Prince William Sound
Regional Citizens' Advisory Council

Assessing Transport and Exposure Pathways and Potential Petroleum Toxicity to Marine Resources in Port Valdez, Alaska

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ABSTRACT

Review of the data from a long-term hydrocarbon-monitoring program at the Alyeska Marine Terminal and a nearby control site suggests Alaska North Slope (ANS) crude oil residues from the terminal's ballast water treatment plant (BWTP) have accumulated in the intertidal mussels within the port. Fortunately, the polynuclear aromatic hydrocarbon (PAH) and saturated hydrocarbon (SHC) levels measured in sediments and mussel tissues and the estimated water-column levels are low and unlikely to cause deleterious effects. From the signature of analytes, we 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 suggest a surface microlayer mechanism may be responsible for seasonal transport of ANS weathered oil residues from the BWTP diffuser to intertidal zones to the north and west of the terminal. The possibility of concentrated contaminants in a surface microlayer combined with the potential for photoenhanced toxicity should be considered in future investigations of potential impacts in Port Valdez.

INTRODUCTION

In the aftermath of the *Exxon Valdez* oil spill (EVOS), the 1990 Oil Pollution Act mandated the formation of the Prince William Sound Regional Citizens' Advisory Council (PWS RCAC) whose duties have included conducting a Long-Term Environmental Monitoring Program (LTEMP) at selected sites throughout Prince William Sound and the nearby Gulf of Alaska since 1993. The program is similar to the National Oceanic and Atmospheric Administration (NOAA) Mussel Watch program including seasonal sampling (March and July) and analyses of intertidal mussels (*Mytilus trossulus*) and marine sediments for polynuclear aromatic hydrocarbons (PAH) and saturated hydrocarbons (SHC), along with a number of biological, physical, and chemical parameters.

This report focuses on LTEMP monitoring within Port Valdez, site of the tanker terminal for the Alaska oil pipeline and the only location in the regional program where slightly elevated hydrocarbon levels are chronically observed. We integrate the Port Valdez LTEMP monitoring results with data from other studies to provide a synthesis on the current levels of hydrocarbon contamination within the Port with the following objectives:

- To document any temporal and geographic trends in hydrocarbon composition and concentration;
- To compare measured total PAH (TPAH) levels in mussels against concentrations known to cause effects (e.g., changes in Scope for Growth) within bivalve populations;
- To compare measured TPAH concentrations in sediments against published screening values that represent threshold concentrations for adverse effects;
- To determine if there are risks to selected sensitive pelagic species of fish from water column or food chain exposures from petroleum discharges;
- To identify sources, events, and transport mechanisms within the Port to explain any temporal and/or geographic trends; and
- To provide recommendations and suggestions for future research efforts in the Port and on how the LTEMP surveys might be modified to capitalize on the findings and conclusions from this review.

Unfortunately, there are no directly-measured PAH exposure values for any biota other than mussels in the Port Valdez environs. Therefore, it is necessary to use water, sediment, and mussels as secondary indicators to estimate what potential water-column or intertidal exposures might be encountered by species of interest. Background information and available data that were reviewed and analyzed included:

- Mussel and sediment PAH and SHC data in the 1993-2000 LTEMP reports and database for the Port Valdez sampling sites at the Alyeska Marine Terminal (AMT) and Gold Creek (GOC) (Figure 1),
- Mussel and water data from RCAC's 2001 Ballast Water Treatment Plant (BWTP) Mixing Zone Study (Salazar et al. 2001), and
- Numerous marine pollution reports from other projects published in the open literature and agency reports including EVOS Trustee Studies and Alyeska's Monitoring Program.

Mussels have long been used as sentinels to monitor coastal ocean pollution because they filter large volumes of water and accumulate both inorganic and organic pollutants. However, since the exposure routes, as well as the rate and extent of PAH uptake are likely different in other species, the level of mussel tissue contamination can only be used as a secondary indicator of exposure. In this study, direct impacts to mussels were evaluated by assessing growth and survival in the field, as well as comparing accumulated residues to literature toxicity values. Petroleum risks were assessed on the basis of total PAH tissue burdens because: the toxicity of ANS to Alaskan species has not been attributable to single PAH compounds or specific homologue groups, TPAH screening values for ANS are readily available, and PAH mixtures may act additively or synergistically (Swartz 1999; Mazet et al. 2001). In undertaking this data analysis and toxicity evaluation, we have evaluated the LTEMP mussel-indicator approach, and concluded that while mussels can certainly document the presence and magnitude of

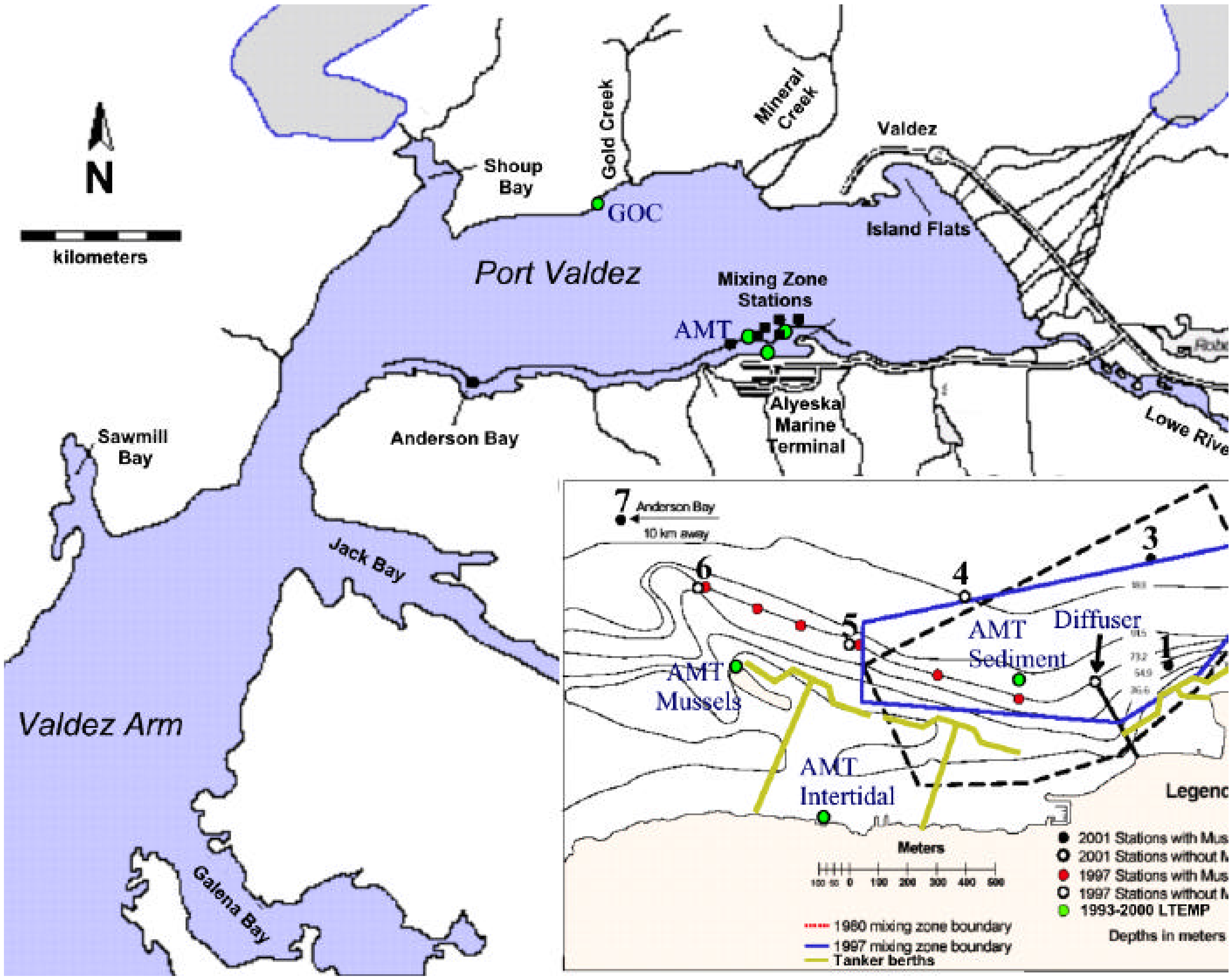


Figure 1. Map of LTEMP and BWTP Mixing Zone stations in Port Valdez. (adapted from Salazar et al. 2001 and KLI 2000)

petroleum hydrocarbon exposure, extreme care should be utilized in attempting to extrapolate the results to other species or to imply precise water-borne concentrations.

To determine if the chronic hydrocarbon levels observed within the Port are potentially detrimental to selected sensitive and commercially important species, we focused on Pacific herring (*Clupea pallasi*) and pink salmon (*Onchorhynchus gorbuscha*) because the eggs and larvae of these species have been shown to be sensitive to PAH contamination in the intertidal zone (Carls, et al. 1999; Heintz et al. 1999; White et al. 1999; Heintz et al. 1995; Marty et al. 1997; Murphy et al. 1999; Bue et al., 1998; Rice et al. 2000; and Roy et al. 1999). While herring do not currently utilize the eastern areas of Port Valdez for spawning, juveniles are found in the area by midsummer (Norcross et al. 1996). Furthermore, because the effects of petrogenic PAHs on egg and larval development are well documented, herring are used here as a surrogate species to conservatively estimate effects on other organisms for which there are only limited data. Pink salmon, on the other hand, do utilize several intertidal streams within the Port for spawning, so comparisons of expected exposure concentrations to measured effects concentrations are directly relevant.

Within the limits of available data, this report incorporates all available information to assess potential impacts to intertidal mussels, benthic invertebrates, and pelagic fish. In doing so, we have found important distinctions in chronic oil transport and exposure pathways and identified data gaps for future monitoring and regulation.

Prior to this report, petroleum pollution sources were known to disperse and partition into water-dissolved and particulate (droplet) phases (Payne and McNabb, Jr. 1984; NRC 1985; Payne et al. 1983, 1984, 1991a,b,c; Payne and Driskell 1999). With the combination of the datasets listed above, we have been able to identify not only the Alaska North Slope crude signature in Port Valdez mussel tissue and sediments, but we have also constructed a cogent scenario linking the partition phases from effluent output to seasonal uptake in mussels and eggs, including possible transport mechanisms.

MATERIALS AND METHODS

Chemistry Assessment

Data on PAH and SHC concentrations within the port came primarily from two sources:

1. Mussel and sediment samples from LTEMP stations AMT and GOC, analyzed as part of the 1993-2000 program (KLI 1994a,b; 1995; 1996; 1997a,b; 1998; 1999; and 2000), and
2. Mussel and water samples analyzed as part of the RCAC's 2001 BWTP Mixing Zone Study (Salazar et al. 2001).

Additional data on mussel tissues and herring eggs from EVOS Trustee studies in 1989-1991 on Naked Island were extracted from the Trustee's database. We also reviewed mussel and sediment data from Alyeska's Monitoring Program (Feder and Shaw 1996) and found it intriguing but unusable for our purposes because it reported only a limited suite of PAHs (i.e., 17 of the 43 analytes considered in LTEMP). The data would have required a significant effort beyond the scope of this report to verify and incorporate into our data interpretation.

From the LTEMP data, we reviewed samples from the Alyeska Marine Terminal (AMT) station and Gold Creek (GOC) stations. According to the LTEMP sample design, the AMT station was sited near the vicinity of the BWTP outfall (Figure 1) to assess possible contamination from daily terminal operations or vessels utilizing the terminal (KLI 1994a). AMT sediments are sampled within the mixing zone at approximately 80 m water depth. This station also replicates an earlier Alyeska monitoring station D-51 as identified in the National Pollutant Discharge Elimination System Permit (U.S. EPA 1989; Feder et al. 2001). The AMT mussel collection site is located on the northeastern side of Saw Island.

The GOC station was selected as a Port Valdez control site due to its physical distance from AMT and tanker operations, and because it, too, had been sampled as part of the AMT permit program in the past (KLI 1994a). At the time of its initial selection, prior studies had indicated that sediments over 1 km from the discharge had remained unaffected (Shaw et al. 1985; KLI 1994a); GOC was 6 km away. Subtidal sediments are collected at approximately 30 m water depth, while the GOC intertidal mussel-collection station is located north of the break in the east-west trending shoreline (Figure 1).

In addition to LTEMP seasonal sampling activities, special event samplings were taken at the terminal following the *T/V Eastern Lion* oil spill in May 1994 and a BWTP spill in January 1997. Reports of the monitoring are prepared each year by Kinnetic Laboratories, Inc. (KLI 1994a,b,c; 1996; 1997a,b; 1998; 1999; and 2000). Additionally, an overall program evaluation and data analysis/synthesis was completed by Payne et al. (1998) and is available online along with the recent annual reports at *www.pwsrcac.org*.

In 1997, a pilot-scale caged-mussel program was successfully deployed in the vicinity of the mixing zone surrounding the offshore diffuser for the Alyeska BWTP (Applied Biomonitoring 1999). In 2001, a fully integrated study was conducted utilizing caged mussel samples, discrete dissolved- and particulate-phase water samples, and passive plastic-membrane devices (the 2001 BWTP Mixing Zone Study, Salazar et al. 2001). These data proved invaluable in delineating exposure pathways. The report is also available online at the PWS RCAC web site.

Additional small datasets were also reviewed. Alyeska sediment monitoring data (2000) were graciously provided as spreadsheets directly from Alyeska. Mussel tissue results (ending in 1995) were obtained from annual reports. Data from the EVOS Fish/Shellfish Impacts Study were retrieved from the EVOS Trustee Hydrocarbon Database, EVTHD (available at *www.afsc.noaa.gov/abl/OilSpill/evthd.htm*).

Typically, the chemistry data were compiled and histogram plots of PAH and SHC were generated for tissues and sediments from individual stations. These plots were used for fingerprint analyses of source signatures, weathering patterns, and identification of dissolved versus particulate (oil-droplet) phases. Temporal trends of hydrocarbon contamination in tissues and sediments were evaluated for each station by time-series plots of total PAH (TPAH), CRUDE Index, and Mytilus Petrogenic Index values (Payne et al. 1998). Target analytes utilized in all of the PWS RCAC programs are listed in Table 1, and include parent and alkyl-substituted PAH from naphthalene through benzo(g,h,i)perylene, as well as saturated hydrocarbons (SHC), which included n-alkanes n-C10 through n-C34 plus pristane and phytane. Abbreviations utilized to designate individual PAH in all the figures and histogram plots utilized in the paper are also shown in the table.

Table 1 List of Analytes, Chemical Abbreviations and Laboratory Datasets

		Laboratory Datasets		
Analytes	**Abbreviation**	**KLI (GERG)**	**NMFS Auke Bay**	**Alyeska (UAF)**
PAH				
Naphthalene	N	x	x	x
C1-Naphthalene	N1	x	x	x
C2-Naphthalene	N2	x	x	x
C3-Naphthalene	N3	x	x	
C4-Naphthalene	N4	x	x	
Biphenyl	BI	x	x	x
Acenaphthylene	AC	x	x	
Acenaphthene	AE	x	x	x
Fluorene	F	x	x	
C1-Fluorenes	F1	x	x	
C2-Fluorenes	F2	x	x	
C3-Fluorenes	F3	x	x	
Dibenzothiophene	D	x	x	
C1-Dibenzothiophene	D1	x	x	
C2-Dibenzothiophene	D2	x	x	
C3-Dibenzothiophene	D3	x	x	
C4-Dibenzothiophene	D4			
Anthracene	A	x	x	x
Phenanthrene	P	x	x	x
C1-Phenanthrene/Anthracene	P/A1	x	x	x
C2-Phenanthrene/Anthracene	P/A2	x	x	
C3-Phenanthrene/Anthracene	P/A3	x	x	
C4-Phenanthrene/Anthracene	P/A4	x	x	
Fluoranthene	FL	x	x	x
Pyrene	PYR	x	x	x
C1-Fluoranthene/Pyrene	F/P1	x	x	
C2-Fluoranthene/Pyrene	F/P2			
C3-Fluoranthene/Pyrene	F/P3			
C4-Fluoranthene/Pyrene	F/P4			
Benzo(a)Anthracene	BA	x	x	x
Chrysene	C	x	x	x
C1-Chrysenes	C1	x	x	
C2-Chrysenes	C2	x	x	
C3-Chrysenes	C3	x	x	
C4-Chrysenes	C4	x	x	
Benzo(b)fluoranthene	BB	x	x	
Benzo(k)fluoranthene	BK	x	x	
Benzo(e)pyrene	BEP	x	x	

Benzo(a)pyrene	BAP	x	x	x
Perylene	PER	x	x	x
Indeno(1,2,3-cd)pyrene	IP	x	x	
Dibenzo(a,h)anthracene	DA	x	x	x
Benzo(g,h,i)perylene	BP	x	x	
Total PAH	TPAH	x	x	x
n-Alkanes				
n-Octane (C8)	C8			
n-Nonane (C9)	C9			
n-Decane (C10)	C10	x	x	
n-Undecane (C11)	C11	x	x	
n-Dodecane (C12)	C12	x	x	
n-Tridecane (C13)	C13	x	x	
n-Tetradecane (C14)	C14	x	x	
n-Pentadecane (C15)	C15	x	x	
n-Hexadecane (C16)	C16	x	x	
n-Heptadecane (C17)	C17	x	x	
Pristane	Pristane	x	x	
n-Octadecane (C18)	C18	x	x	
Phytane	Phytane	x	x	
n-Nonadecane (C19)	C19	x	x	
n-Eicosane (C20)	C20	x	x	
n-Heneicosane (C21)	C21	x	x	
n-Docosane (C22)	C22	x	x	
n-Tricosane (C23)	C23	x	x	
n-Tetracosane (C24)	C24	x	x	
n-Pentacosane (C25)	C25	x	x	
n-Hexacosane (C26)	C26	x	x	
n-Heptacosane (C27)	C27	x	x	
n-Octacosane (C28)	C28	x	x	
n-Nonacosane (C29)	C29	x	x	
n-Triacontane (C30)	C30	x	x	
n-Hentriacontane (C31)	C31	x		
n-Dotriacontane (C32)	C32	x	x	
n-Tritriacontane (C33)	C33	x		
n-Tetratriacontane (C34)	C34	x	x	
n-Pentatriacontane (C35)	C35			
n-Hexatriacontane (C36)	C36			
n-Heptatriacontane (C37)	C37			
n-Octatriacontane (C38)	C38			
n-Nonatriacontane (C39)	C39			
n-Tetracontane (C40)	C40			
Total n-Alkanes	TALK	x	x	

Mussel Tissue Residue Assessment

For mussels, a tissue residue assessment was conducted using tissue chemistry data from LTEMP (Payne et al. 1998; KLI 2000) and the 2001 BWTP Mixing Zone Study (Salazar et al. 2001). These values were compared with the lowest observed effects concentration (LOEC) measured for mussels in other studies using scope for growth as the measured effects endpoint (Widdows and Donkin 1992). Figure 2 is a summary of a variety of laboratory, mesocosm, and field studies conducted by Widdows and his colleagues over a number of years. Based on scope for growth criteria, no or low stress in mussels is

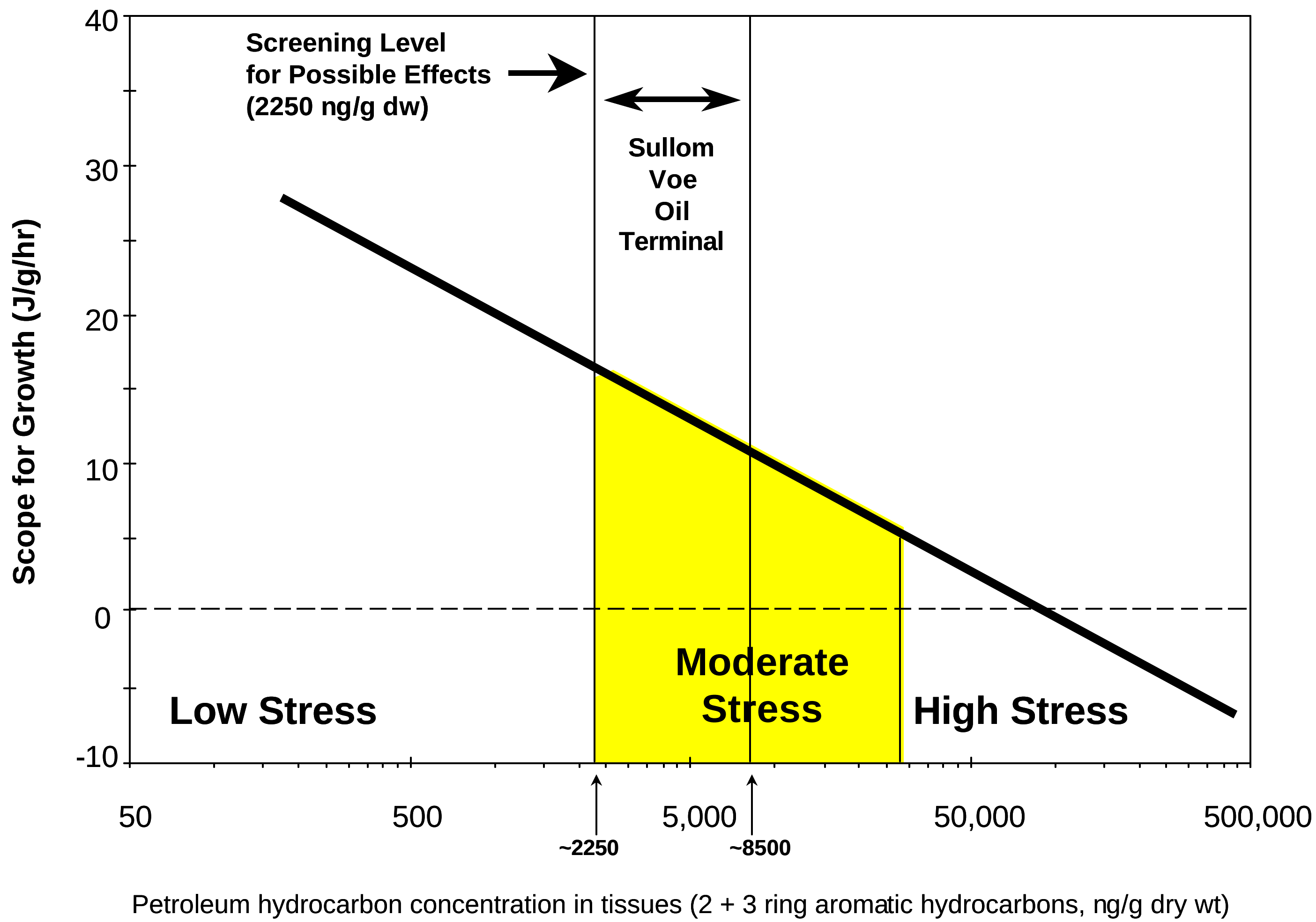


Figure 2. Effects of petroleum hydrocarbons on Scope for Growth in mussels (from Widdows and Donkin 1992).

predicted to occur up to approximately 2,250 ng/g dry wt., moderate stress between 2,500 and 25,000 ng/g dry wt. and high stress above 25,000 ng/g dry wt. As part of the validation of similar exposures and similar effects occurring in similar environments, this figure shows that mussel tissue concentrations between 2,250 and about 8,500 ng/g dry wt. were measured at the Sullom Voe Oil Terminal and that these concentrations were associated with moderate stress on the low to middle range of the effects scale.

Thus, the total PAH concentration of 2,250 ng/g-dry wt. was initially selected for this project as the screening level for possible chronic sublethal effects in mussels. However, in a more recent study, O'Connor (in press) has concluded that scope-for-growth effects might be observed at concentrations as low as 750 ng/g dry weight. Unfortunately, the value was based on UV fluorescence data from HPLC analyses (Widdows et al., 1995), which are not directly comparable with the LTEMP GC/MS results. While O'Connor (in press) now apparently accepts the lower 750 ng/g dry wt. value as the initial effects level for the NOAA Status and Trends (Mussel Watch) data, here again, it is not clear that the effect point is directly comparable to the LTEMP data. The NOAA Mussel Watch analyte list includes only 24 PAH in the total PAH value, whereas, the LTEMP sums 43 PAH analytes to generate a TPAH value. As a result of these uncertainties, we continue to use the original scope-for-growth cutoff of 2,250 ng/g dry wt. in this report. As will be shown below, however, the distinction between the two values becomes moot, because the majority of the mussel tissue burdens (with a few notable exceptions discussed below) in both the LTEMP and the 2001 BWTP Mixing Zone Study samples are below 500 ng/g dry wt.

Benthic Assessment

The focus of the benthic assessment was to identify potential impacts to infaunal assemblages that reside in intertidal and shallow subtidal sediments based on available information on sediment concentrations of TPAH available from the monitoring programs. Moreover, this assessment attempted to identify other exposure routes and mechanisms of toxicity that could impact the biota (e.g., surface microlayer accumulations or photoenhanced toxicity in intertidal habitats).

The assessment involved three different elements.

1. Examine the NOAA ERL's and EPA's ECOTOX AQUIRE database for data on chronic effects on marine species from PAH exposure. The purpose was to derive screening toxicity values for infaunal invertebrates.
2. Review recent literature on the long-term impacts from petroleum hydrocarbons.
3. Identify intertidal and shallow subtidal infaunal species subject to impact in Port Valdez that could be used to supplement the mussel sampling programs.

Pelagic Assessment -- Herring and Salmon

Potential impacts of petroleum contamination in Port Valdez, Alaska to pelagic fish species were assessed from three potential exposure pathways: contact with surface water, uptake of aqueous phase petroleum in planktonic prey, and uptake of petroleum in sediment by epibenthic invertebrate prey. We used a probabilistic assessment of risks focused on Pacific herring (*Clupea pallasi*) and pink salmon (*Onchorhynchus gorbusha*) because of the known sensitivity of these species, their ecological and economic importance in Prince William Sound, and the availability of species-specific toxicity and bioaccumulation information for Alaska North Slope (ANS) crude oil. The sediment to fish pathway was assessed because of the potential for chum salmon fry to feed on epibenthic invertebrates such as harpacticoid zooplankton during their early life stages (Sibert et al. 1977).

Our analysis also incorporated toxicity thresholds determined under ultraviolet radiation (UV) because of the potential for photoenhanced toxicity of petroleum in Prince William Sound (PWS) (Barron and Ka'aihue 2001). ANS crude oil was determined to be greater than 100 times more toxic to shrimp and bivalve embryos when tested under the UV present in aquatic environments, compared to existing toxicity values determined under laboratory light (Pelletier et al. 1997). Also, recent studies with two species of marine copepod zooplankton demonstrate that weathered ANS crude oil is extremely phototoxic (Duesterloh et al., in review).

A probabilistic screening level assessment of risks of petroleum in pelagic species was performed using Latin Hypercube sampling with @Risk software (Palasade Corp., NY) and a simple risk model:

(1) HQ= [exposure]/[screening value]

Probability distributions of Hazard Quotients (HQ) were determined by varying both exposure and the screening values. Concentrations of aqueous phase petroleum (as TPAH) were determined from the 2001 BWTP Mixing Zone Study (Salazar et al., 2001). These data were obtained using high volume water samplers that exclude particulate oil greater than 0.7 µm and are believed to be extremely conservative (protective of the environment) because sampling occurred within and around the perimeter of the mixing zone adjacent to the Alyeska Marine Terminal (AMT). As a result, they are likely to be higher than at any other location within the Port. Sediment concentrations were determined from year 2000 subtidal sampling near Gold Creek and the AMT (KLI, 2000). Concentrations of TPAH in pelagic prey were determined from the probability distribution of TPAH in water and the bioaccumulation factor of TPAH in the marine calanoid zooplankton *Calanus marshallae* (Deusterloh et al., in review) (Table 2).

Table 2. Exposure parameters for assessing risks to pelagic species.

Impacted Media	Concentration range	Exposure Route	BAF	Prey Concentration (mg/kg)
surface water	0.0045 - 0.037[1] (µg/L)	direct contact	--[3]	--[3]
		prey uptake	8000[4]	0.04 - 0.29[6]
sediment	0.11 - 1.5[2] (mg/kg)	prey uptake	model estimated[5]	0.002 - 4.9[7]

1. Minimum and maximum concentrations at most shallow depth (30 m) in Salazar et al., (2001). Triangular statistical distribution (4.5, 17.2, 36.8 ng/L) used in risk modeling.
2. Range of most recent (2000) mean sediment TPAH concentrations at subtidal sampling stations at Gold Creek and the Alyeska Marine Terminal (KL, 2000). Uniform distribution of minimum and maximum values used in risk modeling.
3. Not applicable.
4. Maximum (wet weight basis) for bioconcentration of TPAH by *C. marshallae* exposed to weathered ANS for 24 hours (Deusterloh et al., in review).
5. Determined using Equation 2 (see text).
6. Calculated from maximum water concentration and maximum BAF.
7. Estimated from Latin Hypercube sampling of distribution of sediment concentrations and BAFs.

A simple bioaccumulation model was used to estimate TPAH concentrations in epibenthic invertebrates that may be preyed upon by salmon fry, because of the absence of site- and species-specific bioaccumulation factors:

$$(2) \qquad C_{prey} = [BSAF*(L_{biota}/OC_{sed})*C_{sed}]*DW$$

The TPAH concentration in prey (C_{prey}) was estimated from the biota to sediment accumulation factor (BSAF; lipid and OC normalized), ratio of lipid and OC fractions (L_{biota}/OC_{sed}), concentration in the sediment (C_{sed}), and a dry weight to wet weight conversion (DW = 0.2). C_{prey} was estimated using Latin Hypercube sampling, a triangular distribution (1, 2, 4) of L_{biota}/OC_{sed}, and a triangular distribution (0.04, 1, 8) of BSAF. Literature values for the BSAFs of PAHs ranged from 0.04 to 8, and BSAFs should equal 1 based on equilibrium partitioning theory (Lake 1990; Lotufo 1998; Gewurtz et al. 2000; van Hoof et al. 2001). The DW conversion puts prey concentrations estimated from sediment concentrations (mg/kg sediment dry weight.) on wet weight basis.

A uniform distribution of no observed effect concentrations (NOEC) and lowest observed effect concentrations (LOEC) was used as the screening value in the risk model (Table 3). NOECs and LOECs were determined from the most sensitive response measured in aqueous phase studies with herring eggs (Carls et al. 1999) and dietary studies with pink salmon (Carls et al. 1996) (Table 2). NOECs and LOECs for photoenhanced toxicity were derived from studies of weathered ANS toxicity to herring larvae (Barron et al. unpublished).

Table 3. Risk screening values for herring and pink salmon.

Receptor	Exposure Route	NOEC	LOEC	Source
herring eggs	water	1.8 µg/L	9.1 µg/L	Carls et al. (1999)[1]
herring larvae	water	0.7 µg/L	8 µg/L	Barron et al. (unpublished)[2]
pink salmon	diet	1 mg/kg	13 mg/kg	Carls et al. (1996)[3]

1. Aqueous TPAH threshold for less weathered ANS (>40% naphthalenes) from Carls et al. (1999): resulted in elevated yolk sac edema, but not increased mortality and morbidity (16 d exposure).
2. Values for herring larvae are photoenhanced toxicity thresholds based on preliminary results of Barron and coworkers.
3. Range of dietary NOEC and LOEC from Carls et al. (1996): 8 wk feeding study using fresh ANS crude oil with growth as most sensitive measured response.

RESULTS

Trends in Hydrocarbon Contamination in Water and Mussel Samples From the BWTP Mixing Zone Study

Results from the RCAC's recently completed BWTP Mixing Zone Study (Salazar et al. 2001) were instrumental in providing a fuller perspective of the fate of the BWTP effluent. The LTEMP program has for years tracked the effluent's low-level ANS signature in mussel and sediment samples but elicited little information regarding the uptake processes. Finally, the BWTP study unequivocally demonstrates the weathered signature and partitioning between the dissolved and particulate phases and clarifies the observed patterns of hydrocarbons in tissue and sediment samples.

In the BWTP Mixing Zone Study, two 3.8 L (whole water) grab samples of the BWTP effluent were collected from the pump room before discharge and analyzed for hydrocarbon content. Figure 3 shows the PAH and SHC profiles obtained on those samples along with the filtered water column sample collected at a depth of 200 feet from Station 1 near the diffuser within the mixing zone on 28 April 2001. The raw BWTP effluent contained total PAH at an average concentration of 38 µg/L (ppb), and from the PAH and SHC profiles, it is evident that moderately weathered hydrocarbons are present in both the dissolved and particulate phases. Each of the PAH homologue groups (naphthalenes, fluorenes, dibenzothiophenes, phenanthrenes/anthracenes, etc.) has a significant "water-washed" pattern, with the parent PAH absent or << than the C-1 < C-2 <C-3 alkylated homologues due to weathering during the ballast-water treatment process (Short and Heintz 1997). Naphthalene and C-1 alkylated naphthalenes were almost completely lost from the both samples, implying nearly complete losses of monocyclic aromatic compounds as well. Most of the PAH found in the BWTP effluent samples were likely present as dissolved constituents, with the remainder present as dispersed microdroplets of whole oil. The presence of some dispersed oil droplets are indicated by the relatively uniform pattern of n-alkanes shown in the figure. The preferential losses of the lower molecular weight alkanes compared to fresh ANS oil (Short et al. 1996) is consistent with the preferential losses of the lower molecular-weight PAH and all of the monocyclic aromatic hydrocarbons. Based on the relative abundance of phytane compared to the total PAH, it was estimated that the majority of the PAH was contained in the dissolved phase, with discrete oil droplets accounting for only 10-20 percent of the total PAH in the effluent (Salazar et al. 2001).

The discrete 3.0 L filtered sample (water only, no particulates) collected from the water column within the mixing zone (shown on the right in Figure 3) had the highest overall total dissolved-phase PAH concentration of all the water column samples collected during the program; however, none of the n-alkanes measured in the raw BWTP effluent sample were observed in the water-column sample. The absence of n-alkanes was attributed to sampling only the dissolved components that

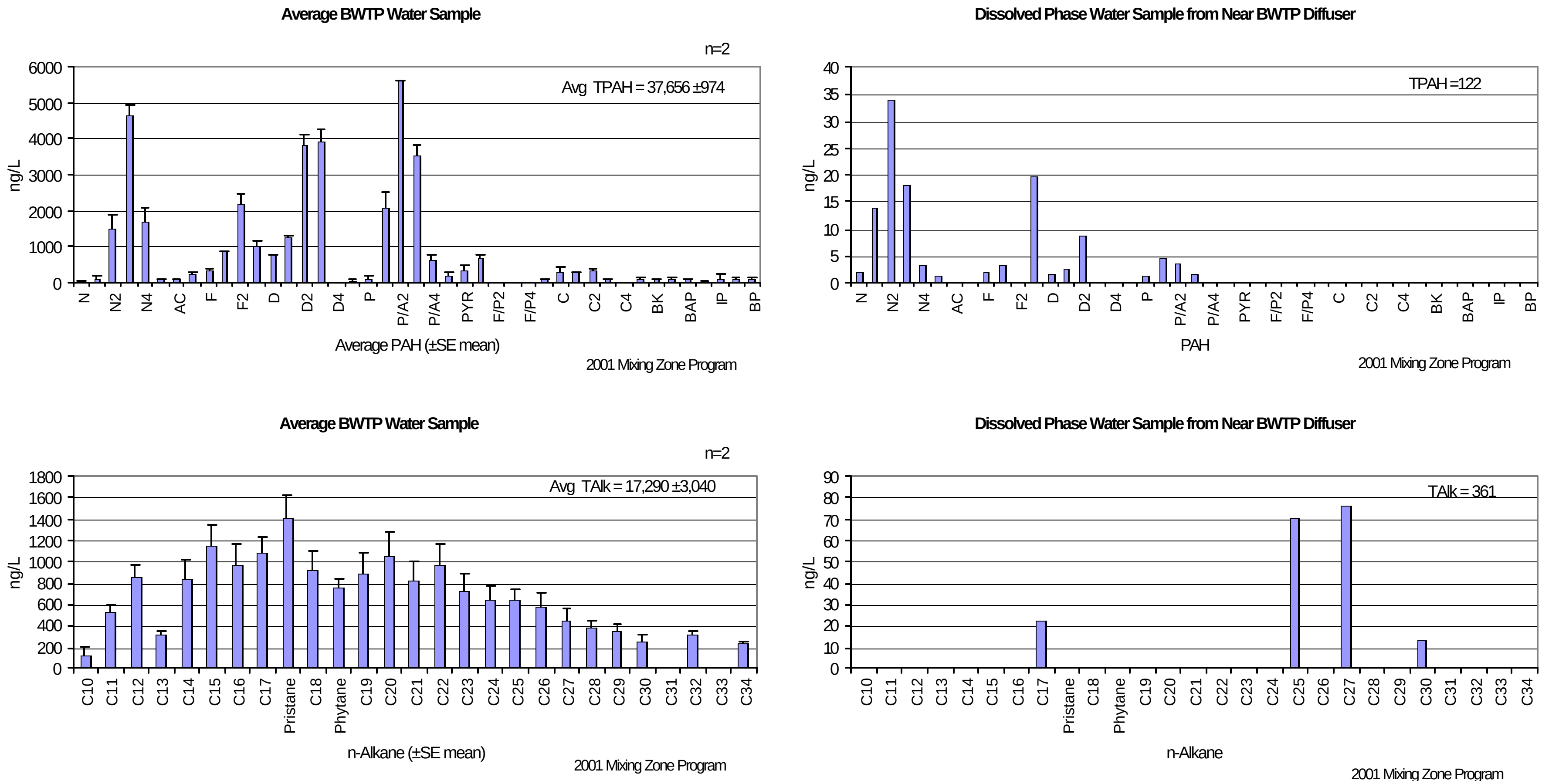


Figure 3. Average PAH and SHC histograms of raw BWTP effluent (n = 2) and the 28 April 2001 dissolved-phase 200-ft depth water sample at Station 1 near the BWTP diffuser within the mixing zone. Abbreviations for PAH and SHC components are given in Table 1. (From Salazar et al. 2001)

diffused from the edge of the effluent plume (i.e., n-alkanes are poorly soluble in water). In fact, none of the discrete 3.0 L filtered water-column samples collected during BWTF Mixing Zone Study were actually obtained within the effluent plume. As a result, the total PAH concentrations for the water-column samples obtained during that program were all extremely low (Table 4) ranging from 14 to 122 ng/L within the mixing zone (above the diffuser) and from 5 to 27 ng/L at all stations (at all depths) outside the mixing zone.

BWTP diffuser modeling studies (Woodward Clyde and ENTRIX 1987) predicted that the effluent would be expected to rise to the surface and be diluted by entraining surrounding water within the mixing zone during the winter months when the water column was not stratified. From April through late fall, however, a vertically stratified water column (Colonell 1980a,b; Colonell et al. 1988) prevents this rise to the surface, which causes the plume to spread horizontally (at a variable depth controlled by the water-column density gradient and the temperature and salinity of the effluent). During the RCAC 2001 BWTP Mixing Zone Study, water sampling depths were fixed at 100 feet, 15-20 feet above the bottom, and halfway in between. As a result, most of the water-column samples collected in February were in fact below the surface layer plume. Most of the evidence suggests that in April, the plume was somewhere between 200 and 250 feet below the surface, and the water sampling program simply missed it on the day the samples were collected. As will be discussed further below, caged mussels and plastic membrane devices (PMDs) did on some occasions during the sampling interval, intersect the plume which was characterized as a relatively thin “pancake” or “ribbon-like” layer of PAH contamination (Salazar et al. 2001).

Figure 4 presents the PAH and SHC histogram plots for two composite averages of caged mussel samples from the 2001 BWTP Mixing Zone Study. The histogram profiles presented on the left represent the mussels from the depths and stations (n = 7) that were identified as being near or within the effluent plume during the two month deployment (Station 1: 100, 150, 200, 250, and 275 feet; Station 3: 250 feet, replicates 1 and 2). These mussels show evidence of hydrocarbon accumulation in both the dissolved and particulate phase with the particulate, dispersed oil droplet phase predominating. The average TPAH concentration was 1,558 ng/g dry wt., and the PAH profile clearly shows the highly weathered, water-washed pattern of predominantly higher molecular weight components (phenanthrenes/anthracenes and chrysenes relative to the naphthalenes) characteristic of whole oil droplets. The SHC profiles show components from both biogenic (as characterized by n-C 15, n-C 17, and pristane) and petrogenic (as characterized by phytane and an homologous series of n-alkanes from n-C 20 through n-C 32) sources. The average TPAH concentration for all of the other subsurface caged mussel samples exposed primarily to the dissolved phase (n = 19) was an order of magnitude lower at 110 ng/g dry wt., and the PAH histogram profile (shown on the right) clearly shows the predominance of the more water-soluble naphthalene homologues over all of the other PAH constituents. The SHC profile for these samples shows a predominance of biogenic components with only a trace of the higher molecular weight n-alkanes associated with particulate-phase oil. These profiles clearly demonstrate the

Table 4. Total PAH (ng/L) in large-volume water samples collected during the RCAC 2001 BWTP Diffuser Study (from Salazar et al. 2001)

Sample Collected on 25 Feb 01

Depth (ft)	**Sta 1**	**Sta 2**	**Sta 3**	**Sta 4**	**Sta 5**	**Sta 6**	**Sta 7**
100	36.8	13.8	13.7 & 15.5	9.8	13.2	10.7	
150							
200	13.7				12.6		10.6
250							
300	15.3				7.2		21.6
350				4.7			
400		10	10 & 7.8				
450							
500							
550							
575				7.6			
600							
650			7.3 & 9.3				
700		12.2					

Sample Collected on 28 Apr 01

Depth (ft)	**Sta 1**	**Sta 2**	**Sta 3**	**Sta 4**	**Sta 5**	**Sta 6**	**Sta 7**
100	16.3	24.9	18.8 & 27.7	4.5	11.9	21.4	23
150							
200	121.8				10.4	22.2	21.1
250							
300	6.7				15.5	27.3	8.3
350				6.6			
400		18.6	30.7 & 4.4				
450							
500							
550							
575	5.9						
600							
650			6.4 & 9				
700		19.9					

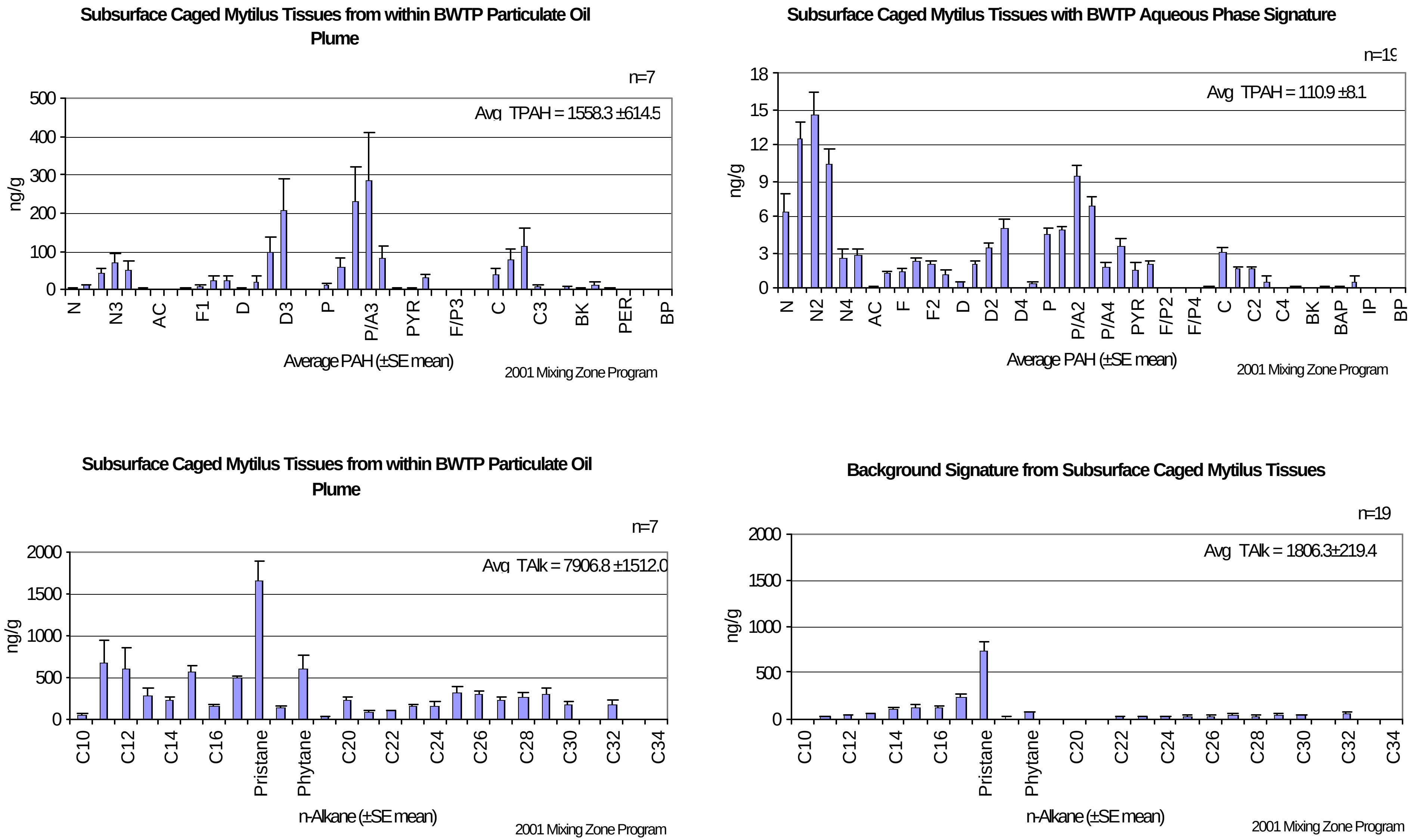


Figure 4. Average PAH and SHC histograms of subsurface caged mussels exhibiting dispersed oil droplet-phase uptake (n = 7) directly from the effluent plume and low-level dissolved-phase PAH uptake from the BWTP diffuser along with background biogenic hydrocarbons (n-alkanes) from the particulate phase (n = 19). From the RCAC 2001 Mixing Zone Study (Salazar et al. 2001). Abbreviations for PAH and SHC components are given in Table 1.

differences obtained in PAH and SHC composition when primarily particulate vs. dissolved components are accumulated by mussels. This theme is reflected again throughout the LTEMP and EVOS data sets. Significantly, these dissolved-phase TPAHvalues from samples collected around the perimeter of the mixing zone are lower in concentration than the clean (control-site) reference samples (calculated at 600 ng/g dry weight) used by Widdows et al. (1995) in their evaluation of the Sullom Voe oil terminal in the Shetland Islands. Those authors went on to state, that the measured TPAH at their control site were among the cleanest measured throughout the British Isles.

Time-Series Observations in Intertidal Mytilus Samples from the 1993-2000 LTEMP

Table 5 lists the total SHC and PAH values of individual samples, seasonal averages, and the coefficient variation for all intertidal mussel samples analyzed from Alyeska Marine Terminal (AMT) and Gold Creek (GOC). In general, the concentrations ranged from 87 ng/g dry wt. to 949 ng/g dry wt., with the exception of the mussel samples collected at AMT following the *T/V Eastern Lion* oil spill when TPAH concentrations exceeded 14,350 ng/g dry wt.

Figure 5 shows the TPAH values as a function of time, and clearly, the parallel trends in overall concentrations at the two stations can be seen. It is also apparent from the figure that concentrations in the summer are generally lower than those observed in the spring. Figure 6 presents the Mytilus Petrogenic Index (Payne et al. 1998) values obtained as a function of time. The Mytilus Petrogenic Index is very similar to the total PAH, except that petrogenic PAH components are weighted to reduce the influence of pyrogenic PAH in the total PAH value. In this way, the contribution from petroleum hydrocarbon contamination is emphasized. In both Figures 5 and 6 the standard error of means is shown for each sample average, and it is clear that the overall trends greatly exceed any variance associated with the measurements.

In attempting to determine the cause of the seasonal trends observed in the figures, we examined the PAH and SHC profiles for each sample and found that they could be differentiated into samples containing primarily dissolved- or particulate-phase oil. The small "p" and "d" shown in Figure 6 represent PAH and SHC profiles coming from primarily particulate- ("p" or oil droplet) or dissolved-phase components ("d"), respectively. The symbol "nd" is used for those samples where PAH components were either not detected (below the MDL) or the measured PAH were believed to be procedural artifacts introduced by the laboratory as discussed by Payne et al. (1998). In the summer of 1999, the overall TPAH level was elevated due to anomalously high concentrations of alkylated fluorenes at both AMT and GOC, and this is denoted by "d & fluorene." What becomes readily apparent after careful examination of Figure 6 is that the summer replicates consistently had a predominantly dissolved-phase signal while the spring replicates consistently had a predominantly particulate-phase signal. This summer versus winter distribution of dissolved versus particulate phases is highly significant (chi sq = 6.93, corrected for continuity; $p < 0.01$; Sokal and Rohlf 1969).

Table 5. Total SHC and PAH values of individual mussel samples, seasonal average and coefficient of variation at AMT and GOC stations, 1993-2000. (Concentrations in ng/g dry weight).

Date	Sample ID	Total SHC	Average	Std Dev	CV	Total PAH	Average	Std Dev	CV
Alyeska Marine Terminal Intertidal Mussel Tissues (AMT-B)									
3-Apr-1993	PWS93TIS0025	23230				376			
3-Apr-1993	PWS93TIS0026	11949				276			
3-Apr-1993	PWS93TIS0027	36982	24054	12537	52	323	325	50	15
17-Jul-1993	PWS93TIS0028	20911				193			
17-Jul-1993	PWS93TIS0029	24974				245			
17-Jul-1993	PWS93TIS0030	17548	21144	3718	18	307	248	57	23
26-Mar-1994	PWS94TIS0025	36648				790			
26-Mar-1994	PWS94TIS0026	15825				865			
26-Mar-1994	PWS94TIS0027	9818	20764	14080	68	738	797	64	8
26-May-1994	PWS94TIS0028	129848				14361			
26-May-1994	PWS94TIS0029	105153				12453			
26-May-1994	PWS94TIS0030	158900	131300	26903	20	16239	14351	1893	13
20-Jul-1994	PWS94TIS0034	12199				1212			
20-Jul-1994	PWS94TIS0035	18311				1376			
20-Jul-1994	PWS94TIS0036	23530	18013	5671	31	2154	1581	503	32
3-Apr-1995	PWS95TIS0025	11176				494			
3-Apr-1995	PWS95TIS0026	25113				646			
3-Apr-1995	PWS95TIS0027	9893	15394	8441	55	411	517	119	23
11-Jul-1995	PWS95TIS0031					79			
11-Jul-1995	PWS95TIS0032					90			
11-Jul-1995	PWS95TIS0033					93	87	7	8
16-Mar-1996	PWS96TIS0001					130			
16-Mar-1996	PWS96TIS0002					132			
16-Mar-1996	PWS96TIS0003					464	242	192	80
12-Jul-1996	PWS96TIS0031					279			
12-Jul-1996	PWS96TIS0032					240			
12-Jul-1996	PWS96TIS0033					169	229	56	24
19-Jan-1997	PWS97TIS0001					523			
19-Jan-1997	PWS97TIS0002					562			
19-Jan-1997	PWS97TIS0003					649	578	64	11
6-Mar-1997	PWS97TIS0007					578			
6-Mar-1997	PWS97TIS0008					547			
6-Mar-1997	PWS97TIS0009					622	582	38	6
14-Jul-1998	PWS98TIS0043	15432				215			
14-Jul-1998	PWS98TIS0044	13279				161			
14-Jul-1998	PWS98TIS0045	16314	15008	1561	10	142	173	38	22
18-Mar-1999	PWS99TIS0016	26121				567			
18-Mar-1999	PWS99TIS0017	29033				594			
18-Mar-1999	PWS99TIS0018	28431	27862	1537	6	502	554	47	9
1-Aug-1999	PWS99TIS0047	39582				649			
1-Aug-1999	PWS99TIS0048	56037				435			
1-Aug-1999	PWS99TIS0049	88512	61377	24898	41	799	628	183	29
26-Oct-1999	PWS99TIS0062	13802				193			
26-Oct-1999	PWS99TIS0063	16779				177			

26-Oct-1999	PWS99TIS0064	12044	14208	2393	17	472	280	166	59
5-Apr-2000	PWS00TIS0025	7040				98			
5-Apr-2000	PWS00TIS0026	10384				97			
5-Apr-2000	PWS00TIS0027	14893	10772	3941	37	187	127	51	40
Gold Creek Intertidal Mussel Tissues (GOC-B)									
19-Mar-1993	PWS93TIS0001	19918				613			
19-Mar-1993	PWS93TIS0002	44451				649			
19-Mar-1993	PWS93TIS0003	33386	32585	12286	38	591	618	29	5
25-Jul-1993	PWS93TIS0055	10391				120			
25-Jul-1993	PWS93TIS0056	13396				133			
25-Jul-1993	PWS93TIS0057	8255	10681	2583	24	128	127	7	5
26-Mar-1994	PWS94TIS0022	15520				651			
26-Mar-1994	PWS94TIS0023	20889				464			
26-Mar-1994	PWS94TIS0024	42605	26338	14341	54	532	549	95	17
20-Jul-1994	PWS94TIS0031	10023				660			
20-Jul-1994	PWS94TIS0032	10316				877			
20-Jul-1994	PWS94TIS0033	12286	10875	1231	11	798	779	110	14
3-Apr-1995	PWS95TIS0022	12640				474			
3-Apr-1995	PWS95TIS0023	14377				378			
3-Apr-1995	PWS95TIS0024	14601	13873	1073	8	1082	645	382	59
11-Jul-1995	PWS95TIS0028					71			
11-Jul-1995	PWS95TIS0029					84			
11-Jul-1995	PWS95TIS0030					78	77	6	8
16-Mar-1996	PWS96TIS0004					127			
16-Mar-1996	PWS96TIS0005					180			
16-Mar-1996	PWS96TIS0006					146	151	27	18
12-Jul-1996	PWS96TIS0028					142			
12-Jul-1996	PWS96TIS0029					75			
12-Jul-1996	PWS96TIS0030					181	133	53	40
6-Mar-1997	PWS97TIS0004					400			
6-Mar-1997	PWS97TIS0005					424			
6-Mar-1997	PWS97TIS0006					350	391	38	10
13-Jul-1998	PWS98TIS0040	23892				138			
13-Jul-1998	PWS98TIS0041	38744				157			
13-Jul-1998	PWS98TIS0042	19983	27539	9898	36	171	156	17	11
18-Mar-1999	PWS99TIS0013	12414				276			
18-Mar-1999	PWS99TIS0014	12776				267			
18-Mar-1999	PWS99TIS0015	31747	18979	11059	58	216	253	32	13
1-Aug-1999	PWS99TIS0044	371823				1116			
1-Aug-1999	PWS99TIS0045	87966				769			
1-Aug-1999	PWS99TIS0046	298656	252815	147377	58	963	949	173	18
26-Oct-1999	PWS99TIS0059	8971				198			
26-Oct-1999	PWS99TIS0060	10222				213			
26-Oct-1999	PWS99TIS0061	12419	10537	1746	17	162	191	26	14
5-Apr-2000	PWS00TIS0028	11465				151			
5-Apr-2000	PWS00TIS0029	9141				122			
5-Apr-2000	PWS00TIS0030	10572	10393	1173	11	136	136	14	11

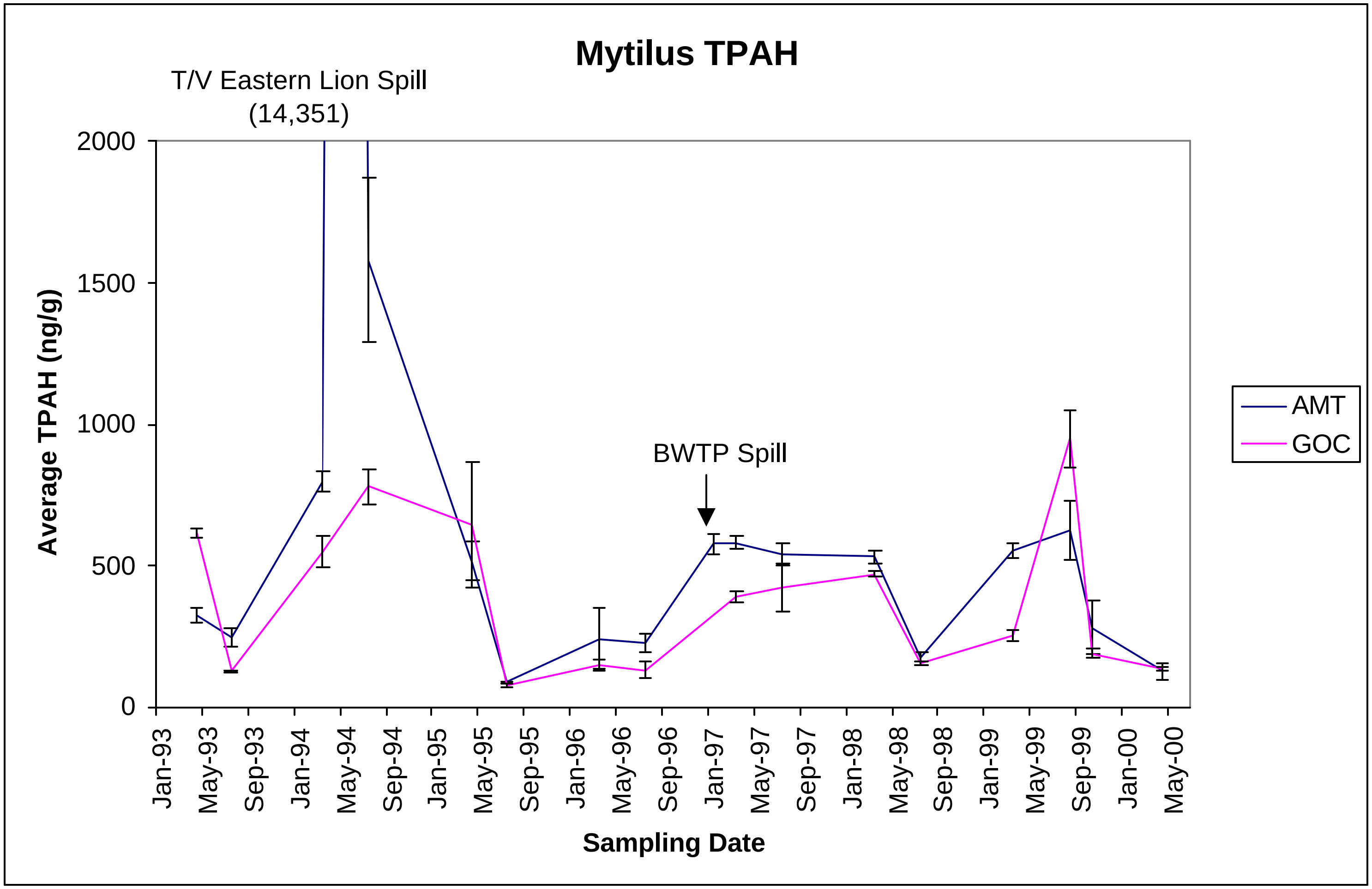


Figure 5. Average total PAH (TPAH) concentrations measured in intertidal LTEMP mussel samples from March 1993 through March 2000. The standard error of the mean for each triplicate analysis is shown by the vertical bars at each sampling time.

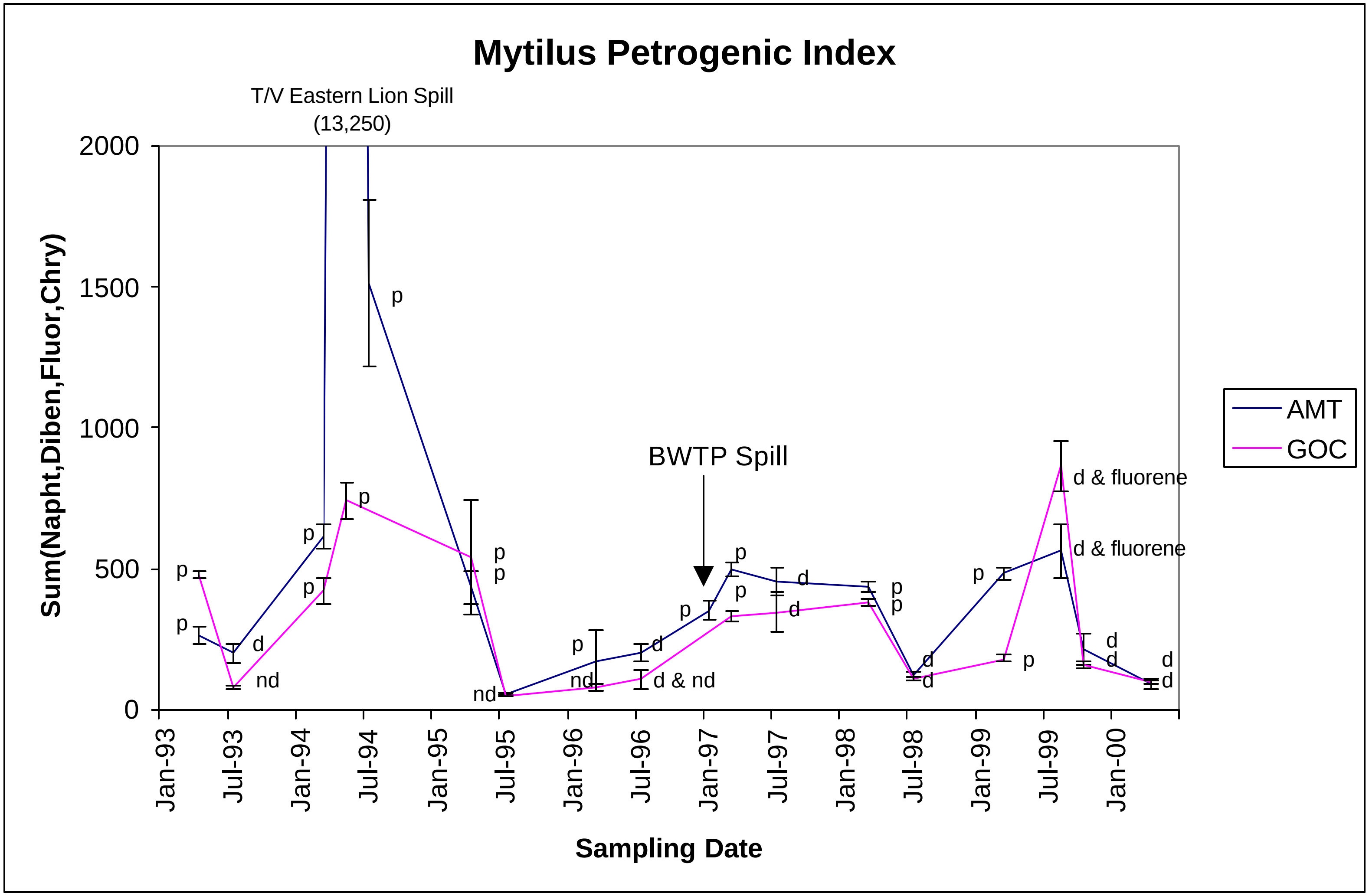


Figure 6. Average Mytilus Petrogenic Index values (Payne et al. 1998) measured in intertidal LTEMP mussel samples from March 1993 through March 2000. The standard error of the mean for each triplicate determination is shown by the vertical bars at each sampling time. The notations "p" and "d" reflect primarily particulate (oil droplet) or dissolved-phase signals, respectively. The notations "nd" and "d & fluorene" reflect samples with non-detected levels of PAH (or analytical artifacts) and dissolved-phase signals predominated by alkylated fluorenes, respectively.

Figures 7 and 8 present the PAH and SHC histogram plots separated by season and dissolved- versus particulate-phase source for all the Alyeska Marine Terminal samples except the non-detects and the mixed phase samples collected immediately following the *T/V Eastern Lion* oil spill. Figure 7 illustrates that in the spring, 22 out of 25 samples can be identified as containing a primarily particulate-phase (dispersed oil droplet) PAH signal that is characterized by higher relative concentrations of higher-molecular-weight alkylated PAH (fluorenes, dibenzothiophenes, phenanthrenes/anthracenes, and chrysenes) compared to the naphthalenes. In contrast, 14 out of 17 summer samples clearly show a primarily dissolved-phase PAH signal that has higher relative concentrations of the naphthalenes compared to the other higher-molecular-weight PAH components. Figure 8 shows the same relative distribution of dissolved- versus particulate-phase sources based on the SHC distributions, except it should be noted that SHC data were not available for all the samples because n-alkanes have not been consistently measured throughout the LTEMP. Also, the SHC data are not as straightforward and easy to interpret.

Specifically, phytane is occasionally observed in the SHC profiles of samples associated with primarily dissolved-phase PAH, and this is at variance with what otherwise might be expected. Phytane is a branched alkane that is nearly insoluble in seawater, resistant to microbial degradation, and almost always associated with crude or refined oils. As a result of its low solubility and environmental persistence, it is generally a good marker compound for whole oil droplets. In general, when particulate phase PAH are suggested by higher relative concentrations of higher-molecular-weight alkylated PAH compared to the naphthalenes, the corresponding SHC profiles are characterized by an evenly repeating series of higher-molecular-weight n-alkanes in the n-C 23 to n-C 32 range with an even:odd carbon ratio approaching unity. This is clearly consistent with dispersed oil droplets contributing the majority of the signal. When the PAH data suggest the hydrocarbon source is primarily from the dissolved phase, however, the corresponding SHC profiles contain significantly reduced levels of higher-molecular-weight n-alkanes, with greater relative concentrations of phytane. Its presence in samples that otherwise can be characterized as containing PAH primarily from the dissolved phase suggests that there may still be traces of extremely weathered oil droplets that have lost most of the PAH to evaporation and dissolution processes and the n-alkanes to microbial degradation. Figures 9 and 10 present the PAH and SHC histogram plots separated by season and dissolved- versus particulate-phase sources for all the Gold Creek samples except the non-detects. In this instance, 18 out of 21 samples showed a particulate phase distribution in the spring, while only three samples exhibited a signal derived from dissolved phase input. In the summer, all 17 of the samples exhibited the characteristic dissolved-phase signal, and no samples were observed with a particulate-phase PAH or SHC distribution.

While these data are not absolute (i.e., there are occasionally samples in the spring that show a dissolved phase signal and there are occasionally samples in the summer that exhibit a particulate phase signal), the general trend of primarily particulate-phase signatures in the spring and dissolved-phase signatures in the summer is supported.

Time-Series Observations in Subtidal Sediment Samples from the 1993-2000 LTEMP

Table 6 presents the total SHC and PAH values of individual sediment samples, seasonal averages, and the associated coefficients of variation for the replicate measurements completed between 1993 and 2000. The TPAH values in the sediments from Gold Creek are uniformly low, ranging from 25

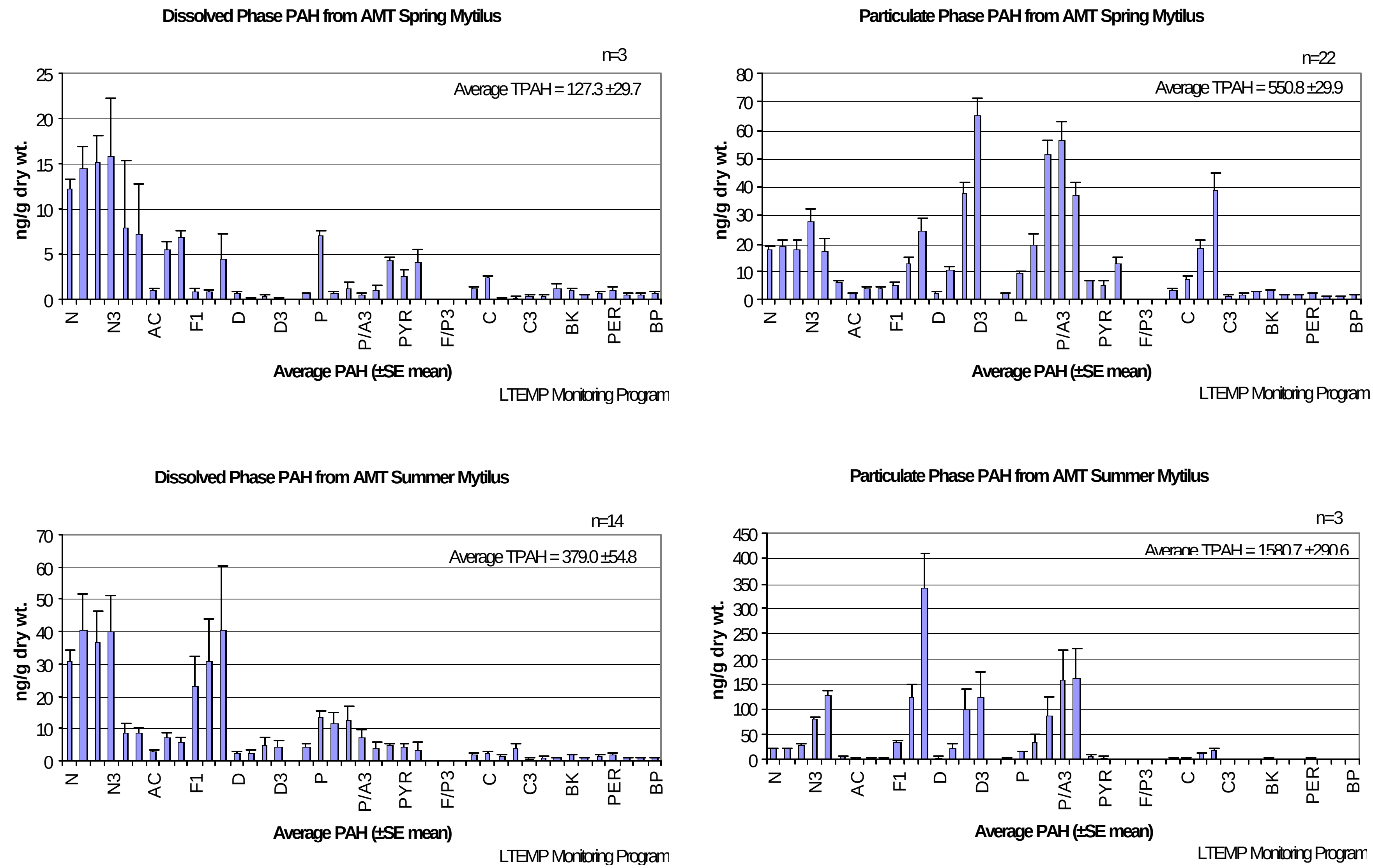


Figure 7. Average PAH histograms from 1993-2000 LTEMP intertidal mussel samples from Alyeska Marine Terminal. The samples are separated by season (Spring at the top of the figure and Summer at the bottom) and physical state of the hydrocarbon source (primarily dissolved phase on the left and primarily particulate (dispersed oil droplets) on the right). The number of samples contributing to each composite is denoted by “n”, which illustrates the predominant particulate-phase signal in the Spring (22 out of 25 samples) and the predominant dissolved-phase signal in the Summer (14 out of 17 samples). Abbreviations for PAH components are given in Table 1.

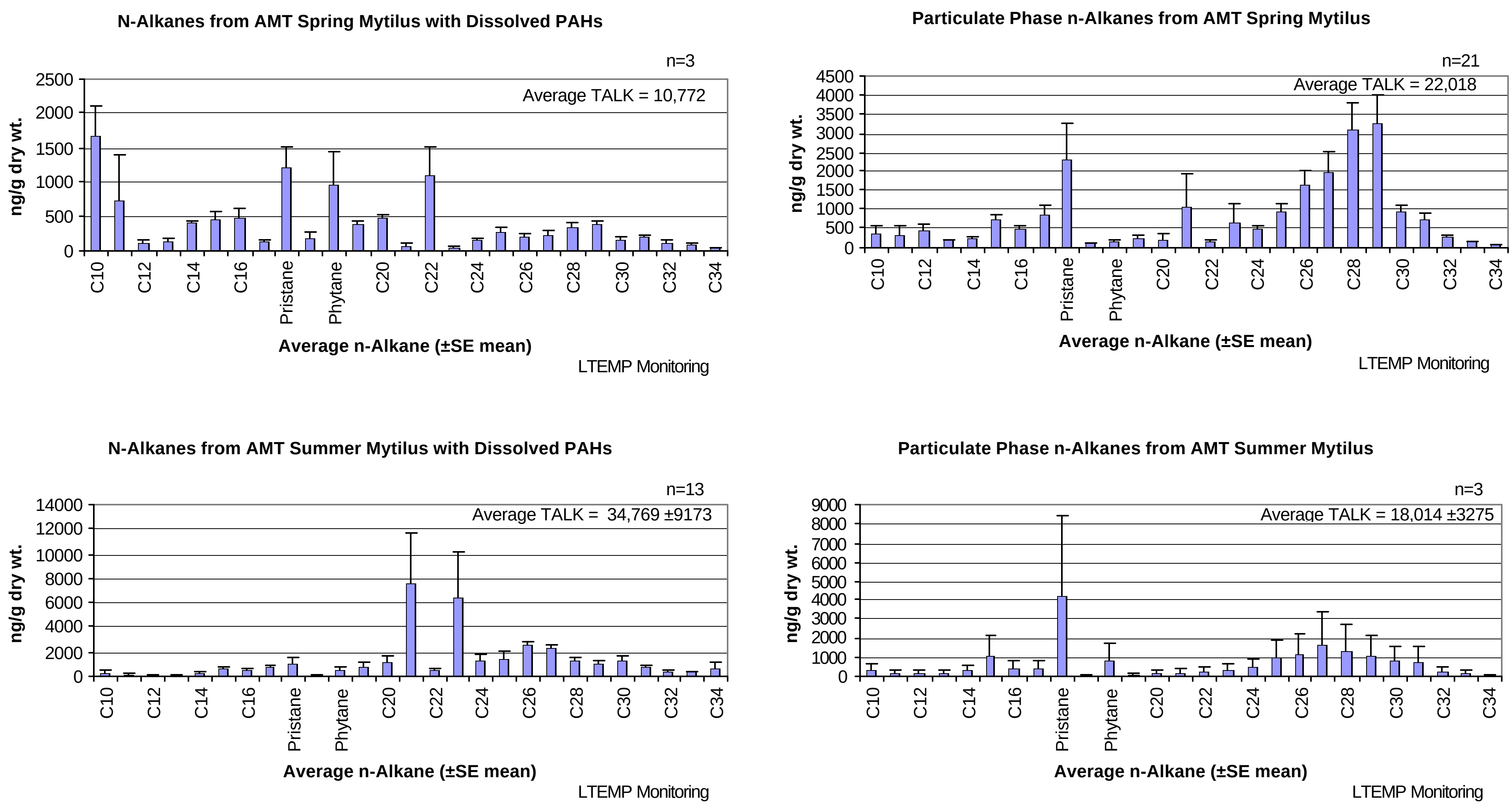
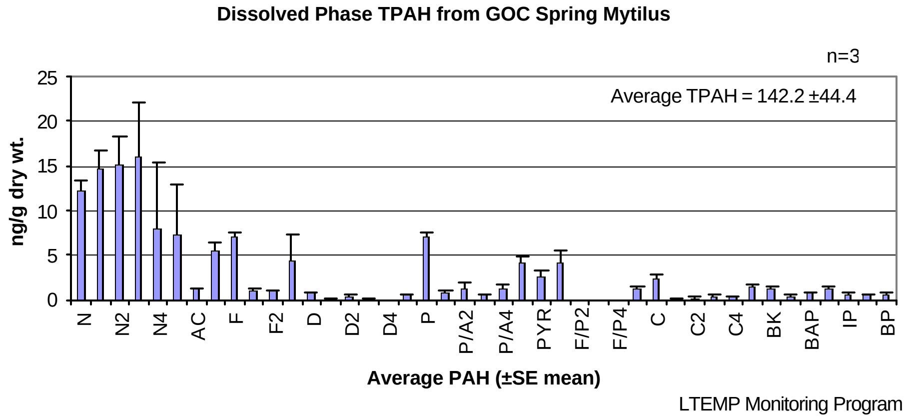
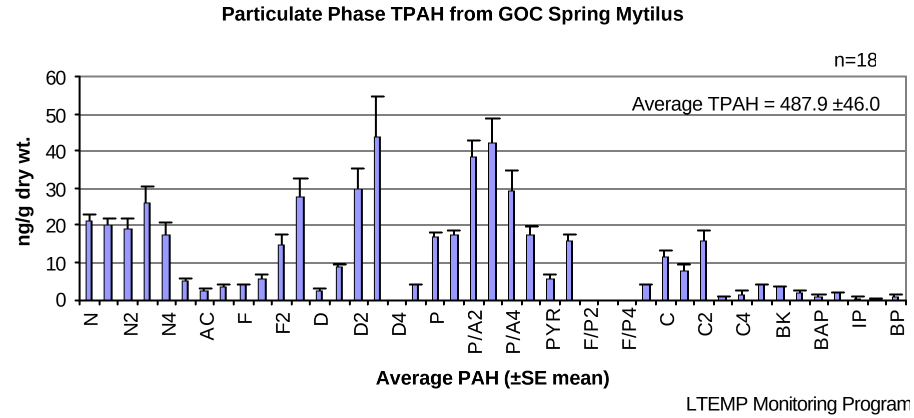


Figure 8. Average SHC histograms from 1993-2000 LTEMP intertidal mussel samples from Alyeska Marine Terminal. The samples are separated by season (Spring at the top of the figure and Summer at the bottom) and physical state of the PAH hydrocarbon source (primarily dissolved phase PAH on the left and primarily particulate (dispersed oil droplets) on the right). The number of samples contributing to each composite is denoted by "n", which illustrates the predominant particulate-phase signal in the Spring (21 out of 24 samples) and the predominant dissolved-phase signal in the Summer (13 out of 16 samples). Abbreviations for SHC components are given in Table 1.





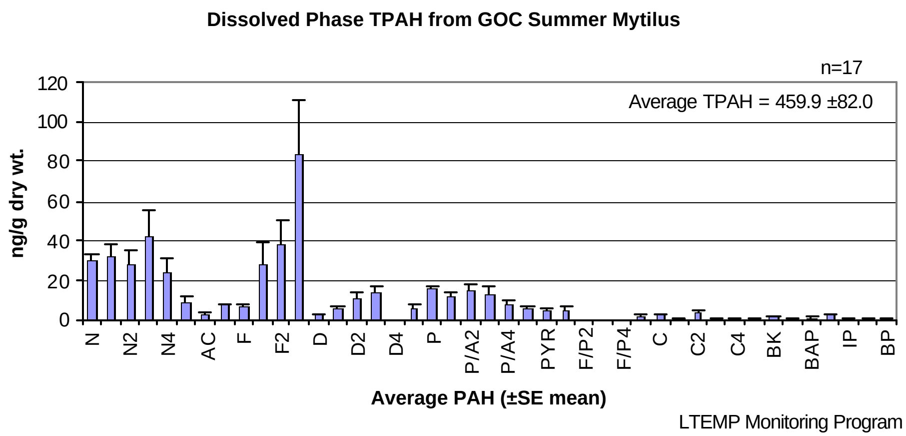
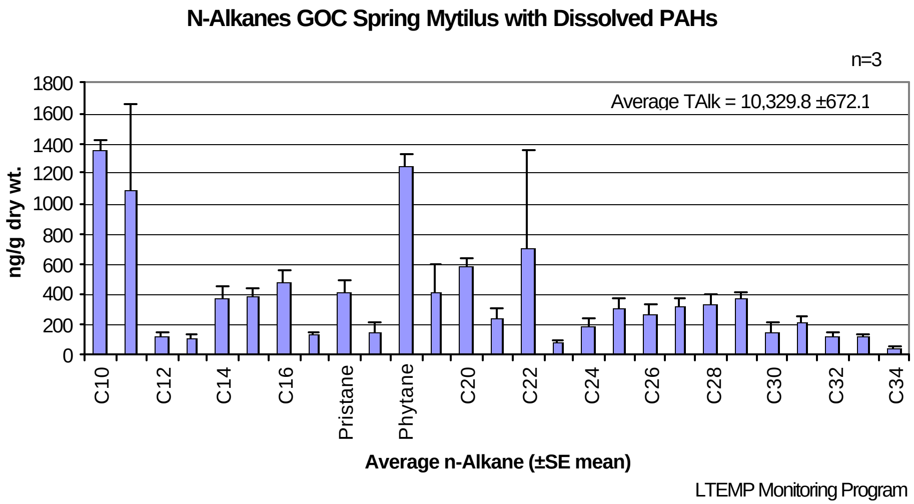
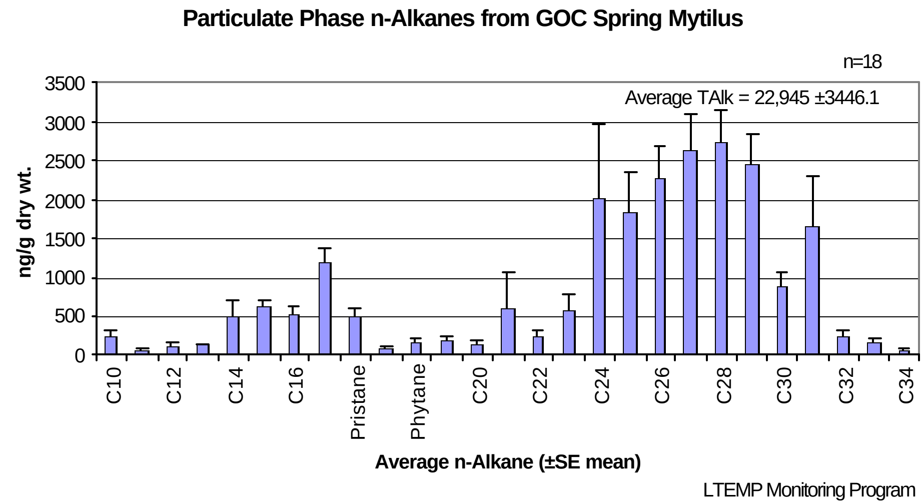


Figure 9. Average PAH histograms from 1993-2000 LTEMP intertidal mussel samples from Gold Creek. The samples are separated by season (Spring at the top of the figure and Summer at the bottom) and physical state of the hydrocarbon source (primarily dissolved phase on the left and primarily particulate (dispersed oil droplets) on the right). The number of samples contributing to each composite is denoted by "n", which illustrates the predominant particulate-phase signal in the Spring (18 out of 21 samples) and the predominant dissolved-phase signal in the Summer (17 out of 17 samples; there were no particulate-phase PAH signals in the summer). Abbreviations for PAH components are given in Table 1.





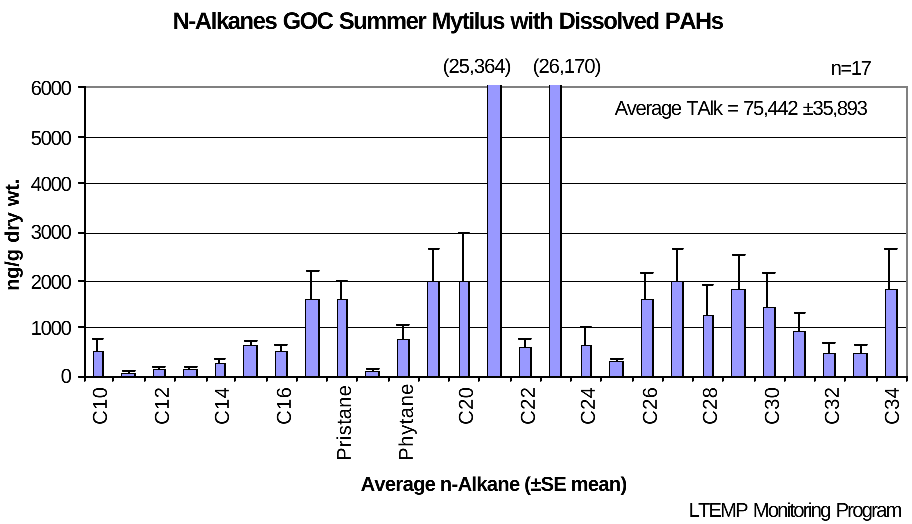


Figure 10. Average SHC histograms from 1993-2000 LTEMP intertidal mussel samples from Gold Creek. The samples are separated by season (Spring at the top of the figure and Summer at the bottom) and physical state of the PAH hydrocarbon source (primarily dissolved phase PAH on the left and primarily particulate (dispersed oil droplets) on the right). The number of samples contributing to each composite is denoted by "n", which illustrates the predominant particulate-phase signal in the Spring (18 out of 21 samples) and the predominant dissolved-phase signal in the Summer (17 out of 17 samples; there were no particulate-phase PAH signals in the summer). Abbreviations for SHC components are given in Table 1.

Table 6. Total SHC and PAH values of individual sediment samples, seasonal average and coefficient of variation at AMT and GOC stations, 1993-2000. (Concentrations in ng/g dry weight).

Date	Sample ID	Total SHC	Average	Std Dev	CV	Total PAH	Average	Std Dev	CV
Alyeska Marine Terminal Subtidal Sediments (AMT-S)									
3-Apr-1993	PWS93PAT0040	1868				196			
3-Apr-1993	PWS93PAT0041	2533				341			
3-Apr-1993	PWS93PAT0042	1873	2091	383	18	191	243	85	35
16-Jul-1993	PWS93PAT0043	1164				146			
16-Jul-1993	PWS93PAT0044	3183				198			
16-Jul-1993	PWS93PAT0045	1707	2018	1045	52	394	246	131	53
26-Mar-1994	PWS94PAT0025	1047				202			
26-Mar-1994	PWS94PAT0026	1698				167			
26-Mar-1994	PWS94PAT0027	1675	1473	369	25	239	203	36	18
20-Jul-1994	PWS94PAT0031	1425				174			
20-Jul-1994	PWS94PAT0032	1242				230			
20-Jul-1994	PWS94PAT0033	1922	1530	352	23	389	264	111	42
3-Apr-1995	PWS95PAT0022	1291				206			
3-Apr-1995	PWS95PAT0023	1093				244			
3-Apr-1995	PWS95PAT0024	1785	1390	356	26	186	212	29	14
11-Jul-1995	PWS95PAT0028	2189				1650			
11-Jul-1995	PWS95PAT0029	1872				362			
11-Jul-1995	PWS95PAT0030	2763	2275	452	20	629	880	680	77
16-Mar-1996	PWS96PAT0004	1109				160			
16-Mar-1996	PWS96PAT0005	1578				311			
16-Mar-1996	PWS96PAT0006	1100	1262	273	22	135	202	95	47
12-Jul-1996	PWS96PAT0025	2265				326			
12-Jul-1996	PWS96PAT0026	1782				201			
12-Jul-1996	PWS96PAT0027	1602	1883	343	18	381	302	92	31
6-Mar-1997	PWS97PAT0001	2203				417			
6-Mar-1997	PWS97PAT0002	1980				449			
6-Mar-1997	PWS97PAT0003	2929	2370	496	21	388	418	31	7
5-Apr-2000	PWS00PAT0004	1465				313			
5-Apr-2000	PWS00PAT0005	1575				335			
5-Apr-2000	PWS00PAT0006	1568	1536	61	4	412	353	52	15
Alyeska Marine Terminal Intertidal Sediments (AMT-L)									
14-Jul-1998	PWS98PAT0043	254				26			
14-Jul-1998	PWS98PAT0044	131				38			
14-Jul-1998	PWS98PAT0045	2492	959	1329	139	123	62	53	85
Gold Coast Subtidal Sediments (GOC-S)									
19-Mar-1993	PWS93PAT0001	941				47			
19-Mar-1993	PWS93PAT0002	436				36			
19-Mar-1993	PWS93PAT0003	1460	946	512	54	58	47	11	23
25-Jul-1993	PWS93PAT0071	1036				57			
25-Jul-1993	PWS93PAT0072	408				31			
25-Jul-1993	PWS93PAT0073	256	567	413	73	25	38	17	45
26-Mar-1994	PWS94PAT0022	1429				60			
26-Mar-1994	PWS94PAT0023	571				45			
26-Mar-1994	PWS94PAT0024	638	879	477	54	106	71	32	45

19-Jul-1994	PWS94PAT0028	385				47			
19-Jul-1994	PWS94PAT0029	378				18			
19-Jul-1994	PWS94PAT0030	737	500	205	41	68	44	25	57
3-Apr-1995	PWS95PAT0019	463				57			
3-Apr-1995	PWS95PAT0020	322				34			
3-Apr-1995	PWS95PAT0021	528	438	105	24	31	41	14	35
11-Jul-1995	PWS95PAT0025	750				67			
11-Jul-1995	PWS95PAT0026	598				59			
11-Jul-1995	PWS95PAT0027	444	597	153	26	31	52	19	36
16-Mar-1996	PWS96PAT0001	588				78			
16-Mar-1996	PWS96PAT0002	470				156			
16-Mar-1996	PWS96PAT0003	523	527	59	11	33	89	62	70
12-Jul-1996	PWS96PAT0028	541				56			
12-Jul-1996	PWS96PAT0029	440				45			
12-Jul-1996	PWS96PAT0030	629	537	95	18	52	51	5	11
6-Mar-1997	PWS97PAT0004	624				54			
6-Mar-1997	PWS97PAT0005	431				39			
6-Mar-1997	PWS97PAT0006	441	499	108	22	40	44	8	19
5-Apr-2000	PWS00PAT0001	590				126			
5-Apr-2000	PWS00PAT0002	668				81			
5-Apr-2000	PWS00PAT0003	918	725	172	24	126	111	26	24
Gold Coast Intertidal Sediments (GOC-L)									
13-Jul-1998	PWS98PAT0040	52				12			
13-Jul-1998	PWS98PAT0041	14				5			
13-Jul-1998	PWS98PAT0042	26	31	19	63	12	9	4	42

ng/g dry wt. to a high of 156 ng/g dry wt. The sediments obtained at Alyeska Marine Terminal exhibit more variability and ranged from a low of 160 ng/g dry wt. to a high of 1,650 ng/g dry wt. observed in July 1995.

Figure 11 presents the mean TPAH concentrations (and associated standard error of the mean) measured in the sediments as a function of time. This figure illustrates the temporal variability and shows that the TPAH concentrations in the sediments at the two sites do not appear to be related. Concentrations for two intertidal samples collected in July 1998 are also shown and are clearly lower than their respective subtidal trend lines.

Figure 12 plots the sediment CRUDE index (Payne et al. 1998) for both stations as a function of time. The CRUDE index combines into a single value many of the numerous individual factors and characteristic ratios that have been used for oil data analysis by chemists and environmental scientists in the past. With this single-value approach emphasizing the petrogenic over the pyrogenic and biogenic signals, some of the variability in the Gold Creek trend line in Figure 11 is reduced, and the importance of the petrogenic influence at the Alyeska Marine Terminal station in the 1993 samples is emphasized.

Figures 13 and 14 present the average sediment PAH and SHC histogram profiles for both Port Valdez stations and allows comparison between the stations by season and intertidal versus subtidal sample location. The PAH concentrations in the intertidal stations are

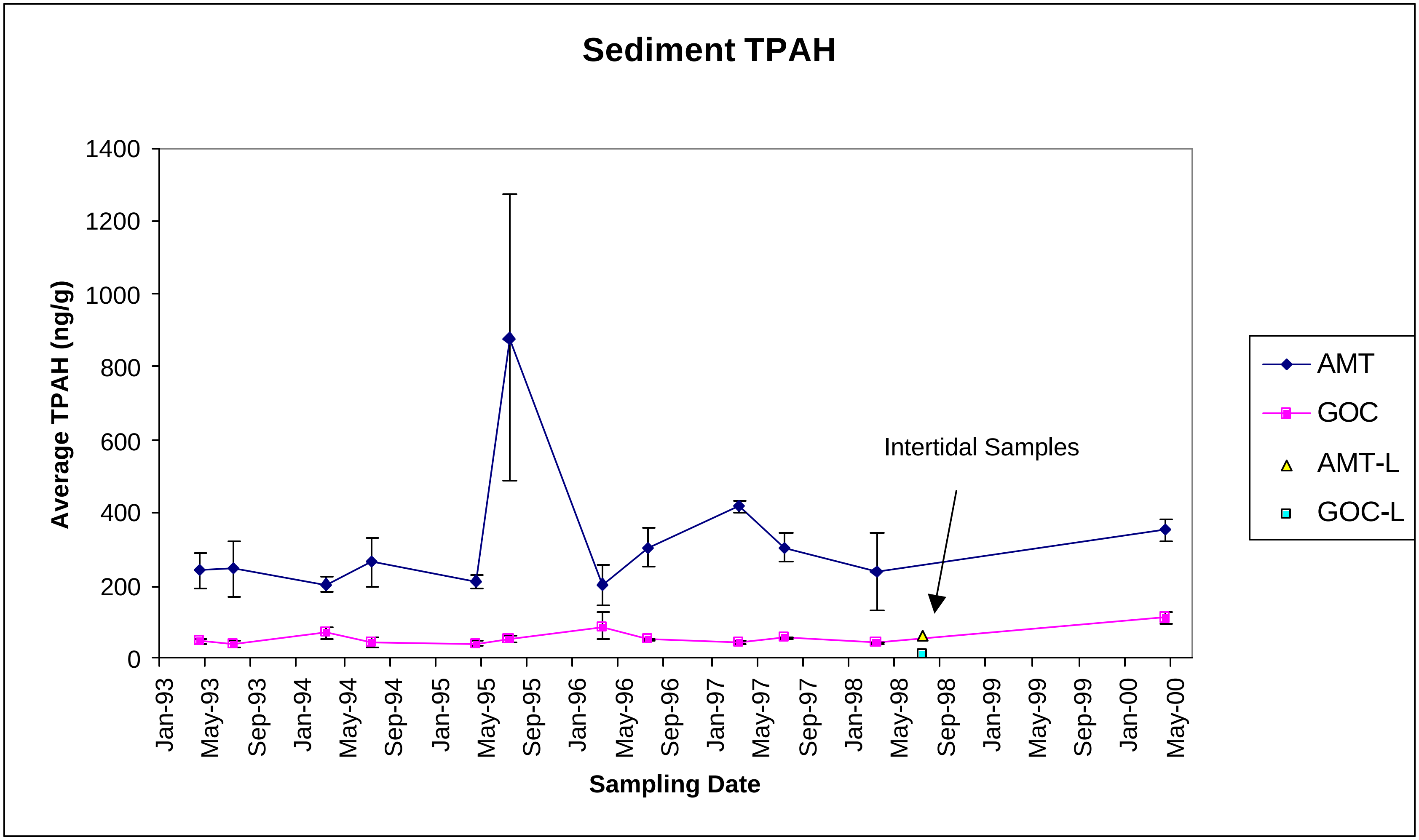


Figure 11. Average total PAH (TPAH) concentrations measured in subtidal (and two intertidal) LTEMP sediment samples from March 1993 through March 2000. The standard error of the mean for each triplicate analysis is shown by the vertical bars at each sampling time.

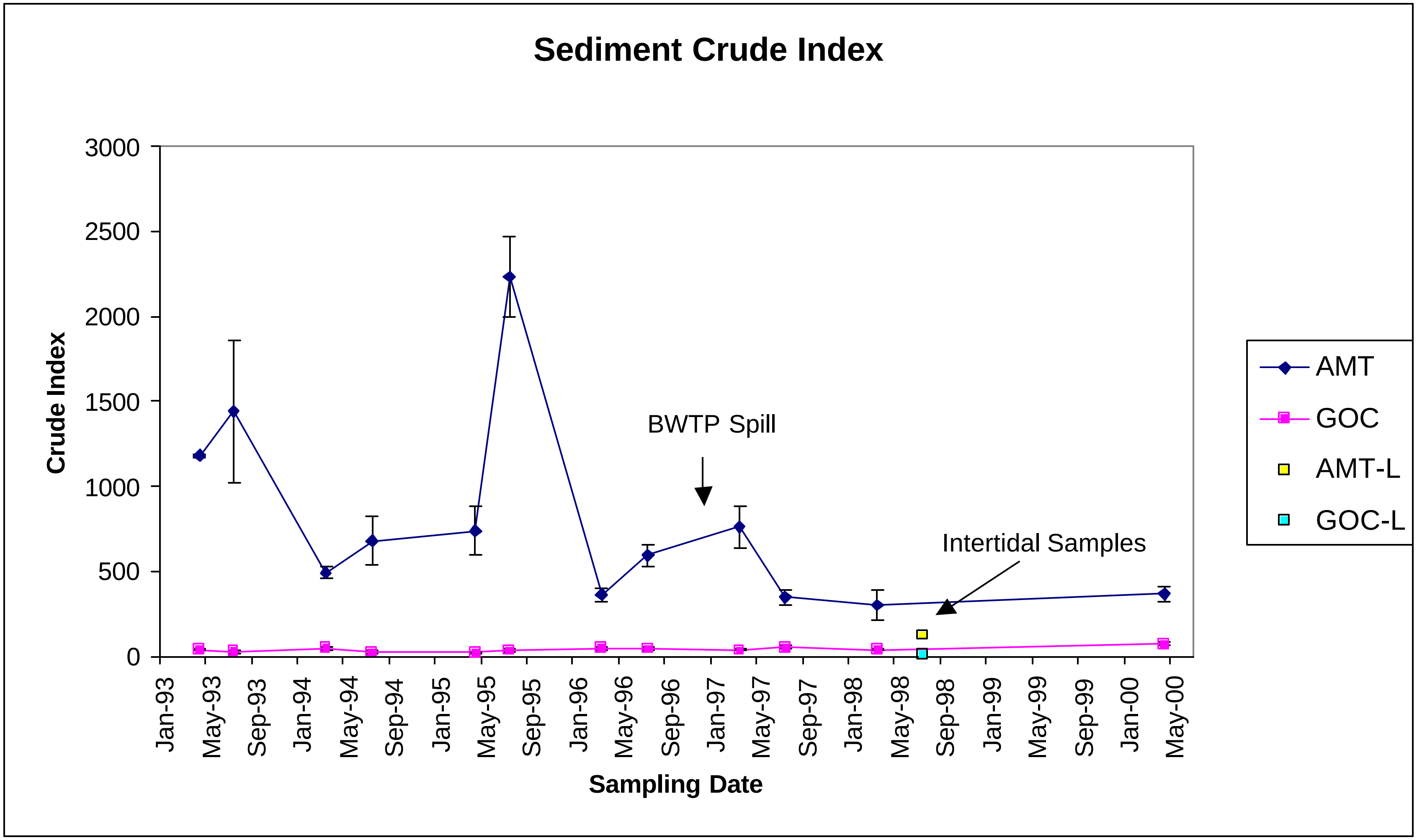


Figure 12. Average CRUDE Index values (Payne et al. 1998) measured in subtidal (and two intertidal) LTEMP sediment samples from March 1993 through March 2000. The standard error of the mean for each triplicate determination is shown by the vertical bars at each sampling time.

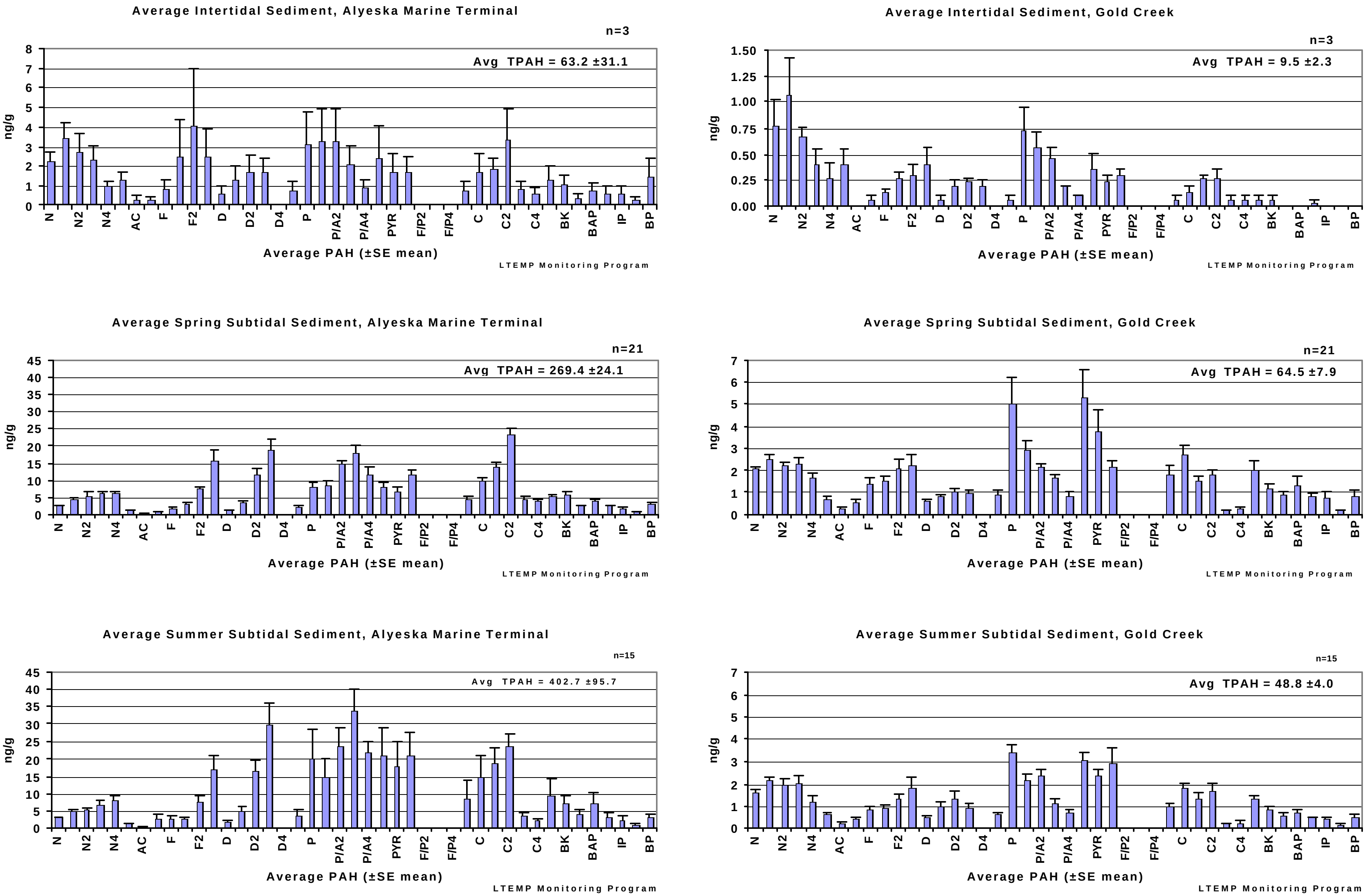


Figure 13. Average PAH histograms of intertidal and subtidal sediments samples from Alyeska Marine Terminal and Gold Creek stations. The subtidal samples are separated by season (Spring in the middle of the figure and Summer at the bottom). The number of samples contributing to each composite is denoted by "n". Abbreviations for PAH and SHC components are given in Table 1.

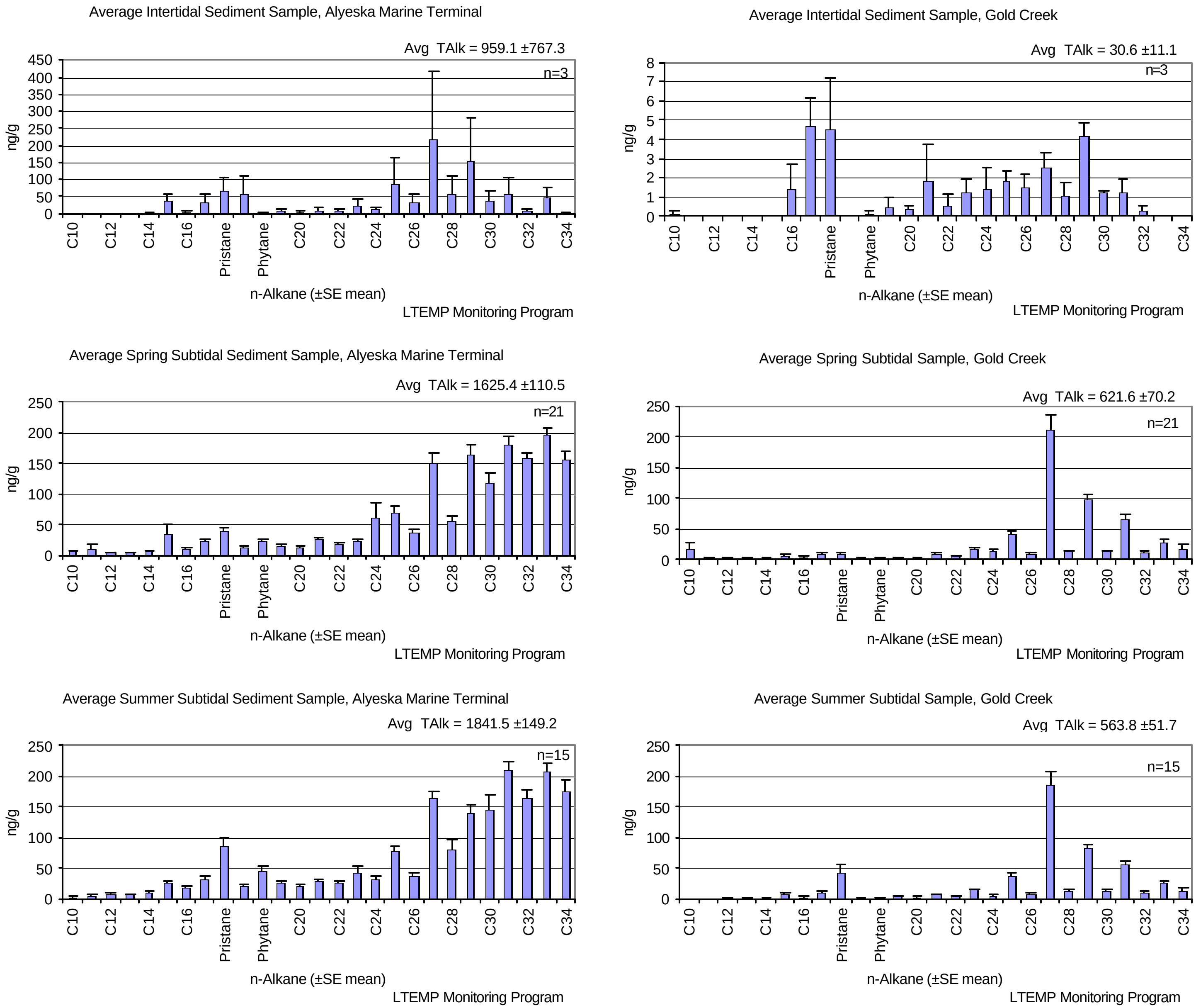


Figure 14. Average SHC histograms of intertidal and subtidal sediments samples from Alyeska Marine Terminal and Gold Creek stations. The subtidal samples are separated by season (Spring in the middle of the figure and Summer at the bottom). The number of samples contributing to each composite is denoted by "n". Abbreviations for SHC components are given in Table 1

significantly lower than the subtidal samples at both locations; however, the compositions are slightly different. The AMT intertidal site collected in July 1998 appears to have both a dissolved- and particulate-phase petroleum signal, while the GOC intertidal sample exhibits characteristics of both a petrogenic and pyrogenic signal.

There does not seem to be a seasonal PAH pattern observed in the sediments (compared to the intertidal mussels) at either AMT or GOC, although the variability is higher at AMT in the summer. The AMT sediments appear to be mostly contaminated by a weathered ANS oil signal, which would be consistent with BWTP diffuser-sourced dispersed oil droplet/suspended particulate material (SPM) interactions and concomitant sedimentation. The GOC sediments, on the other hand, show PAH contamination from a low-level petrogenic source with slightly greater relative input from combustion (pyrogenic) sources. The pyrogenic signal at GOC may be slightly greater in the spring, but it is probably not statistically significant.

The SHC patterns presented in Figure 14 show a predominantly biogenic signal in the two intertidal samples with significant variability observed among the replicates at each site. The subtidal sediments at AMT show a combination of biogenic and very weathered ANS oil signal, again consistent with terrestrial and marine fecal-pellet SPM inputs and significant oil droplet SPM interactions given the elevated level of dispersed oil droplets in the region from the BWTP diffuser (Payne et al. 1989). The subtidal sediments at GOC show a combination of marine and terrestrial biogenic inputs, with very little weathered oil signal in keeping with the extremely low CRUDE index values observed at the site.

Phase Distinctions and the Pitfalls of Using Mussel Concentrations for Predicting Impacts or Concentrations in Other Species

Brown et al. (1996) utilized mussels in Prince William Sound following the *Exxon Valdez* oil spill in 1989 to as a surrogate index of herring egg exposure to oil in the water column. They found a statistically significant correlation between mussel hydrocarbon burdens and anaphase aberrations in herring eggs collected from the intertidal zone in oiled areas. Their results have led some investigators to propose that mussels may be a good surrogate for predicting effects in other species, but as Baumard et al. (1999a,b) emphasized, it is important to recognize the route of exposure in interpreting such assessments. Brown et al. (1996) used mussel tissue residues as a measure of hydrocarbon exposure because of the limited herring egg sample sizes available. In chemical analyses, small sample sizes raise the method detection limits (MDLs) and the sensitivity to detect the PAH hydrocarbons of interest. However, the herring eggs samples were analyzed and even though the MDLs were higher that the original investigators would have liked, the PAH profiles clearly showed that the route of PAH exposure to the herring eggs was completely different from the mussels. Figure 15 presents the average PAH and aliphatic hydrocarbon histogram plots for 50 mussel samples collected from Cabin Bay on Naked Island in Prince William Sound in May and June 1989 and 11 samples collected from the same location in the spring and summer of

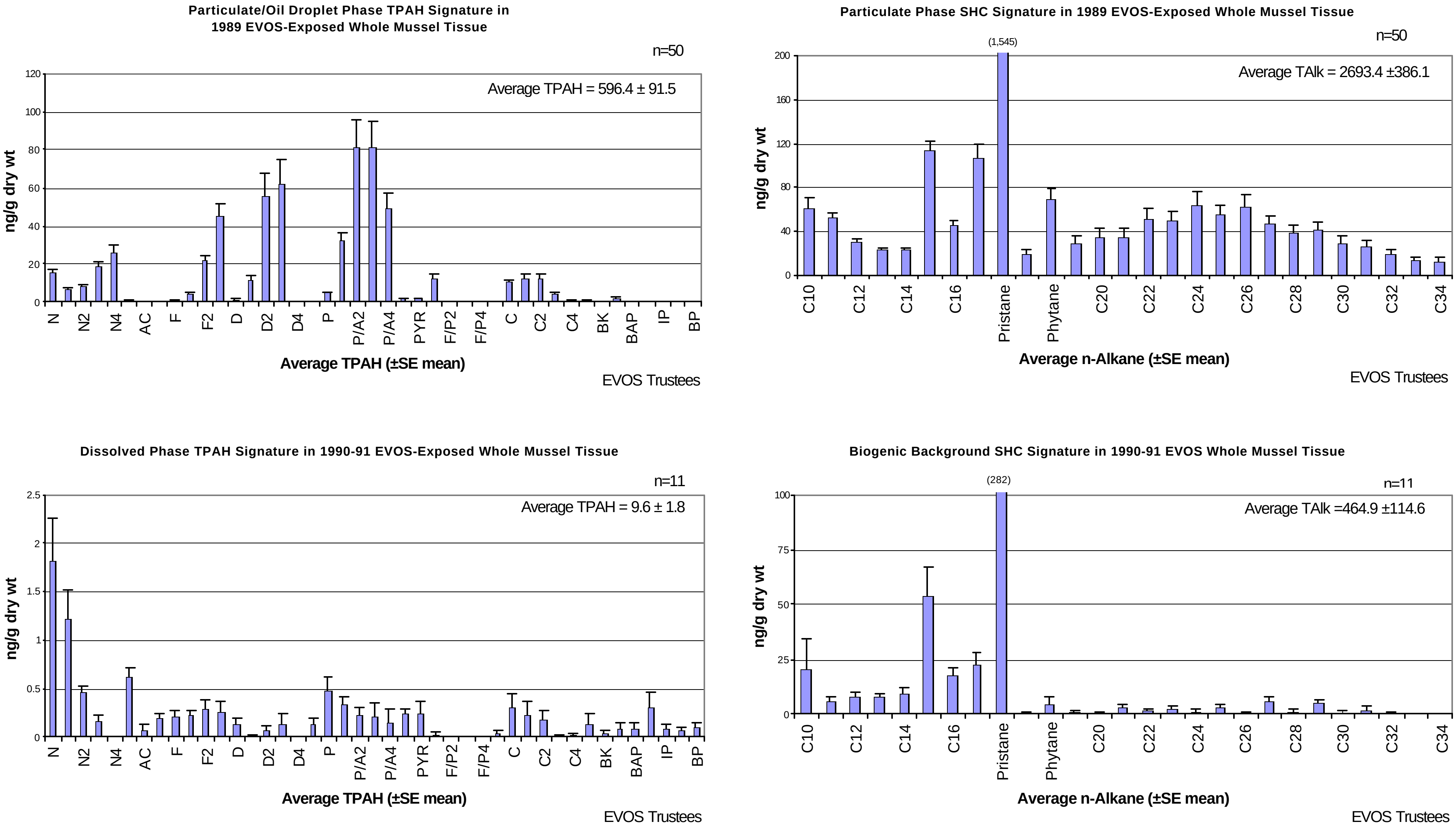


Figure 15. Average PAH and SHC histograms of whole mussel extracts from samples collected from oiled areas of Cabin Bay, Naked Island in Prince William Sound in May 1989 after the *Exxon Valdez* oil spill (EVOS) and again in May/June 1990 and 1991. The number of samples contributing to each composite is denoted by "n." Abbreviations for PAH and SHC analytes are given in Table 1.

1990 and 1991. Figure 16 presents the average PAH and aliphatic hydrocarbon data for 44 separate herring egg samples collected from Cabin Bay in May 1989.

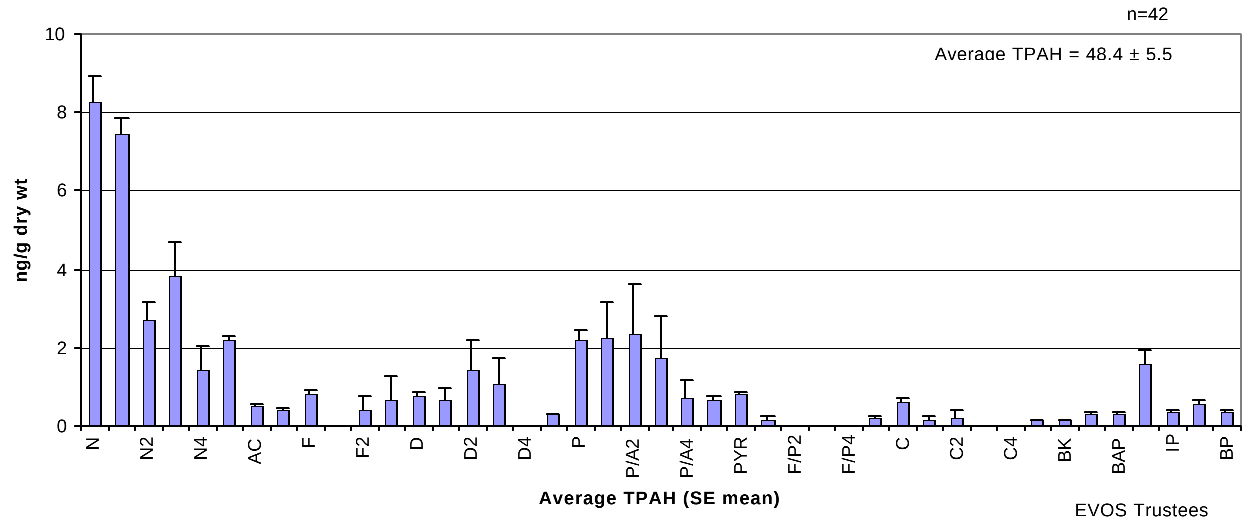
In 1989, the mussels clearly accumulated PAH and aliphatic hydrocarbons from both the dissolved and particulate phases to which they were exposed, however, the particulate (dispersed oil droplet phase) was the predominant source for the accumulated higher molecular weight PAH (C2-dibenzothiophenes through higher alkylated homologues of the phenanthrenes/anthracenes and chrysenes) and the aliphatics (phytane plus n-alkanes from n-C 19 through n-C 34). These higher molecular weight components have only limited water solubilities and have long been associated with the whole oil phase.

In contrast, the histogram plots for the herring eggs collected in 1989 (Figure 16), reflect the selective uptake of only the dissolved-phase (primarily the naphthalene homologues), which are the most water-soluble PAH derived from fresh ANS crude oil (Payne et al. 1984, 1991a,b,c). The SHC profiles for the exposed herring eggs show primarily lower-molecular-weight biogenic alkanes, which accumulate from the lipids in the phytoplankton (n-C15 and n-C17) and calanoid copepods (pristane) that make up the majority of the diet of female herring before depositing their eggs (pers. comm., Jeff Short; Cooney 1993; Blumer et al. 1964). These data demonstrate that the eggs only accumulated PAH from the dissolved phase.

By 1990 and 1991, the mussels were also accumulating primarily dissolved-phase PAH (at significantly reduced overall concentrations) from the more water-soluble hydrocarbons still leaching from the intertidal zone. This is manifest in the histogram plots at the bottom of Figure 15 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 was characterized primarily by lower molecular weight biogenic components (n-C 15, n-C 17, and pristane) with little or no contribution of higher molecular weight n-alkanes from dispersed oil droplets.

In subsequent controlled laboratory experiments using gravel contaminated with lightly and heavily weathered ANS oil (where the naphthalenes and fluorenes had been significantly reduced), it was demonstrated that herring and salmon eggs exposed to the water fraction again accumulated only components from the dissolved phase (Carls et al. 1999; Heintz et al. 1999; Heintz et al. 1995; Marty et al. 1997). Also, the same PAH patterns were obtained when salmon eggs were either exposed directly to the oiled gravel or only to the aqueous phase. The only shift in PAH accumulation occurred when extremely weathered oil was used in those studies. In those instances, the PAH distribution was skewed to the residual higher molecular weight components, which can still partition into the aqueous phase (although at slower rates) when seawater percolates through contaminated gravel. Examination of PAH profiles of other samples in the EVOS database revealed that absorption of PAH into crab eggs was also exclusively through the dissolved-phase in samples analyzed in 1989 following the spill, and more recently, Payne and Driskell (1999, 2000, 2001) documented the selective uptake of dissolved-phase PAH into crab tissues following the release of Bunker C fuel oil and

Dissolved Phase TPAH Signature in 1989 EVOS-Exposed Herring Eggs



Background Biogenic SHC Signature in 1989 EVOS-Exposed Herring Eggs

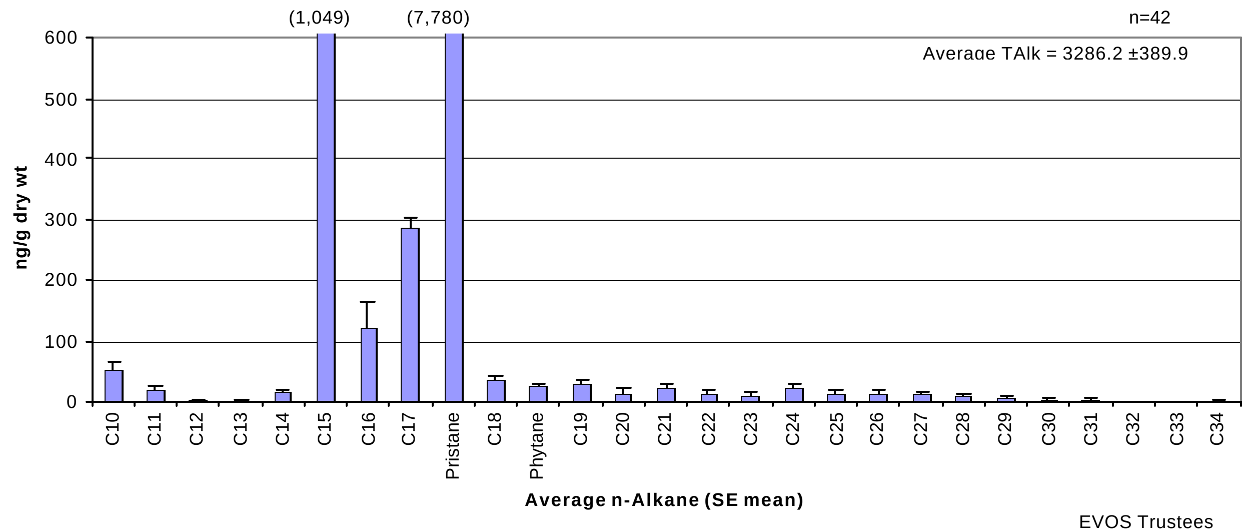


Figure 16. Average PAH and SHC histograms of herring egg extracts from samples collected from oiled areas of Cabin Bay, Naked Island (collocated with the mussel samples in Figure 15) in Prince William Sound in May 1989 after the EVOS. The number of samples contributing to each composite is denoted by “n”. Abbreviations for PAH and SHC components are given in Table 1.

diesel from the *New Carissa* oil spill off the coast of Coos Bay, Oregon in 1999. Mussels and clams collected at the same time, again showed accumulation of PAH and aliphatic hydrocarbons that were primarily associated with the particulate (dispersed) oil droplet phase.

In summary, filter feeder species (e.g., mussels, oysters, clams) primarily accumulate petrogenic hydrocarbons from the particulate phase oil when available. At other times, the signal from dissolved phase components can predominate. Biota with passive uptake (e.g., lipid-rich eggs) will primarily accumulate from the dissolved phase components from the water column.

DISCUSSION

Impact Assessment for Mussels

Comparing PAH concentrations measured in tissues from Port Valdez mussels collected from March 1993 to March 2000 as part of LTEMP to the screening level for possible effects (i.e., 2,250 ng/g dry wt.) suggests that effects are not likely during most years (Figure 7). All measured concentrations were below the 2,250 ng/g dry wt. screening tissue level for possible adverse effects in mussels, and most were below the more conservative 750 ng/g dry wt. based on UV/fluorescence and a more limited set of PAH analyzed by GC/MS. Any impacts to mussels would be overestimated because effects associated with tissue burdens of PAHs are based on a screening level from 17 PAH compounds (Table 1) compared to the 43 PAHs measured in the LTEMP program, i.e., the screening levels likely would be higher if the full suite of PAHs were included. Consistent with an absence of impacts to mussels, Salazar et al. (2001) observed no effects on the growth or survival of mussels deployed in the Port Valdez between January and March 2001.

The highest average concentration of TPAH in mussel tissues ever measured as part of LTEMP was 1,581 ng/g dry wt. This was measured at the Alyeska Marine Terminal (AMT) site in July of 1994. Elevated concentrations associated with the screening level for possible effects were only found in this one of the 16 sampling events between March 1993 and March 2000 (Figure 7). At that time, the elevated concentrations observed at both GOC and AMT were linked to the *T/V Eastern Lion* spill at the terminal in May 1994.

Impact Assessment to Biota in Intertidal and Shallow Subtidal Sediments

Excepting two intertidal sediment samples at the AMT and GOC stations in July, 1998 and the series of mussel tissue data presented above, no directly-measured intertidal exposure data were available to assess potential impacts to other intertidal species. As summarized in Table 6, both intertidal sediment samples contained low levels of hydrocarbons (i.e., 9.5 to 63 ng/g dry wt. TPAH), in fact, even less than nearby subtidal sediments. The AMT intertidal and subtidal sediments showed both a dissolved- and particulate-phase petroleum signature, while the GOC samples exhibited characteristics of both a petrogenic and pyrogenic signal.

The synopsis of mussel data presented above offers new insights into the uptake pathways but the application of the mussel exposure data to other intertidal species has limits. There are concerns that the exposure pathway to mussels may not completely encompass all pathways to other intertidal biota and thus, fail to accurately portray a potentially higher rate of uptake and risk for other important species. A pathway of special concern is through the surface microlayer (Hardy, 1982). The surface microlayer is a very thin film, rich in lipids and fatty acids, that accumulates on the top 50 micrometers of the ocean usually appearing as a patch or streak (often invisible). The concern is that contaminants also accumulate there, concentrating 100 to 10,000-fold either by rising from below (e.g., dispersed oil droplets) or falling from the air (e.g., combustion products). Unfortunately, living both in and beneath the microlayer are concentrations of microbes, zooplankton, floating eggs and larvae, thereby creating a contact exposure route to those species and potentially a contaminated food source for others (e.g., filter-feeding mussels and clams or juvenile salmon and herring). In Port Valdez, surface microlayers are likely to occur but remain to be confirmed.

Earlier studies (Hardy 1982, Hardy et al. 1987a,b, Cross et al. 1987) have demonstrated that a surface microlayer can concentrate PAH by factors of 10^2 -10^4 over dissolved concentrations in the vast bulk of the water column. For example, microlayer samples from Chesapeake Bay contained up to 928 ng/L fluoranthene and up to 440 ng/L benzo(a)pyrene, while sub-surface concentrations of both PAHs were extremely low (0.008 and < 0.002 ng/L respectively) (Hardy et al., 1990). Microlayer concentrations of PAHs and pesticides have been measured at levels many times greater than known toxic concentrations or EPA water quality standards in water off southern California (Cross et al. 1987), Puget Sound (Hardy et al. 1987a and b), and the North Sea (Hardy and Cleary 1992). Furthermore, microlayer PCB concentrations at many sites in Puget Sound exceeded water quality criteria by 130 times.

Laboratory toxicity tests using surface microlayer samples and neustonic fish eggs and larvae have shown toxic effects, including growth inhibition, increased mortality, and chromosomal and developmental abnormalities (Dethelfson et al. 1985; Cross et al. 1987; Hardy et al. 1987a; Gardiner 1992). Also, field studies with fertilized floating fish eggs incubated in the surface microlayer *in situ* displayed marked reduction in hatching success at contaminated sites compared to uncontaminated sites (Hardy et al. 1987a). Concentrations of aromatic hydrocarbons at about half the stations in Chesapeake Bay were equal to or greater than concentrations proven toxic to developing fish embryos (GESAMP 1995). The sea surface microlayer can also contain high concentrations of pyrogenic compounds, which settle as aerosols and concentrate on the sea surface (GESAMP 1995). This aerosol-trap scenario seems highly appropriate for Port Valdez in view of the high volume of marine traffic. However, the areal coverage of any microlayer is highly variable and subject to wind and wave disruption.

Although no data have been collected to support the suggestion, for intertidal biota, the surface microlayer might be the pathway of higher concern relative to the contaminants suspended in the water column. If the surface microlayer were deposited on intertidal sediments during a retreating tide (Gardiner 1992) and adsorbed on the organics in the intertidal sediments, then the concentrated contaminants could be ingested by the numerous invertebrate sediment consumers and their predators.

From previous studies, numerous receptor species have been reported in or on intertidal and shallow subtidal sediments in the eastern portion of Port Valdez (e.g., Lees et al. 1979a,b). A few of the species are listed here by feeding types (Table 7). Suspension feeders, such as mussels, barnacles and some forage fish, filter large volumes of water for passing food particles. Deposit feeders gather the food that falls to the bottom, either selectively vacuuming the surface deposits (*Macoma* clams) or ingesting the mud in bulk

(*Nephtys* polychaete worms). Chemoautotrophs rely on symbiotic bacteria to provide their nutrition rather than directly capturing their own food (*Axinopsida* clam). In such a dynamically complex system, it is difficult to predict the scale and linkages of pollutant transfers through the ecosystem, and even more so without direct-measurement data.

Table 7. Estimated abundance (mean number per sq. m. ± std dev. or visual qualitative abundance) of selected macroinfauna in intertidal and subtidal sediments at the head of Port Valdez.

	Intertidal Habitats			**Shallow Subtidal Habitats (-6 to -18 m)**	
Feeding Behavior Species	**Island Flats**	**Shelf Outside Island Flats**	**Lowe River and Dayville Flats**	Offshore of Island Flats	Off Lowe River, Dayville Flats, and Allison Pt.
Suspension Feeder					
Mytilus trossulus	91 ± 98 (n = 6)*	369 ± 338 (n = 7)	167 ± 269 (n = 4)		
Echiurus echiurus alaskanus		Visually Abundant			
Selective Deposit Feeder					
Macoma balthica	2744 ± 2751 (n = 6)	1313 ± 1123 (n = 7)	1154 ± 669 (n = 4)		
Macoma obliqua				93 ± 93 (n = 12)	44 ± 78 (n = 9)
Non-Selective Deposit Feeder					
Nephtys punctata				Visually Common	Visually Common
Chemoautotrophic Host/Feeder					
Axinopsida serricata			39 ± 25 (n = 4)	373 ± 208 (n = 12)	388 ± 275 (n = 9)

* n = the number of sampling areas in which a species was observed in the specified location.

Using the available data to assess potential impacts to intertidal biota, the total and individual PAH levels from AMT and GOC sediment samples were initially screened against published marine sediment ERLs (Long and Morgan, 1990, Long et al. 1995); no samples exceeded the screening values. Then U. S. EPA's ECOTOX AQUIRE and National Library of Medicine's TOXNET databases were examined for records of chronic effects on comparable marine species (Appendix 2) from several PAHs that have been consistently observed in the water column in Port Valdez (Payne et al. 1998). These included naphthalene, fluorene, phenanthrene, phenanthrenes/anthracenes, dibenzothiophene, fluoranthene, pyrene, and chrysene. In addition, we tabulated data for anthracene and benzo(a)pyrene. The results from screening with the available toxicity records suggest the hydrocarbon levels sampled in Port Valdez never reached values of deleterious effects. However, there are still concerns for unknown effects related to potentially higher concentrations in surface microlayers or from photoenhanced toxicity (discussed below).

Impact Assessment for Pelagic Fish

Potential impacts to pelagic fish were assessed from TPAH exposure to Pacific herring and pink salmon because of the known sensitivity of these species, their ecological and economic importance in Prince William Sound, and the availability of species-specific toxicity and bioaccumulation information for ANS crude oil. Our analysis used the only current aqueous phase petroleum data for Port Valdez (Salazar et al. 2001). We used NOECs and LOECs for "less weathered oil" from Carls et al. (1999) because it most matched the naphthalene dominated PAH composition observed in Port Valdez water samples (Salazar et al. 2001). Aqueous TPAH thresholds for pink salmon were not included in the risk analysis because embryonic exposures to pink salmon will occur only in natal streams, not in the marine environment (Rice et al., 2001). Additionally, assessing risks to herring eggs should be protective of pink salmon from aqueous exposure to petroleum because (1) screening values for herring are very low (<10 µg/L), and (2) toxicity thresholds for salmon fry are substantially higher than for embryonic exposures to salmon (Rice et al. 2001). Our analysis indicated there were no risks posed by the aqueous phase petroleum measured in Port Valdez (Salazar et al., 2001) to pelagic fish (Table 8). Hazard quotients were substantially below one and there was a 0% probability of exceeding an HQ of one, which would be indicative of risk.

To evaluate the consistency of these conclusions, we also assessed risks to pelagic fish using a critical body residue approach, by comparing estimated tissue residues in herring eggs to tissue residue thresholds for abnormal herring embryo development. Egg residues of TPAH were calculated to be 0.007 µg/g from the product of (1) the Bioaccumulation Factor (BAF) of TPAH in herring eggs (55, determined for weathered ANS; Carls et al. 1999) and (2) the maximum observed dissolved-phase PAH concentration within the ballast water mixing zone (0.122 µg/L; observed concentration at 200 foot depth; Salazar et al. 2001). Comparing the calculated worst-case egg residue level from Port Valdez to the published most sensitive LOEC for weathered ANS oil (0.022 µg/g; Carls et al., 1999) also indicates an absence of risks to pelagic fish (HQ = 0.32).

The assessment of risks to pelagic fish species also included consideration of the photoenhanced toxicity of petroleum. Photoenhanced toxicity is the increase in toxicity that is expected under environmental exposures to UV in the water column that is not measured under normal laboratory test conditions with minimal UV. Exposure to the UV in sunlight results in a 2- to greater than 100-fold increase in the toxicity of petroleum, including ANS crude oil (Pelletier et al. 1997), and weathered ANS crude oil (Deusterloh et al., in review; Barron et al., unpublished). Barron and Ka′aihue (2001) concluded that there was potential for photoenhanced toxicity of spilled oil in Prince William Sound based on ambient light levels and expected attenuation (Alexander and Chapman 1980), and the high PAH concentrations measured after the EVOS. At the time, data were not available regarding the chronic low levels of aqueous phase petroleum in Port Valdez. The results of the current evaluation indicate there is negligible potential for photoenhanced toxicity of current levels of aqueous phase petroleum in Port Valdez. This assessment does not, however, consider phototoxic impacts that might be associated with concentrated hydrocarbons in a surface microlayer.

HQs based on preliminary photoenhanced toxicity thresholds for herring larvae (Barron et al. unpublished) were less than 0.05 indicating an absence of risk (Table 8).

Table 8. Calculated hazard quotients (HQs) for pelagic fish using ranges of exposure concentrations (Table 2) and screening values (Table 3).

Receptor	**Exposure Route**	**Range of HQs[1]**	**% Exceedences[2]**
herring eggs	water	0.007 - 0.02	0%
herring larvae	water	0.0009 - 0.04	0%
pink salmon	Diet: water to zooplankton	0.004 - 0.26	0%
	Diet: sediment to epibenthos	0.002 - 4.9	4.3%

1. Range of hazard quotients (HQ)s estimated from Latin Hypercube sampling over distribution of exposure concentrations and screening values.
2. Probability of HQs exceeding one.

Dietary risks of aqueous phase petroleum were evaluated using dietary NOECs and LOECs for pink salmon for unweathered ANS crude oil (Carls et al. 1996); dietary thresholds for herring larvae were not available. Fast growth rates are extremely important in pink salmon fry because of the necessity of growing out of predator-susceptible fish sizes (Rice et al. 2001). Pink salmon screening values may be considered a reasonable surrogate for herring because of the similarity in thresholds for aqueous phase petroleum for these species (Carls et al. 1999; Heintz et al. 1999). Dietary exposures were estimated from TPAH bioaccumulation into a key zooplankton species, *Calanus marshallae*, because calanoid zooplankton can be important prey for salmon and herring in PWS and contain a high proportion of lipid (Deusterloh et al., in review; Kline 1997). Bioaccumulation factors for *C. marshallae* were considered a reasonable maximum because BAFs were substantially lower for both herring eggs (e.g., 55; Carls et al. 1999) and larvae (250; Barron et al., unpublished). Consistent with results for direct exposure to pelagic species, there were no dietary risks estimated from prey uptake of aqueous phase petroleum (Table 8).

The risk analysis did not directly consider consumption of particulate oil, which may be present in Port Valdez at particle sizes of less than 1 µm. Oil globules were ingested by pink salmon fry the year of the *Exxon Valdez* oil spill (EVOS) resulting in reduced growth (Rice et al. 2001). However, the preliminary photoenhanced toxicity thresholds for herring larvae were determined with aqueous phase oil prepared with extreme high energy mixing and 1 micrometer filtration, and should encompass petroleum exposures to particulate oil of less than 1 micrometer that may occur in Port Valdez.

The risk analysis also included an evaluation of dietary risks to salmon fry feeding on surface-dwelling (epibenthic) invertebrates exposed to petroleum in sediment near Gold Creek and AMT in Port Valdez. Species- and site-specific bioaccumulation factors were not available for important prey species such as harpacticoid copepods. Instead, a simple food chain model was used to estimate bioaccumulation using a probability distribution of Biota Sediment Accumulation Factors (BSAFs) for PAH uptake by benthic invertebrates reported in the literature (Lake 1990; Gewurtz et al. 2000; van Hoof et al. 2001). This conservative analysis indicated a 4.3% probability of risks from the sediment-to-prey-to-salmon pathway (Table 8), which likely overestimates actual risks because epibenthos should have substantially lower BSAFs than infaunal invertebrates (Meador et al., 1995). Additionally, growth impacts in field-collected pink salmon fry were not observed one year after EVOS, after petroleum contamination had declined (Rice et al., 2001).

Note that there are substantial uncertainties in the assessment of risks to pelagic fish. Although we have used conservative assumptions and worst case exposure scenarios based on the available data, there are still data gaps and uncertainties associated with potential exposures in the surface microlayer. Additional research is needed to evaluate the spatial extent and any temporal trends in petroleum contamination in the surface microlayer. Bioavailable concentrations of TPAH in the surface microlayer would have to exceed 400 ng/L to pose risks to sensitive pelagic species because concentrations below this threshold have not been reported. For example, Carls et al. (1999) reported a lowest effect concentration of 400 ng/L in herring embryos, and Heintz et al., (1999) reported a toxicity threshold of 1000 ng/L.

Sources of Mussel, Water, and Sediment Contamination and the Influence of Water-Column Stratification and Surface Microlayers on Pollutant Transport

It is apparent that there is widespread but low-level petroleum hydrocarbon contamination in several areas throughout Port Valdez, and that this can be attributed to effluent from the Alyeska Marine Terminal ballast water treatment plant (BWTP) and other ongoing terminal operations. BWTP-derived PAH and n-alkane profiles are observed in the vicinity of the Alyeska Marine Terminal at both the LTEMP and Alyeska monitoring stations, Anderson Bay 10 kilometers west (Salazar et al. 2001), and Gold

Creek, 6 kilometers northwest of the ballast water treatment plant diffuser. BWTP-derived oil was not observed at the Port Valdez small boat harbor in 2001, where the PAH signal reflected primarily combustion derived sources. Salazar et al. (2001) have speculated that the lack of BWTP-derived oil signatures in the small boat harbor can be explained by winds, currents, and freshwater input at the east end of Port Valdez, which prevents surface transport of BWTP particulate-phase oil to the eastern end of the port.

The results of this data evaluation and synthesis effort have shown that measured concentrations of PAH in the water column, subsurface caged mussels, intertidal mussels, and shallow- and deeper-sediment samples are all below toxicity thresholds for chronic and acute effects in sensitive life stages of marine organisms. From the available data, long-term ecological impacts are not predicted to occur in Port Valdez because measured and estimated exposure concentrations do not exceed levels associated with genetic damage, reduced marine fitness, or photoenhanced toxicity in sensitive species (approximately 400 ng/L) (Barron and Ka'aihue 2001; Carls et al. 1999; Marty et al. 1997; Rice et al. 2001; Roy et al. 1999). Contaminant exposures in the intertidal zones and near surface waters may be elevated where petroleum hydrocarbons - may concentrate as a result of surface microlayer effects. Surface microlayer exposures have not been monitored in Port Valdez, nor have they previously been considered a source of potentially significant ecological impacts from petroleum discharges.

After careful evaluation of the seasonally-dependent dissolved versus particulate hydrocarbon signatures in the mussels collected over the last eight years of the LTEMP in Port Valdez, we now believe that the observed hydrocarbon distributions may be explained by a combination of surface microlayer effects and the seasonal development and subsequent breakdown of a stratified water column within the port. These physical oceanographic features directly control the position of the BWTP diffuser plume within the water column, and we now hypothesize that a surface microlayer, which contains higher levels of PAH derived from the BWTP diffuser during the winter period, also allows transport of wind- and current-driven concentrations of PAH to the intertidal zones in early to late spring. Ironically, this occurs at a time when reproduction and other biological activities are at their highest.

These findings may significantly alter the assessment of potential toxicological effects in the future, because the surface microlayer is also host to developing eggs and larval forms of numerous marine organisms that utilize the port. The juxtaposition of these highly carcinogenic (and mutagenic) compounds and the rapidly developing eggs and larvae may be of special concern but to date this phenomenon has not been considered in evaluating any of the LTEMP data in Port Valdez.

The chromatographic profiles of the PAH and n-alkane hydrocarbons associated with the effluent from the BWTP diffuser analyzed as part of the 2001 BWTP Mixing Zone Study (Salazar et al. 2001) demonstrated that the majority of the PAH input into the waters of Port Valdez was in the dissolved-phase and that the PAH were primarily composed of alkylated naphthalenes, fluorenes, and phenanthrenes/anthracenes. Approximately 10 to 20 percent of the hydrocarbons in effluent, however, were associated with discrete but extremely small, dispersed oil droplets; i.e., the particulate phase. These droplets contained a suite of much more highly weathered PAH and SHC, including higher relative proportions of alkylated phenanthrenes/anthracenes and chrysenes, phytane, and n-alkanes between n-C 10 and n-C 32. The PAH profiles observed in the BWTP Mixing Zone Study showed bioavailability and uptake of BWTP diffuser-sourced petroleum hydrocarbons from each of these two physical states. The majority of the subsurface caged mussels demonstrated uptake of primarily dissolved-phase lower molecular weight PAH, comprised of naphthalenes and lower concentrations of fluorenes, and phenanthrenes/anthracenes. The n-alkane patterns associated with those mussels were characterized primarily by biogenic components including n-C 15 and n-C 17 (derived from phytoplankton) and pristane, which is present in the lipid-rich fecal material from herring, pollock, and numerous other fish species that feed heavily on calanoid copepods, primarily *Neocalanus plumchrus*, which dominate the water column in early spring (Cooney 1986). In general, there was little evidence of phytane and higher molecular weight n-alkanes (n-C 23 through n-C 32), which would be indicative of dispersed but highly weathered whole-oil droplets. Several other mussel samples, notably from Station 1 immediately adjacent to the BWTP diffuser (at depths of 100,150, and 200 feet) and the replicate samples from Station 3 (at 250 feet) showed evidence of uptake of petroleum hydrocarbons primarily from dispersed oil droplets or a particulate phase.

Thus, while the majority of PAH released from the BWTP diffuser is in the dissolved phase where it is bioavailable at extremely low (10-30 ng/L) concentrations in the vicinity of the mixing zone, the heavily weathered dispersed oil droplets are actually more persistent. They can be accumulated at significant concentrations when brought into direct contact with mussels and other organisms in specific density-controlled plumes within the water column or at the air-sea interface where they are concentrated in the surface microlayer. In fact, we believe this particulate-phase oil from the BWTP diffuser is the source for much of the petroleum hydrocarbon signature identified in the intertidal mussels analyzed as part of the LTEMP.

This pattern is particularly true in the samples collected in the spring, which should hypothetically reflect mussels (and copepods) ingesting dispersed oil-phase droplets over the winter season when the water column is not vertically stratified and the oil droplets and dissolved components from the BWTP diffuser can reach the surface waters. In the spring with the initiation of freshwater input from melting snow, the water column in Port Valdez becomes more stratified. As the seasons advance and the stratification builds, fewer particulate oil droplets reach the surface and the particulate phase signal fades in mussel tissues. The stratification persists until October or November with the onset of freezing temperatures cooling the upper water surface and limiting freshwater runoff, and winter storms which promote vertical water column mixing.

From the BWTP study, the data suggested the dispersed oil droplets advected away from the AMT diffuser as well-defined ribbon-like plumes, which were entrained between different density layers of the water column (Salazar et al. 2001). During the period of stable water stratification between early spring and fall, effluent from the ballast water treatment plant is primarily entrained in the middle water column regions where it is advected and diluted into the receiving waters of Port Valdez without the opportunity to reach the upper water column and surface layer to a significant extent. These findings were in line with earlier diffuser plume modeling and dye studies and physical oceanographic descriptions of the Port (Colonell 1980a,b, Woodward Clyde & ENTRIX 1987). The exact position of the effluent plume is controlled by time-variable water column stratification, the temperature and salinity of the BWTP effluent, and storm events (including freshwater input enhancing water column stratification and turbulent energy promoting water column turnover).

The mussels collected for the LTEMP at AMT and GOC are clearly coupled as changes in total PAH concentrations are significantly correlated and track over time to a remarkable degree. This is best illustrated by the figure of the Mytilus Petrogenic Index (Figure 6), which demonstrates the parallel trends in hydrocarbon signals observed at these two physically distinct and widely (6 km) separated stations. What also is apparent from the Mytilus Petrogenic Index plot and analysis of individual PAH profiles from all the stations is the fact that the spring signals at both AMT and GOC are predominantly those derived from dispersed oil droplets (also referred to as particulate hydrocarbons). This would be consistent with near surface transport of dispersed oil droplets in or near the surface microlayer during those periods of the year when the lack of water column stratification allows the positively buoyant, yet extremely small oil droplets to slowly rise to the surface where they are then entrained in the surface microlayer (GESAMP 1995) and driven by wind and currents into the intertidal zones at the LTEMP monitoring stations. During the summer, when water column stratification is more pronounced and significantly higher suspended particulate matter (SPM) loads result in more localized oil-droplet/SPM agglomeration and sedimentation, the dispersed oil plume from the BWTP diffuser cannot reach the upper surface layers (Woodward Clyde and ENTRIX, 1987). As a result, the measured hydrocarbons in the intertidal LTEMP stations are significantly lower and generally reflect input primarily from dissolved lower molecular weight PAH rather than the particulate phase.

The hydrocarbon signature in the sediments collected adjacent to the BWTP diffuser and at AMT clearly show input from hydrocarbons associated with the BWTP diffuser and terminal operations. This is not surprising given the higher concentrations of oil introduced in this region (approximately one barrel of heavily weathered ANS crude oil is estimated to be introduced per day from nominal BWTP operations), and oil-SPM interactions from the high loads of suspended sediment and glacially-derived silt present in the water column during much of the year. The immediate proximity of high SPM loads and dispersed oil droplets released from the BWTP would lead to rapid oil-SPM interactions, agglomeration, and sedimentation (Payne et al. 1989, and references therein).

The sediments at GOC, however, are not significantly contaminated with ANS oil, and the PAH profiles suggest input from a variety of sources including lesser amounts of ANS oil (possibly from the Alyeska Marine Terminal), diesel, and atmospheric input of combustion products.

Consequences of Hypothesized Transport and Exposure Mechanisms on Strategies for Future Monitoring Programs and Research Studies

Recently Baumard et al. (1999a,b) discussed the importance of understanding the route of pollutant exposure when using mussels to predict impacts on different marine ecosystems. Specifically, they concluded that the mussels showed different accumulation patterns according to the pollution source they were exposed to (dissolved fraction PAHs versus particulate oil-droplet fraction versus PAH associated with suspended sediments). These findings were then cited in applying caution to monitoring programs and modeling biological uptake of contaminants where the results directly depend on the pollution source and physical state. Similar cautions were recently reported by Baussant et al. (2001a,b) who found that the difference in accumulation of PAH from the particulate (oil droplet) phase by mussels versus the dissolved phase by fish necessitated the utilization of more than one category of animals to assess PAH levels in marine organisms. As considered at length in the preceding sections, the mussels in this study accumulate pollutants from both the dissolved and particulate phases but the results should not be generalized to all species in the Port.

While clearly capable of measuring temporal trends and the physical state of the hydrocarbons released from the BWTP diffuser in Port Valdez, mussels may not be the most appropriate organism for measuring some forms of hydrocarbons, particularly if most of the hydrocarbons are associated with the surface microlayer. Mussels are very suitable for "sampling" hydrocarbons either in dissolved or particulate form in the water column. However, when hydrocarbons become highly concentrated in the surface microlayer (as discussed above), they probably are deposited in surficial sediments during an ebbing tide and then become adsorbed on organic particulates and sediment particles while the tide is out. Once adsorbed onto organic and inorganic particulates, a large proportion of these hydrocarbons probably remains in the surficial sediments during a flooding tide rather than floating back into the surface microlayer. Because these hydrocarbons are in the surface layer rather than the water column, they may not be effectively "sampled" by mussels, which feed in the water column. Rather, these contaminants probably would be more effectively "sampled" by animals such as the clam *Macoma balthica*, which feeds by vacuuming organic-rich particulates residing at the surface of the sediment.

Consider if a PAH were present at 10 ng/L in the dissolved phase, then it could possibly be present in the surface microlayer at 1-10 µg/L given the concentration factors reported by Hardy and others (Hardy 1982, Hardy et al. 1987a,b, Cross et al. 1987). These concentrations may provide elevated exposures to intertidal organisms, and present a scenario for adverse effects that could not be evaluated in this report because of an absence of data.

UV radiation increases the toxicity of PAHs and petroleum (Pelletier et al. 1997; Ankley et al. 1997, 1995). Alexander and Chapman (1980) report that in mid-November to early February the water column is generally well mixed and clear in Port Valdez, and the one percent level of surface sunlight reaches to a 25 m depth. Around the summer solstice, heavy freshwater runoff carrying large quantities of suspended solids and phytoplankton blooms reduce the one percent penetration level to as shallow as 6 meters (Alexander and Chapman, 1980). Barron and Ka'aihue (2001) concluded that photoenhanced toxicity may occur in Prince William Sound from spilled oil, but these authors did not evaluate the potential for photoenhanced toxicity from ballast water discharges or from surface microlayer exposures.

Ankley et al. (1995, 1997) evaluated the effects of exposure to ultraviolet light on survival of a freshwater oligochaete (*Lumbriculus variegatus* – used here as a polychaete surrogate) with tissue burdens of fluorene, anthracene, fluoranthene, and pyrene. They reported that UV irradiation reduces by approximately an order of magnitude the concentrations of tissue residue (and associated water) at which survival effects become apparent for anthracene, fluoranthene, and pyrene (Table 9). For the freshwater oligochaete, anthracene, fluoranthene, and pyrene, water concentrations associated with no effect ranged from 2.5 to 5 µg/L (Ankley et al. 1995, 1997). However, they reported no phototoxic effect on survival for fluorene.

Pelletier et al. (1997) evaluated the response of a clam (*Mulinia lateralis*) and a mysid (*Mysidopsis bahia*) during exposure to several PAHs and petroleum products (most notably anthracene, fluoranthene, and pyrene, and Prudhoe Bay crude) under fluorescent and UV light regimes. The results, summarized in Table 10, indicate that exposure to UV light increases the sensitivity of mysids and clam embryos, larvae, and juveniles, to anthracene, fluoranthene, and pyrene, as well as to Prudhoe Bay crude oil. Moreover, these data indicate that phototoxic concentrations are in the low to sub parts per billion range for mysids and clam embryos, larvae, and juveniles (0.23 to 83 µg/L for the PAHs and 87 µg/L for Prudhoe Bay crude oil. In view of the possibility that these concentrations may be attained in the surface microlayer, there is potential for photoenhanced toxicity in the surface microlayer and in intertidal habitats. During the winter and spring, contaminants in the surface microlayer can become adsorbed on surficial sediments and accumulated in tissues of animals living over, in or on the sediments (e.g., mysids, harpacticoid copepods, or the clam *Macoma balthica*). Subsequently, the contaminated sediments and animals can be exposed to extended periods of UV irradiation during the long days of spring and summer. The studies of Ankley et al. (1995, 1997) and Pelletier et al. (1997) have demonstrated clearly that phototoxicity operates well whether the contaminants are in the water column or in the tissues.

Table 9. Effects of UV radiation on concentrations of selected PAHs in water and tissue at which no survival effects are observed for the oligochaete *Lumbriculus variegatus*.

PAH Compound	Concentration of PAH in Water Associated with Tissue Concentration (µg/L)	No-effect Tissue Concentration of PAH without UV (µg/g)	Concentration of PAH in Water Associated with Tissue Concentration (µg/L)	No-effect Tissue Concentration of PAH with UV (µg/g)
Fluorene	NA	NA*	386	189
Anthracene	36.9	52.4	2.52	3.4
Fluoranthene	143	250	4.7	12.5
Pyrene	80.2	96.2	5.03	10.0

* NA = Not Available

Table 10. Comparison of acute and chronic effects in marine mysids and clams following exposure to several PAHs found in the Ballast Water Treatment Plant effluent or Prudhoe Bay crude and UV (blue rows) or fluorescent light.

Common Name	Scientific Name	Duration of Exposure (days)	Estimated Effects Concentration (µg/L)	Endpoint/ Chronic Effect*
Anthracene				
Mysid	*Mysidopsis bahia*	4	3.6*	LC_{50}
Mysid	*Mysidopsis bahia*	4	535**	LC_{50}
Clam (embryo)	*Mulinia lateralis*	4	6.47*	EC_{50}, Survival & Development
Clam (embryo)	*Mulinia lateralis*	4	4,260**	EC_{50}, Survival & Development
Clam (juvenile)	*Mulinia lateralis*	4	68.9*	LC_{50}
Clam (juvenile)	*Mulinia lateralis*	4	>13,300**	LC_{50}
Clam (juvenile)	*Mulinia lateralis*	4	82.8*	EC_{50}, Growth

Clam (juvenile)	*Mulinia lateralis*	4	>13,300**	EC_{50}, Growth
Fluoranthene				
Mysid	*Mysidopsis bahia*	4	5.32*	LC_{50}
Mysid	*Mysidopsis bahia*	4	63.8**	LC_{50}
Clam (embryo)	*Mulinia lateralis*	4	1.09*	EC_{50}, Survival & Development
Clam (embryo)	*Mulinia lateralis*	4	58.8**	EC_{50}, Survival & Development
Clam (juvenile)	*Mulinia lateralis*	4	1.8*	LC_{50}
Clam (juvenile)	*Mulinia lateralis*	4	3,310**	LC_{50}
Clam (juvenile)	*Mulinia lateralis*	4	>0.81*	EC_{50}, Growth
Clam (juvenile)	*Mulinia lateralis*	4	900**	EC_{50}, Growth
Pyrene				
Mysid	*Mysidopsis bahia*	4	0.89*	LC_{50}
Mysid	*Mysidopsis bahia*	4	24.8**	LC_{50}
Clam (embryo)	*Mulinia lateralis*	4	0.23*	EC_{50}, Survival & Development
Clam (embryo)	*Mulinia lateralis*	4	>11,900**	EC_{50}, Survival & Development
Clam (juvenile)	*Mulinia lateralis*	4	1.68*	LC_{50}
Clam (juvenile)	*Mulinia lateralis*	4	>9,454**	LC_{50}
Clam (juvenile)	*Mulinia lateralis*	4	>0.91*	EC_{50}, Growth
Clam (juvenile)	*Mulinia lateralis*	4	>9,454**	EC_{50}, Growth

Prudhoe Bay Crude				
Mysid	*Mysidopsis bahia*	4	86.6*	LC_{50}
Mysid	*Mysidopsis bahia*	4	157**	LC_{50}
Clam (embryo)	*Mulinia lateralis*	4	86.6*	EC_{50}, Survival & Development
Clam (embryo)	*Mulinia lateralis*	4	>2,540**	EC_{50}, Survival & Development

* EC_{50} under UV light exposure

** EC_{50} under fluorescent light exposure

In summary, after examining the data from BWTP effluent, we concluded that mussels should not be relied upon solely as the receptor with which to measure potential for exposure to various forms of hydrocarbons. Direct testing of organisms or life stages of interest is preferable to extrapolating from surrogate organisms such as mussels (Meador et al., 1995). In addition, if the surface microlayer transport and deposition hypothesis is demonstrated to be true, then the combined effects of microlayer concentrations and photoenhanced toxicity need to be reevaluated in the context of exposed organisms that spend at least some portion of their lives concentrated at the air-sea interface. Likewise, the effects of stranded surface microlayer films on exposed tidal flats may be significantly exacerbated by photoenhanced toxicity.

CONCLUSIONS

- An ANS oil signal that can be attributed to the BWTP effluent is detectable in mussel tissues at both AMT and GOC stations and sediments at AMT.
- The hydrocarbon burdens in the mussels at AMT and GOC are coupled by seasonally-controlled physical oceanographic and biological processes (i.e., stratified layers, entrained plumes, surface microlayers, spring blooms, spawning and feeding behavior).
- Both particulate oil- and dissolved-phases account for patterns of PAH and SHC in mussels. Filter feeding species (e.g., mussels, oysters, clams) primarily accumulate petrogenic hydrocarbons from the particulate phase oil when available. At other times, the signal from dissolved phase components predominate.
- Biota with passive uptake (e.g., lipid-rich eggs) primarily accumulate oil from the dissolved phase components in the water column.
- Mussels should not be the only species used to measure exposure to hydrocarbons. If species other than adult mussels are of interest, direct testing of those organisms (or sensitive life stages) is preferable to extrapolating from surrogate organisms (Meador et al., 1995).
- According to available data and currently accepted methods of toxicological assessment, the low levels of petroleum hydrocarbons in Port Valdez biota appear to be no risk to the biota; however, new insight into the dynamics of the port have identified several data gaps that merit additional investigation.
- The combined potential for concentrated surface microlayer exposures and photoenhanced toxicity may increase the risks to intertidal biota by increasing exposure and lowering the levels of oil necessary to cause adverse effects.
- To fully understand the risks of exposure, it is necessary to know the exposure pathway. The hypothesized transport and uptake mechanisms presented in this report introduce a whole new dynamic into the risk discussion and on how future studies should be designed.
- There are large differences between results from LTEMP and Alyeska mussel monitoring programs that could not be resolved within the scope of this report. Because we are familiar with the strengths and weaknesses in the LTEMP program and have high confidence in the LTEMP results, we are intrigued to find the cause for the differences (e.g., spatial variability, sampling design, or analytic procedures).

RECOMMENDATIONS— SUGGESTED MODIFICATIONS TO THE LTEMP MONITORING PROGRAM

- Continue the LTEMP monitoring program at Alyeska Marine Terminal and Gold Creek to continue to identify temporal trends and the coupling of hydrocarbon contamination at these two locations.
- Initiate a program of surface microlayer sampling (GESAMP 1995) to document the seasonal transport of particulate-phase oil contaminants by advective (wind and current) processes. If a significant surface microlayer is determined to exist (i.e., spatially wide with elevated concentrations) then the potential for ecological impacts, including photoenhanced toxicity, should be investigated.
- Initiate a tissue sampling program using Macoma balthica, a selective deposit feeder that feeds on sediments at the water/sediment interface) to provide greater insight into exposure pathways and potential effects of the surface microlayer in intertidal habitats.
- Attempt to identify the reason for the significant differences in total PAH concentrations measured in the LTEMP vs. the Alyeska Marine Terminal monitoring program. It is not clear why there are such large differences in measured total PAHs in mussel tissues between the two sampling programs. The findings may be pertinent to the NPDES review in assessing the adequacy of the Alyeska monitoring program. For no additional expense, we at the least recommend that Alyeska expand their monitoring to report the full suite of 43 PAH analytes rather the 17 currently reported.
- Initiate a reconnaissance program to identify other intertidal sites that support ambient mussel populations that could be used to obtain a wider geographic evaluation of intertidal contamination within the Port. Because there are only data from three sites with no information on transport processes or geographic fate, there may be other areas receiving more concentrated levels of pollutants.
- Sample shrimp and other species that have been commercially fished or used in subsistence diets from the Port near the BWTP mixing zone and quantify PAH and SHC tissue concentrations. Compare against the same species collected from other locations not influenced by the AMT (possibly west of the Valdez Narrows).
- Sample other species of interest. Direct testing of organisms or life stages of interest is preferable to extrapolating from surrogate organisms such as mussels. *Macoma balthica* may be more appropriate as a deposit-feeding intertidal sentinel species.
- Investigate uptake rates in small invertebrate eggs (e.g., harpacticoids and mysids) to get a better picture of egg susceptibility. Herring and salmon eggs have been shown to be sensitive in taking up PAHs but there is a data gap in looking at smaller egg sizes typical of ecologically important invertebrates.
- If, in Port Valdez, surface microlayers are prevalent, spatially significant and contaminated, or if invertebrate eggs are found to be rapidly saturated by dissolved phase PAH, then additional efforts in the intertidal regions might include near-surface large volume water sampling and collection of eggs (from brooding species) in the intertidal zone for PAH analyses and laboratory controlled studies to look for exposure to developing embryos and larval stages.

- Incorporate a conductivity-temperature-depth (CTD) profiler to identify the overall depth and structure of the water column and possibly a submersible fluorometer to better define the BWTP effluent plume. Then confirm its presence and PAH concentrations by more detailed chemical analyses of discrete filtered 3 L grab samples at specific depths suggested by the CTD and fluorometer data.

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APPENDIX OF POTENTIAL SENTINEL BIOTA FOUND IN PORT VALDEZ

Six of the more important intertidal and shallow subtidal infaunal species, in terms of measuring impacts from chronic hydrocarbon contamination, are listed in Table 7. The mussel *Mytilus trossulus*, an epifaunal organism also commonly found in partially buried mat-like beds on soft substrate, is listed to show abundance and distribution. Average life spans for all of these species are probably at least several years. The criteria used to select these species include:

- Individual size
- Abundance and available biomass
- Feeding behavior
- Ease of collection

The six animals are fairly evenly divided among the four feeding types. Four of the species were observed in the intertidal zone and three were observed in subtidal sediments. Only the clam *Axinopsis serricata* was observed intertidally (low intertidal) and subtidally.

All of these animals were common. Robust populations of suspension feeders were observed only in the intertidal zone. Robust populations of non-selective deposit feeders were observed only on the subtidal slopes of the fjord, in relatively unconsolidated sediments. In contrast, selective deposit feeders were observed both intertidally and subtidally.

Although the softshell clam *Mya arenaria* occurs in some areas in intertidal habitats (Lees et al. 1979a,b), it did not appear to be sufficiently common or widespread to support a sampling program. The only other infaunal suspension feeder that could fulfill this role is the burrowing innkeeper worm, *Echiurus echiurus alaskanus*. This echiuran worm pumps seawater through its semi-permanent U-shaped burrow and strains the water through a funnel-shaped mucous net that it constructs across the bore of the burrow. Like the mussel, it will intercept hydrocarbon droplets and oil adsorbed to suspended particulates. It will also be exposed to dissolved hydrocarbons through dermal contact as the seawater passes through the burrow, but its epidermis may be less receptive to them than the gill membranes of the mussel. Currently, we are not aware of any studies of hydrocarbon effects in *E. echiurus alaskanus*.

The two selective deposit feeders are both clams of the genus *Macoma* (Table 7). The smaller species, *Macoma balthica*, is very abundant and dominates the biological assemblages in terms of abundance, biomass, and function in many intertidal areas in the port. Because of its abundance and its mode of feeding (vacuuming the surface around it with an extensible incurrrent siphon), it is probably a good receptor for hydrocarbons that occur on the surface of the sediment. In areas where its density is high, the potential feeding area (PFA) encompassed by the reach of the siphons can exceed the surface area of the mud flat by more than 2.5 times (Brey 1991). At the estimated densities indicated in Table 7, the PFA for the *M. balthica* populations ranges from about 0.5 to 1.3 times the surface area of the mud flat. Consequently, large proportions of the organic material deposited on the surface of the mud (including hydrocarbons) are likely to be "inhaled" by *M. balthica* soon after settlement. The unfortunate aspect of this situation is that the mass of the hydrocarbons will be divided among a few thousand individuals. However, by relating the number and average size of the individuals used in each sample for hydrocarbon analysis to density and size structure of the sampled population, it may be possible to estimate the mass of hydrocarbons consumed on a unit area basis. Using this information in conjunction with analysis of hydrocarbon residuals in intertidal sediments, it may be possible to construct an estimate of hydrocarbons deposited per unit area.

The subtidal clam species, *M. obliqua,* is considerably larger than *M. balthica* but its density is substantially lower. Although its potential feeding area is far larger, it is likely that the sum of PFAs for the population is about 40 percent of the surface area. Nevertheless, this provides a considerable opportunity for this species to accumulate a substantial proportion of the hydrocarbons deposited on the surface of sediments.

A large burrowing polychaete worm, *Nephtys punctata,* is an important non-selective deposit feeder. Feeding craters and fecal mounds several centimeters in diameter and high can be observed on the soft, unconsolidated sediments of the upper slopes of the fiord. These provide ample evidence of its abundance in these unstable sediments. Because we anticipate that deposited sediments at the sediment/water interface are probably more concentrated than after they become mixed into bulk sediment, it is likely that information provided by bulk deposit feeders is somewhat less accurate than that provided by selective deposit feeders. However, hydrocarbon data from these animals may provide considerable insight into long-term conditions because the feeding behavior of the animals integrates temporal and spatial variation in contaminant conditions in the sediments.

The small clam (*Axinopsida serricata*) has been included only because its abundance and size might be considered to make it suitable as a sentinel species. In fact, it may not be either a suspension or deposit feeder although it has been referred to as the former. The species a member of the bivalve family Thyasiridae, several genera of which are widely recognized to derive their nutrition mainly from chemoautotrophic bacterial symbionts residing in or on the gill filaments. Members of the family typically have a reduced gut, no incurrent siphon, and large fleshy gills poorly adapted for filtration or particulate feeding (Dame, 1996). Consequently, it appears that *Axiinopsis* does not process sediments and that hydrocarbons in seawater passing over the gills would not be filtered or concentrated. Moreover, the hydrocarbons could be metabolized in unexpected ways by the symbionts living thereon because these bacteria are adapted for extracting energy from reactions among sulfur compounds, oxygen, and carbon dioxide. Thus, most of the nutrition is apparently derived from chemical reactions.

Lees et al. (1979a, b) also reported observing numerous juvenile tanner crab on the shallow subtidal shelf and on the soft unstable sediments of the subtidal slopes of Port

Valdez. This suggests these habitats may be important nursery habitats for the tanner crab.

In summary, although several relatively large invertebrates live in intertidal and shallow subtidal sediments of Port Valdez, the most widely distributed and appropriate among them for an additional sentinel species for hydrocarbon contamination appear to be two species of the genus *Macoma*, i.e., *M. balthica* intertidally and *M. obliqua* subtidally.

APPENDIX OF ACQUIRE EXPOSURE CRITERIA RELEVANT TO VALDEZ BIOTA

The PAH constituents are arranged by increasing molecular weight (Table 11); results within each constituent are sorted from shortest to longest duration of exposure.

Concentrations of naphthalenes in the water column generally were higher than for other PAH constituents although the concentration of the parent compound was low. Estimated chronic effects concentrations for naphthalene (parent compound) exposures lasting from 0.002 to 4 days ranged from 0.000085 µg/L (0.085 parts per trillion; a behavioral response in the blue crab *Callinectes sapidus* in a 0.002-day exposure) to 194,000 µg/L (194 ppm; a developmental response in the oyster (*Crassostrea gigas*) larvae in a 2-day exposure; Table 11). In view of their extremely low and high values, and the early life stage for the oyster, both values, based on early studies of hydrocarbon effects, should be viewed with skepticism without confirmatory studies.

Fluorene compounds were moderately concentrated relative to other PAH constituents in the water column. No records on chronic effects were found for fluorene in seawater (Table 11); results for freshwater insects, crustaceans, and fish were tabulated in the absence of seawater data. The estimated effects concentrations may exhibit a tendency to decrease with increased duration of exposure but differences in the endpoints confound this conclusion. Nevertheless, the Maximum Acceptable Toxicant Concentration (the geometric mean of the LOEC and NOEC) for the insect and fish were substantially below 1 ppm.

Dibenzothiophenes were moderately concentrated in the water column relative to other PAH compounds. Only one record was located for chronic effects of dibenzothiophene. This record indicates that mussel feeding behavior is relatively sensitive to the parent compound.

Alkylated homologues of phenanthrene and anthracene generally exhibited the second highest concentrations in the water column. Unfortunately, however, no records whatsoever were located for alkylated phenanthrenes/anthracenes. The only possibly relevant records located were for the parent phenanthrene and anthracene, which had relatively low concentrations compared to other PAH constituents in the water column. Mussels exhibited a change in feeding behavior following exposure to 150 µg/L phenanthrene for ~100 minutes. Brine shrimp, possibly representing larval crustaceans, exhibited intoxication after a 24-hour exposure to 1000 µg/L. Anthracene appears to be somewhat less toxic. Oysters and clams exhibited changes in behavior and growth after 2 and 4 days exposure to 5 and 6.7 ppm anthracene, respectively.

Fluoranthene concentrations in the water column were generally relatively low compared to naphthalenes, fluorenes, dibenzothiophenes, and phenanthrenes/anthracenes. Chronic effects data were available for the blue mussel, six gammarid amphipods, and a clam. NOECs and LOECs for 1-day exposures for gammarids were consistently 3.5 and 35 µg/L, respectively. Four-day EC_{50}s for behavior in five species of gammarids were quite consistent, ranging from 27 to 70 µg/L. The 4-day EC_{50} for growth in the clam was an order of magnitude higher.

Pyrene concentrations in the water column were also generally relatively low compared to naphthalenes, fluorenes, dibenzothiophenes, and phenanthrenes/anthracenes, and it would be expected to exist in the particulate- rather than dissolved-phase. Chronic effects data were available for the blue mussel and a clam. Mussel feeding rates appeared to be sensitive to low concentrations of pyrene. Two measurements for a 4-day EC_{50} for growth in the clam varied considerably, probably as a consequence of a combination of differences in life stage and phototoxicity. Unfortunately, no records were located describing chronic effects for chrysene.

Benzo(a)pyrene concentrations in the water column were quite low relative to other PAH constituents, and it would be expected to exist in the particulate phase (most likely from combustion sources). Chronic effects data were available for three species of fish. Except for the 4-day test, the effects concentrations were all low relative to other PAH compounds. A comparison of the NOECs and LOECs for an enzymatic response in Dover sole following exposure to pyrene and benzo(a)pyrene

Based on a comparative study, it appears that the feeding rate of mussels decreases directly with the molecular weight of the parent compounds. Following 100-minute exposures, the EC_{50}s decreased from 920 µg/L for naphthalene to 40 µg/L for pyrene, the heaviest compound evaluated during this review. This reduction in the EC_{50} suggests that the chronic effect of pyrene on feeding behavior of mussels is about 20 times greater than naphthalene.

Table 11. Chronic effects in bioassays for selected aquatic and marine organisms resulting from exposure to several PAH found in the Ballast Water Treatment Plant effluent.

Common Name	Scientific Name	Duration of Exposure (days)	Estimated Effects Concentration (µg/L)	Endpoint/ Chronic Effect*
FRESHWATER				
Fluorene				
Midge	*Chironomus plumosus*	2	2,350	EC_{50}, Intoxication
Midge	*Chironomus thummi*	2	2,350	EC_{50}, Intoxication

Water flea	*Daphnia magna*	2	430	EC_{50}, Intoxication
Water flea	*Daphnia pulex*	2	212	EC_{50}, Intoxication
Midge	*Chironomus thummi*	30	218	MATC, Behavior
Bluegill	*Lepomis macrochirus*	30	30.4	MATC, Behavior
Bluegill	*Lepomis macrochirus*	30	60.5	MATC, Growth
SEAWATER				
Naphthalene				
Blue crab	*Callinectes sapidus*	0.002	0.000085	EC_{50}, Sensory Detection
Barnacle (larvae)	*Balanus eburneus*	0.04	3,600	EC_{50}, Behavior
Blue mussel	*Mytilus edulis*	0.07	920	EC_{50}, Feeding Behavior
Brine shrimp	*Artemia salina*	1	2,730	EC_{50}, Intoxication
Oyster (embryos)	*Crassostrea gigas*	2	194,000	EC_{50}, Development
Fiddler crab	*Uca pugilator*	4	11,500	EC_{50}, Physiology
Phenanthrene				
Blue mussel	*Mytilus edulis*	0.07	150	EC_{50}, Feeding Behavior
Brine shrimp	*Artemia salina*	1	1000	EC_{50}, Intoxication
Polychaete worm	*Neanthes arenaceodentata*	56	20	EC_{50}, Growth & Reproduction

Anthracene				
Oyster	*Crassostrea gigas*	2	5,000	EC_{50}, Behavior
Clam	*Mulinia lateralis*	4	82.8	EC_{50}, Growth
Clam	*Mulinia lateralis*	4	13,300	EC_{50}, Growth
Dibenzothiophene				
Blue mussel	*Mytilus edulis*	0.07	90	EC_{50}, Feeding Behavior
Fluoranthene				
Blue mussel	*Mytilus edulis*	0.07	80	EC_{50}, Feeding Behavior
Amphipod	*Ampelisca abdita*	1	3.5	NOEC, Biochemical
Amphipod	*Ampelisca abdita*	1	35	LOEC, Biochemical
Amphipod	*Rhepoxynius abronius*	1	3.5	NOEC, Biochemical
Amphipod	*Rhepoxynius abronius*	1	35	LOEC, Biochemical
Amphipod	*Rhepoxynius abronius*	4	35	EC_{50}, Behavior
Amphipod	*Corophium insidiosum*	4	54	EC_{50}, Behavior
Amphipod	*Eohaustorius estuarius*	4	70	EC_{50}, Behavior
Amphipod	*Grandidierella japonicus*	4	27	EC_{50}, Behavior
Amphipod	*Leptocheirus plumulosus*	4	51	EC_{50}, Behavior
Clam	*Mulinia lateralis*	4	0.81	EC_{50}, Growth
Clam	*Mulinia lateralis*	4	900??	EC_{50}, Growth
Pyrene				
				EC_{50}, Feeding

Blue mussel	*Mytilus edulis*	0.07	40	Behavior
Clam	*Mulinia lateralis*	4	0.91	EC_{50}, Growth
Clam	*Mulinia lateralis*	4	9454	EC_{50}, Growth
Benzo(a)pyrene				
Dover sole	*Solea solea*	3	1,000	NOEC, Enzymatic
Dover sole	*Solea solea*	3	5,000	LOEC, Enzymatic
Killifish	*Fundulus* sp.	4	2,650	EC_{50}, Enzymatic
Mummichog (embryos)	*Fundulus heteroclitus*	10	7.112	EC_{50}, Enzymatic

* EC_{50} - Median Effective Concentration for non-lethal endpoints; LOEC – Lowest Observable Effects Concentration; NOEC – No Observable Effects Concentration; MATC - Maximum Acceptable Toxicant Concentration