic due to two factors:

1. While pristine in comparison with sediments from many areas where amphipods have been used as test organisms to assess sediment toxicity, the tested sediments did contain a large mix of trace substances. In this study, we have used the Effects Range methodology developed by Long and Morgan (1990) to relate contaminant concentrations to survival of test organisms. This methodology defines the concentrations of contaminants which have resulted in deleterious biological effects to test organisms (see Section 4.4.1 for a more detailed discussion of ERL and ERM). It has been demonstrated that contaminant mixtures may have a synergistic or additive effect on test organism survival, and that synergistic or additive effects may not be easily elucidated based on analysis of individual contaminant concentrations (Chapman, 1989; Schwartz, 1988, 1995). Methodologies are being developed that may more completely address additive or synergistic biological effects of the mixture of chemicals widely found in sediment analyses, and may prove useful in future analyses of sediments from this study (Thompson, 1998). However, although four of the sediment metals (As, Cr, Cu, and Ni) concentrations exceeded the

ERL, where sediment concentrations are “occasionally” associated with adverse effects, no concentrations exceeded the ERM, the level at which sediment concentrations are “frequently” associated with adverse effects (Long and Morgan, 1990; Long *et al.*, 1995). Concentrations of organic chemicals in the sampled sediments show a similar result. The ERLs for individual and total PAH were not exceeded in any zone or any site.

2. The amphipod *Eohaustorius estuarius* used in this study in 1997 (and widely used elsewhere) is recognized as tolerating highly variable mixtures of grain size, ranging from 0.6 to 100 percent sand. However, it naturally inhabits sandy sediments and some correlation between survival and grain size has been reported by DeWitt *et al.* (1989), and SAIC (1993a; 1993b), with increased mortality associated with decreasing grain size (higher percent silt) (EPA, 1994).

Statistical analysis of all chemical concentrations and amphipod survival demonstrates that percent survival was significantly correlated to two factors in the 1997 samples: 1) concentrations of Zn in the sediments and, 2) percent silt (fine-grained sediments). The three stations with the greatest percent silt were also the stations where amphipods had the poorest survival. Therefore, sediment particle size composition, as has been found previously for this and other amphipod species, probably affected survival. While further investigations may elucidate other factors affecting test organism survival, all indications from the samples collected in 1997 indicate fine grain size of area sediments as the primary factor contributing to low survival in the 1997 sediment bioassays with *Eohaustorius estuarius*.

Concentrations of AVS and SEM also were determined for the sediments collected in 1997 and used in the *Eohaustorius* toxicity tests. As previously mentioned, the underlying principle for using results from AVS-SEM is that metals bound (SEM) with sulfide (AVS) are not bioavailable. Concentrations of AVS in the 27 sediment samples (0 to 2 cm) from this study were all less than 3.1  $\mu\text{mole/g}$ , except for a value of 18.6  $\mu\text{mole/g}$  at station Z0F14. Only five other sites from this study (Z0F1, Z1R13, Z2R13, Z3R11, and Z3R20) yielded AVS levels greater than 1  $\mu\text{mole/g}$ . An AVS value of less than 1  $\mu\text{mole/g}$  was considered below the limit of applicability of the AVS/SEM technique by DiToro *et al.* (1990). Thus, low AVS values in the sediments from outermost Cook Inlet and the Shelikof Strait restrict use of the AVS/SEM approach. By comparison, results for marine sediments from Long Island Sound and Sapelo Island, Georgia, show values of AVS that ranged from less than 0.1 to about 10  $\mu\text{mole/g}$  in the top 1 cm of the sediment and 8 to 43  $\mu\text{mole/g}$  over the top 10 cm of the sediment column (DiToro *et al.*, 1990).

For the 9 sites in outermost Cook Inlet and the Shelikof Strait where amphipod survival was less than 80 percent, AVS levels averaged  $0.7 \pm 1.0 \mu\text{mole/g}$  relative to  $0.4 \pm 0.7 \mu\text{mole/g}$  at 10 stations where survival was greater than 80 percent (excluding the high AVS site Z0F14). Thus, no significant correlation between AVS levels and amphipod survival was observed for the sediments collected in 1997. Concentrations of SEM also were similar between the two survival groups at  $1.0 \pm 0.2 \mu\text{mole SEM/g}$  for the less than 80 percent survival group and  $0.8 \pm 0.4 \mu\text{mole SEM/g}$  for the greater than 80 percent survival group, again showing no relationship in toxicity results among sites as a function of SEM levels in 1997.

A more common use of the AVS and SEM data is to subtract the AVS value from the SEM value [i.e., SEM - AVS] and assume that a negative result means that sufficient sulfide is present in the sediment to bind potentially toxic metals with a high sulfide affinity (Ag, Cd, Cu, Hg, Ni, Pb, and Zn), thereby rendering the sediment less toxic. Overall, excess AVS (a negative result meaning that metals are bound with sulfide) was found at only 4 of the 20 sites sampled in 1997 (2 with greater than 80 percent survival and 2 with less than 80 percent survival), including the site with the lowest percent survival (Z3R11). The SEM-AVS value for the metal-rich site Z0F14 is -17.5  $\mu\text{mole/g}$ , supporting sulfide binding of metals. Once again, no pattern between the results of the amphipod toxicity tests and data for AVS/SEM are observed.

According to the underlying principles of the AVS/SEM test, observed positive numbers for [SEM-AVS] at most sites would correspond with more bioavailable metals. However, in these sediments, a sizeable amount of the SEM is most likely associated with iron oxides that also dissolve with the 1N HCl treatment used. More than 90  $\mu\text{moles Fe/g}$  were released during the SEM treatment, or about 100 times more metal than the total SEM value. Use of the AVS/SEM approach in oxic sediments has been previously shown to be of limited value because of the importance of organic matter and manganese and iron oxides in controlling metal binding (Ankley *et al.*, 1996). The surface few centimeters from all sites were shown by the results of sediment profile imaging to be oxic. Coupled with the observation that most AVS values were less than 1  $\mu\text{mole/g}$ , the lack of relationship between AVS-SEM results and amphipod toxicity is certainly consistent.

In 1998, sediment toxicity tests were conducted on sediments from the seven sites that demonstrated significant toxicity to test organisms in 1997, and in addition, a fine-grained sediment collected from a reference site (figure 2-1) was also tested. This fine-grained reference sediment was tested to assess the test organism's sensitivity to fine-grain size sediments. As discussed in section 3, the test amphipod *Eohaustorius estuarius* (used in 1997) was replaced with the amphipod *Ampelisca abdita*. The site selection and change in test organisms in 1998 was based on the sediment toxicity test results from 1997, which, as discussed above, were not significantly related to measured concentrations of metals or organic compounds. The strongest relationship in the 1997 tests was to grain size, i.e., as grain size decreased, so did survival. *Ampelisca abdita* replaced *Eohaustorius estuarius* in 1998 as an attempt to address the question of the apparent grain-size effect observed with the 1997 sediment toxicity test. *Ampelisca abdita* was selected as an alternative species through conversations with the bioassay laboratory and investigations of the literature. It is thought to be less subject to grain-size effects than *Eohaustorius estuarius*. No significant toxicity (i.e., less than 80 percent) was found in 1998 at the sites with the lowest survival in 1997 or in the fine-grain size "control" site sediments included in 1998. These results indicate that factors affecting survival of test organisms in 1997 were not present in 1998, or that differential survival of test organisms exposed to sediments from the same sites may be explained by differing tolerances between the two amphipod species utilized as test organisms.

#### **4.4.4 P450 Reporter Gene System in Fish and Sediments**

Previous RGS studies have demonstrated that B[a]PEq in excess of 60  $\mu\text{g/g}$  are associated with benthic degradation in sediments. Studies conducted on marine sediments from various parts of the U.S. coastal zone for The National Oceanic and Atmospheric Administration (NOAA) have shown that relatively uncontaminated sediments have produced a response of about 1 to 6  $\mu\text{g/g}$

of B[a]PEq (Anderson *et al.*, 1995; Anderson *et al.*, 1997). The Alaskan sediments analyzed in this study therefore fall within this range of background concentrations. The low levels of CYP1A induction in most fish tissues analyzed, especially the gills, are also consistent with the low RGS P450 response measured in the sediment extracts and in the fish liver composite samples.

#### **4.4.4.1 Sediments**

Petrogenic PAHs ( $r = 0.689$ ) and Total PAHs ( $r = 0.681$ ) were found to correlate significantly ( $p \leq 0.05$ ) with the P450 RGS responses measured on sediment extracts. Numerous individual hydrocarbons, which were included in the summed petrogenic PAH and Total PAH concentrations, also showed significant correlations with the P450 RGS responses.

Total PAH have been found in numerous NOAA Bioeffects studies to correlate highly with the RGS responses measured in those samples from various coastal regions of the country (Anderson *et al.* In Press a). These previous studies have demonstrated that RGS responses to sediments less than about 11 mg B[a]PEq/g are not likely to be associated with biological effects. Levels of RGS response to sediments above about 32 mg B[a]PEq/g may be associated with biological effects, and when the measured response reaches 60 mg B[a]PEq/g and greater, there is likely to be a deleterious impact on the organisms associated with the sediments.

The sediments tested in this investigation were all under 11 mg B[a]PEq/g, and most were equivalent to the lowest responses measured previously from very clean portions of the U. S. coastal zones (Northern Puget Sound and Alaska). The range of RGS responses between 0.5 and 5.0 mg B[a]PEq/g, where nearly all of these samples fell is considered to be a very clean environment.

#### **4.4.4.2 Fish Tissue**

The data on P450 RGS responses to fish tissue were expressed on a lipid weight basis, which always produces higher values than normalization on a dry weight basis, because a smaller portion of the tissue is composed of lipid. Very few of the fish tissue samples tested produced fold induction above the solvent control (1.0 fold induction). Those samples that were above 1.0 fold produced B[a]P equivalent values of 0.3 to 1.0 mg B[a]PEq/g lipid, with one arrow tooth flounder sample having a value of 6.5 mg B[a]PEq/g lipid.

In other studies, the highest observed RGS responses to extracts of tissues were from marine mussels deployed in contaminated areas of San Diego Bay (Anderson *et al.* In Press b). These responses were as high as 295 mg B[a]PEq/g dry weight, and the native clean mussels were at 6 mg B[a]PEq/g dry weight. In a study for the Exxon Valdez trustees the P450 RGS assay was used on 38 samples of whole sand lance collected from various locations in Prince William Sound in 1996, well after the oil spill (1989). These rather lipid-rich fish produced RGS values between 1.5 and 81 mg B[a]PEq/g lipid. The majority of the samples were in the range of 1 to 5, but approximately one-third of the samples were above 10 mg B[a]PEq/g lipid. While it is difficult to compare sand lance directly to the species of fish collected in this investigation, it appears that those in the present study contained much lower levels of inducing compounds.

A more recent study conducted for LGL-Alaska under funding by MMS examined the levels of RGS induction produced by fish collected from both Cook Inlet and the Shelikof Straits. The two species that were collected in adequate numbers from each region were the Pacific sand lance and surf smelt.

Those samples of the two species collected from Cook Inlet in 1998 were found to be higher in RGS responses than the same species collected from the Shelikof Strait.

The results of these investigations demonstrate that the use of a biomarker screening approach provides a good estimate of the levels of inducing compounds, such as high molecular weight PAHs in both sediment and tissue samples.

The responses (both B[a]PEq and TEQ) of the RGS assay to extracts of fish tissue in 1998 were highly correlated with several analytes. (The RGS values are expressed as both B[a]P and Toxic Equivalents, since without chemical confirmation it can not be determined if the response was from exposure to PAHs [B[a]Peq] or from chlorinated hydrocarbons [TEQ]). It is not surprising that for all fish, RGS responses were correlated with C1-fluorenes, C2-fluorenes, and C1-phenanthrenes, since these compounds would be part of a suite of hydrocarbons that could induce the CYP1A1 gene. However, the correlation of RGS with copper and chromium is merely a matter of co-occurrence in the sediments. The solvent extracts applied to the RGS cells would not likely even contain metals.

For Pacific cod collected in 1998, the observed correlations of RGS with fluorenes, phenanthrenes, and fluoranthrene would be expected as noted above. In this case two other metals (zinc and thallium) show a correlation, but these are again merely the result of co-occurrence in the samples.

In conclusion, the results of the RGS assay are in general agreement with the chemical analyses on the same samples, and both types of measurements demonstrate that the collected sediments and tissues are quite low in the concentrations of PAHs, and chlorinated hydrocarbons which induce the CYP1A1 gene.

#### **4.4.5 CYP1A Response in Fish**

The CYP1A response is considered a very sensitive biological response for assessing exposure to a variety of organic pollution conditions, and is widely considered a useful tool for assessing exposure to specific classes of xenobiotic compounds (e.g., PAHs, coplanar polychlorinated biphenyls [PCBs], polychlorinated dibenzofurans, and dibenzodioxins), CYP1A genes code for the major oxidative enzymes induced in fish and other vertebrates by PAHs and chlorinated hydrocarbons (Stegeman and Hahn, 1994). CYP1A and other measures of induction of the cytochrome P450 enzyme system have become common components of contaminant monitoring and effects studies worldwide (e.g., Bucheli and Fent, 1995, Holdaway et al., 1995, McCain et al., 1996, Wirgin and Waldman, 1998, Collier et al., 1998, and Miller et al., 1999), and in Alaska (e.g., Varanasi et al., 1995 and Jewett et al., 2000). Buchelli and Fent, in their 1995 review, cite 75 field studies, 93% of which showed that CYP1A induction is significantly related to contaminant levels in the environment. When coupled with measures of histopathology, i.e., immunohistochemistry (IHC), induction of CYP1A can identify tissue specific-patterns of CYP1A expression to identify target sites and exposure routes for PAH's and other inducing compounds, and can link exposure to xenobiotic compounds to effects at the biochemical, cellular, tissue, and physiological levels. As of yet, however, there are few studies such as this one in which CYP1A has been measured and scored in individual cell types (IHC). This (immunohistochemical) approach not only relates environmental contaminant concentrations to tissue residues and responses, but may also demonstrate the route of exposure (water, diet,

substrate) of biota to environmental contaminants (e.g. Miller et.al., 1989, Spies et al., 1996, Van Veld et. al., 1997).

One study (conducted with a nearly identical methodology) examined cellular response in Embiotocid fish (rainbow surfperch, *Hypsurus caryi*, and rubberlip surfperch, *Rachochilus toxodes*) caught near petroleum seepage in the Santa Barbara Channel, and at control sites. In this study, liver hepatocytes from oiled sites had mean staining indices of 5.6 and 4.2. (rainbow vs rubberlip respectively). These IHC scores have been adjusted based on maximum scores of 15 as used in the present study, as opposed to a maximum score of 25 as used in the surfperch study (the original scores were 9.3 and 7). While at the control sites, liver hepatocyte scores were 2.7 and 2.5 (rubberlip vs rainbow respectively). The original scores being 4.5 and 4.3 (Spies et al., 1996). These values compare to mean values of 2.83, 1.25, and 1.7 (zones 0, 2, and 3 respectively) measured in Pacific halibut (liver hepatocytes) caught in 1997, .25, .09, and 0 (zones 1, 2, and 3 respectively) measured in Pacific halibut in 1998, and 0 to 1.9 measured in all species caught and analyzed in 1998.

There have been several recent studies of hydrocarbon concentrations and effects in Alaska fish stemming from the Exxon Valdez oil spill (EVOS). One study (Jewett et al., 2000) measured the catalytic activity of CYP1A in the form of EROD (ethoxyresorufin *O*-deethylase) as well as using the IHC approach. The measurement of EROD has been the most common means of investigating the CYP1A response to contaminants in both field and laboratory studies up until this point, and the authors are not aware of any other field study of fish from pristine environments in which both approaches (IHC and EROD) were utilized. The fish sampled in the Jewett et al., study (masked greenling, *hexagrammos octogrammus*, and crescent gunnel, *Pholis laeta*) all had mean liver vascular endothelium scores of less than 1, while (with the exception of black cod which had a mean score of 1.2 from Zone 3 in 1997) none of the species from the present study had measurable IHC scores. Vascular endothelium is the first site of contact of inducing compounds in tissues and organs and so should demonstrate early induction and early loss of induction in comparison with other tissues and organs. The total lack of induction (with the exception of black cod) in the fish from the present study indicates either that the fish from Shelikof Strait were less (recently) exposed to inducing compounds than those from the Jewett et al., study, or that there are significant differences between the species in terms of sensitivity to exogenous inducing compounds and or levels of endogenous inducing compounds. Additionally, as exposure through the diet of (metabolized) hydrocarbons lessens with increasing trophic level, it may be expected that higher trophic level fish (halibut and cod) would demonstrate less induction via dietary exposure than lower trophic level fish (gunnels and greenling). The high IHC score for Black cod vascular endothelium is interesting, but difficult to interpret as only 5 fish were sampled, and the mean score of 1.2 came from a single fish with a score of 6.

While direct comparisons of data from IHC versus EROD based studies are somewhat tenuous, the lack of other IHC based studies on Alaska fish initiated the need to make comparisons from studies utilizing other methodologies. EROD is generally considered to be a more sensitive measure of CYP1A induction than IHC. Jewett et al., 2000, utilized EROD due to the low IHC scores in fish from un-oiled sites. Unfortunately, IHC and EROD were not measured in the same fish, making direct comparisons impossible. However, the EROD scores of fish from un-oiled sites were generally lower than those from oiled sites. Another study of Alaska fish stemming from EVOS (Varanasi et al., 1995) utilized aryl hydrocarbon hydroxylase (AHH) to measure P-

4501A (CYP1A) induction in fish from over 50 sites in Prince William Sound, Lower Cook Inlet, and embayments along the Kenai Peninsula and the Alaska Peninsula. AHH is a very similar measure to EROD. The findings in the (Varanasi et al., 1995) study were similar to the Jewett et al., 2000 study in that AHH levels decreased with time and distance from EVOS.

In the tissue assays conducted on fish collected in 1997, the only significant differences observed between zones were in the CYP1A concentrations in the halibut kidney tubules, although a similar progression between zones was seen for all three cell types. In addition, when all three CYP1A response variables were regressed against all of the tissue contaminant concentrations, kidney tubule response did not correlate positively with any tissue measures. Similar results were obtained for the tissues assayed in 1998. In 1997, Halibut were the only fish species caught in significant numbers in all sampled zones, while in 1998, both Halibut and Pacific Cod were caught in sufficient quantities in all sampled zones to allow investigation of differences between CYP1A scores for both species. The results, however, are similar to 1997 in that there was no significant correlation between or within species, scores, and zones. The exception to this is cytoplasmic vacuolation in hepatocytes, which is a non-specific response of these cells that may in some circumstances be linked to contamination.

There is the possibility that the CYP1A responses seen in some cells, i.e, kidney tubules and kidney vascular endothelium, could be due to unmeasured factors. Relatively high levels of kidney cell induction have been noted in other species in circumstances where contaminants are apparently not a factor (Stegeman, personal communication). These tissues could be responding to natural inducers, either endogenous or exogenous.

The low to moderate levels of induction observed in the fish collected in this study could also be a response to contaminants not measured in this study, e.g., chlorinated hydrocarbons such as the PCB. Chlorinated hydrocarbons, especially the coplanar forms of PCB, dibenzofurans, and dioxins, are known inducers of CYP1A in fish (Stegeman *et al.*, 1992). Halibut are piscivorous, and therefore relatively high on the marine food chain, and likely to accumulate some of these globally ubiquitous and slowly metabolized contaminants. In addition, it is well understood that polar, and possibly sub-polar environments, are apparently sinks for chlorinated hydrocarbons that are transported long distances in the atmosphere from lower latitudes. Recent measurement of chlorinated hydrocarbons in the tissues of harbor seals (Small *et al.*, 1998) and killer whales (Matkin *et al.*, unpublished) have confirmed high tissue concentrations of PCBs (high parts per million) that confirm that the Gulf of Alaska receives significant inputs of these biologically active molecules. It is therefore almost certain that fish in the northern Gulf of Alaska ecosystem are also contaminated with such compounds, but probably at 10 to 100 times lower concentrations. One recent study (Ewald et al., 1997) of biotransport of organic pollutants (PCBs and DDTs) by Alaskan Sockeye salmon to their inland spawning lakes in the copper river drainage, found muscle lipid concentrations of PCBs of 670 ng/g and DDTs of 221 ng/g in fish caught in the Gulf of Alaska just prior to upriver migrations. These concentrations are far below levels of concern for human health from consumption, and are 10 times lower than reported in Atlantic salmon from the Baltic Sea (Larsson et al., 1996), and 20 times lower than those reported for salmonids in Lake Ontario (Oliver and Niimi, 1988).

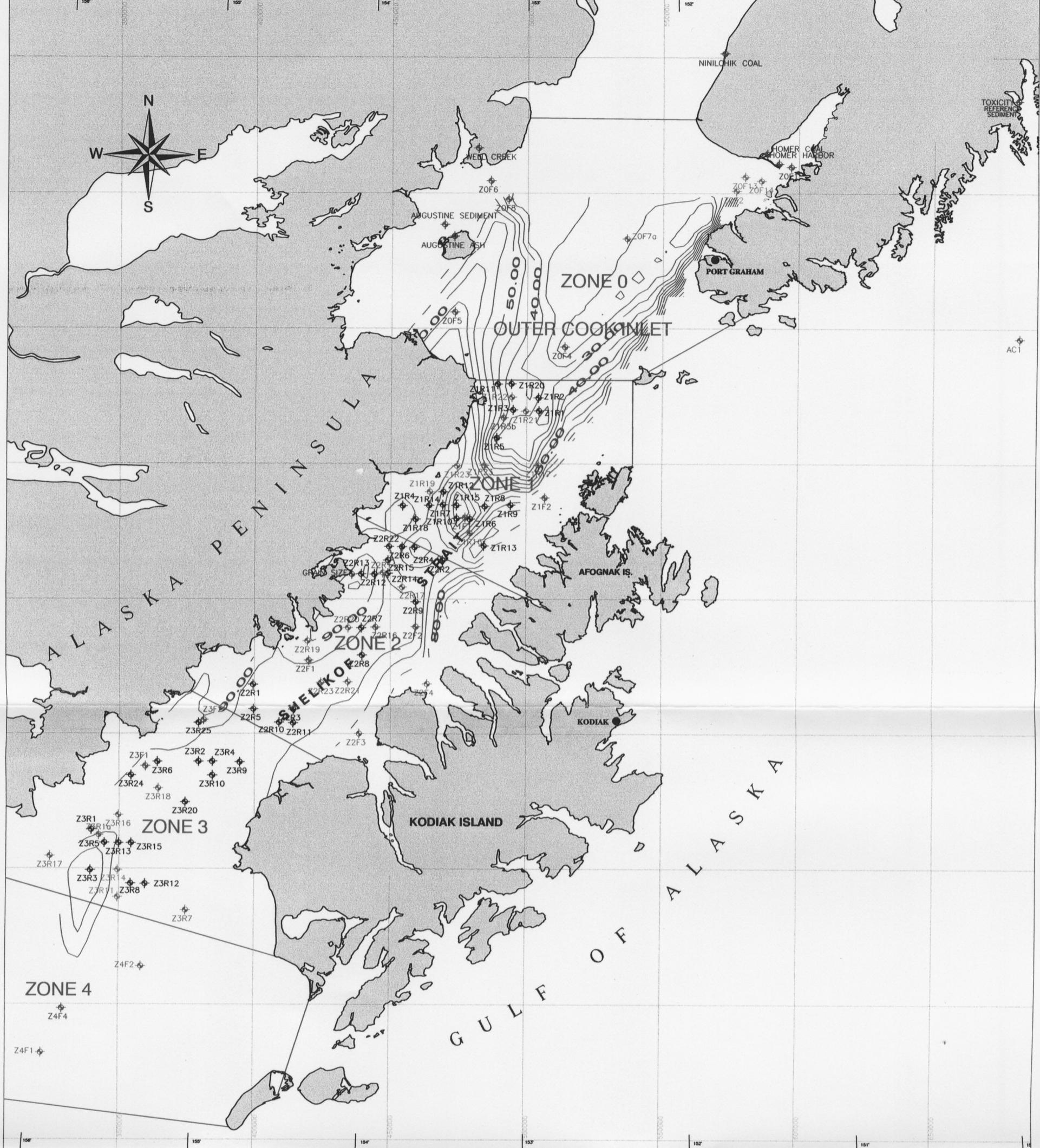
The low induction of CYP1A in gill tissues of all three fish species would be consistent with waterborne sources of contamination being extremely low for these bottom-dwelling fish in

lower Cook Inlet and Shelikof Strait. This finding is also consistent with the low concentrations of PAH and the very low P450 RGS responses seen in sediment extracts in this study. On the other hand, the responses in the liver hepatocytes and the two cell types in the kidney are consistent with some level of inducing compounds in the diet. With the currently available data it is not possible to assign this low to moderate level of CYP1A induction to any particular group of compounds. While serving as a useful benchmark for measures of CYP1A induction in fish from Shelikof Strait and other relatively pristine areas of the world, future studies of fish from this region should attempt to collect greater numbers of fish from which to base statistical analyses and should also collect non-migratory species from lower trophic levels, due to the ability of fish to metabolize PAH. Additionally, other studies of fish from Alaska and other regions intent on determining exposure to xenobiotics have included measurement of bile hydrocarbons (Varanasi et al., 1995, Jewett et al., 2000). These measurements have proven useful in determining recent exposures to PAH. The lack of tissue residue analysis for other CYP1A inducing compounds in the present study hindered the authors in attempting to relate CYP1A induction to PAH alone.

#### **4.4.6 Assessment of Ecological Risk**

Sediment and fish tissue sampling in 1997 and 1998 has provided a picture of contaminants and potentially toxic trace substances in the environment at very low concentrations with an attendant low biological risk. The concentrations of trace metals are consistently below the risk levels identified by Long and Morgan (1990), except for Ni, which has a crustal abundance higher than the designated ERL and ERM concentrations. The concentrations of PAH detected in sediments are also below the ERL identified by Long and Morgan (1990). The P450 RGS results also indicated low to negligible biological risk associated with extractable organic compounds, namely PAH, in the sediments. Sediment bioassays with amphipods produced some low survival rates, but these appear to be related to testing sediments with a high silt content rather than any trace chemicals in the sediments, be they natural or anthropogenic in origin. The levels and patterns of induction of CYP1A in cells of bottom-dwelling fish are consistent with some mild induction by contaminants, but with weak induction in the gills they appear not to be waterborne, but rather from the diet. None of the measured contaminants in the fish tissues correlated with CYP1A induction, but chlorinated hydrocarbons were not measured.

**In summary, in the context of the null hypothesis, our results indicate that the concentrations of organic and metal parameters in the sediments of outermost Cook Inlet and Shelikof Strait do not appear to pose any immediate ecological risk to the marine organisms in the study area.**



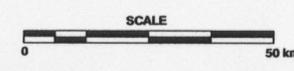
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 N:\CAD\Mms-shelikof\_strait\PDFs\2nd-set\FinalReport-Figure4-8.dwg

**LEGEND**

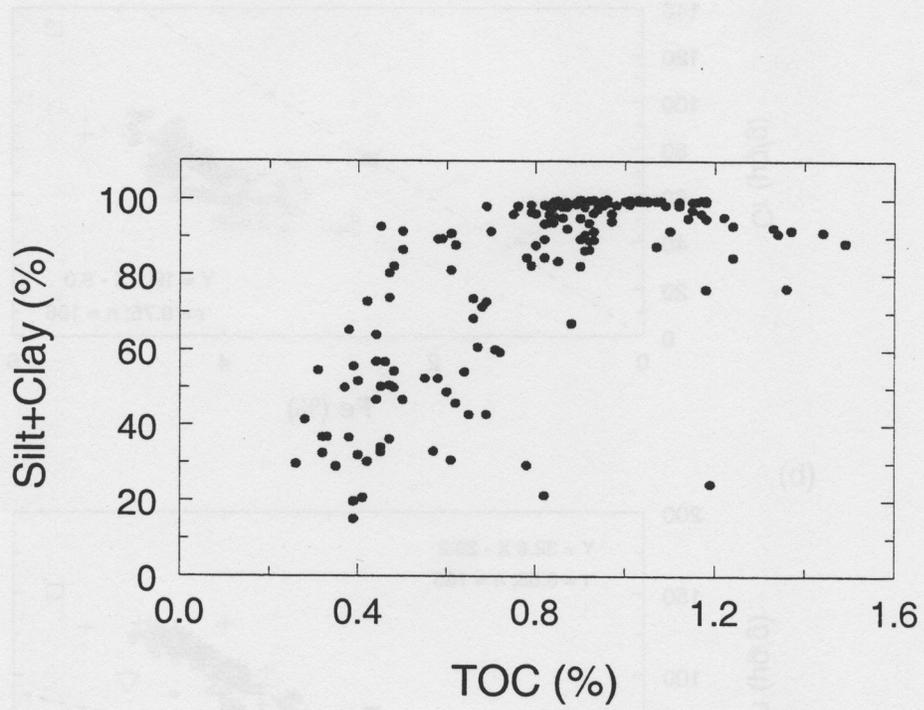
- Z3R7 ◊ 1997 STATION LOCATION
- ZOF1 ◊ 1998 STATION LOCATION
- ZOF2 ◊ 1997 and 1998 STATION LOCATION
- Z4F4 ◊ CORE STATION LOCATION (1997 and/or 1998)
- Z1R23 ◊ FISH STATION LOCATION (1997 and/or 1998)
- WELL CREEK ◊ 1998/1997 SOURCE/REFERENCE STATION
- 60 — GRAIN SIZE IN PERCENT SILT/CLAY

**ZONE DESCRIPTIONS**

- ZONE 1 - NORTH SHELIKOF STRAIT
- ZONE 2 - MID-SHELIKOF STRAIT
- ZONE 3 - SOUTH SHELIKOF STRAIT
- ZONE 4 - OUTER SHELIKOF STRAIT

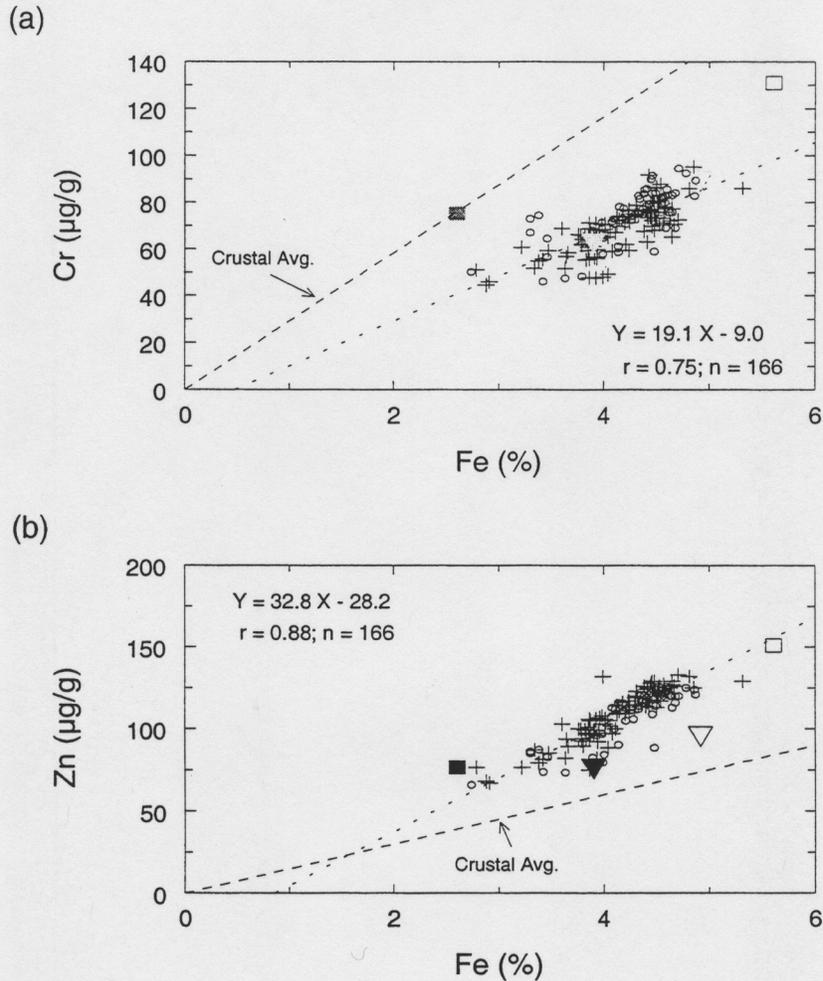


**FIGURE 4-1  
 GRAIN SIZE CONTOUR MAP  
 SHELIKOF STRAIT AND OUTERMOST  
 COOK INLET**

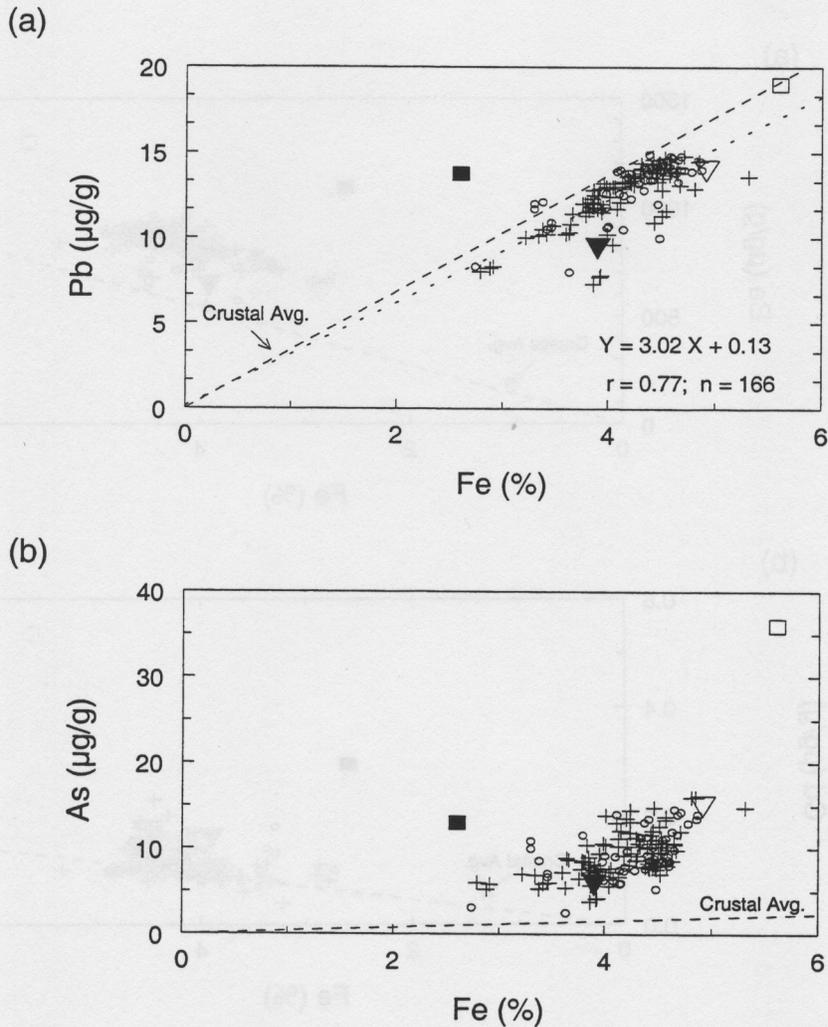


**Figure 4-2: Percent TOC versus Silt + Clay  
for Surficial Sediments for Zones 0, 1, 2, 3 and 4.**

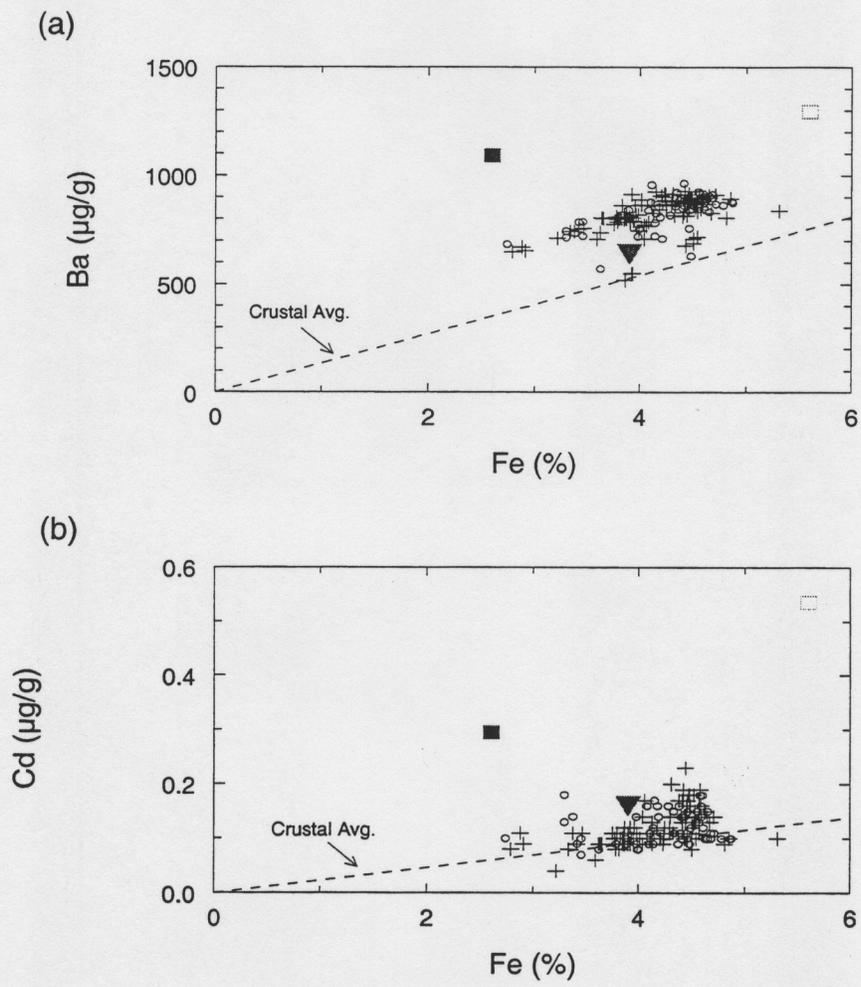
Figure 4-3: Concentrations of Fe versus (a) Cr and (b) Zn in Surficial Sediments from Oyster Creek Lake (Zone 0) and the Shellfish Strait (Zones 1, 2, 3 and 4). Dashed lines show relationship for Average Continental Crust from Wedepohl (1995). Dotted lines and equations are from linear regression for surficial sediments from this study. Symbols are as follows: (+) Surficial Sediments Collected in 1997; (v) Surficial Sediments Collected in 1998; (w) Bottom Sediments from the Sustaina River; (□) Suspended Solids from the Sustaina River; (v) Bottom Sediments from the Copper River and (v) Suspended Solids from the Copper River.



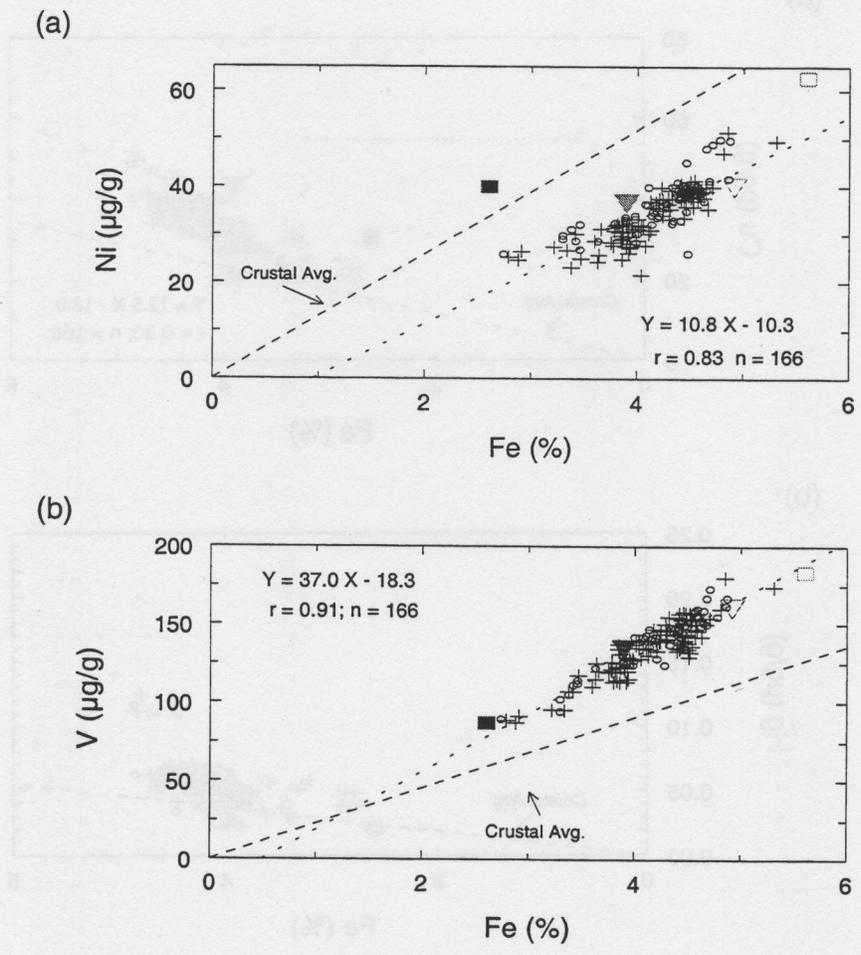
**Figure 4-3: Concentrations of Fe versus (a) Cr and (b) Zn in Surficial Sediments from Outermost Cook Inlet (Zone 0) and the Shelikof Strait (Zones 1, 2, 3 and 4). Dashed Lines Show Relationship for Average Continental Crust from Wedepohl (1995). Dotted Lines and Equations are from Linear Regression for Surficial Sediments from this Study. Symbols are as Follows: (+) Surficial Sediments Collected in 1997, (o) Surficial Sediments Collected in 1998, (■) Bottom Sediments from the Susitna River, (□) Suspended Solids from the Susitna River, (▼) Bottom Sediments from the Copper River and (∇) Suspended Solids from the Copper River**



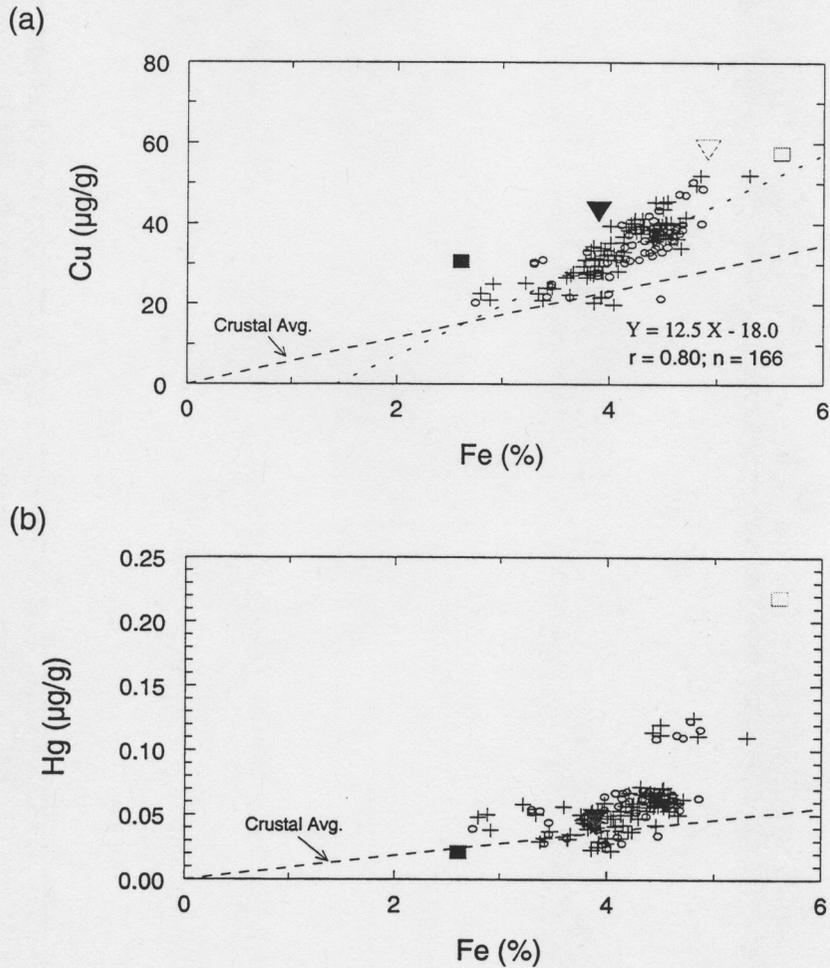
**Figure 4-4: Concentrations of Fe versus (a) Pb and (b) As in Surficial Sediments from Outermost Cook Inlet (Zone 0) and the Shelikof Strait (Zones 1, 2, 3 and 4). Dashed Lines Show Relationship for Average Continental Crust from Wedepohl (1995). Dotted Line and Equation are from Linear Regression for Surficial Sediments from this Study. Symbols are as Follows: (+) Surficial Sediments Collected in 1997, (o) Surficial Sediments Collected in 1998, (■) Bottom Sediments from the Susitna River, (□) Suspended Solids from the Susitna River, (▼) Bottom Sediments from the Copper River and (▽) Suspended Solids from the Copper River**



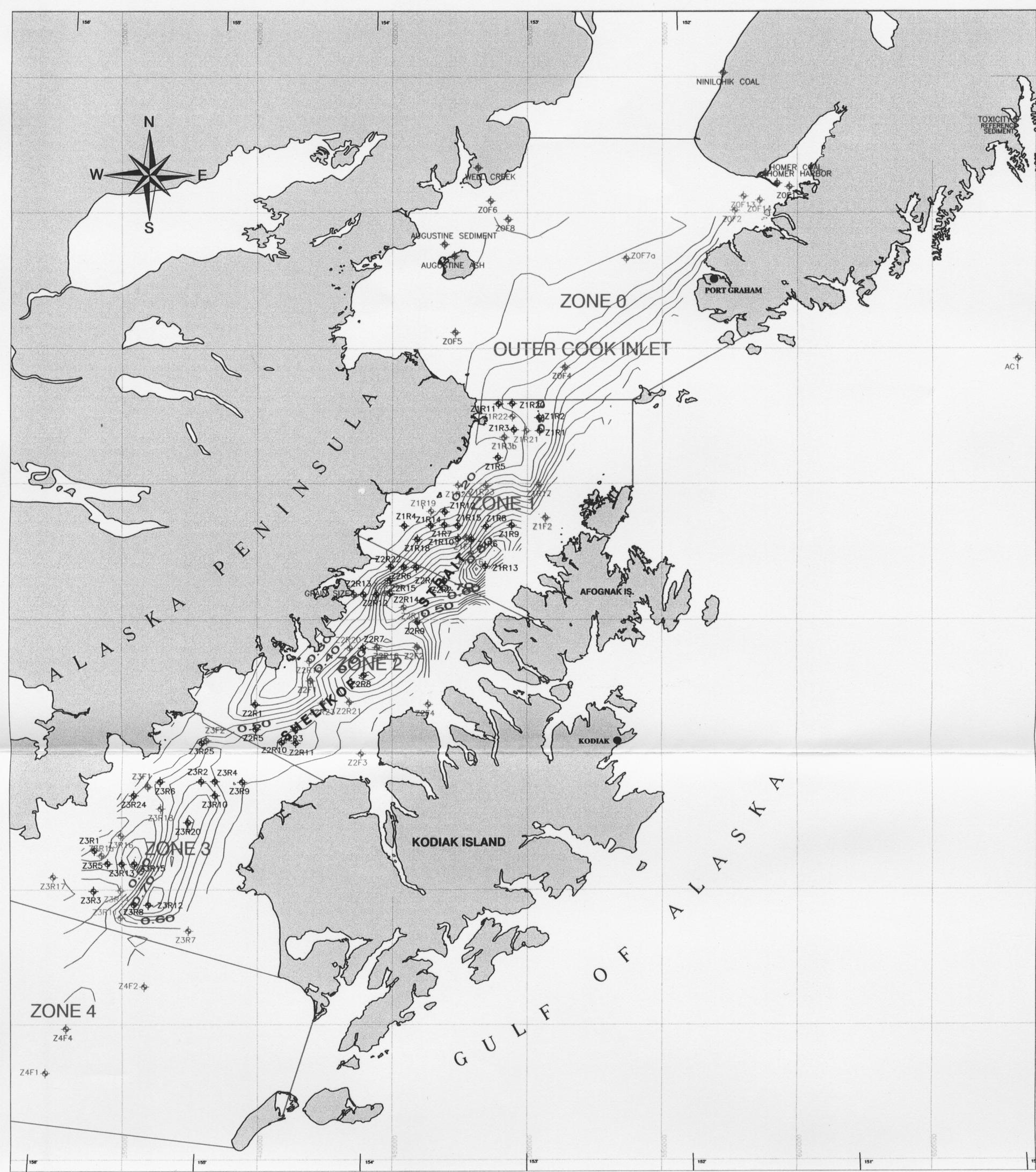
**Figure 4-5: Concentrations of Fe versus (a) Ba and (b) Cd in Surficial Sediments from Outermost Cook Inlet (Zone 0) and the Shelikof Strait (Zones 1, 2, 3 and 4). Dashed Lines Show Relationship for Average Continental Crust from Wedepohl (1995). Symbols are as Follows: (+) Surficial Sediments Collected in 1997, (o) Surficial Sediments Collected in 1998, (■) Bottom Sediments from the Susitna River, (□) Suspended Solids from the Susitna River, (▼) Bottom Sediments from the Copper River and (∇) Suspended Solids from the Copper River**



**Figure 4-6: Concentrations of Fe versus (a) Ni and (b) V in Surficial Sediments from Outermost Cook Inlet (Zone 0) and the Shelikof Strait (Zones 1, 2, 3 and 4). Dashed Lines Show Relationship for Average Continental Crust from Wedepohl (1995). Dotted Lines and Equations are from Linear Regression for Surficial Sediments from this Study. Symbols are as Follows: (+) Surficial Sediments Collected in 1997, (o) Surficial Sediments Collected in 1998, (■) Bottom Sediments from the Susitna River, (□) Suspended Solids from the Susitna River, (▼) Bottom Sediments from the Copper River and (▽) Suspended Solids from the Copper River**



**Figure 4-7: Concentrations of Fe versus (a) Cu and (b) Hg in Surficial Sediments from Outermost Cook Inlet (Zone 0) and the Shelikof Strait (Zones 1, 2, 3 and 4). Dashed Lines Show Relationship for Average Continental Crust from Wedepohl (1995). Dotted Line and Equation are from Linear Regression for Surficial Sediments from this Study. Symbols are as Follows: (+) Surficial Sediments Collected in 1997, (o) Surficial Sediments Collected in 1998, (■) Bottom Sediments from the Susitna River, (□) Suspended Solids from the Susitna River, (▼) Bottom Sediments from the Copper River and (▽) Suspended Solids from the Copper River**



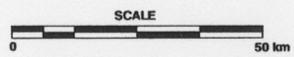
May 17, 2001 - 12:15pm  
 N:\CAD\Mms-shelikof\_strait\32319021.dwg

**LEGEND**

- Z3R7 1997 STATION LOCATION
- Z0F1 1998 STATION LOCATION
- Z0F1 1997 and 1998 STATION LOCATION
- Z4F4 CORE STATION LOCATION (1997 and/or 1998)
- Z1R23 FISH STATION LOCATION (1997 and/or 1998)
- WELL CREEK 1998/1997 SOURCE/REFERENCE STATION
- 0.60 PAH CONCENTRATION IN ug/g DRY WEIGHT

**ZONE DESCRIPTIONS**

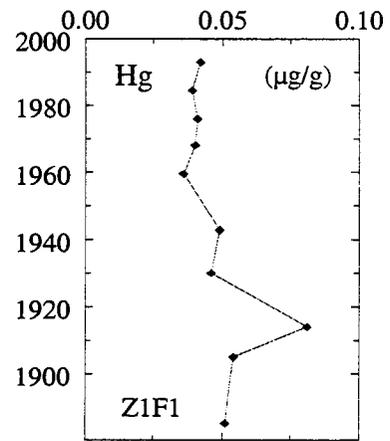
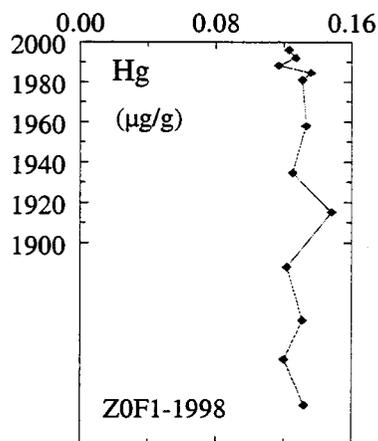
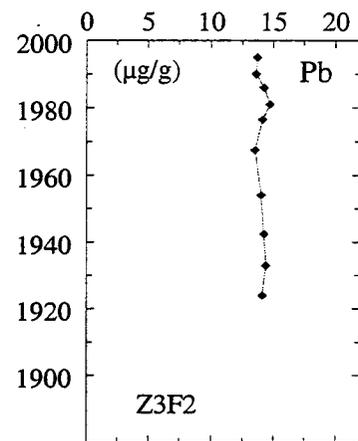
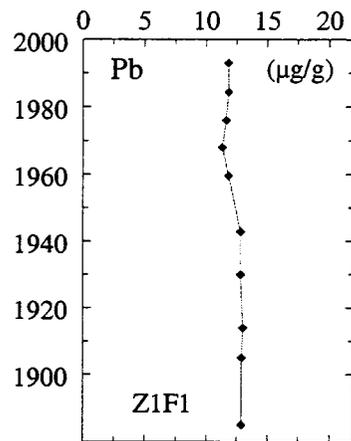
- ZONE 1 - NORTH SHELIKOF STRAIT
- ZONE 2 - MID-SHELIKOF STRAIT
- ZONE 3 - SOUTH SHELIKOF STRAIT
- ZONE 4 - OUTER SHELIKOF STRAIT



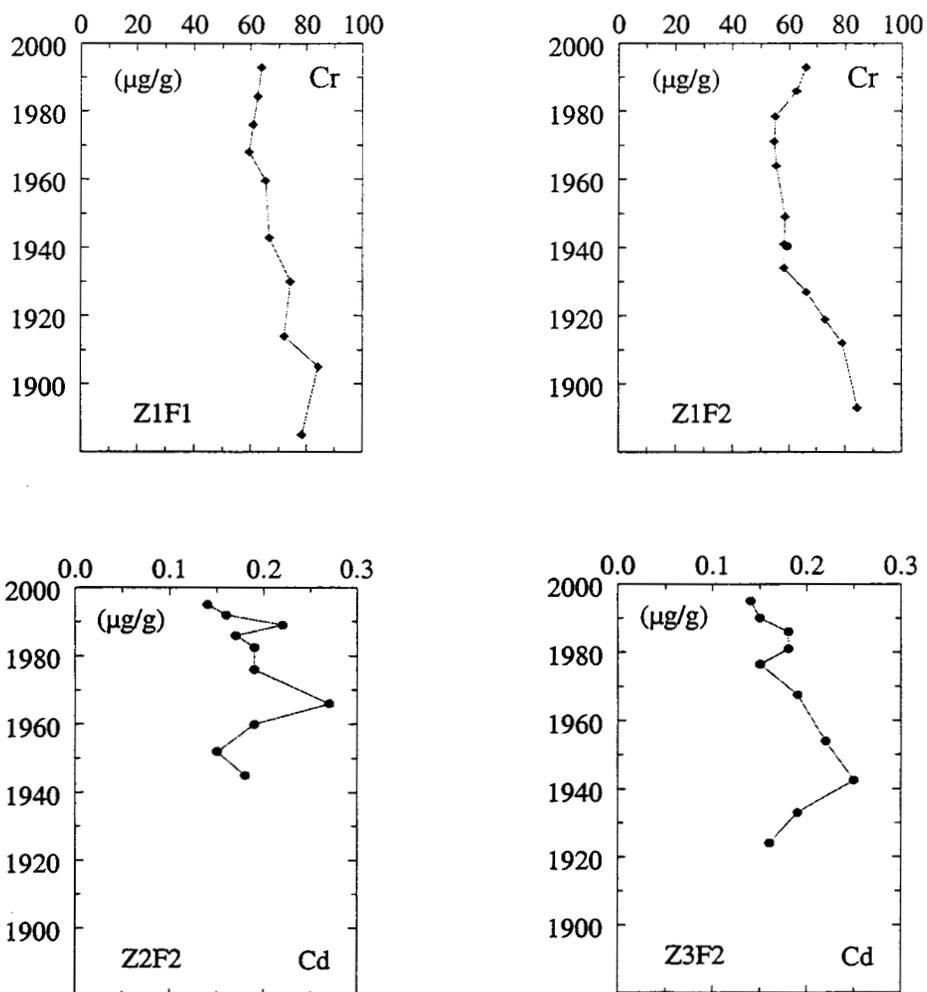
**MMS** Minerals Management Service U.S. Department of the Interior

**Arthur D Little**

**FIGURE 4-8  
 TOTAL PAH CONCENTRATIONS CONTOUR MAP  
 SHELIKOF STRAIT AND OUTERMOST  
 COOK INLET**



**Figure 4-9: Vertical Profiles of Pb and Hg Values in Sediment Cores versus Time (Station identification in lower left hand corner)**



**Figure 4-10: Vertical Profiles of Cr and Cd Values in Sediment Cores versus Time (Station identification in lower left hand corner)**

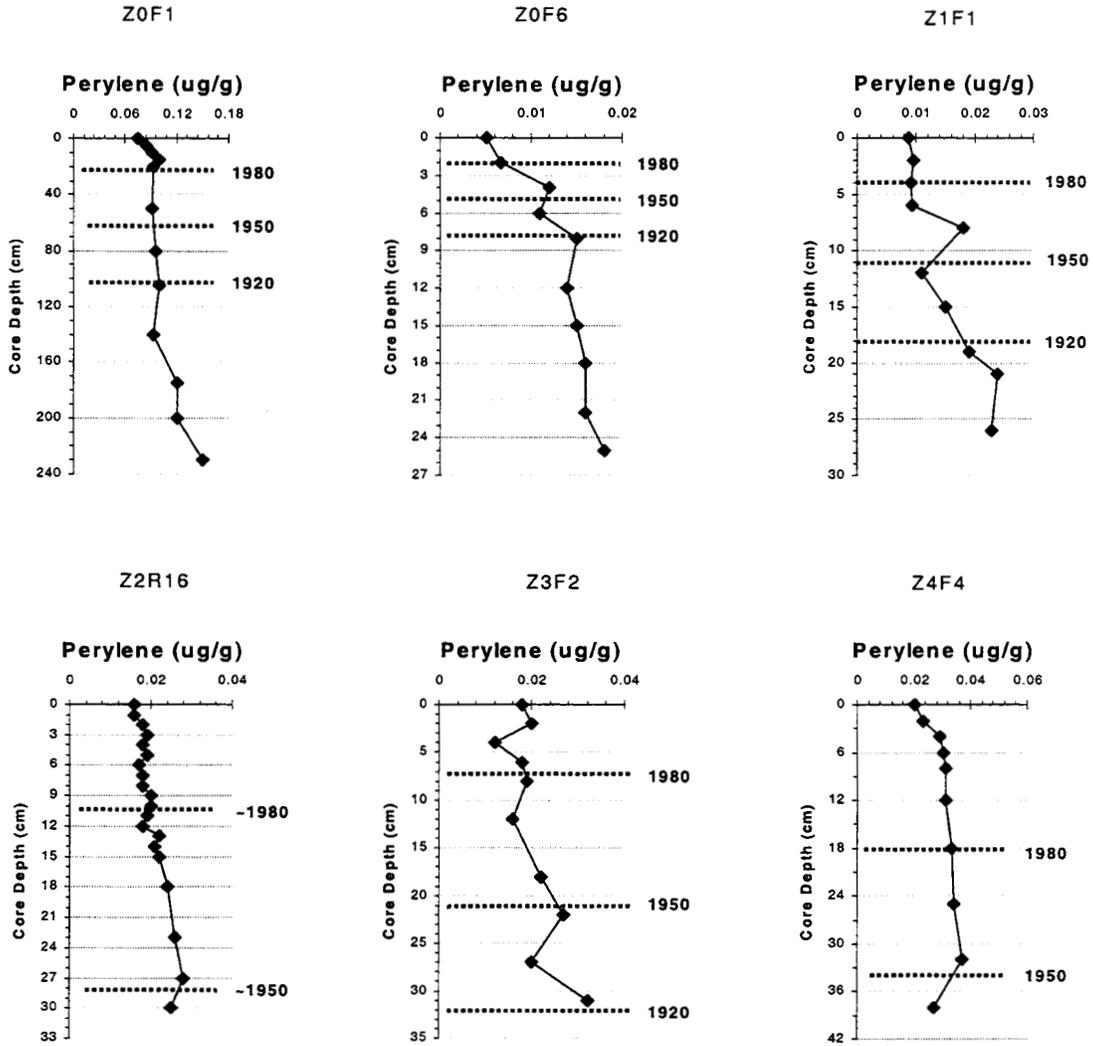
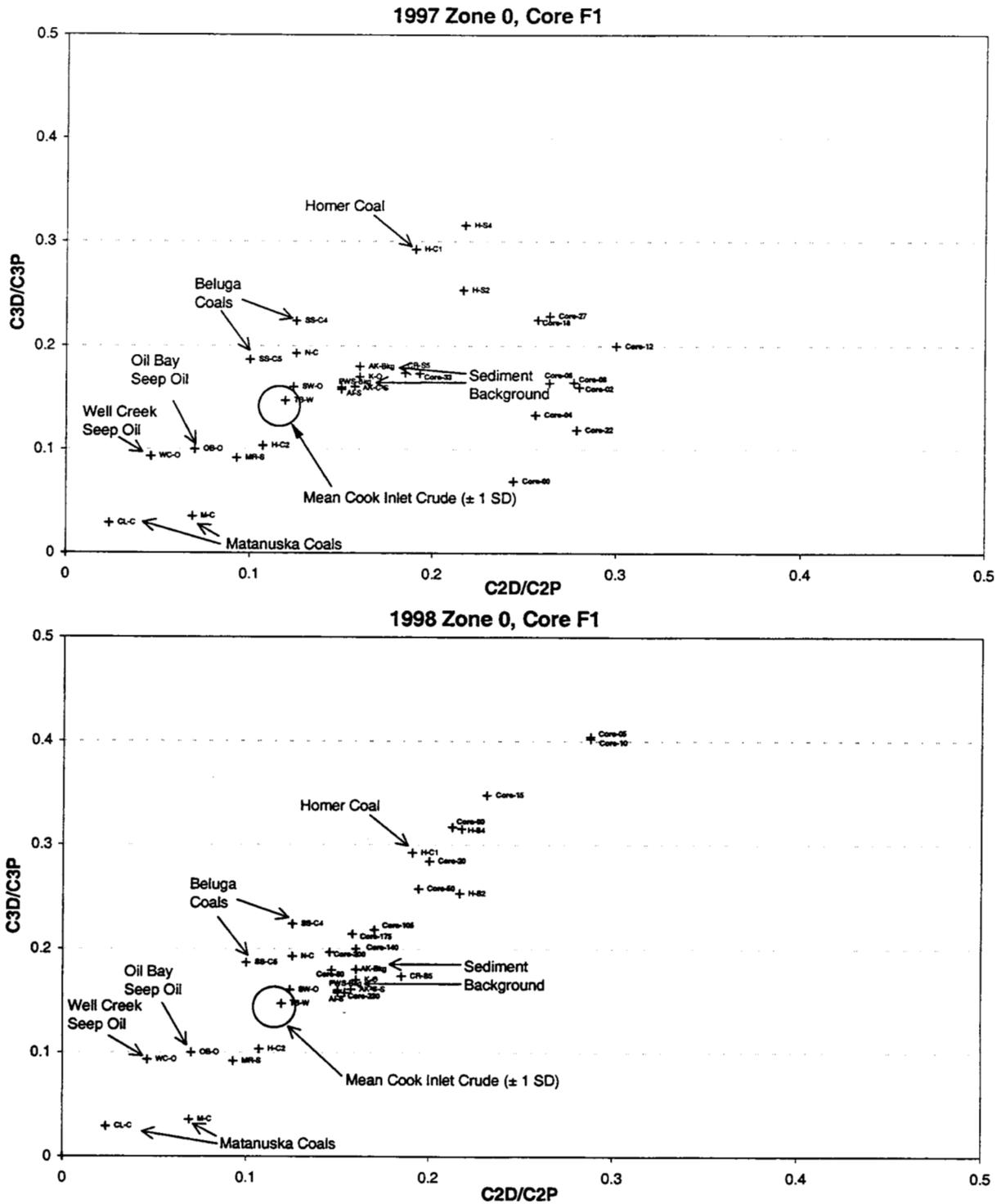


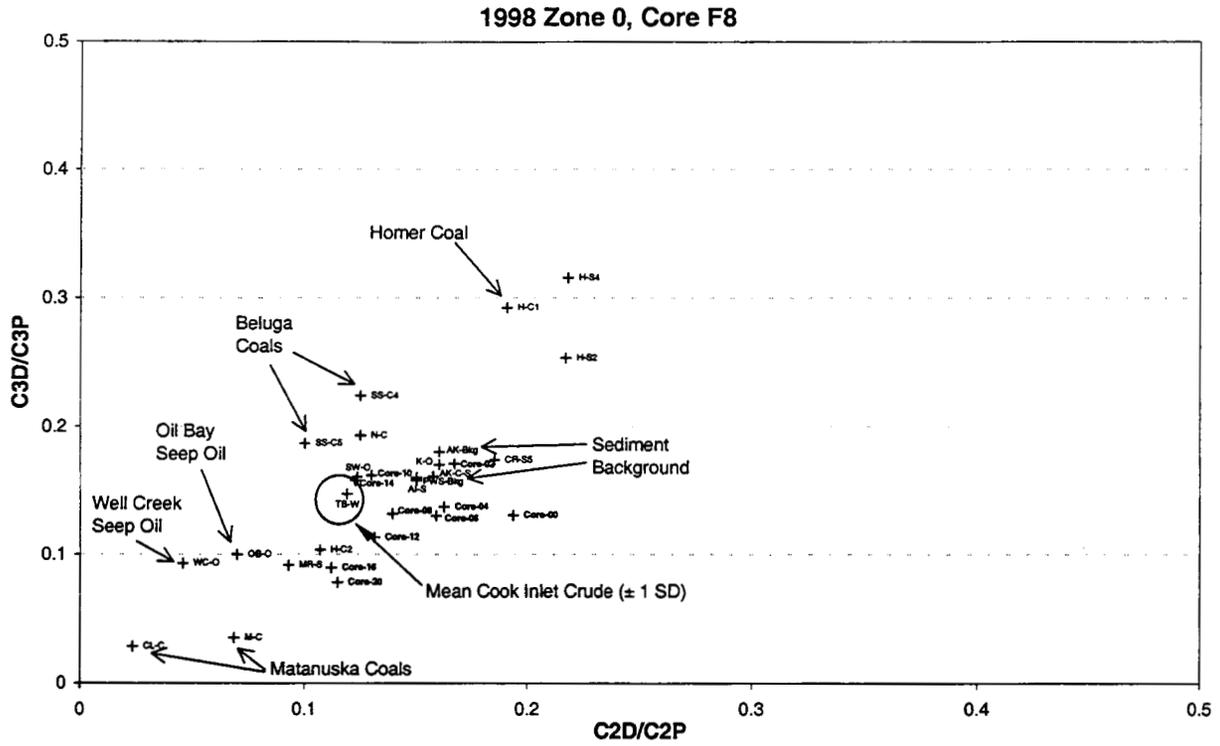
Figure 4-11: Sediment Core Profile of Perylene within each Zone.



**Figure 4-12: Double Ratio Plot of C2D/C2P versus C3D/C3P for Sediment Cores Z0F1 (Core-depth\*) and Sources (abbreviations are in Table 2-2).**

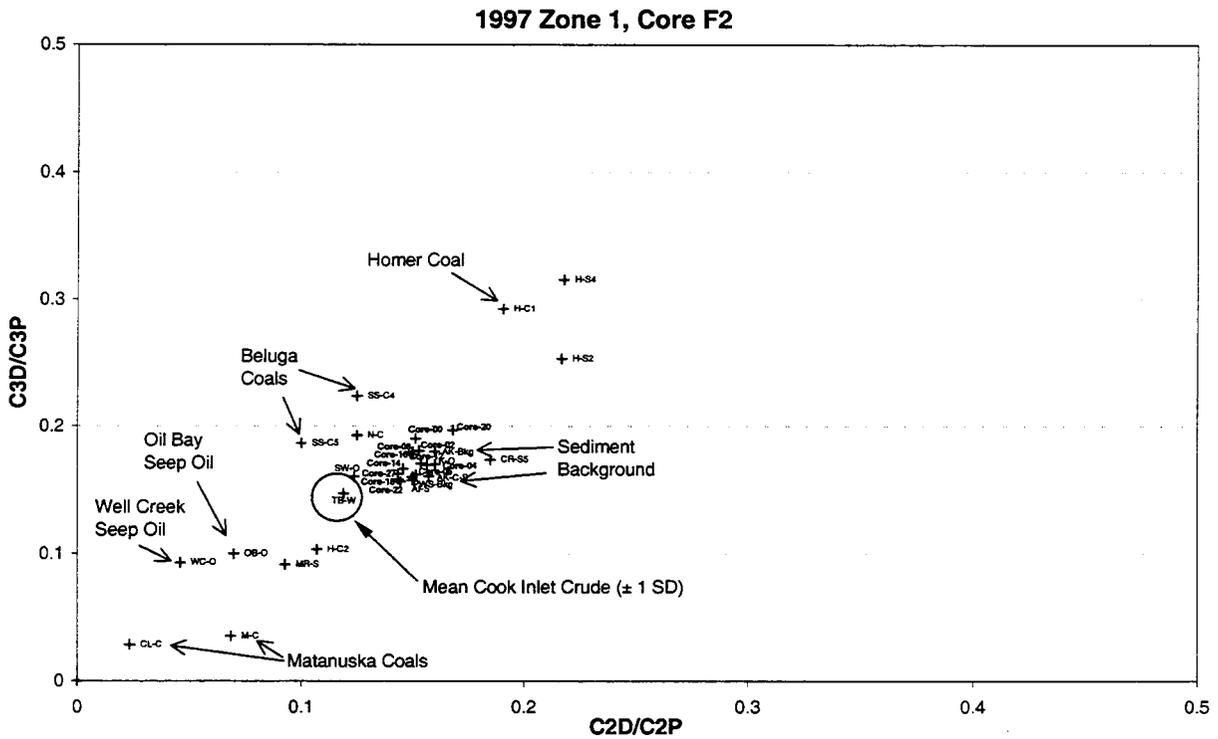
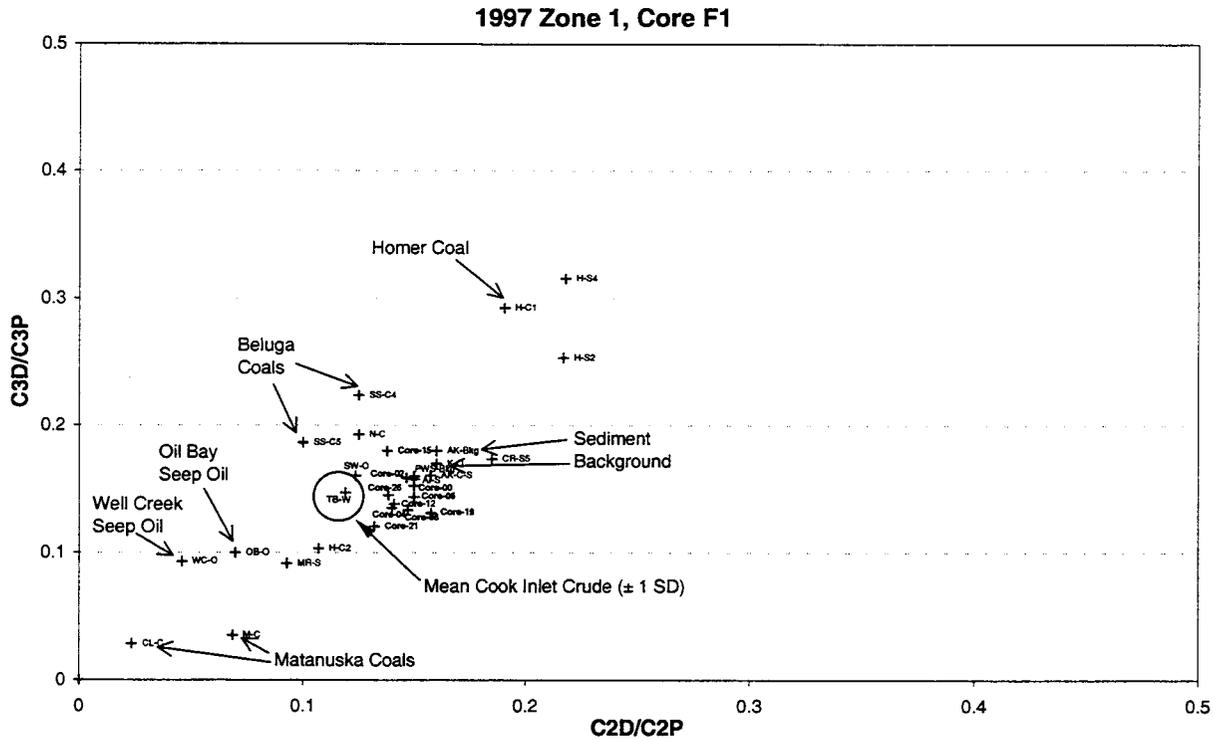
\* for example, Core-12 is the results for the core section taken at the 12 centimeter interval.





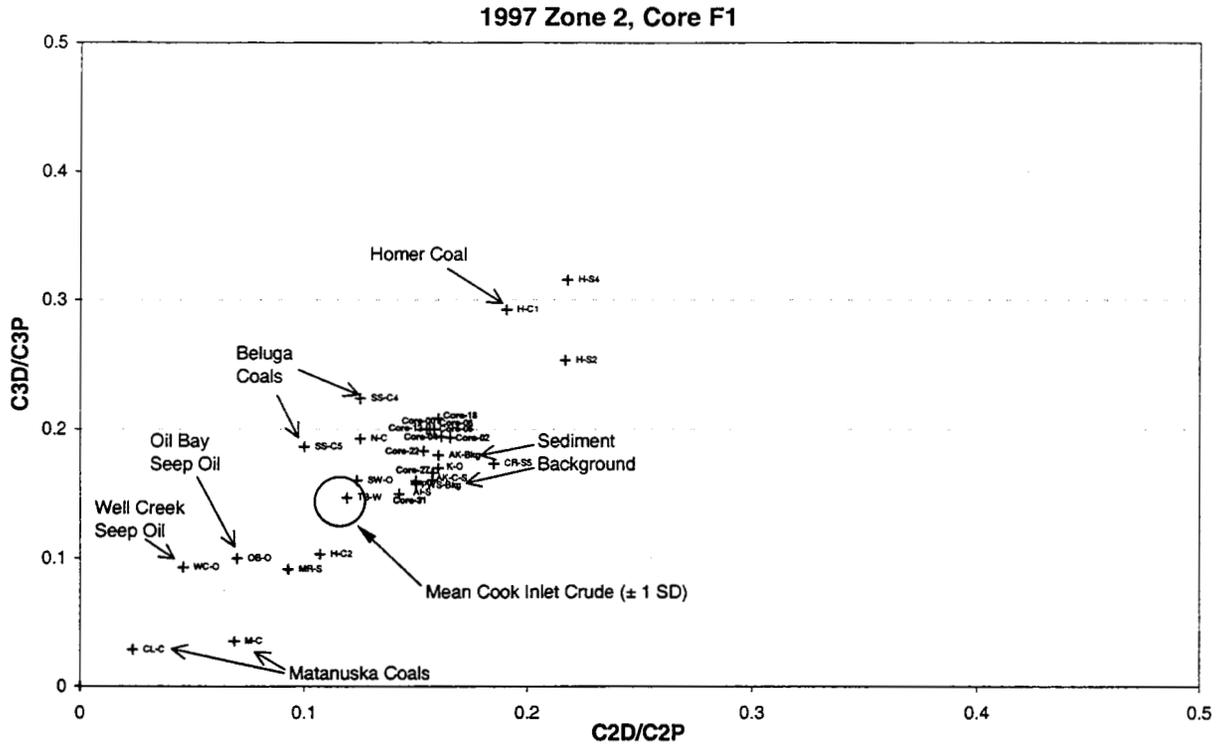
**Figure 4-14: Double Ratio Plot of C2D/C2P versus C3D/C3P for Sediment Core Z0F8 (Core-depth\*) and Sources (abbreviations in Table 2-2).**

\* for example, Core-12 is the results for the core section taken at the 12 centimeter interval.



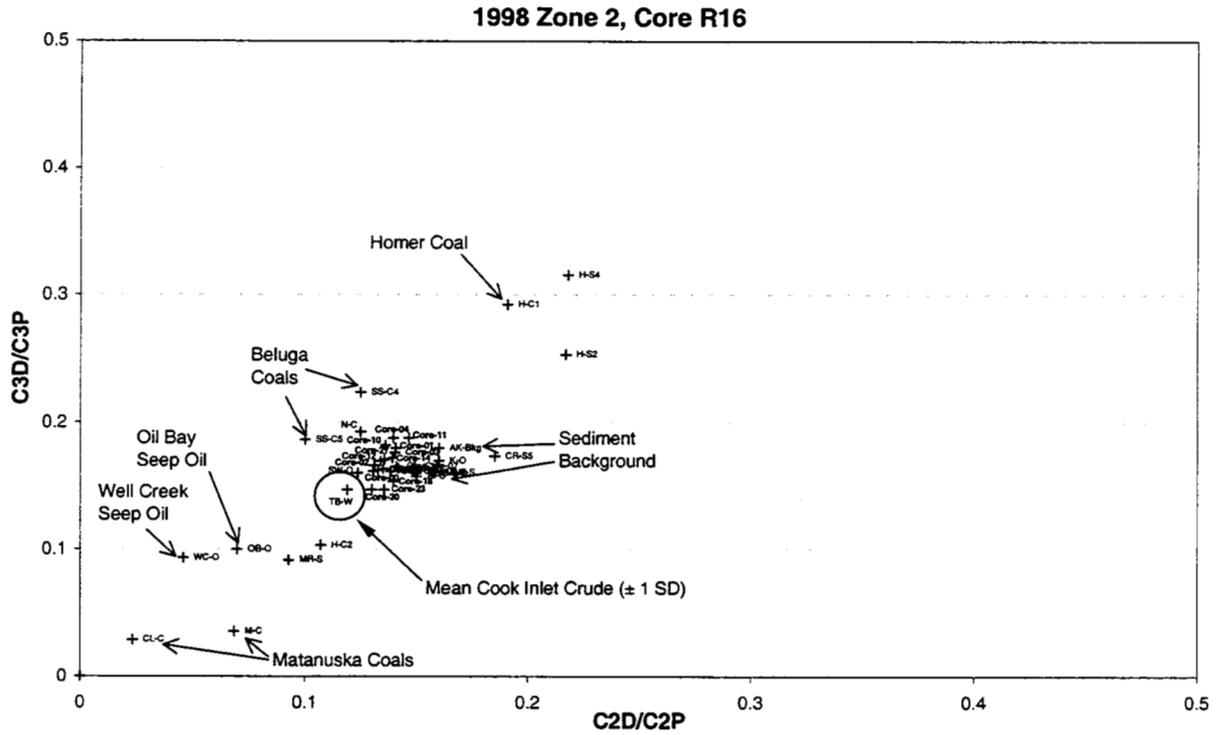
**Figure 4-15: Double Ratio Plot of C2D/C2P versus C3D/C3P for Sediment Cores Z1F1 (top, Core-depth\*), Z1F2 (bottom, Core-depth\*) and Sources (abbreviations in Table 2-2).**

\* for example, Core-12 is the results for the core section taken at the 12 centimeter interval.



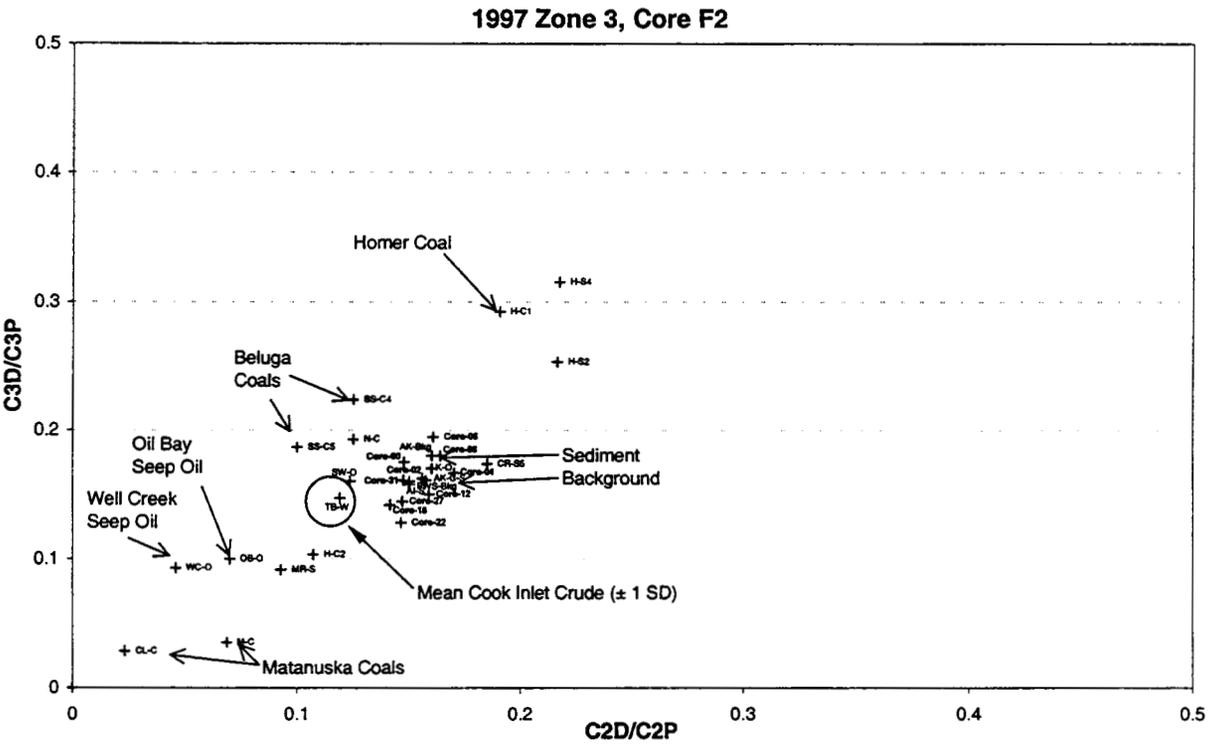
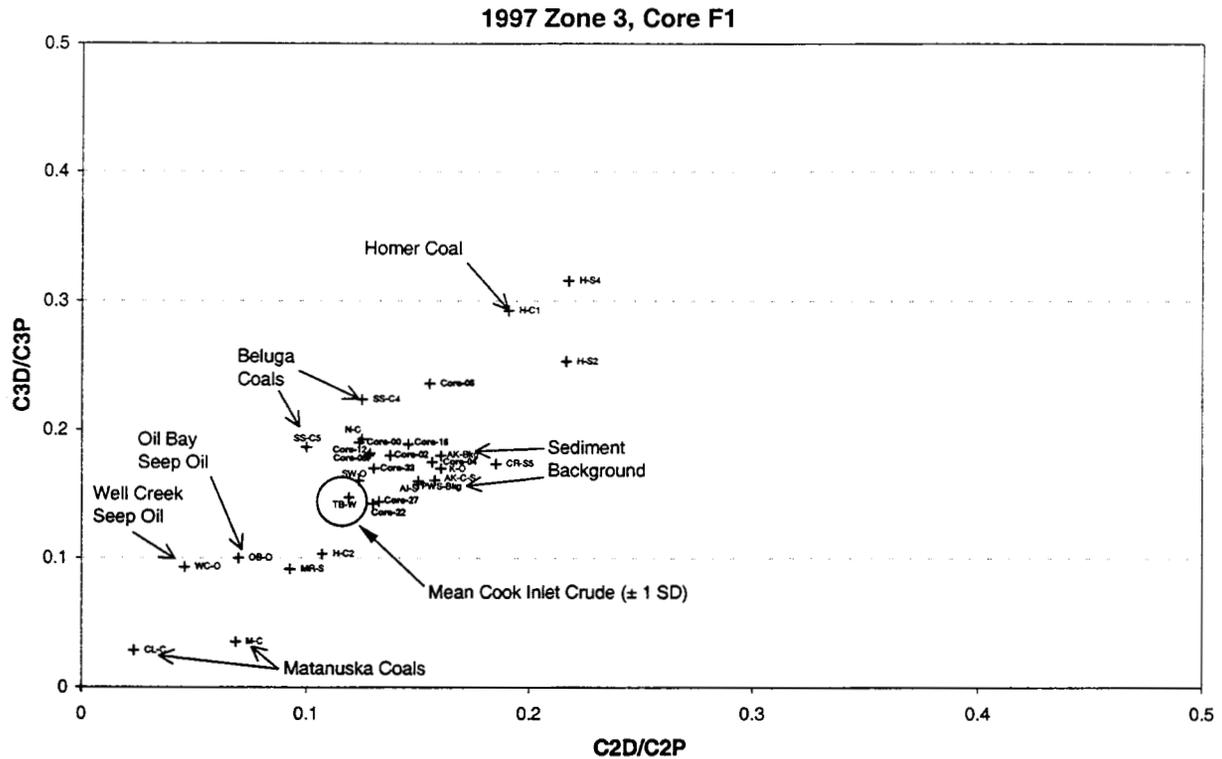
**Figure 4-16: Double Ratio Plot of C2D/C2P versus C3D/C3P for Sediment Cores Z2F1 (top, Core-depth\*), Z2F2 (bottom, Core-depth\*) and Sources (abbreviations in Table 2-2).**

\* for example, Core-31 is the results for the core section taken at the 31 centimeter interval.



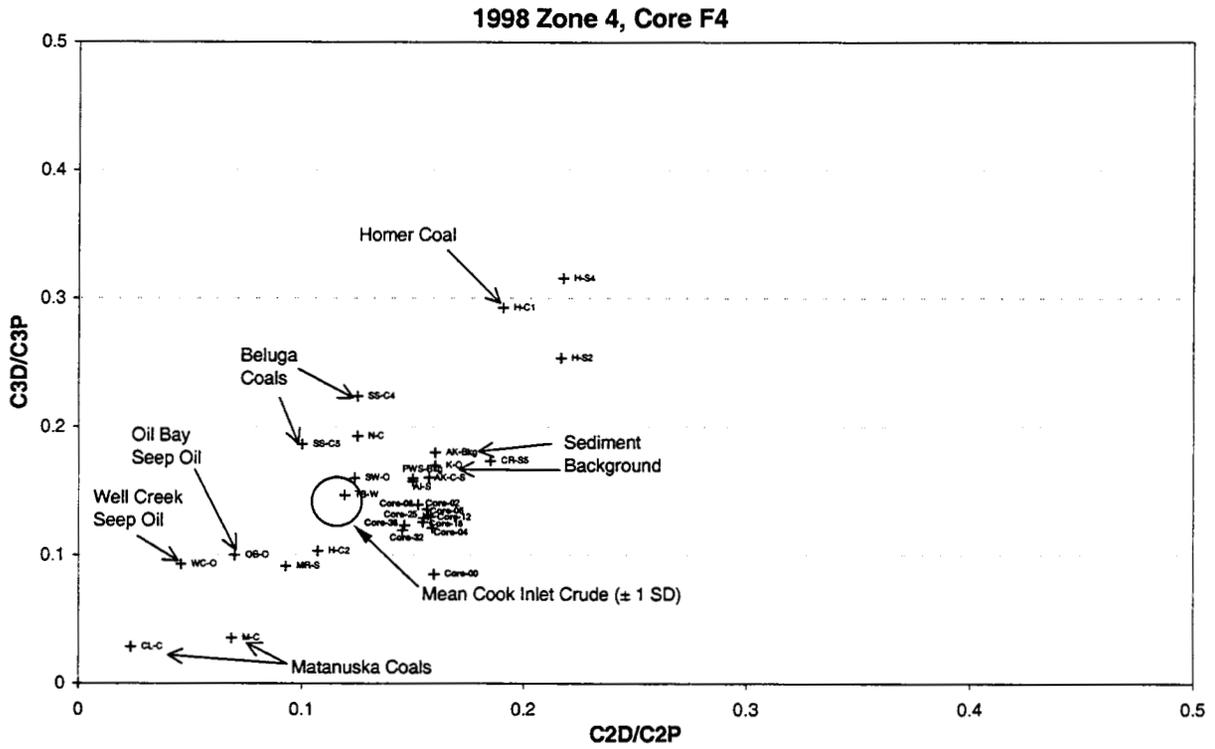
**Figure 4-17: Double Ratio Plot of C2D/C2P versus C3D/C3P for Sediment Core Z2R16 (Core-depth\*) and Sources (abbreviations in Table 2-2).**

\* for example, Core-30 is the results for the core section taken at the 30 centimeter interval.



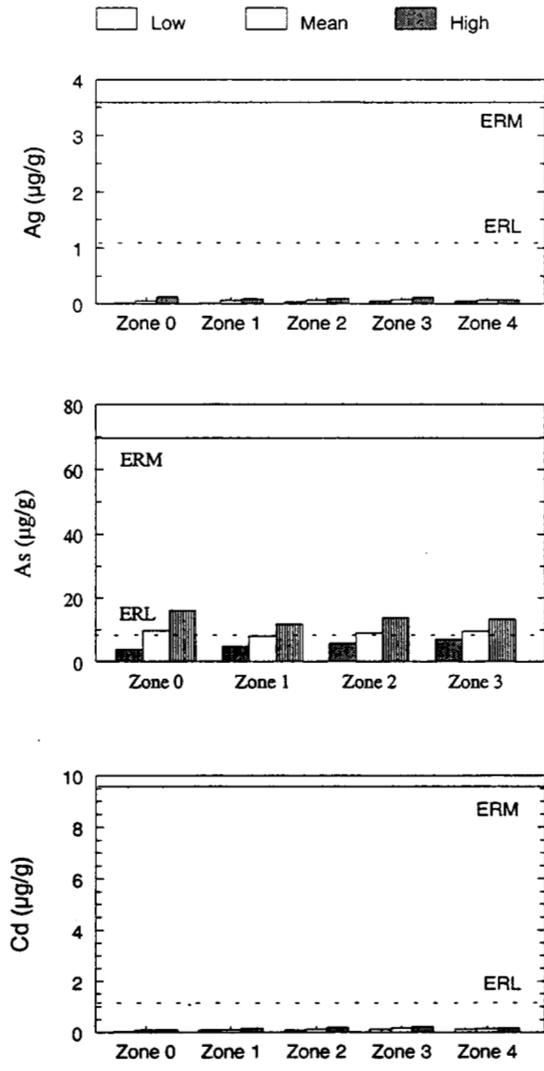
**Figure 4-18: Double Ratio Plot of C2D/C2P versus C3D/C3P for Sediment Cores Z3F1 (top, Core-depth\*) Z3F2 (bottom, Core-depth\*) and Sources (abbreviations in Table 2-2).**

\* for example, Core-05 is the results for the core section taken at the 5 centimeter interval.

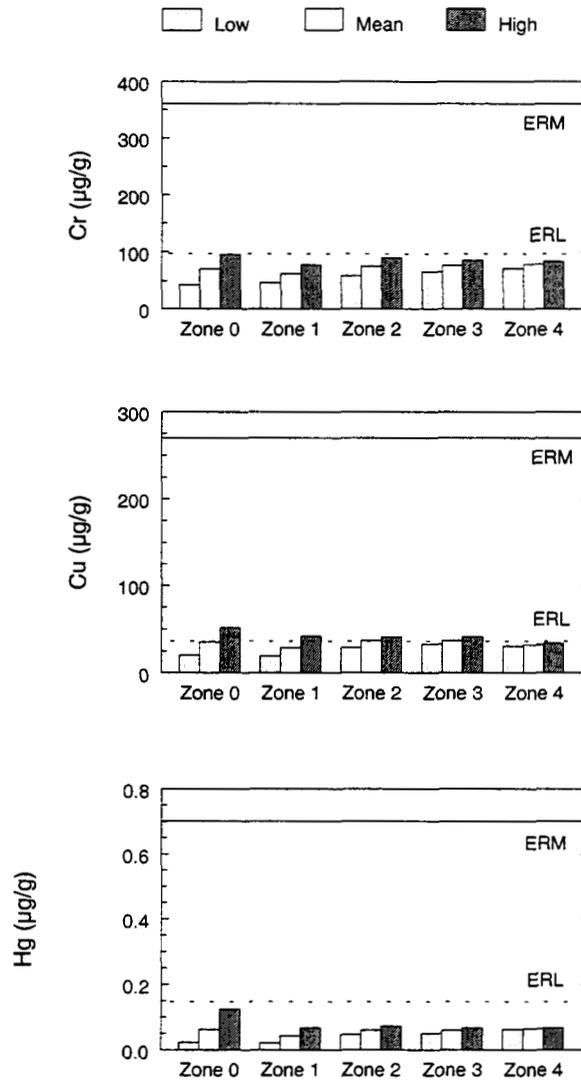


**Figure 4-19: Double Ratio Plot of C2D/C2P versus C3D/C3P for Sediment Core Z4F4 (Core-depth\*) and Sources (abbreviations in Table 2-2).**

\* for example, Core-32 is the results for the core section taken at the 32 centimeter interval.

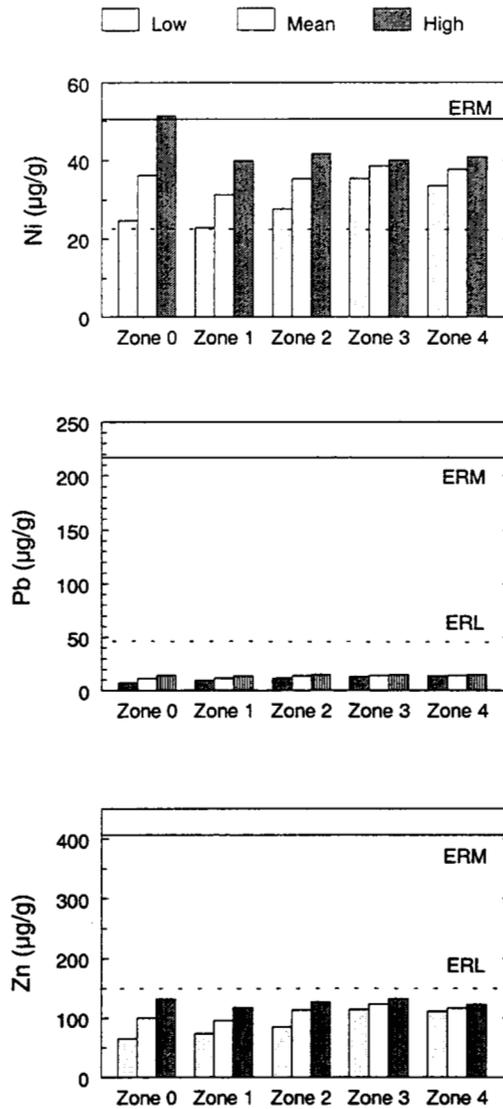


**Figure 4-20: Comparison of Minimum, Mean, and Maximum Concentrations of (a) Ag, (b) As, and (c) Cd for Surficial Sediments from Zones 0, 1, 2, 3 and 4 to the Effects Range Low (ERL) and the Effects Range Medium (ERM) Values (Long *et al.*, 1995).  
ERL = ----; ERM = \_\_\_\_\_**



**Figure 4-21: Comparison of Minimum, Mean, and Maximum Concentrations of (a) Cr, (b) Cu, and (c) Hg for Surficial Sediments from Zones 0, 1, 2, 3 and 4 to the Effects Range Low (ERL) and the Effects Range Medium (ERM) Values (Long *et al.*, 1995).**

ERL = ----; ERM = \_\_\_\_



**Figure 4-22: Comparison of Minimum, Mean, and Maximum Concentrations of (a) Ni, (b) Pb, and (c) Zn for Surficial Sediments from Zones 0, 1, 2, 3 and 4 to the Effects Range Low (ERL) and the Effects Range Medium (ERM) Values (Long *et al.*, 1995).  
 ERL = ----; ERM = \_\_\_\_\_**

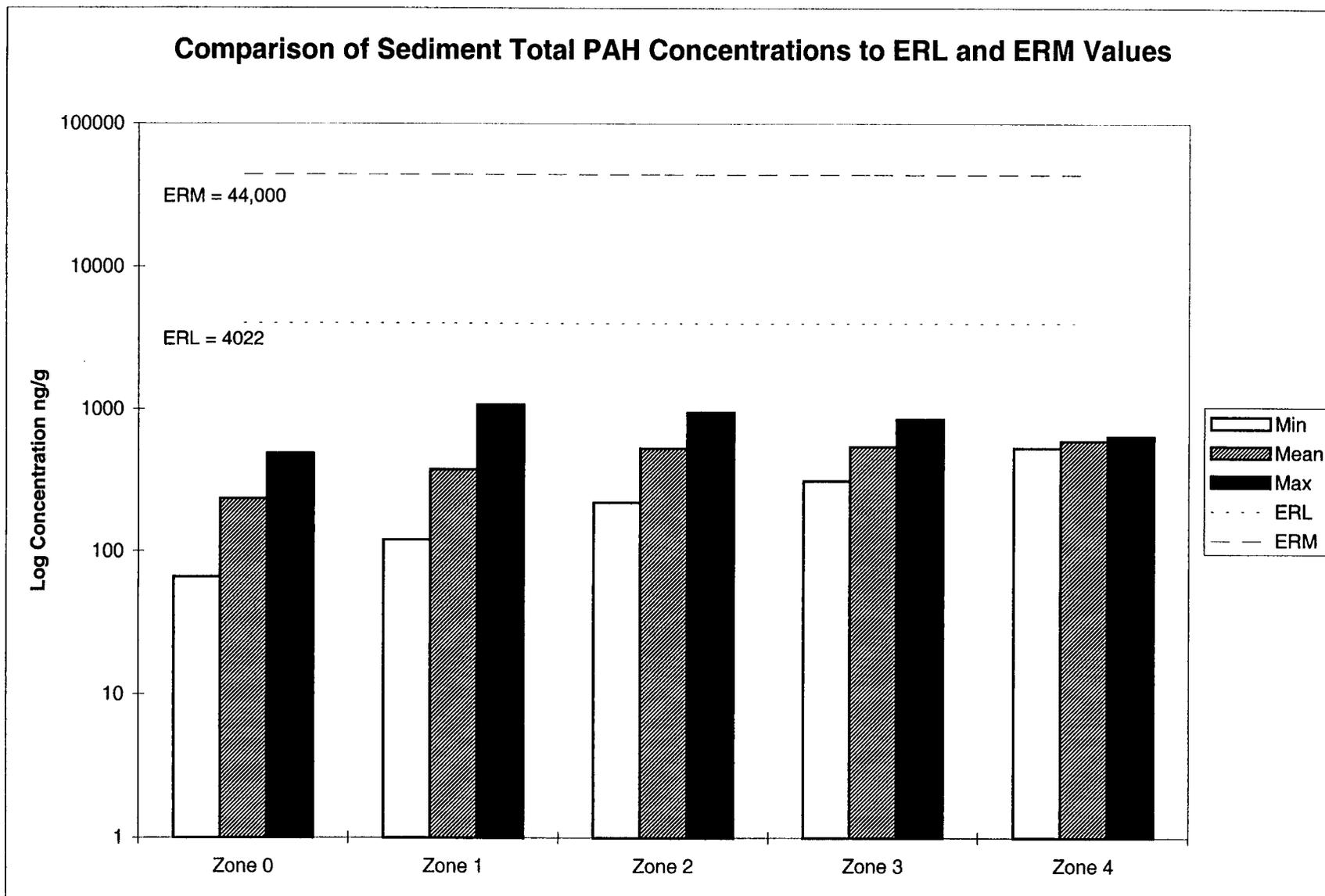


Figure 4-23: Comparison of Sediment Total PAH Concentrations to ERL and ERM Values (Long *et al.*, 1995).

**Table 4-1: Data for Sediment Deposition in Outermost Cook Inlet and the Shelikof Strait**

<b>Zone</b>	<b>Area (10<sup>12</sup> cm<sup>2</sup>)</b>	<b>Sediment Accumulation Rate (gcm<sup>-2</sup>y<sup>-1</sup>)</b>	<b>Total Sediment Deposition (10<sup>6</sup> tons y<sup>-1</sup>)</b>
0	70	0.12	8
1	39	0.24	9
2	37	0.60	22
3	45	0.35	16
4	20-40	0.40	8-16
<b>Total</b>	<b>211-231</b>	<b>--</b>	<b>63-71</b>

**Table 4-2: Metal/Metal Ratios for Bottom and Suspended Sediment from Area Rivers**

<b>Sample</b>	<b>Ni/Be</b>	<b>Fe/Zn</b>	<b>Sn/Sb</b>	<b>Pb/Tl</b>	<b>V/Zn</b>
<b>Susitna River</b>					
Bottom Sediment	25.3	340	1.32	24.8	1.13
Suspended Sediment	23.1	372	1.33	23.7	1.22
Average	24.2	356	1.32	24.2	1.18
<b>Knik River</b>					
Suspended Sediment	28.5	582	0.98	38.1	1.81
<b>Matanuska River</b>					
Suspended Sediment	0	318	1.83	37.0	1.06
<b>Average S-K-M Rivers (83:11:6)</b>	27.3	379	1.31	26.4	1.16
<b>Copper River</b>					
Bottom Sediment	34.4	516	2.24	35.4	1.78
Suspended Sediment	37.2	509	2.40	37.5	1.65
Average	35.8	512	2.32	36.4	1.72

**Table 4-3: Summary of Results from Model for Identifying Sediment Sources in Outermost Cook Inlet and the Shelikof Strait**

Sources	Zone	n	% S-K-M River*
S-K-M Rivers Copper River	Alaska Coastal Current Sediment	4	(0)**
	0 (excluding Z0F1)	7	78 ± 26
	1	14	75 ± 30
	2	17	81 ± 24
	3	10	87 ± 8
	4	10	84 ± 8
	0, 1, 2, 3, 4	58	81 ± 22

Notes:

\* Mean ± 2 standard deviations (i.e., 95% confidence interval)

\*\* Results suggest no inputs from S-K-M Rivers, but possible inputs from source(s) other than the Copper River.

## **5.0 Recommendations**

Based on the results and interpretation of the samples collected from the 1997 and 1998 outermost Cook Inlet and Shelikof Strait field surveys, there are a number of recommendations for future monitoring and scientific studies of the region.

### **Future Monitoring**

- Based on the results of this study, future monitoring of the sediments and biota of the area should be performed if new offshore oil exploration and production activities in the area are planned. In the absence of any oil exploration activities, a smaller, focused sediment and tissue program (chemistry and biology) could be performed over the next 5 to 10 years to confirm the trends reported in this study.
- Future monitoring in the area should include both intertidal and shallow subtidal depositional areas, and embayments (Kamishak Bay, Alaskan Peninsula, Kodiak, and Afognak) of outermost Cook Inlet and the Shelikof Strait. This would add to the baseline data generated for this program, which focused on the deep depositional areas.
- Future studies should include additional samples of seep oils and associated river/stream sediments from the Iniskin Peninsula and the Alaskan Peninsula. These samples would serve to confirm the historical hydrocarbon source relationships observed in this study and add new potential petroleum hydrocarbon sources for evaluation.

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## 7.0 Publications

*Sediment Quality in Depositional Areas of the Shelikof Strait and Outermost Cook Inlet. Sediment Profile Imaging Report.* Prepared by EVS Environmental Consultants under contract to Arthur D. Little, Inc. for U.S. Department of the Interior, Minerals Management Service, Anchorage, Alaska. OCS Study MMS 99-0003. 40 pp.

*Sediment Quality in Depositional Areas of Shelikof Strait and Outermost Cook Inlet, Final Literature Synthesis.* Prepared by Arthur D. Little, Inc. for U.S. Department of the Interior, Minerals Management Service, Anchorage, Alaska. OCS Study MMS 97-0015. 69 pp.



### **The Department of the Interior Mission**

As the Nation's principal conservation agency, the Department of the Interior has responsibility for most of our nationally owned public lands and natural resources. This includes fostering sound use of our land and water resources; protecting our fish, wildlife, and biological diversity; preserving the environmental and cultural values of our national parks and historical places; and providing for the enjoyment of life through outdoor recreation. The Department assesses our energy and mineral resources and works to ensure that their development is in the best interests of all our people by encouraging stewardship and citizen participation in their care. The Department also has a major responsibility for American Indian reservation communities and for people who live in island territories under U.S. administration.



### **The Minerals Management Service Mission**

As a bureau of the Department of the Interior, the Minerals Management Service's (MMS) primary responsibilities are to manage the mineral resources located on the Nation's Outer Continental Shelf (OCS), collect revenue from the Federal OCS and onshore Federal and Indian lands, and distribute those revenues.

Moreover, in working to meet its responsibilities, the **Offshore Minerals Management Program** administers the OCS competitive leasing program and oversees the safe and environmentally sound exploration and production of our Nation's offshore natural gas, oil and other mineral resources. The **MMS Royalty Management Program** meets its responsibilities by ensuring the efficient, timely and accurate collection and disbursement of revenue from mineral leasing and production due to Indian tribes and allottees, States and the U.S. Treasury.

The MMS strives to fulfill its responsibilities through the general guiding principles of: (1) being responsive to the public's concerns and interests by maintaining a dialogue with all potentially affected parties and (2) carrying out its programs with an emphasis on working to enhance the quality of life for all Americans by lending MMS assistance and expertise to economic development and environmental protection.