

# **REFERENCE OILS REPORT**

**Prepared for:**

**Prince William Sound Regional Citizens Advisory Council  
3709 Spenard Road  
Anchorage, Alaska 99503**

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**Prepared by:**

**Kinnetic Laboratories, Inc.  
1102 West 7<sup>th</sup> Avenue  
Anchorage, Alaska 99501**

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## 1.0 INTRODUCTION

The Prince William Sound Regional Citizens' Advisory Council (RCAC) is an independent organization that was formed in 1989 in response to the T/V *Exxon Valdez* oil spill (EVOS). The RCAC was later certified under the Federal Oil Pollution Act of 1990. Operating under a contract with Alyeska Pipeline Service Company, the RCAC acts to minimize the environmental impacts associated with the terminal and the oil transportation tanker fleet. The RCAC's mission includes the performance of research designed to help understand and evaluate environmental impacts associated with oil transportation, including baseline research conducted prior to another spill event.

The goal of the reference oils program, as required by the contract, was to compare chemical analyses of sediment samples performed at the National Marine Fisheries' Auke Bay Laboratory (ABL) with similar analyses performed by Texas A&M's Geochemical and Environmental Research Group (GERG) to supplement data and interpretation provided by these two laboratories in support of the RCAC's Long-Term Environmental Monitoring Program (LTEMP). LTEMP, which was first implemented in 1993, was designed to provide long-term baseline measurements of hydrocarbon levels and sources in sediments and indigenous blue mussels at program sites within the areas of Prince William Sound (PWS) and the Gulf of Alaska represented by the RCAC. The objective of the Reference Oil Project was to provide additional information on the background signatures previously seen during the LTEMP by investigating relative sources of hydrocarbons in the sediments rather than comparing absolute concentrations of those hydrocarbons between samples or laboratories.

This report describes the results of chemical analyses performed on portions of sediment samples collected in 2000 by ABL personnel for a separate project entitled "Evaluation of Yakataga Oil Seeps as Regional Background Hydrocarbon Sources in Benthic Sediments of the Exxon Valdez Spill Area". This project, referred to herein as the Yakataga Project, was funded by the EVOS Trustees to be performed by the National Oceanographic and Atmospheric Association (NOAA), the U.S. Geological Survey (USGS), and Payne Environmental Consultants. For the Reference Oils Project, samples collected for the Yakataga Project were analyzed independently by ABL and GERG. Descriptive and limited data analysis here is performed as called for by the contract in light of the draft manuscript entitled "A Direct Assessment of Hydrocarbon Contributions from Native Coals and from Seep Oils to Marine Sediments of the Northern Gulf of Alaska" (Short, personal communication, 2005). Of the four sample analyzed by both laboratories for the Reference Oils Project, only two were reported in the manuscript by Short (2005).

## 2.0 BACKGROUND

There has been much discussion in the literature regarding the sources of petrogenic hydrocarbon signatures seen in benthic sediments in PWS and Gulf of Alaska (GOA). Background hydrocarbon signatures have been described by various authors over time as originating from California-sourced petroleum that was in use in the area prior to the development of the Cook Inlet and North Slope oil fields; oil seeps, particularly in the near Katalla and in the Yakataga Forelands region; native coal sources found in the region; and, more recently, organic-rich shale deposits that lie under the Malaspina Glacier. Page *et al.* (1995) initially proposed terrestrial seeps as a significant contributor to PAHs in nearshore coastal sediments in GOA. Subsequent work by Page *et al.* in 1997 indicated that oil contributions from these seep sources was considerable. Short *et al.* (1999) questioned this theory, proposing that coal eroding from terrestrial environments was a more likely source due to the lack of PAH weathering that had been shown in the benthic sediments. Short had collected samples from the

Bering River Coal Field (BRCF) to support this conclusion. This potential coal source was questioned by Boehm *et al.* (2000), because ratios of PAH, certain biomarkers, and TOC were substantially lower in the coal samples as reported by Short than those found in benthic GOA sediments.

Work by other researchers using multivariate analyses to help determine relative contributions from various prospective sources in the area was undertaken by Boehm *et al.* in 2001. They concluded that seep oils were still a relatively large contributor compared to potential coal inputs as defined by Short *et al.* in 1999; however, Boehm and his co-authors also identified the dominant source as eroding Tertiary shales potentially located beneath the Malaspina Glacier. Their model included only the BRCF coal sample analysis to help assess the potential coal contributions and at least implied that all the potential hydrocarbon sources in the region had been characterized and were taken into account by the model. This approach was criticized by others (e.g., Van Kooten *et al.*, 2002), whose work included Kulthieth Formation coal as a potential source for background hydrocarbons. According to this study, Kulthieth coal was found to be more oil-prone and more likely to have contributed to background hydrocarbons in GOA sediments. This coal source was shown to have hydrocarbon signatures more closely resembling the Yakataga Forelands oil seep signatures than did the BRCF samples. Mudge (2002) used partial least squares analysis of PAH and biomarkers to further assess the relative contributions of seep oil, coals, shales, and two riverine inputs to the hydrocarbon loading in the GOA. This study concluded that mixed sources with varying relative contributions are present in the study area. Short and Heinz (2002) further investigated these issues and determined that in order to fully understand the potential sources of hydrocarbons in the study area, aliphatic hydrocarbons, particularly the UCM profiles, needed to be included in any diagnostic models. In particular, degradation of seep oils would be evident in the UCM component, the analysis or importance of which prior models had omitted or downplayed. They concluded that the characteristic UCM profile of marine sediments in the GOA was similar to eroding coals or shales in the area. They also concluded that if aliphatics analyses had been included in Boehm's and Mudge's prior source allocation models, seep oils would likely have been eliminated as a significant hydrocarbon source in the area.

The Yakataga Project included PAH and aliphatics analysis as well as that of selected biomarkers (Short, 2005). Environmental samples included benthic sediments as well as riverine and seep samples. Separation of the coal material for analysis allowed more intense examination of the possibility of coal as a potentially dominant contributor to hydrocarbon loads in the GOA. In summary, the project concluded that Yakataga seep oils were responsible for only a very small portion (termed "negligible") of the hydrocarbon load in the GOA sediments, and coal was also responsible for only a small portion (up to 6 % of the total PAHs and 2 % of the total n-alkanes) in the samples. The study concluded that while the major source of the hydrocarbons has still not been definitively identified, benthic sediment geochemistry results and documented oceanographic sediment transport mechanisms along the GOA shoreline indicate that the drainage system of the Malaspina Glacier is responsible for introducing hydrocarbons into the GOA. This substantiates Boehm's earlier claim that organic-rich Tertiary shales from the Malaspina Glacier area is the most likely major hydrocarbon contributor in the region.

### 3.0 METHODS

Station location information and sampling methodology for the Yakataga Project, as well as analytical methodology as performed at ABL, is reported in the manuscript (Short, 2005). While the Reference Oils Project contract implied that LTEMP methodologies would be followed for sample collection, sample collection was performed by ABL and other personnel following Yakataga Project protocols, as described in the manuscript. No methodology comparison is included here. The samples used for the

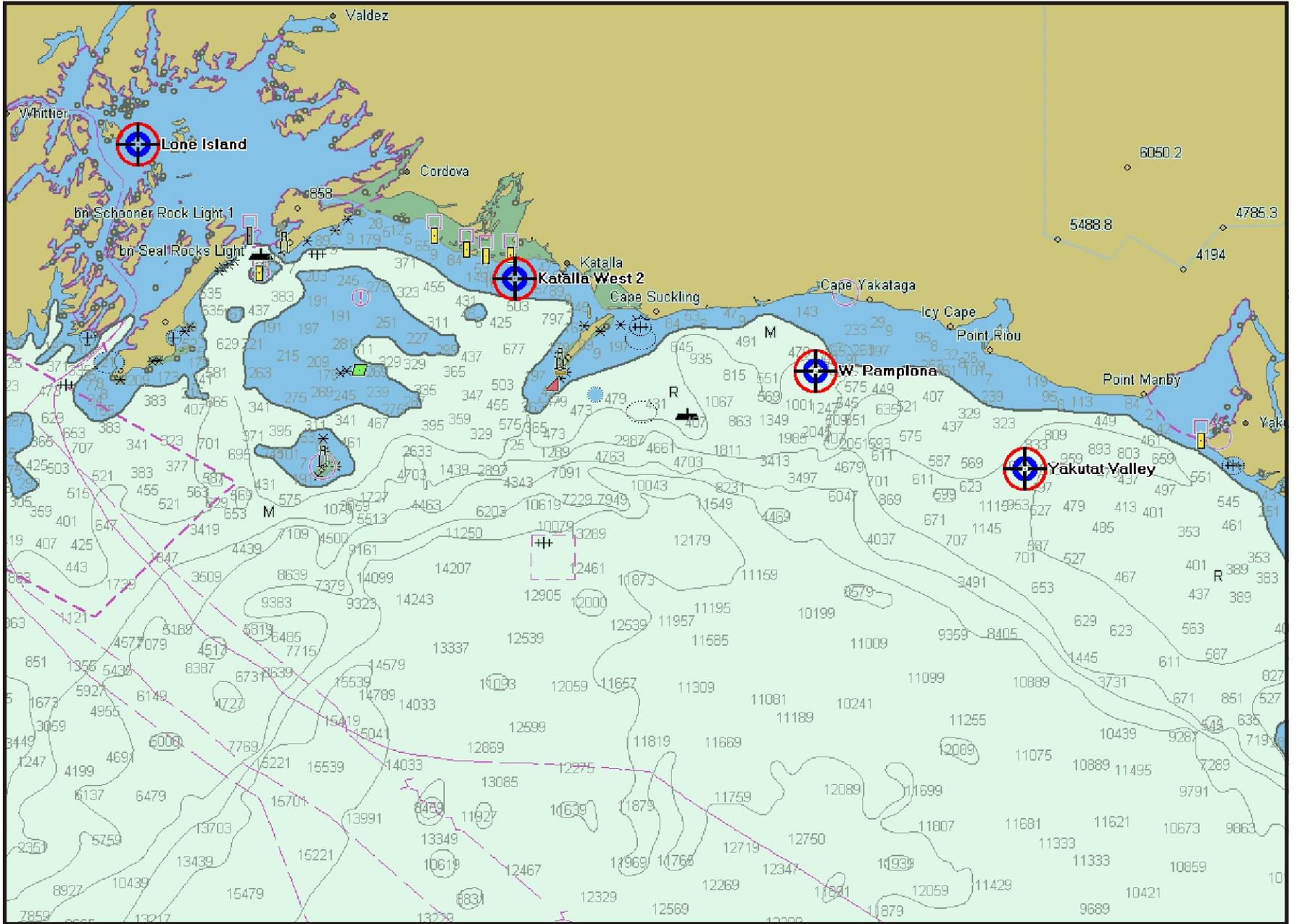
Reference Oils Project were not true sample splits in terms of what would normally be performed as a laboratory split from the same homogeneous sample. The samples consist of additional sediment collected at the time of sampling and basically constitute a field duplicate from the same sampling device. No homogenization or mixing of the sample material was performed in the field prior to subsampling. As a result, differences in analytical results could be caused by laboratory variability or differences in analytical methods as well as natural variability between the samples themselves.

Sampling information reported here was provided by Jeffrey Short of ABL soon after sampling was performed. Four samples (Figure 1 and Table 1) were selected for analysis at GERG at that time based on geographic coverage of the EVOS area, sampling depths, and anticipated inclusion of all the sample results in the final Yakataga Project manuscript. Additional analyses or analysis of additional samples was potentially to be performed for the Reference Oils Program in December 2000 or January 2001 when the Yakataga Project manuscript became available. The personal communication (draft manuscript in preparation for submittal for publishing in 2005) includes, however, results only from Yakutat Valley and West Pamplona Spur. The other two sediment sample results are not included in the manuscript, but data submitted to PWS RCAC and KLI by ABL in Microsoft Excel<sup>®</sup> format have been included in this report.

**Table 1. Location of Sediment Monitoring Stations Analyzed for the Reference Oil Project.**

Station Name	Sampling Depth (meters)	Location
Yakutat Valley	327	59° 25.6'N, 141° 09.4'W
West Pamplona Spur	196	59° 47.7'N, 142° 42.3'W
Katalla West 2	49	60° 08.5'N, 144° 56.2''W
Lone Island 1	740	60° 38.9'N, 147° 4 3.9'W

Sediment samples were analyzed by both laboratories for the hydrocarbon parameters historically used for the LTEMP program as described elsewhere (e.g., Kinnetic Laboratories, Inc. [KLI], 1998), including polycyclic aromatic hydrocarbons (PAH) and aliphatic hydrocarbons (AHC) which included the unresolved complex mixture (UCM). The concomitant parameters of total organic carbon (TOC), total inorganic carbon (TIC), and particle grain size (PGS) distribution were also analyzed by GERG, and TOC and TIC were also determined by ABL. Analyses performed by ABL were performed as described in the manuscript (Short, 2005) and accompanying references, including ABL standard operating procedures (SOPs). Analyses at GERG were performed using the same procedures used in the past on the LTEMP when LTEMP was performed by KLI, as referenced in prior LTEMP reports (e.g., KLI, 1998). Hydrocarbon data were reported by the laboratories on a dry weight basis. While samples analyzed at ABL for reporting in the manuscript were fractionated to separate the lower-density coal-like material from the sediments so each fraction could be analyzed separately, the sample split results provided to KLI for this report were identified as bulk sediment. All samples analyzed at GERG were analyzed in bulk (i.e., there was no separation of the fractions prior to analysis). Appropriate quality assurance/quality control procedures were followed as described in the referenced ABL manuscript and earlier LTEMP reports, along with each laboratory's SOPs. ABL and GERG data were submitted in Microsoft Excel<sup>®</sup> which was used for data entry, data verification, and calculation of summary parameters and diagnostic ratios presented here.



**Figure 1. Sediment Chemistry Stations.**

The opinions expressed in this PWSRCAC-commissioned report are not necessarily those of PWSRCAC.

Sampling and analytical methods varied between the Yakataga Project and the historical LTEMP project, while the analytes lists themselves varied very little between the two laboratories, as provided in the manuscript and earlier LTEMP reports. A number of PAH and AHC parameters and diagnostic ratios are utilized here to help interpret the data (Table 2). Analytes included in the reported summed parameters (e.g., Total PAH [TPAH] and Total AHC [TAHC]) are identical to those historically used by LTEMP but may be different from those reported in the manuscript. Additional analyses performed by USGS on the ABL sediments included petroleum biomarkers (sterane and triterpane) to be used to develop a seep fingerprint to aid in data interpretation, as presented in the Yakataga Project manuscript.

**Table 2. Hydrocarbon and Diagnostic Parameters Used for the Reference Oils Project.**

Parameter	Definition/Relevance
TPAH	Total PAH as defined as the sum of 2 to 5-ring polycyclic aromatic hydrocarbons Naphthalenes through Benzo(g,h,i)perylene and their alkyl homologues, excluding perylene; useful for determining TPAH contamination; includes petrogenic, pyrogenic, and diagenic sources.
FFPI	The fossil fuel pollution index is the ratio of fuel-derived PAH to TPAH and is defined as $FFPI = (N + F + P + D)/TPAH \times 100$ , where:  $N$ (Naphthalene series) = $C_0-N + C_1-N + C_2-N + C_3-N + C_4-N$ $F$ (Fluorene series) = $C_0-F + C_1-F + C_2-F + C_3-F$ $P$ (Phenanthrene/Anthracene series) = $C_0-A + C_0-P + C_1-P + C_2-P + C_3-P + C_4-P$ $D$ (Dibenzothiophene series) = $C_0-D + C_1-D + C_2-D + C_3-D$  FFPI is near 100 for petrogenic PAH; FFPI for pyrogenic PAH is near 0 (Boehm and Farrington, 1984).
TAHC	Total AHC as defined quantifies the total n-alkanes (n-C <sub>10</sub> to n-C <sub>34</sub> ) plus pristane and phytane; represents the total resolved aliphatic hydrocarbons as determined by high resolution GC/FID; includes both petrogenic and biogenic sources.
UCM	The unresolved complex mixture of hydrocarbons of undefined structure that are not separated by gas chromatographic techniques; represented by the total resolved plus unresolved area minus the total area of all peaks that have been integrated (GERG) or the total uncorrected unresolved complex area minus the total peak area (ABL).
CPI	The carbon preference index represents the relative amounts of odd- and even-chain alkanes within a specific boiling range and is defined as follows:  $CPI = 2(C_{27} + C_{29}) / (C_{26} + 2C_{28} + C_{30})$  Odd and even numbered n-alkanes are equally abundant in petroleum but have an odd numbered preference in biological material; a CPI close to 1 is an indication of petroleum and higher values indicate biogenic input (Farrington and Tripp, 1977).
CRUDE Index	The CRUDE index incorporates the other indices to provide a single value which can be used as a relative indication of the probable presence of petroleum hydrocarbons (Payne <i>et al.</i> , 1998):  $CRUDE = (TPAH \times FFPI/100) + (TAHC/CPI^2) + UCM/1000$ (where all concentrations are in the same units)

## 4.0 RESULTS AND DISCUSSION

As noted above, the samples used for the Reference Oils Project consist of additional sediment collected at the time of sampling during the Yakataga Project, basically constituting a field duplicate from the same sampling device although the term sample split is used here. No homogenization or mixing of the sample material was performed in the field prior to subsampling. As a result, any differences seen in analytical results between laboratories could be caused by natural variability between the subsamples themselves as well as differences in analytical methods and laboratory variability. Bearing this in mind, however, paired results from ABL and GERG are presented here (Table 3). Analytical results for the four samples are provided in the appendix.

**Table 3. Sediment Results.**

Location	Yakataga Valley		W. Pamplona Spur		Katalla West 2		Lone Island 1	
	ABL	GERG	ABL	GERG	ABL	GERG	ABL	GERG
TOC (%)	0.62	0.49	0.58	0.47	0.12	0.14	0.79	0.67
TIC (%)	0.58	0.53	0.32	0.29	0.11	0.11	0.23	0.25
Sand (%)	NA	15.2	NA	0.8	NA	96.5	NA	0.4
Silt (%)	NA	48.4	NA	49.3	NA	1.3	NA	30.1
Clay (%)	NA	36.4	NA	49.9	NA	2.2	NA	69.5
TPAH (ppb)	573.5	468.5	2499.0	2002.7	43.6	108.7	1764.0	1253.9
FFPI	82.5	76.6	83.4	78.0	84.9	82.4	85.2	78.7
TAHC (ppb)	684.4	898.0	2546.3	2779.8	96.0	205.8	1778.8	2144.1
UCM (ppm)	1.43	27.70	8.73	26.20	0.98	6.30	7.85	25.30
CPI	2.89	2.02	1.95	1.65	1.48	2.07	1.97	2.00
CRUDE	569	856	2845	2844	91	201	2039	1776

NA = Not Analyzed

### 4.1 TOC and TIC

TOC and TIC were analyzed by both laboratories using different analytical methods. TOC values ranged from approximately 14 to 67 % in the GERG data, and 12 to 79 % in the ABL data (Table 3). TIC values ranged from 11 to 53 % for GERG, and from 11 to 58% for ABL. As expected, the lowest TOC and TIC values were seen at the station in this sample set that exhibited the coarsest sediments (Katalla West 2), which was also the shallowest station sampled (49 m). The highest TOC shown overall was at the deepest station (Lone Island 1).

## 4.2 Particle Grain Size

Sediments from the four stations varied considerably in particle grain size as reported by GERG, with very fine sediments ranging from less than 1 % sand at West Pamplona Spur and Lone Island 1 to coarse sediments showing 96 % sand at the Katalla West 2 station (Table 3). West Pamplona Spur and Lone Island 1 showed the highest degree of finer sediments (silt + clay). As noted above, the station with the highest sand content also exhibited the lowest TOC and TIC values. ABL did not perform particle grain size analysis as part of the Yakataga Project.

## 4.3 Hydrocarbons

### Polycyclic Aromatic Hydrocarbons

Concentrations of TPAH (without perylene) determined by GERG ranged from a low of 108.7 ppb at Katalla West 2 to a high of 2002.7 ppb at West Pamplona Spur (Table 3). ABL found a similar pattern of TPAH at all four stations to that found by GERG with a low of 43.6 ppb at Katalla West 2 and a high of 2499.0 ppb at West Pamplona Spur. The lowest TPAH was seen at same station that also exhibited the coarsest grain size (> 96% sand) and lowest TIC and TOC concentrations. Little difference in FFPI ratios were seen between locations: GERG FFPI ratios ranged from 76.6 to 82.4 while ABL FFPI ratios ranged from 82.5 to 85.2 with slightly higher values seen at each station compared to that seen by GERG. These differences were caused by higher relative concentrations of some of the alkylated homologues (e.g., phenanthrene/anthracene) seen in the ABL data versus slightly higher relative concentrations of some of the 4- and 5-ring pyrogenic PAHs seen in the GERG data (Figure 2). These variations between the two data sets are believed to be due to differences in laboratory methodology where GERG utilizes internal standards and a reference oil to calibrate the alkylated homologues whereas ABL calibrates just the parent compounds.

An inter-laboratory comparison study between GERG and ABL was conducted during 2002 as part of LTEMP; however, due to large differences in sediment sample size and the fact that most analytes were near their MDLs, the study rendered results that were inconclusive (Payne *et al.*, 2003). In general, the study found that PAH analytes were generally higher at GERG versus those measured by ABL. However the results of both laboratories were usually below their respective MDLs. The sediment sample sizes analyzed by ABL was ~ 25 grams (g), whereas those analyzed by GERG were < 3 g. Both laboratories also ran sediment standard reference materials (SRMs) as part of the inter-laboratory study, although the SRMs utilized by GERG and ABL were different. GERG ran SRM 1941b, which is a low-level sediment SRM, and found good agreement between their results and the PAH calibration analytes. ABL ran SRM 1944 which contains substantially higher PAH concentrations and they found good comparison as well; however, ABL's performance on low-level sediments could not be determined. In contrast, the results of this Reference Oils study with sediments that contain higher levels of PAH show good agreement between GERG and ABL for most of the parent compounds with most noticeable differences seen in the alkylated homologues and some of the pyrogenic PAHs.

Individual PAH histograms were normalized to each sample's TPAH concentration to allow easy comparison of relative concentrations between samples that have different absolute concentrations. In order to compare the GOA locations to the one PWS location near Lone Island, the GOA samples were averaged together. Since Katalla West 2 was found to have very coarse grain size, low TIC and TOC concentrations, low PAH (often below MDLs), and low overall hydrocarbon concentrations, this station was excluded from the GOA grouping. A comparison of PAH histograms between ABL and GERG for

GOA and Lone Island 2 is presented in Figure 2. The PAH histogram from the PWS station near Lone Island was found to be very similar to that seen for the GOA. As described above, some differences were seen between the ABL and GERG data that were attributed to differences in laboratory methodology. As noted by Short (2005) and others for the GOA, a large naphthalene hump was seen in all of the PAH fingerprints that was attributed to shale or coal since it did not show signs of degradation as would be expected in a oil seep sample. The PAH signature of all samples very closely matched what has been termed the natural 'background' signature for PWS and GOA where the alkylated phenanthrene/anthracene were found to be approximately ten times larger than the corresponding alkylated dibenzothiophenes as described by Page *et al.* (1995), Short (1999), and others. This pattern was also found by KLI (1995) in deep sediment cores that were obtained at five locations in PWS and at other nearshore LTEMP subtidal sediment sites that had not been influenced by anthropogenic inputs (e.g., KLI, 2000; Payne *et al.*, 1998). The Lone Island sample from PWS and the two samples from GOA collected as part of this program agreed very well with the extended suite of samples for GOA described by Short (2005). Source identification of those samples by Short indicated that an eroding shale source rock formation located beneath the Malaspina Glacier is the most likely source of the hydrocarbons with secondary lesser inputs from other shale and coal sources and minor inputs from oil seeps. This is in agreement with Boehm *et al.* (2001) with respect to identifying eroding shale from the Malaspina Glacier area as the primary source; however, Boehm and co-authors also identified oil seeps as still being an important secondary source of hydrocarbons in the sediments of GOA. Although the jury still appears to be out with respect the relative contribution from oil seep sources, there does appear to be a general agreement that a Tertiary eroding shale formation most likely located beneath the Malaspina Glacier is the primary source of hydrocarbons in the sediments of the GOA which are then transported into PWS.

### **Saturated Hydrocarbons**

Concentrations of TAHC determined by GERG ranged from a low of 205.8 ppb at Katalla West 2 to a high of 2779.8 ppb at West Pamplona Spur (Table 3). ABL found a pattern of TAHC at all four stations similar to that found by GERG with a low of 96.0 ppb at Katalla West 2 and a high of 2546.3 ppb at West Pamplona Spur. As seen with TPAH, the lowest TAHC was seen by both laboratories at the same station that also exhibited the coarsest grain size and lowest TIC and TOC concentrations. Little difference in CPI ratios were seen between locations in the GERG data where CPI ratios ranged from 1.65 to 2.07, while ABL CPI ratios ranged from 1.48 to 2.89 with slightly higher variability seen between stations compared to that seen by GERG. A CPI of approximately 1 would indicate a petrogenic source, whereas CPI ratios in the range of 5-15 would indicate predominately biogenic input typically made up of naturally-occurring plant waxes from terrestrial sources. The CPI of approximately 2 seen in these data would confirm a petrogenic source that is consistent with an oil-bearing shale formation with lesser amounts from biogenic sources.

As with PAH, the individual AHC histograms were normalized to each sample's TAHC concentration to allow easy comparison of relative concentrations between samples that have different absolute concentrations. Overall, the signature of n-alkanes plus pristane and phytane seen in Figure 3 were in good agreement between laboratories and in good agreement between the GOA stations and Lone Island 1 in PWS. As noted previously, some differences were noted between data from the two laboratories; however these differences with respect to AHC concentrations appeared to be small and could have been due to sample variability. The AHC distribution was found to be relatively smooth with minor peaks seen in n-C<sub>15</sub> and pristane, and a small but clear odd-to-even preference evident in the higher molecular

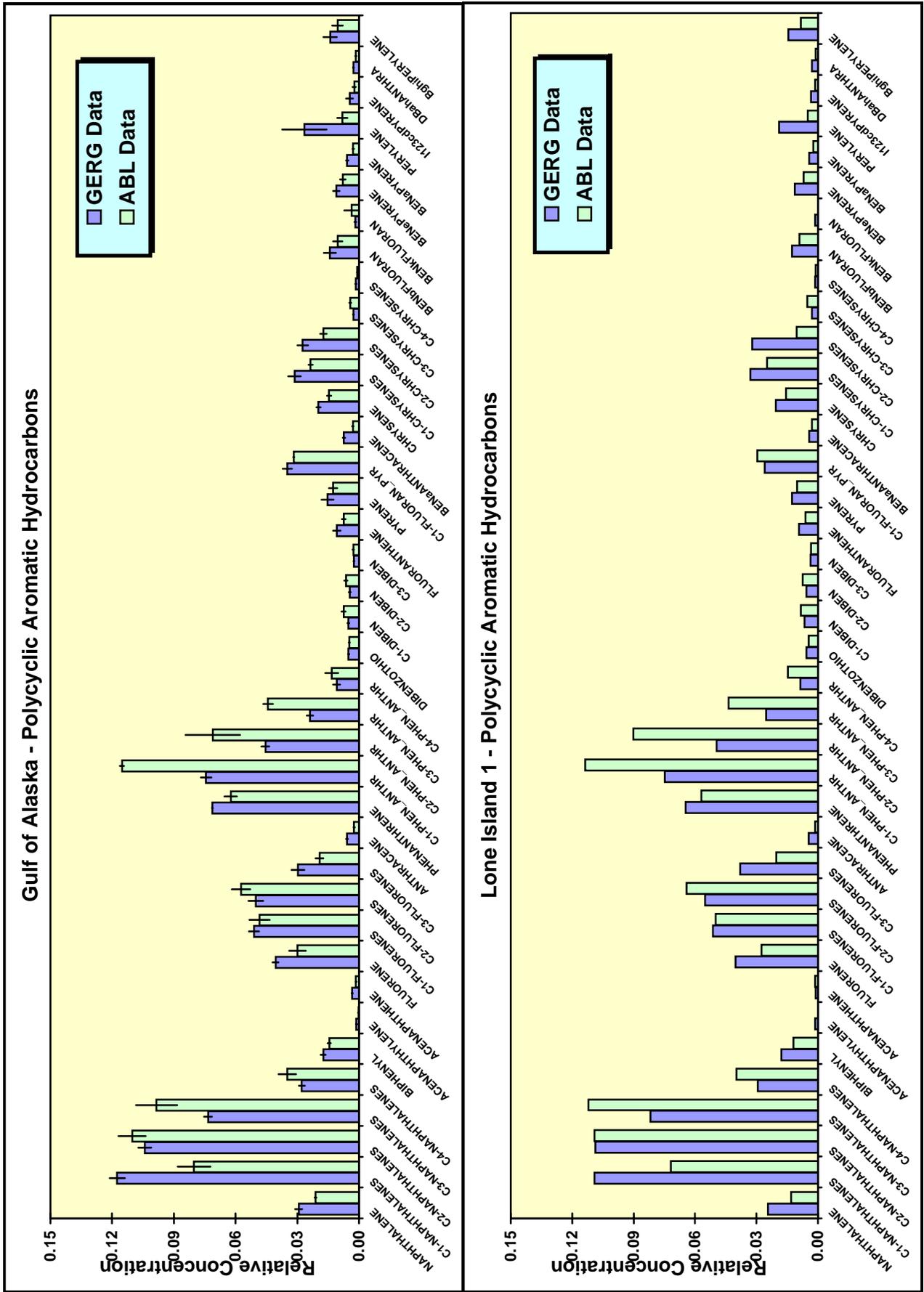


Figure 2. Relative Concentrations of Polycyclic Aromatic Hydrocarbons from Two Gulf of Alaska Sites versus Site in PWS near Lone Island.

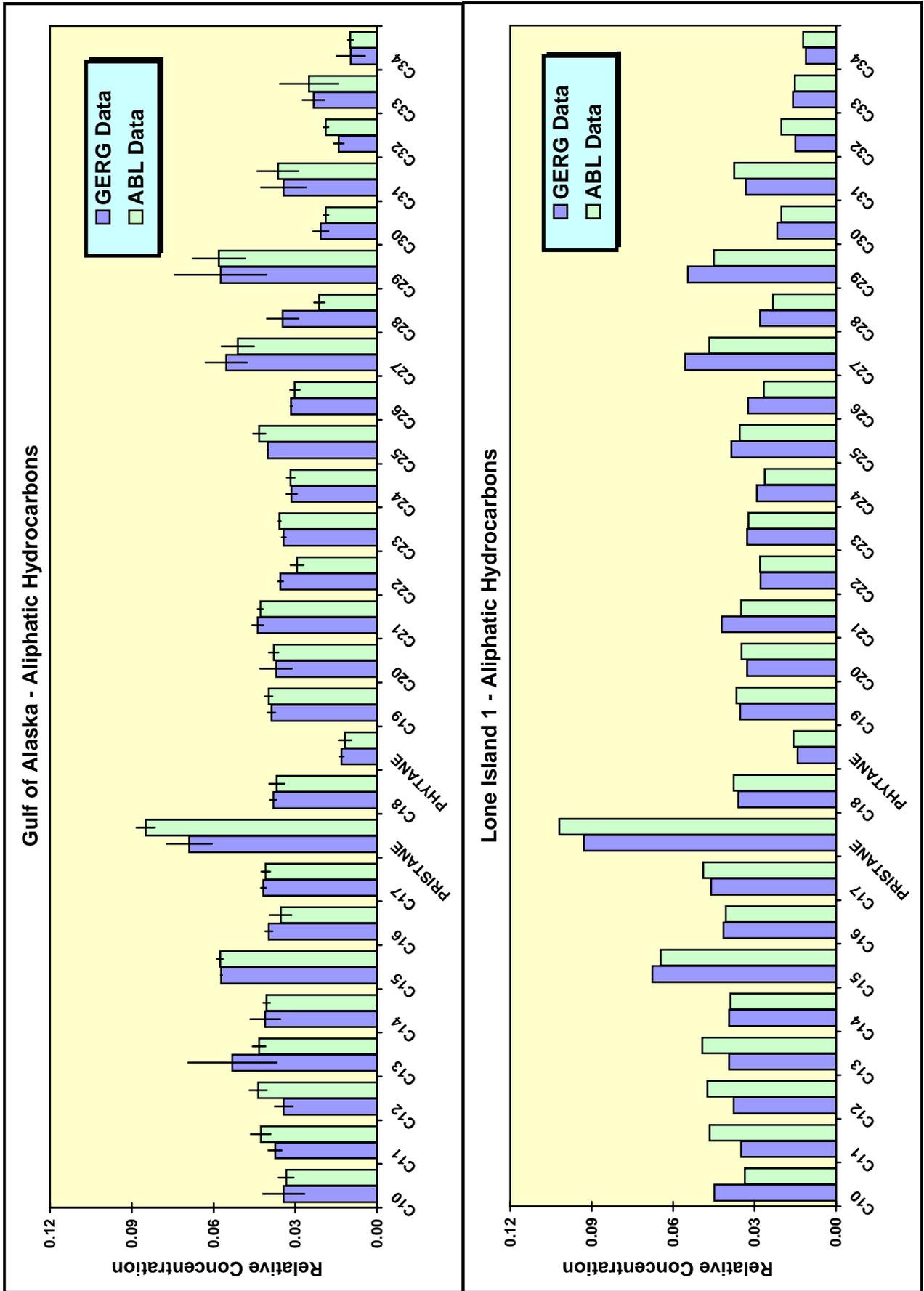


Figure 3. Relative Concentrations of Aliphatic Hydrocarbons from Two Gulf of Alaska Sites versus Site in PWS near Lone Island.

weight alkanes. Overall, the AHC distribution was found to be very similar to that seen by Short (2005) for the eight stations that he examined in GOA which would indicate a similar source for the deep PWS sediments to that seen in GOA.

The UCM in the sediments measured by GERG ranged from a low 6.3 ppm at Katalla West 2 to a high of 27.7 ppm at Yakataga Valley (Table 3). The UCM concentrations measured by ABL were substantially lower than those measured by GERG, ranging from a low of 0.98 ppm at Katalla West 2 to a high of 8.73 at West Pamplona Spur. This large discrepancy between the UCM measured by the two laboratories is much greater than might be expected due to sample variability and is believed to be due to differences in laboratory methodologies and/or their respective definitions of what is quantified as the UCM.

The CRUDE Index which takes into account the petrogenic components of PAH, AHC, and includes UCM was found to range from 201 to 2844 at the four stations analyzed by GERG and from 91 to 2845 by ABL (Table 3). As with TPAH and TAHC, the lowest CRUDE values were seen at Katalla West 2 with the highest at West Pamplona Spur. Good agreement was seen between the two laboratories and within the range of typically variability that would be expected for sample replicates.

## 6.0 CONCLUSIONS

In summary, comparison of analytical results from the Reference Oils Project with those of the Yakataga Project indicated that the background hydrocarbon signatures from the GOA samples were similar to one another and furthermore, that the signature at the Lone Island station in PWS was consistent with that seen in the GOA samples. The actual source of this background signature continues to be somewhat controversial, but at this point in time, the authors that have been involved in the on-going debate regarding this source material in general agree that the most likely source of the predominant hydrocarbon load in GOA and PWS sediments is a Tertiary shale formation most likely located beneath the Malaspina Glacier in Southeast Alaska. Oil seeps and coal material contribute lesser inputs, although the relative contribution from these two secondary sources is still being debated. Data presented in this report also show general good agreement between PAH and AHC signatures from the two laboratories with some notable differences in PAH ascribed to differing laboratory's methodologies. In general, the results from the two laboratories for this project were in much better agreement than those from an inter-laboratory comparison that was previously conducted by RCAC between these same two laboratories.

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## **APPENDIX – Sediment Chemistry Data**

**ABL Data for the PWS RCAC Reference Oils Project**

NOAA Samp No	1105703	1105708	1105712	1105716
USGS Samp No	GOA139	GOA152	GOA130	GOA127
MATRIX	SEDIMENT	SEDIMENT	SEDIMENT	SEDIMENT
STATION	YAKUTAT VALLEY	W. PAMPLONA SPUR	KATALLA WEST 2	LONE ISLAND 1
QCBATCH	R01081	R01081	R01171	R01171
LABSAM1	1105703	1105708	1105712	1105716
dry wt (g)	36.36	37.75	52.15	22.80
wet wt (g)	55.84	65.96	65.94	50.50
solids (%)	65.11	57.23	79.09	45.15
TOC (%)	0.62	0.58	0.12	0.79
TIC (%)	0.58	0.32	0.11	0.23
<b>PAH (ng/g)</b>				
naphthalene	11.85 -	53.96 m	1.47 -	23.13 -
C-1 naphthalenes	41.41 S	220.30 S	3.35 S	126.81 S
C-2 naphthalenes	59.50 m	291.99 m	4.66 -	192.44 m
C-3 naphthalenes	50.68 m	271.02 m	4.46 -	197.59 m
C-4 naphthalenes	17.49 -	97.79 m	2.14 -	70.11 -
biphenyl	8.74 -	34.26 -	0.62 b	21.07 -
acenaphthylene	0.00 a	1.00 b	0.00 a	0.00 a
acenaphthene	0.89 b	3.79 -	0.22 b	2.27 b
fluorene	19.48 -	64.44 m	1.56 -	48.76 -
C-1 fluorenes	30.59 -	108.72 m	2.07 -	88.06 m
C-2 fluorenes	35.52 -	132.17 m	2.84 -	113.22 m
C-3 fluorenes	12.17 -	43.08 -	1.15 b	35.71 -
anthracene	1.20 b	6.67 -	0.13 b	2.40 b
phenanthrene	37.50 -	148.31 m	2.58 -	100.58 m
C-1 phenanthrenes/anthracenes	66.61 m	285.38 m	4.18 -	200.52 m
C-2 phenanthrenes/anthracenes	48.37 m	144.26 m	3.48 -	158.96 m
C-3 phenanthrenes/anthracenes	24.04 -	116.14 m	1.47 -	77.03 m
C-4 phenanthrenes/anthracenes	5.76 -	40.81 -	0.40 b	25.75 -
dibenzothiophene	2.55 -	12.54 -	0.24 b	7.86 -
C-1 dibenzothiophenes	3.76 -	21.20 -	0.36 b	14.63 -
C-2 dibenzothiophenes	3.18 -	18.15 -	0.35 b	13.34 -
C-3 dibenzothiophenes	1.39 b	7.94 -	0.15 b	6.07 -
fluoranthene	4.73 -	16.02 -	0.21 b	10.68 -
pyrene	8.39 -	26.21 -	0.50 b	17.95 -
C-1 fluoranthenes/pyrenes	18.09 -	79.55 m	1.11 b	52.04 -
benz-a-anthracene	1.54 -	8.43 -	0.00 b	5.09 -
chrysene	8.95 -	33.85 -	0.64 b	27.54 -
C-1 chrysenes	12.95 -	61.53 m	0.92 b	43.89 -
C-2 chrysenes	9.03 -	47.17 m	0.33 b	18.23 -
C-3 chrysenes	2.19 -	11.77 -	0.21 b	9.21 -
C-4 chrysenes	0.50 b	2.44 -	0.00 a	1.86 b
benzo-b-fluoranthene	7.18 -	20.33 -	0.43 b	16.07 -
benzo-k-fluoranthene	0.00 a	17.94 -	0.00 a	0.00 a
benzo-e-pyrene	5.30 -	16.23 -	0.37 b	12.29 -
benzo-a-pyrene	1.76 -	6.43 -	0.10 b	3.80 -
perylene	6.11 -	14.32 -	0.31 b	8.65 -
indeno-123-cd-pyrene	1.77 -	3.92 -	0.11 b	2.38 b
dibenzo-a,h-anthracene	1.00 b	3.74 -	0.06 b	1.90 b
benzo-g,h,i-perylene	7.43 -	19.56 -	0.75 b	14.73 -
<b>Total PAH</b>	<b>573.46</b>	<b>2499.03</b>	<b>43.62</b>	<b>1764.00</b>
<b>Specific Isomers (ug/g)</b>				
2-methylnaphthalene	24.14 -	129.84 m	2.11 -	77.22 -
1-methylnaphthalene	17.27 -	90.47 m	1.24 b	49.60 -
2,6-dimethylnaphthalene	18.81	91.20	1.44	62.64
1-methylphenanthrene	12.49	54.31	0.75	36.95
2,3,5-trimethylnaphthalene	9.80	65.64	0.92	35.37
<b>Surrogate Standards (%)</b>				
naph-D8	33.70	38.22	23.88	32.38
acenD10	43.21	56.03	39.31	49.15
phenD10	67.94	74.76	72.49	80.14
chryD12	77.76	82.26	83.86	87.15
peryD12	113.12	141.14	105.95	116.80
benzo-a-pyrD-12	80.39	95.62	90.53	96.58
<b>Diagnostic Parameters</b>				
FFPI	82.49	83.428	84.87	85.204

**ABL Data for the PWS RCAC Reference Oils Project**

NOAA Samp No USGS Samp No MATRIX STATION QCBATCH LABSAM1	1105703 GOA139 SEDIMENT YAKUTAT VALLEY R01081 1105703	1105708 GOA152 SEDIMENT W. PAMPLONA SPUR R01081 1105708	1105712 GOA130 SEDIMENT KATALLA WEST 2 R01171 1105712	1105716 GOA127 SEDIMENT LONE ISLAND 1 R01171 1105716
<b>Aliphatics (ng/g)</b>				
C9	18.37	66.42	5.94	43.46
Alkane, C10- (n-decane)	20.90 b	91.92 -	0.00 b	59.83 -
Alkane, C11- (n-undecane)	26.69 b	117.81 -	3.32 b	82.84 -
Alkane, C12- (n-dodecane)	27.64 b	119.45 -	1.73 b	84.32 -
Alkane, C13- (n-tridecane)	28.00 b	116.19 -	1.94 b	87.67 -
Alkane, C14- (n-tetradecane)	26.89 b	106.39 -	3.73 b	69.00 b
Alkane, C15- (n-pentadecane)	38.65 -	149.63 -	0.52 b	115.00 -
Alkane, C16- (n-hexadecane)	21.47 b	100.14 -	2.66 b	72.14 -
Alkane, C17- (n-heptadecane)	26.84 -	108.18 -	3.65 b	87.11 -
Pristane	55.72 -	224.67 -	19.43 b	181.36 -
Alkane, C18- (n-octadecane)	23.23 b	100.71 -	2.63 b	67.05 -
Phytane	6.39 b	35.87 -	1.01 b	27.98 b
Alkane, C19- (n-nonadecane)	26.25 b	104.97 -	2.51 b	65.25 -
Alkane, C20- (n-eicosane)	24.73 b	100.92 -	1.86 b	61.77 -
Alkane, C21- (heneicosane)	29.96 -	106.72 -	2.56 b	62.23 -
Alkane, C22- (n-docosane)	18.50 b	80.61 -	1.94 b	49.76 -
Alkane, C23- (n-tricosane)	24.21 b	92.02 -	2.78 b	57.19 -
Alkane, C24- (n-tetracosane)	20.69 b	84.28 -	2.75 b	46.72 -
Alkane, C25- (n-pentacosane)	31.10 -	104.31 -	4.31 b	62.96 -
Alkane, C26- (n-hexacosane)	19.39 b	81.41 -	3.94 b	47.17 -
Alkane, C27- (n-heptacosane)	39.02 -	115.06 -	5.83 b	83.02 -
Alkane, C28- (n-octacosane)	13.12 b	58.96 -	3.82 b	41.23 -
Alkane, C29- (n-nonacosane)	46.38 -	122.99 -	5.57 b	80.10 -
Alkane, C30- (n-triacontane)	13.48 b	45.46 -	3.85 b	35.87 b
C31	30.06	73.27	4.52	66.83
C32	13.48 b	45.46 b	3.85 b	35.87 b
C33	24.34	36.27	3.24	27.00
C34	7.30 b	22.61 b	2.07 a	21.51 b
Total AHC	684.42	2546.28	96.04	1778.79
[UCM]	1426.37	8733.10	982.00	7851.38
<b>Surrogate Standards (%)</b>				
C12ALKD	83.08	71.10	67.07	68.17
C16ALKD	84.66	75.77	85.21	86.46
C20ALKD	87.54	74.39	90.33	88.36
C24ALKD	87.07	82.77	87.96	89.49
C30ALKD	93.70	96.06	87.90	91.20
<b>Diagnostic Parameters</b>				
CPI	2.89	1.95	1.48	1.97
CRUDE	569.3	2845.2	90.9	2039.3
<b>Biomarkers (ug/g)</b>				
C27sterane-aaa20R	0.00	0.01	BQL(<0.001)	0.00
C28sterane-aaa20R	BQL(<0.001)	0.01	BQL(<0.001)	0.00
C29sterane-aaa20R	0.00	0.01	BQL(<0.001)	0.01
oleanane (a+b)	0.00	0.00	BQL(<0.001)	0.00
C30 (a,b) hopane	0.00	0.02	BQL(<0.001)	0.02
% biosurr recovery	83.55	85.99	86.19	87.52
(wt.%)	0.62	0.58	0.12	0.79
(wt.%)	0.58	0.32	0.11	0.23

**Qccode key:**

a = no signal

b = signal below lowest calibration standard

m = signal above highest calibration standard

- = signal within calibration range

BQL = below quantitation limit

S = summation of 2-methylnaphthalene and 1-methylnaphthalene

**GERG Data for the PWS RCAC Reference Oils Project**

NOAA SAMP_ID	1105703	1105708	1105712	1105716
KLI SAMP_ID	PWS00NOH0003	PWS00NOH0009	PWS00NOH0013	PWS00NOH0017
MATRIX	SEDIMENT	SEDIMENT	SEDIMENT	SEDIMENT
STATION	YAKUTAT VALLEY	W. PAMPLONA SPUR	KATALLA WEST 2	LONE ISLAND 1
LABSAMP_ID	C35741	C35746	C35750	C35754
BATCH_ID	M3029	M3029	M3029	M3029
dry wt. (g)	12.39	11.57	16.34	8.85
wet wt. (g)	20.39	20.61	20.68	20.12
solids (%)	60.8	56.1	79	44
TOC (%)	0.49	0.47	0.14	0.67
TIC (%)	0.53	0.29	0.11	0.25
<b>PAH (ng/g)</b>				
naphthalene	14.5	55.3	4.7 J	30.6
C-1 naphthalenes	56.8	228.1	15.1	136.9
C-2 naphthalenes	50.3	202.4	14.4	136.3
C-3 naphthalenes	35.3	143.2	12.0	102.6
C-4 naphthalenes	13.7	52.8	5.4	36.9
biphenyl	7.6	37.2	1.8	22.4
acenaphthylene	0.6 J	2.8	0.2 J	1.7
acenaphthene	1.6	7.1	0.5 J	1.4
fluorene	18.3	84.2	3.7	50.3
C-1 fluorenes	22.8	107.3	5.2	64.2
C-2 fluorenes	21.8	107.6	5.0	69.0
C-3 fluorenes	12.4	65.7	2.7	47.7
anthracene	3.0	11.0	0.3 J	5.6
phenanthrene	33.5	142.1	5.6	81.1
C-1 phenanthrenes/anthracenes	33.6	154.2	6.6	93.8
C-2 phenanthrenes/anthracenes	20.4	95.2	4.3	62.0
C-3 phenanthrenes/anthracenes	10.4	50.9	2.2	31.8
C-4 phenanthrenes/anthracenes	4.3	25.3	0.7 J	10.9
dibenzothiophene	2.4	10.3	0.4	7.0
C-1 dibenzothiophenes	2.2	11.4	0.6	8.1
C-2 dibenzothiophenes	1.9	9.8	0.5 J	7.1
C-3 dibenzothiophenes	1.1	5.2	0.2 J	4.4
fluoranthene	5.9	17.8	0.6	11.7
pyrene	8.5	24.9	1.4	15.9
C-1 fluoranthenes/pyrenes	15.3	74.1	2.7	32.6
benz-a-anthracene	3.2	15.8	0.4	5.4
chrysene	9.7	37.4	1.7	25.9
C-1 chrysenes	13.3	68.8	2.6	41.4
C-2 chrysenes	11.6	59.9	2.1	40.3
C-3 chrysenes	1.4	5.1	0.3 J	3.7
C-4 chrysenes	0.7 J	3.5	0.1 J	1.7 J
benzo-b-fluoranthene	8.0	22.4	1.2	16.0
benzo-k-fluoranthene	1.1	2.6	0.0 ND	1.7
benzo-e-pyrene	5.9	18.7	1.0	14.3
benzo-a-pyrene	3.0	10.3	0.4 J	5.4
perylene	17.5	31.5	2.1 J	23.8
indeno-123-cd-pyrene	2.9	5.8	0.3 J	4.3
dibenzo-a,h-anthracene	1.4	5.1	0.3 J	3.6
benzo-g,h,i-perylene	8.1	21.4	1.5	18.2
<b>Total PAH</b>	<b>468.50</b>	<b>2002.70</b>	<b>108.70</b>	<b>1253.90</b>
<b>Specific Isomers (ug/g)</b>				
2-methylnaphthalene	33.3	133.9	9.6	83.2
1-methylnaphthalene	23.5	94.2	5.5	53.7
2,6-dimethylnaphthalene	18.9	108.9	4.2	70.5
1-methylphenanthrene	11.1	51.9	1.9	29.7
1,6,7-trimethylnaphthalene	10.8	64.9	2.9	42.7
<b>Surrogate Standards (%)</b>				
naphthD8	50.5	62	43.9	49.2
acenD10	81.8	67.9	69.4	57.5
phenD10	86.4	78.3	91.9	72.6
chryD12	91.8	91.6	94.3	77.7
peryD12	67	74.9	75.3	56.6
<b>Diagnostic Parameters</b>				
FFPI	76.6	78.0	82.4	78.7

**GERG Data for the PWS RCAC Reference Oils Project**

NOAA SAMP_ID	1105703	1105708	1105712	1105716
KLI SAMP_ID	PWS00NOH0003	PWS00NOH0009	PWS00NOH0013	PWS00NOH0017
MATRIX	SEDIMENT	SEDIMENT	SEDIMENT	SEDIMENT
STATION	YAKUTAT VALLEY	W. PAMPLONA SPUR	KATALLA WEST 2	LONE ISLAND 1
LABSAMP_ID	C35741	C35746	C35750	C35754
BATCH_ID	M3029	M3029	M3029	M3029
<b>Aliphatics (ng/g)</b>				
Alkane, C10- (n-decane)	23.9	116.4	14.4	96.0
Alkane, C11- (n-undecane)	31.4	110.7	5.6	75.0
Alkane, C12- (n-dodecane)	27.7	104.4	5.5	80.7
Alkane, C13- (n-tridecane)	33.1	192.5	7.2	84.6
Alkane, C14- (n-tetradecane)	31.8	129.5	6.4 J	84.4
Alkane, C15- (n-pentadecane)	51.1	159.4	10.8	145.0
Alkane, C16- (n-hexadecane)	34.4	114.2	8.8	88.8
Alkane, C17- (n-heptadecane)	38.3	113.2	8.0	98.6
Pristane	54.4	214.8	20.5	199.2
Alkane, C18- (n-octadecane)	33.2	109.0	7.2 J	77.2
Phytane	10.9	38.6	1.5 J	30.5
Alkane, C19- (n-nonadecane)	36.0	103.9	6.9 J	75.7
Alkane, C20- (n-eicosane)	28.0	119.5	8.7 J	70.3
Alkane, C21- (heneicosane)	41.1	116.1	8.4 J	90.4
Alkane, C22- (n-docosane)	31.0	100.8	7.5 J	59.5
Alkane, C23- (n-tricosane)	30.1	97.1	9.4	70.2
Alkane, C24- (n-tetracosane)	26.4	92.6	8.1 J	62.4
Alkane, C25- (n-pentacosane)	35.8	112.0	14.0	82.7
Alkane, C26- (n-hexacosane)	28.5	87.0	7.4 J	69.4
Alkane, C27- (n-heptacosane)	56.5	132.7	11.3	119.0
Alkane, C28- (n-octacosane)	36.2	80.4	4.3 J	60.1
Alkane, C29- (n-nonacosane)	66.8	112.6	7.6	116.9
Alkane, C30- (n-triacontane)	21.1	49.4	2.3 J	46.5
C31	38.2	72.8	5.1 J	71.1
C32	14.3	33.9	5.0 J	32.3
C33	24.5	53.8	3.1 J	34.1
C34	13.4	12.5	0.8 J	23.7
Total AHC	898.0	2779.8	205.8	2144.1
[UCM]	27.7	26.2	6.3	25.3
TOTAL RAHC	2.2	5.2	0.7	4.0
TRUAHC	29.9	31.4	6.9	29.2
<b>Surrogate Standards (%)</b>				
C12ALKD	63	62	44	52
C20ALKD	87	91	95	72
C24ALKD	86	93	89	71
C30ALKD	99	80	84	62
<b>Diagnostic Parameters</b>				
CPI	2.02	1.65	2.07	2.00
CRUDE	855.5	2844.1	200.8	1776.2
TOC_BATCH	9/6/00	9/6/00	9/6/00	9/6/00
PGS_BATCH	36779	36779	36779	36779
PGS SAMP_ID	PWS00NOP0003	PWS00NOP0009	PWS00NOP0013	PWS00NOP0017
SAND (%)	15.2	0.8	96.5	0.4
SILT (%)	48.4	49.3	1.3	30.1
CLAY (%)	36.4	49.9	2.2	69.5

**QC Qualifier Key:**

J = below method detection limit  
 ND = not detected