

C. Chemistry

1. Quality Assurance/Quality Control

a) Data Quality Indicators

The quality of all chemistry data generated and processed in the program was assessed for Precision, Accuracy, Representativeness, Completeness, Comparability, and Method Detection Limits. Precision and accuracy requirements, as related to surrogate recoveries and analyses of standard reference materials, matrix spike and matrix spike duplicates, and spiked-blanks, followed NOAA Status and Trends analytical requirements. The Case Narratives submitted by the Woods Hole Group Laboratories with each batch of analytical results indicated that the QC data met the criteria for acceptance, and any outliers were identified. Based on the laboratory's and our own evaluation of those data, it was concluded that the precision and accuracy, as reflected in surrogate recoveries and the results of duplicate analyses, duplicate matrix-spike and spiked-blank analyses, and analyses of SRMs, were such that the data could be used for the stated purpose of environmental characterization and trend analysis.

Representativeness begins with sample collection in the field, and with this project, it was assured by the experience of the field sampling team and their knowledge of the intertidal environments within the study areas. Triplicate sediment samples were collected. Two samples were analyzed and the third sample archived to provide the most representative characterization of the study sites that could be practically and economically obtained. In the case of tissue samples, multiple individuals were collected at each site and then composited to provide the most representative samples possible. When sufficient organisms were available, additional samples were collected to provide replicates (of multiple individuals) for tissue analyses as well.

The completeness of the data consists of an estimate of the amount of data expected from the field program versus the amount of data actually entered into the database that is available for interpretation.

$$\text{Percent complete (\%C)} = (v/t) \times 100\%$$

where:

v = number of valid measurements

t = total number of planned measurements

In this program, the data completeness is estimated to approach 100 percent. No samples were lost during shipment and analyses, and the high data acceptance rate allowed useable data to be obtained on essentially every sample collected and analyzed. In fact, as the program evolved, several additional samples were added (e.g., eroded peat from Captain Cook State Beach and Drift River crude oil) as the results of other analyses suggested the need for additional source characterization data.

The Woods Hole Group Environmental Laboratory Standard Operating Procedures contain elements to ensure the comparability of data. In accord with the NOAA Status and Trends Protocols and the Woods Hole Group's documented SOPs, all PAH results are corrected for surrogate recoveries. In addition, all concentrations are reported on a dry weight sample basis (e.g., μg of a particular analyte/gram dry wt of sample extracted). Additional program and laboratory elements that ensure data comparability include:

- Consistency of reporting units;
- Traceability of Standard Reference Materials (SRMs);
- Use of Federal reference (U.S. EPA, NOAA, and ASTM), equivalent, or alternative test procedures and methods; and
- Standardization of data format.

Method Detection Limits (MDLs) are controlled by the volume or weight of sample extracted, extraction efficiencies, component losses during extract fractionation and cleanup, the final concentrated extract volume, the size of the aliquot injected into the analytical instrument, and instrumental sensitivity as determined by replicate analyses of low-concentration standards. Because of limited numbers of individual organisms (e.g., *Macoma balthica*) collected in the field at some locations, it was not always possible to extract as large a sample size as desired. In such instances, the method detection limit for that sample would be higher. To aid in data evaluation of samples with numerous constituents at or just below the method detection limits, actual individual component MDLs were shown by Lees et al. (1999) as a series of dots connected by a solid line at the sample-specific MDL concentration for each PAH histogram plot presented in their report. This same approach is again utilized in this report for all histogram plots of PAH, SHC, and S/T components. It greatly facilitates identifying and quantifying real constituents as opposed to procedural artifacts when analyzing and discussing the data, especially in samples from relatively clean or pristine areas.

b) Field and Laboratory Blanks

The Woods Hole Group Environmental Laboratories provided certified clean I-Chem® jars and shipping coolers for this program. In addition, the laboratory provided distilled/deionized water for the preparation of field blanks. Table 3-7 presents the results from the analyses of all Field and Laboratory Method Blanks completed as part of the program.

Field Blanks were prepared at four randomly selected field sites by opening the sample jars and exposing the open jar and lid to the air for 2-3 minutes (approximately the same amount of time the jar would be open during sample collection). The distilled/deionized water provided by the laboratory was then poured into the jar to act as a "sample" for later analysis. Intertidal sediment samples were collected at each site using disposable, wooden tongue depressors purchased in bulk from a pharmacy. To evaluate the potential from any contaminants leaching from the disposable tongue depressors, one tongue depressor was soaked in the laboratory-supplied distilled/deionized water in a field

sample jar for 3-5 minutes, and that distilled/deionized water was analyzed as a tongue-depressor rinse blank.

Figure 3-41 presents the PAH histogram plots obtained from selected ion monitoring (SIM) GC/MS analyses of a dichloromethane (DCM) solvent rinse of an empty I-Chem[®] jar control sample, the distilled/deionized water shipped directly back to the laboratory in an I-Chem[®] jar, the tongue depressor rinse blank, a Field Blank from Northwest Kalgin Island, and a Field Blank from Polly Creek. The histogram plot generated from the solvent rinse of the empty I-Chem[®] bottle shows no PAH at a method detection limit of 21 ng/liter (parts per trillion). This jar was analyzed separately; on the outside chance that the distilled/deionized water supplied by the laboratory may have been contaminated. As shown by the second histogram in figure, indeed a trace of naphthalene was observed in the distilled/deionized water at concentrations of 24 ng/liter, just above the GC/MS method detection limit of 21 parts per trillion. As will be shown later, this background level of naphthalene contamination in the distilled/deionized water is approximately three orders of magnitude below the µg/Kg (ppb) concentrations measured in some of the field samples. While this background-level contamination in the distilled/deionized water is exceptionally low, it unfortunately manifest itself in all other field blanks prepared using this water. As a result, 23-26 ng/liter concentrations of naphthalene are observed in the tongue depressor rinse blank, the Field Blank from Northwest Kalgin Island, and the Field Blank from Polly Creek. The consistency of the measured naphthalene concentration and the lack of any other PAH constituents strongly suggests that the contaminant was indeed associated with the distilled/deionized water used to prepare the

Table 3-7. Aromatic and aliphatic hydrocarbons measured in field and laboratory method blanks.

Media	Sample ID	Lab ID	TPAH		TAlk		TRC
			µg/Kg	ng/L	µg/Kg	µg/L	µg/Kg
WATER	I-Chem Bottle Blank	45674-05		<21		5.1	
WATER	WHG DI water FB	45674-04		24		9.1	
WATER	Tongue Depressor rinse	45674-06		23		3.3	
WATER	NW Kalgin FB	45674-03		24		3.5	
WATER	N. Tuxedni FB	45674-01		2000		5.2	
WATER	Polly Creek FB	45674-02		26		3.4	
WATER	Old Cannery Creek FB	45674-07		27		7.4	
SEDIMENT	Lab Method BLANK	TS0402B1	<1.0		<100		<100
SEDIMENT	Lab Method BLANK	SS0402B2	<1.0		<100		<100
SEDIMENT	Lab Method BLANK	TS0406B1	<1.8		<100		<100
SEDIMENT	Lab Method BLANK	TS0406B2	<1.2		<100		<100
TISSUE	Lab Method BLANK	ST0417B1	<1.6		310		310
TISSUE	Lab Method BLANK	ST0418B1	<1.6		<130		<130
TISSUE	Lab Method BLANK	ST0418B2	<1.6		<130		<130
TISSUE	Lab Method BLANK	TW0417B2	<1.6		<130		<130

Notes: TPAH measured by SIM GG/MS; TAlk and TRC measured by FID GC. < denotes less than stated method-specific MDL

field blanks and not from the conditions encountered in the field or the sample jars (which were previously demonstrated to be clean) used for sample collection. In any event, it should again be pointed out that at the parts per trillion level, these measured concentrations were three orders of magnitude below values actually measured in field samples.

Figure 3-42 presents the SHC profiles generated from FID/GC analyses of these field blanks. Traces of several contaminants at concentrations just above the method detection limit of 2 µg/liter can be observed in the I-Chem[®] jar blank and in the distilled/deionized

water used to generate the other field blanks. Because all of these constituents are just slightly above the method detection limit, variability among the samples is greater. However, n-C33 appears to be a common constituent at a concentration of approximately 3 µg/liter. Because of its limited water solubility, and its detection in the I-Chem[®] jar bottle blank, this constituent is believed to be associated with the glassware. As will be shown later, however, this background concentration is approximately two orders of magnitude below concentrations measured in actual field samples.

Figure 3-43 presents the PAH histogram plots for the Field Blanks from North Tuxedni Bay and Old Cannery Creek, along with two representative laboratory method blanks generated during the sediment analysis program and a similar laboratory method blank generated during the tissue analysis program. Quite clearly, evidence of contamination from combustion products exists in the PAH histograms obtained at north Tuxedni Bay.

Interestingly, this Field Blank was collected approximately 2-3 minutes after two local residents riding a four-wheeler all-terrain vehicle had visited the site. The wind was absolutely calm at the time the Field Blank was collected, and the four-wheeler was observed to have been smoking badly, with blue-black smoke lingering in the air and easily detected by smell for several minutes after the ignition was turned off. Obviously, traces of the combustion products associated with that vehicular activity were collected in the Field Blank. While these combustion products appear very large at the scale presented in the figure, it should be noted that these maximum concentrations are still three orders of magnitude below concentrations measured in actual field samples. Except for this single instance when the Field Blank was collected under the zero-wind conditions in the proximity of the aforementioned four-wheeler, all other field samples were collected up wind from the helicopter, fixed wing aircraft, or four-wheel drive vehicles used to access the sites. A subsequent Field Blank collected from Old Cannery Creek showed no contamination, other than the previously described naphthalene associated with the distilled/deionized water used to generate all the blanks.

With regard to the Laboratory Method Blanks, no PAH (including naphthalene) were detected at a selected ion monitoring GC/MS method detection limit of 1-2 µg/Kg (ppb) in any of the laboratory method blanks for either sediment or tissue samples. Because all the laboratory method blanks were the same, only three representative samples are presented in the figure.

Figure 3-41. PAH histogram plots of I-Chem sample jar DCM rinse, DI water used to prepare Field Blanks, wooden sampling scoop, and Field Blanks from NW Kalgin Island and Polly Creek.

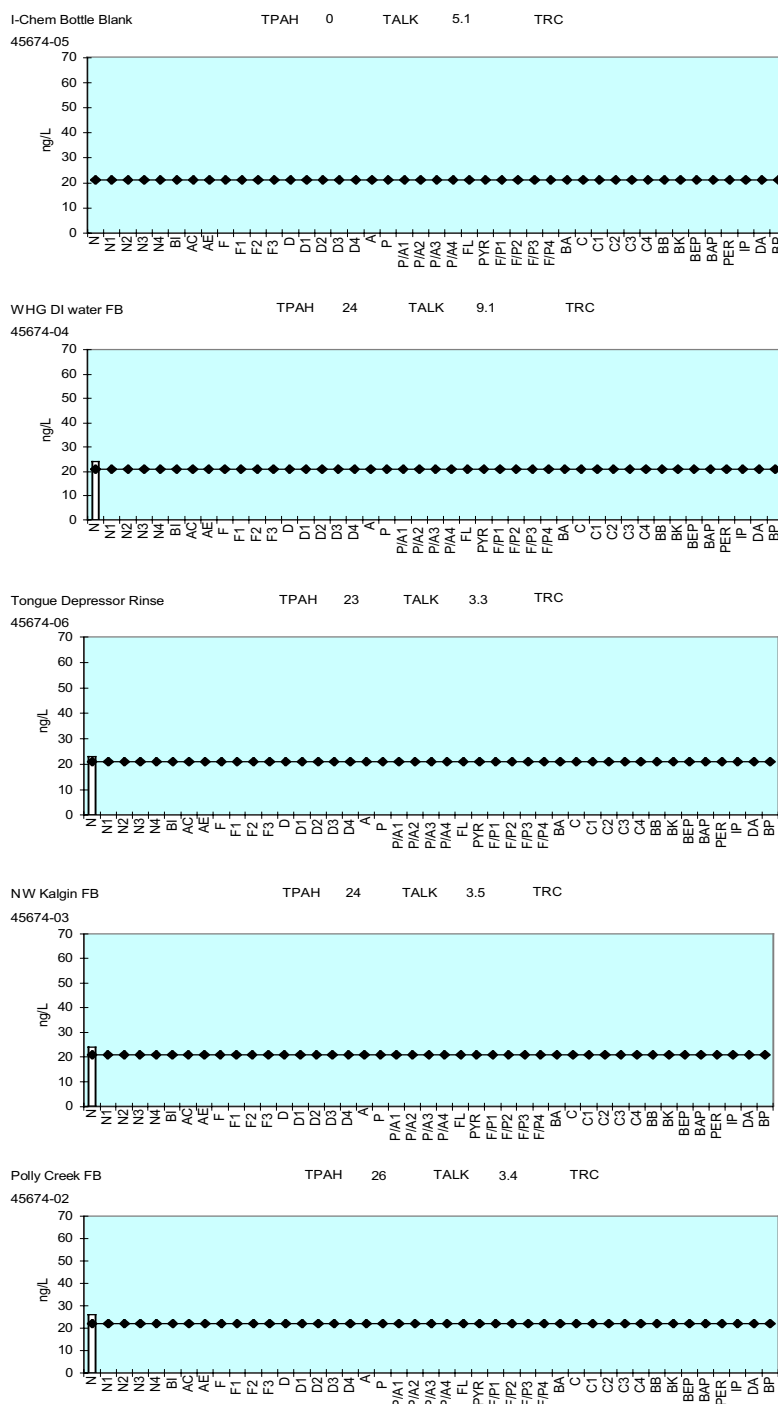


Figure 3-42. SHC histogram plots of I-Chem sample jar DCM rinse, DI water used to prepare Field Blanks, wooden sampling scoop, and Field Blanks from NW Kalgin Island and Polly Creek.

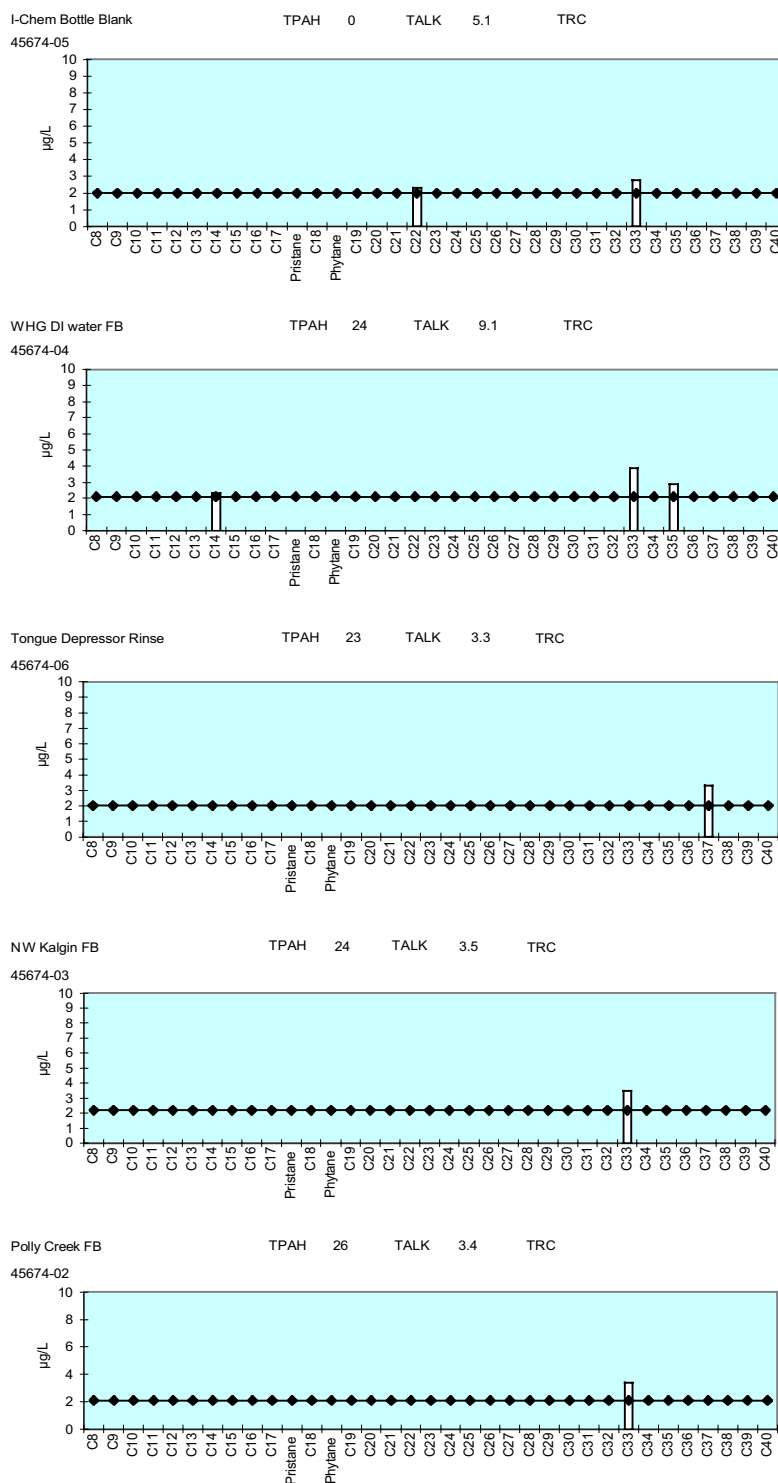
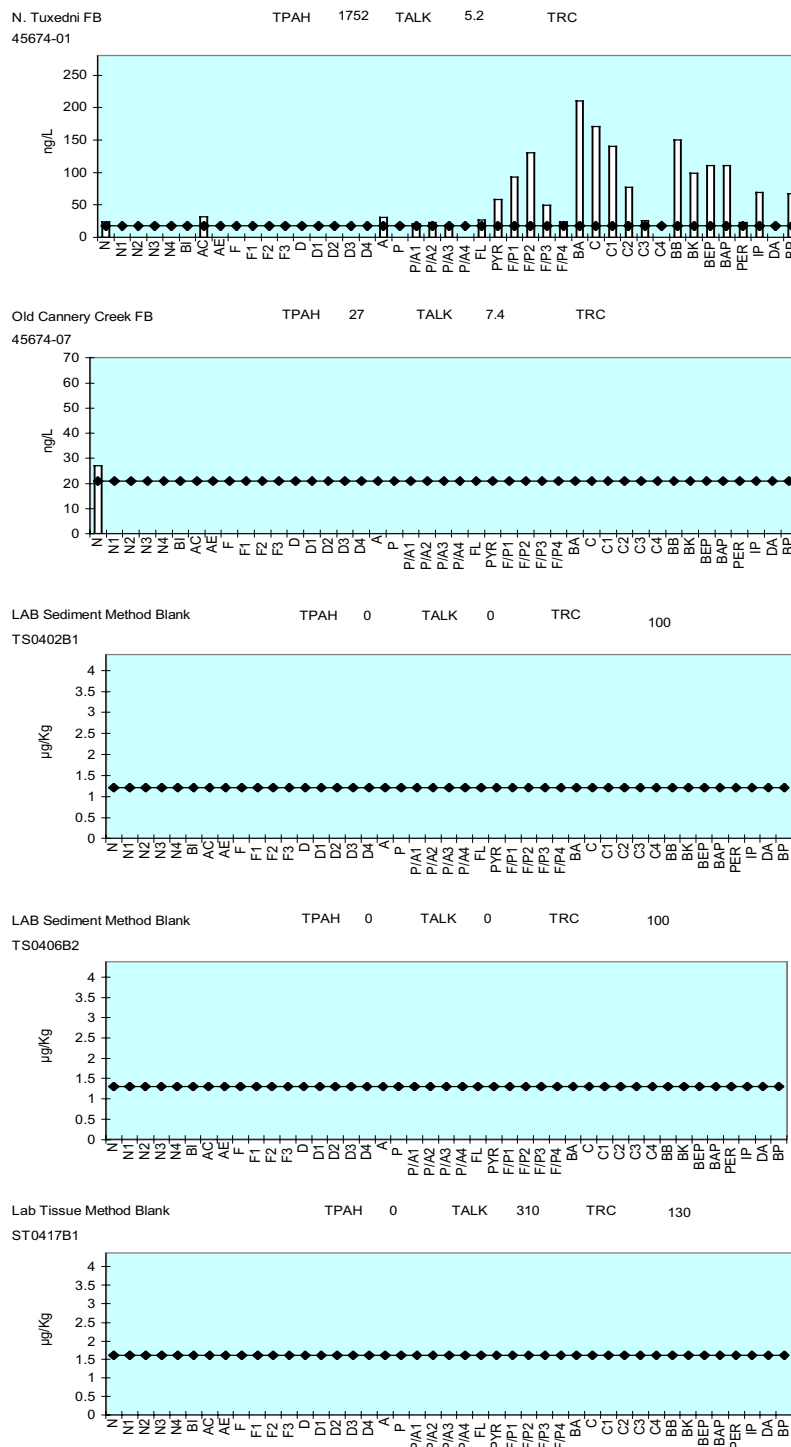


Figure 3-43. PAH histogram plots of North Tuxedni Bay and Old Cannery Creek Field Blanks and representative sediment and tissue Laboratory Method Blanks.



In Figure 3-44, the same near-detection limit background contamination from n-C33 can be observed at 3-4 µg/L in the Field Blanks. As noted previously, this is believed to be

associated with the glass sample jars. SHC laboratory contamination was not observed in any of the Laboratory Method Blanks associated with the sediment analyses; however, a trace of n-C 29 was observed at 310 µg/Kg in one of the Laboratory Method Blanks completed during the tissue analyses. No other SHC components were detected, and the background contamination observed in this single tissue blank was one order of magnitude below concentrations measured in actual field samples.

2. Source Characterization

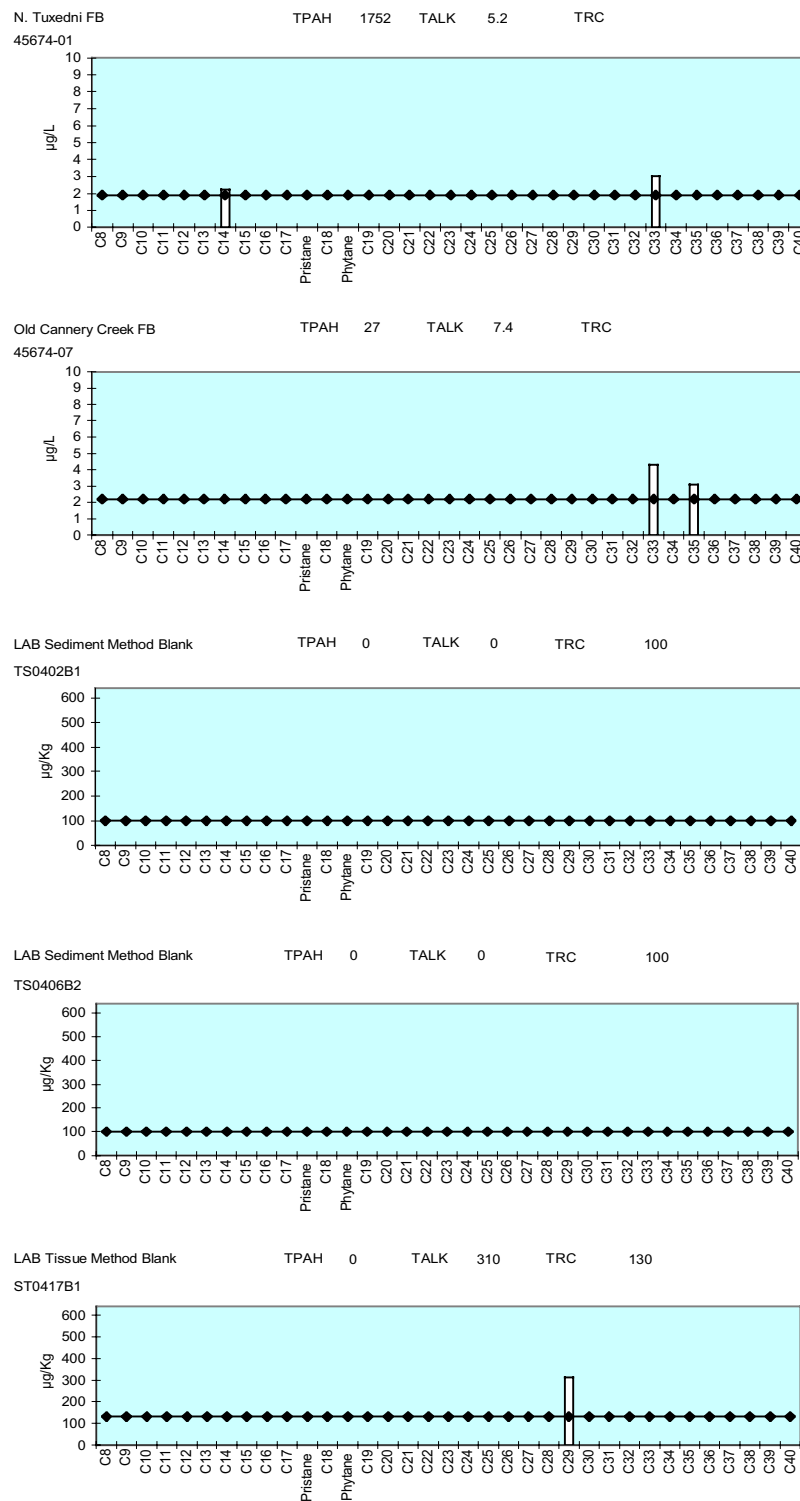
PAH and other hydrocarbons can be introduced to the marine environment from a variety of sources (NRC 1985), and Table 3-8 presents the summary data for TPAH, TPH (or TRC), TALK, TOC, and TKN measured in a number of source-characterization samples that were examined as part of this program. Details of their differing chemical characteristics are discussed in the following sections.

a) Oils and Produced Water

1) Cook Inlet and Alaska North Slope Crude Oils

Figure 3-45 presents the relative distributions of PAH, AHC, and S/T components in Cook Inlet (CI) and Alaska North Slope (ANS) crude oils. The alkylated naphthalenes predominate over the other PAH in both oils, and significantly, the alkylated dibenzothiophenes are drastically reduced in Cook Inlet crude oil compared to ANS crude oil. Taking advantage of these differences, numerous investigators have used double ratio plots of C₃-dibenzothiophene/C₃-phenanthrene versus C₂-dibenzothiophene/C₂-phenanthrene and other diagnostic ratio pairs to differentiate sources (Brown et al., 1980; Overton et al., 1981; Boehm et al., 1989; Sauer and Boehm 1991; Brown and Boehm 1993; Page et al. 1993; Page et al. 1995; and Douglas et al., 1996; Payne et al. 1998; Lees et al. 1999). Compared to the aromatics, the aliphatic constituents are present at significantly higher absolute concentrations, and the relative abundance of individual components differed significantly between the two crude oils. Because of their rapid loss from spilled crude oils by evaporation and microbial degradation processes, however, these aliphatic constituents do not persist in the environment compared to the high molecular weight PAH and the sterane/triterpane constituents. As such, aliphatic (AHC - also referred to as SHC for saturated hydrocarbon) fingerprints are not of much value in source characterization. The sterane/triterpane patterns of the two crude oils do have some similarities with the predominance of S/T 13, S/T 30 and S/T 34 in both samples (see Table 2-3 for definitions of S/T abbreviations). However,

Figure 3-44. SHC histogram plots of North Tuxedni Bay and Old Cannery Creek Field Blanks and representative sediment and tissue Laboratory Method Blanks.



other significant S/T differences that easily allow differentiation between the two sources were observed.

Table 3-8. Aromatic and aliphatic hydrocarbons (plus selected TOC and TKN values) measured in crude oil, coal, and eroding peat source-characterization samples.

		TPAH	TPH or TRC**	TAlk***	TOC	mg/Kg
Crude Oils	Lab ID	µg/Kg	µg/Kg	µg/Kg	mg/Kg dry	
ANS Crude	A20530AK	12,000	540,000,000	64,490,000	n.a.	n.a.
Cook Inlet Crude	CIC053001	9,650	570,000,000	101,060,000	n.a.	n.a.
Drift River Crude	DRC053101	10,500	640,000,000	111,500,000	n.a.	n.a.
East Side						
Clam Gulch Coal	45676-05	4,200	3,200,000	83,390	n.a.	n.a.
Eroding Peat (Capt. Cook St. Park)	45943-01	180	320,000	16,000	>100,000	6,500
Middle of Inlet						
North Shoal Coal	45676-01	1,300	750,000	31,420	n.a.	n.a.
West Side						
No-name Creek Coal	45676-06	31,000	660,000	8,150	>100,000	140
Beluga SW Coal Seam	45676-04	5,900	1,000,000	51,280	n.a.	n.a.
Beluga SW Coal Fines	45676-03	1,600	560,000	36,340	n.a.	n.a.
Beluga SW Coal Chunks	45676-02	5,100	800,000	32,510	>100,000	320

* TPAH represents total PAH as measured by SIM GC/MS

** TPH for oil samples represents total petroleum hydrocarbons measured by FID/GC

TRC for coal and peat samples represents total resolved constituent peaks (but not necessarily petroleum hydrocarbons) measured by FID/GC

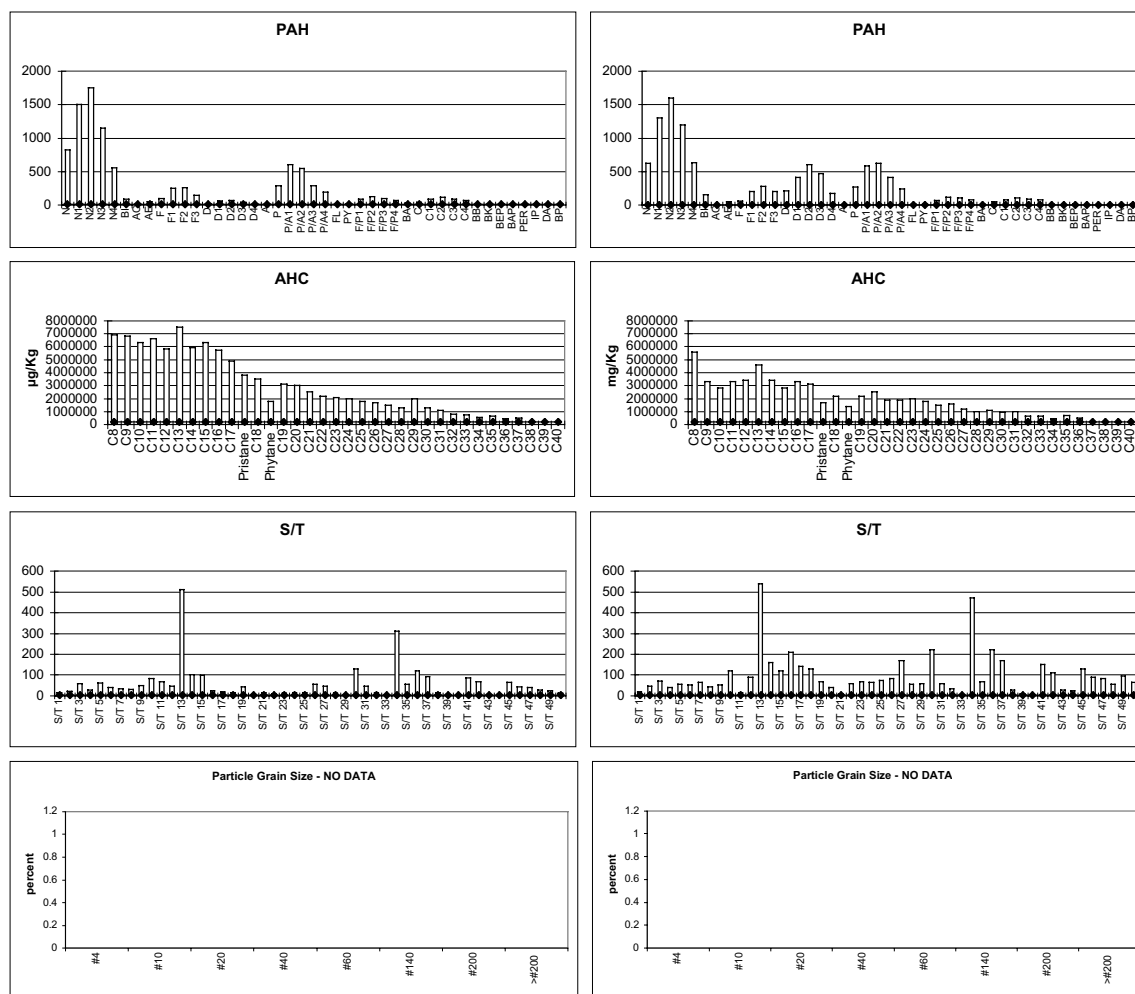
*** TAlk represents the total n-alkanes as measured by FID/GC

n.a. Not available

Most importantly, all of the characterization profiles from both oils are sufficiently different from any of the coal and eroding peat samples characterized in this and other programs (Lees et al. 1999; ADL 2001) to allow easy identification of petroleum contamination in sediments and organisms compared to background PAH derived from other sources. As will be discussed further below, the majority of particulate PAH constituents in coal do not appear to be bioavailable, and they are not detected at significant concentrations in any of the tissues examined in this program. PAH constituents in crude oils and liquid petroleum products, on the other hand, are dissolved by lower molecular weight aromatic (solvent) molecules, and in this more mobile liquid state (with varying degrees of aqueous solubility), they have long been known to

accumulate in the tissues of filter- and detritus-feeding organisms. As such, they can be readily detected in the tissues of monitoring organisms as a result of chronic discharges or a significant oil spill event.

Figure 3-45. Comparison of chemistry profiles for Cook Inlet (CI) and Alaska North Slope (ANS) crude oils.



2) Trading Bay Produced Water

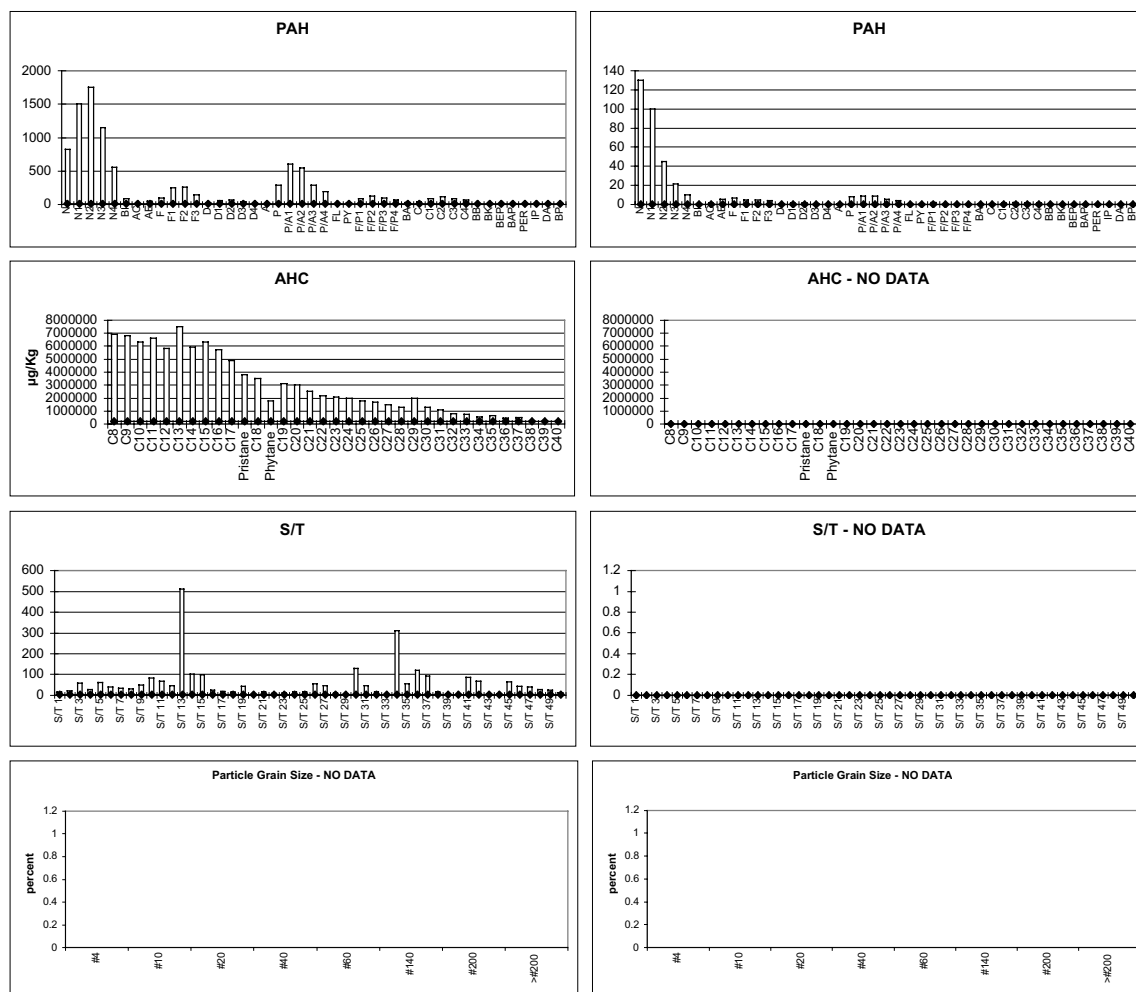
Figure 3-46 presents the PAH and other constituent profiles (when available) for Cook Inlet crude oil compared to the produced water generated from the Trading Bay Tanker Facility. (The produced water sample was analyzed by A.D. Little as part of the 1998 EMP synthesis effort, and that lab did not produce AHC or S/T data.) Clearly, the produced water is significantly enriched in the more water-soluble naphthalene constituents, and this is represented by the predominance of naphthalene over the other alkyl-substituted naphthalene homologues. Because dibenzothiophenes are largely absent in Cook Inlet crude oil, they are also not significantly represented in the PAH

histogram plot for the produced water. Higher molecular weight constituents such as fluoranthenes/pyrenes and alkyl-substituted chrysenes are not sufficiently water-soluble to be represented in the produced water compared to the naphthalene components.

Figure 3-46. Comparison of chemistry profile data for Cook Inlet (CI) crude oil and produced water (PW) released from the Trading Bay Tanker Facility (TF).

Cook Inlet Crude 2

Trading Bay TF PW



b) Cook Inlet Coal Samples

Over the last several years, a significant amount of attention has been directed toward the importance of eroded coal particles as a source of PAH in marine sediments, and an ongoing and often heated debate has ensued in the literature as to the importance of eroding coal and/or source rock versus natural oil seeps as a source of PAH in Prince William Sound, in particular (Short et al. 1997, 1999; Page et al., 1993, 1995, 1996, 1998; and Boehm et al. 2000?). Given the recent attention paid to these and other more

non-traditional PAH sources, Lees et al. (1999) and Payne et al. (1999) suggested that eroding coal may also play an important role in supplying particulate PAH to Cook Inlet. As part of this reconnaissance program, additional samples were collected for source characterization whenever coal was observed as outcrops in the bluffs and scarps above the beach, as part of wave-cut platforms within the intertidal zone, or as accumulations of sand-to-pebble sized particulate fragments between the sand ripples noted along the shorelines and offshore shoals.

The following section presents the source characterization data generated from each of the coal samples collected during this program along with data obtained from collections completed by CIRCAC personnel in 1998 and included in Lees et al. (1999) evaluation of the CIRCAC EMP. All of the samples collected in 1998 were analyzed by A.D. Little Laboratories, while the samples collected in 2000 were analyzed by the Woods Hole Group Environmental Laboratories as part of this program.

Because of the generalized prevailing counter-clockwise currents running from the southwest to the northeast along the east side of Cook Inlet and from the northeast toward the southwest along the west side of Cook Inlet, we will discuss the coal source signatures in an order that follows this general geographical pattern. That is, unlike the south-to-north order used to discuss the sites in the previous sections, we will first go from southwest to northeast (Homer/Clam Gulch/Nikiski) along the east shoreline and then from northeast to southwest (Beluga River SW/North Shoal/No-name Creek) along the west shoreline.

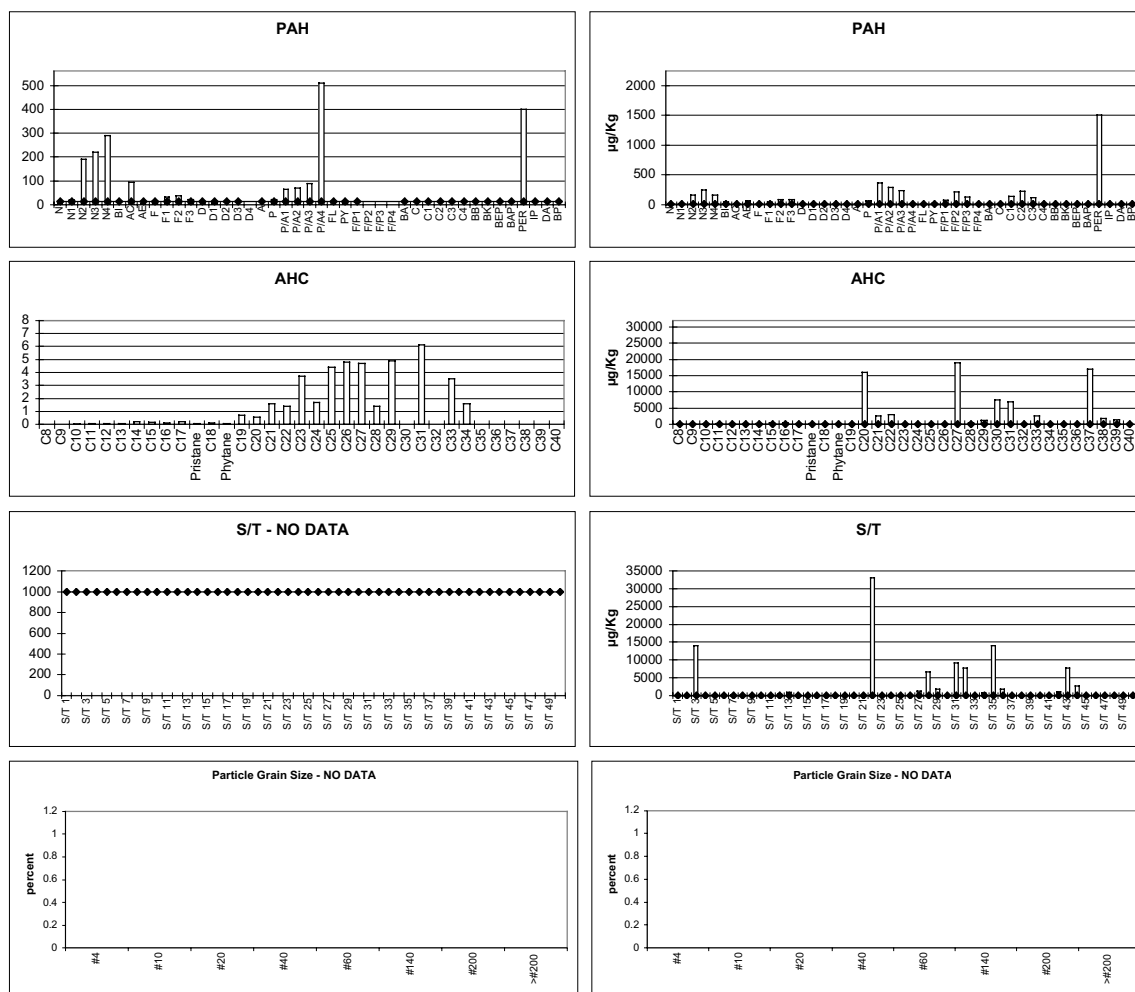
1) Homer Beach Coal (1998) and Clam Gulch Coal (2000)

Figure 3-47 shows the differences in PAH and AHC component distributions in samples of coal collected from Homer in 1998 (analyzed by A.D. Little) and Clam Gulch as part of this program in 2000 (analyzed by the Woods Hole Group Laboratories). While S/T analyses were completed during the CIRCAC 2000 Reconnaissance Program, they were not during the initial screening completed by A.D. Little in 1998, so S/T data are not available for the Homer sample. Obviously, the differences in the PAH and AHC profiles were very strong, with C4-phenanthrene/anthracene being the most predominant PAH in the Homer coal sample followed by perylene and then the C4-, C3-, and C2-naphthalenes, while perylene is three times more concentrated than any other PAH in the Clam Gulch sample and C4-phenanthrene/anthracene is not represented at all. The AHC patterns show absolutely no similarities, and it is also interesting to note the relative abundance differences of PAH vs. AHC for the two samples. The aromatics are two orders of magnitude higher than the aliphatics in the Homer sample, while the aliphatic are an order of magnitude higher than the aromatics in the Clam Gulch sample. As discussed previously, the series of diamonds connected by the solid line at the bottom of each profile represents the laboratory method detection limit (MDL), and the gaps for D4 and F/P2, F/P3 and F/P4 in the profiles for the Homer coal sample indicate compounds that were not part of the analyte list reported by A.D. Little. These compounds include C4 dibenzothiophene and C2, C3, and C4-fluoranthenes/pyrenes.

Figure 3-47 Comparison of chemistry profile data for 1998 Homer coal (analyzed by A.D. Little) and 2000 Clam Gulch coal (analyzed by Woods Hole Group).

Homer Coal 3

Clam Gulch coal



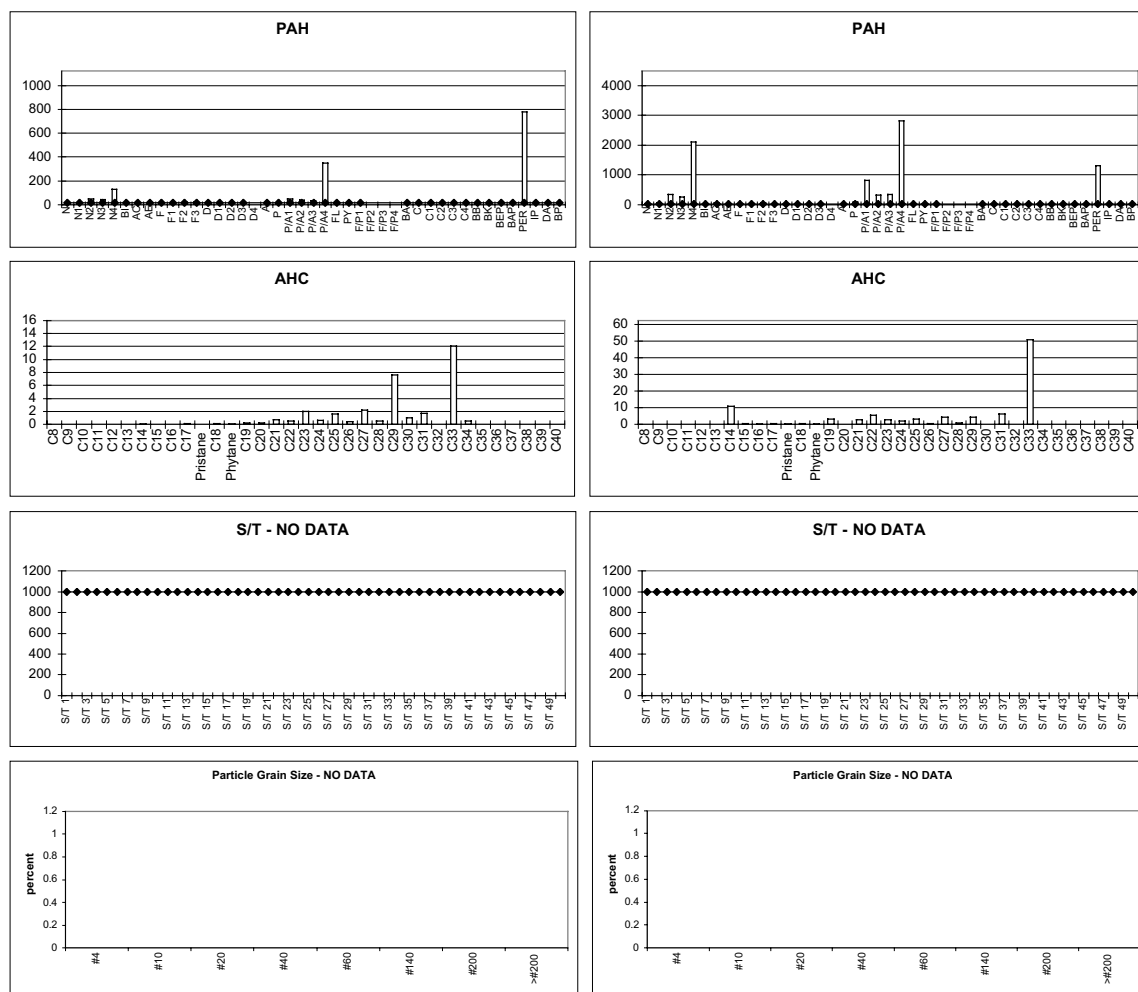
2) Nikiski (1998)

Figure 3-48 shows the differences in relative abundance of individual PAH and AHC components measured in two representative samples of coal collected from the Nikiski bluffs in 1998. The predominance of the C4-naphthalenes and C4 phenanthrene/anthracene is similar to the Homer coal sample; however, the AHC patterns are completely different. Also, the relative abundance of perylene compared to the other PAH is also significantly different in the two samples. In one Nikiski sample perylene predominates (like the coal collected at Clam Gulch, Figure 3-47), while in the other sample, C4-phenanthrene/anthracene is most abundant followed by C4-naphthalenes and then perylene. Also note the different relative concentrations of PAH compared to AHC components in the two coal samples.

Figure 3-48. Comparison of chemistry profile data for two 1998 Nikiski coal samples analyzed by A.D. Little for the 1998 EMP Data Synthesis program.

Nikiski Coal 1

Nikiski Coal 2



3) Beluga Coal Field (1998), Beluga River SW, and North Foreland Area (2000)

Four samples of coal were analyzed from the northwestern portion of the sampling area. One sample was collected in the Beluga coal field in 1998. Three different manifestations of coal were observed in the Beluga River SW/North Foreland area during the 2000 Reconnaissance field survey. On the beach at the 60-65 foot mark at Beluga River SW, coal was observed as 3-4-inch chunks in a 30-foot long swath approximately 6 feet wide laying on the sand/mud. Elsewhere at this site, fine particles of coal were observed between the mud ripples in the lower intertidal zone (near the *M. balthica* collection site). Approximately 4 nm to the southwest, north of North Foreland, a coal outcrop in a wave-cut platform in the upper intertidal zone was observed during our

transit to Nikolai Creek. Several samples were collected at this site by breaking off pieces from the exposed coal seam.

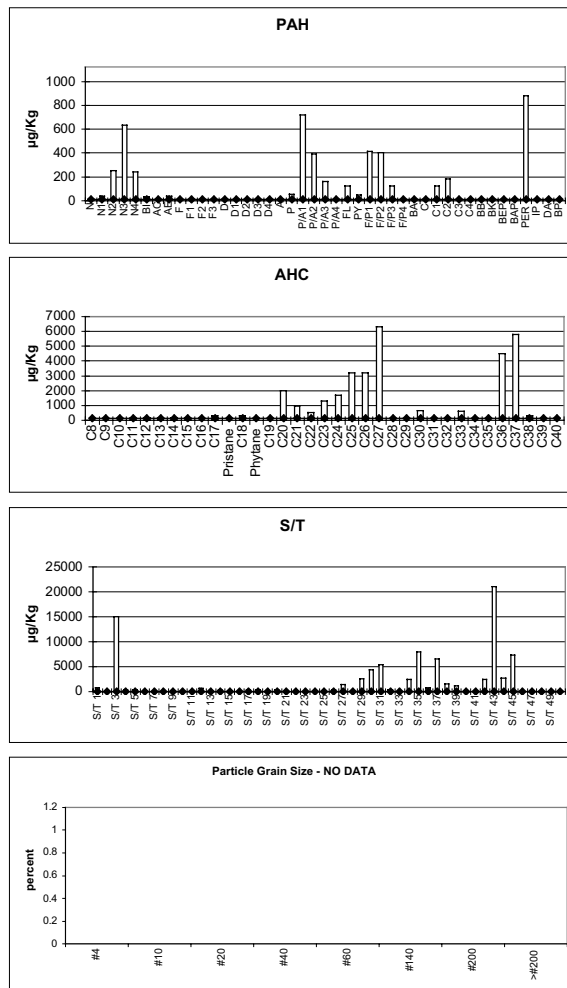
Figures 3-49 and 3-50 show significant variability in aromatic (PAH), aliphatic (AHC), and sterane/triterpane (S/T) composition in four different coal samples identified above. The Beluga River SW chunks and fines and the North Foreland seam samples were analyzed by the Woods Hole Group Laboratories. The Beluga coal field 4 and 5 coal samples (Figure 3-51) were collected during the 1998 EMP data synthesis effort and were analyzed by A.D. Little laboratories. Sterane and triterpane data are not available for those two samples.

Clearly, the differences in relative abundance of the individual constituents in each component class are readily apparent. Perylene is a major component in the three samples analyzed during the FY 2000 reconnaissance program, although the other aromatics are generally present at comparable concentrations. In the two Beluga coal field samples analyzed by ADL, perylene dwarfs all the other components as shown in Figures 3-50 and 51.

The Beluga coal field 4 and 5 coal samples shown in Figure 3-51 were collected in the 1998 EMP synthesis program, and they were analyzed by A.D. Little laboratories. The PAH profiles shown in the figure are presented at a scale (4,000 μ g/Kg) that allows the relative abundance of perylene to be displayed against C4-phenanthrenes/anthracenes and other components. At this scale, however, lower concentrations of C2- and C3-naphthalenes, C1- and C2-fluorenes, and C1-, C2-, and C3-phenanthrene/anthracenes cannot be observed. In actual fact they are present at concentrations ranging from 30 to over 140 ppb in the Beluga River 5 coal samples, and alkylated C1- and C2-phenanthrenes/anthracenes are present between 100 and 150 ppb. These expanded profiles are shown in Figure 3-52, where the individual components at higher concentrations are off scale.

Figure 3-49. Comparison of chemistry profile data from Beluga River SW coal samples.

Beluga River SW coal chunks



Beluga River SW coal fines

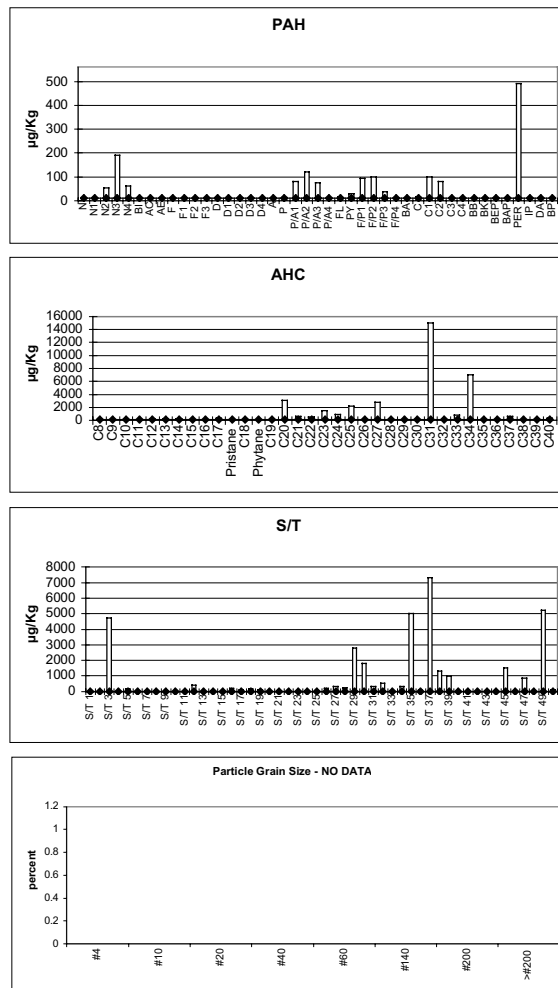


Figure 3-50. Comparison of chemistry profile data from Beluga coal field sample 4 (1998) and North Foreland seam (2000) coal samples.

Beluga coal field sample 4

North Foreland coal seam

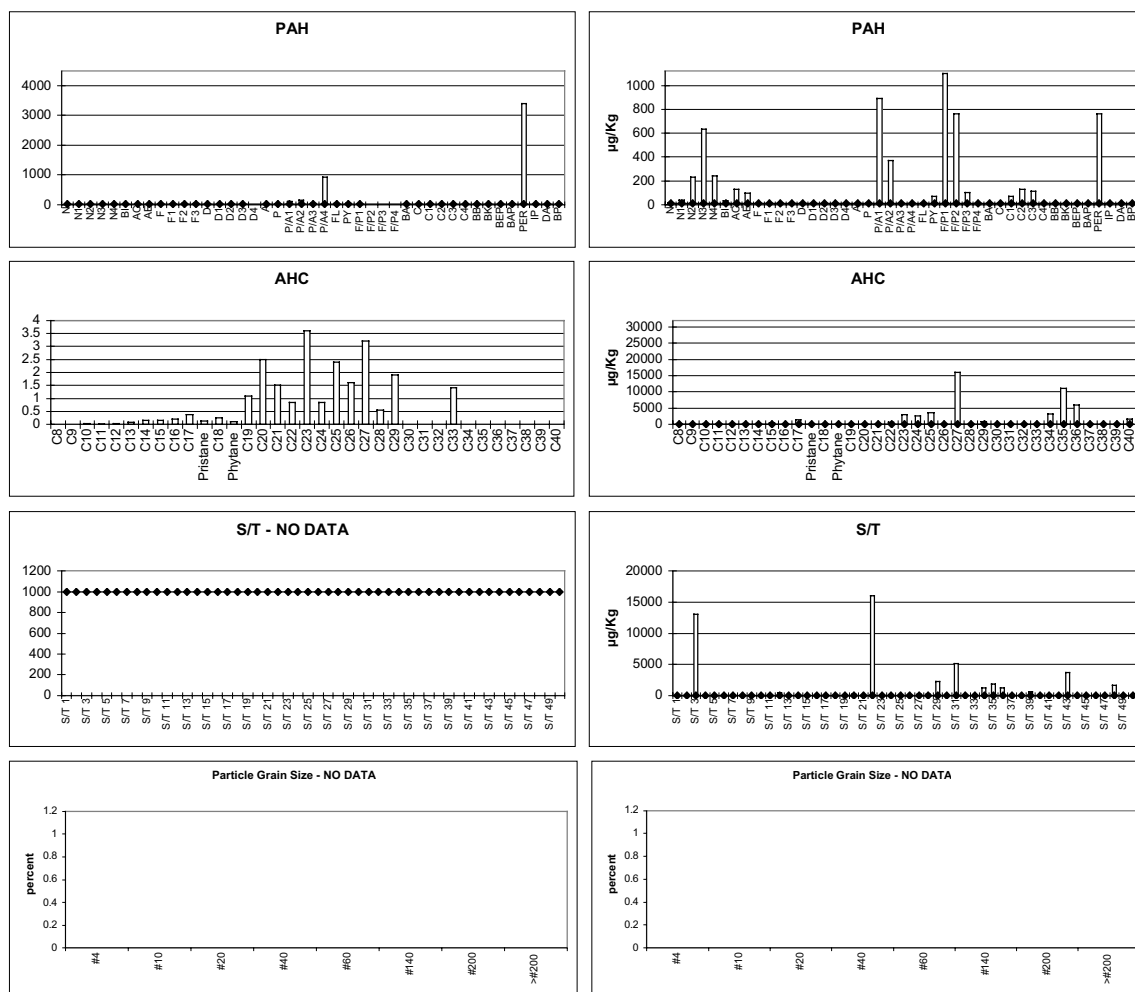


Figure 3-51. Comparison of 1998 Beluga coal field coal samples at higher attenuation to show relative abundance of perylene versus other PAH.

Beluga coal field sample 5

Beluga coal field sample 4

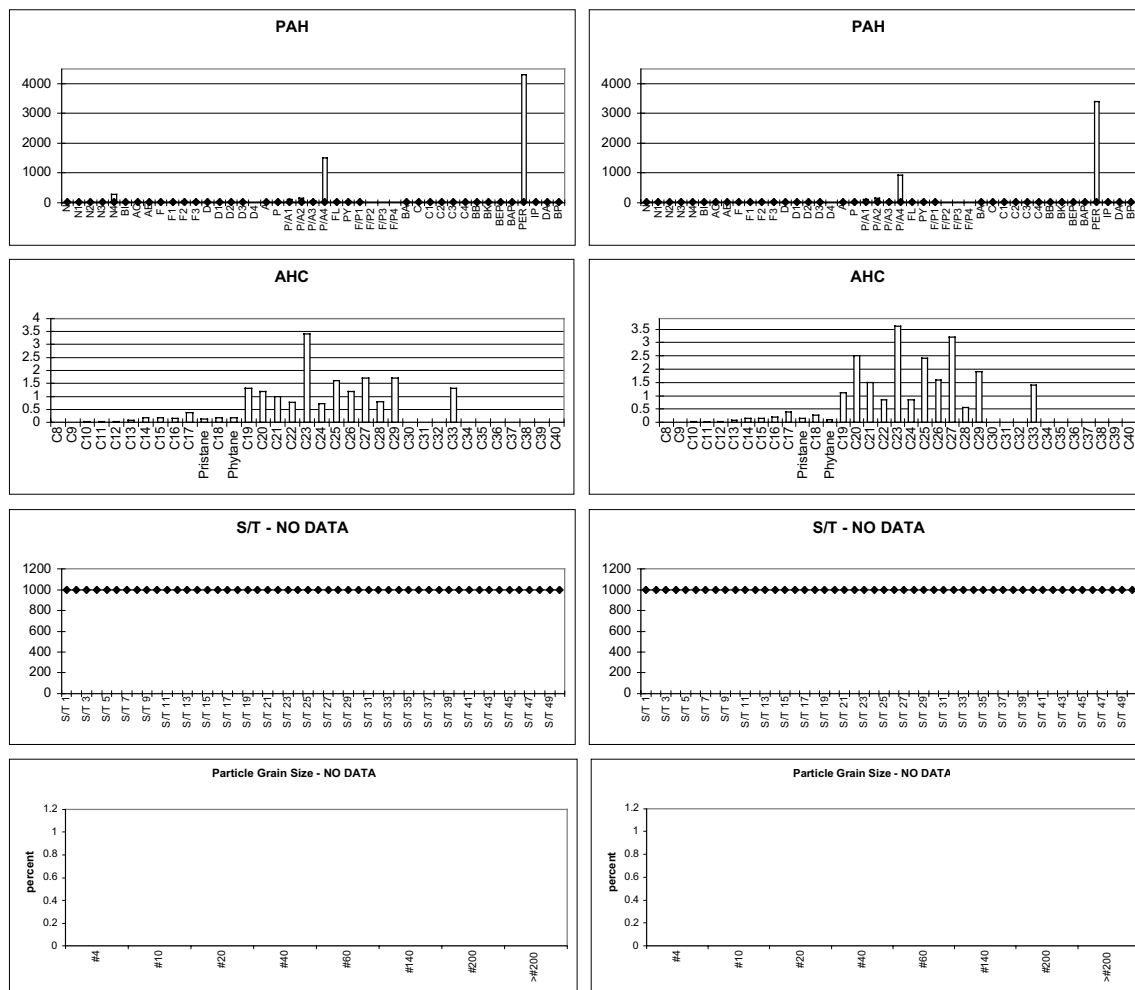
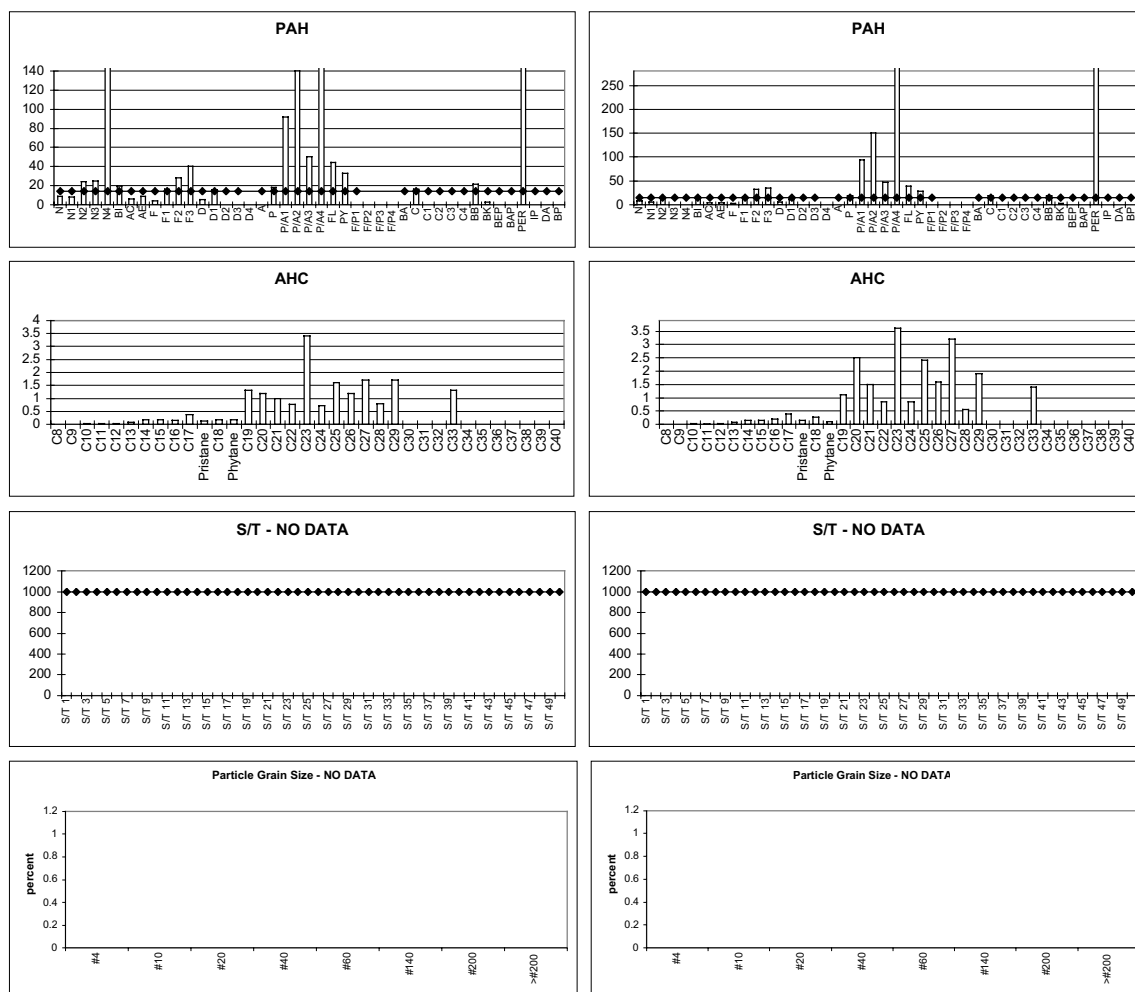


Figure 3-52. Comparison of 1998 Beluga coal field coal samples at lower attenuation to allow evaluation of lower concentration components.

Beluga coal field sample 5

Beluga coal field sample 4



4) North Shoal (2000)

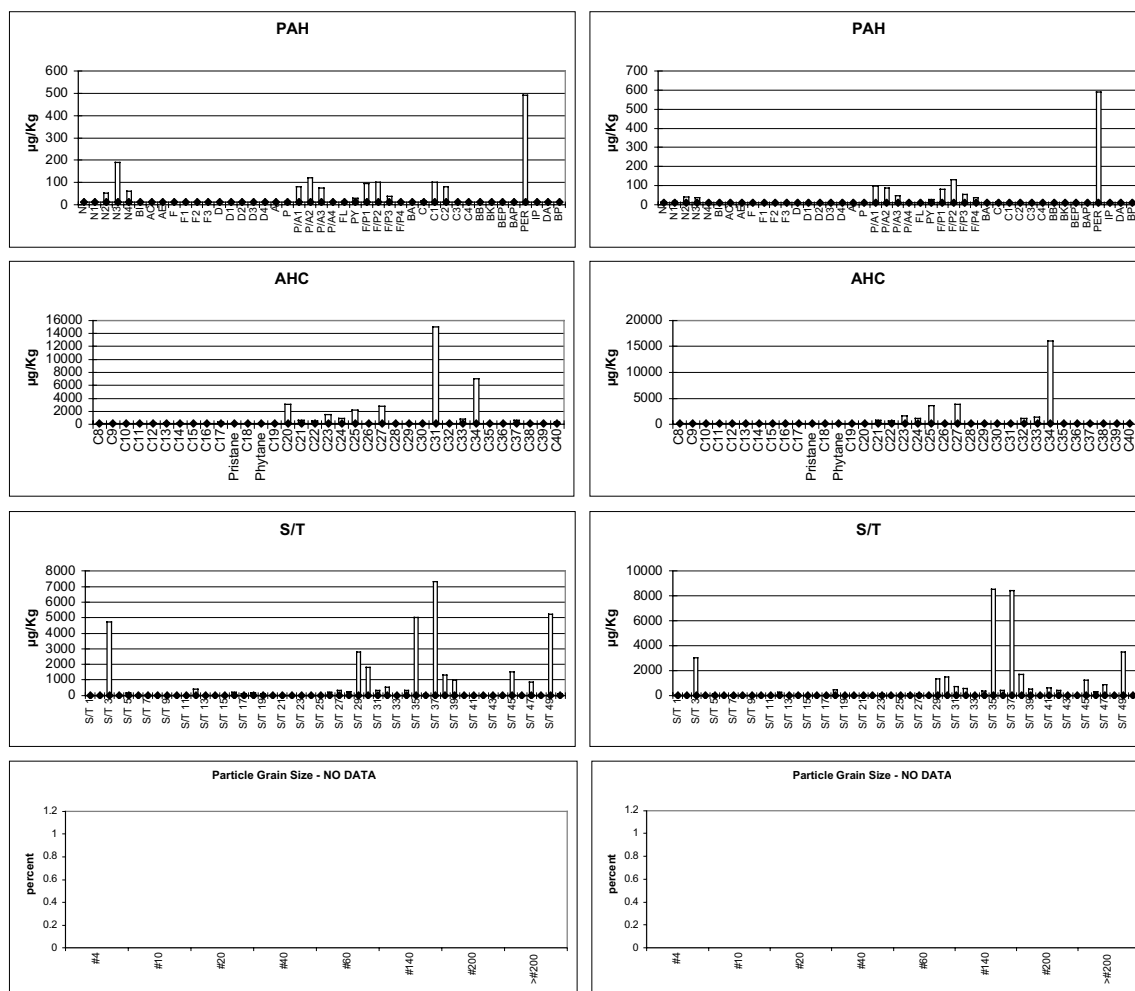
During sampling on the shoal north of Kalgin Island (the North Shoal), sand-sized coal particulates were observed everywhere in the troughs of the current ripples that dominated the exposed sand surface at the site. Of all the coal samples collected and analyzed in this program, it appears that the closest compositional match occurred between the Beluga River SW fines and the particulate coal collected from the North Shoal. Figure 3-53 presents the PAH, AHC, and S/T data for these two samples, and although differences still exist, the similarities are closer than with any other samples examined. In both samples, perylene dominates the PAH fraction, although the naphthalenes are slightly reduced in the North Shoal sample, possibly due to leaching during transport at sea. The aliphatic profiles show many of the same components (n-C 25, n-C 27, and n-C 34) although their relative abundance is different. The sterane

triterpane patterns and absolute concentrations are more similar than any other pair of coal samples evaluated. Based on these data, it appears that the source of the particulate coal observed on the North Shoal could be from the shorelines south of the Beluga River area.

Figure 3-53. Comparison of chemistry profile data for particulate coal samples collected from the shoreline at Beluga River SW and the shoal north of Kalgin Island.

Beluga River SW coal fines

North Shoal coal fines



5) No-name Creek (2000)

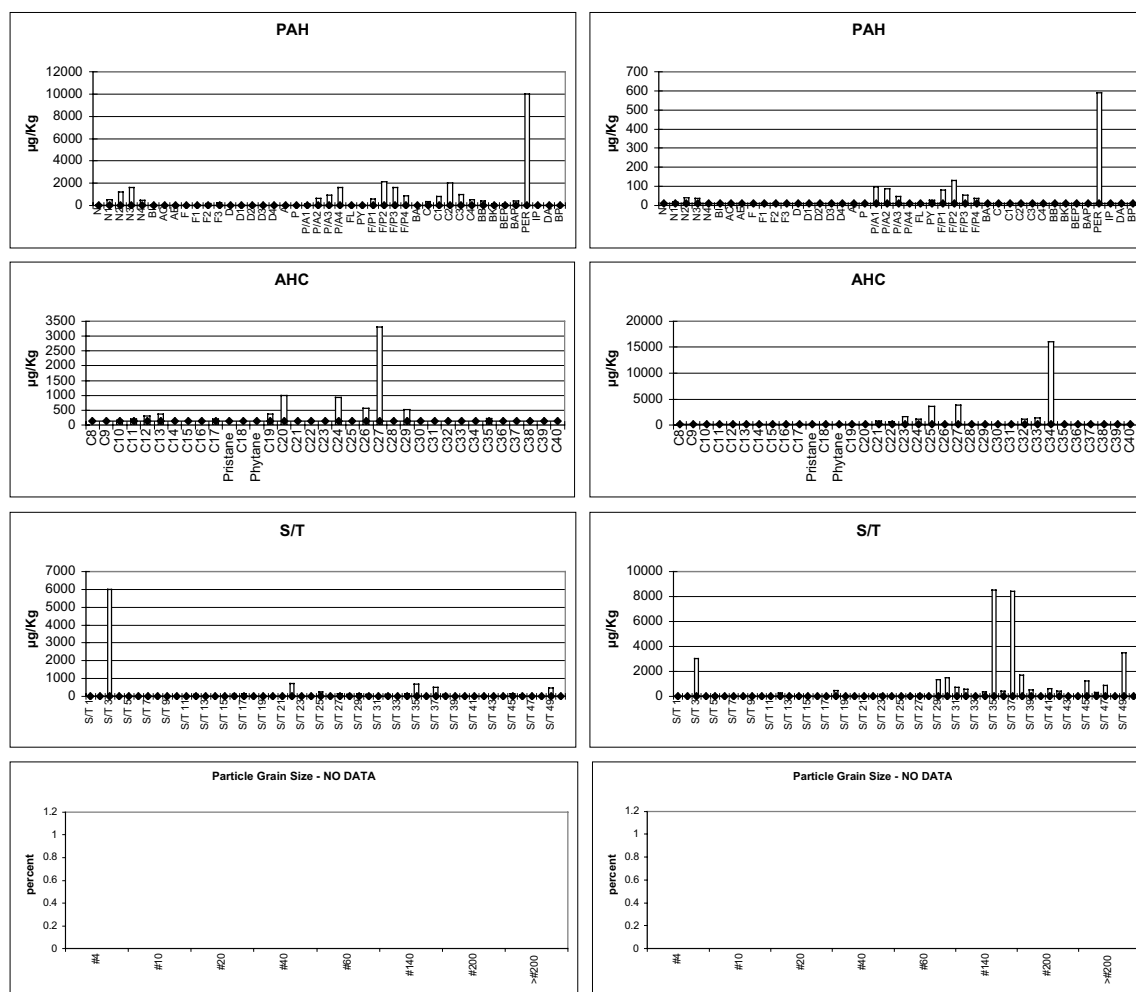
Figure 3-54 presents the PAH, AHC, and S/T data for coal particles collected from No-name Creek and the North Shoal. Both samples are predominated by perylene compared to the other PAH; however, the aromatic profile for No-name Creek coal is more complex and includes a homologous series of alkylated chrysenes. In addition, the relative abundance of aromatics compared to the aliphatics is significantly different. The absolute concentrations of most of the PAH (excluding perylene) in the No-name Creek

coal are of the same order of magnitude as the aliphatic constituents, while the PAH components in the North Shoal coal samples are 40 times lower than the AHC constituents. That is, the coal particles

Figure 3-54. Comparison of chemistry profile data for particulate coal samples collected from No-name Creek and the shoal north of Kalgin Island.

No-name Creek coal fines

North Shoal coal fines



collected from the North Shoal are significantly enriched in aliphatic constituents compared to the aromatics. The coal samples collected from the beach at Beluga River SW and the North Foreland seam also showed this aliphatic component enrichment, although the pattern was reversed in both coal samples from the Beluga coal field collected and analyzed in 1998. The sterane/triterpane patterns and absolute individual S/T component concentrations are also drastically different.

c) Eroding Peat

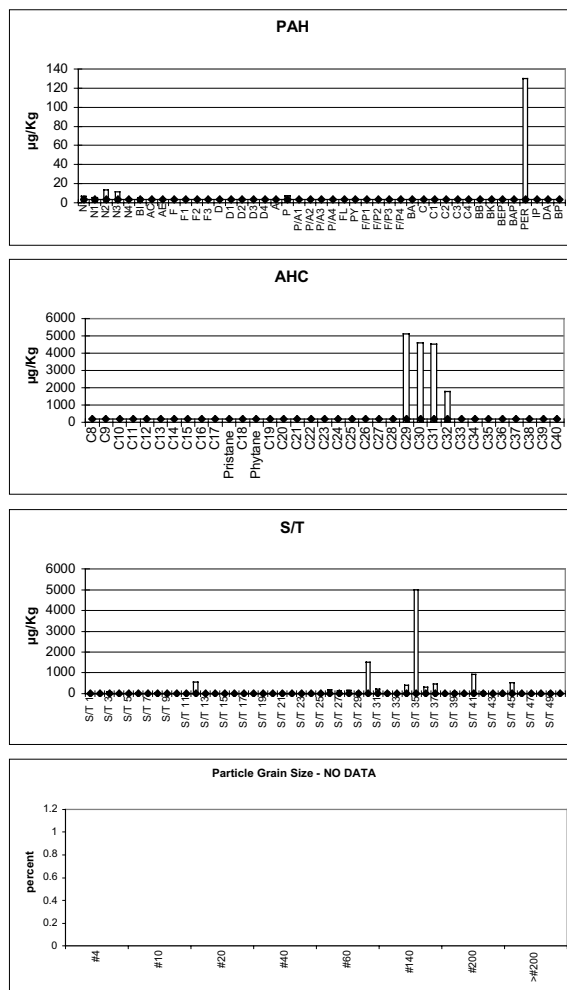
1) Captain Cook State Park

Figure 3-55 presents the PAH, AHC, and S/T data generated from an eroding peat sample collected near Captain Cook State Park. The PAH profile is dominated by perylene; however, a very characteristic pattern of naphthalene, C1-naphthalene, C2-naphthalene, C3-naphthalene, biphenyl, and phenanthrene is apparent when examined at a lower attenuation as shown by the profiles on the right side of the figure. The aliphatic profile is also very characteristic and consists of only n-C29, n-C30, n-C31, and n-C32. The sterane/triterpane pattern for this particular sample is predominated by S/T 30 and S/T 35 (see Table 2-3), although other S/T components are present at lower concentrations, as shown by the profile on the right (note the differences in concentrations scales). The most significant feature of this data set is the very characteristic naphthalene homologue suite and the single appearance of phenanthrene (but no alkylated homologues), and finally perylene. Note also, that this combination of PAH and AHC component profiles is completely different from any of the coal samples examined previously.

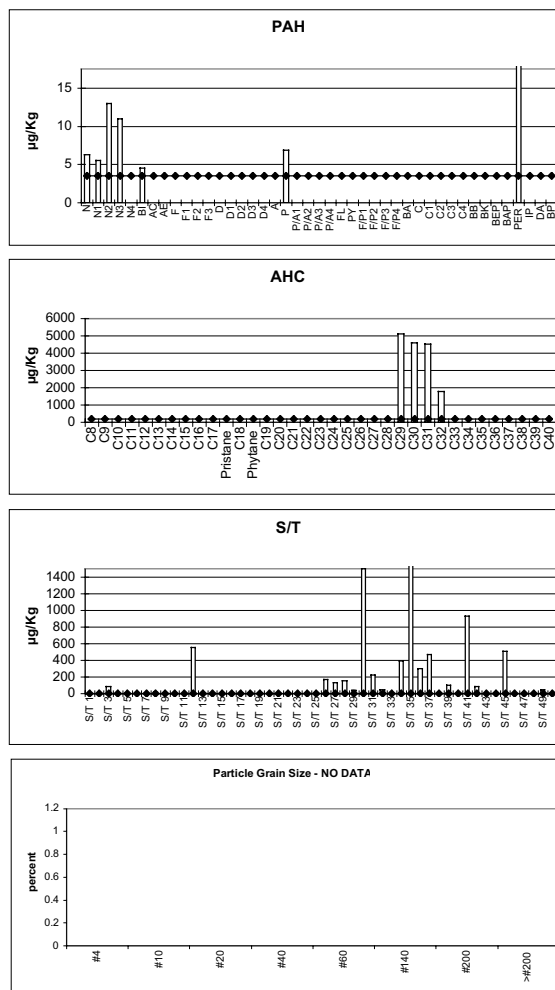
As will be shown in the following sections, this characteristic peat profile, and subtle variations of it, is very common in many of the intertidal sediment samples examined in this program. The relative abundance of the individual naphthalene and S/T components will vary slightly because different eroding peat scarps throughout Cook Inlet no doubt have different organic sources and diagenetic histories. However, the general and distinct grouping of the alkylated naphthalenes, the single phenanthrene, and perylene in the absence of any other aromatics is a striking pattern noted in many of the sediment samples considered in this program. Likewise, the distinct n-C29 through n-C32 pattern will be a common element of many of the tissue sample extracts discussed in the following sections.

Figure 3-55. Chemistry profile data for eroding peat from Captain Cook State Park at two attenuations to allow evaluation of lower-concentration components.

Eroding Peat



Eroding Peat



3. Intertidal Sediments

Specific details regarding the characteristic chemical profiles observed at each station are presented in the following sections. Table 3-9 presents the summary data for TPAH, TALK, TRC, TOC, and TKN measured in the intertidal sediment samples collected during this program. In general, the intertidal sediments were extremely clean, with TPAH values ranging from 0 (no PAH detected at a selected ion monitoring GC/MS MDL of 1.5 ppb) in one of the replicates from the South Shoal to 80 ppb in one of the replicates from Moose Point. Aliphatic hydrocarbons, as measured by total n-alkanes (TALK) and total resolved constituents (TRC) were also largely absent at FID/GC method detection limits ranging from 100-220 ppb. On the few occasions when n-alkanes were observed, they were often at concentrations just slightly above the method detection limit and were generally believed to be of biogenic origin. Evidence of any petroleum hydrocarbon

contamination in any of the intertidal sediments examined was absent, although occasionally PAH associated with combustion products were detected. Traces of PAH derived from eroding peat were frequently encountered, and occasionally evidence of coal was detected. These and other results are discussed below on a site-by-site basis. TOC and TKN, both highly variable, are discussed at greater depth in Sections IIIA and IVA. As stated above (Section IIIA), both TOC and TKN were observed to be positively correlated with particle grain size ($R^2 = 0.81$ and 0.67 , respectively) and to a lesser extent with TPAH ($R^2 = 0.59$ and 0.47 , respectively)

a) East Side of Middle and Upper Cook Inlet

1) Clam Gulch

Figure 3-56 presents the chemistry and particle grain size profiles for the two sediment replicates collected Clam Gulch. One of the sediment samples showed only trace quantities of perylene, which at these detection levels would be consistent with the Clam

Table 3-9. Aromatic and aliphatic hydrocarbons measured in intertidal sediment samples.

	TPAH	TAlk	TRC	TOC	TKN	
East Side of Inlet	µg/Kg	µg/Kg	µg/Kg	mg/Kg dry	mg/Kg dry	Comments
Clam Gulch Rep. 1	2	0	<130	1,900	73	only PER (from coal?), no aliphatics
Clam Gulch Rep. 2	21	0	<120	500	93	traces of combustion products
Kalifornsky Beach Rep. 1	19	0	<140	4,400	210	classic peat profile
Kalifornsky Beach Rep. 2	17	0	<140	2,200	190	classic peat profile
Boulder Point Rep. 1	7	0	<120	-	57	only PER (from coal?), no aliphatics
Boulder Point Rep. 2	4	0	<120	260	56	only PER (from coal?), no aliphatics
Bishop Beach Rep. 1	22	0	<210	9,000	610	classic peat profile
Bishop Beach Rep. 2	41	0	<210	9,500	590	classic peat profile
Moose Point Rep. 1	80	0	<190	6,400	560	peat + combustion products
Moose Point Rep. 2	31	0	<180	7,200	460	classic peat profile
Chickaloon Bay Rep. 1	14	0	<140	3,300	340	classic peat profile
Chickaloon Bay Rep. 2	19	0	<130	4,300	330	classic peat profile
Middle of Inlet						
South Shoal Rep. 1	0	0	<120	350	62	no PAH, no aliphatics
South Shoal Rep. 2	5	0	<120	440	62	MDL levels of N, FL, PY, no aliphatics
SE Kalgin Rep. 1	2	0	<130	110	120	N2 only, no aliphatics

SE Kalgin Rep. 2	2	0	<130	1,100	88	N2 only, no aliphatics
Oldmans Bay Rep. 1	12	0	<140	6,400	280	classic peat profile
Oldmans Bay Rep. 2	22	150	150	3,800	250	classic peat profile
West Shoal Rep. 1	0	0	<130	380	45	no PAH, no aliphatics
West Shoal Rep. 2	55	0	<120	290	50	combustion products, no aliphatics
NE Kalgin Rep. 1	28	0	4,900	2,200	50	classic peat profile
NE Kalgin Rep. 2	23	360	5,200	2,800	210	classic peat profile
NW Kalgin Rep. 1	0	190	190	600	65	no PAH, just n-C 19
NW Kalgin Rep. 2	2	0	<130	570	80	N2 only, no aliphatics
North Shoal Rep. 1	12	0	<110	340	29	traces of combustion products
North Shoal Rep. 2	15	0	<100	450	51	traces of combustion products
Middle Ground Shoal Rep. 1	0	130	130	340	29	no PAH, just n-C 9
Middle Ground Shoal Rep. 2	0	0	<130	390	28	no PAH, no aliphatics
West Side of Inlet						
NE Chisik Island Rep. 1	31	0	<220	11,000	1,000	classic peat profile
NE Chisik Island Rep. 2	48	0	<200	8,600	620	classic peat profile
No. Tuxedni Bay Rep. 1	39	290	18,000	7,100	620	classic peat profile
No. Tuxedni Bay Rep. 2	21	0	17,000	4,900	500	trace of peat
Polly Creek Rep. 1	10	0	<120	1,700	55	only PER (from coal), no aliphatics
Polly Creek Rep. 2	10	0	<130	930	82	only PER (from coal), no aliphatics
No-name Creek Rep. 1	11	270	270	1,600	570	only PER (from coal) and n-C19
No-name Creek Rep. 2	47	0	<140	2,400	120	definite trace of coal PAH
Redoubt Creek Rep. 1	4	160	160	1,000	110	only PER and n-C19
Redoubt Creek Rep. 2	8	0	<140	3,400	240	N2 and PER, no aliphatics
Harriet Point North Rep. 1	5	0	<140	600	48	only PER (from coal), no aliphatics
Harriet Point North Rep. 2	5	0	<130	460	37	only PER (from coal), no aliphatics
Old Cannery Creek Rep. 1	14	350	350	5,900	370	trace of peat and n-C19
Old Cannery Creek Rep. 2	10	0	<140	3,500	230	trace of peat, no aliphatics
West Foreland South Rep. 1	15	0	<130	1,400	99	trace of peat, no aliphatics
West Foreland South Rep. 2	15	0	<150	6,200	350	trace of peat, no aliphatics
West Foreland North Rep. 1	3	0	<140	1,500	97	only PER, no aliphatics
West Foreland North Rep. 2	11	0	<130	760	66	N, FL, PY, BA, PER, no aliphatics
Nikolai Creek Rep. 1	34	0	<180	8,800	540	trace of peat, no aliphatics

Nikolai Creek Rep. 2	29	0	<190	9,000	620	trace of peat, no aliphatics
Beluga River SW Rep. 1	36	0	<160	8,700	390	classic peat profile
Beluga River SW Rep. 2	44	0	<180	6,200	340	classic peat profile

Note: 0 denotes no PAH detected at an MDL of 1-2 ppb, and no n-alkanes detected at the MDL listed for TRC.

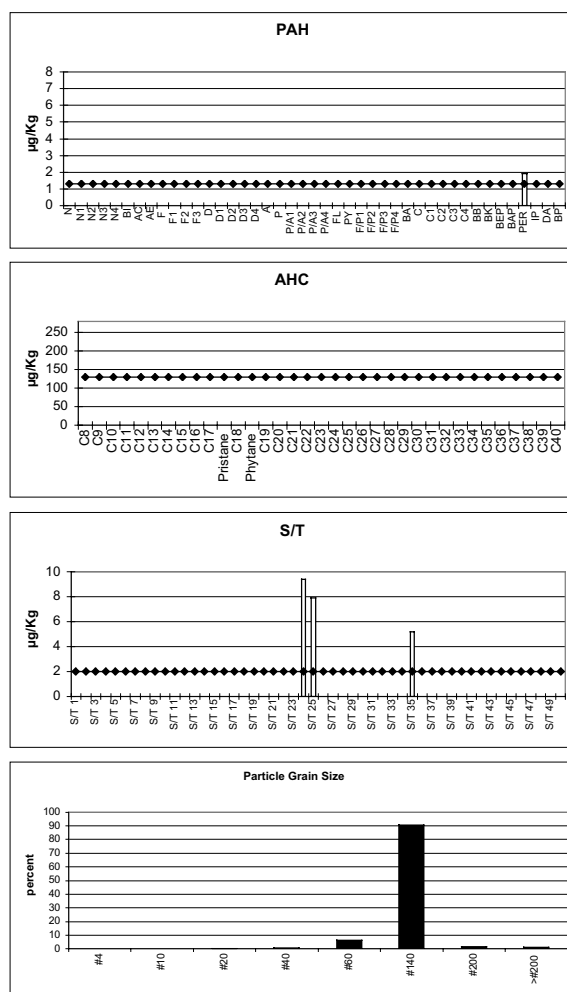
Gulch coal sample collected in the region (see Figure 3-47). The S/T pattern, on the other hand, was not a close match with the Clam Gulch coal reference sample; however, the identified steranes and triterpanes in the sediment samples were just 3-4 times the method detection limit. The other sediment sample from Clam Gulch showed only near method- detection-limit concentrations of a few combustion products plus perylene. No signal of petroleum hydrocarbon contamination or eroding peat was evident in either of the fine-sand sized Clam Gulch sediment samples.

2) Kalifornsky Beach

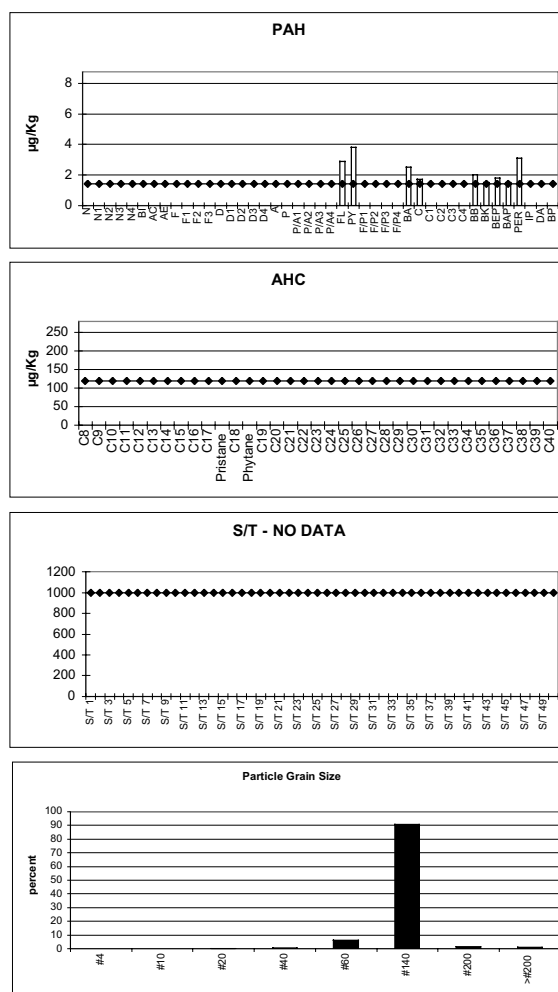
Figure 3-57 presents the chemistry and particle grain size data for sediment replicate 1 from Kalifornsky Beach and the eroding peat reference sample collected further up the coastline at Captain Cook State Park. The PAH patterns observed in both of the sediment replicates from this site were identical and exhibited the classic pattern generated from eroding peat. The overall concentrations were extremely low at 17-19 ppb, and FID GC at an individual component detection limit of 140 ppb detected no aliphatic hydrocarbons.

Figure 3-56. Chemistry and PGS profiles for Clam Gulch sediment replicates.

Clam Gulch Rep. 1



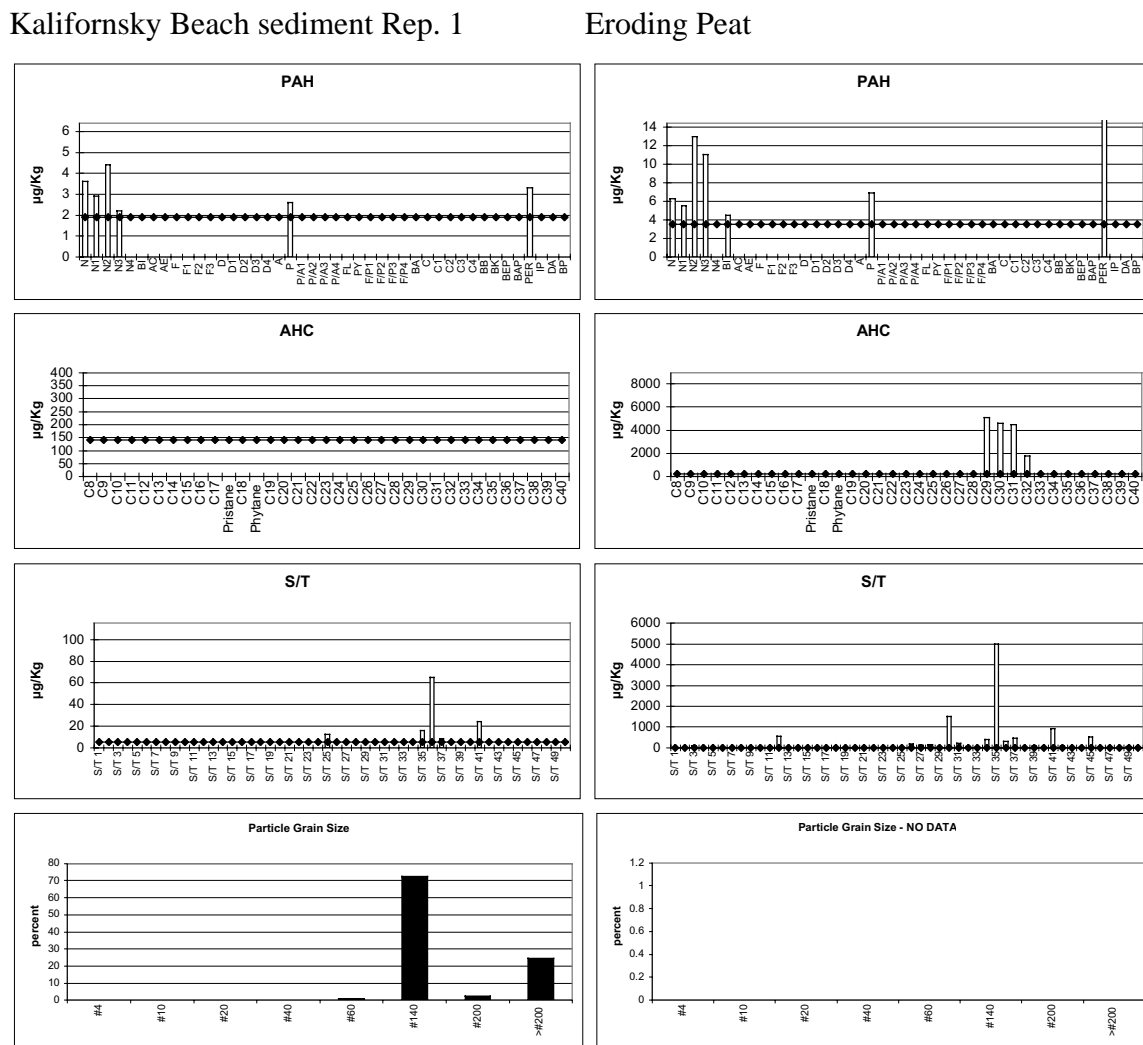
Clam Gulch Rep. 2



With regard to the peat signal observed in both of the sediment samples collected at this (and numerous other) location(s), is important to note the naphthalene and C1- through C3-alkylated naphthalenes at concentrations ranging from 2 to 5 µg/Kg (ppb). These concentrations were just above the method detection limit of 1.5 to 2 ppb in both samples, and it raises the question of whether or not the pattern may be real or some procedural artifact. This suite of naphthalenes did not appear in any of the Field Blanks or Laboratory Method Blanks, although naphthalene itself was observed (at 30 ng/L, part per trillion levels) in the Field Blanks and the deionized/distilled water supplied by the Woods Hole Group Laboratories for preparation of the Field Blanks. As a result, it is believed that the ppb levels of naphthalene and C1- through C3-naphthalenes observed in these (and other) sediment samples are in fact real and not a sampling or laboratory artifact. As noted above, when naphthalene and alkyl-substituted naphthalenes were observed in the reference coal samples, they had a water-washed appearance with

naphthalene often absent, and that is significantly different from the pattern observed in the sediment and eroded peat samples considered here.

Figure 3-57. Chemistry and PGS profiles for Kalifornsky Beach sediment Rep. 1 and an eroding peat reference sample.



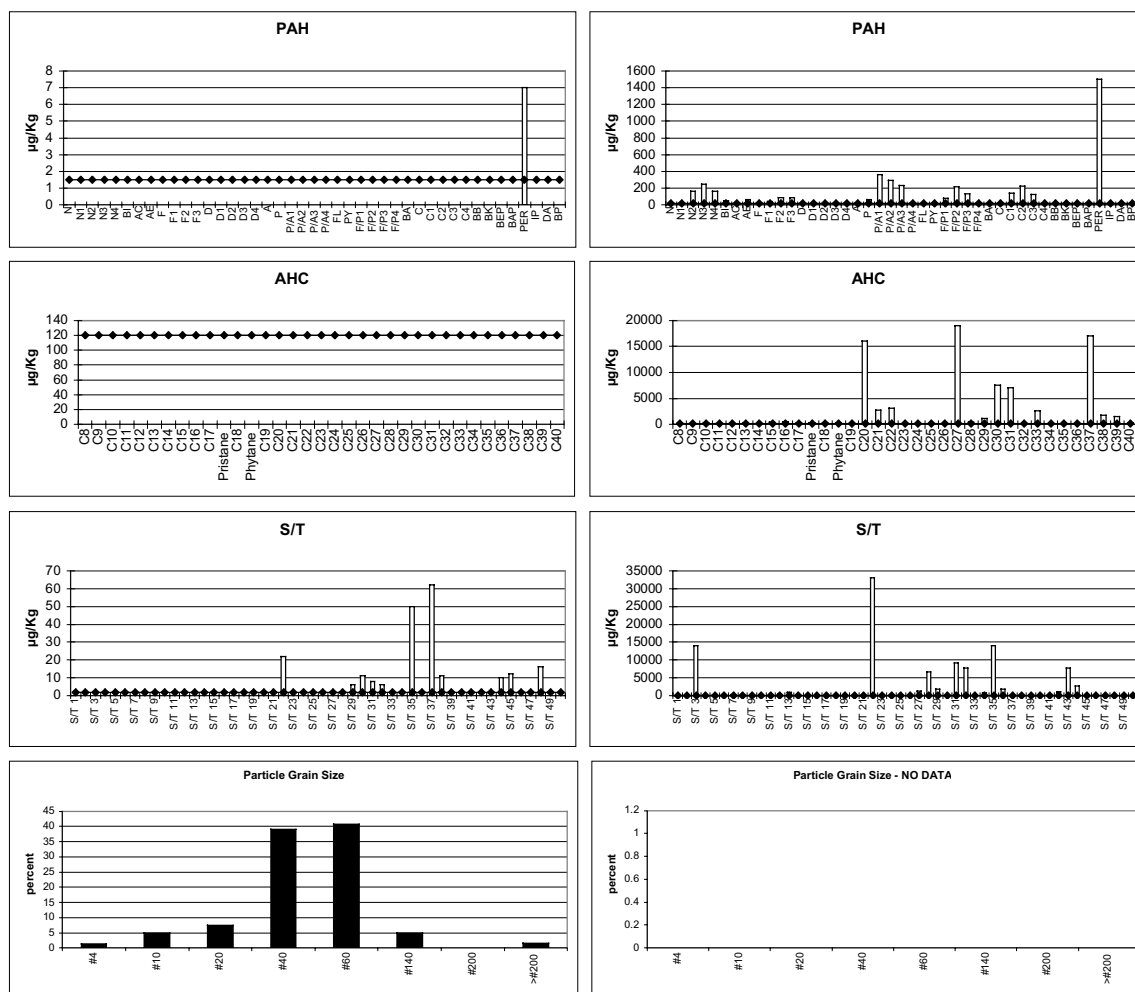
3) Boulder Point

Figures 3-58 and 3-59 present the chemistry and PGS profiles for Boulder Point sediment compared to the coal reference samples from Clam Gulch and the North Shoal, respectively. The coarse- and medium-sand sized sediments at Boulder Point were

Figure 3-58. Chemistry and PGS profiles for Boulder Point sediment Rep. 1 and a Clam Gulch coal reference sample.

Boulder Point sediment Rep. 1

Clam Gulch coal

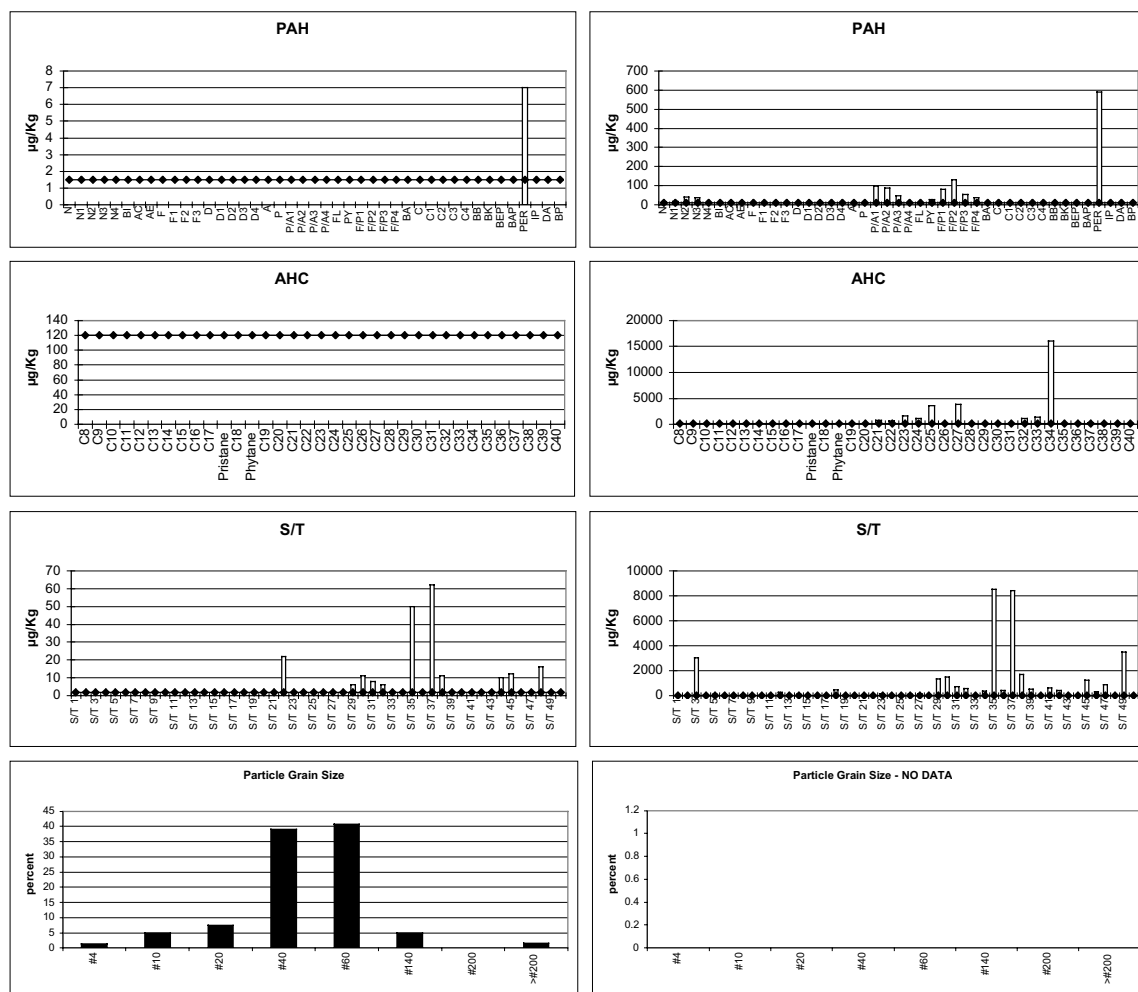


extremely clean and only perylene was identified at measurable concentrations just above the method detection limit of 1.5 ppb. No aliphatics were observed in either sediment sample at a method detection limit of 120 ppb. As described previously, this higher method detection for aliphatics is due to their being measured by FID/GC as opposed to the selected ion monitoring GC/MS technique used for the PAH and S/T fractions. With only perylene detected, it is impossible to identify the source, and the S/T pattern did not match any of the source materials characterized in this program. It was closest, however, to the coal particles isolated from the sand ripples on the shoal North of Kalgin Island (Figure 3-59), and allowing for winnowing of relatively buoyant and finer grained peat fragments (which would not be expected to persist in the coarser-grained higher-energy environment at Boulder Point), it is most likely that the source of perylene in

Figure 3-59. Chemistry and PGS profiles for Boulder Point sediment Rep. 1 and a North Shoal coal reference sample.

Boulder Point sediment Rep. 1

North Shoal coal



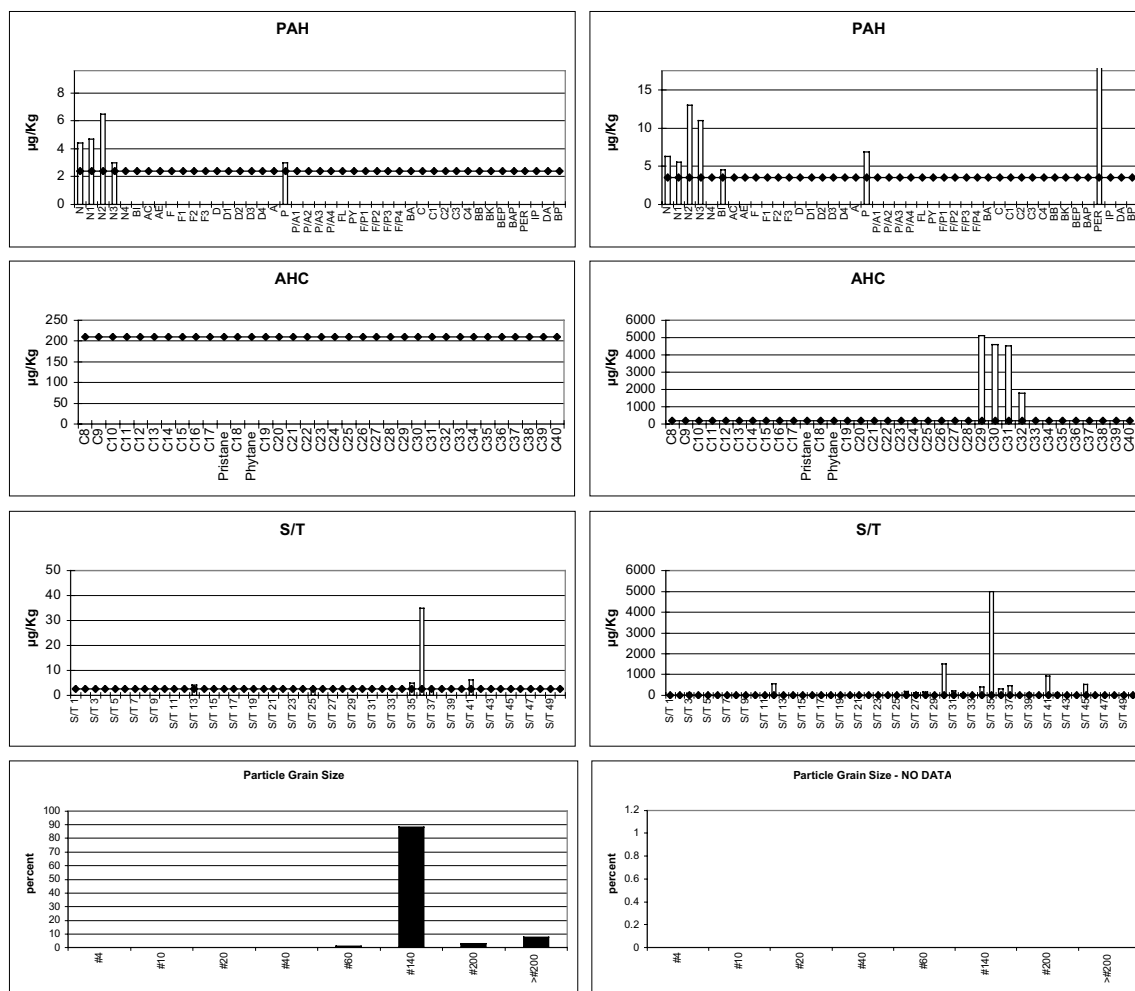
4) Bishop Beach

Figure 3-60 presents the chemistry and PGS profiles for Bishop Beach sediment compared to the eroding peat reference sample collected from Captain Cook State Park.

Figure 3-60. Chemistry and PGS profiles for Bishop Beach sediment Rep. 1 and an eroding peat reference sample.

Bishop Beach sediment Rep. 1

Eroding Peat



The PAH and AHC profiles obtained from both the fine-sand sized sediment replicates at Bishop Beach were identical. Neither sediment sample contained perylene, but they did have trace levels of alkylated naphthalenes and phenanthrene, which are entirely consistent with the pattern observed from eroding peat. The sterane/triterpane profile was predominated by S/T 36, whereas S/T 35 was the predominant sterane triterpane in the single peat sample examined in this program. This same S/T pattern was also observed at Moose Point and Chickaloon Bay further to the north on this side of Cook

Inlet. Evidence of crude oil or refined petroleum product contamination was absent in both Bishop Beach sediment sample.

5) Moose Point

Figure 3-61 presents the chemistry and PGS profiles for both the sediment replicates collected at Moose Point. One of the silt- and clay-sized sediment replicates from this site showed a PAH signal that represented a combination of eroding peat plus combustion products at a total PAH concentration of 80 ppb. This was the highest TPAH concentration measured in any of the intertidal sediment samples examined in the Reconnaissance Program. The other replicate showed PAH components derived only from eroding peat at a total PAH concentration of 31 ppb. Aliphatic components were not detected at an MDL of 190 ppb in the FID GC profiles from either sediment sample. The S/T profile from this site was identical to those observed at Bishop Beach to the southwest and Chickaloon Bay to the northeast. No evidence of PAH derived from coal or petroleum hydrocarbon contamination was observed in the Moose Point samples.

6) Chickaloon Bay

Figure 3-62 presents the chemistry and PGS profiles for Chickaloon Bay sediments compared to the eroding peat sample collected at Captain Cook State Park. Both of the fine-grained sediment samples from Chickaloon Bay were extremely clean and contained only the naphthalene, phenanthrene, and perylene constituents characteristic of eroding peat. Perylene and phenanthrene were just slightly above the method detection limit (at 2.5 ppb) in one sample, and were in fact, absent or below the MDL in the other replicate. The most likely source for these aromatics is eroding peat, although, the S/T pattern (which was identical to the pattern observed at Bishop Beach and Moose Point) showed only low (5 to 23 ppb) concentrations of S/T 36 and S/T 41, while S/T 30 and S/T 41 were the most prominent steranes and triterpanes observed in the single eroding peat sample examined in this program. No evidence of crude oil or refined petroleum product contamination was observed in the Chickaloon Bay sediment samples.

Figure 3-61. Chemistry and PGS profiles for Moose Point sediment replicates.

Moose Point sediment Rep. 1

Moose Point sediment Rep. 2

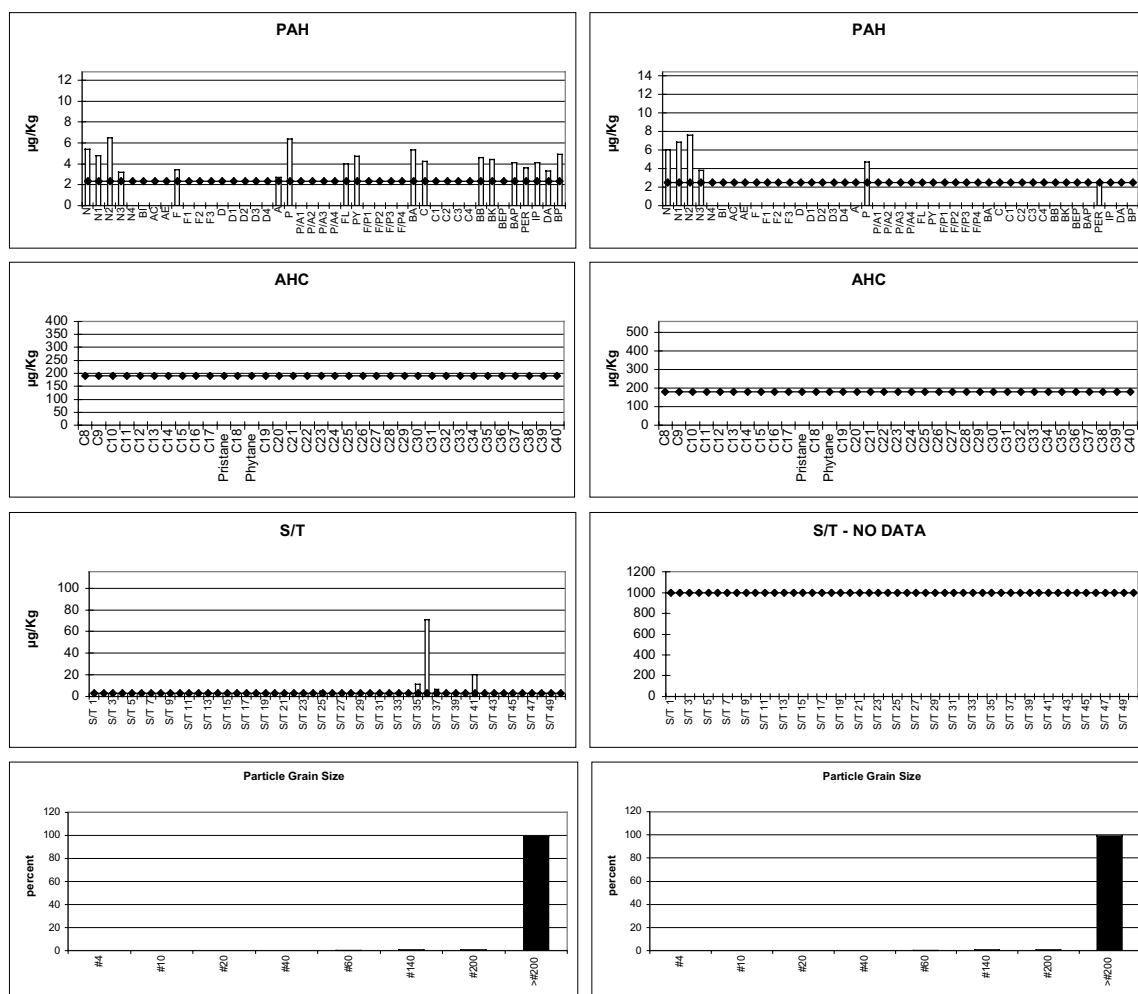
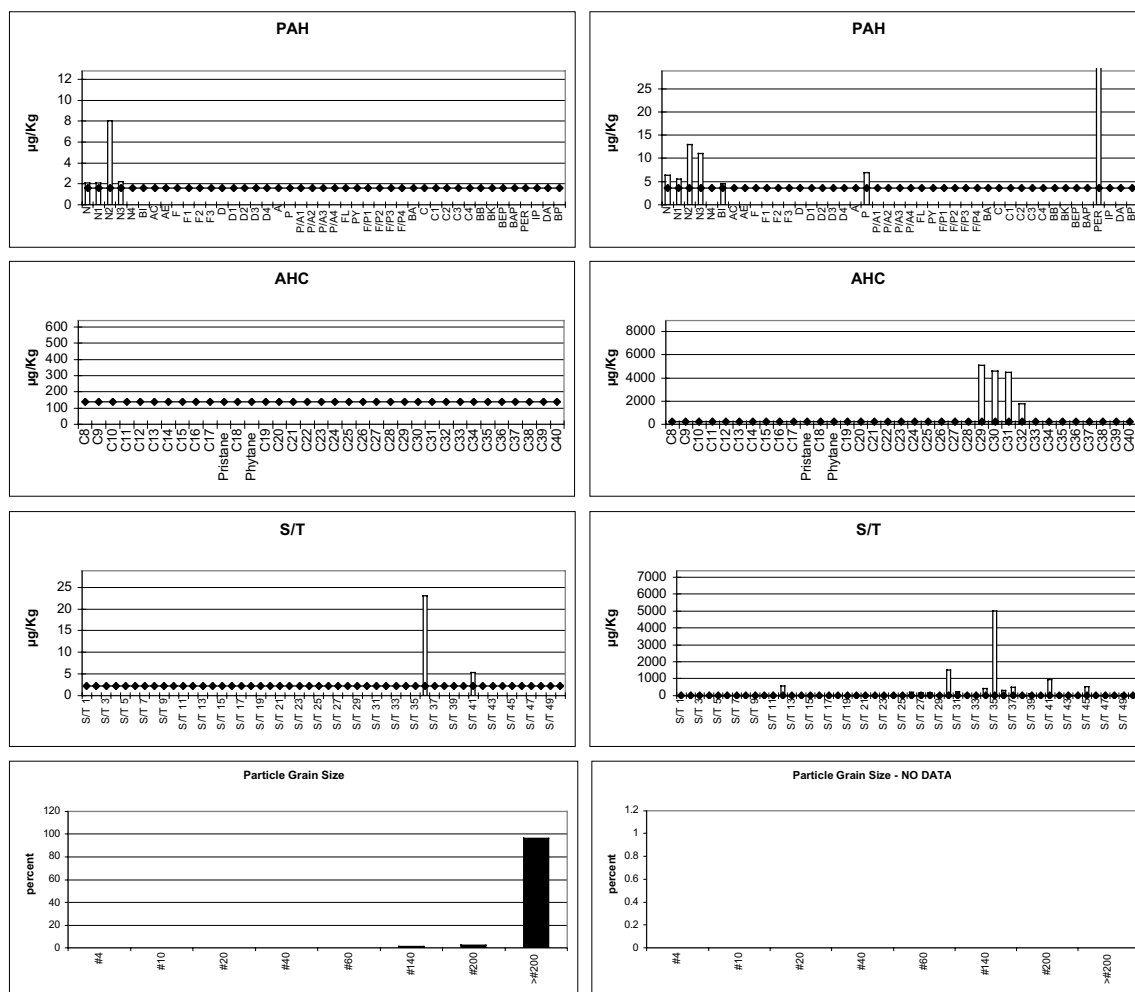


Figure 3-62. Chemistry and PGS profiles for Chickaloon Bay sediment Rep. 1 and an eroding peat reference sample

Chickaloon Bay sediment Rep. 1

Eroding Peat



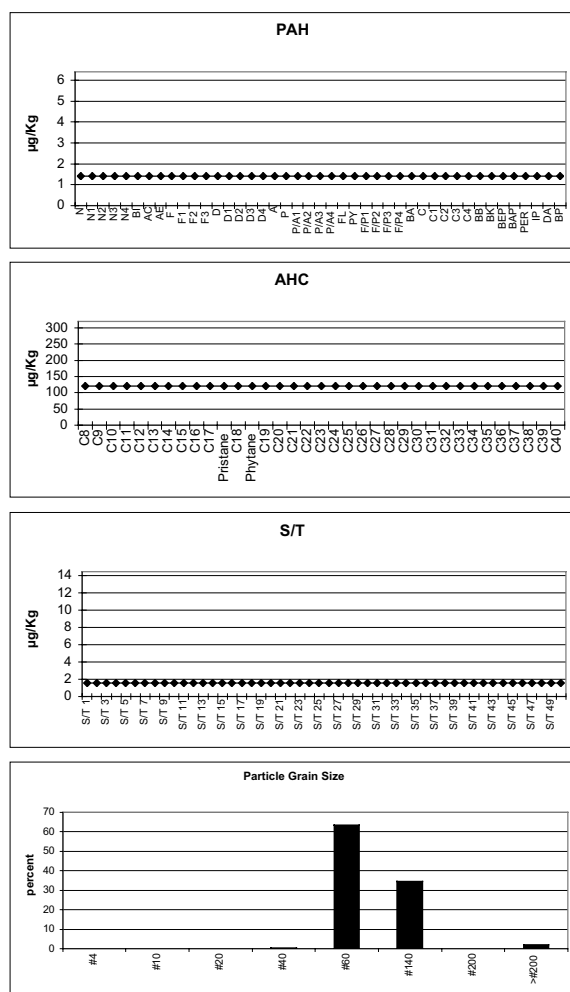
b) Middle of Middle and Upper Cook Inlet

1) South Shoal

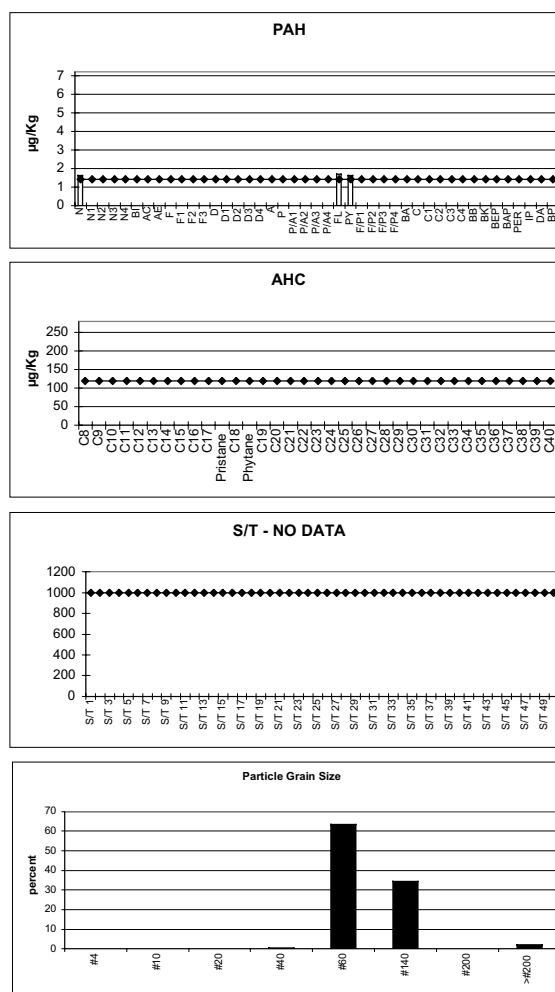
Figure 3-63 presents the chemistry and PGS profiles obtained on both sediment replicates collected from the shoal south of Kalgin Island (South Shoal). One of the medium- to fine-grain sand sized replicates from the South Shoal had no measurable PAH at a method detection limit of 1.5 ppb, while the other replicate contained only traces of naphthalene, fluoranthene, and pyrene (at concentrations at or just slightly above the MDL) to yield a TPAH of only 5 ppb. No peaks were detected in either sample by FID/GC at an individual component detection limit of 120 ppb.

Figure 3-63. Chemistry and PGS profiles for South Shoal sediment replicates.

South Shoal sediment Rep. 1



South Shoal sediment Rep. 2



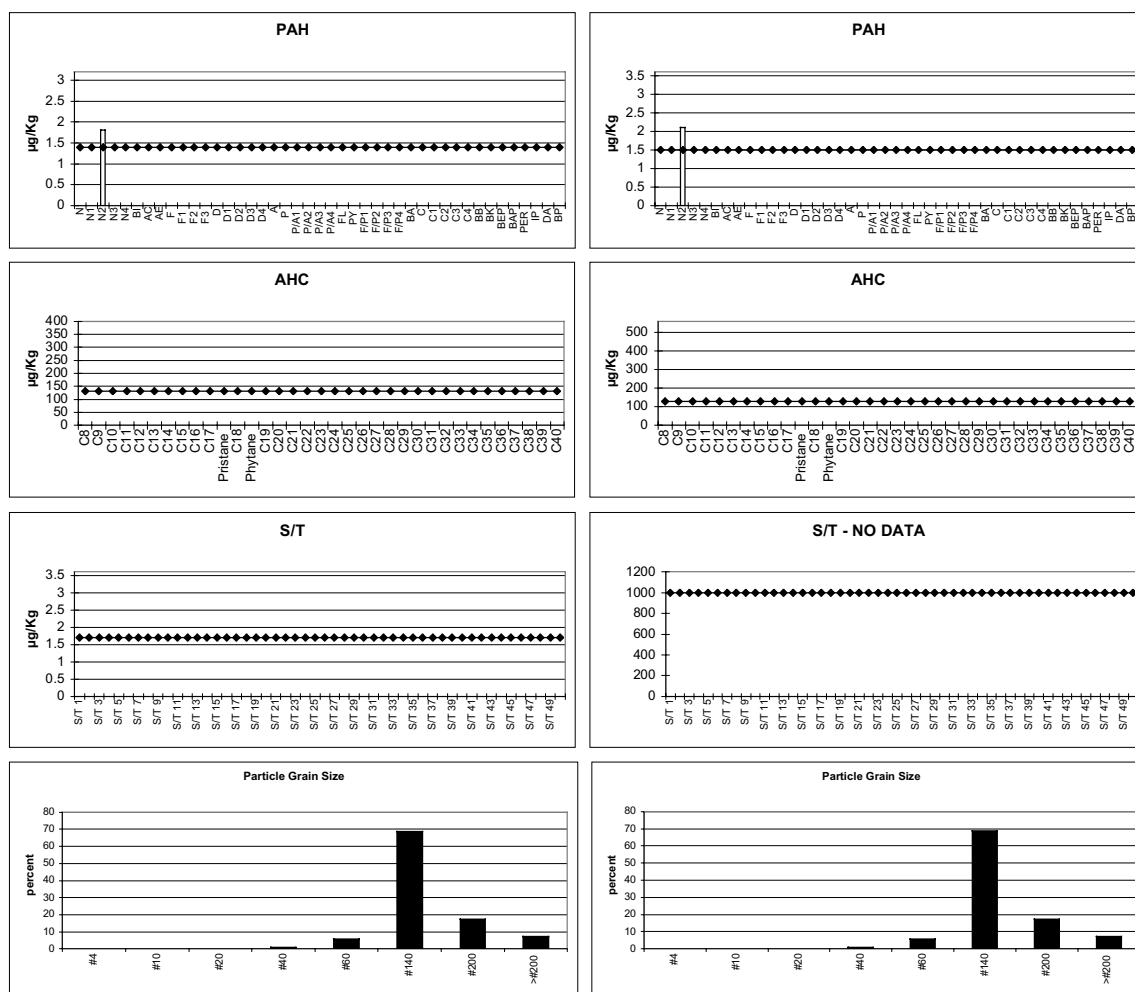
2) SE Kalgin Island

Figure 3-64 presents the chemistry and PGS profiles obtained on both of the sediment replicates collected from this intertidal site on the southeast corner of Kalgin Island. Kalgin SE sediment replicates 1 and 2 contained only C2-naphthalene at 1.8-2 ppb (just above the MDL of 1.4 ppb), and no other PAH, AHC, or S/T components. Indications of signals of coal, peat, or petroleum hydrocarbon contamination were not observed in either of the fine- to very-fine-sand samples.

Figure 3-64. Chemistry and PGS profiles for SE Kalgin Island sediment replicates.

SE Kalgin sediment Rep. 1

SE Kalgin sediment Rep. 2



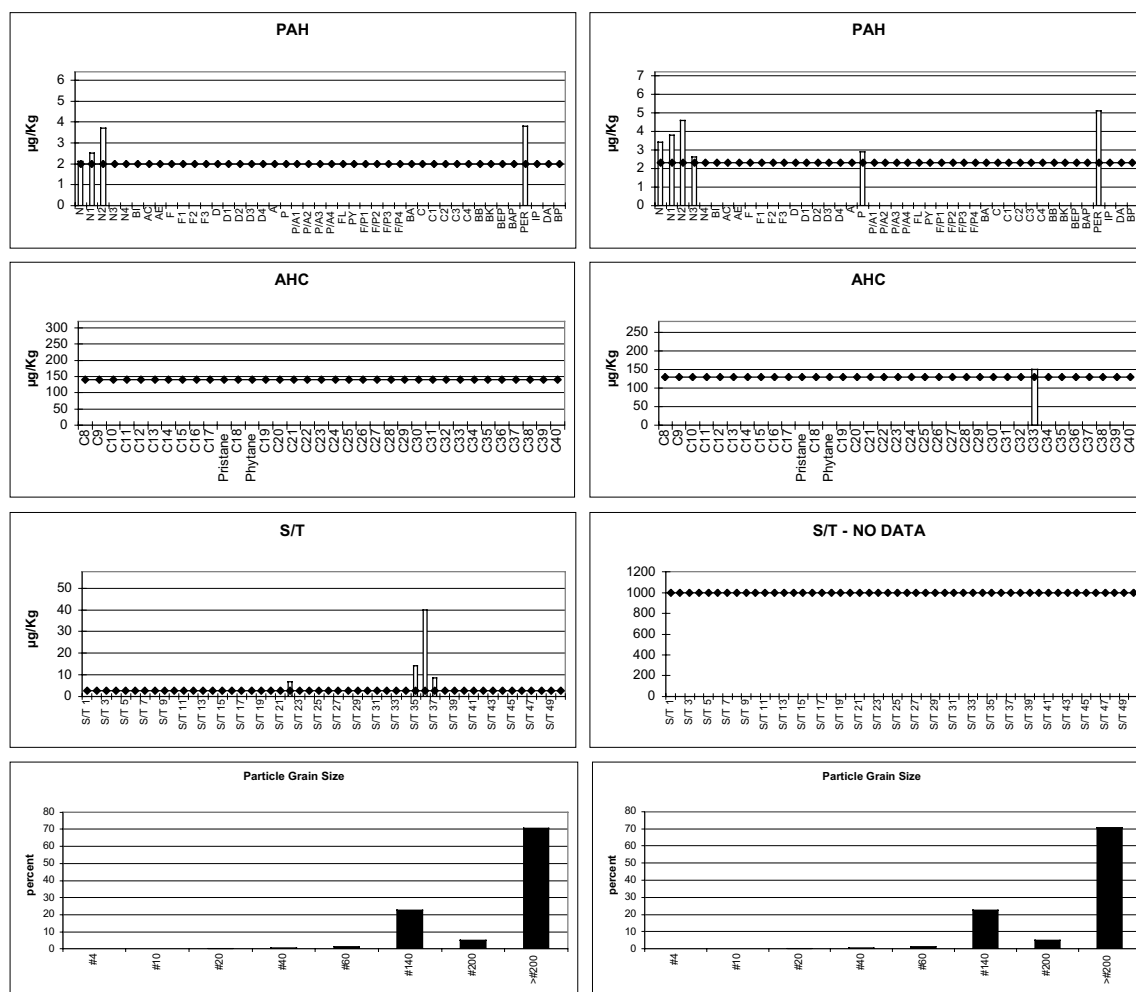
3) Oldmans Bay, Kalgin Island

Figure 3-65 presents the chemistry and PGS profiles obtained on both sediment replicates collected just inside the northwest corner of Oldmans Bay on Kalgin Island. The PGS profile shows the sediments to be primarily silt and clay with traces of fine sand, and the PAH patterns in both samples suggested trace concentrations of eroding peat. The only n-alkane observed was n-C 30 at 150 ppb in replicate 2, just above the method detection limit. The PAH patterns did not show any evidence of petroleum hydrocarbon contamination or particulate coal in either sample.

Figure 3-65. Chemistry and PGS profiles for Oldmans Bay sediment replicates.

Oldmans Bay sediment Rep. 1

Oldmans Bay sediment Rep. 1

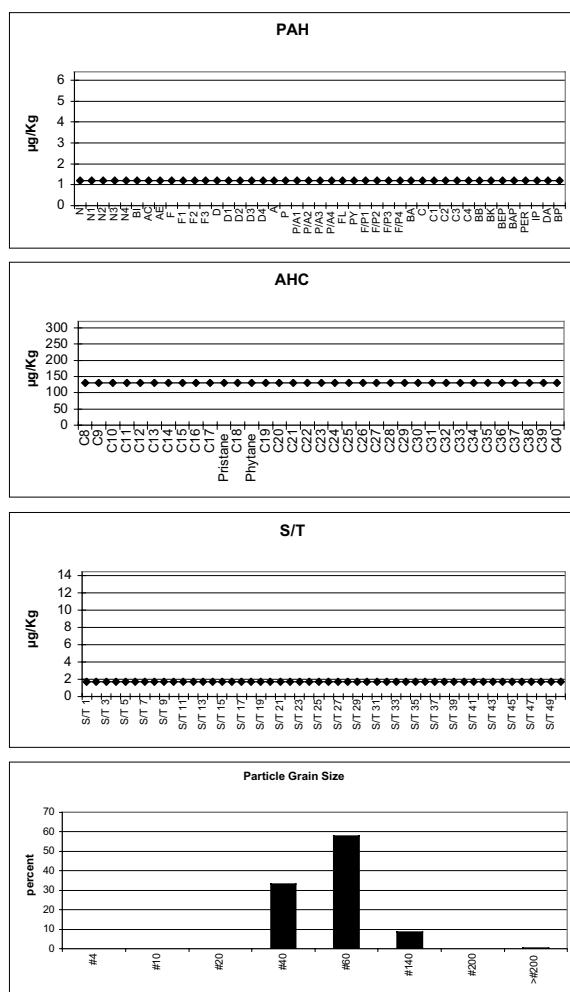


4) West Shoal

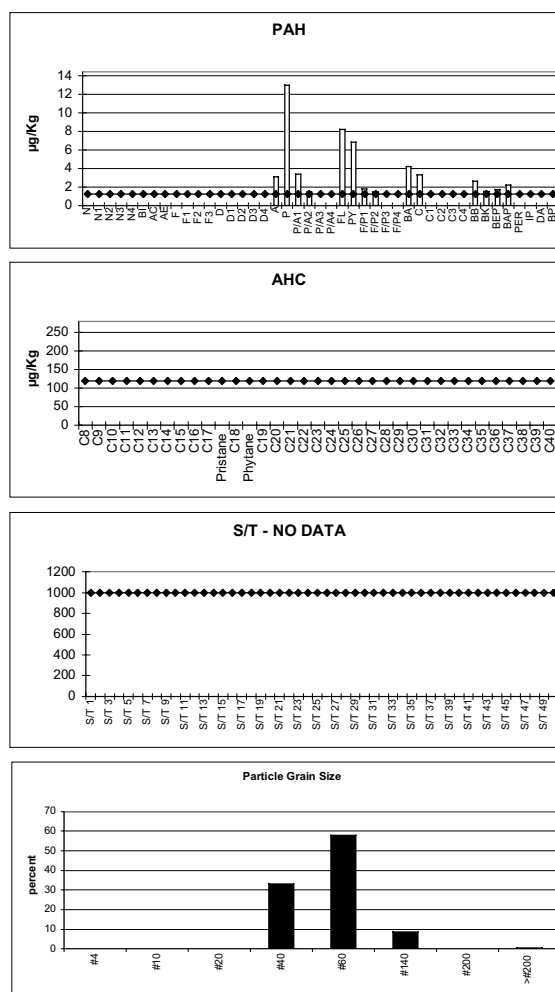
Figure 3-66 presents the chemistry and PGS profiles obtained on both sediment replicates collected from the shoal west of Kalgin Island (West Shoal). One of the coarse- to medium sand sized replicates from the West Shoal showed no evidence of any PAH constituents at a method detection limit of 1 ppb. The other replicate contained what appeared to be intermediate (6-12 ppb) concentrations of anthracene, phenanthrene, C1-anthracenes/phenanthrenes, fluoranthene, pyrene, and C1- to C2-substituted fluoranthene/pyrene homologues, benzo(a)anthracene, and chrysenes plus 2 ppb concentrations of several other combustion products including benzo(b)fluoranthene,

Figure 3-66. Chemistry and PGS profiles for West Shoal sediment replicates.

West Shoal sediment Rep. 1



West Shoal sediment Rep. 2



benzo(k)fluoranthene, benzo(e)pyrene, and benzo a pyrene. At 55 ppb, the TPAH concentration in this sample was the second highest of any sediment sample examined in the program. The source of these primarily combustion-derived PAH is unknown. It is not believed to have come from the helicopter used to access the shoals because all samples were collected 40-50 yards upwind of the helicopter-landing zone. Interestingly, the PAH profile from the combustion products on the West Shoal is significantly different from the profile observed in the North Tuxedni Bay Field Blank (Figure 3-43), where the combustion products were believed to have been generated by the four-wheeler used by nearby residents to investigate our activities on the beach at that site. Neither West Shoal sample showed any trace of aliphatic hydrocarbons at a detection limit of 130 ppb or petroleum hydrocarbon contamination.

5) NE Kalgin Island

Figures 3-67 and 3-68 present the chemistry and PGS profiles obtained on the Replicate 1 sediment sample from NE Kalgin (Replicate 2 was essentially identical) compared to the profiles obtained from the eroding peat and North Shoal coal reference samples, respectively. Both of the intertidal sediment samples at NE Kalgin Island showed traces of alkylated naphthalenes, phenanthrene, and perylene, which were consistent with

Figure 3-67. Chemistry and PGS profiles for NE Kalgin Island sediment Rep. 1 and an eroding peat reference sample.

NE Kalgin sediment Rep. 1

Eroding Peat

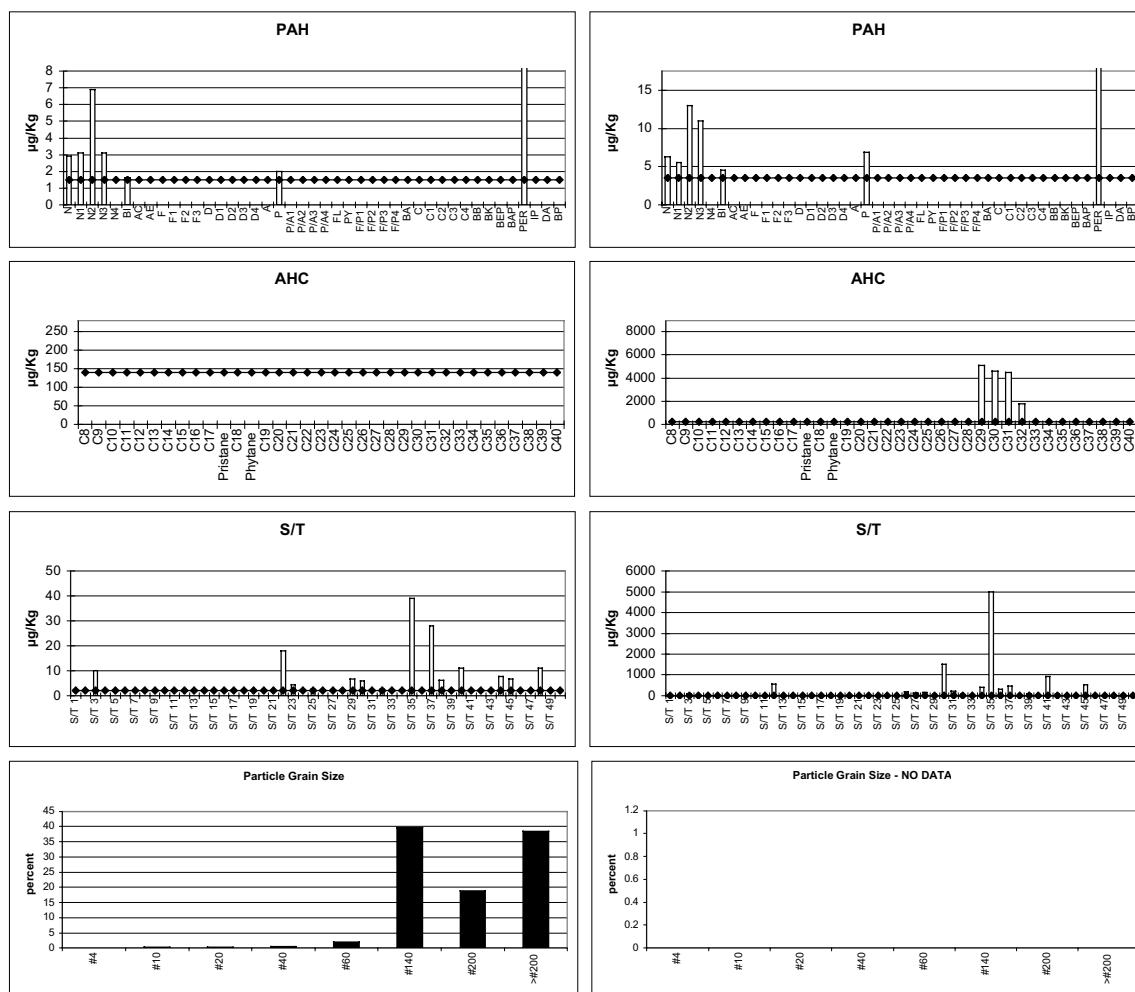
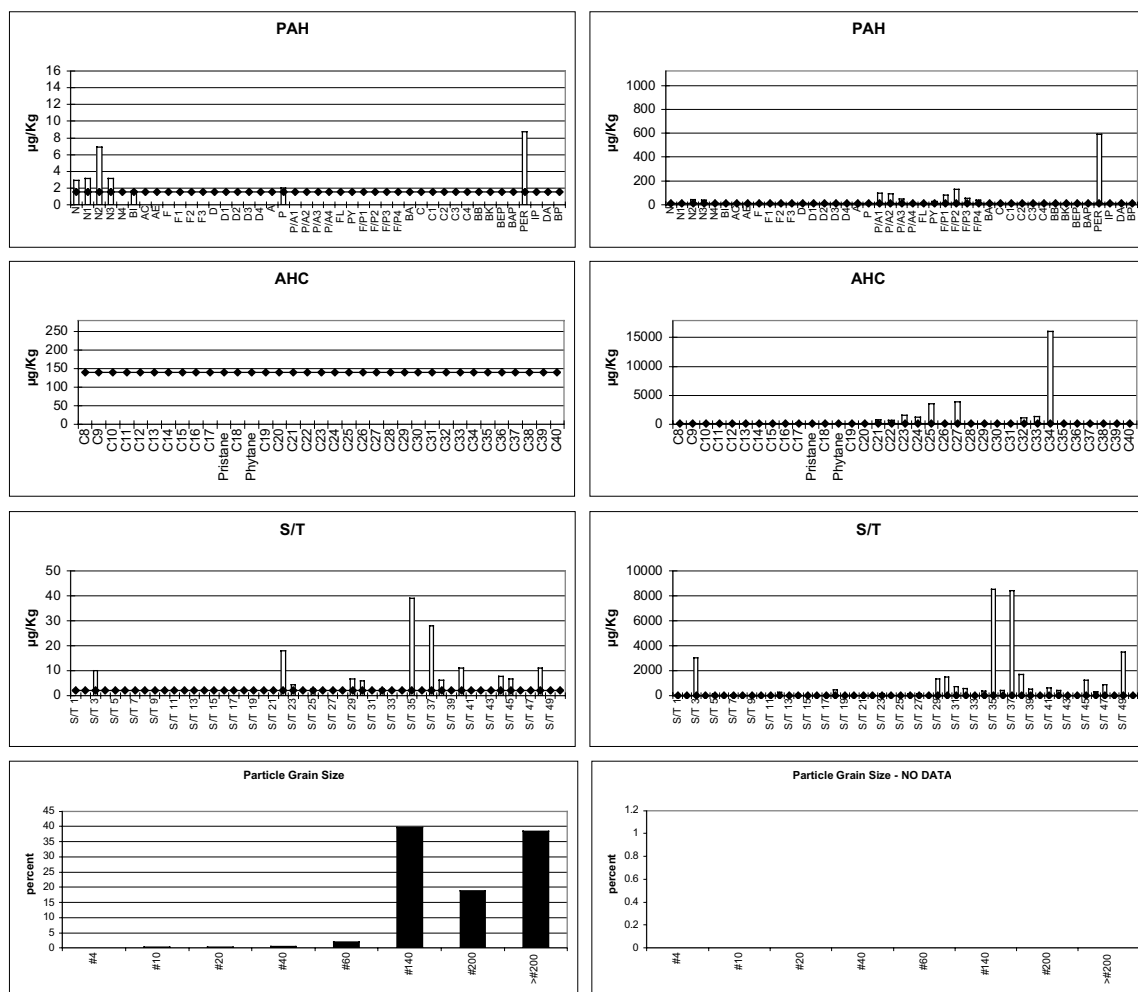


Figure 3-68. Chemistry and PGS profiles for NE Kalgin Island sediment Rep. 1 and the North Shoal coal reference sample.

NE Kalgin sediment Rep. 1

North Shoal coal



One of the replicates contained n-C20 at a concentration of 400 ppb while it was absent in the other one. A confounding factor in coal being the source of PAH is that the coal fragments isolated from the shoals north of Kalgin Island contained phenanthrene/anthracene and fluoranthene/pyrene at concentrations that were 2 times higher than the naphthalenes. None of these intermediate molecular weight PAH components were observed in the NE Kalgin Island sediments. Likewise, phenanthrene was absent in the reference coal, whereas it was present in the sediments. Based on a combination of these factors it seems most likely that the sole source of the PAH observed in the poorly sorted sediments at NE Kalgin Island is due to eroding peat. No signal of petroleum hydrocarbon contamination was observed in either sample.

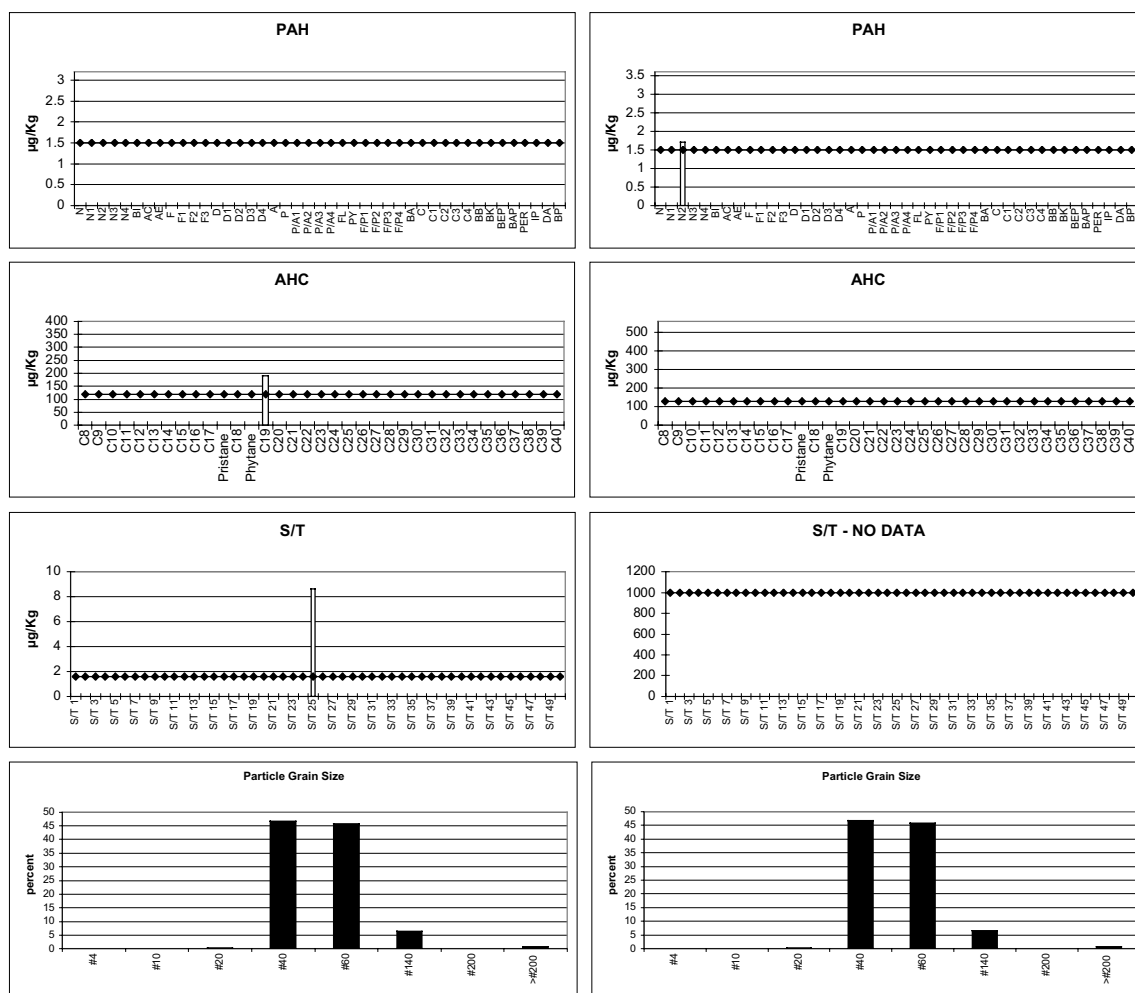
6) NW Kalgin Island

Figure 3-69 presents the chemistry and PGS profiles for both intertidal sediment replicates collected from NW Kalgin Island. Sediment replicate 1 contained no PAH above the MDL of 1.5 ppb, a trace of n-C19 at 180 ppb, and S/T 25 at 8 ppb. Sediment replicate 2 contained only C2-naphthalene at 1.7 ppb (just above the MDL of 1.5 ppb),

Figure 3-69. Chemistry and PGS profiles for NW Kalgin Island sediment replicates.

NW Kalgin sediment Rep. 1

NW Kalgin sediment Rep. 2



and no other PAH or AHC. Evidence of eroding peat, coal, or petroleum hydrocarbon contamination was lacking in both of the coarse- to medium-sand-sized samples.

Interestingly, the grain size distribution at the NW Kalgin Island station was skewed toward much coarser fractions compared to the Northeast Kalgin Island or Southeast Kalgin Island sites. It appears that the eroding peat signature only shows up in the finer-

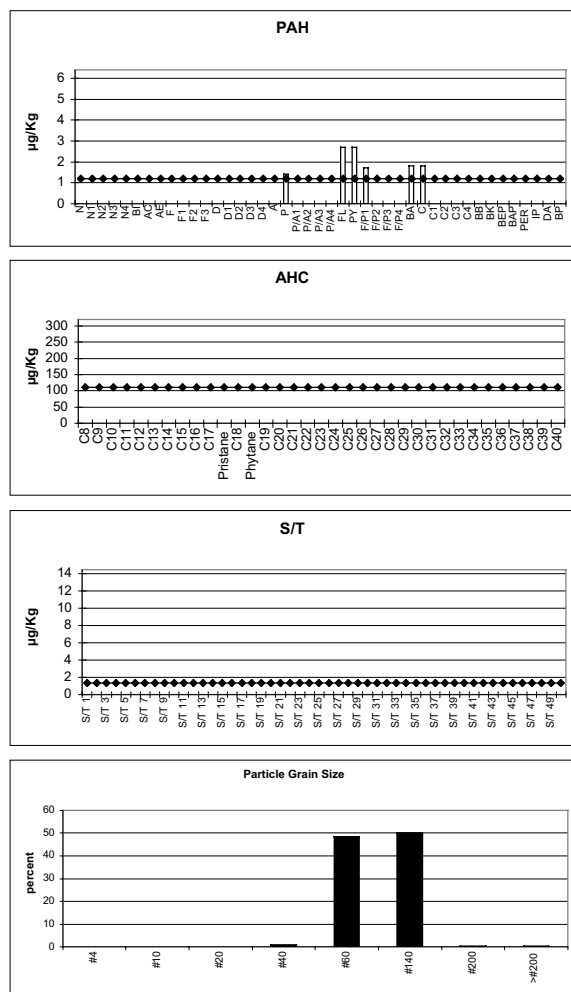
grained sediment samples and is removed from coarser grained sediment materials by wave and current action.

7) North Shoal

Figure 3-70 presents the chemistry and PGS profiles for both sediment replicates 1 and 2 collected from the shoal north of Kalgin Island (North Shoal). Figure 3-71 presents the chemistry profile data for North Shoal sediment replicate 1 compared to the coal particles

Figure 3-70. Chemistry and PGS profiles for North Shoal sediment replicates.

North Shoal sediment Rep. 1



North Shoal sediment Rep. 2

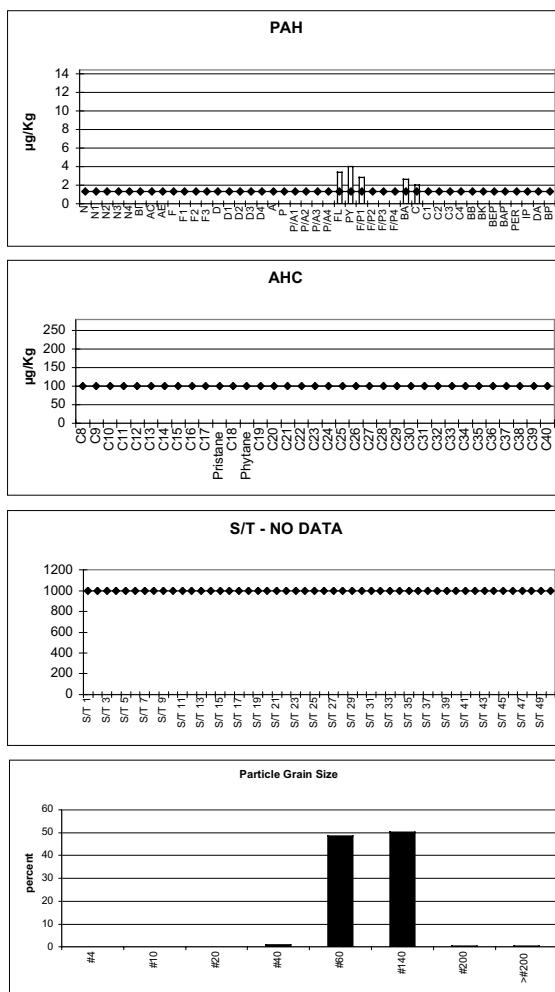
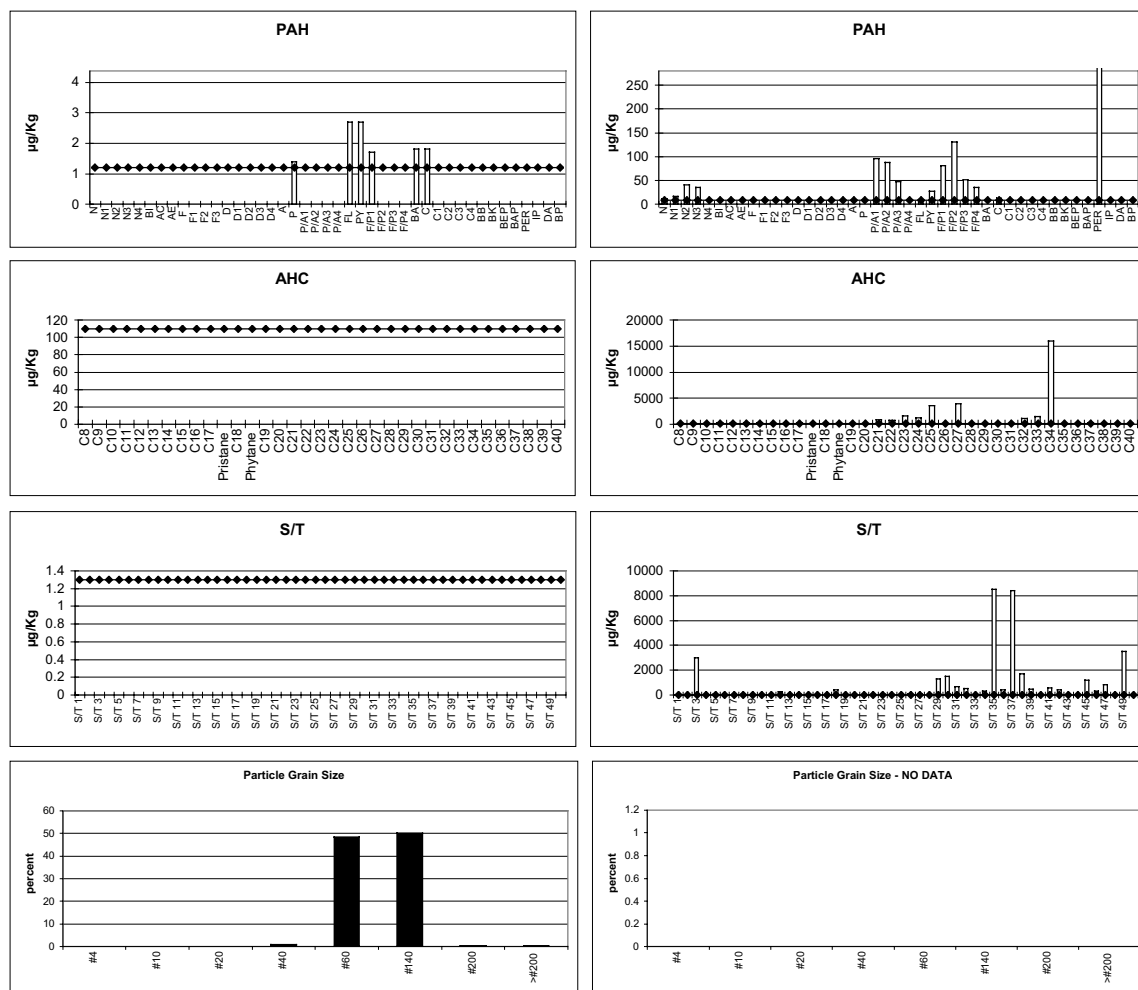


Figure 3-71. Comparison of chemistry profile data from sediments and isolated coal particles collected from North Shoals.

North Shoal sediment Rep. 1

North Shoal Coal



collected from the upper sand surface at the same site. As expected, the peat signal is not apparent in either of the shoal samples because of: 1) the absence of any eroding peat scarps or bluffs in the immediate vicinity of the shoals and 2) the relatively coarse grain size of the constantly re-worked of the shoals themselves. That is, any fine-grained peat fragments would be readily winnowed and washed out of the medium- to fine-sand sized sediments during their agitation and constant turnover by waves and currents at each low-tide exposure. Both North Shoal sediment replicates contained trace levels of fluoranthene, pyrene, C1 fluoranthene/pyrene, benzo(a)anthracene, and chrysene at concentrations that were just 1-2 times the method detection limit. Replicate 1 also contained traces of phenanthrene at the method detection limit of 1.2 ppb. TPAH values in the two samples ranged from 12-15 ppb. The aromatic patterns observed in the sediments are most likely derived from combustion products, although the concentrations are so low that absolute identification of source is impossible. Although coarse sand-

sized particulate coal was observed to collect everywhere in the valleys and depressions of the sand waves covering the exposed surface of the shoal, the less-dense coal particles showed a very different pattern than the trace level PAH concentrations observed in the surrounding sediments themselves (Figure 3-71). In the North Shoal coal sample, concentrations of naphthalene plus higher levels of C1-, C2-, and C3-naphthalenes were at detection-limit levels. However, the PAH profiles were predominated by parent plus alkyl-substituted homologues of phenanthrene/anthracene and parent plus alkyl-substituted homologues of fluoranthenes/pyrenes and the ubiquitous and predominate perylene. None of these components were evident in the sediments themselves, and in fact, the sediments contained easily detectable concentrations of fluoranthene, pyrene, benzo(a)anthracene, and chrysene, which were absent in the coal. Evidently, coal particles are moved by wave and current action along the subtidal sediment surface throughout Cook Inlet; however, their density precludes their burial and deeper incorporation into medium- to fine-sand-sized sediments. This appears to be particularly true on the shoals where waves and currents at each low tide exposure aggressively agitate those sediments. No evidence of any petroleum hydrocarbon contamination was observed in either of the North Shoal sediment samples.

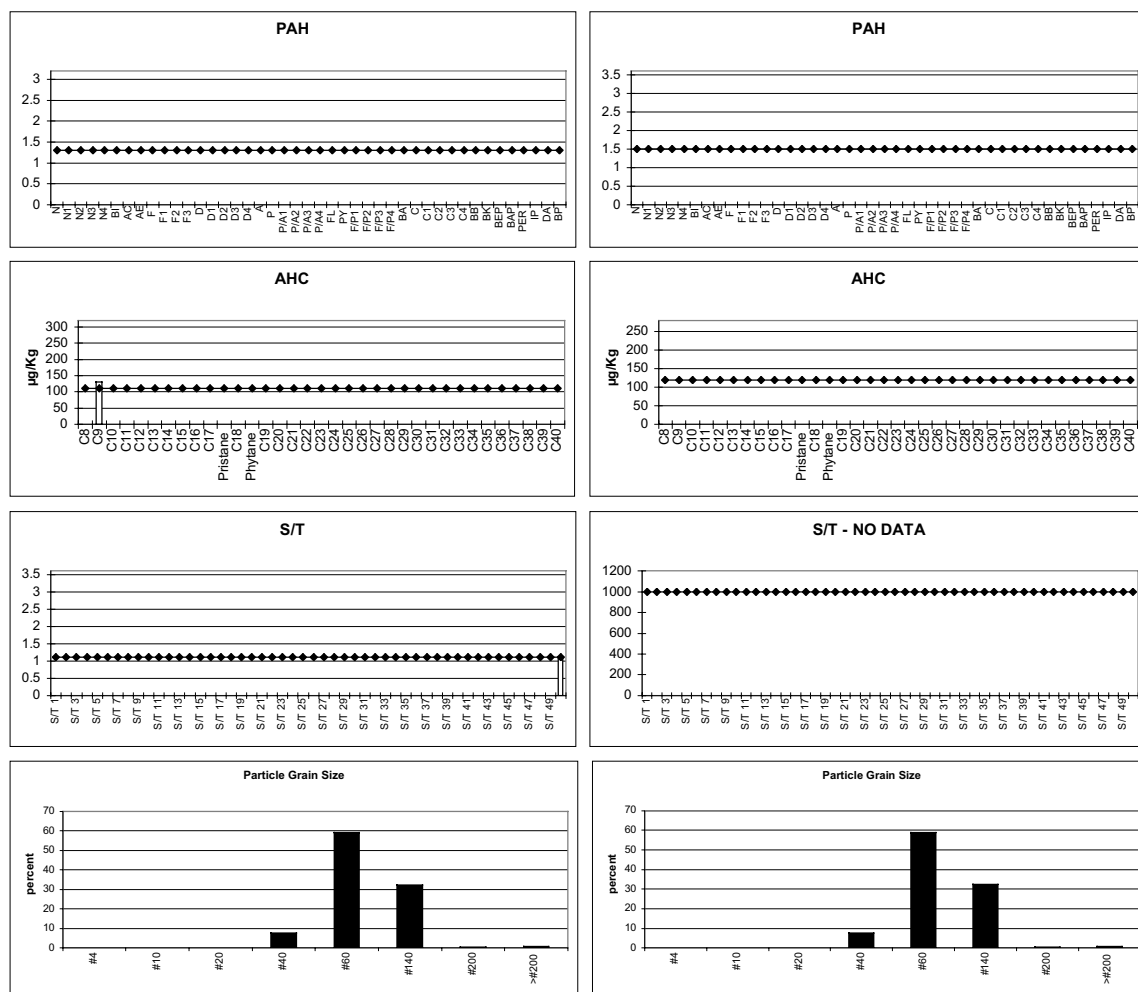
8) Middle Ground Shoal

Figure 3-72 presents the chemistry and PGS profiles for both sediment replicates collected from the Middle Ground Shoals. Neither of the coarse/medium- to fine-sand sized sediment replicates showed a trace of PAH at a method detection limit of 1.3-1.5 ppb. The only component measured was a trace of n-C 9, just above the method detection limit of 110 ppb in replicate 1. Obviously, no evidence of petroleum hydrocarbon contamination was observed in either sediment sample.

Figure 3-72. Chemistry and PGS profiles for Middle Ground Shoals sediment replicates.

Middle Ground Shoal sediment Rep. 1

Middle Ground Shoal sediment Rep. 2



c) West Side of Middle and Upper Cook Inlet

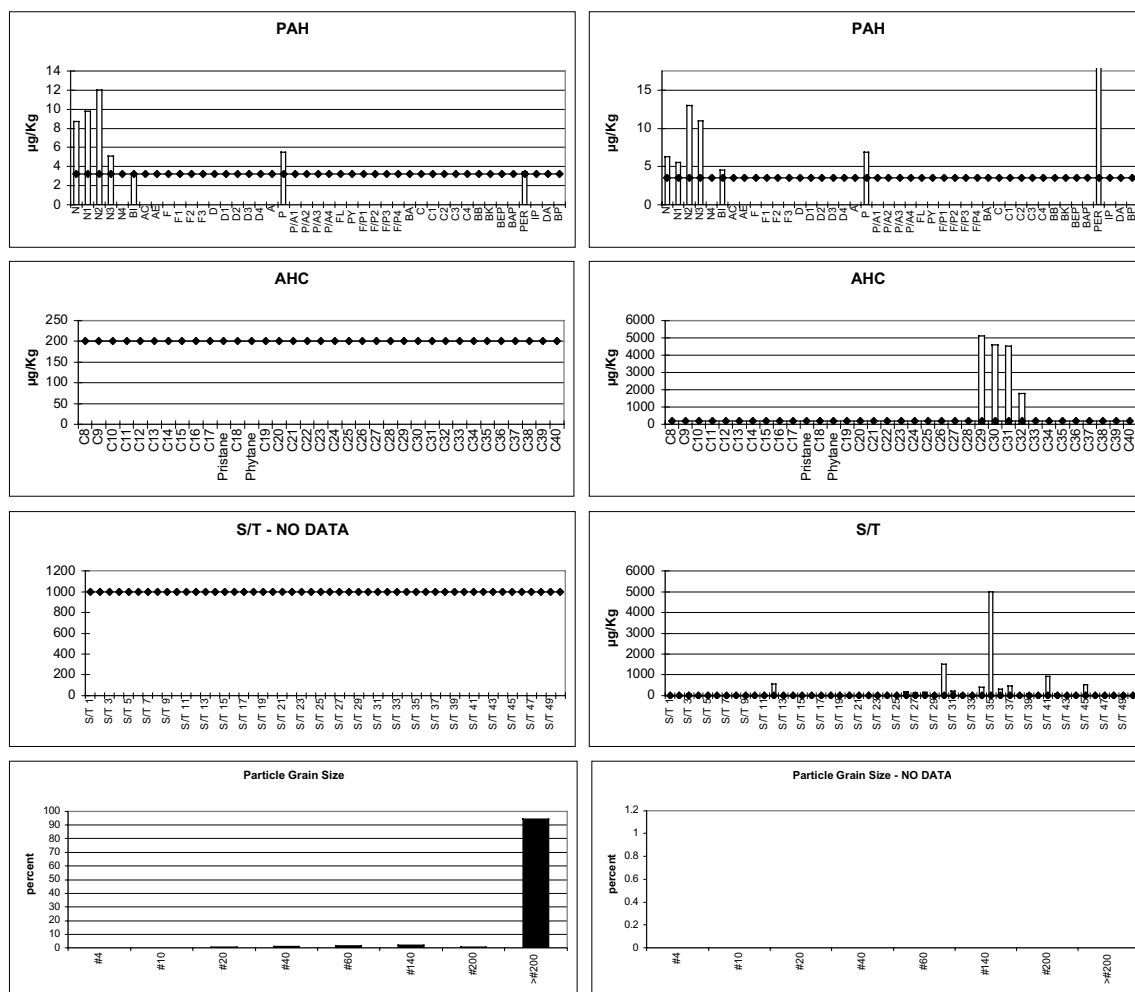
1) NE Chisik Island

Figure 3-73 presents the chemistry and PGS profiles from NE Chisik Island sediment replicate No. 2 compared to the eroding peat reference sample. Replicate 1 contained only alkylated naphthalenes and phenanthrene with only a single sterane/triterpane component, S/T 13 at 11 ppb (just above the MDL 9.5 ppb) detected. The other sediment replicate (shown in the figure) contained the same naphthalene through C3-naphthalene suite and also showed slightly greater than detection-limit concentrations of biphenyl and perylene.

Figure 3-73. Chemistry and PGS profiles for NE Chisik Island sediment Rep. 2 and an eroding peat reference sample.

NE Chisik Island sediment Rep. 2

Eroding Peat



These PAH patterns clearly match the signal derived from eroding peat. Aliphatic components were not detected in either sediment replicate at a method detection limit of 200-220 ppb. Moreover, traces of petroleum hydrocarbon contamination were absent. If coal fragments were present in these silt- and clay-sized sediment samples, they did not match any of the six reference samples analyzed during the 2000 Reconnaissance Program or the six samples examined previously during the CIRCAC data synthesis effort (Lees et al. 1999). It is clear that evidence of any petroleum hydrocarbon contamination was lacking in these sediment sample.

2) North Tuxedni Bay

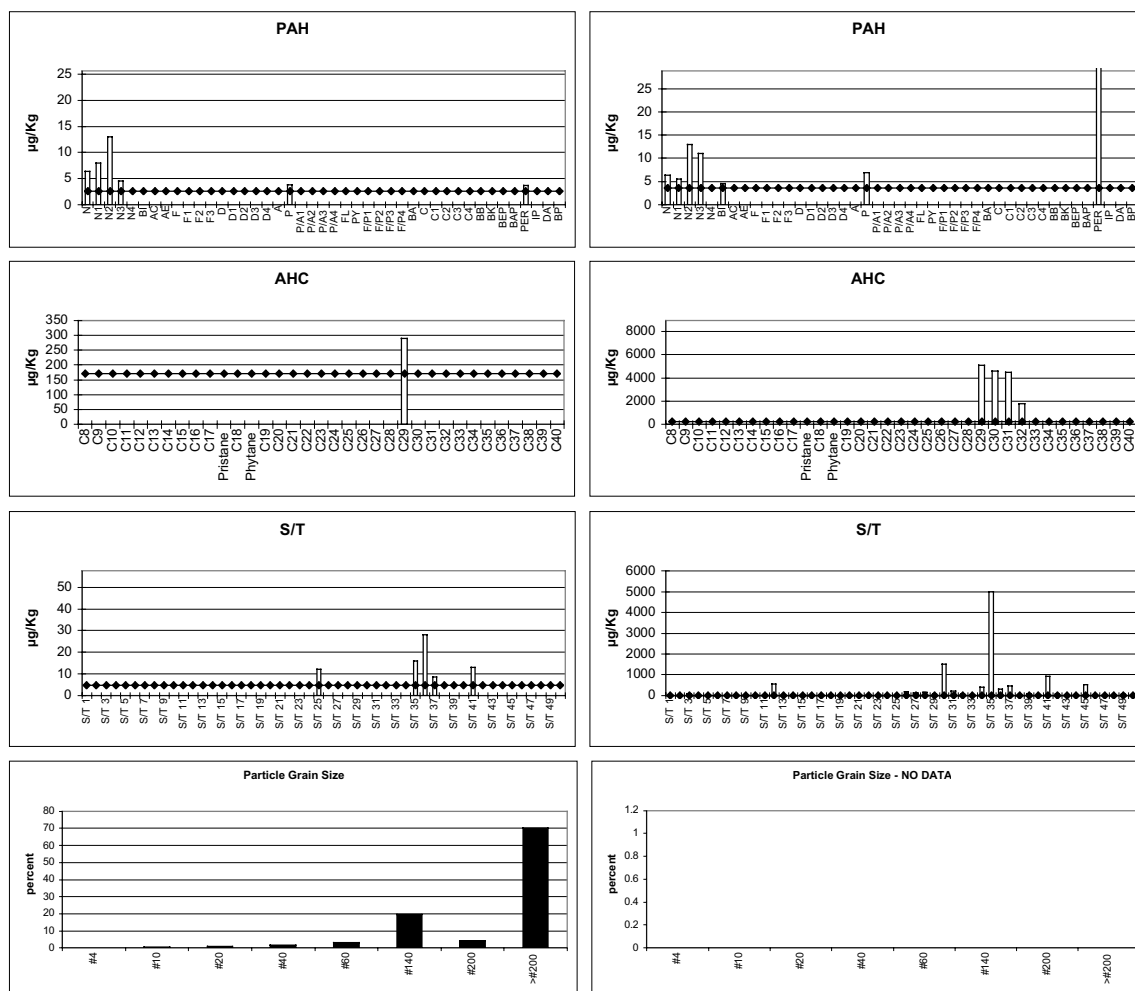
Figure 3-74 presents the chemistry and PGS profiles for sediment replicate 1 collected at North Tuxedni Bay compared to the eroding peat reference sample. Both of the primarily silt- and clay-sized sediment replicates from this site contained the classic PAH profile

derived from eroding peat. TPAH values ranged from 21-39 ppb. The only n-alkane detected was n-C 29 at 290 ppb in replicate 1; however, the FID GC profiles did show the most complex pattern of any of the sediment sites examined the program at total resolved constituent (TRC) concentrations of 17,000-18,000 ppb. These primarily biogenic FID GC profiles are discussed in greater detail in a following section. It should be pointed out

Figure 3-74. Chemistry and PGS profiles for North Tuxedni Bay sediment Rep. 1 and an eroding peat reference sample.

No. Tuxedni sediment Rep. 1

Eroding Peat



at this time, however, that no evidence of petroleum hydrocarbon contamination was observed in either the PAH distribution or the FID GC profiles.

3) Polly Creek

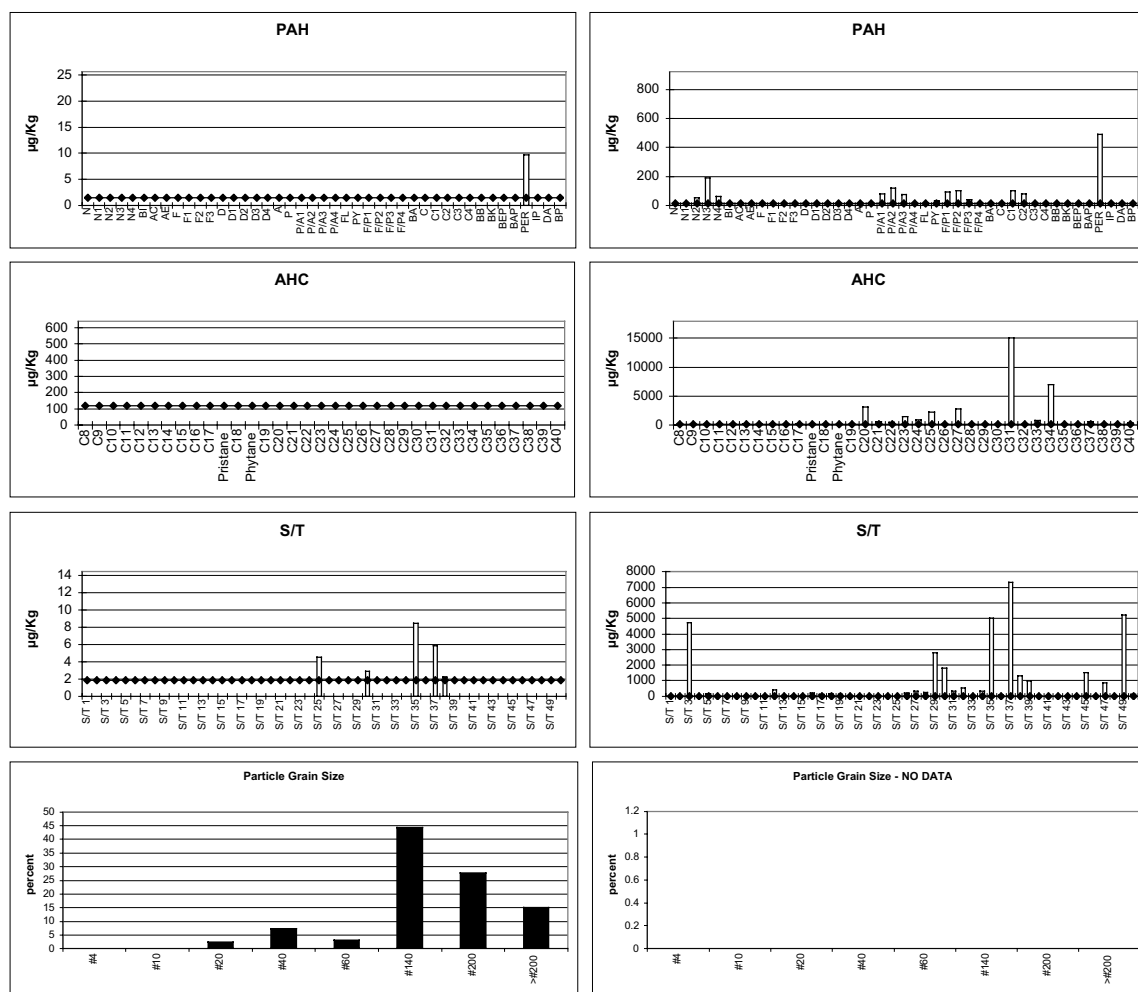
Figure 3-75 presents the chemistry and PGS profiles for sediment replicate 1 from Polly Creek compared to the coarse- to medium-sand sized particulate coal reference sample collected at Beluga River SW. The only PAH measured in either of the sediment samples

was perylene at 10 ppb. No components were measured in the FID GC profile of replicate 1 at a method detection limit of 120 ppb, and replicate 2 contained only a trace of n-C 36, just at the detection limit of 130 ppb. The sediments at the site were fairly

Figure 3-75. Chemistry and PGS profiles for Polly Creek sediment Rep. 1 and a fine particulate coal reference sample.

Polly Creek sediment Rep. 1

Beluga River SW Fine Coal



coarse and very poorly sorted (45 percent fine sand, with 3-7 percent contributions of medium and coarse sand). As a result, it is likely that any fine and less dense particulate fragments from eroding peat would be winnowed from the sediments, and the most likely source of the perylene is fine particulate coal. The S/T pattern observed in the sediment was closer to that observed for Beluga River SW fine coal than to the peat reference sample, although several of the components present in the reference coal samples were absent or below the MDL of 2 ppb in the sediment sample.

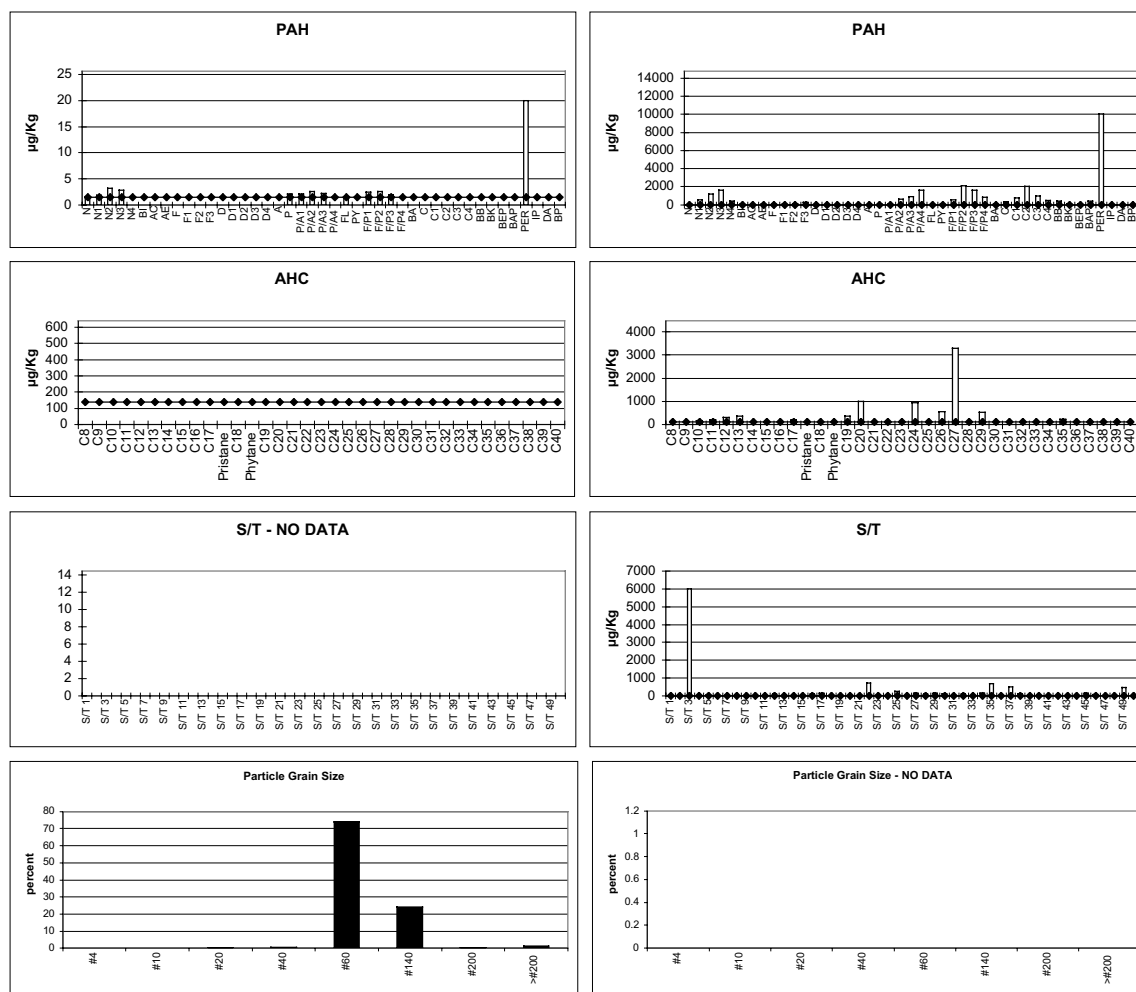
4) No-name Creek

Figure 3-76 presents the chemistry and PGS profiles for sediment replicate No. 2 from

Figure 3-76. Chemistry and PGS profiles for No-name Creek sediment Rep. 2 and fine particulate coal collected from the same location.

No-name Creek sediment Rep. 2

No-name Creek Fine Coal



No-name Creek compared to the particulate coal sample isolated separately at this station. The sediment PAH distribution shown in the figure is consistent with the coal fragments, although the chrysenes series is absent or below the MDL in the sediment. It is unlikely that peat has contributed significantly to the observed PAH because of the measured alkyl-substituted homologues for both the phenanthrene/anthracene series and the fluoranthene/pyrene series. Also, the relatively larger grain size distribution observed for the sediments (primarily medium sand) would tend to preclude eroding peat as a PAH source because peat fragments were generally observed only in the finer-grained sediment locations. Replicate No. 1 from this site contained only perylene at a concentration of 11 ppb, and the FID GC profile showed only one component, n-C 19, at

270 ppb. Interestingly, the sterane/triterpane pattern obtained from replicate 1 for this site (not shown) was identical to the sterane triterpane pattern for Polly Creek (see Figure 3-75), which also contained only perylene (derived from coal) in the sediment samples. As will be discussed in greater detail below, it is interesting that these sediment profiles look nothing like the tissue samples from the razor clam samples collected at either Polly Creek or No-name Creek.

5) Redoubt Creek

Figure 3-77 presents the chemistry and PGS profiles obtained from both sediment replicates collected at Redoubt Creek. Sediment replicate 1 contained perylene at a concentration of 3.7 ppb and a trace of n-C 19 at 160 ppb (just above the method detection limit). Replicate 2 contained both C2 naphthalene and perylene, but no n-alkanes were detected. Although the PAH could have come from either coal or eroding peat, the S/T pattern did not match any of the reference samples. No evidence of any petroleum hydrocarbon contamination was measured in the poorly sorted but primarily silt- and clay-sized sediments collected at this location.

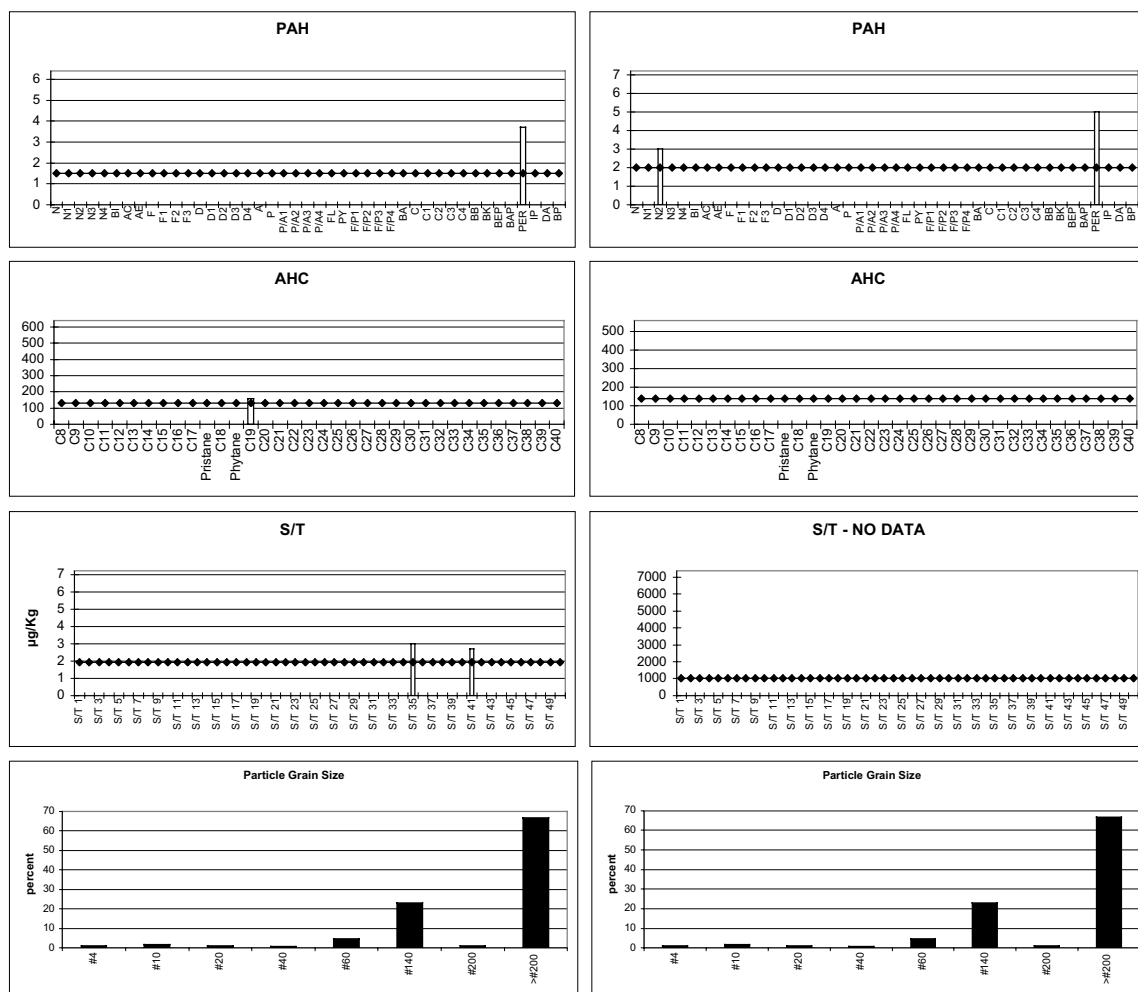
6) Harriet Point North

Figure 3-78 presents the chemistry and PGS profiles for sediment replicate No. 1 collected at Harriet Point compared to the coal reference sample from the shoal north of Kalgin Island (North Shoal). Both of the primarily medium-sand sized sediments from this higher energy beach at Harriet Point showed only traces of perylene and no other PAH constituents. This would be consistent with the PAH signal in either of the Beluga coal field samples collected in 1998. It would also be consistent with the high concentrations of

Figure 3-77. Chemistry and PGS profiles for Redoubt Creek sediment replicates.

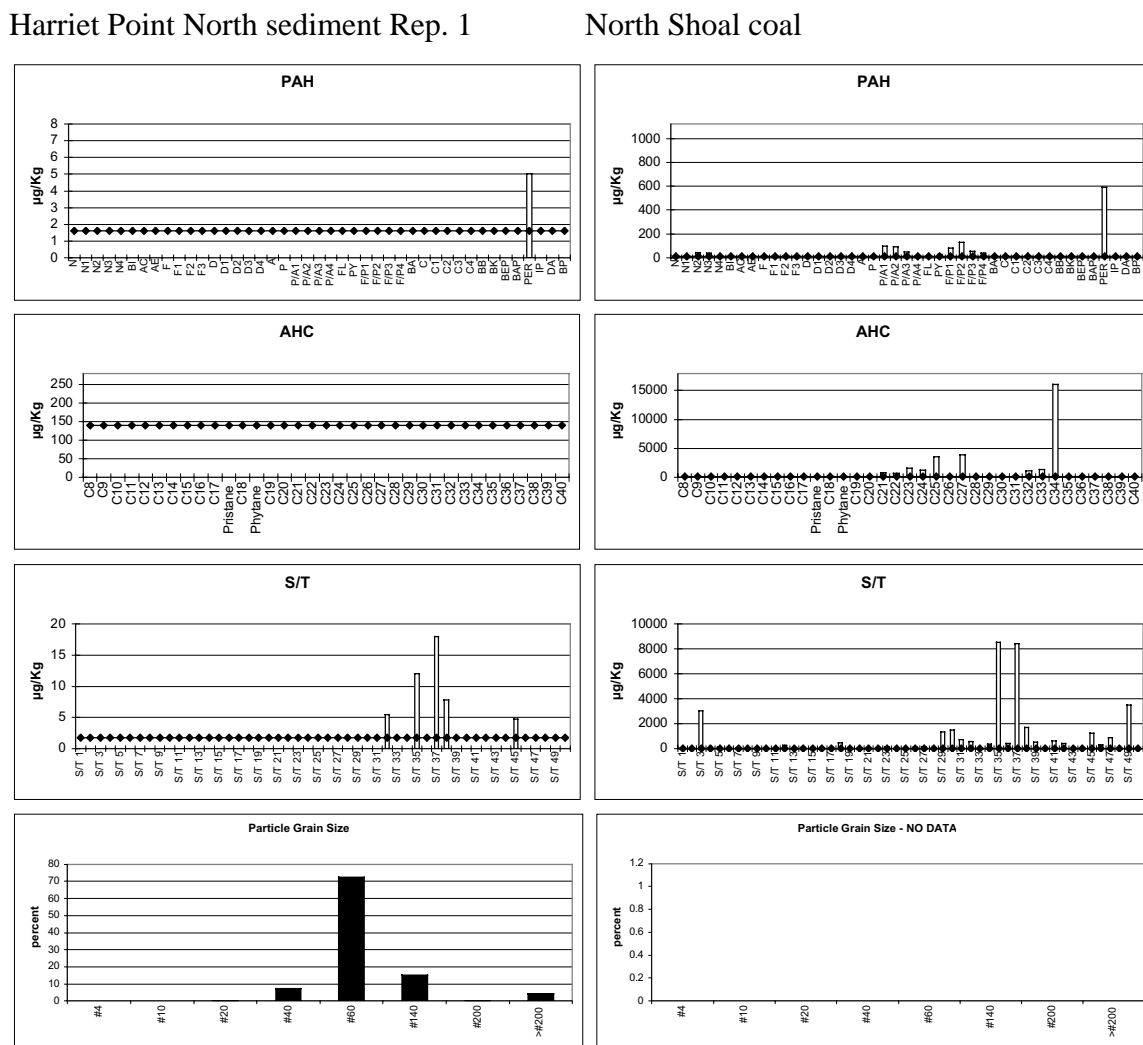
Redoubt Creek sediment Rep. 1
2

Redoubt Creek sediment Rep.



perylene observed in the No-name Creek coal sample collected in 2000; however, none of the other PAH present in the No-name Creek coal sample were observed in these sediment samples. Furthermore, transport of coal from the No-name Creek area to Harriet Point would be unlikely because of the prevailing northeast to southwest currents in the region. Given the relative abundance of perylene to the other PAH in the 1998 Beluga coal field and 2000 Beluga River SW fine coal samples, it is likely that they would have been below the method detection limit of 1.5 ppb in the Harriet Point sediment samples where perylene itself was only detected at 5 ppb. S/T data were not available for the 1998 Beluga River coal samples; however, the S/T pattern in the

Figure 3-78. Chemistry and PGS profiles for Harriet Point sediment Rep. 1 and a North Shoal coal reference sample.



sediments at Harriet Point were consistent with those measured in the Beluga River SW fine coal and North Shoal coal reference samples analyzed in this program. As stated earlier, the coal particles observed on the North Shoal were similar to coal from North Foreland and Beluga River SW. However, it is likely that large coal seams are exposed in several intervening areas (e.g., south of North Foreland). PAH signals representing either eroding peat, crude oil, or refined petroleum product contamination were not present in these coarser grained sediments samples.

7) Old Cannery Creek

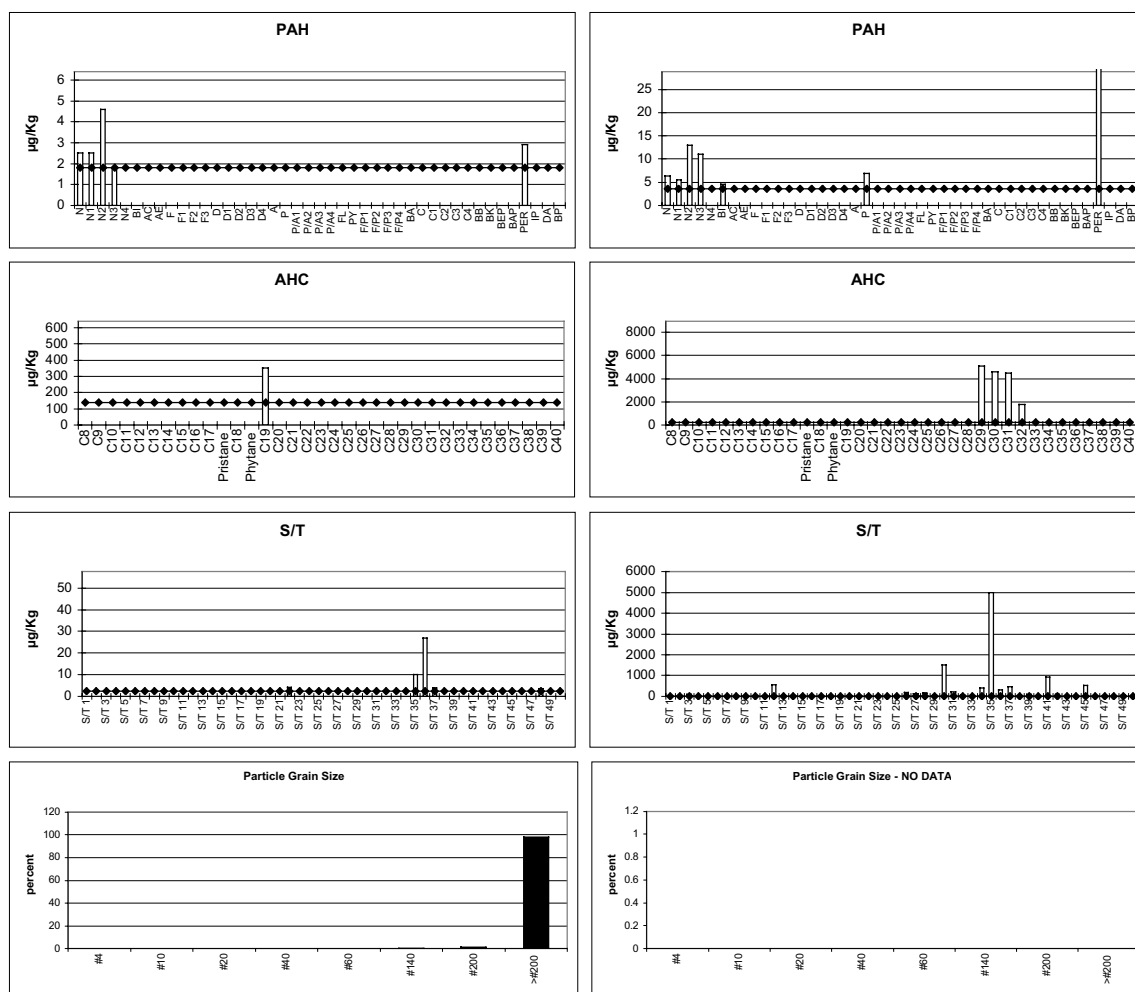
Figure 3-79 presents the chemistry and PGS profiles for sediment replicate 1 from Old Cannery Creek compared to the eroding peat reference sample. The silt- and clay-sized sediments of this site were extremely clean, and only traces of PAH derived from eroding peat were detected at 10-14 ppb in either sample. The only n-alkane identified in the FID

GC profiles was n-C 19 at 350 ppb in replicate 1. Replicate 2 showed no detectable AHC peaks at an individual component detection limit of 140 ppb. No evidence of any petroleum hydrocarbon contamination was observed in either sample.

Figure 3-79. Chemistry and PGS profiles for Old Cannery Creek sediment Rep. 1 and an eroding peat reference sample.

Old Cannery Creek sediment Rep 1

Eroding Peat



8) West Foreland South

Figure 3-80 presents the chemistry and PGS profiles from both sediment samples collected from West Foreland South. The very well sorted and silt- and clay-sized

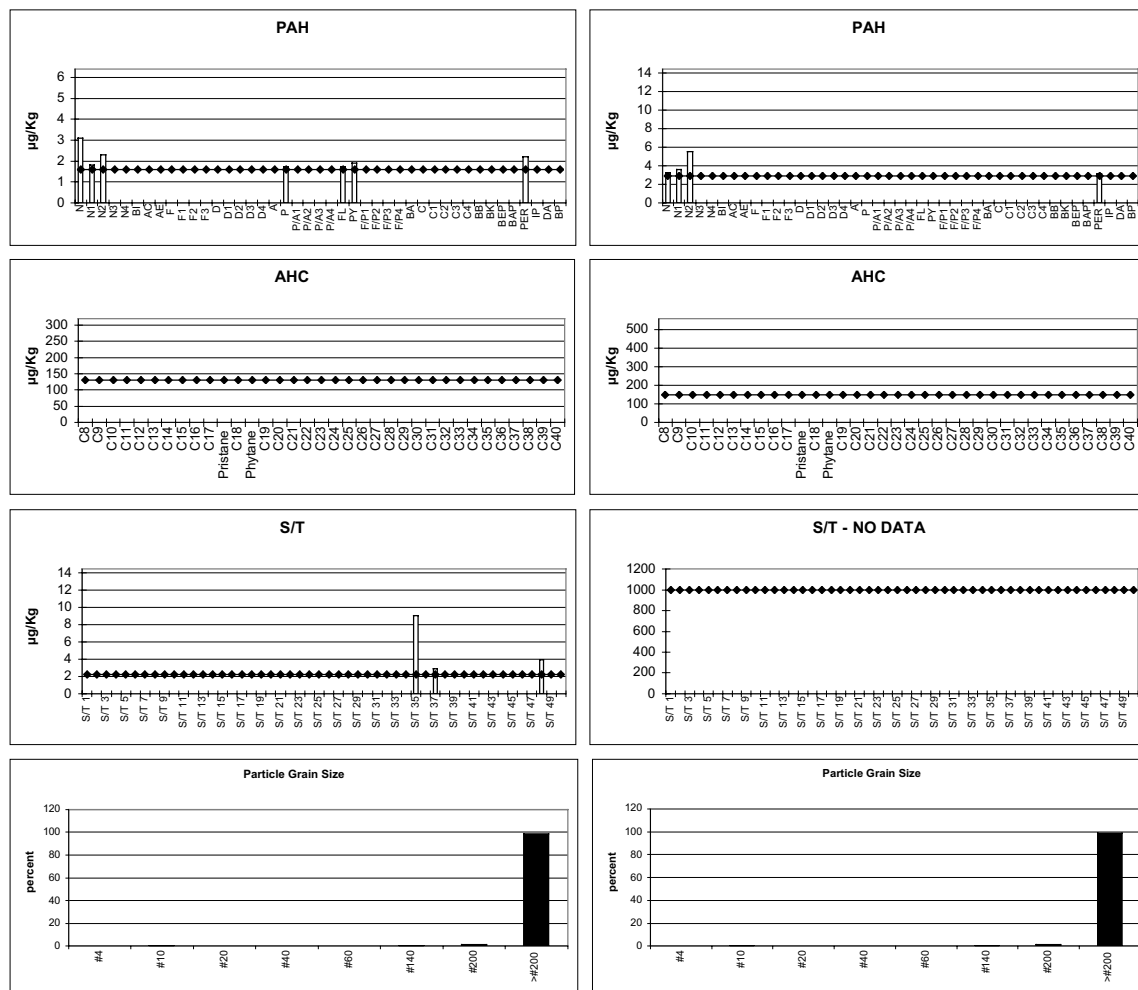
sediment samples from this site were extremely clean, and only traces of PAH derived from eroding peat were observed at or just slightly above the individual component method detection limit of 1.5 and 3 ppb in replicates 1 and 2, respectively. No measurable n-alkanes were observed in either sample at individual-component method

detection limits of 130 and 150 ppb. Neither sample showed any evidence of petroleum hydrocarbon contamination.

Figure 3-80. Chemistry and PGS profiles for West Foreland South sediment replicates.

West Foreland South sediment Rep. 1

West Foreland South sediment Rep. 2



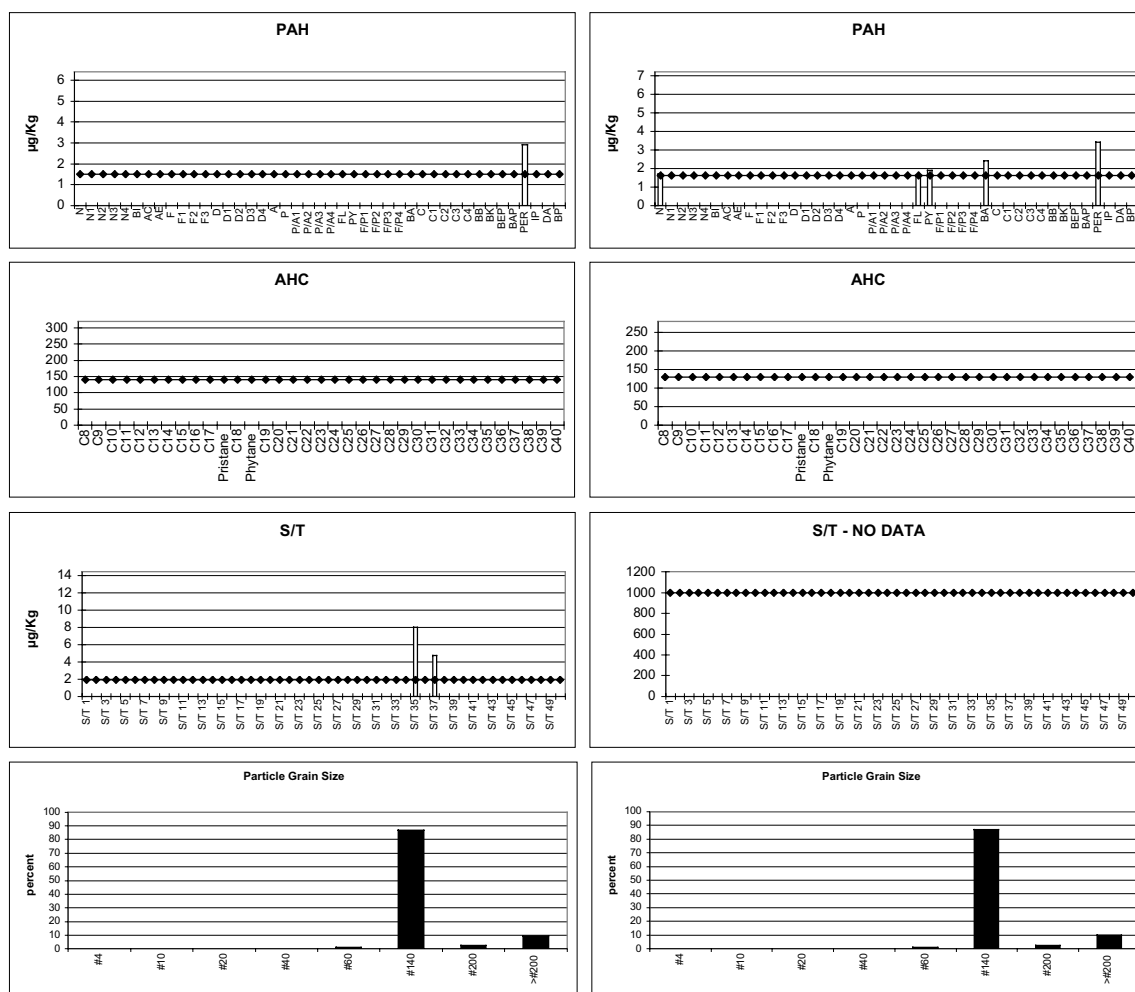
9) West Foreland North

Figure 3-81 presents the chemistry and PGS profiles from both sediment sample replicates collected from the West Foreland. The sediments of this site were extremely clean and only perylene was detected at 3 ppb in replicate 1. Replicate 2 contained traces (just above the method detection limit) of naphthalene, fluoranthene, pyrene, benzo(a)anthracene, and perylene to yield a total PAH value of only 11 ppb. No peaks were detected in either of the FID GC profiles generated from these samples at an individual component detection limit of 130 ppb. At these low concentrations it is impossible to identify the source of the measured PAH in these primarily fine-sand sized sediment samples. No evidence of petroleum hydrocarbon contamination was observed.

Figure 3-81. Chemistry and PGS profiles for West Foreland North sediment replicates.

West Foreland North sediment Rep. 1

West Foreland North sediment Rep. 2



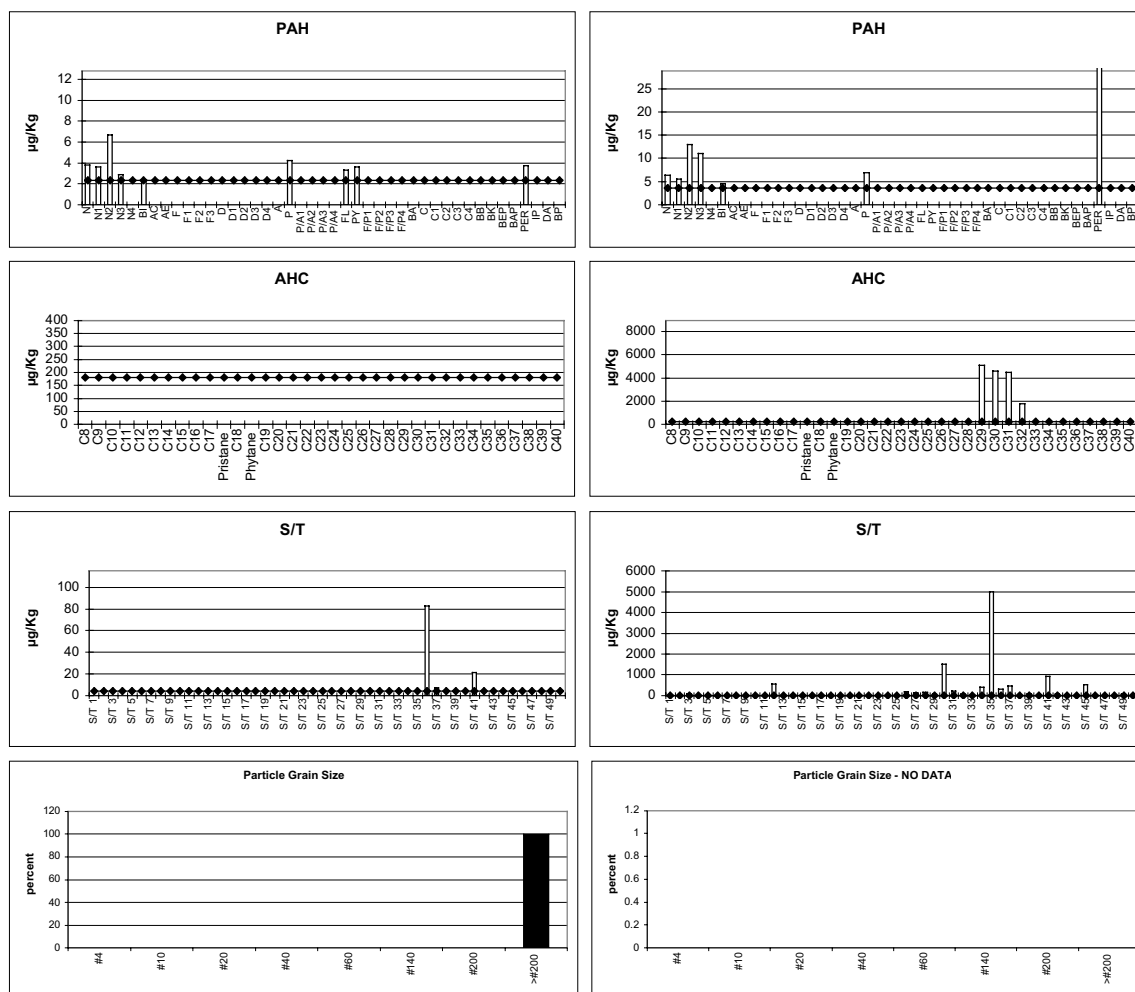
10) Nikolai Creek

Figure 3-82 presents the chemistry and PGS profiles for sediment replicate 1 from Nikolai Creek compared to the eroding peat reference sample. Both replicates were essentially identical, and the PAH profiles in the silt- and clay-sized sediments from this site showed signals from eroding peat at total PAH values of 29-34 ppb. All of the components measured were in the 3-7 ppb range, however, just slightly above the detection limit of 2 ppb. No evidence of petroleum hydrocarbon contamination was lacking in both sediment sample. As will be discussed further below, the PAH profiles in the tissue samples from the *Macoma balthica* collected at this site looked nothing like the surrounding sediment patterns.

Figure 3-82. Chemistry and PGS profiles for Nikolai Creek sediment Rep. 1 and an eroding peat reference sample.

Nikolai Creek sediment Rep. 1

Eroding Peat



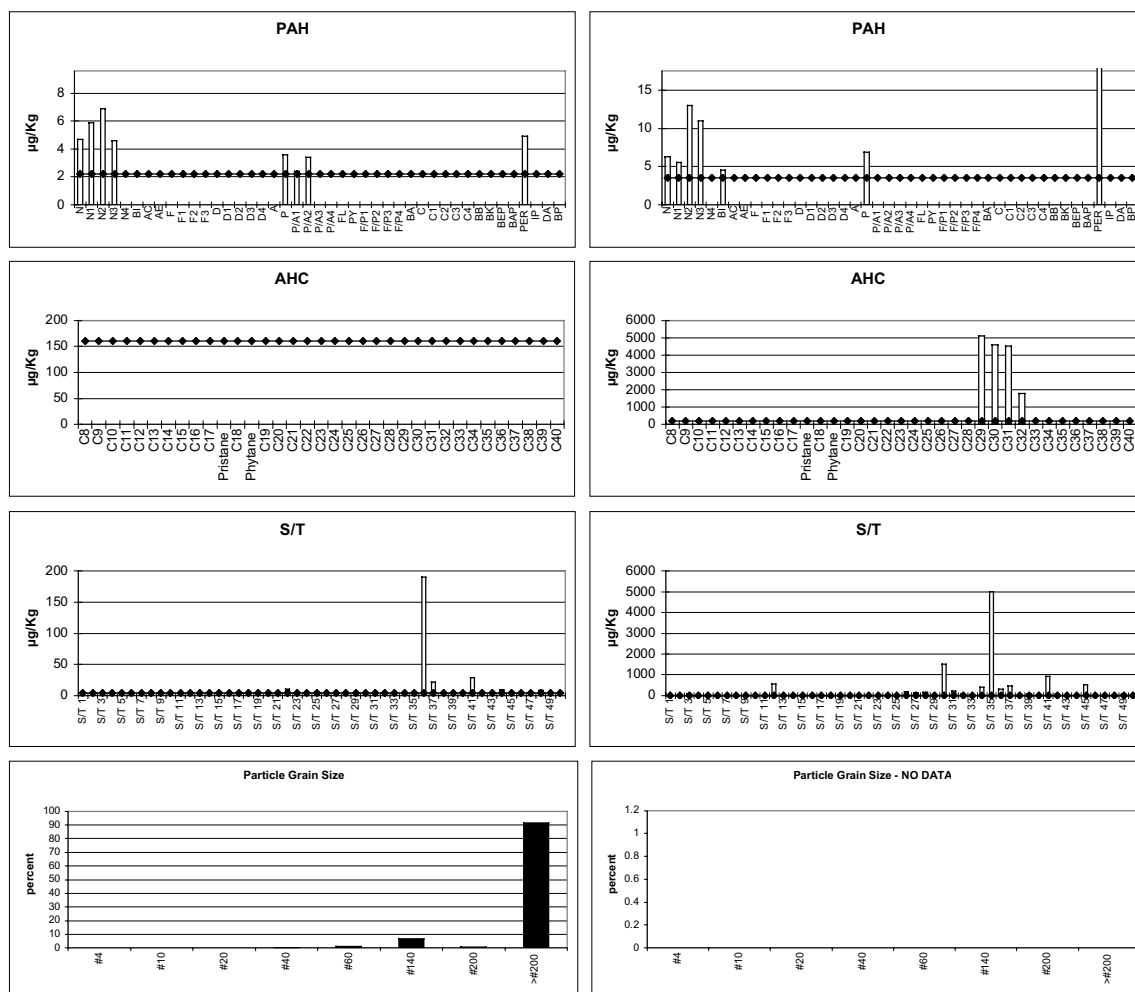
11) Beluga River SW

Figure 3-83 presents the chemistry and PGS profiles for sediment replicate 1 from the Beluga River SW station compared to the eroding peat reference sample. Both sediment replicates at this site were essentially the same, and it was easy to identify eroding peat as the major source of the PAH in the silt- and clay-sized sediment with little or no input from the coal outcrops or sand-sized coal particles also observed in the area. Likewise, no evidence of the PAH signal observed in the coal samples collected in 1998 from the Beluga coal field (see Figures 3-49 through 52) was detected. Parent PAH constituents (naphthalene and phenanthrene) are more abundant compared to their alkylated

Figure 3-83. Chemistry and PGS profiles for Beluga River SW sediment Rep. 1 and an eroding peat reference sample.

Beluga River SW sediment Rep. 1

Eroding Peat



homologues in the sediment samples than in any of the coal reference samples from this region, and the higher molecular weight alkylated homologues of phenanthrene/anthracene and fluoranthene/pyrene observed in the coals are absent in the sediments. N-alkanes were not detected in either sample at a method detection limit of 160 ppb, and no evidence of crude oil or refined petroleum product contamination was observed.

4. Tissue Hydrocarbons

Table 3-10 presents the summary data for TPAH, TALK, and TRC measured in the tissues of the intertidal organisms collected during this program. In general, the intertidal organisms were extremely clean, with TPAH values ranging from no PAH detected (at a selected ion monitoring GC/MS MDL of 8 ppb) in one of the mussel (*Mytilus trossulus*) replicates from Clam Gulch to a high of 1,300 ppb in a *Macoma balthica* sample from Redoubt Creek. Aliphatic hydrocarbons, as measured by total n-alkanes (TALK) and total

resolved constituents (TRC) were consistently higher in the tissue samples than the corresponding sediments (which were almost all non-detect at MDLs ranging from 160-220 ppb). TAlk values ranged from <890 ppb in a Clam Gulch razor clam (*Siliqua patula*) sample to 88,900 ppb in a softshell clam (*Mya arenaria*) sample from Oldmans Bay on Kalgin Island. TRC values were observed to exist over an even wider range from a low of <31,000 for that same Clam Gulch razor clam to over 6,100,000 ppb in a *M. balthica* sample from West Foreland South.

Table 3-10. Aromatic and aliphatic hydrocarbons measured in tissues of intertidal organisms.

		TPAH	TAlk	TRC	
East Side	Lab ID	µg/Kg	µg/Kg	µg/Kg	Comments
Clam Gulch mussel 1	45672-04	84	6,800	420,000	traces of combustion products & peat(?)
Clam Gulch mussel 2	45672-05	<8	3,600	190,000	no PAH detected, nondescript aliphatics
Clam Gulch razor clam 1	45672-01	<20	<890	< 31,000	no PAH detected, no aliphatics
Clam Gulch razor clam 2	45672-02	<15	1,500	38,000	no PAH detected, nondescript aliphatics
Clam Gulch razor clam 3	45672-03	<14	3,480	58,000	no PAH detected, nondescript aliphatics
Kalifornsky <i>Macoma balthica</i>	45672-06	<32	21,600	150,000	no PAH detected, biogenic aliphatics, peat(?)
Bishop Creek <i>Macoma balthica</i>	45672-07	960	50,900	340,000	N2 plus combustion PAH, trace of peat in n-alkanes
Chickaloon Bay <i>Macoma balthica</i>	45672-12	<48	46,600	110,000	no PAH detected, evidence of peat in n-alkanes
Middle of Inlet					
SE Kalgin razor clam	45672-09	<12	10,250	37,000	no PAH detected, trace of peat in n-alkanes(?)
Oldmans Bay <i>Macoma balthica</i>	45672-23	50	40,600	1,600,000	only N detected, evidence of peat in n-alkanes
Oldmans Bay <i>M. arenaria</i> 1	45672-20	130	32,000	4,300,000	only N detected, biogenic aliphatics, peat(?)
Oldmans Bay <i>M. arenaria</i> 2	45672-21	220	88,900	2,200,000	only N & BI detected, trace of peat plus major n-C 18
Oldmans Bay <i>M. arenaria</i> 3	45672-22	100	19,800	1,700,000	only N detected, evidence of peat in n-alkanes
NE Kalgin <i>Macoma balthica</i>	45672-11	<32	50,900	140,000	no PAH detected, evidence of peat in n-alkanes
NE Kalgin <i>Mya arenaria</i>	45672-10	<32	9,700	48,000	no PAH detected, evidence of peat in n-alkanes
West Side of Inlet					
NE Chisik Island <i>Macoma balthica</i>	45672-08	<32	19,400	61,000	no PAH detected, evidence of peat in n-alkanes

No. Tuxedni <i>Macoma balthica</i>	45672-15	47	8,200	8,200	no PAH detected, trace of peat in n-alkanes(?)
No. Tuxedni <i>Mya arenaria</i>	45672-14	43	5,500	5,500	no PAH detected, trace of peat in n-alkanes(?)
Polly Creek razor clam	45672-16	25	6,300	6,300	only N detected, evidence of peat in n-alkanes
No-name Creek razor clam	45672-17	24	5,210	77,000	only N detected, biogenic aliphatics, peat(?)
Redoubt Creek <i>Macoma balthica</i>	45672-18	1,300	14,400	200,000	N plus combustion PAH, evidence of peat in n-alkanes
Redoubt Creek mussel	45672-19	55	12,840	56,000	only N detected, evidence of peat in n-alkanes
West Foreland South <i>Macoma balthica</i>	45672-24	550	33,300	6,100,000	N plus traces of BB & BP, trace of peat in n-alkanes(?)
Nikolai <i>Macoma balthica</i>	45672-13	250	7,000	61,000	N plus combustion PAH, trace of peat in n-alkanes(?)

Note: Because of variable sample sizes, non-detects are listed as < the sample- and method-specific MDLs.

A (?) in Comment column indicates presence of some but not all n-alkanes consistent with eroding peat.

As will be discussed in more detail in the paragraphs below and in the following section on FID GC analyses, the majority of the constituents making up the TRC values were biogenic components that were ingested by the organisms or polar lipid-like materials that were not completely separated from the tissue extracts during fractionation and chromatographic cleanup prior to FID/GC analysis. The TALK, on the other hand, appeared in many but not all cases to include n-C 29, n-C 30, n-C31, and n-C32, which could be attributed to eroded peat that was apparently still present in the gut of the organisms included in the sample. Interestingly, the tissue and surrounding sediment samples consistently produced completely different PAH and AHC profiles, indicating that for the most part, we were not just looking at ingested sediment in the tissue samples. No signals of petroleum hydrocarbon contamination were measured in any of the intertidal tissue samples examined, although occasionally PAH associated with combustion products were detected. Traces of PAH derived from the selective dissolution and partitioning of naphthalene (presumably from eroding peat) were frequently encountered at those sites where higher levels of peat were observed in the sediments; however, no evidence of PAH derived from particulate coal was detected in any of the tissue samples. These and other results are discussed below on a site-by-site basis.

a) East Side of Cook Inlet

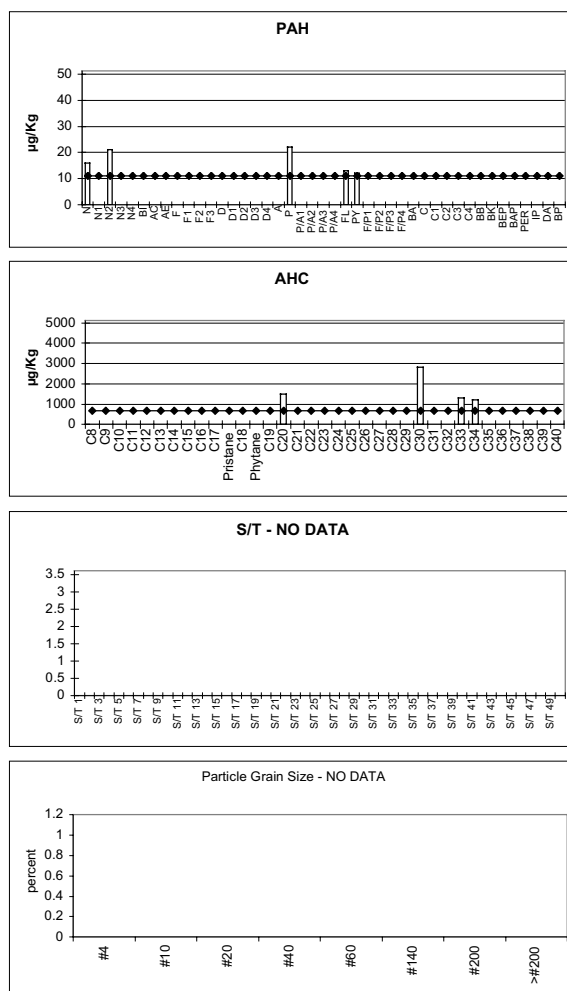
1) Clam Gulch

Figure 3-84 presents the chemistry PAH and AHC histogram plots for the *Mytilus* sample compared to the sediment data collected from this Clam Gulch. The naphthalene, C2 naphthalene, and phenanthrene present just above the MDL in the tissue sample are

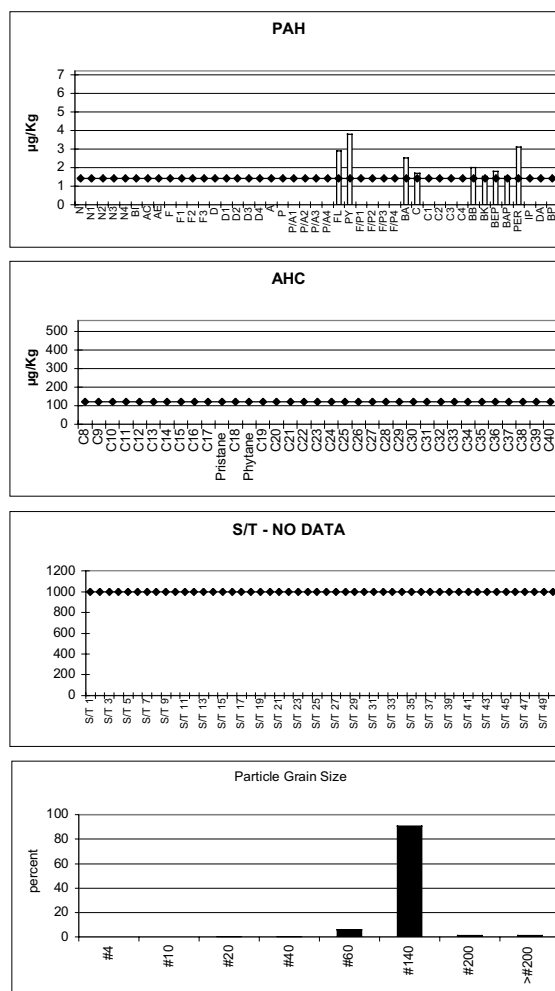
consistent with PAH present in eroding peat. The fluoranthene and pyrene are combustion products, and they along with a number of other higher molecular weight combustion products were detected in the sediments at this site. Concentrations of aliphatic constituents in the tissue extract were too low to draw any definitive conclusions about their source.

Figure 3-84. Chemistry profiles for mussel *Mytilus trossulus* and sediment collected from Clam Gulch.

Clam Gulch mussel Rep 1



Clam Gulch sediment Rep. 2



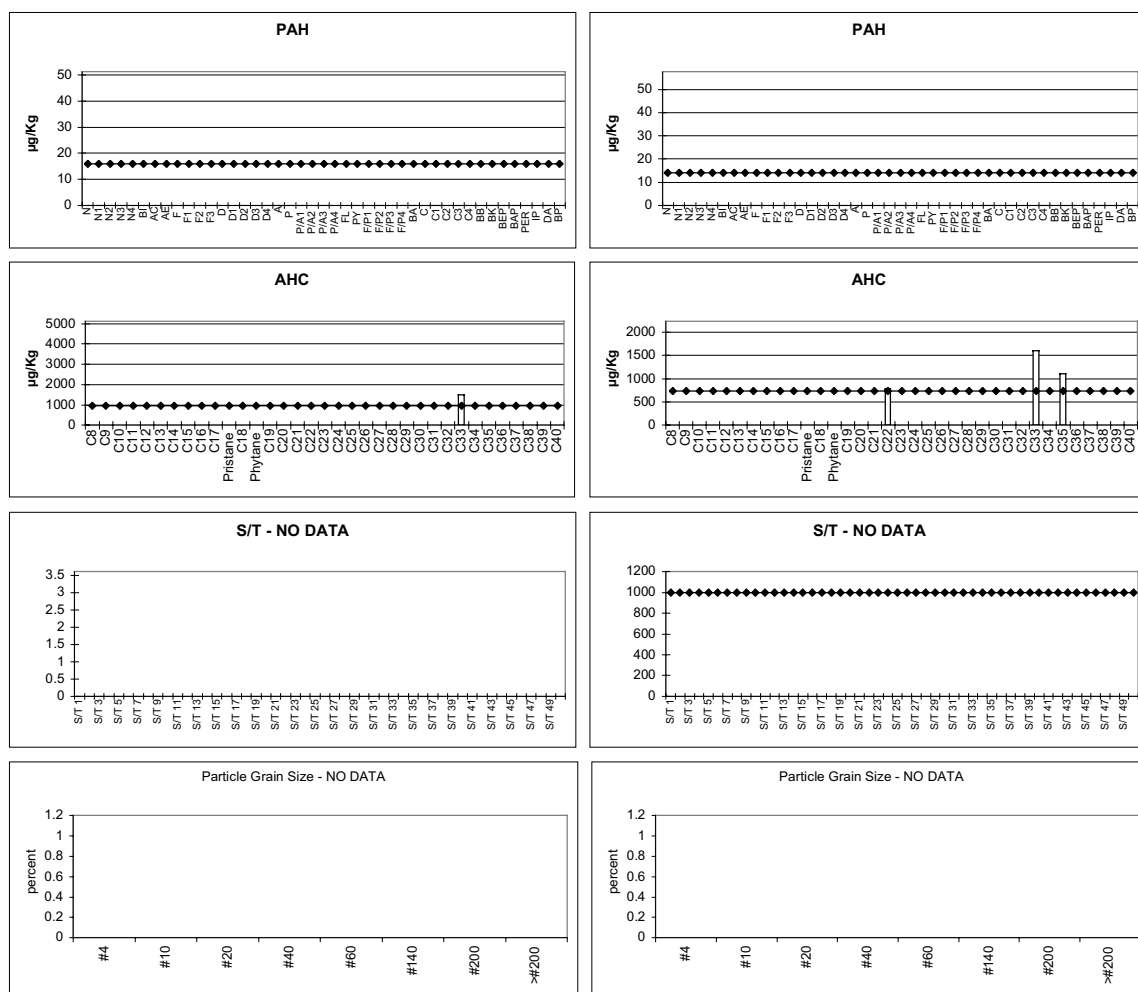
PAH constituents were not detected at MDLs ranging from 14-20 ppb in any of the three razor clam replicates collected at Clam Gulch. Figure 3-85 shows the PAH and AHC profiles for the two razor clam replicates where at least several n-alkanes were detected. As noted above with the *Mytilus* sample from this site, the aliphatic hydrocarbon (AHC) profiles contained too few peaks to draw any conclusions as to the source. Traces of n-C 22, n-C 33, and n-C 35 were detected in two of the three razor clam replicates. No

evidence of the petroleum hydrocarbon contamination was observed in the tissue samples from this location. Likewise, perylene, which was the only PAH observed in one of the sediment replicates, was not observed in any of the tissue samples.

Figure 3-85. Chemistry profiles for two of three razor clam (*Siliqua patula*) replicates collected from Clam Gulch.

Clam Gulch razor clam Rep. 2

Clam Gulch razor clam Rep. 3



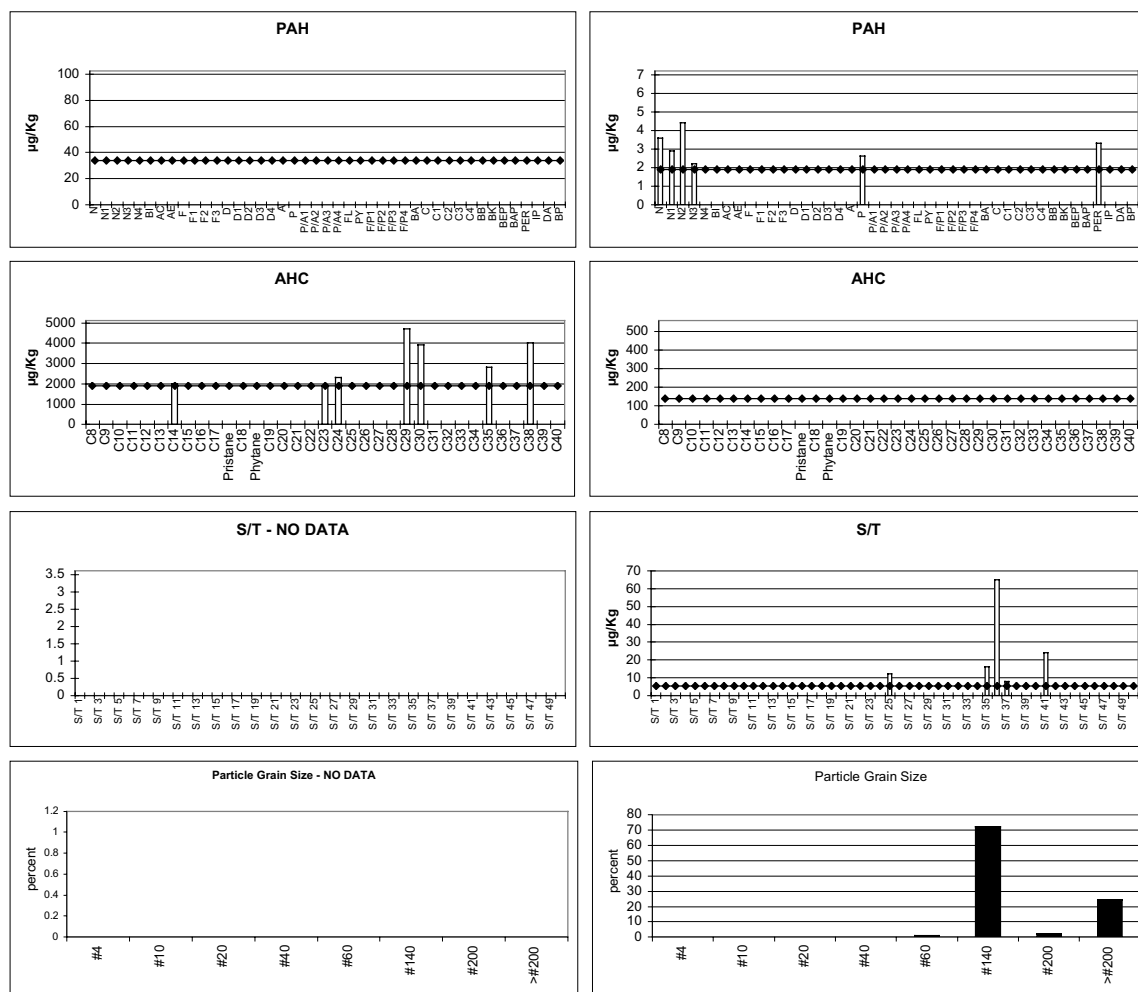
2) Kalifornsky Beach

Figure 3-86 compares the PAH and AHC histograms for the *M. balthica* sample and the sediment collected from this site. PAH was not detected in tissues at a GC/MS method detection limit of 34 ppb, and the few n-alkanes observed cannot be attributed to any one source. The predominance of n-C 29 and n-C 30 is consistent with traces of eroding peat (presumably in the gut), and that would also be consistent with the eroding peat signal observed in the sediments at this site. Evidence of petroleum hydrocarbon contamination in the tissue sample is absent at this site.

Figure 3-86. Chemistry profiles for *Macoma balthica* and sediment collected from Kalifornsky Beach.

Kalifornsky Beach *Macoma balthica*

Kalifornsky Beach sediment Rep. 1



3) Bishop Beach

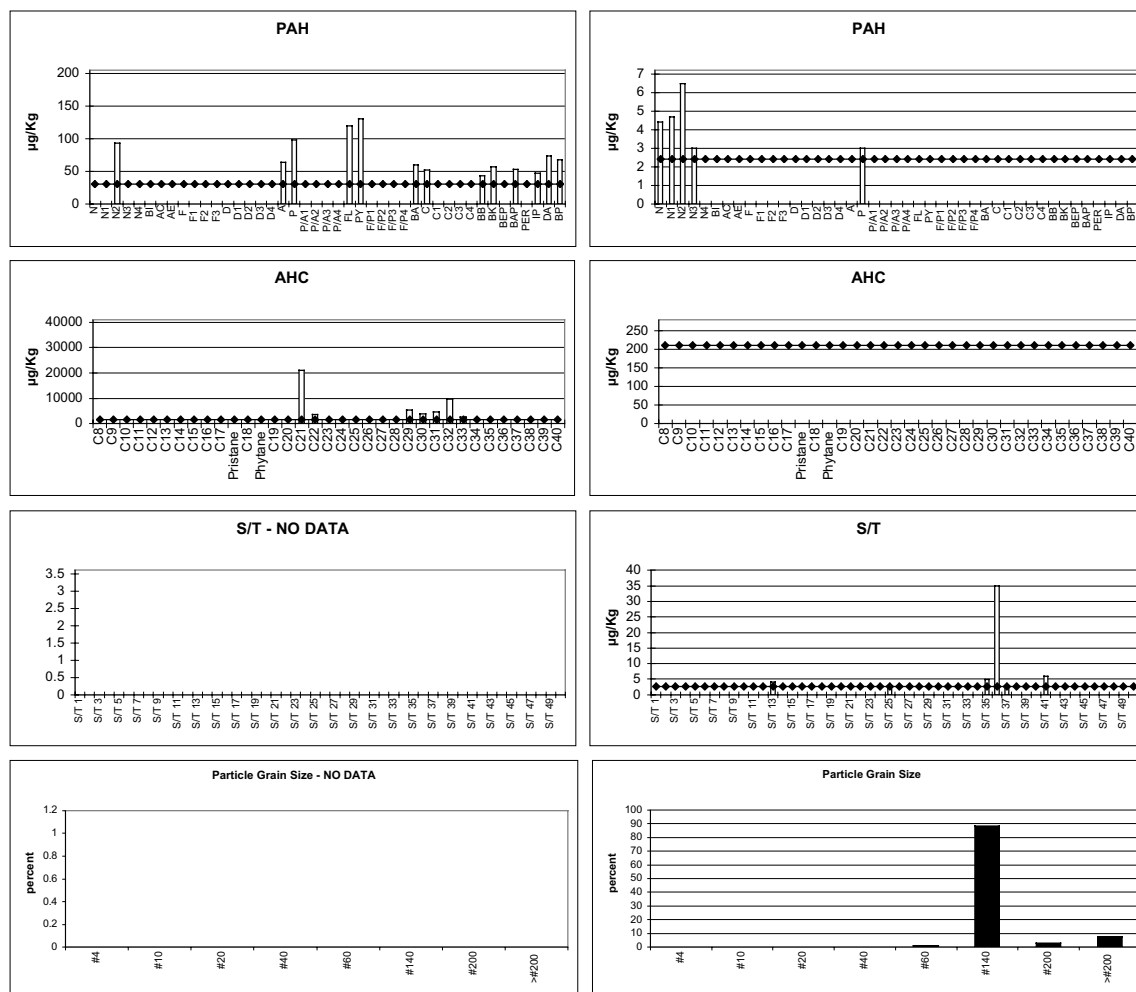
Figure 3-87 presents the chemistry PAH and AHC histograms for the *M. balthica* sample compared to the sediment sample data also collected from this site. The tissue sample shows evidence of PAH contamination by combustion products, and the TPAH concentration value of 960 ppb at this site was the second highest of any tissue samples examined in the program. The PAH profile shows no obvious resemblance to the sediment profile, which contained only the low-level naphthalene suite plus phenanthrene that is characteristic of eroding peat. While the PAH profile for the tissue sample shows no evidence of bioaccumulation of any PAH from the peat (with the possible exception of C2-naphthalene), the AHC profile, with trace concentrations of n-alkanes n-C 29 through n-C 33, suggests the possible presence of peat remnants (presumably in the gut given limited water solubility considerations) within the sample. No evidence of naphthalene

bioaccumulation from the ingested peat or from petroleum hydrocarbon contamination was detected in the tissue sample.

Figure 3-87. Chemistry profiles for *Macoma balthica* and sediment collected from Bishop Beach.

Bishop Creek *Macoma balthica*

Bishop Beach sediment Rep. 1



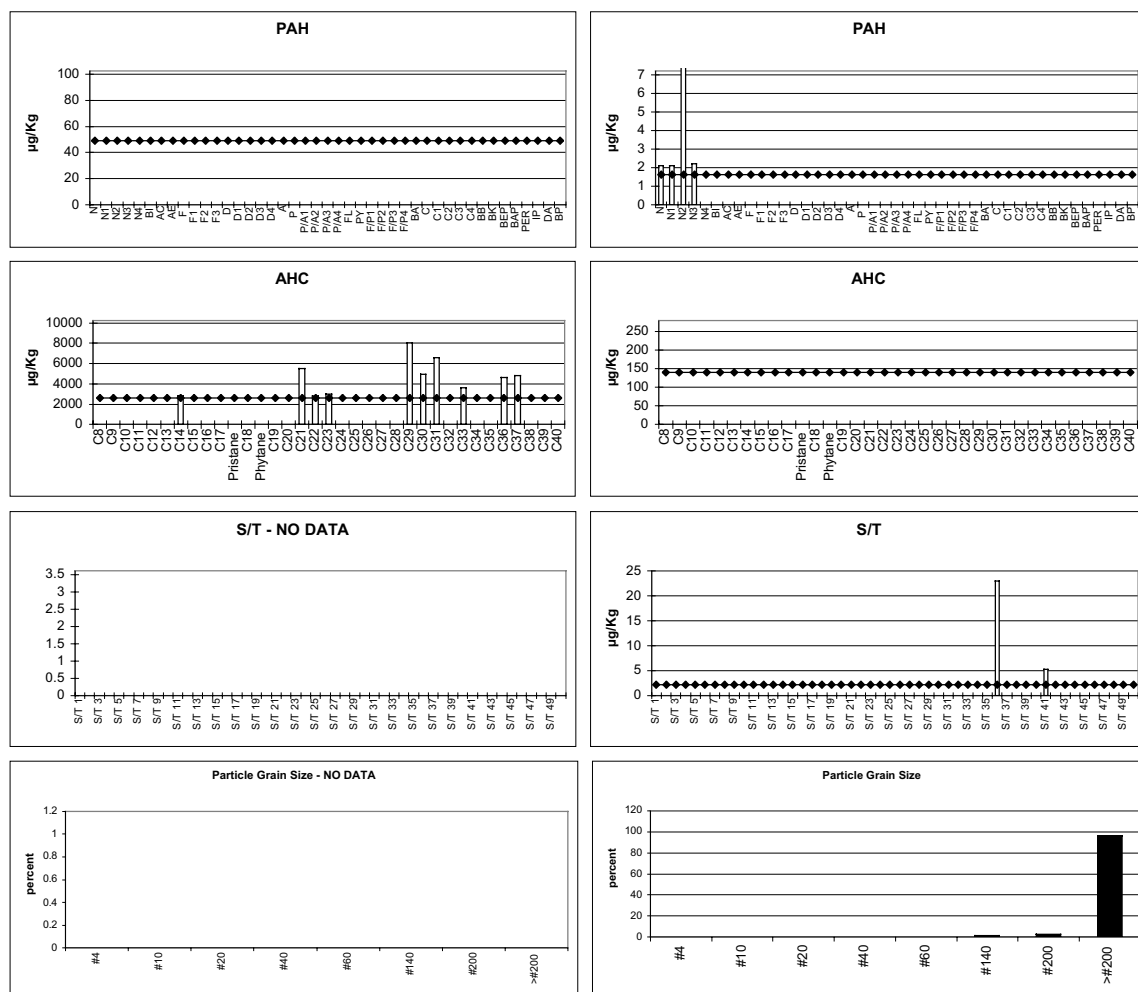
4) Chickaloon Bay

Figure 3-88 presents the chemistry PAH and AHC histogram plots for the *M. balthica* sample compared the sediment data collected from this site. No PAH components were detected at a GC/MS compound specific MDL of 49 ppb. The AHC profile shows a combination of biogenic hydrocarbons and the presence of n-alkanes n-C 29 through n-C 31 possibly due to eroding peat. The sediment PAH profile can be attributed to trace levels of naphthalenes due to eroding peat. Evidence of any petroleum hydrocarbon contamination was not detected in the tissue sample.

Figure 3-88. Chemistry profiles for *Macoma balthica* and sediment collected from Chickaloon Bay.

Chickaloon Bay *Macoma balthica*

Chickaloon Bay sediment Rep. 1



b) Middle of Cook Inlet

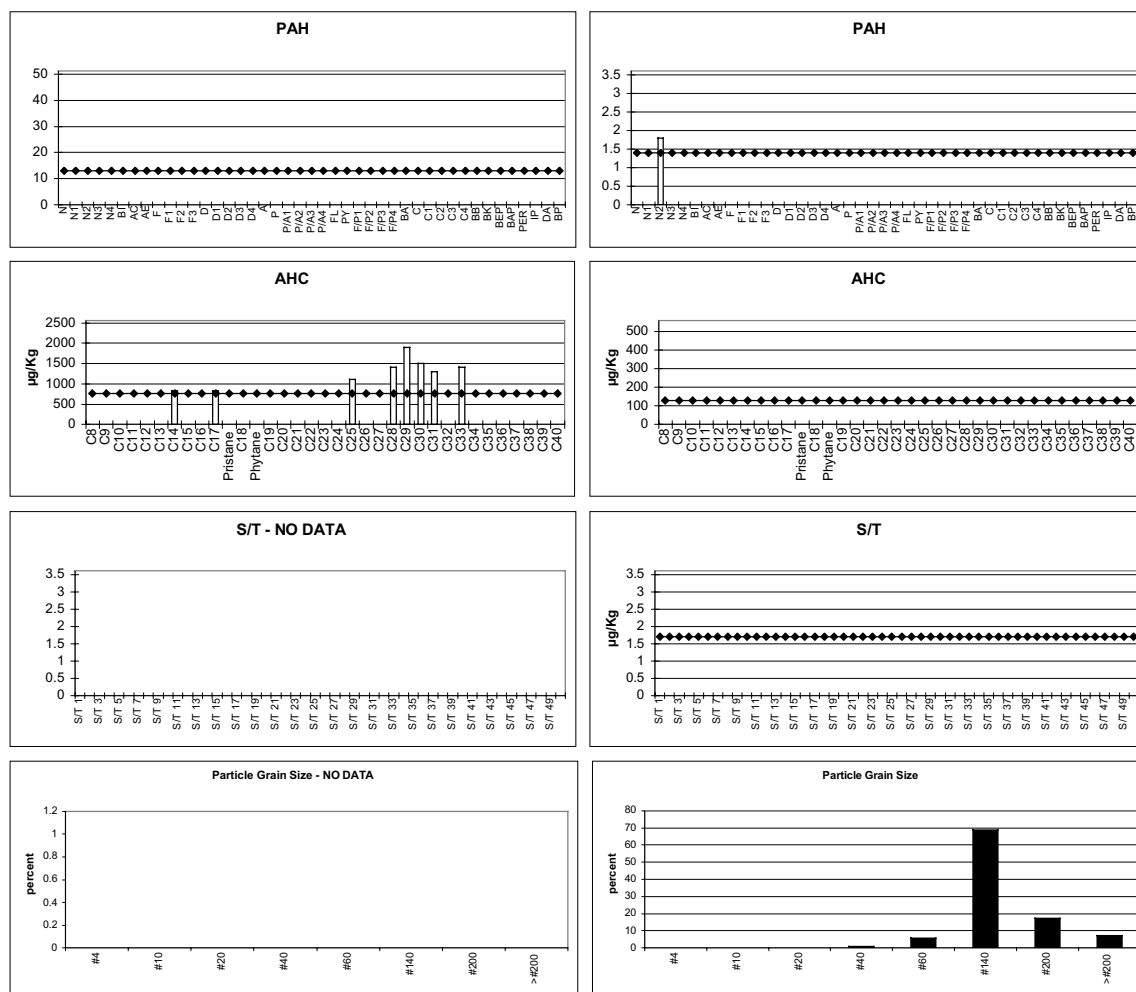
1) SE Kalgin Island

Figure 3-89 presents the chemistry PAH and AHC histogram plots for the single razor clam sample and the sediment collected from this station. PAH signals were not detected in the tissue sample above the GC/MS MDL of 12 ppb, and the AHC profile showed individual n-alkanes that are consistent with traces of eroded peat being present in the gut. Interestingly, in addition to the n-C 29, n-C 30, and n-C 31 constituents that are characteristic of eroded peat, the other detected n-alkanes (n-C 14, n-C 17, and n-C 25)

Figure 3-89. Chemistry profiles for razor clam (*Siliqua patula*) tissues and sediment collected from SE Kalgin Island.

SE Kalgin razor clam

SE Kalgin sediment Rep. 1



were also observed at trace concentrations in the *M. balthica* sample collected from NE Kalgin and in the *M. balthica* sample collected from Oldmans Bay. These other constituents are not components observed in eroding peat. As a result, it is believed that they represent biogenic alkanes associated with suspended particular material, bacteria, decaying algae, or other organic decay products that make up the food of these filter-feeding organisms. No evidence of bioaccumulation of PAH derived from eroding peat, coal, or petroleum hydrocarbons was observed in the tissue sample.

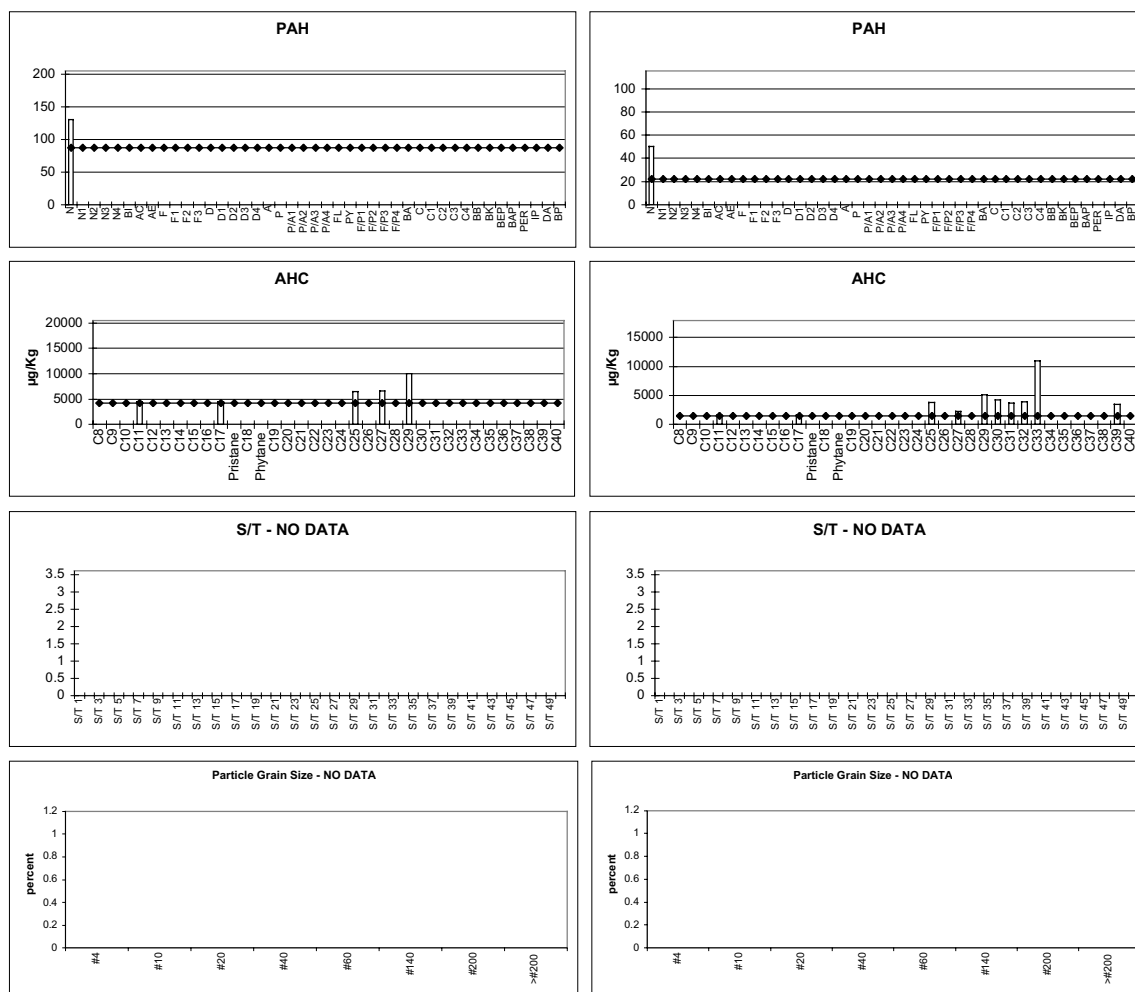
2) Oldmans Bay, Kalgin Island

Figure 3-90 presents the PAH and AHC histogram plots for separate *M. balthica* and *Mya*

Figure 3-90. Chemistry profiles for softshell clam (*Mya arenaria*) and *Macoma balthica* collected from Oldmans Bay, Kalgin Island.

Oldmans Bay *Mya arenaria* Rep. 1

Oldmans Bay *Macoma balthica*



arenaria samples collected from Oldmans Bay. Of all target PAH components, only naphthalene is observed in both organisms above the GC/MS method detection limits shown in the figure. The absence of the other alkylated naphthalene homologues characteristic of peat (which was easily identified in the sediments at this site) leads us to hypothesize that the naphthalene (which has the highest water solubility of all PAH) was partially dissolved in the gut during digestion of the peat fragments and possibly bioaccumulated to allow its detection in the tissues of both species.

The AHC pattern for the *M. balthica* sample shows evidence of the higher molecular weight n-alkanes (n-C 29, n-C 30, n-C 31, and n-C 32) that were identified in the single peat sample analyzed in this program. In addition, trace amounts of n-C 11, n-C 17, n-C 25, and n-C 27 are observed in both the *M. balthica* and *M. arenaria* samples suggesting that these constituents are also part of the food obtained at the sediment water interface by both species. As noted above, these constituents were also observed in the razor

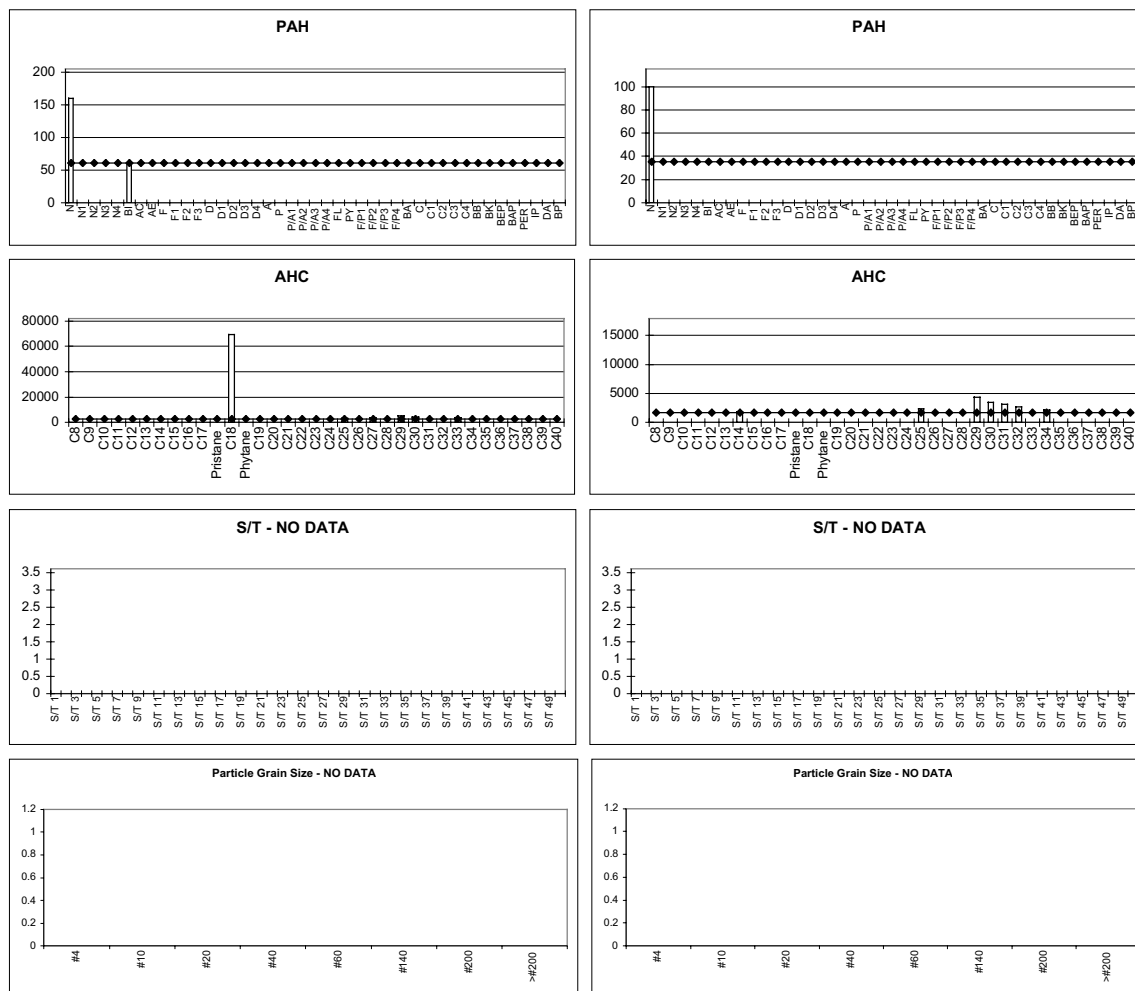
clams from SE Kalgin and the *M. balthica* from NE Kalgin. Based on limited water solubility, particularly for the higher molecular weight n-alkanes, we believe that these constituents are most probably associated with partially digested materials in the gut, although they too could have been assimilated into the tissues of the animals. Without doing additional depuration studies, it is impossible to determine which possibility is in fact the case. No evidence of any petroleum hydrocarbon contamination or bioaccumulation of PAH or n-alkanes associated with particulate coal was detected in either sample.

Figure 3-91 shows the PAH and AHC chemistry profiles for two additional *M. arenaria* sample replicates collected from Oldmans Bay. In addition to the significant concentrations of naphthalene in both samples, replicate 2 (on the left) also shows evidence of detection-limit concentrations of biphenyl, another of the characteristic constituents of eroded peat. Both tissues also show aliphatic hydrocarbons characteristic of eroded peat (n-C 29, n-C 30, n-C 31, and n-C 32), and replicate 2 also contains n-C 18 at significantly elevated concentrations not observed in any of the other tissue samples from this location. The source of the n-C 18 is unknown. Evidence of any petroleum hydrocarbon contamination was absent in both sample.

Figure 3-91. Chemistry profiles for softshell clam (*Mya arenaria*) replicates 2 and 3 collected from Oldmans Bay, Kalgin Island.

Oldmans Bay *Mya arenaria* Rep. 2

Oldmans Bay *Mya arenaria* Rep. 3



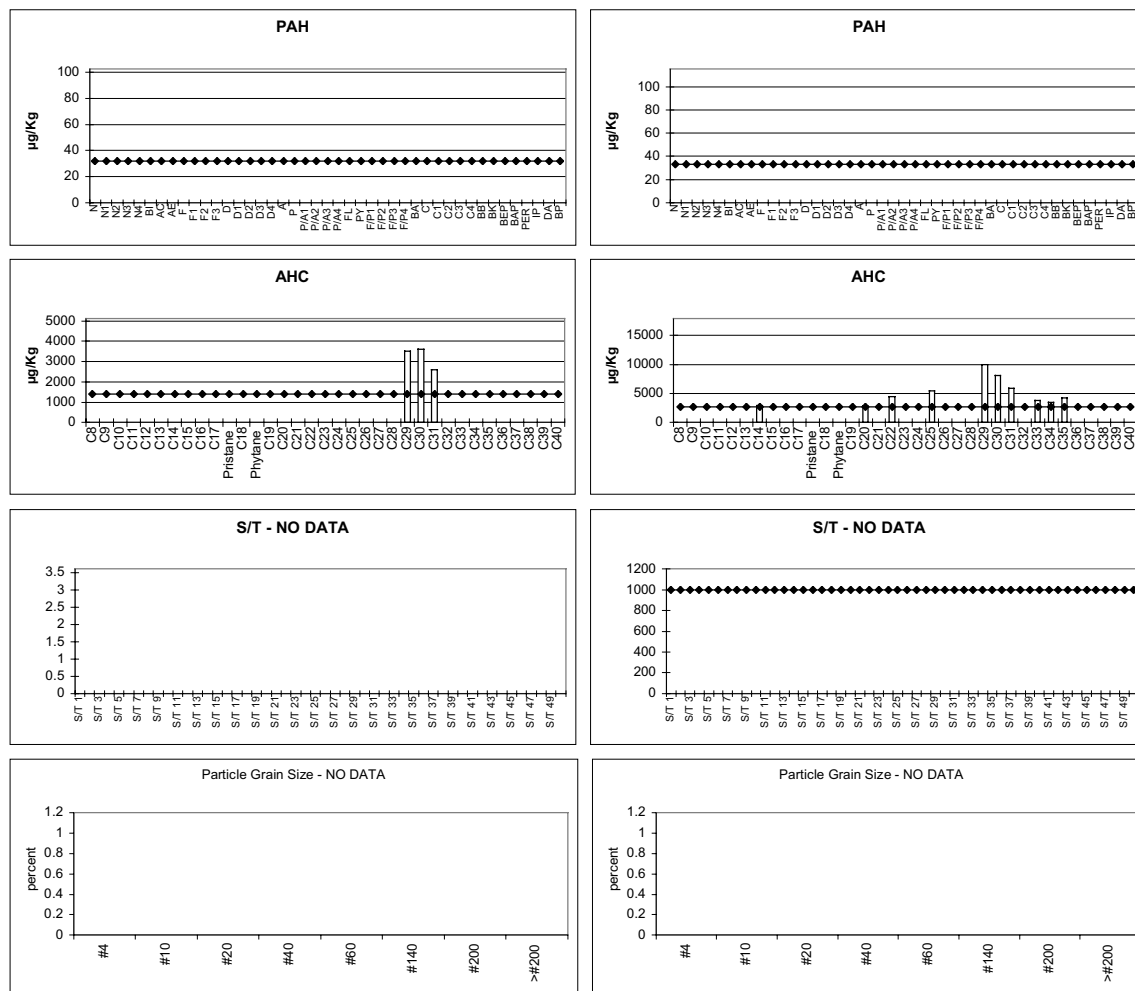
3) NE Kalgin Island

Figure 3-92 presents the chemistry PAH and AHC histogram plots for the *M. arenaria* and *M. balthica* samples collected from the NE Kalgin site. No PAH were detected in either tissue sample at a GC/MS method detection limit of 32 ppb. Both species show evidence of traces of n-C 29, n-C 30, and n-C 31, which is consistent with the aliphatic pattern observed from eroding peat. PAH constituents from eroding peat were the only aromatic components observed in either of the sediment replicates from this station. The biogenic aliphatic hydrocarbon concentrations in *M. balthica* appears to be higher than those observed in the *M. arenaria* samples, and the *M. balthica* also shows traces of several other hydrocarbons (of unknown origin) that are not observed in the *Mya*. No evidence of any petroleum hydrocarbon contamination was observed in either sample.

Figure 3-92. Chemistry profiles for softshell clam (*Mya arenaria*) and *Macoma balthica* collected from NE Kalgin Island.

NE Kalgin *Mya arenaria*

NE Kalgin *Macoma balthica*

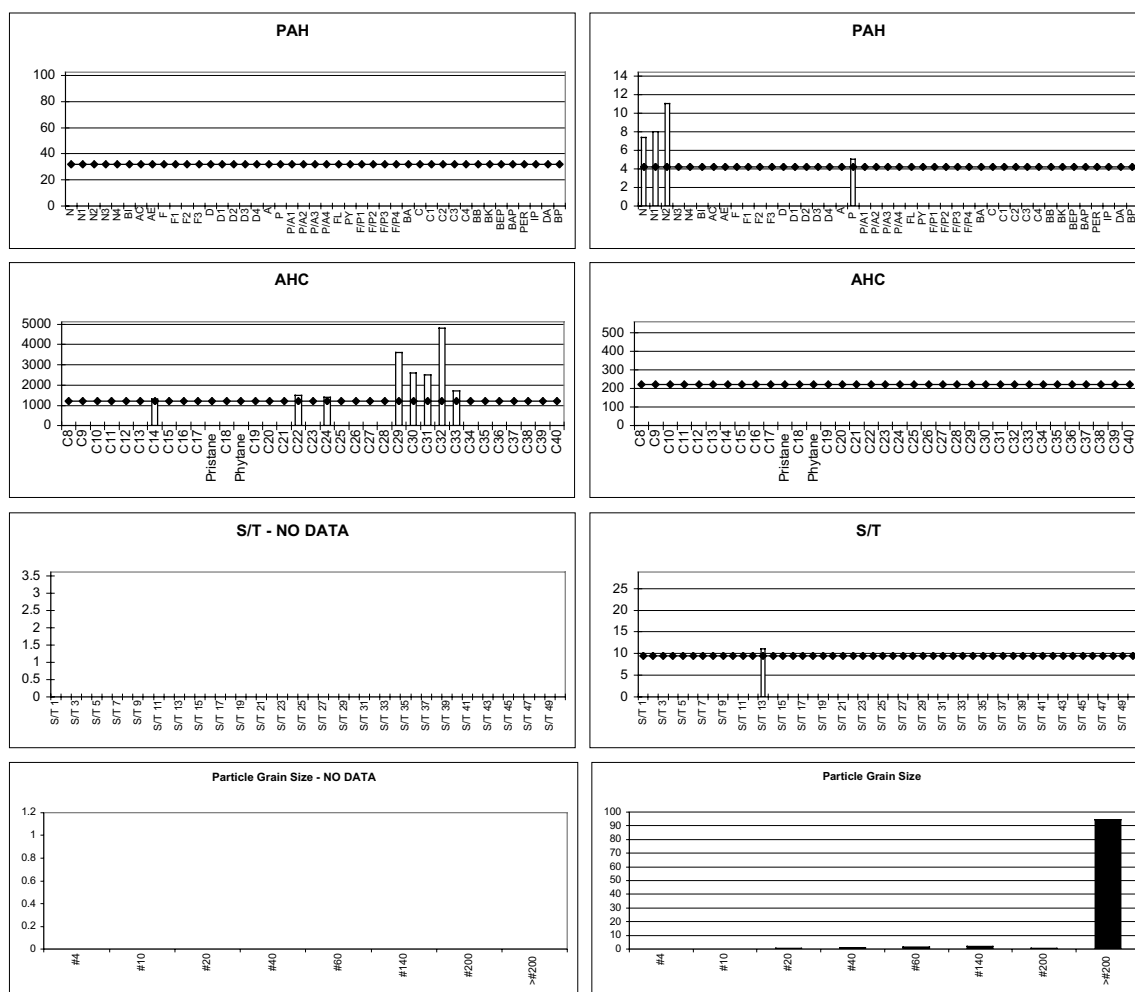


contamination in either the tissue or sediment sample. Likewise, evidence of any accumulation of PAH or AHC from coal not observed.

Figure 3-93. Chemistry profiles for *Macoma balthica* tissues and sediment collected from NE Chisik Island.

NE Chisik *Macoma balthica*

NE Chisik sediment Rep. 1



2) North Tuxedni Bay

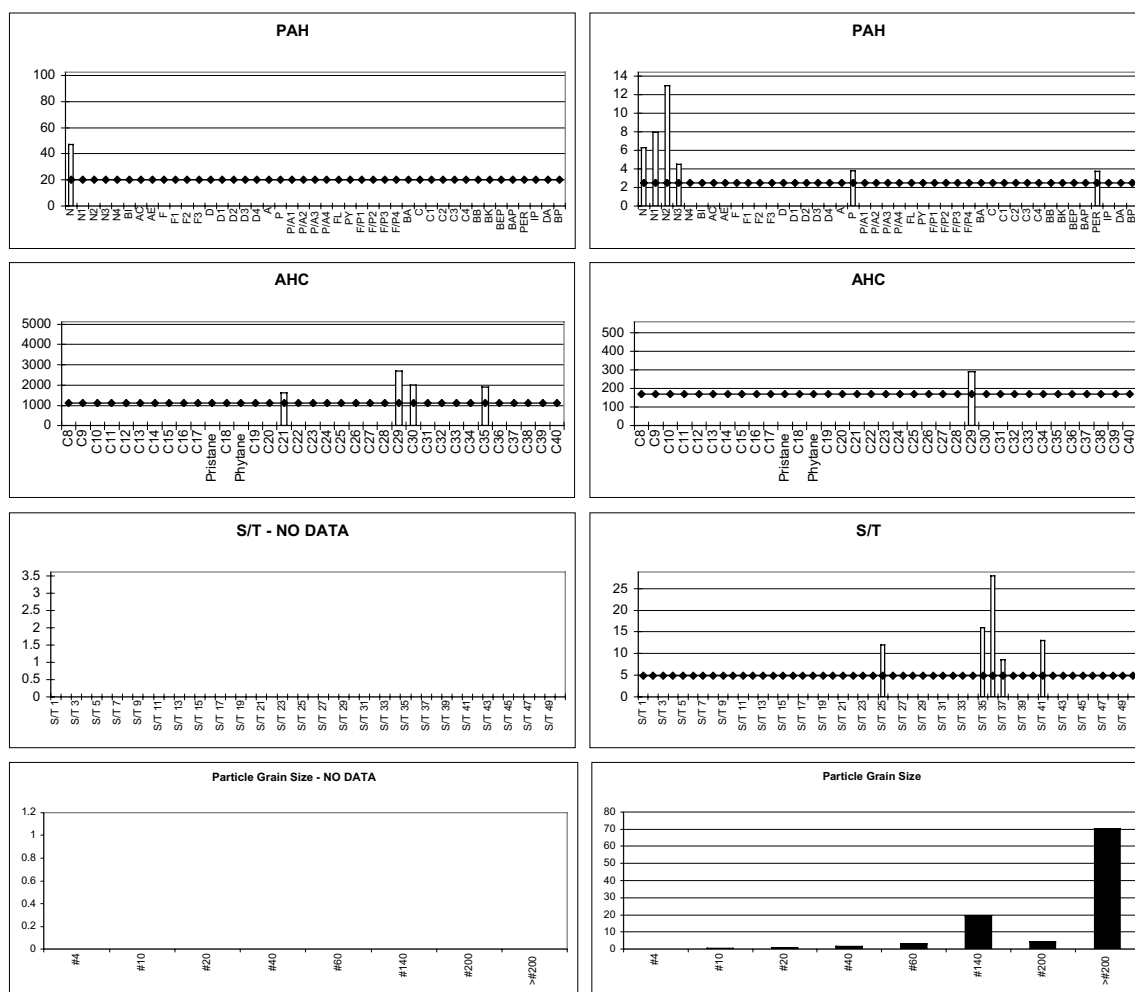
Figure 3-94 presents the chemistry PAH and AHC histogram plots for the *M. balthica* sample and the sediment collected from North Tuxedni Bay. The only PAH detected at a GC/MS MDL of 20 ppb was naphthalene at 47 ppb. As noted above, this is believed to be due to bioaccumulation of naphthalene in the tissues by dissolution of naphthalene from eroding peat ingested during feeding. The AHC profile contains only four components, with n-C 29 and n-C 30 being consistent with the aliphatics characteristic of

eroding peat. The sediment PAH profile clearly shows the pattern associated with eroding peat, although

Figure 3-94. Chemistry profiles for *Macoma balthica* tissues and sediment collected from North Tuxedni Bay.

No. Tuxedni *Macoma balthica*

No. Tuxedni sediment Rep. 1

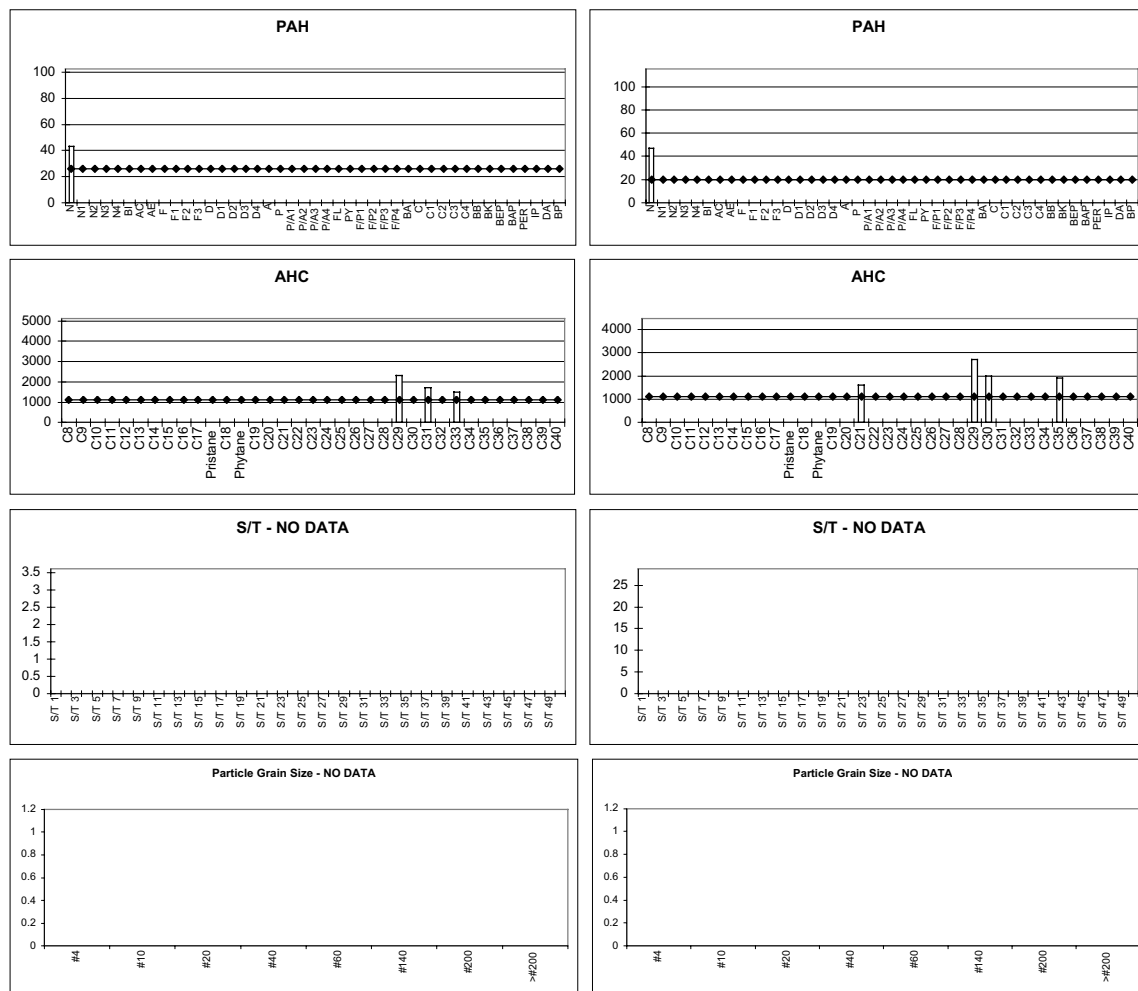


the only aliphatic constituent detected was n-C 29 at 290 ppb. Figure 3-95 allows comparison of the chemistry PAH and AHC histogram plots for the *M. arenaria* and *M. balthica* samples collected at this site. The *M. arenaria* sample contains naphthalene at essentially the same concentrations as the *M. balthica* sample discussed above (duplicated in this figure to facilitate comparisons), and contains only three aliphatic constituents above the FID/GC method detection limit of 1,100 ppb. All three of these constituents are consistent with the higher molecular weight n-alkanes associated with eroding peat. Evidence of any accumulation of hydrocarbons from petroleum contamination or coal is lacking.

Figure 3-95. Chemistry profiles for softshell clam (*Mya arenaria*) and *Macoma balthica* collected from North Tuxedni Bay.

No. Tuxedni *Mya arenaria*

No. Tuxedni *Macoma balthica*



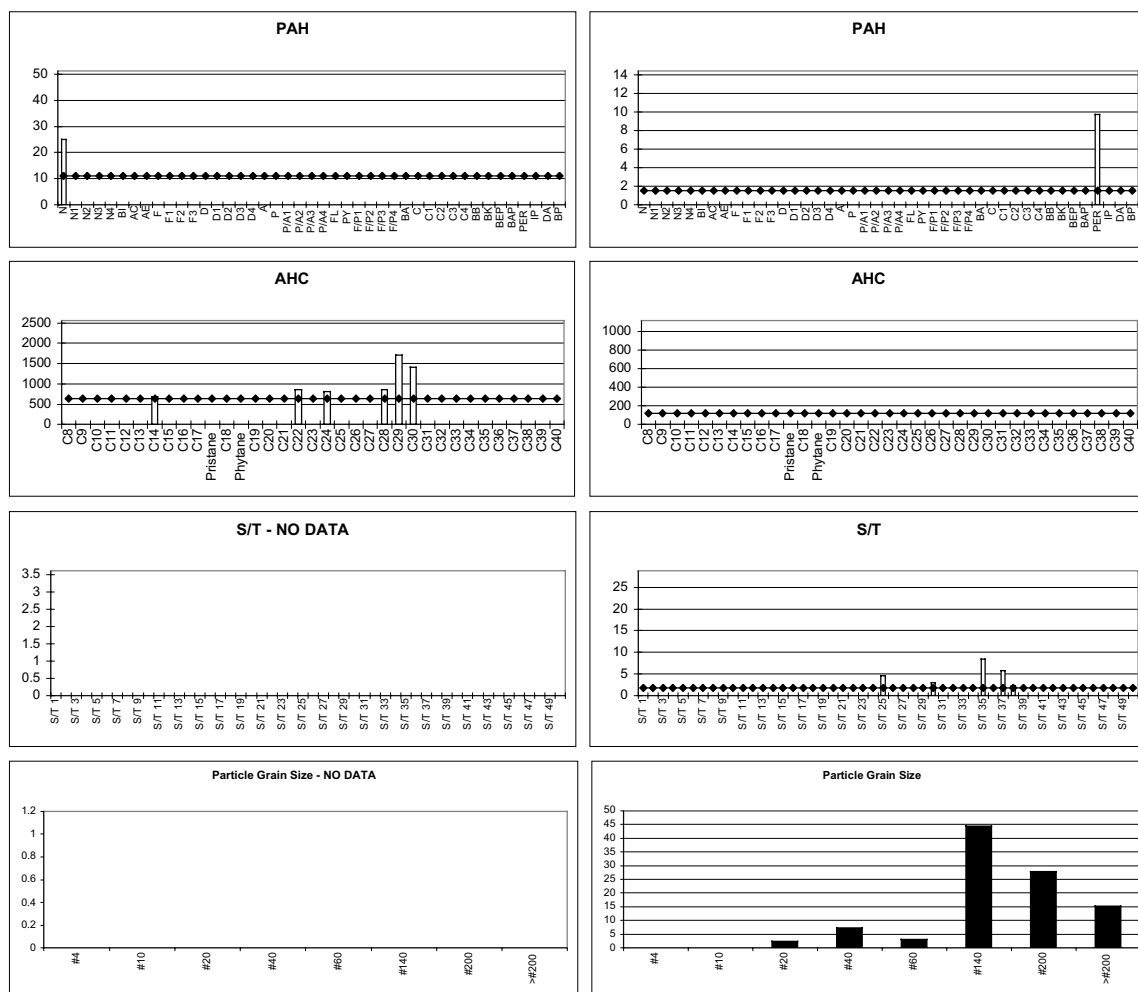
3) Polly Creek

Figure 3-96 presents the chemistry PAH and AHC histogram plots for the single razor clam sample and the sediment collected from Polly Creek. As in most of the other tissue samples collected from the Western side of Cook Inlet, the only PAH observed in the tissue is naphthalene with low-level concentrations of aliphatics (n-C 28, n-C 29, and n-C 30) consistent with eroding peat. The presence of even-carbon numbered n-alkanes (n-C 14, n-C 22, and n-C 24) is somewhat unusual, and was observed in only one other location, the *M. balthica* sample collected from NE Chisik Island. Presumably, these aliphatics

Figure 3-96. Chemistry profiles for razor clam (*Siliqua patula*) tissues and sediment collected from Polly Creek.

Polly Creek razor clam

Polly Creek sediment Rep. 1



represent some unknown component (possibly decaying algae) in the seawater filtered by these organisms. Despite the fact that the sediments from this site contained perylene that was believed to have been derived from particulate coal, evidence of PAH derived from coal was not detected in the tissue sample. Likewise, no evidence of any petroleum hydrocarbon contamination was observed in either the tissue or sediment samples.

4) No-name Creek

Figure 3-97 presents the chemistry PAH and AHC histogram plots for the razor clam tissue sample and particulate coal collected from this beach. Figure 3-98 presents the

Figure 3-97. Chemistry profiles for razor clam (*Siliqua patula*) tissues and coal fragments collected from No-name Creek Beach.

No-name Creek razor clam

No-name Creek coal fragments

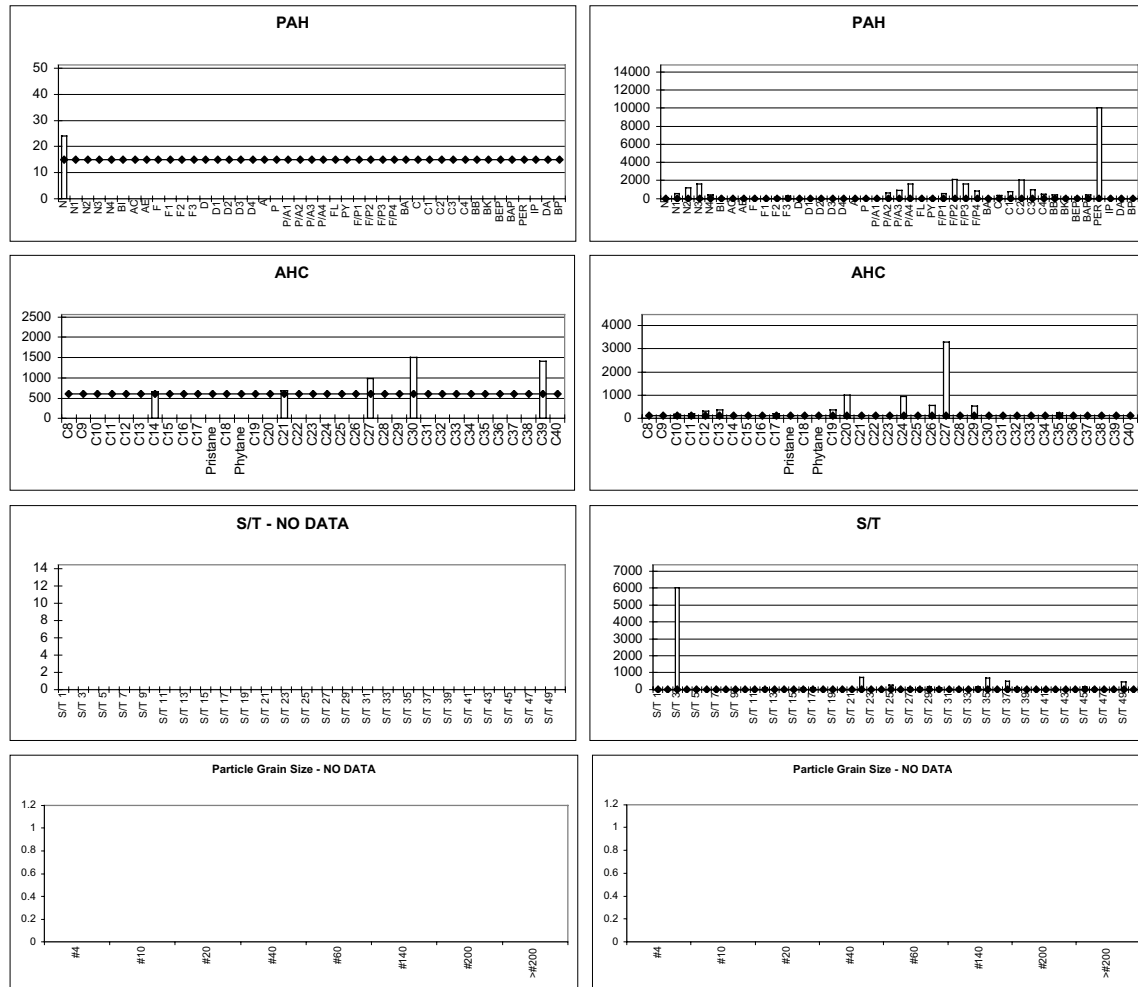
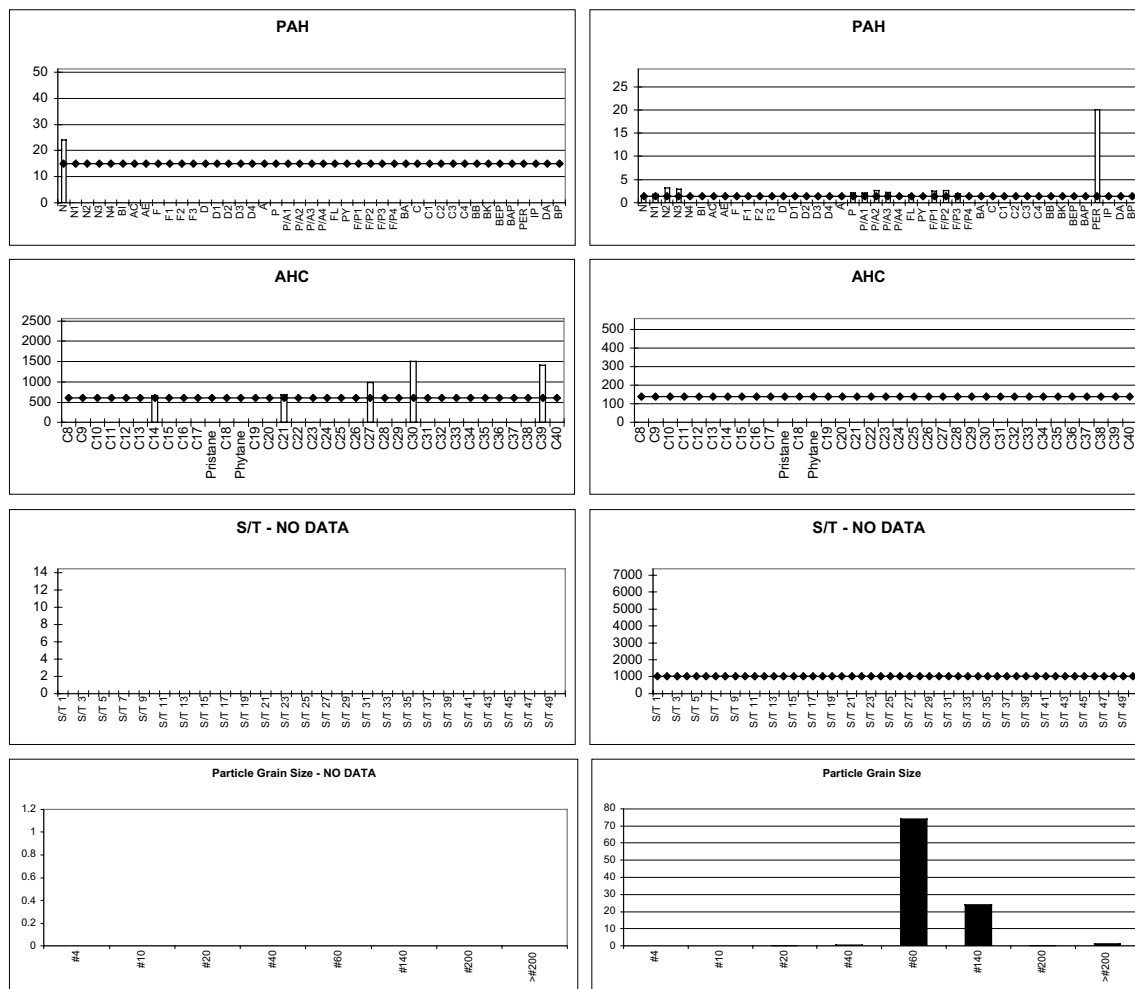


Figure 3-98. Chemistry profiles for razor clam (*Siliqua patula*) tissues and sediment collected from No-name Creek Beach.

No-name Creek razor clam

No-name Creek sediment Rep. 2



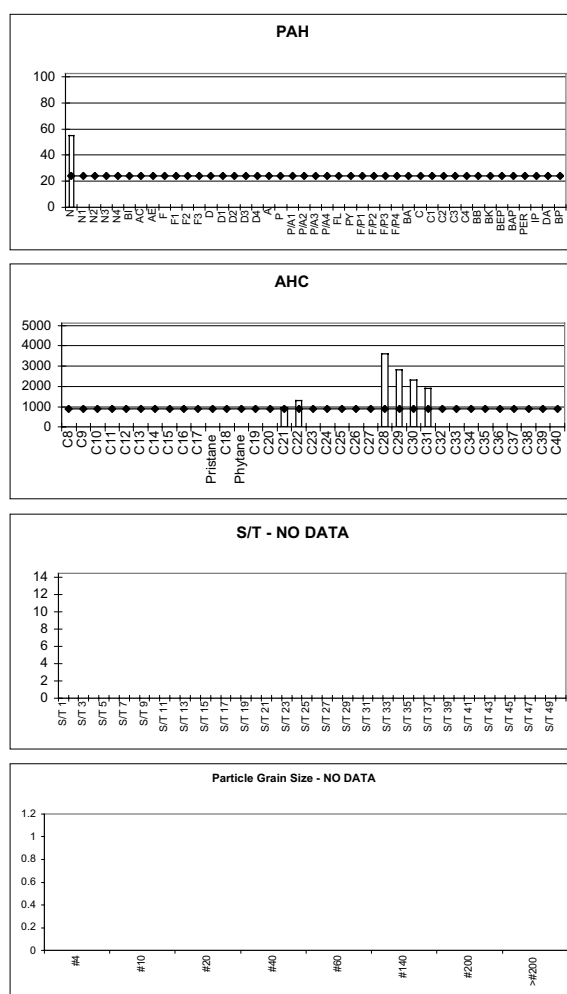
corresponding data for the same razor clam tissue compared to the PAH and AHC histograms for the sediment collected at this site. In this instance, the sediment shows traces of PAH derived from both eroding peat (naphthalene through C3 naphthalene plus phenanthrene) and particulate coal fragments (the alkylated phenanthrene/anthracene and fluoranthene/pyrene homologues). The perylene observed in sediment could have been derived from either eroding peat or particulate coal. As noted earlier at several other sites where coal is noted in the sediments, razor clam tissues do not contain any of the higher molecular weight PAH derived from the coal fragments, and the naphthalene is believed to be due to digestion of eroded peat. The aliphatic profile for the tissue does not provide any real clue as to the source; however, it is clear this tissue sample is not contaminated by petroleum hydrocarbons.

5) Redoubt Creek

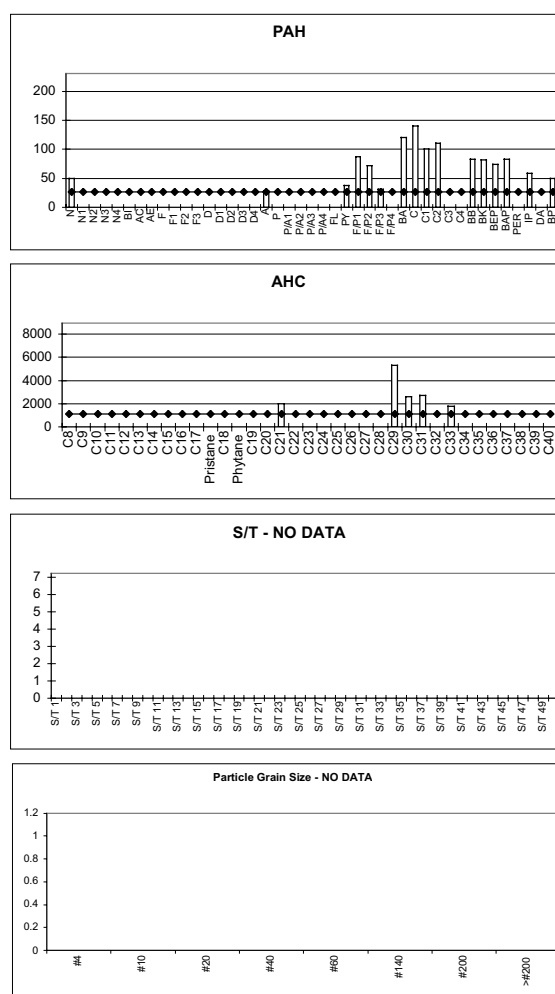
Figure 3-99 presents the PAH and AHC histogram plots for the *Mytilus* and *M. balthica* tissue samples collected at Redoubt Creek. Both samples show evidence of naphthalene uptake due to eroding peat, and several higher molecular weight n-alkanes (n-C 29 through n-C 31) that are consistent with ingestion of eroding peat fragments. The *M. balthica* sample also shows evidence of moderate concentrations of PAH derived from combustion products to yield a TPAH concentration of 1,300 ppb, the highest observed

Figure 3-99. Chemistry profiles for mussel (*Mytilus trossulus*) and *Macoma balthica* tissue samples collected from Redoubt Creek.

Redoubt Creek mussel



Redoubt Creek *Macoma balthica*



in any of the tissue samples analyzed during the Reconnaissance Program. Interestingly, neither of these profiles looks anything like the sediment samples that contained only perylene in both replicates (at 5-8 ppb) and C2-naphthalenes at 3 ppb in replicate 2, and a trace of n-C 19 at 160 ppb in replicate 1. No evidence of petroleum hydrocarbon contamination was observed in either tissue sample.

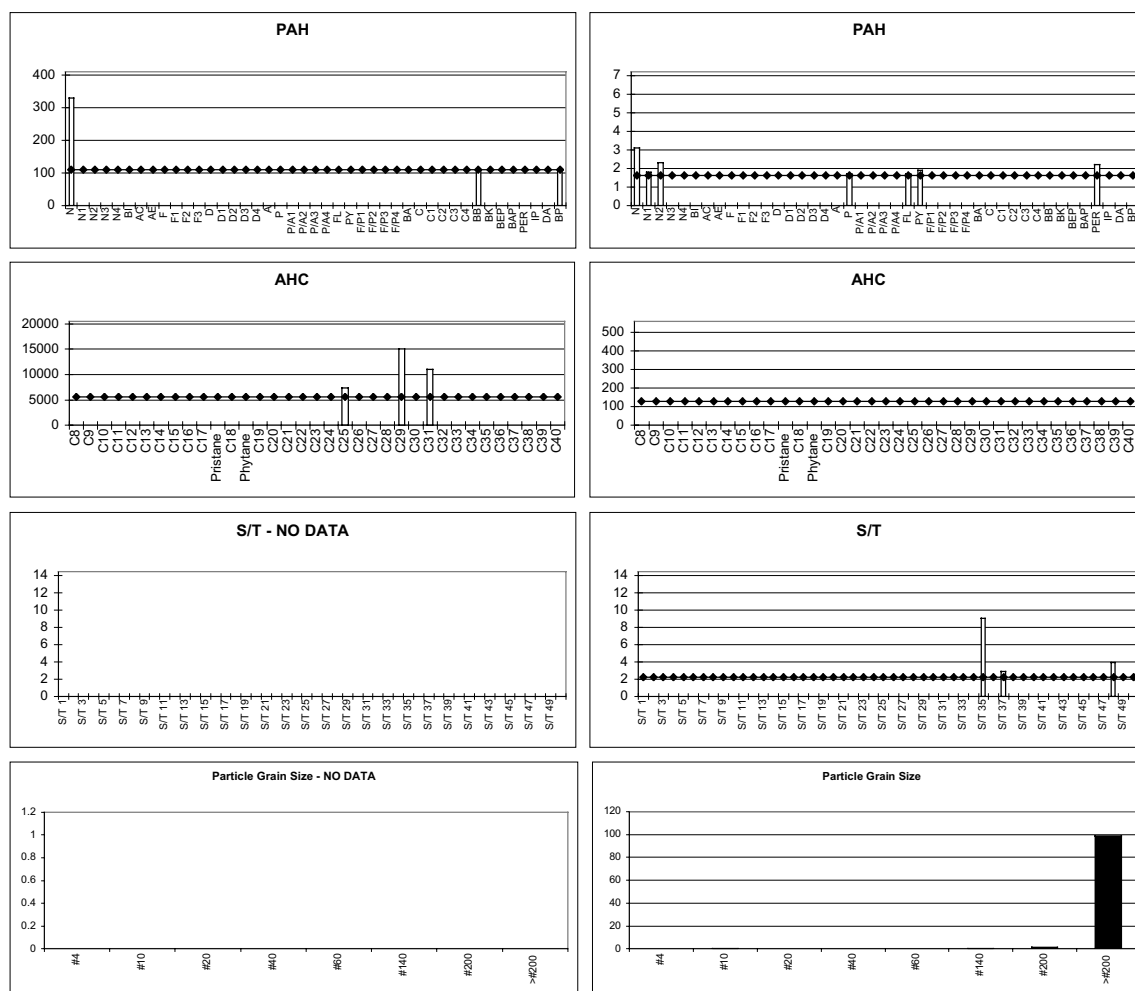
6) West Foreland South

Figure 3-100 presents the chemistry PAH and AHC histogram plots for the *M. balthica* tissue sample and the sediment collected from West Foreland South. The tissue contains the highest concentrations of naphthalene observed in any of the samples examined in

Figure 3-100. Chemistry profiles for *Macoma balthica* tissues and sediment collected from West Foreland South.

West Foreland South *Macoma balthica*

West Foreland South sediment Rep. 1



this program. In addition, concentrations of benzo(b)fluoranthene and benzo(g,h,i)perylene are at the GC/MS method-detection-limit level. As discussed previously we believe that the naphthalene is derived from digestion of eroding peat particles, while the latter two higher-molecular-weight PAH are presumably soot particles that were ingested by the organisms. The AHC profile does not allow identification of the source, although, n-C 29 and n-C 31 are consistent with the higher molecular weight PAH present in eroding peat. The sediment sample at this site shows evidence of PAH derived from eroding peat plus traces of fluoranthene and pyrene,

which are probably combustion products. Interestingly, the FID/GC profile for this tissue sample had the same biogenic cluster of components that were observed between retention times 16 and 22 minutes in all four tissue samples collected from Oldmans Bay, Kalgin Island. These FID/GC data are discussed further in the following section; however, the identity of these biogenic compounds remains unknown and does not correspond with any of the constituents identified by GC/MS. Evidence of any petroleum hydrocarbon contamination was not detected in either the tissue or sediment samples from the station.

7) Nikolai Creek

Figure 3-101 presents the chemistry PAH and AHC histogram plots for the *M. balthica* tissue sample and the sediment collected from Nikolai Creek. The tissue sample shows the presence of naphthalene, which we believe it is derived from digestion of eroding peat fragments plus the obvious pattern of higher-molecular-weight PAH from ingested combustion products. The AHC profile for the tissues shows too few peaks to allow identification of a source; however, the n-C 29 and n-C 30 are consistent with ingestion of eroding peat fragments. The sediment profile clearly shows the characteristic PAH pattern observed from eroding peat, plus fluoranthene and pyrene (also indicative of combustion products). Interestingly, the PAH measured in the sediments are not detected at even trace concentrations in the tissues of the *M. balthica* living within the sediments. No signals of petroleum hydrocarbon contamination were measured in either the tissue or sediment samples from this site.

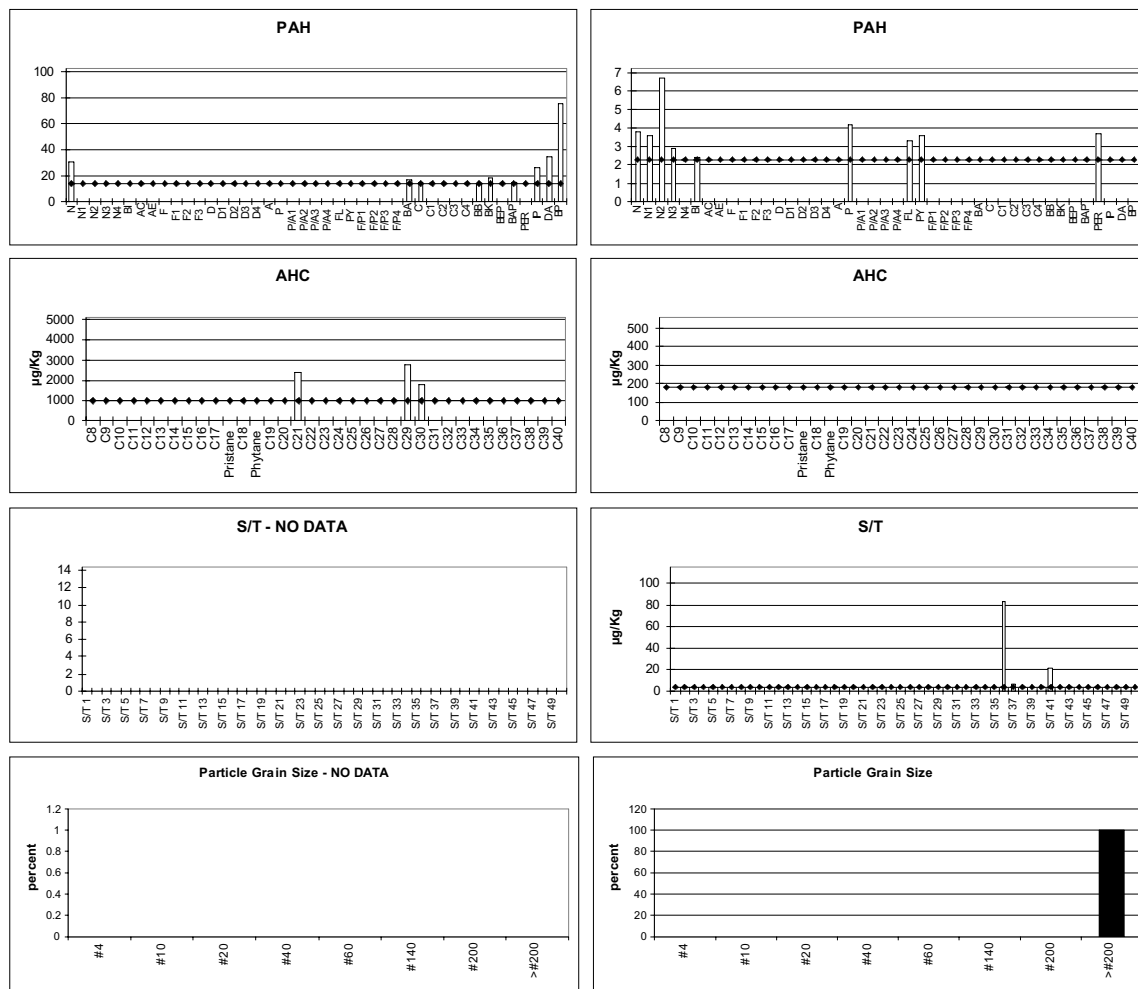
5. FID/GC Pattern Analyses and Additional Comments on Biogenic Component Source Identifications and Geographic Distributions

As discussed in previous section, the GC/MS results for the tissue samples confirmed that no uptake of solid-phase PAH from any coal particulates and only limited uptake of naphthalene had occurred. This constituent may have come from partial dissolution and subsequent bioaccumulation of this sparingly water-soluble PAH from ingested peat fragments. Naphthalene was the only compound detected with any regularity in the tissues, and many samples had no PAH detected at MDLs ranging from 8-32 ppb. No evidence of petroleum hydrocarbon contamination from crude oils or refined products was observed.

Figure 3-101. Chemistry profiles for *Macoma balthica* tissues and sediment collected from Nikolai Creek.

Nikolai *Macoma balthica*

Nikolai sediment Rep. 1



The only organisms that showed evidence of any PAH (primarily trace-level combustion products) other than naphthalene were mussels from Clam Gulch, and *M. balthica* from Bishop Creek, Redoubt Creek, West Foreland South, and Nikolai Creek. These sites were located on both sides of Cook Inlet and no geographic pattern could be established.

Given the extremely clean nature of the tissue samples, and the fact that in general only one or at most a few detection-level PAH components were identified by GC/MS, it was difficult to discern patterns that would allow grouping the samples by species or location. The FID/GC analyses, on the other hand, did allow differentiation of samples by station locations and region (East vs. West shorelines). Those findings and the chromatograms that support them are discussed below.

a) FID/GC Source Characterization

Figures 3-102 and 3-103 presents the flame ionization detector gas chromatographic profiles for Cook Inlet and Alaska North Slope (ANS) crude oils, respectively. Both chromatograms are represented by an evenly repeating series of n-alkanes from n-C 8 through n-C 36. This characteristic picket fence pattern is typical of most fresh crude oils, and can easily be recognized in sediment and tissue samples contaminated with fresh crude oil. Weathering will dramatically alter this pattern, however, so some care must be used when attempting to detect petroleum hydrocarbon contamination in sediments and tissues using FID/GC data alone. Evaporation processes can eliminate n-alkanes below n-C 12-14 after several weeks (Payne et al. 1984), and microbial degradation of the individual n-alkanes can alter the profile leaving only branched and cyclic constituents (represented by an unresolved complex mixture, UCM) in a matter of only a few months during the spring and summer seasons. Microbial degradation is significantly retarded during the colder winter months, and remnants of this pattern can generally be easily identified in sediments containing oil spilled in the late summer or fall until at least the following spring.

An additional confounding feature of the FID/GC profiles of the oils shown in Figures 3-102 and 3-103 is that aside from some relative abundance differences for the lower molecular weight n-alkanes in the n-C 10 through n-C 17 range, the profiles are very similar. With evaporation weathering and microbial degradation these differences become even subtler, and it is impossible to differentiate between weathered residues of Cook Inlet and ANS crude oil by FID/GC alone. In this regard it is necessary to use selected ion monitoring GC/MS to quantify the relative abundance of several of the more recalcitrant PAH constituents remaining in the samples. As discussed above, significant differences in the ratios of alkylated dibenzothiophenes and alkylated phenanthrene/anthracene detected by SIM GC/MS can be used to differentiate weathered crude oil sources.

Figure 3-102 Flame ionization detector gas chromatographic profile of Cook Inlet crude oil reference sample.*

* 10 mg/10 mL post injection volume (PIV). S and IS represent surrogate and internal standards, respectively.

Figure 3-103. Flame ionization detector gas chromatographic profile of Alaska North Slope crude oil reference sample.*

* 10 mg/10 mL PIV. S and IS represent surrogate and internal standards, respectively.

b) Coal Characterization

The ability to differentiate among coal sources observed with the GC/MS results is lost with the less compound-specific FID/GC analyses. Figures 3-104 through 3-106 present the flame ionization detector gas chromatographic profiles obtained on samples of coal from Beluga River SW. Samples included 4-6 in. chunks of coal picked up off the beach (identified as Beluga Point chunks), coal chipped out of exposed seams in wave cut outcrops on the beach north of North Foreland (identified as Beluga Point seams), and sand-sized coal particles deposited on sand ripples in the upper intertidal zone at Beluga River SW (identified as Beluga Point fines). The samples could be differentiated by GC/MS; however, in this case the FID/GC profiles from the three different coals were essentially identical.

Figure 3-107 presents the FID GC profile obtained from the coal sample collected on the shoal north of Kalgin Island. In this case, the similarity with the Beluga River SW fines sample is striking. Overlaying these chromatographic profiles on a light table shows they are essentially congruent. This observation would be in line with the source of particulate coal on the North Shoals being coal transported from the Beluga River/North Foreland area as suggested by the GC/MS results discussed previously.

Figures 3-108 and 3-109 present FID/GC profiles from coal collected from Clam Gulch and No-name Creek, respectively. These profiles have several subtle differences from each other and the samples collected from the Beluga River SW area and the North Shoal. The coal sample from Clam Gulch has a slightly greater predominance of higher molecular weight components compared to the other coal samples, while the coal from No-name Creek is skewed towards a slightly greater relative abundance of lower-molecular-weight constituents. While these differences are extremely subtle and probably only of academic interest, the significant finding from the FID/GC analyses is that the coal signature is very distinct and can be readily differentiated from petroleum hydrocarbon fingerprints. As a result, significant contamination from either source should be readily identifiable if present above the MDLs obtained for the sediment and tissue samples analyzed in this program.

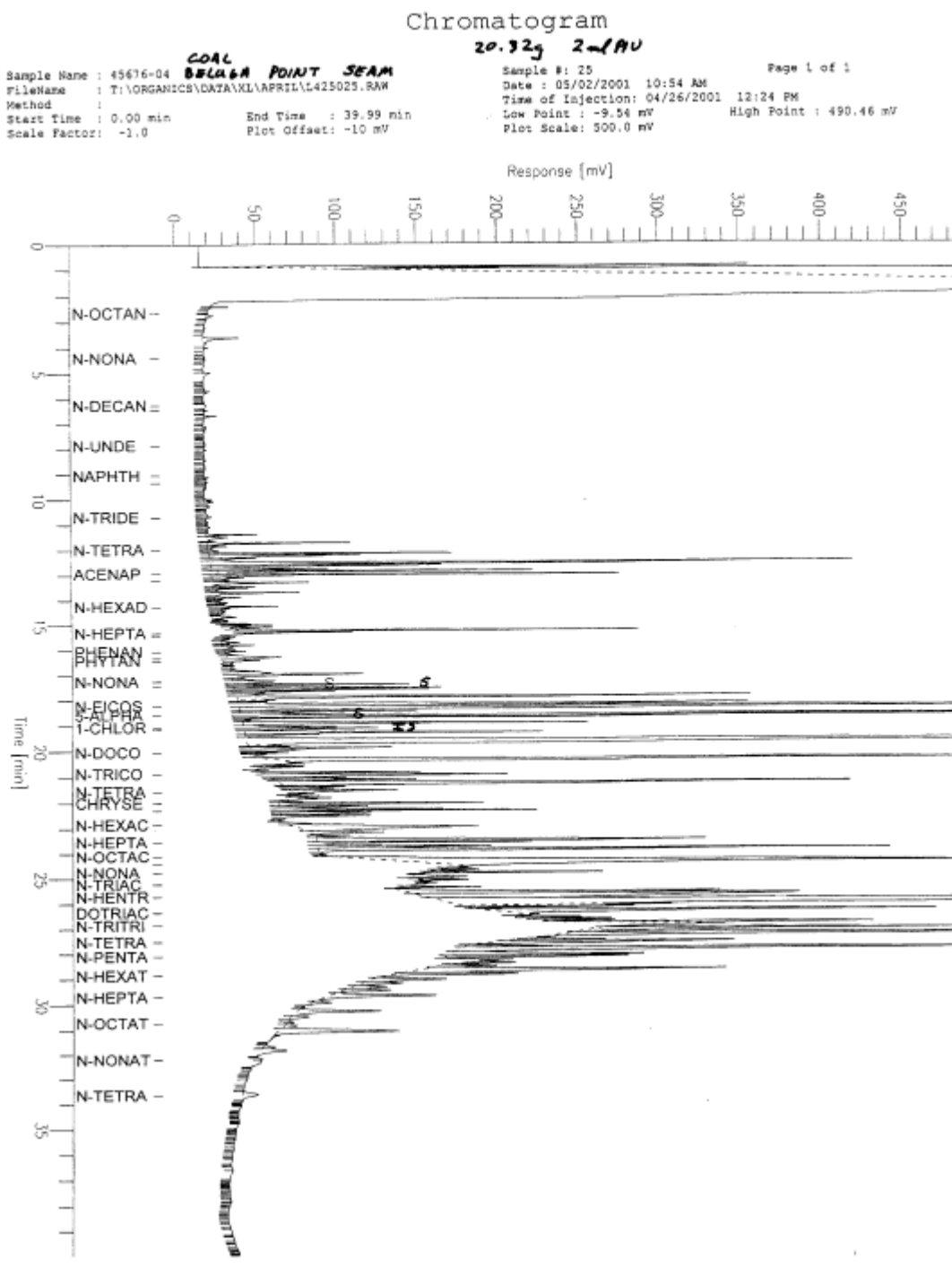
c) Eroding Peat Characterization

Figure 3-110 presents the GC profile obtained from the eroding peat sample collected near Captain Cook State Park. Once again, a distinct profile is obtained, and it is different enough from the coal signatures to easily allow identification in sediments or tissues if present at concentrations above the method specific MDL.

Figure 3-104. Flame ionization detector gas chromatographic profile of Beluga River SW "chunks" coal source reference sample.*

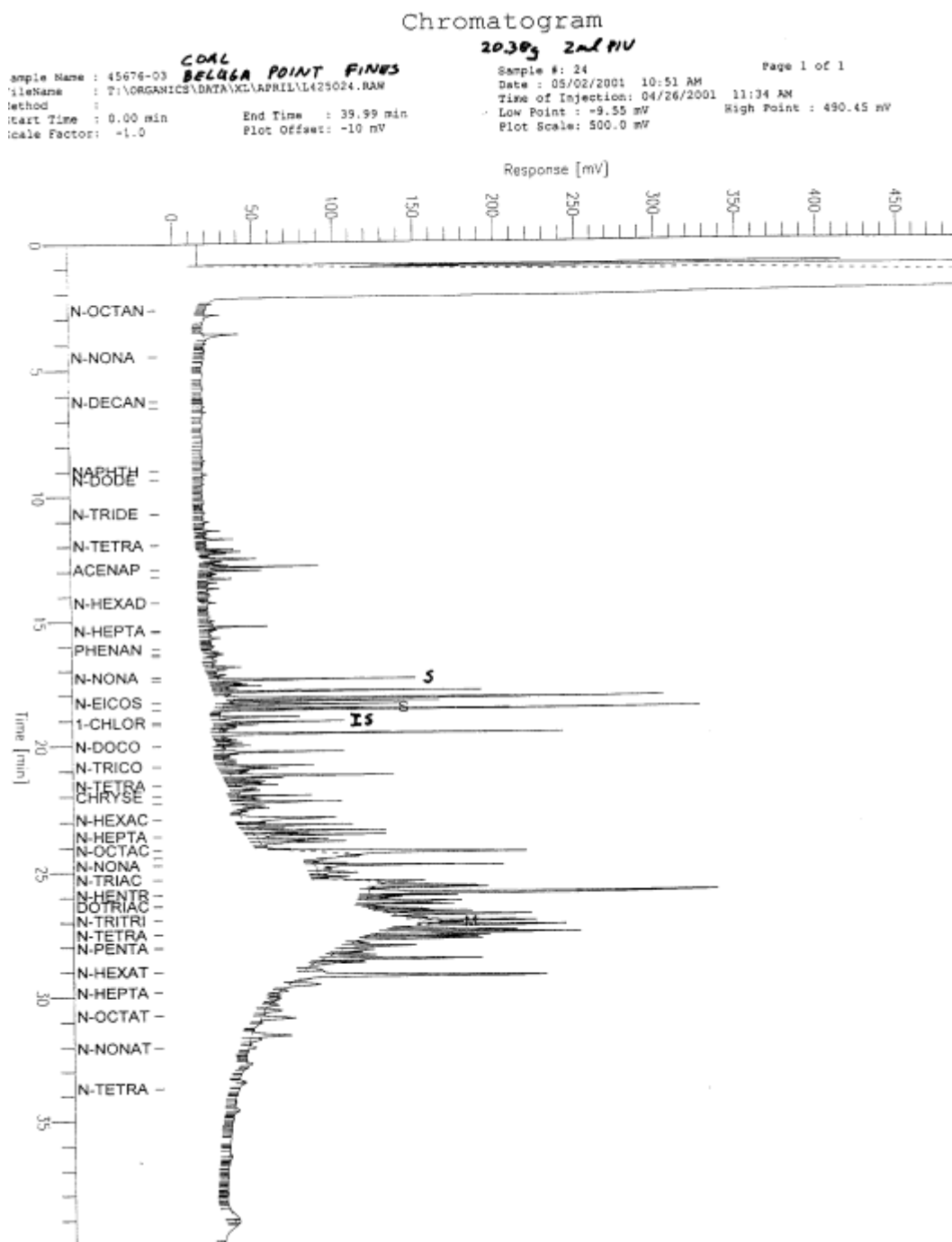
* 20.4 grams extracted/2 mL PIV. S and IS represent surrogate and internal standards, respectively.

Figure 3-105. Flame ionization detector gas chromatographic profile of North Foreland "seam" coal source reference sample.*



* 20.3 grams extracted/2 mL PIV. S and IS represent surrogate and internal standards, respectively.

Figure 3-106. Flame ionization detector gas chromatographic profile of Beluga River SW "fines" coal source reference sample.*



* 20.4 grams extracted/2 mL PIV. S and IS represent surrogate and internal standards, respectively.

Figure 3-107. Flame ionization detector gas chromatographic profile of North Shoal coal source reference sample.*

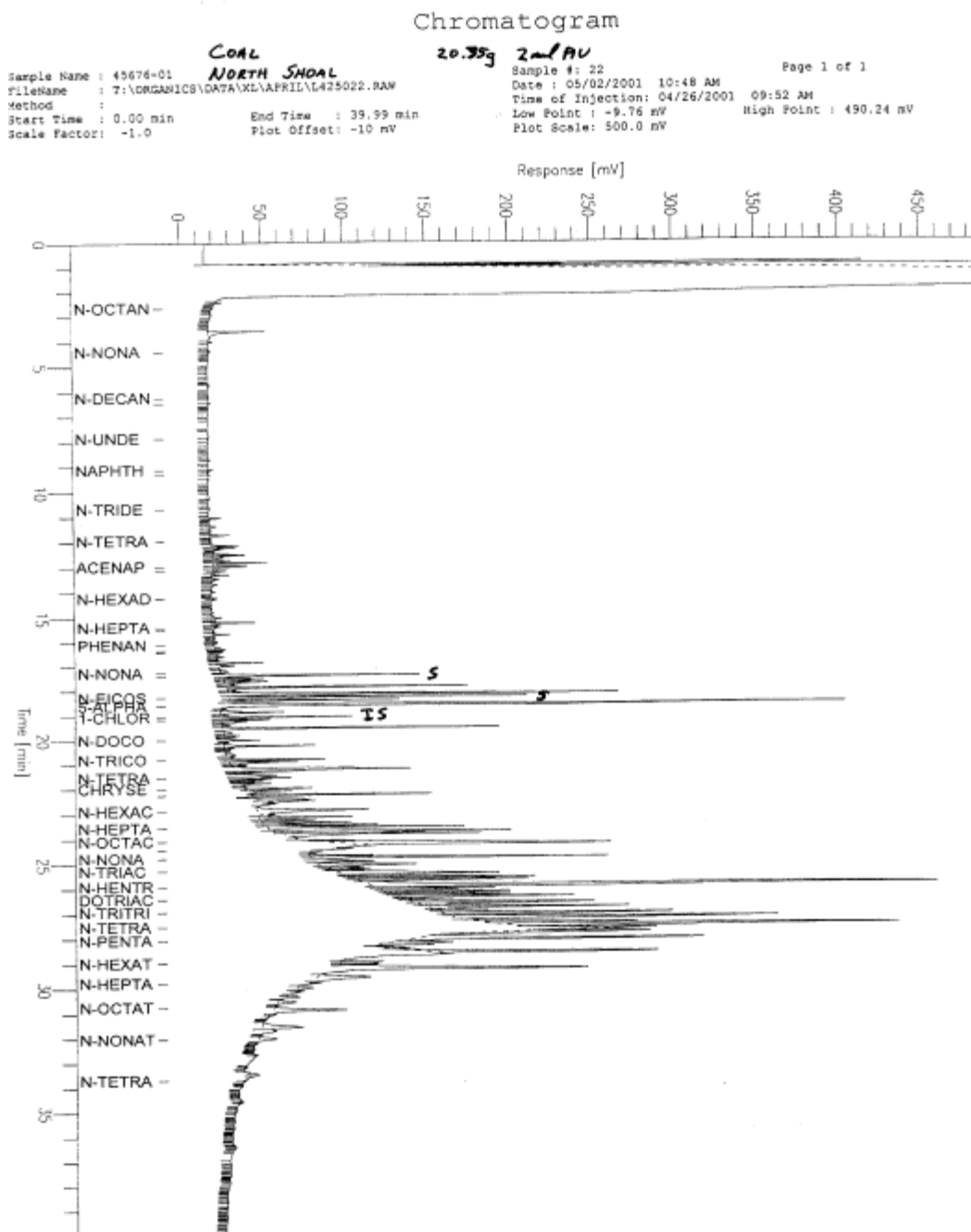
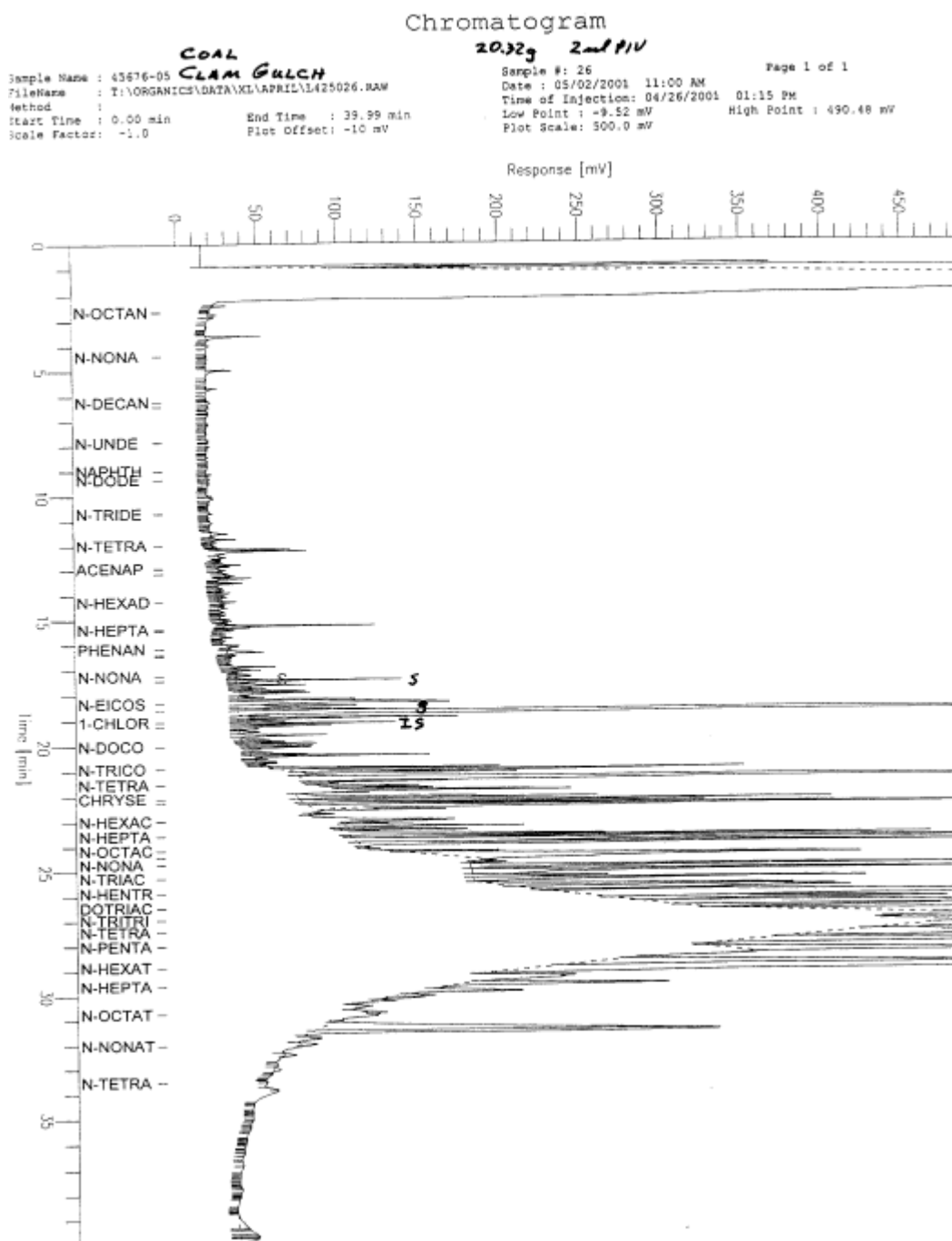
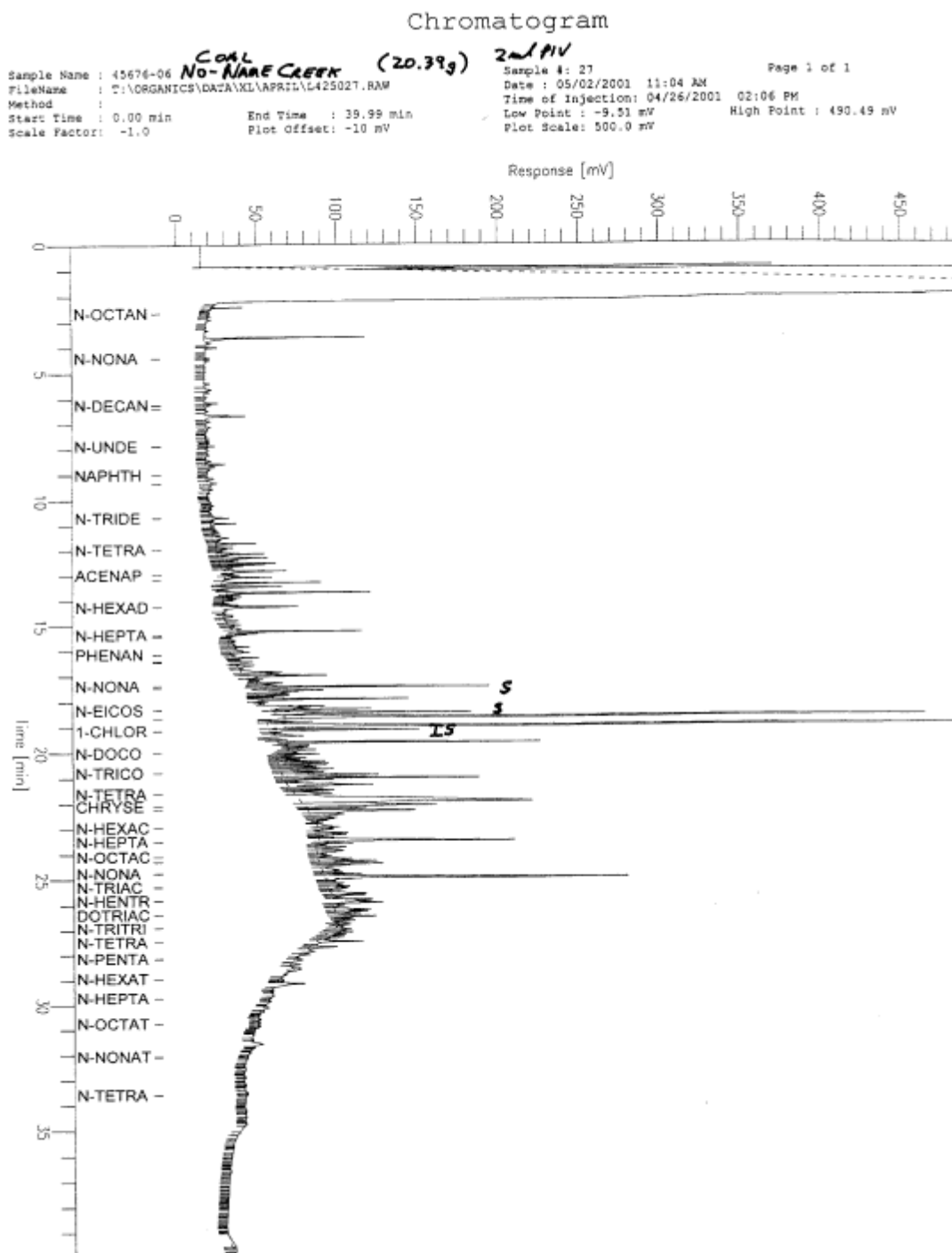


Figure 3-108. Flame ionization detector gas chromatographic profile of Clam Gulch coal source reference sample.*



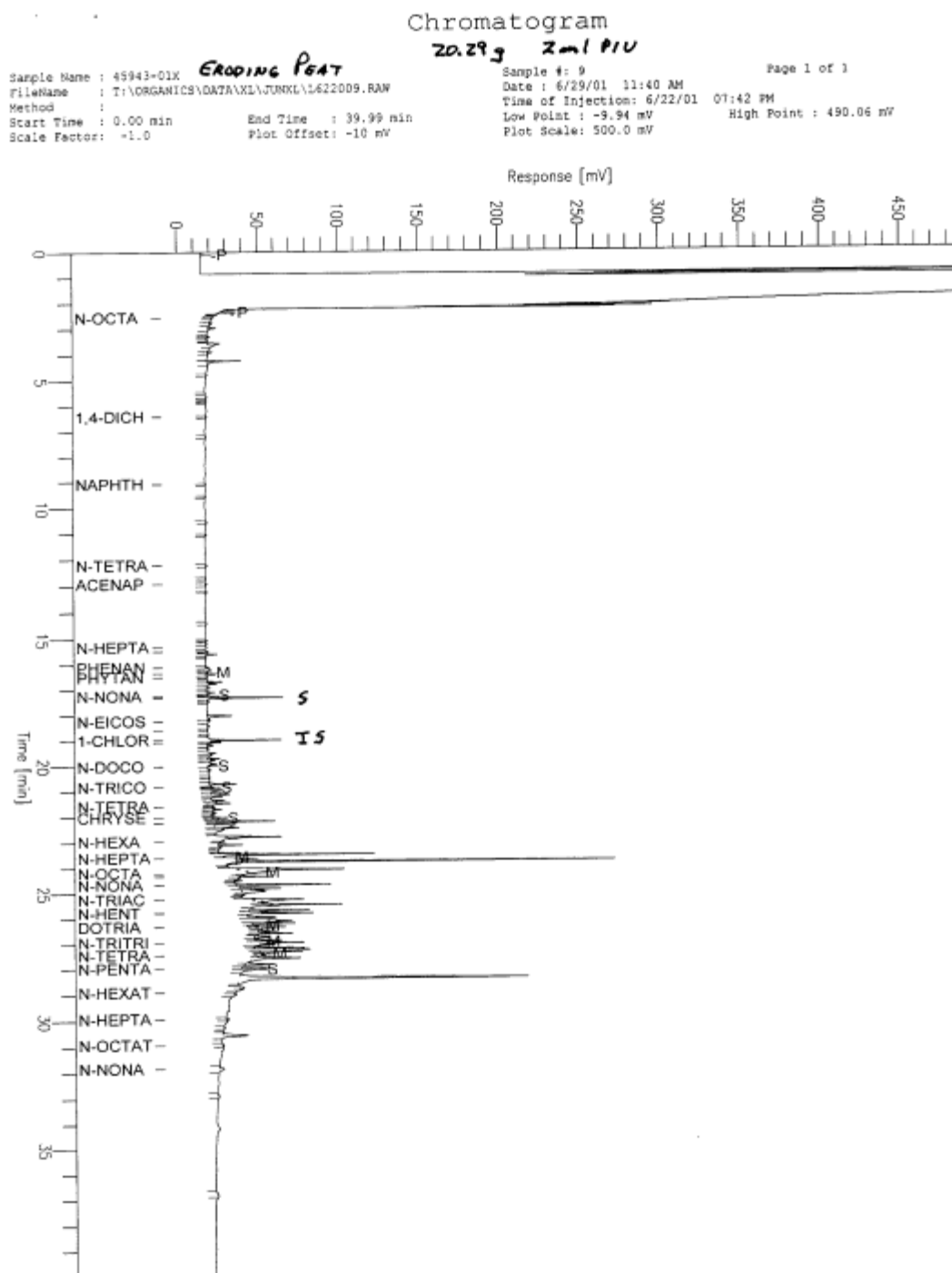
* 20.3 grams extracted/2 mL PIV. S and IS represent surrogate and internal standards, respectively.

Figure 3-109. Flame ionization detector gas chromatographic profile of No-name Creek coal source reference sample.*



* 20.4 grams extracted/2 mL PIV. S and IS represent surrogate and internal standards, respectively.

Figure 3-110. Flame ionization detector gas chromatographic profile of Captain Cook State Park eroding peat source reference sample.*



* 20.3 grams extracted/2 mL PIV. S and IS represent surrogate and internal standards, respectively.

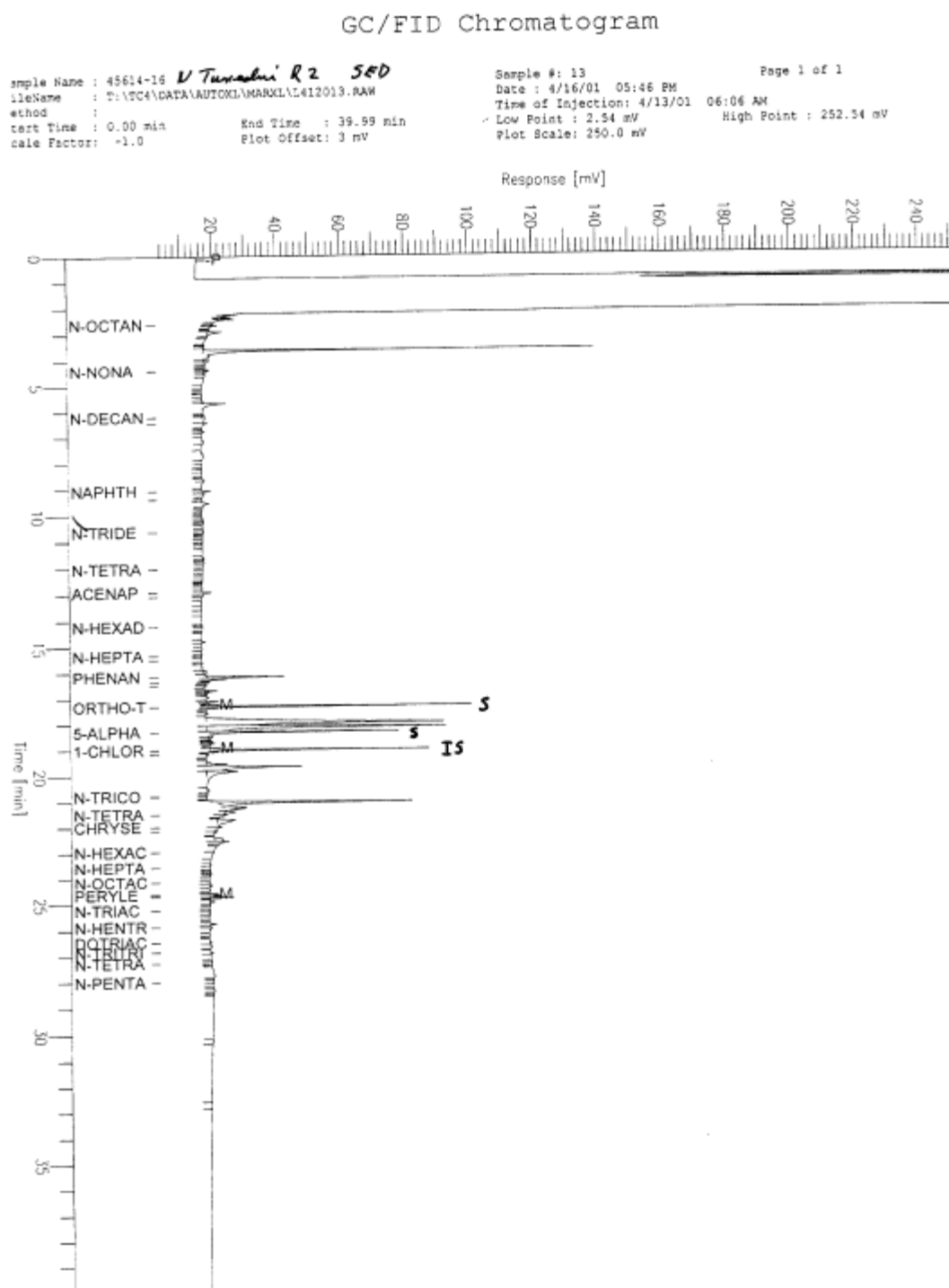
d) Sediment Analyses

The FID/GC profiles for all of the sediment samples analyzed in the Cook Inlet Reconnaissance Program were remarkably similar and extremely clean. With only a few exceptions, individual compounds in the sediment extracts were just above the method detection limit and were only identifiable by the start/stop integration marks before and after the mm-sized peaks appearing along the baseline of most of the chromatograms. Very few peaks larger than the surrogate (S) and internal standard (IS) peaks were detected in any of samples, and only by very careful computer-aided screening of the data was it possible to identify the reported n-alkanes above the baseline noise. In most cases, less than (<) values are reported for total resolved constituents (TRCs), and when they could be identified, total n-alkanes (TAlk) derived from these analyses were presented in Tables 3-9 and 3-10. When individual n-alkanes were successfully identified in the sediment samples, they were generally believed to be of biogenic origin because of an odd carbon-number predominance.

The “less than” total resolved constituent (TRC) values presented in Table 3-9 represent the individual MDLs for the 35 target analytes (n-C8 through n-C40 plus pristane and phytane). In some programs, the MDLs for total resolved constituents are calculated as the sum of the individual component MDLs. For example, if each component had an MDL of 130 ppb, then the total resolved constituents MDL would be 35 times 130 ppb, or “less than” approximately 4,550 ppb. This approach generates anomalously high values for MDLs, and in a tabular format, it leaves the incorrect impression that significant levels of non-alkane resolved components might be present, but under the total MDL. After examining all the FID/GC profiles generated in this program and determining that they were exceptionally clean, we decided to use the individual n-alkane component MDL as the value reported for the total resolved constituent MDL to reinforce the conclusion that the sediments are extremely clean.

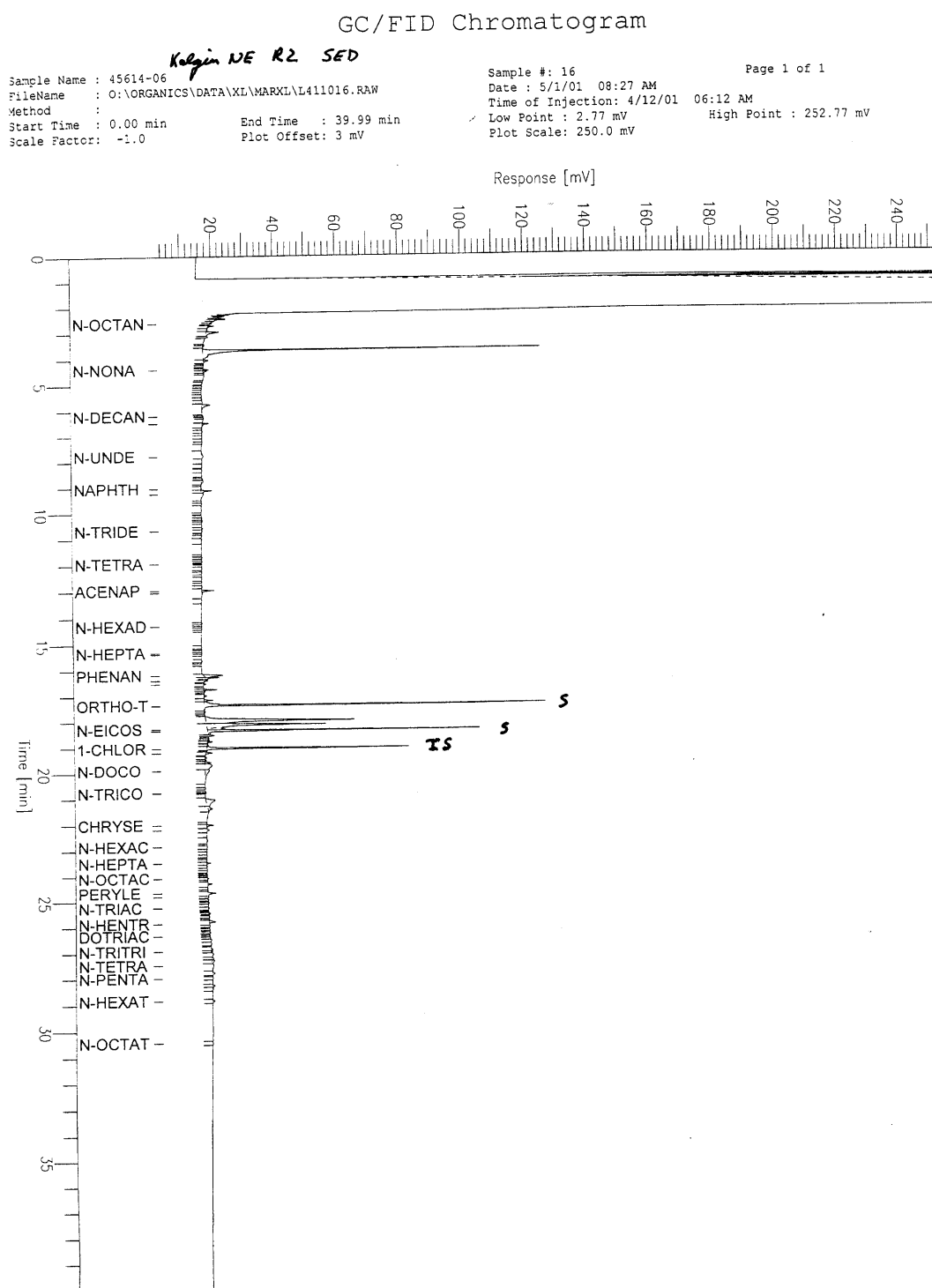
Figures 3-111 and 3-112 present the chromatographic profiles for North Tuxedni Bay and NE Kalgin sediments, respectively. These two stations had the highest total resolved constituent (TRC) values of any of the sediments examined in the program. The TRC range for North Tuxedni Bay was 17,000-18,000 ppb, and at NE Kalgin it was 4,900-5,200 ppb. The chromatograms from both stations are characterized by a doublet (two adjacent and not completely resolved peaks) at retention time ~18 minutes (between the surrogate peaks, labeled “S” in both chromatograms). In addition, the slightly dirtier sample from Tuxedni also shows one component at retention time 16 minutes (present at a higher concentration than observed in the NE Kalgin sediment) plus several poorly resolved peaks in the 19-22 minute retention time range. Only one of these peaks was

Figure 3-111. Flame ionization detector gas chromatographic profile of sediment replicate 2 from North Tuxedni Bay.*



* 20.2 grams extracted/2 mL PIV. S and IS represent surrogate and internal standards, respectively.

Figure 3-112. Flame ionization detector gas chromatographic profile of sediment replicate 2 from NE Kalgin Island.*



* 20.3 grams wet weight extracted/2 mL PIV. S and IS represent surrogate and internal standards, respectively.

identified as an n-alkane, and the rest are presumed to be of biological origin. This was the most complex FID/GC pattern of any of the sediment sites examined the program, and despite the elevated TRC values, no evidence of any petroleum hydrocarbon contamination, coal, or peat was observed in this or any of the other sediment profiles at the 120-210 ppb MDL achieved with the FID/GC method. It was only with the more sensitive selected ion monitoring GC/MS analyses that the PAH signature for peat could be identified in the sediment samples. As discussed previously, the individual component method detection limit by GC/MS was generally 2-8 ppb compared to 120-210 ppb by FID/GC.

e) Tissues

As noted above, the one part of the program where FID/GC profiles allowed segregation and grouping of samples by location was in the tissue analyses, and the TRC data presented in Table 3-10 show significantly elevated concentrations of resolvable components compared to the sediment samples collected from the same stations. TRC values ranged from <31,000 ppb in a razor clam sample from Clam Gulch to 6,100,000 ppb in a *M. balthica* sample composite from the station south of West Foreland. While no evidence of petroleum hydrocarbon contamination of any tissue samples was found, the gas chromatographic profiles identified a number of specific (but unidentified) biogenic components that allowed differentiation among the sites. The data also showed subtle differences in the uptake of these components by species and location.

1) Profiles Unique to Organisms Collected from the East Side of Cook Inlet

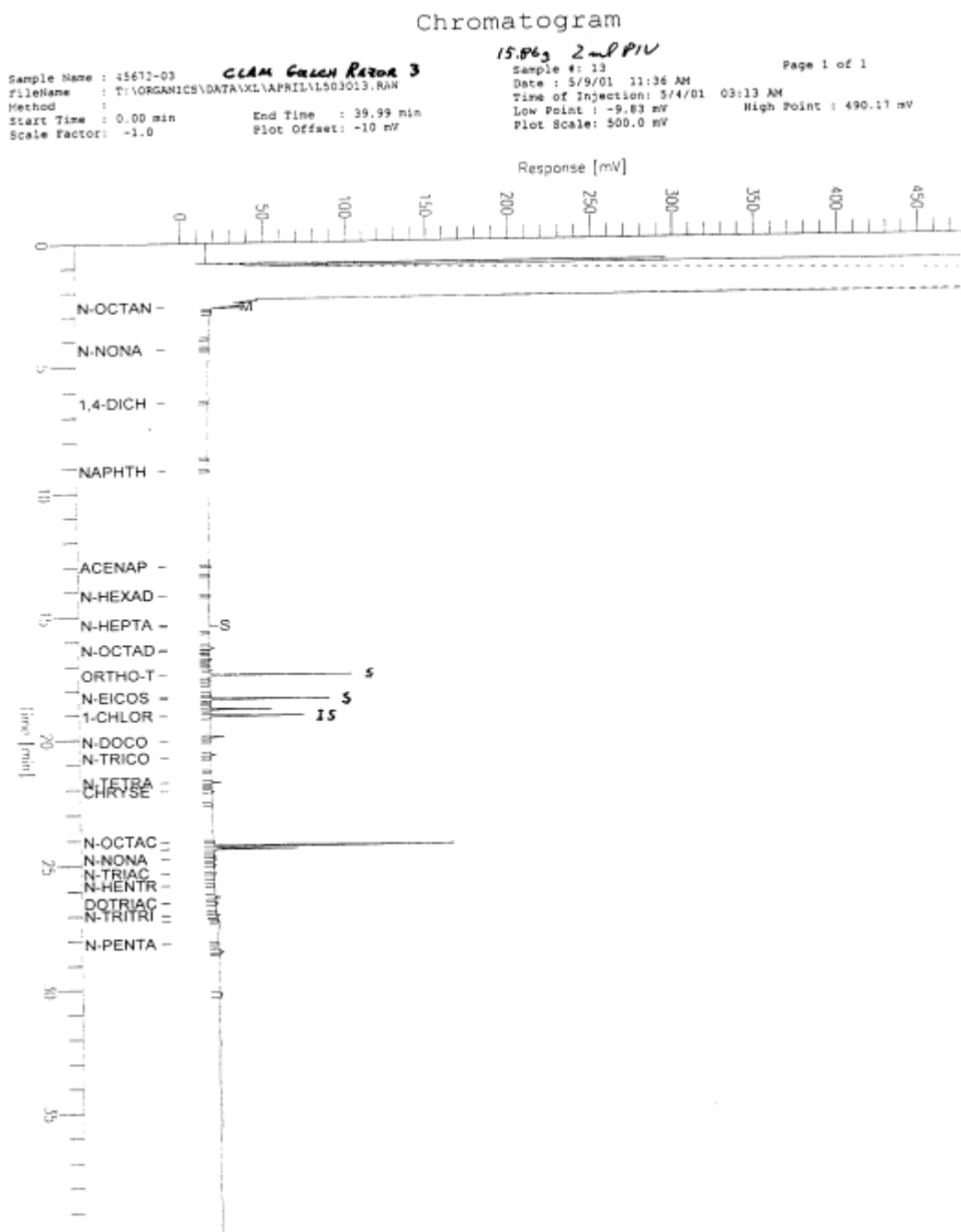
Figure 3-113 presents the gas chromatographic profile obtained on razor clam replicate three from Clam Gulch where a TRC value of 58,000 ppb was measured. Interestingly, less than 1,500 ppb was contributed by n-alkanes. The doublet noted around retention time 24 minutes was only noted in samples collected near Clam Gulch and Kalifornsky Beach. It was observed in razor clams, mussels, and *M. balthica* along this stretch of coastline, and as shown in Figure 3-114 with a TRC value of 420,000 ppb, it was generally more predominant in mussels compared to the other species. The presence of this doublet in the tissue samples from this relatively localized area presumably reflects some unique constituents in the food from this region. The fact that concentrations of this set of compounds are greater in mussels than in either razor clams or *M. balthica* suggests it is primarily associated with the type of particulate material (for example, phytoplankton) suspended in the water column. The fact that concentrations in the razor clams and *M. balthica* are lower suggests that less of this material is being ingested by these organisms, and that its uptake is more limited in those species that obtain a greater proportion of their nutrients from the sediment-water interface where sediment-associated material would be a larger part of their diet. The source of this doublet is unknown; however, based on the chromatographic evidence presented in Figures 3-108 and 3-110, it is not associated with the coal samples in the area or eroding peat.

Figure 3-115 presents the chromatographic profile obtained on the *M. balthica* sample from Bishop Beach, where a TRC value of 340,000 ppb was measured with only 50,900 ppb contributed by n-alkanes. The chromatographic profile is relatively simple with only a few additional resolved peaks observed between retention times 19-21 minutes (immediately after the internal standard, IS peak) and a later unresolved cluster between 26-27 minutes plus a single peak around 28.5 minutes. This pattern was unique to the tissues collected Bishop Beach, and the GC/MS analyses of these tissue extracts showed a variety of alkyl substituted PAH (at significantly lower MDLs) plus several combustion products. The FID/GC profiles for the sediment samples collected at this location showed no peaks at a method detection limit of 210 ppb.

2) Profiles Observed in Organisms Collected from NE and SE Kalgin Island and No-name Creek and Redoubt Creek on the West Side of Cook Inlet

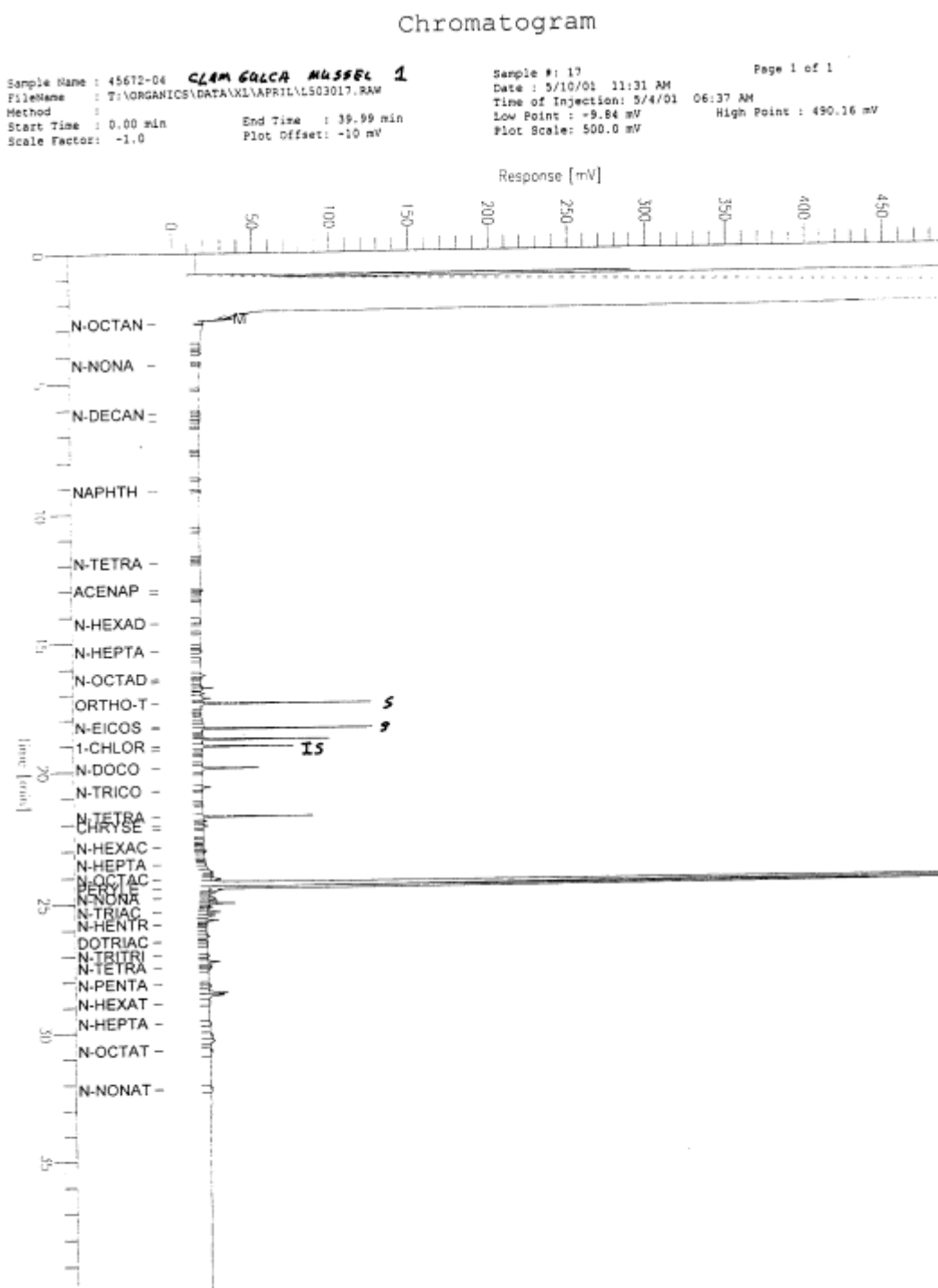
Figures 3-116 through 3-119 show the appearance of a polar (as manifest by peak tailing) and poorly resolved cluster of components between retention times 26 and 28 minutes. They were just beginning to be detected above the baseline noise in Figure 3-115 of the *M. balthica* sample from Bishop Creek, and they become more prominent in the *M. balthica* samples from NE Kalgin (Figure 3-116) reaching a maximum relative concentration in the razor clams collected from No-name Creek (Figure 3-117). This cluster of peaks is presumably due to compounds of biogenic origin because no evidence of any higher molecular weight PAH from coal, peat, or petroleum hydrocarbons was identified by GC/MS in the No-name Creek razor clam sample where these components are the most predominant. Figures 3-118 and 3-119 show evidence of one of these presumably biogenic components from this poorly resolved triplet (but not the other two) in samples of *M. balthica* and *Mytilus* from Redoubt Creek. The greater relative abundance of the unknown polar component in the *M. balthica* sample (Figure 3-78) compared to the *Mytilus* sample at this location (Figure 3-119) suggests that the source might be more closely associated with sedimentary or detrital material than suspended particulate material and associated bacteria in the water column. However, this component was not observed in either of the FID/GC analyses of the sediment samples from this station. It is also interesting to note the small doublet around retention time

Figure 3-113. Flame ionization detector gas chromatographic profile of razor clam composite replicate 3 from Clam Gulch.*



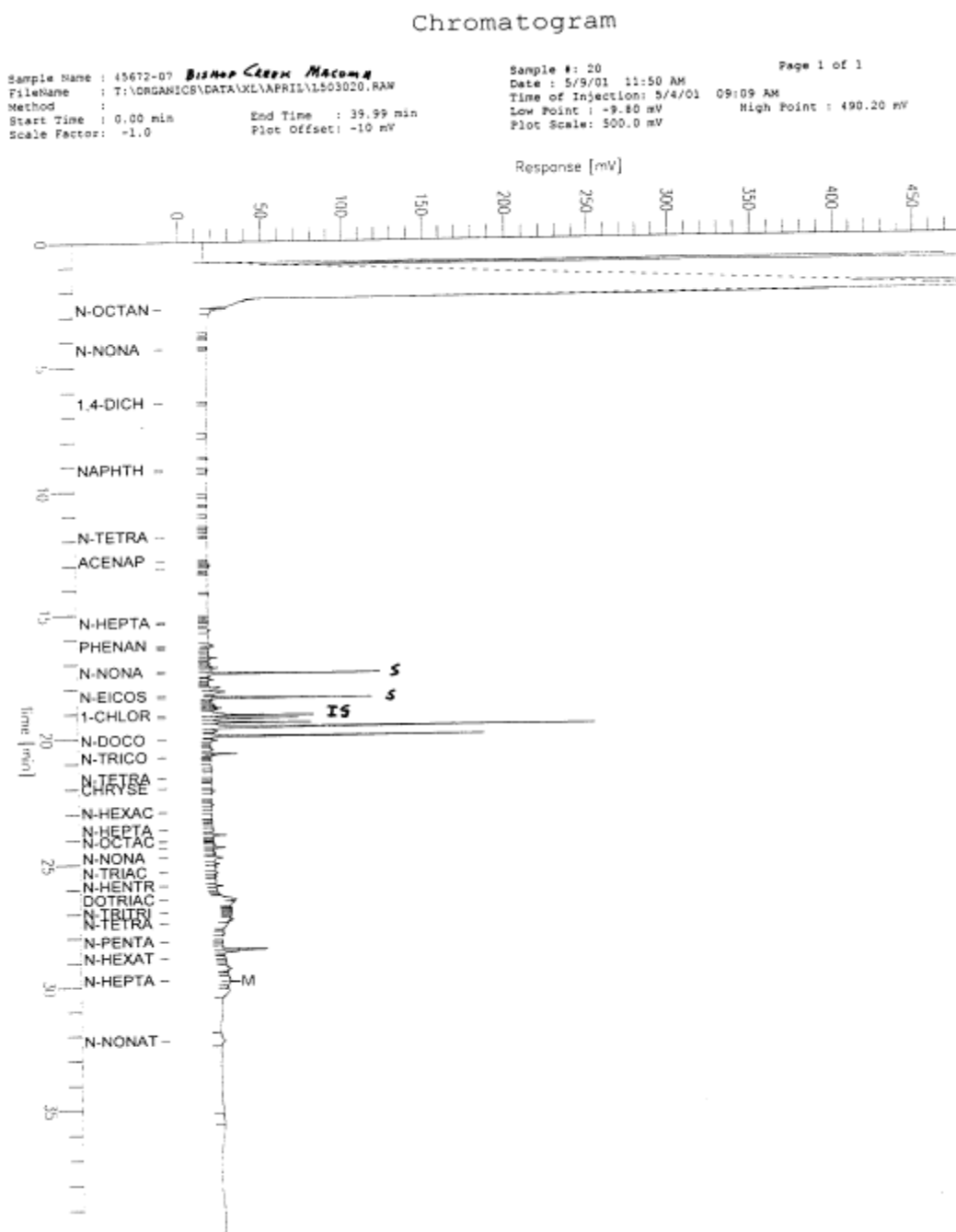
* 15.9 grams wet weight extracted/2 mL PIV. S and IS represent surrogate and internal standards, respectively.

Figure 3-114. Flame ionization detector gas chromatographic profile of mussel composite replicate 1 from Clam Gulch.*



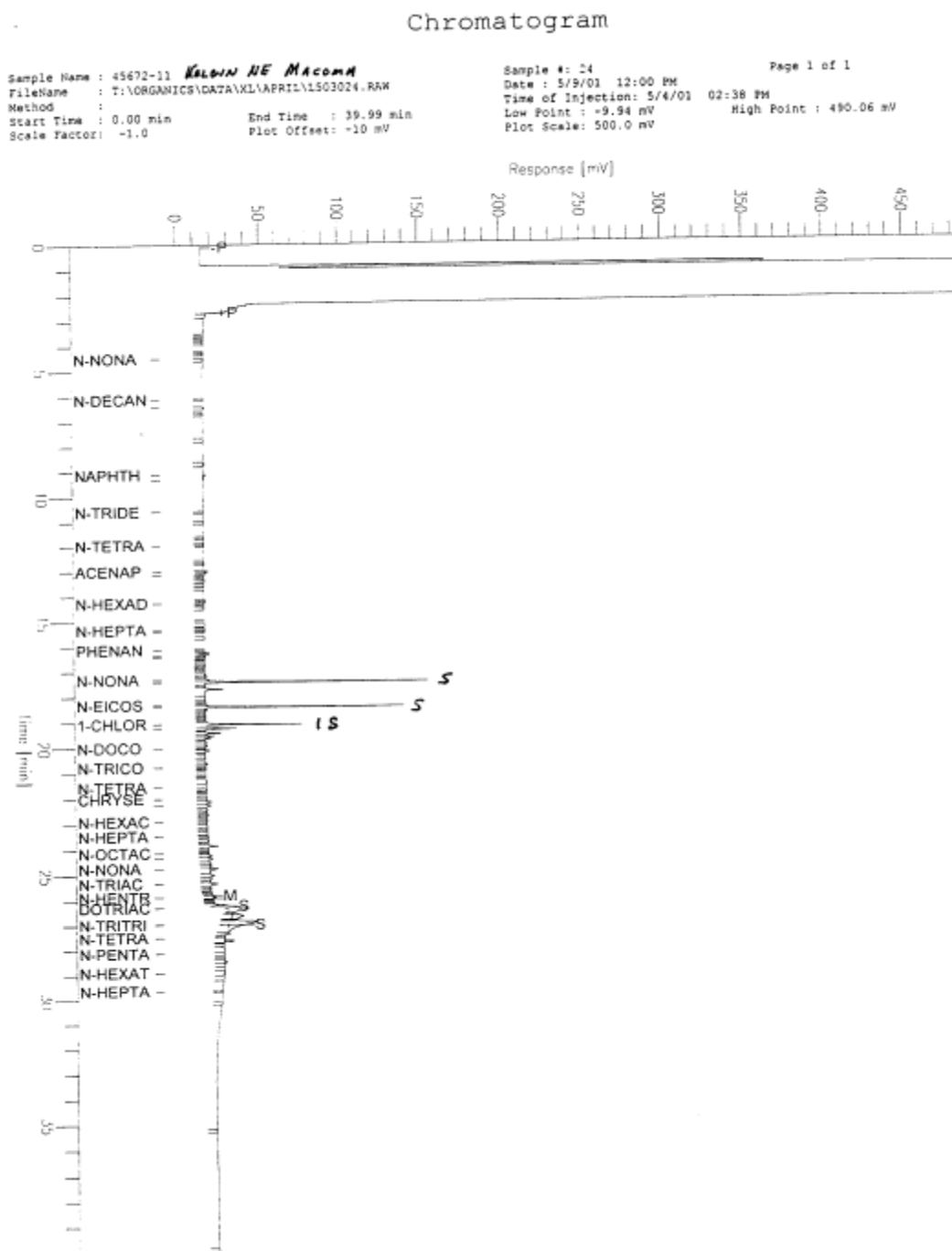
* 15.3 grams wet weight extracted/2 mL PIV. S and IS represent surrogate and internal standards, respectively.

Figure 3-115. Flame ionization detector gas chromatographic profile of *Macoma balthica* composite from Bishops Creek.*



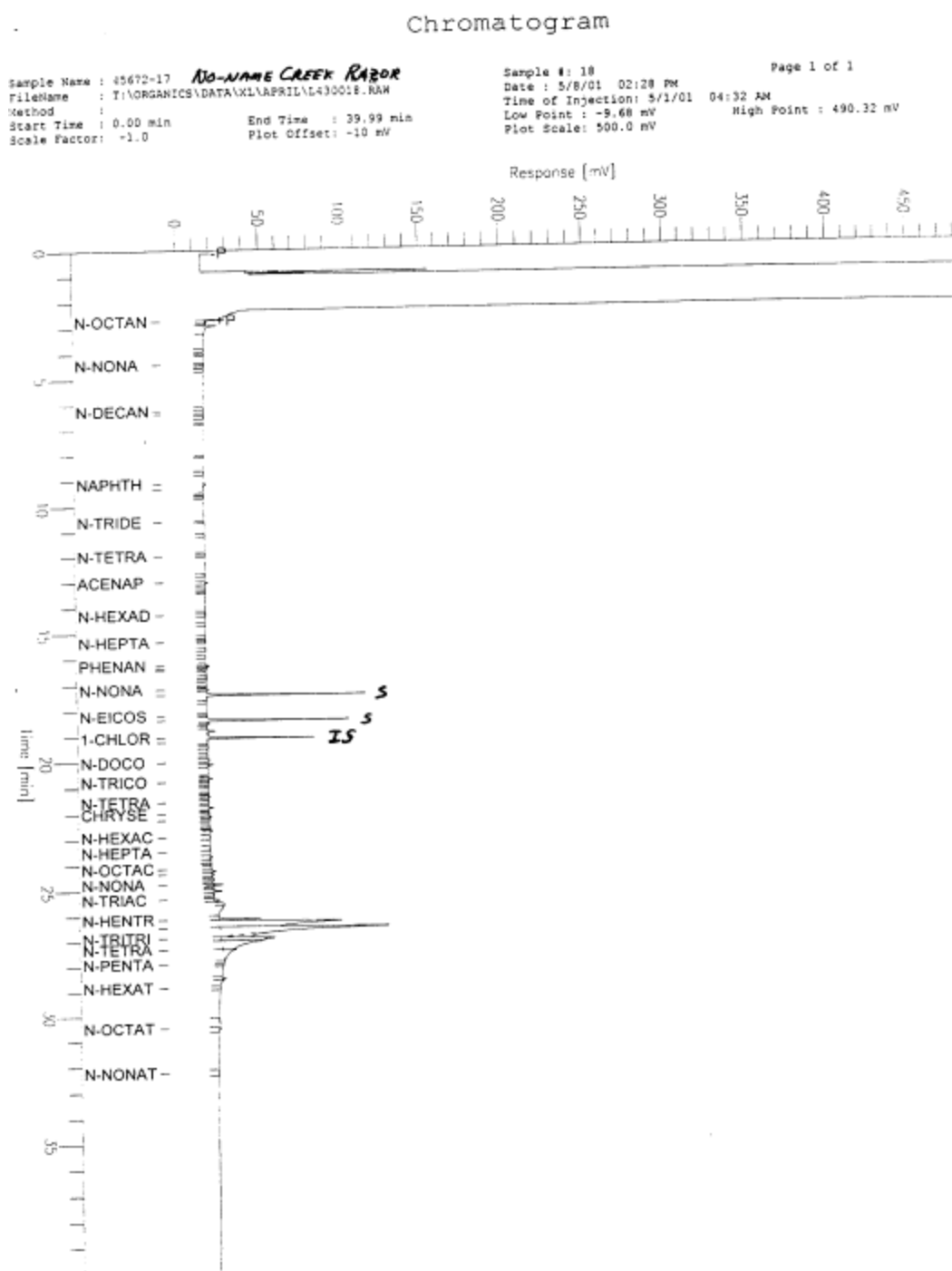
* (7.6 grams wet weight extracted/2 mL PIV. S and IS represent surrogate and internal standards, respectively.

Figure 3-116. Flame ionization detector gas chromatographic profile of *Macoma balthica* composite from NE Kalgin.*



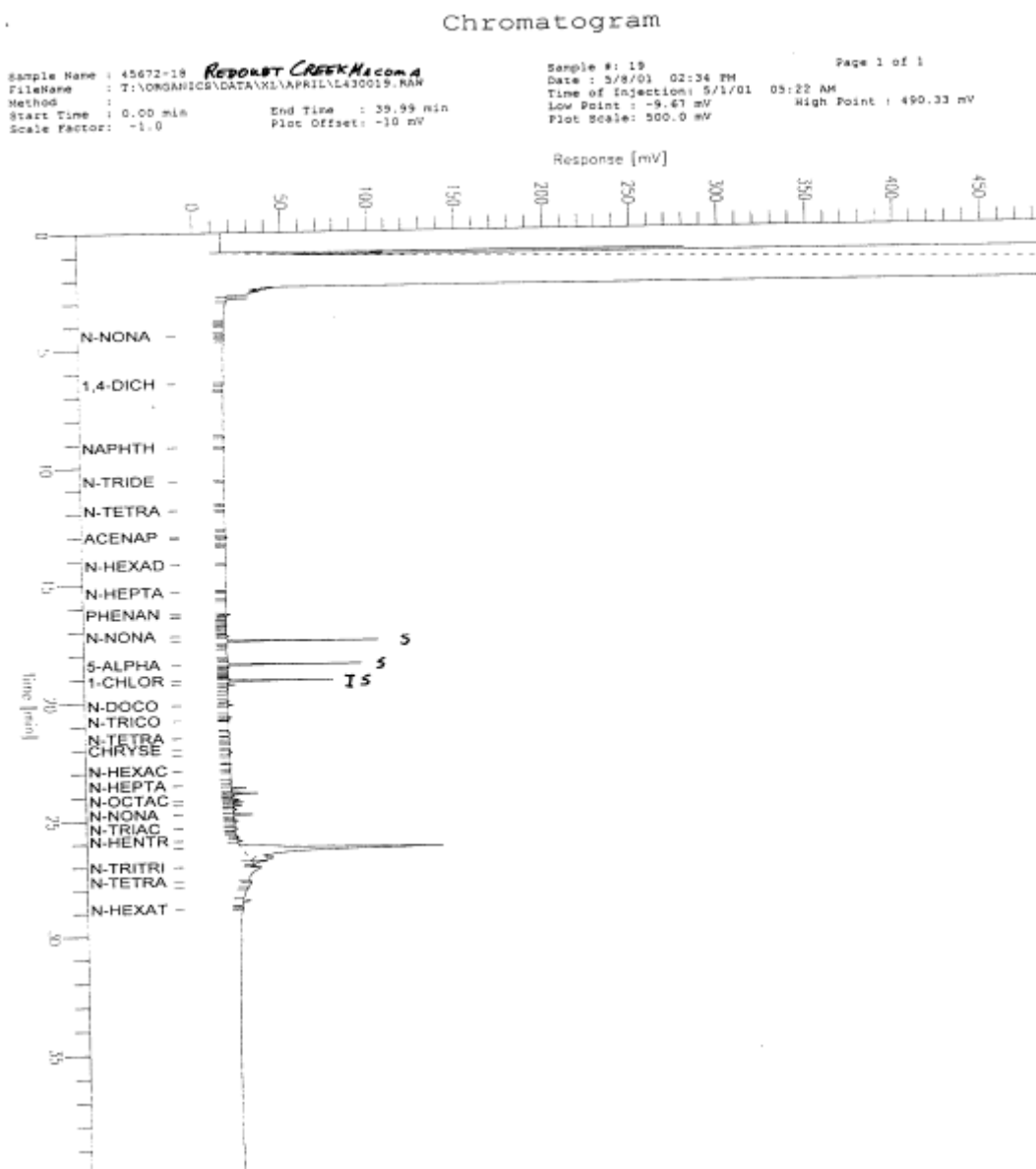
* 3.8 grams wet weight extracted/2 mL PIV. S and IS represent surrogate and internal standards, respectively.

Figure 3-117. Flame ionization detector gas chromatographic profile of razor clam composite from No-name Creek.*



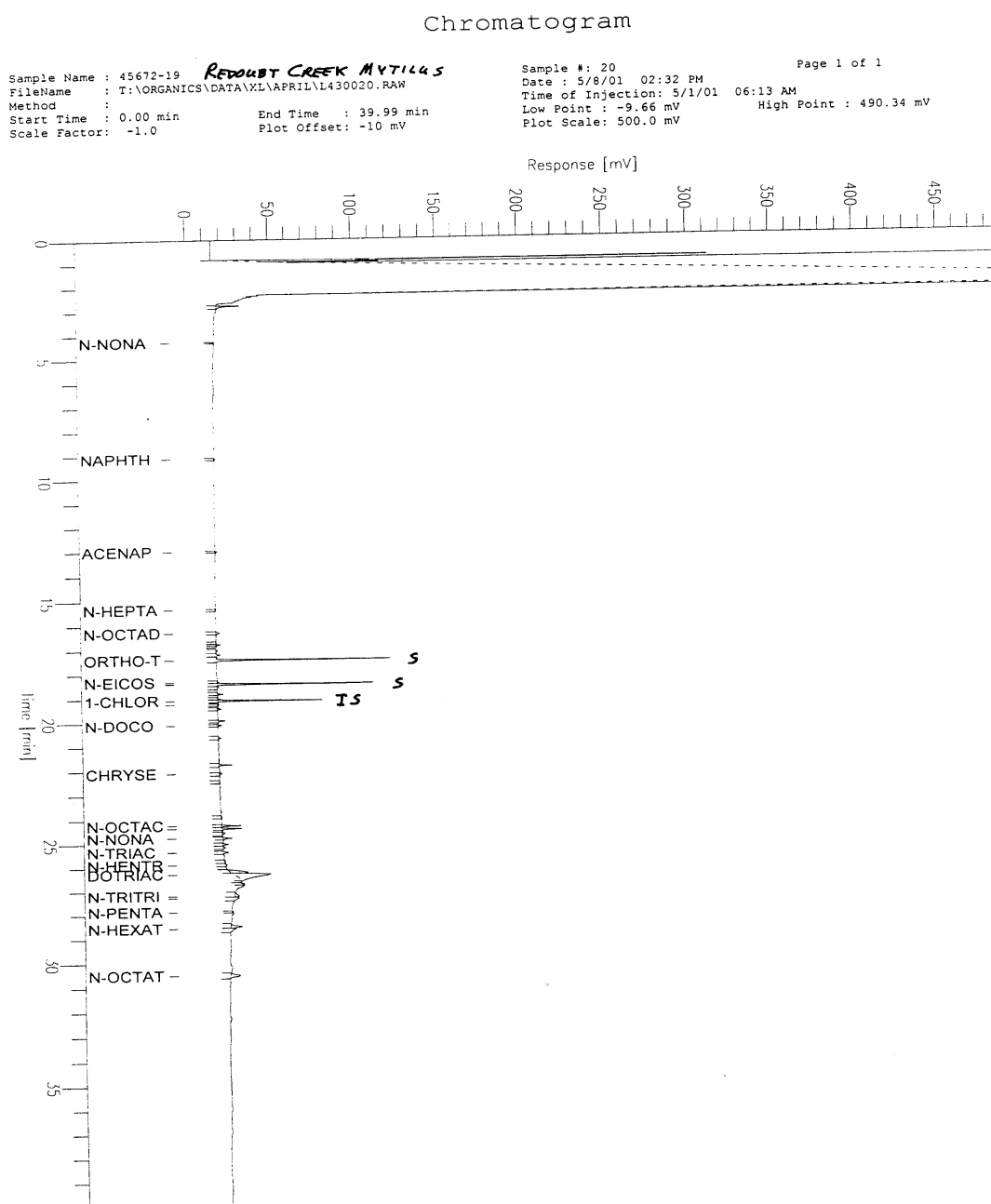
* 15.9 grams wet weight extracted/2 mL PIV. S and IS represent surrogate and internal standards, respectively.

Figure 3-118. Flame ionization detector gas chromatographic profile of *Macoma balthica* composite from Redoubt Creek.*



* 11.7 grams wet weight extracted/2 mL PIV. S and IS represent surrogate and internal standards, respectively.

Figure 3-119. Flame ionization detector gas chromatographic profile of mussel composite from Redoubt Creek.*



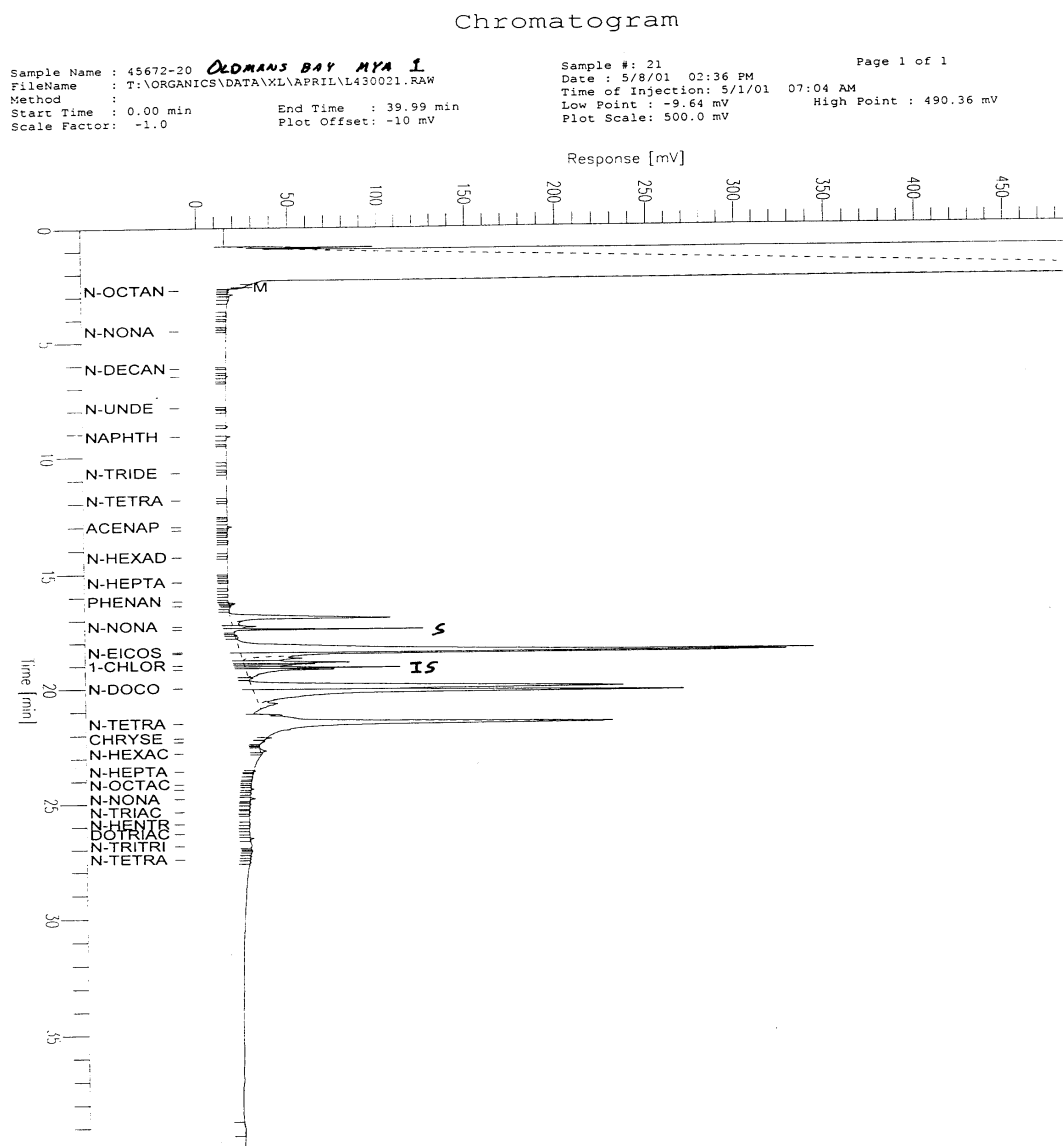
* 16.0 grams wet weight extracted/2 mL PIV. S and IS represent surrogate and internal standards, respectively.

24.7 minutes in Figure 3-119, which corresponds to the largest peaks observed in the filter feeding mussel samples from Clam Gulch (Figure 3-114). Clearly the same set of compounds subject uptake by *Mytilus* is present on both sides of the inlet, however, their concentrations are significant lower in the waters on the west side.

3) Profiles Unique to Oldmans Bay and West Foreland South

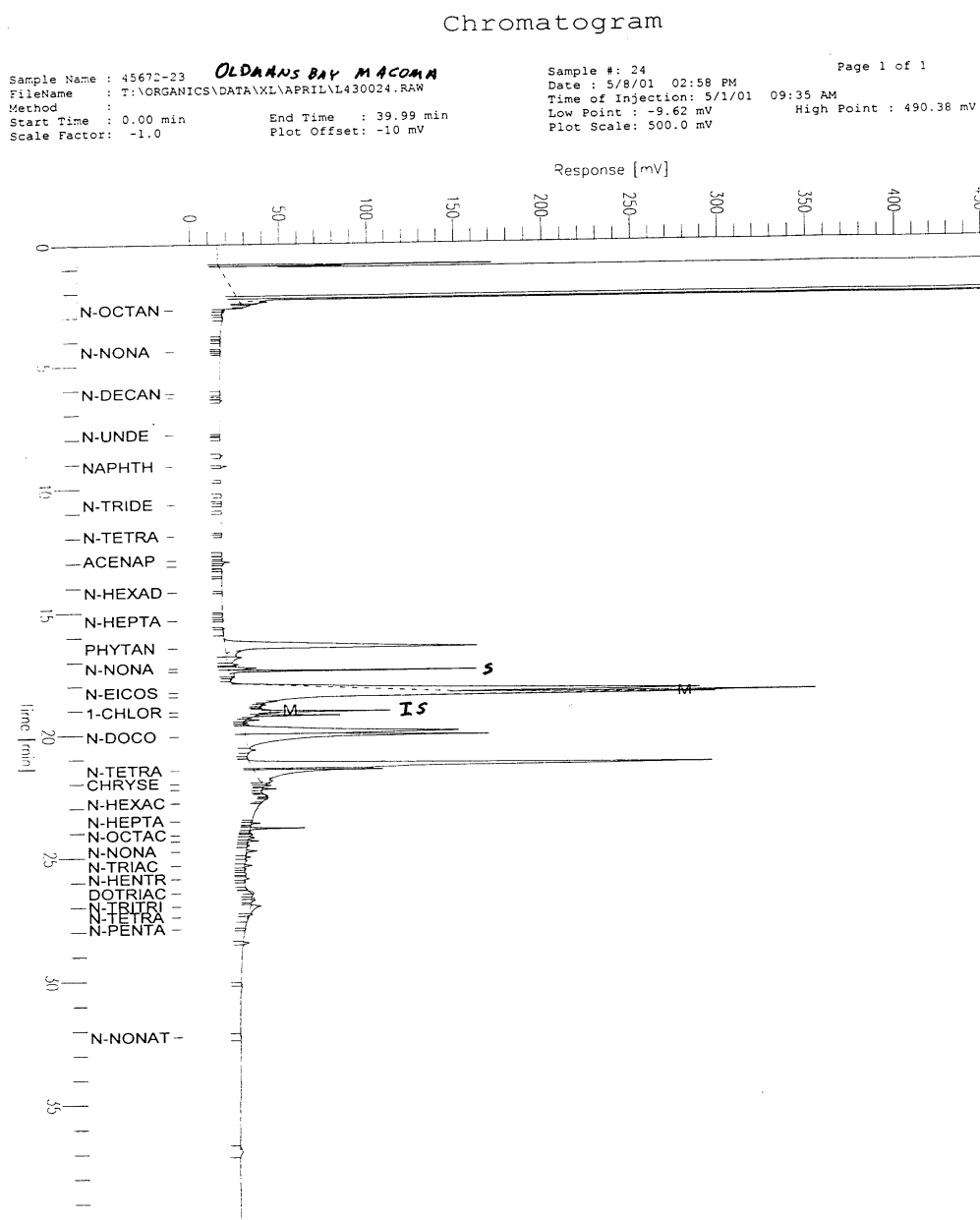
Figures 3-120 and 3-121 present the most unique FID/GC profiles obtained on any of the tissues examined during the reconnaissance program. Both of these samples were collected from Oldmans Bay on Southwest Kalgin Island; however, it should be pointed out that a nearly identical profile was also obtained from the *M. balthica* collected from the station south of the West Foreland. Presumably these peaks represent polar biogenic materials that are associated with detrital materials unique to these southwest facing and somewhat protected sites. TRC values for these sites ranged from 1,700,000 to 6,100,000 ppb. Other than naphthalene, no evidence of any polynuclear aromatic hydrocarbons was observed in the GC/MS data for the samples from Oldmans Bay; however, the sample from West Foreland South contained a huge naphthalene signal (the highest measured in any tissue sample at 330 ppb) and MDL-level concentrations of benzo(b)fluoranthene and benzo(g,h,i)perylene (see Figure 3-100). The retention times of these PAH would not correspond, however, with the biogenic components noted in the FID/GC profiles shown in Figures 3-120 and 3-121. The sediment samples from these locations generally showed no peaks by FID/GC analysis at an MDL of 120-150 ppb, with detection-limit traces of n-C 33 only observed at Oldmans Bay. The more sensitive GC/MS selected ion monitoring method identified the classic signature of eroded peat in the sediments at both locations at TPAH concentrations of 8-22 ppb. The signal from eroded peat does not readily manifest itself in the less sensitive FID/GC profiles for the Oldmans Bay tissue samples shown in Figures 3-120 and 3-121. For this reason we can conclude that the biogenic cluster of peaks observed in both the *M. arenaria* and *M. balthica* samples from Oldmans Bay and West Foreland South was not from peat. By computer-aided enhancement of the FID/GC profiles, it was possible to dig out the n-C 29 through n-C 33 n-alkane signal from eroded peat in one sample each of *M. balthica* and *M. arenaria* from Oldmans Bay. However, the signal was much less apparent in the other two replicates of *M. arenaria* from Oldmans Bay and the *M. balthica* sample from the West Foreland South.

Figure 3-120. Flame ionization detector gas chromatographic profile of *Mya arenaria* composite 1 from Oldmans Bay.*



* 11.2 grams wet weight extracted/2 mL PIV. S and IS represent surrogate and internal standards, respectively.

Figure 3-121. Flame ionization detector gas chromatographic profile of *Macoma balthica* composite from Oldmans Bay.*



* 9.4 grams wet weight extracted/2 mL PIV. S and IS represent surrogate and internal standards, respectively.