Exxon Valdez Oil Spill
Restoration Project Final Report

Final 2005-2006 LTEMP Oil Monitoring Report
Restoration Project 050763

James R. Payne, Ph.D.
Payne Environmental Consultants, Inc.
1991 Village Park Way, Suite 206 B
Encinitas, CA 92024
760-942-1015
jrpayne@sbcglobal.net

William B. Driskell
6536 20th Avenue NE
Seattle, WA 98115
206-522-5930
bdriskell@comcast.net

Jeffrey W. Short, Ph.D. and Marie L. Larsen
Auke Bay Laboratories
Alaska Fisheries Science Center, NOAA Fisheries
Ted Stevens Marine Research Institute
17109 Point Lena Loop Road
Juneau, AK 99801
907-789-6065
jeff.short@noaa.gov
Marie.Larsen@noaa.gov

Prepared for
Joe Banta
Project Manager
Prince William Sound Regional Citizens' Advisory Council
3709 Spenard Road
Anchorage, Alaska 99503
907/277-7222 or 273-6225
banta@pwsrcac.org

December 2008

PWSRCAC Contract 951.06.01

Exxon Valdez Oil Spill Restoration Project Final Report

Final 2005-2006 LTEMP Oil Monitoring Report
Restoration Project 050763

James R. Payne, Ph.D.
Payne Environmental Consultants, Inc.
1991 Village Park Way, Suite 206 B
Encinitas, CA 92024
760-942-1015
jrpayne@sbcglobal.net

William B. Driskell
6536 20th Avenue NE
Seattle, WA 98115
206-522-5930
bdriskell@comcast.net

Jeffrey W. Short, Ph.D. and Marie L. Larsen
Auke Bay Laboratories
Alaska Fisheries Science Center, NOAA Fisheries
Ted Stevens Marine Research Institute
17109 Point Lena Loop Road
Juneau, AK 99801
907-789-6065
jeff.short@noaa.gov
Marie.Larsen@noaa.gov

Prepared for
Joe Banta
Project Manager
Prince William Sound Regional Citizens' Advisory Council
3709 Spenard Road
Anchorage, Alaska 99503
907/277-7222 or 273-6225
banta@pwsrcac.org

December 2008

PWSRCAC Contract 951.06.01
The opinions expressed in this commissioned report are not necessarily those of PWSRCAC

Study History

Preceding this EVOS Trustees Restoration Project, the Long Term Environmental Monitoring Program (LTEMP) began in 1993 as a mandate in the charter of the Prince William Sound Regional Citizen's Advisory Council (PWSRCAC). Aspects of the monitoring program have changed through the years, but mussel tissues are still being sampled biannually at ten fixed locations in Port Valdez, Prince William Sound, and along the outer coast from Seward to Kodiak in addition to subtidal sediments from two sites within Port Valdez. In 2004, joint funding was acquired from the Trustees along with an expansion in program objectives in 2005-2006 to include 1) sampling at random locations of EVOS impact (in addition to the original ten fixed LTEMP sites) to assess lingering oil and 2) exploration of oil levels at human habitation sites and extent of Monterey formation residues (from the 1964 earthquake). Peer-reviewed annual reports, datasets, and program reviews can be obtained from the PWSRCAC with the most recent publications available on their website, *www.pwsrcac.org*.

Abstract

The Long Term Environmental Monitoring Program (LTEMP) has been sampling mussels (and some sediments) twice annually at ten sites in Port Valdez, Prince William Sound, and nearby Gulf of Alaska sites since 1993. Samples are analyzed primarily for polycyclic aromatic and saturated hydrocarbons (PAH and SHC). Indices quantify the proportions of a hydrocarbon signal into dissolved, particulate/oil, and pyrogenic phases. After 1999, a decreasing trend appears in total PAH (TPAH) with current values below 100 ng/g dry weight (and many below 50 ng/g). Most currently measured samples reflect a predominantly dissolved-phase signal. This new low in TPAH likely represents ambient background levels. Furthermore, peaks and lows in total PAH trends and the similarities of the hydrocarbon signatures portray regional-scale dynamics. The five inner Prince William Sound sites have similar composition and behave similarly and yet are different from the three Gulf of Alaska sites. The Disk Island site has recently shown trace amounts of petrogenic signal from buried EVOS oil. The two Port Valdez sites are primarily influenced by the treated ballast water discharge from the Alyeska Marine Terminal.

Key Words

Alaska
Exxon Valdez oil spill
oil monitoring
PAH
Prince William Sound
Northern Gulf of Alaska
intertidal
marine
Mytilus trossulus
sediments
hydrocarbon chemistry

Project data

Current and historical data for this program are maintained by the PWSRCAC LTEMP contractors and supplied along with metadata to the EVOS Trustees. Annual reports and the data are available on request and generally carried on the website, *www.pwsrcac.org*.

Citation

Payne, James R., William B. Driskell, Jeffrey W. Short, Marie L. Larsen. 2008. Final 2005-2006 LTEMP Oil Monitoring Report, Exxon Valdez Oil Spill Restoration Project Final Report (Restoration Project 050763), Prince William Sound Regional Citizen's Advisory Council, Anchorage, Alaska. 137 pp.

PRINCE WILLIAM SOUND RCAC

Long-Term Environmental Monitoring Program

Final 2005-2006 LTEMP Monitoring Report

Photo by Dave Janka, 2005

James R. Payne, Ph.D.

William B. Driskell

Jeffrey W. Short, Ph.D.

Marie L. Larsen

Prince William Sound RCAC Regional Citizens' Advisory Council

December 2008

PWSRCAC Contract 951.06.01

TABLE OF CONTENTS

1 Executive Summary 1
2 Introduction 3
3 Scope 4
4 Methods 4
  4.1 Sampling Design 4
  4.2 Analytic Methods 6
  4.3 Quality Assurance 11
  4.4 Determination of Moisture Content 11
  4.5 Particle Grain Size Determination 11
  4.6 Determination of Total Organic and Total Carbon 12
  4.7 Data Analysis 12
    4.7.1 Hydrocarbon Indices 13
    4.7.2 Data Anomalies 20
  4.8 Data Management 23
5 Results and Discussion 23
  5.1 Sampling and Data Quality 23
    5.1.1 ABL Quality Assurance Chemistry Results 23
    5.1.2 Mussel Populations 24
  5.2 Port Valdez Sediments 24
    5.2.1 Sediment Particle Grain Size 26
    5.2.2 Total Organic and Inorganic Carbon 29
    5.2.3 Sediment Chemistry 30
      5.2.3.1 Alyeska Marine Terminal 32
      5.2.3.2 Gold Creek 32
      5.2.3.3 Constantine Harbor 34
    5.2.4 Summary and Discussion of Sediment Chemistry Results 35
  5.3 Mussel Tissue Chemistry 37
    5.3.1 Regional Trends and Approaches 37
    5.3.2 Port Valdez Stations 41
      5.3.2.1 Alaska Marine Terminal Mussel Tissue Chemistry 41
      5.3.2.2 Gold Creek Mussel Tissue Chemistry 45
    5.3.3 Prince William Sound Stations 46
      5.3.3.1 Disk Island Mussel Tissue Chemistry 47
      5.3.3.2 Knowles Head, Sheep Bay, and Sleepy Bay Mussel Tissue Chemistry 51
      5.3.3.3 Zaikof Bay Mussel Tissue Chemistry 56
      5.3.3.4 Constantine Harbor Mussel Tissue Chemistry 58
    5.3.4 Gulf of Alaska Stations 60
      5.3.4.1 Aialik Bay Mussel Tissue Chemistry 60
      5.3.4.2 Shuyak Harbor and Windy Bay Mussel Tissue Chemistry 63
    5.3.5 Summary and Discussion of Tissue Chemistry Results 68
6 Conclusions 71
7 References 72
8 Appendices 79

Appendix A LTEMP Oil Primer 80
A.1 Regional Sources 80
A.2 Oil Chemistry, Source Allocations, and Weathering Behavior 80
A.3 Mussels as Indicator Organisms 87
Appendix B-1 TPAH and TSHC summary table for Alyeska Marine Terminal and Gold Creek sediment samples, 1993-2006. 89
Appendix B-2 Summary of Sediment TPAH and component fractions, 1993-2006. . 93
Appendix C Tissue TPAH and TSHC summary for LTEMP 2005-2006. 99
Appendix D – PAH plots from the 2005-2006 Tissue Analyses 102
Appendix E – Oiled Sediment and Mussel Histogram Plots from the 2005 GEM Random Pit Sampling Program 113
Appendix F – Nordic Viking Diesel Spill 132

LIST OF FIGURES

Figure 1 Map of the 2005/2006 LTEMP sites. 5
Figure 2 PAH profiles of oil droplets removed by filtration (upper) and the dissolved-phase (lower) of the AMT BWTF effluent, January 2005 (from Payne et al. 2005b). 15
Figure 3 SHC profiles of oil droplets removed by filtration (upper) and the dissolved-phase (lower) of the AMT BWTF effluent, January 2005 (from Payne et al. 2005b). 16
Figure 4 Examples of PAH profiles from LTEMP mussels containing primarily background dissolved-phase components (analytes colored turquoise; top – Knowles Head) and particulate/oil-phase components from a diesel spill (colored gold; middle – Gold Creek), and LTEMP sediments containing primarily low-level combustion products (colored fuchsia; bottom – Gold Creek). White colored analytes are indeterminate. The fractional proportions of each phase (soluble, particulate/oil, and pyrogenic) are shown by the numbers in the upper right-hand corner of each plot with the number of analytes assigned to each group just below (e.g., the bottom replicate was 84% pyrogenic from the 24 fuchsia-coded analytes). 18
Figure 5 PAH procedural artifact patterns (left graphs) common in early LTEMP samples between March 1993 and March 1997. For these samples, homolog data are incomplete. The overlaying solid lines with the blue diamonds represent reported MDLs. Line gaps indicate analytes not reported at the time. SHC analyses (right graphs) were discontinued between 1995 and 1998 due to lipid interference problems. 21
Figure 6 Representative PAH profiles and method detection limits (solid lines with blue diamonds) from July 1997 tissue samples showing highly similar procedural patterns (GC/MS integration artifacts – see Figure 5) plus additional naphthalenes. 22
Figure 7 Time series and time overlays of grain size composition at Alyeska Marine Terminal and Gold Creek, 1993-2006. Sediments were not collected in 1998-99.. 27
Figure 8 Average fine sediment fractions (silt + clay) time series trends (±standard error of means) from GOC and AMT surficial sediment grabs. Note y-axis scale has been clipped for detailed viewing. Sediments were not collected in 1998-99. 28

Figure 9 Time series of total organic and inorganic carbon in AMT and GOC sediment. Dotted lines indicate data gaps. 30
Figure 10 Time series TPAH and relative phase composition of PAH profiles in AMT and GOC sediment samples. Sediments were not collected in 1998-99................. 31
Figure 11 PAH and SHC profiles from representative AMT sediment in July 2005 and March 2006 showing complex, oil/particulate-dominated signatures in a heavily weathered and biodegraded, mixed signal. MDLs indicated with dotted solid line. 33
Figure 12 PAH and SHC data for July 2005 and March 2006 Gold Creek sediments.... 34
Figure 13 PAH and SHC histogram profiles from representative intertidal sediments collected from Constantine Harbor. The line connecting the blue diamonds represents the sample-specific MDL. 35
Figure 14 *Mytilus* TPAH time series (triplicate averages) for all LTEMP stations, 1998-2006.. 38
Figure 15 Regional LTEMP *Mytilus* TPAH time series, 1998-2006.............................. 39
Figure 16 Time series TPAH and relative phase composition of PAH profiles in Alyeska Marine Terminal (AMT) and Gold Creek (GOC) *Mytilus* tissues. Dotted connecting lines without symbols indicate questionable data.. 40
Figure 17 PAH and SHC profiles showing low-level TPAH with variable source signals (combustion-, dissolved-, and oil/particulate-phase) in AMT mussel samples collected in July 2005, October 2005 and March 2006, respectively. MDLs indicated with dotted solid line.. 42
Figure 18 PAH Phase assignments for AMT and GOC mussel samples with other data removed to facilitate visualization of alternating seasonal (winter vs. summer) spikes in dissolved and particulate phases.. 43
Figure 19 Gold Creek mussel PAH and SHC profiles showing low-level TPAH with mixed and variable source signals (combustion products with some particulate/oil-phase components) in July 2005 and March 2006 and a predominant dissolved-phase pattern in October 2005. MDLs indicated with dotted solid line. 47
Figure 20 Time series TPAH and relative phase composition profiles in Disk Island (DII) *Mytilus* tissues. Dotted connecting lines without symbols indicate questionable data. 48
Figure 21 Disk Island *Mytilus* PAH and SHC profiles showing low-level particulate/oil-phase components in July 2004, March 2005, and March 2006. MDLs indicated with dotted solid line.. 49
Figure 22 Trace of fresh sheen of EVOS oil from disturbed sediments on Disk Island (above the LTEMP transect), July 2008. 50
Figure 23 Time series TPAH and relative phase composition profiles in Knowles Head (KNH), Sheep Bay (SHB), and Sleepy Bay (SLB) *Mytilus* tissues. Dotted connecting lines without symbols indicate questionable data. 52
Figure 24 Synchrony in average phase portions between Sheep Bay (SHB), Knowles Head (KNH), and Sleepy Bay (SLB) *Mytilus* PAH since July 1998....................... 53
Figure 25 Representative Knowles Head, Sheep Bay and Sleepy Bay *Mytilus* PAH and SHC profiles showing low-level particulate/oil-phase components in July 2004. MDLs indicated with dotted solid line.. 54
Figure 26 Representative Knowles Head and Sheep Bay *Mytilus* PAH and SHC profiles showing the return to trace-level dissolved-phase components at both sites in July

2005, and the possible (below-MDL) shift to more of a mixed-phase particulate/oil- and combustion-product pattern at Sheep Bay in March 2006. MDLs indicated with dotted solid line. 55

Figure 27 Representative Sleepy Bay *Mytilus* PAH and SHC profiles showing trace-level dissolved- and mixed-phase patterns in July 2005 and March 2006. The SHC profile in July 2005 is difficult to assess, but the March 2006 profile shows above-MDL marine biogenic and heavily weathered petrogenic components. MDLs indicated with dotted solid line 56

Figure 28 Time series TPAH and relative phase composition profiles in Zaikof Bay (ZAB) *Mytilus* tissues. Dotted connecting lines without symbols indicate questionable data. 57

Figure 29 Representative Constantine Harbor *Mytilus* and adjacent intertidal sediment PAH and SHC profiles from samples collected as part of the EVOS Trustees SCAT program in July 2005 and March 2006. MDLs indicated with dotted solid line. 59

Figure 30 Time series TPAH and relative phase composition profiles in Aialik Bay (AIB) *Mytilus* tissues. Dotted connecting lines without symbols indicate questionable data. 61

Figure 31 Representative Aialik Bay *Mytilus* PAH and SHC profiles showing a mixed dissolved- and particulate/oil-phase pattern in March 2005, dissolved-phase components in July 2005, and mixed dissolved- and combustion-phase components in March 2006. The SHC profiles show just-below MDL traces of biogenic and petrogenic components in March 2005, with less-than MDL marine and terrestrial biogenic input in July 2005 and March 2006. MDLs indicated with dotted solid line 62

Figure 32 Time series TPAH and relative phase composition profiles in Shuyak Harbor (SHH) and Windy Bay (WIB) *Mytilus* tissues. Dotted connecting lines without symbols indicate questionable data. 64

Figure 33 Synchrony of *Mytilus PAH* phases between Shuyak Harbor (SHH) and Windy Bay (WIB) since July 1998. Correlations significant at $p<0.001$ and $p< 0.02$, df=14. 65

Figure 34 Representative Shuyak Harbor *Mytilus* PAH and SHC profiles showing a trace-level particulate/oil-phase signal in August 2004 and dissolved-phase patterns in March and July 2005 and March 2006. The higher-molecular-weight n-alkane SHC profiles support the petrogenic PAH phase assignments in August 2004, but not the dissolved-phase pattern in March 2005. The July 2005 and March 2006 SHC profiles suggest biogenic marine input. 66

Figure 35 Representative Windy Bay *Mytilus* PAH and SHC profiles showing a trace-level particulate/oil-phase signal in August 2004 and dissolved-phase patterns in March and July 2005 and March 2006. The SHC profiles support the petrogenic PAH phase assignment in August 2004, but are contradictory in the March 2005 sample. Note that the SHC profiles in August 2004 and March 2005 are very similar to those observed at Shuyak Harbor (Figure 34) as well. MDLs indicated with dotted solid line. 67

Figure 36 Average *Mytilus* TPAH time series and trend lines comparing Prince William Sound and Gulf of Alaska stations' trends. 69

Cover photo by David Janka off *M/V Auklet* showing 2005 pit-digging field crew (left to right): Jeff Short, Bill Driskell, Jim Payne, Clayton Payne, and Wyatt Fournier.

LIST OF TABLES

Table 1. LTEMP Stations 2005-2006. Reported station depths are not tidally corrected. 6
Table 2. Polycyclic aromatic hydrocarbon (PAH) and saturated hydrocarbon (SHC) analytes measured in this study, along with analyte abbreviations, internal and surrogate standards........ 7
Table 3. Hydrocarbon Parameters Used in the LTEMP Data Analysis........ 14
Table 4. Field notes on mussel populations, July 2005-March 2006. 25
Table 5 Total organic and inorganic carbon in sediment replicates at Port Valdez and Constantine Harbor stations........ 29
Table 6 Exact one-tailed probabilities of seasonal phase dominance in mussels at AMT and GOC, 1993-2005 using randomization paired t-tests (1000 trials, n = 13)........ 42
Table 7 Detrended correlations of PAH phases between Sheep Bay (SHB), Knowles Head (KNH), and Sleepy Bay (SLB) *Mytilus* tissue, July 1998-March 2006........ 51
Table 8 Current TPAH concentrations in mussel tissues (ng/g dry wt) relative to recent NOAA Mussel Watch monitoring data and another recovered Alaskan oil-spill event........ 70

LIST OF ABBREVIATIONS

Stations:

AMT	Alyeska Marine Terminal, Port Valdez
AIB	Aialik Bay, west of Seward
COH	Constantine Harbor, Hinchinbrook Entrance, PWS
DII	Disk Island, Knight Island Group, western PWS
GOC	Gold Creek, Port Valdez
KNH	Knowles Head, eastern PWS
SHB	Sheep Bay, eastern PWS
SHH	Shuyak Harbor, Kodiak
SLB	Sleepy Bay, Latouche Island, western PWS
WIB	Windy Bay, Outer Kenai Peninsula
ZAB	Zaikof Bay, Montague Island, central PWS

ABL	NOAA/NMFS Auke Bay Laboratory, Juneau AK
AHC	aliphatic hydrocarbons (same as saturated hydrocarbons – SHC)
ANS	Alaskan North Slope
BWTF	Alyeska Terminal's Ballast Water Treatment Facility
DSI	Dissolved Signal Index
EVOS	*Exxon Valdez* oil spill
EVTHD	*Exxon Valdez* Trustees Hydrocarbon Database
EMAP	US EPA Environmental Monitoring and Assessment Program
GC/FID	gas chromatography/flame ionization detector
GC/MS	gas chromatography/mass spectrometry
GERG	Geochemical and Environmental Research Group, Texas A&M University
KLI	Kinnetic Laboratories, Inc., Anchorage AK
MDL	analytic method detection limit
NIST	National Institute of Standards and Technology
NMFS	National Marine Fisheries Service
NOAA	National Oceanographic and Atmospheric Administration
PAH	polycyclic (or polynuclear) aromatic hydrocarbons
PECI	Payne Environmental Consultants, Inc., Encinitas, CA
PGS	particle grain size
PSI	Particulate Signal Index
PWS	Prince William Sound
SHC	saturated hydrocarbons (same as AHC: n-alkanes + pristane and phytane)
SIM	selected ion monitoring
SRM	NIST standard reference material
TAHC	total AHC
TIC	total inorganic carbon
TOC	total organic carbon
TPAH	total PAH
TSHC	total saturated hydrocarbons (same as total alkanes)
UCM	unresolved complex mixture

1 Executive Summary

From the 2005-06 LTEMP samplings, average tissue hydrocarbon levels remained at trace levels similar to those in recent years (max 61, min 9 ng/g dry weight, ppb). Even the Port Valdez stations, while still reflecting what appears to be very low levels of weathered particulate oil (presumably from the BWTF), continued to report concentrations around 50 ppb. Port Valdez sediments accumulated slightly higher levels, ~70 ppb.

The trace levels seen at sites beyond Port Valdez doubtlessly reflect, oil-wise, the currently pristine nature of the environment. Furthermore, while the dissolved character of the signals points inconclusively to an unknown source(s), the broad-scale similarities suggest incidental geographic input rather than point sources. The only exception to this scenario occurs at the Disk Island site where mussels show a very low but more complex signature that suggests a weathered particulate/whole oil source. Normally, this signature would be too low to identify a source but in all likelihood, it is probably linked to residual EVOS oil seen buried above the transect in 2007 and 2008.

In summary, the LTEMP program is primed for the mission of detecting spill events. In Port Valdez, we see the low-level imprint of human activities in addition to discharge from the Terminal, while elsewhere, we see the trace, dissolved-phase, background signal from an unknown source(s). Any new hydrocarbon inputs to the system have been and will be easily detected.

This year, the program included a new component. Under the auspices of the EVOS Trustees Program, Long-term Monitoring of Anthropogenic Hydrocarbons in the *Exxon Valdez* Oil Spill Region (050763), ten intertidal sites within the Naked-Knight-Southwest Island complex were examined during the 2005 summer program to measure the extent of buried oil still present 16 years after the spill. At EVOS sites previously designated as heavily oiled, a number of random-stratified pits were dug to a depth of ~0.5 m to look for residual oil. Where available, mussels were also collected. Sediments and mussels were analyzed using LTEMP analytical protocols. The results have been published (Short et al., 2007a) and a separate report is being prepared by Dr. Jeffrey Short for this survey plus continuation studies completed in 2006 and 2007. As part of PWSRCAC efforts, PAH and SHC sample profiles are included in Appendix E. Briefly, TPAH levels in the oiled pits ranged from a low of 42 ng/g (on Knight Island) to a high of 567,000 ng/g (on Latouche Island) with the buried oil showing varying states of weathering (from extensively degraded to very fresh). The mussel samples collected from these same beaches (but not necessarily immediately adjacent to the oiled pits) showed low (11 to 42 ng/g dry weight) dissolved-phase TPAH signals very similar to those observed at the traditional LTEMP stations. Although there were still persistent buried EVOS residues at a number of the beaches, they are highly sequestered and do not appear to be bioavailable unless disturbed. Rates of disappearance have diminished to an estimated 4% yr^{-1}. If left undisturbed, Short et al. predict they will be there for decades.

Also attached to this report are the results from chemical analyses of mussel and sediment samples collected in Olsen Bay after the *F/V Nordic Viking* diesel spill in July 2007 (Appendix F). The three October 2007 mussel samples show a low-level, weathered diesel signal (698-1,169 ppb) while the single sediment sample showed very low (2.4 ppb) diesel components.

Prior to delving into the rich technical details of the report, readers unfamiliar with environmental hydrocarbon chemistry may want to examine Appendix A, a primer on basic hydrocarbon chemistry, weathering patterns, and using mussels as indicator organisms.

2 Introduction

The primary objective of the ongoing Long-Term Environmental Monitoring Program (LTEMP) is to collect "…standardized measurements of hydrocarbon background in the EVOS region as long as oil flows through the pipeline." Under Federal and State statutes, the unregulated release of oil into the environment is strictly prohibited; the LTEMP data serve as a sentinel indicator and independent quality control check for Alyeska Marine Terminal and tanker operations throughout the region.

Currently measured variables include polycyclic (or polynuclear) aromatic and saturated (or aliphatic) hydrocarbon levels (PAH and SHC) in mussel (*Mytilus trossulus*) tissues from ten stations between Valdez and Kodiak and sediments from two stations in Port Valdez. The Port Valdez sediment samples are also analyzed for particle grain size and total organic carbon content to validate continuity of the site environments. Sampling and analytical methods are patterned after the protocols developed by the National Oceanic and Atmospheric Administration (NOAA) Status and Trends Mussel Watch Program as fully detailed in the annual Monitoring Reports prepared by Kinnetic Laboratories, Inc. (KLI) and the Geochemical and Environmental Research Group (GERG).

Following the first five years of the program, the collective results from the KLI/GERG team were reviewed in a synthesis paper (Payne et al. 1998). At that time, background oil levels were higher, hot spots were identified, large and small spill events were visible in the data set, and identification of weathered sources was important. Subsequent to this assessment, the PWSRCAC reduced the scope of the program to the current biannual sampling of regional mussel tissues and Port Valdez sediments. Fall mussel sampling was added just in Port Valdez (Alyeska Marine Terminal and Gold Creek) to better track the terminal's discharge. Analyses of aliphatic hydrocarbons in mussel tissues, dropped from the original program in 1995 due to results being confounded from lipid interference, were reinstated in 1998. Improved lab methods have essentially eliminated interference issues at this time.

In 2001, another data evaluation and synthesis review was completed on just the LTEMP results from the Port Valdez sites (Payne et al., 2001). Data from Alyeska Marine Terminal and the Gold Creek control site suggested Alaska North Slope (ANS) crude oil residues from the terminal's ballast water treatment facility (BWTF) had accumulated in the intertidal mussels within the port. Payne et al. (2001) concluded, however, that the PAH and SHC levels measured in sediments and mussel tissues (and the estimated water-column levels) were very low and unlikely to cause deleterious effects. From the analyte signatures, however, they were able to discriminate between particulate- (oil droplet) and dissolved-phase signals in the water column and then correlate those signals with seasonal uptake of hydrocarbons in mussels and with absorption in herring eggs (from other studies). These findings give new insight into the transport and exposure pathways in Port Valdez. The results also suggested a surface microlayer mechanism may be responsible for seasonal transport of ANS weathered oil residues from the BWTF diffuser to intertidal zones to the north and west of the terminal. Payne et al. (2001) concluded that the possibility of concentrated contaminants in a surface microlayer combined with the potential for photo-enhanced toxicity should be considered in future investigations of potential impacts in Port Valdez.

In July 2002, Payne Environmental Consultants, Inc (PECI) and the NOAA/NMFS Auke Bay Laboratory (ABL) began conducting LTEMP operations. Detailed discussions of the transitional 2002/2003 LTEMP samples and interlaboratory comparisons of split samples and Standard Reference Materials (SRMs) supplied by the National Institute of Standards and Technology (NIST) analyzed by both GERG and ABL are presented in Payne et al. (2003a). The results from the 2003/2004 LTEMP and a comprehensive review and synthesis of all analyses completed since the beginning of the program are available in Payne et al. (2005a). Finally, the current program through the 2004-05 results was reviewed by BGES (2007).

3 Scope

This report examines the 2005/2006 samples and trend analyses of over 820 tissue and 150 sediment samples collected historically within Prince William Sound and the surrounding region (Figure 1) in addition to the laboratory quality control results. The reported project year also included cosponsored funding from EVOS Trustees for random sampling at sites previously identified with buried EVOS oil (Short et al. 2004, 2007a). Twenty-three oiled sediment samples from pits still containing oil and 18 tissue samples from nearby mussels were analyzed to assess the rate and state of oil degradation and the exposure of resident biota. These later results will be presented in a separate report to the EVOS Trustees (Short et al., in preparation), but Appendix E contains the histogram plots for PAH and SHC fractions for reference where pertinent to the discussion.

4 Methods

4.1 Sampling Design

For both the tissue and sediment collections, the current sample design followed the previous years' efforts (KLI 2002) with slight modifications. As noted above, mussel tissues are sampled at ten sites and sediments from two sites in Port Valdez on a biannual basis (March-April and July-August) (Figure 1). Mussel tissues are also collected from the two Port Valdez sites in October (inset Figure 1).

For tissues, three replicates were typically taken from random locations spread between the transect end-markers at each site. At Sleepy Bay and Knowles Head, the absence of mussels along the transects (starfish predation) necessitated off-transect sampling. Each replicate of 25-30 mussels was collected by hand using Nitrile® gloves, wrapped in aluminum foil, Ziplock® bagged, labeled, double-bagged and kept chilled until reaching the nearest freezer. The collection site was photographed and GPS coordinates recorded for chain-of-custody documentation. The entire trip collection was eventually air-freighted frozen to the NOAA/NMFS Auke Bay Laboratory in Juneau.

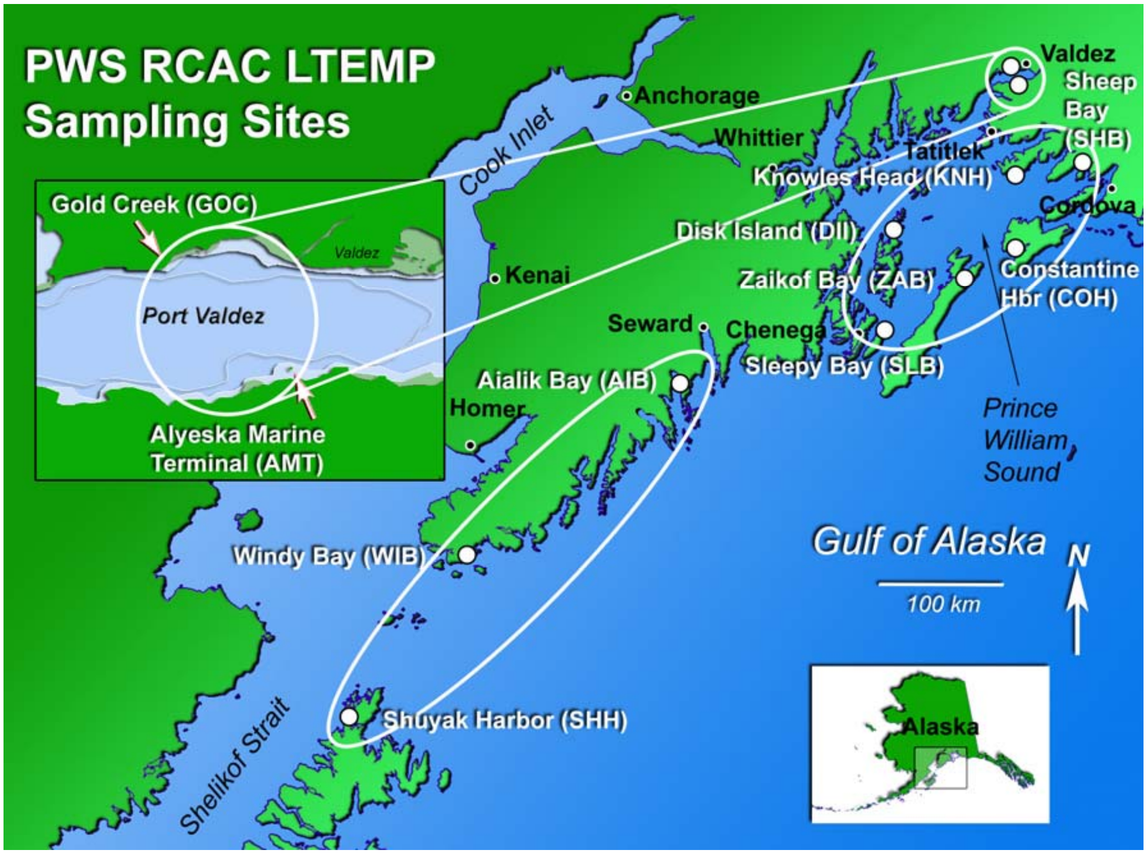


Figure 1 Map of the 2005/2006 LTEMP sites.

Subtidal sediments were collected from the *M/V Auklet* support vessel using a modified Van Veen grab sampler, i.e., the standard pincer-jawed, bucket grab commonly augmented with an encircling stabilization frame to theoretically ensure vertical penetration. Upon retrieval, only the top centimeter of undisturbed sediment was collected from the center of each sample (away from the edges of the grab), scooping with a pre-cleaned spoon into a contaminant-free glass jar. An additional sample was also taken from each grab for particle-grain-size analysis. Water depth and GPS location were recorded for each sample. Prior to sampling at each station, the grab was scrubbed with Alconox® detergent to prevent cross-contamination, rinsed with a previously tested, seawater deck hose, dunked overboard, and the drippings collected as a rinsate blank. The deck hose was also used for rinsing the grab between samples. The sediment samples are immediately frozen onboard and eventually air-freighted to Auke Bay Laboratory in Juneau.

A combination of vessel and float plane is used to access the sampling sites (Table 1). Typically, during PECI field efforts, the *M/V Auklet* is used for the Port Valdez and Knowles Head stations and a float plane to sample all other sites.

Table 1. LTEMP Stations 2005-2006. Reported station depths are not tidally corrected.

Station Location	Station Code	Sample Type	Sampling Date	Average Station Depth	Global Positioning System (GPS) Coordinates	
					Latitude (N)	**Longitude (W)**
Aialik Bay	AIB-B	Intertidal	7/20/2005		59° 52.779'	149° 39.489'
		Mussel	3/4/06		59° 52.733'	149° 39.597'
Alyeska Marine Terminal	AMT-B	Intertidal	7/25/05		61° 5.448'	146° 24.368'
		Mussel	10/2/05		61° 5.452'	146° 24.382'
			3/3/06		61° 5.448'	146° 24.383'
	AMT-S	Subtidal	7/25/05	69 m	61° 5.422'	146°23.589'
		Sediment	3/3/06	69 m	61° 5.431'	146°23.553'
Constantine Harbor	COH-B	Intertidal	7/19/2005		60° 21.061'	146°39.472'
		Mussel	3/4/06		60° 21.061'	146°39.472'
	COH-S	Intertidal	7/19/2005		60° 21.061'	146°39.472'
		Sediment	3/4/06		60° 21.061'	146°39.472'
Disk Island	DII-B	Intertidal	7/19/2005		60° 29.938'	147° 39.513'
		Mussel	3/4/06		60° 29.904'	147° 39.661'
Gold Creek	GOC-B	Intertidal	7/25/05		61° 7.474'	146° 29.653'
		Mussel	10/2/05		61° 7.441'	146° 29.653'
			3/2/06		61° 7.473'	146° 29.652'
	GOC-S	Subtidal	7/25/05	30 m	61° 7.473'	146°29.472'
		Sediment	3/2/06	36 m	61° 7.468'	146°29.469'
Knowles Head	KNH-B	Intertidal	7/19/2005		60° 41.470'	146° 35.018'
		Mussel	3/2/06		60° 41.468'	146° 35.017'
Sheep Bay	SHB-B	Intertidal	7/19/2005		60° 38.795'	145° 59.724'
		Mussel	3/1/06		60° 38.797'	145° 59.723'
Shuyak Harbor	SHH-B	Intertidal	7/17/05		58° 30.115'	152° 37.527'
		Mussel	3/10/06		58° 30.117'	152° 37.530'
Sleepy Bay	SLB-B	Intertidal	7/19/2005		60° 4.082’	147° 49.859'
		Mussel	3/4/06		60° 4.036'	147° 50.001'
Windy Bay	WIB-B	Intertidal	7/17/05		59° 13.129’	151° 31.087'
		Mussel	3/10/06		59° 13.134'	151° 31.097'
Zaikof Bay	ZAB-B	Intertidal	7/19/2005		60° 15.944'	147° 4.994'
		Mussel	3/4/06		60° 15.912'	147° 5.119’

4.2 Analytic Methods

Sediment samples (~50 g wet weight) or whole mussel tissue samples (~10 g wet weight) were spiked with a suite of 5 aliphatic and 6 aromatic perdeuterated hydrocarbon surrogate standards (identified in Table 2) and then extracted with dichloromethane at 100°C and 2,000 psi for 10 min in a Dionex ASE 200 accelerated solvent extractor. The dichloromethane solutions were exchanged with hexane over steam, and separated into aliphatic and aromatic fractions by column chromatography (10 g 2%-deactivated alumina over 20 g 5%-deactivated silica gel; columns for sediments also contained 20 g granular elemental copper and 8 g anhydrous sodium sulfate for removal of sulfur and water, respectively). Aliphatics eluting with 50 mL pentane were analyzed by gas chromatography with a flame ionization detector (GC/FID) following concentration

Table 2. Polycyclic aromatic hydrocarbon (PAH) and saturated hydrocarbon (SHC) analytes measured in this study, along with analyte abbreviations, internal and surrogate standards.

Analytes	**Abbreviation**	**Internal Standard**	**Surrogate Standard**
PAH			
Naphthalene	N	A	1
C1-Naphthalene	N1	A	1
C2-Naphthalene	N2	A	2
C3-Naphthalene	N3	A	2
C4-Naphthalene	N4	A	2
Biphenyl	BI	A	2
Acenaphthylene	AC	A	2
Acenaphthene	AE	A	2
Fluorene	F	A	2
C1-Fluorenes	F1	A	2
C2-Fluorenes	F2	A	2
C3-Fluorenes	F3	A	2
Dibenzothiophene	D	A	3
C1-Dibenzothiophene	D1	A	3
C2-Dibenzothiophene	D2	A	3
C3-Dibenzothiophene	D3	A	3
C4-Dibenzothiophene	D4	A	3
Anthracene	A	A	3
Phenanthrene	P	A	3
C1-Phenanthrene/Anthracene	P/A1	A	3
C2-Phenanthrene/Anthracene	P/A2	A	3
C3-Phenanthrene/Anthracene	P/A3	A	3
C4-Phenanthrene/Anthracene	P/A4	A	3
Fluoranthene	FL	A	3
Pyrene	PYR	A	3
C1-Fluoranthene/Pyrene	F/P1	A	3
C2-Fluoranthene/Pyrene	F/P2	A	3
C3-Fluoranthene/Pyrene	F/P3	A	3
C4-Fluoranthene/Pyrene	F/P4	A	3
Benzo(a)Anthracene	BA	A	4
Chrysene	C	A	4
C1-Chrysenes	C1	A	4
C2-Chrysenes	C2	A	4
C3-Chrysenes	C3	A	4
C4-Chrysenes	C4	A	4
Benzo(b)fluoranthene	BB	A	5
Benzo(k)fluoranthene	BK	A	5
Benzo(e)pyrene	BEP	A	5
Benzo(a)pyrene	BAP	A	5

Perylene	PER	A	6
Indeno(1,2,3-cd)pyrene	IP	A	5
Dibenzo(a,h)anthracene	DA	A	5
Benzo(g,h,i)perylene	BP	A	5
Total PAH	TPAH		5

n-Alkanes

n-Decane	C10	B	7
n-Undecane	C11	B	7
n-Dodecane	C12	B	7
n-Tridecane	C13	B	7
n-Tetradecane	C14	B	8
n-Pentadecane	C15	B	8
n-Hexadecane	C16	B	8
n-Heptadecane	C17	B	8
Pristane	Pristane	B	8
n-Octadecane	C18	B	9
Phytane	Phytane	B	9
n-Nonadecane	C19	B	9
n-Eicosane	C20	B	9
n-Heneicosane	C21	B	9
n-Docosane	C22	B	10
n-Tricosane	C23	B	10
n-Tetracosane	C24	B	10
n-Pentacosane	C25	B	10
n-Hexacosane	C26	B	10
n-Heptacosane	C27	B	10
n-Octacosane	C28	B	10
n-Nonacosane	C29	B	11
n-Triacontane	C30	B	11
n-Hentriacontane	C31	B	11
n-Dotriacontane	C32	B	11
n-Tritriacontane	C33	B	11
n-Tetratriacontane	C34	B	11
Total n-Alkanes	TALK		
Calibrated analytes are identified by boldface. Internal standards: A = hexamethylbenzene; B = dodecylcyclohexane. Surrogate standards: 1 = naphthalene-d8, 2 = acenaphthene-d10, 3 = phenanthrene-d10, 4 = chrysene-d12, 5 = benzo[a]pyrene-d12, 6 = perylene-d12, 7 = dodecane-d26, 8 = hexadecane-d34, 9 = eicosane-d42, 10 = tetracosane-d50, and 11 = triacontane-d62.			

to ~ 1 mL hexane over steam and addition of dodecylcyclohexane as an internal standard to evaluate recoveries of the surrogate standards. PAH constituents from the sample extracts were further purified by gel-permeation high performance liquid chromatography (HPLC). The injection volume was 0.5 mL into dichloromethane flowing at 7 mL/min through two size-exclusion gel columns (Phenomenex, phenogel, 22.5 mm x 250 mm, 100 Å pore size) connected sequentially. The initial 110 mL eluate was discarded, and the following 50 mL was collected and concentrated over a 60–70^o C water bath and exchanged with hexane to a final volume of *ca*. 1 mL, then spiked with hexamethylbenzene as an internal standard for estimating recoveries of the initially added perdeuterated aromatic hydrocarbon surrogate standards.

PAHs in extracts were separated and analyzed with a Hewlett-Packard 6890 gas chromatograph equipped with a 5973 mass selective detector (MSD). The injection volume was 1 µL into a splitless injection port at 300° C. The initial oven temperature was 60° C, increasing at 10° C per minute immediately following injection to a final temperature of 300° C, then held for 12 min. The chromatographic column was a 25 m fused silica capillary (0.20 mm ID) coated with 5% phenyl methyl silicone. The helium carrier gas was maintained at 70 kPa inlet pressure. The gas chromatographic column was eluted into the 70 eV electron impact MSD through a 240° C transfer line. The ionizer temperature and pressure were 240° C and 10^{-5} torr, respectively. The MSD was operated in the selected-ion-monitoring (SIM) mode. The MSD was tuned with mass 69, 102, and 512 fragments of perfluorotributylamine before each batch of samples was analyzed.

Calibrated PAHs were identified based on retention time and ratio of two mass fragment ions characteristic of each hydrocarbon. Calibrated PAHs are identified by bold typeface in Table 2, and include dibenzothiophene and the aromatic hydrocarbons in SRMs supplied by NIST. Chromatographic peaks were identified as a calibrated aromatic hydrocarbon if both ions were co-detected at retention times within ±0.15 minutes (9 seconds) of the mean retention time of the hydrocarbon in the calibration standards, and if the ratio of the confirmation ion to the quantification ion was within ±30% of the expected ratio.

Uncalibrated PAHs include the alkyl-substituted isomers of naphthalene (except the 1- and 2-methyl-substituted homologues), fluorene, dibenzothiophene, phenanthrene/anthracene, fluoranthene/pyrene, and chrysene. Uncalibrated PAHs were identified by the presence, within a relatively wide retention time window, of a single mass fragment ion that is characteristic of the uncalibrated PAH sought. Wider retention time windows were necessary for the uncalibrated PAH because of the range of retention times of the various isomers that are included in an uncalibrated PAH homologue grouping (e.g. C3-phenanthrene).

Concentrations of calibrated PAHs in extracts were estimated by a method employing multiple internal standards and a five-point calibration curve for each calibrated PAH. The deuterated surrogate standards that were initially spiked into each sample are treated as internal standards, where each surrogate compound is associated with one or more calibrated PAHs. A calibration curve for each calibrated PAH and batch of samples analyzed was based on five different hexane dilutions of the PAH standard run before each sample batch or "laboratory string." Each calibration curve was derived from linear regression of (1) the ratio of MSD/SIM quantification ion response of the calibrated PAH and the associated deuterated surrogate standard and (2) the ratio of the amount of calibrated PAH and the amount of deuterated surrogate in the calibration standards. This approach effectively means that all reported analytes are corrected for the appropriate surrogate recoveries.

Concentrations of uncalibrated PAHs in extracts were determined with calibration curves and procedures for the most similar calibrated PAH. The MSD/SIM response to the quantification ion of each uncalibrated PAH homologue isomer were summed; this sum was used in place of the calibrated PAH response in the procedure described above for calculating concentrations of calibrated PAHs. For example, the fluorene calibration curve and procedure was used for all the alkyl-substituted fluorenes identified, but 2,6-dimethylnaphthalene, 2,3,5-trimethylnaphthalene and 1-methylphenanthrene calibration curves were used for C2-naphthalenes, C3-naphthalenes, and for all the alkyl-substituted phenanthrenes, respectively.

Alkanes in extracts were separated and analyzed with a Hewlett-Packard 5890 gas chromatograph equipped with a flame ionization detector (FID). The injection volume was 1 µL into a splitless injection port at 300° C. The 60° C initial oven temperature was maintained for 1 minute, then increased at 6° C per minute to a final temperature of 300° C, then held for 25 min. The detector temperature was 320° C. The chromatographic column was the same as that used for PAH analysis (see above). The helium carrier gas flow rate was 0.80-2.0 mL per minute, and the column effluent was combined with 34 mL per minute nitrogen make-up gas before entering the FID. The FID was operated with hydrogen- and air-flow rates of approximately 33 and 360-410 mL per minute, respectively. Alkane hydrocarbons were identified based on their retention times. Any peak detected above the integrator threshold within ±0.25% of the mean retention time of the alkane in the calibration standards was identified and quantified as that alkane.

Concentrations of calibrated alkanes (Table 2) were determined by an internal-standard method employing a five-point calibration curve for each alkane. The deuterated surrogate standards that were initially spiked into each sample were treated as internal standards, where each surrogate compound was associated with a group of calibrated alkanes. A calibration curve for each calibrated alkane and batch of samples analyzed was based on five different hexane dilutions of the alkane standards. Each calibration curve was derived from linear regression of (1) the ratio of FID response of the alkane and the associated deuterated surrogate standard, and (2) the ratio of the amount of calibrated alkane and the amount of deuterated surrogate in the calibration standards. As with quantitation of the PAH, this approach means that reported concentrations for all n-alkanes are surrogate-recovery corrected.

Amounts of uncalibrated alkane hydrocarbons and the cumulative amount of hydrocarbons in the unresolved complex mixture (UCM) were based on detector responses and the calibration curve for hexadecane. Flame ionization detector response due to the UCM was determined as the difference of the total FID response and the response due to distinguishable peaks using valley-to-valley baseline integrations.

4.3 Quality Assurance

Quality control samples were analyzed with each batch of 12 samples to assess the accuracy and precision of the analysis, and to verify the absence of laboratory contaminants introduced during analysis. Two quality control samples for accuracy assessment were prepared from hydrocarbon standards prepared by NIST (for PAH) or by ABL (for aliphatics), and run with each batch. Precision was assessed by analysis of two NIST standard reference material (SRM) samples analyzed with each batch: SRM 1974a for mussels and SRM 1944 for sediments. The mussel reference is especially appropriate for these analyses because the PAH concentrations are quite low, with many of the PAH analytes present at concentrations near the method detection limits (MDLs). Absence of laboratory contaminants was verified by analysis of one method blank sample with each batch.

Method detection limits (MDLs) were estimated for each calibrated alkane and PAH analyte following the procedure described in Appendix B, 40 Code of Federal Regulations, Part 136. Method detection limits for uncalibrated PAHs were not experimentally determined. Consequently, detection limits for these analytes were arbitrarily assumed as the MDL of the most closely related calibrated PAH analyte. In PAH and SHC bar chart plots throughout this report, MDLs are depicted by a dashed blue line with blue diamonds. They are included for the reader's benefit in assessing the significance of the data particularly where concentrations are at trace levels (far below MDLs). As described below, we are primarily interested in detecting expected multi-analyte patterns rather than the quantifying absolute levels of single analytes.

4.4 Determination of Moisture Content

Weighed aliquots of wet mussel homogenates or of sediments were dried at 100^{o} C for 24 h and re-weighed to determine the moisture content, and the ratio of these wet and dry weights was used to convert PAH and SHC concentrations to a dry weight basis.

4.5 Particle Grain Size Determination

Determination of the distribution of particle grain sizes in the sediment samples was determined by a combination of sieving and pipette methods based on the procedures given by Folk (1974). Implementation of these procedures at ABL (Larsen and Holland 2004) is almost identical with the method described in SOP-8908 at GERG. The ABL procedure differs from the GERG procedure in the sample pre-treatment. At ABL, a somewhat smaller sample aliquot is used (8 – 12 g instead of 15 – 20 g sediment), the minimum amount of hydrogen peroxide is used to oxidize organic matter (typically 30 – 60 mL of 30% H_2O_2 instead of 50 – 100 mL), the sample is not washed with distilled water to remove soluble salts at ABL because of the risk of loosing sediment fines, and only ~ 100 mL of sodium hexametaphosphate solution is used to disperse the sample at ABL instead of 400 mL at GERG. These changes were implemented at ABL because they were specifically optimized for the samples analyzed for the LTEMP program. The effects of these minor procedural differences on the estimates of particle grain size distributions in comparison with results produced at GERG are almost certainly negligible.

4.6 Determination of Total Organic and Total Carbon

Analytical measurements of total organic and total carbon are determined on oven dried and pulverized sediment samples using a Dohrmann DC-85A TOC catalytic combustion (oxygen at 200 mL/min and cobalt oxide on alumina) furnace. The carbon dioxide produced is passed through an acidified liquid sparger (scrubs out entrained water vapor and corrosive species), two scrubbers (copper and tin) and linearized non-dispersive infrared detection, by comparison with results from a calibration curve based on potassium acid phthalate. Total organic carbon (TOC) and total carbon (TC) are determined on samples treated with and without 10% HCl in methanol. Total inorganic carbon is calculated as the difference between TC and TOC.

4.7 Data Analysis

For data analysis, we primarily use standard accepted practices in forensic pattern recognition, which involves subjectively assessing the analyte levels and composition patterns to identify sources and weathering/transport processes (Wang and Stout, 2007). Bar chart PAH and SHC plots for each sample, ordered by increasing molecular weight (number of aromatic rings and degree of alkylation), are scrutinized for relevant details relating to weathering or dissolution behavior. Each replicate is examined separately in order to assess fidelity of the triplicate patterns and avoid any potentially confounding amalgam of replicates with radically differing profiles; identifying the source is more important than the average quantification. Standard errors of the mean are displayed, where practical, for averaged index trends (also tabulated in the appendices).

In the pattern recognition process, we often utilize hydrocarbon data that may fall below laboratory method detection limits (MDLs) as defined by the US Environmental Protection Agency (EPA) (Federal Register, 1986) for assurance of single analyte quantification. We take added confidence in our efforts knowing that false positive identifications of the complex hydrocarbon profiles are minimized based both on prior knowledge of expected multi-analyte patterns (primarily ANS crude, diesel or pyrogenic sources) and on laboratory use of secondary ion confirmations in the SIM analyses. This <MDL practice, an acknowledged conundrum in pattern analysis, has evoked much discussion among PWSRCAC program reviewers, but elicited no comments from peer reviewers and editors at *Marine Pollution Bulletin* (Payne et al., 2008). Furthermore, it appears theoretically and empirically justified for holistically assessing multi-analyte source patterns and for the goals of this project. We refer here to monitoring for anthropogenic hydrocarbon releases; events that typically spike multi-analyte signals at magnitudes well above the current background levels.

For data overviews, an Excel application was developed to plot groups of replicate samples (by station and sampling date) along with the relevant lab method blank. For more detailed comparisons, another Excel application graphs both PAH and SHC analytes with relevant indices from any three samples plus a reference standard (e.g., reference ANS crude, BWTF outfall, etc.).

The ability to discriminate between the dissolved (also called the water-soluble fraction) and particulate/oil-droplet phases, particularly as clues to fate and transport processes, has been essential in our data interpretations. Filter-feeding mussels may acquire waterborne oil signatures from both phases in addition to combustion products (soot) as finely suspended, pyrogenic particles (Baumard et al., 1998; Payne and Driskell, 2003). Note that results are biased when directly comparing a mussel's dissolved-phase PAH levels (absorbed via equilibrium dynamics) versus an ingested oil microdroplet (or contaminated suspended-particulate matter) in that mussels can accumulate particle-bound PAH some 80-fold more effectively than they do an equivalent aqueous concentration of dissolved PAH (Short, 2005). The presence and pattern of insoluble n-alkanes plus phytane can also be used to confirm a sample's particulate/oil-phase burden.

4.7.1 Hydrocarbon Indices

In prior LTEMP studies, several indices, both published and *ad hoc*, have been used with varying degrees of utility to describe LTEMP data trends. Because we use pattern recognition to interpret the data, most of the previously cited indices have become less germane to interpreting the data; we're primarily looking for ANS oil signals and can readily distinguish it through a progression of weathering states. We presently rely on our three derived indices (Table 3) which quantify the dissolved-, particulate/oil-phase, and pyrogenic-source signals in a sample signature in addition to the summary TPAH and TSHC values.

In water, oil partitions by physical equilibrium into two phases, the dissolved phase and the particulate or whole-oil droplet phase. During a 2004/2005 study of the Alyeska Marine Terminal Ballast Water Treatment Facility (BWTF), Payne et al. (2005b,c) utilized a Portable Large Volume Water Sampling System (PLVWSS) to separate (via filtration through a 0.7 μm glass fiber filter) the dissolved- and particulate/oil-phase fractions (Payne et al., 1999) in a sample of the BWTF effluent just before discharge into Port Valdez.

The less water-soluble, higher-molecular-weight PAH (Figure 2 top) and SHC (Figure 3 top) components are readily apparent in the fine particulate phase and finite oil droplets trapped on the glass-fiber filter of the PLVWSS. In the dissolved phase (filtrate – Figure 2 bottom) sample, however, the naphthalenes clearly predominate over all the other PAH, and the presence of the declining but slightly water-soluble C1- and C2-alkylated homologues is in direct contrast to the water-washed pattern (also see Appendix A) obtained for the higher-molecular-weight particulate/oil phase PAH trapped on the filter. Also, almost all of the n-alkanes (Figure 3 bottom) are just barely above (or in most cases below) the MDL in the filtrate (dissolved phase) because of their limited water solubility.

Table 3. Hydrocarbon Parameters Used in the LTEMP Data Analysis.

Parameter	**Relevance**
DSI (mussel tissues and sediments)	Dissolved Signal Index sums the soluble PAH fractions of an oil signature (see accompanying text) DSI = dissolved (naphthalenes + fluorene + C1-fluorene) + dissolved (phenanthrenes) + dissolved (dibenzothiophenes)
PSI (mussel tissues and sediments)	Particulate Signal Index sums the less soluble PAH fractions plus any water-washed groups (see accompanying text) PSI = (C2- + C3-fluorene) + particulate (anthracenes & phenanthrenes) + particulate (dibenzothiophenes) + particulate (fluoranthene/pyrenes) + particulate (chrysenes)
Pyrogenic index (mussel tissues and sediments)	Pyrogenic Index = pyrogenic fraction + pyrogenic (phenanthrenes) + pyrogenic (dibenzothiophenes) + pyrogenic (fluoranthene/pyrenes) + pyrogenic (chrysenes) Where: Pyrogenic fraction = benzo(a)anthracene + benzo(b)fluoranthene + benzo(k)fluoranthene + benzo(e)pyrene + benzo(a)pyrene + indeno(1,2,3-cd)pyrene + dibenzo(a,h)anthracene + benzo(g,h,i)perylene
TPAH (mussel tissue and sediments)	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/anthracene + chrysene, and their alkyl homologues + other PAHs (excluding perylene); useful for determining TPAH contamination and the relative contribution of petrogenic, pyrogenic, and diagenic sources
TSHC (sediments)	Total Saturated 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 (GC/FID); includes both petrogenic and biogenic sources
UCM (sediments)	Unresolved Complex Mixture – petroleum compounds represented by the GC-FID signal for total resolved peaks plus unresolved area under the peaks minus the total area of the resolved peaks quantified with valley-to-valley baseline integration; a characteristic of some fresh oils and most weathered oils.

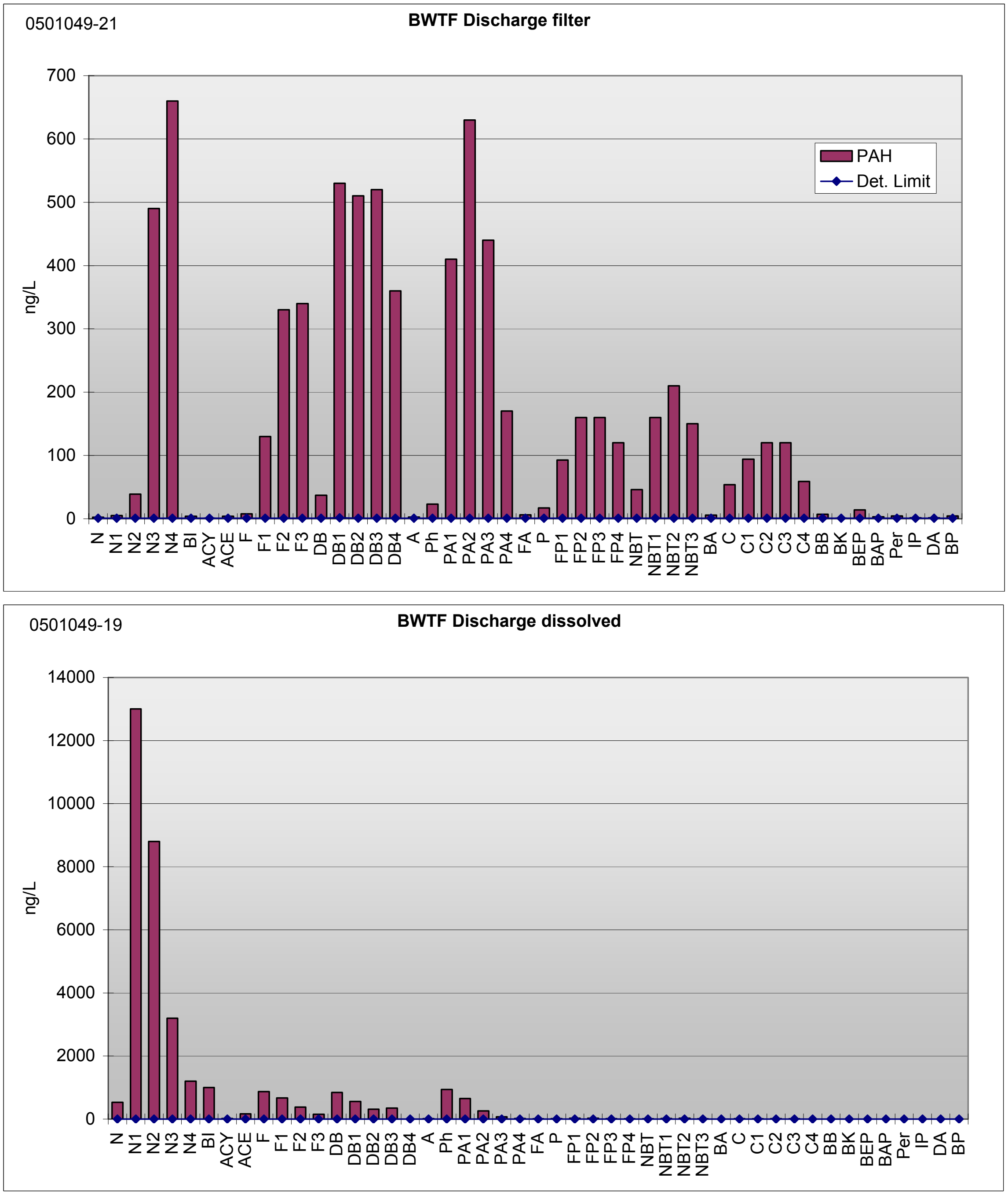
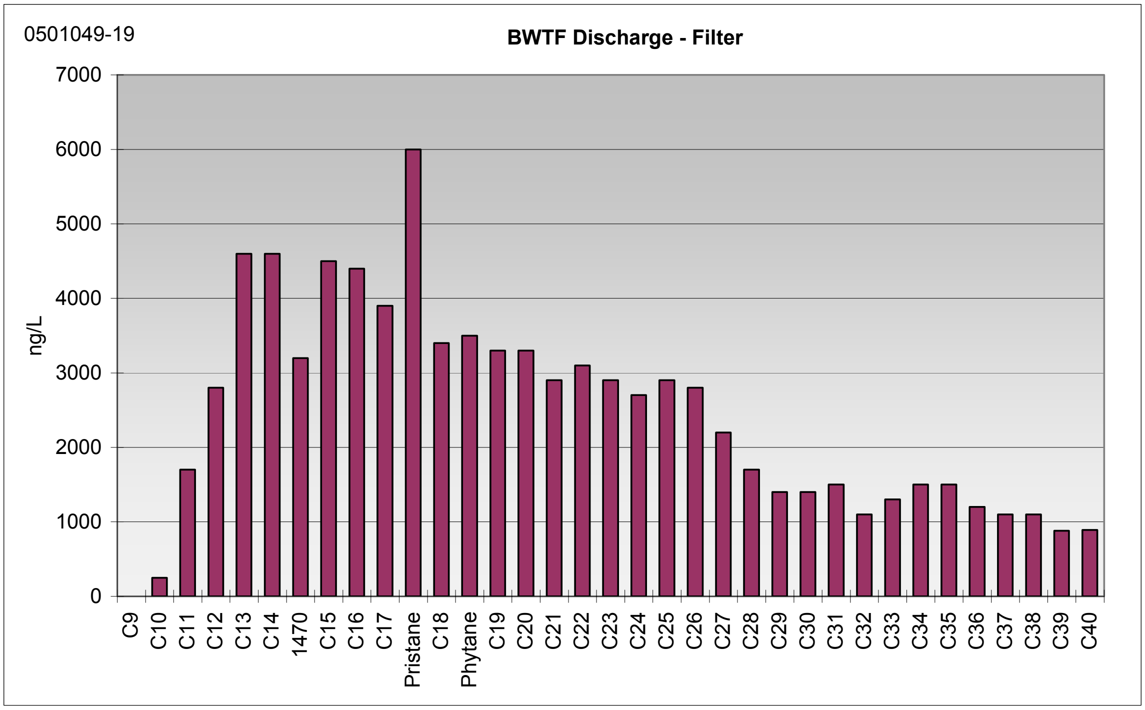


Figure 2 PAH profiles of oil droplets removed by filtration (upper) and the dissolved-phase (lower) of the AMT BWTF effluent, January 2005 (from Payne et al. 2005b).

This partitioning behavior is controlled by the concentration of a given component in the initial oil phase as well as the solubility of that component in both the oil and water phases (i.e., the oil/water partition coefficient). The kinetics of this partitioning is controlled by the oil droplet surface-area-to-volume ratio, the interphase mass-transfer coefficient, and the distance from equilibrium concentrations of a given water-soluble component in the oil and water phases (Payne et al., 1984; NRC 1985, 2003, 2005).



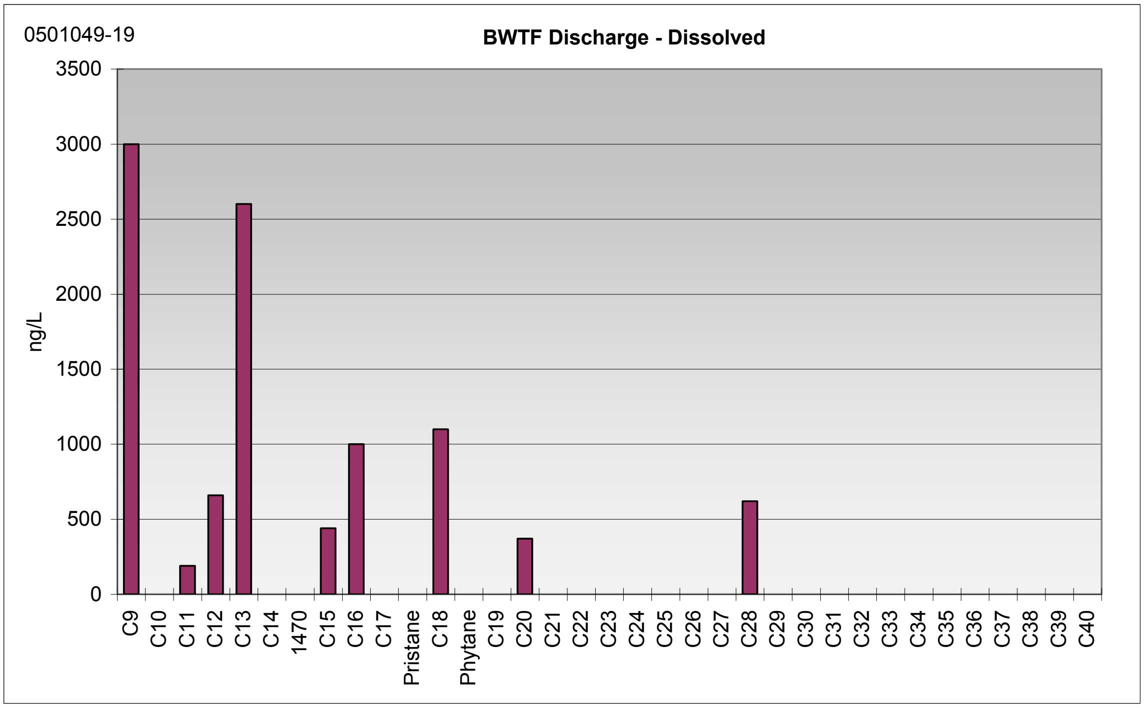


Figure 3 SHC profiles of oil droplets removed by filtration (upper) and the dissolved-phase (lower) of the AMT BWTF effluent, January 2005 (from Payne et al. 2005b).

When oil is spilled at sea, a true equilibrium of oil and water-column concentrations is rarely attained because of the continuing dilution of dissolved components with fresh seawater. Thus, at any given moment, a dynamic (rather than static) equilibrium exists between the oil and water phases.

When filter-feeding indicator organisms (in this case, mussels) are exposed to water containing oil, the resulting PAH profile of the mussel tissue extracts will reflect the physical state of the oil in the water (dissolved- versus particulate/oil-phase) plus any non-soluble pyrogenic (combustion) products (Baumard et al., 1998; Payne and Driskell 2003; also see Appendix A). These signatures are easily differentiated by their plots (examples in Figure 4) although mixtures can be more tricky to tease out. To better illustrate a pyrogenic source, we have included an LTEMP sediment sample. Combustion products generally make up only 20% or less of the total PAH signal in most LTEMP mussel samples (i.e., there are other components present at higher concentrations).

In 2005, Driskell et al. presented original algorithms for discerning the relative portions of dissolved PAH versus particulate versus pyrogenic phases in a crude oil sample (further refined in Payne et al., 2006). Note that the formulations presented here describe the general model but do not represent the complete algorithms. Briefly, the dissolved-signal index (DSI) is summed from the PAH analytes that display water-soluble patterns, which primarily comprise the lighter-molecular-weight analytes (left side of the PAH profiles, e.g., bottom Figure 2 and top Figure 4).

Dissolved Signal Index =
Dissolved (naphthalenes + fluorene + C1-fluorene) + dissolved phenanthrenes + dissolved dibenzothiophenes

The particulate index (PSI) is similarly formulated using less-water-soluble, mid-molecular-weight PAH (e.g., Figure 4 middle).

Particulate Signal Index =
(C2- + C3-fluorene) + particulate (anthracenes & phenanthrenes) + particulate dibenzothiophenes + particulate fluoranthene/pyrenes + particulate chrysenes

A pyrogenic signal is characterized by the higher-molecular-weight PAH plus the suites of middle (3-4 ringed) PAH when they display descending stair-step patterns and are not part of the dissolved signal (e.g., Figure 4 bottom).

Pyrogenic Index =
Pyrogenic fraction + pyrogenic phenanthrenes + pyrogenic dibenzothiophenes + pyrogenic fluoranthene/pyrenes + pyrogenic chrysenes

Where:
Pyrogenic fraction = benzo(a)anthracene + benzo(b)fluoranthene + benzo(k)fluoranthene + benzo(e)pyrene + benzo(a)pyrene + indeno(1,2,3-cd)pyrene + dibenzo(a,h)anthracene + benzo(g,h,i)perylene

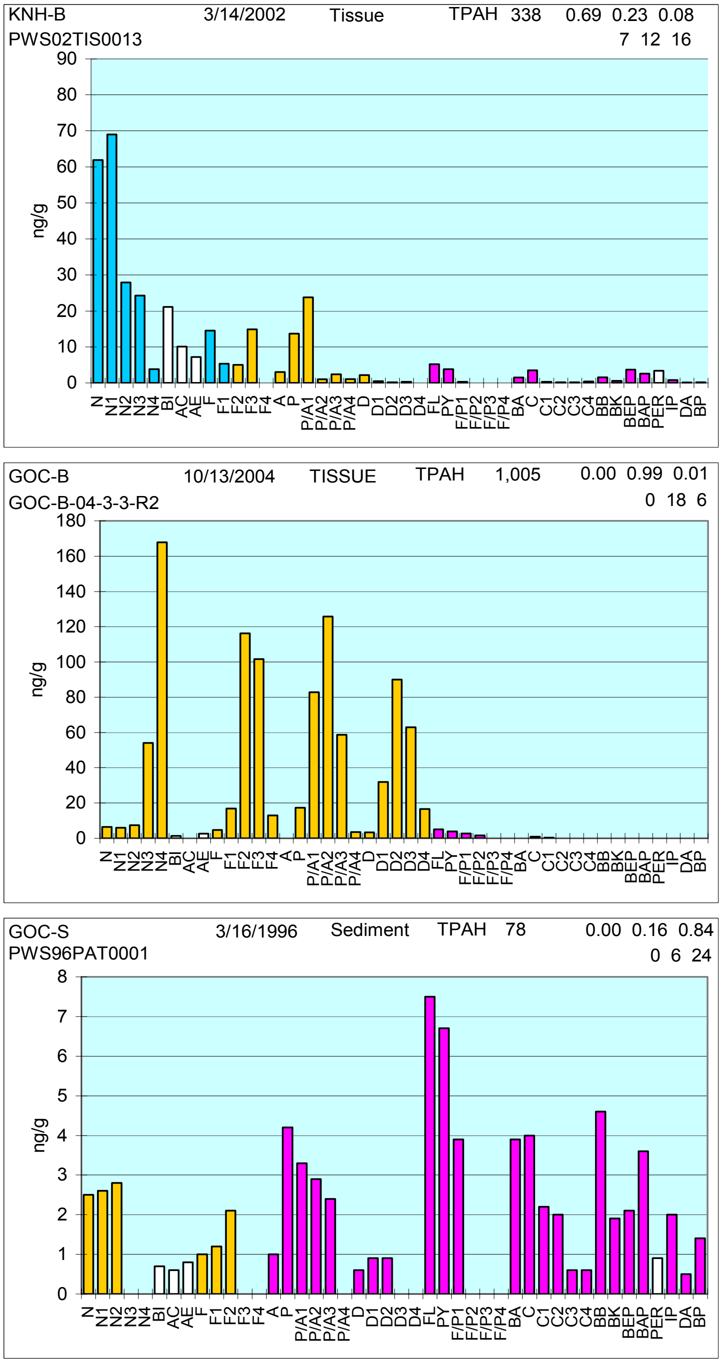


Figure 4 Examples of PAH profiles from LTEMP mussels containing primarily background dissolved-phase components (analytes colored turquoise; top – Knowles Head) and particulate/oil-phase components from a diesel spill (colored gold; middle – Gold Creek), and LTEMP sediments containing primarily low-level combustion products (colored fuchsia; bottom – Gold Creek). White colored analytes are indeterminate. The fractional proportions of each phase (soluble, particulate/oil, and pyrogenic) are shown by the numbers in the upper right-hand corner of each plot with the number of analytes assigned to each group just below (e.g., the bottom replicate was 84% pyrogenic from the 24 fuchsia-coded analytes).

For batch processing the PAH data, algorithms assigning the five multi-state PAH families to dissolved, particulate, or pyrogenic fraction are formulated as Excel logic statements. The logic assigns analytes to a phase based on expected patterns relative to their known dissolution characteristics in water. For example, phenanthrenes would be assigned depending upon both the relative amounts of the parent and alkylated homologues and diagnostic traits from other analyte groups (see Payne et al., 2006 for full description). For example, phenanthrenes in tissues are allocated as dissolved, particulate, or pyrogenic by:

```
IF
    Tissue phenanthrene > max (phenanthrene homologues)
THEN
    IF
        Naphthalenes are dissolved
    THEN
        Dissolved phenanthrenes = sum (all phenanthrenes + anthracene)
    ELSE
        IF
            Pyrogenic fraction > 0
            or
            Fluoranthene or pyrene or chrysene are pyrogenic
        THEN
            Pyrogenic phenanthrenes = sum (all phenanthrenes + anthracene)
        ELSE
            Particulate phenanthrenes = sum (all phenanthrenes + anthracene)
```

Since dissolved phenanthrenes are unlikely to occur in sediments, sediment phenanthrenes and fluorenes are only attributed as pyrogenic or particulate based on:

```
IF
    Sediment phenanthrene > max (phenanthrene homologues)
    and
    (Pyrogenic fraction > 0
    or
    Fluoranthene or pyrene or chrysene are pyrogenic)
    THEN
        Pyrogenic phenanthrenes = sum (all phenanthrenes + anthracene)
ELSE
    Particulate phenanthrenes = sum (all phenanthrenes+ anthracene)
```

Similar logical constructs assess each analyte family (Payne et al., 2006). As each replicate sample is processed through the logic, the individual analytes are plotted color-coded to represent their assignment to a particular phase (plotted in three colors, Figure 4). Phase proportions and number of analytes in each phase appear as labels in the upper right of the plot. This graphic style greatly improves the efficiency of evaluating the 13 years of triplicate LTEMP samples (n>800). In practice, the computer phase assignments are not considered final interpretations. If circumstances suggest mixed sources or small critical differences, we may overrule the assignments based upon other evidence (e.g., similarity to other replicates or SHC patterns suggesting either petrogenic or biogenic components).

4.7.2 Data Anomalies

In the years since LTEMP's inception, analytical chemistry methods and instrumentation have improved. Regrettably, some of the early data with low-level TPAH contain obvious anomalies; lower-concentration samples were incorrectly integrated and merely reflect the laboratory method blanks. Newer GC/MS instrumentation was introduced circa 1997, which resulted in more detections of lower-concentration analytes and more accurate data. To avoid misinterpretations, we have chosen to begin our time series analysis with 1998, although some earlier data that we felt reliably report moderate-to-high TPAH levels are presented. Further details are available in previous annual reports (Payne et al., 2003a, 2005a, 2006).

One issue with early program data occurred with exceptionally clean or low-PAH-level tissue samples when laboratory artifacts were inadvertently reported as real PAH components. We report the data here but flag it as unreliable (discussed below). The problem is detailed in Payne et al. (1998, 2003a, 2005a) but briefly, the issue arose when the early software for the laboratory's GC/MS instrumentation did not automatically integrate all the alkylated PAH homologues (08/07/03 personal communication with Dr. Guy Denoux, GERG Laboratory Director). Most parent PAH components (and methylnaphthalenes) were automatically integrated, but quantification of the remaining C_2-, C_3-, and C_4-alkylated homologues had to be done manually by the GC/MS operator, and then only when a recognizable signal was first observed. As a result, PAH patterns identical to those shown in Figure 5 were often obtained on tissue samples from the cleaner areas and in many of the laboratory procedural blanks (Figure 5). Fortunately, this issue does not appear with sediment chemistry data or with mussel tissue results from later (post 1997) years of the program.

Another procedural artifact discussed at length by Payne et al. (2003a) was anomalously high fluorene and alkylated-fluorene (F, F1, F2, F3) concentrations being reported as a result of incomplete sample cleanup and lipid interference. This was particularly problematic in tissue samples analyzed by GERG from the July 1994, July 1996, and July 1999 sample collections. For reasons presented in last year's report, we elected to simply drop the fluorene contribution to the TPAH and other diagnostic indices for the July 1994, July 1996, and July 1999 tissue samples to eliminate the mega-spikes. Where there was a significant real signal from other PAH, the loss would be minimal and characterization mostly unaffected.

In the July 1997 samples from Disk Island (DII), Gold Creek (GOC), Knowles Head (KNH), Sheep Bay (SHB), and Sleepy Bay (SLB), we noticed that the PAH patterns were remarkably similar (if not identical) and characterized by one or two additional naphthalenes at higher concentrations plus all the other procedural artifacts (Figure 5). In these instances, there were no other alkylated components detected (except

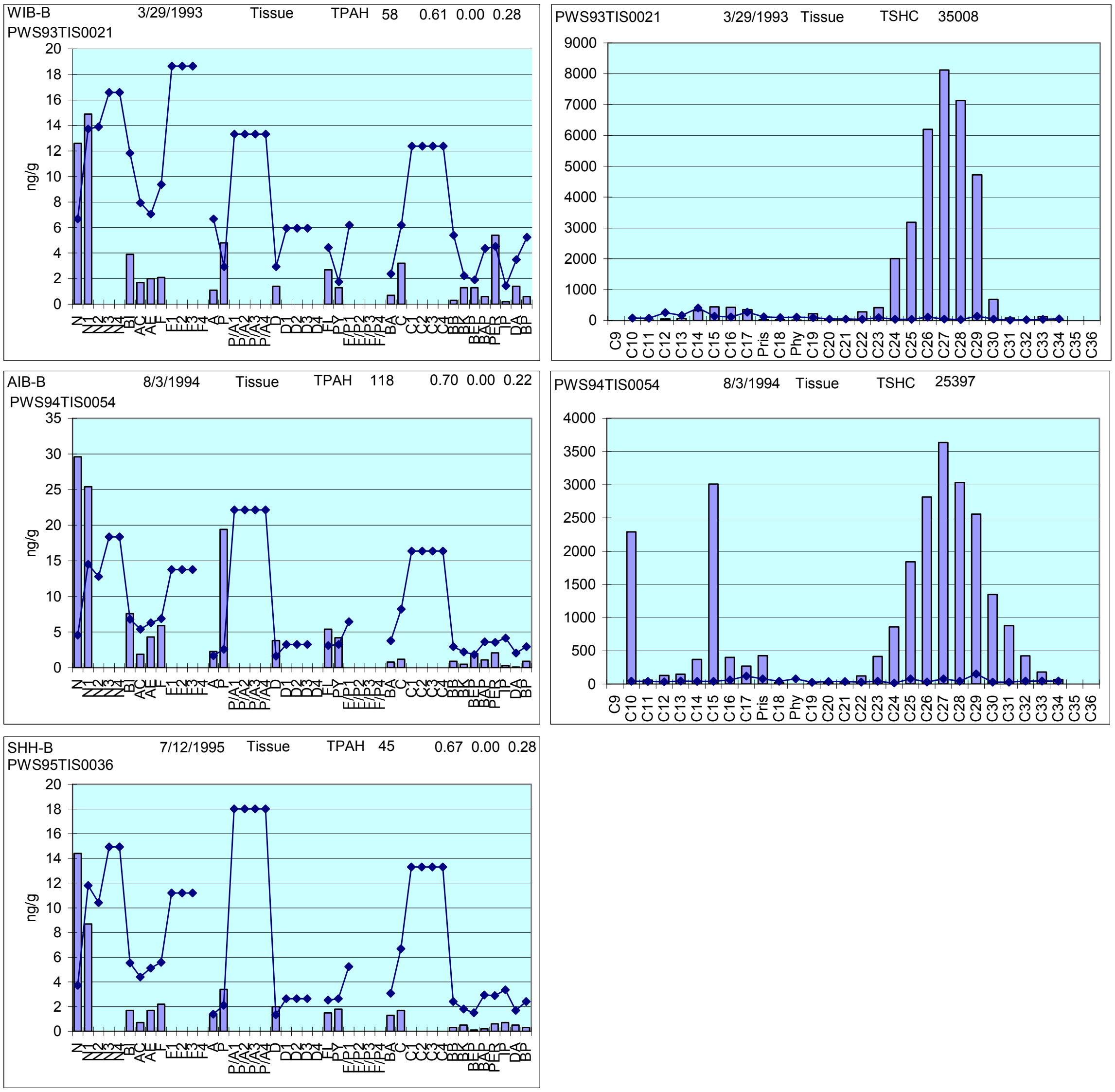


Figure 5 PAH procedural artifact patterns (left graphs) common in early LTEMP samples between March 1993 and March 1997. For these samples, homolog data are incomplete. The overlaying solid lines with the blue diamonds represent reported MDLs. Line gaps indicate analytes not reported at the time. SHC analyses (right graphs) were discontinued between 1995 and 1998 due to lipid interference problems.

for the extra naphthalenes) to suggest that the observed patterns were in fact real (Figure 6), and we concluded that the laboratory may have again erroneously reported concentrations for procedural artifacts plus additional naphthalenes that were manually integrated. For additional details, see Payne et al. (2006). These elevated naphthalenes lead to an apparent region-wide spike in TPAH levels in 1997 with major contributions from the dissolved phase. However, we have little confidence in those data and suspect instead that this apparent trend is really nothing more than an anomaly introduced by changing laboratory integration procedures.

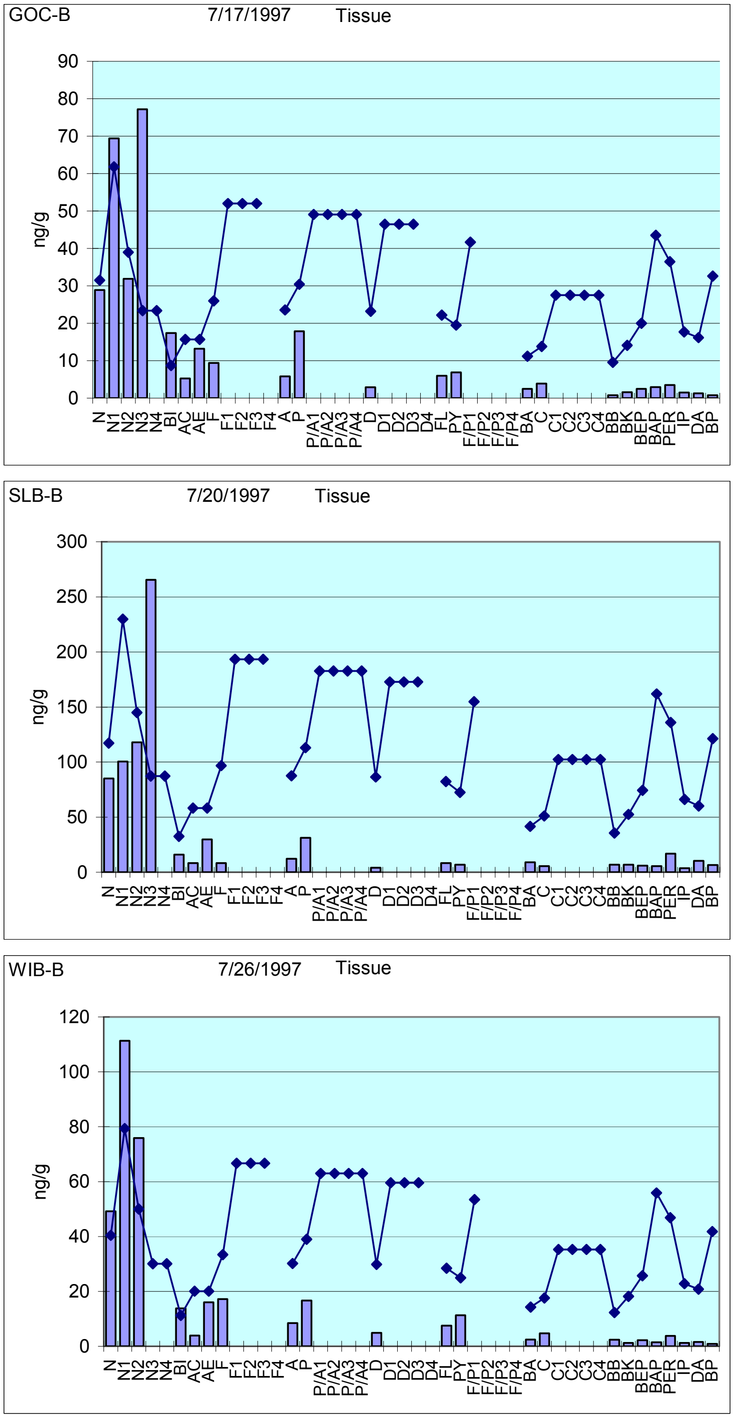


Figure 6 Representative PAH profiles and method detection limits (solid lines with blue diamonds) from July 1997 tissue samples showing highly similar procedural patterns (GC/MS integration artifacts – see Figure 5) plus additional naphthalenes.

Finally, in reviewing these data, we noted that many of the major TPAH peaks in serial plots of early tissue data tended to correlate with extracted sample weights below 1.0 g dry weight (and frequently below 0.5 g). This becomes an issue when the laboratory quantifies the instrument's response on a per gram dry weight of extracted-sample basis because below-normal-sample-weight adjustments arithmetically amplify the results (i.e., a small denominator for the sample dry weight amplifies the final concentration calculation). For this project, we chose to conservatively eliminate only obvious outliers (e.g., samples with half the other triplicates sample weights but twice their concentrations) and address the ramifications in the discussion. Note that even when inflated, there may still be useful information; the analytes' relative concentrations in a low-weight sample may be accurate enough to review phase assignments and source identification, particularly as a confirming signature for the samples' triplicates.

For this year's report, we once again re-examined <u>all</u> the historic tissue data including laboratory blanks and sample sizes, and flagged those samples that were characterized by one of the four patterns discussed above. Then, to avoid propagating questionable data, any questionable data points were excluded in our PAH time series plots. For these plots, values in which we have confidence are represented by symbols on the connecting lines; questionable data have dashed connecting lines between sampling intervals but no symbols. With this approach, legitimate data are easily identified while questionable values are only presented for displaying the complete data set.

4.8 Data Management

Data received in spreadsheet format from ABL were combined with historic data from the LTEMP Microsoft Access database archives. Microsoft Excel pivot tables were used for most data compilations. Graphing and data processing routines (described above) were custom programmed for Excel using Microsoft Visual Basic for Applications (VBA) code.

5 Results and Discussion

5.1 Sampling and Data Quality

5.1.1 ABL Quality Assurance Chemistry Results

The 2005-2006 field samples were processed with a set of quality assurance samples designed to verify analytical accuracy, precision, method cleanliness, and method efficiency. Analysis of the sixteen accuracy-check, instrumental-stability samples (i.e. SRM 1491 or the ABL aliphatic standard) indicated that accuracy for the calibrated compounds were within ABL's targeted range of 85% to 115% of certified or expected values in 97.7% of the observations. Analysis of the three spiked blanks showed that accuracy for the aromatic and aliphatic calibrated compounds were within ± 15% of the expected value in 95% of the observations and analysis of the four SRM 1944 sediment samples showed that accuracy for the PAH were within ± 15% of the certified values in

82% of the observations. The median precision of the PAH (including the uncalibrated compounds) in the twelve SRM 1974b tissue samples analyzed with the mussel batches, expressed as the coefficient of variation, was 22%. The precision for the certified, calibrated analytes above MDL ranged from 12% to 46%. The median precision of the PAH (including the uncalibrated compounds) in the four SRM 1944 samples analyzed with the sediment batches, expressed as the coefficient of variation, was 11%. The precision for the certified, calibrated analytes above MDL ranged from 2% to 18%. The method blanks analyzed with each batch of samples for this report were lower than or near respective MDLs for analytes verifying the absence of positive interferences introduced at the laboratory.

Recoveries of surrogate standards were between 30% and 106% for 99.6% of all surrogate hydrocarbons. These values are within the accepted ranges published in the standard operating procedures (SOP's) for the ABL laboratory and those recommended in NOAA Status and Trends protocols. In accordance with those protocols and to be consistent with procedures utilized at GERG, all individual and total PAH and SHC concentrations have been corrected for surrogate recoveries and are reported on a dry weight basis.

5.1.2 Mussel Populations

One issue of moderate concern is the availability of mussels at some of the sites (Table 4). Some locations have but patchy remnants of former colonies so boldly obvious in earlier KLI photos. At most sites, there is normal attrition in the dominant 6-7 year old mussel age class (based on growth rings) with a 3-4 year old class maturing to fill the space. There are also new 0-3 year old recruits at most locations. The size and robustness of mussels differ substantially among the sampling sites, most likely natural variation from available food resources and predation. The Sleepy Bay site is a chronically impoverished location and is definitely in a transition state. Recruitment is poor and adults are mostly scattered or absent along the transect. Both Knowles Head and Zaikof Bay transects have been stripped by starfish (*Pisaster)* predation in the last year. Nearby off-transect populations have been selected for continued monitoring. As of July 2008, the Knowles Head and Zaikof Bay sites remain impoverished, but sampling off-transect has ample abundance. Sleepy Bay mussels are still scarce but improving.

5.2 Port Valdez Sediments

The primary purpose of the Port Valdez sites is to monitor the regulated discharges (or accidental spills) from the tanker operations at the Alyeska Marine Terminal (AMT), the terminus of the Trans-Alaska oil pipeline. From one nearby site, mussels and subtidal sediments are sampled that are chronically exposed to the diluted discharge of the Alyeska Ballast Water Treatment Facility (BWTF). A reference station, 6 km across the port at Gold Creek (GOC), is also sampled for mussels and subtidal sediments.

Table 4. Field notes on mussel populations, July 2005-March 2006.

Station	Field notes
Aialik Bay	Very good population. Dense, 5-6 yr old, plump and healthy crop of recruits. No predators visible.
Alyeska Marine Terminal	Denser population and not as patchy as Gold Creek.
Disk Island	Healthy, plump, vivid blue shells. No mussels in mid-transect swale. Normally abundant mussels at left end of transect have been mostly stripped; only bysuss threads remain. Otter predation??
Gold Creek	Colony in eroded patchy strips, slippery, silt-covered with reduced shell volume. Suboptimal niche?
Knowles Head	In July 2006, they were completely removed by *Pisaster* predation. Samples were collected off-transect around the outer point which also was under *Pisaster* pressure and will be depleted by next sampling. Scouted out a new outcrop location at north end of bay isolated by long sand beaches.
Sheep Bay	Harvestable mussels discontinuous in mid transect. Shells small (<2 cm) but still 6-7 yr old. Distinct zone in KLI photos no longer visible. 3-4 yr old recruits appearing on upper surfaces.
Shuyak Harbor	Mussels patchy near right end. But healthy and aged 5-6 yr old. Less patchy near left end but slightly smaller. Good recruitment.
Sleepy Bay	Mussels are only in broken shale above the marker and at left end beyond marker. Mostly very small 3-5 yr olds. No mussels in mid-section. Small healthy group found on back side of outcrop beyond left end marker. Almost completely removed by Nucella predation in July 2006. Sampled to left of transect for 3rd replicate.
Windy Bay	Good site. Beds dense and continuous. Mussels healthy, plump and mature. Good recruitment. No visible predators.
Zaikof Bay	By March 2006, this colony had been completely stripped by *Pisaster*; sampling was shifted slightly west of site. Abundant, robust mussels.

During the 2005/2006 LTEMP program, the BWTF treated and discharged an average of five-to-seven million gallons per day (MGD) of oil-contaminated ballast water offloaded from the tankers prior to refilling them with Alaska North Slope (ANS) crude oil. This is a significant reduction in total flow compared to the 16-18 MGD treated in the early 1990s. The ballast-water treatment uses both physical and biological methodologies, which remove most of the BTEX and partially degrade the PAH and SHC components. The treated ballast water is released through a 63 m-long diffuser, approximately 400 m offshore at a depth of 62-82 m.

During warmer months, SHC biodegradation within the facility is very rapid while PAH biodegradation is only partially complete before the effluent is discharged into Port Valdez. During colder months, the biodegradation process is less efficient for both SHC and PAH (Payne et al., 2005b,c). In both seasons, the effluent signature is low level (usually < 300 ppb), but PAH and SHC constituents still appear in local sediments within the mixing zone sampled by the Alyeska Environmental Monitoring Program (EMP) (Blanchard et al., 2005; Shaw et al., 2005) and in mussel and sediment samples historically collected by LTEMP and other PWSRCAC studies (KLI, 2000 and references therein; Payne et al., 2001, 2003a,c,d, 2005a; Salazar et al., 2002). Despite the excellent processing efficiency at the BWTF, the sheer volume processed results in an estimated 0.5-1.4 barrels of highly diluted oil (both as finely dispersed free oil-droplet and dissolved phases – Figure 2 and Figure 3) being discharged daily into the port, with 10-20% of the PAH contributed by the oil-droplet phase (Payne et al., 2005c).

5.2.1 Sediment Particle Grain Size

Sediment grain size plots (Figure 7) show that sediment compositions from the last two samplings are within the range of previous years. The 2002-2003 LTEMP report (Payne et al. 2003a) discusses sources and relevance of this variance. To summarize, the PGS data serve two main purposes to the LTEMP program. First, they ensure that the monitored location has not undergone drastic changes, e.g., slope failures, dredge spoils deposits, etc. Secondly, the silt + clay value allows a rough confirmation or calibration of TPAH levels should it ever become necessary.

From the past and current data, we have noted outlier samples and their effect on the chemistry data but conclude that the outliers represent spatial heterogeneity rather than site changes and more importantly, have not affected the trends nor the interpretation of results. In last year's report, we noted the recent cyclic trend of fines at GOC (Figure 8) seem to reflect seasonal silt deposition. This phenomenon is also observed in the intertidal; at times, the GOC intertidal site becomes slippery with a noticeable cover of silt. Examining the total fines (silt + clay), there appear to be increasing trends over time at both sites (Figure 8) but the sampling design is too confounded to draw any real conclusions (e.g., variance in site location, change in soil labs, consistency in obtaining surface pgs sample). Results do suggest that AMT is a less dynamic regime than GOC, but the sites have always yielded similar soft fines at every sampling and thus represent a good comparative site pairing.

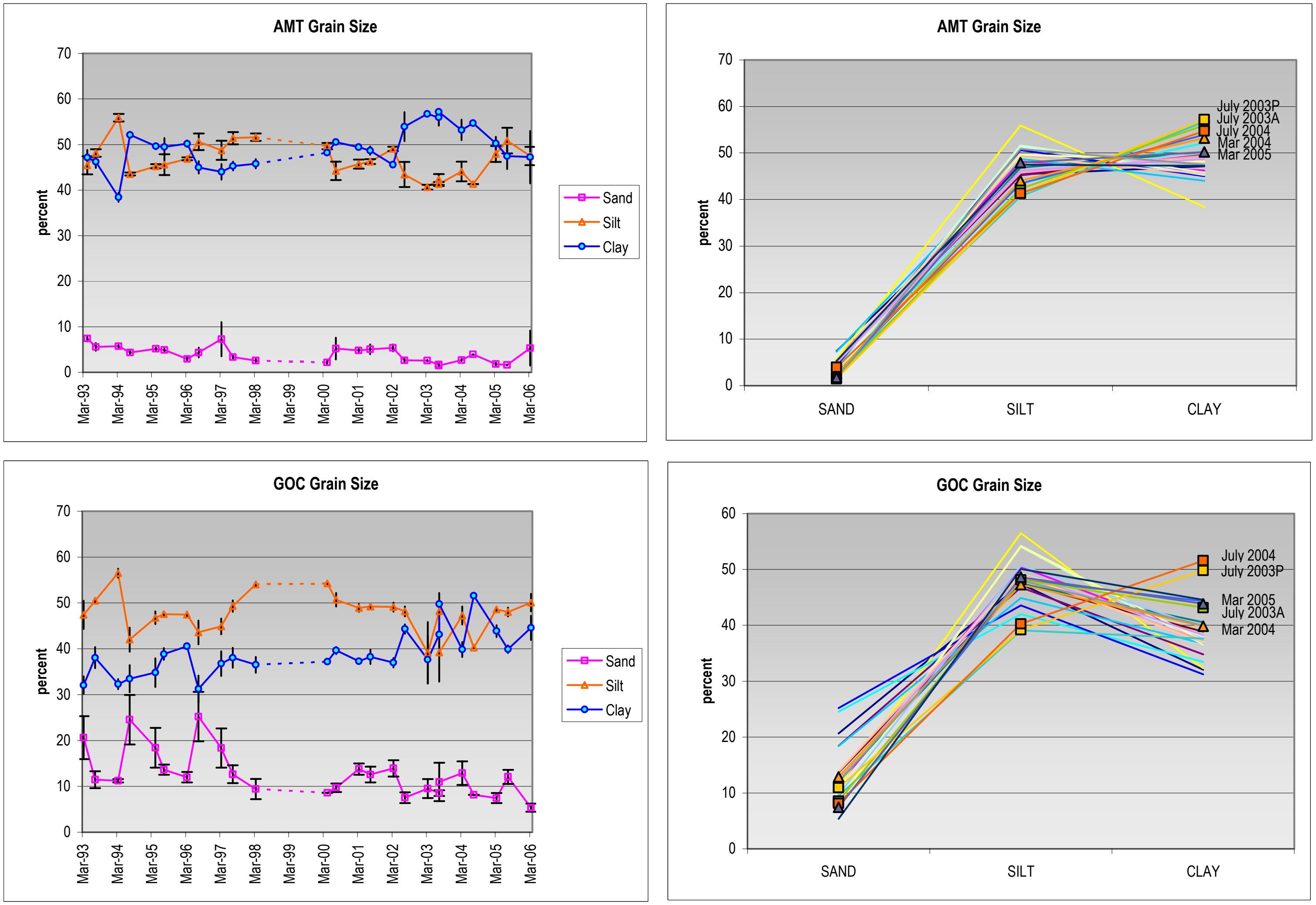


Figure 7 Time series and time overlays of grain size composition at Alyeska Marine Terminal and Gold Creek, 1993-2006. Sediments were not collected in 1998-99.

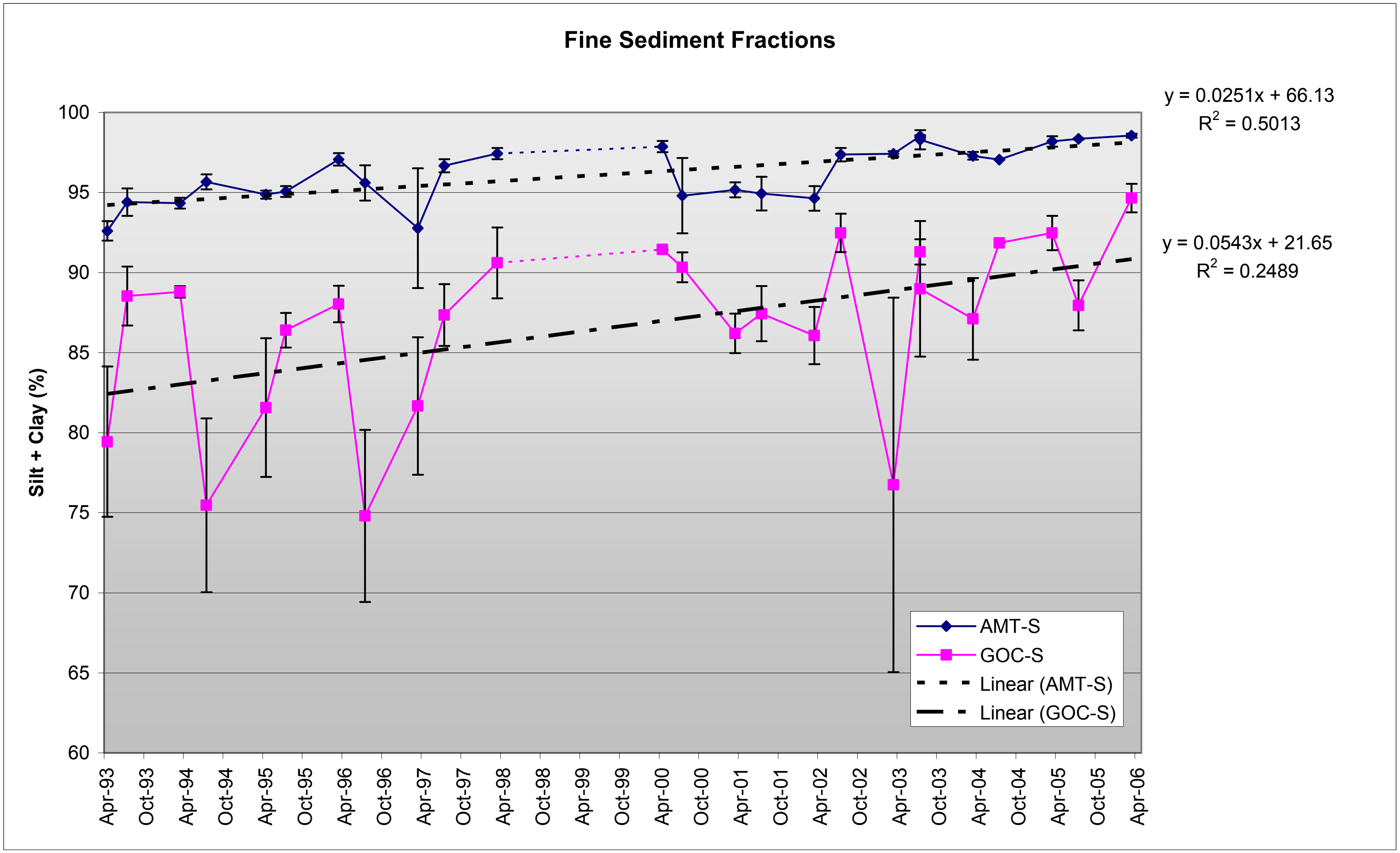


Figure 8 Average fine sediment fractions (silt + clay) time series trends (±standard error of means) from GOC and AMT surficial sediment grabs. Note y-axis scale has been clipped for detailed viewing. Sediments were not collected in 1998-99.

5.2.2 Total Organic and Inorganic Carbon

Although suspended sediment loads are visibly high in the eastern portion of the Port Valdez basin, the carbon contents (Table 5 and Figure 9) are typical of the predominate, organically-poor glacial flour common throughout the Port Valdez and Prince William Sound Basin. At Constantine Harbor (COH), values are similarly low but do show a presumed bump from spring blooms. Even though this site has exposure to oceanic input from Gulf of Alaska, it is often visibly within the diluted, yet still turbid plume of the Copper River.

Table 5 Total organic and inorganic carbon in sediment replicates at Port Valdez and Constantine Harbor stations.

	Jul-05			**Mar-06**		
	% TC	**% TOC**	**% TIC**	**% TC**	**% TOC**	**% TIC**
AMT	0.70	0.69	0.02	0.57	0.57	0.00
AMT	0.63	0.62	0.01	0.59	0.59	0.00
AMT	0.60	0.57	0.04	0.61	0.60	0.01
avg	**0.65**	**0.62**	**0.02**	**0.59**	**0.59**	**0.00**
std dev	0.05	0.06	0.01	0.02	0.01	0.00
GOC	0.59	0.59	0.00	0.62	0.62	0.00
GOC	0.64	0.64	0.00	0.59	0.56	0.03
GOC	0.58	0.59	0.00	0.68	0.65	0.03
avg	**0.60**	**0.61**	**0.00**	**0.63**	**0.61**	**0.02**
std dev	0.03	0.03	0.00	0.04	0.04	0.01
COH	0.90	0.81	0.09	0.75	0.72	0.03
COH	0.70	0.68	0.01	0.90	0.85	0.05
COH	0.70	0.68	0.02	1.12	0.98	0.14
avg	**0.77**	**0.72**	**0.04**	**0.92**	**0.85**	**0.07**
std dev	0.12	0.07	0.05	0.18	0.13	0.06

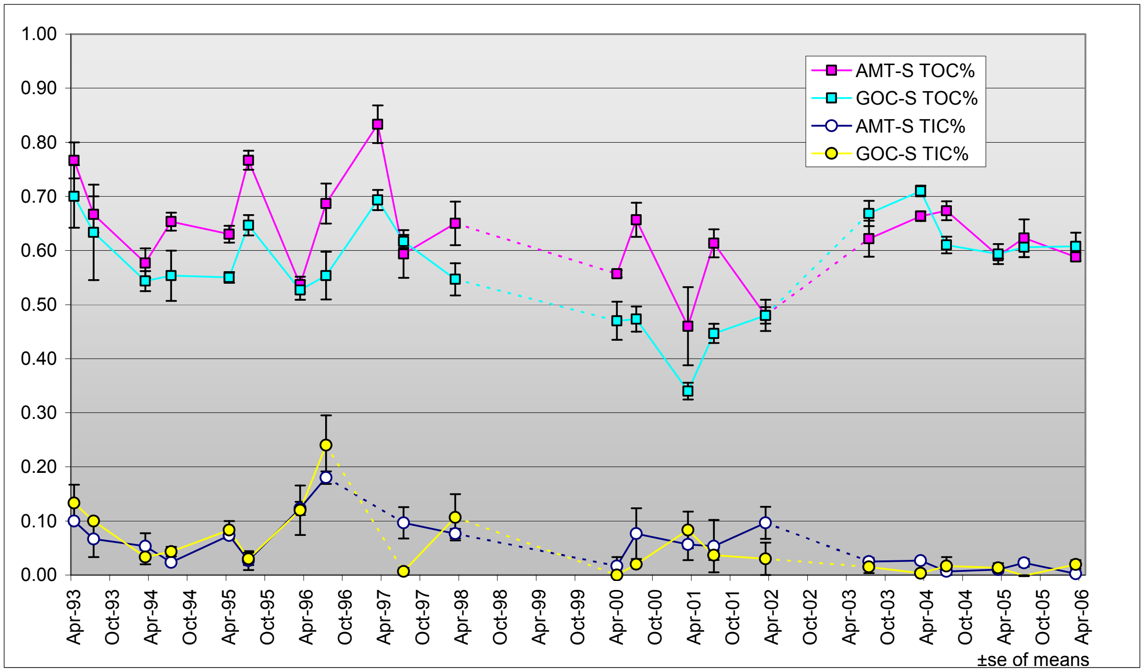


Figure 9 Time series of total organic and inorganic carbon in AMT and GOC sediment. Dotted lines indicate data gaps.

5.2.3 Sediment Chemistry

For a historic recap of the summary sediment chemistry data, Appendix B-1 tabulates the total SHC and PAH values of individual samples, seasonal averages, and the associated coefficients of variation for the replicate measurements completed between 1993 and 2006. In the following sections, these data are discussed for each site separately utilizing a graphical technique first introduced in the 2004-2005 LTEMP report (Payne et al., 2006).

Using the three phase indices developed in Section 4.7.1 plus TPAH, we developed a graphic style (Figure 10) that presents averaged time-series data. The dual-axis, left-hand panels show the relative portions of the TPAH from the three phases (scaled by the left axis) as well as the actual TPAH value (by the logarithmic right axis). The right-hand panels present the same data but scaled as total concentrations (ng/g dry weight on a linear scale) for each phase. Here, the sum of the phases equals the total PAH. This dual-presentation format allows overall trends to be easily identified with the absolute phase magnitudes shown in the right-hand panels, while finer details on relative phase contributions are tracked in the left-hand panels. As a convention, the early samples where procedural artifacts are suspected (1993-1997) are left in context represented by finely-dashed lines; data that we consider reliable have solid symbols. Error bars are omitted for visual clarity.

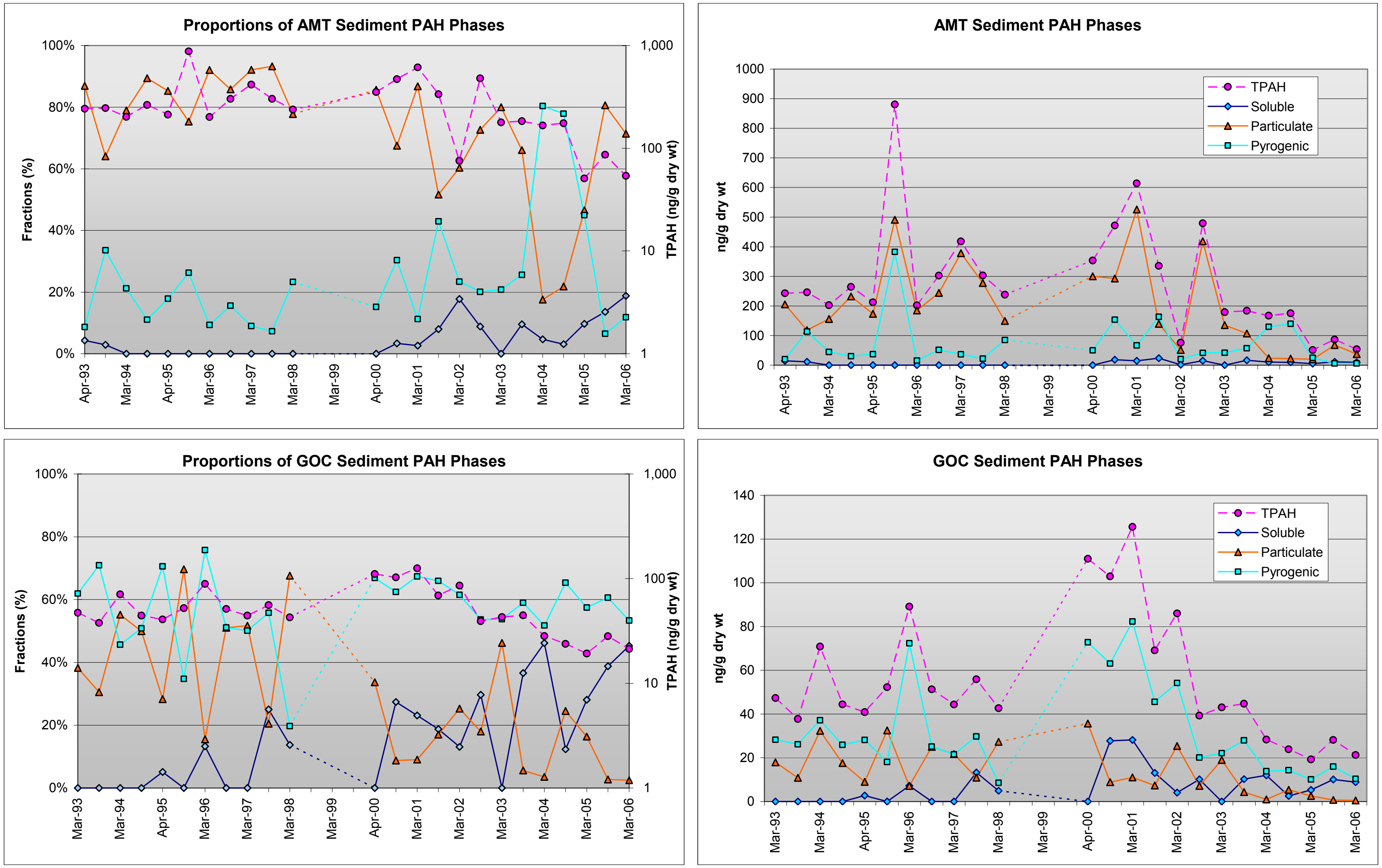


Figure 10 Time series TPAH and relative phase composition of PAH profiles in AMT and GOC sediment samples. Sediments were not collected in 1998-99.

5.2.3.1 Alyeska Marine Terminal

While there has historically been a lot of variability in the sediment TPAH values at this site (top panels in Figure 10), the concentrations have been less variable over the last three years (since March 2003), and have significantly declined compared to the historical range. Also, it is clear that until recently, the majority of the TPAH signal has been associated with the particulate/oil-droplet phase with lesser contributions from pyrogenic components (Figure 10). This is probably the result of free oil droplets from the diffuser interacting with suspended particulate material (SPM) followed by near-field sedimentation (Payne et al. 2003b). In March and July 2004, pyrogenic components were dominant (Figure 10 upper panels), but a more typical, very low, and heavily biodegraded, particulate oil signal has returned in the July 2005 and March 2006 samples (Figure 11). The decline in TPAH in the AMT sediments may reflect lower levels of free oil droplets in the BWTF discharge from reduced discharge volumes, or improvements in the ballast water treatment process efficiency at removing free oil droplets, or both.

As pointed out in previous LTEMP reports (Payne et al., 2003a, 2005a, 2006), we cannot tell from these data if the water-soluble fraction (primarily naphthalenes, which are apparently increasing in proportion to other components over the last three years) is truly bioavailable or simply tied up in the sedimentary matrix. Naphthalenes make up a major component in the deepwater sediments throughout Port Valdez, Prince William Sound, and offshore areas in the Gulf of Alaska from the Copper River to the Shelikof Straits (Short and Babcock 1996; Short et al., 1999, 2007b; Page et al., 1995; Payne et al., 1998, 2006; Saupe, 2004). Our phase-assignment model assigns a dissolved characterization to the naphthalenes because of their decreasing trend with increasing levels of alkylation and their abundance relative to the fluorenes and the phenanthrenes/anthracenes (see Section 4.7.1), but their ubiquitous nature suggests that they are truly tied up in the mineral phase (discussed later).

5.2.3.2 Gold Creek

Just as in the sediment samples from the Alyeska Marine Terminal, there has been considerable variability in the TPAH values at GOC in the past, but the overall TPAH concentrations are generally five-to-ten times lower at GOC (lower panels Figure 10). And just like AMT, the GOC sediments show declining TPAH levels since July 2003 (right-hand graphs Figure 10); however, the overall TPAH levels appear to track primarily with the pyrogenic (combustion) fraction at GOC, whereas they were almost exclusively driven by the particulate/oil-phase at AMT. The relative composition data (lower right Figure 10) show that while the combustion- and particulate/oil-derived constituents in Gold Creek sediments appear to be declining since March 2002, the relative contributions from more soluble, lower-molecular-weight constituents have been increasing since July 2004. This was also observed in the sediments at AMT, but again, we cannot tell from these data alone, if the naphthalenes are truly dissolved in interstitial

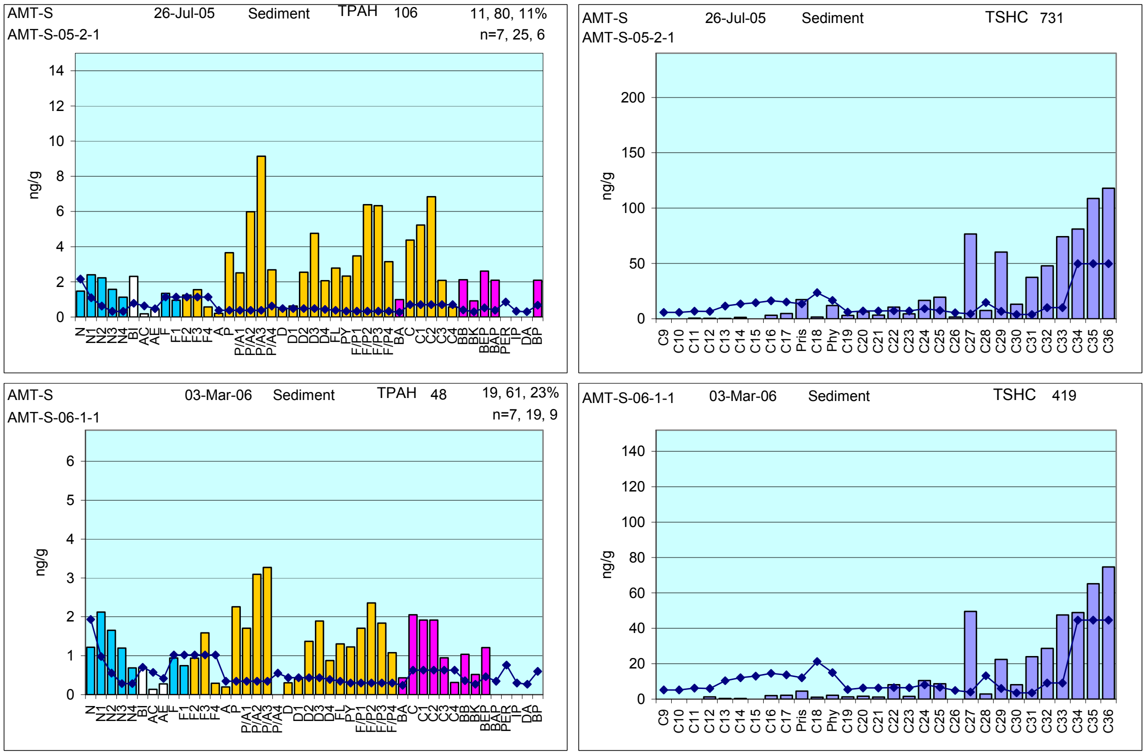


Figure 11 PAH and SHC profiles from representative AMT sediment in July 2005 and March 2006 showing complex, oil/particulate-dominated signatures in a heavily weathered and biodegraded, mixed signal. MDLs indicated with dotted solid line.

water or tied up in the sedimentary matrix. From the histogram plots (Figure 12), it is clear that the phase-assignment model attributes PAH to both dissolved and combustion products, whereas the SHC fraction shows primarily biogenic input reflected by higher-molecular-weight, odd-carbon numbered n-alkanes from terrestrial plant waxes, with traces of below MDL petrogenic components suggested (at least in the July 2005 sample). In this context, however, it is important to note that the overall TPAH levels are very low (above the MDLs but still < 50 ng/g dry weight since July 2002), and we should caution that at very low levels the relative proportional signals can become pretty noisy.

Without additional sterane and triterpane data, it is impossible to determine if the very minor petrogenic signal observed in the sediments at Gold Creek can be attributed to input from the Alyeska Marine Terminal; however, Shaw et al. (2005) concluded from their triterpane data that the sediment profiles at EMP Stations 40 and 50 (near Gold Creek but at greater depths in the Port) contained petrogenic components derived from Alaska North Slope crude oil.

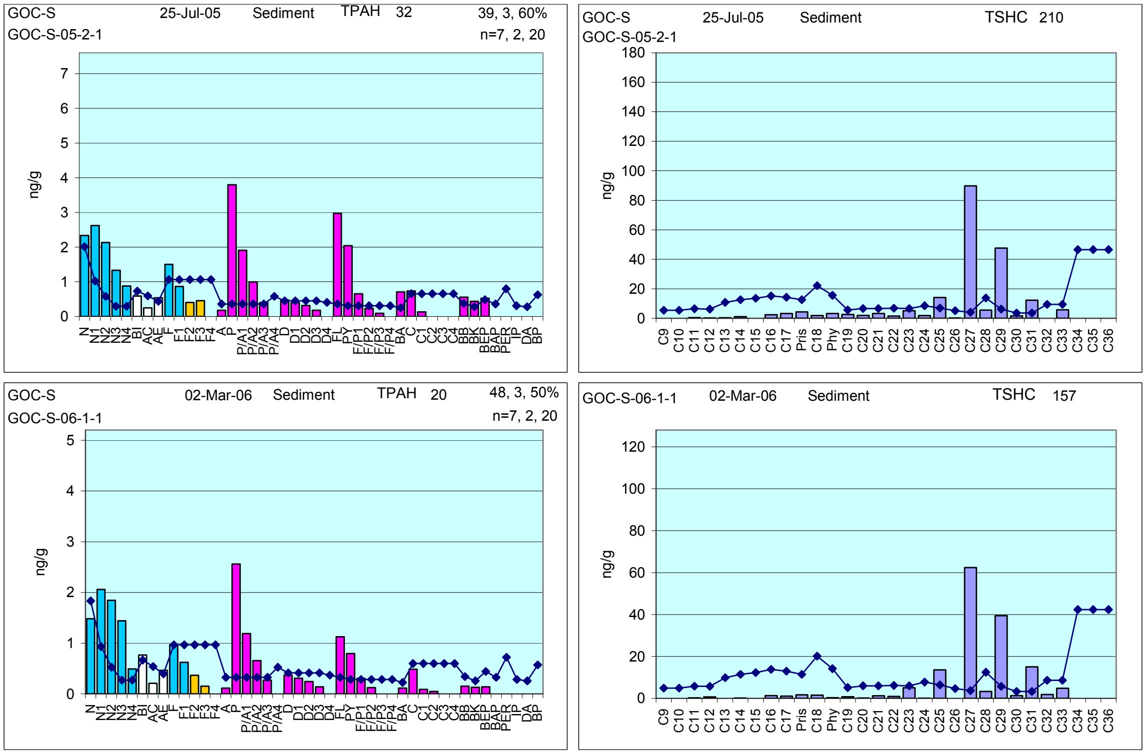


Figure 12 PAH and SHC data for July 2005 and March 2006 Gold Creek sediments.

5.2.3.3 Constantine Harbor

The Constantine Harbor site was added to the program in support of the EVOS Trustees' expanded program objectives. It serves as a non-oiled, sediment reference site primarily influenced by the plume of coastal Gulf of Alaska longshore transport as it sweeps through the Hinchinbrook entrance. TPAH concentrations ranged from 36 to 81 ng/g dry weight, and the PAH composition (Figure 13) reflected sources from outside of Prince William Sound (sediments, coal and organic material (e.g., kerogen), and natural oil seeps introduced to the Alaska Coastal Current by numerous rivers and glaciers along the Gulf of Alaska coastline southeast of the Sound (Karinen et al., 1993, Page et al., 1995; Short and Babcock 1996; Short et al., 2007b). In the PAH plots (Figure 13), the naphthalenes in these sediments are algorithmically assigned as dissolved phase since they typically do occur in the water-soluble fraction. In this case, however, their presence throughout sediments from the Copper River to Shelikof Strait (EMAP program, S. Saupe, 2004) suggests that they are bound up in the solid sedimentary phase and not easily leached out. We tested this leaching effect during the 2007 summer LTEMP/EVOS Trustees SCAT program by collecting filtered interstitial water samples and intertidal sediments from Constantine Harbor but those data are not yet available.

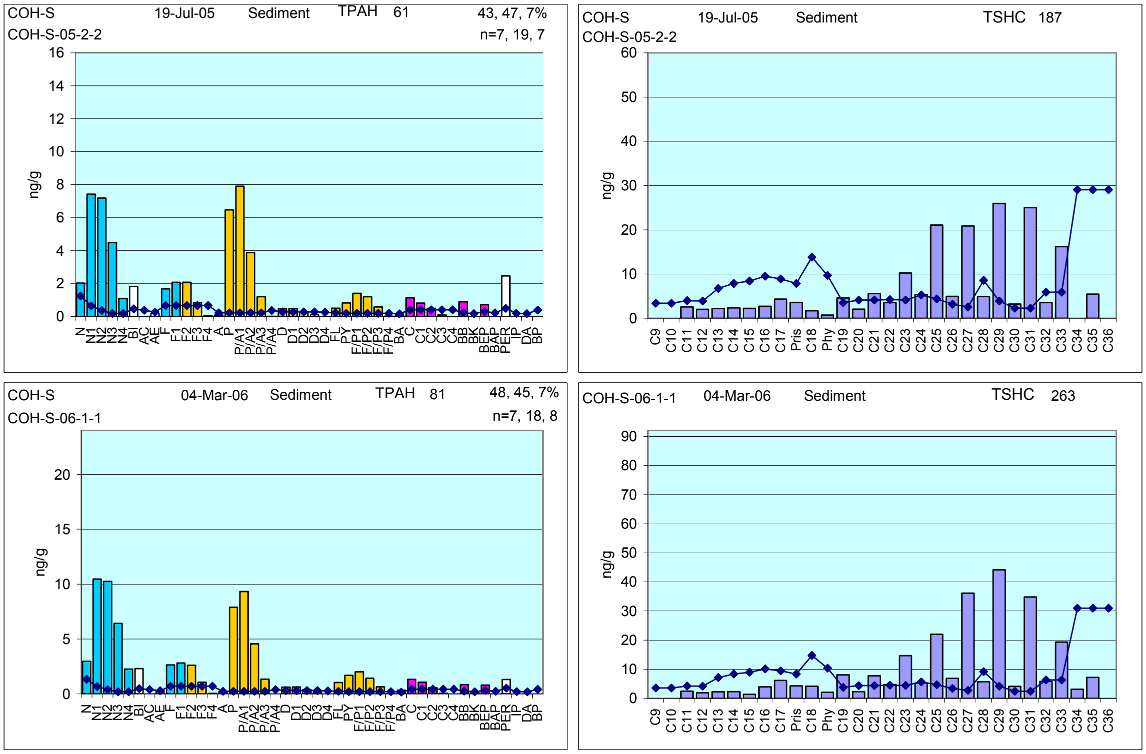


Figure 13 PAH and SHC histogram profiles from representative intertidal sediments collected from Constantine Harbor. The line connecting the blue diamonds represents the sample-specific MDL.

We do not have time-series data from Constantine Harbor as part of the LTEMP program, but data from Karinen et al. (1993) and Short and Babcock (1996) showed higher, and relatively invariant TPAH concentrations (~560 ng/g dry weight) in intertidal sediments collected in 1977-1980 and 1989-1991, respectively. The intertidal sediments collected as part of the LTEMP sampling were obtained from a slightly different area within Constantine Harbor, but the PAH composition was very similar to data reported in earlier studies. The lower concentrations presumably reflect spatial heterogeneity within the Harbor and dilution by local sediments introduced from the surrounding watershed. The SHC profiles reflected terrestrial plant wax components, and a general absence of fresh petroleum (very low or non-detectable levels of phytane). As described by Short and his colleagues, there was no evidence of EVOS oil in the sediments collected as part of this program.

5.2.4 Summary and Discussion of Sediment Chemistry Results

From examination of all the PAH data from both subtidal sediment-sampling sites, it is clear that the sediments adjacent to the Alyeska Marine Terminal are primarily contaminated by a weathered ANS oil signal, which would be consistent with BWTF-diffuser-sourced, dispersed oil-droplet/suspended-particulate-material (SPM) interactions and resulting sedimentation (Payne et al. 1989; 2003a,b). In recent years, the combustion (pyrogenic) components in the sediments at AMT have been variable and appear to be reaching all time lows. The Gold Creek sediments, on the other hand, show generally declining PAH contamination from combustion sources (since March 2001) with lesser contributions from low-level petrogenic sources. These declining combustion product assignments are highly qualified since the TPAH values are so low but may, in fact, reflect lower exhaust emissions from reduced tanker traffic or the concerted local efforts to modify idling tanker operations to mitigate air pollution within the Port.

It is not possible to tell from LTEMP data alone if the low-level petroleum source in the subtidal sediments at Gold Creek is from the BWTF and other activities at Alyeska Marine Terminal, or other sources (boat traffic, sewage and wastewater discharges from the City of Valdez). It may be possible to identify this source through sterane/triterpane analyses of Gold Creek sediments and comparisons to Alyeska Marine Terminal sediments and Alyeska BWTF discharges as part of future LTEMP or other PWSRCAC research activities. Triterpane data from the Alyeska EMP indicate that PAH from their station 40 (deeper and further offshore from the LTEMP GOC station) are consistent with weathered Alaska North Slope crude oil released from the terminal (Shaw et al., 2005).

The SHC patterns observed for the subtidal sediments at Alyeska Marine Terminal (Figure 11) show a combination of biogenic and very weathered ANS oil signals, again consistent with terrestrial and marine copepod fecal-pellet sources along with substantial oil-droplet/SPM interactions given the elevated levels of dispersed oil droplets introduced to the region from the BWTF diffuser (Payne et al. 2001; 2003a,b; 2005b,c; Salazar et al. 2002; Short 2005). In contrast, the SHC profiles from the subtidal sediments at Gold Creek (Figure 12) show a combination of marine and terrestrial biogenic input, with very little weathered-oil signal in keeping with the extremely low TPAH values observed at the site.

The intertidal sediments from Constantine Harbor had lower TPAH values than those reported in previous studies (Karinen et al., 1993; Short and Babcock, 1996), but the PAH and SHC compositional patterns (Figure 13) were consistent with previous findings and represented a non-oiled sediment primarily influenced by the plume of coastal Gulf of Alaska longshore transport as it sweeps through the Hinchinbrook Entrance.

5.3 Mussel Tissue Chemistry

5.3.1 Regional Trends and Approaches

The time series of TPAH data (Figure 14) using the consistently reliable post-1997 data shows generally decreasing trends with a subseries of somewhat synchronous peaks along the timeline. The generally simultaneous TPAH maxima occurred in July 1999, March 2001 (excluding Aialik Bay, Shuyak Harbor, and Windy Bay), March 2002 (again except for Shuyak Harbor and Windy Bay), and July 2002 (for Aialik Bay and Windy Bay only – all the other sites are dropping). These events have been discussed in previous reports couched as possibly ambiguous results or perhaps laboratory artifacts. Using the recently-developed PAH indices, however, we have noted that not only were there synchronous peaks, but in many of the stations, the composition of the trace-level signatures were also similar. After further exploration, three regional patterns became apparent; the Port Valdez, Prince William Sound, and Gulf of Alaska regional stations were each trending in similar fashion (Figure 15) and often with regionally similar, low-level dissolved- and particulate/oil-phase signals. These trends and similarities will be discussed further below, but their discovery prompted us to organize the following sections on mussel tissue chemistry by regions (Figure 15).

This report again emphasizes the importance of examining TPAH data from the perspective of dissolved- and particulate/oil-phase signals. Specifically, when analyzing the LTEMP mussel tissue samples, it is important to recognize that as filter feeders, mussels can accumulate an oil signature from both the dissolved- and particulate/oil-droplet phases, in addition to combustion products (soot) present as finely suspended pyrogenic particles in the water column (Baumard et al. 1998; Payne and Driskell 2003; Short and Springman, 2007). Using the recently developed dissolved-, particulate-, and pyrogenic indices described in Section 4.7.1, we graphically review in this section the mussel-tissue, time-series trends for each site (as shown in Figure 16 for Alyeska Marine Terminal and Gold Creek), and augment that discussion with PAH and SHC plots to further elucidate source signatures as necessary. Recall from Section 4.7.2, higher-concentration data in which we have confidence are represented by solid symbols in Figure 16 and corresponding figures for other stations, while the early, low-concentration samples where procedural artifacts are suspected (1993-1997) are left in context but represented only by finely-dashed lines.

The dual-axis data in the left-hand panels (Figure 16) show the relative percentages of the total PAH (TPAH) from the soluble, particulate (oil phase), and pyrogenic fractions (left axis) as well as the TPAH value (on a logarithmic scale – right axis). The right-hand panels present the same data simply as total concentrations (ng/g dry weight on a linear scale) for each fraction. In the right-hand panels, the sum of the soluble, particulate, and pyrogenic fractions equals the total PAH (dark fuchsia-colored circles). This dual-presentation format allows overall trends to be easily identified with the absolute magnitude of each fraction shown in the right-hand panels, while finer details on relative

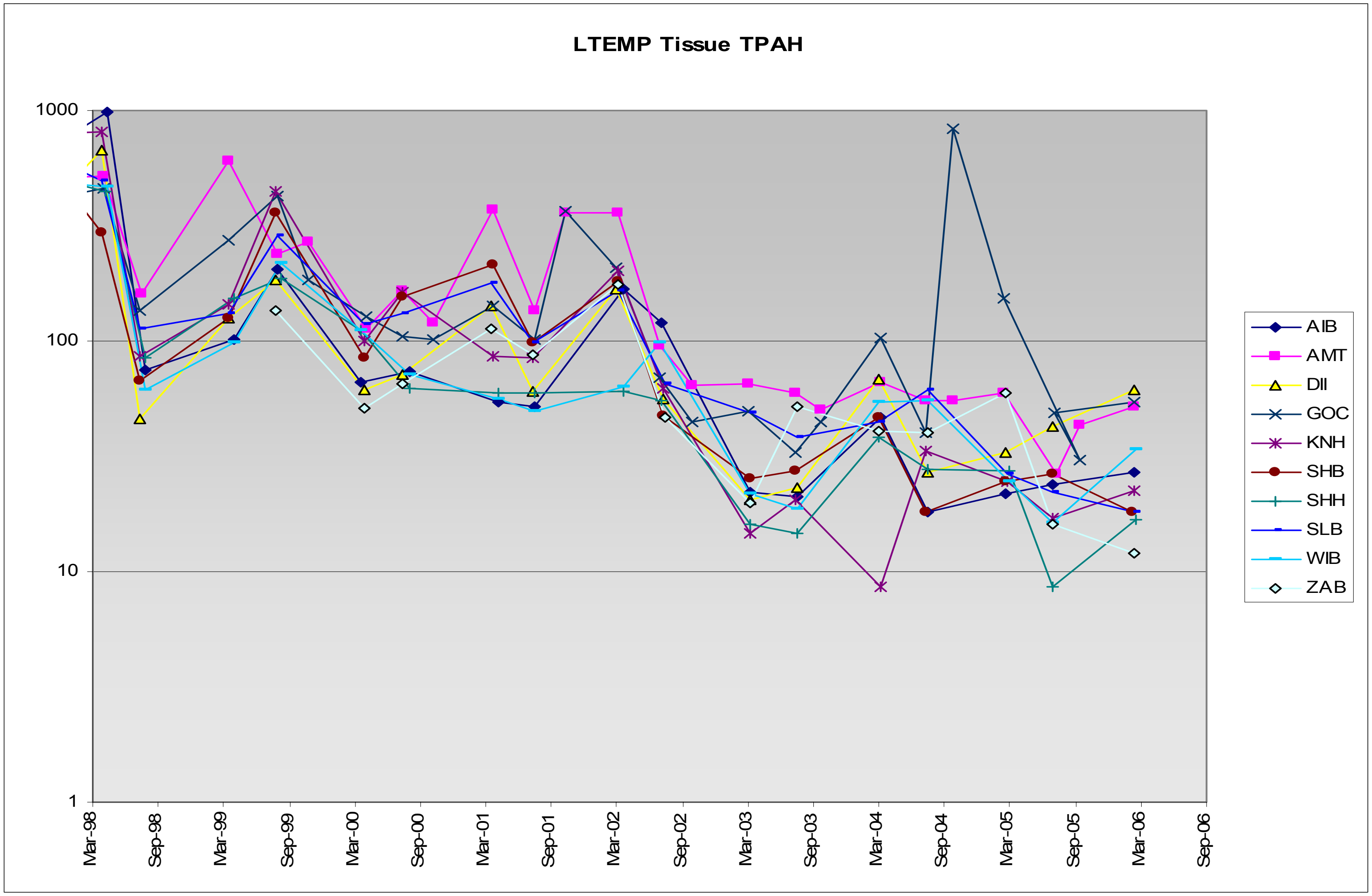


Figure 14 *Mytilus* TPAH time series (triplicate averages) for all LTEMP stations, 1998-2006.

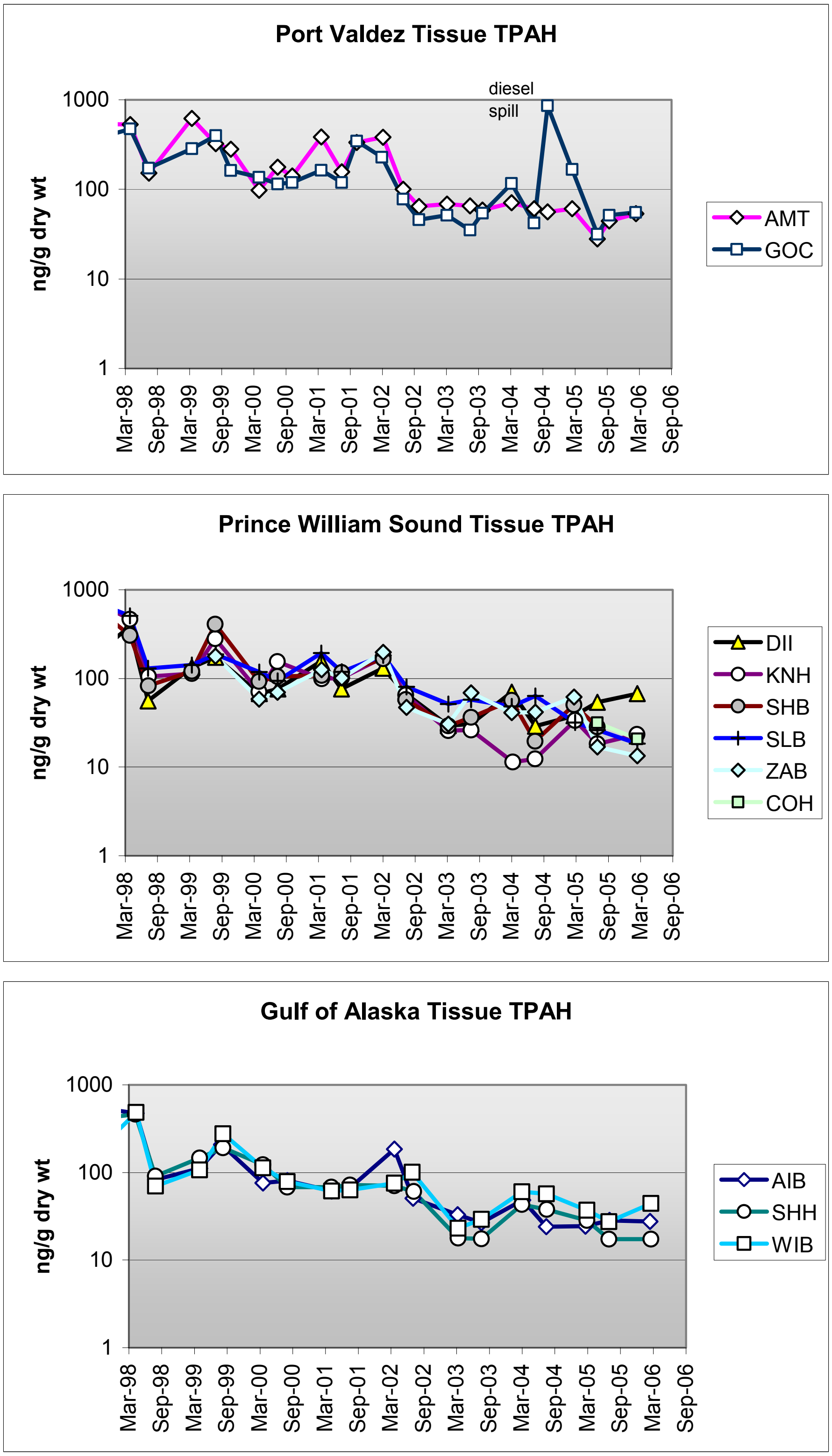


Figure 15 Regional LTEMP *Mytilus* TPAH time series, 1998-2006.

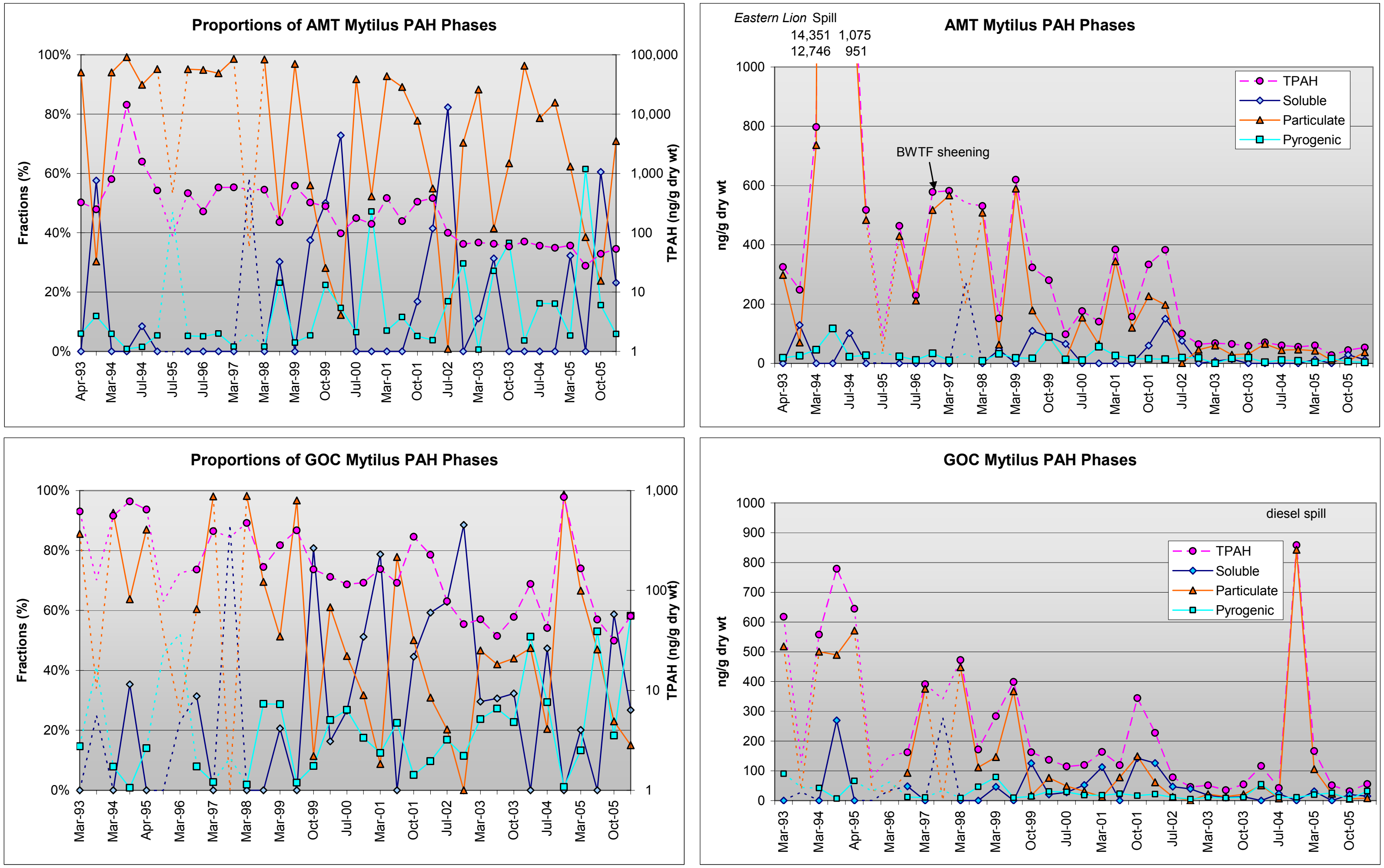


Figure 16 Time series TPAH and relative phase composition of PAH profiles in Alyeska Marine Terminal (AMT) and Gold Creek (GOC) *Mytilus* tissues. Dotted connecting lines without symbols indicate questionable data.

contributions from the different fractions can be tracked in the left-hand panels. In a recent review (BGES, 2007), it was suggested that this information might be better presented using ternary phase plots (dissolved, particulate, pyrogenic) and by separating the seasonal trend results into separate graphs. We agree that these are valid suggestions but find our methods, albeit cluttered, give the reader the complete picture without mentally integrating displays or unwrapping timelines.

In our report for the 2003-2004 program (Payne et al., 2005a), a complete review and detailed discussion of the tissue chemistry data from all stations sampled over the first eleven years of the program was presented in Appendix A-3 – Station Accounts for Tissue Samples; the interested reader is directed to that report for additional information. Appendix B-1 of this document tabulates the total SHC and PAH values of individual tissue samples, sampling averages, and the associated coefficients of variation for the replicate measurements completed between 1993 and 2006. Appendix B-2 does the same for the PAH indices, and Appendix D presents PAH histogram plots for all the tissue analyses from the 2005-2006 program. The following three sections briefly consider the time-series trends noted for the three geographic regions (Figure 14 and Figure 15), Port Valdez, Prince William Sound, and the Gulf of Alaska (see also Figure 1).

5.3.2 Port Valdez Stations

5.3.2.1 Alaska Marine Terminal Mussel Tissue Chemistry

Mussels collected from Saw Island, adjacent to berth 5 at the Alyeska Marine Terminal (AMT), have historically contained the highest and most variable TPAH concentrations of any site in the program (top panels Figure 16). These values reflect input from the daily discharge of treated ballast water from the terminal as well as known spill events, such as the *T/V Eastern Lion* oil spill in May 1994 and the BWTF spill/sheening event in January 1997. Details tracking the descent of TPAH background trend to the current low levels and source-phase variability are described at length in Payne et al. (2006, 2008). In the most recent samples there appears to be more source variability in the low-level TPAH signals (Figure 16), with mixed-phase combustion products, soluble-phase components, and oil/particulate-phase signals observed in July 2005, October 2006, and March 2006, respectively (Figure 17). As noted earlier, however, phase assignments can be tenuous at these extremely low TPAH values.

A striking feature of the AMT data is the alternating saw-tooth pattern for the particulate/oil phase dominating in the spring, and the soluble phase in the summer (excluding the *Eastern Lion* oil spill) (Figure 18, subset of Figure 16 left panel). To facilitate visualization of the seasonal comparisons within the Port, these data have been re-plotted for both the Alyeska Marine Terminal and the Gold Creek (GOC) reference station 6 km across the Port (Figure 18) with all of the other information removed Testing these patterns using randomization, paired-t tests show particulate phases dominate in spring at both sites while dissolved and pyrogenic phases tend to be higher in summer (Table 6).

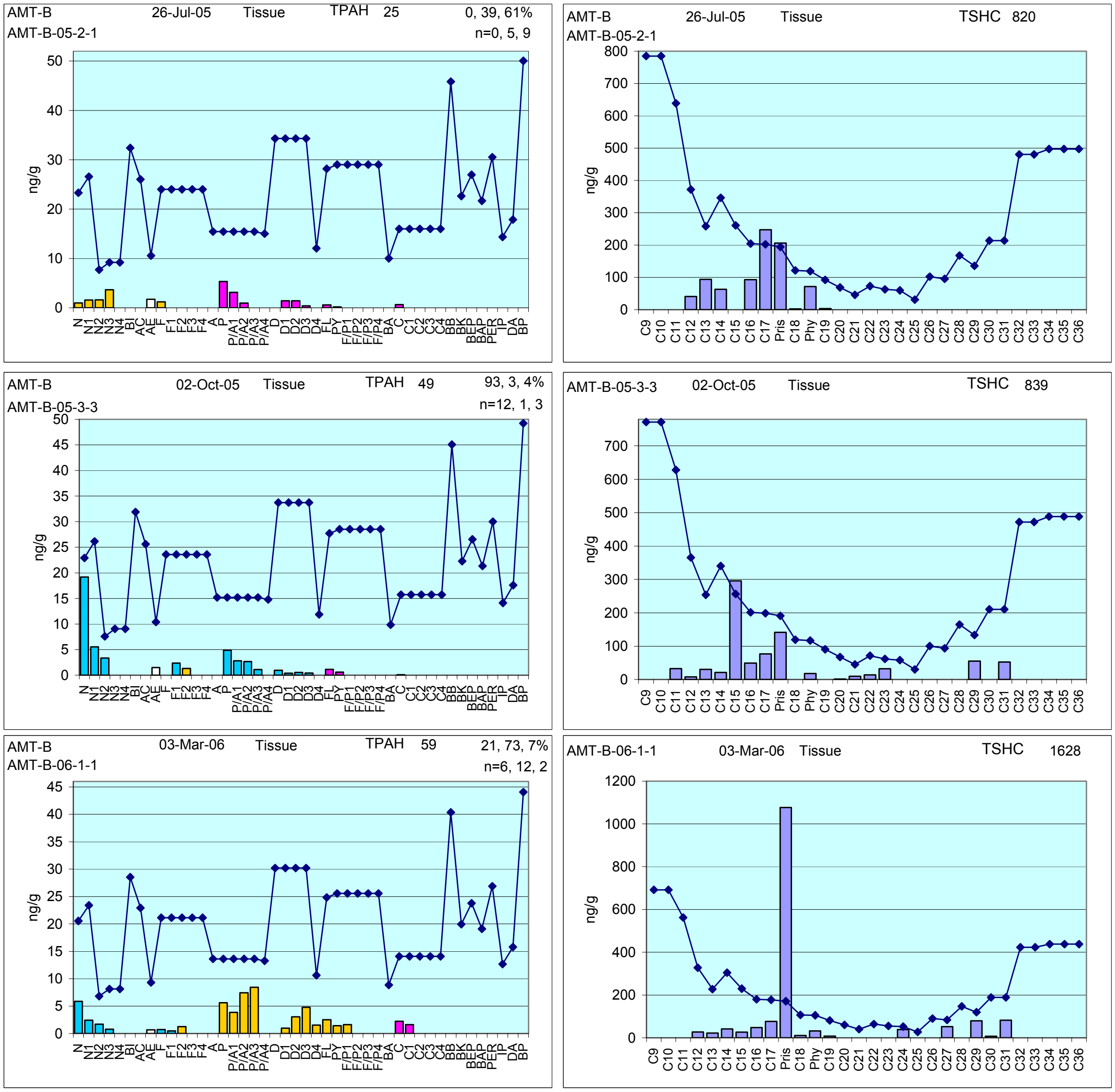


Figure 17 PAH and SHC profiles showing low-level TPAH with variable source signals (combustion-, dissolved-, and oil/particulate-phase) in AMT mussel samples collected in July 2005, October 2005 and March 2006, respectively. MDLs indicated with dotted solid line.

Table 6 Exact one-tailed probabilities of seasonal phase dominance in mussels at AMT and GOC, 1993-2005 using randomization paired t-tests (1000 trials, n = 13).

	Particulate	Dissolved	Pyrogenic
	Spring>Summer	Summer > Spring	Summer > Spring
AMT	0.003	0.074	0.046
GOC	0.054	0.107	0.122

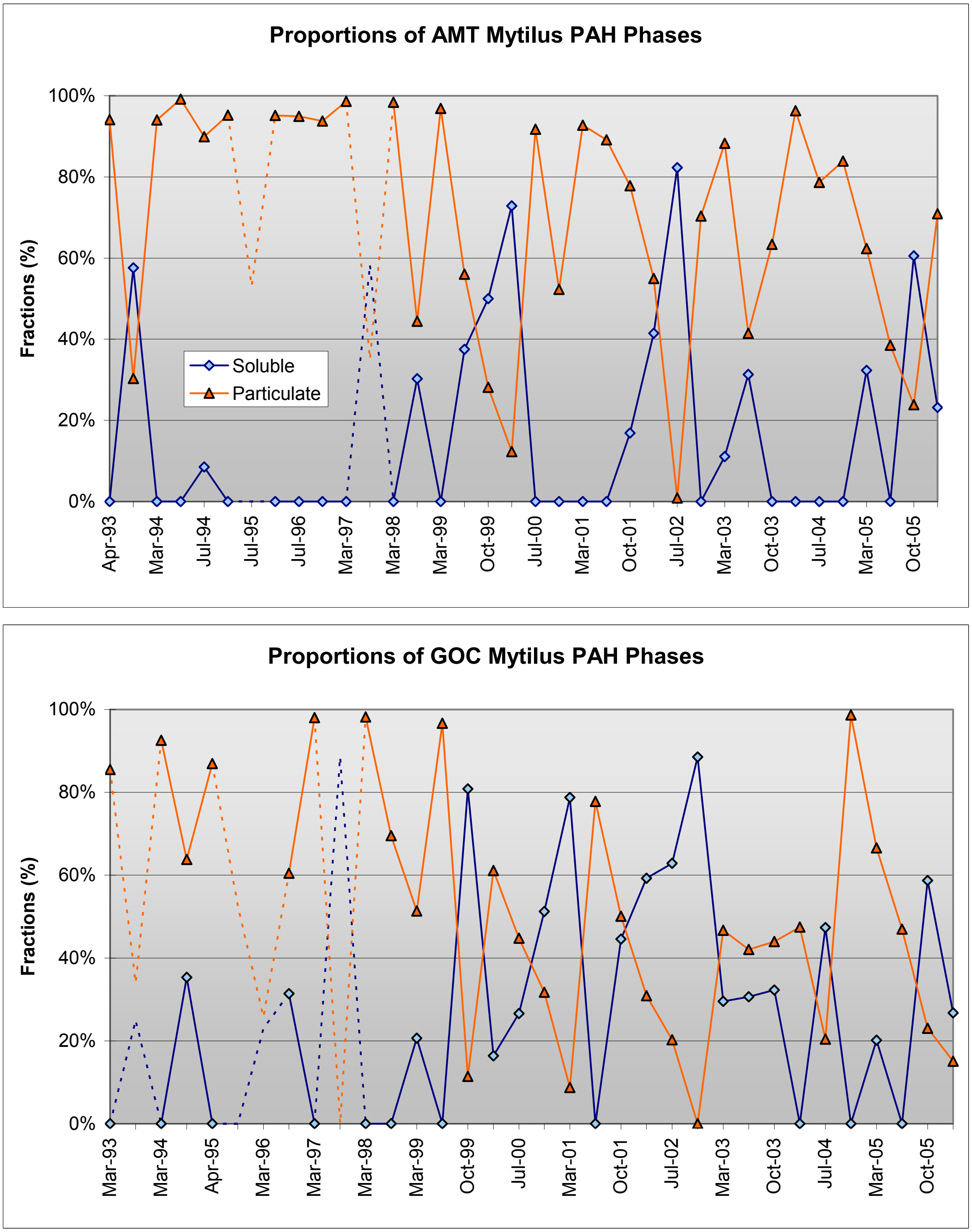


Figure 18 PAH Phase assignments for AMT and GOC mussel samples with other data removed to facilitate visualization of alternating seasonal (winter vs. summer) spikes in dissolved and particulate phases.

To us, this alternating pattern suggests three possible processes: water-column stratification, oil/SPM agglomerate sedimentation, and microbial activity. Relative to the receiving seawater, the BWTF effluent is warmer and less saline, so its behavior and dilution are controlled by the physical oceanography and water-column structure in the Port (Colonell 1980a,b; Woodward Clyde Consultants and ENTRIX 1987). During the period of stable water-column stratification in the Port (late spring, summer, and fall), we believe that the dispersed oil droplets released from the BWTF effluent are primarily entrained beneath the pycnocline (stratified layer) in the middle-water-column regions where they are advected and diluted into the receiving Port waters allowing them to interact with SPM to form agglomerates and sink without ever reaching the upper water column to any significant extent (Payne et al, 2001, 2003b,d). Thus, lower overall TPAH levels with higher dissolved-phase signals (Figure 16 and Figure 18) are often observed in the AMT and GOC intertidal mussels collected in the summer period. During the winter and early spring, however, when the water column is not stratified, the warmer and less-saline BWTF effluent can reach the water surface where it is likely to form a surface microlayer (Hardy 1982; Hardy et al., 1987a,b, 1990; Cross et al., 1987) containing higher levels of weathered oil-droplet-phase SHC and PAH components. Since mussels feed from the surface and upper few meters of the water column, this effect results in the predominance of the particulate/oil-phase signals observed in the intertidal mussels at AMT and (to an even greater extent) GOC during the spring LTEMP collections.

Adding to the stratification effect would be the increased levels of SPM (mostly glacial flour) brought by spring rains and summer glacier melting that would result in increased scavenging and settling of the oil droplets. With the Port's sedimentation rates estimated at 0.4-1.5 cm yr^{-1} (Savoie et al., 2006), one would expect a fairly efficient removal of dispersed oil droplets. And finally, during the warmer months with added insolation, increased surface temperatures, and nutrients from spring blooms, microbial degradation rates might also be expected to increase thus removing more of the particulate/oil phase. In summary, during warmer months, stratification reduces transport to the surface while increased sedimentation and enhanced microbial degradation augment the removal rate of oil droplets before they are acquired by mussels. Without supporting data, we make no attempt to tease out the relative effects of these processes, but the combined results are plainly visible (albeit variable) in the data.

A negative aspect to this seasonal phenomenon is that concentrated contaminants in an upper layer or surface microlayer would also increase risks from photo-enhanced toxicity to near-surface, planktonic biota (Barron and Ka'aihue 2001; Pelletier et al., 1997; Duesterloh et al., 2002; Barron et al., 2003). Supporting this conjecture, Carls et al. (2006) show that in Port Valdez, particle-feeding, *Neocalanus* copepods are capable of concentrating PAH from trace levels in water to detectable levels in tissue, and they had PAH profiles both similar to the BWTF effluent and to the low levels seen in mussels. Furthermore, copepod samples from sites at the western end of the Port and mid Prince William Sound, like the LTEMP mussels, showed a transition from a particulate/oil-phase signature to just a dissolved-phase background signal.

Another feature in the AMT data is the precipitous drop in the overall TPAH values along with significantly reduced seasonal and interannual variability beginning in July 2002 (Figure 16 upper right-hand panel). This is also when the NOAA Auke Bay Laboratory began doing the hydrocarbon analyses. Initially, the coincidence appeared suspicious but the continued seasonal alteration in particulate/oil-phase and dissolved-phase signals, and equivalent or even increased TPAH levels in July 2002 samples from Shuyak Harbor and Windy Bay, compared to March 2002 data generated by GERG (discussed in Section 5.3.4), seem to rule out a systematic bias or laboratory artifact as the reason for the observed decrease in TPAH values. Also, as discussed in Section 5.1.1 on Auke Bay Laboratory quality assurance results, surrogate recoveries have been consistently very good at ABL, further reducing the probability of poor extraction efficiencies or lipid mitigation being a contributing cause.

Similar declines in AMT sediment TPAH burdens over the last four years were discussed in Section 5.2.3.1, and although the sediment PAH profile at the terminal is dominated by a particulate/oil-phase signal (presumably from whole oil droplet/SPM interactions, Figure 10), we also noted an increase in the relative proportion of combustion products (also possibly suggested in the July and October 2004 mussel-tissue data shown in Figure 16). We do not know if the observed decreases in tissue and sediment TPAH burdens reflect reduced BTWF discharge volumes as more double-hulled tankers are brought into the tanker fleet, the decreased flow of ANS crude oil through the pipeline to the terminal, or improved BWTF efficiency at removing particulate/oil-phase PAH, or a combination of all these factors.

5.3.2.2 Gold Creek Mussel Tissue Chemistry

In general, the overall levels of TPAH measured at GOC (Figure 16, bottom graphs) are slightly lower than those at AMT, but the observed peaks and valleys (concentration maxima) track with those at AMT, particularly during the early years of the program when spills or other discharges from the terminal were more frequent. Also, the same seasonally-dependent, saw-tooth pattern of alternating soluble- and particulate/oil-phase signals observed at AMT is apparent (Figure 16, bottom left panel and Figure 18). While many of the lower-TPAH level samples (July 1993, July 1995, March 1996, and July 1997) were subject to the procedural artifact issues discussed in Section 4.7.2 (shown as dashed lines without solid data points in Figure 16), the data for the elevated PAH levels were judged to be of good quality and appear to be related to the known spill events at the terminal across the Port.

In October 2004, the TPAH concentration spikes to the highest levels ever recorded at GOC (830 ng/g), due to a diesel spill which occurred sometime between the July and October 2004 sampling events (Payne et al., 2006). One possible source might be fishing vessels, which before openings, anchor at GOC instead of Valdez Harbor; in July 2005, fishing vessels were anchored in the bight east of GOC Point.

Evidence of the residual diesel signal was observed to persist through the sample collections in March 2005 (Payne et al., 2006). There was no evidence of the diesel spill in any of the AMT mussel samples collected in July or October 2004, and there was no evidence of the diesel signal in the subtidal sediments collected at Gold Creek in March 2005 (Payne et al., 2006). This latter finding should not be a surprise, because very little evidence of oil transfer to near-shore subtidal ($\geq$40 m) sediments has been observed in numerous other spills with similar gravel/cobble intertidal substrates, including the *Exxon Valdez* oil spill in 1989 (O'Clair et al., 1996).

In the most recent tissue samples collected in July and October 2005 and March 2006 (Figure 16), mussel TPAH levels continue to be extremely low (<60 ng/g dry weight). The phase signatures shift from a mixed-phase combustion product signal in July 2005 to a soluble-phase signature in October 2005 and then back to a mixed-phase combustion product pattern in March 2006 (Figure 19). The SHC profiles reflect dominant marine biogenic components in all three samples (NRC 1985).

5.3.3 Prince William Sound Stations

In our 2004/2005 LTEMP report, we presented extended discussions of the 1993-2005 time-series trends for each of the five Prince William Sound stations (Payne et al., 2006). The time-series phase plots for each site were discussed in detail with representative PAH and SHC profiles to illustrate the context of the phase assignments. Rather than repeat that narrative in this year's report, the findings can be briefly summarized. With the exception of Disk Island (DII), the TPAH levels at the other four Prince William Sound stations continued to be extremely low and variable, if not decreasing (generally <60 ng/g dry weight). Furthermore, except for an apparent region-wide increase in the relative proportion derived from a trace particulate/oil-phase signal (also below the MDL; range 12-63 ng/g dry weight) in July 2004, the PAH profiles at these other four sites were dominated by below-MDL, background, dissolved-phase signals. At Disk Island, there does appear to be an increasing trend in TPAH, with a petrogenic signal noted in three of the last four sample collections (since July 2004). As a result, we will examine that station in some more detail. PAH profiles for all of the tissue samples analyzed as part of the 2005/2006 program are presented in Appendix D.

PAH-phase-differentiated, time-series plots for the Prince William Sound stations are presented alphabetically: Disk Island (DII), Knowles Head (KNH), Sheep Bay (SHB), Sleepy Bay (SLB), and Zaikof Bay (ZAB). Representative PAH and SHC profiles from the Prince William Sound stations are presented as contextual information for the time-series plots, when necessary. Constantine Harbor mussels from the EVOS Trustees SCAT program are presented along with intertidal sediment results from that site to illustrate the relationships in hydrocarbon signals between mussel tissues and the surrounding sediment.

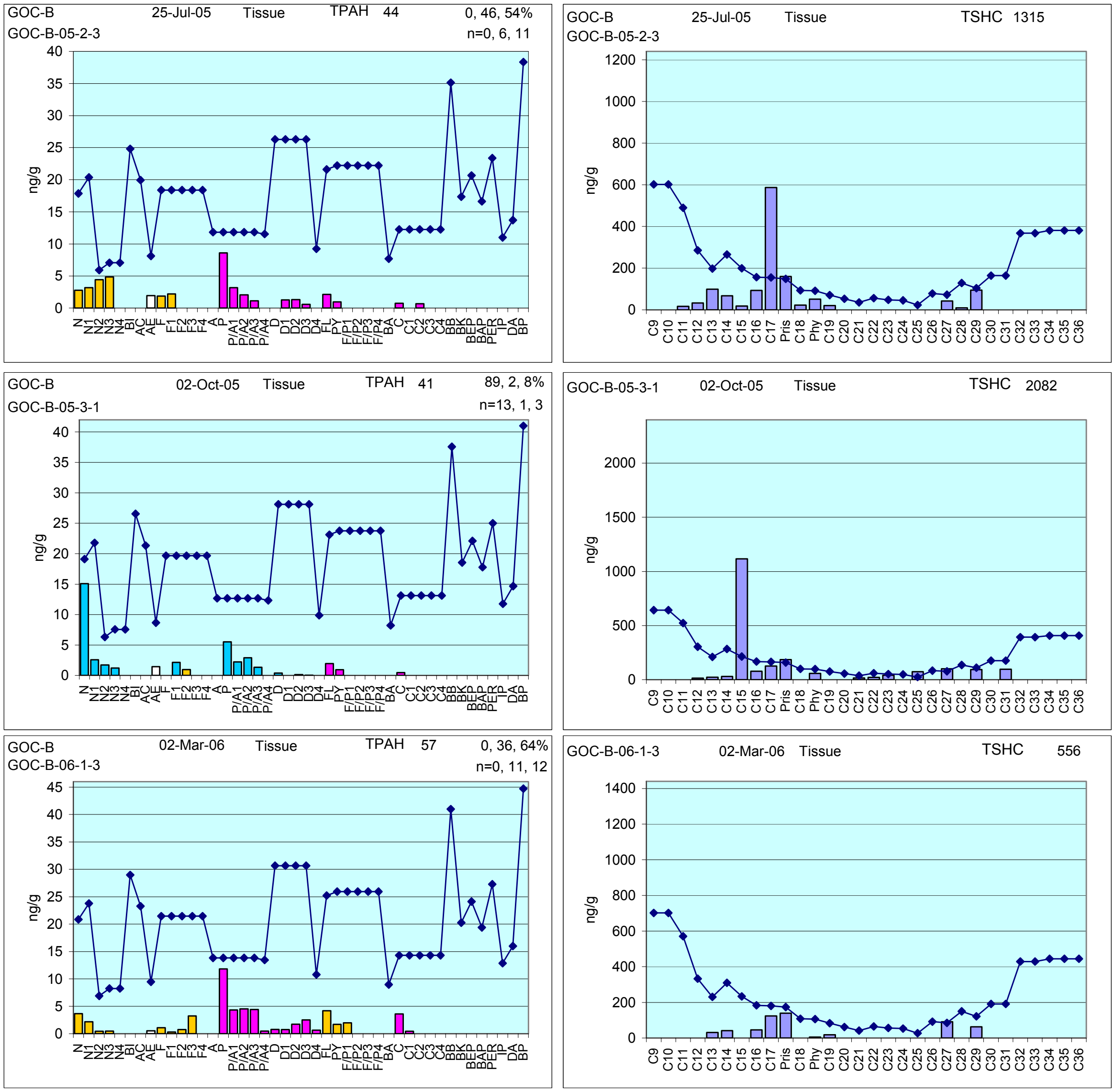


Figure 19 Gold Creek mussel PAH and SHC profiles showing low-level TPAH with mixed and variable source signals (combustion products with some particulate/oil-phase components) in July 2005 and March 2006 and a predominant dissolved-phase pattern in October 2005. MDLs indicated with dotted solid line.

5.3.3.1 Disk Island Mussel Tissue Chemistry

Although the TPAH levels are low, there is a monotonic increase since July 2004 with petrogenic/oil-phase signals dominating in July 2004, March 2005, and March 2006 (Figure 20, left panel). The PAH and SHC profiles (Figure 21) clearly show the characteristic petrogenic profile of weathered EVOS oil even though the TPAH levels are below the sample-weight-adjusted MDLs. The most likely source is from near-surface deposits of buried EVOS oil that were observed above the LTEMP transects in July 2007 and 2008 (Figure 22). These data also suggest that bioavailable oil was being released at

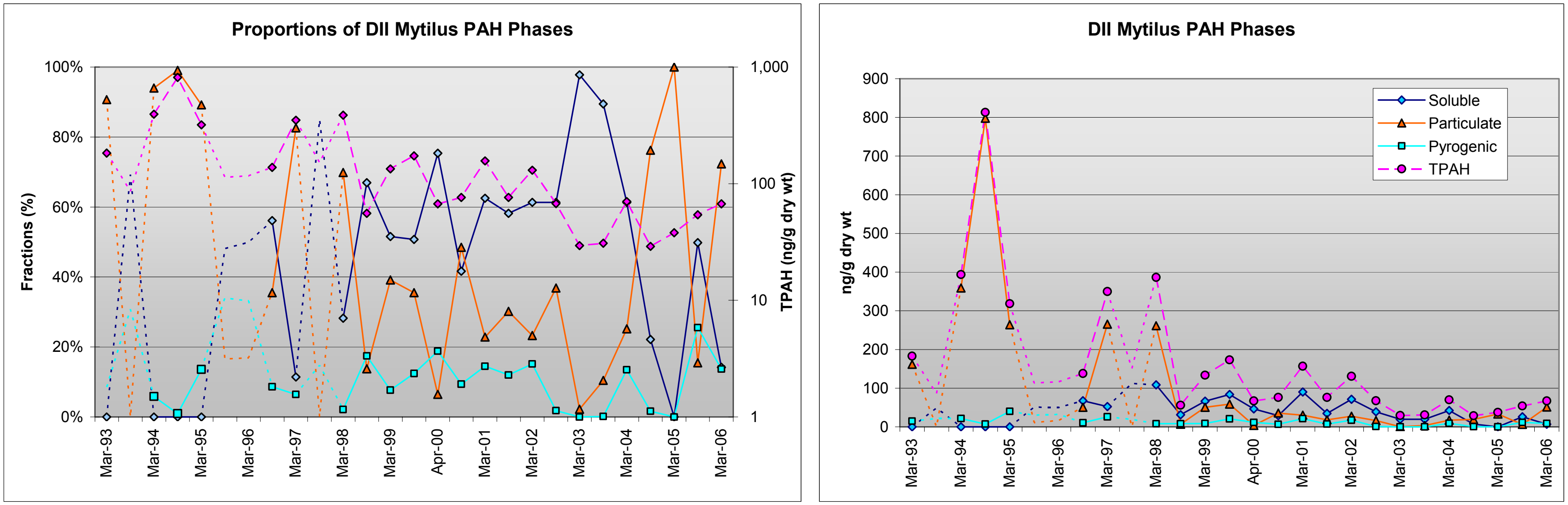


Figure 20 Time series TPAH and relative phase composition profiles in Disk Island (DII) *Mytilus* tissues. Dotted connecting lines without symbols indicate questionable data.

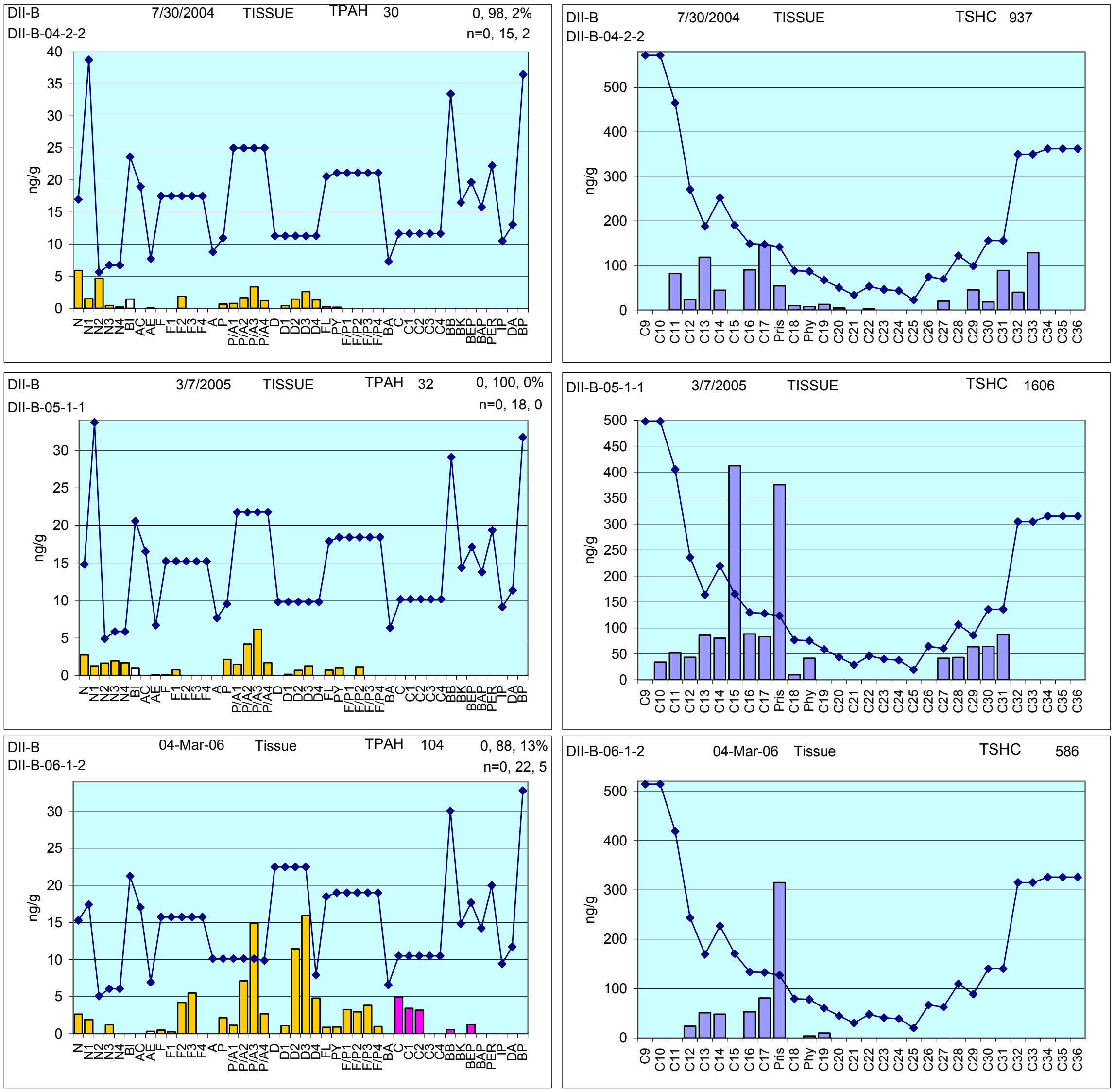


Figure 21 Disk Island *Mytilus* PAH and SHC profiles showing low-level particulate/oil-phase components in July 2004, March 2005, and March 2006. MDLs indicated with dotted solid line.

Figure 22 Trace of fresh sheen of EVOS oil from disturbed sediments on Disk Island (above the LTEMP transect), July 2008.

this site as far back as July (and possibly March) of 2004. The elevated dissolved-phase signals observed in 2003 may also have been from lower-molecular-weight components leaching from this buried oil, but it is it is impossible to confirm from these data.

5.3.3.2 Knowles Head, Sheep Bay, and Sleepy Bay Mussel Tissue Chemistry

Because of their geographic relationship (Figure 1) and their similar TPAH and phase shifts trends since July 1998 (Figure 23, left panels), these three sites are here condensed into one section. During the early sample collections at Sleepy Bay, the data are sketchy, but the higher-concentration signals were dominated by distinctive particulate/oil-phase patterns as buried EVOS oil, released from the intertidal substrate, gradually diminished (Figure 23, bottom left panel). But since July 1998, Sleepy Bay trends with the other central PWS stations. Early lower-concentration data from Sheep Bay and Knowles Head are mostly unreliable as discussed in Section 4.7.2. Since March 2002, the TPAH levels at all three sites have dropped steadily, and although they are currently very low (<30 ng/g dry weight and below laboratory MDLs), the phase assignments based on those low-level PAH signatures show remarkable detrended correlations (Table 7, Figure 24). For example, the PAH and SHC profiles from the July 2004 samples show dramatic shifts to extremely low petrogenic profiles (Figure 25), and while we have a lot of confidence in the distinctive particulate signal from Knowles Head (where PAH are just below MDLS), the Sheep Bay and Sleepy Bay PAH profiles and phase assignments are tenuously assigned as trace-level particulates. However, their SHC patterns show a mixture of biogenic and trace-level petrogenic hydrocarbons which, as separate lines of evidence, support this assignment. In March 2005, there was a synchronous return to the background dissolved-phase signal (Figure 23, Figure 26, and Figure 27). At these ultra-trace levels, however, these phase assignments are very tentative, at best. Only the long series of correlation (16 sampling events at three sites using two different laboratories) provides the authority for these trace-level interpretations. PAH and SHC profiles for the rest of the 2005-06 collections are shown in Appendix D.

Table 7 Detrended correlations of PAH phases between Sheep Bay (SHB), Knowles Head (KNH), and Sleepy Bay (SLB) *Mytilus* tissue, July 1998-March 2006.

Particulate Phase correlations

	SHB	*KNH*	*SLB*
SHB	1		
KNH	0.78	1	
SLB	0.75	0.62	1

Soluble Phase correlations

	SHB	*KNH*	*SLB*
SHB	1		
KNH	0.61	1	
SLB	0.70	0.40*	1

*all values significant at p<=0.01 excepting KNH/SLB at p=0.12 (n=16).

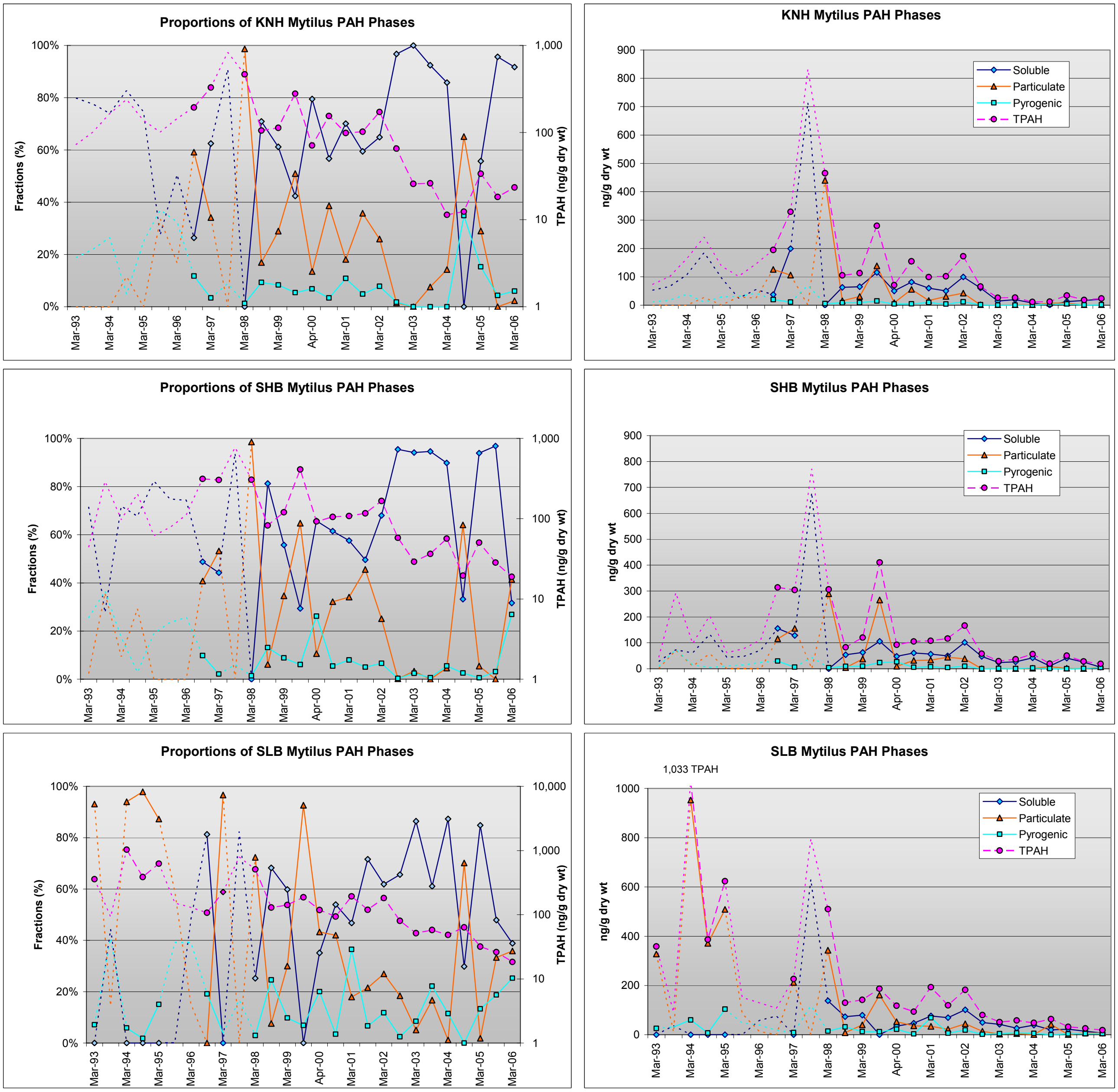


Figure 23 Time series TPAH and relative phase composition profiles in Knowles Head (KNH), Sheep Bay (SHB), and Sleepy Bay (SLB) *Mytilus* tissues. Dotted connecting lines without symbols indicate questionable data.

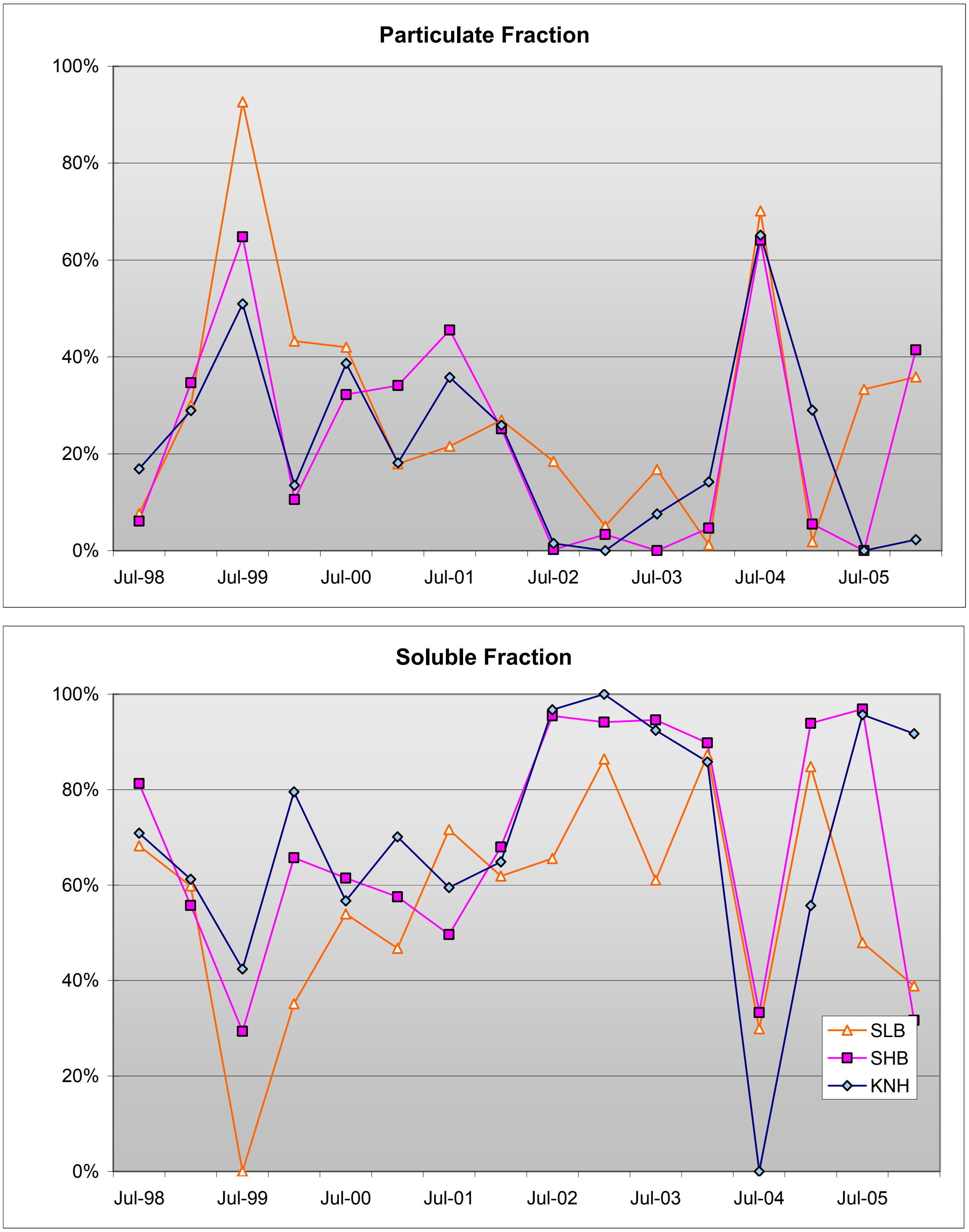


Figure 24 Synchrony in average phase portions between Sheep Bay (SHB), Knowles Head (KNH), and Sleepy Bay (SLB) *Mytilus* PAH since July 1998.

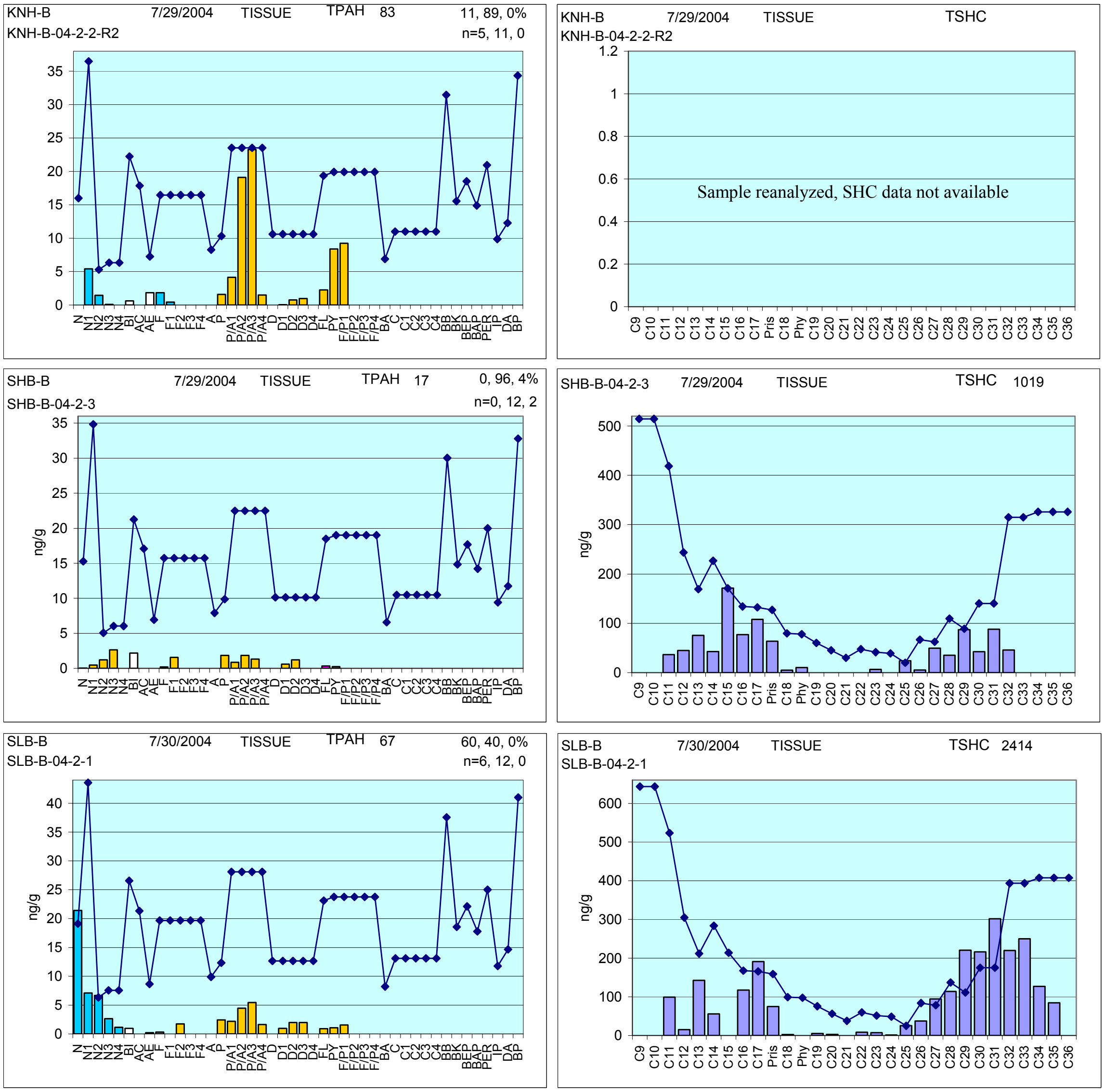
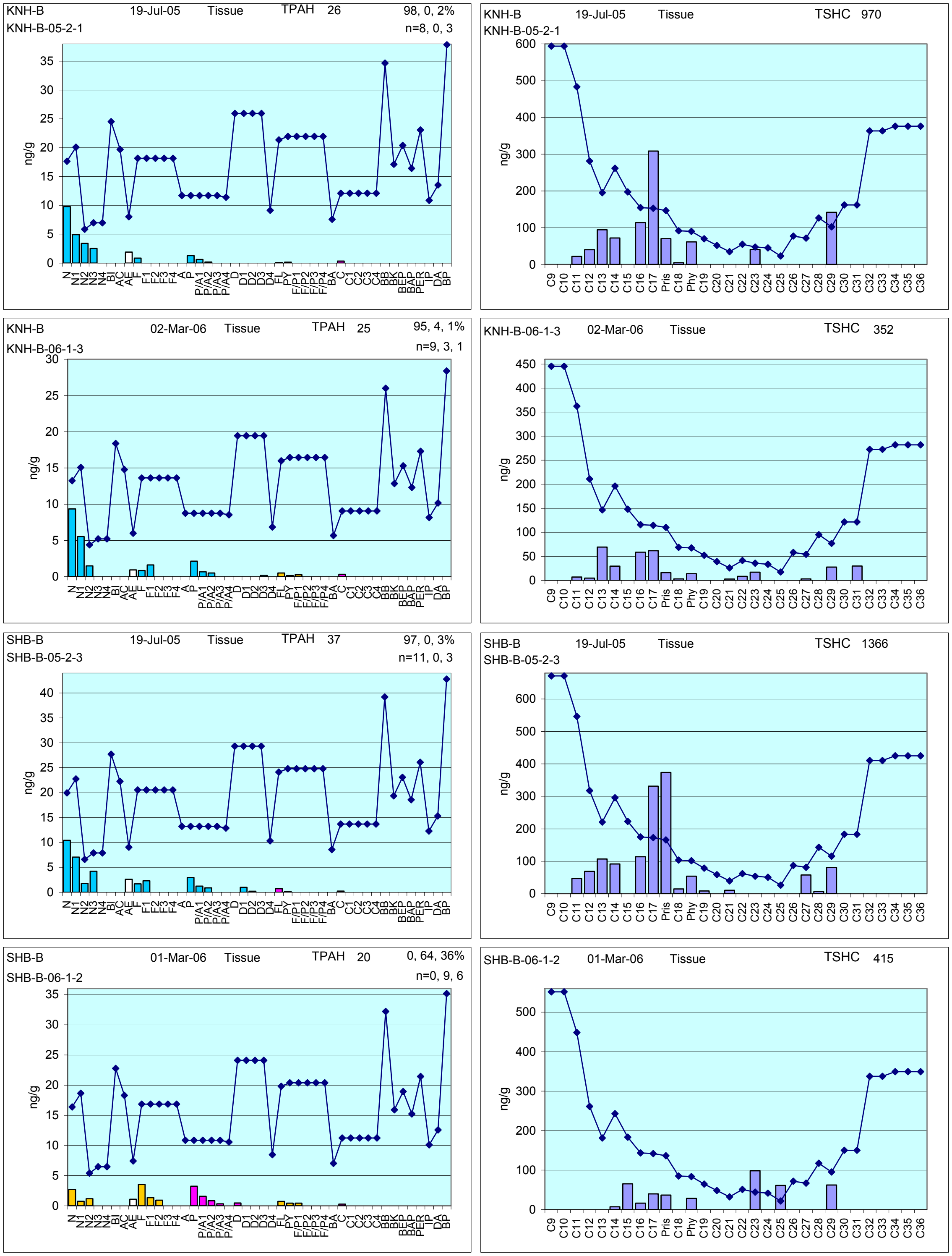


Figure 25 Representative Knowles Head, Sheep Bay and Sleepy Bay *Mytilus* PAH and SHC profiles showing low-level particulate/oil-phase components in July 2004. MDLs indicated with dotted solid line.



KNH-B 19-Jul-05 Tissue TPAH 26 98, 0, 2%
KNH-B-05-2-1 n=8, 0, 3

KNH-B 19-Jul-05 Tissue TSHC 970
KNH-B-05-2-1

KNH-B 02-Mar-06 Tissue TPAH 25 95, 4, 1%
KNH-B-06-1-3 n=9, 3, 1

KNH-B-06-1-3 02-Mar-06 Tissue TSHC 352

SHB-B 19-Jul-05 Tissue TPAH 37 97, 0, 3%
SHB-B-05-2-3 n=11, 0, 3

SHB-B 19-Jul-05 Tissue TSHC 1366
SHB-B-05-2-3

SHB-B 01-Mar-06 Tissue TPAH 20 0, 64, 36%
SHB-B-06-1-2 n=0, 9, 6

SHB-B-06-1-2 01-Mar-06 Tissue TSHC 415

Figure 26 Representative Knowles Head and Sheep Bay *Mytilus* PAH and SHC profiles showing the return to trace-level dissolved-phase components at both sites in July 2005, and the possible (below-MDL) shift to more of a mixed-phase particulate/oil- and combustion-product pattern at Sheep Bay in March 2006. MDLs indicated with dotted solid line.

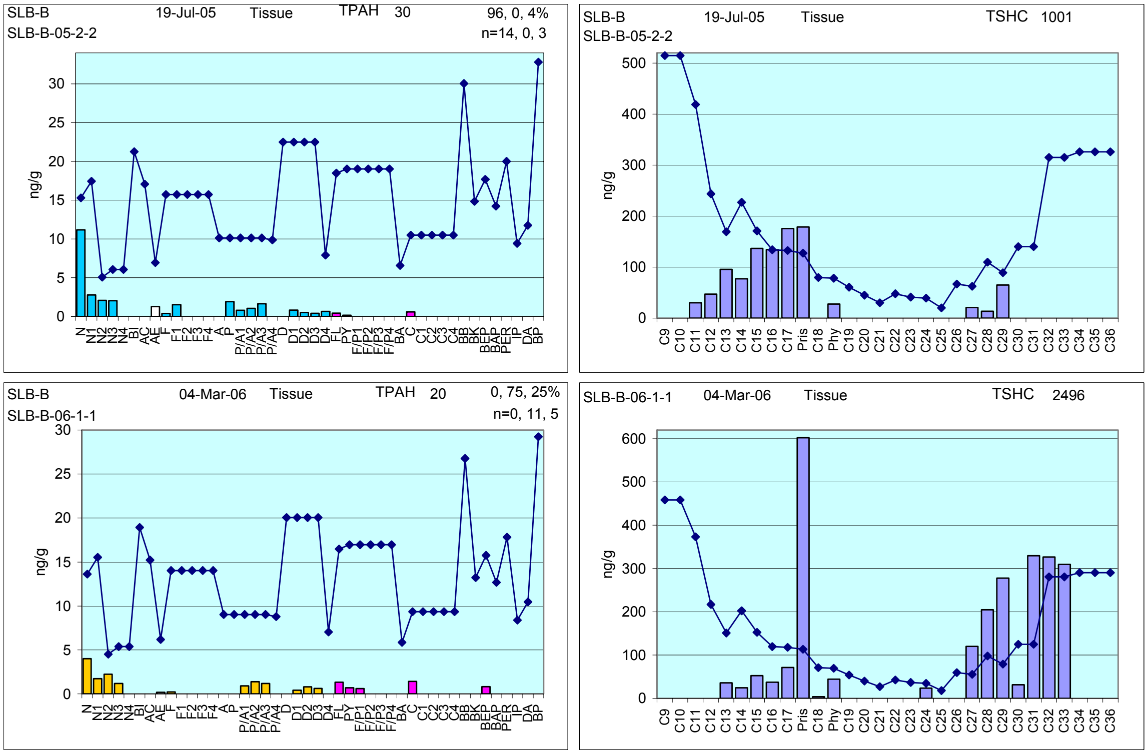


Figure 27 Representative Sleepy Bay *Mytilus* PAH and SHC profiles showing trace-level dissolved- and mixed-phase patterns in July 2005 and March 2006. The SHC profile in July 2005 is difficult to assess, but the March 2006 profile shows above-MDL marine biogenic and heavily weathered petrogenic components. MDLs indicated with dotted solid line

5.3.3.3 Zaikof Bay Mussel Tissue Chemistry

This station was added to the program in 1999 to better assess petroleum hydrocarbon inputs from tanker traffic passing through the Hinchinbrook Entrance to Prince William Sound. TPAH concentrations at Zaikof Bay have been low (less than MDL) and variable over the seven-year sampling period at this site (Figure 28) but over this time frame, the signals have been consistently derived from the dissolved phase (right panel, Figure 28). The maximum TPAH level (197 ng/g dry weight) observed at Zaikof Bay in March 2002 has now dropped to an all-time low (13 ng/g dry weight) in March 2006. Phase patterns at this site do not correlate well with either the nearby central PWS sites or the Gulf of Alaska sites; it behaves uniquely. PAH and SHC profiles from the 2005/2006 collections are shown in Appendix D.

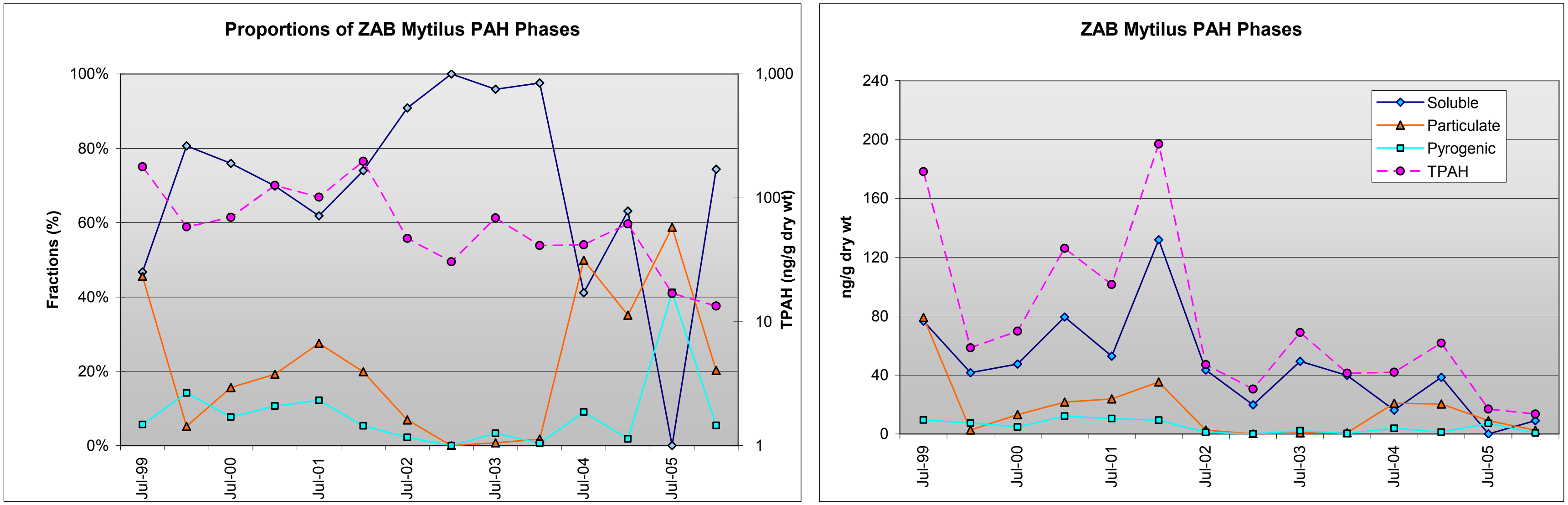


Figure 28 Time series TPAH and relative phase composition profiles in Zaikof Bay (ZAB) *Mytilus* tissues. Dotted connecting lines without symbols indicate questionable data.

5.3.3.4 Constantine Harbor Mussel Tissue Chemistry

This site was added to the 2005/2006 LTEMP as part of the EVOS Trustees SCAT Program undertaken by Auke Bay Laboratory. The location was selected as a reference site because it is known to receive PAH-bearing sedimentary deposits from suspended particulate material introduced to Prince William Sound by the Alaskan Coastal Current sweeping the Gulf of Alaska coastline southeast of the Sound (Karinen et al., 1993, Page et al., 1995; Short and Babcock 1996; Short et al., 2007b). It also was not impacted by oil released from the *Exxon Valdez* oil spill. Along with the mussel samples, intertidal sediments were collected from this site (previously discussed in Section 5.2.3.3). Representative sediment PAH and SHC profiles are re-plotted here along with the corresponding profiles for the mussel tissues (Figure 29) to facilitate comparisons between the mussel tissue burdens and the surrounding sediments.

There are no notable seasonal (July vs. March) differences in the PAH and SHC profiles for either the mussel tissues or intertidal sediments (Figure 29). Like most of the other mussel tissue samples in the Sound, PAH concentrations are all below MDLs, while the sediment profiles are well above. As stated earlier, the sediments show PAH input from suspended particulate material derived from coal and organic material (e.g., kerogen) and natural oil seeps introduced to the Alaska Coastal Current by numerous rivers and glaciers along the Gulf of Alaska coastline southeast of the Sound, and the SHC profiles show the dominant higher-molecular-weight (n-C21 to n-C35) odd-carbon number contribution from terrestrial plant waxes (NRC 1985) introduced by those rivers and the local watershed. In contrast, the mussel tissues show only trace levels of dissolved-phase naphthalenes and either dissolved-phase or particulate-phase phenanthrenes/anthracenes with a few combustion products. Likewise, the tissues do not reflect the higher-molecular-weight, odd-carbon-number n-alkanes, indicating very little assimilation of hydrocarbons from the surrounding sediments. We cannot tell from these data alone if the measured naphthalenes in the mussel tissues were taken up from dissolved traces in the interstitial water in the intertidal zone, or possibly desorbed from traces of ingested sedimentary material inside the mussels. Clearly, however, the mussels did not contain high concentrations of bulk sedimentary material from their surroundings

Mussels have been sampled historically at this site by Auke Bay Lab but unfortunately, these data are from a slightly different part of the spit and thus are not exactly comparable. From June 1989 samples, Short and Babcock (1996) reported TPAH levels of ~650 ng/g dry weight and, similar to the recent samples, with over 50% of the TPAH signal derived from naphthalenes.

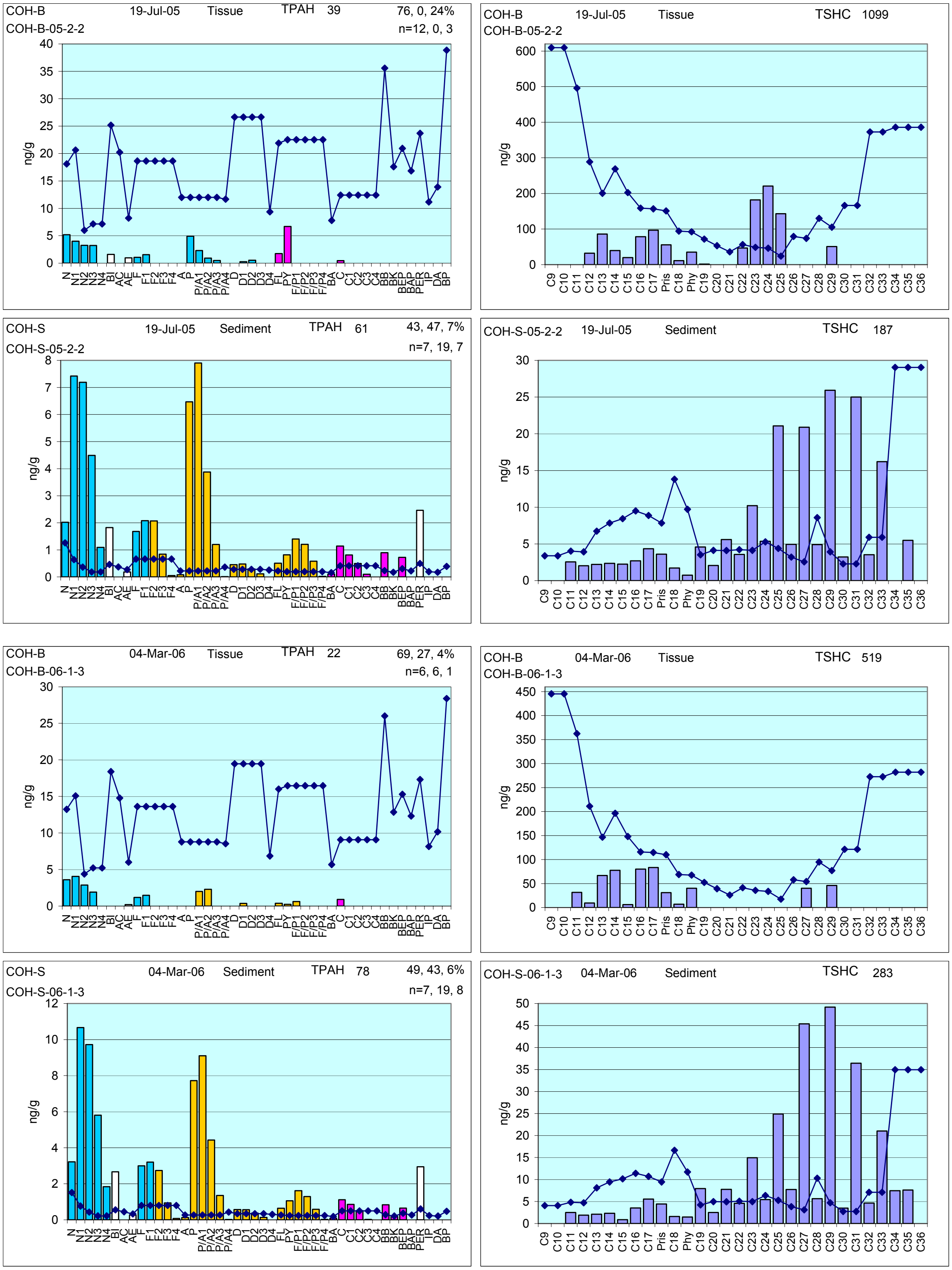


Figure 29 Representative Constantine Harbor *Mytilus* and adjacent intertidal sediment PAH and SHC profiles from samples collected as part of the EVOS Trustees SCAT program in July 2005 and March 2006. MDLs indicated with dotted solid line.

5.3.4 Gulf of Alaska Stations

This section presents the tissue chemistry data from the Gulf of Alaska LTEMP stations, and includes: Aialik Bay (AIB), Shuyak Harbor (SHH), and Windy Bay (WIB). In our 2004/2005 LTEMP report, we presented extended discussions of the 1993-2005 time-series trends for each of Gulf of Alaska stations, and the time-series phase plots for each site were discussed in detail with representative PAH and SHC profiles to illustrate the context of the phase assignments (Payne et al., 2006). Rather than repeat that narrative in this year's report, the findings can be briefly summarized as follows: The below-MDL TPAH concentrations in the mussels at all three sites remain very low (<40 ng/g dry weight), and the PAH-phase differentiated, time-series plots show variable trace-level dissolved-phase contributions at AIB and mixed-phase dissolved- and particulate/oil-phase components at SHH and WIB.

5.3.4.1 Aialik Bay Mussel Tissue Chemistry

The TPAH levels at Aialik Bay appear to have stabilized around 24-28 ng/g dry weight (Figure 30), and dissolved-phase components comprise 50-65% of the signal over the last three years. The particulate/oil-phase contributions appear to have declined steadily since March 2005, and in March 2006 a relative proportional increase in the combustion-derived components is suggested. All of the measured components are well below the laboratory's sample-specific MDL, so these phase assignments, while supported by the PAH and SHC profiles (Figure 31), should be considered as provisional. The rest of the PAH and SHC profiles from the 2005/2006 collections are shown in Appendix D.

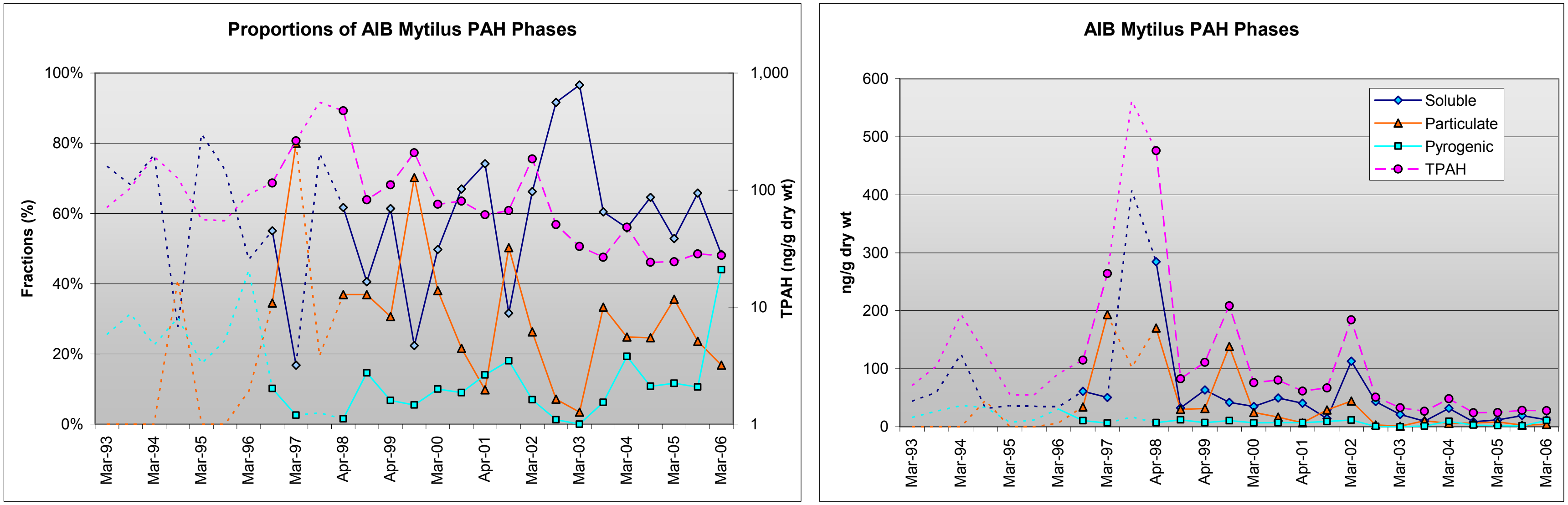


Figure 30 Time series TPAH and relative phase composition profiles in Aialik Bay (AIB) *Mytilus* tissues. Dotted connecting lines without symbols indicate questionable data.

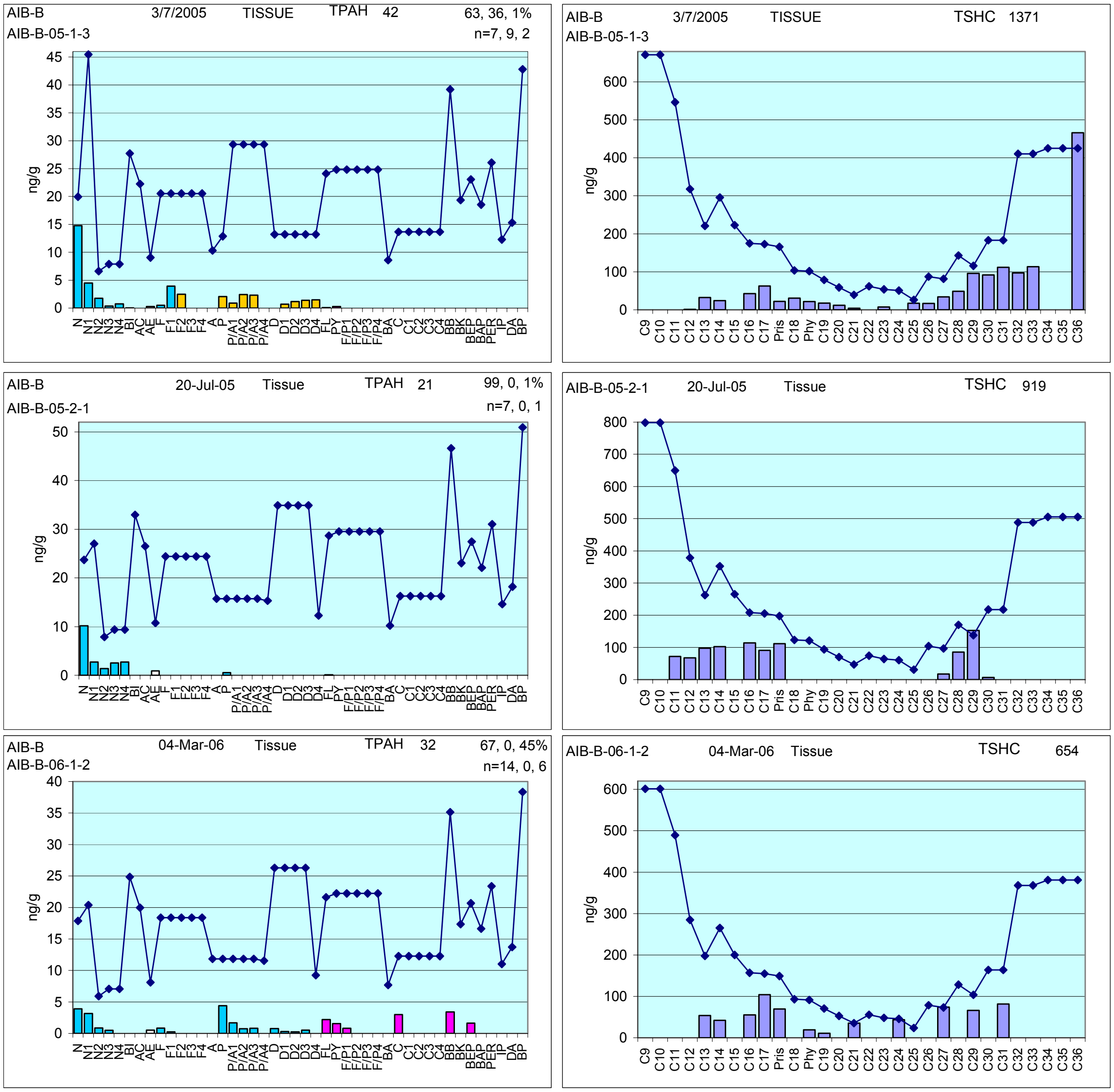
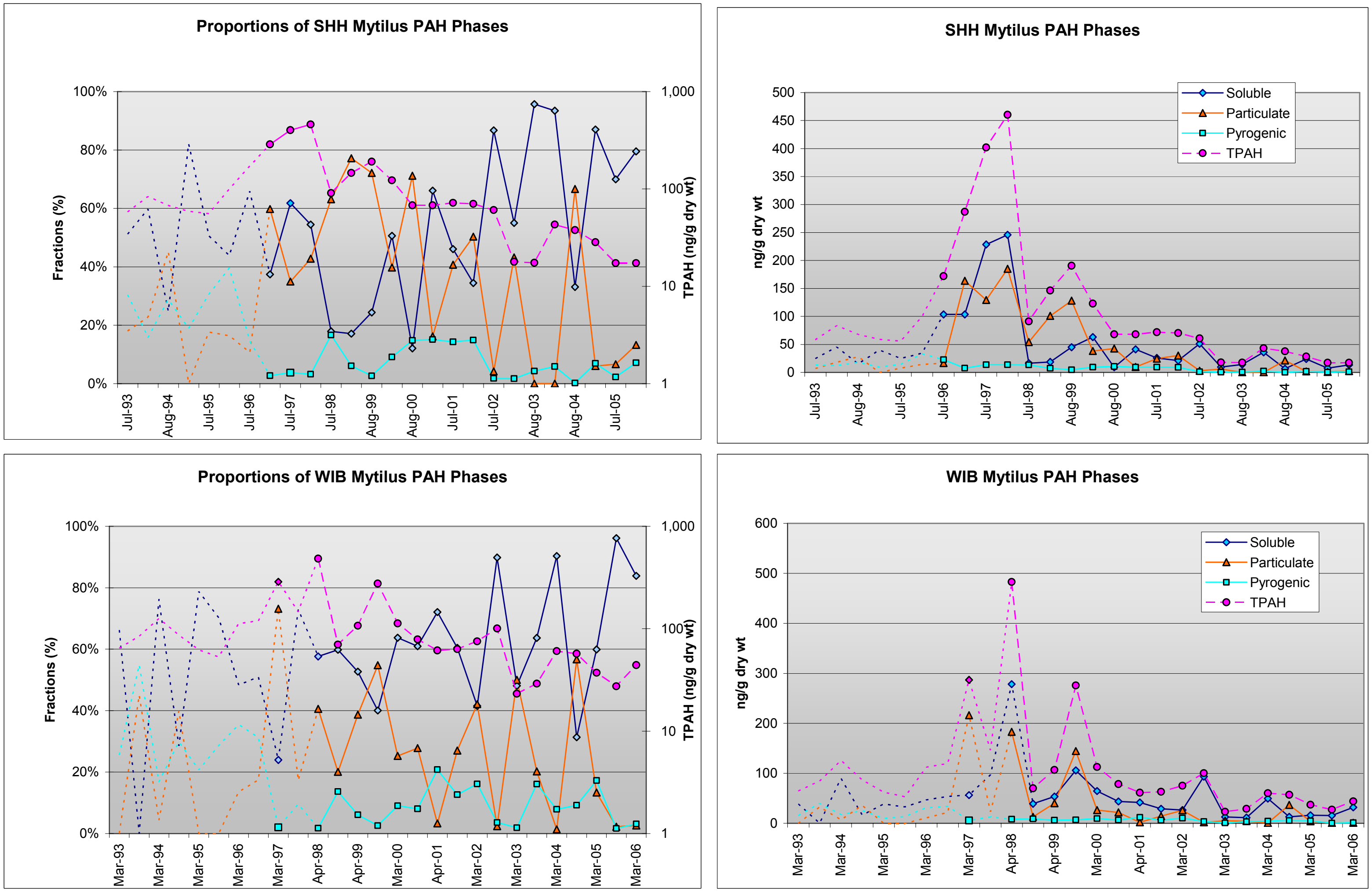


Figure 31 Representative Aialik Bay *Mytilus* PAH and SHC profiles showing a mixed dissolved- and particulate/oil-phase pattern in March 2005, dissolved-phase components in July 2005, and mixed dissolved- and combustion-phase components in March 2006. The SHC profiles show just-below MDL traces of biogenic and petrogenic components in March 2005, with less-than MDL marine and terrestrial biogenic input in July 2005 and March 2006. MDLs indicated with dotted solid line

5.3.4.2 Shuyak Harbor and Windy Bay Mussel Tissue Chemistry

These stations are considered together because of their regional proximity (Figure 1) and similar PAH phase trends (Figure 32 and Figure 33). Detrended correlations from linear regression residuals were 0.80 for particulate phase and 0.59 for dissolved phase ($n=16$, $p < 0.001$, $p < 0.02$). At both stations, TPAH concentrations have continued to decline since March 2004, with Shuyak Harbor having generally lower levels (<20 ng/g dry weight over the last two collections while Windy Bay ranged from 27 to 44 ng/g dry weight). The below-MDL PAH profiles at both sites are predominantly from the dissolved-phase, although there were trace-level PAH patterns suggesting particulate/oil-phase components at both stations in August 2004 (Figure 34 and Figure 35). These phase assignments were corroborated by their very similar, above-MDL SHC profiles that also suggested petrogenic input in August 2004 and March 2005. Curiously, the March 2005 and 2006 PAH profiles reflected only below-MDL dissolved-phase patterns. Lacking more detailed data, it will not be possible to speculate on sources or events driving the synchrony. These limited findings do point out the need for additional laboratory studies to better define and improve MDLs. PAH and SHC profiles from the 2005/2006 collections are shown in Appendix D.


Proportions of SHH Mytilus PAH Phases

SHH Mytilus PAH Phases

Proportions of WIB Mytilus PAH Phases

WIB Mytilus PAH Phases

Figure 32 Time series TPAH and relative phase composition profiles in Shuyak Harbor (SHH) and Windy Bay (WIB) *Mytilus* tissues. Dotted connecting lines without symbols indicate questionable data.

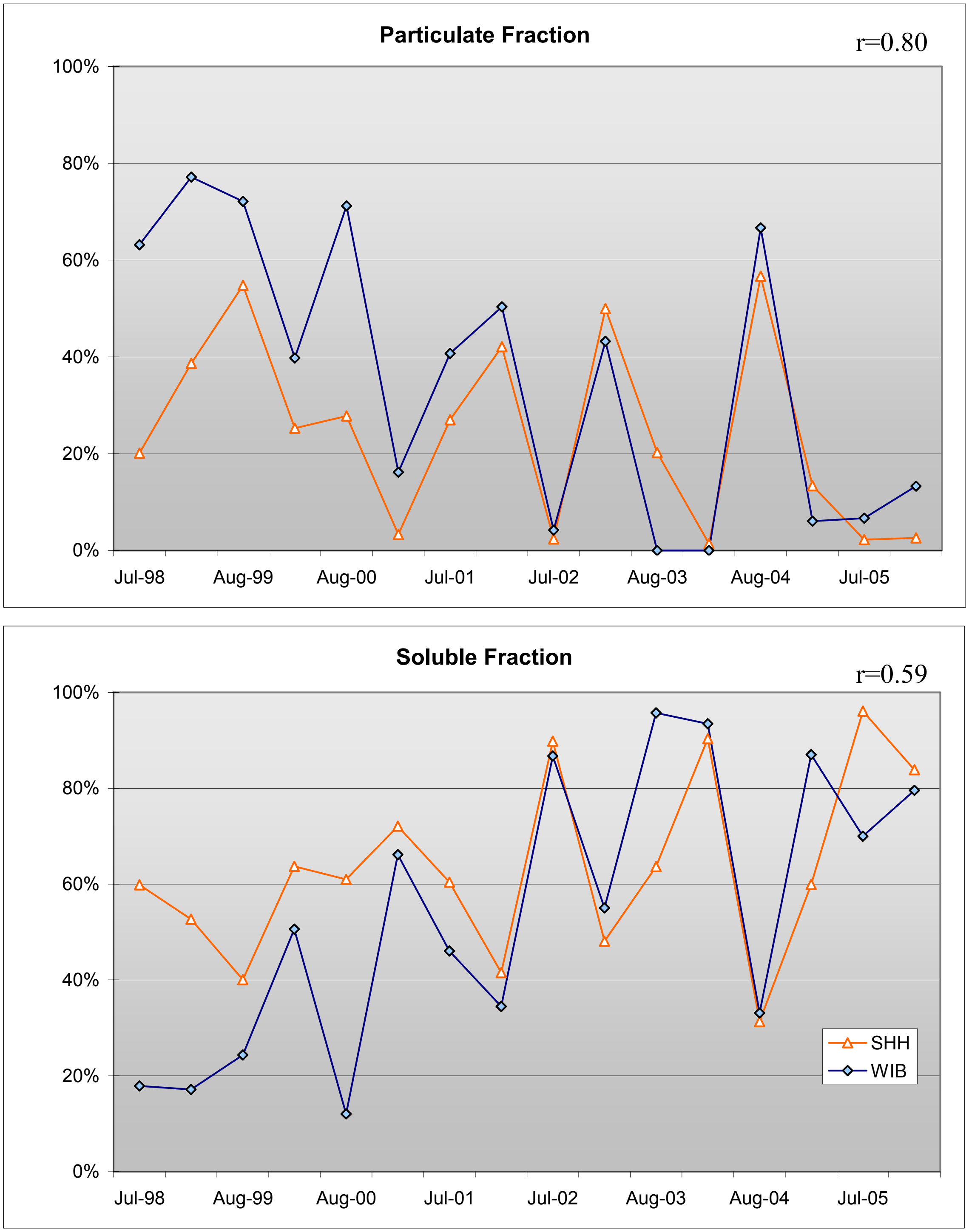


Figure 33 Synchrony of *Mytilus PAH* phases between Shuyak Harbor (SHH) and Windy Bay (WIB) since July 1998. Correlations significant at $p<0.001$ and $p< 0.02$, df=14.

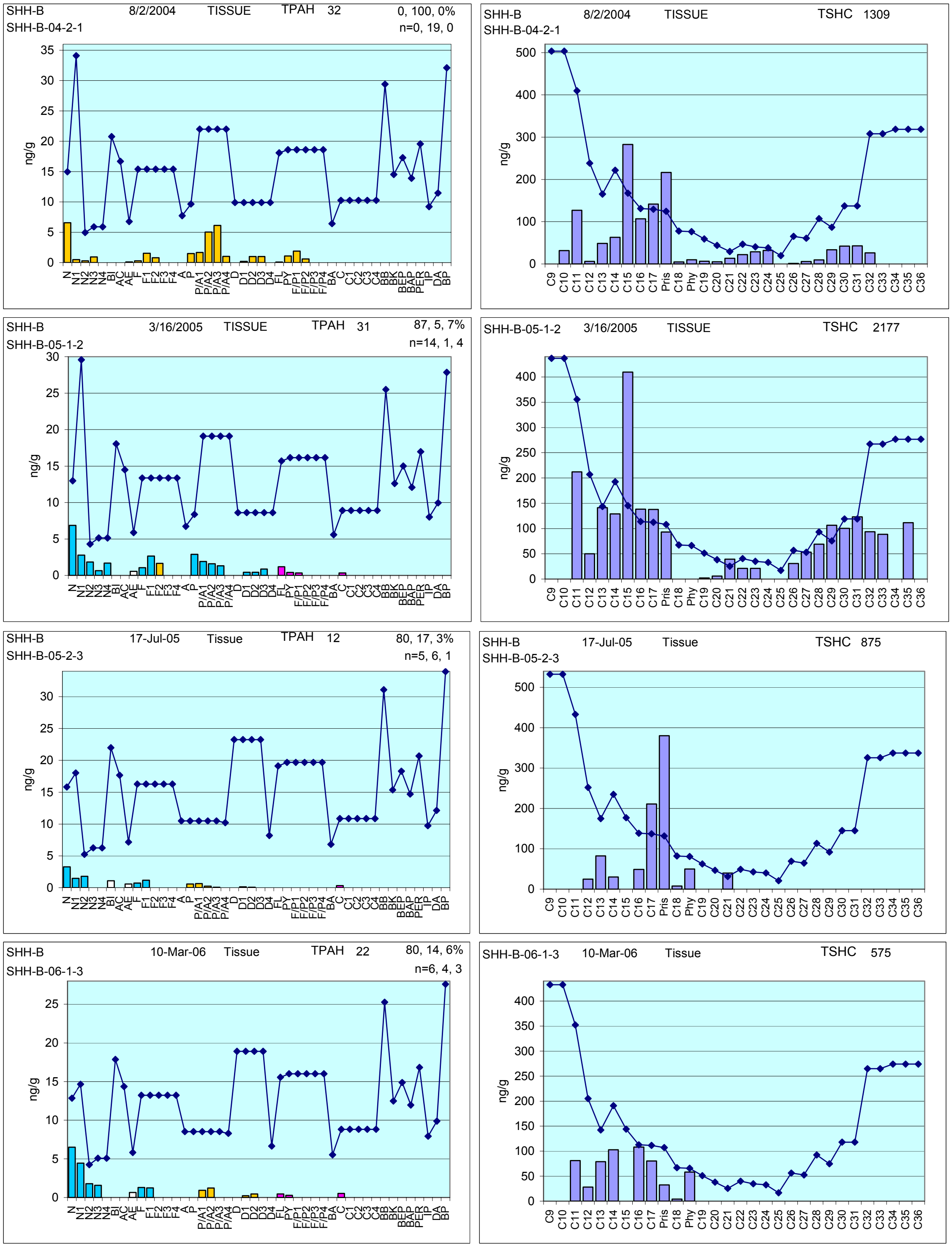


Figure 34 Representative Shuyak Harbor *Mytilus* PAH and SHC profiles showing a trace-level particulate/oil-phase signal in August 2004 and dissolved-phase patterns in March and July 2005 and March 2006. The higher-molecular-weight n-alkane SHC profiles support the petrogenic PAH phase assignments in August 2004, but not the dissolved-phase pattern in March 2005. The July 2005 and March 2006 SHC profiles suggest biogenic marine input.

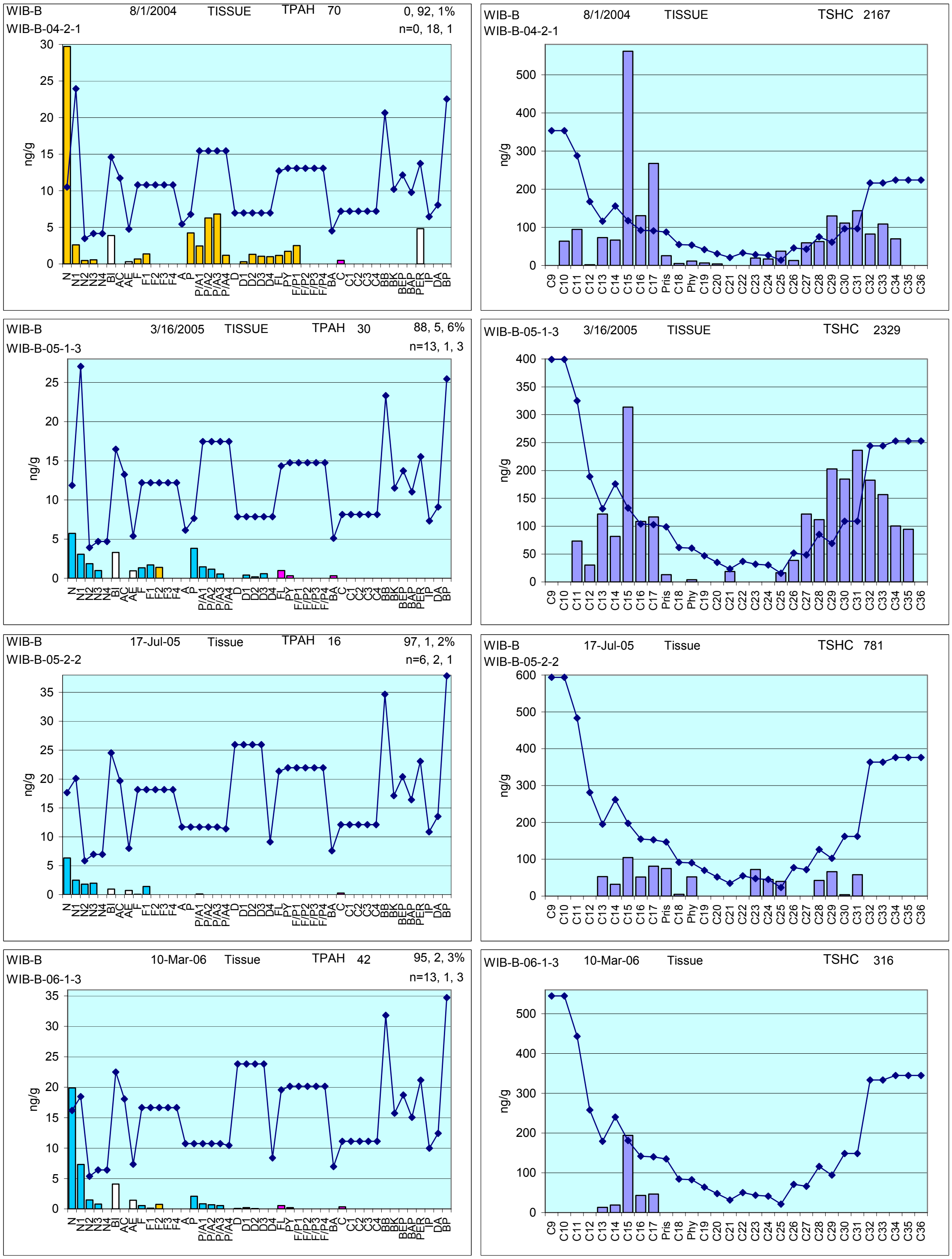


Figure 35 Representative Windy Bay *Mytilus* PAH and SHC profiles showing a trace-level particulate/oil-phase signal in August 2004 and dissolved-phase patterns in March and July 2005 and March 2006. The SHC profiles support the petrogenic PAH phase assignment in August 2004, but are contradictory in the March 2005 sample. Note that the SHC profiles in August 2004 and March 2005 are very similar to those observed at Shuyak Harbor (Figure 34) as well. MDLs indicated with dotted solid line.

5.3.5 Summary and Discussion of Tissue Chemistry Results

In Port Valdez, *Mytilus* tissues exhibit persistent, but very low and declining levels of hydrocarbons directly attributable to the BWTF discharge and terminal/tanker operations. Except for samples collected after major spill events (e.g., the *Eastern Lion* spill in May 1994, the BWTF sheening event in January 1997, and the diesel spill at Gold Creek between July and October 2004), the PAH patterns in Port Valdez tissues largely have been seasonally controlled (Figure 16 and Figure 18). At AMT, a particulate/oil-phase signal is almost always dominant, but there is generally a saw tooth pattern of increased dissolved-phase proportions during the warmer summer/fall period when the water column is more stratified. At GOC, the dominant particulate/oil- and dissolved-phase patterns roughly paralleled the trends observed at AMT until October 1999, with increasing dissolved-phase and combustion product contributions observed after that. Since July 2002, TPAH levels in the AMT mussel tissues have been steadily decreasing. The decreases likely reflect either reduced BTWF discharge volumes as both North Slope oil production decreases and more double-hulled tankers with segregated ballast tanks are brought into the tanker fleet, or improved BWTF efficiency at removing particulate/oil-phase PAH, or a combination of these factors. In mussel tissues, pyrogenic inputs at both AMT and GOC have historically been low, but recently their relative contributions to the overall TPAH levels have become higher and much more variable. One might expect these results as the historic primary source from terminal operations diminishes and minor inputs become more visible, but this suggestion is guarded by the phase-assignment ambiguities with the TPAH values currently averaging around 50 ppb.

For comparison, mussels from a clean reference site used for a similar monitoring program near Sullom Voe, Scotland, one of the major oil terminals in the UK usually have four-fold or higher TPAH burden (Widdows et al., 1995) than mussels immediately adjacent to the Alyeska Marine Terminal (the most consistently contaminated LTEMP monitoring site). We conclude that the very high efficiency of oil removal in the BWTF and effective dispersion at the diffuser combined with reduced tanker traffic, have resulted in remarkably little apparent impact of the discharged PAH on mussel populations within the Port, particularly over the last four years.

In the Sound, with the bulk of EVOS oil either dissipated or the remnants buried and sequestered, regional sites that are physically remote from the chronic input of BWTF discharge are currently looking very clean. Only Disk Island shows what appear to be low (<MDL) but increasing levels of particulate/oil-phase components in mussels over the last four sample collections (July 2004 through March 2006). Having observed pockets of residual oil disturbed and sheening above the LTEMP sampling transect in July 2007 and 2008 (Figure 21 and Figure 22), we assume the trace amounts in 2006 were also of EVOS origin. But overall, the region is getting cleaner. Regressions of log-transformed, average TPAH time series from the five PWS and three GOA stations show parallel decreasing trends (Figure 36). TPAH levels in both regions are dropping at nearly identical rates. This parallelism suggests the decreases are influenced by similar

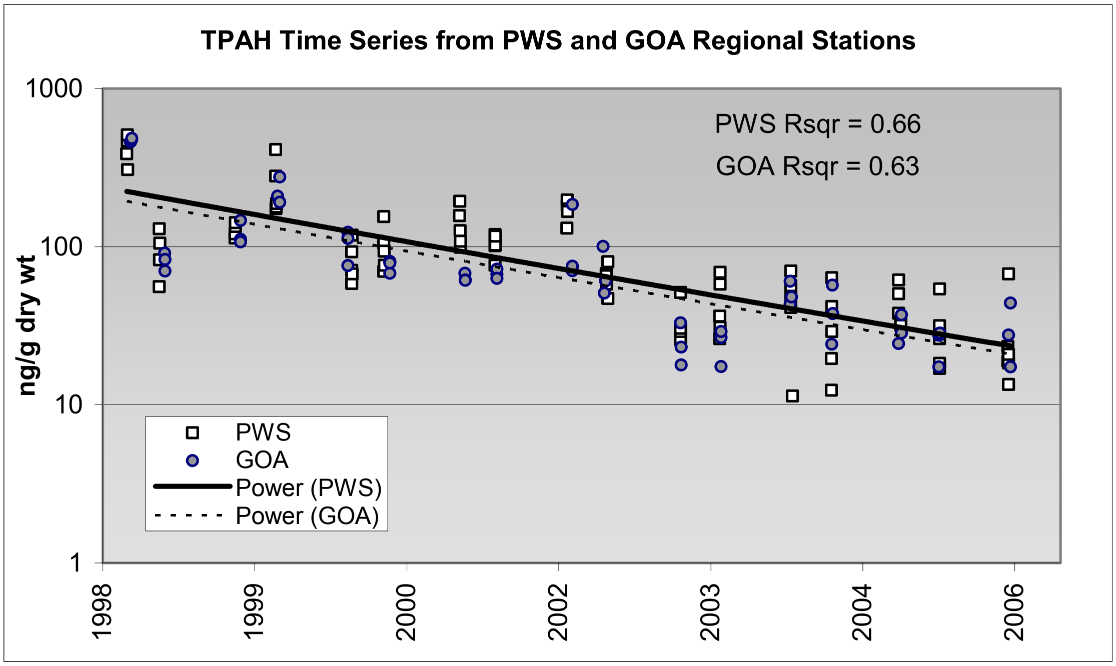


Figure 36 Average *Mytilus* TPAH time series and trend lines comparing Prince William Sound and Gulf of Alaska stations' trends.

(oceanographic-scale?) processes, but the occasional asynchrony of peak events (Figure 15) also suggests regional variation in the dynamics. So what broad-scale sources might appear as an ambient background dissolved signal? Suggestions include atmospheric deposits, forest fires, leaching of water-soluble constituents from the pervasive source-rock (oil shale or coal that constitutes much of the SPM being transported through the region), some upwelling/climate-driven events, a combination of these or some novel mechanism relating to decadal oscillations and/or global warming. There are few data to support or refute any of these concepts, but we are currently favoring atmospheric adsorption and deposition mechanisms (NRC 2003).

Another question is how low will this generally declining trend in TPAH values go? Obviously, at some point, the trend must level out. Follow-up sampling in 2004 for oil residues from the 1997 *M/V Kuroshima* grounding on the Aleutian Chain found TPAH levels between 25 and 85 ng/g dry wt, with an average of 57 ng/g dry wt (Table 8, Helton et al., 2004). This compares favorably with LTEMP's March 2006 range of 13-67 ng/g inside the Sound and 17-44 ng/g at the Gulf of Alaska sites. These data also suggest a natural dissolved-phase background TPAH somewhere below 50 ng/g—a range in which analytical sensitivity is highly susceptible to procedural artifacts. It might easily be the case that the LTEMP data are currently tracking subtle variations in the background PAH, and that we are near or at the minimum.

Table 8 Current TPAH concentrations in mussel tissues (ng/g dry wt) relative to recent NOAA Mussel Watch monitoring data and another recovered Alaskan oil-spill event.

LTEMP (2005/2006)	Valdez	44-55
	PWS	13-67
	GOA	17-44
1997 *M/V Kuroshima*	2004	25-85
West Coast Mussel Watch (sum of 24 analytes)	average	1,928
	Santa Cruz Island	41
	Elliot Bay	46,700
	Alaska	53-144

For relative comparisons, data from the National Status and Trends, Mussel Watch Program (Table 8) show the average PAH concentration in mussels (summing only 24 of the 44 LTEMP analytes) for the remainder of the West Coast is nearly 30 times higher at 1,982 ng/g dry wt. The highest level reported on the West Coast was 46,700 ng/g dry wt at a site in Elliot Bay (Seattle, Washington). The lowest, with 41 ng/g, was from mussels collected on Santa Cruz Island, a National Park 20 miles offshore of Santa Barbara in Southern California. Nationwide from 1986-1996, the 15th, 50th, and 85th percentiles were at 77, 230, and 1,100 ng/g dry wt (O'Connor, 2002). In 2001, the state-wide average TPAH concentration in mussels from the five Alaskan Mussel Watch sites (Ketchikan, Skagway, Port Valdez, Unakwik Inlet, and Cook Inlet) was 86.6 ng/g dry wt with levels ranging from 52.5 to 144 ng/g dry wt. Considering LTEMP results sum nearly twice the number of analytes, the region is exceptionally clean.

Finally, under the auspices of the EVOS Trustees Program, Long-term Monitoring of Anthropogenic Hydrocarbons in the *Exxon Valdez* Oil Spill Region (050763), ten intertidal sites within the Naked-Knight-Southwest Island complex were examined during the 2005 summer program to measure the extent of buried oil still present 16 years after the spill. At EVOS sites previously designated as heavily oiled, 10 to 50 random pits (depending on the beach width) were excavated to a depth of ~0.5 m to look for residual oil. Where available, mussels were also collected in the proximity of any detected oil. Sediments and mussels were analyzed using LTEMP analytical protocols. The results have been published (Short et al., 2007a) but, as part of PWSRCAC efforts, PAH and SHC sample profiles are included in Appendix E. A separate report is being prepared by Dr. Jeffrey Short for this survey plus similar studies completed in 2006 and 2007. Briefly, TPAH levels in the oiled pits ranged from a low of 42 ng/g (on Knight Island) to a high of 567,000 ng/g (on Latouche Island) with the oil showing varying states of weathering (from extensively degraded to very fresh – see Appendix E). The mussel samples collected from these same beaches (but not necessarily immediately adjacent to the oiled pits) showed low (11 to 42 ng/g dry weight) dissolved-phase TPAH signals very similar to those observed at the other ten traditional LTEMP stations. Although there were still persistent buried EVOS residues at a number of the beaches, they are highly sequestered and do not appear to be bioavailable unless disturbed. Rates of disappearance have diminished to an estimated 4% yr^{-1}. If left undisturbed, Short et al. (2007a) predict they will be there for decades.

6 Conclusions

The LTEMP sites are currently reporting stable, trace-level concentrations of biogenic and petrogenic hydrocarbons whereby any new inputs will appear as an easily detected spike above the near pristine background. Utilizing the reliable, post-1998 portions of the dataset, the station trends suggest that TPAH levels have been decreasing in mussel tissues since 1999 and are now at near all-time lows for the LTEMP sites both within and outside of Port Valdez.

At Alyeska Marine Terminal, mussel tissues continue to indicate the accumulation of seasonally influenced, dissolved- and particulate/oil-phase PAH components from the BWTF, but since October 2002, TPAH concentrations have maintained steady within a range of 55-65 ng/g. Sediment conditions at the Alyeska Terminal site, are also improving. After a one and one-half-year plateau at already low TPAH levels, 167-184 ng/g, subtidal sediments have dropped even lower to 50-90 ng/g but still show the weathered-ballast-oil signature plus combustion products (which may or may not be related to terminal activities), and the usual biogenic marine and terrestrial components. These trends most likely reflect the decreased ballast-water throughput for the facility as oil flow through the pipeline and subsequent tanker traffic drops and as double-hulled tankers, carrying segregated, oil-free ballast, come into operation.

Mussel tissue loads at GOC had been consistently low (35-116 ng/g) since July 2002, but a diesel spill sometime between July and October 2004 increased the TPAH values to the highest ever observed at that site, 858 ng/g. Diesel residues were still apparent in mussel tissues collected in March 2005, but TPAH levels have now dropped to the 31-55 ng/g range. TPAH concentrations in GOC sediments are still driven primarily by combustion products, as has always been the case at this site, but are now at all time lows (19-28 ng/g).. There was no evidence of the 2004 diesel spill in the 2005-06 sediment samples at GOC.

Outside Port Valdez, most stations are now showing mussel tissues with less than 70 ng/g TPAH (many with <50 ng/g) and appearing primarily as a dissolved–phase hydrocarbon signal. Based on the regional TPAH trends diminishing to consistently low values, it appears that the final traces of EVOS residues have either stabilized or reached levels that no longer appear in the LTEMP mussel samples (except at Disk Island). From the magnitude and nature of the PAH signal, the bulk of Prince William Sound and the northern Gulf of Alaska reflect only trace background levels of dissolved-phase PAH from an unknown source(s).

Using PAH phase-assignments, we have been able to identify temporal and compositional events that characterize three separate regions comprising Port Valdez, central Prince William Sound, and the outer-coastal Gulf of Alaska stations. Highly significant correlations in synchronous phase shifts since July 1998 demonstrate common influences between Windy Bay (WIB) and Shuyak Harbor (SHH) in the Gulf of Alaska, and between Knowles Head (KNH), Sheep Bay (SHB), and Sleepy Bay (SLB) in PWS. This is further corroborated by regional synchrony of TPAH shifts plus similarity in signatures suggesting that the inner Prince William Sound sites are collectively experiencing one low-level source of hydrocarbons while the outer coastal stations are exposed to a possibly different, common dissolved-phase source. In July/August 2004, both regions showed a dramatic (but below MDL) shift to a common low-level, particulate-PAH source, followed by all stations, except Disk Island, returning to a primarily dissolved-phase signal in 2005 and March 2006. Disk Island is showing recurring trace levels of a particulate signature from activities disturbing EVOS residues buried at the site. The two Port Valdez stations, being mainly influenced by the treated ballast water discharge from the Alyeska Marine Terminal, are trending independently of the regional sites.

7 References

Barron, M.G. & Ka'aihue, L. 2001. Potential for photoenhanced toxicity of spilled oil in Prince William Sound and the Gulf of Alaska waters. *Marine Pollution Bulletin* 43: 86-92.

Barron, M.G., Carls, M.G., Heintz, R. & Rice, S.D. 2003. Evaluation of fish early life-stage toxicity models of chronic embryonic exposures to complex polycyclic aromatic hydrocarbon mixtures. *Toxicological Sciences* 78: 60-67.

Baumard, P. H. Budzinski, and P. Garrigues. 1998. Polycyclic aromatic hydrocarbons in sediments and mussels of the Western Mediterranean Sea. *Environmental Toxicology and Chemistry* 17(5):765-776.

Blanchard, Arny L., Howard M. Feder, and David G. Shaw. 2003. Variations in benthic fauna underneath an effluent mixing zone at a marine oil terminal in Port Valdez, Alaska. *Marine Pollution Bulletin* 46: 1583-1589.

Blanchard, A. L., H. M. Feder, and D. G. Shaw. 2005. Environmental Studies in Port Valdez, Alaska: 2004. Final Report to Alyeska Pipeline Service Co., Inst. Of Marine Science, Univ. Alaska Fairbanks, 221 pp.

Blumer, M., M. Mullin, and D.W. Thomas. 1964. Pristane in the Marine Environment, *Helgolander Wissenshcaftliche Meeresuntersuchungen* 10: 187-201.

Boehm, P.D., D.S. Page, W.A. Burns, A.E. Bence, P.J. Mankiewicz and J.S. Brown, 2001. Resolving the Origin of the Petrogenic Hydrocarbon Background in Prince William Sound, Alaska, *Environmental Science and Technology*, 35(3): 471-479.

Boehm, P.D., and J.W. Farrington. 1984. Aspects of the polycyclic aromatic hydrocarbon geochemistry of recent sediments in the Georges Bank Region. *Environmental Science and Technology* 18: 840-845.

Boehm, P.D., J.S. Brown, and T.C. Sauer. 1989. Physical and chemical characterization of San Joaquin Valley crude oil. Final report prepared for ENTRIX, In., Walnut Creek, California.

Boehm, P.D., J.S. Brown, J.M. Neff, D.S. Page, A.W. Maki, W.A. Burns, and A.E. Bence. 2003. The chemical baseline as a key to defining continuing injury and recovery of Prince William Sound. In Proceedings of the 2003 International Oil Spill Conference. API, Washington, D.C. pp 275-283.

Braunstein Geological & Environmental Services, Inc. (BGES). 2007. Prince William Sound RCAC Long Term Environmental Monitoring Program, Preliminary Review. Prepared for the Prince William Sound Regional Citizens' Advisory Council October 2007, 41 pp.

Brown, D.W., L.S. Ramos, M.Y. Friedman, and W.D. MacLeod, Jr. 1980. Ambient temperature extraction of hydrocarbons from marine sediment -- Comparison with boiling solvent extractions. Pages 313-326 in Petroleum in the Marine Environment, L. Petrakis and F.T. Weiss, eds. Advances in Chemistry Series No. 185. American Chemical Society, Washington, D.C.

Brown, J.S. and P.D. Boehm. 1993. The use of double ratio plots of polynuclear aromatic hydrocarbon (PAH) alkyl homologues for petroleum source identification. Pages 799-801 in Proceedings 1993 Oil Spill Conference. American Petroleum Institute, Washington, D.C.

Carls, M.G. 2006. Nonparametric identification of petrogenic and pyrogenic hydrocarbons in aquatic ecosystems. *Environmental Science and Technology* 40: 4233-4239.

Carls, M.G., Short, J.W. & Payne, J. 2006. Accumulation of polycyclic aromatic hydrocarbons by Neocalanus copepods in Port Valdez, Alaska. *Marine Pollution Bulletin* 52(11), 1480-1489.

Colonell, J.M. 1980a. "Ballast Water Dispersal." In Port Valdez, Alaska: Environmental Studies 1976-1979*,* J.M. Colonell (Ed.), Institute of Marine Science, University of Alaska, Fairbanks, Occasional Publication No. 5. 373 p.

Colonell, J.M. 1980b. "Physical Oceanography". In Port Valdez, Alaska: Environmental Studies 1976-1979*,* J.M. Colonell (Ed.), Institute of Marine Science, University of Alaska, Fairbanks, Occasional Publication No. 5. 373 p.

Cross, J.N., J.T. Hardy, J.E. Hose, G.P. Hershelman, L.D. Antrim, R.W. Gossett and E.A. Crecelius. 1987. "Contaminant Concentrations and Toxicity of Sea-Surface Microlayer near Los Angeles, California," *Marine Environmental Research* 23: 307-323.

Davis, J.B. 1968, Paraffinic hydrocarbons in the sulfate-reducing bacterium, *Desulfovibrio desulfuricaus*. *Chem. Geol*. 3: 155-160.

Douglas, G.S., A.E. Bence, R.C. Prince, S.J. McMillen, and E.L. Butler. 1996. Environmental stability of selected petroleum hydrocarbon source and weathering ratios. *Environmental Science & Technology* 30(7): 2332-2339.

Driskell, W.B., J.R. Payne, and G. Shigenaka. 2005. Revisiting Source Identification, Weathering Models, and Phase Discrimination for *Exxon Valdez* Oil. In Proceedings of Arctic Marine Oil Spill Conference 2005, Calgary, Alberta, Canada. pp 33-58.

Duesterloh, W., Short, J.W. & Barron, M.G. 2002. Photoenhanced toxicity of weathered Alaska North Slope crude oil to the Calanoid copepods *Calanus marshallae* and *Metridia okhotensis. Environmental Science and Technology* 36: 3953-3959.

Farrington, J.W., and B.W. Tripp. 1977. Hydrocarbons in western North Atlantic surface sediments. *Geochim. Cosmochim. Acta* 41: 1627-1641.

Federal Register. 1986. Code of Federal Regulations, Title 40, Part 136, Protection of the Environment. (40 CFR 136). U.S. Government Printing Office, Washington, D.C.

Han, J. and M. Calvin. 1969. Hydrocarbon distribution of algae and bacteria and microbiological activity in sediments, pages 436-443. In Proceedings, National Academy of Sciences. Volume 64. Washington, D.C.; NRC 1985).

Hardy, J.T. 1982. "The Sea-Surface Microlayer: Biology, Chemistry and Anthropogenic Enrichment," *Progress in Oceanography* 11: 307-328.

Hardy, J., S. Kiesser, L. Antrim, A. Stubin, R. Kocan and J.A. Strand. 1987a. The sea-surface microlayer of Puget Sound: Part I. Toxic effects on fish eggs and larvae. *Marine Environmental Research* 23: 227-249.

Hardy, J.T., E.A. Crecelius, L.D. Antrim, V.L. Broadhurst, C.W. Apts, J.M. Gurtisen, and T.J. Fortman. 1987b. The sea-surface microlayer of Puget Sound: Part 2. Concentrations of contaminants and relation to toxicity," *Marine Environmental Research* 23: 251-271.

Hardy, J.T., E.A. Crecelius, L.D. Antrim, S.L. Kiesser, V.L. Broadhurst, P.D. Boehm, and W.G. Steinhauer. 1990. Aquatic surface contamination in Chesapeake Bay. *Marine Chemistry* 28: 333-351.

Helton, Doug, Adam Moles, Jeff Short, Jeep Rice 2004. Results of the *M/V Kuroshima* Oil Spill Shellfish Tissue Analysis 1999, 2000 and 2004. Report to the *M/V Kuroshima* Trustee Council. Prepared by NOAA Office of Response and Restoration, Seattle, Washington and NOAA Auke Bay Laboratory, Juneau, Alaska. December 2004, 7 pp.

Karinen, J.F., M.M. Babcock, E.W. Brown, W.D. MacLeod, Jr., L.R. Ramos, and J.W. Short. 1993. Hydrocarbons in intertidal sediments and mussels from Prince William Sound, Alaska, 1977-1980: characterization and probable sources. NOAA (National Oceanic and Atmospheric Administration) Technical Memorandum NMFS (National Marine Fisheries Service) AFSC-9, Seattle.

Kinnetic Laboratories, Inc. (KLI), 2002. 2000-2002 LTEMP Monitoring Report. Prepared for the Prince William Sound Regional Citizens' Advisory Council Long-Term Environmental Monitoring Program. 94 pp. and appendices.

Larsen, M.L. and L.G. Holland 2004. Standard operating procedure for the determination of particle grain size in marine sediments analyzed at the Auke Bay Laboratory. Auke Bay Laboratory, Alaska Fisheries Science Center, National Marine Fisheries Service, NOAA. Juneau, Alaska.

National Research Council (NRC) 1985. *Oil in the Sea: Inputs, Fates, and Effects.* National Academy Press, Washington, D.C. 601 pp.

National Research Council (NRC) 2003. *Oil in the Sea III: Inputs, Fates, and Effects.* National Academy Press, Washington, D.C. 265 pp.

National Research Council (NRC) 2005. *Oil Spill Dispersants: Efficacy and Effects.* National Academy Press, Washington, D.C. 377 pp.

O'Clair, C.E., J.W. Short, and S.D. Rice. 1996. Contamination of intertidal and subtidal sediments by oil from the *Exxon Valdez* in Prince William Sound. Pages 61-93 *in* S.D. Rice, R.B. Spies, D.A. Wolfe, and B.A. Wright (editors). Proceedings of the *Exxon Valdez* oil spill symposium. American Fisheries Society Symposium 18.

O'Connor, T.P. 2002. National distribution of chemical concentrations in mussels and oysters in the USA. *Marine Environmental Research* 53: 117-143

Overton, E.B., J.A. McFall, S.W. Mascarella, C.F. Steele, S.A. Antoine, I.R. Politzer, and J.L. Laseter. 1981. Identification of petroleum residue sources after a fire and oil spill. Proceedings 1981 Oil Spill Conference. American Petroleum Institute, Washington, D.C., pp 541-546.

Page, D., P.D. Boehm, G.S. Douglas, and A.E. Bence. 1993. The natural petroleum hydrocarbon background in subtidal sediments of Prince William Sound, Alaska. Abstract #089 in Ecological Risk Assessment: Lessons Learned. 14th Annual Meeting, Society of Environmental Toxicology and Chemistry (SETAC) 14-18 November 1993, Houston, TX.

Page, D.S., P.D. Boehm, G.S. Douglas, and A.E. Bence. 1995. Identification of hydrocarbon sources in the benthic sediments of Prince William Sound and the Gulf of Alaska following the *Exxon Valdez* oil spill. Pages 41- 83 in Exxon Valdez Oil Spill: Fate and Effects in Alaskan Waters, ASTM STP 1219, Peter G. Wells, James N. Butler, and Jane S. Hughes, Eds., American Society for Testing and Materials, Philadelphia.

Payne, J.R. and W.B. Driskell. 2001. Source characterization and identification of *New Carissa* oil in NRDA environmental samples using a combined statistical and fingerprinting approach. Proceedings of the 2001 Oil Spill Conference, American Petroleum Institute, Washington, D.C., pp. 1403-1409.

Payne, J.R. and W.B. Driskell. 2003. The importance of distinguishing dissolved- versus oil-droplet phases in assessing the fate, transport, and toxic effects of marine oil pollution. Proceedings of the 2003 Oil Spill Conference, American Petroleum Institute, Washington, D.C., pp 771-778.

Payne, J.R., B.E. Kirstein, G.D. McNabb, Jr., J.L. Lambach, R. Redding, R.E. Jordan, W. Hom, C. de Oliveira, G.S. Smith, D.M. Baxter, and R. Geagel. 1984. Multivariate analysis of petroleum weathering in the marine environment - subarctic. Volume I, Technical Results; Volume II, Appendices. In: Final Reports of Principal Investigators, Vol. 21 and 22. February 1984, U.S. Department of Commerce, National Oceanic and Atmospheric Administration, Ocean Assessment Division, Juneau, Alaska. 690 pp. Volume 21 NTIS Accession Number PB85-215796; Volume 22 NTIS Accession Number PB85-215739.

Payne, J.R., J.R. Clayton, Jr., G.D. McNabb, Jr., B.E. Kirstein, C.L. Clary, R.T. Redding, J.S. Evans, E. Reimnitz, and E. Kempema. 1989. Oil-ice sediment interactions during freezeup and breakup. Final Reports of Principal Investigators, U.S. Dept. Commer., NOAA, OCEAP Final Rep. 64, 1-382 (1989). NTIS Accession Number PB-90-156217.

Payne, J.R., W.B. Driskell, and D.C. Lees. 1998. Long Term Environmental Monitoring Program Data Analysis of Hydrocarbons in Intertidal Mussels and Marine Sediments, 1993-1996. Final Report prepared for the Prince William Sound Regional Citizens Advisory Council, Anchorage, Alaska 99501. (PWSRCAC Contract No. 611.98.1). March 16, 1998. 97 pp plus appendices.

Payne, J.R., W.B. Driskell, M.G. Barron, D.C. Lees. 2001. Assessing transport and exposure pathways and potential petroleum toxicity to marine resources in Port Valdez, Alaska. Final Report Prepared for Prince William Sound Regional Citizens' Advisory Council Contract No. 956.02.1. Prepared by Payne Environmental Consultants, Inc., Encinitas, CA. December 21, 2001. 64 pp plus appendices.

Payne, J.R., W.B. Driskell, and J.W. Short. 2003a. 2002-2003 LTEMP Monitoring Report. Final Report prepared to the Prince William Sound Regional Citizens' Advisory Council, Anchorage, Alaska 99051. PWSRCAC Contract No. 951.03.1. Prepared by Payne Environmental Consultants, Inc., Encinitas, CA. Nov. 6, 2003. 107 pp.

Payne, J.R., J.R. Clayton, Jr., and B.E. Kirstein. 2003b. Oil/suspended particulate material interactions and sedimentation. *Spill Science & Technology Bulletin*, 8(2): 201-221.

Payne, J.R., W.B. Driskell, M.G. Barron, J. A. Kalmar, and D.C. Lees. 2003c. Public comment regarding the Draft NPDES Permit for BWTF at Alyeska Marine Terminal. Final Report prepared for the Prince William Sound Regional Citizens' Advisory Council, Anchorage, Alaska 99051. PWSRCAC Contract No. 551.02.01. Prepared by Payne Environmental Consultants, Inc., Encinitas, CA. June 2, 2003, 21 p.

Payne, J.R., W.B. Driskell, M.G. Barron, D.C. Lees, L. Ka'aihue, and J.W. Short. 2003d. Assessing transport and exposure pathways and potential petroleum toxicity to marine resources in Port Valdez, Alaska. Poster No. PT214 presented at the SETAC 24th Annual Meeting in North America. November 9-13, 2003, Austin, Texas.

Payne, J.R., W.B. Driskell, and J.W. Short. 2005a. 2003-2004 LTEMP Monitoring Report. Final Report prepared for the Prince William Sound Regional Citizens' Advisory Council, Anchorage, Alaska 99051. PWSRCAC Contract No. 951.04.1. Prepared by Payne Environmental Consultants, Inc., Encinitas, CA. April 18, 2005. 123 pp.

Payne, J.R., W.B. Driskell, J.F. Braddock, J. Bailey. 2005b. Hydrocarbon biodegradation in the Ballast Water Treatment Facility, Alyeska Marine Terminal. Final Report prepared for the Prince William Sound Regional Citizens' Advisory Council, Anchorage, Alaska 99051. PWSRCAC Contract Numbers 558.04.01 and 560.2004.01. Prepared by Payne Environmental Consultants, Inc., Encinitas, CA. May 2, 2005. 48 pp.

Payne, J.R., W.B. Driskell, J.F. Braddock, J. Bailey, J.W. Short, L. Ka'aihue, T.H. Kuckertz 2005c. From Tankers to Tissues – Tracking the Degradation and Fate of Oil Discharges in Port Valdez, Alaska. Proceedings of Arctic Marine Oil Spill Conference 2005, Calgary, Alberta, Canada. pp 959-991.

Payne, J.R. and W.B. Driskell, M.R. Lindeberg, W. Fournier, M.L. Larsen, J.W. Short, S.D. Rice, and D. Janka. 2005d. Dissolved- and Particulate-Phase Hydrocarbons in Interstitial Water from Prince William Sound Beaches Containing Buried Oil Thirteen Years After the *Exxon Valdez* Oil Spill, Proceedings of the 2005 International Oil Spill Conference, American Petroleum Institute, Washington, D.C., pp. 83-88.

Payne, J.R., W.B. Driskell, J.W. Short, and M.L. Larsen. 2006. 2004-2005 LTEMP Monitoring Report. Final Report prepared for the Prince William Sound Regional Citizens' Advisory Council, Anchorage, Alaska 99051. PWSRCAC Contract No. 951.05.1. (Restoration Project No. 040724). Prepared by Payne Environmental Consultants, Inc., Encinitas, CA. November 2006. 149 pp.

Payne, J.R., W.B. Driskell, J.W. Short and M.L. Larsen. 2008. Long-term monitoring for oil in the *Exxon Valdez* spill region. *Marine Pollution Bulletin* 56: 2067-2081.

Pelletier, M.C., Burgess, R.M., Ho, K.T., Kuhn, A., McKinney, R.A. & Rybe, S.A. 1997. Phototoxicity of individual polycyclic aromatic hydrocarbons and petroleum to marine invertebrate larvae and juveniles. *Environmental Toxicology and Chemistry* 16: 2190-2199.

Salazar, M., J.W. Short, S.M. Salazar, and J.R. Payne. 2002. Port Valdez Monitoring Report. Prince William Sound Regional Citizens' Advisory Council Contract No. 633.01.1. February 7, 2002. 109 pp plus appendices.

Sauer, T. and P. Boehm. 1991. The use of defensible analytical chemical measurements for oil spill natural resource damage assessment. Proceedings of the 1991 Oil Spill Conference. American Petroleum Institute, Washington, D.C., pp 363-369.

Saupe, Susan 2004. Alaska EMAP coordinator, personal communication.

Savoie, M.A., Savoie, J.M., Trefry, J.H., Semmler, C.M., Woodall, D.W., Trocine, R.P., Brooks, J.M. & McDonald, T. 2006. Port Valdez sediment coring program -- final 2004 monitoring report. Final Report prepared for the Prince William Sound Regional Citizens' Advisory Council, Anchorage, Alaska 99051. (Contract No. 961.04.1) January 2006. 76 pp.

Shaw, D., A.L. Blanchard, and D.L. Hawkins. 2005. Chapter 2 – Hydrocarbon Studies in Environmental Studies in Port Valdez, Alaska: 2004. Final Report to Alyeska Pipeline Service Co., Inst. of Marine Science, Univ. Alaska Fairbanks, 221 pp.

Short, J.W. 2005. Seasonal variability of pristane in mussels (*Mytilus Trossulus*) in Prince William Sound, Alaska. Ph.D. Thesis. University of Alaska, Fairbanks. 204 pp.

Short, J.W. and M.M. Babcock. 1996. Prespill and postspill concentrations of hydrocarbons in mussels and sediments in Prince William Sound. Pages 149-166 *in* S.D. Rice, R.B. Spies, D.A. Wolfe, and B.A. Wright (editors). Proceedings of the *Exxon Valdez* oil spill symposium. American Fisheries Society Symposium 18.

Short, J.W. and K.R. Springman. 2007. Identification of hydrocarbons in biological samples for source determination. Pages 381-403 *in* Oil Spill Environmental Forensics, Z. Wang and S.A. Stout (editors), Elsevier, Inc, Oxford, UK.

Short, J.W., K.A. Kvenvolden, P.R. Carlson, F.D. Hostettler, R.J. Rosenbauer and B.A. Wright. 1999. Natural hydrocarbon background in benthic sediments of Prince William Sound, Alaska: Oil vs. coal, *Environmental Science and Technology*, 33(1): 34-42.

Short, J.W., M.R. Lindeberg, P.A. Harris, J.M. Maselko, J.J. Pella, and S.D. Rice. 2004. An estimate of oil persisting on beaches of Prince William Sound, 12 years after the *Exxon Valdez* oil spill. *Environmental Science & Technology* 38: 19-25

Short, J.W., G.V. Irvine, D.H. Mann, J.M. Maselko, J.J. Pella, M.R. Lindeberg, J.R. Payne, W.B. Driskell, and S.D. Rice. 2007a. Slightly weathered *Exxon Valdez* oil persists in Gulf of Alaska beach sediments after 16 years. *Environmental Science & Technology*. 41(4): 1245-1250.

Short, J.W., J.J. Kolak, J.R. Payne, G.K. Van Kooten. 2007b. An evaluation of petrogenic hydrocarbons in northern Gulf of Alaska continental shelf sediments – The role of coastal oil seep inputs. *Organic Geochemistry* 38(4): 643-670.

Wang, Z. and S.A. Stout. 2007. Oil Spill Environmental Forensics: Fingerprinting and Source Identification. Academic Press, Burlington, MA, USA. 554 pp.

Woodward-Clyde Consultants and ENTRIX, Inc. 1987. Ballast water treatment facility effluent plume behavior. A Synthesis of Findings. Prepared for Alyeska Pipeline Service Company. Walnut Creek, California. March 1987.

8 Appendices

Appendix A LTEMP Oil Primer

Appendix B- 1 TPAH and TSHC summary table for all Alyeska Marine Terminal and Gold Creek sediment samples.

Appendix B-2 Summary of Sediment TPAH and Component Fractions for all Alyeska Marine Terminal and Gold Creek Sediment Grabs

Appendix C Summary of tissue TPAH and TSHC for 2005-2006 program.

Appendix D – PAH plots from the 2005-2006 Tissue Analyses

Appendix E – Oiled Sediment and Mussel Histogram Plots from the 2005 GEM Random Pit Sampling Program

Appendix F – Nordic Viking Diesel Spill

Appendix A LTEMP Oil Primer

This section is included as background material for those readers unfamiliar with oil chemistry or the oil contaminants found in Prince William Sound and central Alaskan coastal regions.

A.1 Regional Sources

In the LTEMP regional environment, oil hydrocarbons arrive from numerous and varied sources. Topping the list would be Alaskan North Slope (ANS) crude including lingering residues from the *Exxon Valdez* oil spill (EVOS); oil products from the Alyeska Marine Terminal (not necessarily ANS); coal, peat and organic-rich shales from vast local and regional deposits; Cook Inlet crude oil; and refined petroleum products that have made their way into the marine environment.

Of primary interest to LTEMP is, of course, ANS crude oil. This crude actually consists of a blend of petroleum from the production fields on the Alaskan North Slope, including Prudhoe Bay, Kuparuk, Endicott, and Lisburne, that together exhibit a chemical fingerprint that is quite distinct from that of oil found in other geographic areas. The EVOS of March 1989 consisted of ANS crude, which over time has weathered to produce a significantly different fingerprint than that of fresh ANS crude. Petroleum that originates from organic-rich shales (or hydrocarbon "source rock") and coal deposits in the Gulf of Alaska also contribute significantly to the natural (or “background") hydrocarbons in the study area, and these also exhibit a distinctly different fingerprint. Recent work shows the source rock signature to be particularly widespread in the deep sediments of PWS, and indeed, appears unchanged in coastal sediments from upstream of the Copper River past the Outer Kenai and through Shelikof Straits (unpublished data, Susan Saupe). Fortunately, animals exposed to these sediments do not seem to accumulate hydrocarbons because these contaminants are not bioavailable. Natural terrestrial oil seeps have also been invoked as hydrocarbon sources, but recent work indicates input from these seeps is insignificant compared with the other sources.

Other petroleum products that may have been introduced into the marine environment in Prince William Sound (PWS) include oil products from source locations other than Alaska. For example, the Great Alaskan Earthquake of 1964 and the resultant tsunamis washed fuel oil and asphalt made from California source oils into Port Valdez, and subsequently into PWS (Kvenvolden et al. 1995). These authors noted that tarballs from these California-sourced products have been found throughout the northern and western parts of PWS. Most recently, hydrocarbons from historic anthropogenic activities (long-abandoned mines, logging operations, camp sites, and fish canneries) in addition to current settlements within PWS have been hypothesized as being additional sources of background hydrocarbon signals (Boehm et al. 2003).

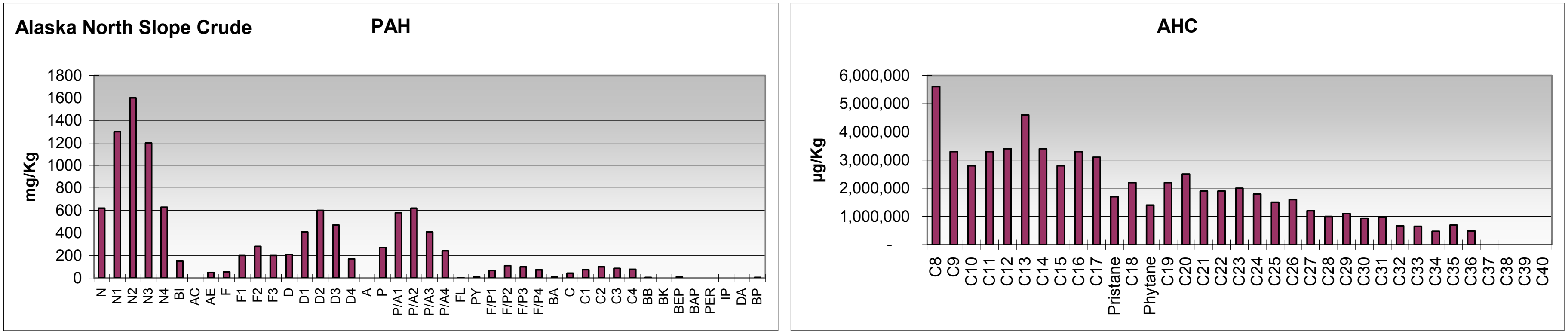
A.2 Oil Chemistry, Source Allocations, and Weathering Behavior

Chemically, oil is a complex mixture of decayed ancient organic matter broken down and modified under geologic heat and pressure. Each deposit is a unique blend but there are commonalities. Hydrocarbons are by far the most abundant compounds in crude oil, accounting for 50-98% of the volume. And in various proportions, all crude blends contain "lighter fractions" of hydrocarbons (similar to gasoline), "intermediate fractions" like diesel or fuel oil, heavier tars and wax-like hydrocarbons, and ultimately residual materials like asphalt. For purposes of the LTEMP chemical analyses, crude oil is identified by its signature blend of just two compositional hydrocarbon groups, the polycyclic aromatic hydrocarbons (PAH) and the saturated (or aliphatic) hydrocarbons (SHC), also referred to as n-alkanes. These two compositional groups encompass the intermediate, heavier tars, and wax-like fractions. As shown by the plots in Figure 1, we work with approximately 44 PAH compounds and 26 SHC components to identify a hydrocarbon source. (Names and abbreviations of the individual analytes shown in this and all following figures are presented in Table 2 in Section 4.2 - Analytic Methods.) These PAH typically account for 2-5% of petroleum by weight (and about 3% of ANS crude).

For source identifications, it is useful to distinguish between five main families of PAH components. In order from light to heavy (left to right in the plots), they are: naphthalenes (N), fluorenes (F), phenanthrenes/anthracenes (P/A), dibenzothiophenes (D), and chrysenes (C).

The naphthalenes are two-ring aromatics (i.e., two 6-carbon rings linked together) and are less persistent in the environment compared to the other higher-molecular-weight groups. They typically disappear from spilled oil by evaporation and dissolution weathering and as such, they may or may not be present in the plots of oil residues or oil-contaminated mussel and sediment samples. Because they dissolve slowly and to a limited extent in water, they can also be detected moving directly from the water column into exposed organisms. 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 oil sources. The dibenzothiophenes (another three-ring compound that also contains sulfur) are important, because they are substantially more abundant in Alaskan North Slope crude oil than in other oil deposits in the region such as Cook Inlet or Katalla crude oil. Finally, the heavier four- and five-ring aromatics (including, the chrysenes (C) through benzo(g,h,i)perylene (BP)) 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.

Chemists have developed a nomenclature to distinguish the various members of each family. The simple parent compounds in each of the five PAH families are referred to as "C_0" (e.g., C_0-naphthalene, here abbreviated simply as "N"). Their other family members, known to chemists as alkyl-substituted homologues, are adorned with an alkyl molecule ($-CH_3$) in a named position around the margin of the PAH ring. These homologues thus become known by their sequence name, e.g., C1-naphthalene (abbreviated as N1), C2-naphthalene (N2), and so on (N3 and N4) (see Figure 1).



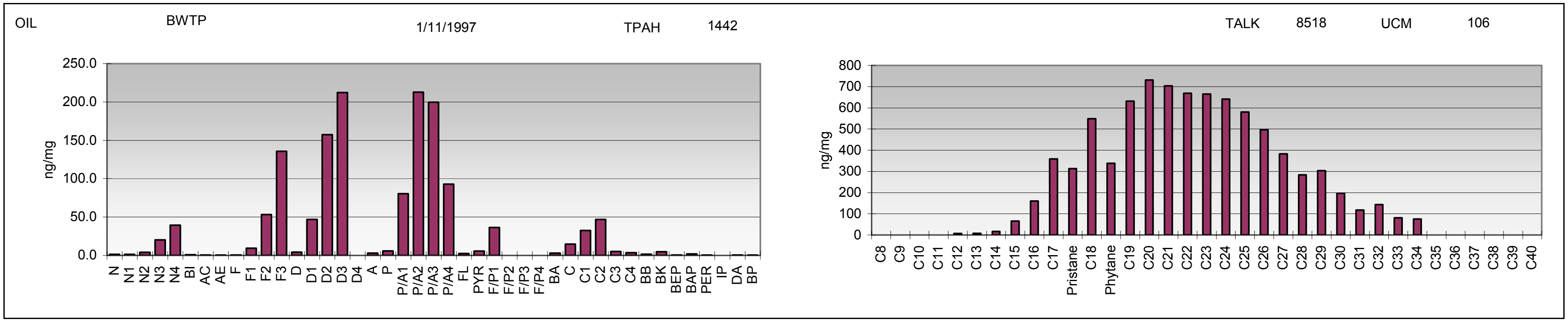
Appendix Figure 1 Example plots of ANS PAH and SHC (also referred to as AHC) components.

Regarding the family structure, it is important to note that petrogenic (petroleum-derived) PAHs have a characteristic fingerprint whereby the parent compounds in each of the five PAH families (e.g., the parent C_0-naphthalene, abbreviated as "N") are usually at lower concentrations than their other family members (see Figure 1). With evaporation/ dissolution weathering, these lower-molecular-weight components are more easily eliminated, thus generating a characteristic "water-washed profile" with the levels of $C_0<C_1<C_2<C_3$ within each PAH group. Eventually, with continued weathering, only the most persistent alkylated phenanthrenes/anthracenes, dibenzothiophenes, and chrysenes are seen, and typically at very characteristic, source-specific ratios in the remaining oil residues (Figure 2).

Likewise, in the SHC fraction, the n-alkanes also clearly show the effects of evaporation weathering with losses of all components with molecular weights below n-C_{14} apparent after several weeks (Figure 2). With continued microbial degradation, the remaining n-alkanes will be selectively removed leaving only the branched compounds, pristane and phytane, which are also removed but at a much slower rate over time. Incidentally, phytoplankton make n-C_{15} and n-C_{17} which mussels can accumulate by feeding on the phytoplankton. Substantial concentrations of pristane are also naturally present in some zooplankton; they biosynthesize it from chlorophyll ingested with the phytoplankton they eat. Therefore, all three compounds can show up in mussel and sediment samples as a result of marine biogenic input. In a spring plankton bloom, these natural aliphatic hydrocarbons can easily dominate the SHC fraction. Phytane, on the other hand, is almost exclusively associated with oil, so its presence in samples can also be used as another indicator of petroleum contamination.

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 because of a similar PAH profile. Pyrogenic PAHs are characterized by high molecular weight PAHs greater than C_3-dibenzothiophene (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 alkyl substitution and molecular weight within a group, i.e., $C_0>C_1>C_2>C_3>C_4$, opposite the trend seen in crude oil and distillate products.

For the aliphatic hydrocarbons, the nomenclature strategy changes. The abbreviation for the aliphatic compound, n-C_{10}, now refers to 10 carbon atoms linked in a straight chain (no cyclic rings). In contrast to the PAHs, aliphatic hydrocarbons can account for more than 70 percent of petroleum by weight. Also, as noted above, aliphatic hydrocarbons can be synthesized by organisms (both planktonic and terrestrial), and may be present as degradation products in some bacteria. As shown in Figure 1, crude petroleum contains a homologous series of n-alkanes ranging from one (methane gas) to more than 30 carbons with odd- and even-numbered n-alkanes present in nearly equal amounts. In contrast, biogenic hydrocarbons (produced by living organisms) preferentially contain specific



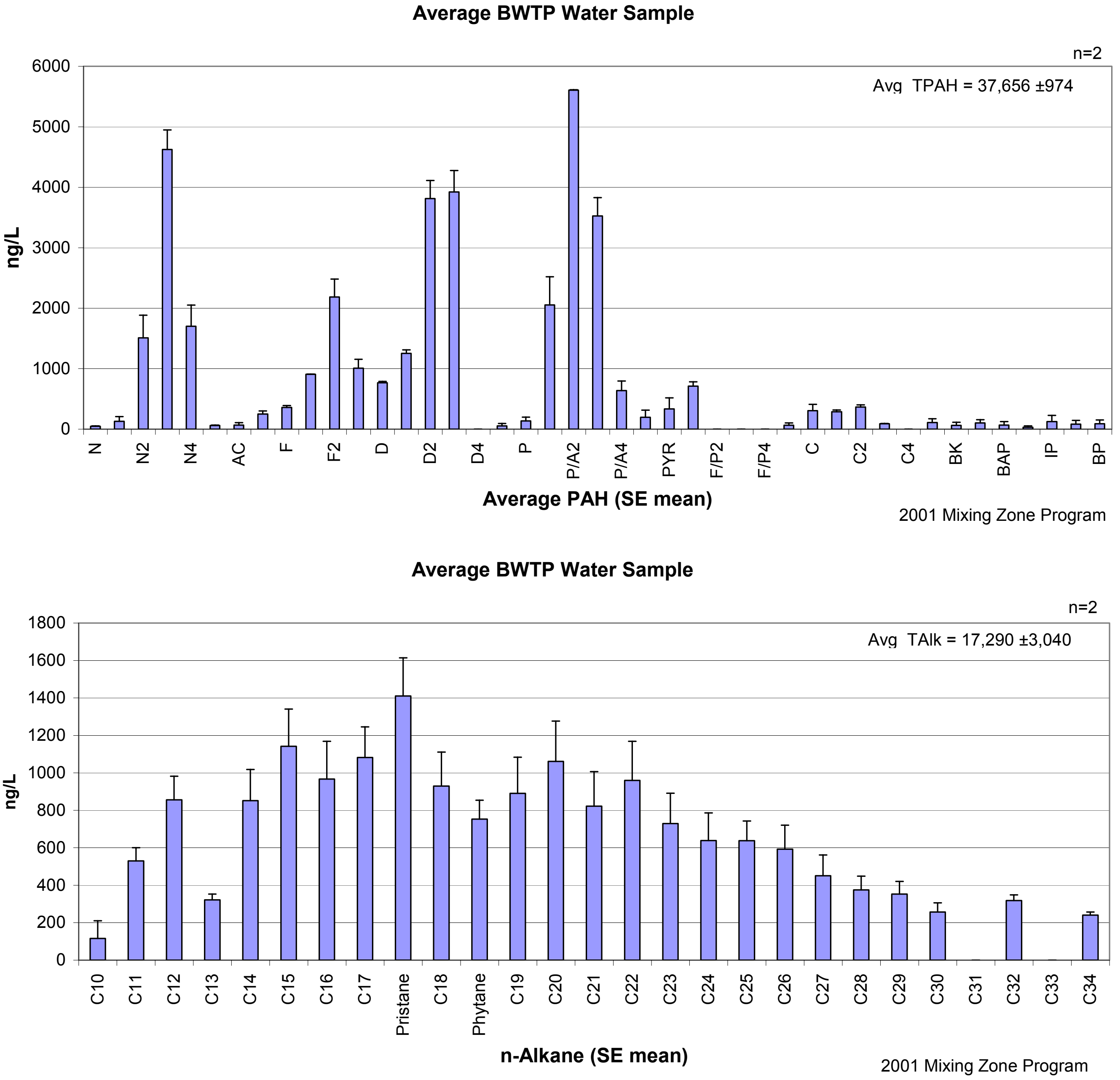
Appendix Figure 2. Plot of weathered ANS from LTEMP 11/97.

suites of normal alkanes with mainly odd-numbered carbons between n-C_{15} and n-C_{33}. In addition to the example of n-C_{15}, n-C_{17}, and pristane from marine plankton cited above, terrestrial plants contribute a predominant odd-numbered carbon pattern including n-C_{25}, n-C_{27}, n-C_{29}, n-C_{31}, and n-C_{33}. These so-called "plant waxes" are commonly observed in marine sediments in depositional areas receiving significant amounts of terrestrial runoff.

Petroleum also contains a complex mixture of branched and cyclic compounds generally not found in organisms. This complex mixture can include oxygenated compounds that produce an "unresolved complex mixture" of compounds (the UCM) in the gas chromatographic profiles. The UCM appears proportionally more prominent in analyses as additional oxygenated compounds are introduced to oil by bacterial and photochemical processes. Thus, the presence and amount of the UCM can be a diagnostic indicator of heavily-weathered petroleum contamination.

Once in water, a crude oil signature can be modified by several processes including evaporation and dissolution weathering, and microbial degradation. We've recently identified another twist in tracking an oil source, the dissolved versus particulate fractions. As a droplet of oil enters water, the more readily-dissolvable components, particularly the naphthalenes, are removed from the droplet thus leaving behind a particulate (or oil droplet) fraction with the "water-washed pattern" mentioned above (low on the parent stock). The receiving water then has the dissolved components signature. In essence, one source produces two signatures in water. This process is readily apparent in the discharge into Port Valdez from the Ballast Water Treatment Facility (BWTF) at the Alyeska Marine Terminal.

Figure 3 presents plots of the PAH and SHC associated with this discharge (Payne et al. 2001; Salazar et al. 2002). In this case, the PAH pattern associated with the colloidal/particulate (oil-droplet) phase shows the depletion of naphthalene (N) and methylnaphthalenes (N1) compared to higher alkylated homologues (N2, N3, and N4), and, to a lesser extent, this same "water-washed pattern" is observed for the fluorenes (F's), dibenzothiophenes (D's), and phenanthrenes/anthracenes (P/A's). The SHC (n-alkane) distribution from the BWTF discharge still shows the presence of minute oil droplets (the water insoluble components that do not dissolve). In addition to evaporation weathering, there is evidence of enhanced microbial degradation from the biological treatment tanks at the BWTF as shown by the depleted concentrations of the n-alkanes compared to pristane and phytane (compare the SHC patterns in Figures 1 and 3).

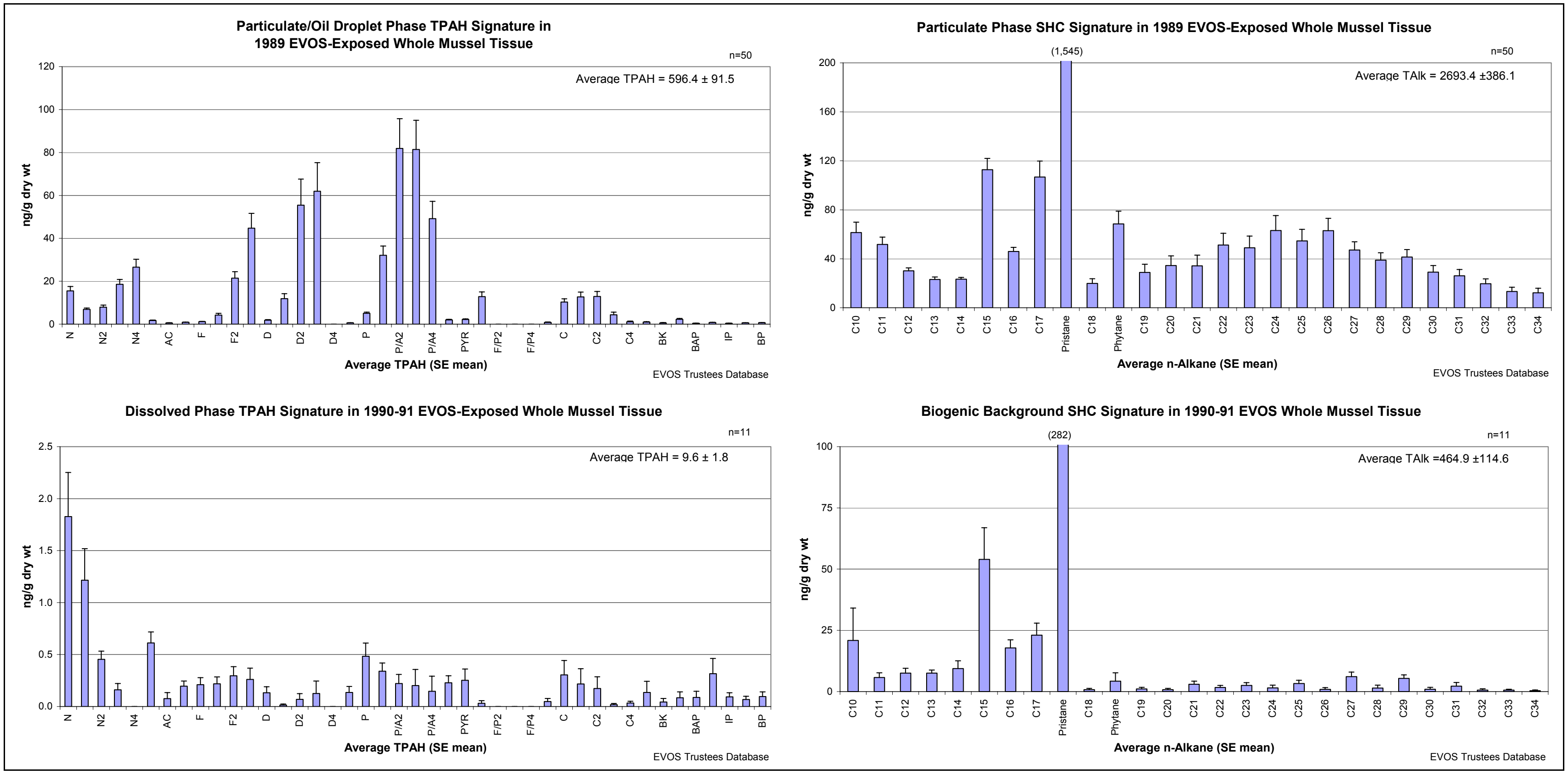


Appendix Figure 3. PAH and SHC plots of effluent from the Alyeska Marine Terminal BWTF (from Salazar et al. 2002).

A.3 Mussels as Indicator Organisms

When analyzing the mussel tissue samples collected as part of LTEMP, it is important to recognize that as filter feeders, mussels can accumulate oil from both the dissolved and particulate/oil-droplet phases. Figure 4 (from Payne et al. 2001) presents examples of mussels collected from oiled areas of Cabin Bay, Naked Island in Prince William Sound in May 1989 immediately after the *Exxon Valdez* oil spill and again in May/June in 1990 and 1991. In 1989, the mussels clearly accumulated PAH and aliphatic hydrocarbons from both the dissolved and particulate phases to which they were exposed; however, the particulate (dispersed oil droplet phase) was the predominant source for the accumulated higher-molecular-weight PAH (C_2-dibenzothiophenes (D2) through higher alkylated homologues of the phenanthrenes/anthracenes and chrysenes) and the aliphatics (phytane plus the even distribution of n-alkanes from n-C_{19} through n-C_{34}). As noted above, these higher-molecular-weight components have only limited water solubilities and have long been associated with the whole oil (droplet) phase. In the post-spill 1990 and 1991 data, the mussels accumulated primarily dissolved-phase PAH (at significantly reduced overall concentrations) from the more water-soluble hydrocarbons still leaching from the contaminated intertidal zone. This is manifest in the plots at the bottom of Figure 4 by the predominant naphthalene and alkyl-substituted naphthalene homologues in greater relative abundance compared to the other PAH. Likewise, the SHC profile for the mussel samples in 1990-1991 is characterized primarily by lower molecular weight biogenic components (n-C_{15}, n-C_{17}, and pristane) with little or no contribution of phytane and higher molecular weight n-alkanes from dispersed oil droplets.

These plots are presented as examples of what should be considered in this report and specifically kept in mind when reviewing the data generated during the past 13 years of the LTEMP. The profiles in Figure 4 are particularly important, because they also illustrate typical patterns of oil contamination (from both particulate and dissolved phases) in the absence of other confounding factors, such as lipid interference.



Particulate/Oil Droplet Phase TPAH Signature in 1989 EVOS-Exposed Whole Mussel Tissue

EVOS Trustees Database

Particulate Phase SHC Signature in 1989 EVOS-Exposed Whole Mussel Tissue

EVOS Trustees Database

Dissolved Phase TPAH Signature in 1990-91 EVOS-Exposed Whole Mussel Tissue

EVOS Trustees Database

Biogenic Background SHC Signature in 1990-91 EVOS Whole Mussel Tissue

EVOS Trustees Database

Appendix Figure 4. Average PAH and SHC plots of whole mussel extracts from samples collected from oiled areas of Cabin Bay, Naked Island in Prince William Sound in May 1989 after the *Exxon Valdez* oil spill (EVOS) and again in May/June 1990 and 1991. The number of samples contributing to each composite is denoted by "n" (from Payne et al. 2001; data from NOAA EVTHD database).

Appendix B-1 TPAH and TSHC summary table for Alyeska Marine Terminal and Gold Creek sediment samples, 1993-2006.

Date	Sample ID	Total SHC	Mean	Std Dev	CV	Total PAH	Mean	Std Dev	CV
Alyeska Marine Terminal Subtidal Sediments (AMT-S)									
3-Apr-93	PWS93PAT0040	1868				196			
3-Apr-93	PWS93PAT0041	2533				341			
3-Apr-93	PWS93PAT0042	1873	2091	383	18.3	191	243	85	35.1
16-Jul-93	PWS93PAT0043	1164				146			
16-Jul-93	PWS93PAT0044	3183				198			
16-Jul-93	PWS93PAT0045	1707	2018	1045	51.8	394	246	131	53.2
26-Mar-94	PWS94PAT0025	1047				202			
26-Mar-94	PWS94PAT0026	1698				167			
26-Mar-94	PWS94PAT0027	1675	1473	369	25.1	239	203	36	17.8
20-Jul-94	PWS94PAT0031	1425				174			
20-Jul-94	PWS94PAT0032	1242				230			
20-Jul-94	PWS94PAT0033	1922	1530	352	23.0	389	264	112	42.2
3-Apr-95	PWS95PAT0022	1291				206			
3-Apr-95	PWS95PAT0023	1093				244			
3-Apr-95	PWS95PAT0024	1785	1390	356	25.6	186	212	29	13.9
11-Jul-95	PWS95PAT0028	2189				1650			
11-Jul-95	PWS95PAT0029	1872				362			
11-Jul-95	PWS95PAT0030	2763	2275	452	19.9	629	880	680	77.2
16-Mar-96	PWS96PAT0004	1109				160			
16-Mar-96	PWS96PAT0005	1578				311			
16-Mar-96	PWS96PAT0006	1100	1262	273	21.7	135	202	95	47.1
12-Jul-96	PWS96PAT0025	2265				326			
12-Jul-96	PWS96PAT0026	1782				201			
12-Jul-96	PWS96PAT0027	1602	1883	343	18.2	381	303	92	30.5
6-Mar-97	PWS97PAT0001	2203				417			
6-Mar-97	PWS97PAT0002	1980				449			
6-Mar-97	PWS97PAT0003	2929	2371	496	20.9	388	418	31	7.3
17-Jul-97	PWS97PAT0029	1124				246			
17-Jul-97	PWS97PAT0030	1477				377			
17-Jul-97	PWS97PAT0031	1892	1498	384	25.7	288	303	67	22.0
29-Mar-98	PWS98PAT0016	1112				120			
29-Mar-98	PWS98PAT0017	1668				451			
29-Mar-98	PWS98PAT0018	972	1251	368	29.4	144	238	185	77.6
5-Apr-00	PWS00PAT0004	1465				313			
5-Apr-00	PWS00PAT0005	1575				335			
5-Apr-00	PWS00PAT0006	1568	1536	62	4.0	412	353	52	14.7
21-Jul-00	PWS00PAT0010	2080				392			
21-Jul-00	PWS00PAT0011	3016				452			
21-Jul-00	PWS00PAT0012	2107	2401	533	22.2	571	472	91	19.4
28-Mar-01	PWS01PAT0001	2987				814			
28-Mar-01	PWS01PAT0002	1803				465			
28-Mar-01	PWS01PAT0003	2659	2483	611	24.6	564	614	180	29.3

Date	Sample ID	Total SHC	Mean	Std Dev	CV	Total PAH	Mean	Std Dev	CV
22-Jul-01	PWS01PAT0010	1044				160			
22-Jul-01	PWS01PAT0011	1276				536			
22-Jul-01	PWS01PAT0012	1969	1429	481	33.7	311	335	189	56.4
15-Mar-02	PWS02PAT0004	2508				10			
15-Mar-02	PWS02PAT0005	2452				68			
15-Mar-02	PWS02PAT0006	3514	2825	598	21.2	149	76	70	92.2
10-Jul-02	AMT-S-02-2-1	473				192			
10-Jul-02	AMT-S-02-2-2	504				158			
10-Jul-02	AMT-S-02-2-3	551	509	39	7.7	1089	480	528	110.2
18-Mar-03	AMT-S-03-1-1	654				134			
18-Mar-03	AMT-S-03-1-2	694				271			
18-Mar-03	AMT-S-03-1-3	594	648	51	7.8	131	179	80	44.7
27-Jul-03	AMT-S-03-2-1P	604				199			
27-Jul-03	AMT-S-03-2-2P	564				132			
27-Jul-03	AMT-S-03-2-3P	522	563	41	7.3	109	147	47	31.7
27-Jul-03	AMT-S-03-2-1A	791				230			
27-Jul-03	AMT-S-03-2-2A	701				286			
27-Jul-03	AMT-S-03-2-3A	496	663	151	22.8	144	220	71	32.4
23-Mar-04	AMT-S-04-1-1	451				128			
23-Mar-04	AMT-S-04-1-2	417				231			
23-Mar-04	AMT-S-04-1-3	352	407	50	12.3	142	167	56	33.6
13-Oct-04	AMT-S-04-2-1	629				93			
13-Oct-04	AMT-S-04-2-2	703				329			
13-Oct-04	AMT-S-04-2-3	402	578	157	27.1	103	175	133	76.3
4-Mar-04	AMT-S-05-1-1	243				65			
4-Mar-04	AMT-S-05-1-2	337				47			
4-Mar-04	AMT-S-05-1-3	350	310	58	18.8	41	51	12	24.5
28-Jul-04	AMT-S-04-2-1	870				93			
28-Jul-04	AMT-S-04-2-2	943				329			
28-Jul-04	AMT-S-04-2-3	608	807	176	0.22	103	175	133	0.76
4-Mar-05	AMT-S-05-1-1	367				65			
4-Mar-05	AMT-S-05-1-2	491				47			
4-Mar-05	AMT-S-05-1-3	455	438	64	0.15	41	51	12	0.24
25-Jul-05	AMT-S-05-2-1	731				106			
25-Jul-05	AMT-S-05-2-2	535				61			
25-Jul-05	AMT-S-05-2-3	677	648	59	15.7	92	86	13	26.9
2-Mar-06	AMT-S-06-1-1	419				48			
2-Mar-06	AMT-S-06-1-2	388				49			
2-Mar-06	AMT-S-06-1-3	670	492	89	31.4	64	54	5	17.1
Alyeska Marine Terminal Intertidal Sediments (AMT-L)									
14-Jul-98	PWS98PAT0043	254				26			
14-Jul-98	PWS98PAT0044	131				38			
14-Jul-98	PWS98PAT0045	2492	959	1329	138.6	123	62	53	84.8
Gold Coast Subtidal Sediments (GOC-S)									
19-Mar-93	PWS93PAT0001	941				47			
19-Mar-93	PWS93PAT0002	436				36			
19-Mar-93	PWS93PAT0003	1460	946	512	54.1	58	47	11	23.4

Date	Sample ID	Total SHC	Mean	Std Dev	CV	Total PAH	Mean	Std Dev	CV
25-Jul-93	PWS93PAT0071	1036				57			
25-Jul-93	PWS93PAT0072	408				31			
25-Jul-93	PWS93PAT0073	256	567	413	73.0	25	38	17	45.2
26-Mar-94	PWS94PAT0022	1429				60			
26-Mar-94	PWS94PAT0023	571				45			
26-Mar-94	PWS94PAT0024	638	879	477	54.3	106	70	32	45.2
19-Jul-94	PWS94PAT0028	385				47			
19-Jul-94	PWS94PAT0029	378				18			
19-Jul-94	PWS94PAT0030	737	500	205	41.1	68	44	25	56.6
3-Apr-95	PWS95PAT0019	463				57			
3-Apr-95	PWS95PAT0020	322				34			
3-Apr-95	PWS95PAT0021	528	438	105	24.1	31	41	14	35.0
11-Jul-95	PWS95PAT0025	750				67			
11-Jul-95	PWS95PAT0026	598				59			
11-Jul-95	PWS95PAT0027	444	597	153	25.6	31	52	19	36.1
16-Mar-96	PWS96PAT0001	588				78			
16-Mar-96	PWS96PAT0002	470				156			
16-Mar-96	PWS96PAT0003	523	527	59	11.2	33	89	62	69.9
12-Jul-96	PWS96PAT0028	541				56			
12-Jul-96	PWS96PAT0029	440				45			
12-Jul-96	PWS96PAT0030	629	537	95	17.6	52	51	6	10.9
6-Mar-97	PWS97PAT0004	624				54			
6-Mar-97	PWS97PAT0005	431				39			
6-Mar-97	PWS97PAT0006	441	499	109	21.8	40	44	8	18.9
17-Jul-97	PWS97PAT0026	514				53			
17-Jul-97	PWS97PAT0027	788				55			
17-Jul-97	PWS97PAT0028	552	618	148	24.0	60	56	3	5.7
29-Mar-98	PWS98PAT0013	341				42			
29-Mar-98	PWS98PAT0014	301				48			
29-Mar-98	PWS98PAT0015	352	331	27	8.1	38	43	5	11.6
5-Apr-00	PWS00PAT0001	590				126			
5-Apr-00	PWS00PAT0002	668				81			
5-Apr-00	PWS00PAT0003	918	725	171	23.6	126	111	26	23.4
20-Jul-00	PWS00PAT0007	966				105			
20-Jul-00	PWS00PAT0008	753				111			
21-Jul-00	PWS00PAT0009	912	877	111	12.7	92	103	10	9.3
28-Mar-01	PWS01PAT0004	904				125			
28-Mar-01	PWS01PAT0005	833				131			
28-Mar-01	PWS01PAT0006	901	879	40	4.6	120	126	5	4.2
21-Jul-01	PWS01PAT0007	311				40			
21-Jul-01	PWS01PAT0008	506				59			
21-Jul-01	PWS01PAT0009	2993	1270	1495	117.8	108	69	35	50.8
15-Mar-02	PWS02PAT0002	1568				91			
15-Mar-02	PWS02PAT0003	1165				33			
15-Mar-02	PWS02PAT0007	1407	1380	203	14.7	134	86	51	59.1
10-Jul-02	GOC-S-02-2-1	188				42			

Date	Sample ID	Total SHC	Mean	Std Dev	CV	Total PAH	Mean	Std Dev	CV
10-Jul-02	GOC-S-02-2-2	147				46			
10-Jul-02	GOC-S-02-2-3	117	151	36	23.9	29	39	9	22.4
18-Mar-03	GOC-S-03-1-1	291				31			
18-Mar-03	GOC-S-03-1-2	368				52			
18-Mar-03	GOC-S-03-1-3	280	313	48	15.4	45	43	11	24.7
27-Jul-03	GOC-S-03-2-1P	203				31			
27-Jul-03	GOC-S-03-2-2P	179				26			
27-Jul-03	GOC-S-03-2-3P	225	202	23	11.4	115	57	50	87.9
27-Jul-03	GOC-S-03-2-1A	283				32			
27-Jul-03	GOC-S-03-2-2A	306				31			
27-Jul-03	GOC-S-03-2-3A	219	269	45	16.8	33	32	1.0	2.1
23-Mar-04	GOC-S-04-1-1	193				33			
23-Mar-04	GOC-S-04-1-2	316				16			
23-Mar-04	GOC-S-04-1-3	132	214	94	43.8	36	28	11	38.7
28-Jul-04	GOC-S-04-2-1	353				22			
28-Jul-04	GOC-S-04-2-2	261				28			
28-Jul-04	GOC-S-04-2-3	150	254	102	0.40	22	24	3	0.14
4-Mar-05	GOC-S-05-1-1	189				17			
4-Mar-05	GOC-S-05-1-2	224				22			
4-Mar-05	GOC-S-05-1-3	271	228	41	0.18	18	19	3	0.13
25-Jul-05	GOC-S-05-2-1	210				32			
25-Jul-05	GOC-S-05-2-2	189				23			
25-Jul-05	GOC-S-05-2-3	148	182	18	17.4	30	28	3	15.5
2-Mar-06	GOC-S-06-1-1	157				20			
2-Mar-06	GOC-S-06-1-2	201				23			
2-Mar-06	GOC-S-06-1-3	250	203	27	23.1	21	21	1	6.6
Gold Creek Intertidal Sediments (GOC-L)									
13-Jul-98	PWS98PAT0040	52				12			
13-Jul-98	PWS98PAT0041	14				5			
13-Jul-98	PWS98PAT0042	26	31	19	63.3	12	10	4	41.8

Appendix B-2 Summary of Sediment TPAH and component fractions, 1993-2006.

			Particulate		Dissolved		Pyrogenic			TPAH	
Sample ID	Sample Date	TPAH ng/g dw	ng/g	portion	ng/g	portion	ng/g	portion	Analytic Lab	Mean	Std Err mean
Alyeska Marine Terminal Sediments (AMT-S)											
PWS93PAT0040	4/3/1993	196	0	0	171.2	0.88	22.5	0.12	GERG		
PWS93PAT0041	4/3/1993	341	43.6	0.13	269.5	0.8	23.9	0.07	GERG		
PWS93PAT0042	4/3/1993	191	0	0	175.3	0.93	13.9	0.07	GERG	243	49
PWS93PAT0043	7/16/1993	145	0	0	125.9	0.87	18.2	0.13	GERG		
PWS93PAT0044	7/16/1993	198	0	0	179.9	0.92	16.3	0.08	GERG		
PWS93PAT0045	7/16/1993	394	33.4	0.09	49.5	0.13	306.4	0.79	GERG	246	76
PWS94PAT0025	3/26/1994	202	0	0	142.8	0.71	57.3	0.29	GERG		
PWS94PAT0026	3/26/1994	167	0	0	151.1	0.92	13.9	0.08	GERG		
PWS94PAT0027	3/26/1994	239	0	0	174.3	0.74	62.6	0.26	GERG	203	21
PWS94PAT0031	7/20/1994	175	0	0	156.2	0.9	16.8	0.1	GERG		
PWS94PAT0032	7/20/1994	230	0	0	204.2	0.9	23.4	0.1	GERG		
PWS94PAT0033	7/20/1994	389	0	0	336.7	0.87	50.2	0.13	GERG	265	64
PWS95PAT0022	4/3/1995	206	0	0	162.2	0.8	41.7	0.2	GERG		
PWS95PAT0023	4/3/1995	244	0	0	193.3	0.8	48.9	0.2	GERG		
PWS95PAT0024	4/3/1995	187	0	0	164.5	0.89	20.4	0.11	GERG	212	17
PWS95PAT0028	7/11/1995	1,650	0	0	526.9	0.32	1108.8	0.68	GERG		
PWS95PAT0029	7/11/1995	362	0	0	339.6	0.95	18.8	0.06	GERG		
PWS95PAT0030	7/11/1995	630	0	0	607.6	0.97	19.5	0.03	GERG	881	392
PWS96PAT0004	3/16/1996	160	0	0	136.8	0.86	21.5	0.14	GERG		
PWS96PAT0006	3/16/1996	311	0	0	297.4	0.96	11.7	0.04	GERG		
PWS96PAT0006	3/16/1996	135	0	0	119.9	0.9	13.6	0.1	GERG	202	55
PWS96PAT0025	7/12/1996	326	0	0	306.2	0.94	19	0.06	GERG		
PWS96PAT0026	7/12/1996	201	0	0	188.3	0.94	11.4	0.06	GERG		
PWS96PAT0027	7/12/1996	381	0	0	110.7	0.31	251.2	0.69	GERG	303	53
PWS97PAT0001	3/6/1997	417	0	0	377	0.91	36.4	0.09	GERG		
PWS97PAT0002	3/6/1997	449	0	0	416.2	0.93	29.3	0.07	GERG		

			Particulate		Dissolved		Pyrogenic		Analytic Lab	TPAH	
Sample ID	**Sample Date**	**TPAH ng/g dw**	**ng/g**	**portion**	**ng/g**	**portion**	**ng/g**	**portion**		**Mean**	**Std Err mean**
PWS97PAT0003	3/6/1997	388	0	0	342.4	0.89	43.2	0.11	GERG	418	18
PWS97PAT0029	7/17/1997	246	0	0	223.5	0.92	18.8	0.08	GERG		
PWS97PAT0030	7/17/1997	377	0	0	341.1	0.92	31.6	0.08	GERG		
PWS97PAT0031	7/17/1997	288	0	0	268.5	0.95	15.4	0.06	GERG	303	39
PWS98PAT0016	3/29/1998	120	0	0	108.9	0.93	8.8	0.07	GERG		
PWS98PAT0017	3/29/1998	451	0	0	210.8	0.47	233.6	0.53	GERG		
PWS98PAT0018	3/29/1998	144	0	0	129.1	0.91	12.1	0.09	GERG	238	107
PWS00PAT0004	4/5/2000	313	0	0	222.7	0.72	86.8	0.28	GERG		
PWS00PAT0006	4/5/2000	335	0	0	303.3	0.91	28.5	0.09	GERG		
PWS00PAT0006	4/5/2000	412	0	0	374.9	0.92	34.2	0.08	GERG	353	30
PWS00PAT0010	7/21/2000	392	0	0	333.5	0.86	54.1	0.14	GERG		
PWS00PAT0011	7/21/2000	452	0	0	397.3	0.89	50.8	0.11	GERG		
PWS00PAT0012	7/21/2000	571	54.5	0.1	147.8	0.26	356.4	0.64	GERG	472	53
PWS01PAT0001	3/28/2001	814	0	0	725.8	0.9	79	0.1	GERG		
PWS01PAT0002	3/28/2001	465	0	0	406.1	0.88	53.9	0.12	GERG		
PWS01PAT0003	3/28/2001	564	43.5	0.08	445.5	0.8	66.9	0.12	GERG	614	104
PWS01PAT0010	7/22/2001	160	20.5	0.13	74.2	0.48	61.5	0.39	GERG		
PWS01PAT0011	7/22/2001	536	51.2	0.1	58.1	0.11	408.9	0.79	GERG		
PWS01PAT0012	7/22/2001	311	0	0	287	0.94	19.4	0.06	GERG	335	109
PWS02PAT0004	3/15/2002	10	4.9	0.53	2.4	0.26	2	0.22	GERG		
PWS02PAT0006	3/15/2002	68	0	0	59	0.88	8	0.12	GERG		
PWS02PAT0006	3/15/2002	149	0	0	94	0.65	51.4	0.35	GERG	76	40
AMT-S-02-2-2	7/10/2002	1,068	0	0	1033	0.98	25.2	0.02	ABL		
AMT-S-02-2-3	7/10/2002	183	23	0.13	98.6	0.55	58.7	0.33	ABL		
AMT-S-02-2-1	7/10/2002	148	21.4	0.15	84.9	0.58	39.8	0.27	ABL	466	301
AMT-S-03-1-1	3/18/2003	127	0	0	94.1	0.75	31.7	0.25	ABL		
AMT-S-03-1-2	3/18/2003	260	0	0	171.7	0.66	87.2	0.34	ABL		
AMT-S-03-1-3	3/18/2003	123	0	0	114.6	0.94	7.2	0.06	ABL	170	45
AMT-S-03-2-1P	7/27/2003	165	14.5	0.09	133.8	0.82	14.1	0.09	ABL		
AMT-S-03-2-2P	7/27/2003	118	12	0.1	58.3	0.5	45.3	0.39	ABL		

			Particulate		Dissolved		Pyrogenic			TPAH	
Sample ID	**Sample Date**	**TPAH ng/g dw**	**ng/g**	**portion**	**ng/g**	**portion**	**ng/g**	**portion**	**Analytic Lab**	**Mean**	**Std Err mean**
AMT-S-03-2-3P	7/27/2003	93	10.1	0.11	75.1	0.82	6.2	0.07	ABL	125	21
AMT-S-03-2-1A	7/27/2003	195	23	0.12	157.6	0.82	11.2	0.06	ABL		
AMT-S-03-2-2A	7/27/2003	265	23.9	0.09	2.9	0.01	232.3	0.9	ABL		
AMT-S-03-2-3A	7/27/2003	126	16.9	0.14	95	0.77	11.2	0.09	ABL	195	40
AMT-S-04-1-1	3/23/2004	121	0	0	21.2	0.18	98.1	0.82	ABL		
AMT-S-04-1-2	3/23/2004	225	30.6	0.14	3.6	0.02	185	0.84	ABL		
AMT-S-04-1-3	3/23/2004	134	0	0	44.9	0.34	85.8	0.66	ABL	160	33
AMT-S-04-2-1	7/28/2004	89	0	0	12.4	0.14	74.7	0.86	ABL		
AMT-S-04-2-2	7/28/2004	321	28.7	0.09	3.4	0.01	280.3	0.9	ABL		
AMT-S-04-2-3	7/28/2004	91	0	0	44.4	0.5	44.7	0.5	ABL	167	77
AMT-S-05-1-1	3/4/2005	106	1.6	0.76	41.8	0.12	4	0.12	ABL		
AMT-S-05-1-2	3/4/2005	61	23.2	0.79	0	0.17	12.3	0.04	ABL		
AMT-S-05-1-3	3/4/2005	92	1.3	0.79	44.3	0.16	1.9	0.05	ABL	86	13
AMT-S-05-2-1	7/25/2005	48	40.9	0.56	12	0.2	3.8	0.24	ABL		
AMT-S-05-2-2	7/25/2005	49	33.2	0.72	10.4	0.2	2.1	0.08	ABL		
AMT-S-05-2-3	7/25/2005	64	34.1	0.74	14.5	0.2	3.6	0.06	ABL	54	5
AMT-S-06-1-1	3/3/2006	61	7.8	0.13	1.1	0.02	50.5	0.85	ABL		
AMT-S-06-1-2	3/3/2006	42	7.6	0.18	23.1	0.56	10.7	0.26	ABL		
AMT-S-06-1-3	3/3/2006	37	0	0	25.5	0.73	9.7	0.27	ABL	47	7
Gold Creek Sediments (GOC-S)											
PWS93PAT0001	3/19/1993	47	0	0	16.3	0.35	29.8	0.65	GERG		
PWS93PAT0002	3/19/1993	36	0	0	12.5	0.35	23	0.65	GERG		
PWS93PAT0003	3/19/1993	58	0	0	25	0.44	31.8	0.56	GERG	47	6
PWS93PAT0071	7/25/1993	57	0	0	15.4	0.28	40.5	0.72	GERG		
PWS93PAT0072	7/25/1993	31	0	0	8.3	0.27	22	0.73	GERG		
PWS93PAT0073	7/25/1993	25	0	0	8.7	0.35	15.9	0.65	GERG	38	10
PWS94PAT0022	3/26/1994	61	0	0	49.1	0.83	10.2	0.17	GERG		
PWS94PAT0023	3/26/1994	46	0	0	27.9	0.63	16.4	0.37	GERG		
PWS94PAT0024	3/26/1994	106	0	0	19.9	0.19	84.9	0.81	GERG	71	18

			Particulate		Dissolved		Pyrogenic			TPAH	
Sample ID	Sample Date	TPAH ng/g dw	ng/g	portion	ng/g	portion	ng/g	portion	Analytic Lab	Mean	Std Err mean
PWS94PAT0028	7/19/1994	47	0	0	26.7	0.59	18.9	0.41	GERG		
PWS94PAT0029	7/19/1994	18	0	0	12.3	0.7	5.2	0.3	GERG		
PWS94PAT0030	7/19/1994	69	0	0	13.6	0.2	53.6	0.8	GERG	44	15
PWS95PAT0019	4/3/1995	57	8.2	0.15	2.6	0.06	45.3	0.81	GERG		
PWS95PAT0020	4/3/1995	34	0	0	10.9	0.33	22.4	0.67	GERG		
PWS95PAT0021	4/3/1995	31	0	0	13.5	0.45	16.8	0.55	GERG	41	8
PWS95PAT0025	7/11/1995	67	0	0	45.6	0.7	19.9	0.3	GERG		
PWS95PAT0026	7/11/1995	59	0	0	28.9	0.51	28.1	0.49	GERG		
PWS95PAT0027	7/11/1995	31	0	0	23	0.79	6.2	0.21	GERG	52	11
PWS96PAT0001	3/16/1996	78	0	0	12.2	0.16	63.7	0.84	GERG		
PWS96PAT0002	3/16/1996	156	11.8	0.08	0	0	140.5	0.92	GERG		
PWS96PAT0003	3/16/1996	33	9.7	0.31	9.1	0.29	12.8	0.41	GERG	89	36
PWS96PAT0028	7/12/1996	56	0	0	26	0.48	28.6	0.52	GERG		
PWS96PAT0029	7/12/1996	46	0	0	23	0.52	21.4	0.48	GERG		
PWS96PAT0030	7/12/1996	53	0	0	25.9	0.5	25.4	0.5	GERG	51	3
PWS97PAT0004	3/6/1997	54	0	0	24.3	0.46	28.1	0.54	GERG		
PWS97PAT0006	3/6/1997	39	0	0	23.8	0.63	14.2	0.37	GERG		
PWS97PAT0006	3/6/1997	40	0	0	17	0.43	22.3	0.57	GERG	44	5
PWS97PAT0026	7/17/1997	53	14.3	0.28	9.7	0.19	27.8	0.54	GERG		
PWS97PAT0027	7/17/1997	55	12.6	0.24	11.4	0.22	28.7	0.54	GERG		
PWS97PAT0028	7/17/1997	60	13	0.23	11.6	0.2	32.8	0.57	GERG	56	2
PWS98PAT0013	3/29/1998	42	14.3	0.35	23.3	0.58	2.8	0.07	GERG		
PWS98PAT0014	3/29/1998	48	0	0	24.8	0.54	20.9	0.46	GERG		
PWS98PAT0015	3/29/1998	38	14.9	0.41	19.4	0.53	2.1	0.06	GERG	43	3
PWS00PAT0001	4/5/2000	127	0	0	32.9	0.27	90.8	0.73	GERG		
PWS00PAT0002	4/5/2000	81	0	0	29.9	0.38	48.5	0.62	GERG		
PWS00PAT0003	4/5/2000	126	0	0	44	0.36	79.1	0.64	GERG	111	15
PWS00PAT0007	7/20/2000	106	26.4	0.26	7.5	0.07	68.1	0.67	GERG		
PWS00PAT0008	7/20/2000	111	32	0.3	10.5	0.1	65.2	0.61	GERG		
PWS00PAT0009	7/21/2000	92	24.8	0.28	8.5	0.1	55.9	0.63	GERG	103	6

			Particulate		Dissolved		Pyrogenic			TPAH	
Sample ID	**Sample Date**	**TPAH ng/g dw**	**ng/g**	**portion**	**ng/g**	**portion**	**ng/g**	**portion**	**Analytic Lab**	**Mean**	**Std Err mean**
PWS01PAT0004	3/28/2001	125	25.2	0.21	10.4	0.09	86	0.71	GERG		
PWS01PAT0006	3/28/2001	131	30.7	0.24	10.8	0.09	84.8	0.67	GERG		
PWS01PAT0006	3/28/2001	120	28.6	0.25	11.8	0.1	76	0.65	GERG	126	3
PWS01PAT0007	7/21/2001	40	0	0	15.7	0.42	21.6	0.58	GERG		
PWS01PAT0008	7/21/2001	59	21.7	0.39	3.1	0.06	31.3	0.56	GERG		
PWS01PAT0009	7/21/2001	108	17.5	0.17	3.1	0.03	83.9	0.8	GERG	69	20
PWS02PAT0002	3/15/2002	91	0	0	38.2	0.43	50.3	0.57	GERG		
PWS02PAT0003	3/15/2002	33	12.3	0.4	1.5	0.06	17.2	0.55	GERG		
PWS02PAT0007	3/15/2002	134	0	0	36.4	0.28	95.2	0.72	GERG	86	29
GOC-S-02-2-1	7/10/2002	42	0	0	19.2	0.48	20.9	0.52	ABL		
GOC-S-02-2-2	7/10/2002	46	16.7	0.38	1.5	0.03	26.2	0.59	ABL		
GOC-S-02-2-3	7/10/2002	29	13.9	0.5	0.7	0.02	13.1	0.47	ABL	39	5
GOC-S-03-1-1	3/18/2003	31	0	0	13.9	0.46	16.4	0.54	ABL		
GOC-S-03-1-2	3/18/2003	52	0	0	23	0.46	27.2	0.54	ABL		
GOC-S-03-1-3	3/18/2003	45	0	0	20.2	0.47	22.5	0.53	ABL	43	6
GOC-S-03-2-1A	7/27/2003	32	13.9	0.47	3.4	0.11	12.5	0.42	ABL		
GOC-S-03-2-2A	7/27/2003	31	11.3	0.38	0.8	0.03	17.6	0.59	ABL		
GOC-S-03-2-3A	7/27/2003	33	12.3	0.41	4.4	0.15	13.4	0.44	ABL	32	0
GOC-S-03-2-1P	7/27/2003	31	13.2	0.46	3.5	0.12	12	0.42	ABL		
GOC-S-03-2-2P	7/27/2003	26	10.6	0.45	2.4	0.1	10.4	0.44	ABL		
GOC-S-03-2-3P	7/27/2003	115	0	0	22	0.19	91.2	0.81	ABL	57	29
GOC-S-04-1-1	3/23/2004	33	14.3	0.45	1.1	0.03	16.1	0.51	ABL		
GOC-S-04-1-2	3/23/2004	16	7.2	0.49	0.6	0.04	7	0.47	ABL		
GOC-S-04-1-3	3/23/2004	36	14.5	0.43	1	0.03	18.2	0.54	ABL	28	6
GOC-S-04-2-1	7/28/2004	22	0	0	8.4	0.41	11.9	0.59	ABL		
GOC-S-04-2-2	7/28/2004	28	0	0	7.5	0.29	18.1	0.71	ABL		
GOC-S-04-2-3	7/28/2004	22	7.5	0.37	0.2	0.01	12.7	0.62	ABL	24	2
GOC-S-05-1-1	3/4/2005	17	0	0	6.8	0.44	8.6	0.56	ABL		
GOC-S-05-1-2	3/4/2005	22	8.8	0.42	0.4	0.02	11.8	0.56	ABL		
GOC-S-05-1-3	3/4/2005	18	7.1	0.41	0.3	0.02	9.7	0.57	ABL	19	2

			Particulate		Dissolved		Pyrogenic		Analytic Lab	TPAH	
Sample ID	**Sample Date**	**TPAH ng/g dw**	**ng/g**	**portion**	**ng/g**	**portion**	**ng/g**	**portion**		**Mean**	**Std Err mean**
GOC-S-05-2-1	7/25/2005	32	69.5	0.03	11.1	0.39	10.8	0.58	ABL		
GOC-S-05-2-2	7/25/2005	23	43.1	0.03	9.4	0.43	2.4	0.54	ABL		
GOC-S-05-2-3	7/25/2005	30	63.5	0.02	12.7	0.33	4.4	0.65	ABL	28	3
GOC-S-06-1-1	3/2/2006	20	23.6	0.03	8.6	0.47	10.3	0.5	ABL		
GOC-S-06-1-2	3/2/2006	23	31.6	0.02	8.8	0.45	3.5	0.52	ABL		
GOC-S-06-1-3	3/2/2006	21	42.5	0.02	11.7	0.42	3.3	0.56	ABL	21	1
Constantine Harbor Sediments COH-S											
COH-S-05-2-1	7/19/2005	36	32.7	0.92	0.0	0.00	2.05	0.06	ABL		
COH-S-05-2-2	7/19/2005	61	28.4	0.47	26.0	0.43	4.26	0.07	ABL		
COH-S-05-2-3	7/19/2005	58	29.1	0.50	23.2	0.40	4.24	0.07	ABL	52	7.8
COH-S-06-1-1	3/4/2006	81	35.7	0.45	37.9	0.48	5.27	0.07	ABL		
COH-S-06-1-2	3/4/2006	70	30.6	0.44	32.3	0.47	4.12	0.06	ABL		
COH-S-06-1-3	3/4/2006	78	33.4	0.43	37.4	0.49	4.28	0.06	ABL	76	3.5

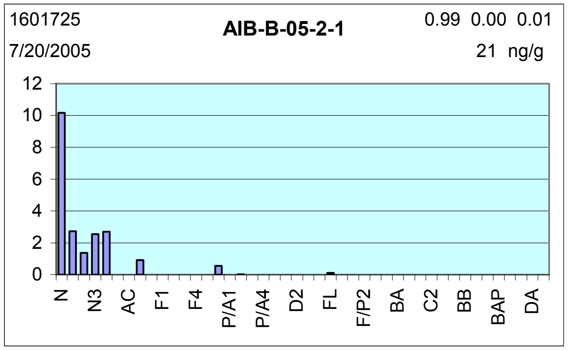
Appendix C Tissue TPAH and TSHC summary for LTEMP 2005-2006.

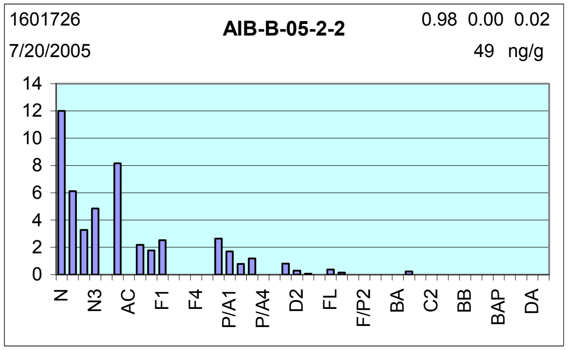
							Particulate		**Dissolved**		**Pyrogenic**	
Sample ID	**TSHC ng/g dw**	**Mean**	**Std error mean**	**TPAH ng/g dw**	**Mean**	**Std error mean**	**ng/g**	**portion**	**ng/g**	**portion**	**ng/g**	**portion**
AIB-B-05-2-1	919			21			20.1	0.99	0	0	0.1	0.01
AIB-B-05-2-2	1915			49			38	0.98	0	0	0.8	0.02
AIB-B-05-2-3	484	1106	424	15	28	10	0	0	8.8	0.71	3.6	0.29
AIB-B-06-1-1	634			27			0	0	12.2	0.47	13.9	0.53
AIB-B-06-1-2	654			32			19	0.6	0	0	12.6	0.4
AIB-B-06-1-3	556	614	30	24	28	2	17.1	0.72	0	0	6.6	0.28
AMT-B-05-2-1	820			25			0	0	9.2	0.39	14.2	0.61
AMT-B-05-2-2	924			35			0	0	14.6	0.43	19.3	0.57
AMT-B-05-2-3	1069	938	72	24	28	4	0	0	7.3	0.33	14.7	0.67
AMT-B-05-3-1	1136			48			41.8	0.88	1.6	0.03	4	0.08
AMT-B-05-3-2	860			36			0	0	23.2	0.65	12.3	0.35
AMT-B-05-3-3	839	945	96	49	44	4	44.3	0.93	1.3	0.03	1.9	0.04
AMT-B-06-1-1	1628			59			12	0.21	40.9	0.72	3.8	0.07
AMT-B-06-1-2	1685			48			10.4	0.23	33.2	0.73	2.1	0.05
AMT-B-06-1-3	877	1397	260	54	53	3	14.5	0.28	34.1	0.65	3.6	0.07
COH-B-05-2-1	559			27			20.8	0.89	0	0	2.5	0.11
COH-B-05-2-2	1099			39			27.7	0.76	0	0	8.9	0.24
COH-B-05-2-3	693	784	162	29	32	4	18.5	0.65	0	0	10	0.35
COH-B-06-1-1	508			18			0	0	16.3	0.91	1.7	0.09
COH-B-06-1-2	723			22			14.2	0.65	5.6	0.25	2.2	0.1
COH-B-06-1-3	519	583	70	22	21	1	15.1	0.69	5.9	0.27	0.9	0.04
DII-B-05-2-1	786			43			0	0	19.1	0.48	20.8	0.52
DII-B-05-2-2	876			48			23.7	0.89	0	0	2.9	0.11
DII-B-05-2-3	932	865	42	71	54	9	51.5	0.84	0	0	9.7	0.16
DII-B-06-1-1	818			54			10	0.21	31.9	0.66	6.1	0.13
DII-B-06-1-2	586			104			0	0	80.5	0.86	13.3	0.14

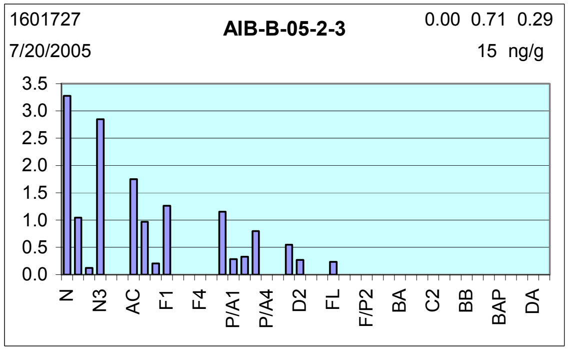
							Particulate		Dissolved		Pyrogenic	
Sample ID	**TSHC ng/g dw**	**Mean**	**Std error mean**	**TPAH ng/g dw**	**Mean**	**Std error mean**	**ng/g**	**portion**	**ng/g**	**portion**	**ng/g**	**portion**
DII-B-06-1-3	617	674	73	44	67	18	10.4	0.25	23.3	0.57	7.3	0.18
GOC-B-05-2-1	2329			54			0	0	29.3	0.56	22.8	0.44
GOC-B-05-2-2	1236			56			0	0	20.7	0.39	32.1	0.61
GOC-B-05-2-3	1315	1627	352	44	51	4	0	0	19.3	0.46	22.7	0.54
GOC-B-05-3-1	2082			41			35.3	0.89	0.9	0.02	3.3	0.08
GOC-B-05-3-2	1445			28			23.7	0.87	1.6	0.06	2	0.07
GOC-B-05-3-3	1731	1753	184	25	31	5	0	0	15	0.61	9.6	0.39
GOC-B-06-1-1	480			53			0	0	11.2	0.22	40.2	0.78
GOC-B-06-1-2	522			57			44.2	0.8	8.3	0.15	2.7	0.05
GOC-B-06-1-3	556	519	22	57	55	1	0	0	20.1	0.36	35.4	0.64
KNH-B-05-2-1	970			26			23.6	0.98	0	0	0.6	0.02
KNH-B-05-2-2	631			14			12.4	0.95	0	0	0.7	0.05
KNH-B-05-2-3	655	752	109	15	18	4	13.1	0.94	0	0	0.8	0.06
KNH-B-06-1-1	331			20			17.5	0.91	1.3	0.07	0.4	0.02
KNH-B-06-1-2	431			26			22.1	0.9	0	0	2.5	0.1
KNH-B-06-1-3	352	371	30	25	23	2	22.3	0.95	0.9	0.04	0.3	0.01
SHB-B-05-2-1	761			20			18.4	0.96	0	0	0.8	0.04
SHB-B-05-2-2	889			27			25	0.98	0	0	0.6	0.02
SHB-B-05-2-3	1366	1005	184	37	28	5	33.7	0.97	0	0	1.1	0.03
SHB-B-06-1-1	391			16			0	0	9.2	0.6	6.1	0.4
SHB-B-06-1-2	415			20			0	0	12.2	0.64	6.8	0.36
SHB-B-06-1-3	325	377	27	20	19	1	18.9	0.95	0	0	1	0.05
SHH-B-05-2-1	1421			28			5.7	0.89	0.4	0.07	0.3	0.04
SHH-B-05-2-2	1857			12			8.6	0.97	0.1	0.01	0.2	0.02
SHH-B-05-2-3	875	1384	284	12	17	5	8.5	0.8	1.8	0.17	0.3	0.03
SHH-B-06-1-1	570			16			12.3	0.81	1.8	0.12	1.1	0.07
SHH-B-06-1-2	741			15			11.1	0.78	2	0.14	1.2	0.08
SHH-B-06-1-3	575	628	56	22	17	2	16.8	0.8	2.9	0.14	1.3	0.06
SLB-B-05-2-1	695			18			15.9	0.95	0	0	0.8	0.05
SLB-B-05-2-2	1001			30			27.1	0.96	0	0	1.2	0.04

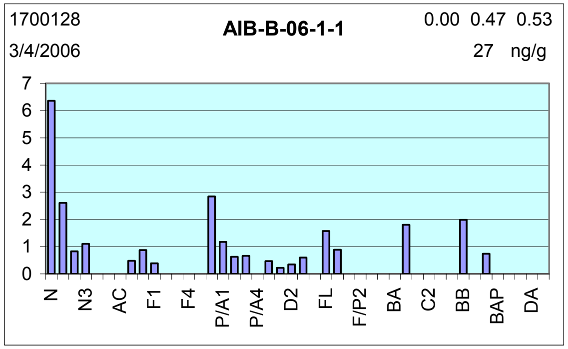
							Particulate		Dissolved		Pyrogenic	
Sample ID	**TSHC ng/g dw**	**Mean**	**Std error mean**	**TPAH ng/g dw**	**Mean**	**Std error mean**	**ng/g**	**portion**	**ng/g**	**portion**	**ng/g**	**portion**
SLB-B-05-2-3	702	799	101	22	23	4	0	0	14.1	0.67	7.1	0.33
SLB-B-06-1-1	2496			20			0	0	14.7	0.75	4.9	0.25
SLB-B-06-1-2	1416			19			7.8	0.43	5.7	0.31	4.8	0.26
SLB-B-06-1-3	1656	1856	327	17	18	1	12.2	0.74	2.1	0.13	2.2	0.13
WIB-B-05-2-1	960			13			10.2	0.98	0	0	0.2	0.02
WIB-B-05-2-2	781			16			14.1	0.97	0.1	0.01	0.3	0.02
WIB-B-05-2-3	572	771	112	53	27	13	22.3	0.93	1.3	0.06	0.3	0.01
WIB-B-06-1-1	63			49			28.3	0.93	1.1	0.04	0.9	0.03
WIB-B-06-1-2	187			41			32.7	0.92	1.1	0.03	1.6	0.04
WIB-B-06-1-3	316	189	73	42	44	3	34.7	0.95	0.7	0.02	1.1	0.03
ZAB-B-05-2-1	675			16			0	0	11.1	0.73	4.2	0.27
ZAB-B-05-2-2	657			24			0	0	9.7	0.43	13.1	0.57
ZAB-B-05-2-3	645	659	9	11	17	4	0	0	6.1	0.61	3.8	0.39
ZAB-B-06-1-1	497			13			10.1	0.78	2.2	0.17	0.6	0.05
ZAB-B-06-1-2	527			11			8	0.74	2.2	0.21	0.6	0.05
ZAB-B-06-1-3	650	558	47	16	13	2	8.8	0.71	2.9	0.23	0.8	0.06

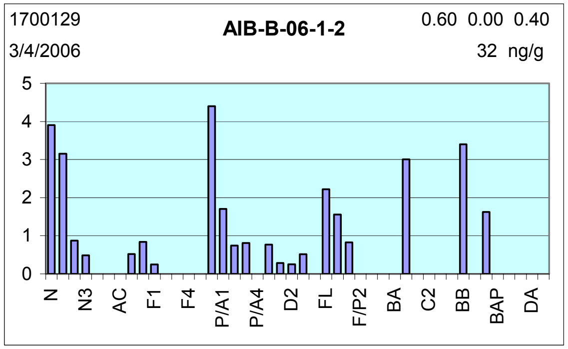
Appendix D – PAH plots from the 2005-2006 Tissue Analyses

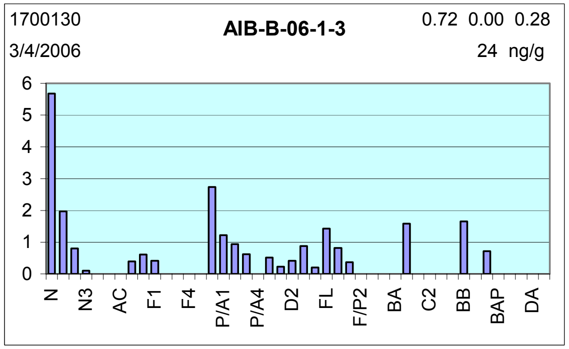


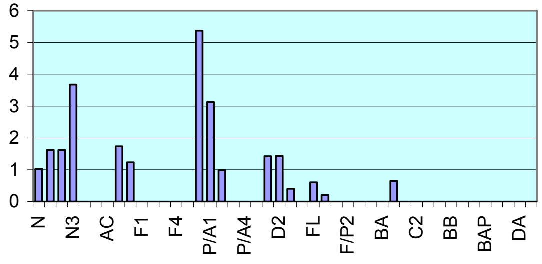






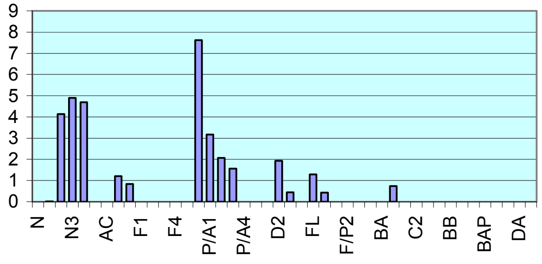






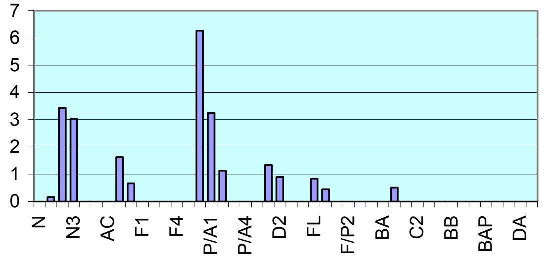
1601731 **AMT-B-05-2-1** 0.00 0.39 0.61

7/26/2005 25 ng/g



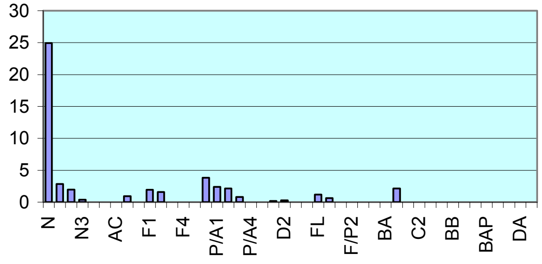
1601732 **AMT-B-05-2-2** 0.00 0.43 0.57

7/26/2005 35 ng/g



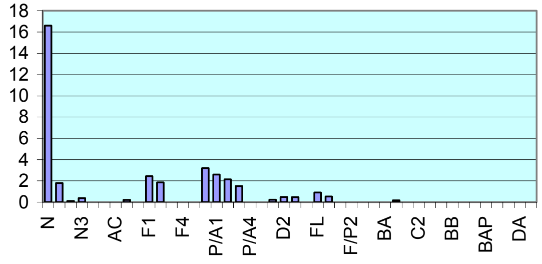
1601733 **AMT-B-05-2-3** 0.00 0.33 0.67

7/26/2005 24 ng/g



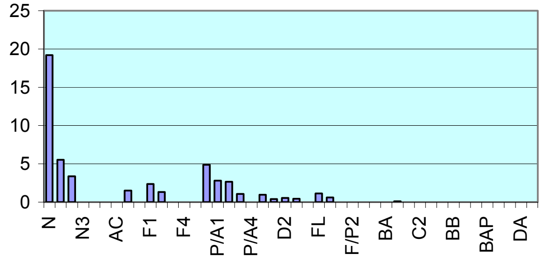
1602104 **AMT-B-05-3-1** 0.88 0.03 0.08

10/2/2005 48 ng/g



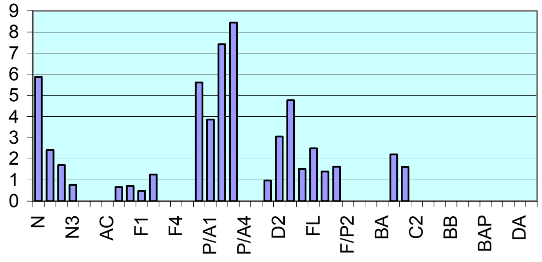
1602105 **AMT-B-05-3-2** 0.00 0.65 0.35

10/2/2005 36 ng/g



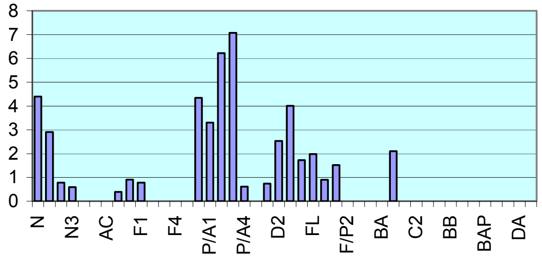
1602106 **AMT-B-05-3-3** 0.93 0.03 0.04

10/2/2005 49 ng/g



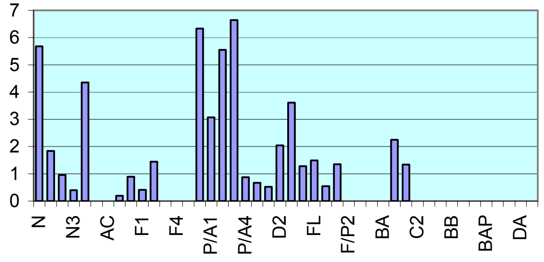
1700123 **AMT-B-06-1-1** 0.21 0.72 0.07

3/3/2006 59 ng/g



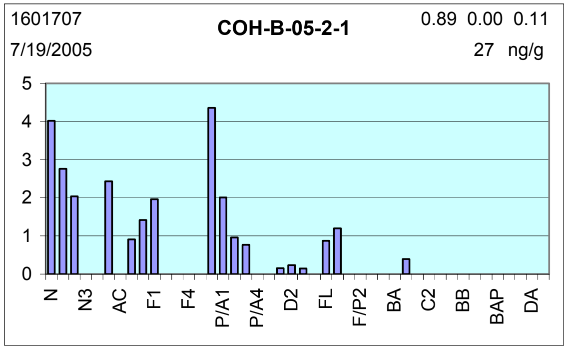
1700124 **AMT-B-06-1-2** 0.23 0.73 0.05

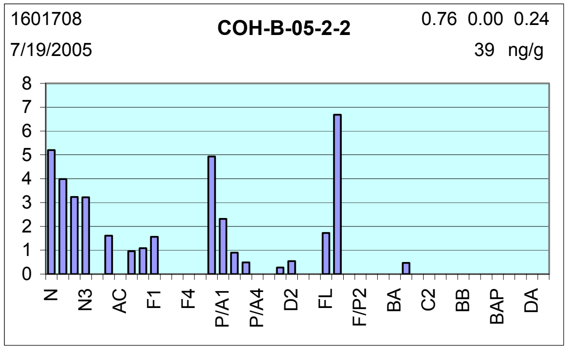
3/3/2006 48 ng/g

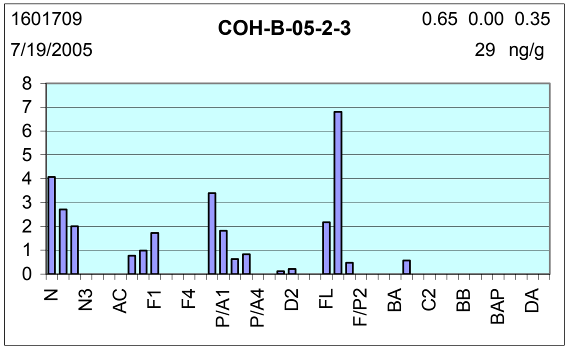


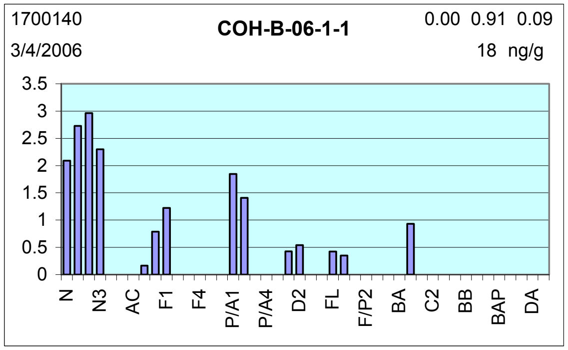
1700125 **AMT-B-06-1-3** 0.28 0.65 0.07

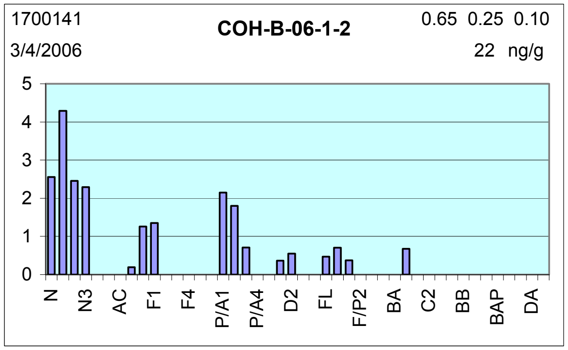
3/3/2006 54 ng/g

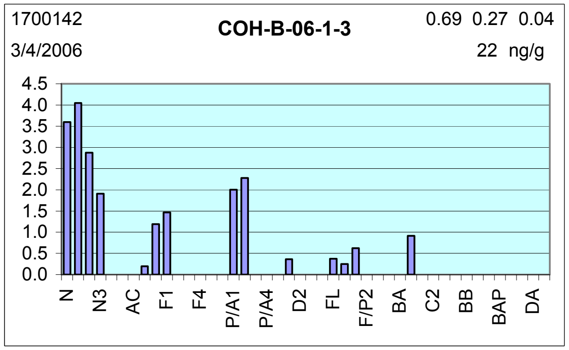

1601707 **COH-B-05-2-1** 0.89 0.00 0.11
7/19/2005 27 ng/g

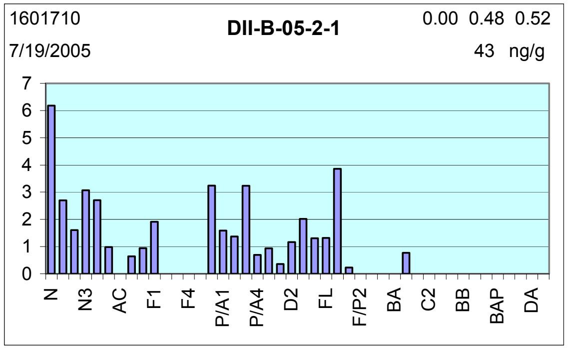

1601708 **COH-B-05-2-2** 0.76 0.00 0.24
7/19/2005 39 ng/g

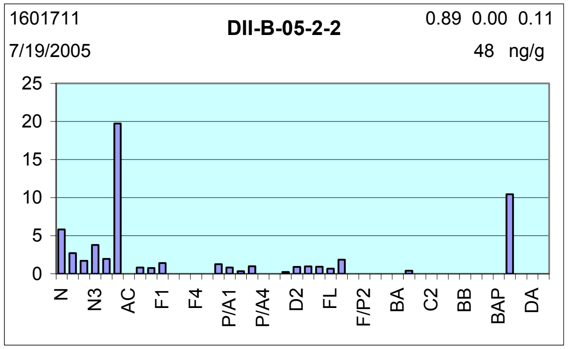

1601709 **COH-B-05-2-3** 0.65 0.00 0.35
7/19/2005 29 ng/g

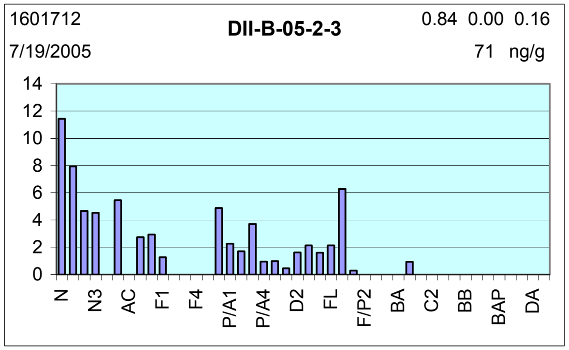

1700140 **COH-B-06-1-1** 0.00 0.91 0.09
3/4/2006 18 ng/g

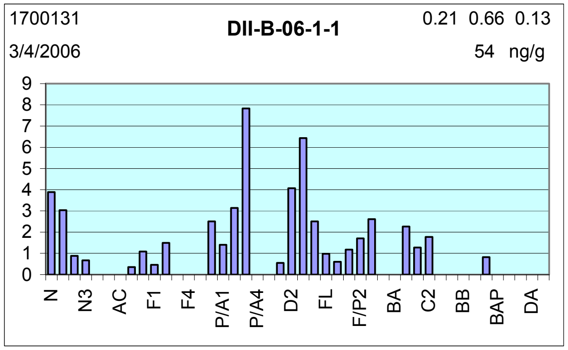

1700141 **COH-B-06-1-2** 0.65 0.25 0.10
3/4/2006 22 ng/g

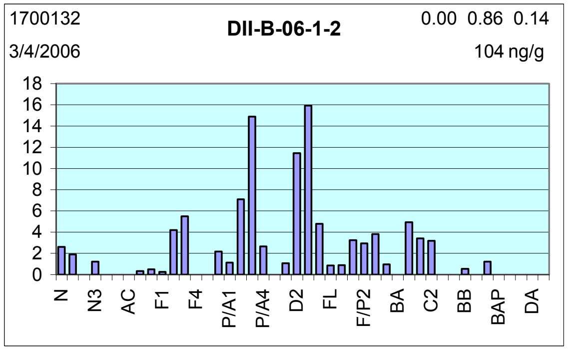

1700142 **COH-B-06-1-3** 0.69 0.27 0.04
3/4/2006 22 ng/g

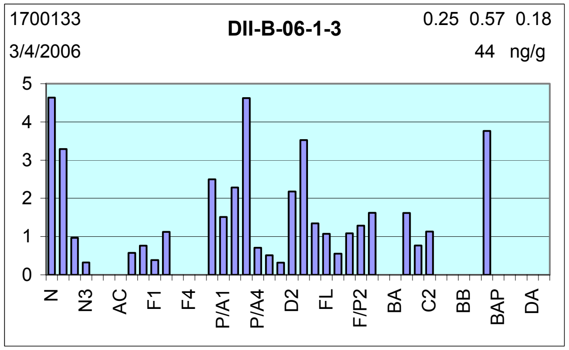

1601710
DII-B-05-2-1
0.00 0.48 0.52
7/19/2005
43 ng/g
7
6
5
4
3
2
1
0
N
N3
AC
F1
F4
P/A1
P/A4
D2
FL
F/P2
BA
C2
BB
BAP
DA

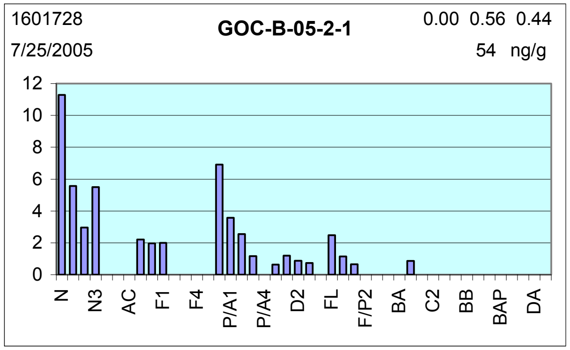

1601711
DII-B-05-2-2
0.89 0.00 0.11
7/19/2005
48 ng/g
25
20
15
10
5
0
N
N3
AC
F1
F4
P/A1
P/A4
D2
FL
F/P2
BA
C2
BB
BAP
DA

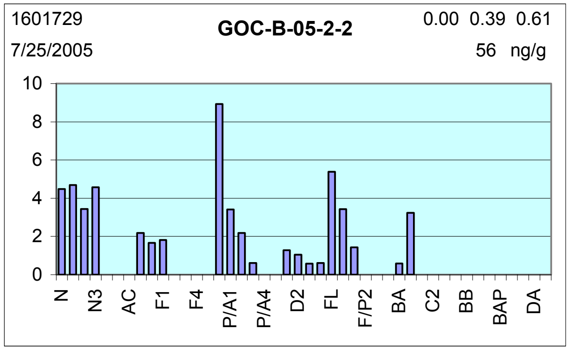

1601712
DII-B-05-2-3
0.84 0.00 0.16
7/19/2005
71 ng/g
14
12
10
8
6
4
2
0
N
N3
AC
F1
F4
P/A1
P/A4
D2
FL
F/P2
BA
C2
BB
BAP
DA

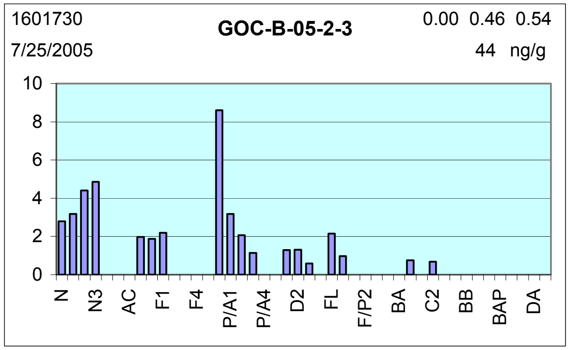

1700131
DII-B-06-1-1
0.21 0.66 0.13
3/4/2006
54 ng/g
9
8
7
6
5
4
3
2
1
0
N
N3
AC
F1
F4
P/A1
P/A4
D2
FL
F/P2
BA
C2
BB
BAP
DA

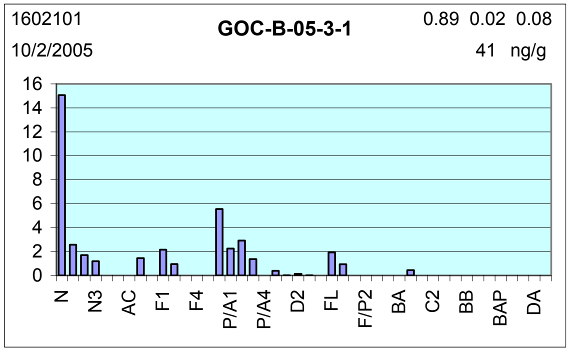

1700132
DII-B-06-1-2
0.00 0.86 0.14
3/4/2006
104 ng/g
18
16
14
12
10
8
6
4
2
0
N
N3
AC
F1
F4
P/A1
P/A4
D2
FL
F/P2
BA
C2
BB
BAP
DA

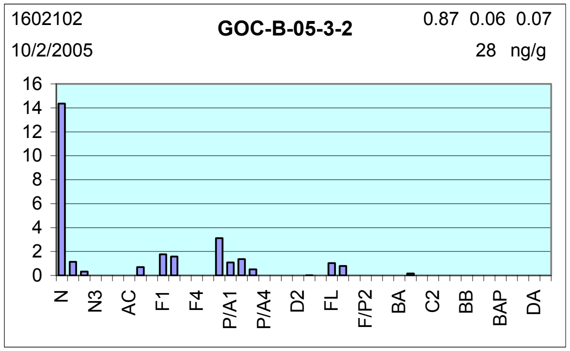

1700133
DII-B-06-1-3
0.25 0.57 0.18
3/4/2006
44 ng/g
5
4
3
2
1
0
N
N3
AC
F1
F4
P/A1
P/A4
D2
FL
F/P2
BA
C2
BB
BAP
DA

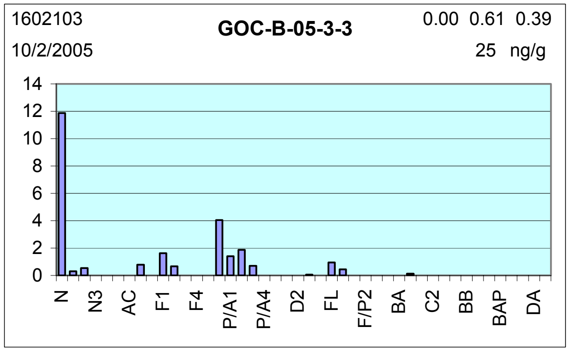

1601728
7/25/2005
GOC-B-05-2-1
0.00 0.56 0.44
54 ng/g
12
10
8
6
4
2
0
N
N3
AC
F1
F4
P/A1
P/A4
D2
FL
F/P2
BA
C2
BB
BAP
DA

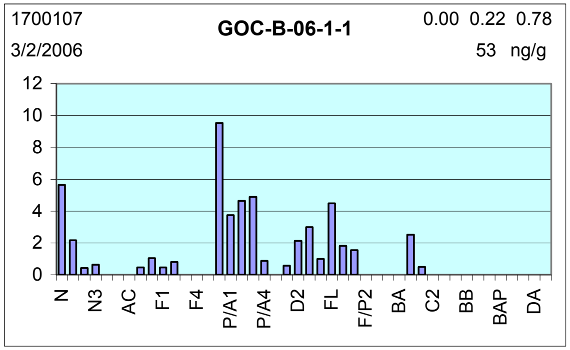

1601729
7/25/2005
GOC-B-05-2-2
0.00 0.39 0.61
56 ng/g
10
8
6
4
2
0
N
N3
AC
F1
F4
P/A1
P/A4
D2
FL
F/P2
BA
C2
BB
BAP
DA

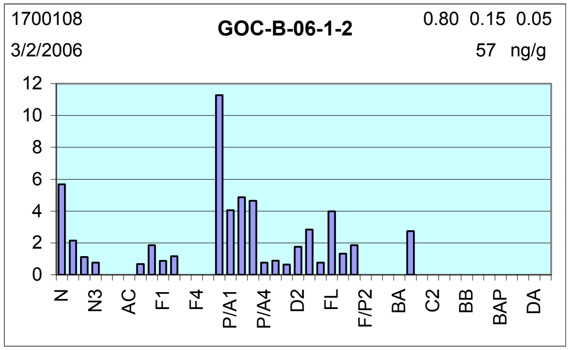

1601730
7/25/2005
GOC-B-05-2-3
0.00 0.46 0.54
44 ng/g
10
8
6
4
2
0
N
N3
AC
F1
F4
P/A1
P/A4
D2
FL
F/P2
BA
C2
BB
BAP
DA

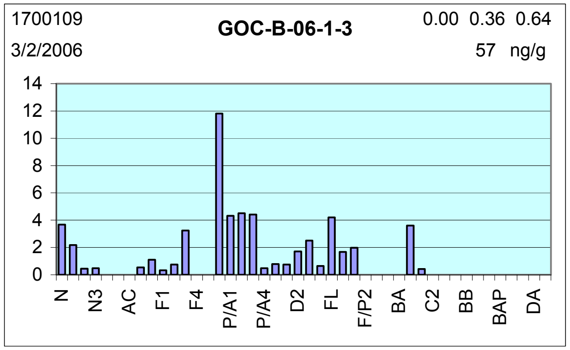

1602101
10/2/2005
GOC-B-05-3-1
0.89 0.02 0.08
41 ng/g
16
14
12
10
8
6
4
2
0
N
N3
AC
F1
F4
P/A1
P/A4
D2
FL
F/P2
BA
C2
BB
BAP
DA

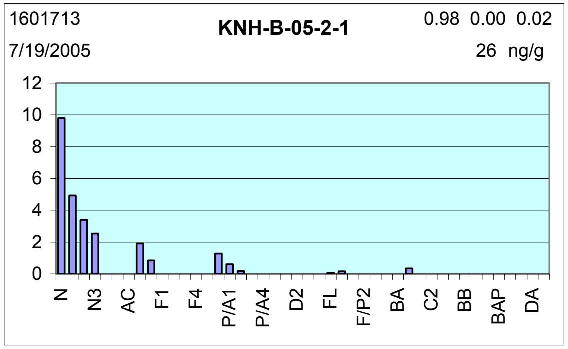

1602102
10/2/2005
GOC-B-05-3-2
0.87 0.06 0.07
28 ng/g
16
14
12
10
8
6
4
2
0
N
N3
AC
F1
F4
P/A1
P/A4
D2
FL
F/P2
BA
C2
BB
BAP
DA

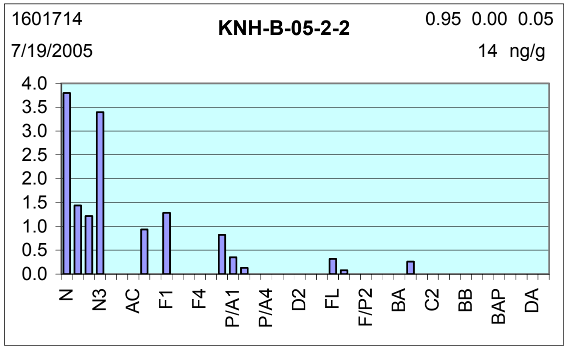

1602103
10/2/2005
GOC-B-05-3-3
0.00 0.61 0.39
25 ng/g
14
12
10
8
6
4
2
0
N
N3
AC
F1
F4
P/A1
P/A4
D2
FL
F/P2
BA
C2
BB
BAP
DA

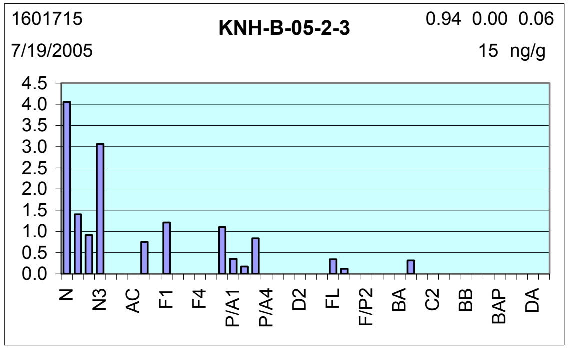

1700107
3/2/2006
GOC-B-06-1-1
0.00 0.22 0.78
53 ng/g
12
10
8
6
4
2
0
N
N3
AC
F1
F4
P/A1
P/A4
D2
FL
F/P2
BA
C2
BB
BAP
DA

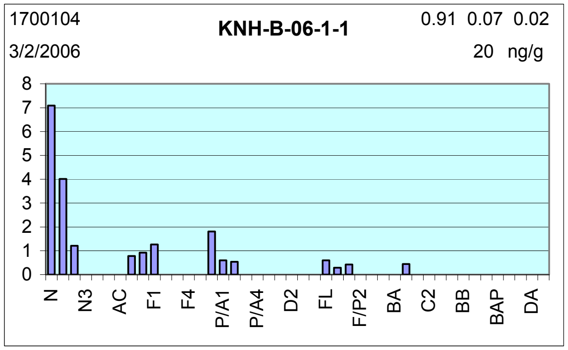

1700108
3/2/2006
GOC-B-06-1-2
0.80 0.15 0.05
57 ng/g
12
10
8
6
4
2
0
N
N3
AC
F1
F4
P/A1
P/A4
D2
FL
F/P2
BA
C2
BB
BAP
DA

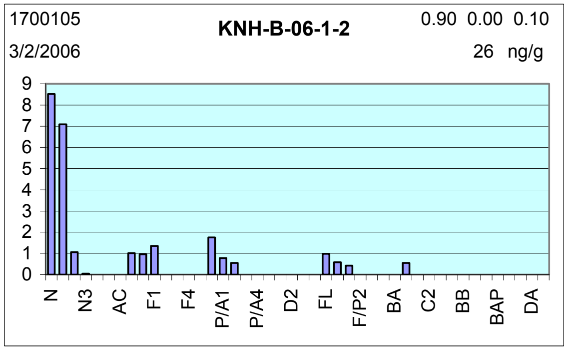

1700109
3/2/2006
GOC-B-06-1-3
0.00 0.36 0.64
57 ng/g
14
12
10
8
6
4
2
0
N
N3
AC
F1
F4
P/A1
P/A4
D2
FL
F/P2
BA
C2
BB
BAP
DA

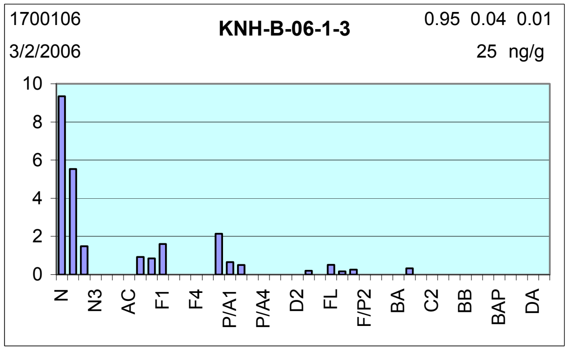

1601713
KNH-B-05-2-1
0.98 0.00 0.02
7/19/2005
26 ng/g
12
10
8
6
4
2
0
N
N3
AC
F1
F4
P/A1
P/A4
D2
FL
F/P2
BA
C2
BB
BAP
DA

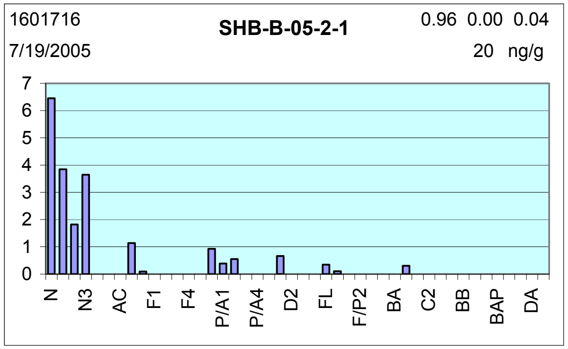

1601714
KNH-B-05-2-2
0.95 0.00 0.05
7/19/2005
14 ng/g
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
N
N3
AC
F1
F4
P/A1
P/A4
D2
FL
F/P2
BA
C2
BB
BAP
DA

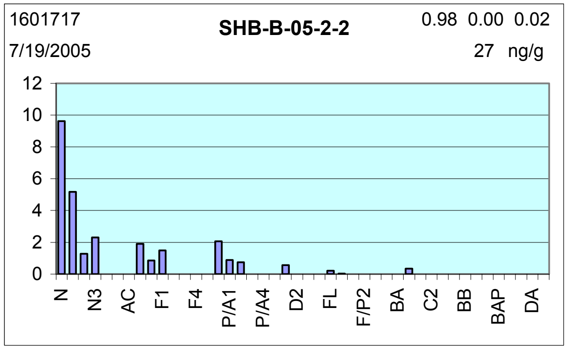

1601715
KNH-B-05-2-3
0.94 0.00 0.06
7/19/2005
15 ng/g
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
N
N3
AC
F1
F4
P/A1
P/A4
D2
FL
F/P2
BA
C2
BB
BAP
DA

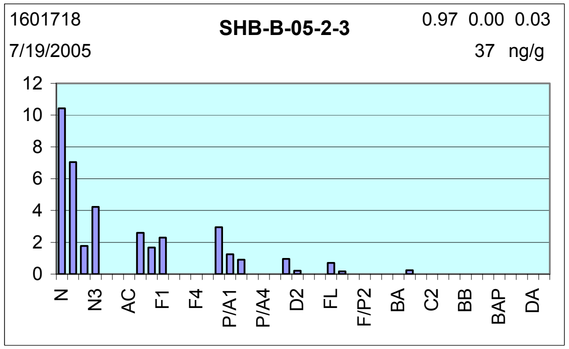

1700104
KNH-B-06-1-1
0.91 0.07 0.02
3/2/2006
20 ng/g
8
7
6
5
4
3
2
1
0
N
N3
AC
F1
F4
P/A1
P/A4
D2
FL
F/P2
BA
C2
BB
BAP
DA

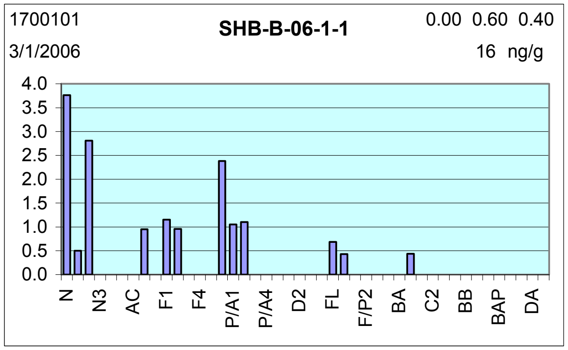

1700105
KNH-B-06-1-2
0.90 0.00 0.10
3/2/2006
26 ng/g
9
8
7
6
5
4
3
2
1
0
N
N3
AC
F1
F4
P/A1
P/A4
D2
FL
F/P2
BA
C2
BB
BAP
DA

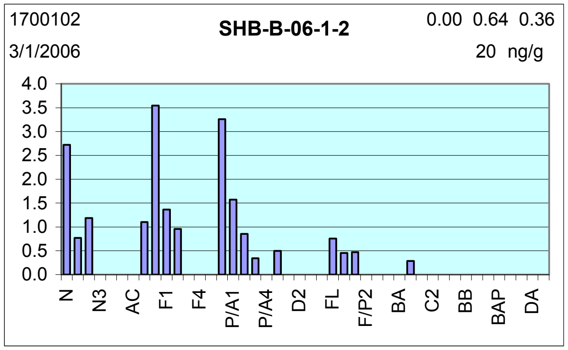

1700106
KNH-B-06-1-3
0.95 0.04 0.01
3/2/2006
25 ng/g
10
8
6
4
2
0
N
N3
AC
F1
F4
P/A1
P/A4
D2
FL
F/P2
BA
C2
BB
BAP
DA

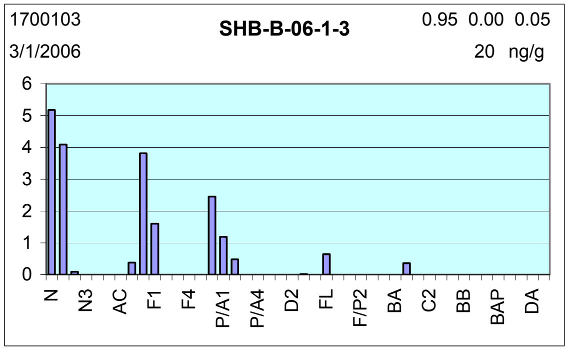

1601716
SHB-B-05-2-1
0.96 0.00 0.04
7/19/2005
20 ng/g
0
1
2
3
4
5
6
7
N
N3
AC
F1
F4
P/A1
P/A4
D2
FL
F/P2
BA
C2
BB
BAP
DA

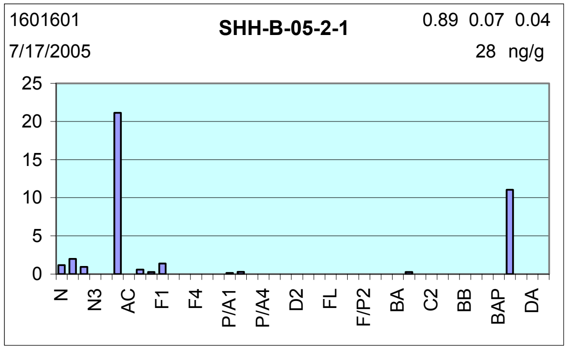

1601717
SHB-B-05-2-2
0.98 0.00 0.02
7/19/2005
27 ng/g
0
2
4
6
8
10
12
N
N3
AC
F1
F4
P/A1
P/A4
D2
FL
F/P2
BA
C2
BB
BAP
DA

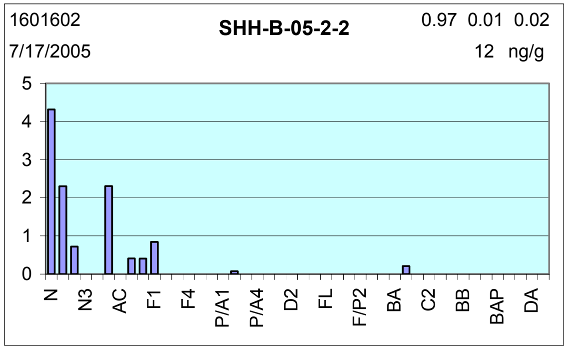

1601718
SHB-B-05-2-3
0.97 0.00 0.03
7/19/2005
37 ng/g
0
2
4
6
8
10
12
N
N3
AC
F1
F4
P/A1
P/A4
D2
FL
F/P2
BA
C2
BB
BAP
DA

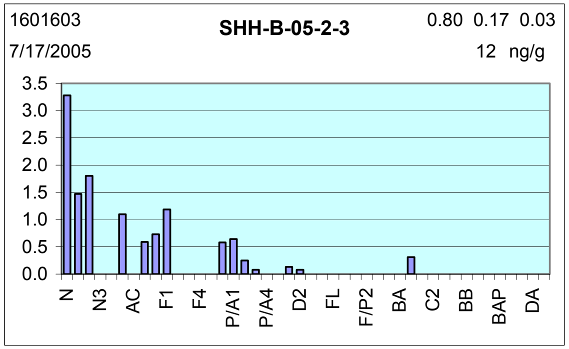

1700101
SHB-B-06-1-1
0.00 0.60 0.40
3/1/2006
16 ng/g
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
N
N3
AC
F1
F4
P/A1
P/A4
D2
FL
F/P2
BA
C2
BB
BAP
DA

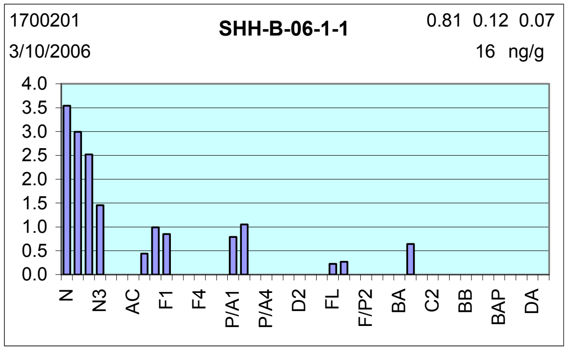

1700102
SHB-B-06-1-2
0.00 0.64 0.36
3/1/2006
20 ng/g
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
N
N3
AC
F1
F4
P/A1
P/A4
D2
FL
F/P2
BA
C2
BB
BAP
DA

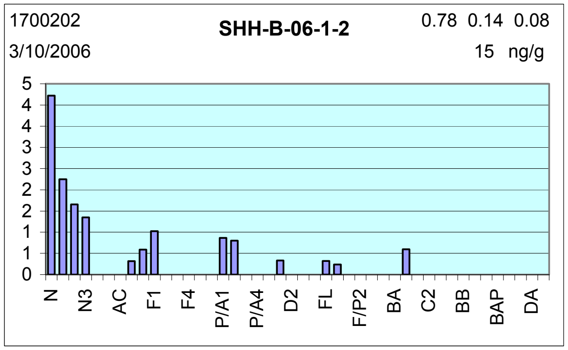

1700103
SHB-B-06-1-3
0.95 0.00 0.05
3/1/2006
20 ng/g
0
1
2
3
4
5
6
N
N3
AC
F1
F4
P/A1
P/A4
D2
FL
F/P2
BA
C2
BB
BAP
DA

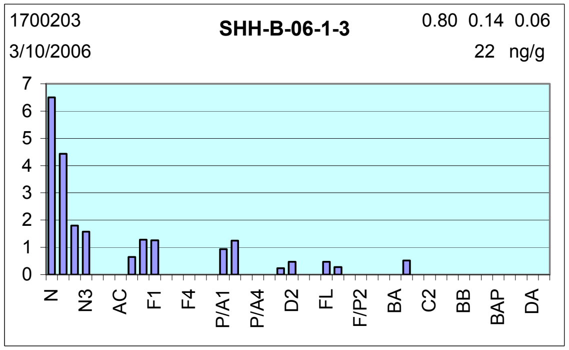

1601601
SHH-B-05-2-1
0.89 0.07 0.04
7/17/2005
28 ng/g
25
20
15
10
5
0
N
N3
AC
F1
F4
P/A1
P/A4
D2
FL
F/P2
BA
C2
BB
BAP
DA

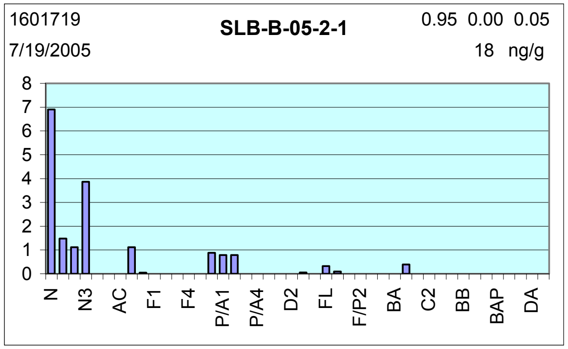

1601602
SHH-B-05-2-2
0.97 0.01 0.02
7/17/2005
12 ng/g
5
4
3
2
1
0
N
N3
AC
F1
F4
P/A1
P/A4
D2
FL
F/P2
BA
C2
BB
BAP
DA

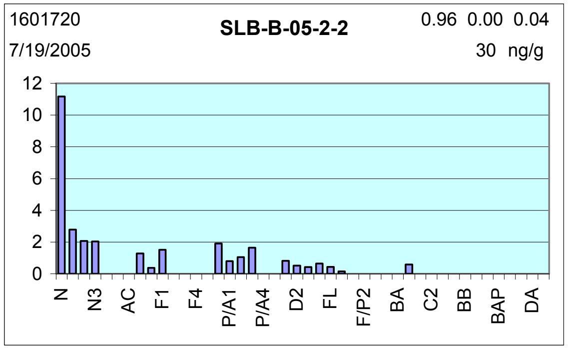

1601603
SHH-B-05-2-3
0.80 0.17 0.03
7/17/2005
12 ng/g
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
N
N3
AC
F1
F4
P/A1
P/A4
D2
FL
F/P2
BA
C2
BB
BAP
DA

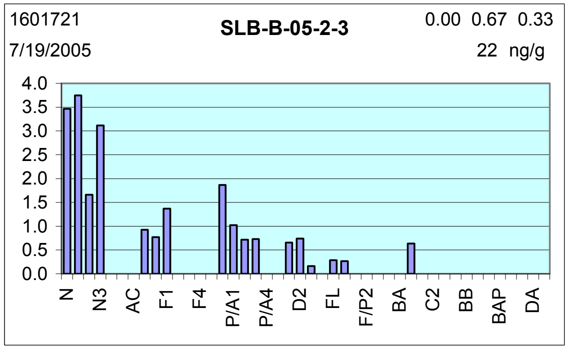

1700201
SHH-B-06-1-1
0.81 0.12 0.07
3/10/2006
16 ng/g
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
N
N3
AC
F1
F4
P/A1
P/A4
D2
FL
F/P2
BA
C2
BB
BAP
DA

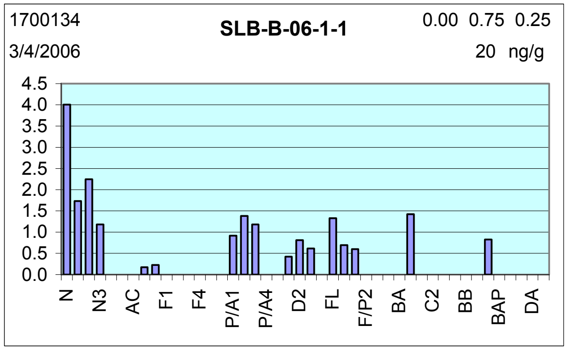

1700202
SHH-B-06-1-2
0.78 0.14 0.08
3/10/2006
15 ng/g
5
4
4
3
3
2
2
1
1
0
N
N3
AC
F1
F4
P/A1
P/A4
D2
FL
F/P2
BA
C2
BB
BAP
DA

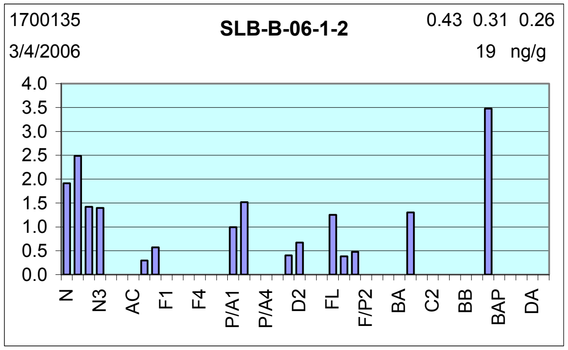

1700203
SHH-B-06-1-3
0.80 0.14 0.06
3/10/2006
22 ng/g
7
6
5
4
3
2
1
0
N
N3
AC
F1
F4
P/A1
P/A4
D2
FL
F/P2
BA
C2
BB
BAP
DA

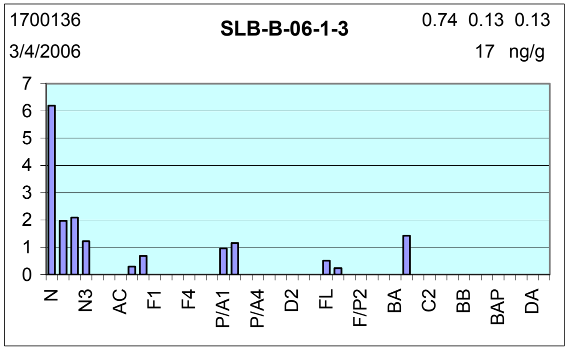

1601719
SLB-B-05-2-1
0.95 0.00 0.05
7/19/2005
18 ng/g
8
7
6
5
4
3
2
1
0
N
N3
AC
F1
F4
P/A1
P/A4
D2
FL
F/P2
BA
C2
BB
BAP
DA

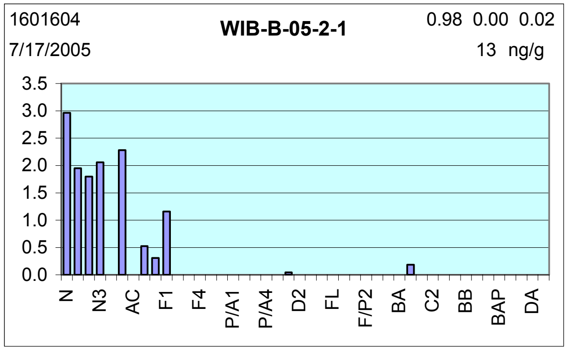

1601720
SLB-B-05-2-2
0.96 0.00 0.04
7/19/2005
30 ng/g
12
10
8
6
4
2
0
N
N3
AC
F1
F4
P/A1
P/A4
D2
FL
F/P2
BA
C2
BB
BAP
DA

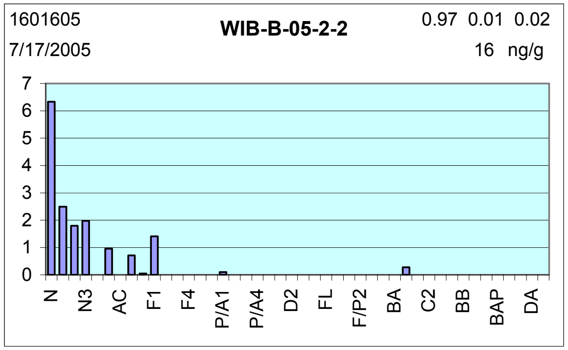

1601721
SLB-B-05-2-3
0.00 0.67 0.33
7/19/2005
22 ng/g
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
N
N3
AC
F1
F4
P/A1
P/A4
D2
FL
F/P2
BA
C2
BB
BAP
DA

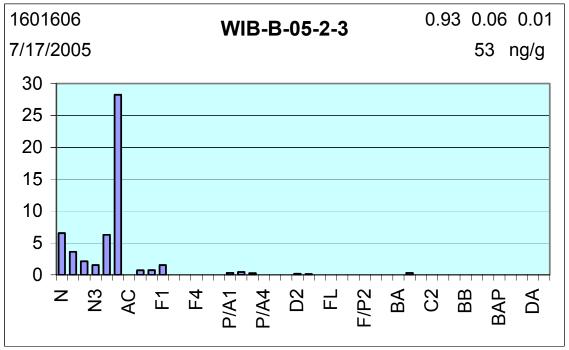

1700134
SLB-B-06-1-1
0.00 0.75 0.25
3/4/2006
20 ng/g
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
N
N3
AC
F1
F4
P/A1
P/A4
D2
FL
F/P2
BA
C2
BB
BAP
DA

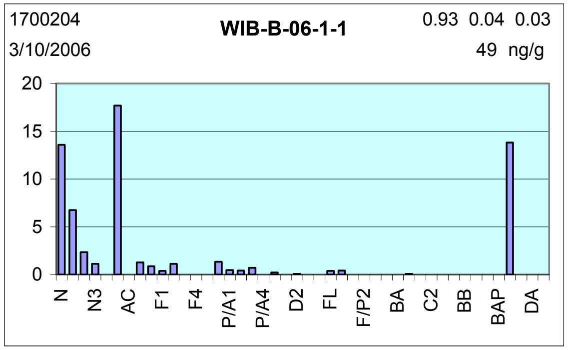

1700135
SLB-B-06-1-2
0.43 0.31 0.26
3/4/2006
19 ng/g
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
N
N3
AC
F1
F4
P/A1
P/A4
D2
FL
F/P2
BA
C2
BB
BAP
DA

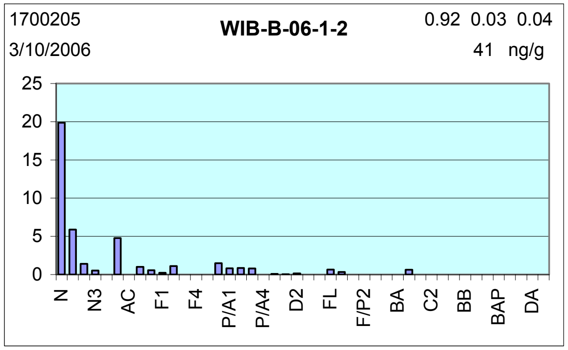

1700136
SLB-B-06-1-3
0.74 0.13 0.13
3/4/2006
17 ng/g
7
6
5
4
3
2
1
0
N
N3
AC
F1
F4
P/A1
P/A4
D2
FL
F/P2
BA
C2
BB
BAP
DA

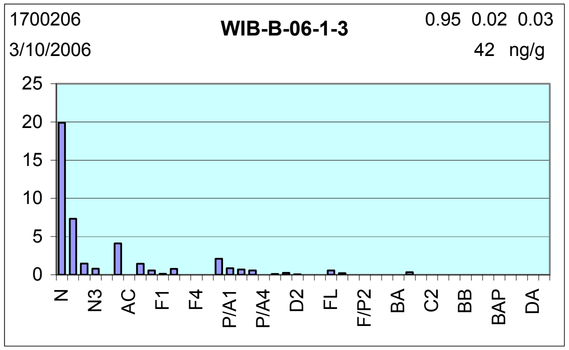

1601604
WIB-B-05-2-1
0.98 0.00 0.02
7/17/2005
13 ng/g
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
N
N3
AC
F1
F4
P/A1
P/A4
D2
FL
F/P2
BA
C2
BB
BAP
DA

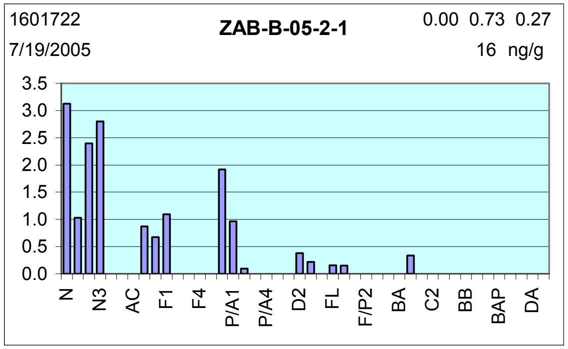

1601605
WIB-B-05-2-2
0.97 0.01 0.02
7/17/2005
16 ng/g
7
6
5
4
3
2
1
0
N
N3
AC
F1
F4
P/A1
P/A4
D2
FL
F/P2
BA
C2
BB
BAP
DA

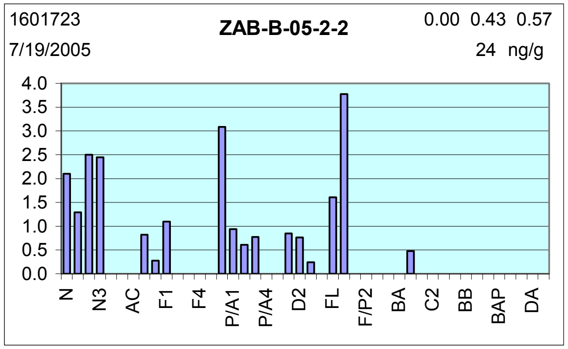

1601606
WIB-B-05-2-3
0.93 0.06 0.01
7/17/2005
53 ng/g
30
25
20
15
10
5
0
N
N3
AC
F1
F4
P/A1
P/A4
D2
FL
F/P2
BA
C2
BB
BAP
DA

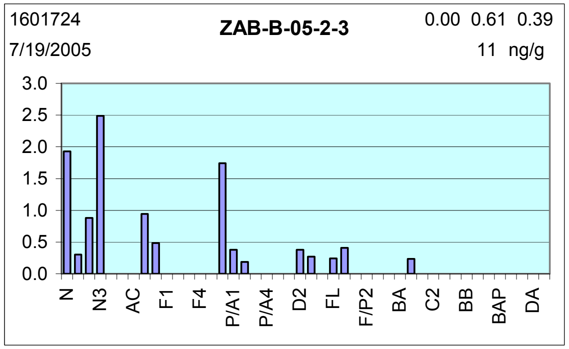

1700204
WIB-B-06-1-1
0.93 0.04 0.03
3/10/2006
49 ng/g
20
15
10
5
0
N
N3
AC
F1
F4
P/A1
P/A4
D2
FL
F/P2
BA
C2
BB
BAP
DA

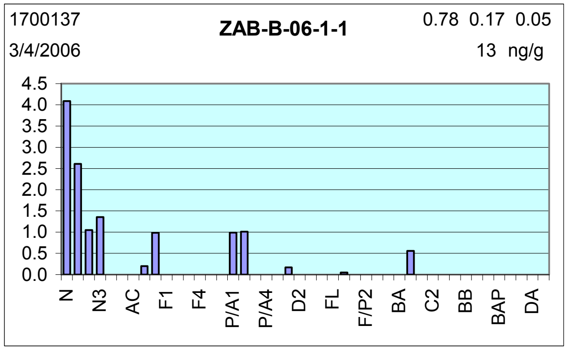

1700205
WIB-B-06-1-2
0.92 0.03 0.04
3/10/2006
41 ng/g
25
20
15
10
5
0
N
N3
AC
F1
F4
P/A1
P/A4
D2
FL
F/P2
BA
C2
BB
BAP
DA

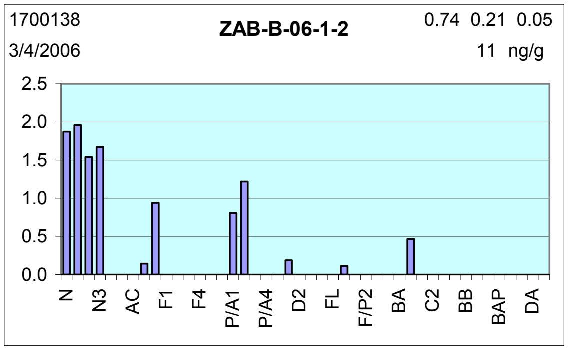

1700206
WIB-B-06-1-3
0.95 0.02 0.03
3/10/2006
42 ng/g
25
20
15
10
5
0
N
N3
AC
F1
F4
P/A1
P/A4
D2
FL
F/P2
BA
C2
BB
BAP
DA

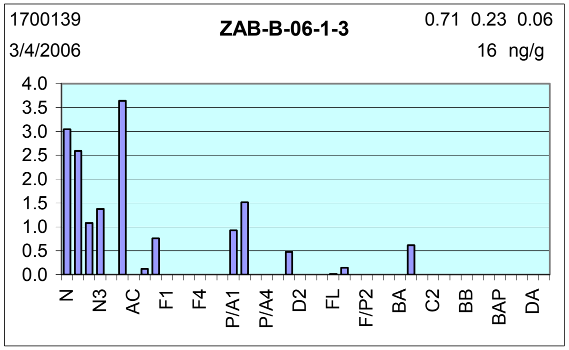

1601722
ZAB-B-05-2-1
0.00 0.73 0.27
7/19/2005
16 ng/g
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
N
N3
AC
F1
F4
P/A1
P/A4
D2
FL
F/P2
BA
C2
BB
BAP
DA


1601723
ZAB-B-05-2-2
0.00 0.43 0.57
7/19/2005
24 ng/g
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
N
N3
AC
F1
F4
P/A1
P/A4
D2
FL
F/P2
BA
C2
BB
BAP
DA


1601724
ZAB-B-05-2-3
0.00 0.61 0.39
7/19/2005
11 ng/g
3.0
2.5
2.0
1.5
1.0
0.5
0.0
N
N3
AC
F1
F4
P/A1
P/A4
D2
FL
F/P2
BA
C2
BB
BAP
DA

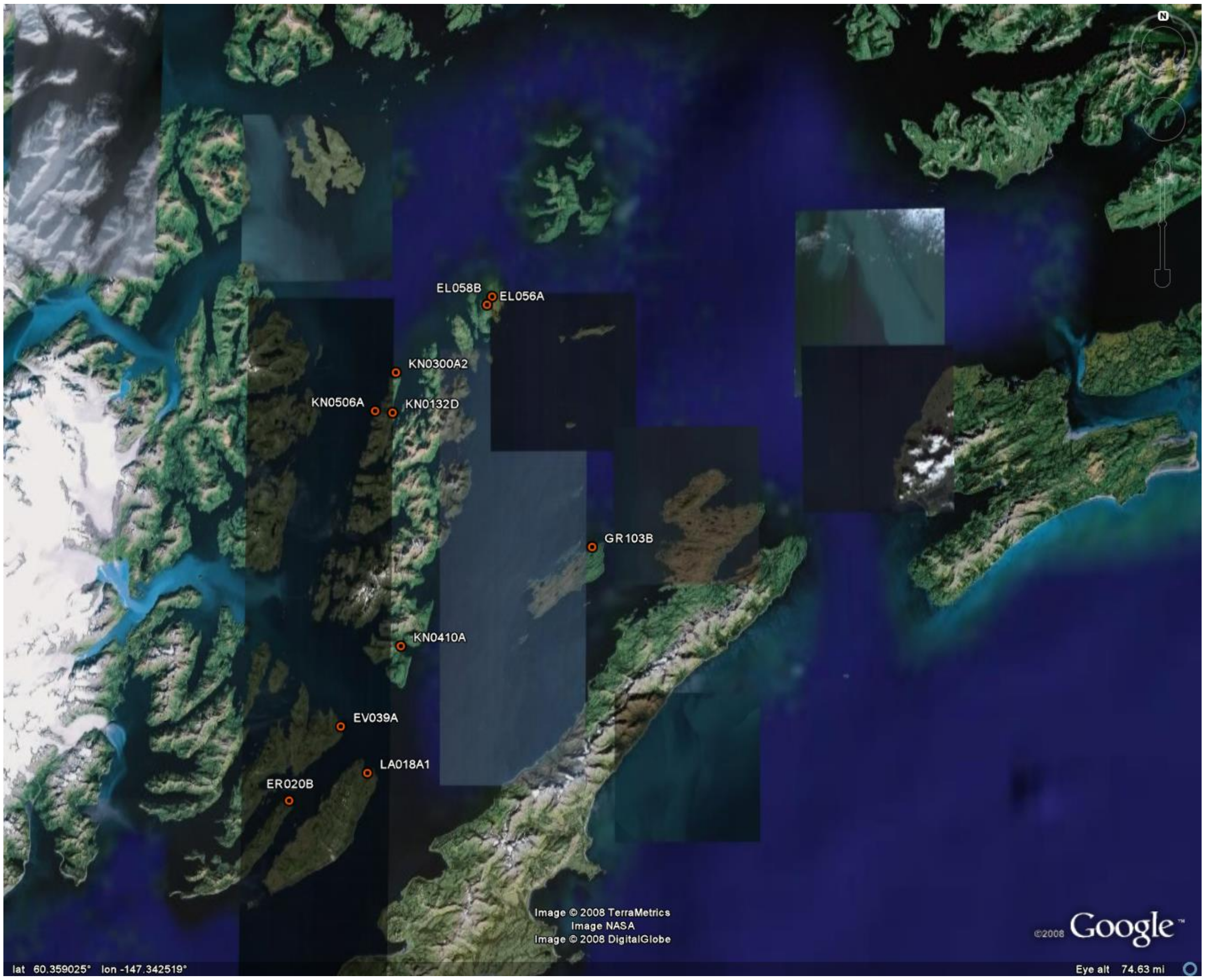

1700137
ZAB-B-06-1-1
0.78 0.17 0.05
3/4/2006
13 ng/g
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
N
N3
AC
F1
F4
P/A1
P/A4
D2
FL
F/P2
BA
C2
BB
BAP
DA

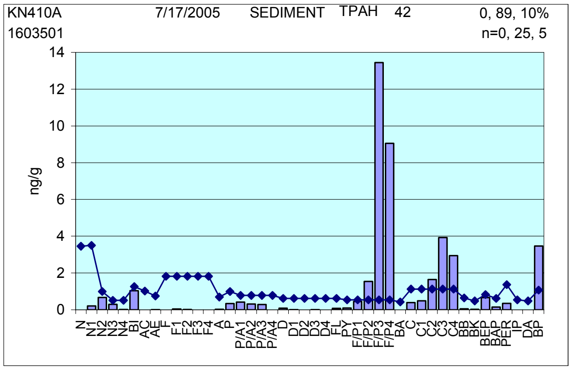

1700138
ZAB-B-06-1-2
0.74 0.21 0.05
3/4/2006
11 ng/g
2.5
2.0
1.5
1.0
0.5
0.0
N
N3
AC
F1
F4
P/A1
P/A4
D2
FL
F/P2
BA
C2
BB
BAP
DA


1700139
ZAB-B-06-1-3
0.71 0.23 0.06
3/4/2006
16 ng/g
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
N
N3
AC
F1
F4
P/A1
P/A4
D2
FL
F/P2
BA
C2
BB
BAP
DA

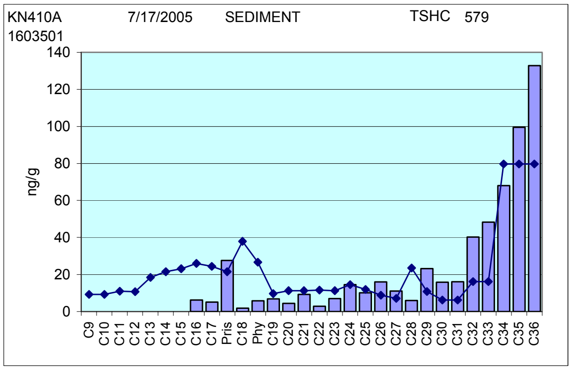
Appendix E – Oiled Sediment and Mussel Histogram Plots from the 2005 GEM Random Pit Sampling Program

The following pages contain PAH and SHC results for samples collected under the 2005 extended LTEMP program assessing the extent of remaining EVOS oil. The sediment samples comprise visibly oiled sediments from stratified random pits. The tissue samples were from nearby mussels, if available. The chain-of-custody images show sample locations. These data will be interpreted in a separate EVOS study report by Dr. Jeffrey Short.

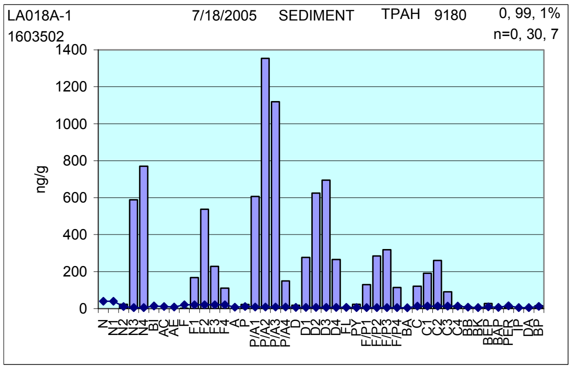




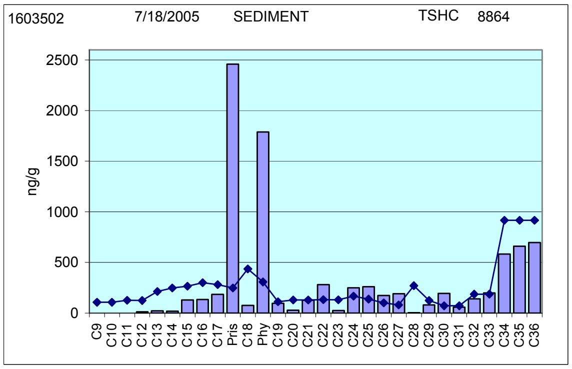
KN410A 7/17/2005 SEDIMENT TPAH 42 0, 89, 10%
1603501 n=0, 25, 5



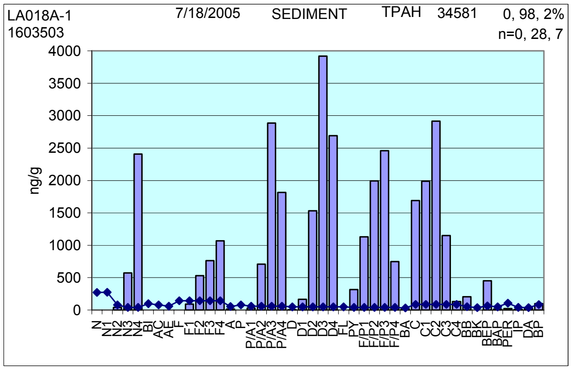
KN410A 7/17/2005 SEDIMENT TSHC 579
1603501



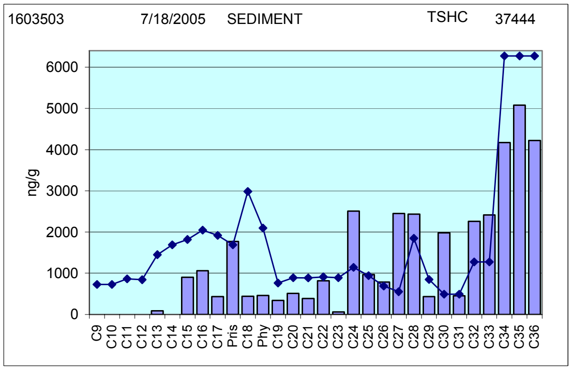
LA018A-1 7/18/2005 SEDIMENT TPAH 9180 0, 99, 1%
1603502 n=0, 30, 7



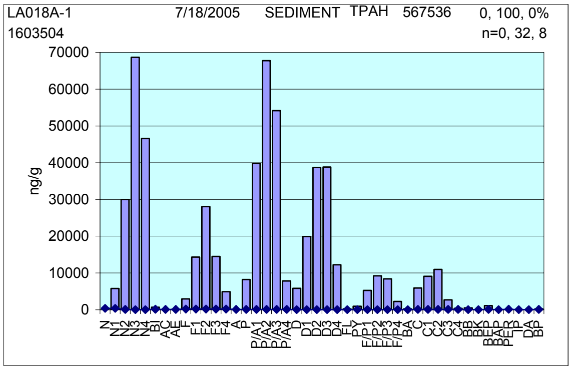
1603502 7/18/2005 SEDIMENT TSHC 8864

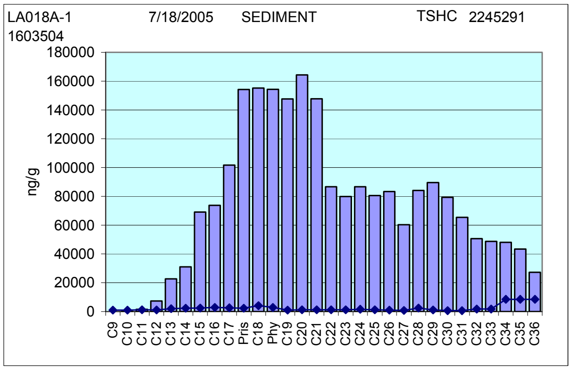


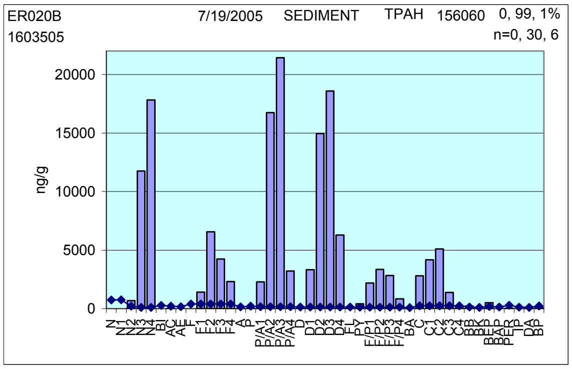
LA018A-1 7/18/2005 SEDIMENT TPAH 34581 0, 98, 2%
1603503 n=0, 28, 7

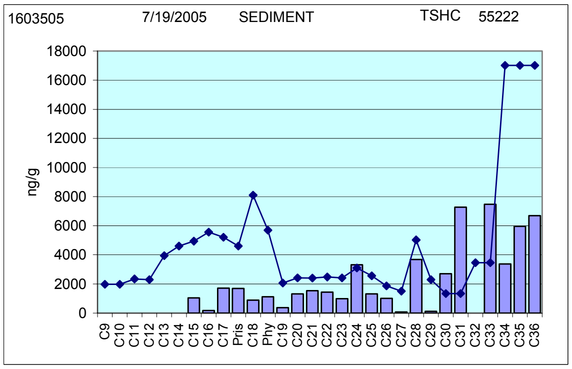


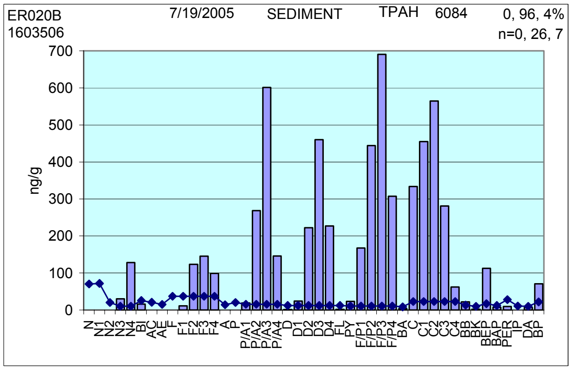
1603503 7/18/2005 SEDIMENT TSHC 37444

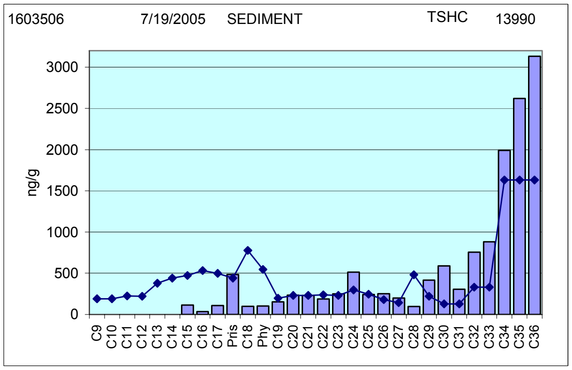

LA018A-1
7/18/2005
SEDIMENT
TPAH 567536
0, 100, 0%
1603504
n=0, 32, 8
ng/g
0
10000
20000
30000
40000
50000
60000
70000
N N1 N2 N3 N4 BI AC AE F F1 F2 F3 F4 A P P/A1 P/A2 P/A3 P/A4 D D1 D2 D3 D4 FL PY F/P1 F/P2 F/P3 F/P4 BA C C1 C2 C3 C4 BB BK BEP BAP PER IP DA BP

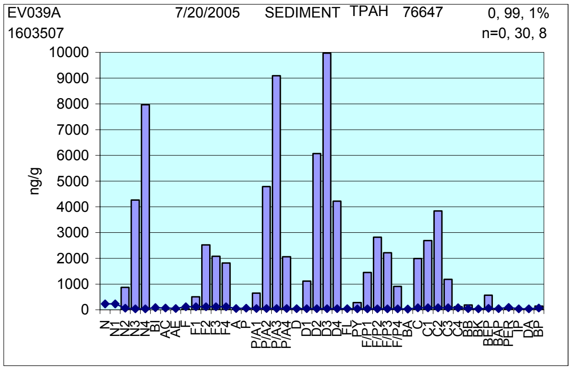

LA018A-1
7/18/2005
SEDIMENT
TSHC 2245291
1603504
ng/g
0
20000
40000
60000
80000
100000
120000
140000
160000
180000
C9 C10 C11 C12 C13 C14 C15 C16 C17 Pris C18 Phy C19 C20 C21 C22 C23 C24 C25 C26 C27 C28 C29 C30 C31 C32 C33 C34 C35 C36

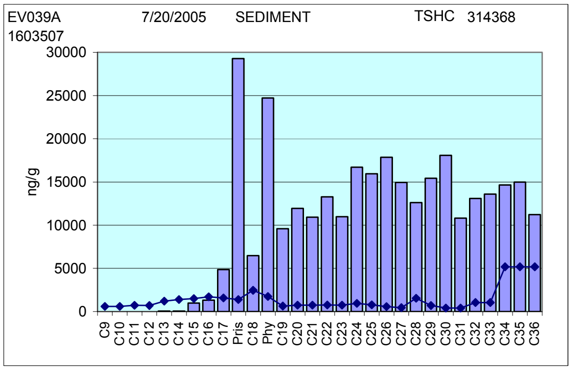

ER020B
7/19/2005
SEDIMENT
TPAH 156060
0, 99, 1%
1603505
n=0, 30, 6
ng/g
0
5000
10000
15000
20000
N N1 N2 N3 N4 BI AC AE F F1 F2 F3 F4 A P P/A1 P/A2 P/A3 P/A4 D D1 D2 D3 D4 FL PY F/P1 F/P2 F/P3 F/P4 BA C C1 C2 C3 C4 BB BK BEP BAP PER IP DA BP

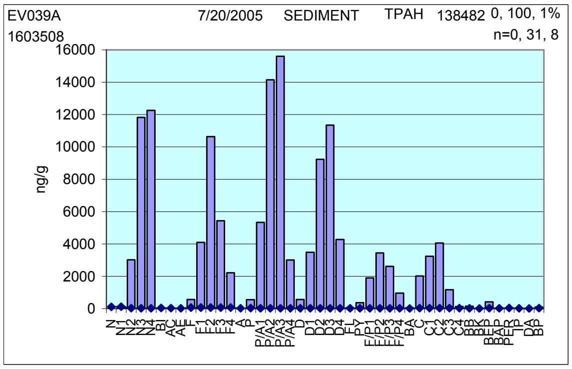

1603505
7/19/2005
SEDIMENT
TSHC 55222
ng/g
0
2000
4000
6000
8000
10000
12000
14000
16000
18000
C9 C10 C11 C12 C13 C14 C15 C16 C17 Pris C18 Phy C19 C20 C21 C22 C23 C24 C25 C26 C27 C28 C29 C30 C31 C32 C33 C34 C35 C36

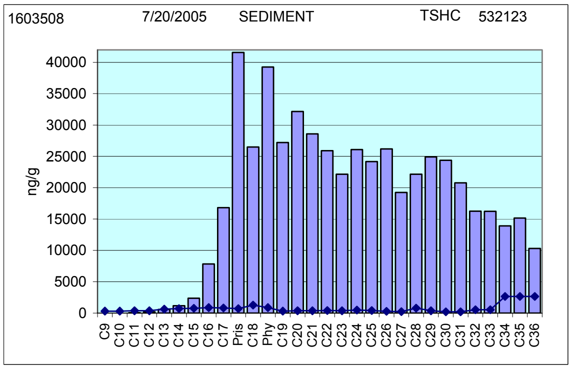

ER020B
7/19/2005
SEDIMENT
TPAH 6084
0, 96, 4%
1603506
n=0, 26, 7
ng/g
0
100
200
300
400
500
600
700
N N1 N2 N3 N4 BI AC AE F F1 F2 F3 F4 A P P/A1 P/A2 P/A3 P/A4 D D1 D2 D3 D4 FL PY F/P1 F/P2 F/P3 F/P4 BA C C1 C2 C3 C4 BB BK BEP BAP PER IP DA BP

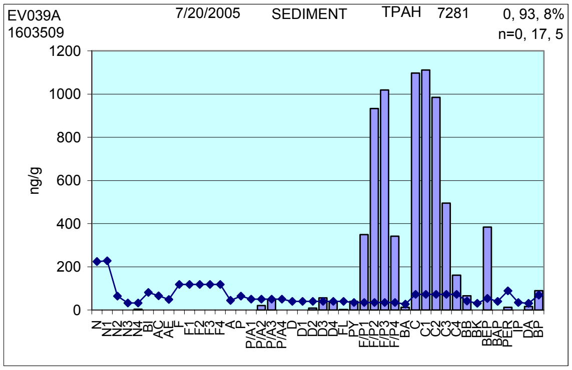

1603506
7/19/2005
SEDIMENT
TSHC 13990
ng/g
0
500
1000
1500
2000
2500
3000
C9 C10 C11 C12 C13 C14 C15 C16 C17 Pris C18 Phy C19 C20 C21 C22 C23 C24 C25 C26 C27 C28 C29 C30 C31 C32 C33 C34 C35 C36

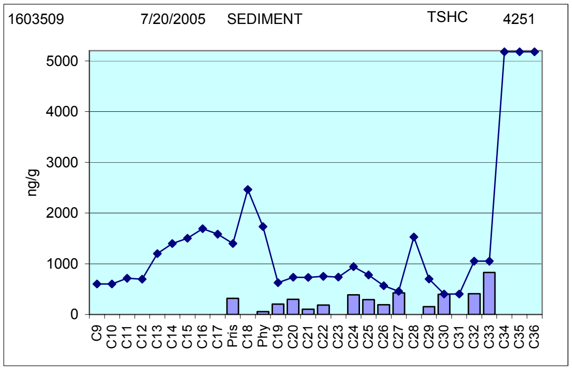

EV039A
7/20/2005
SEDIMENT
TPAH 76647
0, 99, 1%
1603507
n=0, 30, 8
ng/g
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
N N1 N2 N3 N4 BI AC AE F F1 F2 F3 F4 A P P/A1 P/A2 P/A3 P/A4 D D1 D2 D3 D4 FL PY F/P1 F/P2 F/P3 F/P4 BA C C1 C2 C3 C4 BB BK BEP BAP PER IP DA BP

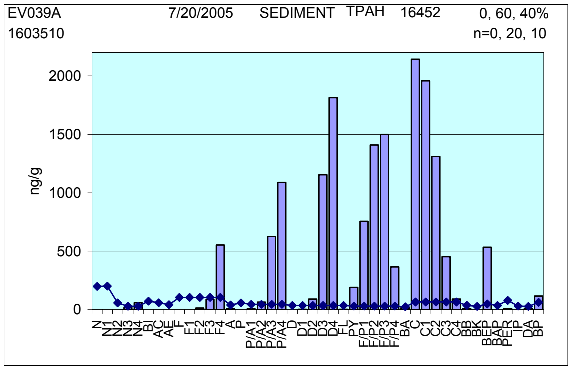

EV039A
7/20/2005
SEDIMENT
TSHC 314368
1603507
ng/g
30000
25000
20000
15000
10000
5000
0
C9 C10 C11 C12 C13 C14 C15 C16 C17 Pris C18 Phy C19 C20 C21 C22 C23 C24 C25 C26 C27 C28 C29 C30 C31 C32 C33 C34 C35 C36

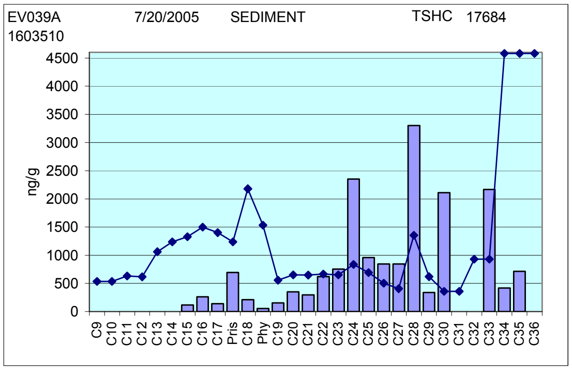

EV039A
7/20/2005
SEDIMENT
TPAH 138482
0, 100, 1%
1603508
n=0, 31, 8
ng/g
16000
14000
12000
10000
8000
6000
4000
2000
0
N N1 N2 N3 N4 BI AC AE F F1 F2 F3 F4 A P P/A1 P/A2 P/A3 P/A4 D D1 D2 D3 D4 FL PY F/P1 F/P2 F/P3 F/P4 BA C C1 C2 C3 C4 BB BK BEP BAP PER IP DA BP

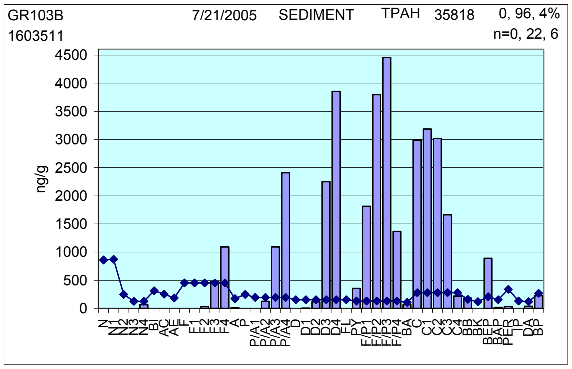

1603508
7/20/2005
SEDIMENT
TSHC 532123
ng/g
40000
35000
30000
25000
20000
15000
10000
5000
0
C9 C10 C11 C12 C13 C14 C15 C16 C17 Pris C18 Phy C19 C20 C21 C22 C23 C24 C25 C26 C27 C28 C29 C30 C31 C32 C33 C34 C35 C36

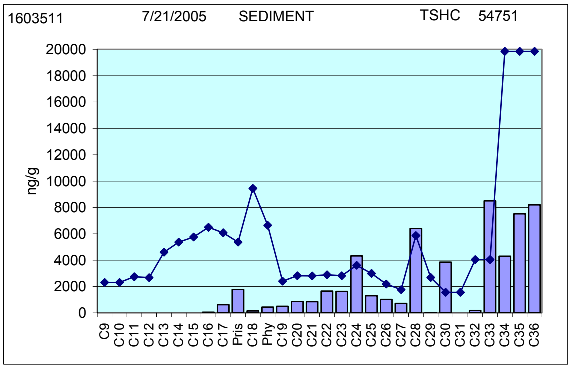

EV039A
7/20/2005
SEDIMENT
TPAH 7281
0, 93, 8%
1603509
n=0, 17, 5
ng/g
1200
1000
800
600
400
200
0
N N1 N2 N3 N4 BI AC AE F F1 F2 F3 F4 A P P/A1 P/A2 P/A3 P/A4 D D1 D2 D3 D4 FL PY F/P1 F/P2 F/P3 F/P4 BA C C1 C2 C3 C4 BB BK BEP BAP PER IP DA BP

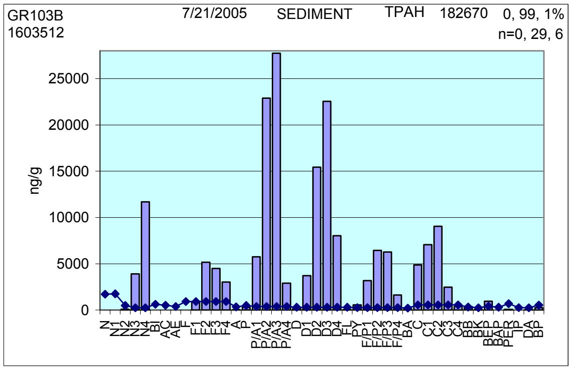

1603509
7/20/2005
SEDIMENT
TSHC 4251
ng/g
5000
4000
3000
2000
1000
0
C9 C10 C11 C12 C13 C14 C15 C16 C17 Pris C18 Phy C19 C20 C21 C22 C23 C24 C25 C26 C27 C28 C29 C30 C31 C32 C33 C34 C35 C36

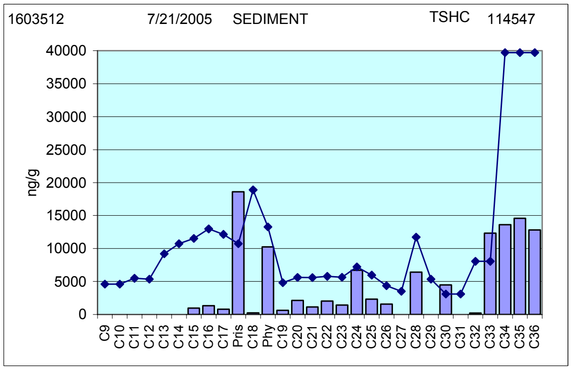

EV039A 7/20/2005 SEDIMENT TPAH 16452 0, 60, 40%
1603510 n=0, 20, 10
ng/g
0
500
1000
1500
2000
N N1 N2 N3 N4 BI AC AE F F1 F2 F3 F4 A P P/A1 P/A2 P/A3 P/A4 D D1 D2 D3 D4 FL PY F/P1 F/P2 F/P3 F/P4 BA C C1 C2 C3 C4 BB BK BEP BAP PER IP DA BP

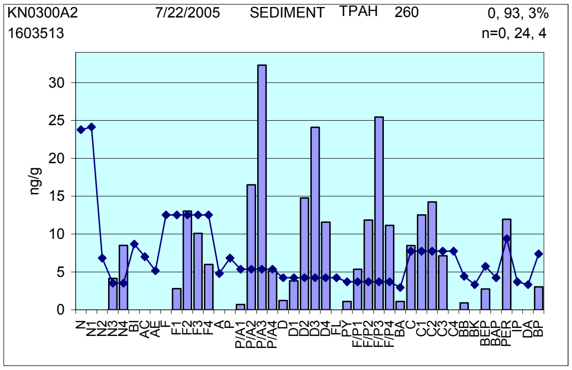

EV039A 7/20/2005 SEDIMENT TSHC 17684
1603510
ng/g
0
500
1000
1500
2000
2500
3000
3500
4000
4500
C9 C10 C11 C12 C13 C14 C15 C16 C17 Pris C18 Phy C19 C20 C21 C22 C23 C24 C25 C26 C27 C28 C29 C30 C31 C32 C33 C34 C35 C36

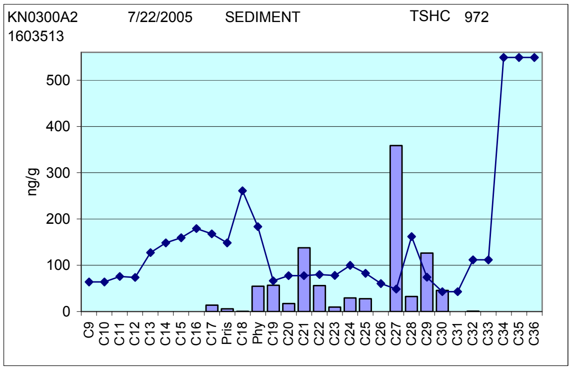

GR103B 7/21/2005 SEDIMENT TPAH 35818 0, 96, 4%
1603511 n=0, 22, 6
ng/g
0
500
1000
1500
2000
2500
3000
3500
4000
4500
N N1 N2 N3 N4 BI AC AE F F1 F2 F3 F4 A P P/A1 P/A2 P/A3 P/A4 D D1 D2 D3 D4 FL PY F/P1 F/P2 F/P3 F/P4 BA C C1 C2 C3 C4 BB BK BEP BAP PER IP DA BP

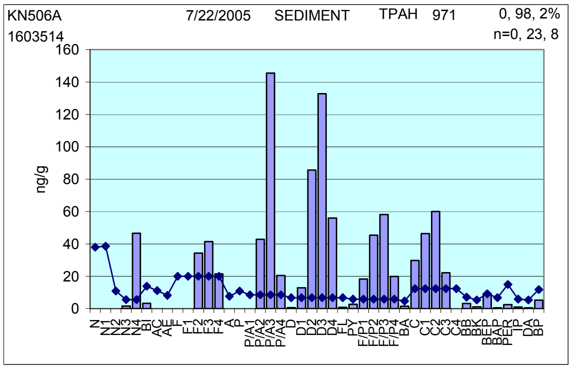

1603511 7/21/2005 SEDIMENT TSHC 54751
ng/g
0
2000
4000
6000
8000
10000
12000
14000
16000
18000
20000
C9 C10 C11 C12 C13 C14 C15 C16 C17 Pris C18 Phy C19 C20 C21 C22 C23 C24 C25 C26 C27 C28 C29 C30 C31 C32 C33 C34 C35 C36

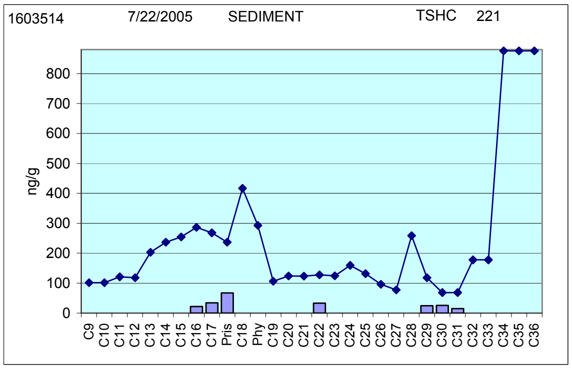

GR103B 7/21/2005 SEDIMENT TPAH 182670 0, 99, 1%
1603512 n=0, 29, 6
ng/g
0
5000
10000
15000
20000
25000
N N1 N2 N3 N4 BI AC AE F F1 F2 F3 F4 A P P/A1 P/A2 P/A3 P/A4 D D1 D2 D3 D4 FL PY F/P1 F/P2 F/P3 F/P4 BA C C1 C2 C3 C4 BB BK BEP BAP PER IP DA BP

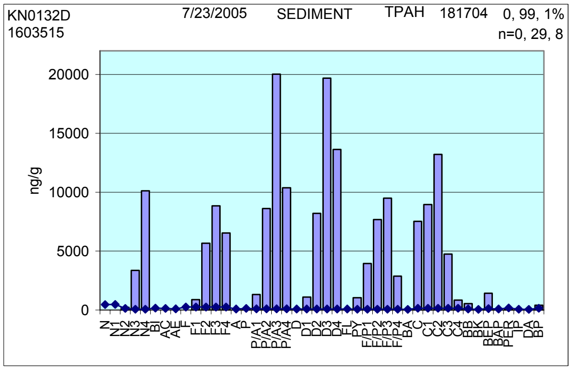

1603512 7/21/2005 SEDIMENT TSHC 114547
ng/g
0
5000
10000
15000
20000
25000
30000
35000
40000
C9 C10 C11 C12 C13 C14 C15 C16 C17 Pris C18 Phy C19 C20 C21 C22 C23 C24 C25 C26 C27 C28 C29 C30 C31 C32 C33 C34 C35 C36

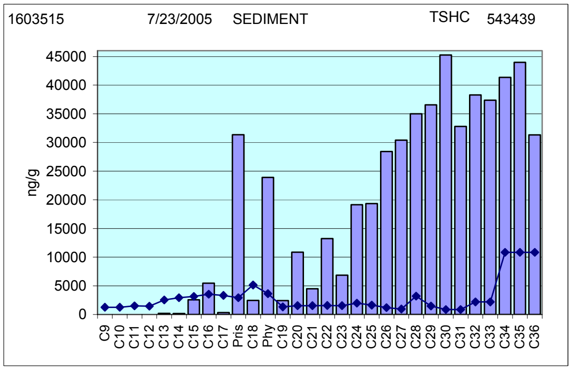

KN0300A2 7/22/2005 SEDIMENT TPAH 260 0, 93, 3%
1603513 n=0, 24, 4
ng/g
0
5
10
15
20
25
30
N N1 N2 N3 N4 BI AC AE F F1 F2 F3 F4 A P P/A1 P/A2 P/A3 P/A4 D D1 D2 D3 D4 FL PY F/P1 F/P2 F/P3 F/P4 BA C C1 C2 C3 C4 BB BK BEP BAP PER IP DA BP

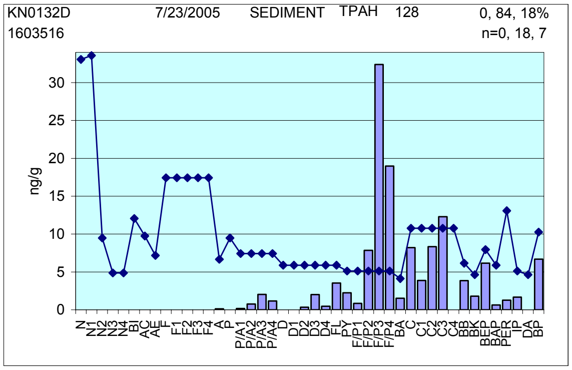

KN0300A2 7/22/2005 SEDIMENT TSHC 972
1603513
ng/g
0
100
200
300
400
500
C9 C10 C11 C12 C13 C14 C15 C16 C17 Pris C18 Phy C19 C20 C21 C22 C23 C24 C25 C26 C27 C28 C29 C30 C31 C32 C33 C34 C35 C36


KN506A 7/22/2005 SEDIMENT TPAH 971 0, 98, 2%
1603514 n=0, 23, 8
ng/g
0
20
40
60
80
100
120
140
160
N N1 N2 N3 N4 BI AC AE F F1 F2 F3 F4 A P P/A1 P/A2 P/A3 P/A4 D D1 D2 D3 D4 FL PY F/P1 F/P2 F/P3 F/P4 BA C C1 C2 C3 C4 BB BK BEP BAP PER IP DA BP

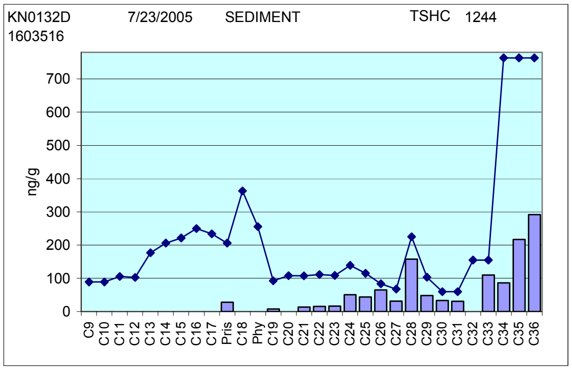

1603514 7/22/2005 SEDIMENT TSHC 221
ng/g
0
100
200
300
400
500
600
700
800
C9 C10 C11 C12 C13 C14 C15 C16 C17 Pris C18 Phy C19 C20 C21 C22 C23 C24 C25 C26 C27 C28 C29 C30 C31 C32 C33 C34 C35 C36


KN0132D 7/23/2005 SEDIMENT TPAH 181704 0, 99, 1%
1603515 n=0, 29, 8
ng/g
0
5000
10000
15000
20000
N N1 N2 N3 N4 BI AC AE F F1 F2 F3 F4 A P P/A1 P/A2 P/A3 P/A4 D D1 D2 D3 D4 FL PY F/P1 F/P2 F/P3 F/P4 BA C C1 C2 C3 C4 BB BK BEP BAP PER IP DA BP

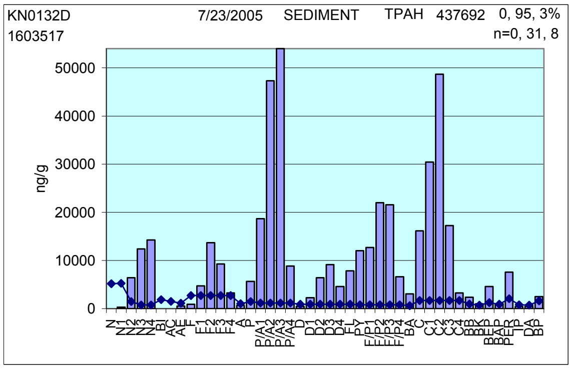

1603515 7/23/2005 SEDIMENT TSHC 543439
ng/g
0
5000
10000
15000
20000
25000
30000
35000
40000
45000
C9 C10 C11 C12 C13 C14 C15 C16 C17 Pris C18 Phy C19 C20 C21 C22 C23 C24 C25 C26 C27 C28 C29 C30 C31 C32 C33 C34 C35 C36



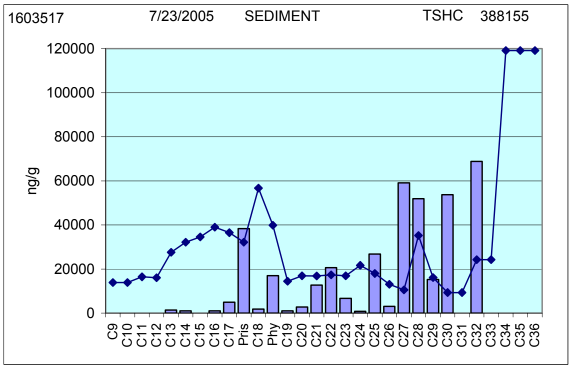
KN0132D 7/23/2005 SEDIMENT TPAH 128 0, 84, 18%
1603516 n=0, 18, 7



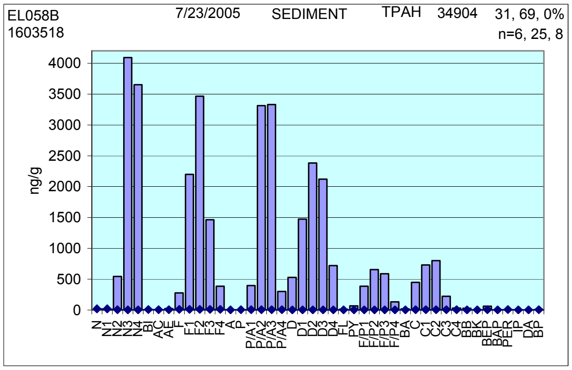
KN0132D 7/23/2005 SEDIMENT TSHC 1244
1603516



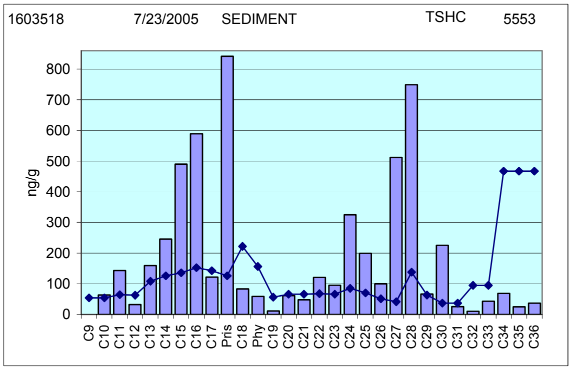
KN0132D 7/23/2005 SEDIMENT TPAH 437692 0, 95, 3%
1603517 n=0, 31, 8



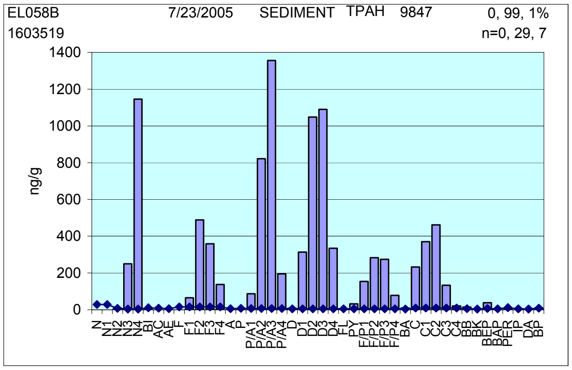
1603517 7/23/2005 SEDIMENT TSHC 388155

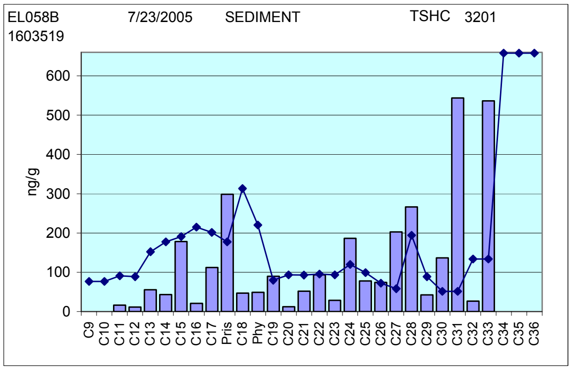


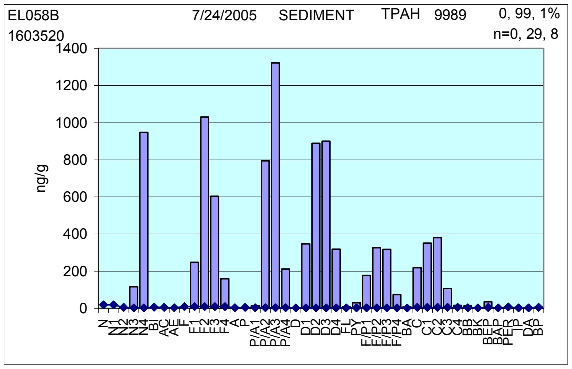
EL058B 7/23/2005 SEDIMENT TPAH 34904 31, 69, 0%
1603518 n=6, 25, 8

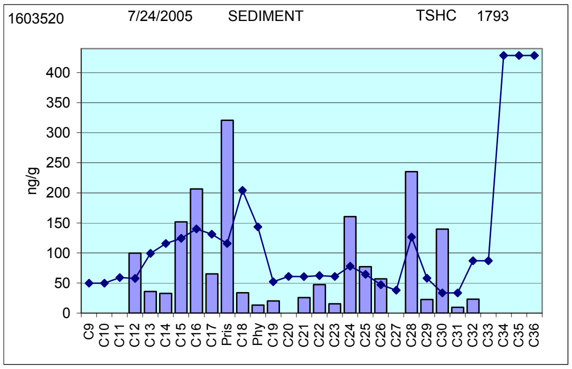


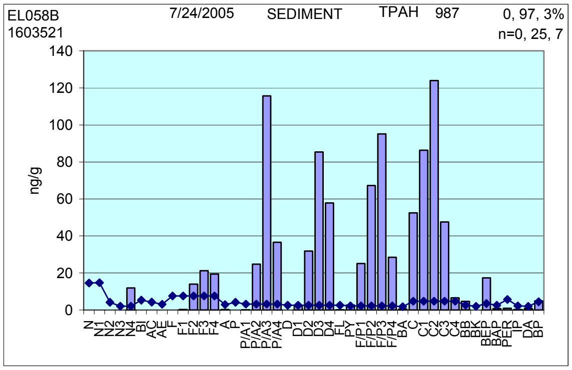
1603518 7/23/2005 SEDIMENT TSHC 5553

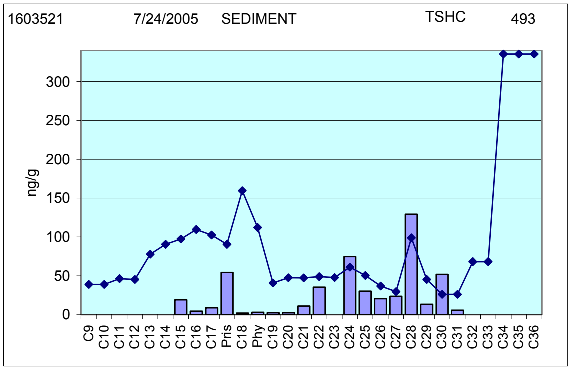

EL058B 7/23/2005 SEDIMENT TPAH 9847 0, 99, 1%
1603519 n=0, 29, 7
ng/g
0 200 400 600 800 1000 1200 1400
N N1 N2 N3 N4 BI AC AE F F1 F2 F3 F4 A P P/A1 P/A2 P/A3 P/A4 D D1 D2 D3 D4 FL PY F/P1 F/P2 F/P3 F/P4 BA C C1 C2 C3 C4 BB BK BEP BAP PER IP DA BP

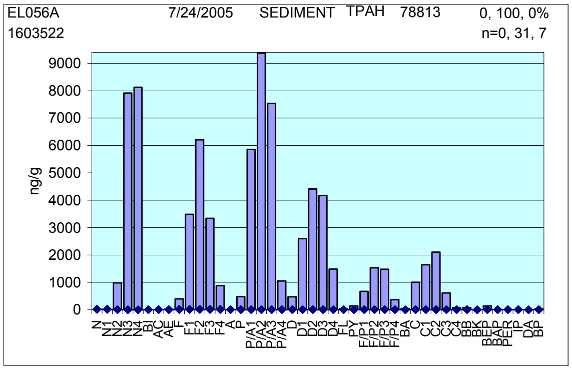

EL058B 7/23/2005 SEDIMENT TSHC 3201
1603519
ng/g
0 100 200 300 400 500 600
C9 C10 C11 C12 C13 C14 C15 C16 C17 Pris C18 Phy C19 C20 C21 C22 C23 C24 C25 C26 C27 C28 C29 C30 C31 C32 C33 C34 C35 C36

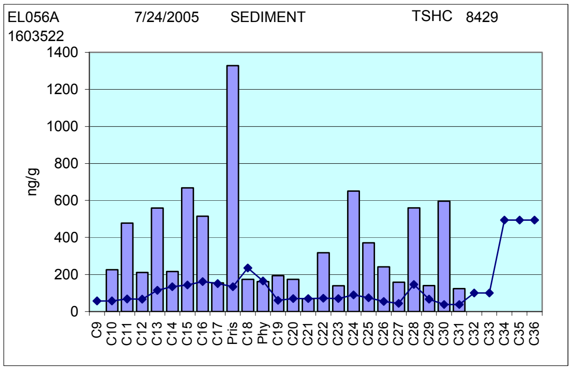

EL058B 7/24/2005 SEDIMENT TPAH 9989 0, 99, 1%
1603520 n=0, 29, 8
ng/g
0 200 400 600 800 1000 1200 1400
N N1 N2 N3 N4 BI AC AE F F1 F2 F3 F4 A P P/A1 P/A2 P/A3 P/A4 D D1 D2 D3 D4 FL PY F/P1 F/P2 F/P3 F/P4 BA C C1 C2 C3 C4 BB BK BEP BAP PER IP DA BP

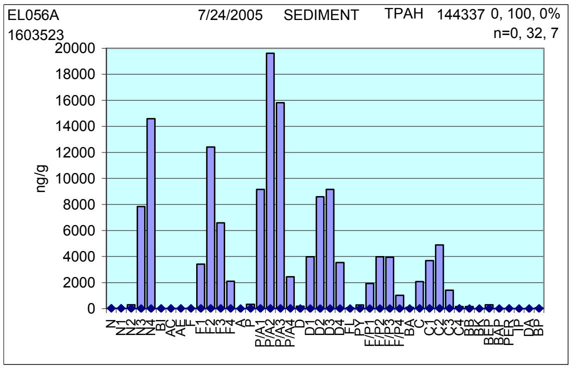

1603520 7/24/2005 SEDIMENT TSHC 1793
ng/g
0 50 100 150 200 250 300 350 400
C9 C10 C11 C12 C13 C14 C15 C16 C17 Pris C18 Phy C19 C20 C21 C22 C23 C24 C25 C26 C27 C28 C29 C30 C31 C32 C33 C34 C35 C36

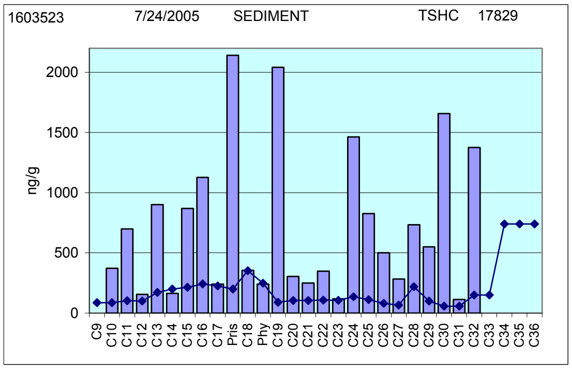

EL058B 7/24/2005 SEDIMENT TPAH 987 0, 97, 3%
1603521 n=0, 25, 7
ng/g
0 20 40 60 80 100 120 140
N N1 N2 N3 N4 BI AC AE F F1 F2 F3 F4 A P P/A1 P/A2 P/A3 P/A4 D D1 D2 D3 D4 FL PY F/P1 F/P2 F/P3 F/P4 BA C C1 C2 C3 C4 BB BK BEP BAP PER IP DA BP

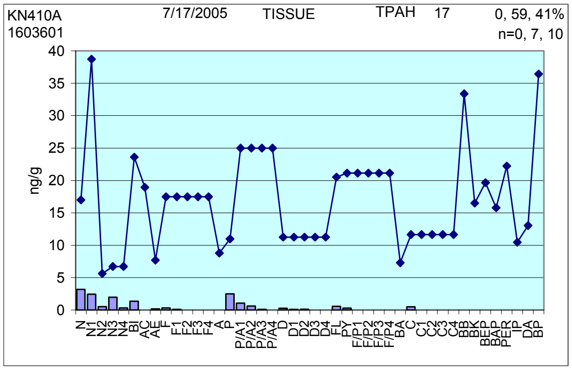

1603521 7/24/2005 SEDIMENT TSHC 493
ng/g
0 50 100 150 200 250 300
C9 C10 C11 C12 C13 C14 C15 C16 C17 Pris C18 Phy C19 C20 C21 C22 C23 C24 C25 C26 C27 C28 C29 C30 C31 C32 C33 C34 C35 C36

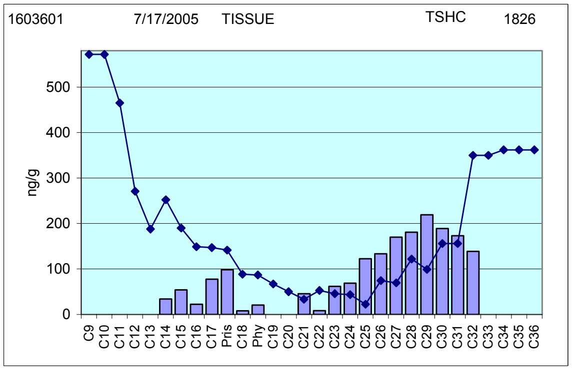

EL056A 7/24/2005 SEDIMENT TPAH 78813 0, 100, 0%
1603522 n=0, 31, 7

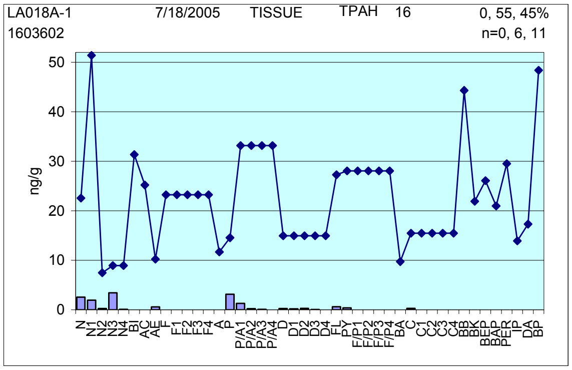

EL056A 7/24/2005 SEDIMENT TSHC 8429
1603522

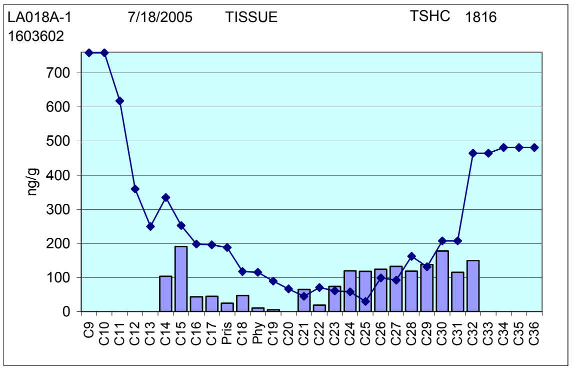

EL056A 7/24/2005 SEDIMENT TPAH 144337 0, 100, 0%
1603523 n=0, 32, 7

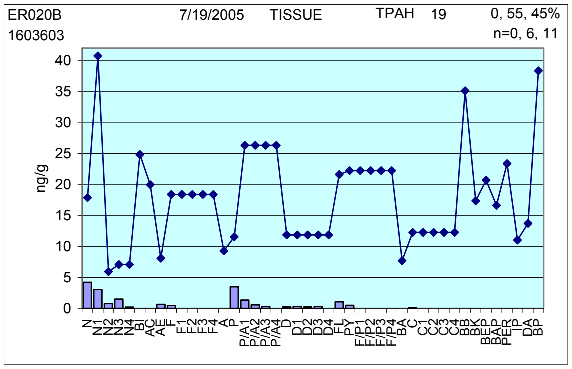

1603523 7/24/2005 SEDIMENT TSHC 17829

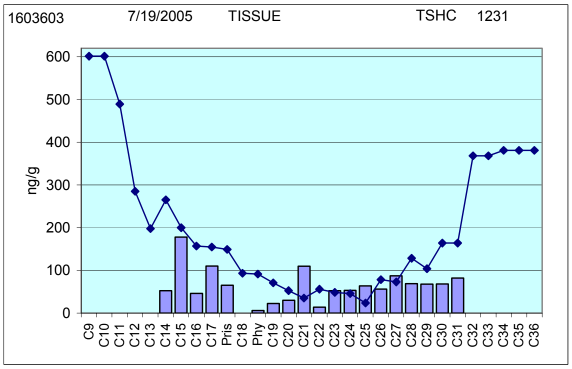

KN410A 7/17/2005 TISSUE TPAH 17 0, 59, 41%
1603601 n=0, 7, 10

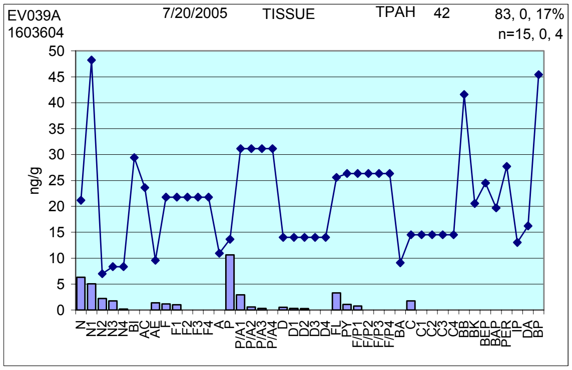

1603601 7/17/2005 TISSUE TSHC 1826

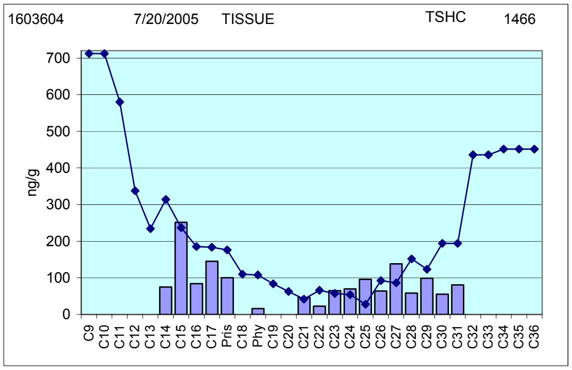

LA018A-1
7/18/2005
TISSUE
TPAH 16
0, 55, 45%
1603602
n=0, 6, 11
ng/g
0
10
20
30
40
50
N N1 N2 N3 N4 BI AC AE F F1 F2 F3 F4 A P P/A1 P/A2 P/A3 P/A4 D D1 D2 D3 D4 FL PY F/P1 F/P2 F/P3 F/P4 BA C C1 C2 C3 C4 BB BK BEP BAP PER IP DA BP

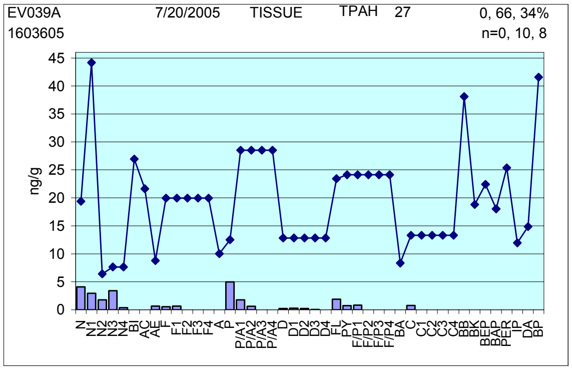

LA018A-1
7/18/2005
TISSUE
TSHC 1816
1603602
ng/g
0
100
200
300
400
500
600
700
C9 C10 C11 C12 C13 C14 C15 C16 C17 Pris C18 Phy C19 C20 C21 C22 C23 C24 C25 C26 C27 C28 C29 C30 C31 C32 C33 C34 C35 C36

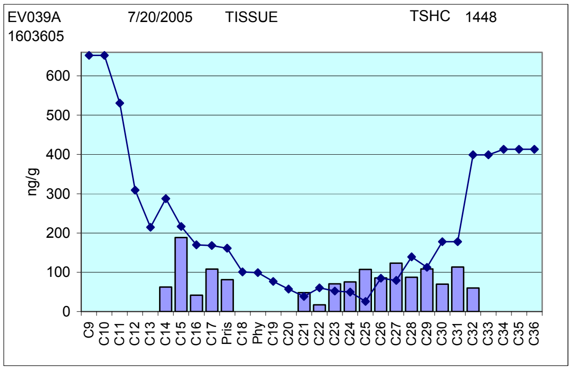

ER020B
7/19/2005
TISSUE
TPAH 19
0, 55, 45%
1603603
n=0, 6, 11
ng/g
0
5
10
15
20
25
30
35
40
N N1 N2 N3 N4 BI AC AE F F1 F2 F3 F4 A P P/A1 P/A2 P/A3 P/A4 D D1 D2 D3 D4 FL PY F/P1 F/P2 F/P3 F/P4 BA C C1 C2 C3 C4 BB BK BEP BAP PER IP DA BP

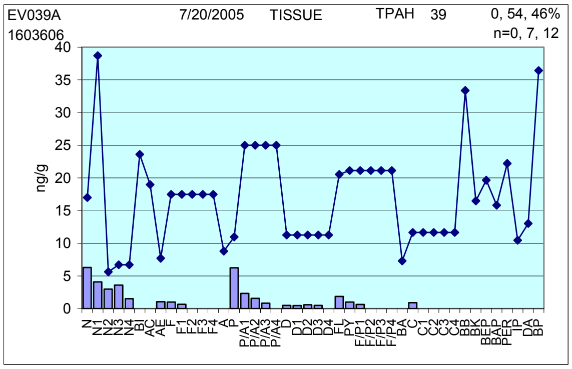

1603603
7/19/2005
TISSUE
TSHC 1231
ng/g
0
100
200
300
400
500
600
C9 C10 C11 C12 C13 C14 C15 C16 C17 Pris C18 Phy C19 C20 C21 C22 C23 C24 C25 C26 C27 C28 C29 C30 C31 C32 C33 C34 C35 C36

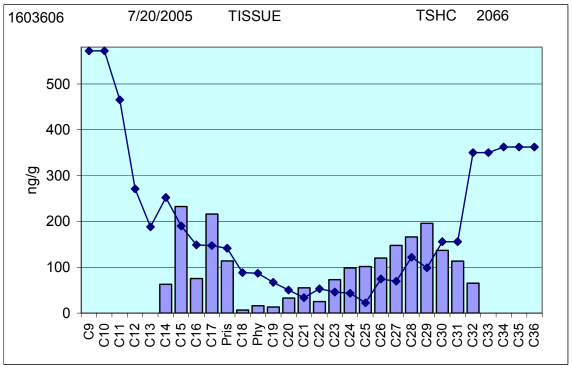

EV039A
7/20/2005
TISSUE
TPAH 42
83, 0, 17%
1603604
n=15, 0, 4
ng/g
0
5
10
15
20
25
30
35
40
45
50
N N1 N2 N3 N4 BI AC AE F F1 F2 F3 F4 A P P/A1 P/A2 P/A3 P/A4 D D1 D2 D3 D4 FL PY F/P1 F/P2 F/P3 F/P4 BA C C1 C2 C3 C4 BB BK BEP BAP PER IP DA BP

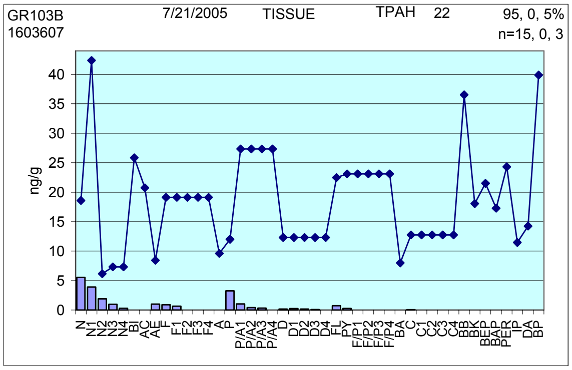

1603604
7/20/2005
TISSUE
TSHC 1466
ng/g
0
100
200
300
400
500
600
700
C9 C10 C11 C12 C13 C14 C15 C16 C17 Pris C18 Phy C19 C20 C21 C22 C23 C24 C25 C26 C27 C28 C29 C30 C31 C32 C33 C34 C35 C36

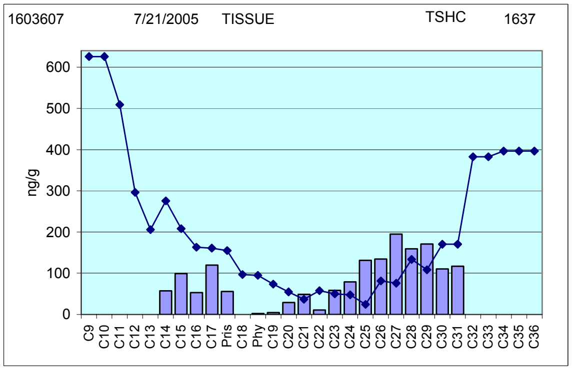

EV039A 7/20/2005 TISSUE TPAH 27 0, 66, 34%
1603605 n=0, 10, 8

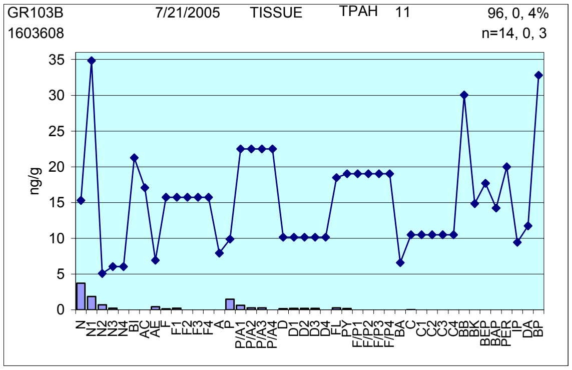

EV039A 7/20/2005 TISSUE TSHC 1448
1603605

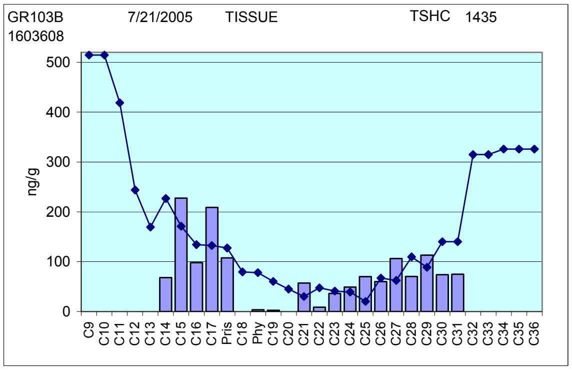

EV039A 7/20/2005 TISSUE TPAH 39 0, 54, 46%
1603606 n=0, 7, 12

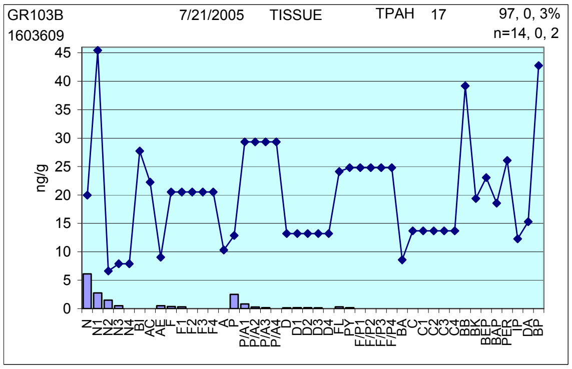

1603606 7/20/2005 TISSUE TSHC 2066

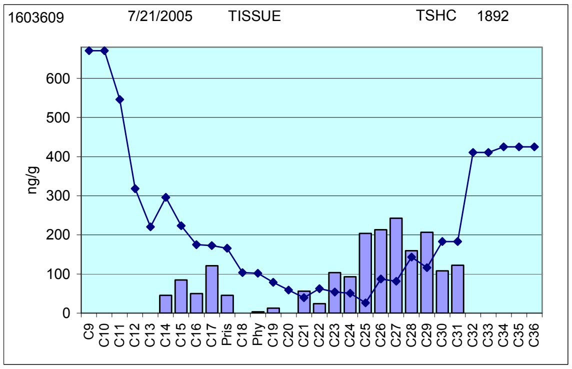

GR103B 7/21/2005 TISSUE TPAH 22 95, 0, 5%
1603607 n=15, 0, 3

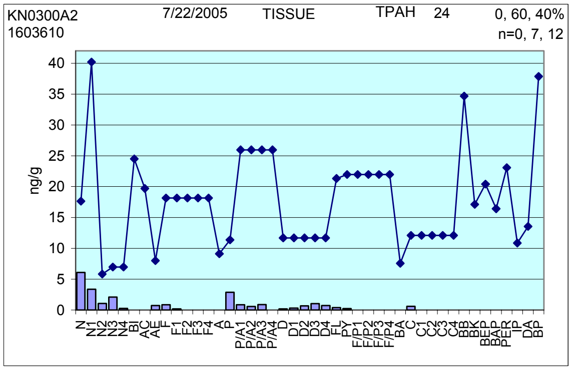

1603607 7/21/2005 TISSUE TSHC 1637

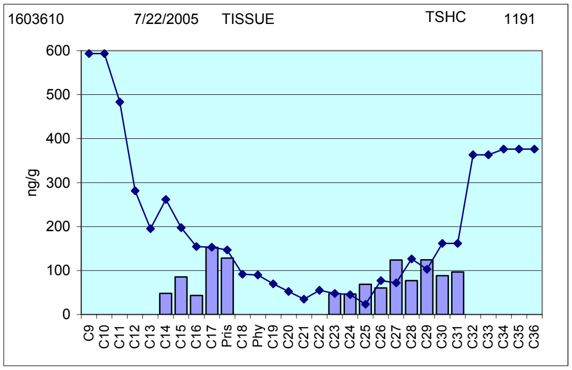

GR103B 7/21/2005 TISSUE TPAH 11 96, 0, 4%
1603608 n=14, 0, 3

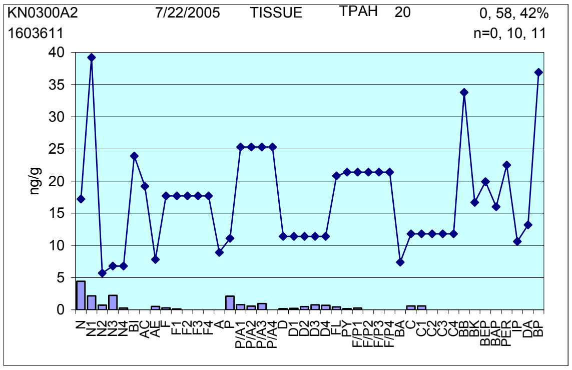

GR103B 7/21/2005 TISSUE TSHC 1435
1603608

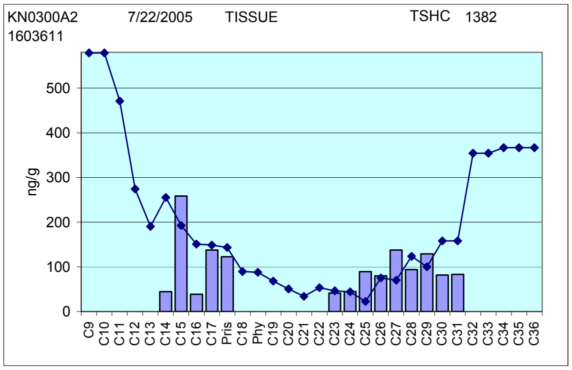

GR103B 7/21/2005 TISSUE TPAH 17 97, 0, 3%
1603609 n=14, 0, 2

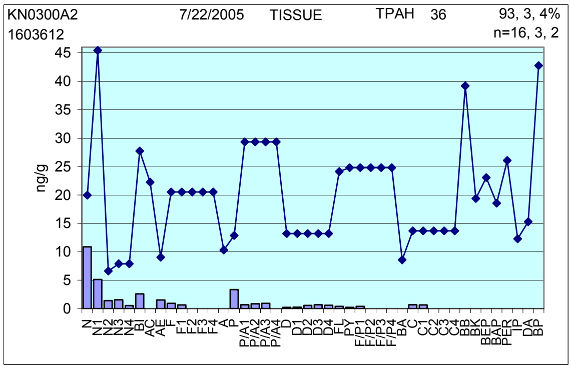

1603609 7/21/2005 TISSUE TSHC 1892

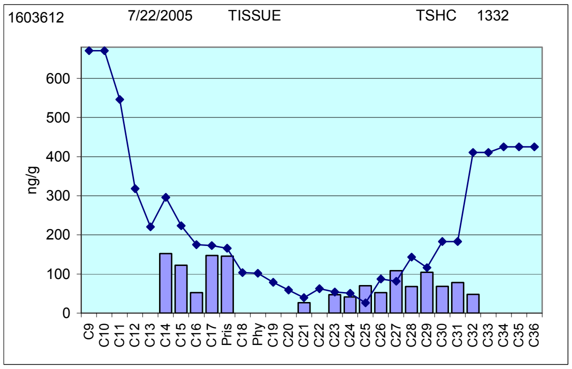

KN0300A2 7/22/2005 TISSUE TPAH 24 0, 60, 40%
1603610 n=0, 7, 12

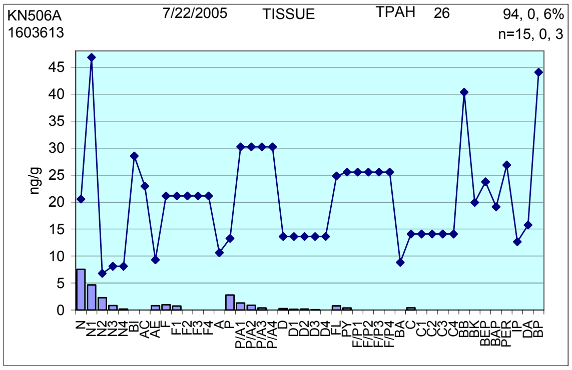

1603610 7/22/2005 TISSUE TSHC 1191

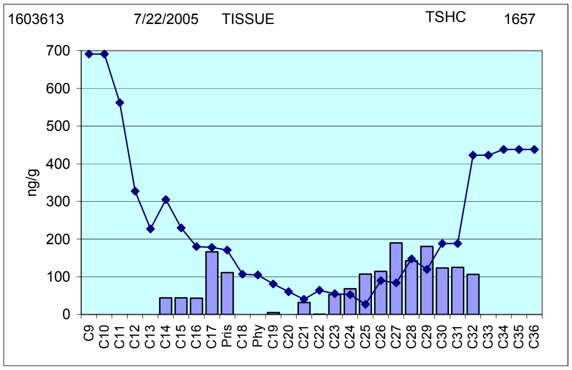

KN0300A2 7/22/2005 TISSUE TPAH 20 0, 58, 42%
1603611 n=0, 10, 11

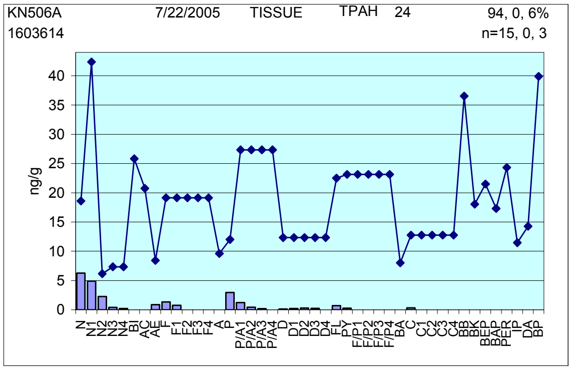

KN0300A2 7/22/2005 TISSUE TSHC 1382
1603611

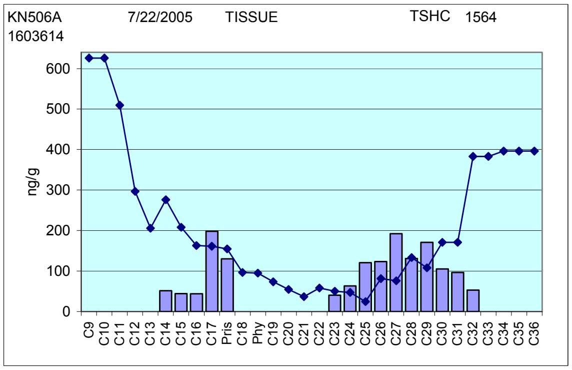

KN0300A2 7/22/2005 TISSUE TPAH 36 93, 3, 4%
1603612 n=16, 3, 2

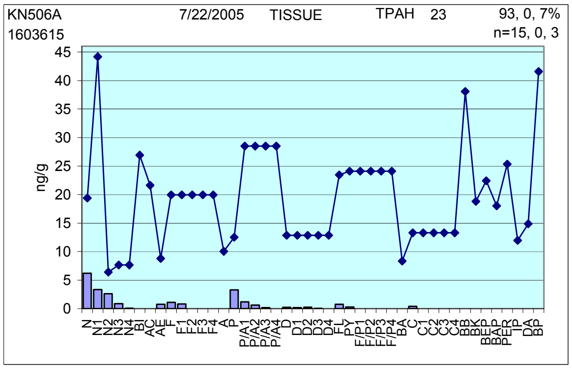

1603612 7/22/2005 TISSUE TSHC 1332

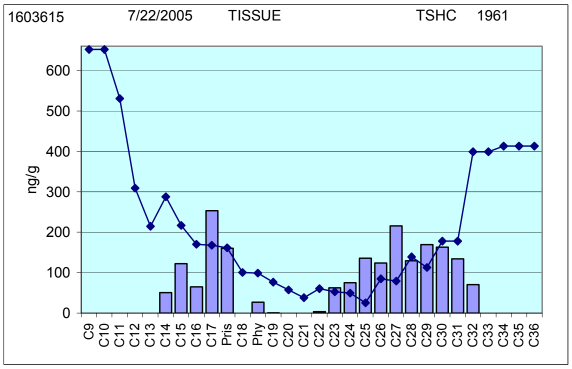

KN506A 7/22/2005 TISSUE TPAH 26 94, 0, 6%
1603613 n=15, 0, 3

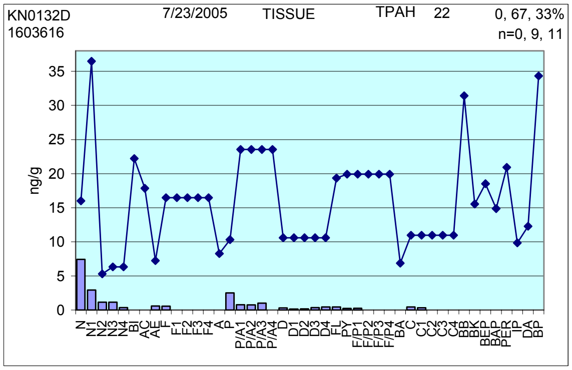

1603613 7/22/2005 TISSUE TSHC 1657

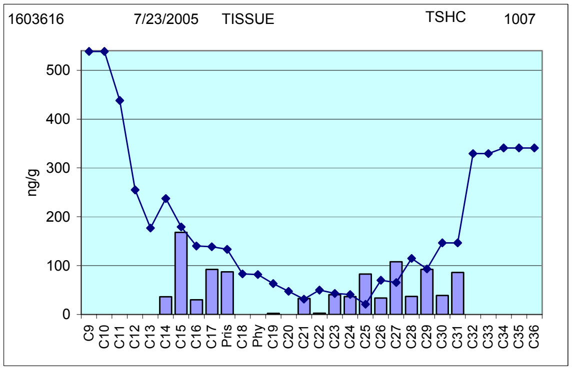

KN506A
1603614
7/22/2005
TISSUE
TPAH 24
94, 0, 6%
n=15, 0, 3
ng/g
0
5
10
15
20
25
30
35
40
N N1 N2 N3 N4 BI AC AE F F1 F2 F3 F4 A P P/A1 P/A2 P/A3 P/A4 D D1 D2 D3 D4 FL PY F/P1 F/P2 F/P3 F/P4 BA C C1 C2 C3 C4 BB BK BEP BAP PER IP DA BP

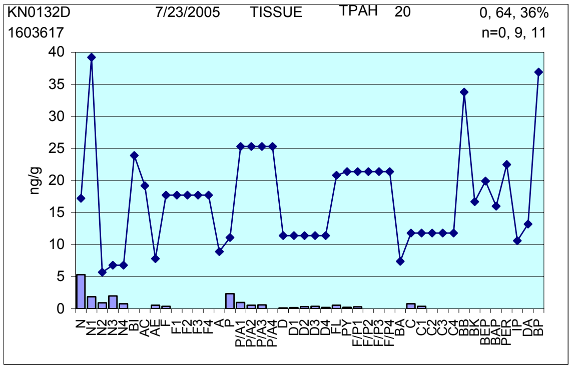

KN506A
1603614
7/22/2005
TISSUE
TSHC 1564
ng/g
0
100
200
300
400
500
600
C9 C10 C11 C12 C13 C14 C15 C16 C17 Pris C18 Phy C19 C20 C21 C22 C23 C24 C25 C26 C27 C28 C29 C30 C31 C32 C33 C34 C35 C36

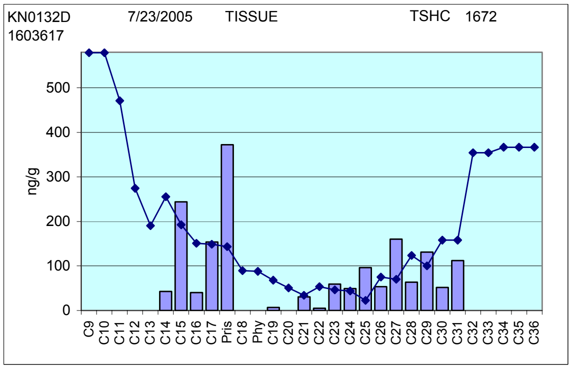

KN506A
1603615
7/22/2005
TISSUE
TPAH 23
93, 0, 7%
n=15, 0, 3
ng/g
0
5
10
15
20
25
30
35
40
45
N N1 N2 N3 N4 BI AC AE F F1 F2 F3 F4 A P P/A1 P/A2 P/A3 P/A4 D D1 D2 D3 D4 FL PY F/P1 F/P2 F/P3 F/P4 BA C C1 C2 C3 C4 BB BK BEP BAP PER IP DA BP

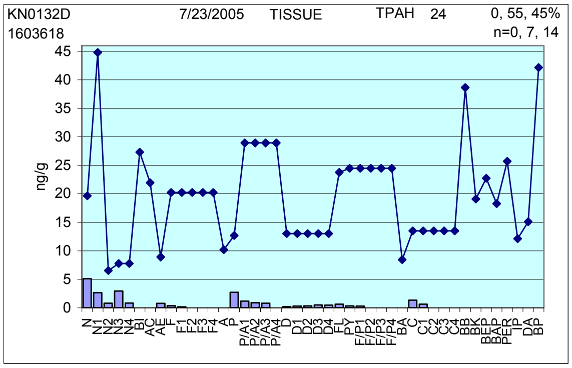

1603615
7/22/2005
TISSUE
TSHC 1961
ng/g
0
100
200
300
400
500
600
C9 C10 C11 C12 C13 C14 C15 C16 C17 Pris C18 Phy C19 C20 C21 C22 C23 C24 C25 C26 C27 C28 C29 C30 C31 C32 C33 C34 C35 C36

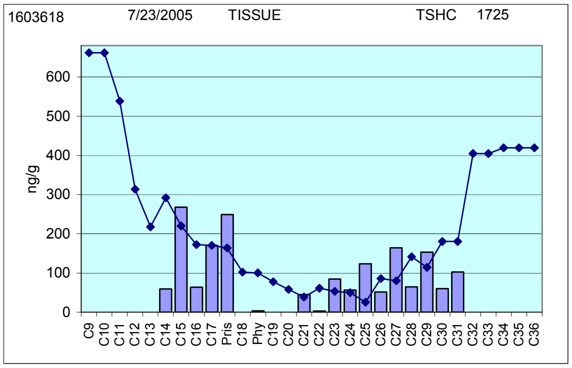

KN0132D
1603616
7/23/2005
TISSUE
TPAH 22
0, 67, 33%
n=0, 9, 11
ng/g
0
5
10
15
20
25
30
35
N N1 N2 N3 N4 BI AC AE F F1 F2 F3 F4 A P P/A1 P/A2 P/A3 P/A4 D D1 D2 D3 D4 FL PY F/P1 F/P2 F/P3 F/P4 BA C C1 C2 C3 C4 BB BK BEP BAP PER IP DA BP

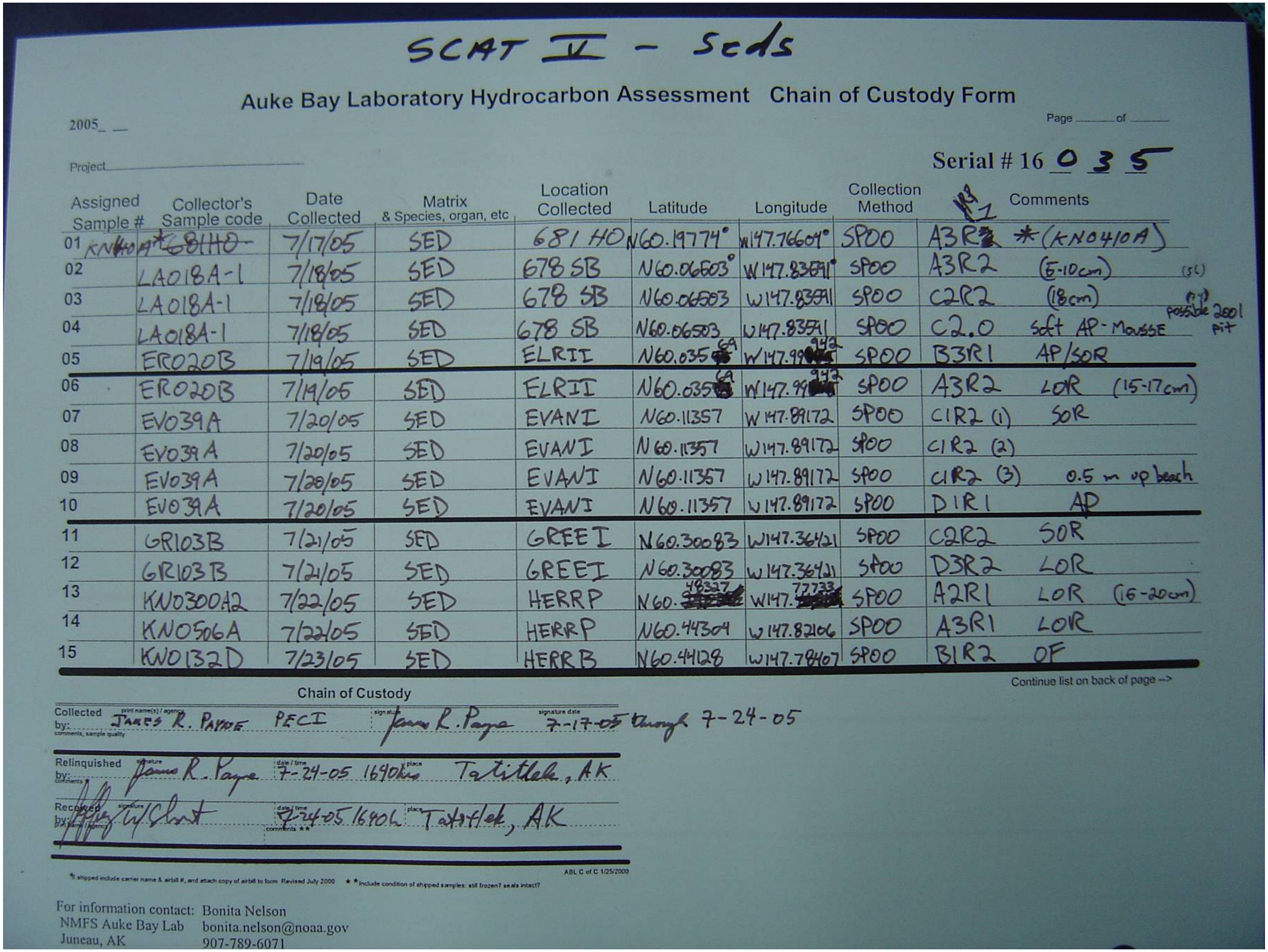

1603616
7/23/2005
TISSUE
TSHC 1007
ng/g
0
100
200
300
400
500
C9 C10 C11 C12 C13 C14 C15 C16 C17 Pris C18 Phy C19 C20 C21 C22 C23 C24 C25 C26 C27 C28 C29 C30 C31 C32 C33 C34 C35 C36


KN0132D
7/23/2005
TISSUE
TPAH 20
0, 64, 36%
1603617
n=0, 9, 11
ng/g
0
5
10
15
20
25
30
35
40
N N1 N2 N3 N4 BI AC AE F F1 F2 F3 F4 A P P/A1 P/A2 P/A3 P/A4 D D1 D2 D3 D4 FL PY F/P1 F/P2 F/P3 F/P4 BA C C1 C2 C3 C4 BB BK BEP BAP PER IP DA BP


KN0132D
7/23/2005
TISSUE
TSHC 1672
1603617
ng/g
0
100
200
300
400
500
C9 C10 C11 C12 C13 C14 C15 C16 C17 Pris C18 Phy C19 C20 C21 C22 C23 C24 C25 C26 C27 C28 C29 C30 C31 C32 C33 C34 C35 C36


KN0132D
7/23/2005
TISSUE
TPAH 24
0, 55, 45%
1603618
n=0, 7, 14
ng/g
0
5
10
15
20
25
30
35
40
45
N N1 N2 N3 N4 BI AC AE F F1 F2 F3 F4 A P P/A1 P/A2 P/A3 P/A4 D D1 D2 D3 D4 FL PY F/P1 F/P2 F/P3 F/P4 BA C C1 C2 C3 C4 BB BK BEP BAP PER IP DA BP


1603618
7/23/2005
TISSUE
TSHC 1725
ng/g
0
100
200
300
400
500
600
C9 C10 C11 C12 C13 C14 C15 C16 C17 Pris C18 Phy C19 C20 C21 C22 C23 C24 C25 C26 C27 C28 C29 C30 C31 C32 C33 C34 C35 C36



SCAT V - Seds

Auke Bay Laboratory Hydrocarbon Assessment Chain of Custody Form

2005_ __

Page ____ of ____

Project____

Serial # 16 0 3 5

Assigned Sample #	Collector's Sample code	Date Collected	Matrix & Species, organ, etc	Location Collected	Latitude	Longitude	Collection Method		Comments
01	KN~~40~~A* ~~681HO~~	7/17/05	SED	681 HO	N60.19774°	W147.76604°	SPOO	A3R2	*(KN0410A)
02	LA018A-1	7/18/05	SED	678 SB	N60.06503°	W147.83591°	SPOO	A3R2	(5-10cm) (SL)
03	LA018A-1	7/18/05	SED	678 SB	N60.06503	W147.83591	SPOO	C2R2	(18cm) (?)
04	LA018A-1	7/18/05	SED	678 SB	N60.06503	W147.83591	SPOO	C2.0	soft AP-MOUSSE possible 2001 pit
05	ER020B	7/19/05	SED	ELRII	N60.03569	W147.99942	SPOO	B3R1	AP/SOR
06	ER020B	7/19/05	SED	ELRII	N60.03569	W147.99942	SPOO	A3R2	LOR (15-17cm)
07	EV039A	7/20/05	SED	EVANI	N60.11357	W147.89172	SPOO	C1R2 (1)	SOR
08	EV039A	7/20/05	SED	EVANI	N60.11357	W147.89172	SPOO	C1R2 (2)	
09	EV039A	7/20/05	SED	EVANI	N60.11357	W147.89172	SPOO	C1R2 (3)	0.5 m up beach
10	EV039A	7/20/05	SED	EVANI	N60.11357	W147.89172	SPOO	D1R1	AP
11	GR103B	7/21/05	SED	GREEI	N60.30083	W147.36421	SPOO	C2R2	SOR
12	GR103B	7/21/05	SED	GREEI	N60.30083	W147.36421	SPOO	D3R2	LOR
13	KN0300A2	7/22/05	SED	HERRP	N60.48327	W147.77733	SPOO	A2R1	LOR (16-20cm)
14	KN0506A	7/22/05	SED	HERRP	N60.44304	W147.82106	SPOO	A3R1	LOR
15	KN0132D	7/23/05	SED	HERRB	N60.44128	W147.78407	SPOO	B1R2	OF

Continue list on back of page -->

Chain of Custody

Collected by: print name(s) / agency JAMES R. PAYNE PECI signature James R. Payne signature date 7-17-05 through 7-24-05
comments, sample quality

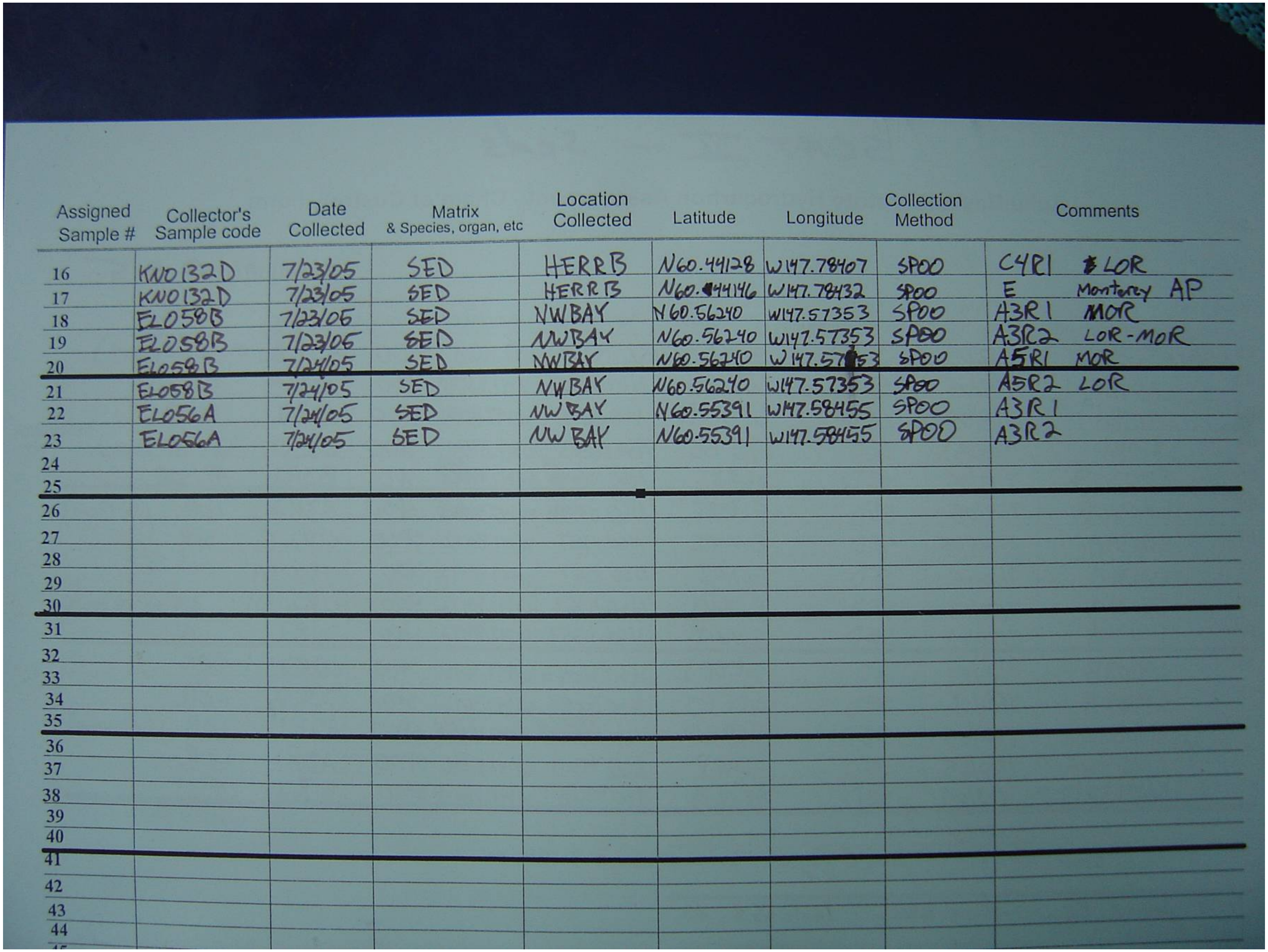
Relinquished by: signature James R. Payne date / time 7-24-05 1640hrs place Tatitlek, AK
comments *

Received by: signature date / time 7-24-05 1640h place Tatitlek, AK
print name / agency comments **

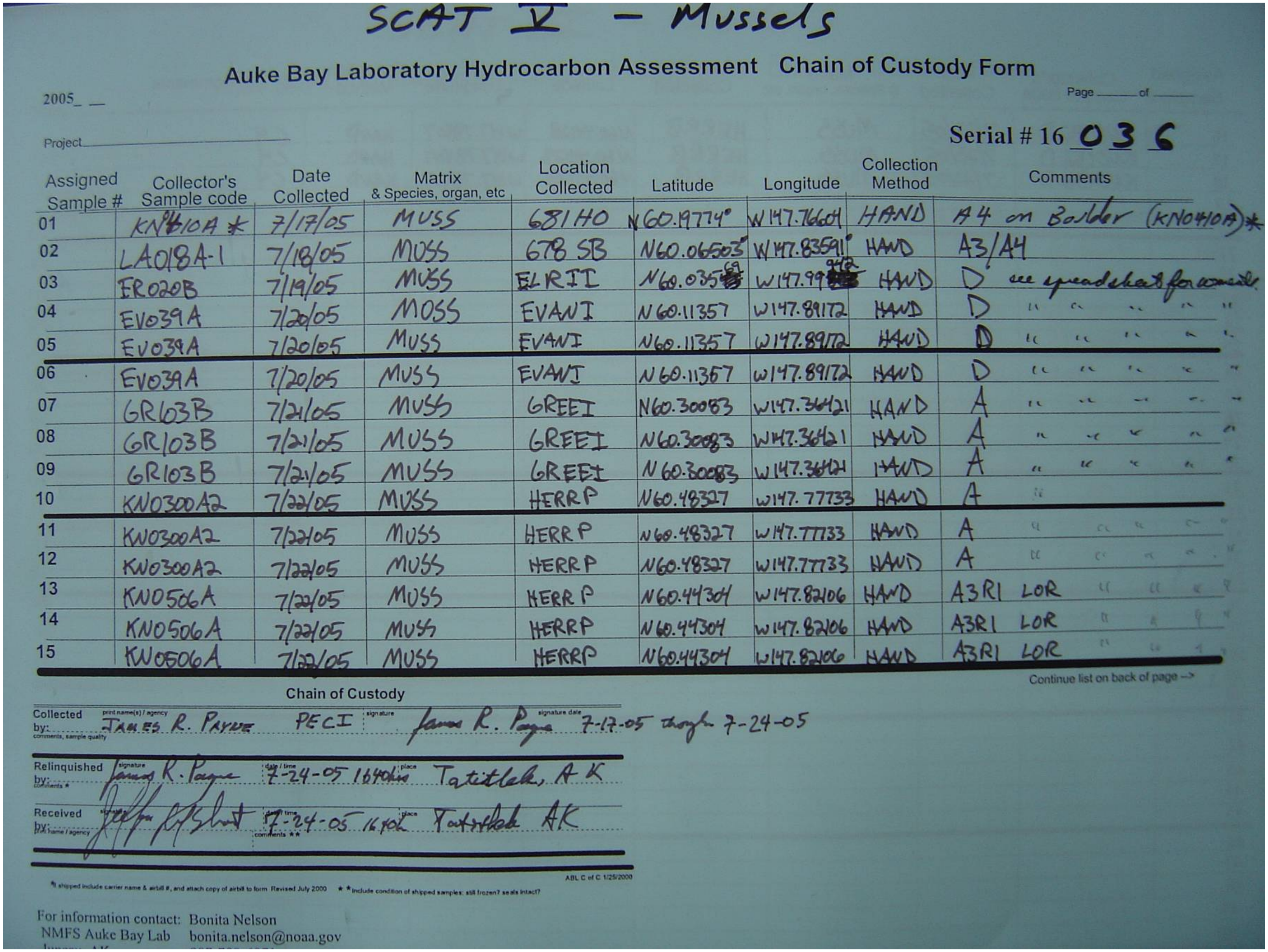
ABL C of C 1/25/2000

* If shipped include carrier name & airbill #, and attach copy of airbill to form Revised July 2000 ** Include condition of shipped samples: still frozen? seals intact?

For information contact: Bonita Nelson
NMFS Auke Bay Lab bonita.nelson@noaa.gov
Juneau, AK 907-789-6071



Assigned Sample #	Collector's Sample code	Date Collected	Matrix & Species, organ, etc	Location Collected	Latitude	Longitude	Collection Method	Comments
16	KN0132D	7/23/05	SED	HERRB	N60.44128	W147.78407	SP00	C4R1 LOR
17	KN0132D	7/23/05	SED	HERRB	N60.44146	W147.78432	SP00	E Monterey AP
18	EL058B	7/23/06	SED	NWBAY	N60.56240	W147.57353	SP00	A3R1 MOR
19	EL058B	7/23/06	SED	NWBAY	N60.56240	W147.57353	SP00	A3R2 LOR-MOR
20	EL058B	7/24/05	SED	NWBAY	N60.56240	W147.57[illegible]53	SP00	A5R1 MOR
21	EL058B	7/24/05	SED	NWBAY	N60.56240	W147.57353	SP00	A5R2 LOR
22	EL056A	7/24/05	SED	NW BAY	N60.55391	W147.58455	SP00	A3R1
23	EL056A	7/24/05	SED	NW BAY	N60.55391	W147.58455	SP00	A3R2
24								
25								
26								
27								
28								
29								
30								
31								
32								
33								
34								
35								
36								
37								
38								
39								
40								
41								
42								
43								
44								



SCAT V – Mussels

Auke Bay Laboratory Hydrocarbon Assessment Chain of Custody Form

2005_ __

Page ____ of ____

Project ______________

Serial # 16 0 3 6

Assigned Sample #	Collector's Sample code	Date Collected	Matrix & Species, organ, etc	Location Collected	Latitude	Longitude	Collection Method	Comments
01	KN0410A *	7/17/05	MUSS	681HO	N60.19774°	W147.76604	HAND	A4 on Bolder (KN0410A)*
02	LA018A-1	7/18/05	MUSS	678 SB	N60.06503°	W147.83591°	HAND	A3/A4
03	ER020B	7/19/05	MUSS	ELRII	N60.03569	W147.99942	HAND	D see spreadsheet for comments
04	EV039A	7/20/05	MOSS	EVANI	N60.11357	W147.89172	HAND	D " " " " "
05	EV039A	7/20/05	MUSS	EVANI	N60.11357	W147.89172	HAND	D " " " " "
06	EV039A	7/20/05	MUSS	EVANI	N60.11357	W147.89172	HAND	D " " " " "
07	GR103B	7/21/05	MUSS	GREEI	N60.30083	W147.36421	HAND	A " " " " "
08	GR103B	7/21/05	MUSS	GREEI	N60.30083	W147.36421	HAND	A " " " " "
09	GR103B	7/21/05	MUSS	GREEI	N60.30083	W147.36421	HAND	A " " " " "
10	KN0300A2	7/22/05	MUSS	HERRP	N60.48327	W147.77733	HAND	A "
11	KN0300A2	7/22/05	MUSS	HERRP	N60.48327	W147.77733	HAND	A " " " " "
12	KN0300A2	7/22/05	MUSS	HERRP	N60.48327	W147.77733	HAND	A " " " " "
13	KN0506A	7/22/05	MUSS	HERRP	N60.44304	W147.82106	HAND	A3R1 LOR " " " "
14	KN0506A	7/22/05	MUSS	HERRP	N60.44304	W147.82106	HAND	A3R1 LOR " " " "
15	KN0506A	7/22/05	MUSS	HERRP	N60.44304	W147.82106	HAND	A3R1 LOR " " " "

Continue list on back of page -->

Chain of Custody

Collected by: print name(s) / agency JAMES R. PAYNE PECI signature James R. Payne signature date 7-17-05 through 7-24-05
comments, sample quality

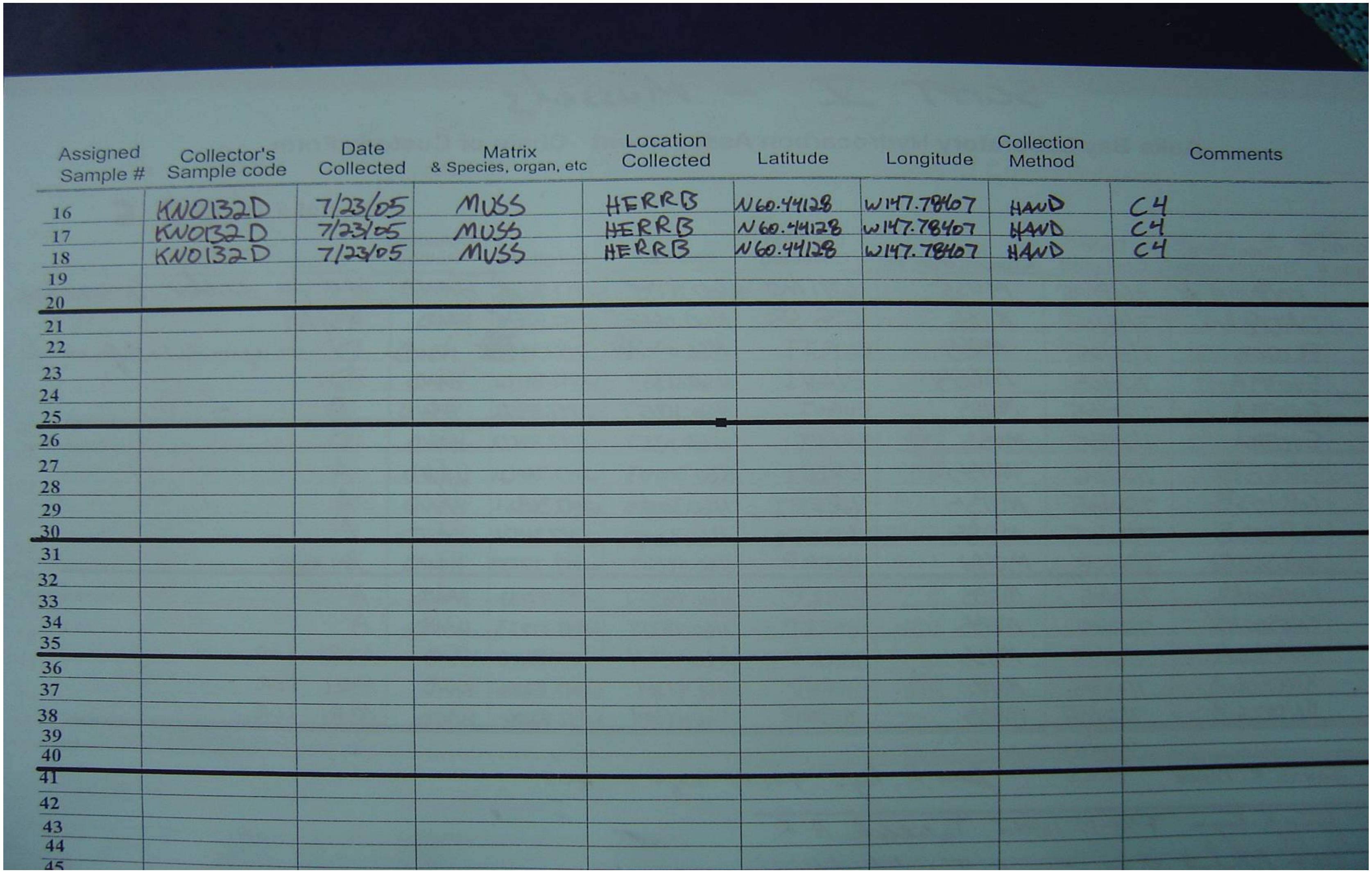
Relinquished by: signature James R. Payne date / time 7-24-05 1640hrs place Tatitlek, AK
comments *

Received by: signature date / time 7-24-05 1640h place Tatitlek AK
print name / agency comments **

ABL C of C 1/25/2000

* If shipped include carrier name & airbill #, and attach copy of airbill to form Revised July 2000 ** Include condition of shipped samples: still frozen? seals intact?

For information contact: Bonita Nelson
NMFS Auke Bay Lab bonita.nelson@noaa.gov

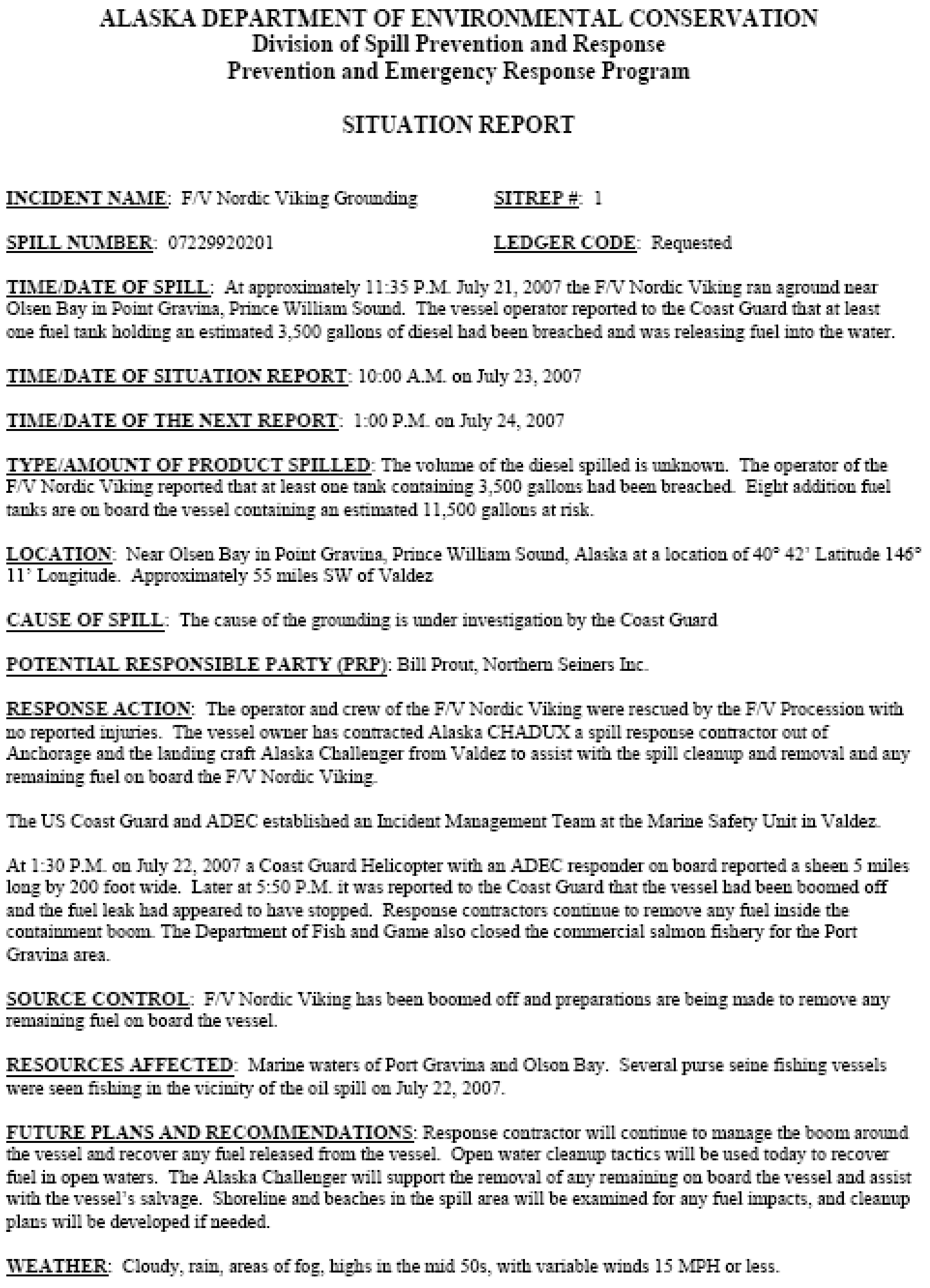


Assigned Sample #	Collector's Sample code	Date Collected	Matrix & Species, organ, etc	Location Collected	Latitude	Longitude	Collection Method	Comments
16	KN0132D	7/23/05	MUSS	HERRB	N60.44128	W147.78407	HAND	C4
17	KN0132D	7/23/05	MUSS	HERRB	N60.44128	W147.78407	HAND	C4
18	KN0132D	7/23/05	MUSS	HERRB	N60.44128	W147.78407	HAND	C4
19								
20								
21								
22								
23								
24								
25								
26								
27								
28								
29								
30								
31								
32								
33								
34								
35								
36								
37								
38								
39								
40								
41								
42								
43								
44								
45								

Appendix F – Nordic Viking Diesel Spill

Nordic Viking Spill *S*ampling

At the request of Joe Banta, the LTEMP project manager, the site of the Nordic Viking grounding and spill incident in Olsen Bay was visited and sampled on 31 July 2007, ten days after the initial incident and clean-up. The location was in proximity to LTEMP's Knowles Head station. At that time, three sites were visited, two in the proximity of the grounding and one along the spill plume. At the later, both a strong smell and sheen were observed and sampled. Joe Banta visited the site in September 2007 but noted neither sheen nor smell. We again sampled the site coincidental to the LTEMP transit from Valdez to Cordova on 28 October 2007. A slight smell was detected and samples were collected from the same locations. The October 2007 samples show a low-level, weathered diesel signal in the three tissue replicates (698-1169 ppb) and the single sediment sample (2.4 ppb). Samples were also collected in December 2007 by ADF&G but have not been analyzed to date.



ALASKA DEPARTMENT OF ENVIRONMENTAL CONSERVATION
Division of Spill Prevention and Response
Prevention and Emergency Response Program

SITUATION REPORT

INCIDENT NAME: F/V Nordic Viking Grounding **SITREP #**: 1

SPILL NUMBER: 07229920201 **LEDGER CODE**: Requested

TIME/DATE OF SPILL: At approximately 11:35 P.M. July 21, 2007 the F/V Nordic Viking ran aground near Olsen Bay in Point Gravina, Prince William Sound. The vessel operator reported to the Coast Guard that at least one fuel tank holding an estimated 3,500 gallons of diesel had been breached and was releasing fuel into the water.

TIME/DATE OF SITUATION REPORT: 10:00 A.M. on July 23, 2007

TIME/DATE OF THE NEXT REPORT: 1:00 P.M. on July 24, 2007

TYPE/AMOUNT OF PRODUCT SPILLED: The volume of the diesel spilled is unknown. The operator of the F/V Nordic Viking reported that at least one tank containing 3,500 gallons had been breached. Eight addition fuel tanks are on board the vessel containing an estimated 11,500 gallons at risk.

LOCATION: Near Olsen Bay in Point Gravina, Prince William Sound, Alaska at a location of 40° 42' Latitude 146° 11' Longitude. Approximately 55 miles SW of Valdez

CAUSE OF SPILL: The cause of the grounding is under investigation by the Coast Guard

POTENTIAL RESPONSIBLE PARTY (PRP): Bill Prout, Northern Seiners Inc.

RESPONSE ACTION: The operator and crew of the F/V Nordic Viking were rescued by the F/V Procession with no reported injuries. The vessel owner has contracted Alaska CHADUX a spill response contractor out of Anchorage and the landing craft Alaska Challenger from Valdez to assist with the spill cleanup and removal and any remaining fuel on board the F/V Nordic Viking.

The US Coast Guard and ADEC established an Incident Management Team at the Marine Safety Unit in Valdez.

At 1:30 P.M. on July 22, 2007 a Coast Guard Helicopter with an ADEC responder on board reported a sheen 5 miles long by 200 foot wide. Later at 5:50 P.M. it was reported to the Coast Guard that the vessel had been boomed off and the fuel leak had appeared to have stopped. Response contractors continue to remove any fuel inside the containment boom. The Department of Fish and Game also closed the commercial salmon fishery for the Port Gravina area.

SOURCE CONTROL: F/V Nordic Viking has been boomed off and preparations are being made to remove any remaining fuel on board the vessel.

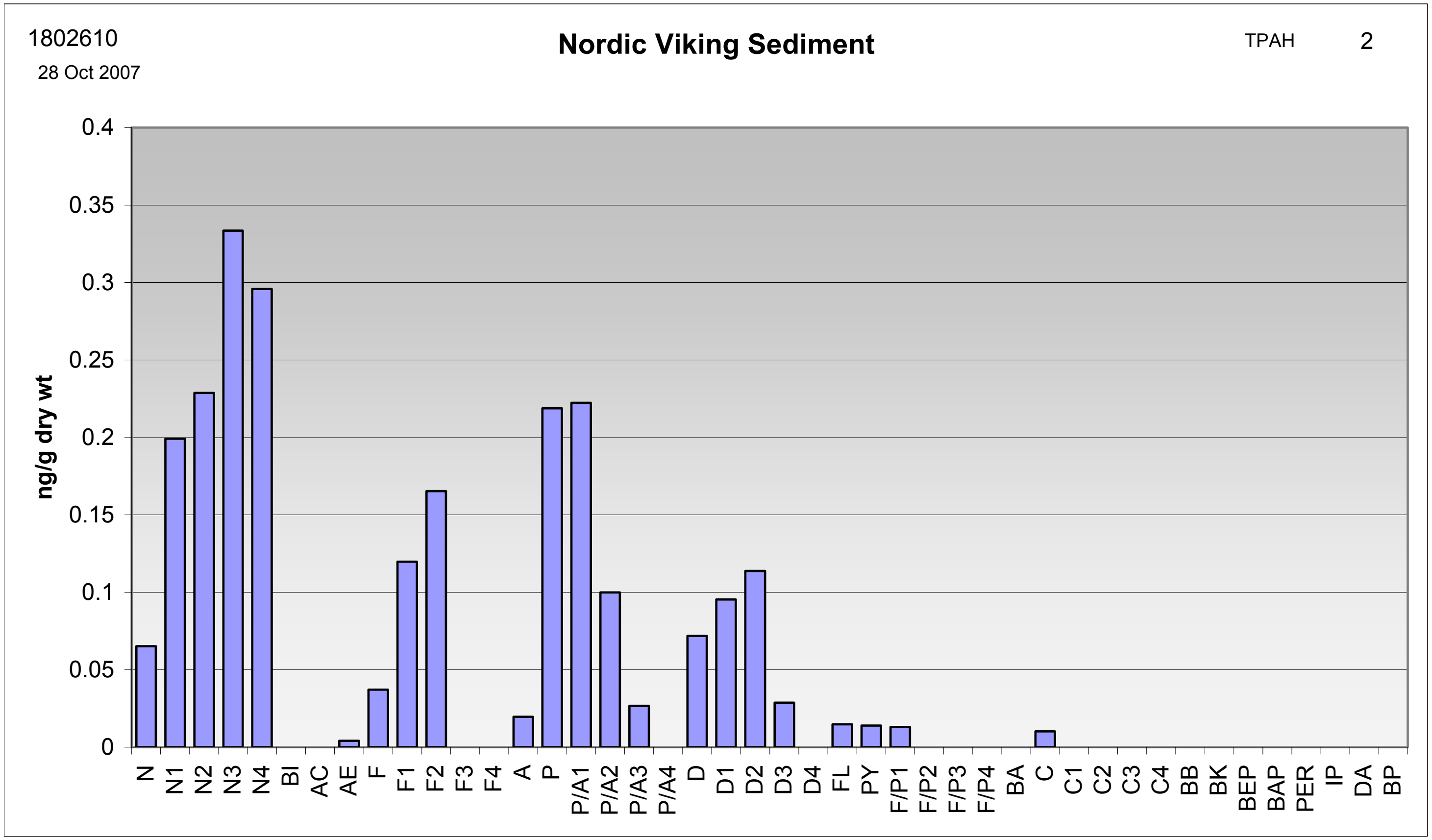
RESOURCES AFFECTED: Marine waters of Port Gravina and Olson Bay. Several purse seine fishing vessels were seen fishing in the vicinity of the oil spill on July 22, 2007.

FUTURE PLANS AND RECOMMENDATIONS: Response contractor will continue to manage the boom around the vessel and recover any fuel released from the vessel. Open water cleanup tactics will be used today to recover fuel in open waters. The Alaska Challenger will support the removal of any remaining on board the vessel and assist with the vessel's salvage. Shoreline and beaches in the spill area will be examined for any fuel impacts, and cleanup plans will be developed if needed.

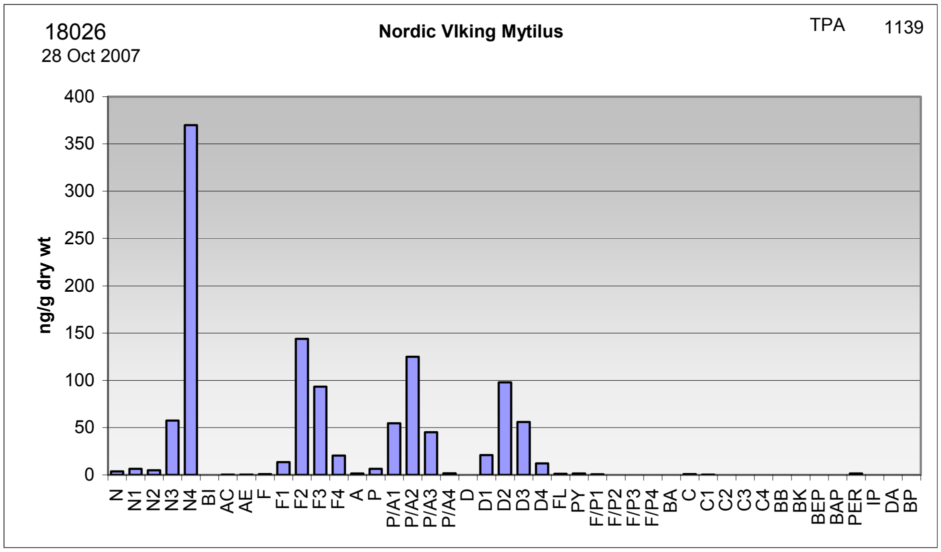
WEATHER: Cloudy, rain, areas of fog, highs in the mid 50s, with variable winds 15 MPH or less.

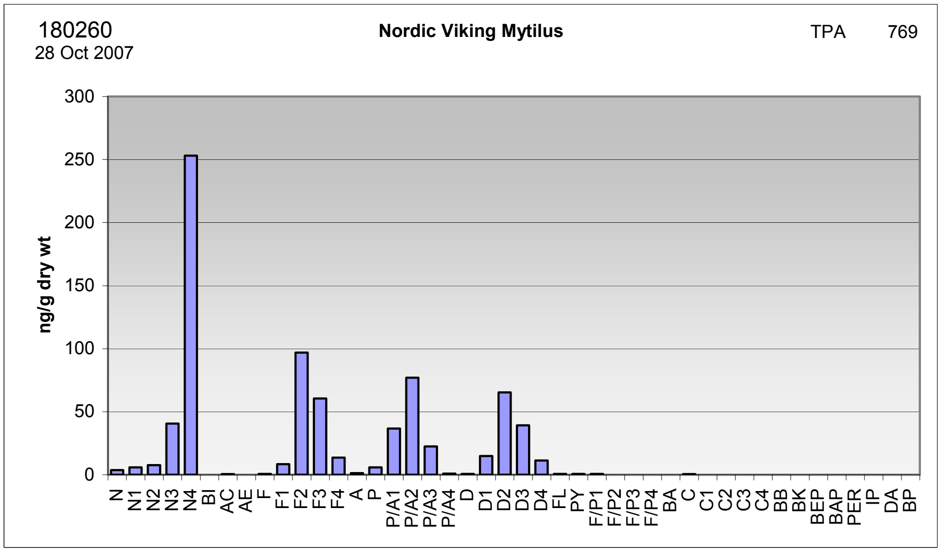
Upper image showing sheen escaping from grounding site on or about 21 July 2007; sampling site is near upper-left corner of image. Lower image shows oil-bearing sediments at sampling site, 31 July 2008. This location was sampled in October.

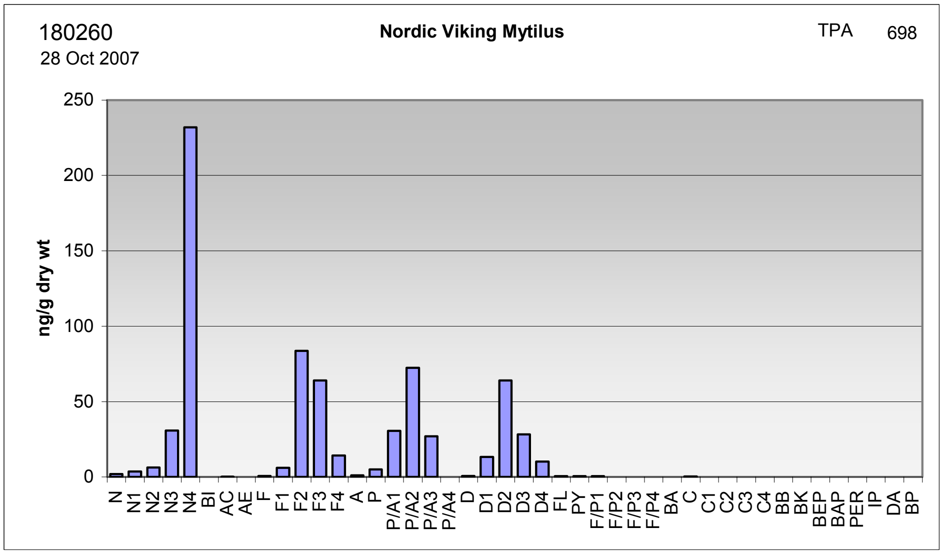

Survey stream
Nordic Viking grounding
Knowles Head
Gravina Island



1802610
28 Oct 2007
Nordic Viking Sediment
TPAH
2
ng/g dry wt
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
N
N1
N2
N3
N4
BI
AC
AE
F
F1
F2
F3
F4
A
P
P/A1
P/A2
P/A3
P/A4
D
D1
D2
D3
D4
FL
PY
F/P1
F/P2
F/P3
F/P4
BA
C
C1
C2
C3
C4
BB
BK
BEP
BAP
PER
IP
DA
BP


18026
28 Oct 2007
Nordic VIking Mytilus
TPA 1139


180260
28 Oct 2007
Nordic Viking Mytilus
TPA 769


180260
28 Oct 2007
Nordic Viking Mytilus
TPA 698