

Natural Hydrocarbon Background in Benthic Sediments of Prince William Sound, Alaska: Oil vs Coal

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The source of the background hydrocarbons in benthic sediments of Prince William Sound (PWS), AK, where the 1989 Exxon Valdez oil spill (EVOS) occurred, has been ascribed to oil seeps in coastal areas of the Gulf of Alaska (GOA). We present evidence that coal is a more plausible source, including (i) high concentrations of total PAH (TPAH), between 1670 and 3070 ng/g, in continental shelf sediments adjacent to the coastal region containing extensive coal deposits; (ii) PAH composition patterns of sediments along with predictive models that are consistent with coal but not oil; (iii) low ratios (<0.2) of triaromatic steranes to methylchrysenes found in sediments and coals, contrasting with the high ratios (11 and 13) found in seep oil; and (iv) bioaccumulation of PAH in salmon collected within 100 m of the Katalla oil seeps but not in filter-feeding mussels collected near oilfield drainages 9 km from the seeps, indicating negligible transport of bioavailable PAH from Katalla seeps to the GOA. In contrast with oil, PAH in coal are not bioavailable, so the presence of coal in these benthic sediments confers no adaptive benefit to biota of the marine ecosystem with respect to PAH insults from anthropogenic sources.

Introduction

The effects of an oil spill on biota are often obscured by pollutants from confounding sources. Hydrocarbons from alternative sources may obscure evidence of exposure to a particular spill, and longer-term effects usually cannot be established with much statistical confidence. The EVOS in PWS appeared to present an opportunity to evaluate the biological impacts of a single large-scale pollution event in the absence of confounding pollutants, because the spill occurred in an area remote from industrial activity, and baseline studies confirmed that hydrocarbon pollutants were negligible in intertidal sediments and mussels throughout much of PWS (1).

The absence of confounding hydrocarbon pollutants in the area affected by the EVOS has been challenged repeatedly

in reports sponsored by Exxon Corporation (2–7). Page et al. (2) conclude that natural oil seeps, identified at Katalla (Figure 1) and elsewhere along the northern coast of the GOA, provide a regional PAH background in subtidal sediments of PWS through transport of oiled sediment by the Alaska Coastal Current (ACC). However, another plausible source of these background PAH is coal (1, 8–10). Page et al. (4) do mention coal as a potential hydrocarbon source for sediment of PWS; however, they dismiss this possibility, not on the basis of comparative geochemistry of relevant Alaskan coals, but rather on the erroneous impression that terrestrial coal deposits (11–13) are not distributed extensively east of the Bering River in coastal regions of the GOA. Distinguishing between these sources is important because PAH in coal are not bioavailable (14) and hence are contaminants but not pollutants capable of causing adverse effects on exposed biota.

We report here evidence linking the PAH distributions found in benthic sediments of the GOA and PWS with distributions found in coals from terrestrial deposits adjacent to the GOA. We compare the PAH distributions of native bulk coal and of particulate coal associated with riverine and beach sediments, with benthic sediments of the GOA continental shelf and of PWS, to determine possible erosional and transport pathways from terrestrial coal deposits to benthic PWS sediments. We compare the PAH distributions of unweathered and weathered oil from Katalla and the PAH distributions of fish and mussels living near the seeps at Katalla to demonstrate that PAH of Katalla oil are subject to characteristic weathering losses and are bioavailable but do not reach the GOA. Furthermore, we show that the hydrocarbon biomarker, oleanane, previously used by Page et al. (4–6) as a specific marker for seep oil, is also present in coal and therefore cannot be used to differentiate oil and coal in this region. Finally, we assess the relative contribution of hydrocarbons from oil seeps and terrestrial coals to the background sediments of the GOA and PWS.

Study Area

The study region includes PWS, the northern GOA, the <1 km² Katalla oilfield (15), and the coal deposits in the Kulthieth Formation (16) that extend about 270 km eastward from the Bering River through the Samovar Hills to Yakutat Bay (Figure 1). The Kulthieth formation is a banded sequence of sandstone, siltstone, shale, and coal with most of the coal in the finer-grained sedimentary sequences (17). The Bering River coal field contains an estimated 3.3×10^9 t, and the Samovar Hills occurrence contains 1.5×10^8 t. The rank of the Bering River coal increases from semibituminous in the west through anthracite at the eastern end of the field (12).

Numerous small and intermittent oil seeps have been identified along the northern GOA coastline near Katalla, Cape Yakataga, the Malaspina Forelands, and the Samovar Hills (15, 18). Oil discharge rates from these seeps have not been estimated, but oil sheens rarely appear in streamwaters that drain these seeps as they encounter the northern GOA (18). Any oil produced by the seeps at Katalla would be hydraulically transported to the mouth of Katalla Slough, a distance of 9 km, where the marine waters of the northern GOA are encountered. Submarine seeps have not been described in the literature for this area. Terrestrial sediments introduced into the northern GOA may be transported into PWS by the ACC as it flushes the Sound, entering through Hinchinbrook Entrance and exiting through Montague Strait (Figure 1).

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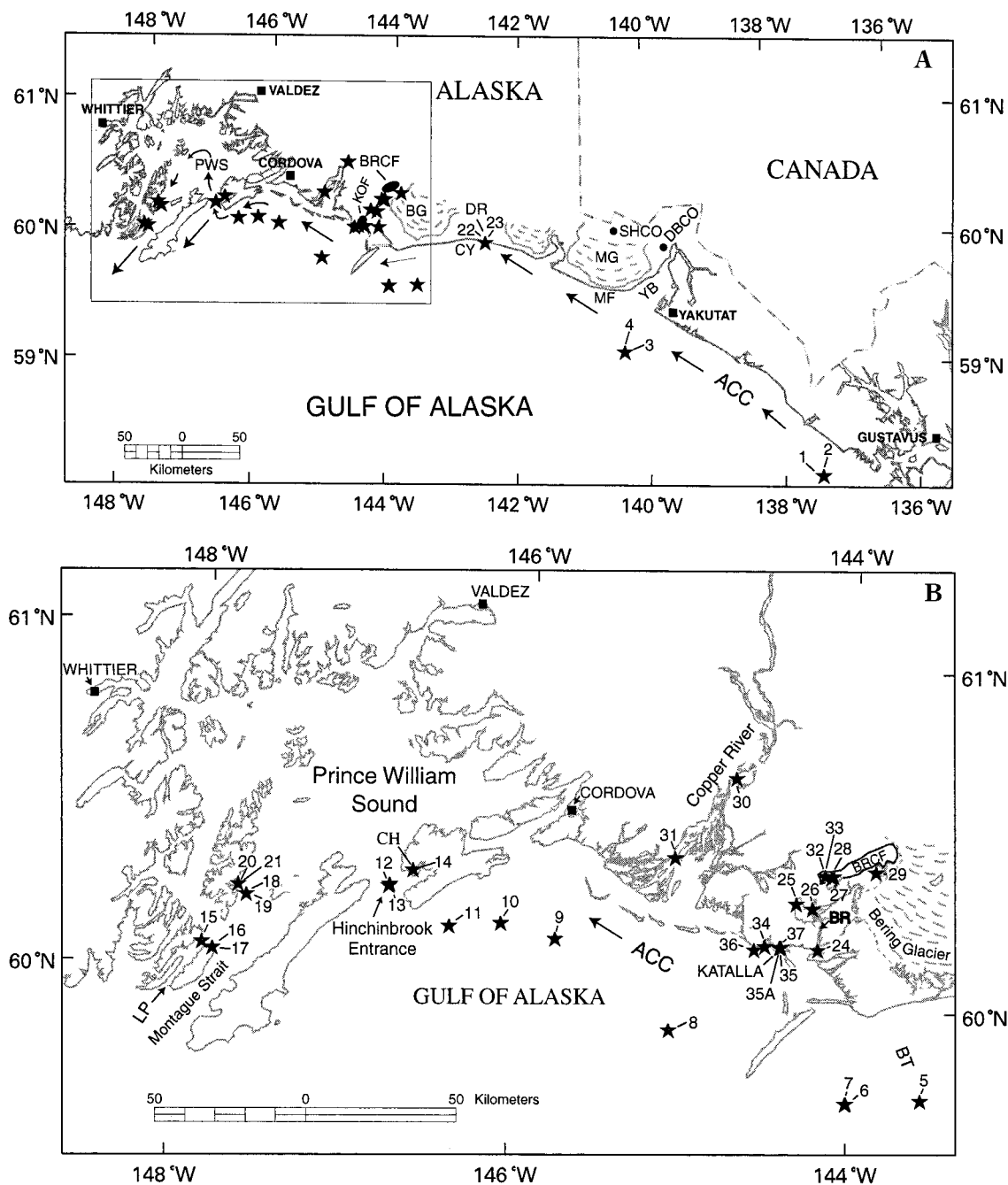


FIGURE 1. Location of sampling stations, major glaciers, positions of benthic samples in the Gulf of Alaska (GOA) and coal in southern Alaska adjacent to the GOA. Abbreviations: ACC, Alaska Coastal Current; BG, Bering Glacier; BR, Bering River; BRCF, Bering River coal field; BT, Bering Trough; CH, Constantine Harbor; CY, Cape Yakataga; DBCO, Disenchantment Bay coal occurrence; DR, Duktoth River; KOF, Katalla oil field; LP, Latouche Passage; MF, Malaspina Forelands; MG, Malaspina Glacier; PWS, Prince William Sound; SHCO, Samovar Hills coal occurrence; YB, Yakutat Bay;

Methods

Sample Collection. Marine sediments (samples 1–21, Table 1) were collected at benthic depths of 100–300 m by a shipboard grab sampler in August and September 1996 at stations along the northern GOA, including inside PWS (Figure 1). Terrestrial sediments (samples 22–31) were collected in June and July 1997 from riparian sediments of the Duktoth, Copper, and Bering Rivers, including tributaries and source lakes of the Bering River. Coal samples were collected from outcrops in the Bering River coal field in 1975 and 1976 (samples 32 and 33) and from coarse sand-sized coal particles (sample 34 collected July 1997) that cover the low-gradient beach at Katalla to depths of about 1 cm (Figure

2). A composite sample of unweathered Katalla oil was obtained from a U.S. Geological Survey (USGS) collection (sample 35), along with a surface sample of exposed seep oil (sample 35A).

Two samples of biota were collected near Katalla to assess the bioavailability of PAH from seep oil. During July 1997, mussels (*Mytilus trossulus*, sample 36) were collected from Whale Island at the mouth of Katalla Slough, and juvenile coho salmon (*Oncorhynchus kisutch*, sample 37) were collected from Oil Creek, which drains the oil-seep area of the Katalla oil field into Katalla Slough. An active oil seep was located about 100 m from the point where the juvenile

TABLE 1. Total Polynuclear Aromatic Hydrocarbon (TPAH) Concentrations in Sediments, Oils, and Coals, and Source Indicator Indices^a

location (no.)	depth	TPAH	MSE(Kat)	MSE(CH)	DPI	OI	RI
Benthic GOA Sediments							
Cross Sound (1)	134	63	2.55	0.48	0.28	0.15	0.5
Cross Sound (2)	132	40	2.86	0.74	0.12	NA	NA
Yakutat Bay (3)	138	96	2.52	0.54	0.10	0.17	<0.1
Yakutat Bay (4)	138	78	2.79	0.59	0.10	NA	NA
Bering Trough (5)	308	3070	1.64	0.25	0.13	0.24	<0.1
East Kayak Island (6)	122	2520	1.82	0.30	0.13	0.25	<0.1
East Kayak Island (7)	120	3150	1.61	0.24	0.13	NA	NA
West Kayak Island (8)	159	4370	1.80	0.23	0.14	0.24	0.1
Pt. Whitney (9)	119	1670	1.66	0.20	0.14	0.24	0.1
C. Hinchinbrook (10)	106	799	1.59	0.21	0.14	0.22	0.1
C. Hinchinbrook (11)	128	1980	1.55	0.23	0.14	0.24	0.1
Hinchinbrook Entrance (12)	270	401	1.75	0.29	0.16	0.22	0.1
Hinchinbrook Entrance (13)	277	326	2.55	0.54	0.13	NA	NA
Constantine Harbor (14)	0	626	2.38	0.25	0.11	0.31	<0.1
LaTouche Passage (15)	255	572	4.41	0.52	0.21	0.37	2.0
Sleepy Bay (16)	145	1090	2.13	0.25	0.13	0.19	0.2
Sleepy Bay (17)	145	1090	2.07	0.26	0.13	NA	NA
East Snug Harbor (18)	264	1990	1.79	0.23	0.12	0.19	0.2
East Snug Harbor (19)	264	1870	2.01	0.25	0.13	NA	NA
NE Snug Harbor (20)	120	1160	2.10	0.26	0.13	0.21	0.1
NE Snug Harbor (21)	120	1150	1.68	0.19	0.14	NA	NA
Terrestrial Sediments							
Duktoth River (22)		5780	2.75	0.86	0.09	0.11	0.2
Cape Yakataga (23)		287	2.07	0.86	0.07	0.22	0.3
Bering River (24)		401	3.83	0.89	0.07	0.17	<0.1
Bering Lake (25)		950	7.28	1.35	0.09	0.12	0
Shepherd Creek (26)		3200	7.21	1.17	0.25	0.13	0
Kushtaka Lake (27)		499	7.50	1.31	0.30	0.10	0
Kushtaka Lake (28)		231	8.46	1.77	0.31	0.12	0
Berg Lake (29)		545	6.99	1.09	0.15	0.12	0
Copper R. delta (30)		21	NA	NA	0.05	NA	NA
Copper R. delta (31)		34	NA	NA	0.17	NA	NA
Bering River Coal Samples							
Queen Vein (32)		58 200	6.46	0.97	0.36	0.11	0
Carbon Ridge (33)		2960	7.20	1.14	0.59	0.08	0
Katalla Beach (34)		34 300	3.25	0.60	0.17	0.12	<0.1
Katalla Seep Oil							
Un-weathered (35)	11	100 000	0 ^b	2.68	0.18	0.12	13
Weathered (35A)		313 000	0.05	1.21	0.18	0.12	11
Katalla Mussels							
Whale Island (36)		8.5	NA	NA	NA	NA	NA
Katalla Salmon							
Oil Creek (37)		156	NA	NA	NA	NA	NA

^a Collection locations are indicated in Figure 1 by the sample numbers following location names here. Depth (m) is the benthic depth of marine sediments. The indexes indicated by MSE(Kat) and MSE(CH) are goodness-of-fit measures of PAH concentration patterns of samples as compared with patterns characteristic of Katalla oil and Constantine Harbor sediments (see Methods). DPI, OI, and RI refer to the ratios: C2-dibenzothiophene/C-2 phenanthrene, oleanane/C₃₀-hopane, and triaromatic sterane/methylchrysene. NA, not analyzed. ^b By definition.

salmon were collected, and oil from the seep entered Oil Creek upstream from the collection point.

Sample Analysis. Procedures for the quantitative determination of PAH are described in ref 19, and for ratios of selected biomarkers in ref 20. Bulk coal samples were pulverized to <0.5 mm particles for analysis. PAH analysis was done on undried samples; biomarker analysis was done on samples air-dried and ground to pass a 30-mesh sieve. Both techniques then utilize dichloromethane extractions of the hydrocarbons followed by fractionation and purification by alumina/silica gel chromatography; PAH samples were further purified by size-exclusion HPLC. PAH were measured by gas chromatography/mass spectrometry (GC/MS) in the selected ion monitoring mode (SIM). PAH analytes included dibenzothiophenes and PAH containing 2–5 rings. Selected biomarker ratios were calculated from GC/MS/SIM chromatograms (*m/z* 191, terpanes and oleanane) and GC/MS scans of unspiked aromatic hydrocarbon fractions

(extracted ion chromatograms, *m/z* 231 for triaromatic steranes and *m/z* 242 for methylchrysenes).

Method detection limits (MDL) were determined experimentally for PAH (21) and generally were 1 ng of PAH/g of sample weight. Concentrations below MDL were treated as 0. All concentrations above MDL are reported on a dry-weight basis.

Data Analysis. Concentrations of TPAH were calculated by summing the concentrations of each of the PAH above MDL. The relative concentrations of PAH were calculated as the ratio of each respective PAH concentration to the TPAH concentration.

Patterns of relative PAH concentrations in samples were compared with patterns characteristic of intertidal sediments at Constantine Harbor (CH) in PWS and of oil from the Katalla oil field by adapting procedures in ref 8. The pattern of relative PAH concentrations in intertidal sediments at CH (from ref 8) was used as a reference pattern because PAH in



FIGURE 2. Particulate coal in strand-lines on the beach at Katalla, AK, near sampling station 34. Photograph by S. Kallick July 1997.

these sediments have remain unchanged since 1977 (1) and are representative of deeper subtidal sediments elsewhere inside PWS (8).

Pattern similarity of the i th sample to CH sediments was calculated as the mean square error [$MSE_i(CH)$] of logarithmically transformed proportions:

$$\frac{1}{14} \sum_{j=1}^{14} \left[\ln \left(\frac{p_{CH,j}}{p_{ij}} \right) \right]^2 = MSE_i(CH) \quad (1)$$

where $p_{CH,j}$ and p_{ij} indicate respective proportions of the j th selected PAH analyte in the reference sample from CH and in the i th sample compared. The 14 selected PAH analytes included in eq 1 are identified in Figure 3 and were selected because they persisted above MDL in the sample set. Values of $MSE(CH) < 0.34$ are not significantly different from the CH sample (8), whereas larger values indicate greater disparity among the compared patterns. The comparison indicated by eq 1 presumes that relative PAH concentration changes from weathering losses do not occur.

Pattern similarity of the i th sample to oil from the Katalla oil field (sample 35) was calculated as

$$\frac{1}{14} \sum_{j=1}^{14} \left[\ln \left(\frac{[\hat{P}]_{Kat,j}}{[P]_{ij}} \right) \right]^2 = MSE_i(Kat) \quad (2)$$

where $[\hat{P}]_{Kat,j}$ and $[P]_{ij}$ indicate respective proportions of the j th selected PAH analyte in Katalla oil and in the i th sample compared, after correction for weathering losses. These weathering losses were assumed to follow the same first-order kinetics that describe PAH losses from oil spilled by the T/V *Exxon Valdez* (8) and are calculated as in ref 8 from the composition of unweathered Katalla oil. The same 14

PAH were compared here as above for the CH pattern. For PAH smaller in size than the selected 14 reference compounds, relative concentrations could be predicted based on k values estimated from a regression relation (Figure 6A of ref 8) of $\ln k$ and total molecular surface area (TSA, in nm^2): $\ln k = -5.10 (\text{TSA}) + 9.92$ ($r^2 = 0.75$, $n = 9$; TSA from ref 22). For PAH larger than the selected 14, weathering is assumed to be negligible ($k = 0$).

In addition, we calculated two specific compound ratios to compare with similar results presented by Page et al. (4, 5): (i) oleanane to hopane (oleanane index, hereafter OI) and (ii) C2-dibenzothiophenes to C2-phenanthrenes/anthracenes (C2D/C2P index, hereafter DPI). The concentrations of C2-phenanthrenes/anthracenes used in the latter ratio were determined from a calibration curve based on the detector response to phenanthrene [following the method used by Page et al. (4, 5)] rather than 1-methylphenanthrene, which was used for all other purposes in this report.

We also present a new PAH biomarker index, the $[C_{26}(R) + C_{27}(S)]$ triaromatic sterane ($m/z 231$)/methylchrysene ($m/z 242$) ratio, called here the refractory index (hereafter RI) because these PAH are common to most crude oils (23), including Katalla; are not generally found in coals; and are among the most resistant to weathering processes. Other aliphatic biomarker ratios are presented in ref 20; however, these data are not included here because they fail to discriminate between coal and oil in these sediments. Instead, they indicate predominantly recent terrigenous biogenic sources.

Results

Katalla Oil and Bering River Coal Samples. The RI values for the unweathered and weathered Katalla oil are 13 and 11 as compared to values < 0.1 for the Bering River coal (compare

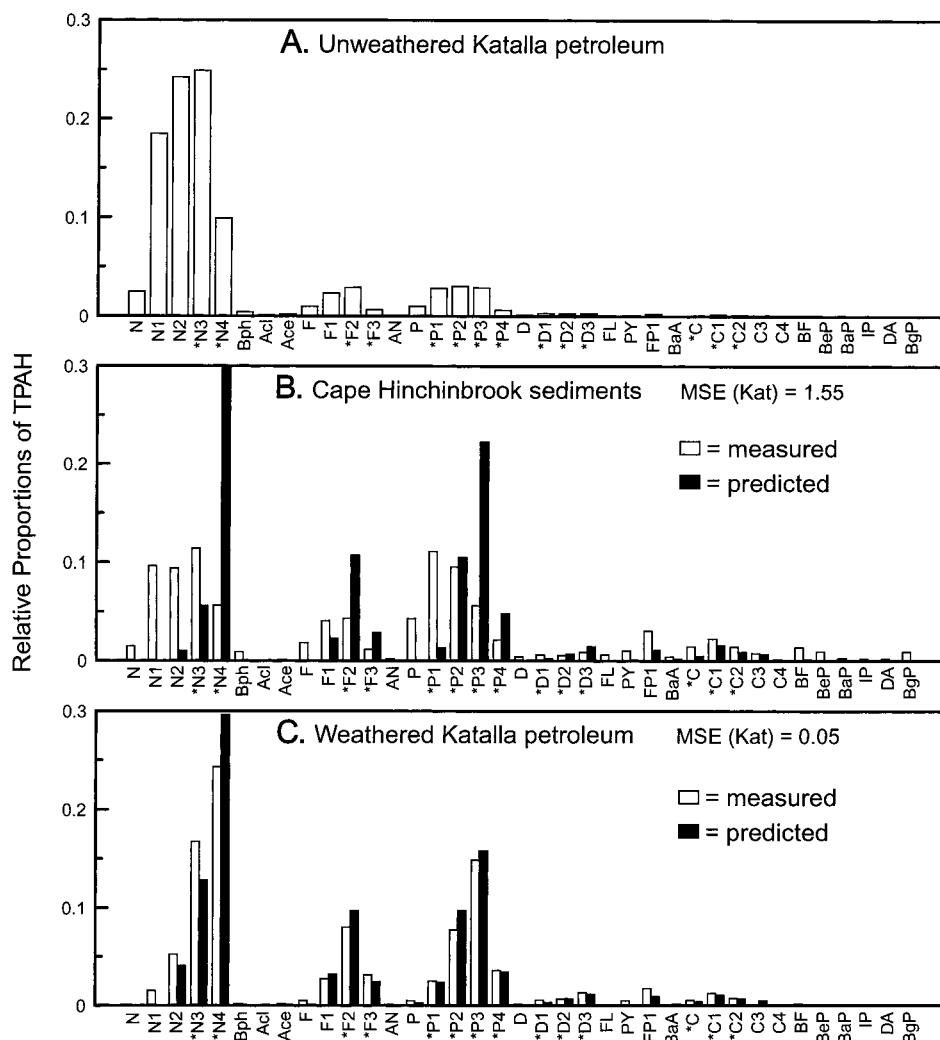


FIGURE 3. (A) Relative PAH concentrations measured in unweathered Katalla oil (sample 35). (B) Relative PAH concentrations measured in benthic sediments near Cape Hinchinbrook (sample 11) compared with predicted concentrations based on weathering of Katalla oil. (C) Comparison of predicted and measured relative PAH concentrations in an actual sample (35A) of weathered Katalla oil. MSE is a goodness-of-fit statistic of measured and predicted relative PAH concentrations (see Methods). The PAH analytes are abbreviated with numbers indicating alkyl carbon atoms as follows: N, naphthalenes; Bph, biphenyl; Acl, acenaphthylene; Ace, acenaphthene; F, fluorenes; AN, anthracene; P, phenanthrenes/anthracenes; D, dibenzothiophenes; FL, fluoranthene; PY, pyrene; FP1, C1-fluoranthenes/pyrenes; BaA, benz[a]anthracene; C, chrysenes; BF, benzo[b+k]fluoranthene; BeP, benzo[e]pyrene; BaP, benzo[a]pyrene; IP, indeno[1,2,3-c,d]pyrene; DA, dibenz[a,h]anthracene; BgP, benzo[g,h,i]perylene. The 14 PAH selected to calculate the MSE statistics of model fits in eqs 1 and 2 are indicated by an asterisk (*).

samples 32–35, Table 1). In contrast, values of the OI and DPI for the coal samples bracket those for the oil samples. The OI range from 0.08 to 0.12 in the coal samples as compared with 0.12 in the oil samples, and the DPI range from 0.17 to 0.59 for coal as compared with 0.18 for oil. The DPI value for particulate coal collected from the beach at Katalla (Figure 2) is 0.17, almost identical with the corresponding value for Katalla oil. Thus, of these three indexes, only the RI has clearly different values for Bering River coal as compared with Katalla oil.

Comparison of relative PAH concentrations of Katalla oil before and after exposure to the environment shows that substantial weathering losses of PAH occur before seep oil enters the GOA (Figure 3A,C). The seep oil collected at Katalla had already lost substantial proportions of the lower molecular weight PAH before entering Oil Creek. The MSE(Kat) value of 0.05 for the weathered seep oil (sample 35A, Table 1) indicates that the model used to account for weathering losses in eq 2 predicts the 14 selected PAH concentrations that on average differ from observed concentrations within $\exp \pm [\text{MSE(Kat)}]^{1/2}$, which is within 25% (Figure 3C). In

contrast, the MSE(CH) value of 1.21–2.68 for seep oil indicates that these relative PAH concentrations differ from corresponding concentrations at CH by over a factor of 3 on average.

The PAH composition patterns of the coal samples resemble the CH pattern much more than any weathered Katalla oil pattern. The coal sample most similar to the CH pattern is from the beach at Katalla, with an MSE(CH) of 0.60 (sample 34, Table 1). The other two coal samples (samples 32 and 33, Table 1) are less similar, with MSE(CH) of 0.97 and 1.14. However, the MSE(Kat) values of 3.25–7.2 for these coals indicate PAH composition patterns that are very different from weathered Katalla oil, implying discrepancies over a factor of 6 on average.

Benthic GOA Sediments. The PAH in benthic sediments increases dramatically between Yakutat Bay and Bering Trough along the trajectory of the ACC (Table 1, Figure 1). Concentrations of TPAH increase from <100 ng/g at stations east of Bering Trough to 799–4370 ng/g at stations from Bering Trough to Cape Hinchinbrook. At Hinchinbrook Entrance and inside PWS, TPAH concentrations range from

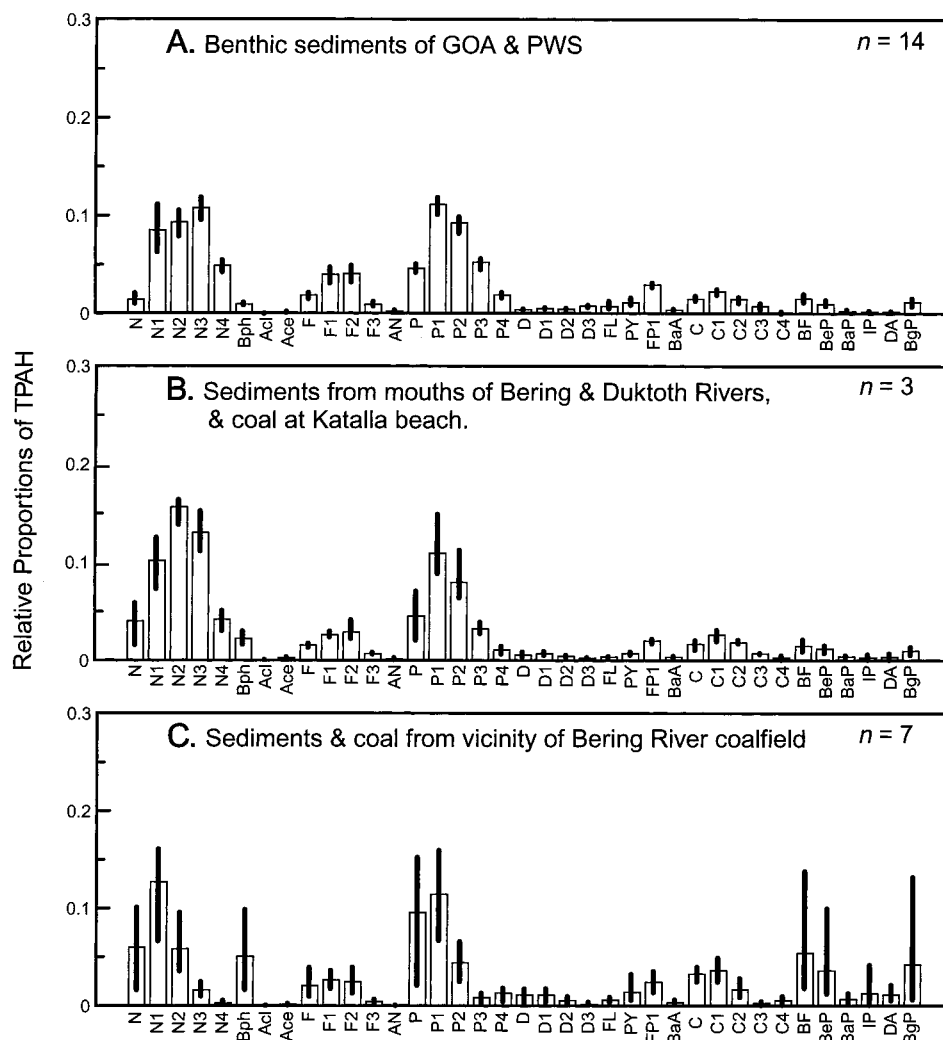


FIGURE 4. Proportions of PAH relative to total PAH (TPAH) in (A) benthic sediments of the Gulf of Alaska (GOA) west of Yakutat (samples 6-12, 14, and 16-21; $n = 14$), (B) sediments from the mouths of the Bering and Duktorth Rivers and particulate coal on the beach at Katalla (samples 22, 24, and 34; $n = 3$), and (C) sediments and native coal from the Bering River coal field and vicinity (samples 25-29, 32, and 33; $n = 7$). Vertical bars indicate ranges.

326 to 1990 ng/g. Westward of Yakutat Bay, the OI ranges from 0.19 to 0.37, and the DPI ranges from 0.11 and 0.21 (Table 1). The RI is very low (≤ 0.2) except at one station (LaTouche passage, sample 15), where it is 2.0 (Table 1).

Composition patterns of PAH in sediments of Bering Trough and westward into PWS are generally consistent with the CH pattern. The MSE(CH) value calculated for 14 of the 16 subtidal samples collected is ≤ 0.30 (Table 1), which is not significantly different from the CH pattern (8). The two higher MSE(CH) values of 0.54 and 0.52 result from low proportions of C3-fluorenes and -dibenzothiophenes at Hinchinbrook Entrance and at Latouche Passage.

In contrast, the PAH composition patterns of the benthic sediments are substantially different from the Katalla oil pattern, as indicated by MSE(Kat) values that range from 1.55 to 4.41 (Table 1). The MSE(Kat) value of 1.55 at Cape Hinchinbrook (sample 11, Table 1) indicates that discrepancies among PAH proportions in sediments as compared with oil usually exceed a factor of 3, after accounting for weathering losses, with even greater discrepancies at the remaining stations. Note that these discrepancies are minimized by accounting for weathering losses. The less substituted PAH homologues are present at higher relative concentrations in benthic sediments at Cape Hinchinbrook and elsewhere when compared with relative concentrations predicted for weathered Katalla oil (Figures 3B and 4A). This

indicates that weathering losses of PAH expected for Katalla oil do not occur in these benthic sediments.

Terrestrial Samples. The PAH in sediments collected from drainages of the Duktorth and Bering Rivers, but not the Copper River, are often substantial (Table 1). The TPAH concentration of 5780 ng/g in sediments at the mouth of the Duktorth River exceeds the concentration found in any of the benthic sediments collected from the GOA. In sediments from the Bering River drainage, TPAH concentrations range from 231 to 3200 ng/g. In contrast, TPAH concentrations in sediments collected from the Copper River delta are < 50 ng/g.

Values of the OI, DPI, and RI for terrestrial sediments from the Bering and Duktorth River drainages are similar to those of benthic GOA sediments. In these riverine samples, the OI ranges from 0.10 to 0.22, the DPI ranges from 0.07 to 0.31, and the RIs are ≤ 0.3 .

Similar PAH composition patterns characterize sediments collected near the mouths of the Duktorth and Bering Rivers and particulate coal from the beach at Katalla (Figure 4B) and resemble the pattern characteristic of benthic sediments in the GOA and in PWS (compare Figure 4, panels A and B). Relative proportions of most PAH are nearly identical among these samples, with generally decreasing proportions of more alkyl-substituted homologues.

As with the coal samples, comparison of MSE(CH) and MSE(Kat) values indicates that PAH composition patterns of the terrestrial samples resemble the CH pattern more closely than any weathered Katalla oil pattern. Most of the MSE(CH) values range from 0.86 to 1.35, but most of the MSE(Kat) values exceed 3 (Table 1). Samples collected closer to the Bering River coal field contain lower proportions of more substituted naphthalenes than samples collected closer to the GOA. Proportions of C3- and C4-naphthalene homologues are consistently less than 3% of TPAH in samples of sediments or native coal collected near or within the coal field (Figure 4C) as compared with proportions above 10% in Katalla beach coal or in sediments from the mouths of the Bering and Duktoth Rivers (Figure 4B). However, proportions of PAH homologues other than naphthalenes are more similar among the coal and sediment samples collected (compare Figure 4, panels A–C) with the C1- or C2-homologues most abundant. This includes five-ring PAH, which are evident in coal and sediment samples, but not in the seep-oil samples (compare Figures 3 and 4).

Samples collected near the Bering River coal field also show greater variability among patterns of PAH proportions. Proportions of PAH in benthic samples from the GOA or PWS are usually within 1% of the mean (Figure 4A) as compared with more than 3% in terrestrial samples (Figure 4B), and the greatest ranges are associated with samples collected nearest the Bering River coal field (Figure 4C). This increased variability indicates that the PAH composition of coal beds within the Bering River field is not homogeneous.

Tissue Samples. The distribution of PAH detected in coho salmon at Oil Creek is generally consistent with weathered Katalla oil, although the accumulated TPAH burden of 156 ng/g was so low that some PAH characteristic of the oil are below MDL. The PAH homologue groups detected in order of decreasing abundance are phenanthrene/anthracenes > chrysenes > fluoranthene/pyrenes > fluorenes \approx naphthalenes, and the distributions of alkyl-substituted homologues within each group are consistent with those of weathered Katalla oil (Figure 3C). In contrast, only methylchrysenes were detected above MDL in the mussels collected from the mouth of Katalla slough, at a TPAH concentration of 8.5 ng/g.

Discussion

The available evidence is uniformly consistent with the hypothesis that coal is the source of PAH in the benthic sediments of PWS and the northern GOA. This evidence includes (i) the geological setting, which leads to a straightforward process for the transformation and transport of bulk coal in source beds to fine-grained coal particles in benthic sediments; (ii) the geographic distribution of source coal beds; (iii) the similar geochemical analyte profiles of sediments and coals but not oil; (iv) the persistence of lower molecular weight PAH in sediments, indicating absence of weathering; and (v) the absence of bioaccumulated PAH in mussels proximal to the Katalla beach coal, indicating absence of bioavailability from coal. Although some of this evidence does not contradict the hypothesis of oil seeps as a dominant PAH source, much of the evidence does.

Large active glaciers (Figure 1) promote the erosion, pulverization, and transport of coal from the Kulthieth Formation to the northern GOA. These glaciers overlie most of the Formation, and in this century have undergone significant retreat, interrupted by several surging events (24, 25). This glacial activity has exposed progressively larger coal-bearing areas to hydraulic erosion and flushing. Coal seams that remain underneath these glaciers are exposed to powerful erosive forces, which pulverize coal outcrops before hydraulic flushing to the adjacent GOA. The extensive folding and fragmentation of the Formation from tectonic activity

(26) results in coal deposits that have been subjected to high temperatures and pressures, causing coal beds to fracture into easily eroded pods or lenses of widely varying composition. Coals eroded from exposed outcrops of these deposits become progressively more mixed during hydraulic transport, consistent with our observation that PAH composition patterns converge with decreasing variability en route to the benthic sediments of the GOA.

Further erosion and transport processes are clearly visible at the beaches near Katalla, where abrasion of dispersed particulate coal by wave action on the low-gradient sand/coal beaches may be readily observed (Figure 2). The specific gravity of these coals (~ 1.2) is low enough to permit long-distance transport of fine coal particles by the ACC but high enough to permit deposition in calmer waters of PWS.

Geographically, the increase in sediment TPAH concentration in benthic GOA sediments collected west of Yakutat Bay corresponds with the eastern extent of the Kulthieth Formation. Transport of eroded coal from the Formation is supported by the pattern similarity of the high PAH content we found at the Duktoth River. The higher TPAH concentration we measured in the silty Duktoth River sediment as compared with benthic GOA sediments is consistent with dilution of Duktoth sediments by noncoal bearing sediment entrained from the east in the ACC.

The coal source is also consistent with the observed absence of PAH weathering losses and absence of bioavailability. Weathering losses of PAH confined within a solid matrix such as coal would proceed much more slowly than PAH dissolved within a liquid such as oil. Also, PAH confined within coal particles cannot migrate readily into biological tissues, so coal-PAH are not readily bioavailable (14). Hence, we find the absence of PAH in mussels at Katalla despite the presence of particulate coal on adjacent beaches.

In contrast to coal, both visual and analytical results indicate that PAH introduced into the GOA from oil seeps is negligible. Visually, the usual absence of sheens near reported seeps at Yakataga, the Malaspina Forelands, or on Katalla Slough suggests miniscule oil production rates. Analytically, the PAH composition patterns of the PWS and GOA sediments (Figure 4A) are nearly identical with coal on the beach at Katalla (Figure 4B) but are clearly different than Katalla oil, weathered or not (compare Figures 3A, 3B, and 4B). Also, the $RI \leq 0.2$ indicates the near-absence of triaromatic steranes as compared with methylchrysenes for coal and for most of the sediment samples. In contrast, the RI of Katalla oil is about 100-fold higher. Triaromatic steranes are thus clearly present in Katalla oil and are among the most resistant to weathering, so their absence from GOA sediments contraindicates the Katalla oil source. Finally, PAH in Katalla oil clearly are bioavailable prior to entering the northern GOA, as indicated by the appearance of PAH in juvenile salmon at Oil Creek 100 m downstream from the oil seeps there, but oil production rates are so small that these PAH fail to reach mussels 9 km away at the mouth of Katalla Slough. These analytical results confirm the negligible contributions of PAH from Katalla oil to benthic sediments suggested by the visual evidence.

In contrast to coal, it is not clear how oil produced from seeps at Katalla and elsewhere might be transported to subtidal sediments of the GOA and PWS in an unweathered state. To sink in seawater, oil must associate with higher density particles (e.g., sediment grains). These grains must be small enough (<0.1 mm) to persist for days within the mixed layer of the GOA during transport across 100 km distances. The ratio of surface area to volume for particles of this size exceeds 10^4 m $^{-1}$. Therefore, oil transported by suspended sediments should experience rapid loss of lower molecular weight PAH (27). We observed such losses in seep oil at Katalla before it even reached the adjacent slough en

route to the GOA but did not observe corresponding losses among PAH in the benthic sediments of the GOA or PWS.

The natural barriers that suppress the incorporation of oil into benthic sediments are demonstrated by other studies on the environmental fate of oil. For example, several EVOS studies have confirmed that spilled oil did not appreciably contaminate the subtidal sediments of PWS in water deeper than about 20 m (2, 4, 5, 9, 10). Substantial fluxes of oil to subtidal sediments were observed only adjacent to heavily oiled beaches (10). The transported oil collected in sediment traps lost virtually all the lower molecular weight PAH due to weathering. It therefore seems highly unlikely that seep oil can be transported unaltered across 100-km distances to the deeper parts of PWS when oil spilled from the EVOS was found only in the shallow subtidal zone and weathered rapidly.

The previously reported identification of seep oil as the source of the background PAH in PWS (2, 4–6) was based on two geochemical parameters, the presence of oleanane and the DPI, which have proved inadequate to distinguish seep oil from coal in the study area. The OI and the DPI remain at the same low levels whether in coal samples, onshore or offshore sediment samples, or oil samples and so cannot be used to identify an oil source as implied in refs 6 and 28. However, other PAH ratios do contradict an oil source here. For example, ratios of alkyl-substituted phenanthrenes to like-substituted chrysenes are around 1–2 for benthic GOA sediments in contrast to about 10 for Katalla oil (regardless of weathering state; see Figure 3). Also, the MSE(Kat) statistic reported here summarizes the simultaneous agreement of 14 such ratios and indicates that discrepancies among these analytes in GOA sediments and Katalla oil usually exceed a factor of 3.

We conclude that coal is the major source of background PAH in PWS and that the contributions from oil sources such as Katalla are probably negligible. Because PAH in coal are not bioavailable, the presence of coal in the benthic sediments of this region confers no adaptive benefit to biota of the marine ecosystem with respect to episodic PAH insults from anthropogenic pollution sources. Prince William Sound has suffered two such major insults in the recent past: from fuel oil and asphalt released out of tanks that ruptured at Valdez during the 1964 earthquake (29–31) and from the EVOS 25 years later. Apart from the impacts of these events, most of PWS should be considered pristine with regard to oil pollution. That the background hydrocarbons are due to coal and not to chronic oil pollution makes the area ideal as a natural laboratory to study the long-term effects of these catastrophic oil pollution events.

Acknowledgments

The authors thank R. Sanders for coal samples from the Bering River field; S. Kallick and M. Twitchell for sample collection at Katalla; the crew of the NOAA ship *Ranier* for assistance with collection of subtidal sediments from the GOA and PWS; and M. Larsen, L. Holland, and J. Lunasin for PAH analysis. The research described in this paper was supported in part by the *Exxon Valdez* Oil Spill Trustee Council. However, the findings and conclusions presented by the authors are their own and do not necessarily reflect the views or position of the Trustee Council.

Literature Cited

- (1) Short, J. W.; Babcock, M. M. Prespill and postspill concentrations of hydrocarbons in mussels and sediments in Prince William Sound. In *Proceedings of the Exxon Valdez Oil Spill Symposium*; Rice, S. D., et al., Eds.; American Fisheries Society Symposium 18; American Fisheries Society: Bethesda, MD, 1996; pp 149–166.
- (2) Page, D. S.; Boehm, P. D.; Douglas, G. S.; Bence, A. E. Identification of hydrocarbon sources in the benthic sediments of Prince William Sound and the Gulf of Alaska following the *Exxon Valdez* oil spill. In *Exxon Valdez Oil Spill: Fate and Effects in Alaskan Waters*; Wells, P. G., Butler, J. N., Hughes, J. S., Eds.; ASTM, STP 1219; ASTM: Philadelphia, 1995; pp 41–83.
- (3) Boehm, P. D.; Douglas, G. S.; Burns, W. A.; Mankiewicz, P. J.; Page, D. S.; Bence, A. E. *Mar. Pollut. Bull.* **1997**, *34*, 599–613.
- (4) Page, D. S.; Boehm, P. D.; Douglas, G. S.; Bence, A. E.; Burns, W. A.; Mankiewicz, P. J. *Environ. Toxicol. Chem.* **1996**, *15*, 1266–1281.
- (5) Page, D. S.; Boehm, P. D.; Gilfillan, E. S.; Bence, A. E.; Burns, W. A.; Mankiewicz, P. J. Effects of the *Exxon Valdez* oil spill on the subtidal organic geochemistry of two bays in Prince William Sound, Alaska. In *Proceedings of the 19th Arctic & Marine Oilspill Program Technical Seminar*; 1996; pp 1195–1209.
- (6) Page, D. S.; Boehm, P. D.; Douglas, G. S.; Bence, A. E.; Burns, W. A.; Mankiewicz, P. J. *Mar. Pollut. Bull.* **1997**, *34*, 744–749.
- (7) Bence, A. E.; Kvenvolden, K. A.; Kennicutt, M. C. *Org. Geochem.* **1996**, *24*, 7–42.
- (8) Short, J. W.; Heintz, R. A. *Environ. Sci. Technol.* **1997**, *31*, 2375–2384.
- (9) O'Clair, C. E.; Short, J. W.; Rice, S. D. Contamination of intertidal and subtidal sediments by oil from the *Exxon Valdez* in Prince William Sound. In *Proceedings of the Exxon Valdez Oil Spill Symposium*; Rice, S. D., et al., Eds.; American Fisheries Society Symposium 18; American Fisheries Society: Bethesda, MD, 1996; pp 61–93.
- (10) Short, J. W.; Sale, D. M.; Gibeau, J. C. Nearshore transport of hydrocarbons and sediments after the *Exxon Valdez* oil spill. In *Proceedings of the Exxon Valdez Oil Spill Symposium*; Rice, S. D., et al., Eds.; American Fisheries Society Symposium 18; American Fisheries Society: Bethesda, MD, 1996; pp 40–60.
- (11) Sanders, R. B. Alaska's coal resources, an international view. In *Transactions of the Third Circumpacific Energy and Mineral Resources Conference*; Watson, S. T., Ed.; American Association of Petroleum Geologists: Tulsa, OK, 1982; pp 507–512.
- (12) Wahrhaftig, C.; Bartsch-Winkler, S.; Stricker, G. D. Coal in Alaska. In *The Geology of Alaska: The Geology of North America, Vol. 1*; Plafker, G., Berg, H. C., Eds.; Geological Society of America: Boulder, CO, 1994; pp 937–978.
- (13) Holloway, C. D. *Map showing coal fields and distribution of coal bearing rocks in the eastern part of southern Alaska*; U.S. Geological Survey Open File Report 77-169D; 1 map sheet, scale = 1:1,000,000; USGS: Denver, CO, 1977.
- (14) Chapman, P. M.; Downie, J.; Maynard, A.; Taylor, L. A. *Environ. Contam. Toxicol.* **1996**, *15*, 638–642.
- (15) Magoon, L. B., III. Petroleum Resources in Alaska. In *The Geology of Alaska: The Geology of North America, Vol. 1*; Plafker, G., Berg, H. C., Eds.; Geological Society of America: Boulder, CO, 1994; pp 398–450.
- (16) Miller, D. J. *Geology of the southeastern part of the Robinson Mountains, Yakataga District, Alaska*; U.S. Geological Survey Oil and Gas Investigations map M-187, 2 sheets, scale 1:63,360; USGS: Denver, CO, 1957.
- (17) Plafker, G.; Miller, D. J. *Reconnaissance geology of the Malaspina District, Alaska*; U.S. Oil and Gas Investigations Map OM-189, scale 1:125,000; USGS: Denver, CO, 1957.
- (18) Blasco, D. P. Occurrences of oil and gas seeps along the gulf coast of Alaska. *Offshore Technology Conference Abstracts*; Society of Petroleum Engineers—American Institute of Mechanical Engineers: Houston, TX, 1976.
- (19) Short, J. W.; Jackson, T. J.; Larsen, M. L.; Wade, T. L. Analytical methods used for the analysis of hydrocarbons in crude oil, tissues, sediments, and seawater collected for the Natural Resources Damage Assessment of the *Exxon Valdez* oil spill. In *Proceedings of the Exxon Valdez Oil Spill Symposium*; Rice, S. D., et al., Eds.; American Fisheries Society Symposium 18; American Fisheries Society: Bethesda, MD, 1996; pp 140–148.
- (20) Carlson, P. R.; Kvenvolden, K. A.; Hostettler, F. D.; Rosenbauer, R. J.; Warden, A. *Fate of spilled oil in Prince William Sound: Diary of a Forensic Geology Study*; U.S. Geological Survey Open-File Report 97-518; USGS: Denver, CO, 1997.

- (21) Glaser, J. A.; Forest, D. L.; McKee, G. D.; Quave, S. A.; Budde, W. L. *Environ. Sci. Technol.* **1981**, *15*, 1426–1435.
- (22) Pearlman, R. S.; Yalkowsky, S. H.; Banerjee, S. J. *Phys. Chem. Ref. Data* **1984**, *13*, 555–562.
- (23) Killops, S. D.; Howell, V. J. *Estuarine Coastal Shelf Sci.* **1988**, *27*, 237–261.
- (24) Post, A. J. *Glaciol.* **1969**, *6*, 229–240.
- (25) Molnia, B. F.; Post, A. *Phys. Geogr.* **1995**, *16*, 87–117.
- (26) Plafker, G.; Moore, J. C.; Winkler, G. R. Geology of southern Alaska margin. In *The Geology of Alaska: The Geology of North America, Vol. 1*; Plafker, G., Berg, H. C., Eds.; Geological Society of America: Boulder, CO, 1994; pp 398–450.
- (27) Mackay, D.; Paterson, S.; Boehm, P. D.; Fiest, D. L. Physical-chemical weathering of petroleum hydrocarbons from the Ixtoc I blowout—chemical measurements and a weathering model. In *Proceedings of the 1981 Oil Spill Conference*; American Petroleum Institute Publication 4334; API: Washington, DC, 1981; pp 453–460.
- (28) Douglas, G. S.; Bence, A. E.; Prince, R. C.; McMillen, S. J.; Butler, E. L. *Environ. Sci. Technol.* **1996**, *30*, 2332–2339.
- (29) Kvenvolden, K. A.; Hostettler, F. D.; Rapp, J. B.; Carlson, P. R. *Mar. Pollut. Bull.* **1993**, *26*, 24–29.
- (30) Kvenvolden, K. A.; Carlson, P. R.; Threlkeld, C. N.; Warden, A. *Geology* **1993**, *21*, 813–816.
- (31) Kvenvolden, K. A.; Hostettler, F. D.; Carlson, P. R.; Rapp, J. B.; Threlkeld, C.; Warden, A. *Environ. Sci. Technol.* **1995**, *29*, 2684–2694.

Received for review February 6, 1998. Revised manuscript received August 17, 1998. Accepted September 28, 1998.

ES980130W