Technical Evaluation of the Environmental Monitoring Program for Cook Inlet Regional Citizens Advisory Council

Submitted by:

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Table of Contents

List of Tables

List of Figures

Executive Summary

Background and Purpose of the CIRCAC Environmental Monitoring Program

The Cook Inlet Regional Citizens Advisory Council (CIRCAC), a citizen's oversight council for oil industry operations in the Cook Inlet region, was established according to Section 5002 of the Oil Pollution Act of 1990 (OPA '90). One of the CIRCAC mandates is to conduct monitoring to assess environmental impacts of oil industry operations in Cook Inlet. To this end, the CIRCAC Environmental Monitoring Committee (EMC) was formed in 1991 and initiated steps to develop and manage an Environmental Monitoring Program (EMP) for Cook Inlet. Based on a 1992 model recommended by Cook Inlet RCAC contractors, a pilot study was initiated in 1993 to provide data as a baseline for conducting longer-term environmental monitoring. Additional environmental monitoring studies were conducted annually from 1994 through 1997. The major objective of the EMP has been to determine if operations associated with the oil industry in Cook Inlet are having adverse effects on the surrounding ecosystem. These studies were also intended to document the sources, magnitude, and spatial and temporal trends of any observed impacts.

Overall Goal of Technical Evaluation

The goal of this evaluation project is to analyze and synthesize the existing data and to provide guidance to CIRCAC in developing a strategy and scope for the future sampling and analytical programs comprising its EMP.

This report provides a technical evaluation of the EMP. It is based on the results of the studies conducted from 1993 to 1997. Conclusions and interpretations of the data also take into account data from recent or continuing studies by the EPA and MMS that were not available when this program was initially designed. Specific objectives of this evaluation are to:

- Summarize the existing EMP data contained in various annual reports into one technical report.
- Evaluate the specific methods (e.g., toxicity testing and analytical chemistry procedures) and environmental monitoring approaches (e.g., the Sediment Quality Triad) used during the EMP.
- Evaluate the effectiveness of the existing data for use as a baseline against which future chronic or acute oil-industry impacts can be measured.
- Recommend a strategy and methods for further environmental monitoring efforts to assess temporal and spatial oil-industry impacts to the Cook Inlet ecosystem.

An additional goal of this evaluation was to assess the physical range of the plumes from industrial discharges into Cook Inlet by modeling dilution and distance from point-sources. The objective for this exercise was to provide insight into maximum area of potential impact from the discharges from oil and gas facilities. The relevant question was, given dispersion and dilution conditions in the upper inlet, how far away from the respective discharges might one expect to be able to detect the hydrocarbons released from those discharges using state-of-the-art detection limits. This information was desired to help focus future sampling programs and direct the selection of sampling methods, target organisms, and sampling locations.

Description of Environmental Monitoring Program Approach, 1993-1997

The principal strategy used to drive the monitoring program was the Sediment Quality Triad (SQT) approach, which is structured to determine if:

- Contaminants exist in the sediments or water at measurable concentrations;
- Concentrations of contaminants found in the sediments can potentially cause mortality or sublethal (chronic) effects to organisms that might be exposed to them; and
- Organisms living in the areas at risk exhibit ecological or biological indications of having been exposed to the potential contaminants.

The SQT is not designed to develop a functional understanding of baseline conditions for all biological resources in an area of concern, nor is this a primary goal of the EMP.

The EMP was initially designed to detect whether contaminants contained in permitted discharges from the oil industry were accumulating in the inlet and, if so, whether they were affecting or could affect organisms at various trophic levels. Due to the extremely high sediment loads in the areas of Cook Inlet where oil industry operations are concentrated, and because many of the chemical compounds found in industry discharges are known to adsorb strongly onto the surface of sediments, the EMP focused mainly on collecting subtidal samples from areas of potential deposition. This was an attempt to determine whether sediment-sorbed contaminants are accumulating in depositional areas downstream of oil industry operations.

The EMP consistently measured polynuclear aromatic hydrocarbons (PAH) in sediments. PAH in tissues of mussels and clams were also measured during several years. Sediment toxicity was evaluated during most years using a variety of tests with differing sensitivity. Aliphatic hydrocarbons (AHC) and trace metals were measured in only two surveys. In the first years of the EMP, semipermeable polymeric membrane devices (SPMDs or "lipid bags") and mussels in cages were suspended in the water column to measure concentrations of petroleum hydrocarbons from produced water discharges. In later surveys, fish, mussels, and clams were collected once to evaluate exposure to petroleum hydrocarbons through examination of biomarkers in tissues.

Secondary variables measured to support interpretation of the hydrocarbon measurements and toxicity testing data included total organic carbon (TOC), sediment particle grain size, lipid content in blue mussel (*Mytilus*) tissues, shell characteristics (length and volume) for mussels and clams (*Macoma*); and weight of total tissue for the mussels.

Summary of the Results of the CIRCAC Environmental Monitoring Program

Geographic and Temporal Coverage by the Environmental Monitoring Program

During the five years of the Environmental Monitoring Program (1993 through 1997), sediment and/or tissue samples were collected at 87 different sites distributed in eight general areas (Table 1-1), i.e., seven in Cook Inlet and one in northwestern Shelikof Strait. The number of sites sampled and the number of years in which sampling occurred varied among the areas. Sampling generally occurred annually during midsummer.

Sampling areas were selected to represent conditions upstream and downstream of, and proximate to, the most intensive oil industry activities, and in areas where deposition of fine-grained sediments was known or suspected to occur. Additionally, areas known to be environmentally sensitive or important foraging areas for seabirds were included.

Sediment and tissue samples were collected from upper Cook Inlet upstream (based on net flow rather than tidal currents) of the discharges (the Beluga region); areas where effluents were discharged (Trading Bay and the Forelands area); the lower inlet, including two embayments on the west side of Cook Inlet (Tuxedni and Chinitna Bays); Kamishak Bay; Kachemak Bay; southern lower Cook Inlet (the "Null Zone"); and northwestern Shelikof Strait (Capes Douglas, Nukshak, and Chiniak).

Activity	Sampling Period: 1993	1994	1995	1996	1996	1997	1997
	Type or Name of Program: Pilot Monitoring Program						
	Phase 1; 4 regions	Phase 2; 1 region, 3 sites	Environmental Monitoring Program; 4 regions	Lake Clark Bivalve Program; 1 region, 9 sites	Shelikof Strait Program, 1 region	Cook Inlet Sediment Toxicity & Hydrocarbon Study, 3 regions	Kenai River Estuary Sediment Character-ization
	Regions Sampled: Upper Cook Inlet, Trading, Kamishak, and Kachemak Bays	Granite Point, Trading Bay, and East Forelands	East Forelands, Trading Bay, "Null Zone", Kachemak and Kamishak Bays	Tuxedni and Chinitna Bays	Capes Douglas, Nukshak, and Chiniak	East Forelands, Trading, Kamishak, and Kachemak Bays	Kenai River estuary, delta, and N and S of river mouth
	Depth Stratum Sampled: Subtidal	Subtidal	Subtidal	Intertidal	Intertidal and Subtidal	Subtidal	Subtidal
Sediment							
Sediment PAHs (Total and alkylated homologs)	12	18	15		9	12	12
Sediment Aliphatic Hydrocarbons					9	12	12
Sediment Trace Metals					9		
Sediment Grain Size	12	18	15		9	12	12
Total Organic Carbon	12	18	15		9	12	12
Lipid Bag Sampling for PAH in Water Column	2	3	3				
Mytilus							
Mussel Watch - PAH Burdens in *Mytilus*	2						
PAH Burdens in Resident *Mytilus*					9		
Trace Metals Burdens in Resident *Mytilus*					9		
Physiological Condition of *Mytilus*	2				9		
Lipid Content in *Mytilus* Tissues					9		
Macoma							
Population Density and Condition of *Macoma*	6		15	9			
PAH Burdens in *Macoma* spp. Tissues	6			9			
Trace Metals Burdens in *Macoma* spp. Tissues				9			
Various Bivalves							
Population Density and Condition of Various Benthic Bivalves			11				
Toxicity Testing							
Sediment Toxicity - *Ampelisca abdita*	12	18				12	
Echinoderm Larval Development						12	
Microtox Testing of Sediments			15		9	12	
P450 Reporter Gene System Sediment Testing					9	12	
Bioaccumulation/Bile Metabolites							
P4501A Reporter Gene System Fish Tissue Testing			2				
P450 Reporter Gene System Bivalve Tissue Testing				5	9		
Bile Metabolites & Liver Enzyme Induction Analyses			2				
Contractor	A. D. Little	A. D. Little	Kinnetic Labs	Kinnetic Labs	Kinnetic Labs	Kinnetic Labs	Kinnetic Labs

Table 1-1 Summary of monitoring tasks and activities conducted during the CIRCAC Environmental Monitoring Program

General Sampling Strategy

The EMP examined 12 lines of evidence for tracking hydrocarbon contributions and impacts from oil and gas activities in the inlet. These include:

1) PAH concentrations in sediments;

2) aliphatic hydrocarbon concentrations in sediments;

3) PAH concentrations in SPMD as an indication of hydrocarbons in the water column;

4) PAH concentrations in mussel tissues;

5) PAH concentrations in *Macoma* tissues;

6) toxicity tests on amphipods;

7) toxicity tests using echinoderm larval development;

8) Microtox testing;

9) P450 reporter gene system assays of sediments;

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11) P4501A assays of halibut liver; and,

12) analyses of halibut tissues for bile metabolites and liver enzyme induction, which indicate exposure to hydrocarbons.

Table 1-1 summarizes which approaches were used during each of the five field seasons. The various approaches address the question of potential hydrocarbon contamination from the three principal directions dictated by the Sediment Quality Triad. Approaches 1 through 3 are useful primarily for determining if the contaminants exist in the sediments or water at measurable concentrations. Approaches 6 through 9 address whether or not the concentrations of a contaminant found in the sediments could potentially cause mortality or sublethal (chronic) effects to organisms that might be exposed to them. Finally, the remaining five approaches (4, 5, 10, 11, and 12) are useful for determining if organisms living in the areas at risk exhibited indications of exposure to the potential contaminants. These elements basically fulfill the needs of the Sediment Quality Triad strategy.

Patterns Observed in Environmental Monitoring Program Studies

The CIRCAC Environmental Monitoring Program employed a diverse suite of sampling and analytical methodologies to examine a wide variety of potential indicators for oil contamination in the inlet and in northwestern Shelikof Strait. Results to date indicate the following:

Analytical Methods

Switching laboratories, extraction methodologies, and contractors midway through the program has not had a significant negative impact on data quality or data comparability

- minor differences with alkyl-substituted PAH ratios have been noted, and they can affect Double Ratio plots when trying to identify and resolve very subtle differences in potential sources.

Sediment Hydrocarbon Burdens

- Sediment samples exhibit extremely low levels of PAH (40-50 times below NOAA ERL concentrations)

  1. the sources are varied and mixed, but they cannot be directly attributed to Cook Inlet oil and gas development operations.
  2. no evidence of EVOS or ANS oil was observed in any of the subtidal sediments (including Shelikof Strait).

- The modeling efforts presented in this report describe the mechanisms responsible for the weakness of the hydrocarbon signal in Cook Inlet. Studies conducted in 1993 by the University of Alaska for the Minerals Management Service (MMS), and currently by MMS and the U.S. Environmental Protection Agency corroborate this finding.

- The sediments do not contain adequate concentrations of hydrocarbon to cause mortality or sublethal effects to organisms exposed to them.

- No relationship was observed between toxicity and PAH concentrations in sediments in the entire suite of toxicity tests. Toxicity tests using amphipods and echinoderm larvae showed significant toxicity in several cases, but these effects appeared related to other environmental factors such as concentration of fine sediments or ammonia rather than PAH.

Tissue Hydrocarbon Burdens

- Subtidal organisms living in the region have neither been accumulating nor exposed to high levels of hydrocarbons from Cook Inlet oil and gas activities.

- In a few instances, minimal exposure of intertidal organisms to petroleum products has occurred:

  1. extremely weathered EVOS residues plus fresh diesel were encountered in mussels at one site in Shelikof Strait.

  2. mixtures of diesel and very low-level combustion-derived (pyrogenic) hydrocarbons were noted in tissues of *Macoma balthica* from Tuxedni Bay.

  3. fresh oil seep signals (natural sources) were possibly observed in tissues of *Macoma balthica* from Chinitna Bay.

  4. analytical or procedural artifacts contribute to and interfere with many of the low-level PAH analyses in tissues.

Hydrocarbon Sources

- Subtidal coal outcrops or river-borne particulate coal from terrestrial sources may contribute significant levels of PAH to the sediments throughout the region.

- Total naphthalenes/TPAH ratios tend to increase with sand-sized particulates suggesting a particulate coal-derived source for much of the PAH observed in the sediments.

- Samples from up the Kenai River show a PAH signature similar to samples from other areas in the inlet. These upriver samples from terrestrial sources most likely represent erosion of coal deposits in the watershed area.

- Very few of the low-level PAH signatures for either sediments or tissues could be directly tied to specific sources; the samples suggest either undocumented sources or mixtures from multiple sources.

Water Column Hydrocarbons

- Deployment of caged mussels near produced water discharge outfalls failed to show any evidence of PAH accumulation but this could have been due to extreme stress in the deployed mussels due to high suspended-particulate loads or other environmental factors.

- Despite technical difficulties, SPMDs did show evidence of a produced water PAH signal in the Trading Bay area and what was presumably a weathered diesel signal in Kachemak Bay.

- Numerous procedural blank and method development problems still plague the SPMD approach.

In summary, it appears, based on the overwhelming weight of evidence from the many aspects of the EMP, that hydrocarbon contamination or effects related to hydrocarbon exposure are either lacking or, if observed, occurred at levels very near the detection limit for the particular approach. Ninety-nine percent of the observations found no evidence of contamination from oil activities in Cook Inlet or effects that could be related to hydrocarbon concentrations in the sediment. The only methodology that exhibited a relevant response was the SPMD (lipid bag) when arrays were placed near the produced water discharge in Trading Bay. Some approaches exhibited responses to environmental factors, but none exhibited a significant correlation with petroleum hydrocarbons.

Evaluation of Program Approaches

When the EMP program began in 1993, there was a distinct paucity of data on hydrocarbon levels in Cook Inlet. The Environmental Monitoring Committee (EMC) had

to decide how, what, and where to sample for optimal evaluation of whether the Cook Inlet oil industry was affecting the environment. In view of its concern about the fate of contaminants discharged into sediment-laden waters, and given its limited annual budget, the EMC appropriately placed its initial focus on determining whether petroleum hydrocarbon contaminants were accumulating in sediments or representative organisms. The Sediment Quality Triad approach is a scientifically accepted method used in national programs for monitoring pollutant effects in the environment.

The EMP has provided researchers and managers with significant data that were not previously available from other sources. Specifically, PAH concentrations were measured throughout the program area. These measurements have provided valuable information on patterns of accumulation and sources of hydrocarbons in the inlet. The total sampling effort, however, was relatively small and the physical characteristics (such as current and sediment deposition rates) varied considerably among the areas sampled. Since the inception of the EMP, however, several federal agencies have contributed significant funds towards analyzing whether oil industry contaminants are presently or were historically accumulating in Cook Inlet or downstream areas. These data were incorporated into the current evaluations.

After five years of EMP studies, corroborating evidence from the current MMS Program and this study's dilution modeling results indicate that the traditional SQT concept no longer seems the most effective monitoring approach. Toxicity tests generally yielded negative results. The suite of toxicity tests did show some toxic responses, but they appear unrelated to hydrocarbon contaminants. The viability of the mussels in the mussel-watch arrays was poor under the harsh conditions characteristic of the upper inlet. Nevertheless, these experiments still provided useful information. SPMDs acquired some signal but technical problems limited interpretation. Mussels also showed a signal but since they are not found naturally in the upper and middle inlet, they were only collected from the northwestern Shelikof Strait. The EMP collected clams (*Macoma balthica*), an important forage species for several migrating seabirds and numerous fish species, from two intertidal areas of Cook Inlet. However, PAH body-burden measurements in subtidal species failed when, despite much effort, inadequate numbers were collected.

While the EMP provided no real time-series data, several general areas were visited more than once; the latter results were similar to those found during previous visits. However, the data are not usable for statistical comparisons among years. Furthermore, because all sampling has occurred during the summer, no seasonal comparisons can be made. Given the results of the study, however, we do not expect that concentrations of the chemicals or toxicity measured during the EMP would have significant seasonal differences. In summary, while there have been inconsistencies and lack of continuity in the program during the past five years as CIRCAC has tried various methods and altered sampling emphasis from year to year, the overall results indicate little or no adverse water column or benthic impacts from oil-and-gas development activities to date.

Recommended Changes in Program Strategy

Based on our evaluation of the data from the EMP and on the results of other ongoing studies in Cook Inlet, we have several recommendations for strategic changes to the program:

1) Continue to measure hydrocarbon concentrations, but consistently sample for aliphatics, PAHs, and specific chemical biomarkers such as steranes and triterpanes.

2) Replace toxicity testing with the more specific P4501A assay on tissues of resident organisms except for specific cases where contaminant levels begin to appear suspect. Toxic impacts were rare during the EMP and did not correlate well with PAHs. Moreover, it is difficult to differentiate between toxicity in response to target contaminants and other unmeasured contaminants.

3) Replace the strategy of absolute random sampling within regions with a modified stratified random strategy. Monitoring an area such as Cook Inlet, which is highly variable in bathymetry and physical environment, can only be effective by one of two approaches: 1) establish permanent monitoring sites and revisit those locations repeatedly through time; or 2) if a total random sampling design is desired, sample at enough stations to account for the high degree of variability observed within the regions. Random sampling within a general area (e.g., Trading Bay) has an unknown (presumably large) component of variance that will usually confound the results.

4) Replace subtidal sampling with intertidal sampling. Extensive baseline data for hydrocarbons and trace metals will soon be available for depositional areas in Cook Inlet through the MMS program. Focus instead on areas that are most likely to be affected in the event of spilled oil. Collective experience at oil spills suggests that intertidal assemblages have a greater likelihood of exposure to hydrocarbons than subtidal assemblages.

5) Focus the sampling program on soft-substrate habitats. In Cook Inlet, intertidal soft-bottom biological assemblages are far more uniform than subtidal assemblages, and intertidal sampling programs are easier to design and more cost effective. Moreover, they support large long-lived populations of potential target species.

6) Identify the most suitable biological target species for use as sentinel organisms. This may require additional surveys of intertidal assemblages. Robust populations of the razor clam (*Siliqua patula*) can be sampled on sandy beaches from many areas of Cook Inlet, and robust populations of the bivalve *Macoma balthica* can be found in many protected mud flats, even in some areas in the upper inlet. Soft-shell clams (*Mya* spp.) are another widespread candidate for use as a sentinel organism in mud flats. All of these species are long-lived (at least 10 years) and therefore are good indicators of long-term conditions in a location.

7) Establish a baseline program in several areas where trajectory modeling predicts the highest probabilities of exposure to crude oil in the event of a catastrophic spill. During the EVOS, the absence of adequate background data to assess impacts or measure recovery of the resources resulted in problems. CIRCAC's current data sets are not adequate to characterize levels of abundance and variation in background contaminants and biological resources. A more comprehensive data set could be achieved by rotating annually between sandy beach and mud flat habitats within a small number of different geographic regions. A two- to three-year rotation plan should suffice to cover the inlet, establish a credible time-series database, and fill in some of the obvious data gaps.

8) Discontinue trace metals monitoring in sediment and tissues. The discharge plume modeling conducted during this evaluation suggests a very low probability of trace metal accumulation in sediments from produced water discharges in Cook Inlet. Moreover, the results from the EMP and the MMS studies show no indication that trace metal residues from oil and gas activities have accumulated over time in the active reaches of Cook Inlet.

9) The analytical chemistry program has pretty much stabilized with the utilization of the current laboratory contractor for the last three years of the EMP. Nevertheless, several areas could be modified with regard to source oil characterization and analyses of samples with extremely low concentrations of PAH (particularly tissues).

10) Complete additional in-depth source characterizations of coal and other organic sources of hydrocarbons from strategic locations.

11) Undertake a systematic water sampling program in the region of a produced water diffuser to examine the dissolved and dispersed oil droplet plume. Furthermore, sample dissolved and particulate oil fractions in receiving water downstream of diffuser sites for source characterization, to document oil-SPM adsorption behavior, and to validate PLUME model predictions.

12) Conduct a limited set of weathering and sedimentation studies to obtain more definitive data on coal vs. oil PAH sources and their respective fates after release into the marine environment in Cook Inlet. Specific experiments should be designed and completed to evaluate: 1) produced water/SPM interactions and subsequent weathering (leaching) and biodegradation; 2) leaching/biodegradation of PAH from suspended coal particulates; 3) sedimentation rates and resuspension behavior of coal vs. background sediments as function of particle grain size, organic content, salinity, and flocculation behavior.

13) EMC is also tasked to provide data to the public. The CIRCAC website would seem an appropriate vehicle for this task and should include their study reports, as well as this summary report. Finally, the data could be disseminated as compressed spreadsheets for those keenly interested in the studies. Another helpful product would be a bibliography of Cook Inlet publications and lending libraries that hold them.

Finally, we recommend the original objectives be modified for the continuation of the EMP. Two of the original objectives remain the same but the original objective directing toxicity testing is replaced with one directing conduct of specific baseline studies.

- Objective A: Determine if the potential contaminants associated with the activity or area are becoming incorporated in the sediments or water mass at measurable concentrations.

- Objective B: Determine through bioaccumulation and biomarker studies if organisms living in the areas at risk have been exposed to the potential contaminants.

- Objective C: Develop a comprehensive understanding of baseline conditions for a small suite of sentinel organisms on sandy beach and mud flat habitats at several intertidal locations within Cook Inlet where trajectory modeling indicates a high likelihood of exposure to crude oil in the event of a catastrophic spill.

Recommended Monitoring Program

A qualitative ecological risk assessment (a formal evaluation technique) was used to focus the monitoring options in order to optimize the information obtained within the available budget. Based on this analysis, it appears that dilution by the receiving water reduces the concentrations of potential chemical stressors to the point that the exposure route is interrupted before it reaches most potential receptors. Thus, these stressors can be removed from consideration as valid chemical of concern to the nearest known benthic resources. In other words, under current levels of input, the program should not expect to find any major acute or chronic impacts. As a result, the monitoring program can be focused on gathering baseline data while watching for low-level effects in the biota rather than looking for acute impacts with expensive toxicity tests.

Framework for Monitoring Program

To date, it appears the EMP has been searching for contaminants and effects in areas where hydrocarbons discharged from permitted outfalls could become deposited following adsorption onto suspended particulates. However, based on the inability of the program to detect significant results during five years of sampling using a wide variety of techniques throughout the region, a change in strategy appears in order. Dilution modeling conducted as part of this study and the recent publication of corroborating evidence from an MMS study support this position.

Dual Focus Monitoring Program

Working from the assumption that the basic mission of the EMP is to identify sources, magnitudes, and spatial and temporal trends in pollution from the oil industry, we suggest a two-pronged program to address both potential chronic and acute effects to the environment.

1) The EMP should continue looking for chronic effects from industry operations, but should concentrate these efforts in the upper Inlet. Although our dilution modeling shows that under normal conditions we would not expect to see any significant (or perhaps detectable) PAH concentrations outside of the mixing zone of most of the discharges, events happen.

2) As the second "prong," we strongly suggest that the EMC conduct its monitoring program with a view toward establishing baseline data for future acute events. It is highly likely that a catastrophic spill in any location in the inlet would impact areas not covered by an upper inlet monitoring program. Moreover, because the habitats in the lower inlet are typically far richer and more productive than those in the upper inlet, they are far more at risk. The EMP should use existing studies or surface trajectory models to identify the shorelines at greatest risk. They should also consider the sensitivity of various habitats to oiling. We believe that intertidal habitats are at greater risk from exposure to hydrocarbons than subtidal habitats and are the most logical place to focus the sampling.

3) Within the monitoring program, several one-time surveys or analyses should be conducted to fill data gaps. The first would be a one-time reconnaissance of selected intertidal habitats within Cook Inlet. To our knowledge, most of the shoreline in the upper inlet has not been surveyed and the resources living there are undefined. Surveys in this area would provide valuable information on intertidal assemblages on hard and soft substrates, characterize the sediments and geomorphology of the shoreline, and possibly identify biological resources that, because of their proximity to the contaminant sources, would be more appropriate as sentinel species. We also recommend one-time chemical analyses to better understand the multiple PAH sources (e.g. particulate coal) within the region and thus, better understand the processes creating background levels of hydrocarbons observed in the sediments.

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Patterns Observed in Environmental Monitoring Program Studies

The CIRCAC Environmental Monitoring Program employed a diverse suite of sampling and analytical methodologies to examine a wide variety of potential indicators for oil contamination in the inlet and in northwestern Shelikof Strait. Results to date indicate the following:

Analytical Methods

- Switching laboratories, extraction methodologies, and contractors midway through the program has not had a significant negative impact on data quality or data comparability
  - minor differences with alkyl-substituted PAH ratios have been noted, and they can affect Double Ratio plots when trying to identify and resolve very subtle differences in potential sources.

Sediment Hydrocarbon Burdens

Sediment samples exhibit extremely low levels of PAH (40-50 times below NOAA ERL concentrations)

- the sources are varied and mixed, but they cannot be directly attributed to Cook Inlet oil and gas development operations.
- no evidence of EVOS or ANS oil was observed in any of the subtidal sediments (including Shelikof Strait).

- The modeling efforts presented in this report describe the mechanisms responsible for the weakness of the hydrocarbon signal in Cook Inlet.
  - Studies conducted in 1993 by the University of Alaska for the Minerals Management Service (MMS), and currently by MMS and the U.S. Environmental Protection Agency corroborate this finding.
- The sediments do not contain adequate concentrations of hydrocarbon to cause mortality or sublethal effects to organisms exposed to them.
- No relationship was observed between toxicity and PAH concentrations in sediments in the entire suite of toxicity tests.
  - Toxicity tests using amphipods and echinoderm larvae showed significant toxicity in several cases, but these effects appeared related to other environmental factors such as concentration of fine sediments or ammonia rather than PAH.

Tissue Hydrocarbon Burdens

- Subtidal organisms living in the region have neither been accumulating nor exposed to high levels of hydrocarbons from Cook Inlet oil and gas activities.

- In a few instances, minimal exposure of intertidal organisms to petroleum products has occurred:

  - extremely weathered EVOS residues plus fresh diesel were encountered in mussels at one site in Shelikof Strait.

  - mixtures of diesel and very low-level combustion-derived (pyrogenic) hydrocarbons were noted in tissues of *Macoma balthica* from Tuxedni Bay.

  - fresh oil seep signals (natural sources) were possibly observed in tissues of *Macoma balthica* from Chinitna Bay.

  - analytical or procedural artifacts contribute to and interfere with many of the low-level PAH analyses in tissues.

Hydrocarbon Sources

- Subtidal coal outcrops or river-borne particulate coal from terrestrial sources may contribute significant levels of PAH to the sediments throughout the region.

- Total naphthalenes/TPAH ratios tend to increase with sand-sized particulates suggesting a particulate coal-derived source for much of the PAH observed in the sediments.

- Samples from up the Kenai River show a PAH signature similar to samples from other areas in the inlet. These upriver samples from terrestrial sources most likely represent erosion of coal deposits in the watershed area.

- Very few of the low-level PAH signatures for either sediments or tissues could be directly tied to specific sources; the samples suggest either undocumented sources or mixtures from multiple sources.

Water Column Hydrocarbons

- Deployment of caged mussels near produced water discharge outfalls failed to show any evidence of PAH accumulation but this could have been due to extreme stress in the deployed mussels due to high suspended-particulate loads or other environmental factors.

- Despite technical difficulties, SPMDs did show evidence of a produced water PAH signal in the Trading Bay area and what was presumably a weathered diesel signal in Kachemak Bay.

- Numerous procedural blank and method development problems still plague the SPMD approach.

In summary, it appears, based on the overwhelming weight of evidence from the many aspects of the EMP, that hydrocarbon contamination or effects related to hydrocarbon exposure are either lacking or, if observed, occurred at levels very near the detection limit for the particular approach. Ninety-nine percent of the observations found no evidence of contamination from oil activities in Cook Inlet or effects that could be related to hydrocarbon concentrations in the sediment. The only methodology that exhibited a relevant response was the SPMD (lipid bag) when arrays were placed near the produced water discharge in Trading Bay. Some approaches exhibited responses to environmental factors, but none exhibited a significant correlation with petroleum hydrocarbons.

Evaluation of Program Approaches

When the EMP program began in 1993, there was a distinct paucity of data on hydrocarbon levels in Cook Inlet. The Environmental Monitoring Committee (EMC) had to decide how, what, and where to sample for optimal evaluation of whether the Cook Inlet oil industry was affecting the environment. In view of its concern about the fate of contaminants discharged into sediment-laden waters, and given its limited annual budget, the EMC appropriately placed its initial focus on determining whether petroleum hydrocarbon contaminants were accumulating in sediments or representative organisms. The Sediment Quality Triad approach is a scientifically accepted method used in national programs for monitoring pollutant effects in the environment.

The EMP has provided researchers and managers with significant data that were not previously available from other sources. Specifically, PAH concentrations were measured throughout the program area. These measurements have provided valuable information on patterns of accumulation and sources of hydrocarbons in the inlet. The total sampling effort, however, was relatively small and the physical characteristics (such as current and sediment deposition rates) varied considerably among the areas sampled. Since the inception of the EMP, however, several federal agencies have contributed significant funds towards analyzing whether oil industry contaminants are presently or were historically accumulating in Cook Inlet or downstream areas. These data were incorporated into the current evaluations.

After five years of EMP studies, corroborating evidence from the current MMS Program and this study's dilution modeling results indicate that the traditional SQT concept no longer seems the most effective monitoring approach. Toxicity tests generally yielded negative results. The suite of toxicity tests did show some toxic responses, but they appear unrelated to hydrocarbon contaminants. The viability of the mussels in the mussel-watch arrays was poor under the harsh conditions characteristic of the upper inlet. Nevertheless, these experiments still provided useful information. SPMDs acquired some signal but technical problems limited interpretation. Mussels also showed a signal but since they are not found naturally in the upper and middle inlet, they were only collected from the northwestern Shelikof Strait. The EMP collected clams (*Macoma balthica*), an important forage species for several migrating seabirds and numerous fish species, from two intertidal areas of Cook Inlet. However, PAH body-burden measurements in subtidal species failed when, despite much effort, inadequate numbers were collected.

While the EMP provided no real time-series data, several general areas were visited more than once; the latter results were similar to those found during previous visits. However, the data are not usable for statistical comparisons among years. Furthermore, because all sampling has occurred during the summer, no seasonal comparisons can be made. Given the results of the study, however, we do not expect that concentrations of the chemicals or toxicity measured during the EMP would have significant seasonal differences. In summary, while there have been inconsistencies and lack of continuity in the program during the past five years as CIRCAC has tried various methods and altered sampling emphasis from year to year, the overall results indicate little or no adverse water column or benthic impacts from oil-and-gas development activities to date.

Recommended Changes in Program Strategy

Based on our evaluation of the data from the EMP and on the results of other ongoing studies in Cook Inlet, we have several recommendations for strategic changes to the program:

1) Continue to measure hydrocarbon concentrations, but consistently sample for aliphatics, PAHs, and specific chemical biomarkers such as steranes and triterpanes.

2) Replace toxicity testing with the more specific P4501A assay on tissues of resident organisms except for specific cases where contaminant levels begin to appear suspect. Toxic impacts were rare during the EMP and did not correlate well with PAHs. Moreover, it is difficult to differentiate between toxicity in response to target contaminants and other unmeasured contaminants.

3) Replace the strategy of absolute random sampling within regions with a modified stratified random strategy. Monitoring an area such as Cook Inlet, which is highly variable in bathymetry and physical environment, can only be effective by one of two approaches: 1) establish permanent monitoring sites and revisit those locations repeatedly through time; or 2) if a total random sampling design is desired, sample at enough stations to account for the high degree of variability observed within the regions. Random sampling within a general area (e.g., Trading Bay) has an unknown (presumably large) component of variance that will usually confound the results.

4) Replace subtidal sampling with intertidal sampling. Extensive baseline data for hydrocarbons and trace metals will soon be available for depositional areas in Cook Inlet through the MMS program. Focus instead on areas that are most likely to be affected in the event of spilled oil. Collective experience at oil spills suggests that intertidal assemblages have a greater likelihood of exposure to hydrocarbons than subtidal assemblages.

5) Focus the sampling program on soft-substrate habitats. In Cook Inlet, intertidal soft-bottom biological assemblages are far more uniform than subtidal assemblages, and intertidal sampling programs are easier to design and more cost

effective. Moreover, they support large long-lived populations of potential target species.

6) Identify the most suitable biological target species for use as sentinel organisms. This may require additional surveys of intertidal assemblages. Robust populations of the razor clam (*Siliqua patula*) can be sampled on sandy beaches from many areas of Cook Inlet, and robust populations of the bivalve *Macoma balthica* can be found in many protected mud flats, even in some areas in the upper inlet. Soft-shell clams (*Mya* spp.) are another widespread candidate for use as a sentinel organism in mud flats. All of these species are long-lived (at least 10 years) and therefore are good indicators of long-term conditions in a location.

7) Establish a baseline program in several areas where trajectory modeling predicts the highest probabilities of exposure to crude oil in the event of a catastrophic spill. During the EVOS, the absence of adequate background data to assess impacts or measure recovery of the resources resulted in problems. CIRCAC's current data sets are not adequate to characterize levels of abundance and variation in background contaminants and biological resources. A more comprehensive data set could be achieved by rotating annually between sandy beach and mud flat habitats within a small number of different geographic regions. A two- to three-year rotation plan should suffice to cover the inlet, establish a credible time-series database, and fill in some of the obvious data gaps.

8) Discontinue trace metals monitoring in sediment and tissues. The discharge plume modeling conducted during this evaluation suggests a very low probability of trace metal accumulation in sediments from produced water discharges in Cook Inlet. Moreover, the results from the EMP and the MMS studies show no indication that trace metal residues from oil and gas activities have accumulated over time in the active reaches of Cook Inlet.

9) The analytical chemistry program has pretty much stabilized with the utilization of the current laboratory contractor for the last three years of the EMP. Nevertheless, several areas could be modified with regard to source oil characterization and analyses of samples with extremely low concentrations of PAH (particularly tissues).

10) Complete additional in-depth source characterizations of coal and other organic sources of hydrocarbons from strategic locations.

11) Undertake a systematic water sampling program in the region of a produced water diffuser to examine the dissolved and dispersed oil droplet plume. Furthermore, sample dissolved and particulate oil fractions in receiving water downstream of diffuser sites for source characterization, to document oil-SPM adsorption behavior, and to validate PLUME model predictions.

12) Conduct a limited set of weathering and sedimentation studies to obtain more definitive data on coal vs. oil PAH sources and their respective fates after release into the marine environment in Cook Inlet. Specific experiments should be

designed and completed to evaluate: 1) produced water/SPM interactions and subsequent weathering (leaching) and biodegradation; 2) leaching/biodegradation of PAH from suspended coal particulates; 3) sedimentation rates and resuspension behavior of coal vs. background sediments as function of particle grain size, organic content, salinity, and flocculation behavior.

13) EMC is also tasked to provide data to the public. The CIRCAC website would seem an appropriate vehicle for this task and should include their study reports, as well as this summary report. Finally, the data could be disseminated as compressed spreadsheets for those keenly interested in the studies. Another helpful product would be a bibliography of Cook Inlet publications and lending libraries that hold them.

Finally, we recommend the original objectives be modified for the continuation of the EMP. Two of the original objectives remain the same but the original objective directing toxicity testing is replaced with one directing conduct of specific baseline studies.

- Objective A: Determine if the potential contaminants associated with the activity or area are becoming incorporated in the sediments or water mass at measurable concentrations.

- Objective B: Determine through bioaccumulation and biomarker studies if organisms living in the areas at risk have been exposed to the potential contaminants.

- Objective C: Develop a comprehensive understanding of baseline conditions for a small suite of sentinel organisms on sandy beach and mud flat habitats at several intertidal locations within Cook Inlet where trajectory modeling indicates a high likelihood of exposure to crude oil in the event of a catastrophic spill.

Recommended Monitoring Program

A qualitative ecological risk assessment (a formal evaluation technique) was used to focus the monitoring options in order to optimize the information obtained within the available budget. Based on this analysis, it appears that dilution by the receiving water reduces the concentrations of potential chemical stressors to the point that the exposure route is interrupted before it reaches most potential receptors. Thus, these stressors can be removed from consideration as valid chemical of concern to the nearest known benthic resources. In other words, under current levels of input, the program should not expect to find any major acute or chronic impacts. As a result, the monitoring program can be focused on gathering baseline data while watching for low-level effects in the biota rather than looking for acute impacts with expensive toxicity tests.

Framework for Monitoring Program

To date, it appears the EMP has been searching for contaminants and effects in areas where hydrocarbons discharged from permitted outfalls could become deposited following

adsorption onto suspended particulates. However, based on the inability of the program to detect significant results during five years of sampling using a wide variety of techniques throughout the region, a change in strategy appears in order. Dilution modeling conducted as part of this study and the recent publication of corroborating evidence from an MMS study support this position.

Dual Focus Monitoring Program

Working from the assumption that the basic mission of the EMP is to identify sources, magnitudes, and spatial and temporal trends in pollution from the oil industry, we suggest a two-pronged program to address both potential chronic and acute effects to the environment.

1) The EMP should continue looking for chronic effects from industry operations, but should concentrate these efforts in the upper Inlet. Although our dilution modeling shows that under normal conditions we would not expect to see any significant (or perhaps detectable) PAH concentrations outside of the mixing zone of most of the discharges, events happen.

2) As the second "prong," we strongly suggest that the EMC conduct its monitoring program with a view toward establishing baseline data for future acute events. It is highly likely that a catastrophic spill in any location in the inlet would impact areas not covered by an upper inlet monitoring program. Moreover, because the habitats in the lower inlet are typically far richer and more productive than those in the upper inlet, they are far more at risk. The EMP should use existing studies or surface trajectory models to identify the shorelines at greatest risk. They should also consider the sensitivity of various habitats to oiling. We believe that intertidal habitats are at greater risk from exposure to hydrocarbons than subtidal habitats and are the most logical place to focus the sampling.

3) Within the monitoring program, several one-time surveys or analyses should be conducted to fill data gaps. The first would be a one-time reconnaissance of selected intertidal habitats within Cook Inlet. To our knowledge, most of the shoreline in the upper inlet has not been surveyed and the resources living there are undefined. Surveys in this area would provide valuable information on intertidal assemblages on hard and soft substrates, characterize the sediments and geomorphology of the shoreline, and possibly identify biological resources that, because of their proximity to the contaminant sources, would be more appropriate as sentinel species. We also recommend one-time chemical analyses to better understand the multiple PAH sources (e.g. particulate coal) within the region and thus, better understand the processes creating background levels of hydrocarbons observed in the sediments.

Technical Evaluation of the Environmental Monitoring Program for Cook Inlet Regional Citizens Advisory Council

1. INTRODUCTION

The Cook Inlet Regional Citizens Advisory Council's (CIRCAC) Environmental Monitoring Committee (EMC), created in response to the Oil Pollution Act of 1990, initiated several environmental studies between 1993 and 1997 as part of its overall Environmental Monitoring Program (EMP). The major objective of the EMP has been to determine if operations associated with the oil industry in Cook Inlet are having adverse effects on the surrounding ecosystem. If such impacts were detected, these studies were also intended to document the sources and magnitude of the impacts and spatial and temporal trends.

Littoral Ecological & Environmental Services (LEES) and its team are pleased to submit this synthesis report analyzing data from the first five years of the EMP. To support the major objective of the EMP, the goals of this report are to: 1) summarize, analyze, and synthesize the existing data and reports from the EMP; 2) evaluate the methods and approaches employed during the EMP; 3) determine the value of the existing database(s) for establishing or defining baseline conditions; and 4) provide recommendations to CIRCAC regarding the design of further monitoring efforts to assess oil-related impacts to the ecosystems in Cook Inlet.

This project has involved seven major tasks.

- integrate and compile the various data sets into a comprehensive database or set of consistently formatted databases.

- summarize the results found in the database(s) into technical and non-technical reports describing: 1) the distribution of hydrocarbons in sediments, the water column, and tissues of bivalves and fishes; 2) evidence of trace metals contamination in sediments and mussel tissues; and 3) sediment toxicity testing.

- examine analytical data for sediments and tissues for potential contaminants from oil production, shipping, refineries.

- perform modeling studies to develop an understanding of the scale over which the potential contaminants resulting from oil and gas activities in Cook Inlet could be detected.

- evaluate the methods and approaches used in the EMP so as to determine what changes, if any, are required in the basic framework of the program so that it provides the information desired by the EMC.

- evaluate the information contained in the database in order to assess whether the data meet the needs of CIRCAC to measure future chronic or acute impacts from activities of the oil industry.

- develop a new monitoring program.

1.1 Report Organization

The report is divided into nine major sections. Section 1, the Introduction, includes discussions of CIRCAC's Environmental Monitoring Program in Cook Inlet and Shelikof Strait, including its goals and objectives, monitoring approaches, and its geographic and temporal coverage. Section 2 describes the goals of this synthesis effort. Section 3 provides a brief Methods section. Section 4 presents the results of the Environmental Monitoring Program and the PLUMES modeling study conducted for the preparation of this report. Section 5 is a discussion of the findings and effectiveness of the EMP. Section 6 provides recommendations for the strategy to be followed in the development of the future monitoring program and for key elements of the program. Section 7 identifies Literature Cited. Section 8 is a Glossary, List of Acronyms, and a list of polycyclic (or polynuclear) aromatic hydrocarbon (PAH) abbreviations used in graphical presentations of PAH fingerprints. Appendix A comprises the ninth section.

1.2 Description of CIRCAC's Environmental Monitoring Project

Two major goals of CIRCAC's Environmental Monitoring Program (EMP) are to: 1) determine if oil-industry operations in Cook Inlet are having adverse effects on the surrounding ecosystem; and, if so, 2) document their sources, magnitude, and spatial and temporal trends. The principal strategy used to drive the program was the Sediment Quality Triad (SQT) approach, which is structured to: 1) determine if contaminants exist in the sediments or water at measurable concentrations; 2) determine whether or not the concentrations of a contaminant found in the sediments can potentially cause mortality or sublethal (chronic) effects to organisms that might be exposed to them; and finally, 3) determine if organisms living in the areas at risk have been exposed to the potential contaminants. A mussel watch approach is presented as a second strategy but it actually falls within the structure of the SQT. The SQT is not designed to develop a functional understanding of baseline conditions for the biological assemblages and resources in an area of concern nor is this a primary goal of the EMP.

Within the framework of the SQT, sediment and tissue samples have been collected from several sampling locations in each of eight general areas (Figure 1-1). These are:

1) The Beluga region in upper Cook Inlet

2) Granite Point, Trading Bay and the East Forelands area in the middle inlet

3) The Kenai River and its delta

4) Tuxedni and Chinitna Bays on the west side of Cook Inlet

5) Kamishak Bay

6) Kachemak Bay

7) the "Null Zone" (i.e., southern lower Cook Inlet), and

8) Capes Douglas, Chiniak, and Nukshak in northwestern Shelikof Strait.

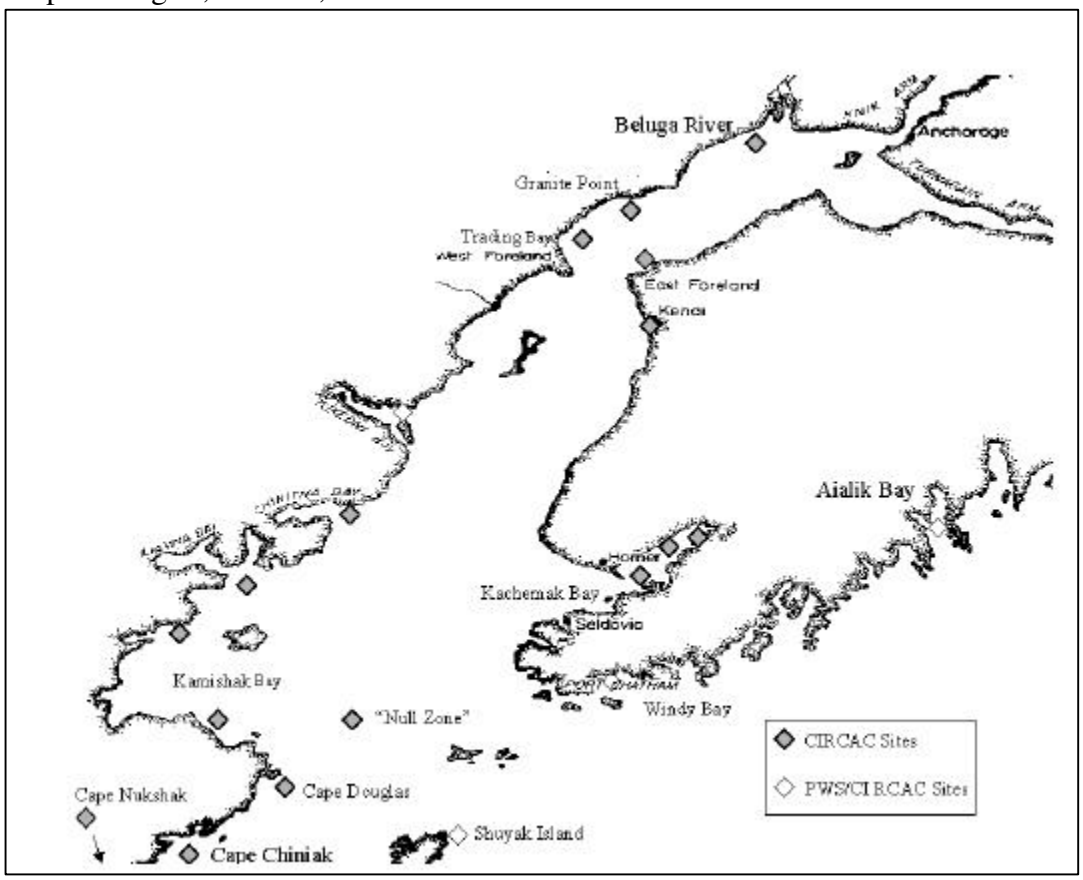


Figure 1-1 Areas sampled during the Cook Inlet RCAC Environmental Monitoring Program – 1993 through 1997.

The primary environmental properties measured during the EMP include: 1) polycyclic (or polynuclear) aromatic hydrocarbons (PAH) in: a) intertidal or shallow subtidal sediments; and b) tissues of mussels, *Macoma balthica*, or *Macoma* spp. from intertidal or subtidal habitats; and 2) sediment toxicity (Table 1-1). PAHs, reported either as total PAH or as alkylated homologs, were measured for the purpose of evaluating hydrocarbon baseline conditions and the introduction of hydrocarbons into the environment. Trace metals (collected during one survey only) in sediments are typically evaluated to monitor the magnitude of industrial and anthropogenic contributions and predict potential impacts to the marine biota. Trace metals analyses in sediments and tissues were incorporated into the EMP in an effort to detect known metal constituents in the produced water effluents

and to emulate the National Oceanic and Atmospheric Administration (NOAA) National Status and Trends Mussel Watch Program, which monitors a broad array of contaminants in a wide variety of locations along all coasts of the U. S. Analyses of aliphatic hydrocarbon (AHC) in sediments and tissues from two surveys were incorporated into the EMP to provide a broader view of petroleum hydrocarbon conditions.

In the first three years of the EMP, mussels in cages and semipermeable polymeric membrane devices (SPMDs) were suspended in the water column with the objective of measuring petroleum hydrocarbons (Table 1-1). In later surveys, fish were collected to evaluate exposure to petroleum hydrocarbons through examination of biomarkers in tissues or organs.

Activity	Sampling Period: 1993	1994	1995	1996	1996	1997	1997
	Type or Name of Program: Pilot Monitoring Program						
	Phase 1; 4 regions	Phase 2; 1 region, 3 sites	Environmental Monitoring Program; 4 regions	Lake Clark Bivalve Program; 1 region, 9 sites	Shelikof Strait Program, 1 region	Cook Inlet Sediment Toxicity & Hydrocarbon Study, 3 regions	Kenai River Estuary Sediment Character-ization
	Regions Sampled: Upper Cook Inlet, Trading, Kamishak, and Kachemak Bays	Granite Point, Trading Bay, and East Forelands	East Forelands, Trading Bay, "Null Zone", Kachemak and Kamishak Bays	Tuxedni and Chinitna Bays	Capes Douglas, Nukshak, and Chiniak	East Forelands, Trading, Kamishak, and Kachemak Bays	Kenai River estuary, delta, and N and S of river mouth
	Depth Stratum Sampled: Subtidal	Subtidal	Subtidal	Intertidal	Intertidal and Subtidal	Subtidal	Subtidal
Sediment							
Sediment PAHs (Total and alkylated homologs)	12	18	15		9	12	12
Sediment Aliphatic Hydrocarbons					9	12	12
Sediment Trace Metals					9		
Sediment Grain Size	12	18	15		9	12	12
Total Organic Carbon	12	18	15		9	12	12
Lipid Bag Sampling for PAH in Water Column	2	3	3				
Mytilus							
Mussel Watch - PAH Burdens in *Mytilus*	2						
PAH Burdens in Resident *Mytilus*					9		
Trace Metals Burdens in Resident *Mytilus*					9		
Physiological Condition of *Mytilus*	2				9		
Lipid Content in *Mytilus* Tissues					9		
Macoma							
Population Density and Condition of *Macoma*	6		15	9			
PAH Burdens in *Macoma* spp. Tissues	6			9			
Trace Metals Burdens in *Macoma* spp. Tissues				9			
Various Bivalves							
Population Density and Condition of Various Benthic Bivalves			11				
Toxicity Testing							
Sediment Toxicity - *Ampelisca abdita*	12	18				12	
Echinoderm Larval Development						12	
Microtox Testing of Sediments			15		9	12	
P450 Reporter Gene System Sediment Testing					9	12	
Bioaccumulation/Bile Metabolites							
P4501A Reporter Gene System Fish Tissue Testing			2				
P450 Reporter Gene System Bivalve Tissue Testing				5	9		
Bile Metabolites & Liver Enzyme Induction Analyses			2				
Contractor	A. D. Little	A. D. Little	Kinnetic Labs	Kinnetic Labs	Kinnetic Labs	Kinnetic Labs	Kinnetic Labs

Table 1-1 Summary of monitoring tasks and activities conducted during CIRCAC's Environmental Monitoring Program.

Secondary variables measured to support interpretation of the hydrocarbon measurements and toxicity testing data include: total organic carbon (TOC), sediment particle grain size, lipid content in mussel tissues, shell characteristics (length and volume) for the mussels and *Macoma*; and weight of total tissue for the mussels.

1.3 Geographic and Temporal Coverage of the Environmental Monitoring Program

During the five years of the Environmental Monitoring Program (1993 through 1997), sediment and/or tissue samples were collected at approximately 87 different sites distributed in eight general areas. Seven of the regions are located in Cook Inlet and one is located on the northwestern shore of the Alaska Peninsula in northeastern Shelikof Strait (Figure 1-1).

The number of sites sampled and the number of years in which sampling occurred varied considerably among the regions. Sampling generally occurred annually during mid-summer. The greatest number of samples was collected from Trading Bay (15), where sampling was conducted in all years except 1996. Twelve samples were collected in the East Forelands region; sampling was conducted there in 1994, 1995, and 1997. Nine samples were collected in both Kamishak and Kachemak Bays; these bays were both sampled in 1993, 1995, and 1997. The nine remaining regions were only sampled once during the five-year program. Samples were collected at three sites in the Beluga area in 1993. Samples were collected at six sites in the Granite Point area in 1994. Samples were collected at three sites in the "null zone" in the southern portion of lower Cook Inlet in 1995. In 1996, samples were collected at four and five sites in Tuxedni and Chinitna Bays, respectively, and at three sites in Shelikof Strait (i.e., Capes Douglas, Nukshak, and Chiniak). In 1997, sediment samples were collected at 25 locations in or near the Kenai River estuary; PAH was analyzed for twelve samples.

2. GOALS AND OBJECTIVES

2.1 Environmental Monitoring Program Goals and Objectives

Studies carried out during the first five years of the EMP provided thirteen lines of evidence related to detection of hydrocarbon contributions from oil and gas activities in the inlet. The lines of evidence examined included:

1) PAH concentrations in sediments

2) Aliphatic hydrocarbons in sediments;

3) PAH analyses of SPMD as an indication of hydrocarbons in the water column;

4) PAH analyses for mussel tissues,

5) PAH analyses for *Macoma* tissues;

6) Toxicity tests on amphipods,

7) Toxicity tests using echinoderm larval development,

8) Microtox© testing,

9) P450 reporter gene system testing of sediments,

10) P450 reporter gene system testing of bivalve tissues,

11) P4501A testing of halibut liver, and,

12) analysis of halibut tissues for bile metabolites and liver enzyme induction which indicate exposure to hydrocarbons, and,

13) source allocation or hydrocarbon fingerprinting to identify the likely sources of observed hydrocarbons in water, sediments, and tissues.

These approaches come at the question of potential hydrocarbon contamination from three principal directions. Approaches 1 through 3 are useful primarily for determining if the contaminants exist at measurable concentrations in the sediments or water column. Approaches 6 through 9 address whether or not the concentrations of a contaminant found in the sediments can potentially cause mortality or sublethal (chronic) effects to organisms that might be exposed to them. Finally, the remaining five approaches (4, 5, 10, 11, and 12) are useful for determining if organisms living in the areas at risk have been exposed to the potential contaminants. These elements basically fulfill the needs of the Sediment Quality Triad strategy.

2.2 Synthesis Program Goals

This project's goal is to analyze and synthesize the existing data and provide guidance to CIRCAC in developing the strategy and scope for the future sampling and analytical programs comprising its Environmental Monitoring Program. The program has four major objectives:

- Summarize the existing data, results, and interpretations into a technical report, a combined database, and a non-technical report.

- Evaluate the methods and environmental monitoring approaches used by the EMC, including the evaluation of specific methodology such as the Sediment Quality Triad, toxicity testing, and water quality monitoring methods.

- Evaluate the effectiveness of the existing data as baseline information against which future chronic or acute oil-industry impacts can be measured.

- Recommend further environmental monitoring efforts for assessing temporal and spatial oil-industry impacts to the Cook Inlet environment.

3. METHODS

Methods employed during the Environmental Monitoring Program are detailed in the various reports and these descriptions are not repeated in this synthesis report. It should be noted, however, that the analyses utilized by the EMP to assess hydrocarbons, trace metals, toxicity, and water quality are rigorous, used widely in the scientific community, and provide scientifically and legally defensible results. All are either Environmental

Protection Agency (EPA)-approved methods or potentially more sensitive experimental methods that are being evaluated nationally.

An important objective of the early years of the EMP was to identify methods that were sensitive to the types of contamination being monitored. Thus, in some cases, a wide variety of methodologies was employed over the five years. For example, four different methods were employed to evaluate sediment toxicity, i.e., assays evaluating amphipod survival, echinoderm larval development, bioluminescence produced by bacteria (Microtox), and the P450 Reporter Gene System. Each type of assay looks at different fractions of the sediment (e.g., whole sediment vs. porewater) and has different strengths and weaknesses. Moreover, it was useful to evaluate the screening potential of the less expensive tests. The echinoderm larval development test was run to provide data that could be compared to results of an earlier Minerals Management Service study.

Hydrocarbons were primarily measured as PAH although analyses were conducted for aliphatic hydrocarbon in several regions during 1997. The analytical methods employed for extraction and analysis of PAH and aliphatic hydrocarbons are based on NOAA protocols but, unfortunately, extraction methods differed by the two labs contracted to run the analyses at different times during the program. Both laboratories contracted for the hydrocarbon analyses are widely recognized to be among the best analytical laboratories in the country.

Except for the modeling used to examine the potential behavior of contaminants released into the receiving waters in effluents from oil production and processing facilities, the methods employed during the development of this synthesis were generally relatively simplistic and uncomplicated. The following sections include descriptions of the conceptual approach to this synthesis, the data management scheme, the rudimentary statistics employed, and the modeling and models employed to describe the dispersion and dilution of effluents emitted from the various outfalls considered.

3.1 Conceptual Approach for Synthesis

Our conceptual approach to accomplish the above objectives was to compile and summarize the data, examine the validity of the collection and analytic methods, reassess findings against laboratory Method Detection Limit (MDL) and Quality Control (QC data, and interpret the significance of the results in context of the applicability of the methods. We then synthesized the refined data to gain a perspective on the accomplishments of the program. Synthesis was followed by an abbreviated screening ecological risk assessment to help formulate future objectives. Finally, we suggested our best alternatives for continuing the monitoring program.

3.2 Data Management

Data from the following reports were placed in the database:

A. D. Little. 1995a. Cook Inlet Pilot Monitoring Study - Final Report: Phase I of an overall program entitled : Design and Implementation of a Prototype Environmental Sampling Program for Cook Inlet, Alaska. Prepared for Cook Inlet Regional Citizens Advisory Council, Kenai, Alaska.

A. D. Little. 1995b. Cook Inlet Pilot Monitoring Study - Final Report: Phase II of an overall program entitled : Design and Implementation of a Prototype Environmental Sampling Program for Cook Inlet, Alaska. Prepared for Cook Inlet Regional Citizens Advisory Council, Kenai, Alaska.

A. D. Little. 1998a. Sediment quality in depositional areas of Shelikof Strait and outermost Cook Inlet - Final Literature Synthesis. For Minerals Management Service. OCS Study MMS97-0015.

A. D. Little. 1998b. Sediment quality in depositional areas of Shelikof Strait and outermost Cook Inlet - Draft Interim Report. For Minerals Management Service. OCS Study MMS97-0015.

Kinnetic Laboratories Inc. (KLI). 1996. Final Report – 1995 – Cook Inlet Environmental Monitoring Program. Prepared for Cook Inlet RCAC Environmental Monitoring Committee. January 1996.

Kinnetic Laboratories Inc. (KLI). 1997a. Final Report - 1996 - Cook Inlet Shelikof Strait Project. Prepared for Cook Inlet RCAC Environmental Monitoring Committee. December 1997.

Kinnetic Laboratories Inc. (KLI). 1997b. Data Summary - 1996 Lake Clark bivalve analyses. Prepared for Cook Inlet RCAC Environmental Monitoring Committee. August 1996.

Kinnetic Laboratories Inc. (KLI). 1998a. Final Report - 1997 Cook Inlet sediment toxicity and hydrocarbon study. Prepared for Cook Inlet RCAC Environmental Monitoring Committee. June 1998.

Kinnetic Laboratories Inc. (KLI). 1998b. Draft Data Report - 1997 Kenai River estuary sediment characterization study. Prepared for Cook Inlet RCAC Environmental Monitoring Committee. May 1998.

Using the existing Kinnetic Laboratories, Inc. (KLI) database structure, A. D. Little's (ADL) data were transferred from the supplied spreadsheets and put into the KLI format. Pertinent portions of the data were exported to Excel spreadsheets for manipulation prior to statistical analysis. Notably absent from the ADL spreadsheets were data for sampling

dates, raw data for toxicity tests, MDLs, and some laboratory QC data for PAHs. A request was made to ADL but no additional data were received by time of this report.

3.3 Statistical Analyses

The approach to source analysis of hydrocarbon is often referred to as fingerprinting. Pattern matching is the primary technique; no statistical analyses were employed.

Significance of differences between several variables has already been analyzed by the respective contractors using parametric and non-parametric approaches. For these data, we will simply be summarizing the results and assessing the interpretations.

Significance of differences in the toxicity tests has been determined by the contractors using standardized non-parametric approaches developed for analysis of toxicity testing results. In some cases, the statistical interpretation was assessed by comparing the standardized results with results based on randomization testing techniques (Edgington 1995). This method of analysis requires no assumption of data distribution or equality of variances as do the classic parametric tests (analysis of variance, t tests, etc).

3.4 Modeling

To date, CIRCAC's monitoring efforts have been spread widely throughout the inlet in an attempt to locate oil-impacted areas where either aqueous or sediment-bound contaminants may have been transported. From out experience in Cook Inlet, we suspected that discharges from the platforms would be rapidly diluted before reaching downstream receptors. The modeling study undertaken for this report was designed to assess that physical range of concern by looking at dilutions and distances from the point sources. To this end, we have focused on the naphthalene aromatic hydrocarbons (rather than other organics) both as indicators of potential petroleum pollution and as one of the more traceable chemical signals (based on relative concentration) being released by the oil industry. Various metals are also byproducts of oil production; however, in Cook Inlet discharges, they diluted out within short distances.

Two forms of models are routinely used for assessing oil pollution in Cook Inlet: mixing zone modeling of the discharges from oil production platforms and shore facilities (as required for National Pollutant Discharge Elimination System (NPDES) permits), and surface trajectory modeling for oil spill planning and response. These models work on different scales, one for local effects and the other for basin-wide processes. Both have inherent limitations.

3.4.1 Surface Trajectory Models

Three models have been constructed for tracking surface spills in Cook Inlet: NOAA HAZMAT's hindcast model, CIRCAC's model and the Mineral Management Service's COZOIL model. These models work on a basin-wide scale and all use estimates of tidal and wind components to calculate surface water movements at any particular location in the inlet. Notably absent are programming elements designed to deal with 1) discontinuities where two masses of water, significantly different in density, meet (e.g.,

where the fresher, sediment-laden, outward-flowing western waters adjoin the incoming oceanic waters in mid-inlet) and 2) the highly dynamic rip tides around Kalgin Island.

3.4.2 PLUMES, The Mixing Zone Model

For the local scale, EPA's modeling program, PLUMES, is commonly used to evaluate the size of mixing zones around a discharge point versus the dilutions of pollutant compounds. In Cook Inlet, PLUMES (version 3.1) has been heavily relied on for NPDES permit applications. The applicants and regulating agencies agree that while the results likely do not represent actual field conditions, the results do provide an order-of-magnitude estimate of the mixing zone's size. Alaska Department of Environmental Conservation (ADEC), the final permitting authority in Cook Inlet, is more interested in assuring that specific pollutants are diluted to safe exposure levels within tens of meters versus a thousand meters rather than the veracity of the model's specific estimate (pers comm, Robert Dolan, ADEC).

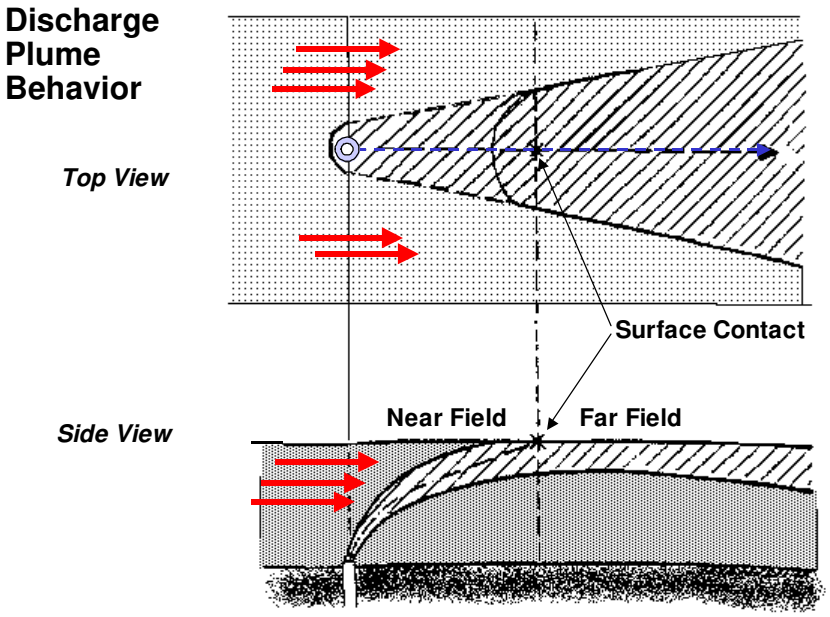


Figure 3-1. Discharge plume behavior.

The actual model is a theoretical mathematical construct depicting the near-field behavior of a plume for a given diffuser configuration (e.g., flow rates, number and size of nozzles, depth, spacing and angle of discharge), as the plume transits from the discharge nozzle until it hits the surface (or bottom; Figure 3-1). Based on fluid dynamics, the model estimates mixing zone dilution (given the specific velocity and density of the discharge relative to the surrounding water) by calculating how much of the surrounding waters will be entrained into the plume as it rises. Then, as the plume leaves the near-field, estimates

of far-field dilution are calculated using the Brooks equation, a generic algorithm appropriate for open coastal waters like Cook Inlet. The Brooks equation calculates dilution using the "4/3 power law" which is a non-robust estimator driven by initial dilution, plume width and time-in-transit. It works by continuously increasing the dispersion by the 4/3 power of the local plume field width.

$$S=S_a\ (erf\ ((1.5/\ (1+8ab^{4/3}t/b^2)^3-1)^{1/2}\ ))^{-1}$$

where:

S = centerline dilution in the far-field plume

S_a = initial dilution of plume leaving mixing zone

erf = standard error function

a = dispersion coefficient (.0001-.0005 $m^{2/3}sec^{-1}$)

b = width of plume at the end of initial dilution

t = time of travel from the point of the end of initial dilution (edge of the mixing zone) to the point of interest.

For our purposes, one of the model's limitations is that it is a two dimensional model concerned only in the plume's change in depth and downstream transport at a given current velocity. It has no provision for varying either the local or far-field current velocities or directions with a changing tide. Another limitation is that it calculates far-field dilution by conservatively reporting the plume's centerline concentration rather than estimating average dilution of the spreading plume (a very difficult and unreliable task given the unknown physical conditions downstream). Some modelers suggest that average plume concentration is approximately half that of the centerline value (Parametrix, Inc. 1998).

3.4.3 Modeling Methods

For this study, the PLUMES model was used to calculate dilutions and travel distances expected during the succession of tidal currents throughout an average tide cycle. To do this, we have taken the modeling details previously reported for the NPDES permit applications (Table 3-1), added a series of local currents specific for each oil platform or shore facility and repeatedly run the PLUMES model to calculate expected far-field dilutions and distance traveled during each tidal stage (Table 3-2). Local current data for the specific discharge locations were estimated from the CIRCAC trajectory model (generously compiled by Doug Jones).

Table 3-1. Produced water dilution model input parameters.

	Outfall Configuration				Effluent Conditions			Ambient Conditions		
Facility	Depth (ft)	Diameter (in)	Vertical Angle (degrees)	Distance to Shore (mi)	Flow (ft^3/sec)	Temperature C	Salinty (ppt)	Season	Temperature C	Salinity (ppt)
Granite Point Production Facility	57	3	90	7.2	0.15	21	21	Summer	12.5	20
								Winter	4	32
Trading Bay Production Facility	35	16	0	1.9	4.24	32	26	Summer	12.5	20
								Winter	4	32
East Foreland Treatment Facility	27	7	0	0.14	0.31	32	22	Summer	12.5	27
								Winter	4	32
Tyonek A	75	4	-25	6.1	0.0028	22	4	Summer	12.5	17
								Winter	4	32
Bruce	53.7	3	90	1.6	0.01	22	15	Summer	12.5	17
								Winter	4	32
Baker	102	2	90	7	0.065	22	16	Summer	12.5	17
								Winter	4	32
Dillon	81	3	90	3.7	0.195	32	19	Summer	12.5	20
								Winter	4	32
Anna	71.2	10	90	2.5	0.0694	32	15	Summer	12.5	20
								Winter	4	32
Tesoro PM	11	8	-85		1.67	12.5	27	Summer	10	0
								Winter		
Tesoro 001A	11	8	-85		1.23	12.5	27	Summer	10	0
								Winter		

(from Parametrix, 1995,1998)

Platform Dillon

FLOOD Velocity (m/s)	Time (hr)	Distance (m)	Cumul. distance	Tidal transport	Farfield velocity	Effluent Concentration (%)	Dilution	Width	Distance	Naphthalene Concentration (ug/L)	Dilution	Width	Distance
0.421	0.4	606	606	51883	0.010	0.000259	387000	462	51900	3.429	5759	9.808	356
0.992	0.8	1429	2035	50866	0.010	0.000128	780000	394	50900	2.429	5759	6.389	669.1
1.731	1.2	2493	4528	48905	0.009	0.000093	1070000	309	48900	2.429	5759	4.837	1005
2.378	1.6	3424	7951	45946	0.009	0.000091	1090000	229	45900	2.429	5759	4.127	1264
2.839	2	4087	12039	42191	0.008	0.000107	935000	164	42200	2.429	5759	3.777	1435
3.148	2.4	4533	16572	37881	0.007	0.00014	712000	113	37900	2.429	5759	3.587	1544
3.370	2.8	4853	21425	33188	0.006	0.000211	472000	69.7	33200	2.429	5759	3.467	1620
3.479	3.2	5009	26434	28257	0.005	0.000379	263000	37.1	28300	2.429	5759	3.412	1657
3.457	3.6	4979	31413	23263	0.004	0.000529	188000	19.8	24400	2.429	5759	3.423	1650
3.324	4	4787	36199	18380	0.003	0.0008144	12.45	16.07	17080	2.429	5759	3.491	1605
3.069	4.4	4420	40619	13777	0.003	0.001087	13.69	14.48	12940	2.429	5759	3.633	1516
2.723	4.8	3921	44540	9606	0.002	0.001526	14.85	12.97	9147	2.429	5759	3.857	1392
2.254	5.2	3246	47786	6023	0.001	0.002158	15.6	11.99	6107	2.429	5759	4.239	1216
1.673	5.6	2409	50195	3195	0.001	0.003052	15.79	11.7	3758	2.429	5759	4.92	980.1
1.022	6	1471	51667	1255	0.000	0.008632	17.94	8.902	1174	2.429	5759	6.295	683.9
0.361	6.4	519	52186	260	0.000	0.02442	17.85	8.906	242.3	2.429	5759	10.59	317.7
		52186				100	1		0				

EBB Velocity (m/s)	time (hr)	dist(m)	Cumul. distance	Tidal transport	Farfield velocity	Effluent Concentration (%)	dilution	width	Distance	Naphthalene Concentration (ug/L)	dilution	width	Distance
-0.472	0.4	680	680	45756	0.006	0.000278	359000	382	45800	2.429	5759	9.263	387.4
-1.188	0.8	1711	2391	44561	0.006	0.000136	735000	309	44600	2.429	5759	5.839	763.6
-1.829	1.2	2634	5025	42388	0.005	0.000115	868000	237	42400	2.429	5759	4.706	1046
-2.446	1.6	3522	8548	39309	0.005	0.000123	815000	166	39300	2.429	5759	4.069	1290
-2.920	2	4205	12753	35446	0.004	0.000158	631000	107	35400	2.429	5759	3.724	1464
-3.210	2.4	4622	17376	31032	0.004	0.00024	415000	64	31000	2.429	5759	3.552	1565
-3.311	2.8	4768	22143	26337	0.003	0.000417	239000	35	26300	2.429	5759	3.497	1600
-3.286	3.2	4732	26875	21587	0.003	0.000558	178000	20	22600	2.429	5759	3.511	1592
-3.177	3.6	4574	31450	16934	0.002	0.0008176	121600	16	16460	2.429	5759	3.57	1554
-2.964	4	4268	35717	12513	0.002	0.001088	91390	15	12590	2.429	5759	3.696	1479
-2.639	4.4	3801	39518	8478	0.001	0.001526	65160	13	8936	2.429	5759	3.917	1362
-2.160	4.8	3111	42629	5023	0.001	0.002158	46070	12	5916	2.429	5759	4.33	1179
-1.552	5.2	2235	44864	2350	0.000	0.00610	16290	9	2090	2.429	5759	5.108	928
-0.856	5.6	1232	46096	616	0.000	0.01726	5759	7	600.5	2.429	5759	6.878	600.5
		46096				100	1		0				

Table 3-2. Example worksheet of input data and PLUME modeling results.

The model runs for each site were structured by the tidal current data. The currents were broken into 0.4 hr segments, so the PLUMES model was run to track each physical parcel (0.4 hr segment) of water as it exited the discharge point and was transported by succeeding currents in the progress of the tidal cycle. The final cumulative tidal transport for each block was calculated as the sum of the succeeding tidal stage velocities times 0.4 hours. As a result, the initial block of water passing by the discharge nozzle at slack tide would typically end up tens of kilometers away by the next slack tide. Average far-field current velocities were then calculated as final tidal transport divided by time-in-transit. Then the data were entered into the model. The actual input for each run was local tidal stage velocity, average far-field velocity during the remainder of the tide cycle and far-field distance of interest. The model would then calculate effluent concentration, dilution, plume width and distance traveled (Table 3-2). Flood and ebb tides were run as separate data sets since direction vectors are not a parameter of the PLUMES model. An example plot of dilution versus distance traveled is shown in Figure 3-2.

After the final dilution curves were defined for each tidal stage, an actual TAqH (total aqueous hydrocarbons) or TAH (total aromatic hydrocarbons [benzene, ethylene, toluene, xylene only]) value from NPDES data was input for the specific location. These model runs were intended to estimate the distance at which the laboratory method detection limit (MDL) would be reached, i.e., the distance beyond which it would be impossible to detect the compounds. For this exercise, the MDL for an individual PAH was estimated to be 0.025 ug/L for typical samples, a sensitivity routinely attained by top PAH analytical laboratories. Since we were mostly interested in detecting a single compound as a traceable signal rather than the presence of all 39 target PAHs, we presumed that if the sum of the five naphthalene congeners (C_0N-C_4N) reached levels near 0.1 ug/L then detection was possible. Thus, we extracted from the model runs the distance at which the actual naphthalene discharge (as a percentage of TAqH or TAH) was diluted to approximately 0.1 ug/L and suggest that these distances are estimates of the range of detectable pollution from the discharge points. We consider these results to be an over-estimate of actual detectable distance for three reasons:

1. Most commercial labs report results at less sensitive MDLs (typically 1.0 ug/L or higher). The decision to use a more sensitive 0.1 ug/L MDL for these calculations greatly expanded the range of detection around the discharge points.

2. The PLUMES model is not robust in calculating far-field dilutions (i.e., in cases where detectable naphthalene was transported significantly beyond the mixing zone). Many physical processes not included in the theoretical basis of model could affect the rates of dilution (e.g., boundary constraints, stratification in the water column or the unknown mixing dynamics in the vicinity of the tidal rips).

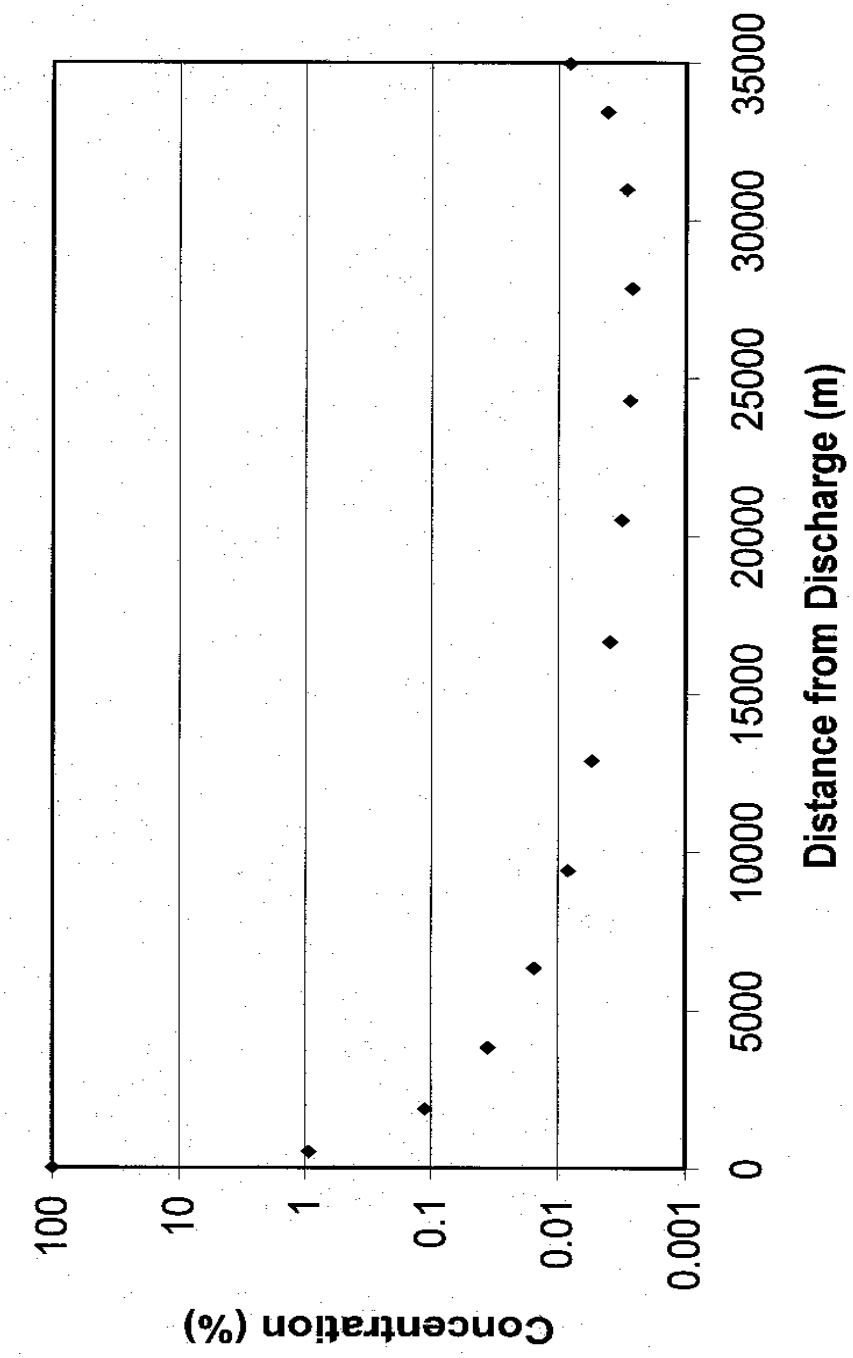


Figure 3-2. Relationship between effluent concentration (%) of naphthalene and distance from discharge at end of flood tide in summer at Tyonek A.

The modeling results are based on predicted concentrations in the centerline of the plume rather than the average plume-wide concentrations. Finding and sampling the plume's centerline, assuming it would still be intact several kilometers downstream, is an improbable task. Note that this modeling exercise is only intended to track naphthalene as a representative and the dominant PAH contaminant in its aqueous state. In upper Cook Inlet, there is the additional complication of PAH compounds adsorbing onto suspended sediment particles. For the modeling tasks, it was assumed that during tidal transport, the suspended sediments would remain suspended and would dilute at the same rate as aqueous phase compounds.

4. RESULTS

The results of the EMP focus primarily to three questions. The studies were designed to determine whether or not:

1) Contaminants derived from oil and gas activities in Cook Inlet can be observed at measurable concentrations in sediments or the water column.

2) Contaminants found in the sediments can potentially cause mortality or sublethal (chronic) effects to organisms that might be exposed to them.

3) Organisms living in the areas at risk have been exposed to the potential contaminants.

These elements basically fulfill the needs of the Sediment Quality Triad strategy.

Studies conducted during the EMP present thirteen lines of direct evidence that address questions regarding hydrocarbon concentrations and sources in Cook Inlet. These include:

1) PAH concentrations in sediments

2) Aliphatic hydrocarbons in sediments;

3) PAH analyses of SPMD as an indication of hydrocarbons in the water column;

4) PAH analyses for mussel tissues,

5) PAH analyses for *Macoma* tissues;

6) Toxicity tests on amphipods,

7) Toxicity tests using echinoderm larval development,

8) Microtox© testing,

9) P450 reporter gene system testing of sediments,

10) P450 reporter gene system testing of bivalve tissues,

11) P4501A testing of halibut liver

12) Analysis of halibut tissues for bile metabolites and liver enzyme induction which indicate exposure to hydrocarbons, and,

13) Source allocation or hydrocarbon fingerprinting to identify the likely sources of observed hydrocarbons in water, sediments, and tissues.

The results of the EMP studies are described in the sections below.

4.1 Overview of Sediment Conditions

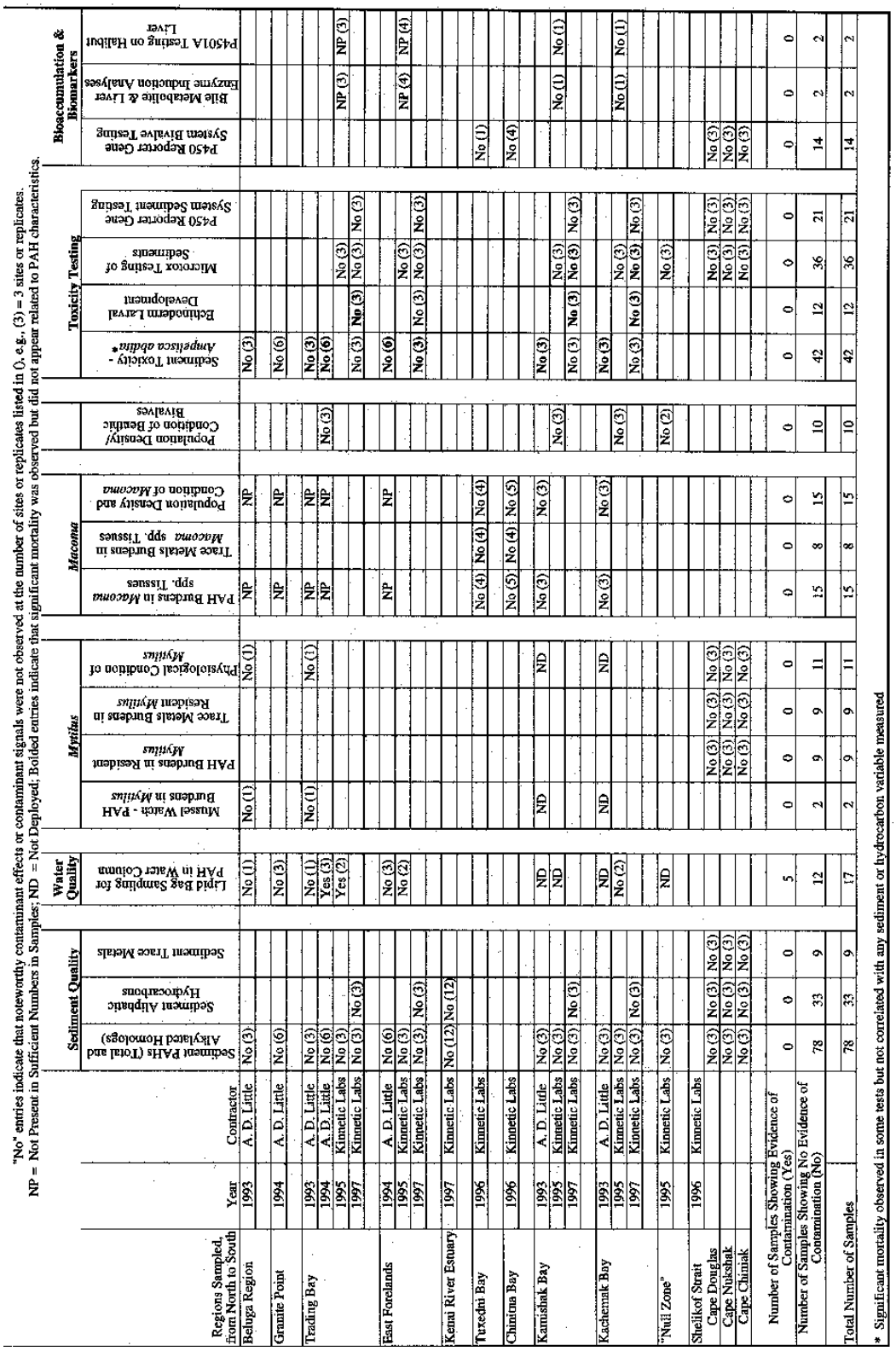
A variety of approaches was used to characterize potential contaminant concentrations in subtidal sediments in Cook Inlet and in intertidal and subtidal sediments along the Alaska Peninsula in northern Shelikof Strait (Tables 1-1 and 4-1). Analysis for polycyclic aromatic hydrocarbons (total PAH and the alkylated homologs), conducted at nearly every region examined, was the most commonly used approach. PAH was analyzed in sediments in all years of the EMP and for all regions in which subtidal sediments were collected. Samples were collected in vicinity of Beluga River, Granite Point, Trading Bay, East Forelands, Kenai River estuary, Kamishak Bay, Kachemak Bay, the "null zone", and Capes Douglas, Nukshak, and Chiniak on the northeastern shore of Alaska Peninsula in Shelikof Strait. The only areas in which hydrocarbons were not assessed in sediments were Chinitna and Tuxedni Bays. Unfortunately, the data are somewhat inconsistent temporally because the extraction procedure was changed from sonication to Soxhlet as a consequence of a change in analytical contractors. The importance of this difference is addressed in detail in Section 4.8.2 below. Aliphatic hydrocarbons were analyzed at a limited number of sites only in 1997. These data are therefore of limited use for spatial or temporal comparisons. The information provided for trace metals is also limited. Trace metals in sediments were analyzed for three locations along the northeastern shore of the Alaska Peninsula only in 1997.

In addition to the chemical analyses for potential contaminants outlined above, particle grain size and total organic carbon content of the sediments were analyzed. These sediment properties can exert important influences on the distribution of petroleum hydrocarbons and other contaminants and are useful in interpreting observed distribution patterns.

4.1.1 Distribution of Total PAHs

PAHs in the sediments were analyzed for 78 sites in seven distinct regions covering Cook Inlet and northwestern Shelikof Strait during the EMP (Tables 4-1 and 4-2). The overall average concentration (± standard error (SE)) for total PAH (TPAH) over the duration of the EMP was 83.4 ± 9.2 nanograms/gram (ng/g = parts per billion) dry weight. Average concentration of TPAH for individual sediment samples ranged from 6 ng/g dry weight at the East Forelands in 1995 to 469 ng/g dry weight outside the Kenai River in 1997 (Figure 4-2). TPAH concentrations in samples collected in most regions within a specific survey

varied substantially. Differences between lowest and highest values measured in an area



"No" entries indicate that noteworthy contaminant effects or contaminant signals were not observed at the number of sites or replicates listed in (), e.g., (3) = 3 sites or replicates.
NP = Not Present in Sufficient Numbers in Samples; ND = Not Deployed; Bolded entries indicate that significant mortality was observed but did not appear related to PAH characteristics.

Regions Sampled, from North to South	Year	Contractor	Sediment Quality: Sediment PAHs (Total and Alkylated Homologs)	Sediment Quality: Sediment Aliphatic Hydrocarbons	Sediment Quality: Sediment Trace Metals	Water Quality: Lipid Bag Sampling for PAH in Water Column	*Mytilus*: Mussel Watch - PAH Burdens in *Mytilus*	*Mytilus*: PAH Burdens in Resident *Mytilus*	*Mytilus*: Trace Metals Burdens in Resident *Mytilus*	*Mytilus*: Physiological Condition of *Mytilus*	*Macoma*: PAH Burdens in *Macoma* spp. Tissues	*Macoma*: Trace Metals Burdens in *Macoma* spp. Tissues	*Macoma*: Population Density and Condition of *Macoma*	Population Density/ Condition of Benthic Bivalves	Toxicity Testing: Sediment Toxicity - *Amphelisca abdita**	Toxicity Testing: Bethinoderm Larval Development	Toxicity Testing: Microtox Testing of Sediments	Toxicity Testing: P450 Reporter Gene System Sediment Testing	Bioaccumulation & Biomarkers: P450 Reporter Gene System Bivalve Testing	Bioaccumulation & Biomarkers: Bile Metabolite & Liver Enzyme Induction Analyses	Bioaccumulation & Biomarkers: P4501A Testing on Halibut Liver
Beluga Region	1993	A. D. Little	No (3)			No (1)	No (1)			No (1)	NP		NP		No (3)							
Granite Point	1994	A. D. Little	No (6)			No (3)					NP		NP		No (6)							
Trading Bay	1993	A. D. Little	No (3)			No (1)	No (1)			No (1)	NP		NP		No (3)							
	1994	A. D. Little	No (6)			Yes (3)					NP		NP	No (3)	No (6)							
	1995	Kinnetic Labs	No (3)			Yes (2)														NP (3)	NP (3)	
	1997	Kinnetic Labs	No (3)	No (3)											No (3)	No (3)	No (3)	No (3)	No (3)			
East Forelands	1994	A. D. Little	No (6)			No (3)					NP		NP		No (6)							
	1995	Kinnetic Labs	No (3)			No (2)											No (3)			NP (4)	NP (4)	
	1997	Kinnetic Labs	No (3)	No (3)											No (3)	No (3)	No (3)	No (3)	No (3)			
Kenai River Estuary	1997	Kinnetic Labs	No (12)	No (12)																		
Tuxedni Bay	1996	Kinnetic Labs									No (4)	No (4)	No (4)							No (1)		
Chinitna Bay	1996	Kinnetic Labs									No (5)	No (4)	No (5)							No (4)		
Kamishak Bay	1993	A. D. Little	No (3)			ND	ND			ND	No (3)		No (3)		No (3)							
	1995	Kinnetic Labs	No (3)			ND								No (3)			No (3)			No (1)	No (1)	
	1997	Kinnetic Labs	No (3)	No (3)											No (3)	No (3)	No (3)	No (3)	No (3)			
Kachemak Bay	1993	A. D. Little	No (3)			ND	ND			ND	No (3)		No (3)		No (3)							
	1995	Kinnetic Labs	No (3)			No (2)								No (3)			No (3)			No (1)	No (1)	
	1997	Kinnetic Labs	No (3)	No (3)											No (3)	No (3)	No (3)	No (3)	No (3)			
"Null Zone"	1995	Kinnetic Labs	No (3)			ND								No (2)			No (3)					
Shelikof Strait	1996	Kinnetic Labs						No (3)	No (3)	No (3)										No (3)		
Cape Douglas			No (3)	No (3)	No (3)												No (3)	No (3)	No (3)			
Cape Nukshak			No (3)	No (3)	No (3)			No (3)	No (3)	No (3)							No (3)	No (3)	No (3)	No (3)		
Cape Chrinak			No (3)	No (3)	No (3)			No (3)	No (3)	No (3)							No (3)	No (3)	No (3)	No (3)		
Number of Samples Showing Evidence of Contamination (Yes)			0	0	0	5	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Number of Samples Showing No Evidence of Contamination (No)			78	33	9	12	2	9	9	11	15	8	15	10	42	12	36	21	14	2	2	
Total Number of Samples			78	33	9	17	2	9	9	11	15	8	15	10	42	12	36	21	14	2	2	

* Significant mortality observed in some tests but not correlated with any sediment or hydrocarbon variable measured

Table 4-1. General summary of results from studies conducted during the CIRCAC Environmental Monitoring Program.

Regions Sampled, from North to South	Year	Total Polycyclic Aromatic Hydrocarbons in Sediments (ng/g dry weight)							
		Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Average	SE
Beluga Region	1993	47	29	105	--	--	--	60.3	28.1
Granite Point	1994	25	39	12	37	73	51	39.5	9.4
Trading Bay	1993	58	15	47	--	--	--	40.0	16.0
	1994	110	100	92	38	56	97	82.2	12.7
	1995	55	49	64	--	--	--	56.3	5.4
	1997	119	97	100	--	--	--	105.0	8.3
East Forelands	1994	8	84	39	32	24	33	36.7	11.4
	1995	32	9	6	--	--	--	15.7	10.2
	1997	156	19	136	--	--	--	103.7	52.2
Kenai River Estuary	1997	469	99	116	125	3	180	182.1	47.1
from offshore into river		108	131	121	200	529	104		
Kamishak Bay	1993	37	31	26	--	--	--	31.3	4.0
	1995	33	54	30	--	--	--	38.8	9.2
	1997	75	63	67	--	--	--	68.2	4.4
Kachemak Bay	1993	54	10	39	--	--	--	34.4	15.6
	1995	51	51	58	--	--	--	53.2	2.8
	1997	93	50	51	--	--	--	64.6	17.7
"Null Zone"	1995	116	124	130	--	--	--	123.3	4.9
Shelikof Strait	1997								
Cape Douglas		114	82	102	--	--	--	99.4	11.2
Cape Nukshak		114	120	135	--	--	--	123.2	7.8
Cape Chiniak		110	123	88	--	--	--	106.9	12.5

Table 4-2 Summary of concentrations of Total Polycyclic Aromatic Hydrocarbon in sediment from hydrocarbon analyses conducted during studies for the Environmental Monitoring Program.

ranged from 12 to 912 percent and averaged 216 percent (excluding the measurements from the Kenai River study, which were extremely variable). The most uniform measurements were observed in Kamishak Bay and the least uniform at the East Forelands (again excluding the Kenai River measurements).

Regional averages for all years sampled ranged from 39.5 ± 9.4 ng/g dry weight for Granite Point (sampled only in 1994) to 182.1 ± 47.1 ng/g dry weight for the Kenai River estuary, sampled at 12 sites in 1997. Generally, distribution of TPAH in the sediments sampled during the EMP did not appear to exhibit predictable patterns. TPAH concentrations were below the inlet's average (in order of increasing TPAH) in the Granite Point region, Kamishak Bay, the East Forelands region, Kachemak Bay, the Beluga region, and Trading Bay, and above average at the Shelikof Strait sites, the "Null Zone", and in the Kenai River Estuary. Concentrations of TPAH are all below average in the regions that are closest to oil production and shipping activities, except in the Kenai River estuary. Except for some samples in the Kenai River study, higher concentrations are found at the sites most distant from the sources of oil contamination.

Because sampling sites generally were not occupied more than once during the EMP, the data set is not well designed to assess temporal trends. Nevertheless, an attempt was made in 1997 to reoccupy some of the stations established in 1993 or 1994. However, this attempt was only partially effective. Examination of the geographic coordinates indicates that the locations of the sites sampled in 1997 only generally approximated those sampled in 1994. All of the sites were located more than 60 m apart and differed in water depth by between 1 and 8 meters. In some cases, the locations may have differed by several nautical miles. Moreover, comparison of the PAH data may have been further confounded by methods differences because the extraction procedures were different in these two years. TPAH concentrations were approximately twice as high in 1997 as in 1993 (Table 4-2; compare Trading Bay, Kamishak Bay, and Kachemak Bay for 1993 and 1997). However, the difference is substantially greater than the difference reported for the two methods by KLI (1997).

While discussing the levels of TPAH in the sediments and the possible spatial and temporal patterns, it is important to compare these data with the information available on the ability of the analyses to detect PAHs and on the potential toxicity of these compounds. Generally, the Method Detection Limits (MDL) for the analytical procedures used in the EMP for TPAH were approximately 10 ng/g dry weight. The point here is that the concentrations reported in this study are relatively close to the MDL for these analytical procedures.

The potential toxicity of a wide variety of potential contaminants has been reported by Long et al. (1995). Based on their evaluation of a large number of studies describing the toxicity associated with different concentrations of contaminants, they described three levels of potential toxicity. For each contaminant, these ranges are separated by two derived values, i.e., the effects range-low (ERL) and the effects range-median (ERM). Concentrations below the ERL are in a range considered to have minimal effects, i.e., effects would only rarely be observed. Concentrations between the ERL and the ERM are in a range where effects would occasionally occur. Concentrations above the ERM are in

a range where effects would frequently occur. According to the analyses by Long et al. (1995), the ERL and ERM for TPAH are 4,020 and 44,792 ng/g dry weight, respectively. The ERL for TPAH is about 50 times higher than the concentrations of TPAH reported in these studies. In general, Cook Inlet sediments are very clean. Further insight into the potential toxicity of the PAH found in the sediments of Cook Inlet and Shelikof Strait will be provided by an examination of patterns in distribution of the alkylated homologs in a later section.

4.1.2 Distribution of Aliphatic Hydrocarbons

Total aliphatic hydrocarbons (TAHC) in the sediments were analyzed at twelve sites in four regions of Cook Inlet and in twelve areas on the Kenai River estuary in 1997 (Tables 4-1 and 4-3). Concentrations in Cook Inlet ranged from 49.5 to 2000.3 ng/g and averaged 906 ± 201 ng/g (SE). Highest concentrations were observed in Kachemak Bay, where concentrations were more that twice as high as the second highest region (Trading Bay). The lowest individual concentration (49.5 ng/g dry weight) occurred at the East Forelands. The lowest average concentration was observed in Kamishak Bay. Except in the vicinity of the East Forelands, variation in concentrations within a region was fairly low (Table 4-3). Concentrations in the Kenai River estuary ranged from 225.3 to 3139.3 ng/g dry weight and averaged 1705.8 ng/g. Generally, they were higher than all other regions sampled except Kachemak Bay. Relative to position within the estuary, TAHC were quite variable and exhibited no apparent spatial trend.

Regions Sampled, from North to South	Year	Total Aliphatic Hydrocarbons (ng/g dry weight)				
		Site 1	Site 2	Site 3	Average	SE
Trading Bay	1997	895.2	658.0	905.1	1183.4	98.9
East Forelands	1997	285.6	49.5	1470.2	777.4	538.3
Kamishak Bay	1997	408.1	409.1	332.3	938.1	31.2
Kachemak Bay	1997	2000.3	1816.5	1639.4	1937.9	127.6
Kenai River estuary	1997	2816.0	2770.5	225.3	1670.7	285.5
		1325.1	848.7	3139.3		
		952.1	748.0	1382.9		
		1228.9	2349.9	2682.4		

Table 4-3. Summary of concentrations of Total Aliphatic Hydrocarbon in sediment from hydrocarbon analyses conducted during studies for the Environmental Monitoring Program.

4.1.3 Distribution of Trace Metals

Analysis of trace metals in sediments was conducted only in 1996 for the nine subtidal sites sampled at three capes in northwestern Shelikof Strait (Table 4-1) and therefore provide a very limited data set (KLI 1997). The metals examined include aluminum, arsenic, barium, cadmium, chromium, copper, nickel, lead, vanadium, and zinc. Generally, concentrations of the trace metals were relatively low. All but aluminum and vanadium exhibited strong correlations ($r = 0.77$ to 0.91) with fine fraction of the sediments (i.e., silt + clay). ERLs and ERMs for cadmium, chromium, copper, lead, and zinc exceed the concentrations observed in the sediments by a substantial margin. ERL values are not available for aluminum, barium, and vanadium. Arsenic and nickel concentrations were above ERL values but fell within the range observed previously in Cook Inlet and Shelikof Strait by Robertson and Abel (1979). Moreover, the concentrations for arsenic at these sites are lower than the ambient concentration of arsenic in the Susitna River particulates (KLI 1997) and the concentration of nickel is lower than the average observed in the Earth's crustal materials (A. D. Little 1998b). All indications are that the trace metals observed are derived from natural crustal rather than anthropogenic sources.

4.1.4 Sediment Characteristics - Particle Grain Size and Total Organic Carbon

The major sediment characteristics, particle grain size and total organic carbon, were measured for each sediment sample, primarily for use in normalizing hydrocarbon concentrations. By themselves, these data are irrelevant to the objective of describing hydrocarbon conditions and therefore have not been summarized or discussed in this report.

4.2 Sediment Toxicity Testing

The types of sediment toxicity tests used to assess sediment quality at a variety of locations in Cook Inlet include: survival of the amphipod *Ampelisca abdita* following exposure to bulk sediments; echinoderm larval development testing following exposure to pore water extracted from sediments; Microtox© testing; and Cytochrome P450 reporter gene system testing (Table 4-1). Amphipod toxicity was tested for sediments collected during three surveys (1993, 1994, and 1997). Microtox© testing was also conducted in three surveys (1995, and two studies in 1997). Testing using the P450 reporter gene system was conducted in two surveys (1995 and 1997). Finally, echinoderm larval development testing was used in 1997. The purpose of conducting four types of tests in 1997 was to compare the effectiveness of these tests on the same sediment and thereby provide a basis for selecting the best method in future monitoring studies.

4.2.1 Toxicity Tests

4.2.1.1 Amphipod Sediment Testing with *Ampelisca abdita*

Sediment toxicity to amphipods was tested at 42 sites during the EMP (Table 4-1 and 4-4). Significant mortality was observed at several locations in each survey for which

Regions Sampled, from North to South	Year	% Survival in Amphipods*						Average % Survival
		Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	
Beluga Region	1993	80	83.5	80	–	–	–	81.2
Granite Point	1994	76	79	78	80	70	83	77.7
Trading Bay	1993	**71**	**73**	78	–	–	–	74.0
	1994	**68**	84	**43**	86	67	77	70.8
	1997	99	94	99	–	–	–	97.3
East Forelands	1994	95	**70**	78	**56**	85	**71**	75.8
	1997	**52**	**69**	**10**	–	–	–	43.7
Kamishak Bay	1993	**61**	78	83	–	–	–	74.0
	1997	90	93	88	–	–	–	90.3
Kachemak Bay	1993	86	**66**	**65.5**	–	–	–	72.5
	1997	94	90	92	–	–	–	92.0

* Significant mortality observed in some tests but not correlated with any sediment or hydrocarbon variable measured.

4-4. Summary by region of percent survival in amphipod toxicity tests conducted during studies for the CIRCAC Environmental Monitoring Program.

amphipod testing was employed, based on standardized statistics applied to toxicity testing data. In 1993, Table significant mortality was reported for two samples from Trading Bay, one from Kamishak Bay, and two from Kachemak Bay. In 1994, significant mortality was observed in two samples from Trading Bay and three from the East Forelands area. In 1997, mortality was observed only in the three samples from the East Forelands area. In all cases, PAH concentrations in the sediments were two or more orders of magnitude below the ER-L value for Total PAH (4,022 parts per billion (ppb); Long et al. 1995) and comparisons between the levels of toxicity in the amphipod tests and TPAH in the sediments did not exhibit any appreciable correlations. It was suggested each time that amphipod testing was conducted that ammonia may have been the cause of the observed toxicity but ammonia was measured only in 1997. At that time, it was found in some of the samples but at levels that are deemed acceptable (KLI 1998a).

The standardized testing applied to toxicity test results appears to be quite conservative. Using standardized testing, significant mortality was reported in 30 percent of the amphipod tests performed by A. D. Little and 25 percent performed by KLI. In contrast, where the results of replicated tests for control and treatment tests for the amphipod tests are compared using randomization t-tests, substantially higher numbers of significant differences were observed. Mortality was significantly higher in fourteen of eighteen (78 percent) and five of twelve (42 percent) samples in the 1994 and 1997 data sets, respectively (raw data were not available for evaluation of the 1993 data).

The EPA has indicated (Anon. 1994) that mortality of the amphipod *Ampelisca abdita* is elevated in sediments with low concentrations of fine sediments (silt and clay). This condition is characteristic of most of the sediments sampled in this program. The level of significance showed a significant positive correlation with percent silt+clay in 1997 ($r = 0.74$; $p = 0.006$) but surprisingly was unrelated in the 1994 data set ($r = 0.06$).

4.2.1.2 Microtox © Testing

Microtox© testing was conducted on sediments from 36 sites distributed among Trading Bay, East Forelands, Kamishak and Kachemak Bays, the "Null" zone, and three sites in Shelikof Bay during the EMP (Table 4-1 and 4-5). Significant inhibition of bacterial bioluminescence was observed in two samples from Kamishak Bay and one sample from Kachemak Bay (Table 4-5). However, the Microtox© results did not correlate with any variables related to sediment hydrocarbons, implying that the observed effects are not related to petroleum hydrocarbons in the sediments. In fact, the Microtox© system has recently been shown to respond primarily to the presence of elemental sulfur in the sediments rather than other contaminants (Jacobs et al. 1992). Elemental sulfur is a common constituent in anaerobic sediments. It is innocuous to the infauna but when it is co-extracted from sediments with the contaminants of concern by the solvents used in the Microtox© procedure, it is toxic to the bacteria used in the procedure.

Regions from North to South	Year	Toxicity of Sediment Extract in Microtox Tests, EC_{50} in mg/mL		
		Site 1	Site 2	Site 3
Trading Bay	1995	>1.63	>1.63	>1.63
	1997	3.26	>1.63	>1.63
East Forelands	1995	>1.63	>1.63	>1.63
	1997	>1.63	>1.63	>1.63
Kamishak Bay	1995	>1.63	>1.63	>1.63
	1997	>1.63	**0.935**	**3.18**
Kachemak Bay	1995	>1.63	>1.63	>1.63
	1997	**1.77**	4.05	>1.63
"Null Zone"	1995	>1.63	>1.63	>1.63
Shelikof Strait	1997			
Cape Douglas		>1.63	>1.63	>1.63
Cape Nukshak		>1.63	>1.63	>1.63
Cape Chiniak		>1.63	>1.63	>1.63

* Significant mortality observed in some tests but not correlated with any sediment or hydrocarbon variable measured

Table 4-5. Summary of results from Microtox© testing studies conducted during the Environmental Monitoring Program.

4.2.1.3 P450 Reporter Gene System

The P450 reporter gene system was used to evaluate exposure of sediments to petroleum hydrocarbons at 21 sites during the EMP in 1997 (Table 4-1 and 4-6). It was being evaluated as a less costly "screening" method. Testing was performed on sediments from Trading Bay, the East Forelands area, Kamishak Bay, Kachemak Bay, and Cape Douglas, Cape Nukshak, and Cape Chiniak in Shelikof Strait. No significant induction of folding was observed in the testing. Highest values in sediment assays were observed for Trading Bay and Cape Nukshak. Lowest values were from East Forelands and Kachemak Bay. Overall, the values observed in both sediments and tissues in Shelikof Strait were higher than those observed in Cook Inlet..

Regions Sampled, from North to South	Year	P450 RGS Toxicity Testing (µg B(a)PEq/g)				Average
		Site 1	Site 2	Site 3	Site 4	
Sediment Assays						
Trading Bay	1997	2.10	1.50	2.50	–	2.03
East Forelands	1997	0.10	0.20	0.20	–	0.17
Kamishak Bay	1997	0.80	0.50	0.90	–	0.73
Kachemak Bay	1997	0.50	0.20	0.40	–	0.37
Shelikof Strait	1997					
Cape Douglas		0.69	0.92	1.04	–	0.88
Cape Nukshak		2.89	1.66	2.50	–	2.35
Cape Chiniak		0.99	0.91	0.83	–	0.91
Tissue Assays						
Tuxedni Bay - *Macoma balthica*	1996	3.76	–	–	–	3.76
Chinitna Bay - *Macoma balthica*	1996	0.00	1.08	0.61	0.00	0.42
Shelikof Strait - *Mytilus trossulus*	1996					
Cape Douglas		5.29	5.40	2.80	–	4.50
Cape Nukshak		0.37	0.77	2.25	–	1.13
Cape Chiniak		3.31	2.73	3.04	–	3.03

Table 4-6. Summary of results for P450 Reporter Gene System assays for sediments and tissues from studies conducted during the Environmental Monitoring Program.

P450 reporter gene systems were used to evaluate exposure of tissues to petroleum hydrocarbons at 14 sites during the EMP (Table 4-1 and 4-6). Testing was performed on tissues of *Macoma balthica* from Tuxedni and Chinitna Bays and the blue mussel (*Mytilus trossulus*) from Cape Douglas, Cape Nukshak, and Cape Chiniak in Shelikof Strait.

Highest responses were observed in tissues from *M. balthica* from Tuxedni Bay and *M. trossulus* from Cape Douglas.

All of the values observed are well below the level considered to be indicative of serious contamination (60 µg B(a)P Eq/g, J. W. Anderson personal communication). In fact, most are well within a range considered representative of baseline conditions (Anderson 1996). The lack of correlation with any of the hydrocarbon variables measured indicates that petroleum hydrocarbons were not driving the P450 response at any of the sites examined. The EMP did not analyze chlorinated organic compounds which are also known to induce responses in the P450 reporter gene system (RGS) assay. However, preliminary data from an EPA subsistence study (1998) found only very low traces of polychlorinated biphenyls and methylmercury in "sea bass" and cadmium in snails, chitons and octopus collected in another region of Cook Inlet.

4.2.1.4 Echinoderm Larval Development Testing

Echinoderm larval development was used in the 1997 survey to evaluate toxicity of sediments at 12 sites during the EMP (Table 4-1 and 4-7). Testing was performed using porewater from sediments collected at Trading Bay, East Forelands, Kachemak and Kamishak Bays. Significant toxicity was observed in all the samples from Kachemak and Kamishak Bays and one from Trading Bay (Table 4-7). However, the relationship between level of toxicity and concentration of petroleum hydrocarbons was poor whereas the relationship between levels of toxicity and initial concentrations of ammonia in the pore water was high (KLI 1998a). These results suggest that ammonia is a more likely cause of the observed mortality than petroleum hydrocarbons.

		Echinoderm Toxicity (EC_{50} in % Test Fluid)				
Regions Sampled, from North to South	Year	Site 1	Site 2	Site 3		Average EC_{50}
Trading Bay	1997	**72.1**	>100	>100		>90.7
East Forelands	1997	>100	>100	>100		>100
Kamishak Bay	1997	**11**	**17**	**6.3**		11.4
Kachemak Bay	1997	**35.9**	**15.9**	**27.8**		26.5

* Significant mortality observed in some tests but not correlated with any sediment or hydrocarbon variable measured

Table 4-7. Summary of results for larval echinoderm toxicity studies conducted during the Environmental. Monitoring Program.

4.2.2 Toxicity Patterns

The toxicity data do not provide a compelling argument for contaminant effects of any type in the regions sampled in Cook Inlet or Shelikof Strait. There is a general paucity of evidence from within or among the various types of toxicity tests performed suggesting temporal or spatial trends . Amphipod and Microtox© tests were the only kinds of toxicity test performed in two or more surveys. The fact that sediments from Trading Bay and the East Forelands area caused significant amphipod mortality in the tests in most years sampled (Table 4-4) could be interpreted as an indication of chronic sediment problems in these regions. However, based on an EPA report on amphipod testing (Anon. 1994) and the low concentrations of TPAH observed in the sediments in these regions, sediment grain size (i. e., paucity of fine sediments) appears to be a far more likely cause of the mortality in these tests.

Agreement among toxicity tests in findings of toxicity would provide a strong argument for impacts. However, the only year that more than one toxicity test was performed concurrently was 1997, when the results of four different toxicity tests were compared for the same sediments. The only agreements in findings of significant effects were between the echinoderm larval development and the Microtox© tests for Kamishak Bay and Kachemak Bay.

The fact that the average concentration of TPAH in sediments in Cook Inlet is only about 1/50th of the NOAA ER-L for TPAH (Long et al. 1995) provides insight into the lack of a correlation between toxicity and TPAH. TPAH concentrations in the sediments sampled in Cook Inlet are more than an order of magnitude below the level considered by Long et al. (1995) to represent the concentration at which minimal effects would occur.

4.2.3 Implications of Ambient and Testing Temperature Differences

Because of the temperatures at which they are conducted, it is likely that the toxicity tests all provide a considerably conservative estimate of the potential toxicity of the sediments in Cook Inlet. Temperatures used for the tests are all considerably higher than the ambient temperatures of the sediments in Cook Inlet. Typically, the level of toxicity of sediments is directly related with sediment temperature (Winger and Lasier 1993; McGee et al. 1993). Thus, a sediment sample will be more toxic at high temperature than at a low temperature. Therefore, sediments from Cook Inlet will typically exhibit greater toxicity in lab tests than in their natural setting.

4.3 Hydrocarbon Analyses for *Macoma* and *Mytilus* Tissues

PAH concentrations were measured in bivalve tissues in only two surveys (Table 1-1). In 1993, measurements were made on mussels (*Mytilus trossulus*) and deposit-feeding clams (*Macoma balthica*). The mussels were suspended in cages in the water column for 30 days in Trading Bay and near the Beluga River, using an approach similar the NOAA Mussel Watch program. The *M. balthica* were collected from subtidal sediment samples

in Kachemak and Kamishak Bays (Table 4-1). Many of the mussels in the mussel watch experiment died and the approach was discontinued. Moreover, sufficient quantities of *Macoma* could not obtained in the 1994 survey, and that approach was also discontinued. In 1996, PAH analyses were conducted on: 1) resident intertidal mussels collected from three sites in Shelikof Strait; and 2) resident intertidal populations of *Macoma balthica* from four sites in Tuxedni Bay and five sites in Chinitna Bay (Table 4-1).

This data set for TPAH in bivalve tissues (Table 4-8) is small but it provides some useful data regarding baseline conditions of bivalves in Cook Inlet and northwestern Shelikof Strait as well as general conditions in Cook Inlet. Moreover, it provides insight into the difficulties of PAH analysis at the low concentrations encountered in this region.

The TPAH concentrations shown Table 4-8 differ from those reported in the relevant EMP reports. Many of the values are based on recalculations of data reported by A. D. Little (ADL) and Kinnetic Laboratories, Inc. (KLI). ADL (1995a and b) reported TPAH in two forms, one including and one excluding perylene. Neither included C_0-naphthalene. KLI also omitted perylene from their TPAH values. Because of the importance of perylene in Cook Inlet coal samples and the potential for suspension-feeding bivalves to ingest fine particulate coal, one value of TPAH that we have included in this table includes perylene.

The most notable finding in Table 4-8 is that TPAH concentrations in all of the bivalves examined are very low. All of the areas sampled were apparently quite clean with reported concentrations ranging from 29.4 to 531.8 ng/g dry weight (Table 4-8). In 1993, the total PAH values were uniformly low (generally < 100 ng/g dry weight) in all but one of the samples, which represented subtidal exposures of caged mussels and native subtidal populations of *Macoma*. In 1996, the TPAH concentrations in the intertidal

Target Species	Site or Source	Year Sampling Level	Concentration of TPAH Homologs* (ng/g dry weight) 1993 TPAH	1993 TPAH + perylene	1996 TPAH	1996 TPAH + perylene
		Wild Collected Bivalves				
Macoma balthica						
	Kamishak Bay 1	Subtidal	50.0	50.0		
	Kamishak Bay 2	Subtidal	36.0	41.0		
	Kamishak Bay 3	Subtidal	45.0	50.0		
	Kachemak Bay 1	Subtidal	42.0	55.0		
	Kachemak Bay 2	Subtidal	38.0	45.0		
	Kachemak Bay 3	Subtidal	79.0	92.0		
	Chinitna Bay - 1	Intertidal			311.2	319.5
	Chinitna Bay - 2	Intertidal			271.1	275.8
	Chinitna Bay - 3	Intertidal			348.6	356.3
	Chinitna Bay - 4	Intertidal			402.4	412.0
	Tuxedni Bay - 1	Intertidal			295.5	300.6
	Tuxedni Bay - 2	Intertidal			371.5	374.2
	Tuxedni Bay - 3	Intertidal			362.9	367.4
	Tuxedni Bay - 4	Intertidal			407.9	414.4
	Annual Average		48.3	55.5	346.4	352.5
	Std. Dev.		15.8	18.5	49.7	50.3
Mytilus trossulus						
	Cape Douglas - 1	Intertidal			384.5	385.4
	Cape Douglas - 2	Intertidal			130.2	132.2
	Cape Douglas - 3	Intertidal			151.6	154.6
	Cape Nukshak - 1	Intertidal			320.3	321.3
	Cape Nukshak - 2	Intertidal			498.3	501.7
	Cape Nukshak - 3	Intertidal			531.8	534.3
	Cape Chiniak - 1	Intertidal			206.8	211.8
	Cape Chiniak - 2	Intertidal			177.8	179.8
	Cape Chiniak - 3	Intertidal			252.0	256.0
	Annual Average		–	–	294.8	297.5
	Std. Dev.		–	–	148.8	148.6
		Experimental Mussel Watch Arrays				
Mytilus trossulus						
	Pre-exposure TPAH Concentration for Source Mussels					
	Halibut Cove	Subtidal	95.6	96.6		
	After 1-month Deployment in Cages					
	Beluga - surface	Subtidal	79.2	79.7		
	Beluga - mid depth	Subtidal	96.7	96.7		
	Beluga - deep	Subtidal	163.0	163.0		
	Trading Bay - surface	Subtidal	49.0	52.0		
	Trading Bay - mid depth	Subtidal	29.4	29.4		
	Trading Bay - deep	Subtidal	32.4	32.4		
	Survey Average		75.0	75.5		
	Std. Dev.		50.6	50.3		

* The TPAH concentrations shown in this table are based on recalculations of the data reported by A. D. Little (ADL) and Kinnetic Laboratories, Inc. (KLI). ADL (1995a and b) reported TPAH in two forms. One included perylene and the other didn't. Neither included C0-naphthalene. KLI reports did not include Co-naphthalene in their reported TPAH values. Because of the importance of perylene in Cook Inlet coal samples and its possible uptake by suspension-feeding bivalves, we have included a value of TPAH in this table the includes perylene.

Table 4-8. Summary of concentrations of Total Polycyclic Aromatic Hydrocarbon (ng/g) in bivalve species from hydrocarbon analyses conducted during studies for the Environmental Monitoring Program.

Macoma samples in Tuxedni Bay and Chinitna Bay appeared to be substantially higher (200-400 ng/g dry weight) than the earlier measurements for this species collected subtidally in Kamishak and Kachemak Bays. As an indication of how low the concentrations are, most of the chromatogram peaks were below the MDLs in both years. In contrast, TPAH concentrations cited by Reish et al. (1993) for bivalves in California, Australia, the Netherlands, Trinidad, and France range from 35 to 27,000 ng/g TPAH dry weight and average 5,076 ng/g. Highest concentrations were reported for France and Trinidad. Concentrations observed in 1991 in mussels from Prince William Sound exposed to EXXON Valdez oil spill (EVOS) oil in 1989 averaged about 3,500 ng/g dry weight (Houghton et al. 1993). Mussels collected near a cannery in Seward for the same study to assess conditions in a port had a concentration of 6,200 ng/g TPAH dry weight. TPAH concentrations in mussels collected from Prince William Sound for the Long-Term Environmental Monitoring Program (LTEMP) program between 1993 and 1997 at sites exposed to EVOS oil in 1989 averaged 368 ng/g dry weight.

The reported concentrations differed substantially between years. Concentrations in *Macoma balthica* averaged 48 and 364 ng/g in 1993 and 1996, respectively. Similarly, concentrations in *Mytilus trossulus* averaged 75 and 295 ng/g in these years. These differences may be a consequence of differences in sampling levels, which differed between years for each species or differences in analytical method. The 1993 samples were all subtidal whereas the 1996 samples were all intertidal. However, great care must be taken to examine the individual PAH profiles to ensure that perceived TPAH differences actually represent different hydrocarbon burdens in the tissues and not laboratory artifacts or systematic bias introduced by changing laboratories between 1993 and 1996. The extraction procedures and the analytical labs differed between years. Moreover, it should be noted that many of the individual PAH components were observed at concentrations that were just slightly above their respective MDLs. The MDLs for the two labs conducting these analyses differed substantially. Finally, the lab conducting the analyses in 1996 reported substantial PAH concentrations in its procedural blanks. The concentrations reported in these blanks are large enough to partially account for the reported differences in TPAH levels between years. With this in mind, and in view of the absence of repeated sampling at any sites, it does not appear fruitful to compare these results between years or sampling levels.

Total lipid concentrations were measured for the tissues of the mussels used for PAH analyses from Shelikof Strait (Table 1-1). This measurement was taken because it was thought, as a consequence of the lipophilic nature of PAHs, that it would be helpful in normalizing hydrocarbon concentrations in tissues. It is now recognized that lipid normalization of PAH concentrations in tissue is not useful (Gosling 1992; Sericano et al. 1990; Widdows et al. 1987; and Payne et al. 1998).

The mussels deployed in the mussel watch experiment provide insight into the level of contamination of the marine environment in Cook Inlet. The source mussels from Halibut Cove actually exhibited a low-level diesel signal before deployment. At the end of the 1-month deployments in Beluga River and Trading Bay areas, PAH concentrations decreased substantially at Trading Bay but increased slightly at Beluga River. This

indicates that seawater in Trading Bay was even cleaner than Halibut Cove. The fingerprint for the Trading Bay produced water was not apparent in the mussels deployed in the vicinity of the outfall. The mussels in the Beluga region had slightly higher concentrations of alkylated naphthalenes following deployment, and one sample had assimilated some benzo(a)pyrene. All had depurated most of the alkylated fluorenes and phenanthrenes that were present in the Halibut Cove control samples before being transplanted. The data from the mussel watch deployments must be viewed with a certain amount of suspicion, however. The animals used in these experiments were greatly stressed by the environmental conditions in the areas of deployment. Many of the caged mussels died during the one-month deployment and the remainder were in very poor condition when the program was terminated. The causes of stress were probably high loads of Total Suspended Solids (TSS) and lack of suitable food (phytoplankton).

4.4 Bioaccumulation and Biomarkers in Fishes

In 1995, fishes were collected with trawls, longlines, and rod-and-reel at several locations throughout Cook Inlet for the purpose of assessing exposure to hydrocarbons through analysis for bile metabolites and cytochrome P4501A (Tables 1-1 and 4-1). Collection sites included the East Forelands, Trading Bay, the "null zone" in the outer reaches of lower Cook Inlet, and Kamishak and Kachemak Bays (KLI 1996). Catches were erratic and were not adequate for the analyses at the East Forelands or Trading Bay. The only fish species examined was Pacific halibut (*Hippoglossus stenolepis*).

This single data set provides a one-time view of PAH exposure in one species of demersal fish in two regions in the inlet, i.e., Kachemak and Kamishak Bays. Concentrations of bile metabolites were low or below detection limits in the samples from both locations, indicating low exposure to hydrocarbons. In the P4501A analyses, values from Kachemak Bay were significantly higher than those from Kamishak Bay, indicating a higher level of exposure to hydrocarbons in Kachemak Bay. However, indicators of exposure were low in samples from both areas and agree with the findings of the bile metabolite and sediment PAH studies.

4.5 Lipid Bag Assessment of PAH in Water Column

Semi-permeable polymeric membrane devices (SPMDs or lipid bags) were deployed in the water column at a couple of sites during three early surveys (1993, 1994, and 1995) to assess PAHs in the water column (Tables 1-1 and 4-9). Most were deployed in the vicinity of terminal facilities in Trading Bay or Granite Point but one array was in the Beluga River region, ostensibly "upcurrent of existing offshore production activities" (A. D. Little 1995a), and one was deployed in Kachemak Bay. (Based on the results of the modeling study reported below, the Beluga River site does appear, in fact, to be effectively outside the influence of petroleum activities in middle and upper Cook Inlet even though it is downstream of these activities on a flooding tide.) Questions arose regarding the applicability and accuracy of the method and it was discontinued in later surveys.

Regions Sampled, from North to South	Year	Contractor	Surface	Mid	Bottom	Field Blank	Proc Blank	Lab Blank	Significant Results
Beluga Region	1993	A. D. Little	94.2	96.7	163.2	248.0			No (1)
Granite Point	1994	A. D. Little	1984.7	2072.0	1075.8	300.7			No (3)
Trading Bay	1993	A. D. Little	49.0	29.4	32.4	224.4			No (1)
	1994	A. D. Little	**5693.0**	**5620.0**	**5591.3**				Yes (3)
	1995	Kinnetic Labs	**11949.6**		**16458.9**	2443.4			Yes (2)
East Forelands	1994	A. D. Little	2866.7	1610.8	2030.0	224.5			No (3)
	1995	Kinnetic Labs	4605.6		6494.7	2403.8			No (2)
Kachemak Bay	1995	Kinnetic Labs	5545.4		7635.9	2513.9			No (2)
Control-93	1993	A. D. Little					95.6		
Proc Blank-94	1994	A. D. Little					12.0		
Proc Blank-94	1994	A. D. Little					390.0		
Lab Blank - 95	1995	Kinnetic Labs						718.3	
Lab Blank - 95	1995	Kinnetic Labs						2823.2	
Proc Blank - 95	1995	Kinnetic Labs					35.7		

Table 4-9. Summary of concentrations of Total Polycyclic Aromatic Hydrocarbon in the water column in hydrocarbon analyses of SPMDs conducted during studies for the Environmental Monitoring Program.

Perhaps a more difficult problem is correlating SPMD results with realistic exposures to the biota, the object of concern in this study. Although an SPMD may to some extent indicate the exposure to aqueous PAHs, uptake across respiratory tissue is only one of the exposure pathways to the local biota. Suspended oil droplets readily adsorb onto organic particulates in the water column. These particulates are consumed by filter-feeding organisms at all scales, from microbes to plankton to clams to fish; there is potentially high availability of PAHs through handling and digestion of the particulates. Thus, if a study design is unable to directly sample the local biota, SPMDs do not provide a complete evaluation of potential pathways.

Finally, in many areas in upper Cook Inlet, the water column tranmissivity is very limited; the sediment loads are so high, light can only penetrate a few centimeters. Knowing that PAHs adsorb onto organic particulates, we can assume under these conditions that the aqueous phase will not be the predominant form of PAHs. The question then becomes, what is the nature of the PAH uptake in SPMD under conditions of high suspended sediment loads?

4.6 Trace Metals in Bivalves

Trace metal concentrations in bivalve tissues were examined during the EMP in 1996 (Tables 1-1 and 4-1). Analyses were conducted for intertidal populations of: 1) the blue mussel *Mytilus trossulus* from three locations in northwestern Shelikof Strait (Capes Douglas, Nukshak, and Chiniak; KLI 1997a); and 2) *Macoma balthica* from Chinitna and Tuxedni Bays, in lower Cook Inlet (KLI 1997b). The bivalves were not depurated (allowed to self-cleanse after collection) in either case. Moreover, sediment samples were not collected for trace metals analysis at either of the intertidal sites at which bivalves were collected and therefore the influence of ingested sediments cannot be evaluated. While the NOAA Mussel Watch program does not depurate bivalves as a standard practice in its program, this nevertheless has the potential to confound analyses aimed at determining true tissue loading of trace metals in areas with high TSS loading, especially in the case of suspension feeders where there is a high likelihood that the target species will ingest fine inorganic particulates. In cases when animals have not been depurated, the level of contaminants reported from tissue analysis will reflect analytes in the gut contents as well as those found in the tissues. In most natural settings, trace metals found in sediments in the gut of deposit and suspension feeders are usually in the form of highly insoluble mineral salts and "invisible" to the animal. In this form, they generally do not pose a threat to the condition of an animal. Nevertheless, these metals become available for quantitation during the acid extraction typical of analytical methods and the concentration of these metals will be included in the value reported as "tissue" concentrations. Inclusion of the concentrations associated with sediments could lead to erroneous conclusions.

We have not summarized or analyzed the data for trace metals in bivalves. Based on effluent data from produced water discharges, the trace metals of most concern are arsenic, copper, lead, mercury, and zinc (Parametrix, Inc. 1995), None of these analytes exhibited concentrations higher than 60 ppb at the edge of the mixing zones for the respective facilities. Consequently, based on the results of the modeling study described

below, the likelihood of detecting signals of these constituents in sediments or clam tissues as far away as Tuxedni Bay is very small. Moreover, the inability to distinguish in the data from the tissue samples between actual metals in tissues and signals contributed by ingested sediment inorganics reduces the value of the measurements still further. Consequently, these data are of questionable relevance in addressing the effects from the activities of the oil industry.

4.7 Physiological Condition of Bivalves

Sizes of mussels, *Macoma* spp., and a few other bivalve species were measured as tissue weight and shell volume, and these data were used to calculate a condition factor for comparison among sites (Tables 1-1 and 4-1). Because these data sets lack spatial and temporal consistency, they are not useful to the objectives of the program and have not been summarized or evaluated any further. Moreover, this and other approaches to describing the condition of target populations are subject to a variety of problems related to the effects of lack of uniformity in food availability and variability in environmental condition such as temperature and salinity on growth, reproduction, and other physiological processes that are used to evaluate condition.

4.8 Comparability of Hydrocarbon Analytical Methods

4.8.1 Correction for Surrogate Compound Recoveries

The NOAA Status and Trends analytical protocol specifies correction of target analyte concentrations for surrogate recoveries. While not explicitly stated in either of their reports, ADL (A.D. Little 1995a,b) did correct for surrogate recoveries in reporting target PAH analyte data for the EMP (personal communication, John Brown, 1998). In the ADL draft final report for the 1997 Minerals Management Service (MMS) study of Shelikof Strait and Outermost Cook Inlet (ADL 1998b), it was stated that the data were not surrogate-recovery corrected. On checking this statement with John Brown of ADL, he indicated that the data were, in fact, corrected for surrogate recoveries, so the data generated in that effort should be comparable with their earlier studies. In concurrence with the NOAA protocols, Geochemical and Environmental Research Group of Texas A&M University (GERG) also corrected their data for surrogate recoveries, except when samples had to be excessively diluted (due to high analyte concentrations), in which case 100% surrogate recovery was assumed (personal communication, Guy Denoux, 1998). What KLI did report with regard to surrogate recoveries was that "analyte results were not corrected when surrogate recoveries fell outside the 40 to 120 percent limits, but that the affected values were qualified using the appropriate qualifier" (KLI 1996). In general, the majority of surrogates were recovered within quality assurance acceptance ranges by both laboratories.

4.8.2 Sonication Versus Soxhlet Extraction Procedures

Another and more confounding factor in evaluating the data from the two laboratories was changing from sonication to Soxhlet extraction procedures when GERG began the PAH analyses in 1995. Before undertaking the full suite of sediment sample analyses from the 1995 field program, GERG (KLI 1996) completed an intralaboratory calibration exercise

where they compared sonication and Soxhlet extraction procedures on sediment sample splits from the 1994 East Forelands and Trading Bay sites (obtained from ADL). The results of this intralaboratory method comparison showed significant under-representation of alkyl-substituted PAH (particularly naphthalenes, fluorenes, phenanthrenes/ anthracenes, dibenzothiophenes, and chrysenes) by sonication versus Soxhlet when employed by GERG. The GERG Soxhlet procedure did, however, yield TPAH and Fossil Fuel Pollution Index (FFPI) values that were in close agreement with values previously obtained at ADL, so the two procedures were considered to be comparable (see Table 4-10). Based on those data, Soxhlet extractions were employed in the program from that time until the present. What was not considered at that time, was the affect the differing extractions efficiencies had on individual alkylated-PAH recoveries, and how those differences would affect double ratio analyses. Table 4-10 also presents the double ratio data generated from GERG's Soxhlet-extraction-based procedure versus ADL's results using sonication.

The TPAH values obtained by the two methods at the two laboratories were remarkably close in two out of the three intercalibration samples. Likewise, the FFPI values were almost identical in two out of the three samples (although it was a different pair that gave the closest agreement). Unfortunately, however, the values for the double ratio pairs differ drastically. In the Trading Bay and East Forelands samples the Soxhlet procedure gave consistently better relative recoveries of the higher molecular weight C_3-naphthalenes, C_4-naphthalenes, C_3-fluorenes, C_3-phenanthrenes/anthracenes, and C_4-phenanthrenes/anthracenes compared to the sonication procedure. In contrast, the sonication extraction procedure yielded consistently higher concentrations of perylene.

Sample	Lab/Procedure	TPAH	FFPI	N2/F2	N3/F3	D2/P2	D3/P3	C2/P2	C3/P3
Trading Bay RCAC940500OR	ADL/sonication	113	80.6	3.67	1.90	0.21	0.17	0.32	0.33
	GERG/soxhlet	117	82.2	2.11	0.69	0.41	n.a.	0.67	n.a.
	GERG/sonication	89.1	84.4	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Trading Bay RCAC940600OR	ADL/sonication	115	73.3	3.44	2.03	0.17	0.14	1.6	0.32
	GERG/soxhlet	110	80.5	1.45	1.55	n.a.	n.a.	0.78	n.a.
	GERG/sonication	74.8	81.0	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
East Forelands RCAC941700OR	ADL/sonication	92.3	83.6	4.78	n.a.	0.26	n.a.	0.22	0.29
	GERG/soxhlet	114	80.6	2.08	1.49	0.21	0.18	1.14	n.a.
	GERG/sonication	87.9	75.7	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.

Notes: N2/F2 = C_2-naphthalenes/C_2-fluorenes; N3/F3 = C_3-naphthalenes/C_3-fluorenes;

D2/P2 = C_2-dibenzothiophenes/C_2-phenanthrenes; D3/P3 = C_3-dibenzothiophenes/C_3-phenanthrenes;

C2/P2 = C_2-chrysenes/C_2-phenanthrenes; C3/P3 = C_3-chrysenes/C_3-phenanthrenes.

n.a. = not applicable (component not reported or division by zero)

Table 4-10. Interlaboratory comparability data for sediments extracted by sonication (at ADL) versus Soxhlet (at GERG) extraction.

These data indicate that the use of Double Ratio Plots (Brown et al. 1980; Overton et al. 1981; Boehm et al. 1989; Sauer and Boehm 1991; Brown and Boehm 1993; Page et al. 1993; Page et al. 1995; and Douglas et al. 1996) for source identifications will be more tenuous than if all the analyses had been completed in one laboratory.

4.8.3 Method Detection Limits

Another potential problem with trying to interpret data from two different laboratories is the influence introduced by different method detection limits (MDLs). ADL never delivered complete sample-specific MDL data for the 1993 and 1994 data sets; however, an MDL of 10 ng/g dry weight was noted for 1993 tissue samples (ADL 1995a), and a range of 0.5–5.0 ng/g dry weight was claimed for sediments in the 1994 survey (ADL 1995b). Representative MDL values for 1994 were provided, but not on an individual sample-specific basis (corrected for sample weight extracted), and ADL suggested that the 1994 values were representative of those obtained in 1993. In contrast, GERG provided MDL data that could be linked to each sample analyzed, and as such, compound-specific MDLs were calculated for each sample to reflect the actual weight of sediment or tissue extracted. The MDLs in 1995 and 1996 sediments analyzed at GERG generally ranged from 2-4 ng/g dry weight, while slightly lower values (1-2 ng/g dry weight) were reported in 1997. Because of smaller sample sizes and problems with lipid interference, individual component MDLs for tissue samples analyzed at GERG generally ranged from 10-30 ng/g dry weight.

To aid in data evaluation of samples with numerous constituents at or just below the method detection limits, actual individual component MDLs (when available) are shown as a solid line along the bottom of each aromatic hydrocarbon histogram plot presented in this report. It should be remembered, however, that the MDL values shown for 1993 and 1994 ADL data are "representative" in that sample-specific MDL data were not provided for either program year.

Although somewhat controversial, concentration data that fall below the MDL are often taken as estimated values, and their inclusion in a data set is generally considered valid and useful, particularly when assessing very low-level environmental contamination (EPA 1993). Except for the exclusion of naphthalene by ADL noted below in Section 4.8.5, ADL and KLI utilized all values and estimated values when calculating summed or ratio parameters. In defending this approach, KLI (1996) claimed, “due to the rigorously-defined statistically-based concept of the MDL (as defined by the EPA; Federal Register 1986), that data below the MDL are more likely to contain false negatives (reporting non-detects when concentrations actually do exist) than false positives (reporting erroneous values above non-detect when no such concentrations exist).” In actual fact, this may not be the case for some tissue samples where the MDLs were particularly high due to extremely small sample sizes. In certain cases, background electronic noise associated

with the Gas Chromatography/Mass Spectrometer (GC/MS) Selected Ion Monitoring (SIM) analyses of tissue samples contributed to a quantifiable signal that was magnified to a high PAH concentration by the inclusion of a small value for the total sample weight extracted in the denominator of the data reduction algorithm. When all of the "quantifiable" peaks (including those at or just below a particularly high MDL) were summed to generate a TPAH value, the result was anomalously high due to the contribution generated from the electronic noise associated with the GC/MS method. This issue is discussed further below under Field and Analytical/Procedural Blanks, and recommendations for modifying data reduction procedures for reporting TPAH are presented in Section 6.3.

For parameters where individual analytes were used for calculating statistical values (e.g., means) or indices, KLI converted non-detect (N.D.) or zero (0) concentrations to an assigned value of 0.05 ng/g dry weight, which was less than one-half the lowest reported concentration in the data set. KLI claimed that this method has been shown to cause less bias in estimating population parameters than several alternative methods (Gilbert 1987). ADL did not discuss how they dealt with zero or non-detect values in either of their reports.

4.8.4 Exclusion of Perylene from TPAH Calculations

Both ADL and GERG consistently omitted perylene from the TPAH values reported in their studies. This is a common practice among hydrocarbon geochemists because perylene is largely attributed to biological sources, and it is not a major component in petroleum (LaFlamme and Hites 1978; Wakeman et al. 1980; Venkatesan 1988). As will be discussed in more detail in Section 4.10 below, however, perylene is a major component in the relatively young and immature coal deposits that surround much of Cook Inlet. It is widely observed in most of the sediment samples examined in the EMP, and in future studies it should be reported in the text/table narratives and not just buried in the data base. Perhaps it would be advisable to report TPAH with and without perylene to assist in tracing coal-derived signals in sediment (and to a lesser extent) tissue samples.

4.8.5 Field, Analytical, and Procedural Blanks

Both ADL and GERG had occasional problems with apparent contamination of field blanks and procedural laboratory/method blanks. The most common contaminant observed by ADL was naphthalene at concentrations ranging from 2-28 ng/g dry weight in 1993 laboratory/method blanks and 8-24 ng/g dry weight in 1994 field equipment and laboratory/method blanks. This background contamination was particularly problematic with the cleaner 1993 tissue samples where the overall TPAH levels were generally very low and just above the method detection limits. Although primarily just a problem with tissues, ADL reported both the sediment and tissue TPAH values without naphthalene in their 1993 and 1994 project reports (ADL 1995a, b). Naphthalene has been included in the database generated for CIRCAC in this program, and it makes up part of the TPAH reported with all the histograms in this report.

Blanks associated with the SPMD components of the EMP were particularly problematic (for both ADL and GERG), and they are considered separately in a later section (4.13) where the SPMD results are presented in detail.

The field and laboratory/method blanks generated by GERG were represented by a very characteristic and persistent pattern of extremely low-level parent PAH components. Figure 4-1 presents representative histogram plots for PAH concentrations in sediment and tissue samples from the 1996 Cape Chiniak site along with associated field and procedural blanks. See Table 4-11 for a list of the 39 target analytes considered in the EMP along with the respective abbreviations used to identify them in the histogram plots presented throughout this report. As illustrated in Figure 4-1, the contaminant analytes in the field and method blanks were usually less than 2 ng/g dry weight, below the MDL, and well below the levels observed in most of the field (particularly sediment) samples examined in the program. Nevertheless, it should be noted that the same patterns of PAH components are present in the tissue sample (CAC-B-96) and the associated blanks. Because of the influence of a small extracted sample size and the concomitant higher MDL (10-25 ng/g dry weight), the TPAH for the tissue is calculated to be over 200 ng/g dry weight. In actual fact, the GC/MS signal may not be that much larger for the tissue sample compared to the blanks, it just appears that way due to the small sample weight used to calculate the final sample concentrations. In this tissue sample example, the only components that are significantly above the MDL (and possibly even real) are the naphthalenes, phenanthrene, and anthracene. Even then, there is a real chance of background laboratory or field introduction of naphthalene, which is often a trace contaminant in certain solvents (G. Denoux, personal communication 1998). As noted above, naphthalene contamination was certainly a problem at ADL during the first two years of the EMP.

The pattern observed for the tissue and blanks shown in Figure 4-1 has been characterized in other areas by Bence and Burns (1995) as a “procedural artifact.” In reality, the detection of these spurious signals probably has more to do with electronic noise in the GC/MS instrumentation run under the SIM mode than with the actual detection of background components. Specifically, the conformation ion is typically not within the QC criteria at these low levels, but the data are reported in a conservative manner to ensure that no individual PAH components are missed. Their presence in the blanks shows what the influence of instrument noise would be during analyte quantitation in extremely low-level samples, and caution should be exercised in examining tissue-sample data, were this signal can sometimes contribute to unrealistically high TPAH values. None of the KLI/GERG data have been corrected by subtracting

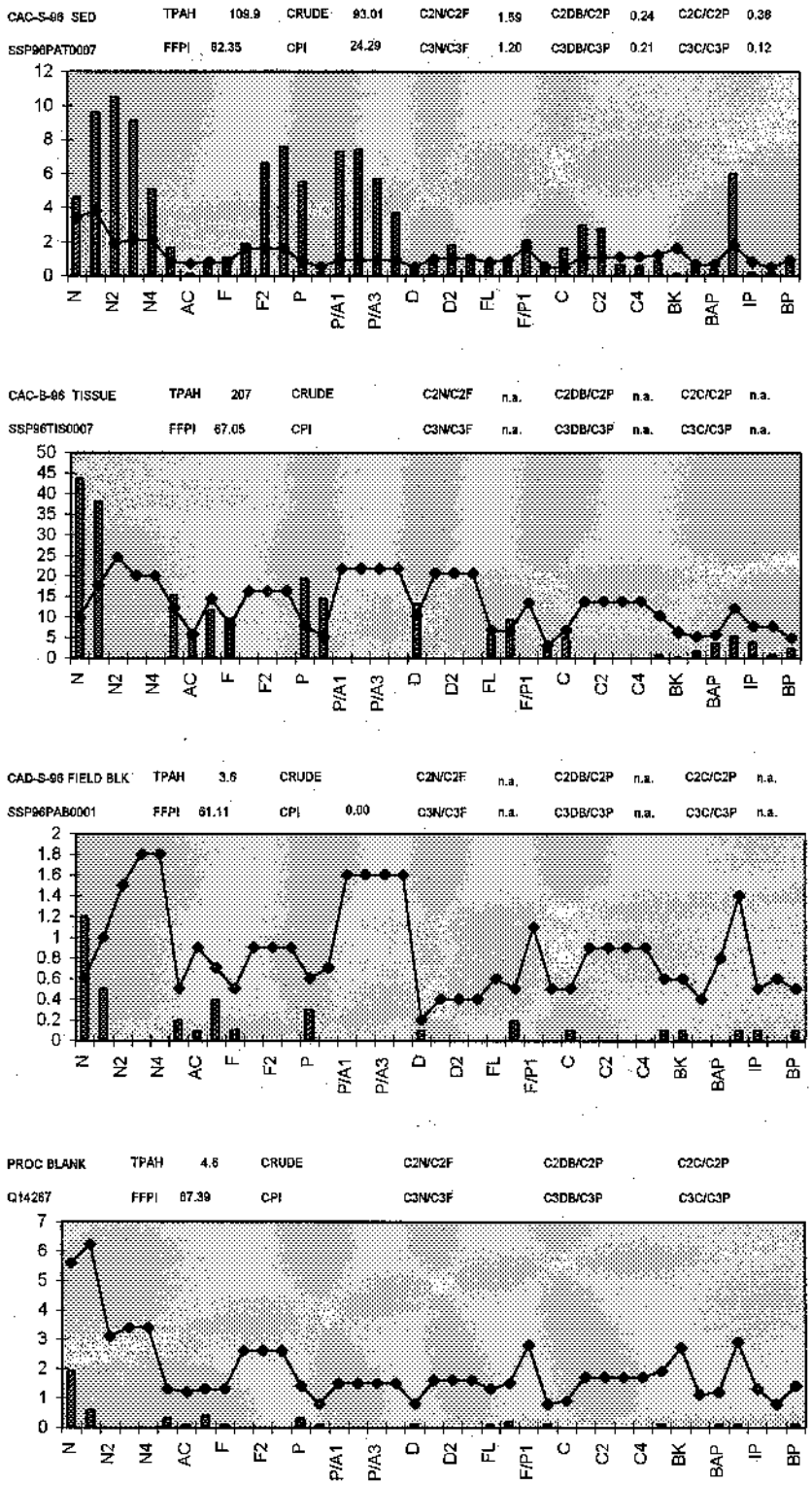


Figure 4-1 Histogram plots for Cape Chiniak sediment and tissue samples and associated field and procedural blanks.

PAH	Abbreviation
Naphthalene	N
C1-Naphthalenes	N1
C2-Naphthalenes	N2
C3-Naphthalenes	N3
C4-Naphthalenes	N4
Biphenyl	BI
Acenaphthylene	AC
Acenaphthene	AE
Fluorene	F
C1-Fluorenes	F1
C2-Fluorenes	F2
C3-Fluorenes	F3
Phenanthrene	P
Anthracene	A
C1- Phenanthrene /Anthracene	P/A1
C2- Phenanthrene /Anthracene	P/A2
C3- Phenanthrene /Anthracene	P/A3
C4- Phenanthrene /Anthracene	P/A4
Dibenzothiophene	D
C1-Dibenzothiophene	D1
C2-Dibenzothiophene	D2
C3-Dibenzothiophene	D3
Fluoranthene	FL
Pyrene	PY
C1-Fluoranthenes/Pyrene	F/P1
Ben(a)anthracene	BA
Chrysene	C
C1-Chrysenes	C1
C2-Chrysenes	C2
C3-Chrysenes	C3
C4-Chrysenes	C4
Ben(b)fluoranthene	BB
Ben(k)fluoranthene	BK
Ben(e)pyrene	BEP
Ben(a)pyrene	BAP
Perylene	PER
Indeno(1,2,3-c,d)pyrene	IP
Dibenzo(a,h)anthracene	DA
Benzo(g,h,i)perylene	BP
Total PAH	TPAH

Table 4-11 List of EMP target analytes and abbreviations used in figures.

background/blank component concentrations in any of the KLI reports. Likewise, the data have been used "as is" to generate the database deliverable and histograms discussed in this report.

4.8.6 Overall Conclusions Regarding Analytical Procedures

Notwithstanding the aforementioned concerns, it should be noted that from an overall perspective, switching laboratories, extraction methodologies, and contractors mid-way through the program has not had a significant negative impact on data quality or data comparability. As noted above, minor differences with alkyl-substituted PAH ratios have been noted, and they can affect Double Ratio plots when trying to identify and resolve subtle differences in potential sources. Fortunately, however, these differences are not significant enough to affect the overall conclusions reached in evaluating and summarizing the EMP to date.

4.9 Sources of Hydrocarbons Measured in the EMP

4.9.1 Target Analytes

Petroleum contains monoaromatic and polycyclic aromatic hydrocarbons (PAH), both of which can be toxic to organisms. Monoaromatic hydrocarbons such as benzene, toluene, and xylene(s) are highly volatile and are quickly lost into the environment through evaporation and dissolution processes (Payne et al. 1983, 1984, 1991a,b,c; Payne and McNabb, Jr. 1984). These compounds do not persist in the marine environment for long periods of time and have not been included in the target analyte list in any of the Cook Inlet RCAC EMP studies. Petroleum also contains an extensive suite of PAHs, and the amount and composition of the PAH fraction can be effectively used as a tracer of petroleum contamination. In general, PAHs are more resistant to microbial breakdown than many aliphatic hydrocarbons, and thus, they tend to persist in the environment longer. PAHs also exhibit varying degrees of individual and combined toxicity to marine organisms (French 1998), and they serve as an indication of petroleum exposure in organisms. Based on consideration of the petroleum chemistry, biological hydrocarbons (i.e., analytic interference), and toxicological effects, PAH were chosen as the preferred organic tracers of petroleum contamination in the earlier EMP studies. Aliphatic hydrocarbons (AHC) were added to the target analyte list in 1996 with the Shelikof Strait Project.

4.9.2 Biogenic Hydrocarbons

Polycyclic aromatic hydrocarbons are generally divided into three main sources: biogenic, petrogenic, and pyrogenic. The most abundant biogenic PAH is perylene, which is believed to be formed during the early stages of diagenesis -- the breakdown of organic matter by (predominantly) biotic and abiotic processes in marine sediments (LaFlamme and Hites 1978; Wakeman et al. 1980; Venkatesan 1988). High concentrations of perylene are often observed in high depositional areas receiving significant concentrations of organic material, and perylene concentrations often increase with depth, especially in

anoxic sediments (Tan and Heit 1981; ADL 1998b). Perylene generally occurs in very low concentrations in petroleum, and because of its biogenic origin, it is usually not classified as a petrogenic PAH. As a result, it has been excluded from the summation of TPAH in all the EMP data analyses to date. As will be noted below, perylene is a predominant component in coal samples collected throughout Cook Inlet, and it was observed at high relative (compared to other PAH) concentrations in many Cook Inlet sediments examined throughout the EMP study efforts. As such, its inclusion in the data analysis of future studies is recommended.

4.9.3 Petrogenic Hydrocarbons

Petrogenic PAHs include all of those commonly identified in crude oil, its refined products, and many coals. While hydrocarbons are ubiquitous in the marine environment, petrogenic hydrocarbons can be individually recognized and are often used as tracers of oil contamination (Brassell et al. 1978; Boehm and Requejo 1988; Kennicutt and Comet 1992). Potential reported sources of petrogenic PAHs in the Cook Inlet study areas include: Cook Inlet crude oil from production and shipping operations; produced water discharges; Alaska North Slope (ANS) crude oil including EXXON VALDEZ Oil Spill (EVOS) residues; refined petroleum products (fuel oil, diesel, etc.); and seep oils from Oil Bay (and elsewhere) within Cook Inlet, as well as Katalla, Yakataga, and other eastern Gulf of Alaska seeps. Additional "non-petroleum" PAH sources that also contain the petrogenic signal (in addition to other characteristic PAHs) include coal particles introduced from glacial and water erosion of terrestrial deposits; municipal wastewater discharges; and atmospheric fallout of combustion products. Techniques for attempting to differentiate among these sources are discussed below.

Figure 4-2 presents example histogram plots of the observed distribution of the 39 target EMP PAH constituents (in order of increasing molecular weight) in fresh Cook Inlet crude oil, produced water from the Trading Bay diffuser outfall, fresh ANS/EVOS crude oil, and diesel refined from ANS crude oil. The individual PAH constituents are listed in Table 4-11 along with the respective abbreviations used in all the histogram plots presented in this report.

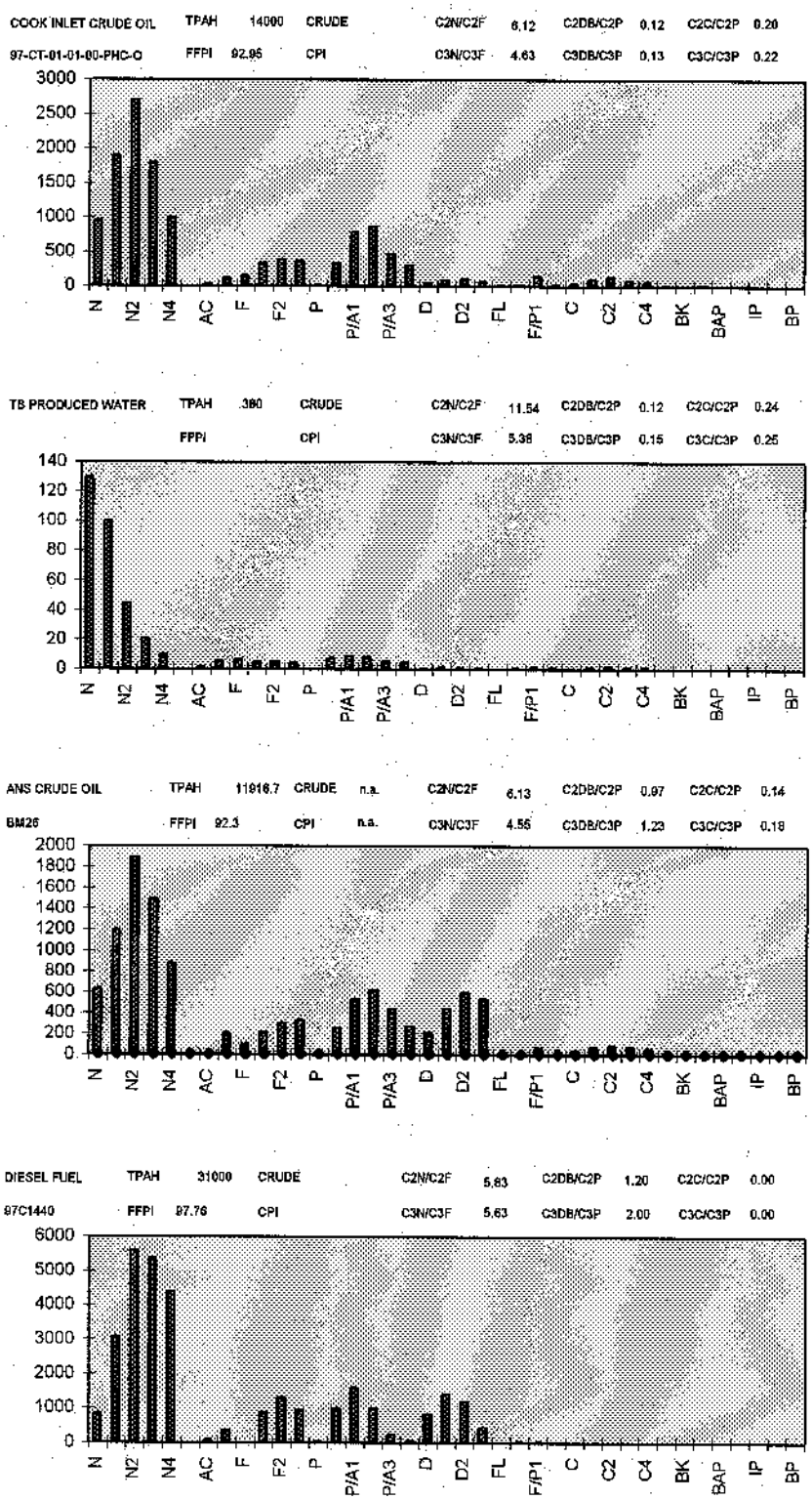


Figure 4-2 Histogram plots of PAH distributions in Cook Inlet crude oil, Trading Bay produced water effluent, Alaska North Slope crude oil, and diesel fuel distilled from ANS oil.

For purposes of the Cook Inlet EMP data evaluation, it is useful to distinguish between five main groups of PAH components. The naphthalenes (which are two-ring aromatics) are less persistent in the environment compared to the other higher-molecular-weight groups, and they are subject to loss from spilled oil by evaporation and dissolution weathering. As such, they may or may not even be present in well-weathered oil-contaminated samples obtained from the environment. The fluorenes, anthracenes, and phenanthrenes (which are all three-ring aromatics) are each more persistent in the environment, and as such, they can act as markers to help differentiate among different sources. The dibenzothiophenes (another three-ring compound that also contains sulfur) are important because they are characteristic of Alaskan North Slope crude oil, but not Cook Inlet or Katalla crude oil. Finally, the four- and five-ring aromatics (including, the chrysenes through benzo(g,h,i)perylene) are important because: 1) they can help distinguish between crude oils and refined products (such as diesel oil) that may have been produced from a particular crude oil; and 2) they are also representative of combustion by-products.

Petrogenic PAHs have a characteristic fingerprint where the parent compounds (i.e., C_0-naphthalene (N), C_0-fluorene (F), C_0-phenanthrene (P), C_0-dibenzothiophene (D), and C_0-chrysene (C)) are usually at lower concentrations than their alkyl-substituted homologues (i.e., C_1-naphthalenes (N1), C_2-naphthalenes (N2), C_1-fluorenes (F1), etc.). With weathering, this feature becomes more prominent because the more soluble parent compound (C_0) disappears before the alkyl homologue (C_1), which in turn disappears more quickly than C_2, etc. Thus, a characteristic "water-washed profile" is generated where the $C_0<C_1<C_2<C_3$ within each PAH group in the residual oil phase. Conversely, the distribution of dissolved PAH components, as exhibited in the produced water sample shown in Figure 4-2, shows primarily alkyl-substituted naphthalenes with significantly depleted fluorenes and phenanthrenes/anthracenes (compared to the starting crude oil) and only traces of higher-molecular weight components. This distribution reflects the preferential dissolution of the naphthalenes with their higher solubility compared to the other PAH. Eventually, with continued weathering, only the higher alkylated naphthalenes, phenanthrenes/anthracenes, dibenzothiophenes, and chrysenes persist in oil residues at very characteristic and source-specific ratios. Figure 4-3 demonstrates this change in PAH distributions due to observed and computer-model-predicted weathering of Katalla crude oil (Short et al. 1999). Figure 4-3C clearly shows the rapid and selective loss of naphthalene, C_1-naphthalene, and C_2-naphthalene compared to the fresh oil in Figure 4-3A. Interestingly, the sediments from Cape Hinchinbrook (near the Katalla seep oil source) still have significant concentrations of naphthalene, C_1-naphthalene, C_2-naphthalene, and C_3-naphthalene (Figure 4-3B) suggesting a source other than Katalla seep oil. This is discussed further below.

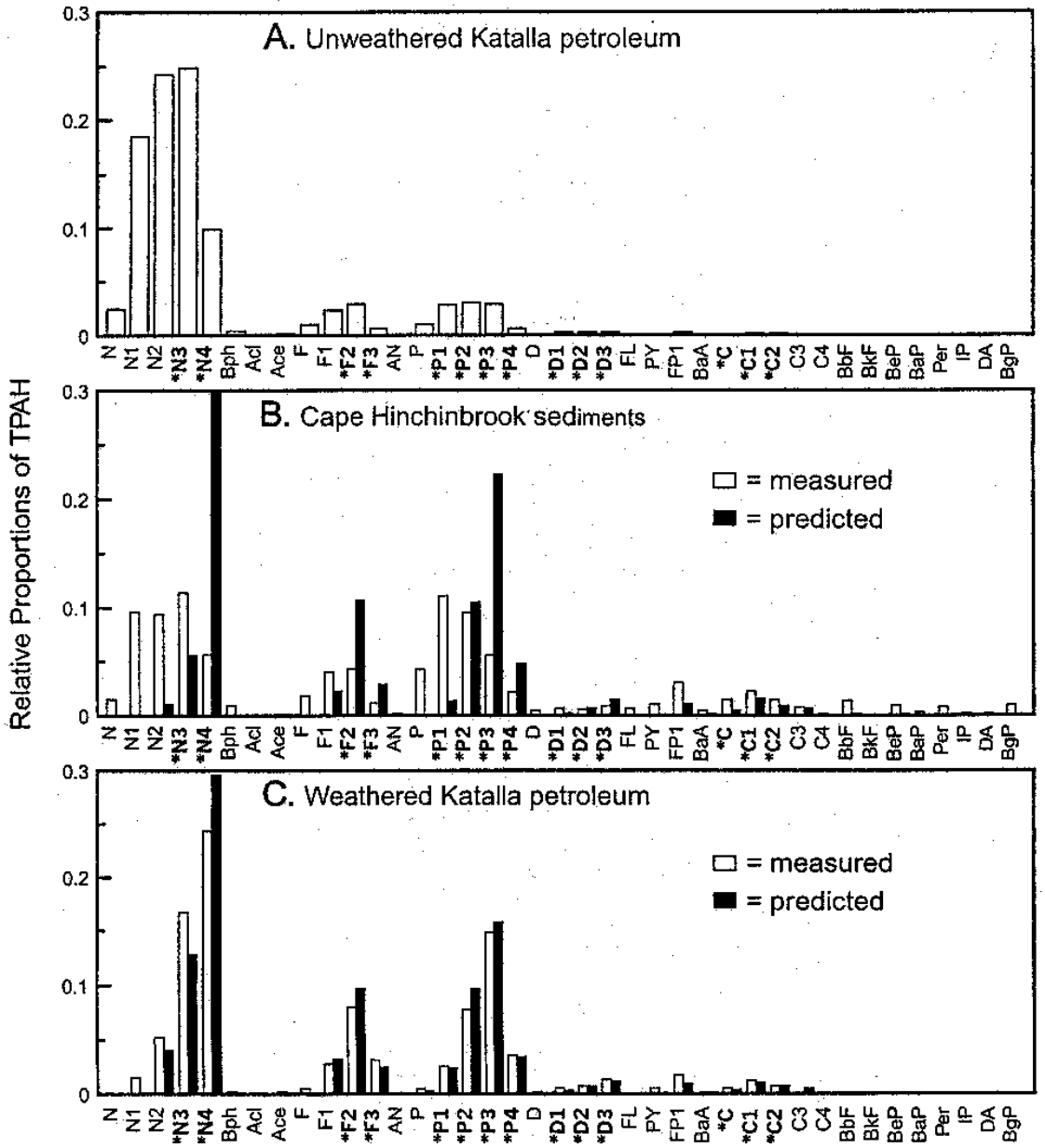


Figure 4-3. Histogram plots showing the relative concentrations of 39 target PAH observed in unweathered Katalla seep oil, Cape Hinchinbrook sediments showing measured and predicted PAH distribution if the source was Katalla seep oil, and weathered Katalla seep showing measured and predicted PAH composition. Reproduced from Short et al. 1999.

In contrast to the PAHs, which may make up anywhere from 1 to 20 percent of many crude oils by weight, aliphatic hydrocarbons can account for more than 70 percent of the measured components in the same sample. Aliphatic hydrocarbons can also be synthesized by organisms (both plankton and terrestrial). Most crude oils contains an homologous series of n-alkanes with one to more than 30 carbons, with odd- and even-carbon numbered n-alkanes present in nearly equal amounts. On the other hand, biogenic hydrocarbons produced by living organisms preferentially contain specific suites of normal

alkanes with odd numbers of carbon atoms from 15 to 33. Petroleum also contains a complex mixture of branched and cyclic compounds generally not found in organisms, although the latter may be found as degradation products in some bacteria. This complex mixture can include oxygenated compounds that produce an unresolved complex mixture of compounds (the unresolved complex material (UCM)) on gas chromatographic profiles when petroleum is extensively biodegraded. The presence and amount of the UCM can be a diagnostic indicator of heavily weathered petroleum contamination.

4.9.4 Pyrogenic Hydrocarbons

Pyrogenic PAHs come from combustion sources including atmospheric fallout and surface runoff from the burning of fossil fuels (diesel, heating oil, gasoline, etc.) and from other pyrogenic sources such as forest fires and camp fires. Creosote, which is used to preserve wood pilings, is also usually included in this category. Pyrogenic PAHs are characterized by high molecular weight PAHs, greater than C_3-dibenzothiophenes (D3), and by high concentrations of the parent compounds compared to their alkyl homologues. A typical pattern for pyrogenic PAHs is decreasing concentration with increasing molecular weight within a group (i.e., $C_0>C_1>C_2>C_3>C_4$). It has been noted, however, that the PAH in diesel soot has primarily a petrogenic signature (Bence and Burns 1995; Burns et al. 1997).

4.9.5 Municipal Wastewater Discharges

PAHs in municipal wastewater discharges have not been analyzed as part of the CIRCAC EMP, however, ADL analyzed a final effluent source sample from the Point Woronzof Municipal Waste Treatment Facility as part of the MMS Shelikof Strait Program (ADL 1998). Figure 4-4 presents the flame ionization detector FID/GC chromatogram, PAH histogram plot, and triterpane extracted ion chromatogram obtained on that sample.

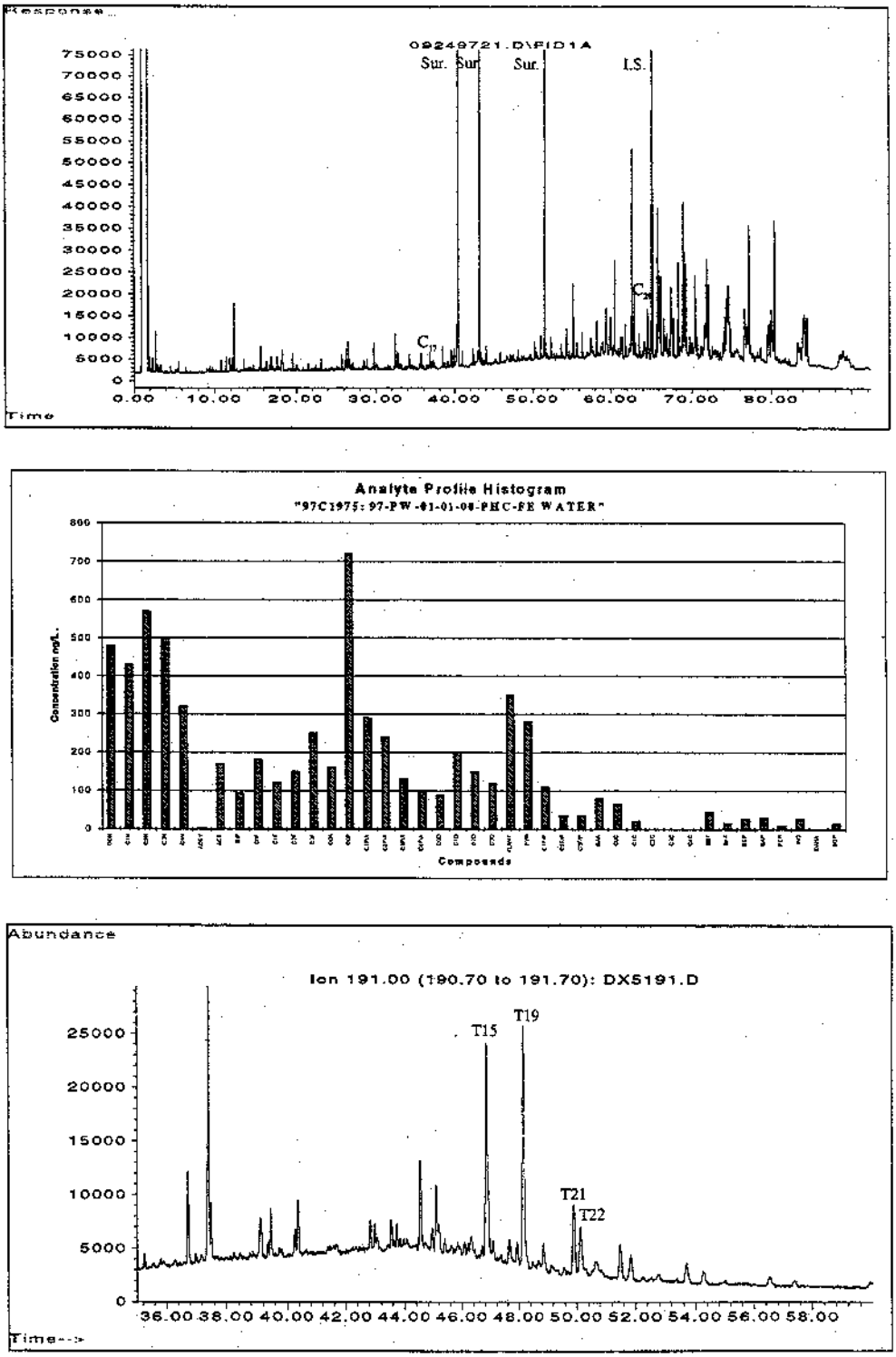


Figure 4-4 Characterization of Point Woronzof Municipal Waste Treatment Facility final effluent.

Clearly, there are significant (100-500 ng/L) concentrations of the full suite of 2-, 3-, and 4-ring PAH, with trace levels of 5- and 6-ring PAH. Three of the most abundant

compounds are phenanthrene, fluoranthene, and pyrene, which are indicative of pyrogenic or combustion related sources (e.g., urban runoff); however, the complete series of C_1- through C_4-alkyl naphthalenes, phenanthrenes, and dibenzothiophenes are characteristic of petroleum sources. It is estimated that approximately 30 million gallons (114,000,000 L) of treated wastewater are discharged per day from the Point Woronzof facility (Mark Savoie, personal communication, 1998), and this is approximately 10 times greater than the combined produced water volumes discharged daily near Trading Bay (see Section 4.14). Therefore, the municipal wastewater discharges do represent a real and significant source of PAH to the marine environment. It is critical to note, however, that the concentrations in the Point Woronzof Municipal Waste Treatment Facility discharge are in ng/L, three orders of magnitude lower than the produced water discharges at Trading Bay. As a result, approximately 100 times more PAH is introduced from produced water discharges than municipal wastewater sources. Thus, the municipal wastewater plant does not appear to be a significant source of PAH compared to produced water discharges from the oil production facilities north of the East and West Forelands.

4.9.6 Particulate Coal

Coal has recently been suggested as an alternative and dominant source for the most of the PAH in offshore southcentral Alaskan sediments (Short et al. 1999). Short et al. propose that the natural hydrocarbon background in sediments of Prince William Sound comes, not from seep oils (Page et al. 1995, 1996a, 1996b, 1997), but from coal located in terrestrial deposits along the northern coast of the Gulf of Alaska. Short et al. state that these coal sources have been eroded over geologic time by glaciers and steams, and particulate coal has been transported by the Alaskan Coastal Current into Prince William Sound. Based on an analysis of the data presented by Short et al. and the results of the EMP efforts within Cook Inlet, we now believe that these and other coal sources must be considered as major contributors to the observed sedimentary PAH burdens within Cook Inlet as well.

Figure 4-5 (reproduced from Short et al. 1999) shows the proportions of PAH relative to TPAH in 1) benthic sediments of the Gulf of Alaska, 2) sediments from the mouths of the Bearing and Duktoth Rivers, and particulate coal from the beach at Katalla, and 3) sediments and native coal from the Bering River coal field and vicinity. The vertical bars denote ranges and clearly show the greater heterogeneity of the coal and sediments near the Bering and Duktoth River sources compared to the overall average signal obtained by the time the coal particles and river sediments are mixed and transported into the Gulf of Alaska and Prince William Sound. Evidence cited by Short et al. that coal is the source of PAH in the benthic sediments of the northern Gulf of Alaska includes: 1) the geological setting, which leads to the straightforward erosion and transport of bulk coal in source beds to fine-grained coal particles in benthic sediment, 2) the geographic distribution of the source coal beds, 3) the similarity of PAH and geochemical analyte profiles of coal and sediments, 4) the lack of PAH weathering as seen in the persistence of lower molecular weight PAH (primarily naphthalenes) following release into the environment, 5) the absence of bioaccumulated PAH in mussels and therefore the lack of bioavailability of coal versus oil, and 6) the relative volume of oil released from the Katalla seeps versus the sediment bed load transport from the Bering and Duktoth Rivers.

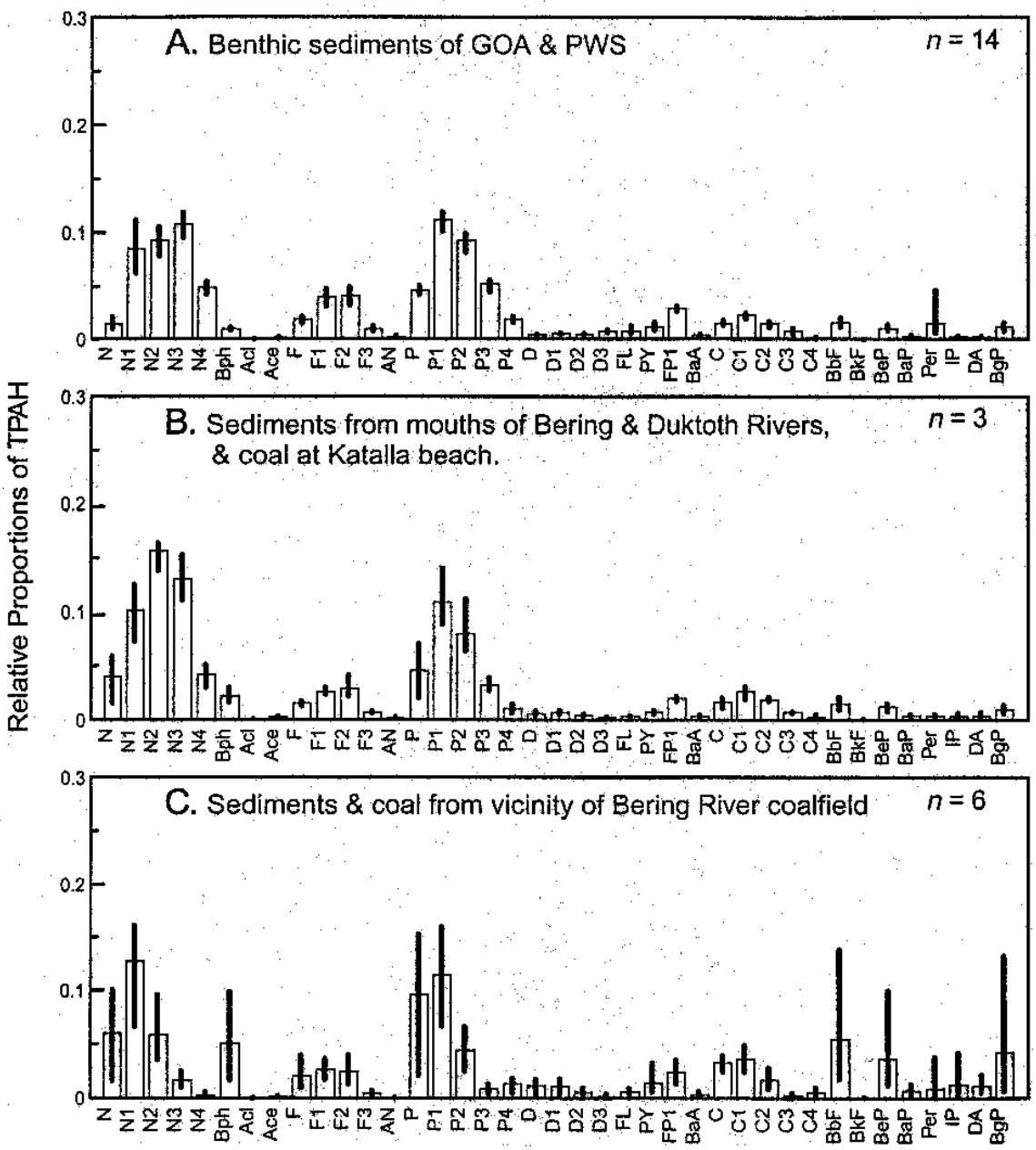


Figure 4-5 Histogram plots showing PAH concentrations relative to TPAH in benthic sediments of the Gulf of Alaska and Prince William Sound, sediments from the mouths of the Bering and Duktoth Rivers, particulate coal on the beach at Katalla, and sediments and coal from the vicinity of the Bering River coal field. (Reproduced from Short et al. 1999).

In essentially all of the EMP Project reports to date, the sources of PAH in the sediments in question are attributed to Katalla seep oil, Cook Inlet crude oil (seep and production activities), and (only very recently) "coal sources in the area" (KLI 1998). While largely overlooked until recently, the importance of coal-derived PAH in Cook Inlet sediments will be considered in greater detail in the following sections. Also, an increased awareness of coal as a major potential source for PAH to Cook Inlet sediments will have an impact

on suggested directions for additional research and monitoring program activities designed to differentiate oil and coal sources to better segregate and assess oil production-activity impacts within Cook Inlet.

4.9.7 Integration of Analytical Parameters for Data Evaluation and Source Identification

Through the investigation of petroleum weathering and persistence in the marine environment, numerous investigators have developed an innovative suite of characteristic ratios, sums, and other indices to aid them in identifying petroleum signatures and distinguishing petrogenic from pyrogenic and biogenic sources. Table 4-12 summarizes a number of the different factors that have been used in the EMP data analyses.

Factor	Relevance
TPAH (oil, tissue, and sediment samples)	Total PAH as determined by high resolution GC/MS with quantification by selected ion monitoring; defined as the sum of 2 to 5-ring polycyclic aromatic hydrocarbons: Naphthalene + fluorene + dibenzothiophene + phenanthrene + chrysene, and their alkyl homologues + other PAHs (excluding perylene); useful for determining TPAH contamination and the relative contribution of petrogenic, pyrogenic, and diagenic sources
FFPI (oil, tissue and sediment samples)	The Fossil Fuel Pollution Index is the ratio of fossil-derived PAHs to TPAH and is defined as follows: FFPI = (N + F + P + D)/TPAH x 100 where: N (Naphthalene Series) = C_0-N + C_1-N + C_2-N + C_3-N + C_4-N F (Fluorene series) = C_0-F + C_1-F + C_2-F + C_3-F P (Phenanthrene/Anthracene series) = C_0-A +C_0-P + C_1-P/A + C_2-P/A + C_3-P/A + C_4-P/A D (Dibenzothiophene Series) = C_0-D + C_1-D + C_2-D + C_3-D FFPI is near 100 for petrogenic PAH; FFPI for pyrogenic PAH is near 0 (Boehm and Farrington 1984)
TAHC (sediments)	Total aliphatic hydrocarbons quantifies the total n-alkanes (n-C_{10} to n-C_{34}) + pristane and phytane; represents the total resolved hydrocarbons as determined by high resolution gas chromatography with flame ionization detection (FID-GC); includes both petrogenic and biogenic sources
UCM (sediments)	Petroleum compounds represented by the total resolved plus unresolved area minus the total area of all peaks that have been integrated; a characteristic of some fresh oils and most weathered oils
CPI (sediments)	The carbon preference index represents the relative amounts of odd and even carbon number n-alkanes within a specific boiling range and is defined as follows: CPI = 2(C_{27} + C_{29})/(C_{26} + 2C_{28} + C_{30}) Odd and even carbon-numbered n-alkanes are equally abundant in petroleum but have an odd numbered preference in biological material; a CPI close to 1 is an indication of petroleum and higher values indicate biogenic input (Farrington and Tripp 1977)

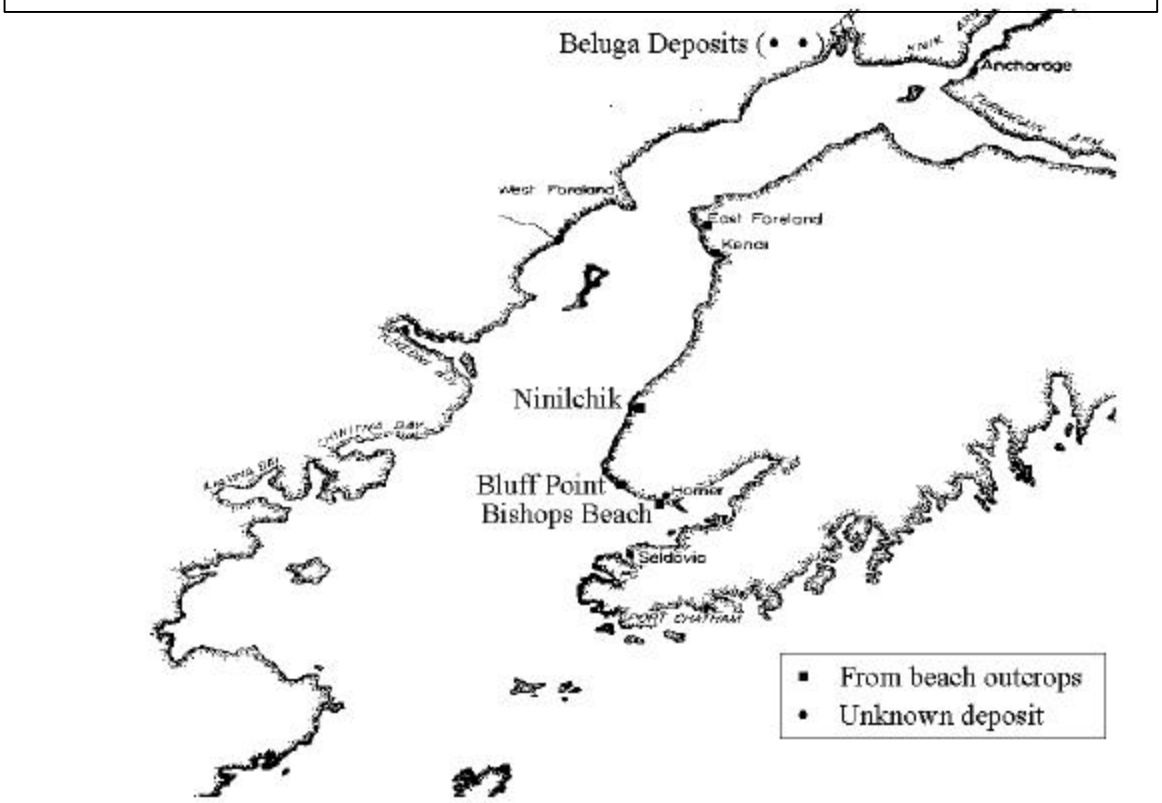
CRUDE Index (sediments)	An empirical summation of TPAH, TAHC and UCM (which were readily available parameters or indices in the KLI-summarized EMP data base) weighted to assess the petrogenic fractions (Payne et al. 1998). See additional discussion in Section 4.11.2. CRUDE = (TPAH x FFPI/100) + (TAHC/CPI^2) + UCM/1000
MPI (tissues and sediments missing TAHC data)	The Mytilus Petrogenic index isolates the FFPI fraction of TPAH (same as first term in CRUDE) (Payne et al. 1998). This was again derived to utilize summary data from the KLI-generated EMP data base for tissues where aliphatic data were not available. Note: this also equates to the sum of the N + F + P + D. MPI = TPAH X FFPI/100

Table 4-12. Hydrocarbon Parameters Used in the EMP Data Analysis (Adapted from KLI 1997).

In examining the oil chemistry data for this program, we used a fairly standard approach based on historical precedent and experience for analyzing the data. Initially, the common indices of TPAH, total AHC (TAHC) and UCMs (when available), and ratio indices such as FFPI, Carbon Preference Index (CPI), CRUDE Index, and Mytilus Petroleum Index (MPI) were examined and plotted to evaluate any obvious trends in the data. Detailed examination of the aromatic and (to a lesser extent) aliphatic hydrocarbon histogram profiles was then undertaken on all the samples with additional emphasis on unusual samples or "hot spots" identified by the trend analyses. These parametric and visual data analyses were then integrated with the results from several double ratio plot approaches to produce the final assessments on each suite of samples discussed below.

4.10 Characterization of Coal Samples Collected Within Cook Inlet

At the beginning of this data evaluation project, five additional samples of surface coal from several areas within Cook Inlet were obtained by CIRCAC for PAH and AHC analyses. The locations of these coal sample collection sites are shown in Figure 4-6. These samples were analyzed by ADL as part of their ongoing MMS-sponsored Shelikof Strait and Outermost Cook Inlet Sediment Quality Program. Through cooperative agreement, the data from those analyses were provided to CIRCAC for evaluation in the current project. Figures 4-7 and 4-8 present the AHC and PAH histogram plots obtained from these analyses.



-6 Cook Inlet coal sampling sites, 1997 98.

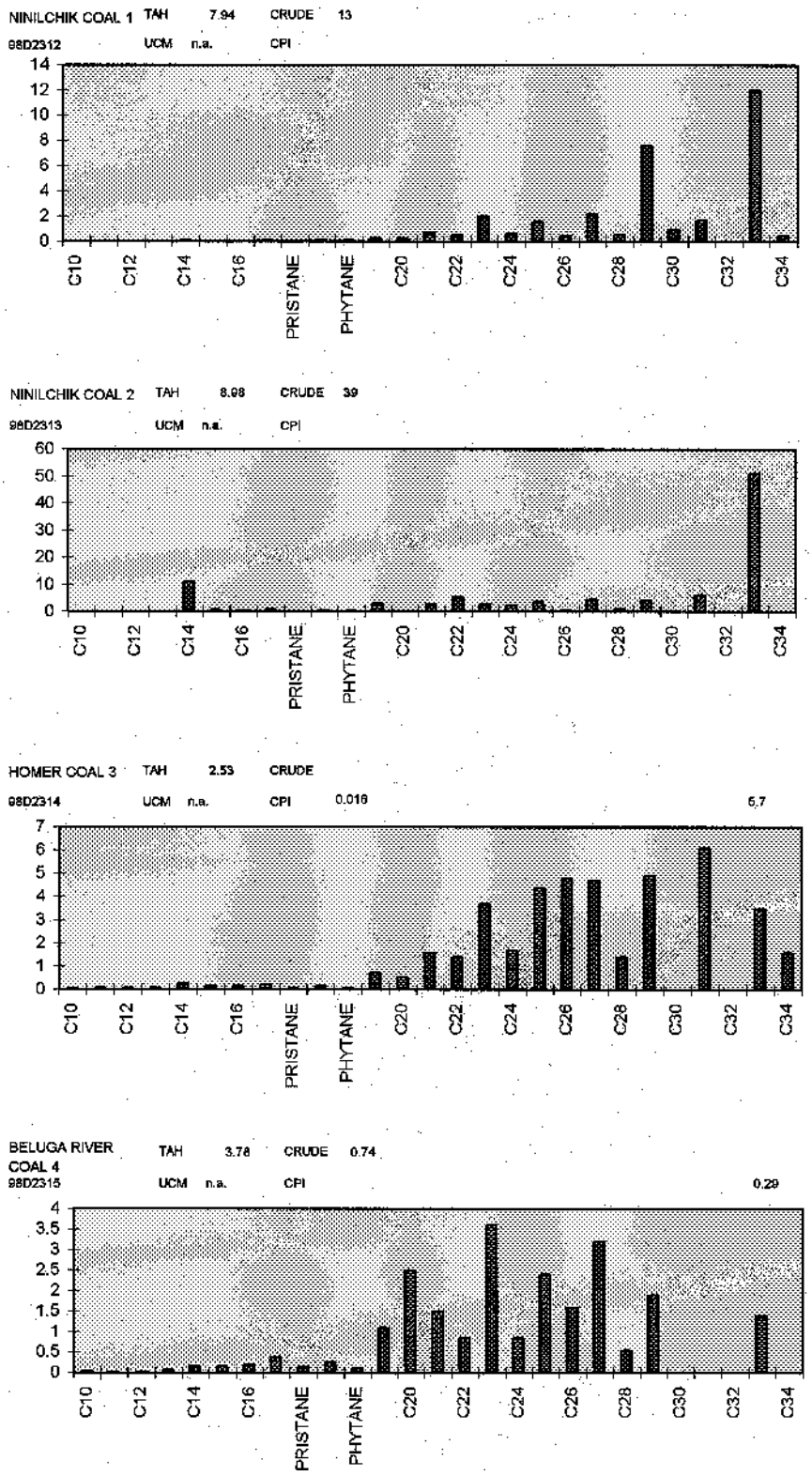


Figure 4-7 Aliphatic hydrocarbon histogram profiles of selected coal samples from Cook Inlet.

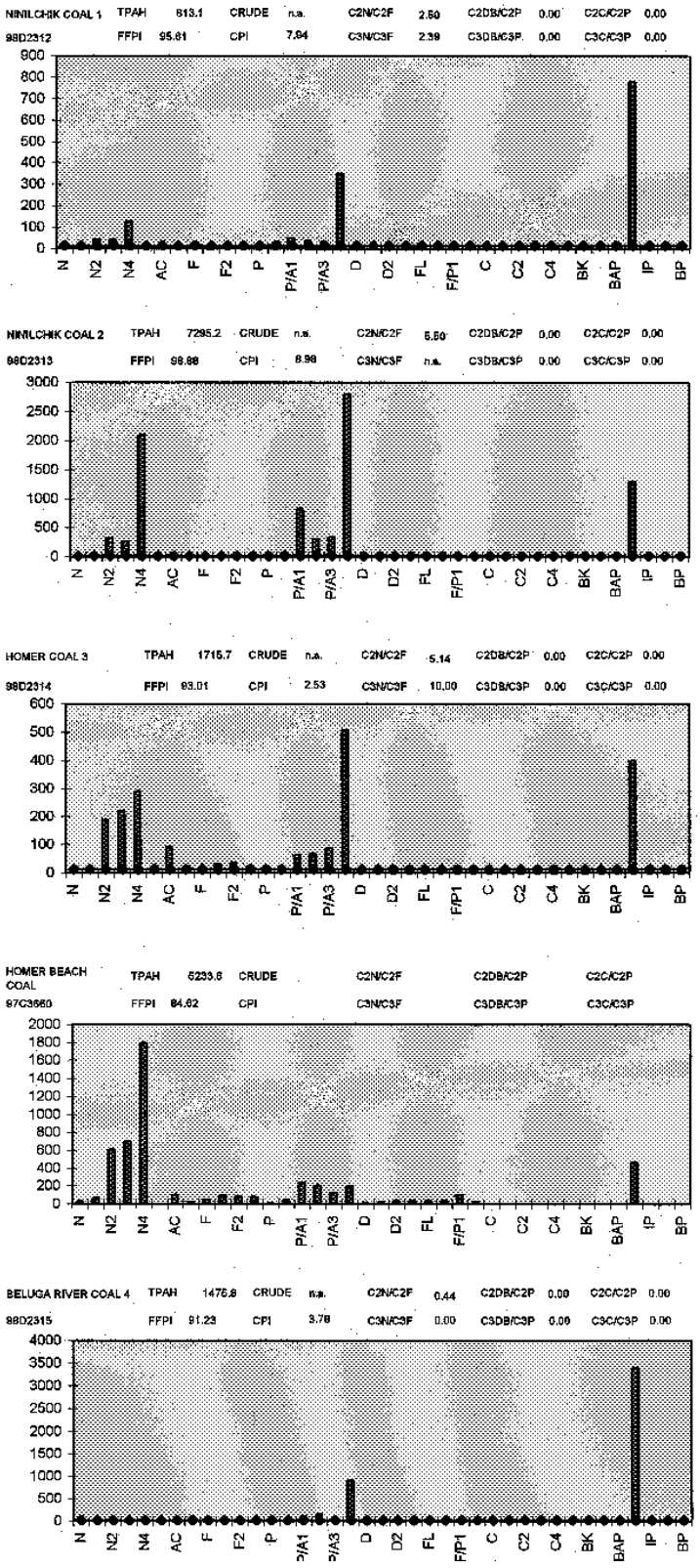


Figure 4-8 PAH profiles of selected coal samples from Cook Inlet.

The AHC histograms show a variable but generally consistent odd-carbon predominance among the higher molecular weight n-alkanes that reflects a relatively recent terrestrial biogenic source in the samples. The PAH histograms show a predominant perylene component and only a limited series of other PAH constituents that again reflects the recent biogenic contribution to the coal. The coal samples from Homer and Ninilchik contain high concentrations of a water-washed suite of naphthalenes with C_4-naphthalenes predominating, along with an abundant suite of phenanthrenes/anthracenes with C_4-phenanthrenes/anthracenes in greatest abundance. The Beluga coal field samples contained only significant PAH contributions from C_4-phenanthrenes/anthracenes and perylene. As shown by the data in Figure 4-8, the concentrations of individual measured PAH are in hundreds (and in some cases thousands) of ng/g dry weight; however, it is quite likely that numerous other PAH are also present at much lower concentrations in each of these samples. It is suspected that these other PAH were "diluted out" (reduced to concentrations below the laboratory detection limit) when the final sample extracts were analyzed. Often with such samples, it is necessary to dilute the extract to keep the extremely high concentrations of C_4-naphthalenes, C_4-phenanthrenes/anthracenes, and perylene on scale and within the linear range of the GC/MS instrumentation. It is our understanding that these samples are being reanalyzed by ADL to identify lower concentration PAHs, but those data were not available at the time of this writing.

These PAH signatures and the relative absence of other PAH are consistent with the coal being relatively young and immature. The perylene is high because of huge terrigenous plant flux into a coal that has only recently (in geologic time) been formed. Coal from the Susitna regions is mostly lignite and subbituminous, and it is considered to be an immature, low rank coal (Marritt 1990). Rank is the basis of coal classification in the natural series from lignite to anthracite and refers to the degree of metamorphism and maturity of the coal (DNR 1993). Higher rank indicates greater metamorphism. Bituminous coals and anthracites are considered to be high-rank; subbituminous coals and lignites, low-rank. In contrast to the coal samples collected by CIRCAC and discussed above, coal from the Matanuska field (which is drained by the Matanuska River into upper Knik Arm) is primarily bituminous, semianthracitic, and anthracitic. Likewise, coal from the Katalla region is a higher rank coal that is more mature. Bering River coal is primarily anthracite, meta-anthracite, and bituminous. As such, these more mature coals would be expected to contain a wider range of geologically formed PAH as previously shown in Figure 4-5. With this maturation process, the odd-carbon predominance of the AHC fraction is also attenuated, and the resultant profile of the Gulf of Alaska coals is more like a petrogenic signature (J. Short, personal communication, 1998).

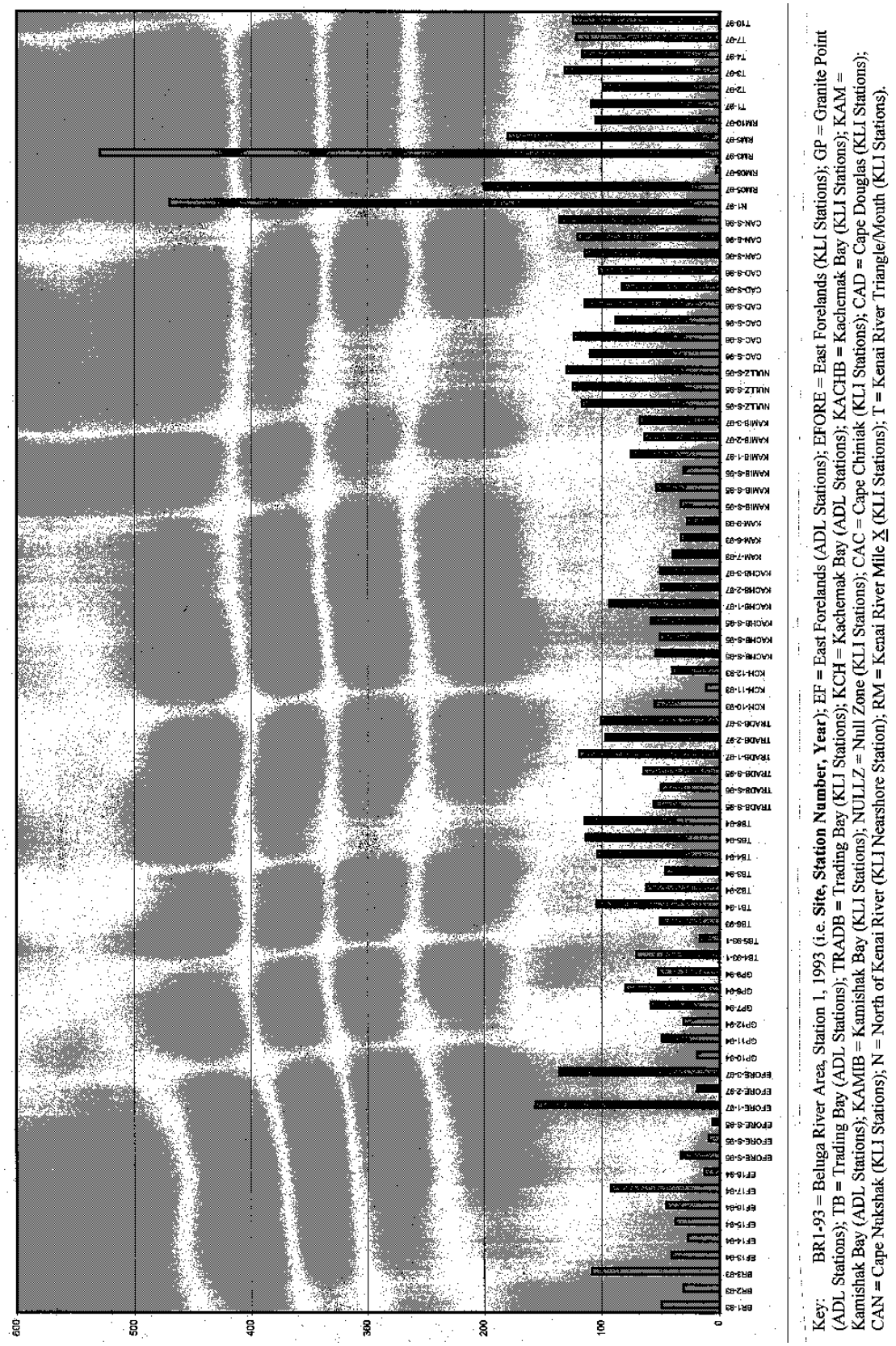
Two characteristics of coal particulates that are important in considering their behavior after release to marine waters and sediments are their significantly reduced weathering losses and limited bioavailability. Evaporation and dissolution losses of PAH confined within a solid matrix such as coal would proceed much more slowly than PAH dissolved within a liquid such as oil. This weathering behavior would contribute to a high total naphthalene signal in the sediments. Also PAH confined within coal particles cannot migrate readily into biological tissues, so coal-derived PAH may be considered to be

toxicologically inert compared to oil-derived PAH (Short et al. 1999; Chapman et al. 1996).

4.11 Cook Inlet Sediment PAH Loading and Composition

4.11.1 Total Polynuclear Aromatic Hydrocarbon Burdens

All of the CIRCAC EMP Projects have shown the ubiquitous presence of low concentrations of PAH throughout the study sites considered to date. As shown in Figure 4-9, the TPAH concentrations within Cook Inlet are generally less than 100 ng/g dry weight (usually less than 50 ng/g dry weight). Slightly higher concentrations (approaching 100 ng/g dry weight) were observed in the Shelikof Strait sites of Cape Douglas, Cape Chiniak, and Cape Nukshak, in the Null Zone, and in the sediments associated with the Kenai River, the river mouth, the East Forelands, and Trading Bay.

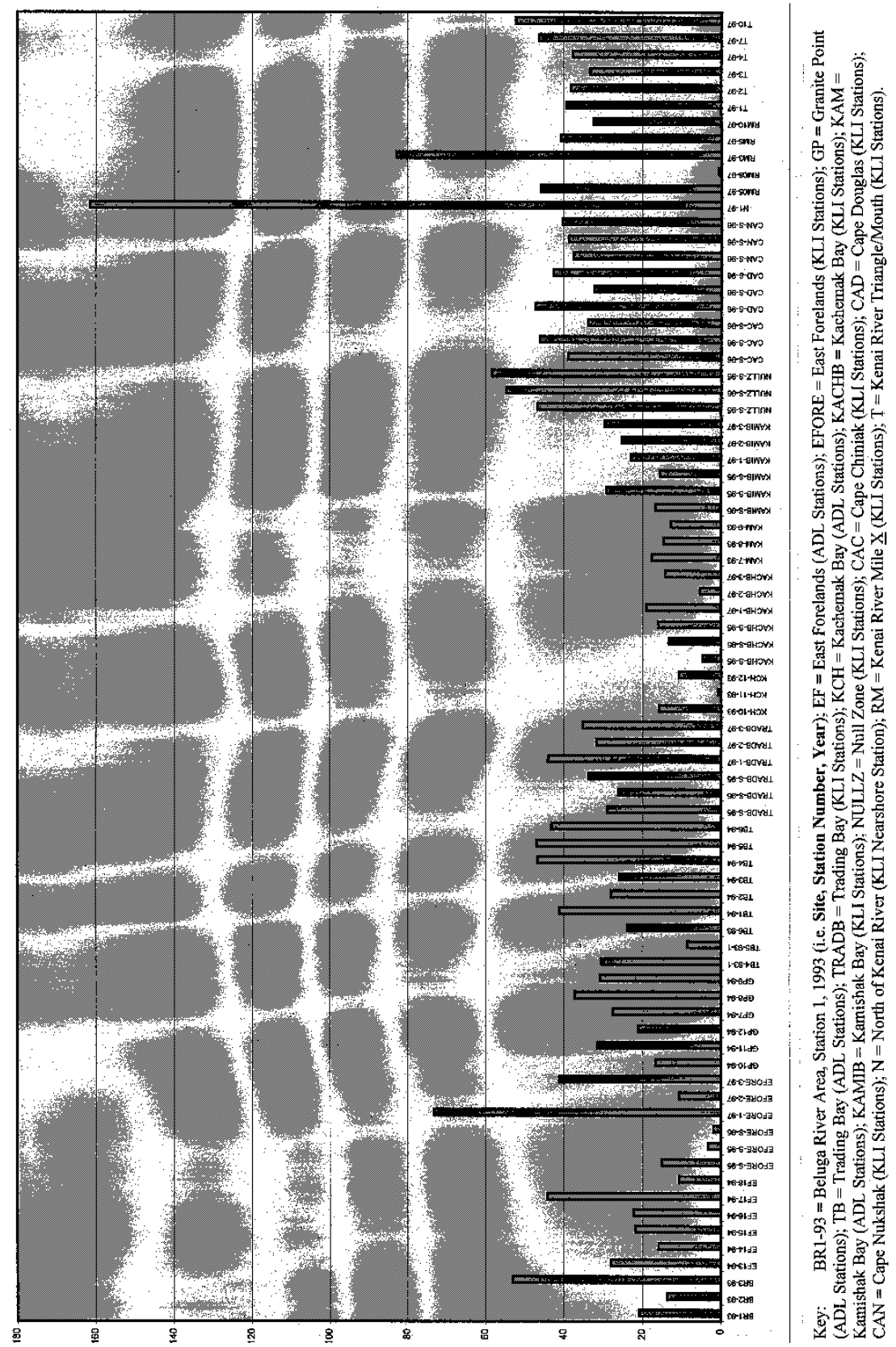


Key: BR1-93 = Beluga River Area, Station 1, 1993 (i.e. **Site, Station Number, Year**); EF = East Forelands (ADL Stations); EFORE = East Forelands (KLI Stations); GP = Granite Point (ADL Stations); TB = Trading Bay (ADL Stations); TRADB = Trading Bay (KLI Stations); KCH = Kachemak Bay (ADL Stations); KACHB = Kachemak Bay (KLI Stations); KAM = Kamishak Bay (ADL Stations); KAMIB = Kamishak Bay (KLI Stations); NULLZ = Null Zone (KLI Stations); CAC = Cape Chiniak (KLI Stations); CAD = Cape Douglas (KLI Stations); CAN = Cape Nukshak (KLI Stations); N = North of Kenai River (KLI Nearshore Station); RM = Kenai River Mile X (KLI Stations); T = Kenai River Triangle/Mouth (KLI Stations).

Figure 4-9 Total PAH in EMP sediment samples from 1993 through 1997.

As noted earlier, the PAH concentrations at all of these sites are generally a factor of forty times less than the ER-L of 4,022 ng/g dry weight associated with adverse biological effects as defined by Long et al. (1993).

Interestingly, the majority of the PAH signal observed in most of the subtidal sediment samples is derived from the sum of the C_1-C_4-naphthalenes as shown by Figure 4-10. Note the striking similarity in the patterns for TPAH and total naphthalenes when Figures 4-9 and 4-10 are compared, with the total naphthalenes often contributing up to 50% of the TPAH.



Key: BR1-93 = Beluga River Area, Station 1, 1993 (i.e. **Site, Station Number, Year**); EF = East Forelands (ADL Stations); EFORE = East Forelands (KLI Stations); GP = Granite Point (ADL Stations); TB = Trading Bay (ADL Stations); TRADB = Trading Bay (KLI Stations); KCH = Kachemak Bay (ADL Stations); KACHB = Kachemak Bay (KLI Stations); KAM = Kamishak Bay (ADL Stations); KAMIB = Kamishak Bay (KLI Stations); NULLZ = Null Zone (KLI Stations); CAC = Cape Chiniak (KLI Stations); CAD = Cape Douglas (KLI Stations); CAN = Cape Nukshak (KLI Stations); N = North of Kenai River (KLI Nearshore Station); RM = Kenai River Mile X (KLI Stations); T = Kenai River Triangle/Mouth (KLI Stations).

Figure 4-10 Total naphthalenes in EMP sediment samples from 1993 - 1997.

4.11.2 CRUDE Index

To aid in the evaluation of complex hydrocarbon data sets, we recently developed the CRUDE Index to encompass many of the parametric indices presented in Table 4-12 into a single value that indicates the likely presence of crude oil or refined products in environmental samples (Payne, et al. 1998). It is essentially an empirical weighted summation with emphasis towards petrogenic indicators.

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

Recall from Table 4-12 that the FFPI is roughly the proportion of selected compounds in TPAH that tend to be present in petrogenic rather than pyrogenic sources, i.e., as FFPI approaches 100, it confirms a petrogenic source. Therefore, the first term in the CRUDE Index uses the FFPI/100 to isolate the petrogenic fraction of TPAHs (i.e., the sum of the naphthalenes, fluorenes, phenanthrenes/anthracenes, and dibenzothiophenes as opposed to the pyrogenic components). In a similar fashion, the second term uses the CPI to distinguish between petrogenic and biogenic sources of aliphatic hydrocarbons. A higher CPI indicates a biological source of aliphatics, so in the second term, a higher CPI lessens the contribution of TAHC to the overall CRUDE Index value. Because TAHC is often larger than TPAH, the CPI is squared (in the denominator) to de-emphasize this component. On rare occasions with fresh oils, the CPI may become less than 1.0 which, when squared, affects the TAHC term in an unintended manner. In these cases (as happened only twice in the Prince William Sound Regional Citizens Advisory Council [PWS RCAC] Long-Term Environmental Monitoring Program [LTEMP] study), the CPI can be adjusted to 1.0. The final term of the CRUDE Index is the unresolved complex mixture (UCM), an enigmatic hump observed on gas chromatograms of highly weathered and polar products that cannot be adequately separated. The UCM is typically so large that it is measured in a higher magnitude of weight. To de-emphasize its mass, it is divided by 1000 (other formulations of CRUDE left it out entirely but dividing seemed to work best).

The CRUDE index is extremely useful in summarizing the five commonly used indices, and it truly aids in tracking the probable presence of petrogenic hydrocarbons. It should be noted, however, that it is a somewhat subjective *empirical* index, and that the CRUDE index values are not directly comparable to total hydrocarbon loading, such as TPAH or TAHC. Nevertheless, it is extremely useful in a relative sense, and can be used to highlight the presence of crude oil and track changes in relative hydrocarbon concentrations over time or distance.

Figure 4-11 presents a graphical depiction of CRUDE Index values obtained on the 1996 and 1997 data sets from the CIRCAC EMP. Because the CRUDE Index required input on aliphatic hydrocarbon parameters, it could not be applied to the data from any of the earlier programs. Likewise there are no time-series data for any single station over the 1996 and 1997 program years, so the CRUDE Index can only be used to examine within-station-replicates homogeneity and to compare among stations between the two years.

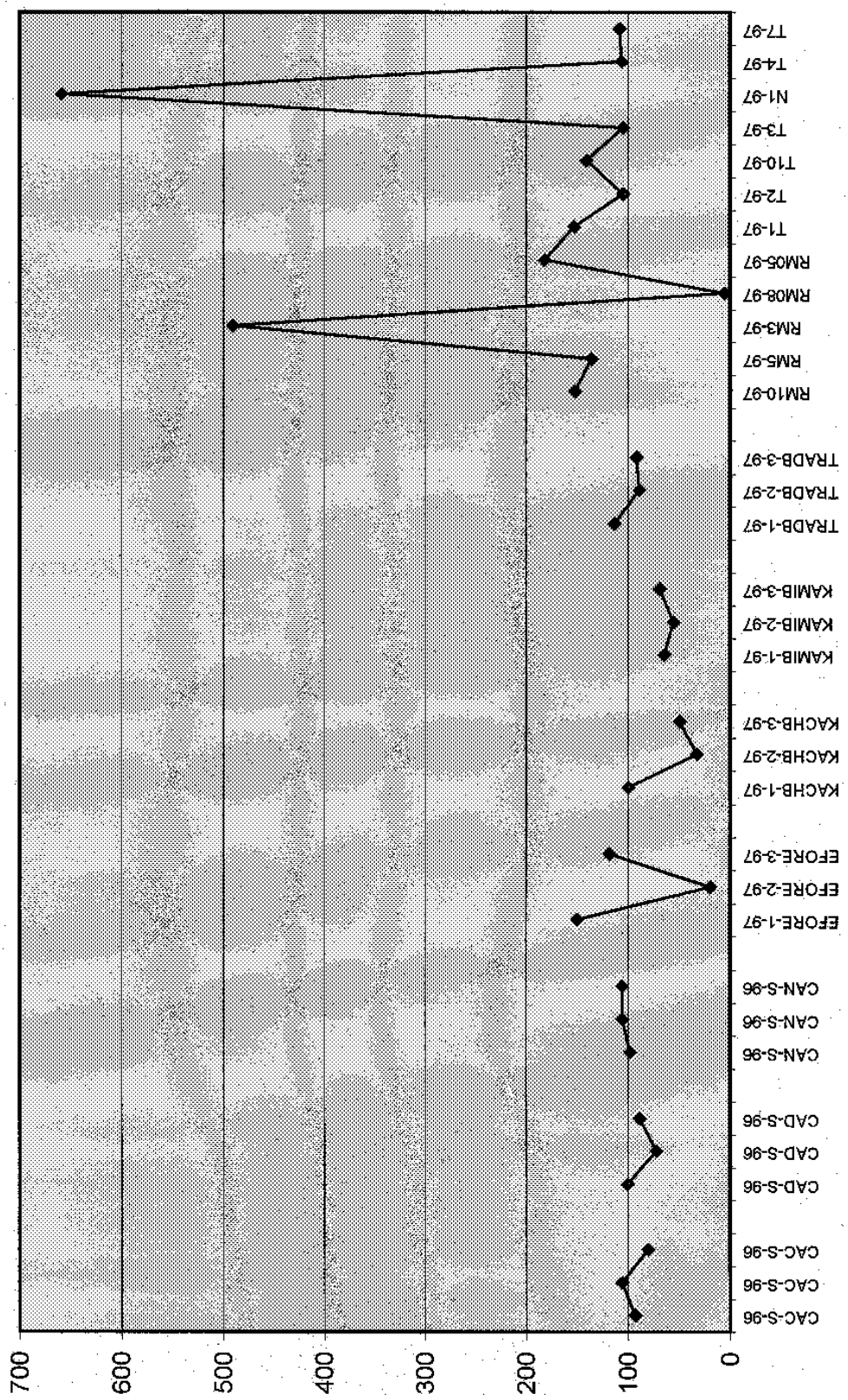
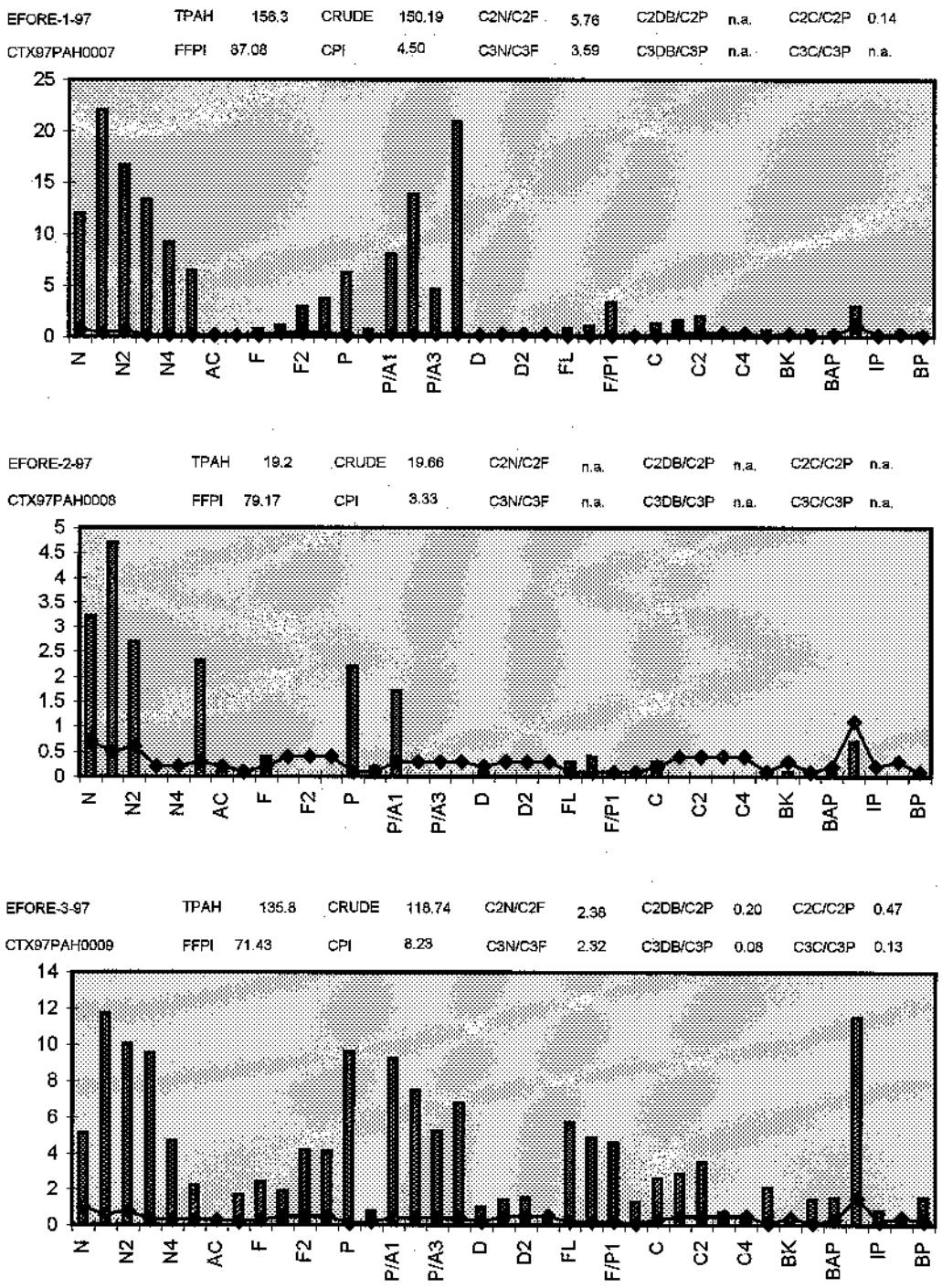


Figure 4-11 CRUDE Index values for 1996 and 1997 EMP sediment samples.

Fairly low and relative constant CRUDE Index values were obtained for Cape Chiniak, Cape Nukshak, and Cape Douglas in the Shelikof Strait area in 1996, and at Kamishak Bay and Trading Bay in 1997. More within station variability was observed at the East Forelands and Kachemak Bay stations in 1997. The significant variability in the East Forelands and Kachemak Bay CRUDE Index values in 1997 are easily explained by the dramatic changes in the histogram plots for those stations shown in Figures 4-12 and 4-13, respectively. Note that replicate 2 at the East Forelands is devoid of C_3- and C_4-naphthalenes, all the alkylated fluorenes, and the C_2, C_3, and C_4-phenanthrenes/ anthracenes. In fact, there are only six components that are above the method detection limit. In Figure 4-13 the influence of TPAH and FFPI on the CRUDE Index values are quite apparent, as shown by the data presented immediately above each histogram plot. Replicate 2 has noticeably more pyrogenic components compared to lower molecular weight PAH, and the TPAH, FFPI, and CRUDE Index are concomitantly lower. It is also interesting to note the strong similarity to the Homer coal patterns shown in Figure 4-8. Finally, Figure 4-14 illustrates the almost identical PAH fingerprints in three replicates that have essentially the same CRUDE Index values.



-12 Histogram plots for 1997 sediments at East Forelands showing en CRUDE Index values and PAH distribution.

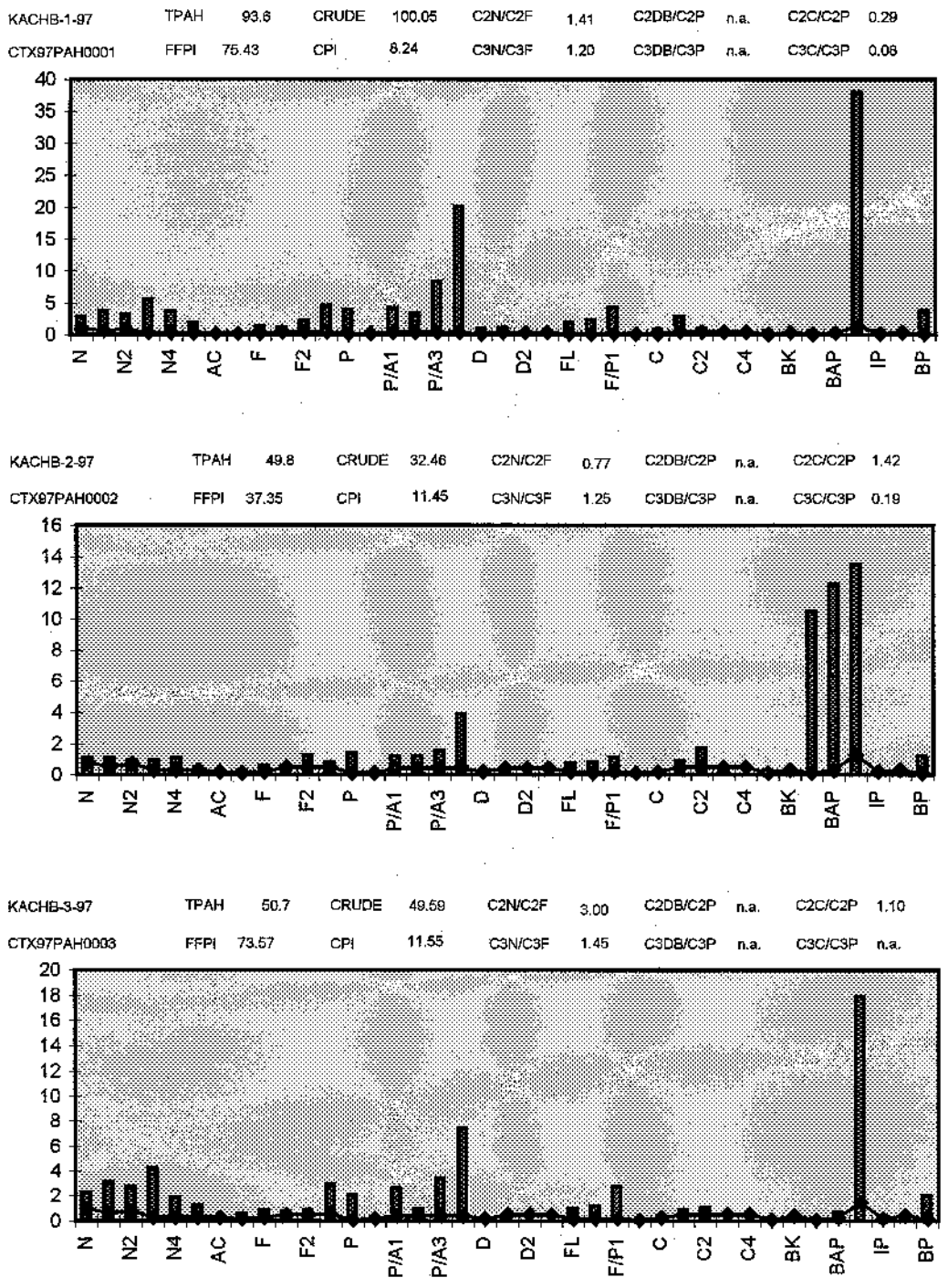


Figure 4-13 Histogram plots for 1997 sediments at Kachemak Bay showing relationship between CRUDE Index values and TPAH and FFPI.

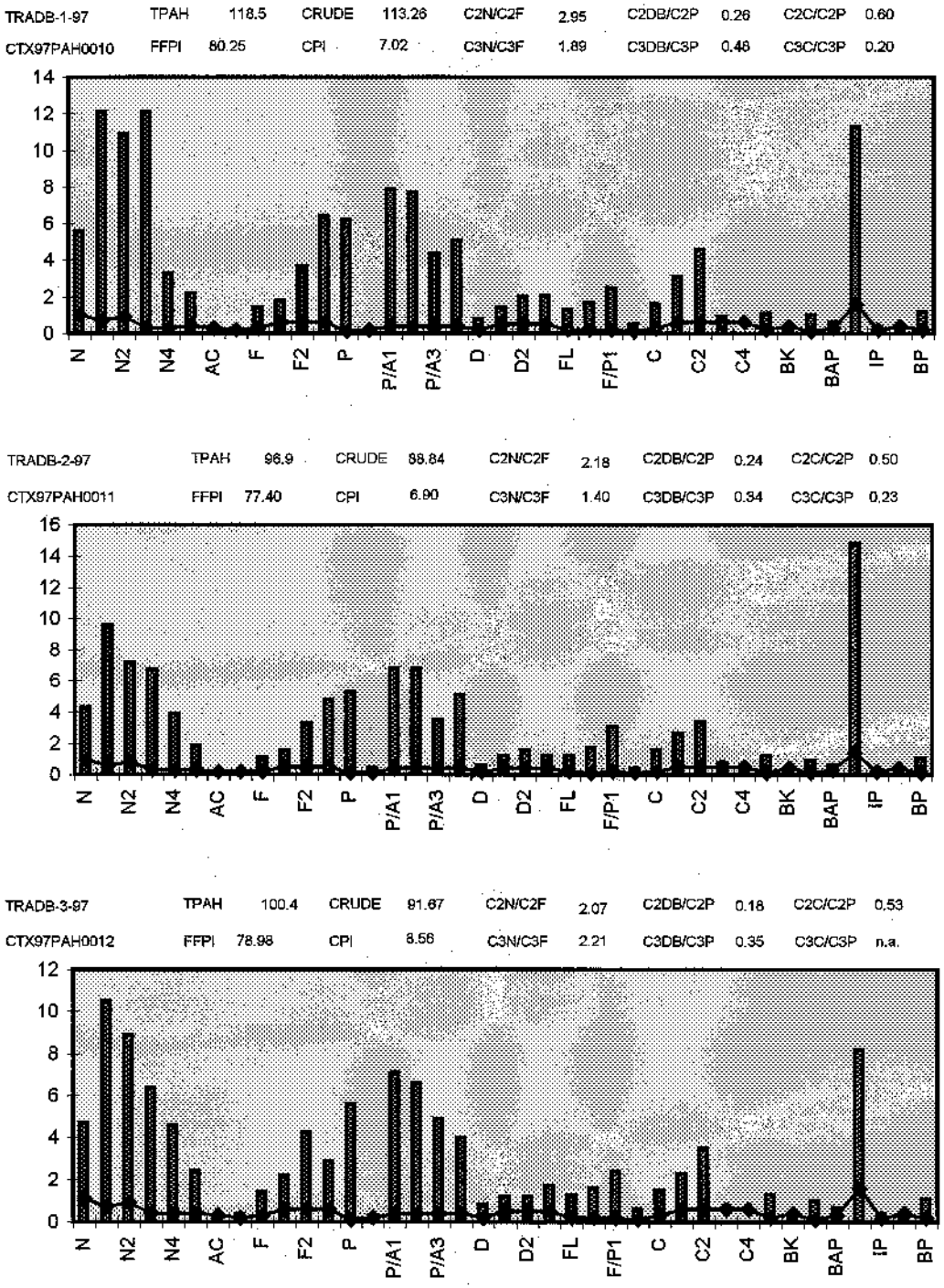


Figure 4-
profiles in replicate samples having similar CRUDE Index values.

-11 is the
-

Delta Triangle sedime
left to right starting 10 miles upriver (RM10), going down river to 0.5 miles into the river

mouth (RM05), then from just outside the river mouth (T1) trending to the northwest, and endi -15). Finally, the last

deeper station (T7) approximately 2000 meters to the southwest. In selecting the samples -grained

differences in grain size would not be an important factor. In actual fact, differences in the

it would have been more useful if samples with a wider range of grain-
had been selected. For example, stations N1 and RM3, which yielded the highest CRUDE -sand concentrations at 14

highly variable CRUDE Index values ranging from 6 to almost 136, and yet, they had

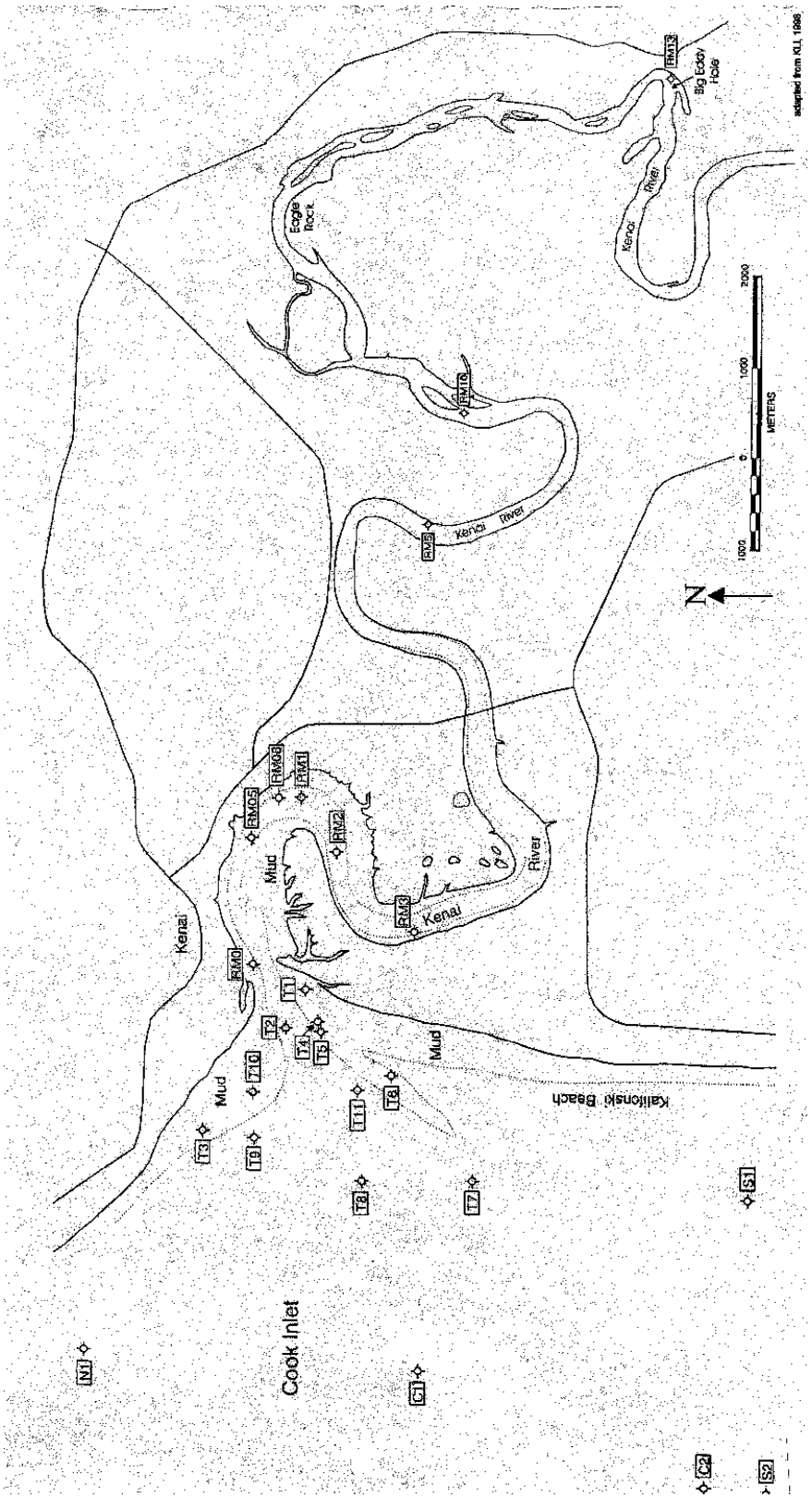


Figure 4-15 1997 Kenai River sediment sampling locations.

While more PAH analyses on additional samples with wider grain-size distributions are clearly needed to complete an in-depth trend analysis, it is important to note, that the observed relationship between sand content and higher CRUDE Index values goes counter to the generally accepted notion that higher PAH concentrations are associated primarily with finer-grained sediments. The CRUDE Index data show intermediate levels of a "petrogenic" presence upriver at stations RM10 and RM5, with a maximum at station RM3, three miles from the river mouth. The value then falls off dramatically at station RM08 (0.8 miles upriver near the Kenai City Dock) only to increase again at RM05, 0.3 miles further downstream and at station T1, at the river mouth itself. CRUDE Index values then generally tended to decrease gradually as samples were collected in the mudflats to the northwest (T2, T10, and T3) and to the southwest (T4 and T7). The exception to these generally decreasing trends as samples were collected further from the river mouth is station N1. This station was located further offshore in deeper and coarser (14% sand) sediments out of the mudflats to the northwest of the river mouth.

Figures 4-16 and 4-17 present the PAH histogram plots for the river sediments and offshore triangle delta sediments, respectively. The samples are arranged from up river (RM10) to the river mouth in Figure 4-16, and then from the southwest (T7), to just off of the river mouth (T1), and then in a trend line to the northwest ending a N1 in Figure 4-17. The histogram plots for the upriver samples in Figure 4-16 show significant concentrations of alkylated naphthalenes, fluorenes, phenanthrenes/anthracenes, dibenzothiophenes, and even chrysenes, in addition to a major contribution from perylene. The alkylated fluorene and chrysene patterns in the upriver samples do not match Cook Inlet crude oil (see Figure 4-2), and except for the perylene, these samples bear a closer resemblance to the background signals obtained in Prince William Sound shown in Figure 4-5. A significant increase in petrogenic components is then noted at RM3, presumably from increased boating activities and river traffic closer to the mouth, and this pattern is consistently observed at the river mouth itself (RM05). The sudden and unmistakable drop in PAH signature at RM08 (and concomitant decrease in CRUDE Index value) is difficult to explain. The site is close to the Kenai docks, the grain size distribution is nearly identical to RM05, and there is no physical or geological reason to expect such a dramatic and complete loss of a hydrocarbon signal. With the exception of perylene, all of the components are below the MDL, and they resemble the procedural analytical artifacts presented in Figure 4-1. We suspect that an error in sample custody, tracking, or labeling may have occurred with this sample (or its extract) in the laboratory. The upstream river sediment pattern then continues to be observed in the sediments from the mudflats shown in Figure 4-17, with a significant decrease in the petrogenic signal (compared to RM3 and RM05) as the samples are collected further from the river mouth itself. The perylene contribution continues to be a significant factor, and the increase in the C_4-phenanthrenes/anthracenes in the T1 sample suggests a contribution from along-shore transport of Ninilchik coal particles. As slightly coarser samples are collected from further offshore at N1, the relative contribution from the alkyl-substituted naphthalenes and phenanthrenes/anthracenes continues to increase.

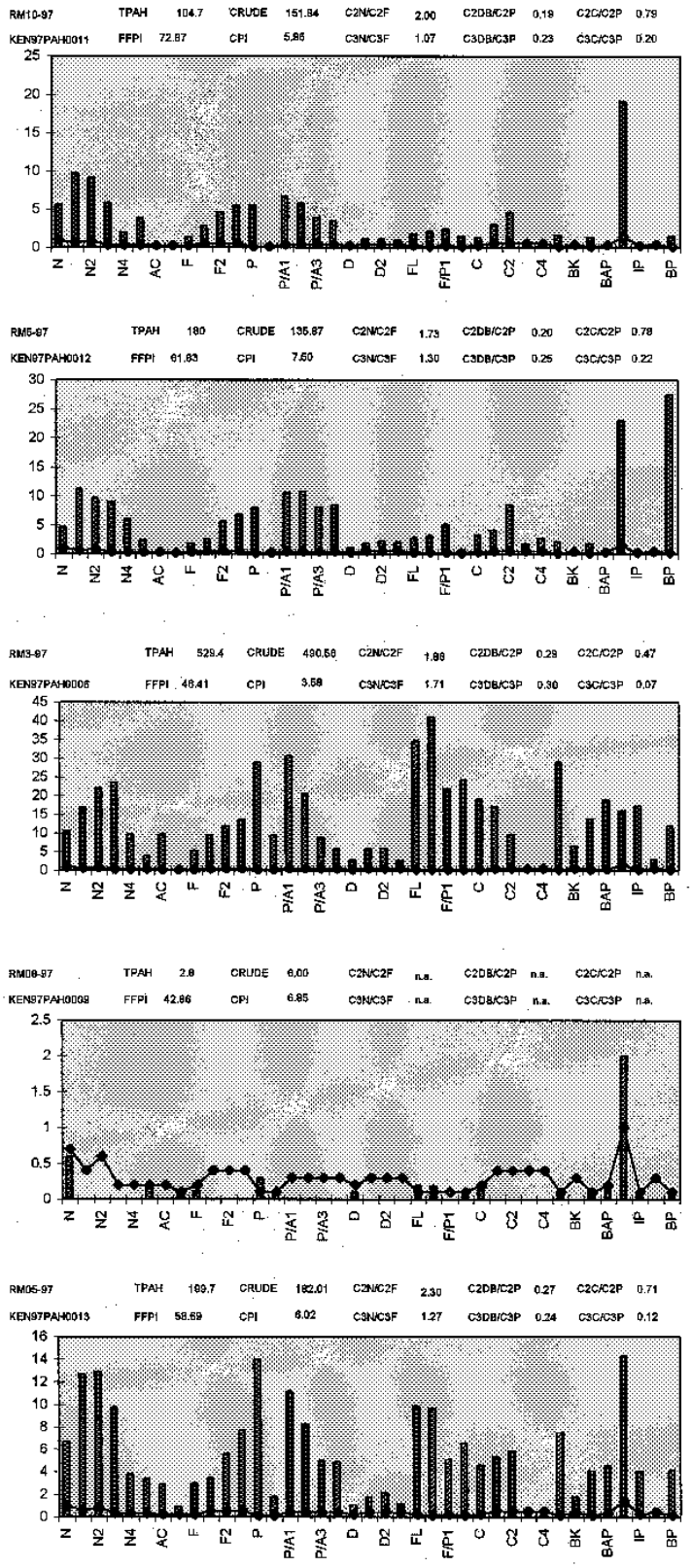


Figure 4-16 PAH profiles of 1997 Kenai River sediments descending from upriver to the mouth.

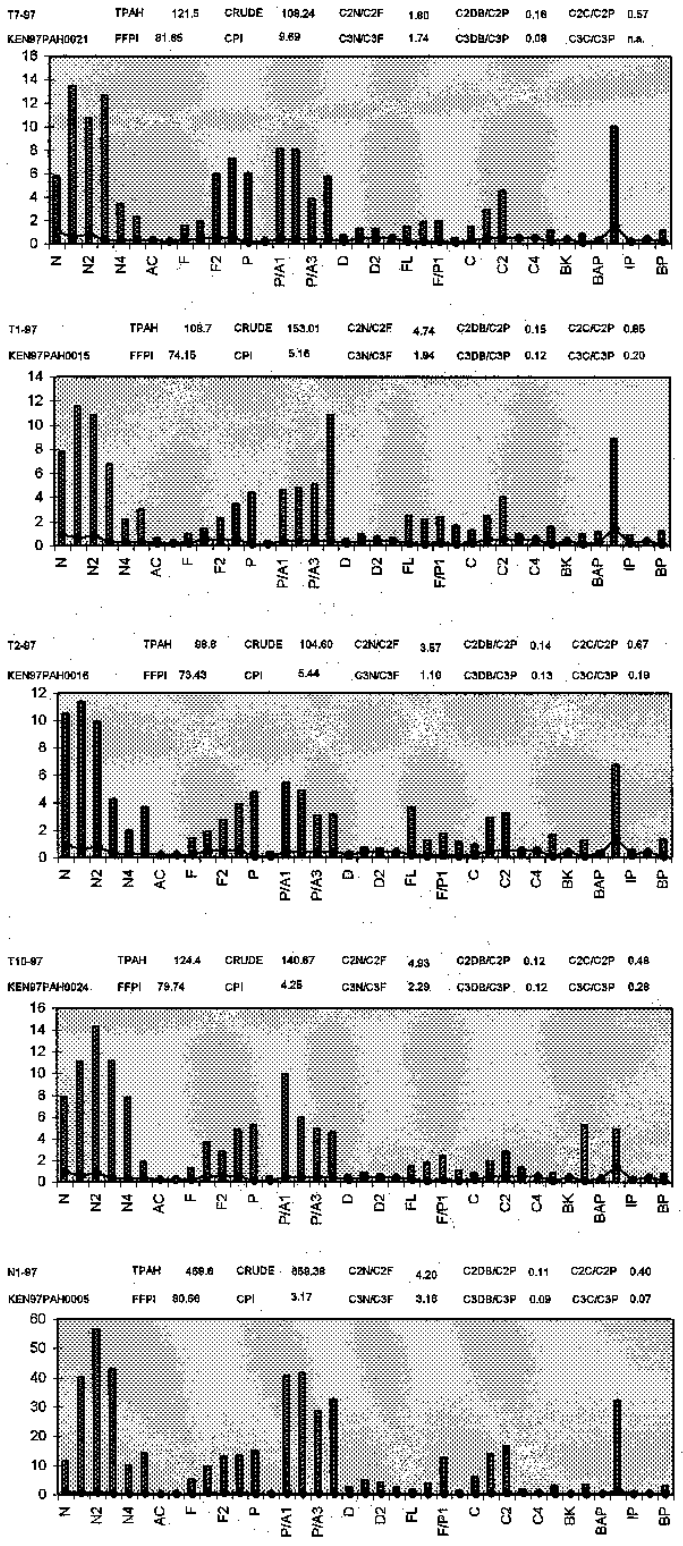


Figure 4-
the SW, then to the river mouth, and finally trending NW to Station N1, farthest offshore.

The strength and utility of the CRUDE Index approac
generalized overview of hydrocarbon burdens and trends can be observed from this limited application to the data. Unfortunately, the required aliphatic data were only available for re, the rest of the EMP program data were evaluated with the Mytilus Petrogenic Index, which was initially developed for tissue

4.11.3 Mytilus Petrogenic Index

c Index is essentially just the first term of the CRUDE Index defined above, and actually reduces down to the sum of the naphthalenes, fluorenes,

Mytilus Petrogenic Index was initially derived to make use of the available parameterized

in this program, because it does not require any AHC data. Figure 4-
Mytilus Petrogenic Index values obtained for all the sediment samples analyzed thus far in

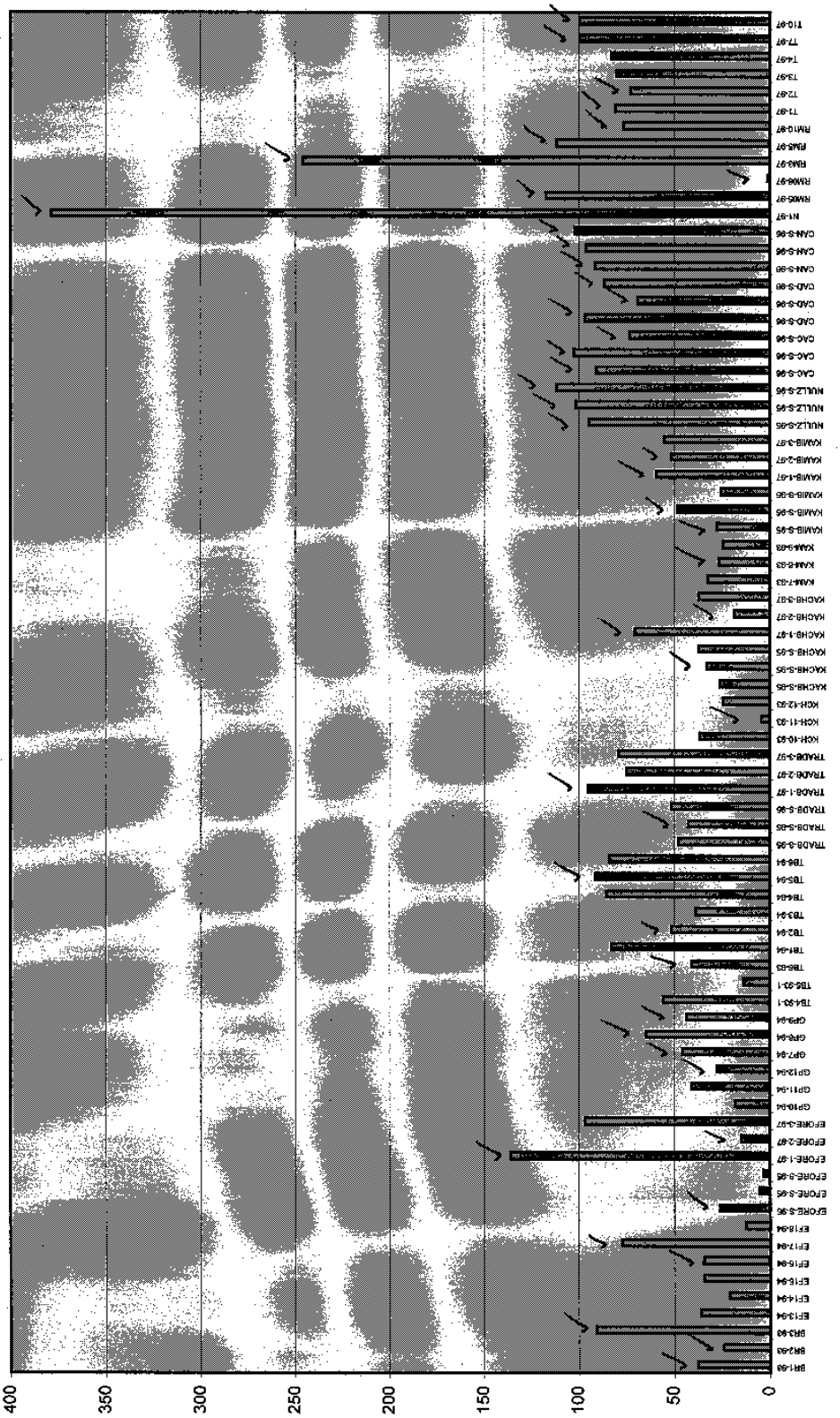


Figure 4-18 Application of Mytilus Petrogenic Index calculations to 1993-1996 EMP sediment data set.

In general, the values are all quite low, generally below 100; however, there are some apparent differences among samples within a given year, or among samples at a given station over time. Samples showing the greatest apparent spatial or temporal differences for a given station were selected for more detailed analyses, and comparative histogram plots were prepared to elucidate any changes in the PAH profiles responsible for the apparent trends. Histogram plots for samples shown with a "check mark" in Figure 4-18 are presented in Figures 4-19 through 4-28. Depending on the number of samples available and the observed differences, anywhere from three to five histograms are presented per station per figure. Additional discussions on some of the trends observed in these figures are presented in Sections 4.11.5 and 4.11.6.

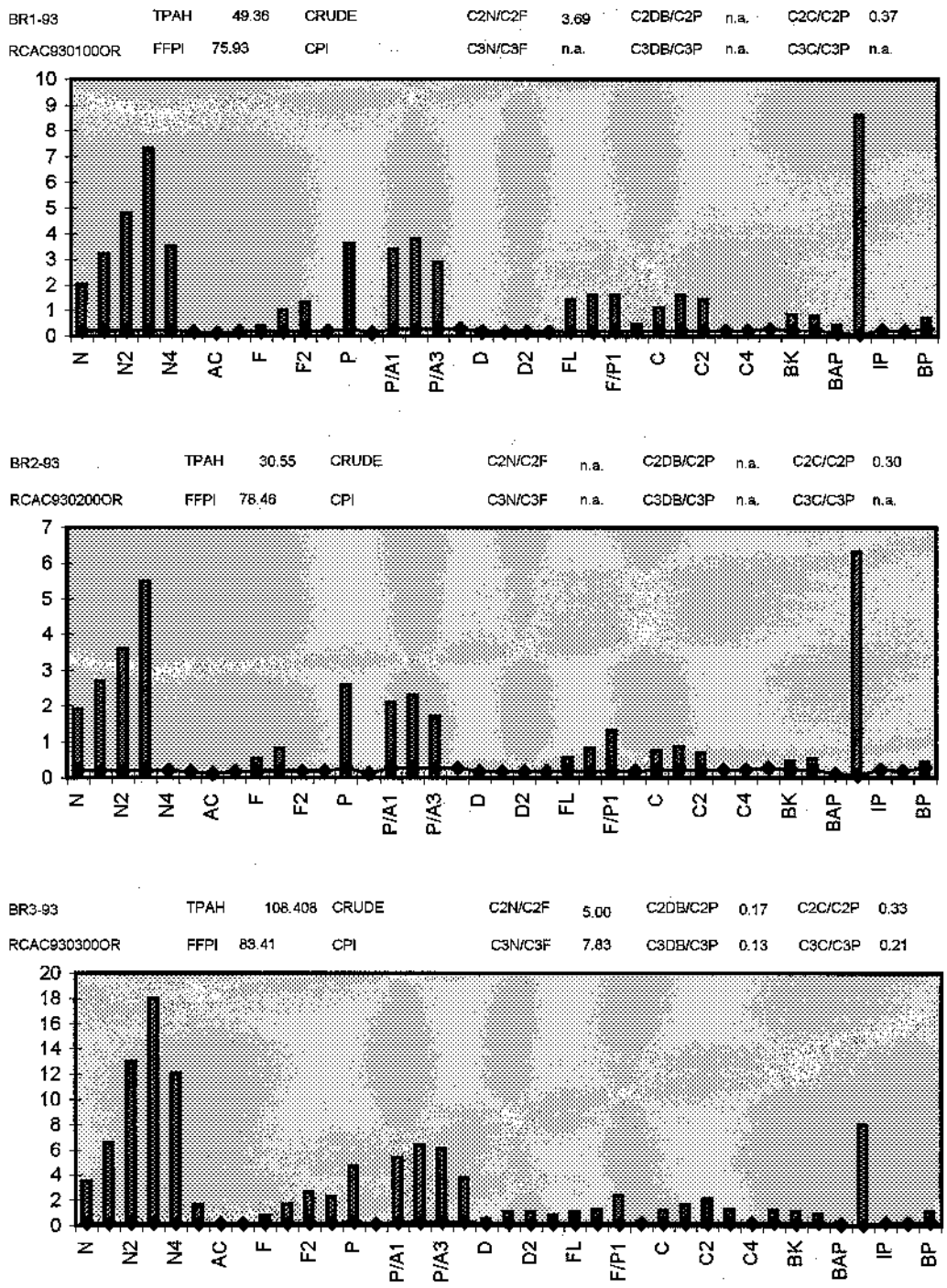


Figure 4-19 Representative PAH histogram plots for 1993 Beluga River area sediments.

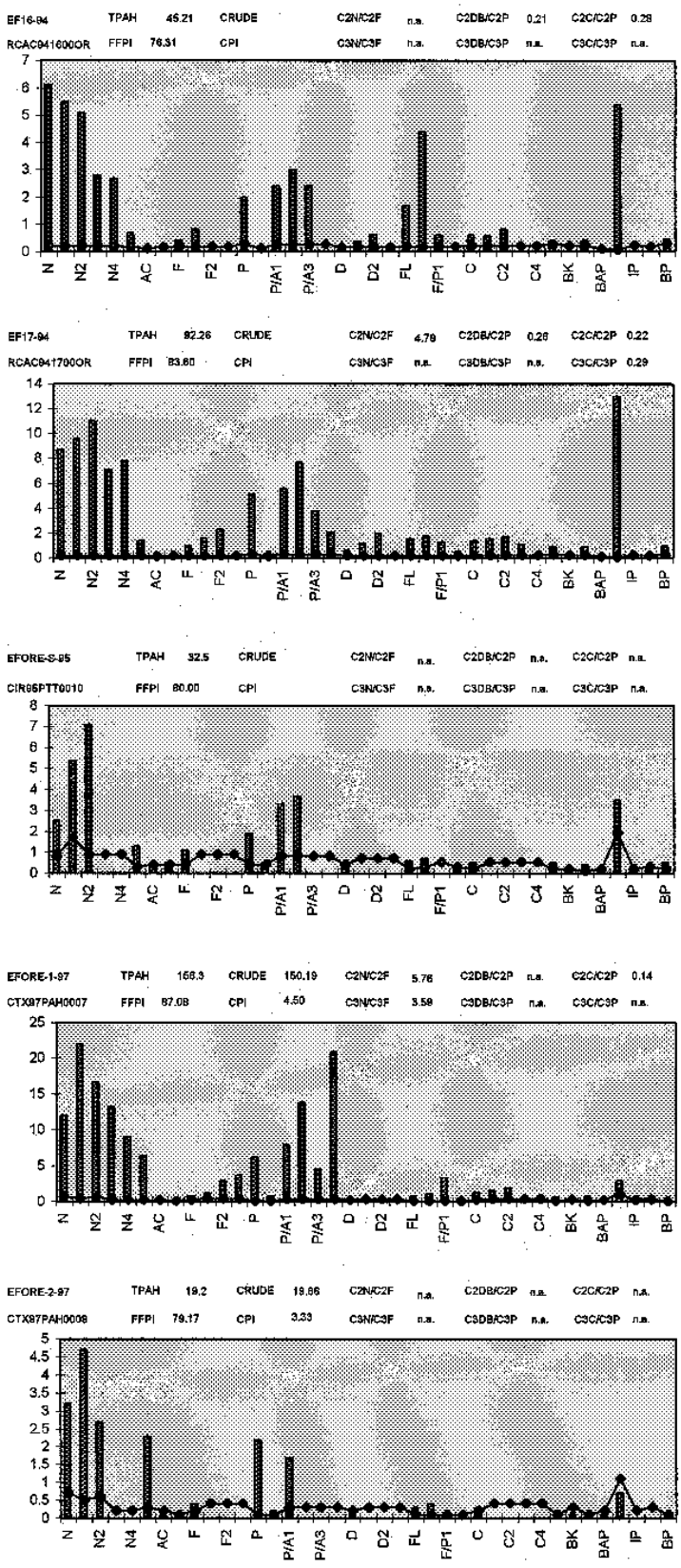


Figure 4-20 PAH profiles of selected 1994-1997 East Forelands sediments.

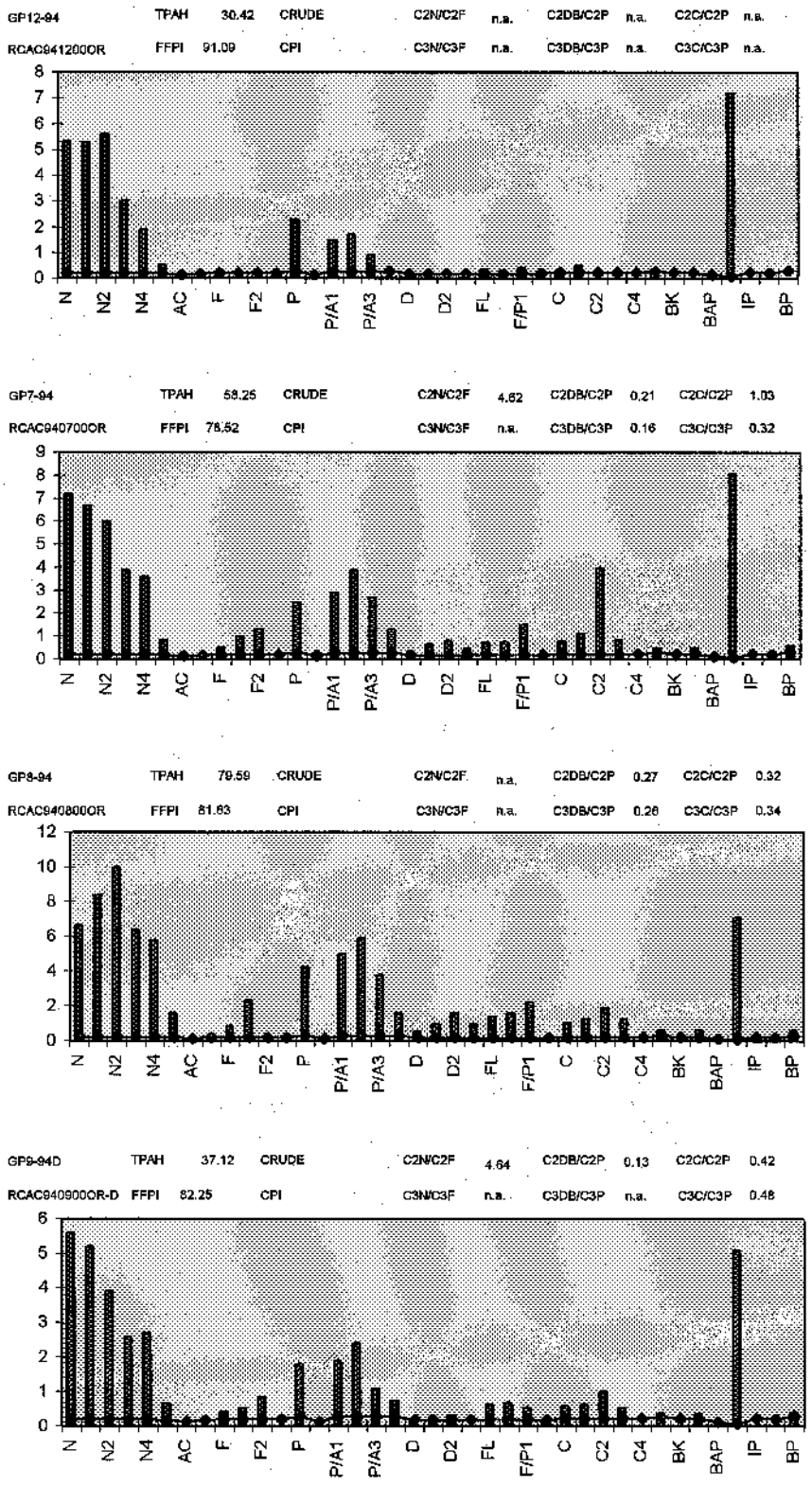
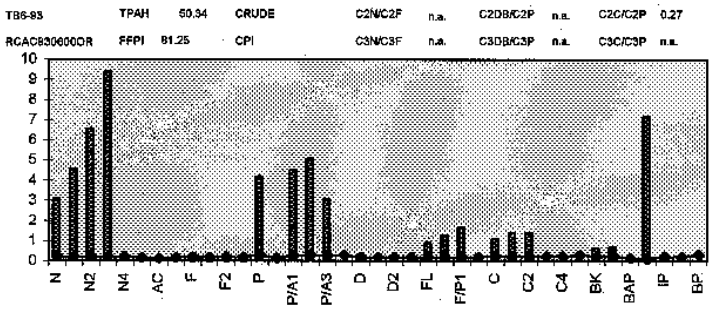
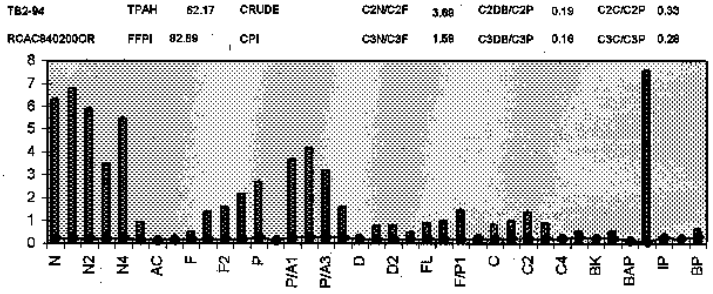
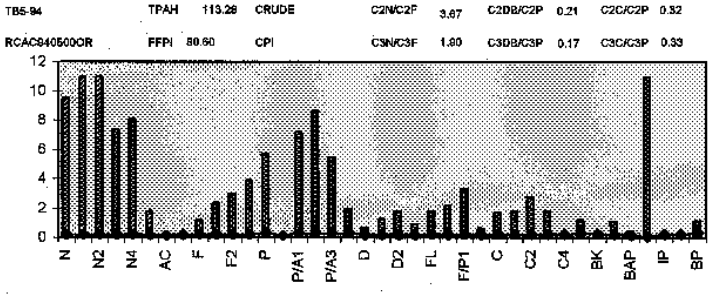
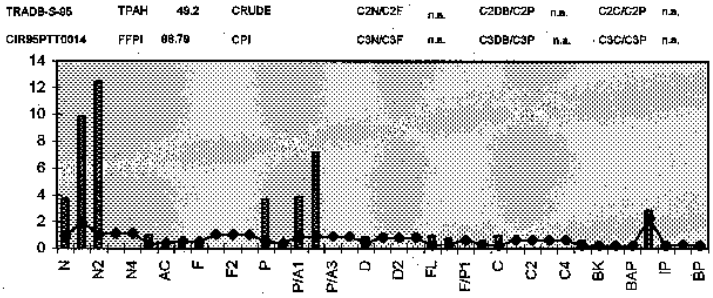

GP12-94 TPAH 30.42 CRUDE C2N/C2F n.a. C2DB/C2P n.a. C2C/C2P n.a.
RCAC941200OR FFPI 91.09 CPI C3N/C3F n.a. C3DB/C3P n.a. C3C/C3P n.a.
GP7-94 TPAH 58.25 CRUDE C2N/C2F 4.62 C2DB/C2P 0.21 C2C/C2P 1.03
RCAC940700OR FFPI 78.52 CPI C3N/C3F n.a. C3DB/C3P 0.16 C3C/C3P 0.32
GP8-94 TPAH 79.59 CRUDE C2N/C2F n.a. C2DB/C2P 0.27 C2C/C2P 0.32
RCAC940800OR FFPI 81.63 CPI C3N/C3F n.a. C3DB/C3P 0.26 C3C/C3P 0.34
GP9-94D TPAH 37.12 CRUDE C2N/C2F 4.64 C2DB/C2P 0.13 C2C/C2P 0.42
RCAC940900OR-D FFPI 82.25 CPI C3N/C3F n.a. C3DB/C3P n.a. C3C/C3P 0.48
N N2 N4 AC F F2 P P/A1 P/A3 D D2 FL F/P1 C C2 C4 BK BAP IP BP

Figure 4-


TB6-93 TPAH 50.34 CRUDE C2N/C2F n.a. C2DB/C2P n.a. C2C/C2P 0.27
RCAC830600OR FFPI 81.25 CPI C3N/C3F n.a. C3DB/C3P n.a. C3C/C3P n.a.
N N2 N4 AC F F2 P P/A1 P/A3 D D2 FL F/P1 C C2 C4 BK BAP IP BP


TB2-94 TPAH 62.17 CRUDE C2N/C2F 3.69 C2DB/C2P 0.19 C2C/C2P 0.33
RCAC840200OR FFPI 82.89 CPI C3N/C3F 1.58 C3DB/C3P 0.16 C3C/C3P 0.28
N N2 N4 AC F F2 P P/A1 P/A3 D D2 FL F/P1 C C2 C4 BK BAP IP BP


TB5-94 TPAH 113.28 CRUDE C2N/C2F 3.67 C2DB/C2P 0.21 C2C/C2P 0.32
RCAC840500OR FFPI 80.60 CPI C3N/C3F 1.80 C3DB/C3P 0.17 C3C/C3P 0.33
N N2 N4 AC F F2 P P/A1 P/A3 D D2 FL F/P1 C C2 C4 BK BAP IP BP


TRADB-S-95 TPAH 49.2 CRUDE C2N/C2F n.a. C2DB/C2P n.a. C2C/C2P n.a.
CIR95PTT0014 FFPI 88.79 CPI C3N/C3F n.a. C3DB/C3P n.a. C3C/C3P n.a.
N N2 N4 AC F F2 P P/A1 P/A3 D D2 FL F/P1 C C2 C4 BK BAP IP BP

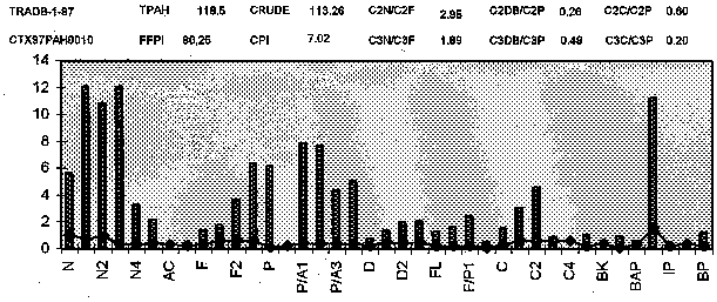
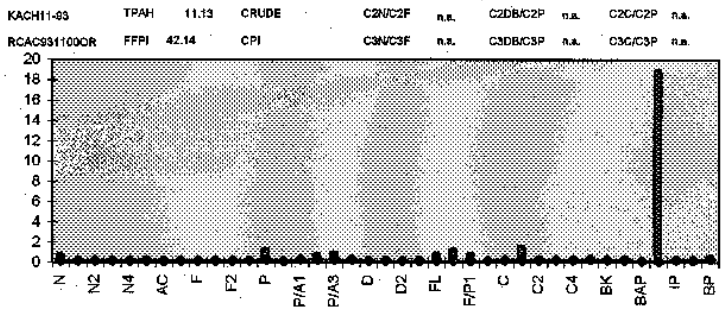
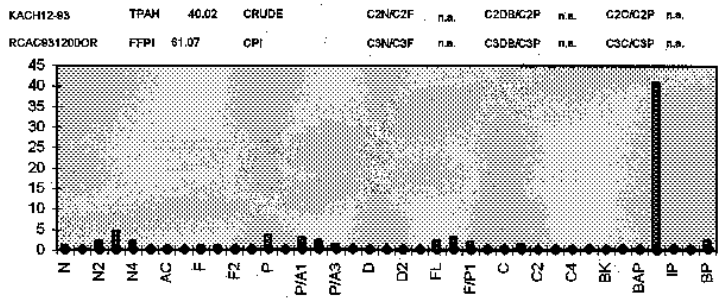
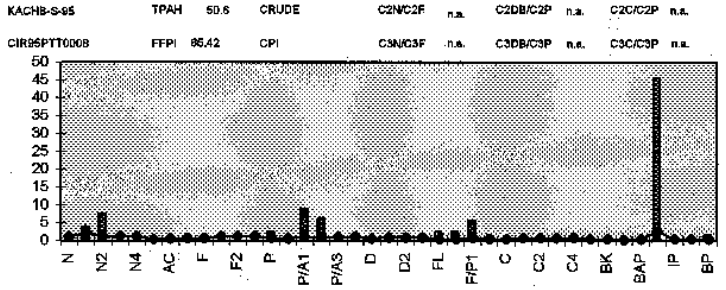
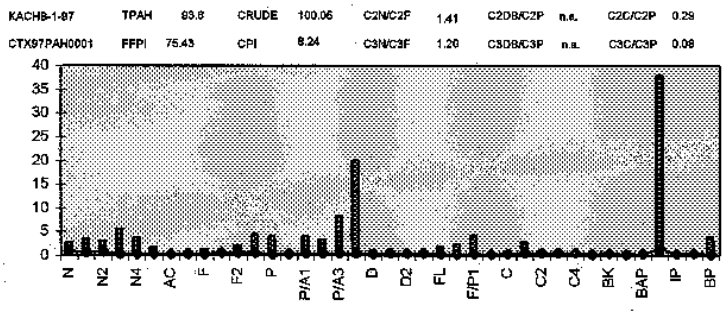

TRADB-1-97 TPAH 119.5 CRUDE 113.26 C2N/C2F 2.95 C2DB/C2P 0.26 C2C/C2P 0.60
CTX97PAH0010 FFPI 80.25 CPI 7.02 C3N/C3F 1.89 C3DB/C3P 0.49 C3C/C3P 0.20
N N2 N4 AC F F2 P P/A1 P/A3 D D2 FL F/P1 C C2 C4 BK BAP IP BP

Figure 4- profiles of selected 1993-


KACH11-93 TPAH 11.13 CRUDE C2N/C2F n.a. C2DB/C2P n.a. C2C/C2P n.a.
RCAC931100OR FFPI 42.14 CPI C3N/C3F n.a. C3DB/C3P n.a. C3C/C3P n.a.
N N2 N4 AC F F2 P P/A1 P/A3 D D2 FL F/P1 C C2 C4 BK BAP IP BP


KACH12-93 TPAH 40.02 CRUDE C2N/C2F n.a. C2DB/C2P n.a. C2C/C2P n.a.
RCAC931200OR FFPI 61.07 CPI C3N/C3F n.a. C3DB/C3P n.a. C3C/C3P n.a.
N N2 N4 AC F F2 P P/A1 P/A3 D D2 FL F/P1 C C2 C4 BK BAP IP BP


KACHB-S-95 TPAH 50.6 CRUDE C2N/C2F n.a. C2DB/C2P n.a. C2C/C2P n.a.
CIR95PTT0008 FFPI 86.42 CPI C3N/C3F n.a. C3DB/C3P n.a. C3C/C3P n.a.
N N2 N4 AC F F2 P P/A1 P/A3 D D2 FL F/P1 C C2 C4 BK BAP IP BP


KACHB-1-97 TPAH 93.6 CRUDE 100.06 C2N/C2F 1.41 C2DB/C2P n.a. C2C/C2P 0.29
CTX97PAH0001 FFPI 75.43 CPI 8.24 C3N/C3F 1.20 C3DB/C3P n.a. C3C/C3P 0.08
N N2 N4 AC F F2 P P/A1 P/A3 D D2 FL F/P1 C C2 C4 BK BAP IP BP

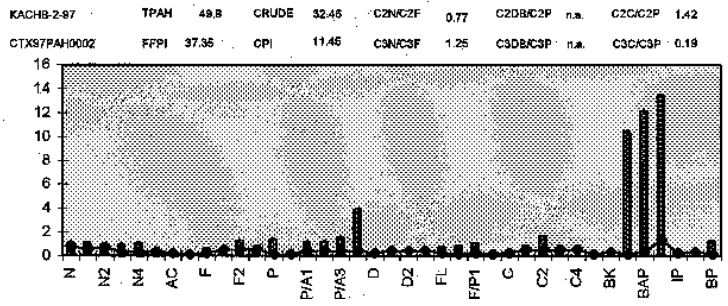
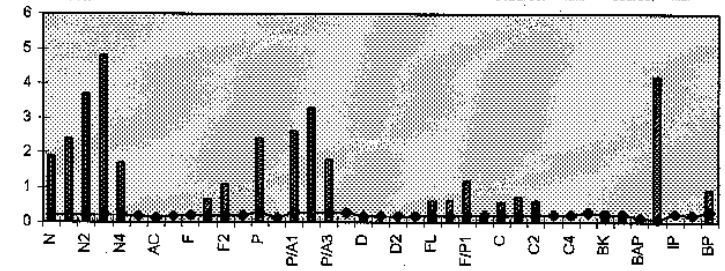
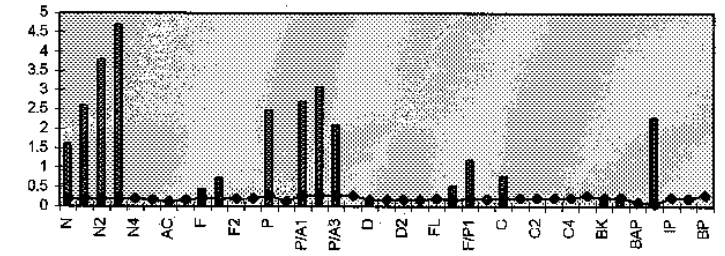

KACHB-2-97 TPAH 49.8 CRUDE 32.46 C2N/C2F 0.77 C2DB/C2P n.a. C2C/C2P 1.42
CTX97PAH0002 FFPI 37.35 CPI 11.45 C3N/C3F 1.25 C3DB/C3P n.a. C3C/C3P 0.19
N N2 N4 AC F F2 P P/A1 P/A3 D D2 FL F/P1 C C2 C4 BK BAP IP BP

Figure 4- -1997 Kachemak Bay sediments.

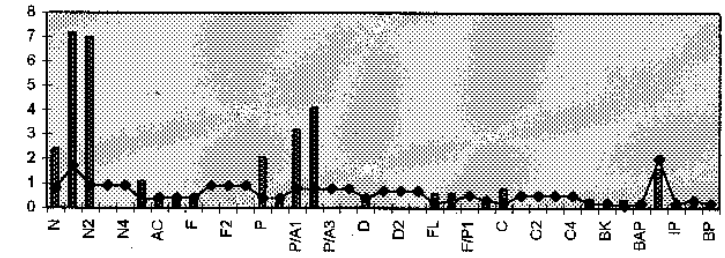
KAMI8-93 TPAH 32.64 CRUDE C2N/C2F 3.36 C2DB/C2P n.a. C2C/C2P 0.19
RCAC930800OR FFPI 81.40 CPI C3N/C3F n.a. C3DB/C3P n.a. C3C/C3P n.a.



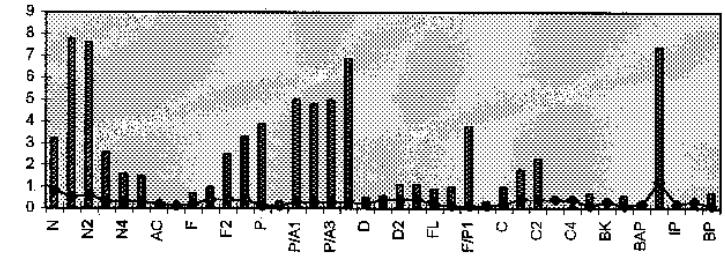
KAMI9-93 TPAH 27.5 CRUDE C2N/C2F n.a. C2DB/C2P n.a. C2C/C2P n.a.
RCAC930900OR FFPI 89.05 CPI C3N/C3F n.a. C3DB/C3P n.a. C3C/C3P n.a.



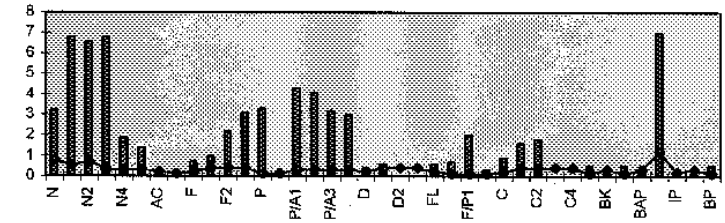
KAMIB-S-95 TPAH 32.8 CRUDE C2N/C2F n.a. C2DB/C2P n.a. C2C/C2P n.a.
CIR95PTT0004 FFPI 83.23 CPI C3N/C3F n.a. C3DB/C3P n.a. C3C/C3P n.a.



KAMIB-1-97 TPAH 75.1 CRUDE 84.33 C2N/C2F 3.04 C2DB/C2P 0.23 C2C/C2P 0.48
CTX97PAH0004 FFPI 79.23 CPI 9.20 C3N/C3F 0.79 C3DB/C3P 0.22 C3C/C3P n.a.



KAMIB-2-97 TPAH 63.2 CRUDE 55.82 C2N/C2F 3.09 C2DB/C2P n.a. C2C/C2P 0.44
CTX97PAH0005 FFPI 81.33 CPI 9.63 C3N/C3F 2.19 C3DB/C3P n.a. C3C/C3P n.a.



-24 PAH profiles of selected 1993 1997 Kamishak Bay sediments.

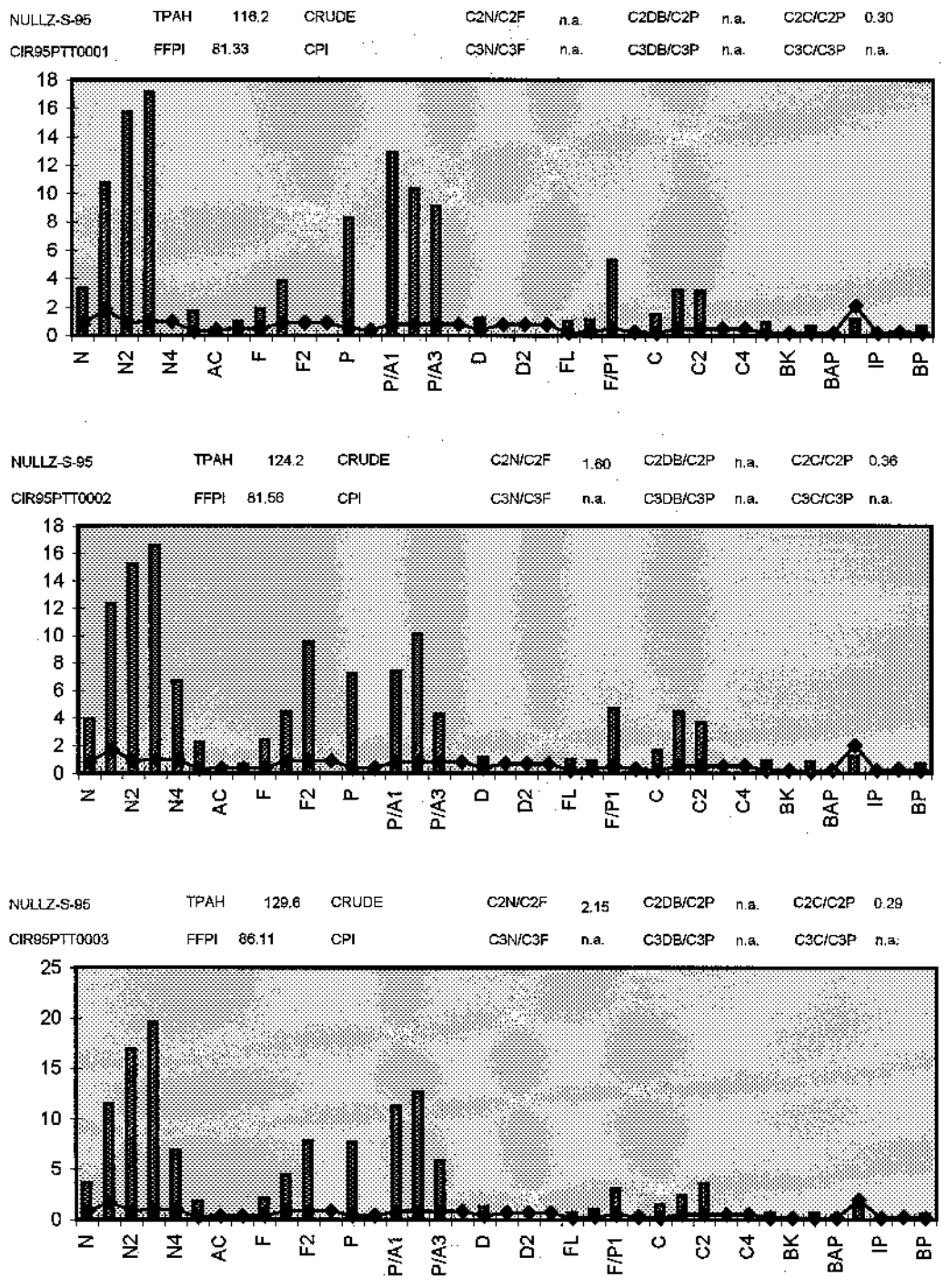


Figure 4-25 Representative PAH histogram plots for 1995 Null Zone sediments.

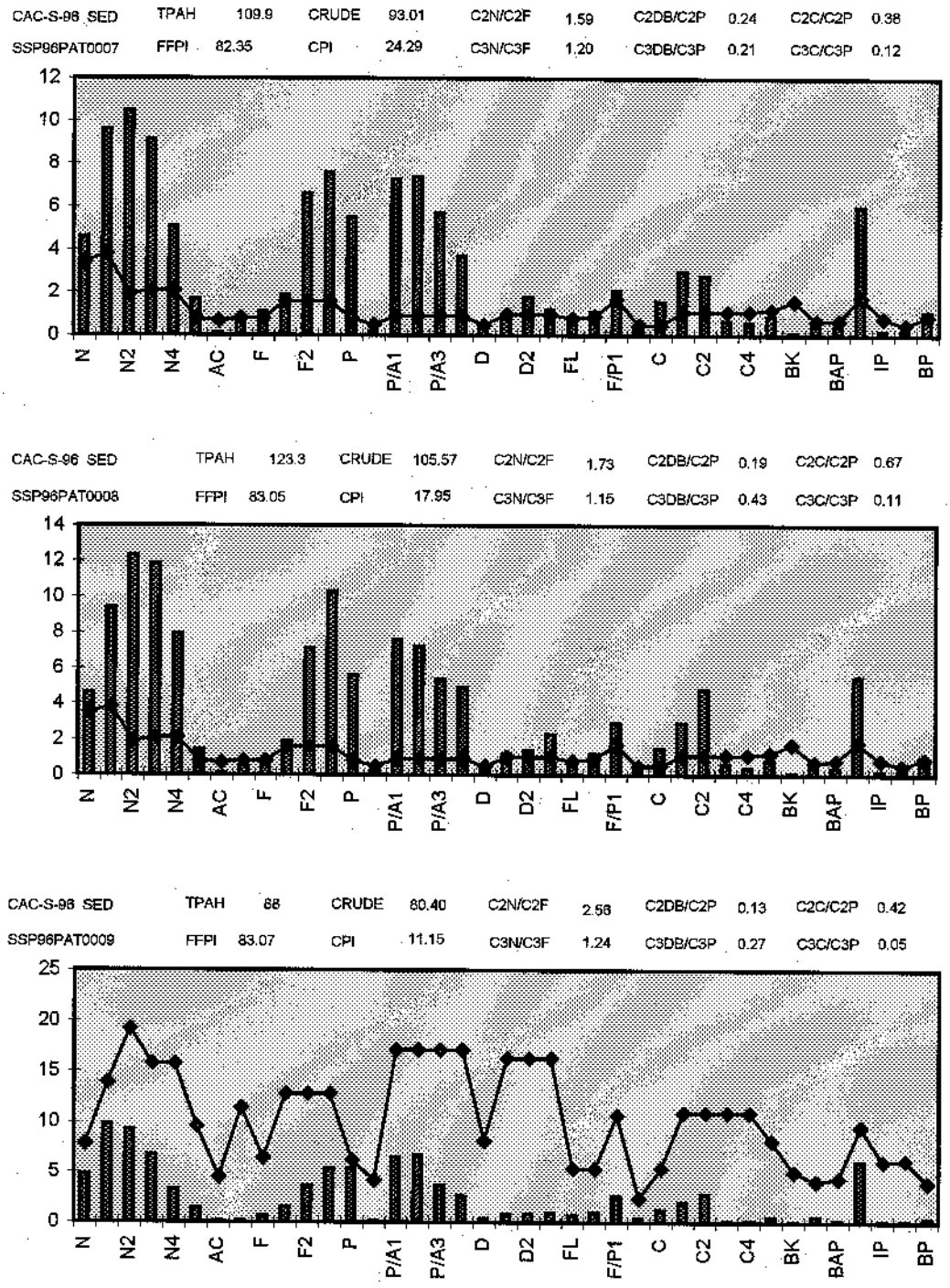


Figure 4-26 PAH histogram plots for the 1996 Cape Chiniak (Shelikof Strait) sediments.

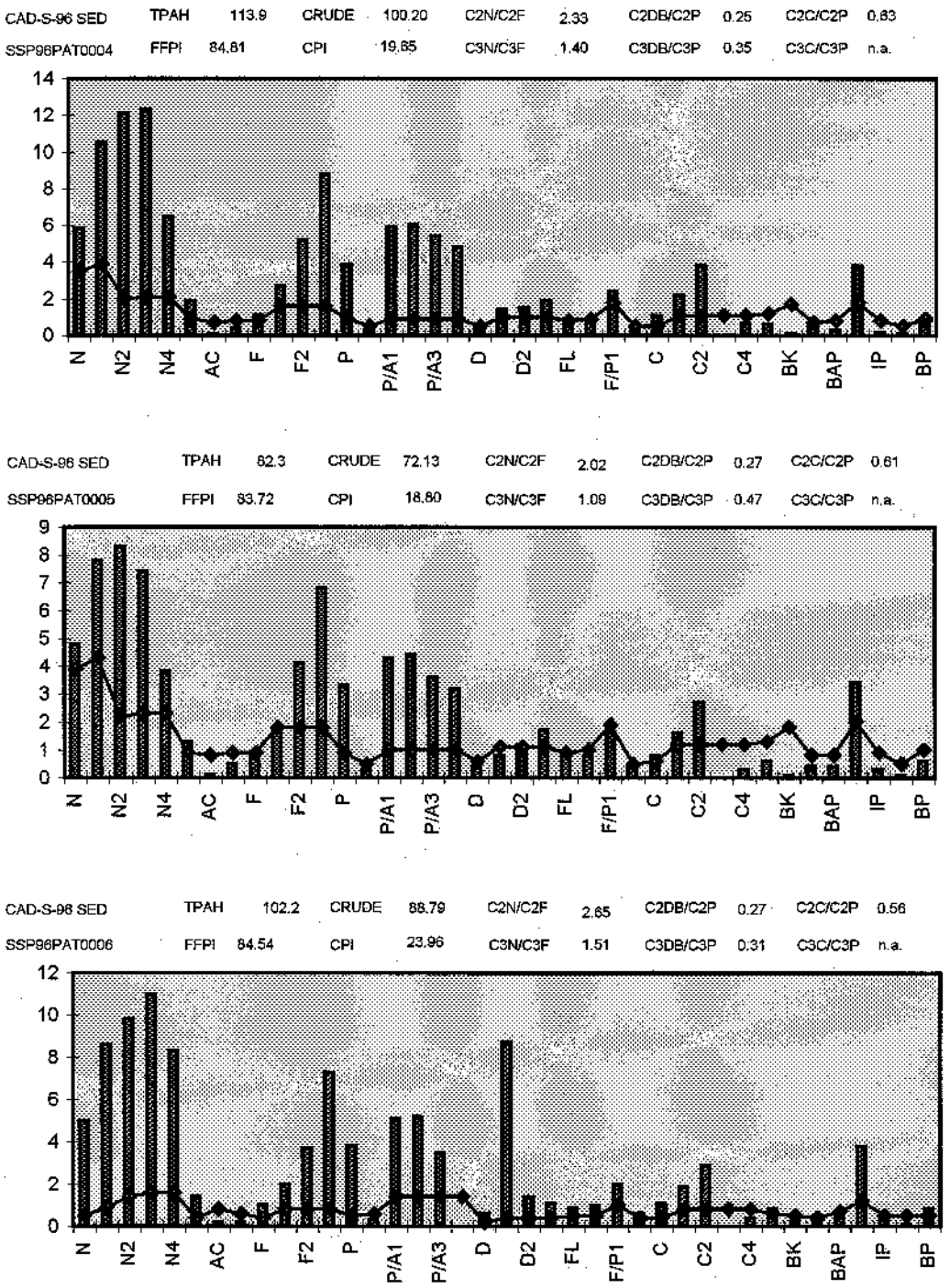


Figure 4-27 PAH histogram plots for the 1996 Cape Douglas (Shelikof Strait) sediments.

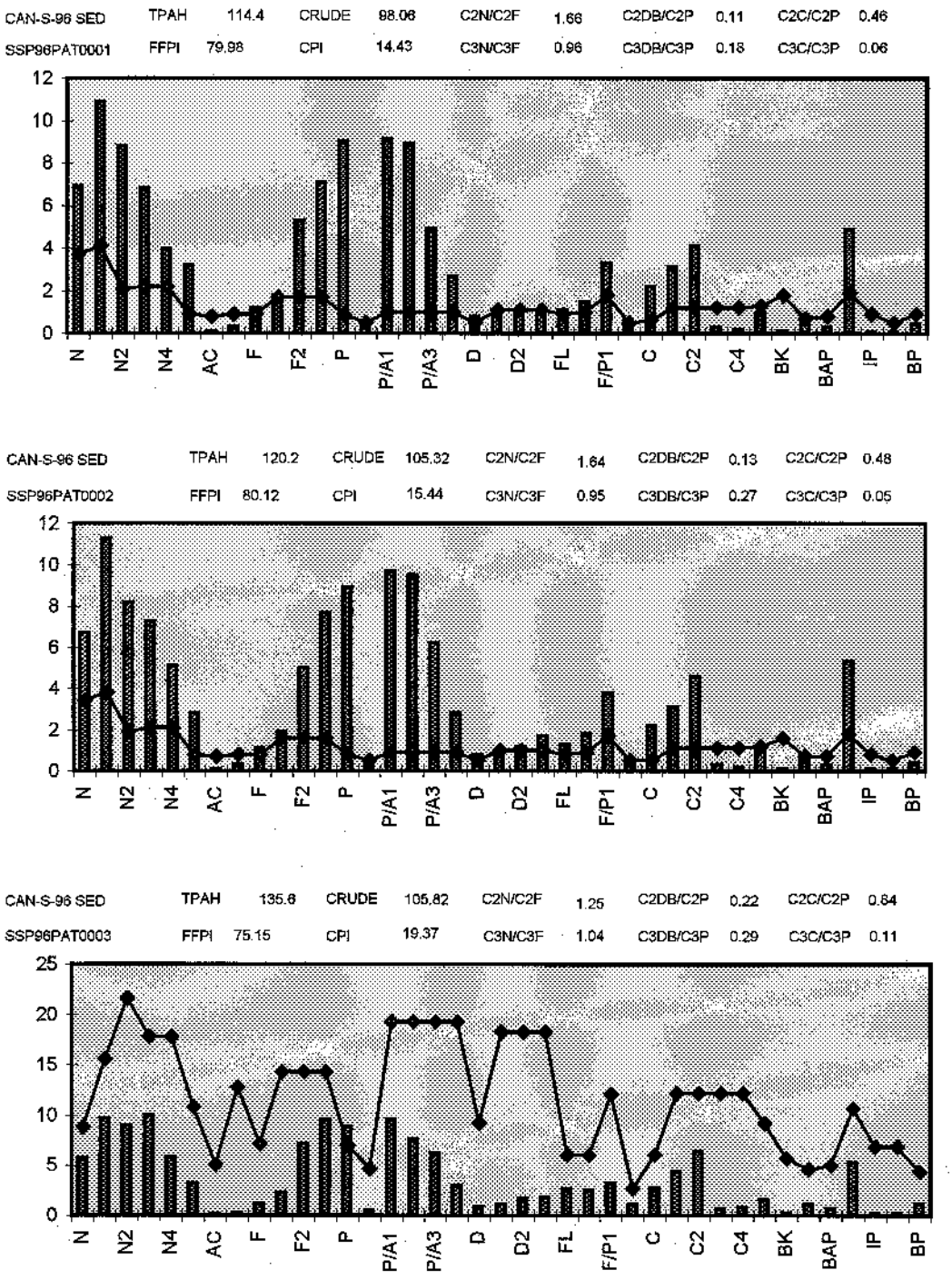


Figure 4-28 PAH histogram plots for the 1996 Cape Nukshak (Shelikof Strait) sediments.

4.11.4 Characterization of Multiple Sources by Double-Ratio Analyses

Double-ratio-plots of C_3-dibenzothiophene/C_3-phenanthrene versus C_2-dibenzothiophene/ C_2-phenanthrene and other diagnostic ratio pairs are graphically depicted to differentiate

sources of hydrocarbon contamination in extremely complex environmental samples (Brown et al. 1980; Overton et al. 1981; Boehm et al. 1989; Sauer and Boehm 1991; Brown and Boehm 1993; Page et al. 1993; Page et al. 1995; and Douglas et al. 1996).

Figure 4-29 presents the double ratio plot for C_3-dibenzothiophenes/C_3-phenanthrenes versus C_2-dibenzothiophenes/C_2-phenanthrenes for all the sediments analyzed in the EMP plus Point Woronzof municipal wastewater treatment effluent and ANS crude oil. Clearly the majority of samples cluster together in the lower left-hand corner of the figure suggesting a relatively common source with little evidence of significant contributions from Point Woronzof or ANS crude oil. Figure 4-30 presents an expanded view of the clustered data set from the lower left-hand corner of Figure 4-29 and allows better analysis of more subtle influences of different sources at a much higher degree of resolution. At this increased level of detail, the Cook Inlet crude oil reference samples and the Trading Bay produced water samples can be seen to cluster together tightly, with most of the Trading Bay sediments and Kenai triangle-delta samples also in the same general group. The rest of the samples tend to be separated from the more obvious Cook Inlet crude oil source by higher levels of both C_2- and C_3- alkylated dibenzothiophenes. It is interesting to note that Katalla seep oil falls within the Cook Inlet crude oil subgroup, while the Kenai River sediments, seep oil from Oil Bay, and the samples from more extreme distances from the production operations near the East and West Forelands diverge.

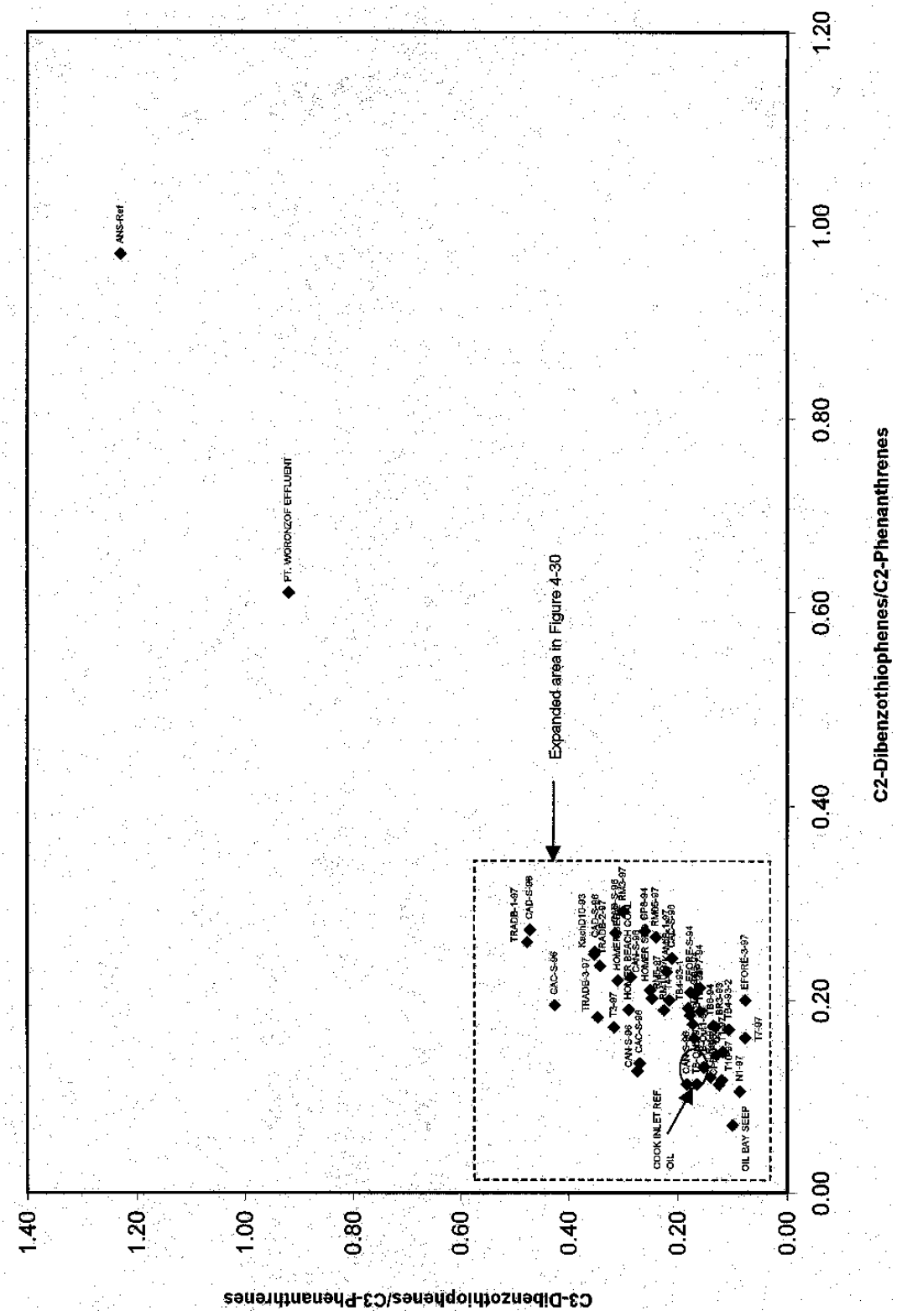


Figure 4-29 Double-ratio analysis of C3-dibenzothiophene/C3-phenanthrene versus C2-dibenzothiophene/C2-phenanthrene.

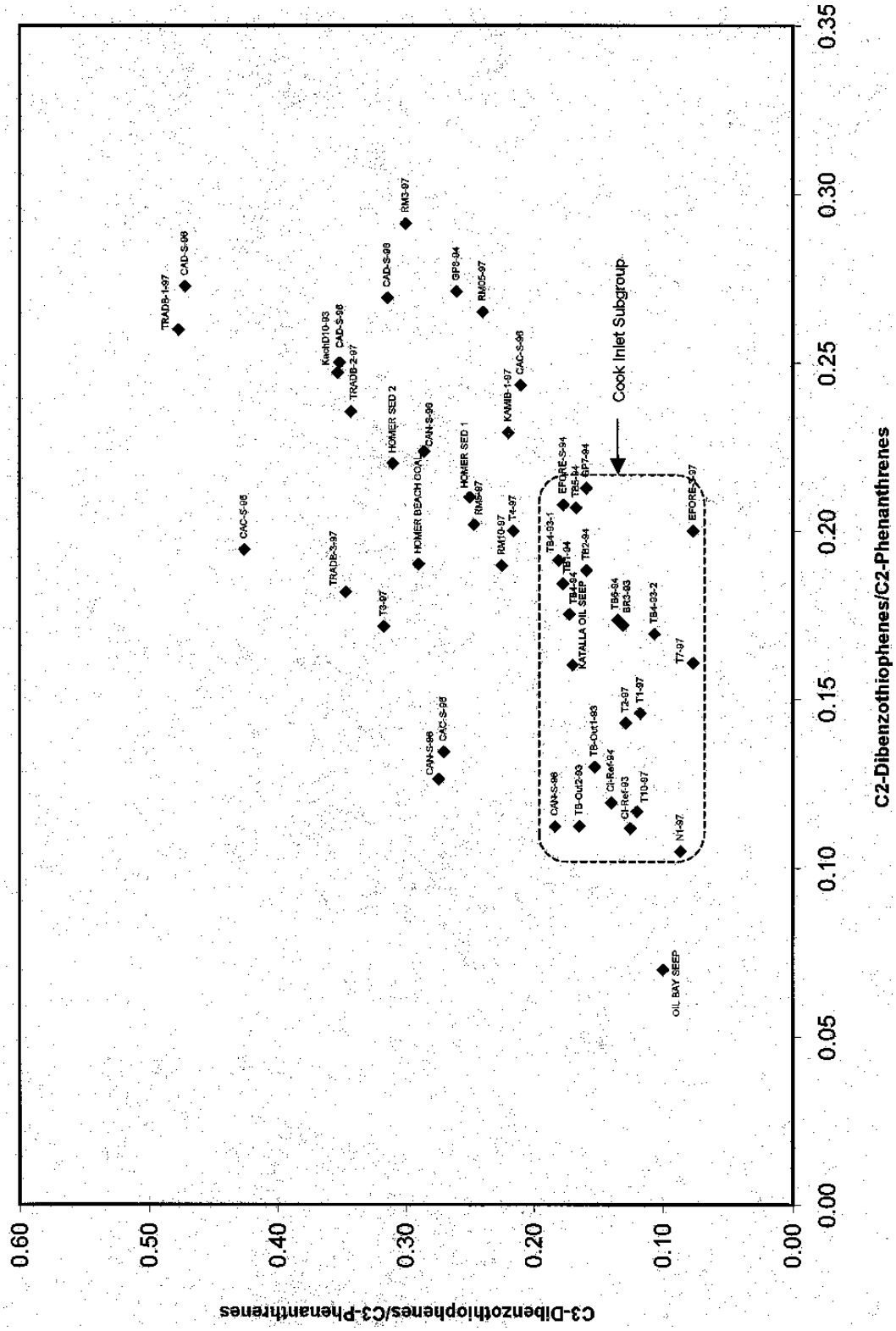


Figure 4-30 Expanded-axis double-ratio analysis of C3-dibenzothiophene/C3-phenanthrene versus C2-dibenzothiophene/C2-phenanthrene.

identification is confounded by the fact that two different laboratories using different

required for these double ratio analyses were often at or just above the MDL where quantification
further interpretation of the available data (ADL is expected to reanalyze the coal samples). In addition, because of the low overall PAH concentrations in the sediments, benzothiophenes and/or phenanthrenes were not detected in numerous samples. Therefore, the size of the sample set generating legitimate values is not very large. Finally, -30 may simply reflect the mult
sources of PAH that are present in this geographically and environmentally diverse study area.

4.11.5
Contamination

s, previous
investigators have identified multiple potential sources for the low but finite hydrocarbon

1998a,b). In all of these studies, however, there has been little evidence of direct oil production-
assist in this effort, aliphatic hydrocarbons (AHC) were added to the target analyte list in the 1996 and 1997 programs, but in general, the data
background biogenic signals that are consistent with terrestrial plant waxes, marine algae, and the Cook Inlet coal samples discussed earlier. A few exceptions to this generalization o correlate those limited AHC observations
with the PAH profiles presented in Section 4.11.3 and shown in Figures 4 19 through 4-

The aliphatic histogram for 1997 East Forelands Replicate 2 suggested a trace of diesel -2 ng/g dry weight concent -alkanes between n C_{13} - C , but the profile was dominated by 3- -carbon n C_{25} through n- $_{33}$ plant waxes. Furthermore, as shown in Figure 4 20 no confirming evidence was observed in the PAH profi
C_{3} $_{4}$-
phenanthrene/anthracene components are above the detection limit. All three samples in Kamishak Bay in 1997 showed a smal -alkane pattern suggesting a trace of

components, but the presence of chrysenes in the PAH profiles (Figure 4-
it is more likely fresh crude oil. The dibenzothiophene/phenanthrene ratios and the

they clearly eliminate seep oil from Oil Bay. The offshore sediment sample at Station N1 collected during the K
hydrocarbons in the AHC analysis. In this instance a fresh Cook Inlet crude oil source was suggested by the PAH histogram plot shown in Figure 4 17 and the double ratio analyses in Figure 4 30. The aliphatic hydrocarbon profiles for Kenai River mouth samples RM05 and RM3 also suggested a low level diesel pattern, but the corresponding

PAH profiles in Figure 4-16 rule out both diesel and Cook Inlet crude oil as a source (also see Figure 4-30). At RM05 and RM3 there is clearly a pyrogenic signal contributing to the PAH pattern, but up river at Stations RM5 and RM10, there is no petroleum hydrocarbon signal in the AHC profiles, and the source of the PAH is more likely particulate coal.

The aliphatic hydrocarbon patterns in the 1997 Trading Bay sediments, show a trace of what looks like well weathered diesel plus predominant biogenic components. That signal is inconsistent, however, with the high alkyl-substituted naphthalenes in the PAH profiles in Figure 4-14, which suggest a fresh (not weathered) "petroleum" source. Also, the dibenzothiophenes and chrysenes are too high compared to the phenanthrenes for it to be Cook Inlet crude, and they are too low to correspond with Point Woronzof effluent or ANS oil. An alternative source such as particulate coal must be considered as a definite possibility.

4.11.6 Correlation with Other Measured Parameters, and Geographic Distinctions of Special Significance

In examining the data for upper Cook Inlet sediments, an increase in the total C_0-C_4-naphthalenes/TPAH ratio with increasing grain size (percent sand) was noted for Granite Point and to a lesser extent the East Forelands (Figure 4-31). In fact, the naphthalene signal at those areas was limited almost exclusively to sediments containing greater that 40 percent sand-sized particulates by weight. This probably reflects the stronger current regimes at those stations that would tend to scour and remove finer-grained materials leaving only larger (and evidently) naphthalene-enriched particles behind. This observation begged the question as to the source of larger naphthalene-laden particles in those areas, and it led to a wider investigation of the entire EMP sediment data set to see if this trend was apparent elsewhere within Cook Inlet. Figure 4-32 presents the same analysis (total C_0-C_4-naphthalenes/TPAH versus percent sand) for all available sediment data. In this case, a computer-generated linear regression/trend line clearly shows an overall increase in the total alkylated-naphthalenes contribution to the TPAH as the percent sand-size fraction increases. This trend is counter to the generally accepted notion that PAH and other petroleum constituents are usually associated with finer grained sediments, with higher surface-area-to-volume ratios and higher concomitant adsorptive capacities. Instead, it suggests a separate, particulate source for total naphthalenes such as pulverized coal perhaps from the Matanuska River (transported through Knik Arm) or the Kenai River for the Granite Point and East Forelands regions, respectively.

The highest TPAH and total C_0-C_4-naphthalenes observed in any of the EMP efforts were at station N1-97, which was located just North of the Kenai River mouth (where the prevailing long-shore current would carry most of the sediments from the Kenai River). The second highest values for TPAH and total naphthalenes were from station RM3-97, which was three miles up the Kenai River. In addition to the high relative naphthalene contribution at RM3-97 there is also a significant contribution from pyrogenic PAH, which was higher at that location than at any other station on the river. The grain size distribution at that station was over 60% silt with only 12% sand. Ten miles up-river, at RM10-97, the total naphthalenes contributed over 30% of the TPAH signal with an

additional 20% of the TPAH derived from perylene. At that location, the grain size distribution showed over 23% sand, and there was very little combustion derived PAH

contamination in the aliphatic fraction at that station. Therefore, the observed PAH distribution is believed to be from background coal particulates introduced fr
and glacial erosion of scattered coal seams and deposits throughout the watershed that drains into the Kenai.

The total C_0 C_4 naphthalenes/TPAH values at Trading Bay were much more uniform with grain size compared to Granite Point or the East F -31 and 4 32). If anything, there was a relatively larger absolute number of samples at Trading Bay with -50%) total naphthalene/TPAH values. total naphthalenes at Trading Bay, one from larger particle sizes such as coal and the other from naphthalene laden produced- discharges that can interact with finer- water column. The produced water discharges at Trading Bay are responsible for -borne) C -C - naphthalenes being injected into the water column every day (see Section 4.14). These ssolved constituents can rapidly interact

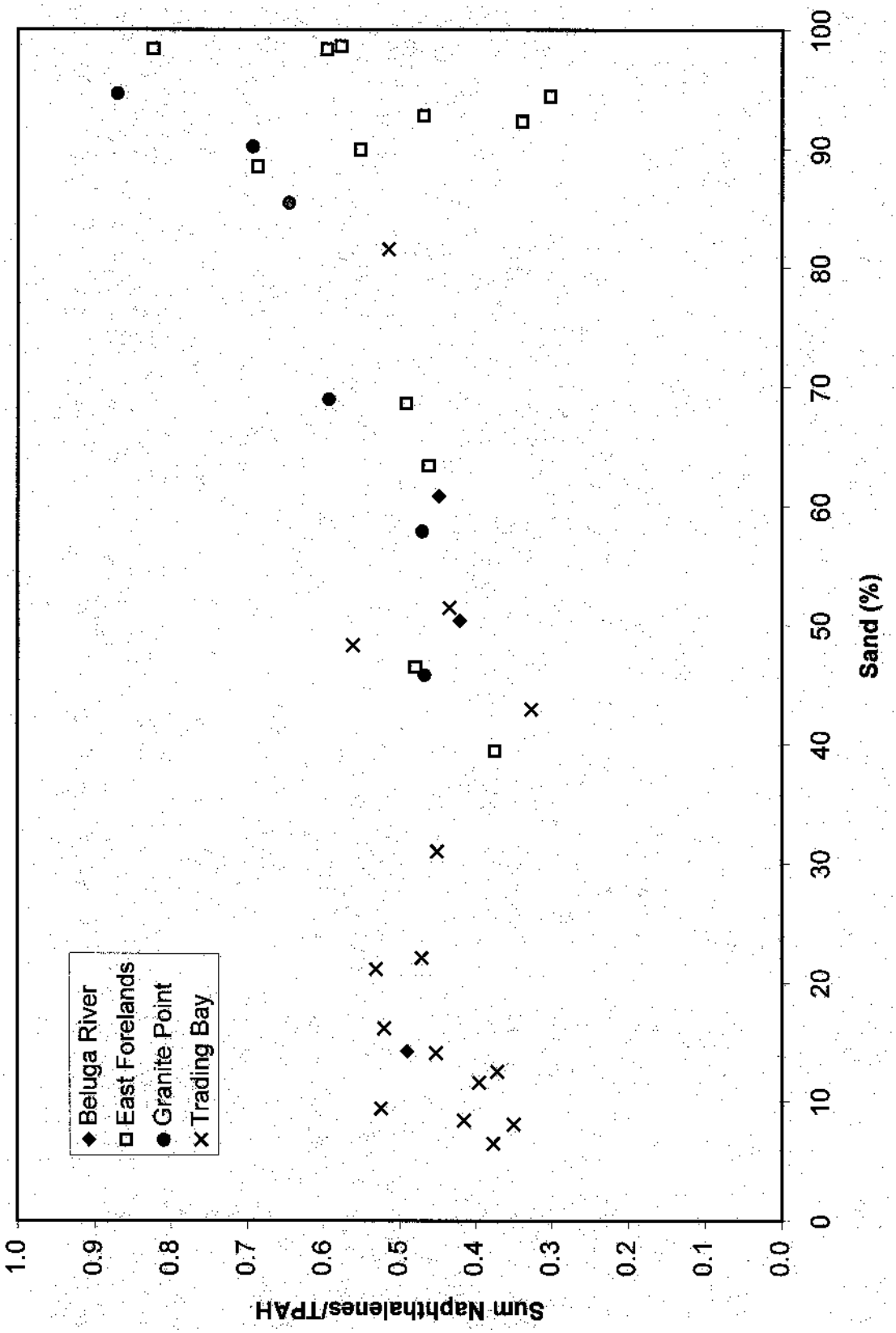


Figure 4-31 Total naphthalenes/TPAH for upper Cook Inlet sediments.

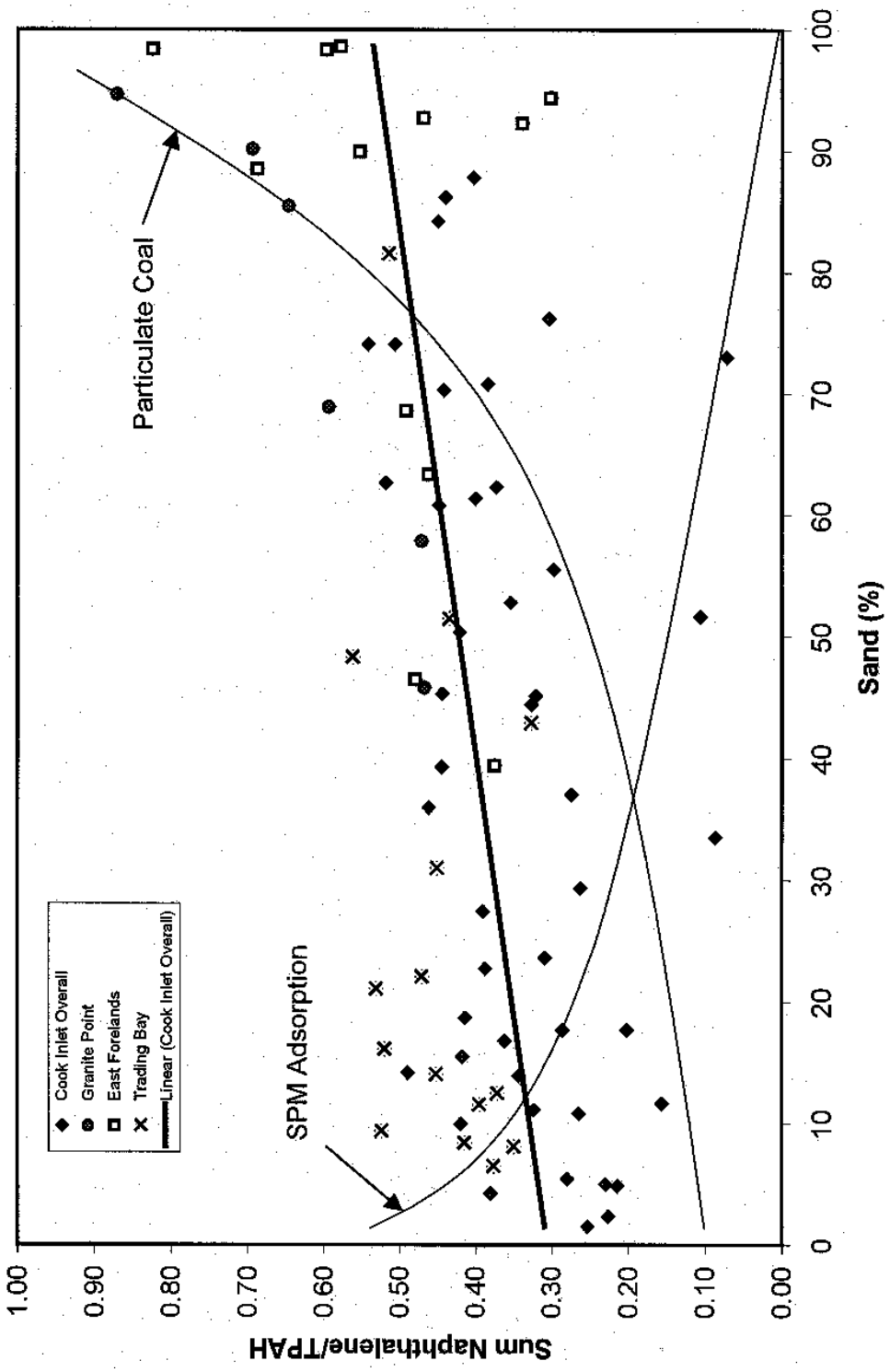


Figure 4-32 Total naphthalenes/TPAH versus sand for all upper Cook Inlet sediments.

with and be adsorbed by the high SPM loads in the region. From oil/SPM kinetics studies (Payne et al. 1989), it is known that the rate of oil-droplet SPM interactions is proportional to SPM particle number density, and presumably this is also true for

dissolved component adsorption onto SPM. That is, the greater the number of smaller particles the faster the reaction rate. Once these oil droplet/SPM particles have interacted to form agglomerates, they behave like larger particles and generally settle faster. As a caveat, however, it should be noted that we do not know if this effect would be sufficient to increase sedimentation rates in the presence of the high current regimes in the area. If increased sedimentation due to oil/SPM agglomeration did occur in the vicinity of the diffusers, then a PAH signal like the ones observed in 1993 and 1994 might be expected. During the laboratory analyses, however, the oil/SPM agglomerates would not be perceived as being larger particles and the total naphthalenes would tend to cluster with smaller grain sizes (as observed in Figure 4-31) reflecting their origins in finer-grained suspended particulate material. Specifically, the settled oil-SPM agglomerates are not identified as "larger" particles because the sediments are treated with an oxidizer to remove organic carbon before grain-size determinations by either sieving or pipette analyses. This treatment would tend to break up the oil-SPM agglomerates into smaller particles before the analysis. The sample aliquots used for PAH analyses are not sized before extraction and GC/MS analysis.

Figure 4-32 presents a generalized schematic to explain the two sources of alkylated naphthalenes observed in the Cook Inlet sediments. Naphthalenes associated with larger particle sizes are most likely derived from particulate coal introduced by glacial and water erosion of terrestrial deposits. These larger particles can be transported by currents within Cook Inlet, but they would also tend to settle more rapidly in localized geographic areas leading to the trend of increased total naphthalene versus grain size dependence observed at Granite Point. Smaller coal particles would be subject to greater transport from their river-borne sources, and they would be harder to trace. Naphthalenes introduced to the sediments by oil/SPM interactions would be predominantly associated with the smaller SPM and sediment grain size fractions as observed near the point source discharges of dissolved and dispersed components introduced at the Trading Bay oil production facilities. Thus, in areas where high total naphthalenes/TPAH values are associated with smaller grain size fractions, the sources could be from either oil/SPM interactions or finer-grained coal-particulates that eventually settled out of the water column. In areas where high total naphthalenes/TPAH are associated with larger particle sizes, the source is most likely particulate coal. Obviously, both mechanisms can be responsible for naphthalene burdens in intermediate grain-sized sediments. However, the fact that the overall trend line in Figure 4-32 shows an increase in total naphthalenes/TPAH values with increasing percent sand, suggests that particulate coal is an important source of C_0-C_4-naphthalene burdens throughout Cook Inlet.

In other areas, the influence of a distinct source is much easier to identify. Specifically, the coal signal from the Homer region (Figure 4-8) can be readily observed in the sediments from Kachemak Bay (Figure 4-23), and the influence of coal in this region has been noted by both KLI (1998a) and ADL (1998b). In fact, this finding should not be particularly surprising because fine coal particulates have been noted as a nuisance interferant in numerous subtidal and intertidal infaunal samples analyzed by Lees and Driskell over the last 25 years. In addition, "coal tides" (deposits of coal particles and chunks in the intertidal zone and along the high-tide berm) are a common event in the

pieces to supplement firewood supplies for wood and coal-

Somewhat to our surprise, it was not possible to readily identify a distinct signal from the

(Figure 4- nt (Figure 4-
Beluga River season, there is a hint of the C_4 phenanthrenes/anthracenes and perylene signal that could be derived from Beluga River coal, but the dominant alkyl substituted naphthalenes, fluoren
be Cook Inlet crude oil clearly mask or overwhelm the signal. Likewise, at Granite Point there are peaks for C -phenanthrenes/anthracenes and perylene that are consistent with oal, but the majority of the PAH signal comes from somewhere else. The patterns are similar to fresh Cook Inlet crude oil (there is very little weathering of the

importantly the chrysenes in most of the samples are a little too high to yield a definitive

4.11.7 Mass Balance Considerations for TPAH and Total Naphthalenes

alkylated homologues) into the sediments. Naphthalenes were chosen because they are

PAH group in produced waters discharged into the inlet. The question then becomes how muc
anthropogenic or industrial sources? Assuming that the high sediment loads transiting the inlet deposit an estimated average of 2 centimeters (cm)/year and that all the naphthalene

liberal estimate), the calculation goes as follows.

^{2} (6357 miles as estimated from a grid map). Assuming the average concentratio
centimeter (cc) and using 2 centimeter (cm) of sediments as the average annual deposit, Cook Inlet receives roughly 127.14 x 10 ng/yr or 28,098 lbs/yr or in liquid form, 9.19 gal/day of naphthalene from

16,300 km x 10^6 ^{2}/ km x 10^4 ^{2}/ m x 39 x 10^- kg/cubic centimeters (cc) x 2 cm/yr = 12,714 kg /yr

12,714 kg/yr x 2.21 lb/kg = 28,098 lbs/yr

How much total nap -production facilities in Cook Inlet? From

gallons/day or 9326 lbs/year (Table 4-
adsorbed onto particles that then sank inside the inlet, the amount would equate to 1/3rd

of the amount found in the sediments. This is a liberal estimate but it suggests that at least 2/3rds of the background naphthalene is entering the system from non-point sources.

Discharge	Total Discharge Flow		Effluent			
	Gallon/day	Liters/day	TAqH/l	fraction		ug N/d
Anna	44,139		20428	0.129		447,371,257
Baker	41,341		21006	0.039		129,258,982
Bruce	6,360		70536	0.031	2165.5	
	124,023	477,010		0.050	699.3	
	1,781	6,849		0.070	4.8	
001A		1,370,157	0		0	0
PM		1,017,028	119		32.7	33,256,801
Drift River	300,000	0		0.110	1.7	
Forelands		758,324	15360*		2657.3	2,015,078,922
Trading Bay	2,696,698		7330	0.107		**8,134,795,814**
Granite	95,402	366,931		0.078	1172.3	
	4,136,772	15,858,445			10966	11,578,368,015 ug/month
						4,226,104,325,415 ug/yr
Est. naphthalene discharge = 3.05 gal/day or 91.6 gal/month or 1,099 gal/yr						

Table 4 13. Mass balance considerations for TPAH and total naphthalenes in produced water from discharges in Cook Inlet.

4.11.8

Sediment samples exhibit extremely low levels of PAH (40 50 times below ER-concentrations). The sources are varied and mixed, but they cannot be directly attributed to Cook Inlet oil and gas development operations. There is no evidence of EVOS or oil in any of the subtidal sediments (including Shelikof Strait).

Total naphthalenes/TPAH ratios tend to increase with sand-sized particulates suggesting a particulate coal-derived source for much of the PAH observed in the sediments. River-borne sources of particulate coal from terrestrial sources are believed to contribute significant levels of PAH to the sediments throughout the region.

Very few of the low-level PAH signatures for sediments could be directly tied to specific sources; the samples suggest undocumented or multiple sources.

4.12 Hydrocarbon Analyses of Tissue Samples

4.12.1 TPAH and Mytilus Petrogenic Index Data Analyses

As in the analysis of sediment hydrocarbon data, tissue data were first screened by examining total PAH values and selected diagnostic ratios or other indices to look for obvious geographic, tidal height, or species-specific trends.. Figure 4-33 presents the total PAH, *Mytilus* Petrogenic Index values, and total C_0-C_4-naphthalene concentrations for all tissue samples analyzed during the 1993-1997 EMP. It should be noted that, as in the case of sediments, total naphthalenes are a major factor in the overall PAH signal in tissues, and total naphthalenes tend to parallel the trends observed with TPAH and MPI.

As will be discussed below, the absolute magnitude of the differences in TPAH values for most of the 1996 *Macoma* samples are supported by differences in the PAH profiles for those samples. Thus, it can be concluded (as suggested by Figure 4-33) that the intertidal *Macoma* in Tuxedni and Chinitna Bays in 1996 had higher TPAH loading than the subtidal *Macoma* in Kamishak and Kachemak Bays in 1993 The situation for the mussels is more complicated; however, the trends suggested in Figure 4-33 are generally supported by individual PAH profiles. One of the mussel samples from Cape Chiniak (replicate 3) is higher than the other two. Likewise, one of the samples from Cape Douglas (replicate 1) exhibits a low-level petrogenic signal, whereas the other two show no petroleum hydrocarbon contamination and only procedural artifacts. At Cape Nukshak (with the highest MPI values), there is evidence of petroleum hydrocarbon contamination in all three samples, and replicate 1 is slightly less contaminated that the other two. Finally, total C_0-C_4-naphthalenes in all the samples generally make up 30-60 percent of the TPAH signal.

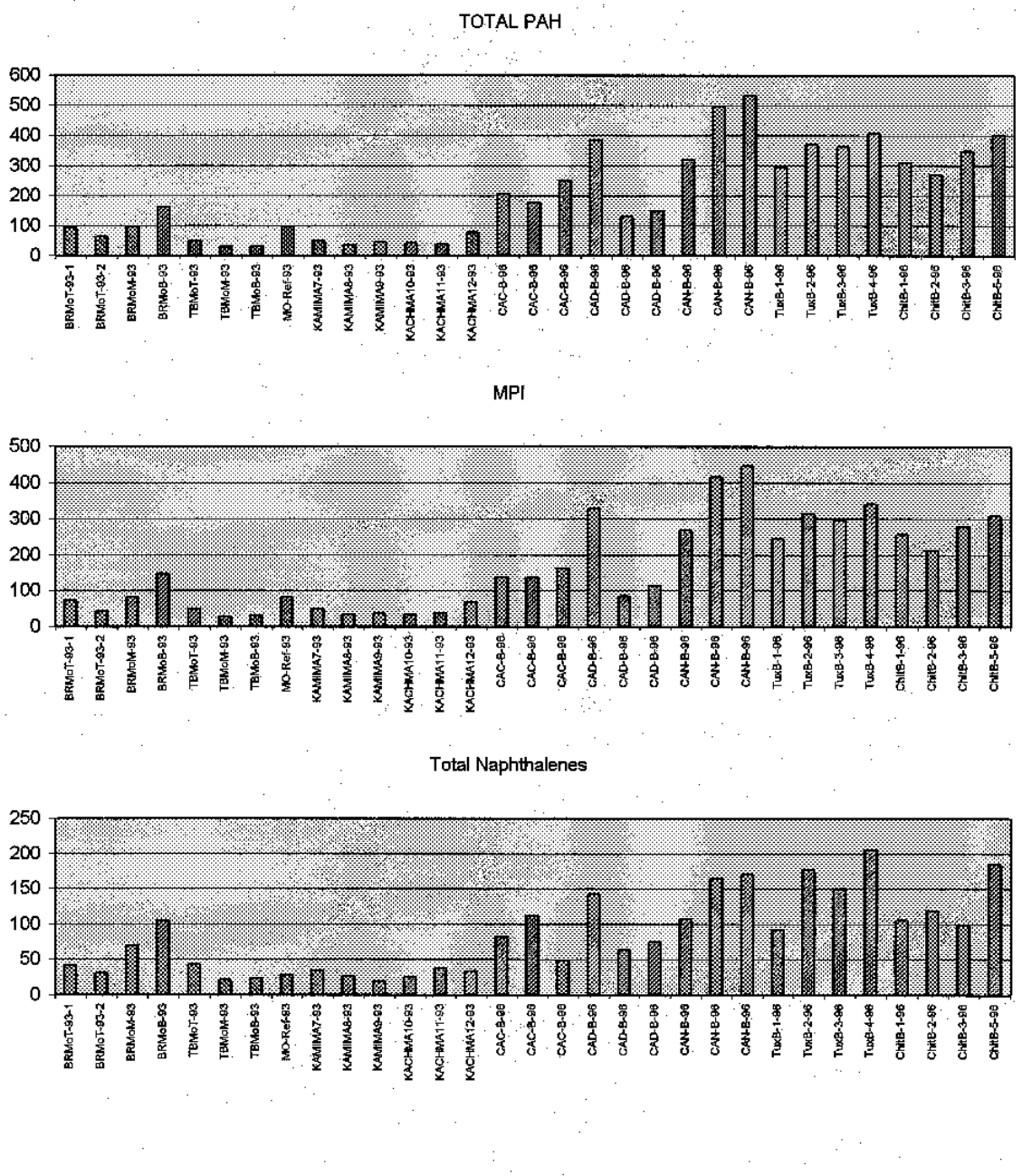


Figure 4-33. Total PAH, Mytilus Petrogenic Index values, and total naphthalenes for all tissue samples analyzed during the 1993-1997 EMP. Concentrations for TPAH and Total Naphthalene are in ng/g dry weight. BRMo and TBMo denote Mytilus moorings (T = top, M = middle, B = bottom) at Beluga River and Trading Bay, respectively. MO-Ref is the control Mytilus population sample (from Halibut Cove) before mooring deployment. KAMI MA and KACH MA denote Macoma sp from Kamishak Bay and Kachemak Bay, respectively. CAC, CAD, and CAN represent resident Mytilus at Capes Chiniak, Douglas, and Nukshak, respectively. TuxB and ChitB denote Macoma sp at Tuxedni and Chinitna Bays. Year of sampling is shown with each station id.

-33 Total PAH, Mytilus Petrogenic Index values, and total naphthalenes -1997 EMP.

4.12.2 Characterization of PAH Histogram Plots and Identification of Laboratory

Figure 4 34 presents the PAH histogram plots obtained on the Beluga River moored *Mytilus* n the figure are from laboratory splits of the uppermost caged mussel tissue homogenate. It is somewhat disturbing that the PAH profiles do not match very closely, and this is also ples from the middle and bottom depths again bear closer resemblance to the top sample (replicate 1), bottom). Also note the appearance of the C_3 naphthalenes in the middle and bottom Halibut Cove contained a more predominant petroleum (diesel) and pyrogenic profile before being transplanted to the Beluga River region. The loss of the al and phenanthrenes/anthracenes after deployment at the Beluga River mooring site reflects the organism's ability to depurate these intermediate molecular weight constituents even as the alkylated naphthalenes increased (particularly in the mid depth and near- samples) over the 30- analyses (shown in Figure 4- $_{1}$- $_{3}$- -34 are real and represent -column exposures over the deployment period. There does not appear to Likewise, there is not a strong signal from the Susitna River sediments, which were the alkylated naphthalenes would be produced water discharges (also shown in Figure 4- unoff from Anchorage and the Point Woronzof wastewater treatment facility. The mussel deployment station was at twice that longitudinal distance from Anchorage. Because of the extremely low individual not possible to identify the source of the observed PAH signal in the mussels transplanted to the Beluga River area.

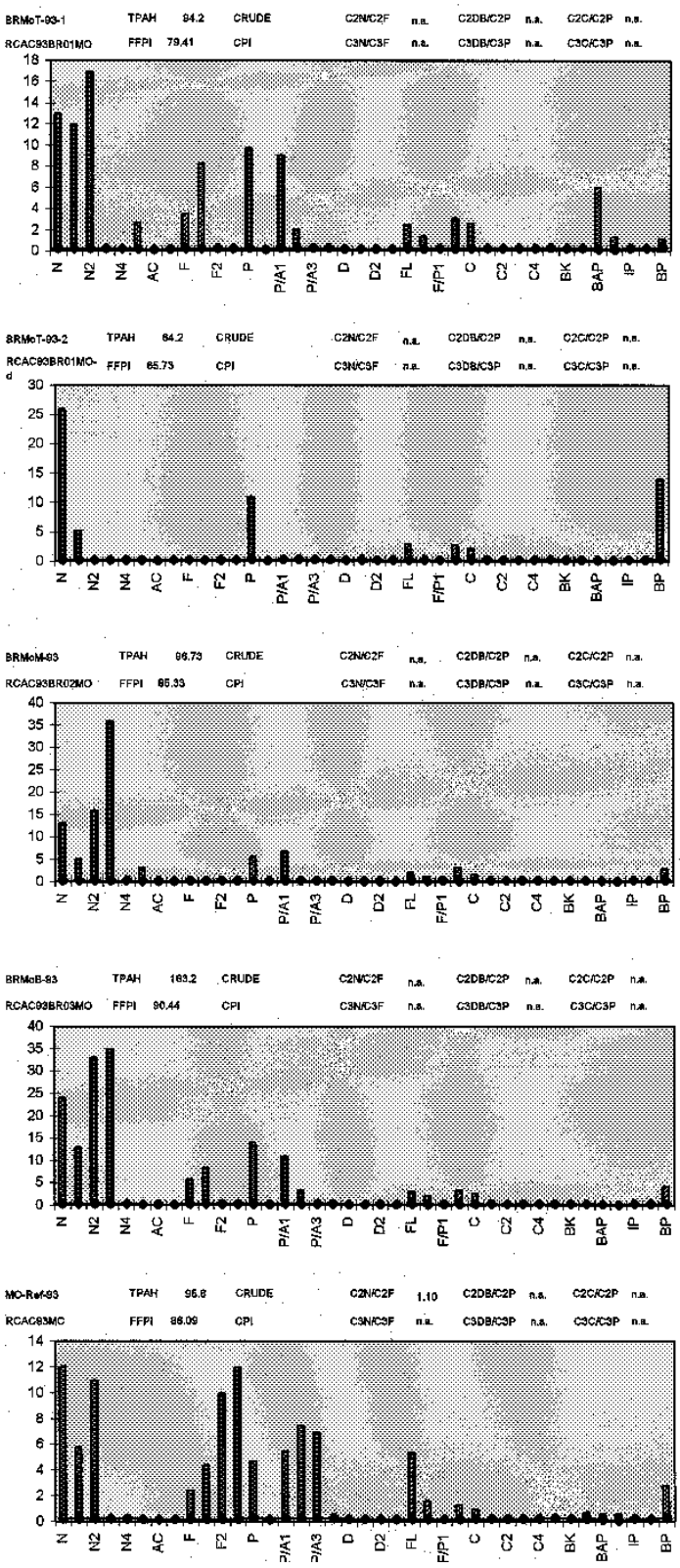


Figure 4-34 Beluga River moored *Mytilus* and background control (source) samples from Halibut Cove.

Figure 4-35 presents PAH histogram profiles from the moored mussel array placed in Trading Bay in 1993. To allow a better comparison with potential laboratory contamination and the known source for most of the PAH introduced into the region, the PAH profiles from an associated ADL laboratory procedural blank and a 1993 Trading Bay produced water analysis are also shown in the figure. The field-deployed samples show low but finite concentrations of both naphthalene and phenanthrene that could be associated with laboratory contamination; however, they also show C_1-naphthalenes and C_2-naphthalenes that may have originated from the dissolved (and oil-borne) alkylated naphthalene components associated with the produced water discharges. The limited sample size and laboratory method detection limits do not allow detection of any other PAH constituents in the tissues that are common to the presumed produced water source. In addition, the Trading Bay deployed mussel samples were cleaner than the Beluga River samples and the pre-exposure control samples from Halibut Cove (as also reflected in Figures 4-33 and 4-34). Clearly, the mussels were able to depurate their background signal from Halibut Cove; however, it is surprising that they didn't exhibit a more pronounced produced water signal. It is estimated that the caged-mussel array was located only 4-5 nautical miles from the Trading Bay diffuser.

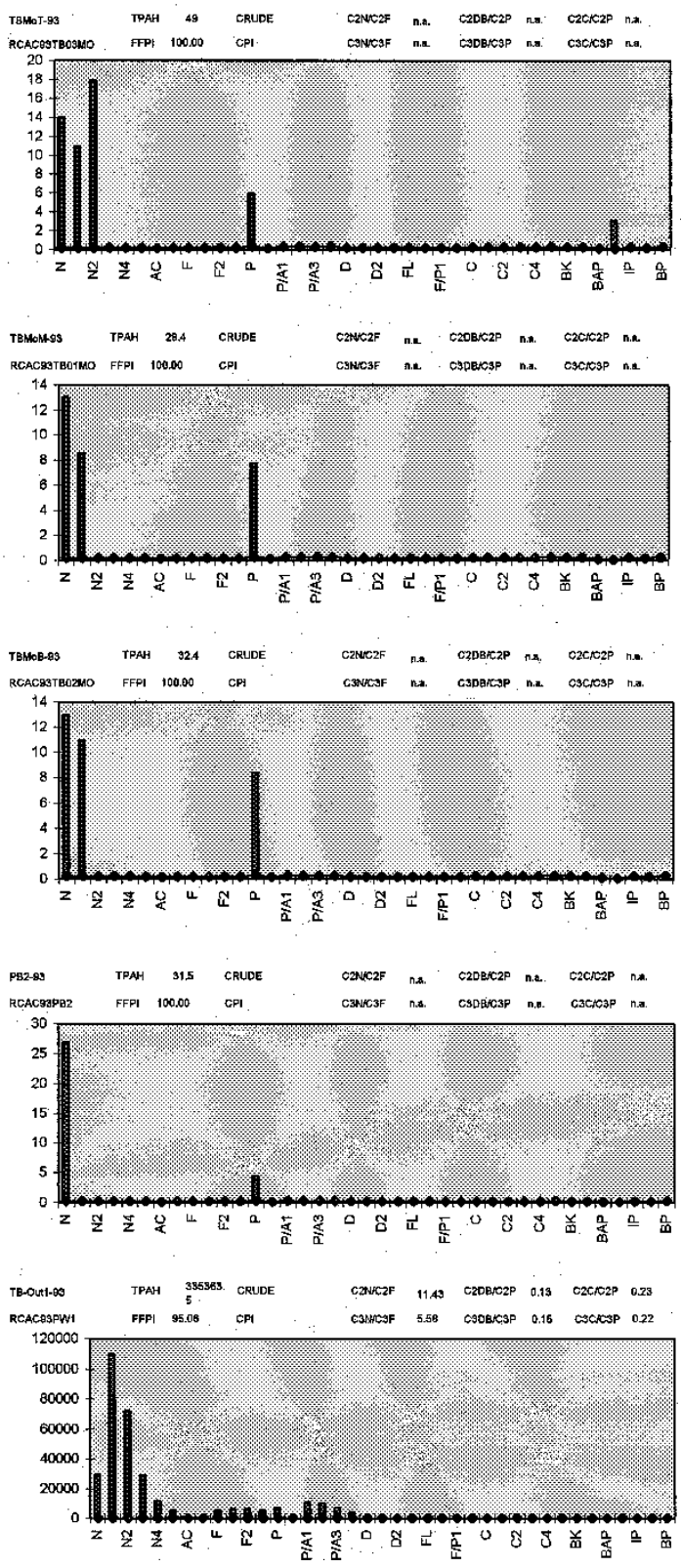


Figure 4- ored *Mytilus*
Trading Bay produced water samples collected in 1993.

Figure 4-36 shows the PAH distribution in the subtidal 1993 *Macoma* samples from Kamishak Bay. In this case, the first replicate exhibits only components that are also observed in the ADL laboratory procedural blank. The second and third replicates do contain several additional constituents that suggest additional PAH input from other sources, but the concentrations are very low (generally < 6 ng/g dry weight) and source identification is impossible. The perylene component is consistent with several coals from the Cook Inlet area, but the C_1-naphthalenes, and alkylated phenanthrenes/- anthracenes could be derived from either fresh oil or coal. The fluoranthene, pyrene, benzo(a)anthracene, and chrysene reflect combustion sources.

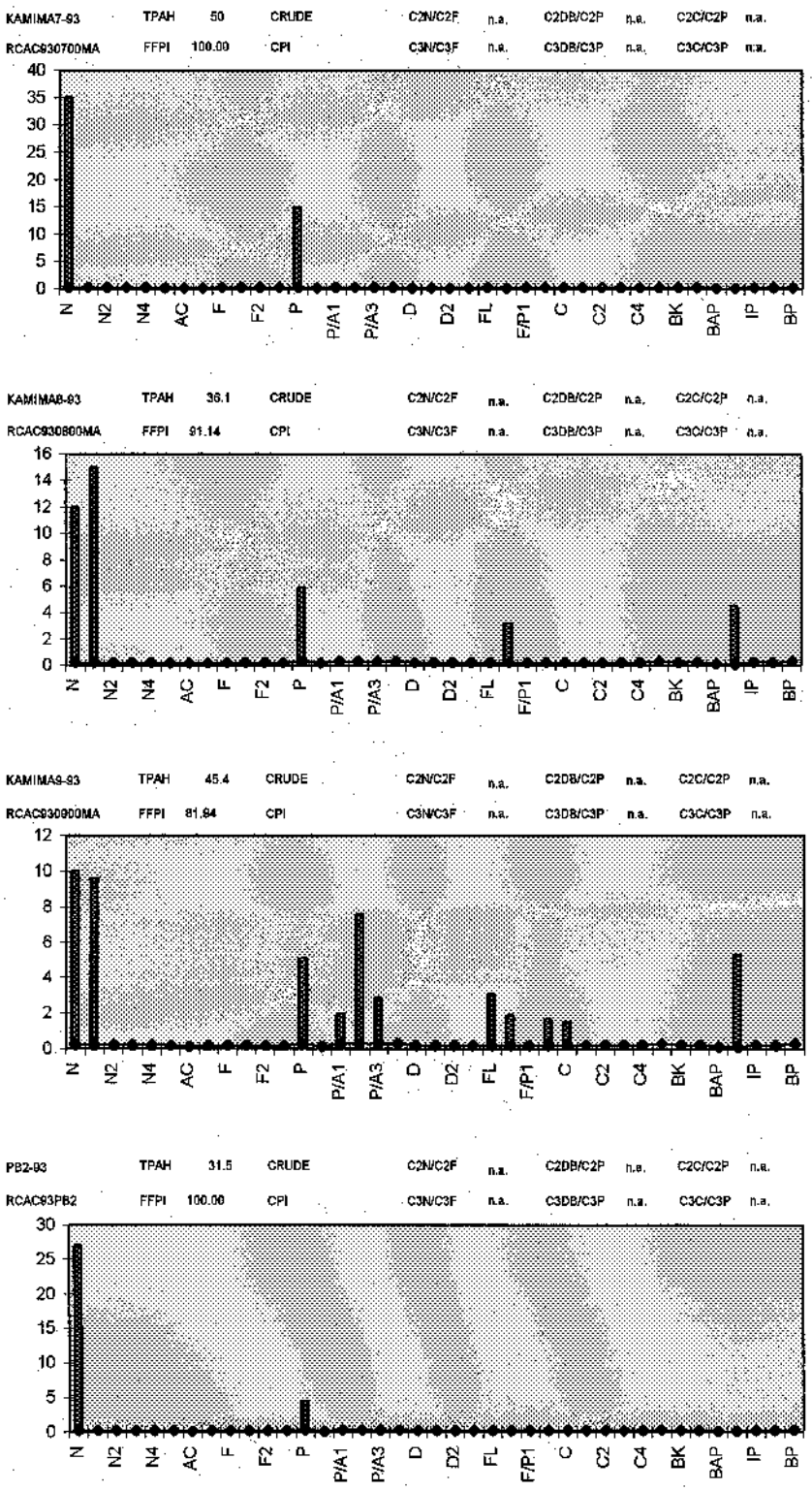


Figure 4-36 PAH histogram plots for 1993 Kamishak Bay *Macoma* sp. and representative procedural blank run by ADL.

Figure 4-37 presents the PAH histogram plots for the subtidal *Macoma* samples collected from Kachemak Bay. The first two samples were very clean and, after correcting for

naphthalene which could have been introduced by the laboratory, only biogenic/coal-derived perylene remained in one sample with higher levels of perylene and low levels of C_1-naphthalenes, phenanthrene, fluoranthene, and pyrene observed in the other. These latter constituents reflect a background combustion source. Only one sample contained any higher alkylated naphthalenes or phenanthrenes/anthracenes (in addition to the ubiquitous perylene) suggesting either a fresh diesel (petrogenic) or particulate coal source.

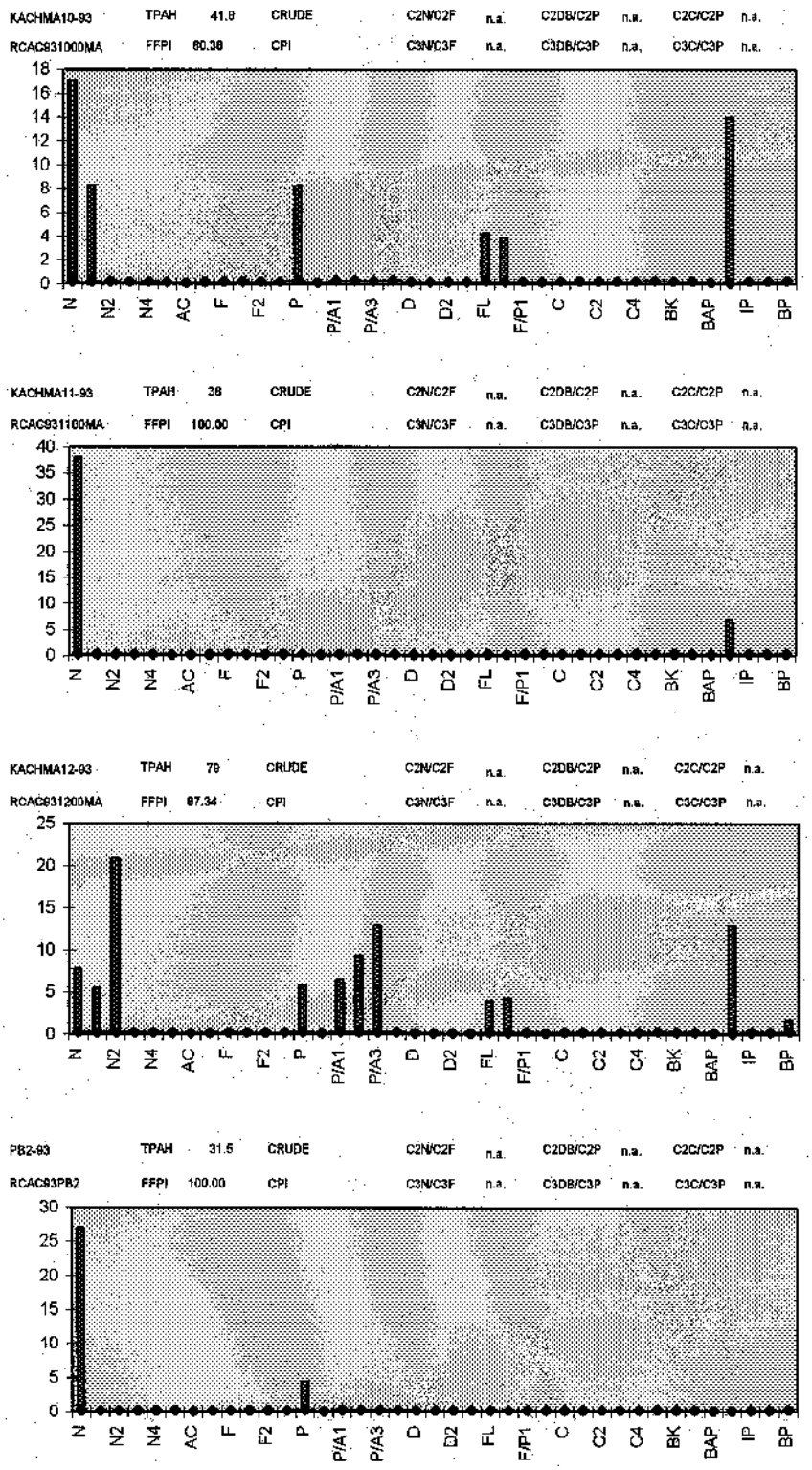


Figure 4-37 PAH histogram plots for 1993 Kachemak Bay *Macoma* sp. and representative procedural blank run by ADL.

Figure 4-38 contains the PAH histograms for the 1996 intertidal mussel samples collected from Cape Chiniak in the Shelikof Strait. These tissue samples, analyzed by GERG,

provide an excellent example of a problem with background electronic noise associated with the GC/MS SIM analyses of low-level samples within that laboratory. While relatively high (178-252 ng/g dry weight) TPAH values were reported for all three samples obtained at this site, only one replicate (SSP96TIS0009) contains any evidence of actual hydrocarbon contamination. The other two samples exhibit the "procedural artifact" pattern identical to the one observed in the GERG laboratory/method blank that is shown at the bottom of the figure. In actual fact, the GC/MS signal may not be that much larger for the first two tissue samples compared to the blank, it just appears that way due to the small sample weight used to calculate the final sample concentrations. Only two components (naphthalene and C_1-naphthalenes) were appreciably above the MDL in the first two replicates, and these constituents were also represented in the blank. As noted in Section 4.8.5, the background electronic noise in the GC/MS contributes to a quantifiable signal that is magnified to a high TPAH concentration by the inclusion of a small numerical value (for the total sample weight extracted) in the denominator of the data reduction algorithm. As a result, the TPAH values for the first two replicates are probably too high by a factor of two to three, and it is only through evaluation of the PAH histogram patterns that the real PAH signal can be sorted out. This is exemplified with sample SSP96TIS0009 where the alkylated C_1-fluorenes, C_1-phenanthrenes/ anthracenes, C_1-chrysenes, and C_2-chrysenes at concentrations well above the MDL suggest the presence of a well-weathered oil residue. Because of the absence of key analytes, however, it is impossible to identify the source in even this sample without additional diagnostic data (e.g. steranes and triterpane biomarkers). Perylene is not a major component in any of the samples, suggesting that the particulate coal and sediments from within Cook Inlet do not contribute greatly to the PAH signal in these intertidal mussels.

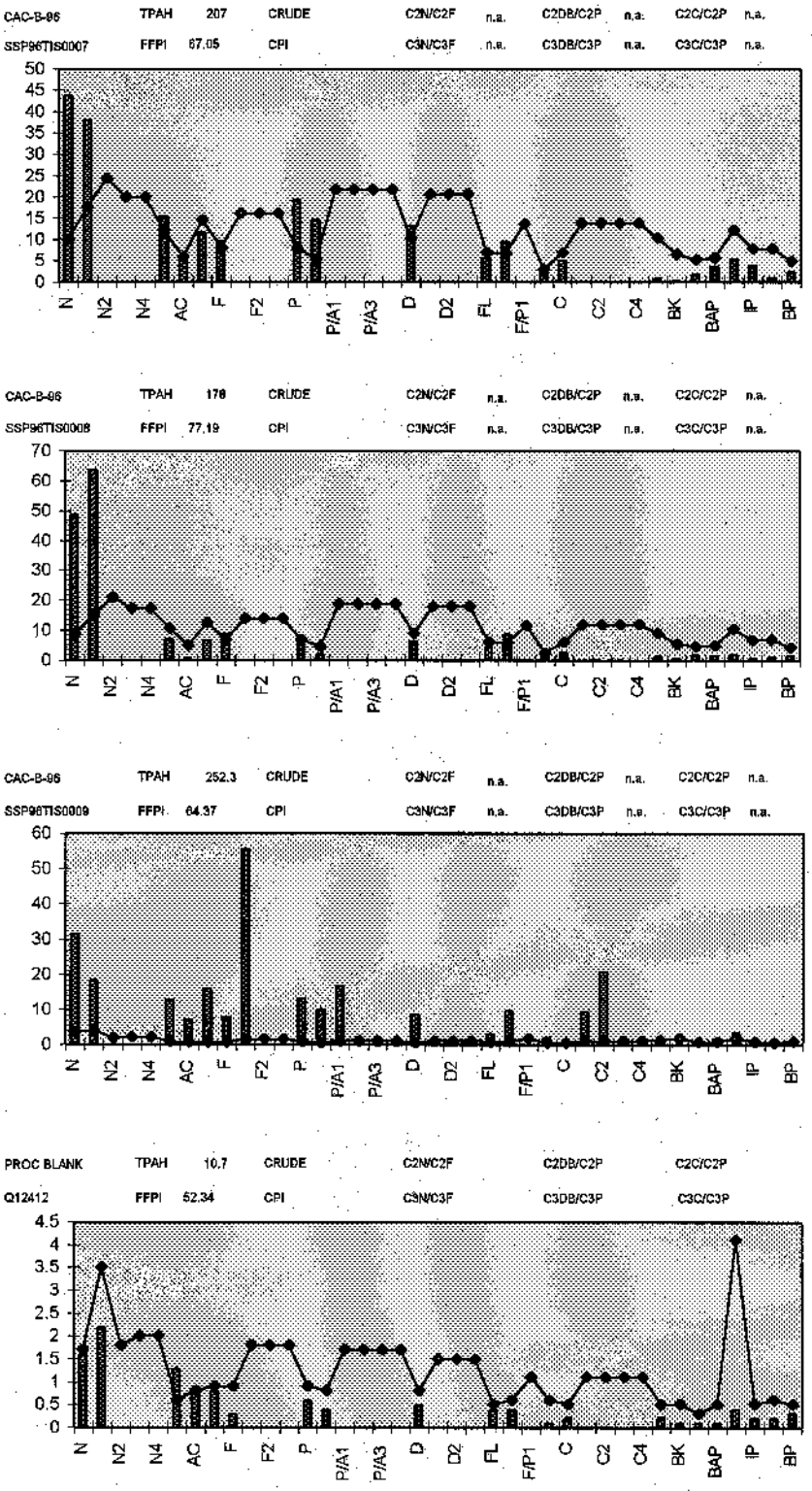


Figure 4-38 PAH histogram plots for 1996 Cape Chiniak intertidal *Mytilus* sp. and representative procedural blank run by GERG.

Figure 4-39 shows the PAH profiles from the 1996 intertidal *Mytilus* samples at Cape Douglas, and here again, only one of the three replicates actually contains any evidence of recent hydrocarbon contamination. In this case, the first sample in the figure (SSP96TIS0004) shows alkylated C_0-C_4-naphthalenes, C_0-C_3-fluorenes, and C_0-C_2-phenanthrenes/anthracenes (below the MDL) with a characteristic water-washed appearance ($C_0<C_1<C_2<C_3<C_4$) that suggests a weathered petroleum source. The concentrations are still very low, and definitive source identification is not possible. The fluorenes are much to high compared to the phenanthrenes/anthracenes, however, for it be consistent with Cook Inlet, ANS, or Katalla crude oil. The other two samples in the figure exhibit the pattern associated with procedural artifacts, and these constituents shouldn't be included in the calculation of a TPAH value. Perylene is not a major component in any of the samples, suggesting that the particulate coal and sediments from within Cook Inlet do not contribute greatly to the PAH signal in these intertidal mussels.

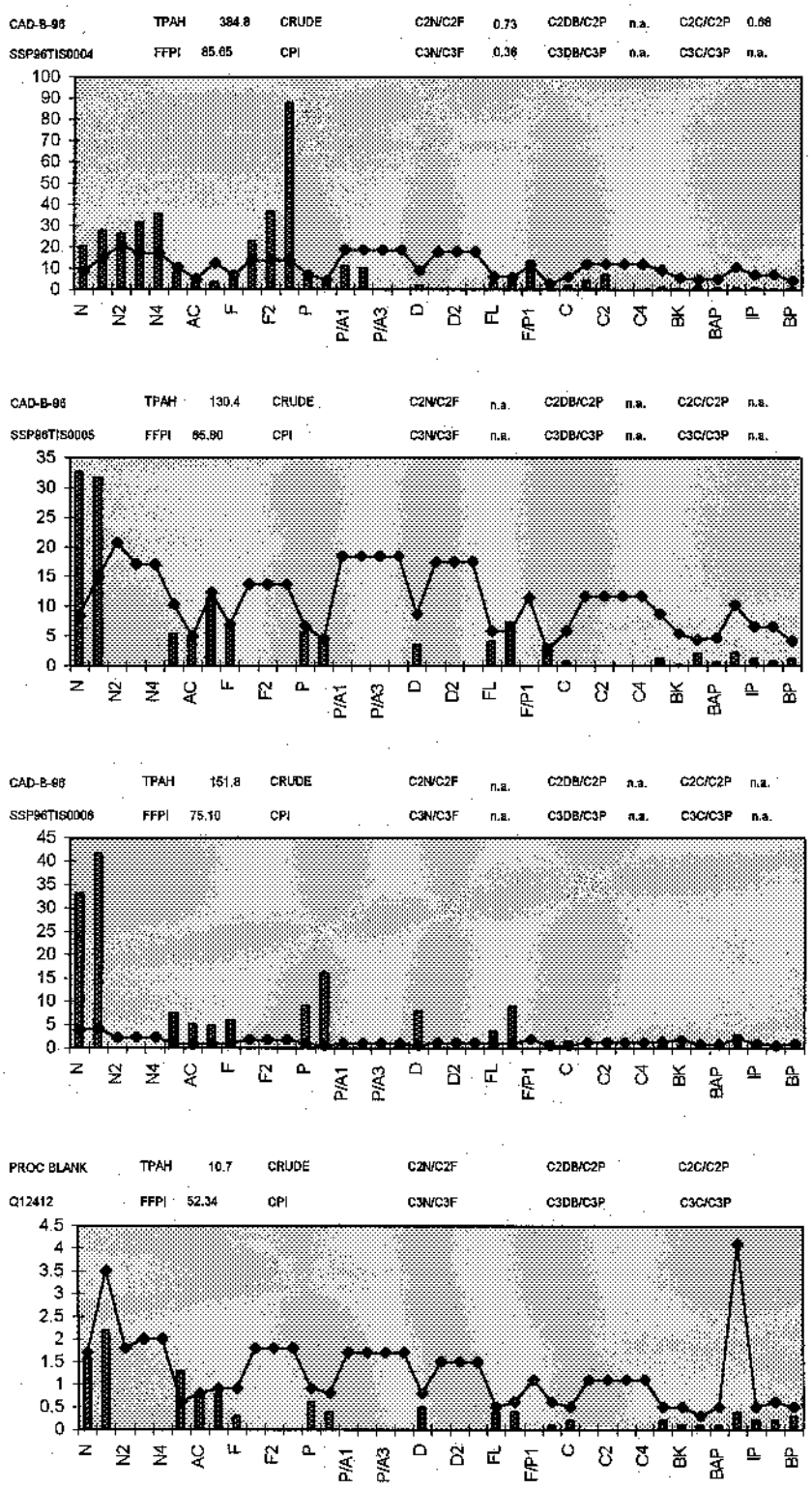


Figure 4 39 PAH histogram plots for 1996 Cape Douglas intertidal *Mytilus* and representative procedural blank run by GERG.

Figure 4 40 presents the PAH histogram plots from the 1996 intertidal *Mytilus* Cape Nukshak. This is the one station in the Shelikof Strait Program that showed consistent evidence of petroleum hydrocarbon contamination in all examined. The PAH patterns are almost identical, and they are consistently different from the GERG procedural artifact pattern in the laboratory/method blank. The tissue sample h little evidence of evaporative weathering. Diesel as a sole contaminant can be ruled out by the alkylated chrysenes, and

Cook Inlet crude oil as the source. Cook Inlet seep oil would have also undergone much

Shelikof Strait region. As in the other 1996 Shelikof Strait stations, perylene is not a major component in any of the sa from within Cook Inlet do not contribute greatly to the PAH signal in these intertidal mussels. Finally, the fluorenes are much too high compared to the be consistent with fresh ANS oil. The possibility of fresh diesel recontamination of an area that had been previously

remains the most likely scenario.

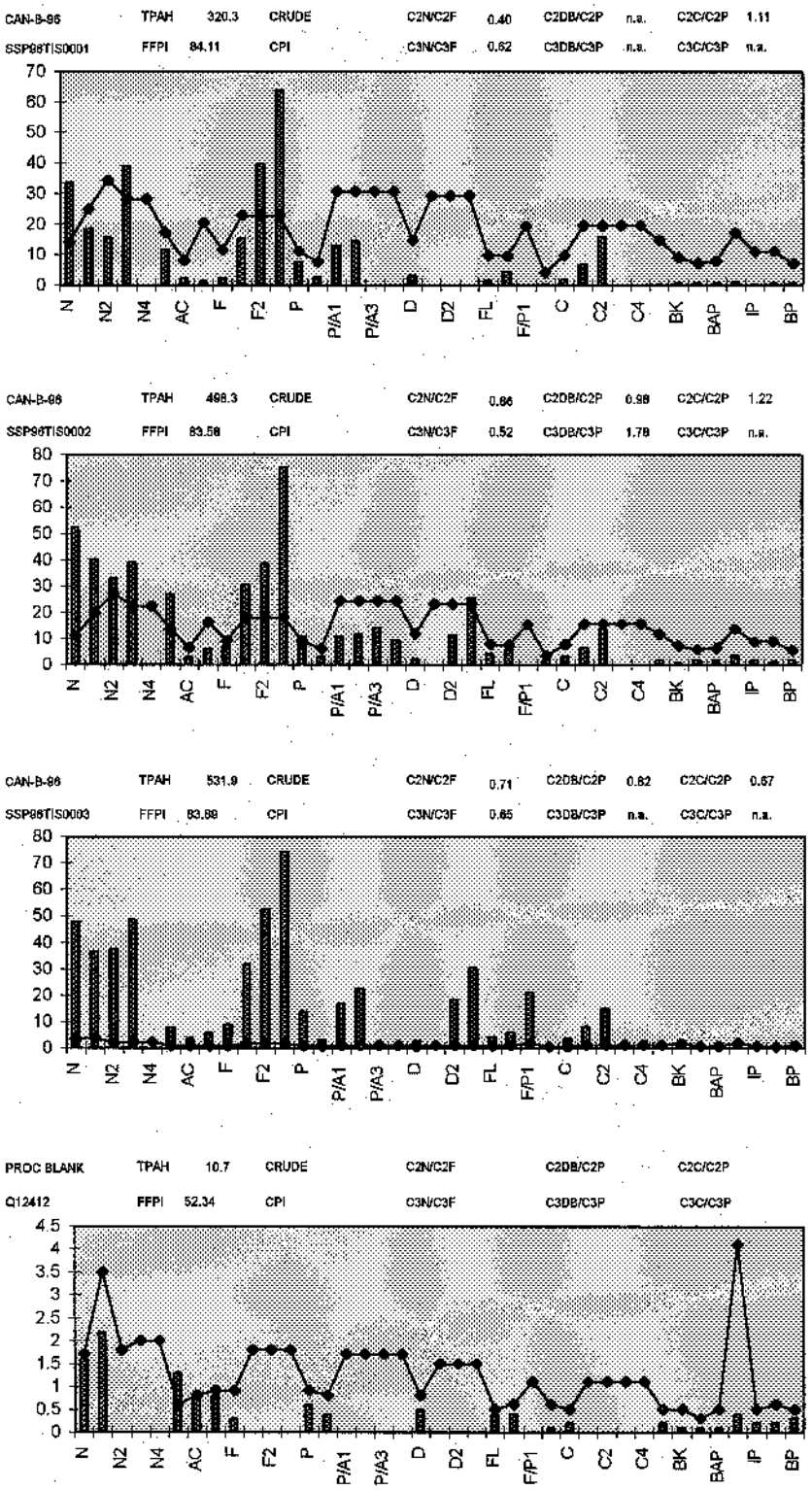


Figure 4-40 PAH histogram plots for 1996 Cape Nukshak intertidal *Mytilus* sp. and representative procedural blank run by GERG.

Figure 4-41 shows the PAH data obtained on the 1996 intertidal *Macoma* samples from Tuxedni Bay. Four replicate samples were collected from this region using hand corers and, although somewhat variable, evidence of fresh petroleum hydrocarbon contamination is apparent in all four samples. TPAH concentrations ranged from 300-400 ng/g dry weight, and in this instance, those levels are believed to be fairly accurate. It is true that the MDLs are fairly high, and that many of the individual constituents are at or below the MDL; however, the measured constituents are different from the ones observed in the laboratory blanks. Perylene is not a major component as was observed in Kamishak and Kachemak Bays. Based on the high concentrations of C_0-C_3-naphthalenes it appears that the oil source is very fresh, and the pattern is consistent with a diesel signature plus trace levels of pyrogenic chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(e)-pyrene, benzo(a)pyrene, indeno(1,2,3-c,d)pyrene, dibenzo(a,h)anthracene, and benzo(g,h,i)perylene.

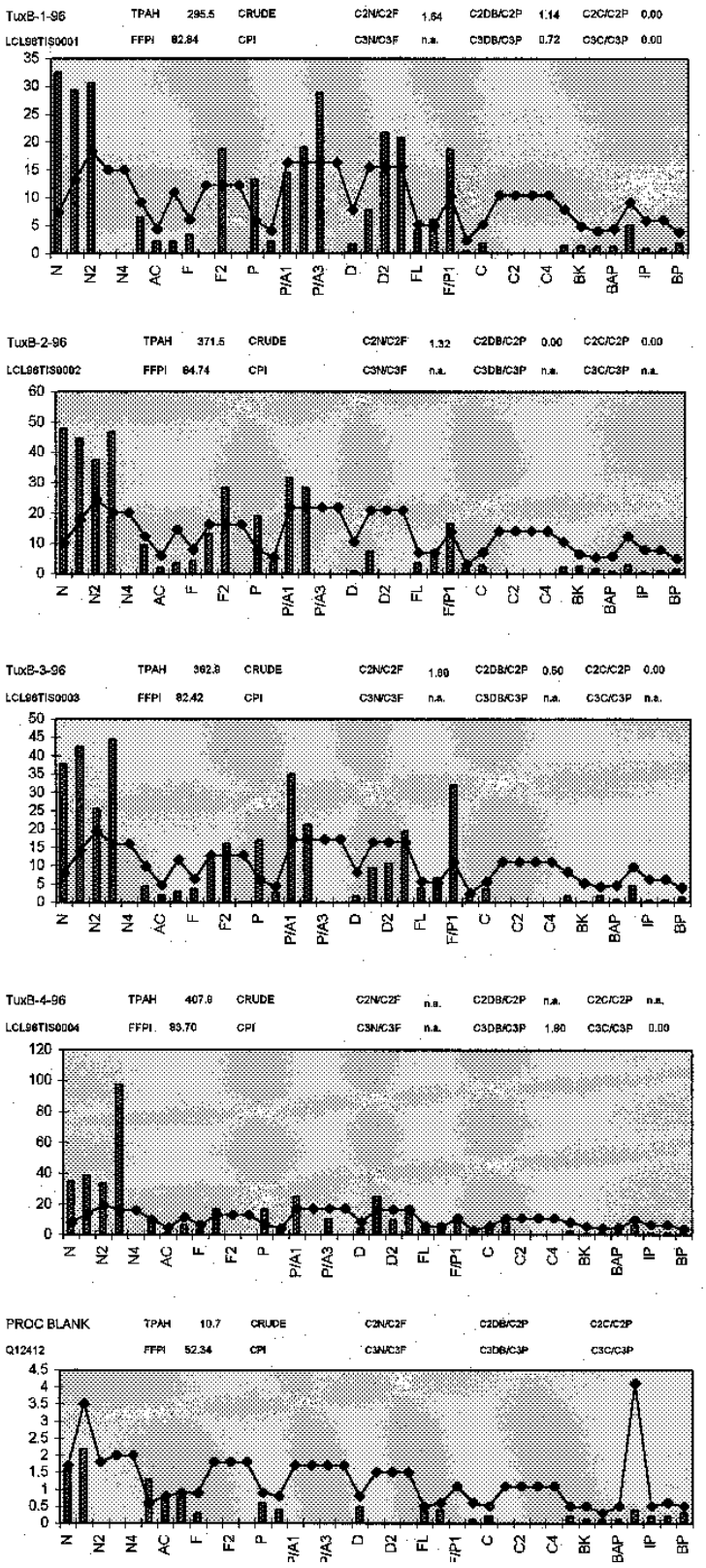


Figure 4-41 PAH histogram plots for 1996 Tuxedni Bay *Macoma* sp. and representative procedural blank run by GERG.

-42 presents the final set of PAH profiles obtained on the 1996 intertidal samples from Chinitna Bay. Like Tuxedni Bay, the tissues appear to be contaminated by a source. Unlike Tuxedni Bay the presence of an increasing series of chrysenes (C_0 $_1$<C2) ead, the contamination could be from a localized and yet uncharacterized seep. There is a pyrogenic signal similar to the at Tuxedni Bay.

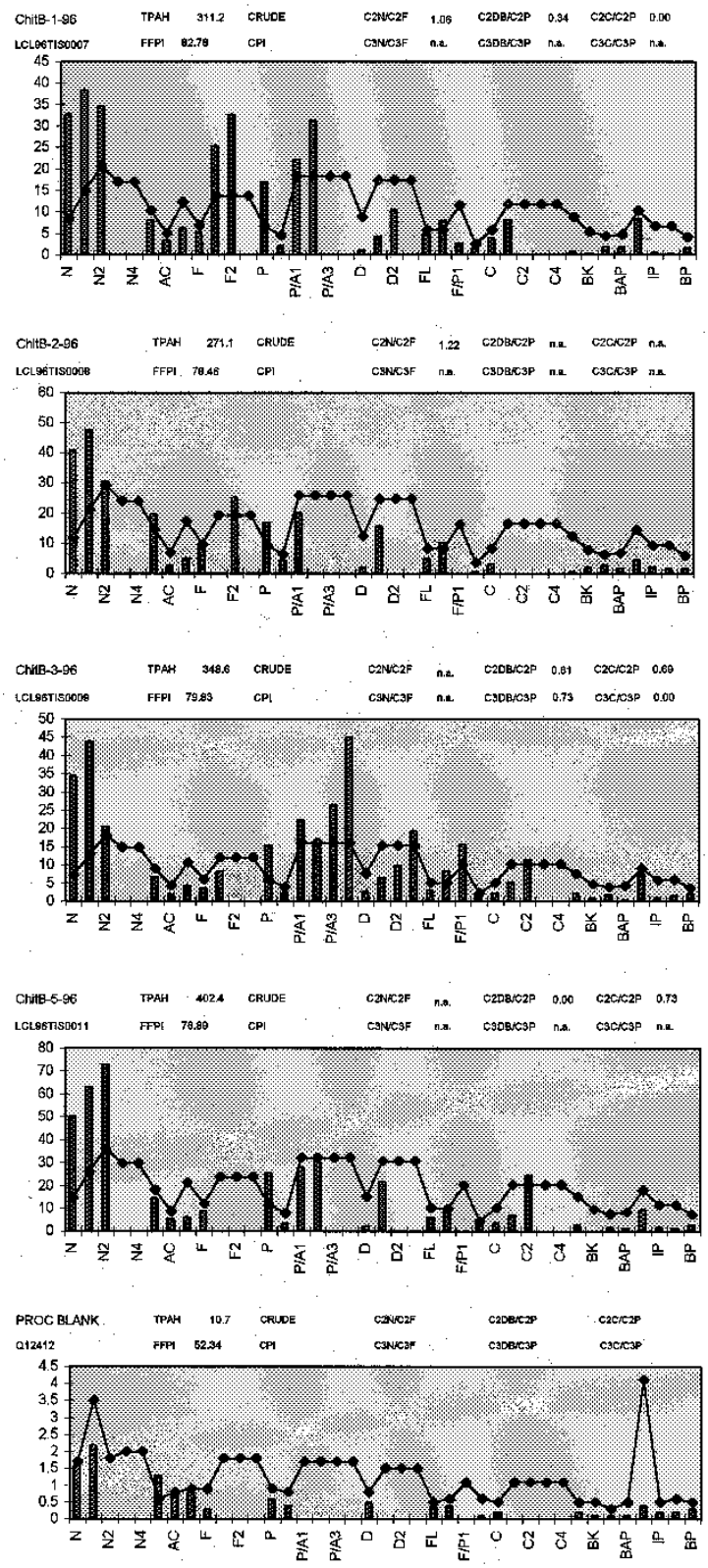


Figure 4-42 PAH histogram plots for 1996 Chinitna Bay *Macoma* sp. and representative procedural blank run by GERG.

4.12.3 Conclusions from Hydrocarbon Analyses of Tissues

To summarize, subtidal organisms living in the region have neither been accumulating nor exposed to high levels of hydrocarbons from Cook Inlet oil and gas activities. Deployment of caged mussels near produced water discharge outfalls failed to show any evidence of PAH accumulation, but this could have been due to extreme stress in the deployed mussels due to high suspended particulate loads or other environmental factors.

There is evidence of variable petroleum contamination in the intertidal tissues examined to date in the EMP.. In a few instances, minimal exposure of intertidal organisms to petroleum products has occurred. The sources of oil observed in intertidal organisms have ranged from extremely weathered EVOS plus fresher diesel in the Shelikof Straits,

to mixtures of diesel and pyrogenic constituents at Tuxedni Bay, and possibly fresh seep oil in Chinitna Bay. The intertidal areas within the Shelikof Strait show more variability in PAH signal and source than in the intertidal zones of Tuxedni and Chinitna Bays.

There are problems with false positives in calculating TPAH values in samples analyzed at GERG due to electronic noise during GC/MS SIM analyses. This is particularly true for subtidal samples and cleaner intertidal areas

Very few of the low-level PAH signatures found in tissues could be directly tied to specific sources; the samples suggest undocumented or multiple sources. Taken in total, the data do not show evidence of direct Cook Inlet oil or produced water contamination in the intertidal or subtidal areas examined thus far.

4.13 Results of Semi-Permeable Polymeric Membrane Devise (SPMD) Testing and Analyses of Cook Inlet Waters

Moorings supporting surface, mid-depth, and bottom SPMDs were deployed by ADL at two sites in Cook Inlet in 1993 and at three sites in 1994. Likewise, KLI deployed surface and near bottom SPMD moorings at three locations in 1995. Figure 4-43 presents the TPAH, Mytilus Petrogenic Index values, total C_0-C_4-naphthalene concentrations, and Total naphthalene/TPAH ratios for the complete SPMD data set generated thus far in the EMP.

The first three parameters reported in Figure 4-43 illustrate very low SPMD concentrations (in units of ng/SPMD device) for the moorings in the Beluga River area and near Trading Bay (presumably near the produced water diffusers) in 1993. Significantly greater PAH loading were obtained from the East Forelands and Trading Bay deployments in 1994, with similar values obtained by KLI in Kachemak Bay and East Forelands waters in 1995. Trading Bay results in 1995 appeared to increase by almost a factor of two. Interestingly, the relative percent of C_0-C_4-naphthalene/TPAH was essentially constant (ranging between 50-60%) at all stations in 1993 and 1994, with much more variability noted with the KLI deployments in 1995.

Interpretations of these apparent trends are facilitated by detailed examination of the PAH -44 through 4 51 in the order of field deployment as listed in Figure 4 43. The first major finding in examining all these figures is the tremendous problems encountered with obtaining clean SPMD two deployments by ADL at Beluga River and Trading Bay (Figures 4- -45, to the field deployed samples, so the results were essentially useless. There did appear to -deployed SPMDs to a pattern that more refinement before useable data could be obtained. In the 1994 ADL deployments at the cleaner (see Figures 4- -48) and a definite pattern of alkylated naphthalenes, othiophenes approaching the distribution expected from produced water discharges was obtained. There were still problems with $^{1-}$ $^{3-}$ associated with the method were usually a factor of two to– signals measured in the field- background/blank problem for the intermediate- -molecular weight PAH largely appeared to be solved.

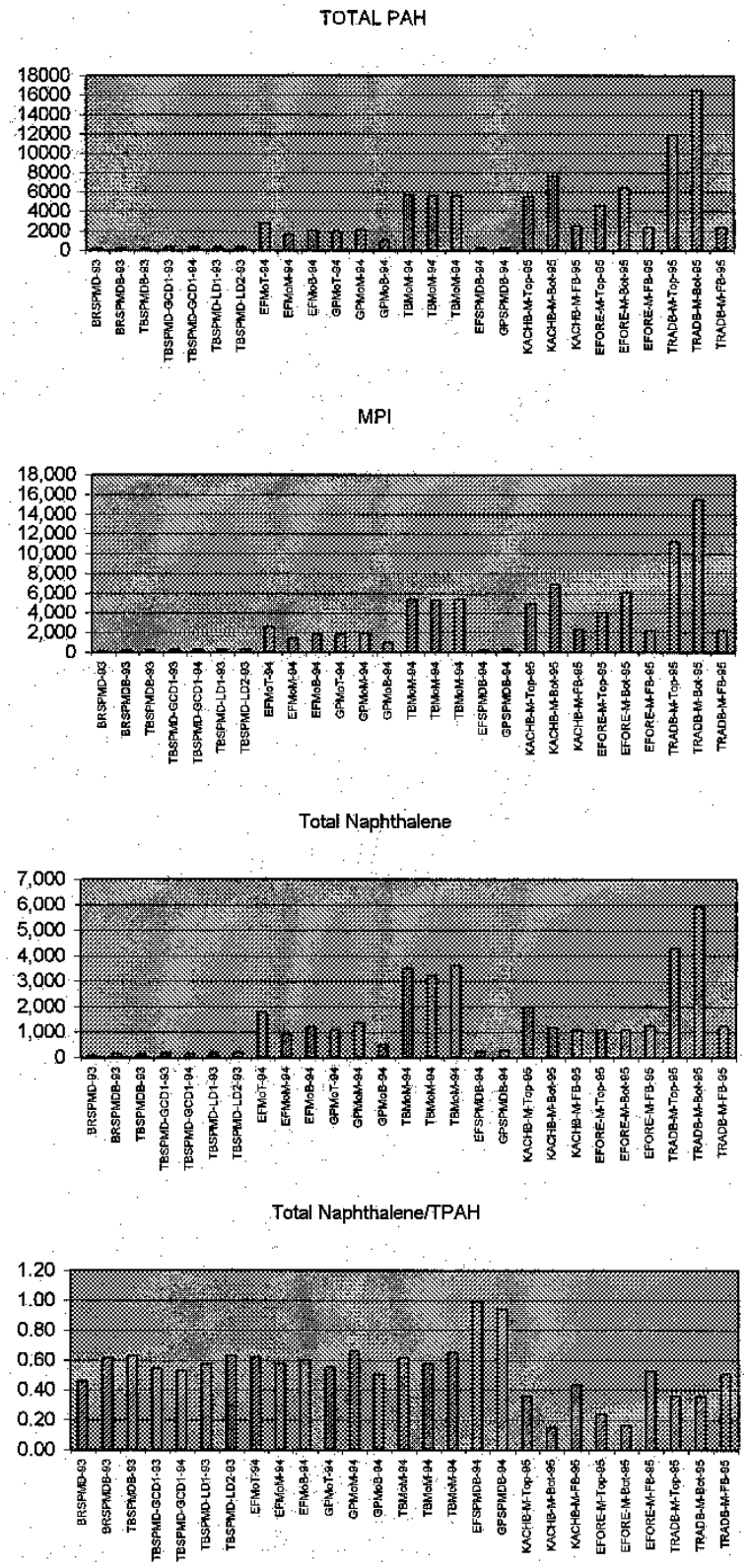


Figure 4-43 TPAH, Mytilus Petrogenic Index values, total naphthalenes, and total naphthalene/TPAH values for SPMD samples examined in the 1993-1995 EMP.

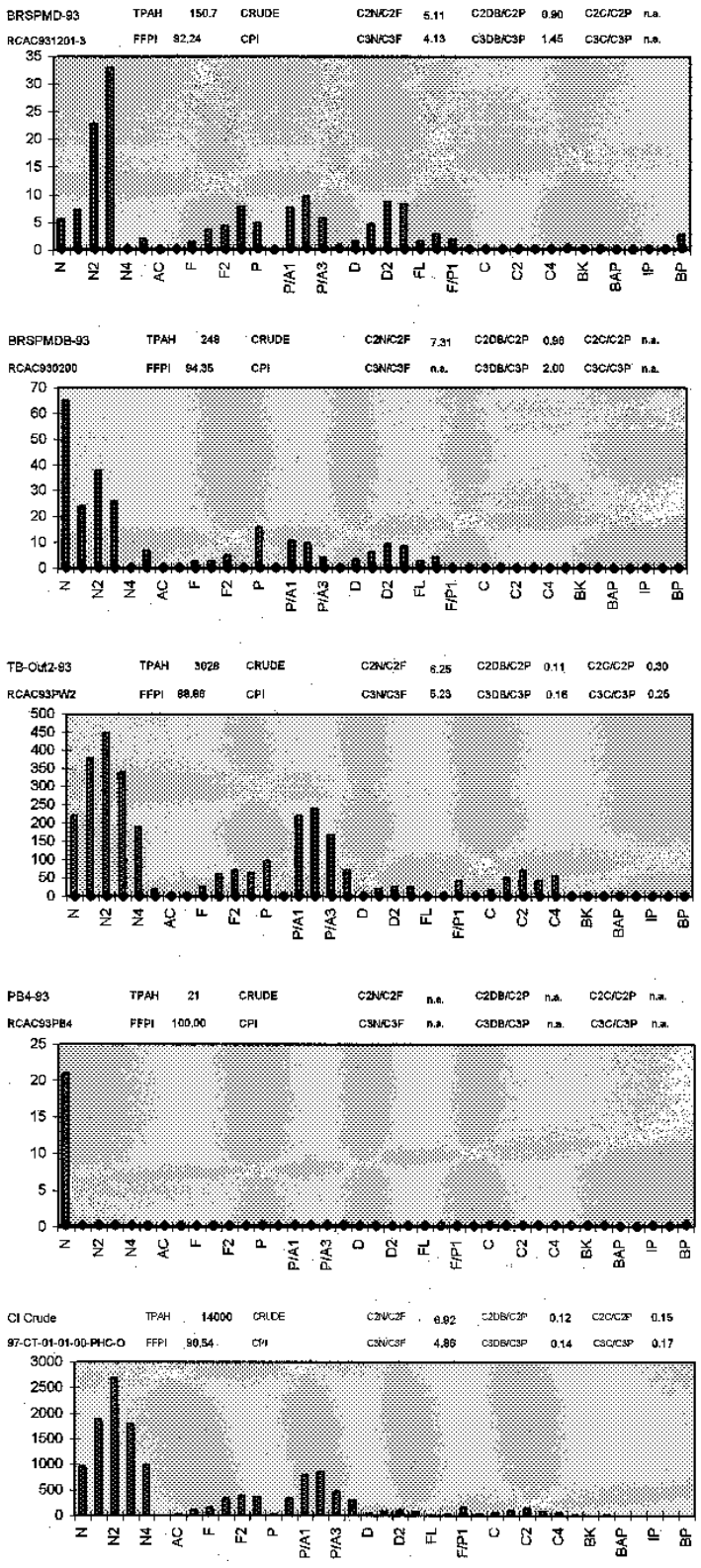


Figure 4 44 PAH histogram plots for 1993 Beluga River SPMD field sample, SPMD Method Blank, Trading Bay Outfall 2, ADL laborat
Inlet crude oil sample.

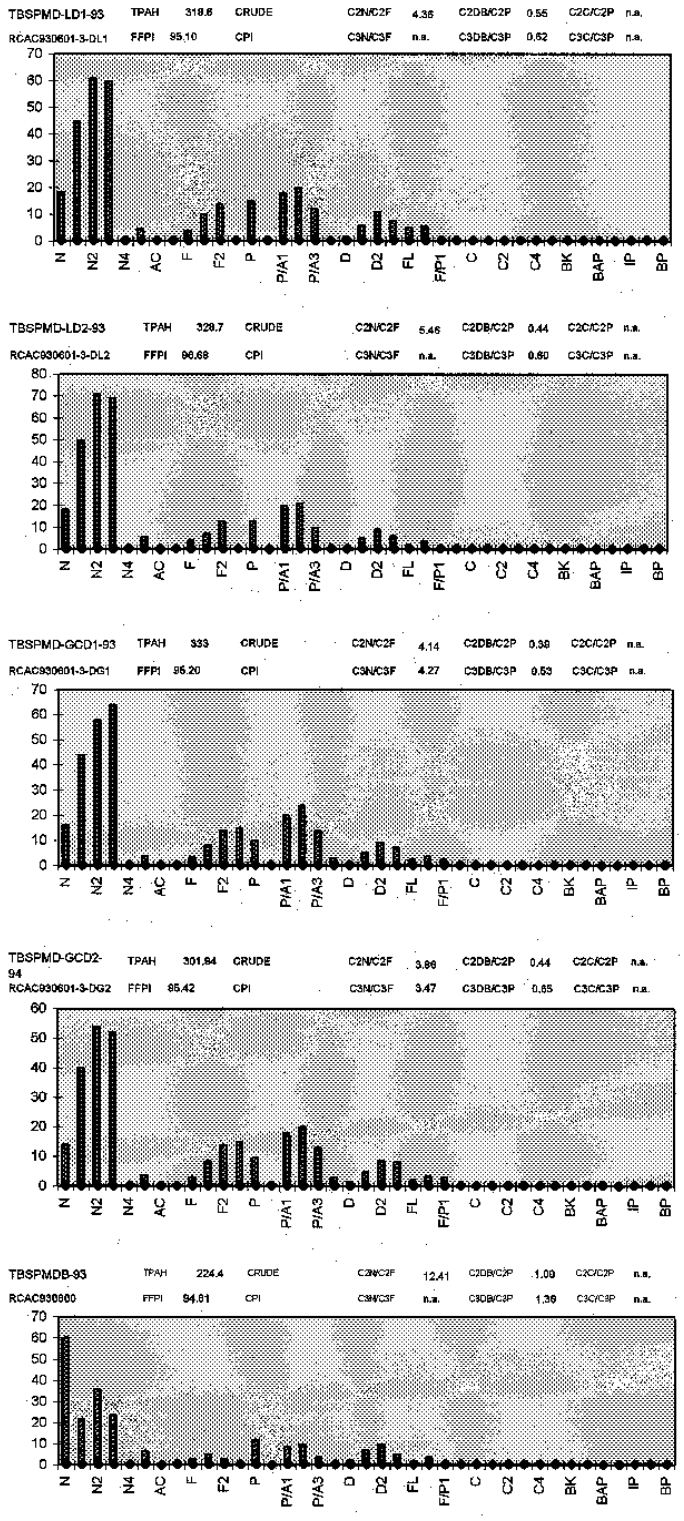


Figure 4-45 PAH histogram plots for 1993 Trading Bay SPMD field sample duplicates; SPMD field sample GCMS duplicates; and Trading Bay SPMD method blank.

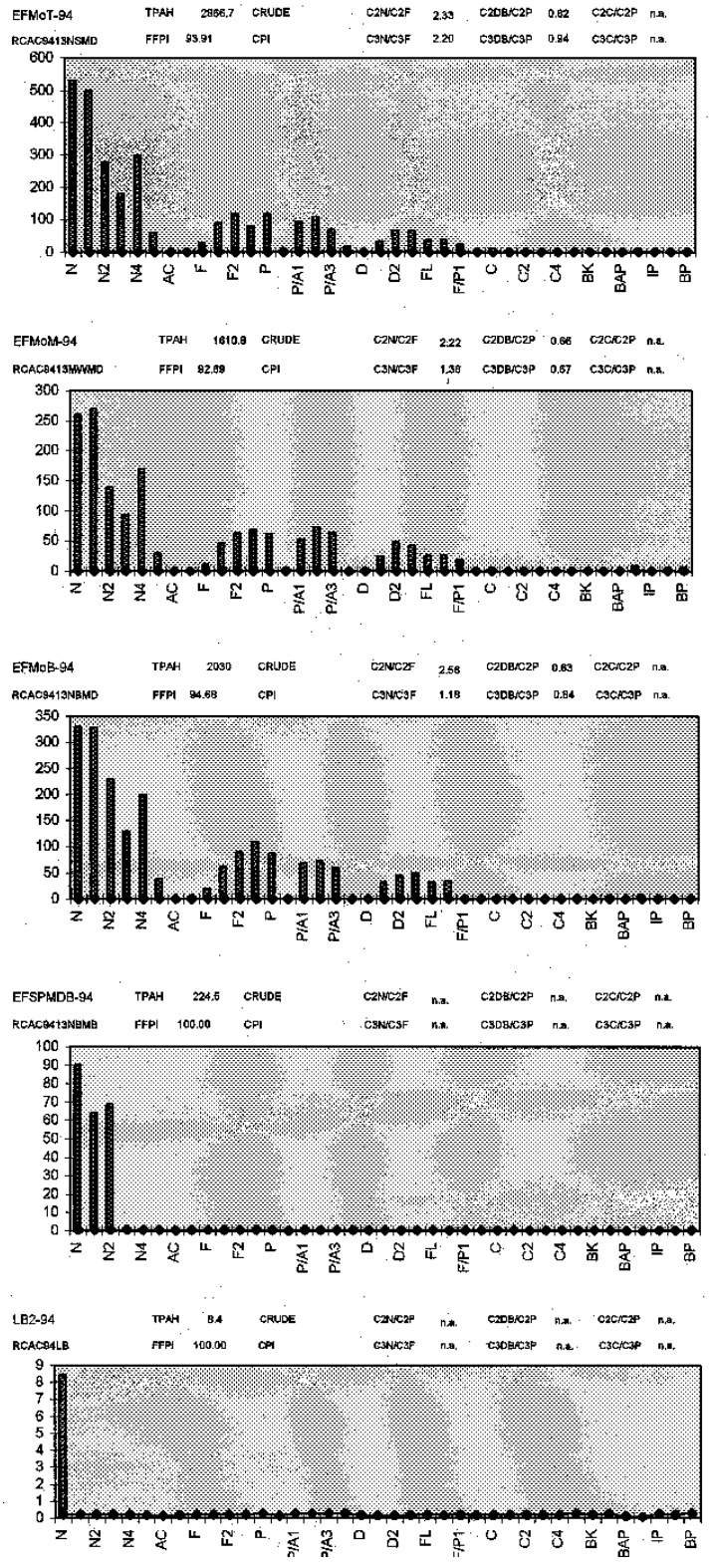
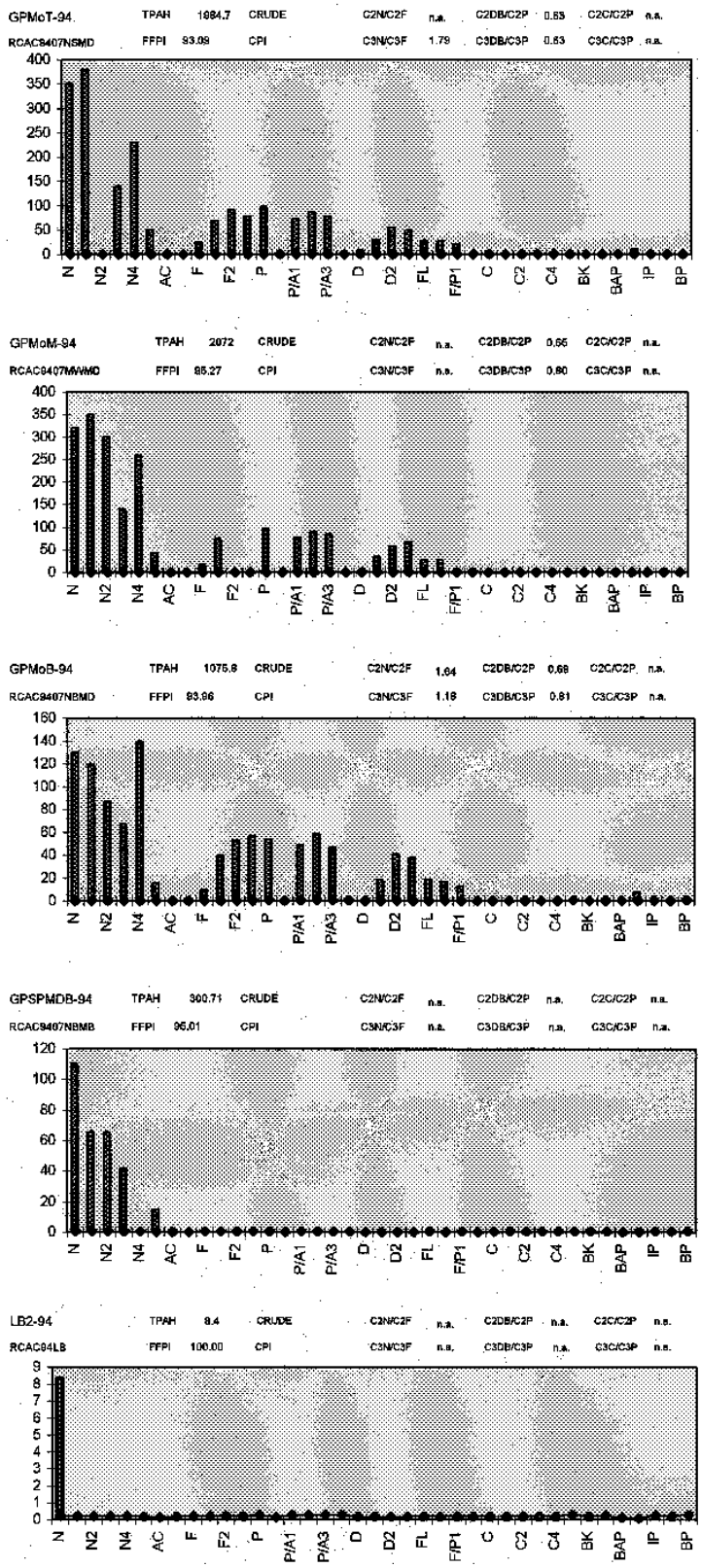


Figure 4- t upper, middle, and bottom SPMD field samples; SPMD blank; and ADL laboratory blank.



-47 PAH histogram plots for 1994 East Forelands upper, middle, and

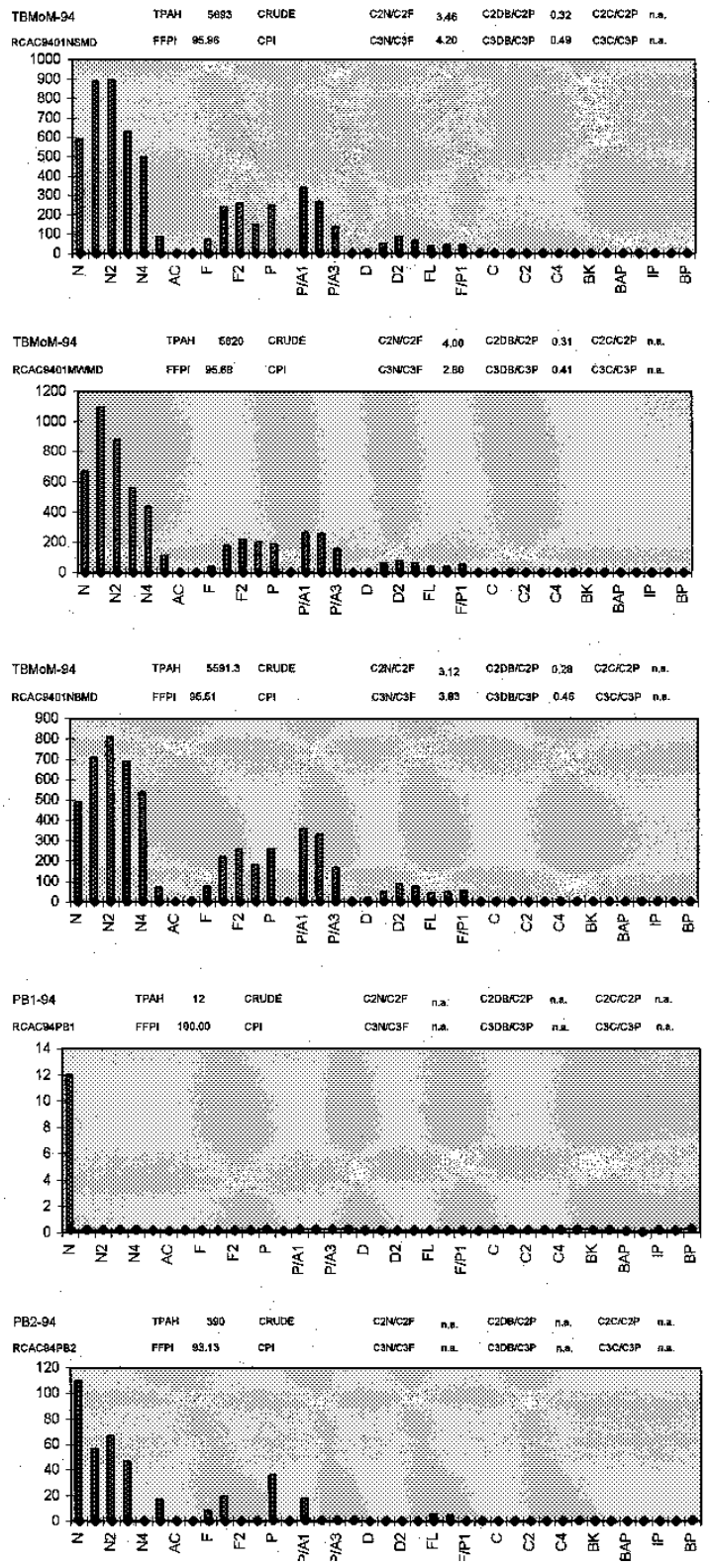
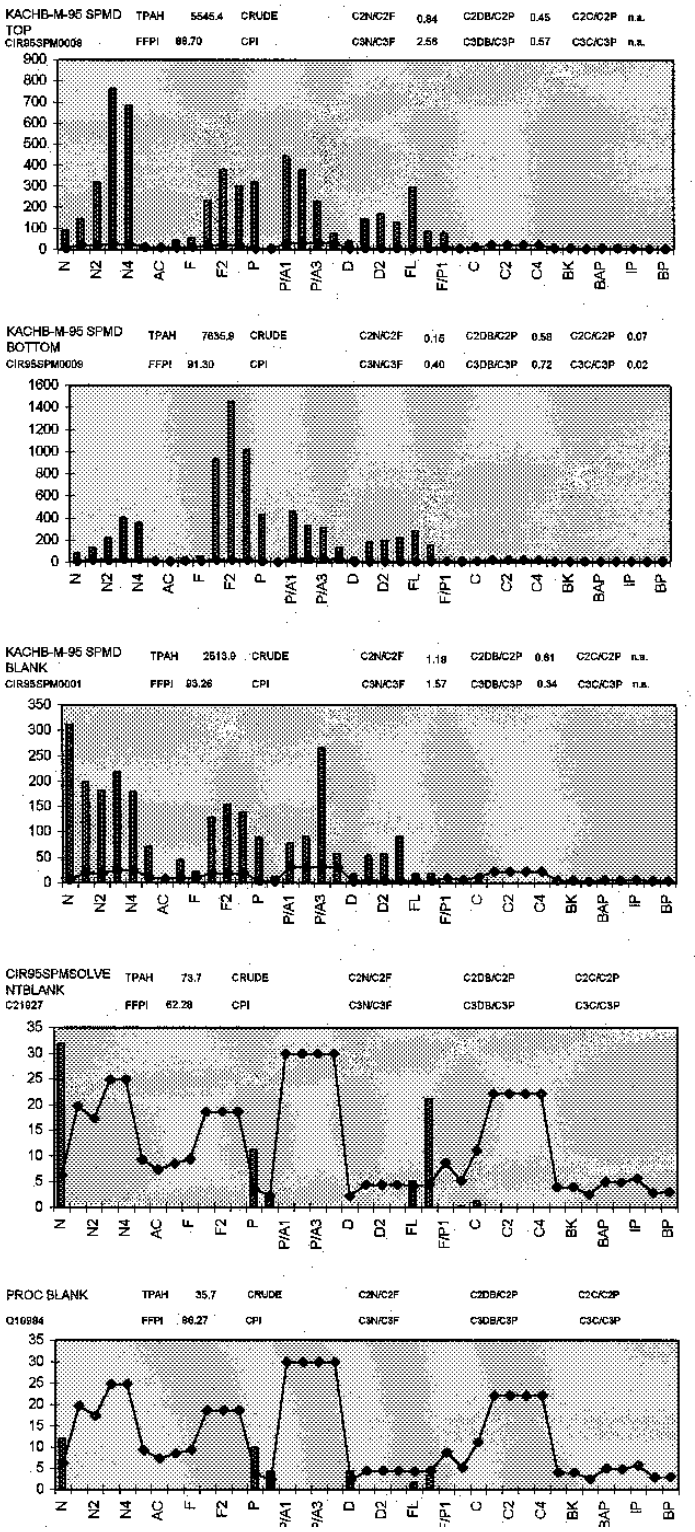


Figure 4- m plots for 1994 Trading Bay upper, middle, and bottom SPMD field samples; SPMD blank; and ADL procedural blank.



-49 PAH histogram plots for 1995 Kachemak Bay upper and bottom solvent blank.

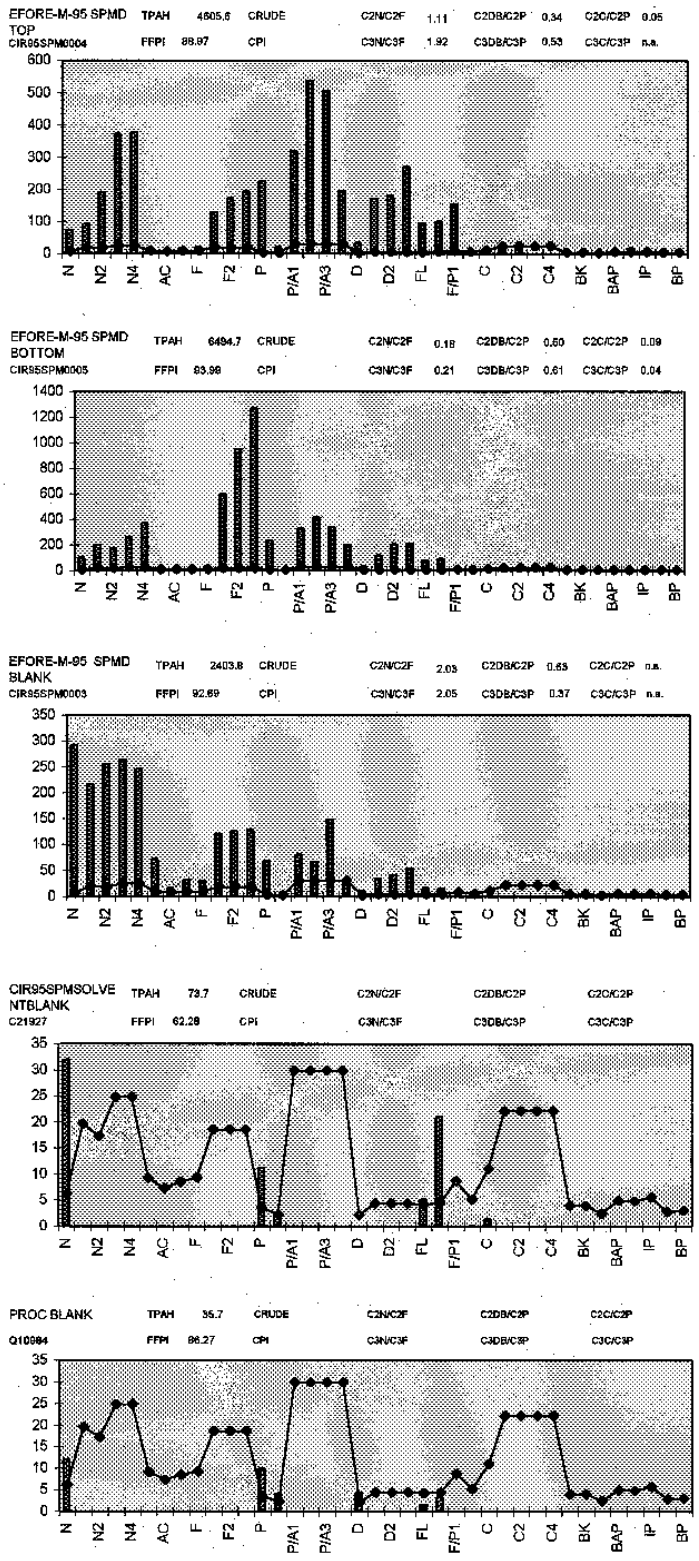


Figure 4-50 PAH histogram plots for 1995 East Forelands upper, and bottom SPMD field samples; SPMD blank; GERG SPMD procedural blank; and GERG solvent blank.

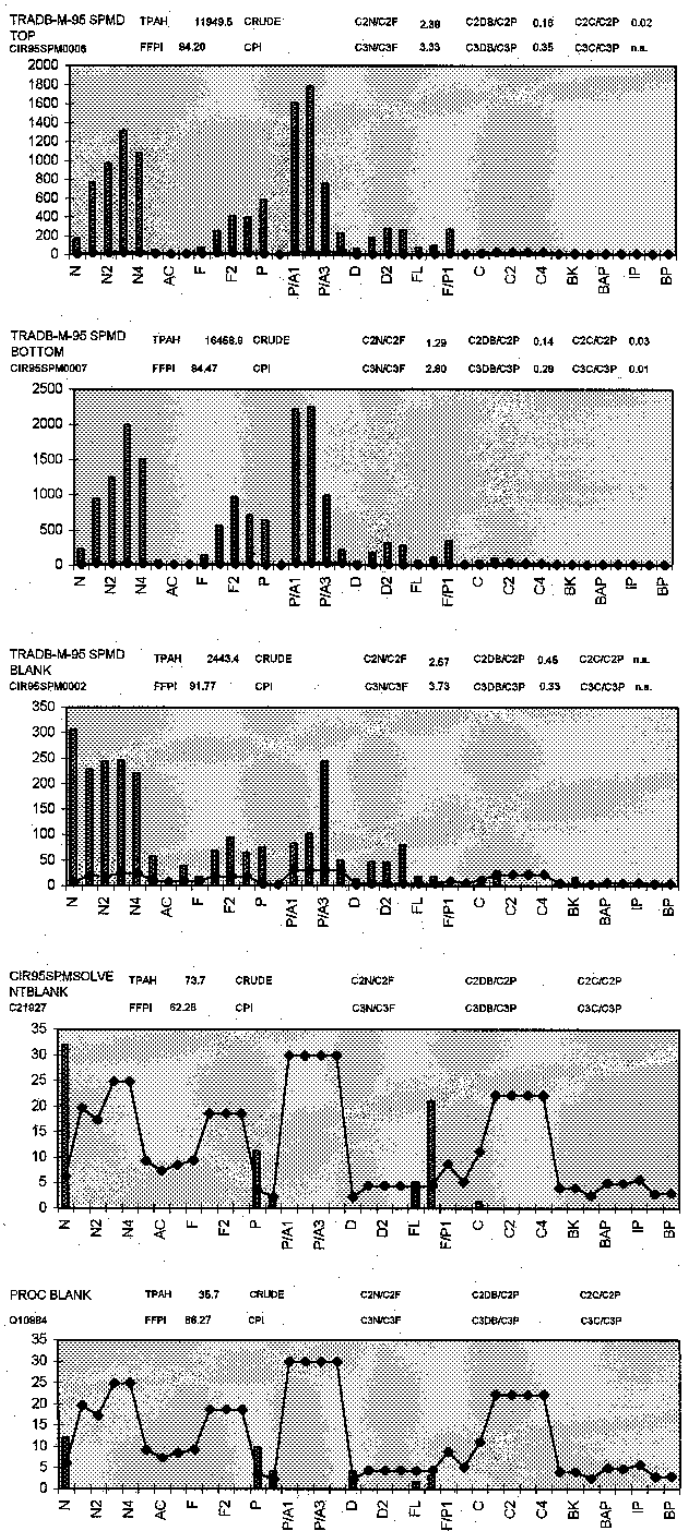


Figure 4-
field samples; SPMD blank; GERG SPMD procedural blank; and GERG solvent

When KLI attempted its first field deployment in 1995, considerable background/blank problems were again encountered with the SPMD lipid matrix, and the results were cceptable. Closer examination of the PAH histograms presented in Figures 4 49 through 4-
contamination is indeed washed out of the SPMDs upon deployment. Furthermore, the background contaminant sig
Cook Inlet crude oil and the dissolved compounds that are major constituents of the produced water discharges.

In conclusion, despite technical difficulties, SPMDs did show evidence of a produced

signal in Kachemak Bay. There are still numerous procedural blank and method development problems that appear to plague this particular approach, but on reanalysis the available data, the approach appeared to work slightly better than originally reported by either ADL or KLI.

4.14

Proposed mixing zones from the NPDES application and our far field calculations are contrasted i -14. Also included is the distance to MDL dilution for naphthalene -52 and presented

that initiated the tide cycle was also transported the farthest before reaching MDL

be the least diluted when leaving the mixing zone. Subsequent blocks of water typically

were met within the mixing zone with the most distant transport occurring at mid-
with peak tidal currents. Finally, in all cases, the last blocks in the tide cycle remained

tide cycle were not sufficient to transport and dilute the plume.

	Constituent	Effluent Concentration (ug/L)	Proposed Mixing Zone (m)*	Initial Dilution Factor	Percent Naphthalene in Effluent	Est. Distance (m) to MDL Dilution (m) at Flood**	Maximum Tidal Transport (m)		
							Ebb	Flood	Ebb
Granite Point Production Facility	TAqH***	15029	955	3877	7.8	2295	2282	10558	10277
Trading Bay Production Facility	TAqH	7330	1420	974	10.7	41000	24000	41382	31440
East Forelands Treatment Facility	TAH	15360	412	3762	17.3	23200	21800	70237	39459
Platform Tyonek A	TAqH	68	20	17	7.0	800	1000	34964	38063
Platform Bruce	TAqH	70536	867	18164	3.1	2556	2354	34086	28924
Platform Baker	TAqH	21006	837	5409	3.9	823	955	7146	27035
Platform Dillon	TAqH	14071	405	3609	5.0	1657	1600	51883	45756
Platform Anna	TAqH	20428	363	5233	12.9	2544	2700	29916	26620
Tesoro Treatment Facility (001A)	TAqH	34	13	39	ND				
Tesoro Treatment Facility (PM)	TAqH	354	18	37	21.1				

* where mixing zone limits for TAqH = 15 ug/L or TAH = 10 ug/L
** total naphthalenes method detection limit (MDL) = 0.1ug/L
*** TAqH = Total Aqueous Hydrocarbons

Table 4-14 Proposed hydrocarbon discharge, NPDES mixing zones, and calculated distance to detection limits for total naphthalenes.

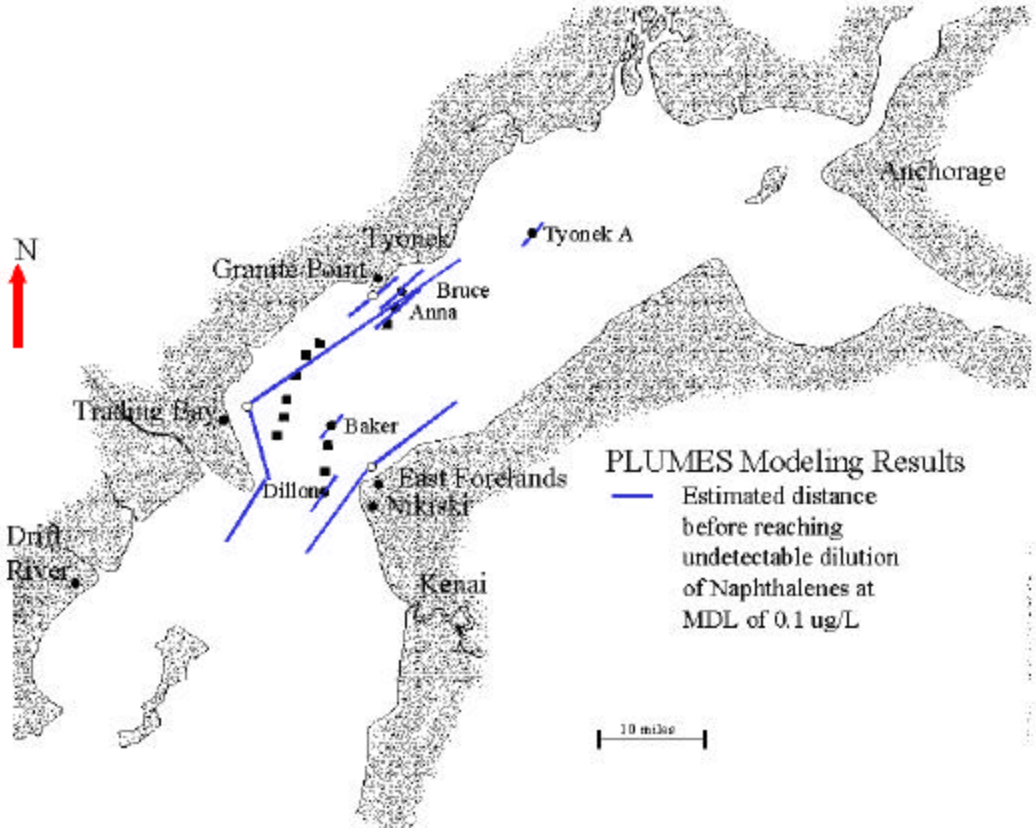


Figure 4-52 Limits of detectability for naphthalene from specified discharges in middle Cook Inlet.

Separate runs of the model were made for flood and ebb conditions because it was suggested that, in general, blocks of water travel in Cook Inlet farther during ebb than during flood tides due to massive inputs from the northern rivers; Nelson and Whitney 1996). This observation was not true for all of our data; although there were differences in average cycle lengths, the predominant direction was often reversed. Initially, separate runs were made for winter and summer in order to accommodate differences in water temperatures. However, seasonal temperature variations made little difference in the results and so seasonal runs were discontinued. In the NPDES application for the Tesoro refinery, the consultant also ran the model with a variation in discharge depth due to changing tide height but this factor, too, was found to have little effect on the size of the mixing zone (Parametrix, Inc. 1995)

The most extreme results from the modeling came from Trading Bay and East Forelands production facilities. The model predicted the Trading Bay discharge would be detectable throughout its tidal excursion up to 25 miles (41 kilometers) away on the flood and 14.4 miles (24 kilometers) on the ebb. The East Forelands discharge was calculated to be detectable slightly over 12 miles (20 kilometers) away. Apparently, since the average peak currents around Trading Bay and East Forelands run in excess of 4 knots, the long detection distances are more a result of a greater volume of discharge (relative to the other point sources modeled) rather than less tidal mixing.

Model Limitations

The PLUMES model has been favorably reviewed in actual field tests using dye dilution studies (Huang et al. 1997) but still the model's aut -field -field results tend to break down with distance from the -quantified initial unter stochastic mixing processes. This is particularly true in the highly energetic tidal regime of upper Cook Inlet and the tidal rips around

deficiencies in the available input data. In many of the model runs, the range calculations

velocities. So, from our own data we know that the currents and transport rates are different than those th
realistic, the far-
trajectory model in a massive numerical simulation approach.

orithm comes from using average far-
velocities rather than actual time-
depicting dilution versus distance for each block of water (Figure 4-
simplifies the more complex actual event (simulated in Figure 4 53b). Prior to each block of water reaching its final location at the end of the tide cycle, the concave curves showing -53a) tend to over estimate the actual dilution.
This unavoidable in
requires that far-
dynamically changing series of tidal currents. However, the resulting inaccuracy is not considered signi

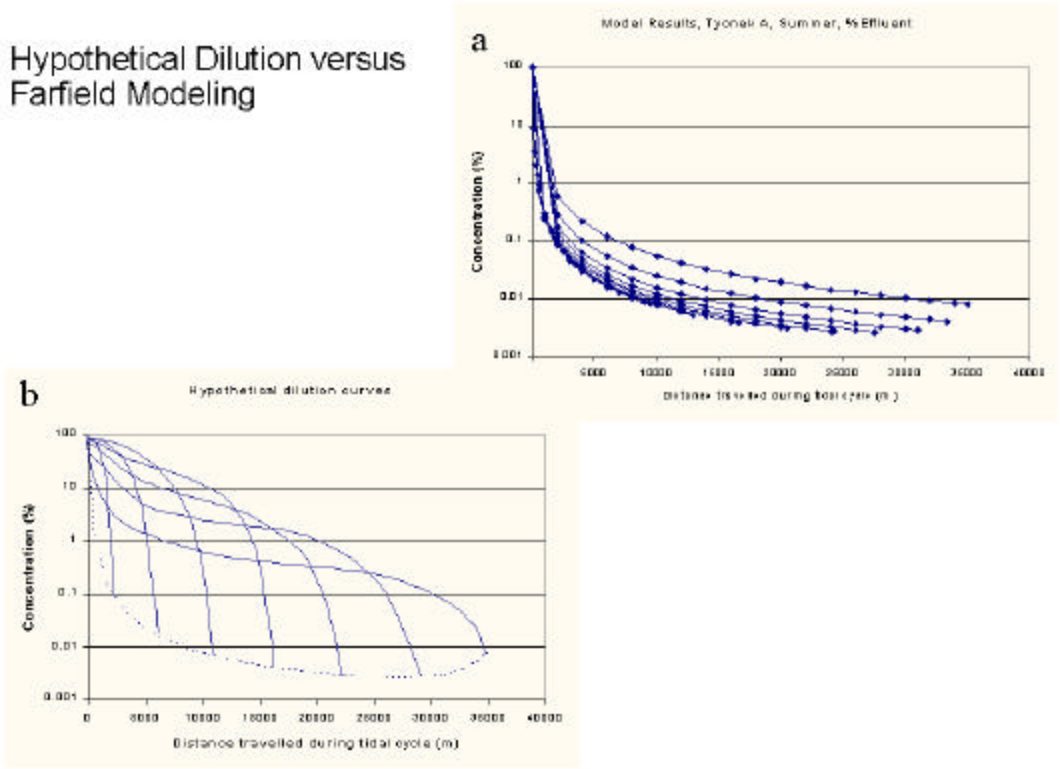


Figure 4-53 Hypothetical dilution curves for naphthalene in produced water effluent and distance traveled by water blocks during tidal cycle.

Realistically, the more extreme results of the model are accompanied with very low confidence estimates. For example, the ranges from Trading Bay and the East Forelands encompass the rips around Kalgin Island, a significant omission in the far-field calculations.

It is also important to keep in mind that while this modeling exercise was used to assess distances to which pollutants might travel before falling below levels of analytical detection, the mandated environmental safety exposure limits were met within the immediate area of the mixing zone.

In summary, results from PLUMES modeling shows that dilution progresses quickly beyond the boundaries of the near-field mixing zone at upper Cook Inlet discharges. Most plumes were undetectable beyond their mixing zone. However, using the sensitive MDLs (0.1 ug/L) attainable by top analytical laboratories and TPAH values from the NPDES applications, it seems theoretically possible to track naphthalene from some discharges a significant distance beyond their mixing zones. But the results also suggest some spectacular (albeit low confidence) values. For example, the model predicts that the East Forelands and the Trading Bay effluents could be tracked for 14 miles and 25 miles, respectively, from their discharges. At best, the modeling results reported here should be considered indicative of the dilution processes occurring in the upper Inlet but only as very

-field conditions, particularly where long distances are

5. _____

5.1 Patterns Observed in the Environmental Monitoring Program Studies

The Environmental Monitoring Program has sampled extensively in a wide variety of areas in the inlet and in northwestern Shelikof Strait. Moreover, the program employed a variety of potential indicators for contamination. While the design of the program has not been conducive to a useful body of data and important findings regarding the condition of Cook Inlet. The oil and gas activities. One finding that appears time after time in the discussions of results indicates there is little evidence of exp related to oil and gas activities in Cook Inlet. This strong trend is represented in Table 4- above.

direct evidence of hydrocarbon contributions from oil and gas activities in the inlet. These

1) PAH concentrations in sediments

2) aliphatic hydrocarbons in sediments;

4) PAH analyses f

5) PAH analyses for tissues;

7) toxicity tests using echinoderm larval development,

8) Microtox©

9) P450 reporter gene system testing of sediments,

10) P450 reporter gene system testing of bivalve tissues,

11) P4501A testing of halibut liver, and,

indicate exposure to hydrocarbons, and,

the likely sources of observed hydrocarbons in water, sediments, and tissues.

These approaches come at the question of potential hydrocarbon contamination from three principal directions. Approaches 1 through 3 are useful primarily for determining if the contaminants exist in the sediments or water at measurable concentrations. Approaches 6 through 9 address whether or not the concentrations of a contaminant found in the sediments can potentially cause mortality or sublethal (chronic) effects to organisms that might be exposed to them. Finally, the remaining five approaches (4, 5, 10, 11, and 12) are useful for determining if organisms living in the areas at risk have been exposed to the potential contaminants. These elements basically fulfill the needs of the Sediment Quality Triad strategy.

Regarding the question of whether hydrocarbons contributed to Cook Inlet by oil and gas activities, data contained in the EMP database indicate that neither PAH or aliphatic hydrocarbons in sediments exhibit spatial patterns that can be related to petroleum activities in the inlet. The PAH fingerprints were generally not characteristic of Cook Inlet or Alaska North Slope crude. In fact, the fingerprint observed was often similar to that of forms of coal from one of the several sources in the inlet. The SPMDs provided one of the few results that suggested exposure to hydrocarbons introduced to Cook Inlet by the oil industry. SPMDs deployed in Trading Bay assimilated PAH with a fingerprint similar to that found in the produced water effluents discharged from the Trading Bay facility.

With respect to whether the sediments contain hydrocarbons at concentrations that could cause mortality or sublethal effects to organisms exposed them, the entire suite of toxicity tests exhibited no relationship between toxicity and PAH concentrations in the sediments. In fact, toxicity test using amphipods and echinoderm larvae showed significant toxicity in several cases but it appeared related to other environmental factors such as concentration of fine sediments or ammonia rather than PAH.

Concerning whether organisms living in the region appear to have been exposed to hydrocarbons contributed to Cook Inlet by oil and gas activities, again, the evidence in the EMP database indicates that there has been no exposure or, if exposure has occurred, it has been minimal and probably involved hydrocarbons from unrelated activities such as small vessel operations. Generally, hydrocarbons observed in tissues appeared to represent refined products or pyrogenic hydrocarbons. The hydrocarbons observed often appeared to represent coal.

It appears, based on an overwhelming weight of evidence from the many aspects of this sampling program, that hydrocarbon contamination or effects related to hydrocarbon contamination are either lacking or, if they were observed, occurred at levels very near the levels of detection for the particular method. Ninety-nine percent of the observations summarized in Table 4-1 found no evidence of contamination from oil activities in Cook Inlet or effects that could be related to hydrocarbon concentrations in the sediment. The only methodology that exhibited a response was the SPMD (lipid bag) when arrays were placed near the produced water discharge in Trading Bay. Some approaches exhibited responses to environmental factors but none of these responses exhibited a correlation with petroleum hydrocarbons.

study of lower Cook Inlet and Shelikof Strait for the Minerals Management Service

approaches to address the question of whether there have been changes in conditions since the advent of the oil indu
is just as compelling as that which we have summarized for the EMP. A similar study in Cook Inlet by the Environmental and Natural Resources Institute (ENRI), University of (1995) produced similar conclusions.

Evaluation of Methods and Environmental Monitoring Approaches Used by

5.2.1 Sediment Quality Triad

contamination included elements to assess: 1) sediment contaminants; 2) sediment toxicity

communities living in or associated with the sediments is impaired as a result of exposure to the contami
contaminants of concern exhibit a relatively strong gradient within the study area so that the organisms at risk can exhibit a strong response if, in fact, they are affected by. The

areal range of the contaminant field is considered to assure that sampling occurs on an appropriate scale. Furthermore, the types of organisms identified for toxici
should be selected carefully to assure that they are appropriate for the sediment characteristics found in the study area. Furthermore, care must be taken to assure that the tudies such as P450
assays can be found in adequate numbers to support the analytical needs. The earlier

Initially, the EMP included elements that supported each of the three aspects of the triad. pect covering populations or communities, represented solely by an assessment of the physiological condition of populations of the bivalve spp., was implemented less vigorously than the other legs. This was due to a failure to identify through use of existing literature or with a reconnaissance survey, what bivalve species were found throughout the inlet and whether populations of a single

weakened by adopting multiple species of as the target "species". It was further weakened by the inherent weaknesses of the condition factor approach itself, for example,

affecting growth rates and survival. This problem was compounded by the difficulties of

spatial heterogeneity of bivalve assemblages. It was difficult to be assured of locating

influences of substantial habitat and environmental differences on the distribution of bivalves. Consequently, this part of the program was unsuccessful in the

the EMP because of an inability to collect the target species, *Macoma*, and this leg of the triad was never re-established.

In effect, it appears that after the bivalve condition approach proved ineffective, it was replaced by the bioaccumulation and biomarkers approaches in the later years of the program. In fact, given the difficulties of dealing with the effects of the broad array of environmental factors on recruitment, growth, and reproductive rates, examination of biomarkers that indicate a metabolic response to a contaminant may provide a far stronger approach to assessing impacts. It is unfortunate, however, that biomarkers and bioaccumulation approaches were given only minimal emphasis in later years. Biomarkers were only measured in fish from two regions and in mussels or *Macoma balthica* from five locations in two regions.

In the case of the CIRCAC, the general concept of the SQT is appropriate but because of the low concentrations of contaminants, not all elements are relevant. The toxicity tests indicated that the sediments are not sufficiently contaminated to affect resident organisms. Thus, it appears that standard toxicity testing will not produce any additional insight into spatial or temporal patterns of contamination unless contaminant loading increases considerably or "hot spots" are discovered during future sampling. Therefore, it seems feasible to discontinue standard toxicity testing until contaminants are observed at higher concentrations. However, the other elements of the SQT (hydrocarbon analysis of sediments and condition of specific resident organisms) should be continued. Relevant factors that should be evaluated to assess condition include tissue burdens of hydrocarbons and response in P4501A assays.

5.2.2 Hydrocarbon/Sediment Topics

5.2.2.1 Surface oil evaporation/dissolution/microbial degradation

Crude oils (and refined distillate products) consist of literally hundreds, if not thousands, of individual hydrocarbon components. When a crude oil or refined product is released to the marine environment, these individual components are immediately subject to a wide variety of weathering processes, including: evaporation, dissolution, adsorption onto suspended particulate material, photochemical oxidation, and microbial degradation (Payne et al. 1983; 1984; Payne and McNabb, Jr. 1984; Payne and Phillips 1985a; National Research Council 1985). A surface slick can undergo physical-properties changes in viscosity and density due to water-in-oil emulsion (mousse) formation (Payne and Phillips 1985b), and physically (and chemically) dispersed oil droplets are subject to dispersion and advection throughout the water column (National Research Council 1989). Eventually, these dispersed oil droplets can also interact with suspended particulate material (SPM) leading to sedimentation (Payne et al. 1987; 1989; Boehm 1987).

In general, the lighter-molecular-weight aromatics (e.g., benzene, toluene, xylenes, and other C_3-C_4 alkyl-substituted benzenes) do not persist in an oil slick for more than several hours. Intermediate-molecular-weight PAHs (e.g., naphthalene and fluorene, and their respective C_1-C_4 alkyl-substituted homologues) are removed over a matter of days to weeks, such that their initial concentrations in a given oil are not reflected in residues

The higher- -weight PAHs (e.g., phenanthrene, dibenzothiophene, chrysene, and $_{1-4}$ alkyl substituted homologues) are more persistent, and ratio

of oil residues collected after numerous spill events (Brown et al. 1980; Overton et al. 1981; Boehm et al. 1989; Saue
1993; Page et al. 1995; and Douglas et al. 1996; Burns et al. 1997). This approach was also utilized in Section 4.11.4 to characterize the multiple sources contributing to the PAH s program.

will not retain significant concentrations of naphthalene, C_1 naphthalenes, and C_2 naphthalenes compared to the higher molecular weight PAH. With continued weathering

the phenanthrenes/anthracenes, dibenzothiophenes, and chrysenes persist (Burns et al. 1997).

5.2.2.2 H adsorbed onto SPM

dissolved lower molecular-
suspended particulate material (SPM) has not been studied to the same extent as surface oil weathering. Recent work by Henrichs et al. (1997) and Braddo
however, suggests that individual PAH may be more environmentally persistent after adsorption onto SPM. Henrichs et al. (1997) reported that adsorption of phenanthrene completely, rapidly
reversible by suspension of the exposed sediment into clean seawater. Longer adsorption

dissolved aromatic concentration nor, in most cases, with the addition of a water soluble fraction (WSF) of hydrocarbons from crude oil. Braddock and Richter (1998) found that -adsorbed phenanthrene and naphthalene both became more ing organic carbon content of the
sediment (SPM). Sediments pre aged abiotically for 30 days with phenanthrene showed lowered mineralization rates in subsequent bioassays; however, there was still evidence of her directly or following desorption). In
contrast, the mean mineralization rate for naphthalene implied that more of the sediment adsorbed naphthalene was biologically unavailable. Taken together, these studies suggest that naphthalene and phenanthrene
microbial degradation after they are adsorbed onto suspended particulates. As such, these investigators concluded that individually adsorbed PAH could persist for decades in n Lower Cook Inlet.

-SPM interactions.

individual dissolved constituents from fresh and weathered ANS crude oil and

variety of Alaskan coastal regions. While not addressing the longer-
availability of the oil- oil droplet-

interactions overwhelmed dissolved constituent-SPM adsorption by many orders of magnitude. In all experimental runs the SPM was in at least 100-fold excess of the oil droplet density, such that the reaction was pseudo-first order (dependent on oil concentration) and SPM "loss" could be neglected. This is also a condition that closely resembles the water-column environment that would be encountered in most of Cook Inlet where SPM loading have been measured from 200 to 2,000 mg/L (i.e., up to 2 percent) (Burbank 1977, Dames & Moore 1978). Physical and chemical properties of the SPM types investigated included: particle number density per unit mass, the fraction of the total SPM fraction occurring in the 0-2 μm particle size range, total organic carbon, specific density, and background total (based on gas chromatography) resolved hydrocarbon content. Results of statistical analyses indicated that of the five independent variables, particle number density per unit mass showed the highest correlation ($r = 0.902$) with the values for the reaction coefficient. A slightly lower degree of correlation ($r = 0.798$) existed with the values for sediment fractions comprising the 0-2 μm particle-size range. The remaining three variables (TOC, specific density, and background total GC resolved hydrocarbon content) showed no significant correlation with the reaction coefficient ($r = 0.355$, 0.032, and 0.321, respectively).

Given the relatively high SPM loading (200-1,000 mg/L) and requisite turbulence to keep the SPM in suspension, all of the oil droplets in each experiment quickly reacted (within 15-20 minutes) with the SPM to form an oil-SPM agglomerate. These oil-SPM agglomerates were then subject to relatively rapid sedimentation after the turbulence was removed, and oil-SPM agglomerates were carefully transferred into a settling chamber (Payne et al. 1989). The sedimentation rates of the oil-SPM agglomerates were largely controlled by the initial SPM particle size (diameter) and the size of the resultant oil-SPM agglomerate. Increasing amounts of oil in the stirred reaction vessel experiments also produced higher settling velocities for oil-SPM agglomerates in follow-on settling chamber studies.

These data imply that physically (or chemically) dispersed oil droplets will interact with high concentrations of SPM, and that the resulting oil-SPM agglomerates can lead to enhanced transport of whole oil droplets to the sediments in lower-turbulence depositional areas.

5.2.2.3 Microbial and physical/chemical weathering of oil-droplet/SPM agglomerates

Unfortunately, no systematic studies have been completed on the bioavailability or evaporation/dissolution weathering of whole oil droplet-SPM agglomerates while still in suspension in the water column. Based on what is known about weathering of free oil droplets, however, it can be inferred that the oil-SPM agglomerate would still be subject to the same oil-phase diffusion-controlled weathering behavior (although possibly at a slower rate due to decreased surface area to-volume ratios for larger agglomerates). It is important to note, however, that this would be true for only as long as the turbulence regime is sufficient to keep the oil-SPM agglomerate in suspension. After turbulence is removed, free oil droplets above about 20 μm in diameter tend to return to the water surface (where evaporation predominates), while oil-SPM agglomerates would tend to settle out of the water column (where only oil-phase diffusion-controlled dissolution and

re significant factors). It is known that bacteria are more likely to be associated with particulate surfaces in the water column (Subba Rao and Alexander 1982; van Loosdrecht et al. 1990), and this may enhance bacterial utilization of the hydrocarbons the oil phase; however, this is clearly an area that requires further investigation.

Weathering of Deposited Oil

Several studies have examined the potential for microbial degradation of hydrocarbons in sediments contaminated by acute inputs such
et al. 1980; Karl 1992; Braddock et al. 1993; Braddock et al. 1995). Likewise, studies have involved additions of relatively high concentrations of hydrocarbons to sediments in 81) and the laboratory (Bauer and Capone 1985; 1988). Unfortunately, much of the research to date has focused on microbial degradation and

may be of greater concern to the environment; and yet, the effects of low level additions

In a study aimed at examining microbial activities in areas of deposition of sediments with drocarbon accumulation nor for
altered microbial activities in areas predicted to be the sites of fine grained sediment deposition from Cook Inlet (Atlas et al. 1983). In their study emphasis was placed on levels of hydrocarbons from Cook
Inlet oil production activities (Atlas et al. 1983; Bartha and Atlas 1987). Similar findings -dated sediment cores collected in outer Cook um- -related hydrocarbon

which microorganisms utilize adsorbed hydrocarbons in sedimentary environments.

ats in Kasitsna Bay and Sadie Cove
(Kachemak Bay) Alaska with three concentrations (0.1, 1.0, and 50 parts per thousand

allowed to weather *in situ* environment for one year, and then they were retrieved for biological and chemical analyses. Significant inhibition of biological activity

concentration, and chemical analyses showed no evidence of microbial degradation of

There did appear to be a factor of two- -three abiotic loss (presumably from dissolution) PAH in the 15-
sample spiked with 50 ppt fresh crude. However, the abiotic PAH decreases in the 50 ppt weathered -30% (individual PAH in the 3 12 µg/g dry weight range) due to their lo
process before sediment spiking. At 1 ppt there was chromatographic evidence of bacterial degradation of the aliphatic fraction (overall loss of n alkanes and decreased n-$_{17}$/pr -C ratios); however, the approximate two-
200- -substituted naphthalenes. on or
microbially mediated processes. At the 0.1 ppt total oil spike level, there was extensive

microbial degradation/removal of the non-water-soluble aliphatic fraction after one year, and most of the PAH were not detected at an individual concentration of < 30 ng/g dry weight. Again, it is impossible to say if the PAH removal was due to dissolution or microbial activity; however, microbial co-metabolism is likely, given the active microbial degradation of the aliphatic fraction. More importantly, the results do provide evidence that 30-300 ng/g dry weight concentrations of PAH from bulk oil contamination of sub-tidal sediments are capable of being removed by a combination of abiotic and biological processes in approximately one year. That is, when sediment-laden oil droplets or oil-coated sediments (as opposed to pure compounds adsorbed onto sediments) are allowed to weather under natural conditions, individual PAH can be removed at environmentally significant rates. These findings may help to explain the fact that to date, significant PAH accumulations from offshore oil and gas resource development activities have not been observed in depositional areas within outer Cook Inlet and Shelikof Strait (ADL 1998).

5.2.2.5 Coal as a major alternative source for the observed PAH in Cook Inlet sediments

Given the oil weathering scenarios discussed in the previous section, it becomes increasingly implausible to believe that the ubiquitous presence of PAH (and particularly the high relative concentrations of C_1-C_4-naphthalenes compared to the other PAH) throughout much of the study region can be due primarily to production operations and natural seeps. This is particularly true when one realizes that the majority of the surface sediments (and even age-dated sediment core samples predating Alaskan oil development) from the Gulf of Alaska, Prince William Sound, Outer Cook Inlet, and Shelikof Strait also have a similar background signal.

Coal has recently been suggested as an alternative and dominant source for the most of the PAH in offshore south-central Alaskan sediments (Short et al. 1999). Short et al. propose that the natural hydrocarbon background in sediments of Prince William Sound comes, not from seep oils (Page et al. 1995, 1996a, 1996b, 1997), but from coal located in terrestrial deposits along the northern coast of the Gulf of Alaska. Short et al. state that these coal sources have been eroded over geologic time by glaciers and steams, and particulate coal has been transported by the Alaskan Coastal Current into Prince William Sound. Based on an analysis of the data presented by Short et al. and the results of the EMP efforts within Cook Inlet, we now believe that these and other coal sources must be considered as major contributors to the observed sedimentary PAH burdens within Cook Inlet as well.

In essentially all of the EMP Project reports the sources of PAH in the sediments in question are attributed to Katalla seep oil, Cook Inlet crude oil (seep and production activities), and (only very recently) "coal sources in the area" (KLI 1998a). While largely overlooked until recently, the importance of coal sources of PAH in the Cook Inlet sediments will need to be considered in greater detail in designing future research and monitoring program activities. One area of particular significance requiring additional study is in examining the long-term fate of oil/SPM agglomerates and the weathering behavior and bioavailability/leachability of PAH associated with particulate coal. This research will provide additional data on the relative importance of PAH inputs to benthic

environments from natural (particulate coal) versus oil exploration and production-

5.2.3 Trace Metals Analysis

luated to monitor the magnitude of industrial and anthropogenic contributions and predict potential impacts to the marine

Administration (NOAA) National Status and Trends Mussel Watch Program, which

broad array of contaminants released by a wide spectrum of industrial activities (O'Connor 1992; NOAA 1987). Trace metals analysis in se
incorporated into the EMP in an effort to emulate the data collected by the Status and Trends program and possibly to assess potential contamination from metals in produced
ness of the sampling locations to the sources of trace metals, the sampling program did not appear to contribute materially to

of the relationship between metals concentrations in produced water discharges and the

The strongest evidence for the absence of a signal from produced water metals in
Quality in Depositional Areas of Shelikof Strait and Outermost Cook Inlet" of age dated sediment cores. Long cores of sediments were collected, sliced sequentially and age dated using naturally occurring radioisotopes and then analyzed for various trace metal concentrations

following commencement of OCS oil and gas development in Cook Inlet.

Toxicity Testing and Biomarkers

Toxicity testing and biomarkers analyses including methods that evaluated whether

sediments, and if animals exposed to the sediments in Cook Inlet exhibited metabolic products or biomarkers indicating a phys

On several occasions, results of the toxicity tests indicated some toxic effects. However,

concentrations of hydrocarbons in the sediment. In some cases, a correlation was

in the sediment or initial concentrations of ammonia in the sediment (the echinoderm tests). The Microtox text consistently exhibited no effects. P450 reporter gene system

the range of normal background values.

s to petroleum hydrocarbons. Testing was performed on tissues of and the blue mussel ( ). Strongest responses were observed in tissues from *M.* from Tuxedni Bay and *M. trossulus* the

values observed are well below the level considered to be indicative of serious contamination. As above for sediment, most of the responses are well within a range considered representative of baseline conditions. The lack of correlation with any of the hydrocarbon variables measured indicates that petroleum hydrocarbons were not driving the P450 response at any of the sites examined. Kinnetic Labs (1998) suggested that "chlorinated organic compounds" not measured during this program may be the cause of higher values observed for sediments from sites in Trading Bay and, by inference, Shelikof Strait. Preliminary data from the EPA subsistence study (1998) did find trace levels of PCBs in "sea bass" but these samples were collected in a different region of the inlet. .

5.2.5 SPMDs

Water masses in upper Cook Inlet are characterized by strong turbulent currents, extreme tidal changes, large seasonal variations in salinity and water temperature, and high concentrations of suspended particulates. Phytoplankton productivity is very low because the high sediment loading results in a very thin euphotic zone. This leads to poor food availability for filter feeders. Because of these environmental conditions, the paucity of hard substrate, and ice scour, mussels and other bivalves commonly used as sentinel species in monitoring programs have been found to be uncommon in the upper or middle inlet.

In concept, semipermeable polymeric membrane devices would be an ideal device to sample hydrocarbons in the water column for this area. The device consists of a loop of dialysis tubing filled with a oily (lipid) fluid which absorbs PAH compounds from the water. It is designed to mimic the respiratory uptake of contaminants (adsorption through the gills) by biota without the problems of separating the dissolved PAHs versus the wide range of PAHs associated with particulate and dissolved organic carbon (Priest et al. 1992). In practice, however, there are some limitations, and it is imperative to evaluate very carefully what question is being asked (i.e., what aspect of hydrocarbon chemistry is to be measured) before designing a monitoring program that incorporates SPMDs.

The device works by establishing an equilibrium between the concentration of a given PAH within the water versus the concentration within the SPMD. In the suite of target PAHs, the mid-weight compounds require about 3-4 weeks to equilibrate, a time similar to uptake in mussels. However, the lighter weight compounds equilibrate in a much shorter time (e.g., naphthalene - 1 day) which makes them highly sensitive to minor variations in ambient levels of the lighter fractions. This also makes the device very susceptible to contamination in field handling and laboratory storage. In contrast, the higher weight compounds show poor uptake performance because the molecules are too large to easily pass through the semipermeable membrane. Thus, the SPMD which needs to be immersed for 3-4 weeks to get an adequate sample of the mid-weight PAHs is over- or under-sampling the lighter and heavier ends of the target PAHs. This is difficult to correlate with actual ambient concentrations.

Because of the background blank contamination problem, all previous investigators have been reluctant to place much emphasis on the results; however, the SPMD program in 1994 (ADL 1995a) and (to a lesser extent) in 1995 (KLI 1996) were not complete

failures. In fact, the data do provide evidence that produced water or other point source dispersed hydrocarbons can be potentially tracked for considerable distances if the procedural/blank problems can be solved.

Additional work with this approach has been continued on other projects at GERG, and some additional improvements have been made (personal communication, Guy Denoux, 1998). Nevertheless, the CIRCAC EMP program should not be used as a vehicle to support continued method development and field trials of this very interesting, but problem-plagued approach. However, the existing SPMD data (for what they are worth), do show that water-borne contaminants may, in fact, be transmitted for greater distances than we had previously thought of predicted by our modeling approaches.

Therefore, we believe that a water sampling programs should be considered, but that a more standard approach should be used. Under contract to NOAA, we have developed a large volume (4-20 L) water sampling system that allows simultaneous filtration of the sample at the time of collection to facilitate separate analyses of the dissolved and particulate phases (Payne 1997; Payne et al. 1999). The use of this, or a similar approach would improve CIRCAC's ability to profile the extent and duration of production water discharges and their exposure to marine organisms.

We recommend an approach to ensure that adequate volumes of water will be collected to meet critical detection limit requirements, and that provisions are taken to differentiate between truly dissolved components and the dispersed oil droplet and SPM phases. Systematic sampling in a grid or down plume transect would generate more reliable data that could more accurately reflect water-column conditions as they actually exist in the vicinity of the diffusers in the mixing zone and further down field.

In past water sampling programs, insufficient volumes have been collected and PAH method detection limits were too high to support toxicity and modeling efforts. In addition, PAH analyses of unfiltered water samples were confounded by the facts that: 1) a significant, but unknown fraction of discrete oil droplets in the water column will rise to the surface in less turbid water; or 2) be adsorbed to SPM and potentially sink. Unfortunately, we do not have adequate data to evaluate either phenomenon. In addition, high levels of dispersed oil droplets will raise detection limits of dissolved PAH. As a result, it is impossible to determine how much of the PAH is in the truly dissolved state where it can persist as a toxic fraction to exposed organisms and how much is simply associated with oil droplets or SPM that are subject to relatively rapid removal by re-surfacing, or sinking, respectively.

A field-portable water-sampling system described by Payne (1997) and Payne et al., (1999) would allow adequate volumes of seawater to be collected to meet the required quantitation requirements to support CIRCAC's PLUME-modeling and toxicity efforts. In addition, the system has been designed to allow water-sample filtration at the time of collection to provide critical differentiation between truly dissolved constituents and dispersed oil/SPM agglomerates. The system can be quickly and easily deployed from fixed structures (production platforms, breakwaters, etc.) and/or vessels of opportunity to provide essential data to allow three dimensional PAH tracking and model verification.

Data collected with the system can be used to document exposure conditions and thereby provide information relating to toxicity issues in a more enlightened manner.

5.3 Relevance of Sampling Strategies Employed

Based on the information available for the environment and biological assemblages in Cook Inlet, we suggest the habitats and receptors sampled were not the most appropriate or reliable for identifying hydrocarbon insults to the inlet. Although the sampling design was driven by a justifiable belief that hydrocarbons released in Cook Inlet would adsorb to particulates and become deposited in subtidal sediments, it is just as likely that the hydrocarbons would settle out in intertidal depositional areas such as Tuxedni Bay or Chinitna Bay. In hindsight, subtidal habitats and organisms do not appear to have provided the highest level of sensitivity to potential hydrocarbon contamination. The weakness of the hydrocarbons signals observed in sediments and difficulties associated with sampling subtidal populations appears to have caused the program to evolve toward a more chemically or toxicity-based program. Because of the ease and lower expense of identifying suitably comparable sampling area and locating target organism for analysis, we are suggesting that intertidal sampling would be a more appropriate and cost-effective sampling strategy for future monitoring.

It appears that, with the exception of Kamishak Bay, all of the regions sampled have depositional and scoured areas. However, based on sediment grain size, the East Foreland, Granite Point, and Kamishak Bay are areas of lower deposition whereas Kachemak Bay, Trading Bay, and the Beluga area are areas of higher deposition. It is apparent from the data that sediments in most of the areas are very patchy. Grain size varies dramatically among samples from within each area. Nevertheless, based on sediment characteristics, it appears that much of the sampling has been focused in portions of the inlet characterized by high energy regimes and low deposition.

Three types of criteria were used to select sampling regions. Regions were selected to represent: 1) areas where impacts from the oil industry were not expected, i.e., reference areas, 2) areas (preferably depositional) near or downstream from oil industry facilities where impacts were expected (e.g., Trading Bay). From this perspective, the Sediment Quality Triad approach was a valid choice for assessing the region. However, after four years of searching and finding that contaminants are not accumulating in subtidal sediments, and considering the recent arrival of corroborating evidence from the MMS study and this study's dilution modeling, the SQT approach no longer seems the most effective approach to monitoring (see discussion in section 5.2.1).

5.3.1 Evaluation of Spatial Relevance of Regions and Habitats Sampled

CIRCAC has shown commendable persistence in searching for possible accumulations of oil pollution throughout the inlet. However, all of the regions examined are relatively large and are likely to be somewhat heterogeneous while the sampling effort was small. Fortunately, the results have been mostly negative and there now are two more solid pieces of information corroborating CIRCAC's results.

The current MMS study in lower Cook Inlet and Shelikof Strait (ADL 1998b) seems to

from oil industry are diluted, transported, and buried in undetectable quantities in Shelikof

multiple lines of evidence (i.e., PAH signatures, metals ratios, age-
biomarkers, etc.) suggest that signals of oil pollution from oil and gas activities in the inlet

modeling study done for this CIRCAC project supports the MMS findings by also suggesting that the strong local currents makes the effluent dischar
platforms and shore facilities undetectable within kilometers (or less) from the source.

limited spatially and in terms of replication. However, although they are less conclusive

consistent with those of that study. At this point, however, given the results of the modeling predictions in this report and the paradigm of dis
adsorption, and burial, the program should discontinue trying to detect chronic subtidal traces of contaminants from the oil industry.

Where the intensity of physical factors is most harsh, habitat and receptor diversity is poor
scour and gouging, sediment instability, and velocity and turbulence of tidal currents from the upper to the lower inlet are accompanied with an increase in the diversity o
and habitats. Based on monitoring for the Anchorage wastewater discharge, Bakus (1979) reported that infaunal assemblages were extremely impoverished in the upper inlet.
lower Cook
Inlet were impoverished relative to assemblages at similar depths near Kachemak Bay

reported by Bakus (1979) or on sandy beaches in lower Cook Inlet (Lees and Rosenthal

long-
sand beaches or in protected mud flats in embayments on both sides of lower Cook Inlet.

of abundance on beaches or mud flats in the central or upper inlet.

that CIRCAC's
monitoring approach should focus on sampling at the point source (end of pipe) of the

sure to detect effluents, the information would serve only as expensively verification of
-permitted level without

fulfill a narrow regulatory objective and would have no linkage to assessing impacts in the

nor information regarding potential impacts or the final destination of the pollutants.

5.3.2 Evaluation of Temporal Coverage

Two important aspects of temporal coverage in monitoring program are long-term patterns and seasonal variation. Repeated sampling over time which is designed to provide time-series data for trend analysis for either years or for seasons. The EMP sampled annually, with only a few regions being reoccupied more than one time. Thus, the program has provided only a very limited set of time-series data. The repeat visits did not follow a true repeated-measures sampling design because the majority of sites were sampled only once. In fact, specific sites were not resampled. Instead, new random sites were sampled within each region in subsequent years.

Because of funding limitations, field work for the EMP has been performed only in mid-summer. Consequently, the program also cannot assess seasonal changes. Considerable evidence has been reported describing the manner in which animals and plants living in Cook Inlet respond to the extreme seasonal changes, for example, by migrating to deeper water (e.g., fish in Rosenthal and Lees 1976) or slowing growth (e.g., kelps in Lees et al. 1980). It is well known from several OCSEAP programs that various biological assemblages change dramatically with the seasons. Therefore, in view of the low concentrations of hydrocarbons encountered and the low frequency with which effects have been observed in Cook Inlet, it appears pointless to spend any of the limited research funds available to the EMP for a study of seasonal patterns in the biota.

Indeed, the PWS RCAC's LTEMP program found the early spring samplings (April) to show differences in mussel condition but little else of significance. We recommended they drop that phase of their monitoring program (Payne et al. 1998).

5.3.3 Relevance and Suitability of Target Species

As stated before, in our experience in Cook Inlet, mussels are neither common nor viable in the sediment-laden waters throughout most of the inlet. Therefore, while mussels may be suitable target species in Kachemak Bay and Shelikof Strait, they are generally inappropriate in middle and upper Cook Inlet. Instead, many large bivalves (e.g., razors, cockles, Alaska surf, soft shell, or little-neck clams [*Siliqua, Clinocardium, Spisula, Mya*, and *Protothaca*]) are commonly available in the intertidal or shallow subtidal throughout all but the very upper portion of the inlet (e.g., Lees and Houghton 1977; Lees et al. 1980). These suspension-feeding species, which are adapted to live in depositional or at least fine-grained soft sediments, would be much more appropriate as monitoring species in the region most likely to experience effects from discharges by the oil industry.

One problem with using clams for monitoring is that the ability of marine invertebrates to metabolize PAHs varies widely within and between phyla. For example, recent studies have shown mussels (*Mytilus edulis*) have the ability to metabolize PAHs while some crabs species cannot (Meador et al. 1995). In addition, they have also found relatively short half-lives for many PAHs (e.g., two to six days for naphthalene and phenanthrene in clams and mussels).

Several concerns are enumerated for previously selected species.

The Pacific halibut, *Hippoglossus stenolepis*
commercial value, is unavailable for sampling in many parts of Cook Inlet.

migratory behavior.

is rare to nonexistent on the west side of the inlet and north of Ninilchik on the east side of the inlet because of ice scour and/or high

Macoma balthica is far more common
than in the subtidal zone. Other bivalves are better candidates in the subtidal.

Highly susceptible to exposure to the contaminant of concern.

Relatively sedentary so that it is representative of conditions in a specific area.

Relatively long lived so that it is representative of long term conditions in an area.

Constitutes an important component of the food web or valuable resource

Finally, from NPDES applications (Parametrix 1995, 1998), theoretical concentrations of c and the aromatic hydrocarbons, benzene, chrysene and indeno(1,2,3-
fish and shellfish were of concern as potentially attributable to produced water discharges from the oil production facilities. Although the risk assessment models found no

higher priority in monitoring than the standard suite of target PAHs.

Evaluation of Navigation

There are two aspects to navigation in terms of sampling strategy. First is accuracy in

during subsequent samplings and that the site can be assessed in relation to other data, e.g., maps of sediment transport or species migration
system (GPS) navigation, there should be little concern about accurately describing the position of a fixed station.

The second aspect of navigation is the ability (or motivation) to reoccupy a specific GPS described
reestablish position at a particular sampling site. But generally, it is a difficult task to navigate winds, currents, and choppy seas to drift across a site just as the grab

sediment. However, such is the true task of monitoring. In order to establish a true time series at a monitoring site, the sampling *must* be restricted to a single location rather than collecting random samples from a general vicinity. The latter is appropriate for describing the variation in a sampling area (e.g., Trading Bay) but it makes data impotent to assess whether observed variations between samples comes from: 1) spatial differences in the sampling area; or 2) real temporal changes occurring area-wide since samples were collected in the previous sampling period. Only replicate sampling from within a fixed site reduces the statistically confounding effects of area-wide variation.

So, how much tolerance should there be around each sampling location? The appropriate response is that the data will tell how much tolerance is needed, and the amount of tolerance will be specific to each site.. For example, if, at a subtidal site, replicate samples show dramatic change of grain size parameters or PAHs or depth, then the sampling team should spend more effort trying to hit the location. But if samples are being drawn from a vast subtidal sand plain of mostly similar depth, then drifting a couple of hundred meters would likely have little effect. In contrast, because of the known patchiness of the intertidal and the ease of collecting a sample therein, an intertidal location should have a fixed monument or some other ability to relocate within centimeters of previous samplings. Again, the purpose of monitoring is to determine what changed at a site with the measurements including as little variation between replicates as possible.

Sampling variance also affects the power of a monitoring program. Statistical power is the probability of getting a statistically significant result given that there is a real biological effect in the population being studied. If a particular test is not statistically significant, is it because there is no effect or because the study design makes it unlikely that a real biological effect would be detected? The study design incorporates the variables of sample size, variance and accepted level of significance (typically 0.05). Given any three of the variables, the fourth can be calculated. For example, "Based on variability observed in the existing baseline data, how large of a change (%) must occur in the future to be significantly different from this year if we collect 10 samples?"

A well-designed sampling program will have some estimate of the sampling variance based on prior knowledge from similar studies or from pilot programs mobilized to establish sites and measure the variance. Knowing the actual variance allows the statistician to then back-calculate the necessary sample size to achieve the desired sensitivity objectives of the program. In our studies on Cook Inlet beaches, we have typically collected 10 samples of intertidal infauna to assess seasonal population changes. But the calculations must be based on a specific query. If we were only interested in the common species, 10 samples was probably overkill but, in contrast, if we were also interested in the changes in rarer species, then the variance of mean abundance might be too high to detect meaningful change with just 10 samples.

For CIRCAC studies, over-sampling in the first year is recommended to assess variance. Adjustments can then be made to the sampling design following the considerations of statistical adequacy.

Knowledge of Baseline Conditions

One of the lessons learned from the EXXON VALDEZ Oil Spill (EVOS) was that most of -spill natural resources along a major tanker route were poorly documented. If a

and scientists to make informed operational decisions, to assess impacts, to litigate, or

Cook Inlet is very sparse. There are maps of environmentally sensitive coastlines based on geomorphology a
intertidal communities are undocumented. Chemical body burdens and sediment loading data are even more sparse.

Granted that it is beyond the scope of EMC to know all things about the natural and

provide hints or deeper understanding of the inlet's processes. For example, measuring sediment quality and body burdens in suspension or surface deposit feeders suggests not

bioavailability and risk of bioaccumulation in higher trophic levels. These research topics are well suited for a monitoring program while others, like gathering
physical oceanographic data, would serve to eliminate data gaps and further the understanding and predictability of the inlet's natural processes.

5.5

According to CIRCAC's mandate, EMC is responsible for "...
and dissemination of environmental literature and information for use in committee and Council activities and by the public." Thus, one of the objectives of this study is to mplete. Although the KLI and ADL
data have been effectively combined, a portion of the data is not yet available from earlier

and MMS studies on sediment quality and tidal rips) are still in preparation and should

be an on-
database for CIRCAC studies. The database submitted with this report will follow that

EMC is also tasked to provide data to the public. The CIRCAC website would seem an -
tech
of it). Finally, the data itself could be disseminated as ZIP-
those keenly interested in the studies. Another helpful product would be a bibliography of

5.6 Bivalve Studies

Macoma balthica,
, and several other subtidal clams to support an analysis of the

than once from any of the small number of stations. The observations provided no useful information for this program.

Moreover, similar information was collected for mussels in the mussel watch deployments in the upper and lower inlet. In this case, the mussels were highly stressed by environmental conditions in the region. Many of the animals died from the exposure.

Because these data sets lack spatial and temporal consistency, they were not useful to the objectives of the program. Moreover, this and other approaches to describing the condition of target populations are subject to a variety of problems related to the effects of lack of uniformity in food availability and variability in environmental condition such as temperature and salinity on growth, reproduction, and other physiological processes that are used to evaluate condition. We recommend that this approach be discontinued in future monitoring studies unless environmental conditions can be carefully controlled.

Recommended Monitoring Program

The above cited studies by CIRCAC and MMS have been unable to identify any significant signals suggesting historic accumulations of petroleum hydrocarbons metal residues in the active reaches of Cook Inlet that could have originated from activities of the oil industry. Moreover, the PLUMES modeling described above for this om these discharges to produce detectable levels of PAH in the sediments of the inlet. In the preliminary Ecological Risk Assessment to identify strategies that will lead to a more

6.1 Strategy for Monitoring-

Ecological risk assessment (ERA) is a process that evaluates the likelihood that adverse e to one or more environmental stressors. This approach will help determine: 1) which contaminants may dispersion reduce the concentrations below levels where these contaminants can cause a (receptors) could potentially come into contact with contaminants; 5) what concentrations of the contaminants are required to cause biological problem pathway between the source of the contaminant and the receptor.

and focus a risk assessment (*Framework for Ecological Risk Assessment* PA 1992). In this case, we have used this stepwise approach to sort through the many options that potentially be examined in the EMP. The purpose of this exercise was to reduce the be obtained with the budget available for monitoring.

and products in a very cost effective manner. An ERA requires that a physical or chemical stressor not only has the ability to cause adverse effects but also co occurs with or contacts biological resources of interest (e.g., organisms, populations, communities, or ecosystems) for a sufficient period of time and at a sufficient concentration or dose to elicit an identifiable adverse effect. The ERA can help identify potential environmental

Tier 1 in a stepwise approach prima pose risk. Available data are coupled with a characterization of appropriate exposure pathways, biological receptors, and resulting estimates of risk for each stressor under -case scenarios. target or most- maximal; and 2) a diverse, multitrophic level aquatic community is present and the biological int

these types of data comprises three primary phases (USEPA 1992): problem formulation, analysis, and risk characterization. The intent and elements of these phases are described briefly below. For the purposes of identifying the appropriate region, habitats, and target species for the monitoring program, we will limit this assessment to the problem formulation component of the Tier 1 approach.

6.1.1 Problem Formulation.

Problem formulation includes: 1) a preliminary characterization of exposure and effects; 2) designation of biological resources considered for protection 3) examination of available data and data needs; 4) and site-specific factors that may influence the feasibility, scope, and objectives of the risk assessment. The problem formulation phase provides an early identification of key factors to be considered, which in turn will lead to a more scientifically sound risk assessment. In a screening risk assessment, it is possible that examination of available data and regulatory guidelines may demonstrate that the stressors are not of environmental significance and do not pose an environmental risk. In such an instance, the ERA can be concluded.

The activity driving the conduct of this exercise is the chronic discharge of produced water and other combined effluents (not tanker spills) produced during the operation of oil production rigs and processing and refinery facilities. The objective of the exercise is to estimate the magnitude of ecological risks associated with the chemical constituents in this effluent and identify the most relevant target species and regions for a program to monitor in order to detect the presence or accumulation of these constituents and biological effects in biological resources.

The ecosystem at risk in this region includes the habitats comprising the water mass, hard substrates, and sediments in the middle inlet and the northern reaches of lower Cook Inlet. Based on the physical characteristics of the substrate and the water mass and the physical dynamics and rigors of the area, this region appears to be marginal habitat for most of the biological assemblages known to occur there. However, robust populations of several infaunal organisms are known to exist in intertidal sediments at least as far north as Polly Creek on the west side of the inlet and Clam Gulch on the east side (e.g., Lees and Houghton 1997).

6.1.2 Identification of Ecological Receptors of Concern.

An ecological receptor is an organism, population, or community that is potentially exposed to stressors either at a location of release (e.g., a discharge or spill) or as a result of chemical migration to offsite areas. The purpose of identifying site-specific ecological receptors is to focus an analysis on the potential for onsite stressors to adversely affect biological resources of concern, particularly sensitive or commercially valuable species or species protected by regulatory criteria. Sensitive species can include those afforded protection by federal, state, or local regulations as well as species serving as indicators of the general health of food webs and ecosystems in an area (i.e., sentinel species such as mussels). All wildlife species occurring in the vicinity of a contaminated or discharging site are potential ecological receptors of concern.

on these habitats as well as demersal, pelagic, and anadromous fish and marine mammals

depend on review of the information presented below and an evaluation of the stressors identified in the effluent.

Realistically, a very limited subset of this broad group of receptors is at risk of being

based on the modeling completed during this program, hydrocarbons are diluted to the point within the permitted mixing
Concentrations of hydrocarbons this low are far below the level at which biological effects have been observed over extended periods of exposure. In cases where the concentrations exceed their MDLs beyond the limits of the mixing zone,
the plumes typically do not come into contact with areas known to support significant

planktonic organisms, pelagic and anadromous fish, and most marine mammals are likely

and from the river systems are probably the most significant biological resource passing through or
nearby river systems, it is quite likely that they enter their spawning rivers very quickly after arriving there. With regard to more the sedentary demersal fish assemblages,
on trawling conducted in the middle inlet (e.g., KLI 1996), populations of demersal fishes are sparse and do not constitute an important resource.

Based on this analysis, the only type of resource that can be considered to include realistic recepto
razor clam resources living in the intertidal zone at Clam Gulch and Polly Creek are the most important known benthic resources in this region. In view of the fact that ubsistence fisheries for clams or other benthic resources are not widely known north of these areas, it is likely that significant resources do not exist. However, we are unaware dal zone
between Polly Creek on the west and Clam Gulch on the east and the mud flats in the

Kasilof River in 1976 (Lees and Rosenthal 1976). This lapse in resource information

Island and Kenai, this data gap seems very significant. Moreover, these appear to be the closest valuable resources available for assessing potential signals o
discharges in the middle inlet.

Stressor Identification and Source Characterization

Stressors for an ecological risk assessment most commonly include chemicals of concern (COCs) in sediments and water in the study area that have
impact natural populations or ecosystems. Sources for these COCs can include discharges from industrial or waste treatment facilities and other types of development activities. For rocarbons associated with oil and gas
activities in the middle inlet. They include dissolved and particulate components that are

collectively referred to as Total Aqueous Hydrocarbons; the state water quality standards for TAqH is 15 µg/L (ADEC 1996).

6.1.4 Identification of Exposure Pathway

An exposure pathway is the means by which a stressor is transported to and received by a target receptor. A complete exposure pathway must include each of the following components (USEPA 1992):

- a transport medium for the stressor;
- a source and mechanism for release of a stressor to the environment;
- a point of contact for the stressor on/in the target receptor; and
- a viable and realistic exposure route for the stressor at the exposure point for the target receptor.

The effluents discharged from production facilities and platforms in middle Cook Inlet comprise a definite "source and mechanism for release" of stressors. The receiving waters of the inlet constitute a transport medium for the stressors. All potential target receptors have multiple points of contact for exposure to stressors in the effluents. Examples of potential points of contact are epidermis, gills, and alimentary canals. However, based on extremely low concentrations indicated by the modeling effort for most of the stressors, there does not appear to be a "viable and realistic exposure route from the source (discharge ports) to the exposure points on the target receptors. All of the stressors fall below their MDLs 10 or more miles away from the beaches where significant clam resources are known to live, adding substantially to the dilution of the hydrocarbons before they would enter the area of concern.

Based on this analysis of the potential stressors in the produced water effluent, it appears that dilution by the receiving water brings the concentrations so low that the exposure route is interrupted. Normally, they would be removed from consideration as valid potential stressors to the nearest known benthic resources. However, because of the high level of concern related to these discharges, it seems prudent to continue monitoring the system but to revise the strategy and framework for the monitoring program.

6.2 Formulation of Recommended Sampling Program

Generally, the objectives of the original EMP, under the Sediment Quality Triad strategy, were to determine: 1) if the contaminants exist in the sediments or water at measurable concentrations: 2) whether or not the concentrations of a contaminant found in the sediments could potentially cause mortality or sublethal (chronic) effects to organisms that might be exposed to them; and 3) if organisms living in the areas at risk had been exposed to the contaminants of concern (specifically petroleum hydrocarbons). Based on the results from that approach and on our ERA problem formulation discussions above, we suggest a partial revision of these objectives for a continued monitoring program in Cook Inlet. The first two of the objectives listed below were among the original objectives and

re
toxicity testing, would change.

area are becoming incorporated in the sediments or water mass at measurable

Objective B: Determine through bioaccumulation and biomarker studies if organisms

Objective C: Develop a comprehensive understandin
small suite of sentinel organisms on sandy beach and mud flat habitats at several locations within Cook Inlet where trajectory modeling indicates the spill.

because the previous testing did not find any toxicity attributable to hydrocarbons and, additionally, concentrations of PAH in the sediments are 40 to 50 times NOAA's ER-

6.2.1 Dual Focus Program

magnitudes, spatial and temporal trends in pollution from the oil industry, we suggest the EMC needs to conside -focus program based on chronic versus potential acute

First, the EMP must continue looking for chronic effects from industry operations in upper inlet; this is their charter mandate. Although our dilution ows that we wouldn't expect to see any significant (or perhaps detectable) concentrations outside of the mixing zone under normal conditions,

The second focus, objective C, is another approach to the charter goals. It

acute discharge of oil on the surface of the inlet. Moreover, it can be accomplished concurrently with the other two objectives. In l experience during the EVOS, where pre- documented, we strongly suggest that the EMC conduct their monitoring program with a goal of establishing baseline data for future acute events.

In actuality, there may be no discernible difference in the methods of sampling in pursuing

However, if the EMC decided that their mandate (or budgetary allowance) was only to accomplish the local chronic would suggest that the most cost- vicinity of the discharges. Far- highly improbable.

However, a catastrophic spill in any other location in the inlet would be sure to impact areas not covered by solely monitoring the upper inlet. Existing studies have highlighted high risks areas throughout the inlet both in terms of the most probable shorelines to be impacted and the sensitivity of various habitats to oiling (Michel et al. 1978; Schlueter and Rauw 1981). It is our assumption that, despite the intense turbulence of the waters in Cook Inlet, there is a strong likelihood that some oil from a surface spill will be driven onto the shoreline by winds. Although a significant amount of the spilled oil may be entrained into the water column and adsorbed onto the SPM, we believe that it will be dispersed extensively, to a point where it will be difficult to detect. Consequently, we argue that the intertidal zone, rather than the subtidal, should be the habitat of concern and the most logical place to focus the sampling. The spatial coverage should focus especially along the regions of highest potential spill impact.

In the case of a catastrophic discharge of aqueous effluents (e.g., rupture of a ballast water pipeline or sunken barge filled with refined product), the intertidal zone may not be the site of greatest impact. However, due to the numerous technical difficulties in subtidal sampling, high variance is often a problem with benthic data sets. Based on our PWS studies, it seems likely that nearby intertidal locations would still incur some level of impact and would be immensely easier to evaluate based on previous years of data.

6.2.1.1 Intertidal Habitats

Collective experience at oil spills suggests that intertidal assemblages have a greater likelihood of exposure to hydrocarbons than subtidal assemblages and hydrocarbons and associated effects is far simpler to detect in intertidal habitats. Both rocky and soft intertidal habitats are common in Cook Inlet. However, rocky habitats are nearly nonexistent on the east side of the inlet north of Kachemak Bay where gravel and sand beaches predominate. On the west side, mud beaches are common in the embayments with rocky and fine textured substrates scattered along the exposed coasts. The biological assemblages on the hard substrates in the middle and upper inlet are severely disturbed by the winter ice that scours the rocks annually. Thus, on the west side, the rocky intertidal biota is generally impoverished, relatively ephemeral, and probably less important to the other species in the marine community than subtidal species or burrowing species in soft habitats (Lees and Houghton 1977). Because most of the populations in rocky habitat are relatively short-lived, they have less time to accumulate the contaminant body burdens.

In contrast, deeper burrowing forms in soft habitats are substantially more sheltered and thus are frequently longer lived and larger than rock-dwelling species. Moreover, soft bottom assemblages in Cook Inlet are far more uniform in intertidal than in subtidal assemblages (Driskell and Lees 1977; Lees and Houghton 1977; Lees 1978; Lees et al. 1980) and therefore, sampling programs can provide statistically more robust data. Moreover, it is easier at intertidal sites to control important variables such a sediment grain size and elevation than at subtidal sites. This allows better "control" over these factors where they are important to the results of other analyses (e.g., the influence of the fine fraction in sediments and hydrocarbon or trace metals concentrations.) Therefore, considering these conditions and the limited budget of the EMC, we suggest the EMP should focus on soft intertidal substrates to the exclusion of rocky sites.

there is value in continuing infrequent but periodic sampling of subtidal sediments near the

metals associated with produced water discharges or refinery effluents.

Field Sampling Plan

Considering the limited budget of the EMC, we would suggest two alternative concepts

greater number of sites in a rotating annual visit plan. The first alternative allows the EMC to b
to know a few sites very well. The second alternative builds the temporal patterns over a longer length of time but gives a better spatial overview of the inlet. Each option tradeoff in temporal or spatial coverage but either could still be the basis of long term monitoring.

We favor the second option and think it could work in this manner. Divide the inlet into 5 or 6 geographic regions (e.g., upper Inlet, east side, w
Shelikof) and every year the field team would visit a different region. With travel logistics reduced, more data could be collected from more sites within each region. If the program , collections might be made by float plane, visiting 2 to 3 sites per low tide. Finally, there is a compromise plan whereby the inlet would be

6.2.1.3 Random Site Selection

During the aftermath of the EVOS event, there was debate over the significance of findings from the three intertidal studies (NOAA, Trustees, Exxon) based on the *ad hoc* in the eld beginning 4 days post spill. It used non-
methods for selecting sites while the other two studies arrived much later with completely randomized sites selected from geographic information system (GIS) information.

their final results represented the best estimate of a given parameter for all of PWS. In contrast, the design was limited to saying their results (with more intensive

PWS but may be biased as a summary estimate.

-term monitoring plan and should be h all available knowledge and input from multiple interests. Pilot studies may be justified in regions that are sparsely surveyed. In Cook Inlet, we would

sampling design. Regarding site selection, it seems more important to select sites that

line statistical value that accurately reflects regional variance. The latter may be important

natural processes of the region. Moreover, because of limitations in time, funding, and adequate scientific resources, the truly random approach will probably

sufficient replication to provide a realistic description of the systems being examined. The resulting data set will therefore be characterized by high variability and will consequently gloss over the existence of major effects.

An important part of the role of the modified stratified random approach in site selection is identification of appropriate and inappropriate sampling habitats and regions within these habitats. Initially, decisions must be made on the characteristics for appropriate sampling habitats. Issues to be considered include substrate and sediment type, biological resources, exposure to physical and chemical stresses, elevation, access, and previous scientific research in the areas. For example, in Kamishak Bay, we know that, in terms of hydrocarbon exposure, the southern part of the bay will be different from the northern part because there are natural seeps in Oil Bay. Both regions may be acceptable but they should be placed in separate strata. There is little point in randomly selecting sites around the coastline if we would be better served selecting sampling locations with foresight on sediment transport, spill risk, and wave exposure. Furthermore, it is worthwhile to consider areas where previous studies have been performed because those studies provide a useful historic perspective.

When the appropriate sampling areas have been separated from the inappropriate areas, it is then possible to commence rational and random selection of sampling areas. At this time, it is advisable to select from within the appropriate areas the actual sampling sites by a random process. Following selection of the actual sampling sites, a random process should be used to select the individual locations for repeated sampling (by either quadrat or core sampler) at carefully selected elevations within each newly selected sampling site. The positions of these individual sampling locations should then be mapped and, if possibly, physically marked to facilitate relocation and resampling in subsequent surveys.

6.2.2 Sampling Methods

Although there are many aspects of an intertidal community that could be examined in monitoring study, time and costs would require focusing on just a few. We would recommend a quick survey approach collecting population data (e.g., transect burrow counts and length-weights on a modest sample size of macro infauna), tissue samples for bio-markers and hydrocarbon body burdens of select species, and surface sediments. We would not recommend toxicity testing unless other results justified the expense. We would also not recommend subtidal sampling for reasons stated above.

We also see a need for a ground survey to document the biota along the western shoreline from Tuxedni Bay to the West Forelands, on Kalgin Island and along the eastern shoreline from Kasilof and Kenai. We found no survey data describing these regions.

6.3 Relevant Habitats and Receptors of Concern

The various environmental features and the infaunal biota for sand beaches or on mud flats are generally fairly uniform over great distances on both the east and west sides of Cook Inlet. Therefore, it is easier to identify suitable target species for use as sentinel organisms. For example, robust populations of the razor clam (*Siliqua patula*) can be sampled on sandy beaches from Clam Gulch to at least Homer on the east side of the inlet,

and from Polly Creek to Amakdedori on the west side. Likewise, robust populations of the bivalve *Macoma balthica* can be found on protected mud flats from Kasilof to Port Graham on the east side of the inlet and from at least Tuxedni Bay to Amakdedori on the west side. The soft-shell clam *Mya arenaria* is another widespread candidate for use as a sentinel in mud flats. All of these species are long-lived (at least 10 years) and therefore are somewhat good indicators of long-term conditions in a location. In many cases, the larger specimens of clams are used for human subsistence and, in the case of razor clams, harvested commercially

6.3.1 Analysis of PAH in Bivalve Tissues

Analysis of bivalve tissues for PAH provides very useful information and we recommend that it be included in any future monitoring studies for the EMP. We recommend that all specimens collected for tissue analysis be allowed to purge in clean seawater (i.e., depurate) for 24 hours in order to eliminate sediment from the alimentary tract and the mantle cavity, etc. Analysis with undepurated animals has the strong potential to indicate erroneous levels of contaminants because the concentration of contaminants included in gut contents is analyzed concurrently with the tissue concentrations. Consequently, the concentrations reported are higher than is accurate for tissue concentrations.

6.4 Summary of Recommended Sampling Program

The monitoring program we propose would work like this. First, we recommend conducting a one-time reconnaissance in the region just south of the East and West Forelands. The proposed survey areas include: West Forelands south to Polly Creek on the west side of the inlet; 2) sites on Kalgin Island; and 3) East Forelands south to Clam Gulch on the east side of the inlet. The objective of this survey is to describe intertidal assemblages on hard and soft substrates and identify biological resources that could be used as sentinel species.

In line with the one-time survey, we also recommend several one-time analyses to better understand the PAH sources within the region and thus, better understand the processes creating the background levels in the sediments. The tasks include collection and analysis of several poorly defined PAH sources such as coal from other sites in Homer and around Cook Inlet, archived coal samples at UAF, natural oil seeps, PAH in terrestrial litter and other upstream sources in the Matanuska and Susitna Rivers.

Second, we recommend sampling selected species in intertidal areas with soft sediments in areas of lower Cook Inlet that have been identified as being at risk of suffering: 1) chronic effects from exposure to effluents from discharges (based on the modeling program described in this report) or 2) acute effects from exposure to crude oil released during a catastrophic event (based on trajectory modeling studies). Likely areas for evaluation of chronic effects include: the west and east sides of the inlet south of the Forelands, and Kalgin Island. Likely areas for establishing baseline data sets for evaluation of acute impacts from catastrophic events include: Clam Gulch (sandy), Deep Creek (sandy), Mud Bay at the base of Homer Spit (muddy), and Port Graham (muddy) on the east side of the inlet; and Polly Creek (sandy), Chinitna Bay (muddy), Bruin Bay (muddy), Amakdedori Beach (sandy), and Douglas River (muddy) on the west side of the inlet. Each sampling

site would be permanently marked during the first survey to facilitate replicate sampling during subsequent surveys.

The target organisms recommended for this study are all clams and occur in appropriate habitats throughout the region. They include *Macoma balthica* and *Mya arenaria* in the mud flats and the razor clam *Siliqua patula* on sandy beaches. We recommend that only a limited suite of variables be measured for each site and species. For sediments, these variables include: PAHs, P450 reporter gene system assays, particle grain size, and total organic carbon. For the clams, these variables include: animal density, based on counts of burrows in quadrats for *Mya* and *Siliqua* and *Macoma* in core samples; PAHs in tissues and P450 reporter gene system assays for all three species. In addition, we recommend measuring shell length and annual growth checks for a limited number of specimens in each species to provide an estimate of size and age structure of the populations at each sampling location.

6.5 Suggestions for Further Analytical Chemistry Work

6.5.1 Hydrocarbons

Include perylene in summation of TPAH. Present data both with and without perylene.

Be more consistent in correcting PAH concentration data for surrogate recoveries

Conduct library search (or laboratory studies) to identify and add selected biomarkers (unique to coals and/or source oils) to target analyte lists.

Modify calculation and reporting of TPAH in low concentration samples with high MDLs and numerous components reported below the MDL. This will correct for spurious electronic noise signal contributing to background signal when using GC/MS SIM. Try new TPAH data reduction algorithm developed by Payne and Denoux that defines TPAH as follows:

$$\text{TPAH} = \Sigma \text{ (each component/component-specific MDL) x average MDL}$$

This approach will normalize each component concentration to its detection limit and absolutely minimize the contribution from low-level components at or below their respective detection limits. Then by multiplying the sum by the average MDL for all analytes, the overall value of the TPAH result is brought back to the correct order of magnitude. This will correct for anomalously high values of TPAH in samples that have very high detection limits and excessive electronic noise.

Screen lab data so that electronic noise signal in low concentration samples is eliminated. It contributes to TPAH and generates spurious data. If it can be identified as noise at the laboratory, do not include it in the data deliverable.

Insist on minimum 10 g sample size (especially with tissues) to keep MDLs lower and avoid problems of over reporting TPAH because of small denominator in data reduction algorithm.

Have the lab continue to run source oils for double ratio determinations during each year of the program to account for possible changes in analytical procedures and any variation in the source oil or new products.

6.5.2 Additional In-Depth Source Characterization

Sample coal outcrops and coal tides (in Homer and elsewhere).

Characterize additional oil seeps in Chinitna Bay and elsewhere.

Characterize PAH in terrestrial litter (leaves, decaying organic matter, etc.).

Obtain additional upstream river sources (Matanuska & Susitna Rivers).

Analyze PAH distribution in archived coal samples at UAF (Rao 1986).

Analyze additional samples from Kenai River study with larger percent sand loading. Samples C1 & S2 at a minimum. Include coarser sediments from Kenai area C1 and S2 to look for total naphthalenes in coarser coal fragments/particles.

Undertake dissolved and particulate water sampling down stream of diffuser sites for source characterization and model validation. Complete a systematic water sampling program in the region of the Produced water diffuser to examine dissolved and dispersed oil droplet plume. Filter water samples at the time of collection to facilitate differentiation of dissolved phase and particulate/oil phase. Use to document adsorption behavior onto SPM and to validate PLUME model predictions.

Biomarkers – add several sterane tri-triterpane biomarkers that are characteristic Cook Inlet, Crude, Cook Inlet seep oils, and different coal sources.

6.5.3 Weathering Studies

Evaluate leaching/biodegradation of PAH from suspended oil-droplet/SPM agglomerates. Individual/dissolved PAH adsorbed onto SPM has already been investigated to limited extent, but additional data are needed on oil-droplet/SPM behavior with multiple PAH constituents.

Produced water/SPM interactions and subsequent weathering (leaching) and biodegradation should be investigated to better understand true fate of PAH loading from produced water discharges into heavy SPM-laden waters of Cook Inlet.

Characterize leaching/biodegradation of PAH from suspended coal particulates to rule out weathering behavior in assessing relative magnitude of oil versus particulate coal input and bioavailability of PAH in marine environment.

Obtain a sample of Produced Water for controlled produced water/SPM interaction studies and subsequent weathering and sedimentation experiments.

6.5.4 Sedimentation Studies

Characterize sedimentation rates and resuspension behavior of coal versus background sediments as function of particle grain size, organic content, salinity, flocculation behavior.

Examine chemical composition of coal fines and coal slurries (characterize dissolved vs. particulate phases for PAH and other organics as well as potential metals of environmental concern).

Examine naphthalene/TPAH ratios and grain size data in age dated cores from MMS programs to further evaluate importance of coal-derived PAH input over time.

6.5.5 Toxicity Studies

Toxicity testing of coals in fine and coarse state and as slurries (evaluate both particulate and dissolved phase).

6.6 Physical Oceanographic Studies

A crucial part of a well-designed monitoring program involves physically selecting sampling sites appropriate for the program's objectives. One category of sites in the EMP would be locations that would be likely to be impacted in a spill event. However, from our EVOS experience, shorelines beyond the direct path of the spill were incompletely oiled, for example, the windward side but not the lee side of an embayment might be oiled as tidal currents carried the slick past the mouth. A similar situation may occur in Cook Inlet depending on numerous factors including prevailing winds, shoreline topography, and tidal currents. Filling data gaps in physical oceanography would be pertinent to both the EMP and PROPS committee projects.

The physical oceanographic characteristics of Cook Inlet also determine the transport pathways of the suspended sediments and any oil products adsorbed on their surface. It is germane to the EMP to identify the transport pathways both at basin-scale and at a local scale near the sampling sites. In fact, modeling efforts are hampered by the lack of data regarding currents and turbulence in Cook Inlet.

7. Summary

During the five years of the Environmental Monitoring Program (1993 through 1997), sediment and/or tissue samples were collected at 87 different sites distributed in 13 discrete regions. Nine of the regions are located in Cook Inlet and three are located on the northeastern shore of the Alaska Peninsula in northwestern Shelikof Strait. Studies conducted during the EMP provide twelve lines of evidence that could provide direct evidence of hydrocarbon contributions from oil and gas activities in the inlet. These include: chemistry analyses for 1) PAH and 2) aliphatic hydrocarbons in sediments; 3) PAH analyses of SPMDs as an indication of hydrocarbons in the water column; PAH analyses for 4) mussel and 5) mud clam tissues; a suite of toxicity tests, including 6) amphipod, 7) echinoderm larval development, and 8) Microtox bacterial assay, P450 reporter gene system assays of 9) sediments and 10) bivalve tissues, 11) P4501A testing of halibut liver, and finally, 12) analysis of halibut tissues for bile metabolites and liver enzyme induction, which indicate exposure to hydrocarbons.

These approaches come at the question of potential hydrocarbon contamination from three principal directions. Approaches 1 through 3 are useful primarily for determining if the contaminants exist in the sediments or water at measurable concentrations. Approaches 6 through 9 address whether or not the concentrations of a contaminant found in the sediments can potentially cause mortality or sublethal (chronic) effects to organisms that might be exposed to them. Finally, the remaining five approaches (4, 5, 10, 11, and 12) are useful for determining if organisms living in the areas at risk have been exposed to the potential contaminants.

Analysis for polycyclic aromatic hydrocarbons was conducted for all but one of the regions examined. PAH concentrations reported in this study are very low. They averaged about 1/50th of the level estimated by NOAA to cause minimal effects in marine organisms. Moreover, distribution of PAH in sediments did not appear to exhibit predictable patterns. Except for the Kenai River, higher concentrations are found at the sites most distant from the sources of oil contamination, but these may be the depositional regions.

SPMDs were deployed in the water column in the vicinity of terminal facilities in Trading Bay or Granite Point, in the Beluga River region, and in Kachemak Bay during three early surveys to assess PAHs in the water column. The SPMDs provided one of the few data sets that suggested exposure to hydrocarbons introduced to Cook Inlet by the oil industry. SPMDs deployed in Trading Bay assimilated PAHs with a fingerprint similar to that found in the produced water effluents discharged from the Trading Bay facility.

Regarding the question of whether hydrocarbons contributed to Cook Inlet by oil and gas industry activities are accumulating in Cook Inlet, data contained in the EMP database indicate that neither PAH nor aliphatic hydrocarbons in sediments exhibit spatial patterns that can be related to petroleum activities. The PAH fingerprints were generally not characteristic of Cook Inlet or Alaska North Slope crude. The sources are varied and mixed but they cannot be directly attributed to Cook Inlet oil and gas development operations. In addition, no evidence of EVOS or ANS oil was observed in any of the

subtidal sediments (including Shelikof Strait). In fact, the fingerprint observed in many cases was similar to that of forms of coal from one of the several coal sources in the inlet.

PAH concentrations were also measured in mussel and clam (bivalves) tissues. Measurements were made on: mussels deployed in cages suspended in the water column in Trading Bay and near the Beluga River; mud clams collected from subtidal sediment samples in Kachemak and Kamishak Bays; resident intertidal mussels collected from three sites in Shelikof Strait; and resident intertidal populations of mud clams from Tuxedni Bay and Chinitna Bay. The mussel watch experiments were deemed unsuccessful. Moreover, sufficient quantities of subtidal mud clams could not obtained, and that approach was also discontinued. The most notable finding is that PAH concentrations in all of the bivalves examined are very low. Concentrations observed were about $1/50^{th}$ of the concentrations observed in mussels in Prince William Sound and Seward in 1991. Based on hydrocarbon "fingerprints," the predominant sources were coal, diesel, and a non-Cook Inlet crude oil.

P450 reporter gene system assays were used during the EMP to evaluate exposure of clams to petroleum hydrocarbons. Highest responses were observed in tissues from mud clams from Tuxedni Bay and mussels from Cape Douglas. All of the values observed were well within a range considered representative of baseline conditions. Moreover, correlation analysis suggests that petroleum hydrocarbons were not driving the observed P450 response.

Fishes were collected at several locations throughout Cook Inlet to assess exposure to hydrocarbons through analysis for bile metabolites and P4501A reporter gene system assays. The only fish species examined, Pacific halibut (*Hippoglossus stenolepis*), was evaluated once; specimens came from Kachemak and Kamishak Bays. Concentrations of bile metabolites were low or below detection limits in the samples from both locations, indicating low exposure to hydrocarbons, but values indicated a higher level of exposure to hydrocarbons in Kachemak Bay than in Kamishak Bay.

Several types of sediment toxicity tests were used to assess impairment of sediment quality in Cook Inlet. Significant mortality was observed in amphipods following exposure to bulk sediments from samples from Trading Bay, the East Forelands, Kamishak Bay, and Kachemak Bay. However, correlations between the degree of toxicity to the amphipods and concentrations of PAH in the sediments were not significant. Instead, the level of mortality showed a significant positive relationship with percent silt+clay in 1997. In fact, EPA has reported that mortality of the amphipod used in this study is elevated in sediments with low concentrations of fine sediments such as occur in many areas of Cook Inlet.

Significant toxicity was observed in echinoderm larval development tests performed using porewater from sediments from Kachemak and Kamishak Bays. However, the relationship between level of toxicity and concentration of petroleum hydrocarbons was poor. The relationship between levels of toxicity and initial concentrations of ammonia in the pore water was high, however, suggesting that ammonia was a more likely cause of the observed mortality than petroleum hydrocarbons.

The P450 reporter gene system assay was performed on sediments from Trading Bay, the East Forelands, Kamishak Bay, Kachemak Bay, and thee locations in Shelikof Strait. Highest values in sediment assays were observed for Trading Bay and Cape Nukshak, but no significant effects were observed in the testing.

The toxicity data provide a compelling argument that contaminant effects related to hydrocarbon contamination are lacking in the regions sampled in Cook Inlet or Shelikof Strait. There is scant evidence from the various types of toxicity tests performed to suggest either temporal trends or spatial patterns. Based on the low concentrations of PAH observed in the sediments (relative to suggested levels of PAH causing measurable effects, sediment grain size and ammonia appear to be far more likely causes of the mortality observed in these tests. Average concentrations of PAH in sediments in Cook Inlet are only about 1/50th of the NOAA guideline for minimal effects from PAH.

PLUMES modeling studies were performed during the preparation of this report to provide estimates for how far away from the discharges from oil and gas facilities the discharged hydrocarbons could be detected. The modeling indicates that dilution progresses quickly beyond the boundaries of the near-field mixing zone at upper Cook Inlet discharges. Most plumes were undetectable beyond their mixing zone. However, using the sensitive MDL (0.1 ug/L) attainable by top analytical laboratories and PAH values in the effluents from the NPDES applications, it seems theoretically possible to track PAHs from some discharges a significant distance beyond their mixing zones. The most extreme results from the modeling were predicted for Trading Bay and East Forelands production facilities. The model predicted the Trading Bay discharge, with average peak currents around Trading Bay and East Forelands in excess of 4 knots, would be detectable throughout its tidal excursion up to 25 miles (41 kilometers) away on the flood and 14.4 miles (24 kilometers) on the ebb. The East Forelands discharge was calculated to be detectable slightly over 12 miles (20 kilometers) away.

Throughout the diverse variety of methodologies employed to examine a wide variety of potential indicators for contamination in a wide variety of areas in the inlet and in northwestern Shelikof Strait, the finding that appears time after time is that the various analyses were unable to establish a relationship between signals for hydrocarbons and observed effects in the sediments or tissues. Concentrations of hydrocarbons in the sediments are at least 50 times than those that could cause mortality or sublethal effects to organisms exposed them. Likewise, the entire suite of toxicity tests exhibited no relationship between toxicity and PAH concentrations in the sediments. Regarding the question of whether organisms living in the region appear to have been exposed to hydrocarbons from Cook Inlet oil and gas activities, again, the evidence in the EMP database indicates there has been little or no exposure. Generally, hydrocarbons observed in tissues were barely above detection limits and, when observed, they appeared to represent refined products or pyrogenic hydrocarbons. In some cases, the hydrocarbons observed appeared to represent coal.

It appears, based on an overwhelming weight of evidence from the many aspects of this program, that hydrocarbon contamination or effects related to hydrocarbon contamination are either lacking or, if they were observed, occurred at levels very near the levels of

detection for the particular method. Ninety-nine percent of the observations found no evidence of contamination from oil activities in Cook Inlet or effects that could be related to hydrocarbon concentrations in the sediment.

Recommended strategic changes to the program are as follows:

1) Discontinue the toxicity testing element of the program.

2) Discontinue the strict random sampling strategy within regions.

3) Replace subtidal sampling with intertidal sampling.

4) Establish a baseline program in several of the sites where trajectory modeling predicted a high likelihood of exposure to crude oil in the event of a catastrophic spill..

5) Discontinue trace metals monitoring in sediment and tissues.

We recommend the following objectives be adopted to focus the continuation of the EMP.

Objective A: Determine if the potential contaminants associated with the activity or area are becoming incorporated in the sediments or water mass at measurable concentrations.

Objective B: Determine through bioaccumulation and biomarker studies if organisms living in the areas at risk have been exposed to the potential contaminants.

Objective C: Develop a comprehensive understanding of baseline conditions for a small suite of sentinel organisms on sandy beach and mud flat habitats at several locations within Cook Inlet where trajectory modeling indicates the likelihood of exposure to crude oil is high in the event of a catastrophic spill.

A recommendation for a revised approach to the monitoring program for Cook Inlet has been developed based on a qualitative problem formulation exercise and the modeling efforts conducted for this study. Based on this analysis, benthic assemblages in soft substrates are the only type of resource that may include realistic receptors. For this program, the stressors are petroleum hydrocarbons associated with oil and gas activities in the middle inlet. Based in the modeling exercise using PLUMES, concentrations of the most abundant hydrocarbon are diluted quite rapidly following discharge. Nevertheless, the effluents discharged from production facilities and platforms in middle Cook Inlet do comprise a definite “source and mechanism for release” of stressors. Also, the receiving waters of the inlet constitute a transport medium for the stressors, and all potential target receptors have multiple points of contact for exposure to stressors in the effluents, e.g., epidermis, gills, and alimentary canals. Based on extremely low concentrations indicated by the modeling effort for the stressors, however, there does not appear to be a “viable and realistic exposure route from the source (discharge ports) to the exposure points on the target receptors. All of the stressors fall below their MDLs 10 or more miles away from the beaches where significant clam resources are known to live. Consequently, the stressors would be substantially more diluted before they would enter the area of concern.

We recommend a two-pronged program to address both potential chronic effects and acute effects to the environment. First, the EMP must continue looking for chronic effects from industry operations in upper inlet. Secondly, the EMC should conduct its monitoring program with a view toward establishing baseline data for future acute events. We recommend that sampling be focused in the intertidal zone rather than the subtidal.

The proposed monitoring program is described below.

First, we recommend conducting a one-time reconnaissance survey to describe intertidal assemblages on soft substrates and identify biological resources that could be used as sentinel species in the region just south of the East and West Forelands. In line with the one-time reconnaissance survey, we recommend one-time analyses of several poorly defined PAH sources. Second, we recommend sampling selected species in intertidal areas with soft sediments in areas of lower Cook Inlet that have been identified as being at risk of suffering chronic effects from exposure to effluents from discharges or acute effects from exposure to crude oil released during a catastrophic event.

The target organisms recommended for this study are all clams and occur in appropriate habitats throughout the region. They include mud clams and soft-shell clams in the mud flats and razor clams on sandy beaches. For sediments, we recommend evaluating PAHs, P450 reporter gene system assays, particle grain size and Total Organic Carbon. For the clams, we recommend measuring animal density, PAHs in tissues, and P450 reporter gene system assays.

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Glossary

9.1

(Adapted from KLI 1997a, CIRCAC Final Report)

A

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ADL - Arthur D. Littl

AHC Aliphatic hydrocarbon

Aliphatic hydrocarbons Fully saturated normal alkanes (paraffins) and branched alkanes, n C10 to n-
(C20) which are often the most abundant isoprenoids in petroleum hydrocarbons.

Ampelisca abdita Amphipod species used for solid-

Anadromous – Fish that go up rivers to spawn

Anthropogenic Resulting from the influence of human activities (refers to hydrocarbon input)

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

ASTM American Society of Testing and Materials

B

–

B[a]PEq Benzo[a]pyrene equivalents

BETX Benzene/ethyl benzene/toluene/xylene

- including microbiota (refers to hydrocarbon input)

C

cc -

CIRCAC - Cook Inlet Regional Citizens Advisory Council

cm - Centimeter

CPI – Carbon Preference Index

CRUDE Index - A summation of TPAH, TAHC and UCM weighted to assess the petrogenic fractions (Payne et al. 1998)

D

Demersal – Living in association with the seafloor

Depurate – Flush or purge of sediments and associated contaminants

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

E

EMC - Environmental Monitoring Committee

EMP - Environmental Monitoring Program

ENRI - Environment and Natural Resources Institute, University of Alaska Anchorage

EPA - U.S. Environmental Protection Agency

ERA – Ecological Risk Assessment

ERL – Effects Range - Low

ERM – Effects Range - Median

EVOS - *T/V Exxon Valdez* oil spill (March 1989)

F

FFPI - Fossil fuel pollution index

Fossil fuel pollution index (FFPI) - The fossil fuel pollution index is the ratio of fossil-derived PAHs to total PAHs

calculated as FFPI = ~ + F + P + D)[1?AH x 100, where:

N (Naphthalene series) = C0-N + C1-N + C2-N+C3-N+C4-N

F (Fluorene series) = C0-F + C1-F + C2-F + C -F

P (Phenanthrene/Anthracene series) = C0-A +C0-P + C1-P+C2-P+C3-P+ C4-P

D (Dibenzothiophene series) = C0-D + C1-D + C2-D + C3-D.

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

FID/GC - Flame ionization detector/gas chromatogram

G

g - Gram

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

GC/MS - Gas chromatography with mass spectrometry.

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

GIS - geographic information system

Global Positioning System - A satellite-based navigation system

GPS - Global positioning system

K

KLI - Kinnetic Laboratories, Inc.

L

L - Liter

LTEMP – Long-Term Environmental Monitoring Program being performed for the PWS RCAC

M

m - Meter

MDL - Method detection limit

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

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

µg - Microgram

µg/g - Micrograms per gram or parts per million

µm - Micron

Microtox~ sediment bioassay - A toxicity testing method based on emission of light by the bacterium,

mg/L - Milligrams per liter (parts per million)

min – Minutes

MMS – Minerals Management Service

MPI - Mytilus Petroleum Index

N

ND – Non-detect

Near-field - area within the mixing zone of a discharge source

ng/g - Nanograms per gram (parts per billion)

NOAA - National Oceanic and Atmospheric Administration

NOS - NOAA National Ocean Services

NPDES – National Pollutant Discharge Elimination System

Null - A database value description which means "not applicable"

P

P450 RGS -
P450 in test cells (a reporter gene system – organic contaminants; measures benzo[a]pyrene equivalents (B[a]PEq) and toxic equivalents.

PAH -

Particle grain size - Percent gravel, sand, silt, and clay

Pelagic –

Petrogenic Resulting from natural geologic processes which originally form

Planktonic Floating, weakly swimming or drifting plant or animal life of the sea

- ne size and dilutions of effluents

Polycyclic (or polynuclear) aromatic hydrocarbons (PAH) 2- -ring polycyclic consisting of unsubstituted (parent) compounds, such as naphthalene, and substituted such as C1-

ppb

ppt Parts per thousand (‰)

- Prince William Sound

PWS RCAC - egional Citizens Advisory Council

- Resulting from the activity of fire or very high temperature (Refers to creosote)

Q

- Quality control

R

RCAC - Regional Citizens Advisory Council

RGS – Reporter Gene System

S

SD – Standard deviation

SE – Standard error

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

SIM - Selected ion monitoring

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

SPM - Suspended particulate materials

SPMD - Semipermeable polymeric membrane device

SQT – Sediment Quality Triad

T

TAH – Total aromatic hydrocarbons

TAHC - Total aliphatic hydrocarbons

TaqH - Total aqueous hydrocarbons

TOC - Total organic carbon

Total aliphatic hydrocarbons - See aliphatic hydrocarbons

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

Total polycyclic aromatic hydrocarbons - See polycyclic aromatic hydrocarbons

TPAH - Total polycyclic aromatic hydrocarbons

TSS – Total suspended solids

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US U. S. Environmental Protection Agency

Van Veen grab Device used for collection of subtidal marine sediments

WSF – Water soluble fraction

ZIP – A commonly used utility to compress computer files

9.2 List of Chemical Abbreviations Used for Hydrocarbon Compounds

List of Target Analytes for PAH Analyses in CIRCAC Monitoring Programs

PAH	Abbreviation used in Graphics
Naphthalene	N
C1-Naphthalenes	N1
C2-Naphthalenes	N2
C3-Naphthalenes	N3
C4-Naphthalenes	N4
Biphenyl	BI
Acenaphthylene	AC
Acenaphthene	AE
Fluorene	F
C1-Fluorenes	F1
C2-Fluorenes	F2
C3-Fluorenes	F3

Phenanthrene	
	A
C1 Phenanthrene /Anthracene	
- Phenanthrene /Anthracene	P/A2
C3-	P/A3
C4 Phenanthrene /Anthracene	
	D
C1 Dibenzothiophene	
-Dibenzothiophene	D2
C3-	D3
Fluoranthene	FL
Pyrene	
-Fluoranthenes/Pyrene	F/P1
Benzo(a)anthracene	
	C
C1 Chrysenes	
-Chrysenes	C2
C3-	C3
C4 Chrysenes	
	BB
Benzo(k)fluoranthene	BK
Benzo(e)pyrene	
	BAP
Perylene	PER
Indeno(1,2,3-	IP
Dibenzo(a,h)anthracene	DA
Benzo(g,h,i)perylene	
	TPAH

Appendix A - Modeling Data

A Platform Anna

FLOOD

Nearfield Velocity (m/s)	Tidal Transport (m)	Avg Farfield Velocity(m/s)	Napthalene Conc (ug/L)	Dilution	Plume Width	Distance (m)
0.30	29916	1.43	0.080	32480	17	605.9
0.87	29075	1.50	0.080	32480	10	1353
1.33	27490	1.53	0.080	32480	8	1862
1.62	25364	1.53	0.080	32480	7	2156
1.78	22914	1.52	0.080	32480	7	2312
1.88	20276	1.48	0.080	32480	7	2412
1.97	17498	1.43	0.080	32480	6	2498
2.02	14620	1.35	0.080	32480	6	2544
1.99	11728	1.25	0.080	32480	6	2518
1.88	8941	1.13	0.080	32480	7	2405
1.68	6379	0.98	0.080	32480	7	2216
1.41	4152	0.82	0.080	32480	8	1942
1.09	2352	0.65	0.080	32480	9	1602
0.73	1041	0.48	0.114	22970	9	913.6
0.36	258	0.36	0.322	8121	8	245.2
			2635	1	0.3	0
EBB						
0.14	26620	1.27	0.099	26500	38	2700
0.53	26138	1.34	0.080	32480	12	934
0.89	25118	1.40	0.080	32480	10	1372
1.22	23604	1.43	0.080	32480	8	1740
1.48	21664	1.43	0.080	32480	7	2012
1.67	19397	1.42	0.080	32480	7	2204
1.81	16893	1.38	0.080	32480	7	1601
1.89	14230	1.32	0.080	32480	7	2421
1.91	11493	1.23	0.080	32480	7	2435
1.83	8803	1.11	0.080	32480	7	2359
1.66	6292	0.97	0.080	32480	7	2193
1.42	4078	0.81	0.080	32480	8	1950

	2252	0.63		32480	9	
0.74	914		0.114	22970	9	922.1
0.27	192	0.27	0.322	8121	9	196.2
			2635	1	0.3	0

B Platform Baker

FLOOD

Nearfield Velocity (m/s)	Tidal Transport (m)	Avg Farfield Velocity(m/s)	Napthalene Conc (ug/L)	Dilution	Plume Width	Distance (m)
0.191	7146	0.58	0.10	8169	10	258
0.485	6659	0.62	0.10	8169	6	515
0.749	5771	0.62	0.10	8169	5	709
0.905	4580	0.58	0.10	8169	5	815
0.918	3268	0.50	0.10	8169	5	823
0.801	2030	0.40	0.10	8169	5	745
0.611	1013	0.28	0.10	8169	6	611
0.398	287	0.40	0.10	8169	7	445
			813	1		0
EBB						
0.323	27035	0.83	0.10	8169	8	382
0.417	26502	0.86	0.10	8169	7	461
0.553	25804	0.87	0.10	8169	6	568
0.661	24929	0.89	0.10	8169	5	647
0.740	23920	0.90	0.10	8169	5	703
0.822	22795	0.90	0.10	8169	5	759
0.904	21552	0.91	0.10	8169	5	814
0.997	20183	0.90	0.10	8169	4	875
1.071	18694	0.90	0.10	8169	4	922
1.102	17130	0.88	0.10	8169	4	941
1.124	15527	0.86	0.10	8169	4	955
1.103	13923	0.84	0.10	8169	4	942
1.105	12334	0.82	0.10	8169	4	943
1.095	10750	0.79	0.10	8169	4	937
1.075	9187	0.75	0.10	8169	4	924

1.046	7660		0.10	8169		906
0.995	6191		0.10	8169		873
0.944	4796	0.61	0.10	8169	5	841
0.860	3497	0.54	0.10	8169	5	785
0.768	2325	0.46	0.10	8169	5	723
0.625	1322	0.37	0.10	8169	6	621
0.431	562	0.26	0.10	8169	7	472
0.175	126	0.17	0.10	8169	10.5	242
			813	1		0

C Platform Bruce

FLOOD

Nearfield Velocity (m/s)	Tidal Transport (m)	Avg Farfield Velocity(m/s)	Napthalene Conc (ug/L)	Dilution	Plume Width	Distance (m)
0.27	34086	1.63	0.07	32650	7	525
0.93	33225	1.71	0.07	32650	4	1329
1.53	31454	1.75	0.07	32650	3	1934
1.93	28960	1.75	0.07	32650	2	2294
2.14	26029	1.72	0.07	32650	2	2476
2.21	22897	1.67	0.07	32650	2	2535
2.23	19697	1.61	0.07	32650	2	2556
2.23	16482	1.53	0.07	32650	2	2553
2.18	13309	1.42	0.07	32650	2	2507
2.07	10253	1.29	0.07	32650	2	2415
1.88	7408	1.14	0.07	32650	3	2251
1.62	4885	0.97	0.07	32650	3	2017
1.27	2801	0.78	0.07	32650	3	1682
0.87	1262	0.58	0.07	32650	4	1264
0.44	319	0.44	0.07	32650	5	765
	0	0.44	2165	1		0
EBB						
0.07	28924	1.39	0.07	32650	13	194
0.55	28477	1.46	0.07	32650	5	900
1.01	27352	1.52	0.07	32650	3	1419

	25602	1.55		32650	3	
1.73	23340		0.07	32650		2110
1.91		1.51	0.07		2	2273
	17920	1.46		32650	2	
2.00	15048		0.07	32650		2354
1.99		1.30	0.07		2	2344
.91		1.18	0.07		2	2279
	6733	1.04		32650	3	
1.50	4393		0.07	32650		1904
1.18		0.68	0.07		3	1590
	1042	0.48		32650	4	
0.33	234		0.07	32650		608
			2165			0

D

FLOOD

Nearfield Velocity (m/s)	Tidal (m)		Napthalene Conc (ug/L)	Dilution		Distance (m)
0.421		2.32	0.12		9.808	356
	50866	2.44		5759	6.389	
1.731	48905		0.12	5759		1005
2.378		2	0.12	5759		1264
2.839		2.55	0.12		3.777	1435
	37881	2.51		5759	3.587	
3.370	33188		0.12	5759		1620
3.479		2.31	0.12		3.412	1657
	23263	2.15		5759	3.423	
3.324	18380		0.12	5759		16
3.069	13777		0.12	5759		1516
2.723		1.48	0.12		3.857	1392
	6023	1.20		5759	4.239	
1.673	3195		0.12	5759		980
1.022		0.58	0.12		6.295	684
	260	0.36		5759	10.59	

	0		699	1		0
EBB						
0.472	45756	2.35	0.12	5759	9.263	387
1.188	44561	2.48	0.12	5759	5.839	764
1.829	42388	2.56	0.12	5759	4.706	1046
2.446	39309	2.60	0.12	5759	4.069	1290
2.920	35446	2.59	0.12	5759	3.724	1464
3.210	31032	2.54	0.12	5759	3.552	1565
3.311	26337	2.44	0.12	5759	3.497	1600
3.286	21587	2.31	0.12	5759	3.511	1592
3.177	16934	2.14	0.12	5759	3.57	1554
2.964	12513	1.93	0.12	5759	3.696	1479
2.639	8478	1.68	0.12	5759	3.917	1362
2.160	5023	1.40	0.12	5759	4.33	1179
1.552	2350	1.09	0.12	5759	5.108	928
0.856	616	0.86	0.12	5759	6.878	601
			699	1		0

E East Forelands Outfall

FLOOD

Nearfield Velocity (m/s)	Tidal Transport (m)	Avg Farfield Velocity(m/s)	Napthalene Conc (ug/L)	Dilution	Plume Width	Distance (m)
0.65	70237	3.15	0.100	26500	96.3	23200
1.67	68566	3.28	0.099	26700	36.7	11200
2.70	65420	3.37	0.100	26400	22.3	8100
3.60	60884	3.38	0.100	26500	16.5	7200
4.15	55304	3.34	0.099	26700	14.4	7100
4.38	49162	3.25	0.100	26500	13.5	7000
4.45	42804	3.13	0.100	26500	13.2	6900
4.44	36403	2.97	0.099	26600	13.3	6800
4.34	30082	2.79	0.099	26600	13.6	6600
4.14	23976	2.56	0.100	26500	14.3	6300
3.84	18231	2.30	0.099	26800	15.7	6000
3.45	12982	2.00	0.100	26400	17.3	5500

2.94	8381	1.66	0.099	26600	20.6	5000
2.29	4615	1.28	0.100	26600	26.5	4400
1.49	1894	0.88	0.246	10800	16.6	1890
0.57	410	0.57	1.095	2410	9.38	410
	0		2657	1		0
EBB						
0.40	39459	2.03	0.100	26600	157	21800
1.26	38263	2.13	0.099	26700	49	9400
1.95	35952	2.17	0.099	26700	31	7000
2.40	32820	2.17	0.100	26400	25	6200
2.75	29111	2.13	0.099	26900	22	5900
2.95	25007	2.04	0.100	26500	20	5600
2.98	20737	1.92	0.100	26500	20	5400
2.88	16518	1.76	0.099	26800	21	5200
2.68	12515	1.58	0.099	26700	23	4900
2.41	8850	1.37	0.101	26200	25	4500
2.07	5624	1.12	0.100	26400	29	4100
1.61	2975	0.83	0.129	20500	29	2970
1.01	1088	0.50	0.356	7410	17	1090
0.25	181	0.25	2.318	1140	10	181
	0		2657	1		0

F Granite Pt Outfall

FLOOD

Nearfield Velocity (m/s)	Tidal Transport (m)	Avg Farfield Velocity(m/s)	Napthalene Conc (ug/L)	Dilution	Plume Width	Distance (m)
0.17	10558	0.44	0.10	11900	35.3	1400
0.36	10173	0.46	0.10	11570	13.17	1302
0.52	9538	0.46	0.10	11570	10.96	1714
0.63	8712	0.45	0.10	11570	9.998	1967
0.68	7771	0.43	0.10	11570	9.586	2095
0.68	6791	0.41	0.10	11570	9.586	2095
0.65	5832	0.39	0.10	11570	10	2026
0.60	4931	0.36	0.10	11570	10	1905

0.56	4096	0.33	0.10	11570	11	1807
0.52	3321	0.31	0.10	11570	11	1706
0.49	2599	0.28	0.10	11570	11	1624
0.44	1930	0.24	0.10	11570	12	1520
0.40	1321	0.20	0.10	11570	12	1411
0.32	800	0.16	0.14	8183	12	919
0.23	401	0.11	0.29	4092	10	429
0.10	161	0.07	0.57	2046	10	141
0.06	44	0.06	1.62	723	8	48
	0		1172	1		0
EBB						
0.05	10277	0.49	0.10	11800	122	3900
0.24	10068	0.52	0.10	11900	25.6	1400
0.43	9585	0.53	0.10	11570	12.05	1487
0.61	8835	0.53	0.10	11570	10.27	1497
0.66	7918	0.52	0.10	11570	9.723	2051
0.71	6928	0.51	0.10	11570	9	2169
0.76	5866	0.48	0.10	11570	9	2282
0.75	4773	0.44	0.10	11570	9	2262
0.70	3729	0.40	0.10	11570	9	2130
0.62	2784	0.35	0.10	11570	10	1946
0.53	1959	0.30	0.10	11570	11	1736
0.44	1261	0.25	0.14	8183	10	1162
0.34	699	0.19	0.20	5786	10	743
0.22	295	0.14	0.40	2893	8	317
0.09	68	0.09	1.62	723.3	6	63
	0		1172	1		0

G Trading Bay Outfall

FLOOD

Nearfield Velocity (m/s)	Tidal Transport (m)	Avg Farfield Velocity(m/s)	Napthalene Conc (ug/L)	Dilution	Plume Width	Distance (m)
0.39	41382	1.74	0.93	7880	473	41000
0.67	40618	1.82	0.91	8050	288	30000

1.15	39304	1.88	0.92	8000	170	21000
1.59	37332	1.92	0.96	7640	115	16000
1.99	34757	1.93	0.91	8050	95.4	14000
2.35	31633	1.91	0.93	7890	78.4	12000
2.60	28074	1.86	0.91	8020	71.6	11000
2.72	24245	1.77	0.94	7830	66.5	10000
2.73	20317	1.66	0.93	7910	66.9	9500
2.65	16440	1.52	0.92	7920	69.3	9000
2.48	12745	1.36	0.93	7920	74.1	8500
2.22	9361	1.18	0.94	7820	82.5	8000
1.86	6421	0.99	1.18	6200	78.8	6420
1.44	4044	0.80	2.08	3520	59	4040
0.97	2315	0.64	4.47	1640	42	2310
0.58	1199	0.56	11.10	661	27	1200
0.54	390	0.54	23.00	317	13	390
	0		784	1		0
EBB						
0.84	31440	1.75	0.95	7730	224	24000
1.23	29946	1.81	0.92	7930	156	19000
1.62	27893	1.84	0.97	7540	111	15000
1.94	25328	1.85	0.97	7540	91.6	13000
2.16	22375	1.83	0.96	7660	83.3	12000
2.27	19187	1.78	0.98	7450	76.8	11000
2.30	15897	1.70	0.92	7940	80.8	11000
2.27	12608	1.59	0.98	7500	77.4	10000
2.15	9425	1.45	0.99	7370	80	9430
1.93	6486	1.29	1.51	4840	59	6490
1.61	3935	1.09	2.65	2760	41	3940
1.20	1908	0.88	5.87	1240	25	1910
0.72	521	0.72	18.00	404	13	521
	0		784	1		0

H Platform Tyonek A

FLOOD

Nearfield	Tidal	Avg Farfield	Napthalene	Plume

Velocity (m/s)	Transport (m)	Velocity(m/s)	Conc (ug/L)	Dilution	Width	Distance (m)
0.70	34964	1.94	0.10	46.9	1.11	800
1.42	33437	2.02	0.09	51.3	0.54	500
1.99	30978	2.05	0.08	60.5	0.39	400
2.36	27841	2.04	0.09	53.5	0.27	300
2.58	24281	1.98	0.08	62.9	0.28	300
2.68	20494	1.90	0.11	42.1	0.18	200
2.67	16644	1.78	0.10	45.5	0.19	200
2.54	12891	1.63	0.10	47.1	0.21	200
2.30	9408	1.45	0.10	47.3	0.25	200
1.96	6344	1.26	0.11	44.9	0.30	200
1.56	3814	1.06	0.12	40.5	0.37	200
1.15	1868	0.87	0.13	36.2	0.50	200
0.72	522	0.72	0.10	49	1.12	300
	0		4.76	1		0
EBB						
0.34	38063	1.55	0.10	49.4	2.14	1000
0.43	37507	1.63	0.09	54.2	1.99	1000
0.88	36562	1.69	0.10	48.2	0.895	600
1.30	34992	1.74	0.08	56.3	0.661	500
1.66	32860	1.76	0.08	57.1	0.477	400
1.95	30260	1.75	0.10	49.1	0.326	300
2.17	27292	1.72	0.08	58.8	0.332	300
2.35	24037	1.67	0.12	40.9	0.207	200
2.48	20564	1.59	0.10	47	0.22	200
2.52	16968	1.47	0.09	52.7	0.241	200
2.45	13393	1.33	0.08	57.9	0.275	200
2.27	9997	1.16	0.08	62.1	0.329	200
2.03	6901	0.96	0.07	68	0.423	200
1.71	4207	0.73	0.06	76.4	0.612	200
1.29	2048	0.47	0.13	36.7	0.435	100
0.73	596	0.21	0.08	60.8	1.39	100
0.05	36	0.03	0.05	92	11.2	100
	0		4.76	1		0