Exxon Valdez Oil Spill
Restoration Project Final Report

Evaluation of Yakataga Oil Seeps as Regional Background Hydrocarbon Sources in Benthic Sediments of the *Exxon Valdez* Spill Area

Restoration Project 01599
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Restoration Project 00599
Annual Report

Study History: This project was initiated in FY00.

Abstract: Hydrocarbon distributions among samples of water, suspended particulate matter (SPM), and riparian sediment collected from Yakataga District coastal watersheds were compared with northern Gulf of Alaska benthic sediment geochemistry to determine the fate of petroleum-seep derived hydrocarbons in the fluvio-marine environment. Only the Johnston Creek drainage conveyed a detectable (~4 $\mu g\ L^{-1}$ total PAH) load of seep-derived hydrocarbons to the Gulf of Alaska. The Yakataga District petroleum seeps collectively account for a negligible proportion of the hydrocarbon burden in Gulf of Alaska benthic sediments. Coaly material was separated from Gulf of Alaska sediment samples using a heavy liquid, but this material accounted for only a small portion of the total PAHs (1–6%) and total *n*-alkanes (0.4–2%) in these samples. The remainder of the hydrocarbon burden in these sediments is associated with the denser siliciclastic material. The major source(s) for these hydrocarbons remains elusive, but the combination of benthic sediment geochemistry and well-documented long-shore sediment transport processes clearly implicates the glaciofluvial drainage system of the Malaspina Glacier as a prominent vector by which this hydrocarbon load is introduced into the Gulf of Alaska.

Key Words: *Exxon Valdez*, coal, crude oil, petrogenic rock, fingerprinting, Gulf of Alaska, oil seeps, Kulthieth Formation, Poul Creek Formation, Yakataga Formation.

Project Data: The data herein consist of hydrocarbon analyses of polycyclic aromatic hydrocarbons and aliphatic hydrocarbons in riparian waters and sediments near Cape Yakataga, Alaska, and adjacent benthic marine sediments from the Gulf of Alaska from Yakutat Bay to Cape St. Elias. These data are stored as Excel workbooks. The data custodian is Jeffrey Short, Auke Bay Laboratory, 11305 Glacier Highway, Juneau Alaska 99801-8626, Ph: 907.789.6065, email: Jeff.Short@noaa.gov.

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Table of Contents

Executive summary	6
Introduction	8
Objectives	10
Methods	10
Results	17
Discussion	25
Conclusions	32
Acknowledgments	32
Literature Cited	33

List of Tables

Table 1. Site Information for Benthic and Riparian Sample Stations.

Table 2. Polycyclic Aromatic Hydrocarbon Distribution Between Dissolved and Particulate Phases at Yakataga District River Sample Stations.

Table 3. Percentage of Hydrocarbons Associated with the Float Fraction (Coaly Material).

List of Figures

Figure 1. (A) Satellite image depicting sediment transport along the northern Gulf of Alaska coastline. Image courtesy of NASA Earth Observatory website: <http://earthobservatory.nasa.gov/Newsroom/NewImages/Images/Alaska_tmo_2003234_lrg.jpg>. (B) Inset from Figure 1A. Map of the northern Gulf of Alaska showing the sample locations for the marine (1-9) and fluvial (10-17) stations. The locations of the Katalla and Yakataga Districts are also denoted, along with the Kosakuts River (KOS), Marvitz Creek (MC), Samovar Hills (SH) area, and the Sullivan Anticline (SA).

Figure 2. (A) Detailed map (inset from Figure 1B) depicting the surficial geology of the Yakataga District. The geologic base was traced from USGS Map I-610 (Miller, 1971). Solid black circles indicate the Big River and Duktoth River sample stations. (B) Inset map showing sampling stations on Johnston and Munday Creeks. The solid triangles denote the approximate locations at which seep oil samples were collected. Other documented seep locations (from Miller, 1971) are shown as white triangles.

Figure 3. Total ion current (TIC) chromatograms illustrating the prominent UCMs in the aliphatic fractions of (A) Munday Creek and (B) Johnston Creek seep oil samples.

Figure 4. Histograms of relative hydrocarbon distributions within seep oil samples collected from Johnston Creek (gray) and Munday Creek (black): (A) PAHs, and (B) aliphatic hydrocarbons. Note the different scale for the sterane and triterpane concentrations, and that relative sterane and triterpane concentrations from the Munday Creek sample have been multiplied by a factor of 20.

Figure 5. Histograms of relative hydrocarbon distributions within bulk riparian sediments collected from stations devoid of recently documented oil seeps: (A) PAHs, and (B) aliphatic hydrocarbons. Note different scale for the steranes and triterpanes. Total PAH and total *n*-alkane concentrations (ng g^{-1} dry wt. sediment) are given in brackets.

Figure 6. Histograms of relative PAH distributions among bulk riparian sediments collected downstream from the Munday Creek oil seep at stations (A) 17, (B) 16, and (C) 15. Corresponding relative PAH distributions from the seep oil sample and the bulk riparian sediment sample (station 14) collected upstream of the seep are overlain for comparison. Histograms of relative aliphatic hydrocarbon distributions among bulk riparian sediments collected downstream from the Munday Creek oil seep at stations (D) 17, (E) 16, and (F) 15. Corresponding aliphatic hydrocarbon distributions from the seep oil sample and the bulk riparian sediment sample (station 14) collected upstream of the seep are overlain for comparison. Arrows indicate direction of flow. Total PAH and total *n*-alkane concentrations (ng g^{-1} dry wt. sediment) are given in brackets.

Figure 7. Histograms of relative hydrocarbon distributions in bulk riparian sediment collected from stations located downstream of the Johnston Creek oil seep: (A) PAHs, and (B) aliphatic hydrocarbons. Corresponding hydrocarbon distributions from the seep oil sample and the bulk riparian sediment sample (station 12) collected upstream of the seep are overlain for comparison. Total PAH and total *n*-alkane concentrations (ng g^{-1} dry wt. sediment) are given in brackets. Note that the relative sterane and triterpane concentrations in the seep oil sample have been divided by a factor of 10.

Figure 8. Histograms showing the relative PAH distributions among dissolved and suspended particulate matter phases in river water samples collected from Munday Creek stations (A) 14, (B) 17, (C) 16, and (D) 15. The total (dissolved + particulate) PAH concentrations, expressed in ng L^{-1}, are given in brackets. Asterisks denote target analytes whose concentrations are below the MDL.

Figure 9. Histograms showing the relative PAH distributions among dissolved and suspended particulate matter phases in river water samples collected from Johnston Creek stations (A) 12 and (B) 13. The total (dissolved + particulate) PAH concentrations, expressed in ng L^{-1}, are given in brackets. Asterisks denote target analytes whose concentrations are below the MDL.

Figure 10. Histograms depicting average relative hydrocarbon distributions in northern Gulf of Alaska benthic sediments: (A) PAHs, and (B) aliphatic hydrocarbons. The tick marks indicate the range of values encountered. Relative hydrocarbon distributions in SPM samples collected from the mouths of the Duktoth River (station 10) and Johnston Creek (station 13) are overlain for comparison. Total PAH and total *n*-alkane concentrations (ng g^{-1} dry wt. sediment) are given in brackets.

Figure 11. Histograms of relative hydrocarbon distributions in low-density (float) material separated from riparian sediments: (A) PAHs, and (B) aliphatic hydrocarbons. The relative hydrocarbon distributions from two area coal samples are plotted for comparison. Total PAH and total *n*-alkane concentrations (ng g^{-1} dry wt. sediment) are given in brackets.

Figure 12. Histograms comparing the average relative hydrocarbon distributions in northern Gulf of Alaska benthic sediments to corresponding distributions in samples of siltstone from the Kulthieth Formation and organic-rich shale from the Poul Creek Formation: (A) PAHs, and (B) aliphatic hydrocarbons. The tick marks indicate the range of values encountered. Total PAH and total *n*-alkane concentrations (ng g^{-1} dry wt. sediment) are given in brackets.

Executive Summary

Exxon-sponsored scientists have claimed that the benthic sediments of the northern GOA and PWS, including the region polluted by the Exxon Valdez oil spill, had already been contaminated by crude oil from natural oil seeps. EVOS Trustee scientists, who found evidence of native coal contamination in the region, subsequently challenged this conclusion. Resolution of hydrocarbon inputs from these natural sources has implications for the interpretation of EVOS Trustee studies. Some of these studies have found evidence of long-term exposure of biota to toxic polycyclic aromatic hydrocarbons (PAH) in the spill region. PAH are bioavailable from crude oils but not from coals or petrogenic shales. If the PAH associated with the natural hydrocarbon background are sequestered in refractory matrixes such as coals or shales instead of crude oils from natural seeps, then they would not be bioavailable, and therefore could not account for the biological indications of PAH exposure.

The objective of this project is to compare hydrocarbon contributions from native coals, petrogenic shales, and natural seepage crude oils to the nearshore benthic sediments of the northern Gulf of Alaska (GOA), including Prince William Sound (PWS). Three compartments were sampled, including (1) terrestrial outcrops of petrogenic shales, native coals, and terrestrial oil seeps, (2) riparian sediments and waters of streams that receive natural seep-oils, and (3) benthic sediments of the northern GOA, including Prince William Sound (PWS). The first compartment provides a chemical characterization of prospective natural hydrocarbon sources in the region. The second provides a basis for estimating the flux of hydrocarbon inputs from oil seeps to the GOA, and the third provides a direct assessment of the proportion of PAH in benthic sediments attributable to coal.

Hydrocarbon distributions among samples of water, suspended particulate matter (SPM), and riparian sediment collected from Yakataga District coastal watersheds were compared with northern Gulf of Alaska benthic sediment geochemistry to determine the fate of petroleum-seep derived hydrocarbons in the fluvio-marine environment. Petroleum samples collected near seep sources along Johnston and Munday Creeks contained hydrocarbon patterns indicative of moderate degradation, including the extensive loss of low-molecular weight *n*-alkanes ($<nC_{14}$) and the presence of large, bimodal, aliphatic unresolved complex mixtures (UCMs). After entering the fluvial systems, the petroleum seep oils had a pronounced effect on hydrocarbon concentrations in both the dissolved and SPM fractions. The dissolved phase contained markedly increased concentrations of low-molecular weight polycyclic aromatic hydrocarbons (PAHs), e.g., naphthalenes and fluorenes, reflecting the water-washed component of the seep oil. The corresponding SPM fraction exhibited more prominent UCMs and greater proportions of the higher-molecular weight constituents, e.g., chrysenes, alkylated phenanthrenes, and triterpane biomarkers. Riparian sediments collected nearer the seep sources tended to reflect the bulk composition of the seep oils, indicating that the riparian sediments may be coated with oily films, but this geochemical overprinting was not observed in samples collected from stream mouths. Of the watersheds sampled, only the Johnston Creek drainage conveyed a detectable (~4 $\mu g\ L^{-1}$ total PAH) load of seep-derived hydrocarbons to the Gulf of Alaska. The majority of this load (~ 61%) was associated with the SPM.

The Gulf of Alaska benthic sediments are broadly characterized by abundant naphthalene homologs, relatively smooth *n*-alkane envelopes (nC_9 through nC_{34}) punctuated by elevated levels of nC_{27}, nC_{29}, and nC_{31}, and small UCMs. Despite marked variations in absolute hydrocarbon concentrations among benthic sediment samples, the PAHs, aliphatic hydrocarbons, and UCMs are highly intercorrelated. Considering the magnitude of sediment loads delivered to the Gulf of Alaska and the strong relationship among hydrocarbon constituents, the Yakataga District petroleum seeps account for a negligible proportion of the hydrocarbon burden in Gulf of Alaska benthic sediments. Coaly material was separated from Gulf of Alaska sediment samples using a heavy liquid, but this material accounted for only a small portion of the total PAHs (1–6%) and total *n*-alkanes (0.4–2%) in these samples. The remainder of the hydrocarbon burden in these sediments is associated with the denser siliciclastic material. The major source(s) for these hydrocarbons remains elusive, but the combination of benthic sediment geochemistry and well-documented long-shore sediment transport processes clearly implicates the glaciofluvial drainage system of the Malaspina Glacier as a prominent vector by which this hydrocarbon load is introduced into the Gulf of Alaska.

The PAH and aliphatic hydrocarbon compositions of aqueous, SPM, and riparian sediment samples indicate that fluvial systems draining the Yakataga Forelands convey a substantive petrogenic hydrocarbon burden to the Gulf of Alaska continental shelf. The geochemical signatures of individual drainage basins vary, depending on both the types and proportions of exposed rock formations. Active petroleum seeps within these drainage basins readily overprint these geochemical signatures, and seep-derive hydrocarbons undergo fluvial transport largely through oil-SPM associations. However, the combination of modest seepage rates and high SPM loads serves to rapidly attenuate the influence of petroleum seeps on fluvial geochemistry. As a result, of the fluvial systems studied, only Johnston Creek was found to convey a discernible load of seep-derived hydrocarbons to the Gulf of Alaska.

Total hydrocarbon concentrations in Gulf of Alaska benthic sediments are highly variable; however, the relative geochemical fingerprints recorded in these sediments are remarkably similar. The persistence of this geochemical fingerprint argues against a labile hydrocarbon source, e.g., oil-SPM associations, that would undergo substantial alteration during coastal marine transport. The prominence and persistence of *n*-nonane indicates that hydrocarbons sequestered in eroded coal and shale particles sampled here are little affected by weathering processes, and persist in transport from terrestrial sources to the benthic sediments of the northern Gulf of Alaska. These hydrocarbons include the *n*-alkanes, Ph and perylene, which retain information regarding their sources as well as the hydrocarbon biomarkers. Comparison of hydrocarbon concentration patterns that characterize northern Gulf of Alaska sediments with those characterizing known hydrocarbon sources or inputs reveals significant discrepancies in every case, indicating the dominant sources of hydrocarbons in these sediments remain to be identified. The geographic association of hydrocarbons in the benthic sediments with inputs from the Malaspina Glacier, along with the regional dominance of this glacier as source of sediments, suggests that the dominant sources of hydrocarbons in benthic sediments of the northern Gulf of Alaska are probably located beneath it. Finally, previous assessments of hydrocarbon source contributions to the benthic sediments of the northern Gulf of Alaska based on statistical hydrocarbon source allocation models are not reliable, because the inventory of

sources included in these models is not complete, and because analytes with high discriminating power were not included.

Introduction

Scientists contracted by Exxon Corporation have claimed that benthic coastal sediments of the northern Gulf of Alaska (GOA), including Prince William Sound (PWS), receive crude oil produced naturally by terrestrial oil seeps at Katalla and Yakataga. If true, this suggests that the marine biota of the EVOS spill area are adapted to oil pollution, thus promoting recovery of species exposed to toxic components of oil spilled from the T/V *Exxon Valdez*. Thus, fauna that show induction of cytochrome-P450 in the spill area may be responding to natural oil pollution and not to the spilled oil. A recent study by Trustee scientists casts considerable doubt on oil from Katalla as a candidate source of hydrocarbons in these sediments, hence sources near Cape Yakataga have been emphasized by the Exxon team. This study compares hydrocarbon transport from oil seeps with shale and coal deposits in drainages where oil seeps, particulate coal or shale particles have been located in the Cape Yakataga area, to resolve their relative contributions to benthic sediments offshore of these drainages in the GOA. Resolution of hydrocarbons derived from coal will be achieved by physical separation, with less dense coal particles floated off from the more-dense inorganic fraction of sediments in an aqueous brine solution of intermediate density.

Northern Gulf of Alaska benthic sediments record a natural, petrogenic hydrocarbon burden for which there are several possible terrigenous sources, including petroleum seeps, organic-rich rocks (i.e., source rocks), organic-lean rocks, and coal beds. Fluvial transport is generally regarded as the pathway by which this natural hydrocarbon burden is delivered to the Gulf of Alaska, with subsequent transport by the Alaska Coastal Current serving to disperse these hydrocarbons over a broader area (Fig. 1A) (Armentrout, 1983; Page et al., 1996). Concentrations of PAHs in benthic sediments from the continental shelf adjacent to the Yakataga District (Fig. 1B) are typically among the highest measured in the Gulf of Alaska and Prince William Sound (Page et al., 1995; Bence et al., 1996; Short et al., 1999; Boehm et al., 2001). The spatial distribution of PAHs supports the inference that point sources, i.e., fluvial inputs, are the primary source of hydrocarbons to the Gulf of Alaska.

Recent studies have attributed significant proportions of this petrogenic background signature to petroleum seeps (Page et al., 1997; Boehm et al., 2001; Mudge, 2002). The combination of numerous prospective hydrocarbon sources and the ability of oil components to partition among free oil droplets, the dissolved phase, and suspended particulate material (SPM; for a review, see Payne et al., 2003) poses a significant challenge to resolving hydrocarbons derived from petroleum seepage. For example, Page et al. (1997) inferred that pre-anthropogenic PAH distributions in Prince William Sound benthic sediments were derived from onshore and submarine petroleum seeps in the eastern Gulf of Alaska. They estimate that between 0.4×10^6 and 1.3×10^6 L a^{-1} [360 and 1200 ton a^{-1}] of petroleum equivalents accumulate in Prince William Sound alone. However, this estimate conflicts with a previous assessment by McGee (1972) that the total amount of oil input to the Gulf of Alaska by coastal seeps constituted only

approximately 40,000 L a^{-1} [30 gallons d^{-1}]. Furthermore, the eastern Gulf of Alaska is apparently devoid of any reported submarine petroleum seeps (McGee, 1972; Rosenberg, 1972). Short et al. (1999) later emphasized the importance of particulate coal from the Bering River coal field as a hydrocarbon source, although recent work has shown that these coal beds are unable to satisfy constraints imposed by organic carbon budgets and, hence, are not likely major PAH sources (Boehm et al. 2001). This inability to adequately resolve hydrocarbon inputs from among various prospective sources may stem from inadequate identification of relevant sources as well as from possible genetic relationships between sources (Van Kooten et al., 2002), resulting in overlapping geochemical signatures (Mudge, 2002).

Statistical analyses of geochemical data have been used recently to discern contributions derived from individual hydrocarbon sources (Boehm et al., 2001; Mudge, 2002). For example, Boehm et al. (2001) calculated that seep oils accounted for approximately 40-70% of the total hydrocarbon burden in eastern Gulf of Alaska benthic sediments, and that contribution gradually declined to roughly 10-15% in the Prince William Sound area. Using a partial-least squares method and the same data set, Mudge (2002) determined that seep oil accounted for 18% of the total hydrocarbon burden among all benthic sediments sampled. Although more conservative, the latter value still requires a release of petroleum that greatly exceeds previously estimated seepage rates from McGee (1972). The large disparity between model results and field observations represents a significant incongruity between the magnitude of a given source and proportion of the hydrocarbon burden attributed to that source. This incongruity may exist because seepage rates have been significantly underestimated, or because outputs from the source-allocation models may have overestimated the seep-oil contribution, perhaps due to an inability to resolve contributions from hydrocarbon sources that are similar in composition. A more detailed evaluation of the fate of petroleum-seep derived hydrocarbons during fluvial transport from the seep to the Gulf is needed to resolve this matter.

Blasko (1976) conducted a survey of both the aqueous geochemistry of streams and the petroleum geochemistry of hydrocarbon seeps and produced oil from the Katalla and Yakataga Districts (Fig. 1B). The amount of free-phase oil, determined on a mg L^{-1} basis, was found to decline sharply immediately downstream of the seeps. Oil concentrations measured at the stream mouths were near detection limits, implying minor input of free-phase oil into the Gulf of Alaska. However, this approach neglected changes in oil partitioning among the aqueous phase and SPM; hence, these data may not be sensitive enough to resolve the magnitude of seep-derived hydrocarbons that reach the Gulf of Alaska.

This study builds on the earlier work of Blasko (1976), and directly tests the hypothesis that petroleum seeps from the Yakataga District constitute a substantial portion of the total hydrocarbon burden recorded in Gulf of Alaska benthic sediments. Our objectives are to: (1) characterize the hydrocarbon signature of petroleum seep oils entering Yakataga Forelands coastal watersheds, (2) determine the phase-associations of seep oils during fluvial transport to the Gulf, (3) compare the hydrocarbon compositions among fluvial SPM and Gulf of Alaska benthic sediment samples to discern the influence of coastal petroleum seeps on benthic sediment geochemistry, and (4) assess the significance of other sources contributing hydrocarbons to the fluvio-marine environment. Water samples, SPM, and riparian sediments were collected from petroleum seep-affected streams and from streams with no recently

documented seeps to evaluate the influence of seep oils on sediment and aqueous geochemistry. Multiple samples were collected from fluvial systems with known seeps to determine the extent to which the oil seep-derived geochemical signature was attenuated prior to reaching the Gulf of Alaska. A suite of hydrocarbons, including PAHs, *n*-alkanes, and other petroleum biomarkers were analyzed to develop a geochemical fingerprint that could be used to determine the fate of seep-derived hydrocarbons during fluvio-marine transport. Samples from other prospective hydrocarbon sources, including source rocks and coal beds, were analyzed to delineate the significance of these sources. A heavy-liquid separation procedure was used to isolate and directly quantify the proportion of the sediment hydrocarbon burden associated with lower-density, i.e., coaly, material. These data were then combined to evaluate the influences of these prospective hydrocarbons on sediment geochemistry in the northern Gulf of Alaska fluvio-marine environment.

Objectives

This project has 1 objective:

1. Measure contributions of hydrocarbons from oil seeps and from terrestrial coal deposits to benthic marine sediments adjacent to the northern GOA margin from Icy Bay to the Duktoth River.

Methods

A. Study Area

The study area is located along the northern Gulf of Alaska and extends generally from Yakutat Bay to the Katalla region (Figs. 1&2). This region includes large, piedmont glaciers such as the Malaspina and Bering Glaciers, numerous glacial meltwater streams, and generally smaller, non-glacial streams fed by surface runoff and ground water. Geologically, this area is part of the Yakutat micro-continent which docked against and deformed the southern Alaska borderland in the Miocene (Plafker et al., 1994). The Yakutat terrane consists primarily of thick, Eocene to Miocene fluvial to marine sedimentary rocks of the Kulthieth, Poul Creek, and Yakataga Formations (Figure 2A&B). These sedimentary formations have been deformed and uplifted during collision of the Yakutat terrane with southern Alaska and are well exposed in a series of east-west thrust structures that generally parallel the Alaska coastline.

The Kulthieth Formation contains fresh water fluvial sands, siltstones, and shale, and commonly contains coal beds (Plafker, 1987). Coal samples collected from the Kulthieth Formation are unusual in that they contain Type I/II kerogen and will generate oil during thermal maturation (Van Kooten et al., 2002), rather than gas as is typical for most coal deposits. The Kulthieth Formation ranges in thermal maturity from highly overmature ($R_o \sim 1.8$-3.5) for oil generation in the thrusted hinterland, to mature ($R_o \sim 0.5$-1.0) for oil generation in outcrop exposures near the Kosakuts River and in recycled Kulthieth Formation coal fragments included in the Yakataga Formation near the coast (Fig. 2A). Oil-prone coal beds from the Kulthieth

Formation may be the source rocks for the numerous surface oil seeps observed near the Sullivan anticline east of Cape Yakataga and the Samovar Hills (Van Kooten et al., 2002).

The Poul Creek Formation is a marine shale with subordinate marine siltstone and sand. The organic-rich shale facies of the Poul Creek Formation are present at the western part of the study area near Katalla and Kayak Island (Plafker, 1987). In this area, the Poul Creek Formation is thermally immature to mature ($R_o < 1.0$) for oil generation, but is strongly oil-prone during thermal maturation. The Poul Creek Formation is the source of the oil produced from the Katalla oil field and in numerous, nearby surface seeps. The organic facies of the Poul Creek Formation probably grades to siltstone between Kayak Island and Cape Yakataga. Exposures of the organic facies at Cape Yakataga are lacking, but could be perennially covered by beach gravels.

The Yakataga Formation is a roughly 5-km thick glaciomarine sedimentary unit consisting largely of diamictites and sandstones with interbedded mudstones (Eyles et al., 1991). Extensive Pleistocene glaciers delivered large volumes of unsorted sedimentary debris to the coast where marine processes redistributed much of the material in the offshore environment. The Yakataga Formation represents a very rapid rate of sedimentation and contains relatively low (<1 wt.%) organic carbon concentrations (Armentrout, 1983). The Yakataga Formation is known to contain recycled kerogen (Armentrout, 1983) and occasionally, recycled coal clasts from the Kulthieth Formation are found.

The northern Gulf of Alaska is recognized as a potential petroleum province in part because of the abundance of surface oil seeps. Oil seeps are particularly numerous in the Katalla region, along the Sullivan anticline east of Cape Yakataga, and in the Samovar Hills, an area now part of the Wrangell-St. Elias National Park (Plafker, 1987). The most prolific seep, based on occasional estimates of oil volume and the areal extent of oil saturated ground, is located at Johnston Creek on the Sullivan anticline (e.g., Blasko, 1976). Relatively prolific seeps are also present at Munday Creek (which includes seeping gas), near Oily Lake in the Samovar Hills, and at the site of the old Katalla oil field in the Katalla District. These seeps occur along about 260 km of coastline and are related to Poul Creek Formation source rocks in the west and Kulthieth Formation source rocks in the east.

The Katalla region seeps are located downstream along the Alaska Coastal Current from the continental shelf sediments containing elevated hydrocarbon levels, (Feely et al., 1979; Fig. 1A). Furthermore, previous geochemical analyses have shown that the geochemical fingerprint associated with Katalla petroleum seeps does not compare well with the fingerprint recorded in benthic sediments offshore (Page et al., 1998), and oil production rates from the largest of these seeps is so small that these hydrocarbons are not readily evident in nearby aquatic biota immediately downstream of them (Short et al., 1999). The Katalla seeps are therefore also probably insignificant sources of hydrocarbons to the benthic sediments of the Gulf of Alaska.

In this study we examine the effects of the oil seeps on the fluvial geochemistry of Johnston and Munday Creeks, in comparison with two nearby streams that are unaffected by oil seeps, Big River and Duktoth River. It should be noted that one seep was reported north of the Yakataga River within the Duktoth River drainage by Miller (1957). However, Blasko (1976) did not encounter any petroleum seeps in the Duktoth and Yakataga River drainage basins during

his investigation. An intensive ground and air search in 1994 by one of us (GVK) also failed to document a petroleum seep in this area, possibly because the seep is ephemeral, is no longer active, or is so small it escaped visual detection. Given these possible scenarios, the petroleum seep documented by Miller (1957) is not likely to exert a discernible effect on the hydrocarbon budget of the Duktoth River drainage basin; hence, we consider the fluvial sediments collected from this station as devoid of any influence from petroleum seeps. All four streams have substantial SPM loads from glacial sources, and they drain basins that receive > 2 m of precipitation annually (Reed and Elliot, 1979), which is seasonally variable but substantial in all seasons. Johnston Creek, Munday Creek and Big River are relatively short (<10 km) and drain basins of 15-25 km^2 in area, whereas the Duktoth River channel is >24 km long and drains a basin exceeding 400 km^2 (Figs. 2A&B). The gradients of these streams exceed 15 m km^{-1} over most of their reaches. The high precipitation and steep stream-channel gradients result in turbulent flows along nearly the entire reaches of these streams.

B. Sample Collection

Samples of benthic sediment were collected at nine stations along the northern Gulf of Alaska continental shelf from southwest of Yakutat to Cape St. Elias (stations 1 – 9, Fig. 1B; Table 1). Riparian sediments and water samples were collected from four coastal watersheds that discharge into the northern Gulf of Alaska. We sampled a total of eight stream stations (stations 10 – 17, Figs. 1B, 2A&B; Table 1). Each of the four fluvial systems was sampled within roughly 0.5 km of the fluvio-marine interface (stations 10, 11, 13, and 15, Figs. 2A&B) to monitor hydrocarbon inputs to the Gulf of Alaska. Four additional fluvial stations were located on streams receiving seep oil to examine both the pre-seep hydrocarbon levels and the persistence of the seep oil signature during fluvial transport. Of these four additional stations, three were located within the Munday Creek drainage basin (Fig. 2B): one station (#14) was situated on Munday Creek just upstream of the confluence of Munday Creek and a tributary draining a petroleum seep; one station was located on the tributary draining the seep (#17), just prior to the confluence of the tributary and Munday Creek; and one station (#16) was located on Munday Creek at a point 30 m downstream of the input from the seep. On Johnston Creek, one station located upstream of the petroleum seeps was sampled (#12); inclement weather precluded the collection of additional samples from this drainage basin.

Riparian Sediment, Dissolved and Suspended Particulate Matter

Samples of riparian sediment were collected from the waterline of stream banks during September 2001 and stored in precleaned glass jars with polytetrafluoroethylene (PTFE)-lined lids. Water samples (3.8 L) were collected at each fluvial station and filtered through pre-combusted 0.7 □m glass fiber filters (GFFs) using procedures and equipment described in Payne et al. (1999). The filtered water samples were immediately spiked with a mixture of six deuterated PAH surrogate standards in 500 □L acetone and then extracted with two successive 100 ml aliquots of dichloromethane (DCM), which were subsequently combined. The SPM samples retained on the GFFs were wrapped in two layers of DCM-rinsed aluminum foil. All water and sediment samples were stored at -20°C within 8 h of collection.

Gulf of Alaska Benthic Sediments

Samples of benthic sediment were collected from the northern Gulf of Alaska during May 2000 aboard the M/V *Auklet*. The samples were taken with Van Veen grab and Ship-Eck dredge samplers deployed from the vessel. The benthic sediment samples were immediately apportioned on deck into aliquots for PAHs, biomarkers, and density separation. The apportioned samples were stored in precleaned glass jars with PFTE-lined lids and immediately frozen.

Prospective Hydrocarbon Sources

An aliquot of Munday Creek seep oil was skimmed (3 Sept 2000) from the surface of a pond feeding a tributary located about 20 m upstream from the confluence with Munday Creek. The pond serves as a natural collection point for the seep, located farther up the tributary, and episodically feeds into the Munday Creek drainage (McGee, 1972). A sample of Johnston Creek seep oil was collected (26 Sept 1998) from an oil-coated rock located adjacent to the stream channel. A coal sample was collected (5 Sept 2000) from an outcrop of the Kulthieth Formation near the headwaters of the Kosakuts River (~ 530 m elevation), a tributary of the Kaliakh River. A sample of organic-rich (~ 6.7 wt. % organic carbon) shale from the Poul Creek Formation was collected (5 Sept 2000) from an intertidal bench located on the eastern shore of Kayak Island. George Plafker (USGS – Menlo Park, CA) provided us with a siltstone sample (~0.49 wt. % organic carbon) collected from an outcrop of the Kulthieth Formation at Marvitz Creek in the Samovar Hills on 12 Aug 1982.

C. Density Fractionation of Sediment Samples

A density fractionation technique was developed to physically isolate lower-density coal clasts ($\rho \sim 1.2\text{-}1.9$ g cm^{-3}) from bulk sediment samples (Kolak et al., 2000). The heavy liquid used in this procedure was prepared from a mixture of zinc iodide and organic-free water, yielding a fluid density of ~2.00 g cm^{-3}. Bulk sediment samples were thawed and the standing water decanted. The fractionation was conducted in a separatory funnel by slowly dispersing small aliquots (< 5 g) of thawed sediment in the heavy liquid. In this manner, an entire bulk sediment sample (~250 g wet sediment) was completely fractionated in less than 24 h. Both the lower-density (float) and higher-density (sink) fractions were rinsed several times with organic-free water to remove excess zinc iodide. Following the density-separation procedure, the float and sink fractions were further subsampled, with aliquots taken for PAH/*n*-alkane and for biomarker analysis. PAH fractions were refrozen until extraction, whereas fractions for biomarker analysis were dried in a forced-air convection oven at 40°C. The float and sink fractions were extracted subsequently to ascertain the proportion of hydrocarbons associated with clastic material derived from coal beds (Ghosh et al., 2000; Kolak et al., 2000)

D. Extraction, Cleanup and Analytical Procedures

n-Alkanes and Polycyclic Aromatic Hydrocarbons

All samples were analyzed for aliphatic and aromatic hydrocarbons (excluding sterane and triterpane biomarkers, see 4.3.2) following procedures summarized in Short et al. (1996). Aliquots from wet bulk sediment or sink fraction samples (20-50g dry wt. basis), float fraction samples (1.8-130 mg dry wt.), and GFF samples (1-20g wet wt.) were each added to anhydrous sodium sulfate for dehydration, and spiked with 500 □L of a hexane solution containing eleven perdeuterated surrogate hydrocarbon standards. The mixture of sample, sodium sulfate, and surrogate standards was agitated mechanically for 3 successive periods of 16 h, 6 h, and 16 h with each of 3 successive 100 mL DCM aliquots. Each DCM aliquot was removed by filtration following each agitation period, and all three aliquots were later combined (ca. 300 mL DCM total). Both sediment and water sample extracts were then reduced in volume over steam and exchanged with hexane to a final volume of ~ 1 mL. Oil samples were dissolved in DCM, spiked with the same suite of perdeuterated surrogate hydrocarbon standards, exchanged with hexane to precipitate the asphaltenes, and then processed in the same manner as the sediment and water samples.

The sample extracts were separated into aliphatic and aromatic hydrocarbon fractions using 5%-deactivated silica gel/activated-alumina (20g:10g, + 5g Cu for sulfur removal) column chromatography. The aliphatics were eluted with 50 mL pentane, followed by the aromatics with 250 mL of a 1:1 pentane:DCM mixture. Both fractions were reduced in volume over steam to a final volume of ~ 0.5 mL, and the aliphatic fraction was analyzed on a gas chromatograph (GC) equipped with a flame ionization detector (FID). The aromatic fraction was further purified by gel-permeation high performance liquid chromatography (HPLC).

The aliphatic hydrocarbons analyzed included the *n*-alkanes from *n*-nonane (nC_9) through *n*-tetratriacontane (nC_{34}), pristane (2,6,10,14-tetramethylhexadecane; abbreviated as Pr) and phytane (2,6,10,14-tetramethylheptadecane; Ph). These aliphatic hydrocarbons were separated on an HP Ultra 2 column (25mx0.25mmx0.33□m). Samples were injected (1 □L) in the splitless mode, and run using the following temperature program: initial temperature 60°C, hold 1.0 min; ramp 10°C min^{-1} to 300°C; hold 25 min. Helium (0.9 mL min^{-1}) was used as the carrier gas. Aliphatic hydrocarbon concentrations were determined using an internal-standard method employing a five-point calibration curve for each target analyte, with the perdeuterated surrogate standards treated as the internal standards.

Following purification, the aromatic fractions were analyzed using a GC equipped with a mass-selective detector (MSD) operated in the selective-ion-monitoring (SIM) mode. Aromatic hydrocarbons were separated on an HP Ultra 2 column (25mx0.25mmx0.33□m) with helium carrier gas (1.0 mL min^{-1}). The following temperature program was used during the analyses: the initial temperature was 60°C (no hold), followed by a 10°C min^{-1} ramp to 300°C, and held for 15 min at final temperature. The aromatic hydrocarbons analyzed included both parent homolog and alkyl-substituted naphthalenes, fluorenes, dibenzothiophenes, phenanthrenes, and chrysenes (abbreviated as NX, FX, DX, PX and CX, where X = number of alkyl-substituted carbon atoms ranging from 0 to 3 or 4), along with biphenyl (bip), acenaphthene (ace), acenaphthylene (acn), anthracene (ant), fluoranthene (flu), pyrene (pyr), methyl-fluoranthene/pyrene (FP1), benzo-a-anthracene (baa), benzo-b-fluoranthene (bbf), benzo-k-fluoranthene (bkf), benzo-e-pyrene (bep), benzo-a-pyrene (bap), perylene (per), indeno-1,2,3-

c,d-pyrene (icp), dibenzo-*a,h*-anthracene (dba), and benzo-*g,h,i*-perylene (bgp). The concentrations of N1 and the unsubstituted PAHs were determined in a manner similar to that used for the aliphatic hydrocarbons. Calibration curves for the other alkyl-substituted PAHs were calculated using the most similar PAHs: 2,6-dimethylnaphthalene was used for N2; 2,3,5-trimethylnaphthalene was used for N3 and N4; and 1-methylphenanthrene was used for the P1-P4 homologs.

Samples were extracted and analyzed in batches of 12 along with two reference samples, a method blank and a spiked method blank for quality control. Method detection limits (MDLs) varied inversely with sample aliquot size and are summarized in Short et al. (1996). These MDLs are approximately 1 ng g^{-1} dry wt. sediment for the benthic and riparian samples, 1 ng L^{-1} to 8 ng L^{-1} for the water samples, 2 ng g^{-1} to 20 ng g^{-1} dry wt. sediment for the bulk SPM samples, and 100 to 15,000 ng g^{-1} dry wt. for the float fraction of the density-separated sediments. Sample precision is generally better than ± 20% based on the combined results of the reference samples, and accuracy is generally better than ± 15% based on comparison with National Institute of Standards and Technology standards used for the spiked blanks.

Sterane and Triterpane Biomarkers

Sterane and triterpane biomarkers were extracted from sediment, coal, and rock samples using a microwave-assisted solvent extraction technique. A sample aliquot (15 g of dry sediment; 0.5-5 g of coal or rock) was loaded into a glass extraction vessel and then spiked with 10 □L of a surrogate solution containing d_4-C_{27}□□□20R-cholestane. The vessel was sealed immediately following the addition of 40 mL of a 1:1 (v/v) acetone:DCM mixture. The loaded extraction vessels were heated to 115°C in the microwave oven (MARSX; CEM Corp., Matthews, NC) during an 8-minute ramp stage, and then held at temperature for 15 minutes. Two separate 15-g aliquots of sediment were extracted when the sample was known to contain low total organic carbon levels. The extracts from these two aliquots were subsequently combined and treated as a single sample. A method blank was processed with each round of extractions. Sample extracts were filtered through GFFs, evaporated, and the aliphatic biomarker fraction was isolated using silica/alumina gel column chromatography as described in Van Kooten et al. (2002).

Sterane and triterpane biomarkers were analyzed on a Hewlett Packard 6890 GC interfaced with a 5973 MSD operated in the SIM mode. Biomarker extracts were injected (1 μL) in the splitless mode and analyzed on an HP5-MS column (30mx0.25mmx0.25μm) using the following temperature program: initial temperature was 150°C (held 0.5 min), then temperature was ramped 30°C min^{-1} to 200°C, followed by a 1°C min^{-1} ramp to 300°C, followed by a 10°C min^{-1} ramp to 320°C; the final temperature was held for 5 min. Each sample extract was spiked with 5□-cholane as an internal standard; external standards were analyzed with each sample set to generate concentration-response calibration curves. Response curves were generated for the following analytes: C_{27}-ααα20(R)-cholestane, C_{28}-ααα20(R)-methylcholestane, C_{29}-ααα20(R)-ethylcholestane, 18α+β(H)-oleanane, and 17(α),21(β)-C_{30}-hopane. The names of these target analytes will be abbreviated in the following manner: C_{27}S, C_{28}S, C_{29}S, ol, and hop, respectively. Certified standards for the biomarker surrogate, internal standard and target analytes were purchased from Chiron AS (Trondheim, Norway). The regular steranes were quantified using

the area response of the m/z 217 ion fragment whereas oleanane and hopane were quantified using the area response of the m/z 191 ion fragment. The MDLs for the aliphatic biomarkers varied inversely with sample size. For bulk sediment samples, the MDLs for $C_{27}S$, $C_{28}S$, $C_{29}S$, ol, and hop were determined as 0.7, 3.2, 0.9, 0.7 and 2.1 ng g^{-1} dry weight sediment, respectively. Surrogate recoveries for the overall extraction and fractionation procedure were 94% ± 17% (mean ± 1 standard deviation).

E. Organic and Inorganic Carbon Analysis

The total organic carbon (TOC) concentrations in all sediment samples were determined from the difference between measured total carbon (TC) and total inorganic carbon (TIC) contents. The TC content of a sample aliquot was measured by combusting the sample at 1000°C and quantifying the CO_2 evolved using a coulometric titration method. For TIC content, a second sample aliquot was digested in a warm, perchloric acid solution, and the CO_2 evolved was titrated in a similar manner.

F. Data Presentation

To facilitate comparison among samples, the individual PAH concentrations in a given sample have been normalized to its respective total PAH (TPAH) concentration. Comparison of these relative PAH patterns allows evaluation of changes in PAH content resulting from such processes as water washing, volatilization, etc. The *n*-alkane assemblages (including Pr, Ph, steranes, and triterpanes) were similarly normalized to the total *n*-alkane (TNA) concentration in a given sample. Hydrocarbon distributions within SPM and aqueous samples are expressed relative to the total concentration (dissolved+particulate) per L river water. All hydrocarbon concentrations are reported to three significant figures. Hydrocarbon concentrations in sediment and SPM samples are given on a dry weight basis unless specified otherwise.

Results

A. Geochemical Characterization of Seep Oil Samples

The geochemical characteristics of the Johnston and Munday Creek seep oils indicate that these samples were weathered prior to entering the fluvial systems. This weathering is particularly evident in the prominent, bimodal UCMs present in the aliphatic fractions (Figs. 3A&B). Greater losses of PAH with fewer rings and alkyl substituents are also evident (Fig. 4A). The TPAH in these samples constitute 0.6 to 1.1 wt.% of the seep oils, but losses of the naphthalenes and unsubstituted fluorene, dibenzothiophene and phenanthrene are nearly complete. The P2 and P3 homologs are the most abundant PAH in these samples. Both seep oil samples contain relatively low amounts of the higher molecular weight PAHs, particularly benzo-ghi-perylene, indeno-1,2,3-c,d-pyrene, and perylene.

In addition to the losses of lower molecular weight PAH, the paucity of *n*-alkanes relative to other hydrocarbon constituents in these seep oil samples is indicative of light to moderate biodegradation (*sensu* Peters and Moldowan, 1993). Total *n*-alkane concentrations for the

Johnston and Munday Creek seep oil samples are 152 and 3,380 μg g^{-1} oil, respectively. The Munday Creek seep oil sample contains essentially no *n*-alkanes below nC_{14} (Fig. 4B), while the *n*-alkane fingerprint of the Johnston Creek seep oil sample indicates a more gradual loss of *n*-alkanes below nC_{19}. Compared to the *n*-alkanes, Pr is generally more abundant in both seep samples whereas Ph is substantially less so (Fig. 4B). The relative *n*-alkane patterns in both seep oil samples appear erratic, in part due to analytical interferences from the large UCMs, and do not resemble the smooth envelopes typical of undegraded oil samples. The UCM concentrations in the Johnston and Munday Creek seep oil samples are roughly 43,900 and 247,000 □g UCM g^{-1} oil, respectively, yielding TNA:UCM ratios with values of 0.003 and 0.014, respectively.

The sterane and triterpane biomarker patterns are nearly identical in both seep oil samples (Fig. 4B). In both samples, the relative biomarker concentrations increase in the following manner: $C_{27}S < C_{28}S < C_{29}S <$ ol < hop. However, the relative biomarker concentrations in these samples differ roughly by a factor of 20, owing to the higher TNA content in the Munday Creek seep oil sample.

B. Eastern Foreland Stream Station Unaffected by Oil Seeps

The Duktoth River (station 10) and Big River (station 11) drainage basins are unaffected by petroleum seeps, as are riparian sediments collected from Johnston and Munday Creek stations located *upstream* of known seep occurrences (stations 12 and 14, respectively). The relative hydrocarbon concentration patterns in these samples therefore provide an indication of the baseline geochemical signature prior to any overprinting from petroleum seeps. Bulk riparian sediment samples collected from the Big River, Johnston Creek and Munday Creek have TPAH concentrations ranging from 206 ng g^{-1} to 424 ng g^{-1}, nearly an order of magnitude lower than in the Duktoth River sample (2,820 ng g^{-1}). All four samples have broadly similar relative PAH patterns (Fig. 5A), marked by substantial proportions of unsubstituted and lower molecular weight PAH, e.g., N0-N4. The naphthalenes are the most abundant homologous series, followed by the phenanthrenes, fluorenes, and chrysenes. Subtle compositional differences distinguish the Duktoth River sample: the most abundant alkyl-substituted homolog within a series typically has 1-2 alkyl carbon atoms in the Duktoth River sample whereas the most abundant homologs in the three remaining samples have 2-3 alkyl carbon atoms, and perylene is relatively less abundant in the Duktoth River sample.

The Duktoth River riparian sediment sample also has a much higher TNA concentration (4640 ng g^{-1}) than corresponding concentrations in the samples collected from the Big River, and Johnston and Munday Creeks (479-765 ng g^{-1}). Unlike the seep oils, all four of these riparian sediment samples contain relatively smooth *n*-alkane envelopes and have appreciable amounts of the lower molecular weight homologs, including nC_9 (Fig. 5B). All four sediment samples have relatively low UCM concentrations, ranging from roughly 6 to 16 □g UCM g^{-1}. The TNA:UCM ratios for these samples have values ranging from 0.08 to 0.29.

Inspection of the relative aliphatic hydrocarbon patterns reveals additional characteristics of the Duktoth River riparian sediment sample that are distinct from the other three samples. The *n*-alkane envelopes recorded in the Johnston Creek, Munday Creek, and Big River samples

are punctuated by peaks at the nC_{27}, nC_{29} and nC_{31} homologs, but these features are not observed in the Duktoth River sample. Phytane is relatively more abundant than most of the *n*-alkanes in the Johnston Creek, Munday Creek, and Big River samples, but this relationship is reversed in the Duktoth River sample. Although $C_{29}S$ is the dominant sterane in all four samples, the Johnston Creek, Munday Creek, and Big River samples have sterane concentrations that are similar to concentrations of individual *n*-alkanes, whereas steranes in the Duktoth sample are substantially less abundant (Fig. 5B). Oleanane is substantially less abundant than the steranes and hopane from the Johnston Creek, Munday Creek and Big River samples, but oleanane is present at levels comparable to the steranes and hopane in the Duktoth River sample.

C. Eastern Foreland Stream Stations Downstream of Oil Seeps - Munday Creek

The influence of seep oil hydrocarbons on Munday Creek riparian sediments is most clearly evident in the sediment sample collected from the tributary station (#17), located just upstream of the confluence with Munday Creek. The TPAH and TNA concentrations in this sample are 11,300 ng g^{-1} and 4,510 ng g^{-1}, respectively, an order of magnitude or more greater than corresponding concentrations measured upstream of the seep (Figs. 6A&D). The phenanthrenes/anthracenes and chrysenes are the most abundant homologous series, followed by the naphthalenes. The relative concentrations of phenanthrenes/anthracenes and naphthalenes in this sample are intermediate between those found in Munday Creek seep oil and those in riparian sediment collected upstream of the seep (Fig. 6A). In contrast, the relative abundances of chrysenes and perylene in sediment from station 17 are broadly similar to those determined in Munday Creek seep oil.

As with Munday Creek seep oil, riparian sediment from station 17 contains much lower relative concentrations of low-molecular weight *n*-alkanes ($<nC_{14}$; Fig. 6D) and has a more erratic distribution of *n*-alkanes than sediment from station 14 (upstream). Likewise, the aliphatic fraction of riparian sediment from station 17 contains a large UCM (1,210,000 ng UCM g^{-1}). As a result, the TNA:UCM ratio in this sample has a value of 0.004, similar to that of the seep oil sample. The triterpanes are more abundant than the regular steranes in the riparian sediment sample.

The riparian sediment samples collected from stations 16 and 15, located downstream from the petroleum seep, have nearly identical TPAH concentrations: 230 and 219 ng g^{-1}, respectively. The relative PAH abundances in these two samples are also quite similar (Figs. 6B&C). Naphthalenes are the most abundant homologous series in both samples, and perylene is conspicuously abundant in each. These features are in stark contrast to those characterizing sediment from station 17 and the Munday Creek seep oil. Instead, the two downstream samples are nearly identical with the riparian sediment collected upstream of the seep (station 14), both in terms of TPAH concentration and relative hydrocarbon abundances.

Concentrations of *n*-alkanes in the riparian sediments from stations downstream of the seep corroborate the variations in PAH compositions. Concentrations of TNA downstream of the seep (station 16) and at the mouth of Munday Creek (station 15) are 498 ng g^{-1} and 511 ng g^{-1}, respectively, compared with 479 ng g^{-1} at station 14 upstream of the seep. The relative

abundances of *n*-alkanes, steranes, and triterpanes at these downstream stations are also nearly identical to those measured upstream at station 14 (Figs. 6E&F). The UCM concentrations in these downstream sediments, 5,200 ng g^{-1} and 4,900 ng g^{-1} (stations 16 and 15, respectively) are markedly lower than in sediment from the seep-oil tributary, but are comparable to the concentration measured upstream of the seep (5,770 ng g^{-1}). The TNA:UCM ratios in the two downstream samples both have values approaching 0.10, substantially greater than the corresponding ratios in Munday Creek seep oil and in sediment from the seep oil tributary.

D. Eastern Foreland Stream Stations Downstream of Oil Seeps - Johnston Creek

The TPAH concentration measured in riparian sediment at the Johnston Creek mouth (524 ng g^{-1}; station 13) is slightly greater than that measured upstream at station 12 (424 ng g^{-1}), and this difference may reflect the influence of the Johnston Creek oil seep. The relative PAH distribution in riparian sediment from station 13 (Fig. 7A) contains approximately equal abundances of naphthalenes and phenanthrenes/anthracenes. The relative concentrations of each of these two homologous series is intermediate between the corresponding relative concentrations found in Johnston Creek seep oil and in riparian sediment collected upstream of the seep. However, the relative abundances of fluorene, methyl-fluorene, the chrysenes, and perylene in riparian sediment from the Johnston Creek mouth more closely resemble those measured in riparian sediment upstream of the seep than those in Johnston Creek seep oil.

In contrast to the PAH, the TNA concentration measured in riparian sediment from the Johnston Creek mouth (755 ng g^{-1}; station 13) is nearly identical to that measured in sediment upstream of the seep (765 ng g^{-1}; station 12). Likewise, the relative distributions of *n*-alkanes, steranes, and triterpanes in these sediment samples are nearly identical (Fig. 7B). The concentrations of aliphatic UCMs for stations 13 and 12 are also quite similar, and yield TNA:UCM ratios of 0.10 and 0.09, respectively. The relative concentration of hopane in riparian sediment from the Johnston Creek mouth is greater than oleanane, but comparable to the abundances of the three regular steranes. These features contrast with the seep oil signature, where the relative hopane abundance is nearly an order of magnitude greater than the corresponding sterane concentrations. The absolute hopane concentrations at the two Johnston Creek stations are nearly identical (23 ng g^{-1} at station 12 versus 24 ng g^{-1} at station 13), and are lower than the hopane concentration measured in seep oil (685 ng g^{-1}) by roughly a factor of 30. This disparity indicates that hopane concentrations may be very sensitive to hydrocarbon inputs derived from petroleum seeps.

E. Fluvial Transport of Dissolved and Particulate Hydrocarbons

Hydrocarbon compositions of the dissolved and SPM samples collected from the Munday Creek main stem differ markedly. Dissolved PAH concentrations in the main stem of Munday Creek are relatively low (TPAH $\leq$ 365 ng L^{-1}), with nearly all the PAHs (> 90%) associated with the SPM (Table 2). Total PAH concentrations in SPM, on a sediment mass basis, vary among the three main stem stations by nearly a factor of two (514 ng g^{-1} SPM – 908 ng g^{-1} SPM). However, per unit volume of stream water, these SPM-associated PAH concentrations are

substantially lower at the mouth (923 ng L^{-1}) than at the stations nearer the seep source (2,790 ng L^{-1} – 4,720 ng L^{-1}) (Table 2). The relative PAH distributions associated with SPM from the three main stem stations (stations 14, 15 and 16) are nearly identical (Figs. 8A, C, & D), as are the corresponding patterns of *n*-alkanes, steranes, and triterpanes (data not shown). These patterns closely resemble those observed in the corresponding riparian sediment samples from these stations. Both riparian sediment and SPM samples share the naphthalenes as the dominant PAH homologous series, and both are relatively enriched in perylene. These SPM samples also contain relatively low, but detectable levels of higher-molecular weight PAHs. Conversely, the most abundant dissolved PAH homologs are the phenanthrenes/anthracenes, followed by the naphthalenes, dibenzothiophenes, fluorenes, and then the chrysenes (Figs. 8A, C, &D). The dissolved concentrations of the higher molecular weight PAHs are below the MDLs. The same dissolved PAH pattern is found at the upstream Johnston Creek station (#12; Fig. 9A). Aliphatic hydrocarbon concentrations were below the MDLs in all aqueous samples collected, except for nC_{27} (679 ng L^{-1}) at Munday Creek station 16.

In contrast with the Munday Creek main stem samples, the PAH concentration and distribution within the water sample collected from the seep oil tributary (station 17) clearly reflects the influence of seep oil. Most of the PAH (86%; Table 2) are associated with the dissolved phase at this station, and the TPAH concentration of the dissolved phase (2,100 ng L^{-1}) substantially exceeds dissolved TPAH concentrations measured in stations along the Munday Creek main stem ($\leq$ 365 ng L^{-1}). The dissolved phase PAHs are dominated by the naphthalene homologs, followed by lesser amounts of fluorenes and phenanthrenes (Fig. 8B). The absolute TPAH concentration SPM-associated TPAH concentration at this station (337 ng L^{-1}) is substantially lower than at the main stem stations, in part because the SPM concentration is commensurately lower (0.33 g L^{-1}) in the tributary. On a sediment mass basis, the TPAH concentration of SPM-associated PAH is slightly greater at station 17 (1,020 ng g^{-1} SPM) than at the main stem stations (714 ng g^{-1} SPM – 907 ng g^{-1} SPM). The barely evident pattern of relative abundances of the SPM-associated PAHs at station 17 is a characteristic water-washed crude oil pattern, consisting of phenanthrenes/anthracenes followed by chrysenes as the most abundant homologous series remaining with the oil/particulate phase, and it clearly exhibits preferential losses of the more water-soluble, less-substituted alkyl homologs within each series (Fig. 8B). Also, perylene is notably absent in this sample. In addition, the distribution of *n*-alkanes in the station 17 SPM is erratic (data not shown), but the TNA:UCM ratio (0.011) is nearly identical to that of Munday Creek seep oil. Finally, oleanane and hopane are present in station 17 SPM at significantly greater concentrations relative to the steranes, similar to the riparian sediment from this station as well as in the Munday Creek seep oil sample.

The concentration and distribution of PAH in water samples from Johnston Creek confirm the presence of a measurable seep-derived hydrocarbon load that is conveyed to the northern Gulf of Alaska. At station 12 above the seep-oil input, the combined TPAH concentration is quite low (338 ng L^{-1}), with the dissolved and SPM-associated proportions nearly equal (Table 2). Perylene is abundant in the SPM, and the relative abundances of the other SPM-associated PAH are broadly similar to that of the riparian sediments at station 12 (compare Figs. 9A and 5A), as are the distribution patterns of the biomarkers (data not shown). On a sediment mass basis, the TPAH concentration of the SPM is 585 ng g^{-1}, similar to the concentration in riparian sediment from station 12 (Fig. 5A), and only slightly lower than

concentrations associated with the SPM in the main stem stations of Munday Creek. The aliphatic hydrocarbons are too often below the MDL to make meaningful comparisons for this sample.

At station 13, near the mouth of Johnston Creek and downstream of the seep oil input, the concentrations and patterns of relative hydrocarbon abundance in the water sample are dramatically different than upstream station 12, and clearly indicate the influence of seep oil. The TPAH concentration of the combined phases at station 13 is almost tenfold those at station 12, with 71% of the PAH associated with the SPM (Fig. 9B and Table 2), and on a sediment mass basis the TPAH concentration is 5,170 ng g^{-1} SPM. As at the oil seep tributary station on Munday Creek (station 17), the pattern of relative abundances of the SPM-associated PAH at station 13 is a characteristic water-washed crude oil pattern, with phenanthrenes/anthracenes followed by chrysenes and fluorenes the most abundant homologous series present, preferential losses of the less-substituted alkyl homologues within each series, and negligible perylene (Fig. 9B). In addition, the distribution of *n*-alkanes in the station 13 SPM is erratic, but the TNA:UCM ratio is 0.008, with oleanane and hopane relatively more abundant than the steranes (e.g., see Fig. 10B), as in Johnston Creek seep oil. Hence, nearly all of the dissolved and SPM-associated PAH at station 13 appear to derive from the Johnston Creek oil seep, and enter the northern Gulf of Alaska at combined concentrations on the order of 4 μg L^{-1}.

The relative abundance patterns of SPM-associated hydrocarbons found at the stations near the mouths of the Duktoth (#10) and Big Rivers (#11) closely resemble patterns evident in the respective riparian sediments at each station (Fig 5), including the differences in relative abundances of perylene, Ph and the biomarkers relative to the *n*-alkanes that distinguish sediments in the Duktoth drainage from the oil seep drainages to the east. The high SPM concentration (2.75 g L^{-1}) and high TPAH concentration associated with SPM (5,040 ng g^{-1} SPM) yield a TPAH concentration of 13,900 ng L^{-1} in the Duktoth River. Because the Duktoth River drainage basin area is >16 times those of either Johnston or Munday Creeks (Fig. 2A), the Duktoth River can be expected to discharge a commensurately greater volume of water to the Gulf of Alaska. As a result, the Duktoth River conveys a much larger hydrocarbon load (~80 fold) to the Gulf of Alaska than either Johnston or Munday Creeks.

F. Gulf of Alaska Benthic Sediments

Total PAH concentrations in benthic sediments collected from stations along the northern Gulf of Alaska continental shelf increase abruptly from 62 ng g^{-1} at station 1, located southwest of Yakutat Bay, to 580 ng g^{-1} or greater at the other stations (Fig. 1B; Appendix A). The highest TPAH concentration was measured in benthic sediment from station 5 in Icy Bay (5,680 ng g^{-1}) . Total PAH concentrations at the remaining stations generally increase with proximity to Icy Bay. Despite the large variations in absolute TPAH concentrations, benthic sediments from stations 2-9 display a remarkably similar PAH fingerprint (Fig. 10A). All the samples from stations 2-9 contain similar relative concentrations of naphthalene and phenanthrene homologs. These two homologous series are the most abundant, followed by the fluorenes, chrysenes, and dibenzothiophenes, and perylene is only a minor constituent.

The TNA concentrations measured in benthic sediments range from 256 ng g^{-1} at station 1 to 4,690 ng g^{-1} at station 5 in Icy Bay. As with the PAHs, the relative *n*-alkane distributions among the benthic sediments from stations 2-9 are remarkably similar and contain a relatively smooth *n*-alkane envelope from nC_9 through nC_{34} (Fig. 10B). The aliphatic constituents showing the highest degree of variability among stations are Pr, Ph, and the higher-molecular weight odd *n*-alkanes (nC_{27}, nC_{29}, nC_{31}, and nC_{33}). The relative concentrations of sterane and triterpane biomarkers are also quite similar among the benthic sediment samples. These biomarker compounds are present at conspicuously lower abundances relative to the *n*-alkanes. Concentrations of the aliphatic UCM in the Gulf of Alaska sediments range from 1,426 ng g^{-1} sediment (station 2) to 23,300 ng g^{-1} (station 5).

Compared to SPM from fluvial systems in the adjacent Yakataga District, the mean TPAH concentrations in northern Gulf of Alaska benthic sediments are lower by approximately a factor of two. The Duktoth River and Johnston Creek transport SPM with the highest PAH content, and of these two the Duktoth River SPM sample is more comparable with the mean Gulf of Alaska benthic sediments (Fig. 10A). The relative abundance of naphthalene homologs in the benthic sediments are appreciably greater than those in Johnston Creek SPM, but are only slightly lower than corresponding concentrations in Duktoth River SPM. Conversely, Gulf of Alaska benthic sediments contain relatively lower abundances of phenanthrenes/anthracenes than the Johnston Creek SPM, but are similar to Duktoth River SPM abundances.
Comparisons among the aliphatic hydrocarbon patterns confirm the comparisons based on PAH. The relatively uniform *n*-alkane distribution in the benthic sediments is in marked contrast to the more erratic *n*-alkane distribution characteristic of Johnston Creek SPM (Fig. 10B). The relative abundances of steranes and triterpanes in Johnston Creek SPM are similar to those of Johnston Creek seep oil, but are substantially greater than those measured in Gulf of Alaska benthic sediments while these biomarkers in the Duktoth River SPM are comparable with Gulf of Alaska benthic sediments. The geochemical fingerprint of Duktoth River SPM also contains a relatively uniform distribution of *n*-alkanes, and the low relative Ph abundance in the Duktoth River SPM matches the low abundance in the Gulf of Alaska sediments.

Despite the general similarity between Duktoth River SPM and offshore benthic sediment, there are some noteworthy differences. The Duktoth River SPM generally contains a smaller proportion of lower molecular weight *n*-alkanes ($<nC_{16}$), and a larger proportion of higher molecular weight *n*-alkanes ($>nC_{18}$), than the benthic sediments. Also, the relative abundances of the nC_{27}, nC_{29}, and nC_{31} *n*-alkanes are less pronounced in the Duktoth River SPM sample than in Gulf of Alaska benthic sediment. The TNA:UCM ratios for the benthic sediments range from 0.201 to 1.149, which are substantially greater than the TNA:UCM ratios of either the Duktoth River or Johnston Creek SPM, 0.058 and 0.008, respectively.

The combined suite of hydrocarbons analyzed in the Gulf of Alaska benthic sediments are highly intercorrelated. In addition, the UCM is also closely correlated with TNA and with TPAH ($r > 0.93$, $P < 0.001$). Of the 1,653 product-moment correlation coefficients for pairwise correlations among the 58 most abundant hydrocarbons analyzed in each of the 8 Gulf of Alaska sediments (excluding station 1 where most analytes were below the MDL), all are above 0.69, with 80% above 0.9 (the excluded analytes are near or below MDL), indicating the *n*-alkanes,

hydrocarbon biomarkers and PAH are all highly intercorrelated within and among each other in these samples.

G. Geochemical Signature of Local Coal Samples and Density-Fractionated Sediments

Geochemical analyses of coal samples collected from outcrops within the study area were compared with density-fractionated riparian sediments to provide additional information regarding prospective hydrocarbon sources in the fluvio-marine environment. The relative PAH distributions in coal samples (Fig. 11A) are comparable to corresponding distributions in the float fraction samples in that the naphthalene homologous series is most abundant, followed by the phenanthrenes, fluorenes and chrysenes. The coal sample collected from the Kosakuts River area contains a larger proportion of the parent and less-alkylated homologs (e.g., N0, N1, P0 and P1), whereas the Samovar Hills area coal sample contains a larger proportion of the more alkylated homologs (e.g., N3, N4, P3 and P4). Given this distinction, the Kosakuts River area coal sample appears to bear a stronger resemblance to the float fraction samples than the Samovar Hills area coal sample. The resemblance between the Kosakuts River coal sample and Duktoth River float fraction sample is particularly strong. The other three float samples contain abundant perylene, fluoranthene, and methylfluoranthene/methylpyrene, which are not nearly as prominent in the Kosakuts River area coal sample.

The relative distributions of aliphatic constituents in the float fractions isolated from the riparian sediments show some subtle distinctions (Fig. 11B). The float fraction obtained from the Duktoth River sample contains a relatively larger proportion of smaller *n*-alkanes ($<nC_{17}$) and a relatively smaller proportion of higher molecular weight *n*-alkanes ($>nC_{23}$) than the material isolated from the three remaining riparian sediments. Furthermore, the distribution of *n*-alkanes in the Duktoth River float fraction gradually declines from nC_{20} out to nC_{34}, whereas the other three samples exhibit a less uniform distribution that is punctuated by relatively high concentrations of the nC_{29}, nC_{31}, and nC_{33} homologs. As with other sediments from the Duktoth drainage, the float fraction contains little Ph compared with most of the *n*-alkanes.

The similarities between the geochemical signatures of the local coal samples and the benthic and riparian sediment samples prompted a more detailed study of density fractionation to determine the extent to which low-density coaly material contributed to the overall hydrocarbon burden in fluviomarine sediments. The low-density material isolated from the bulk sediment samples was inspected under a binocular microscope and found to consist primarily of clasts eroded from coal beds, rather than recent organic detritus. Although the coaly material isolated from the sediment samples represents only a very small portion of the total mass of the initial sample (generally less than 0.10%; Table 3), it contains TPAH and TNA concentrations as high as 839,000 ng g^{-1} and 430,000 ng g^{-1}, respectively. This component of the sediment contributes up to 11% of the TNA burden in the riparian and benthic sediment samples (Table 3). The largest contribution is found on Johnston Creek upstream of the seep oil influence (station 12). The mean percentage of TNA burden derived from the coaly material is somewhat greater in the riparian samples than in the offshore benthic sediments. The coaly material accounts for an even greater proportion of the TPAH burden in the sediment samples, ranging from 4.5 % to 28.8% at the main stem riparian stations, and from 1.1% to 6.1% at the northern Gulf of Alaska offshore

benthic stations. Again, the highest contribution was found at the upstream Johnston Creek sample (station 12), in which the largest mass of float fraction was obtained.

Given the apparent modest contribution from coal to the total hydrocarbon burden in the fluvial and marine sediments, samples of siltstone (Kulthieth Formation) and organic-rich shale (Poul Creek Formation) were evaluated to assess the potential contributions from these relatively more extensive geologic sources. Despite the marked difference in organic carbon and TPAH content between these two samples (see sec. 4.1.3 above and Fig. 12A), the relative PAH distributions for both samples are broadly similar. Both samples contain a large proportion of naphthalenes with markedly lesser amounts of phenanthrenes and chrysenes (Fig. 12A). These distributions differ from the average pattern recorded in Gulf of Alaska benthic sediments, where naphthalenes and phenanthrenes are present in roughly equal proportions. The fluorene homologous series is also more prominent in the average PAH distribution from Gulf of Alaska sediments relative to the pattern in the siltstone and shale samples.

The relative *n*-alkane distributions present in the siltstone and shale samples are generally similar and contain substantial proportions of the lower molecular weight homologs (< nC_{14}; Fig. 12B). The siltstone sample contains a noticeable spike in Pr relative to the *n*-alkanes, and the *n*-alkane distribution is not smooth and appears somewhat skewed toward the higher molecular weight homologs, notably nC_{22} through nC_{26}, and nC_{31} and nC_{32}. The organic-rich shale from the Poul Creek formation contains a similar Pr spike, but has a much more regular *n*-alkane distribution that exhibits a gradual decline from lower to higher molecular weight homologs. This latter fingerprint appears to compare more favorably with the average signature from the Gulf of Alaska sediments, but there are some noticeable differences. For example, Pr levels in the Gulf of Alaska samples are only slightly greater relative to *n*-alkane levels, whereas Pr in the Poul Creek and Kulthieth samples exceeds the proportions of individual *n*-alkanes by a factor of four or greater. Relative abundances of Ph in Gulf of Alaska sediments are lower than most *n*-alkanes, unlike the Poul Creek and Kulthieth samples. The Gulf of Alaska sediments also show relative enrichments in nC_{27}, nC_{29}, and nC_{31} homologs, which may be an indication of a thermally immature source or terrestrial plant waxes. This feature appears largely subdued in the distribution from the Poul Creek shale and is absent in the Kulthieth siltstone. The Poul Creek and Kulthieth samples contain appreciably similar distributions of sterane and triterpane biomarkers, with the Poul Creek sample slightly more enriched in hopane. Contrary to the seep oil signatures, the relative proportions of these biomarker constituents fall near the range of values encountered in Gulf of Alaska sediments.

Discussion

A. Fate of Seep-Derived Hydrocarbons

Despite the presence of a substantive hydrocarbon signature in the upstream fluvial samples, the SPM, aqueous, and riparian sediment samples analyzed from Johnston and Munday Creeks collectively demonstrate the influence of Yakataga oil seeps on fluvial geochemistry. The hydrocarbon distributions among these samples, especially in those collected near the seep sources, clearly illustrate oil partitioning and association with clastic material. The seep-derived

hydrocarbons overprinted PAH patterns in SPM and riparian sediments located nearer the seeps. The UCM, sterane, and triterpane biomarker distributions also reflect the characteristic hydrocarbon pattern of the seep oils. If adsorption of dissolved-phase PAH was the process by which seep-derived hydrocarbons became associated with SPM, then this scenario may lead to enriched abundances of PAH relative to the aliphatic constituents because of the greater affinity of the aromatic π-electrons for the active sites on the sediments (ET&C, 1999). However, this enrichment is not observed. Instead, the connection among the hydrocarbon classes likely indicates that fluvial transport of seep-derived hydrocarbons in this setting occurs largely as free-phase oil associated with the SPM. In a detailed study of oil-SPM interactions that used a variety of oil types and nine representative Alaskan sediment/SPM sources, Payne et al. (2003) found that dissolved component-SPM interactions in simulated coastal or open-ocean conditions were insignificant compared to whole oil droplet-SPM interactions and sedimentation. Interestingly, those authors also found that whole oil droplet-SPM interactions were significantly retarded in fresh water (0 parts per thousand salinity, ppt) compared to waters with salinities ranging from 14-30 ppt. They concluded that there was evidently a breakpoint between 0 and 14 ppt in estuarine environments where ionic interactions or particle-solute interactions prevented significant oil droplet/SPM particle-particle collisions and sticking. In other studies, McCourt and Shier (1998), Lee et al. (2001), Le Floch et al. (2002), and Owens and Lee (2003) have reported that oil/SPM interactions can occur in fresh or low-salinity waters, and such interactions are believed to be important in freshwater streams with high SPM loads and extremely turbulent conditions, which describe the streams we sampled here.

This free phase oil-sediment association may consist of oil-coated sediment grains, or of oil-sediment flocs consisting of microscopic oil droplets covered by a surface layer of clay-sized sediment particles (Bragg and Yang, 1995; Payne et al., 2003). Oil-mineral aggregate (OMA) formation does not appear to be restricted to clay minerals or clay-sized (< 2□m) particles, as some studies have documented OMAs on the scale of 50□m or larger (Owens and Lee, 2003; Payne et al., 2003). Based on these findings, we believe that the abundant sediment loads measured in the streams sampled in this study provide ample opportunity for conveying oil seep-derived hydrocarbons into the Gulf of Alaska as oil-SPM aggregates. Indeed, previous work has shown that the relatively high concentrations of free-phase oil measured nearer the Johnston and Munday Creek seep sources (2,340 mg L^{-1} and 1,340 mg L^{-1}, respectively) declined precipitously downstream from the seeps and approached limits of detection, (<0.1 mg L^{-1}) at the stream mouths (Blasko, 1976). The rapid loss of free-phase oil during fluvial transport in these drainages likely coincides with an increase in the degree of oil-SPM association, and this scenario is clearly reflected in the increased hopane content in the SPM from the Johnston Creek mouth relative to SPM collected further upstream.

Association of free-phase oil with the riparian sediment and SPM provides a large specific surface area for the oil that promotes weathering losses of PAH through dissolution and evaporation of the more volatile components (Bragg and Yang, 1995; Short and Heintz, 1997; Payne et al., 2003). The dissolution losses from the oil give rise to an aqueous PAH distribution containing enhanced levels of the more readily soluble, lower molecular weight constituents. The PAH distribution resulting from this dissolution process manifests itself through the greater proportions of naphthalenes and fluorenes and lesser amounts of phenanthrenes and chrysenes in the aqueous phase (Fig. 8B) relative to the corresponding proportions measured in the Munday

Creek seep oil (Fig. 4A). The particularly high concentration of dissolved PAH measured at the Munday Creek seep-oil tributary (station 17) likely resulted from dissolution of the more water-soluble PAH into the relatively clear water (the measured SPM load was only 0.33 g L^{-1}). Subsequent transport beneath the extensive surface oil slicks present on ponds along the tributary enhanced PAH dissolution relative to that expected from the entrained load of oil-coated SPM. Because of the relatively lower turbulence and SPM load in the oil-seep tributary, over 86% of the measured PAH associated with the aqueous phase.

Upon entering Munday Creek, this load of dissolved PAHs concentrations in Munday Creek is immediately diluted by the large volume of receiving water in the main stream channel compared to the oil-seep tributary. The flow of the seep oil tributary constituted a small fraction (< ~10%) of the total discharge though the main channel, based on our visual estimate. This flow estimate is consistent with the observed dilution of dissolved PAH as the seep oil tributary waters enter the main stem: the increase in dissolved PAH content from station 14 to station 16 corresponds with a roughly ten-fold dilution of the dissolved PAH load from the seep oil tributary station 17. Furthermore, the SPM load of the main channel exceeded that of the seep oil tributary by more than a factor of ten (Table 2). The combination of higher SPM load and increased discharge rate readily overwhelms seep inputs from the tributary. As a result, the SPM phase collected from stations further downstream of the seep show no discernible evidence of seep-derived hydrocarbons.

Unlike Munday Creek, waterborne seep oil hydrocarbons are detectable near the mouth of Johnston Creek because the Johnston Creek oil seep is larger, and this fluvial system carries a relatively smaller SPM load. Discharge rates from petroleum seeps can be highly variable and are difficult to estimate accurately. However, the surficial area affected by the Johnston Creek petroleum seeps is visually estimated at ~ 2 hectares, or ~3-5 times larger than the corresponding area affected by the Munday Creek petroleum seeps, suggesting commensurately higher average oil seepage rates at Johnston Creek. Dilution of dissolved PAH by the main stem waters of Johnston Creek also accounts for the lower proportion of dissolved versus SPM-associated PAH we found at station 13 near the mouth of Johnston Creek (29% TPAH dissolved, Table 2) compared with station 17 on the seep oil tributary of Munday Creek (86% dissolved).

Seep oil production from the Johnston Creek seep was sufficiently large that introduction of these hydrocarbons into the marine waters of the northern Gulf of Alaska was detectable, albeit at low TPAH concentrations on the order of 4 μg L^{-1} (dissolved + SPM-associated). Boehm et al. (2001) also concluded that Johnston Creek seep oil associated with Johnston Creek sediments downstream from the seep would be discharged to the GOA and that the hydrocarbons would be sorbed to fine SPM rather than existing as oil droplets or as sheens on top of the water. The histograms for the SPM and dissolved-phase hydrocarbon burdens presented here confirm those findings and offer the first quantitative assessment of this hydrocarbon load.

The geochemical data presented here are tempered by the fact that this sample set represents conditions during a single hydrologic event, whereas oil seep production rates and the subsequent effects on fluvial geochemistry are temporally variable. Blasko (1976) observed that seep oil pooled in a pond prior to draining into Johnston Creek and postulated that significant rainfall could cause a "spillover" effect resulting in a much larger release of oil to the creek.

Such ephemeral releases of seep oil may substantially increase the concentration (and flux) of seep-derived hydrocarbons delivered to the Gulf of Alaska relative to the values measured during this sampling campaign. Nonetheless, the low discharge concentration of aqueous PAH we measured near the mouth of Johnston Creek is much more compatible with McGee's (1972) estimate of 40,000 L a^{-1} [30 gallons d^{-1}] oil input to the northern Gulf of Alaska from all seeps combined than it is with Page et al.'s (1997) estimate of $\geq 1.3 \times 10^6$ L a^{-1} [360 and 1200 ton a^{-1}].

Even fluxes of seep oil PAH considerably larger than 4 μg L^{-1} into the northern Gulf of Alaska are unlikely to be detectable in marine sediments beyond the immediate vicinity of the oil seep creek mouths, because of dilution by PAH-laden sediments from other sources in the region. While this contribution is clearly measurable in Johnston Creek, the observed discharge rates from the Johnston Creek watershed are so small compared to those of neighboring fluvial systems, especially the Duktoth River, that the hydrocarbon flux released into the Gulf of Alaska coastal marine environment is readily overwhelmed by inputs from these larger drainage basins. Likewise, the SPM and associated hydrocarbon loads from the Duktoth River are miniscule relative to the $>1.5 \times 10^7$ m^3 of SPM (Gustavson and Boothroyd, 1987) derived annually from the Malaspina Glacier. Given this context, hydrocarbon contributions from the Yakataga petroleum seeps to the benthic sediments along the northern Gulf of Alaska continental shelf are probably undetectable except near the mouths of the streams receiving the seep oils.

B. Regional Variations in Hydrocarbon Sources to the Fluvio-marine Environment

The sediments we sampled from the Yakataga Foreland streams showed clear and consistent hydrocarbon composition differences in comparison with sediments from the Duktoth River, reflecting erosion of geochemically distinct surface rocks within these respective drainages. For example, the hydrocarbon content of the Duktoth sediment is nearly an order of magnitude higher than the Yakataga Foreland stream sediment, and probably reflects the sediment contribution of the organic-rich Kulthieth Formation. The aerial extent of exposed Yakataga and Poul Creek Formations varies widely in the drainage areas of Johnston Creek, Big River, and Munday Creek (Fig. 2), but riparian samples from all three areas are geochemically very similar. The Poul Creek Formation underlies about 80%, 45%, and 20% of the drainage area for Johnston Creek, Munday Creek, and Big River, respectively. The Duktoth River drainage is much larger with more diverse geology than the drainages of the Yakataga Foreland streams. Fluvial sand, siltstone, and coal of the Kulthieth Formation underlie about 35-40% of the Duktoth drainage area, and large areas of the drainage are also covered by glacial ice.

We interpret the geochemical characteristics of stream sediment from the Yakataga Forelands as related primarily to organic material derived from the marine Poul Creek Formation, which makes up a significant portion of the drainage geology in the Yakataga Forelands (Figs. 2A&B). The streams of the Yakataga Forelands drain extensive exposures of both the Yakataga and Poul Creek Formations, but Poul Creek organic matter likely dominates the geochemical signature of the stream sediment. The Poul Creek Formation at the Yakataga Forelands is composed of marine siltstone and shale deposited slowly in an offshore environment. The organic-rich black shale member of the Poul Creek Formation, exposed at Kayak Island about 125 km to the west, is not found at Yakataga despite extensive Poul Creek

exposures at Yakataga and along the coast, and has likely graded into siltstone at the Yakataga Forelands. Even where organically lean, Poul Creek shale and siltstone still routinely contain 0.5 – 1.0 wt. % TOC, and occasionally up to 1.5% TOC, based on numerous analyses from the offshore Y-0211 (Yakutat) well (Flett, 1992). These Poul Creek subsurface samples also have low, but detectable, hydrocarbon generative potential indicated by Rock-Eval analysis and routinely contain extractable C_{15+} hydrocarbons up to nearly 500 ppm (Flett, 1992, Fig. 102). In the Y-0211 well, the Yakataga Formation contains about 0.25% TOC on average, and only 3 of 32 samples show either detectable generative hydrocarbon potential or extractable C_{15+} hydrocarbons (Flett, 1992, Fig. 102). Both the Yakataga and Poul Creek Formations are immature for oil generation in the Y-0211 well, as indicated by vitrinite reflectance (R_o) of 0.47 for Poul Creek samples at about 2130 m (Flett, 1992). These geochemical characteristics suggest the Poul Creek Formation may be a more important source of hydrocarbons in eroding sediments than the Yakataga Formation.

Perylene is found in elevated relative concentrations (4-9% of TPAH) in all of the bulk stream sediment samples from the Yakataga Forelands and high, but variable, perylene also occurs in the SPM fraction (1-11% of TPAH) at these sample sites. None of the sediment fractions from the Duktoth River contain significant perylene, nor do analyzed samples of the Poul Creek shale, Kulthieth siltstone, or Kulthieth coals. The perylene in the Yakataga sediment and SPM may be related genetically, and apparently reflects the incorporation of perylene-bearing sediment as entrained and suspended material. Perylene can form in recent sediments during early diagenesis (Venkatesan, 1988). We consider that the perylene content is related to the surface sedimentary environment in the stream and does not reflect the perylene content of the rock formations in the stream drainage. The low aqueous solubility of perylene may constrain the dissolved concentration of this hydrocarbon in Yakataga stream waters.

The geochemical characteristics of the Duktoth sediment reflect a small contribution (<~5%) by lithologically distinct coal and a large contribution (>~95%) possibly from finely dispersed organic (coaly) particles in fine-grained sediment from the fluvial Kulthieth Formation. The Duktoth River sediment and coal sample from the Kosakuts River area are broadly similar, but not identical. The close geochemical similarity between the Duktoth sink fraction and the Kosakuts coal suggests the possibility that finely dispersed, comminuted coal or kerogen associated with the denser sediment fraction constitutes an important source of hydrocarbons to the Duktoth sediment. Six coal samples collected from the Kulthieth Formation within the Duktoth River drainage basin exhibit high thermal maturity, yielding R_o values ranging from 1.8–2.5 (Van Kooten et al., 2002). The difference in thermal maturity between the primary lithologies comprising the Dutktoth and Yakataga Forelands drainages likely enhances the disparity in observed geochemical signatures.

The systematic hydrocarbon differences that distinguish Duktoth River and Yakataga Foreland sediments indicate these hydrocarbons are preserved in the sediment and reflect the geological characteristics of the stream drainages. Normal alkanes derived from crude oils are usually degraded rapidly by microbial activity following introduction into receiving waters, and the lower molecular weight *n*-alkanes are subject to rapid volatility losses unless sequestered within a refractory matrix. The preservation of these typically labile constituents suggests they are sequestered within a matrix that is relatively resistant to weathering (Barrick et al. 1980),

such as coal or kerogen disseminated within a siliciclastic rock. Preservation of these *n*-alkanes has been documented elsewhere in the coastal sediments of Alaska and arctic Canada (Steinhauer and Boehm, 1992; Yunker et al., 1993).

D. Sources of Hydrocarbons in Northern Gulf of Alaska Benthic Sediments

Similar to the onshore fluvial systems, hydrocarbons are preserved in the marine sediments of the northern Gulf of Alaska and retain information about their hydrocarbon sources. The consistent intercorrelation among all the most abundant hydrocarbons analyzed implies these hydrocarbons likely originate from the same source. Prospective hydrocarbon sources that closely match the PAH distribution of the northern Gulf of Alaska sediments should therefore match the distribution of aliphatic and biomarker hydrocarbons as well.

Comparison of relative hydrocarbon abundances shows that sampled Yakataga Foreland streams may be dismissed as a significant source of sedimentary hydrocarbon in Gulf of Alaska benthic sediments. The sediments from the Yakataga Forelands contain 4-9% perylene relative to TPAH, and high Pr and Ph concentrations relative to TNA. The GOA benthic sediments contain very little (<<1%) perylene relative to TPAH and lower concentrations of Pr and, especially, Ph relative to TNA than the Yakataga Foreland stream sediments. In addition, the TNA:UCM ratio characteristic of Gulf of Alaska sediments is substantially higher than that of Yakataga Foreland stream sediments. These relationships indicate the Yakataga streams are only minor contributors to the Gulf of Alaska benthic sediments.

The patterns of relative hydrocarbon abundances in Duktoth River sediments and the coal samples from Samovar Hills or the Kosakuts River also exhibit significant discrepancies from the Gulf of Alaska pattern. Although these samples all contain relatively little perylene and phytane, the *n*-alkane and hydrocarbon biomarker patterns of the prospective source samples differ appreciably from that of the Gulf of Alaska sediments (Figs. 10 & 11). Relative abundances of aliphatics in the coal sample from the Kosakuts River closely resembles those of coaly material floated from sediments from the Duktoth River (Fig. 11), and relative abundances of the hydrocarbon biomarkers of the Kosakuts coal are also fairly similar, with $C_{27}S < C_{28}S < C_{29}S <$ ol < hop in the Kosakuts coal sample (Van Kooten et al., 2002), at concentrations comparable with the *n*-alkane concentrations. If this suite of aliphatic and hydrocarbon biomarkers is typical of the Kulthieth Formation, then the hydrocarbon signatures of the Kaliakh and Duktoth River discharges are likely to be similar, with neither more than a minor perturbation of the dominant Gulf of Alaska pattern.

In agreement with Boehm et al. (2001), we suspect the dominant source of hydrocarbons in the northern Gulf of Alaska sediments is an organic-rich shale, most likely somewhere beneath the Malaspina Glacier. The close intercorrelation of the PAH, aliphatic and biomarker hydrocarbons in the Gulf of Alaska sediments strongly suggests a single dominant source or collection of closely related sources, with minor perturbations from local inputs derived from coal beds and other siliciclastic units of varying organic carbon contents and thermal maturities located to the west of the Malaspina Glacier. Sediments eroded by the Malaspina Glacier are clearly a major source of hydrocarbons to the Gulf of Alaska, because the abrupt increase of hydrocarbons in the Gulf of Alaska sediments coincides with sedimentary discharges from the

glacier downstream of the Alaska Coastal Current (Fig. 1). On both a sediment mass basis and an organic carbon basis (Van Kooten et al. 2002), the highest concentration of PAH in northern Gulf of Alaska sediments we observed was at station 5 within Icy Bay, directly in front of the large sediment discharge from the Malaspina Glacier into the Bay (Fig. 1), indicating this discharge may be an especially concentrated input of hydrocarbon-laden sediments to the Gulf of Alaska. The high concentrations of sedimentary hydrocarbons at stations 3, 4, and 5 along the perimeter of the Malaspina Glacier, together with the high intercorrelation of hydrocarbons at these stations, suggests a terrestrial source of hydrocarbon-rich sediment of nearly uniform hydrocarbon composition beneath this glacier that is sufficiently large to produce a geochemically similar discharge along its entire face, from Yakutat to Icy Bays. If so, the combination of high sediment discharge rates and high concentrations of hydrocarbons in the discharged sediments would result in a massive input to the northern Gulf of Alaska sediments, with a hydrocarbon abundance pattern that could only be perturbed to a minor extent by the much smaller sediment discharges to the west (Fig. 1B).

F. Implications for Hydrocarbon Source Apportionment Models

Our results demonstrate that the hydrocarbon source-apportionment models previously used for evaluating hydrocarbon burdens in northern Gulf of Alaska benthic sediments do not accurately predict the fate of hydrocarbons in the fluvio-marine environment. Our analyses of the geochemical fingerprints within fluvial and coastal marine sediments show that the Yakataga seep oils exert a negligible influence Gulf of Alaska benthic sediment geochemistry. The least-squares source allocation model of Boehm et al. (2001) predicts that seep oils are a substantial hydrocarbon source: seep-oil contributions to the PAH burden of offshore benthic sediments adjacent to the Yakataga district in the range between 35–75%, and that roughly 5–90% of the petrogenic hydrocarbons in the riparian sediments from the Yakataga District are derived from oil seeps. Our results from hydrocarbon analyses of physically separated coaly particles are comparable to estimates from the source allocation models. Boehm et al. (2001) predict that coal beds account for 0-8% of the total petrogenic hydrocarbons in riparian sediments from the Yakataga District, and analyses of our float fractions show that coaly particles account for 0–28% and 0–11% of the total PAH and n-alkane sediment burdens, respectively. The disparity between model outputs and geochemical analyses for different prospective hydrocarbon sources is likely the result of two interacting factors.

One crucial assumption implicit in the hydrocarbon source apportionment models of Boehm et al. (2001) and of Mudge (2002) is that the inventory of potential hydrocarbon source signatures used as model inputs is complete. Omission of a single significant source from the inputs of these kinds of models may lead to serious source allocation errors. In addition to excluding low-maturity Kulthieth Formation coal as a prospective source, Boehm et al. (2001) were unable to consider sources beneath glaciers and hence unavailable for sampling. Lacking access to authentic endmember samples, a thorough inventory of sediment and especially SPM samples from streams draining from the Malaspina Glacier into the Gulf of Alaska may at least permit a more realistic allocation of hydrocarbon contributions to the marine sediments. Boehm et al. (2001) did include samples of glacial flour from the Malaspina Glacier in their model, but it

is not clear whether these samples adequately represent hydrocarbon inputs derived from the Malaspina to northern Gulf of Alaska sediments.

Omission of hydrocarbon analytes that have high discriminating power further hampers the performance of the Boehm et al. (2001) and Mudge (2002) models. Inclusion of a large number of analytes in such models is no guarantee of accuracy, if the analytes are highly intercorrelated. In the present case, perylene, Ph and the *n*-alkanes retain important information regarding their sources. These analytes are frequently omitted from hydrocarbon source allocation efforts because they are often subject to interferences and degradation. The possibilities of perylene production by diagenesis, Ph introduction from anthropogenic pollution, and microbial decomposition of *n*-alkanes have often precluded their consideration as reliable indicators of hydrocarbon sources, but these concerns are not applicable to the northern Gulf of Alaska sediments. Perylene is characteristically abundant in the terrestrial sediments of the Yakataga Forelands, whether in bulk riparian sediments, coaly material separated from them or the remaining inorganic sediment, or in SPM transported to the Gulf of Alaska, but perylene is a characteristically minor PAH in the Gulf of Alaska sediments. Likewise, the characteristically low Ph concentrations of the Gulf of Alaska sediments in comparison with the *n*-alkanes places another important constraint on mixtures of potential hydrocarbon sources evaluated by the source allocation models, as does the entire spectrum of *n*-alkanes, which are usually rapidly biodegraded but not in the present case. We therefore expect that inclusion of these hydrocarbons in the source allocation models would alter their predictions substantially.

Conclusions

The PAH and aliphatic hydrocarbon compositions of aqueous, SPM, and riparian sediment samples indicate that fluvial systems draining the Yakataga Forelands convey a substantive petrogenic hydrocarbon burden to the Gulf of Alaska continental shelf. The geochemical signatures of individual drainage basins vary, depending on both the types and proportions of exposed rock formations. Active petroleum seeps within these drainage basins readily overprint these geochemical signatures, and seep-derive hydrocarbons undergo fluvial transport largely through oil-SPM associations. However, the combination of modest seepage rates and high SPM loads serves to rapidly attenuate the influence of petroleum seeps on fluvial geochemistry. As a result, of the fluvial systems studied, only Johnston Creek was found to convey a discernible load of seep-derived hydrocarbons to the Gulf of Alaska.

Total hydrocarbon concentrations in Gulf of Alaska benthic sediments are highly variable; however, the relative geochemical fingerprints recorded in these sediments are remarkably similar. The persistence of this geochemical fingerprint argues against a labile hydrocarbon source, e.g., oil-SPM associations, that would undergo substantial alteration during coastal marine transport. The prominence and persistence of *n*-nonane indicates that hydrocarbons sequestered in eroded coal and shale particles sampled here are little affected by weathering processes, and persist in transport from terrestrial sources to the benthic sediments of the northern Gulf of Alaska. These hydrocarbons include the *n*-alkanes, Ph and perylene, which retain information regarding their sources as well as the hydrocarbon biomarkers. Comparison of hydrocarbon concentration patterns that characterize northern Gulf of Alaska sediments with

those characterizing known hydrocarbon sources or inputs reveals significant discrepancies in every case, indicating the dominant sources of hydrocarbons in these sediments remain to be identified. The geographic association of hydrocarbons in the benthic sediments with inputs from the Malaspina Glacier, along with the regional dominance of this glacier as source of sediments, suggests that the dominant sources of hydrocarbons in benthic sediments of the northern Gulf of Alaska are probably located beneath it. Finally, previous assessments of hydrocarbon source contributions to the benthic sediments of the northern Gulf of Alaska based on statistical hydrocarbon source allocation models are not reliable, because the inventory of sources included in these models is not complete, and because analytes with high discriminating power were not included.

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Tables

Table 1. Site Information for Benthic and Riparian Sample Stations.

Station ID	Station Name	Latitude (N)	Longitude (W)	Depth (m)
Gulf of Alaska				
1	Southwest Yakutat	59° 24.3'	139° 49.7'	154
2	Yakutat Valley	59° 25.6'	141° 09.4'	327
3	Yakutat Bay	59° 40.2'	139° 58.2'	158
4	Point Riou	59° 43.1'	141° 39.3'	81
5	Icy Bay	60° 00.0'	141° 23.3'	102
6	East Yakataga	59° 56.3'	142° 02.0'	41
7	West Yakataga	59° 58.8'	142° 40.9'	106
8	Pamplona Spur	59° 47.7'	142° 42.3'	196
9	Cape St. Elias	59° 39.9'	144° 25.6'	151
10	Duktoth River	60° 05.389'	142° 30.024'	NA
11	Big River	59° 58.611'	141° 45.967'	NA
12	Johnston Cr. – upstream	60° 01.926'	141° 53.406'	NA
13	Johnston Cr. – mouth	60° 00.833'	141° 54.616'	NA
14	Munday Cr. – upstream	60° 02.714'	141° 57.244'	NA
15	Munday Cr. – mouth	60° 00.999'	141° 56.418'	NA
16	Munday Cr. – downstream of tributary	60° 02.411'	141° 57.511'	NA
17	Munday Cr. – seep tributary	60° 02.436'	141° 57.494'	NA

Table 2. Polycyclic Aromatic Hydrocarbon Distribution Between Dissolved* and Particulate Phases at Yakataga District River Sample Stations.†

Station ID	Station Name	PAHs, dissolved (ng L^{-1})	PAHs, particulate (ng g^{-1} SPM)	SPM (g L^{-1})	PAHs, particulate (ng L^{-1})	PAHs, Total (ng L^{-1})	PAHs, dissolved (%)
No Recently Documented Petroleum Seeps							
10	Duktoth R. - mouth	482	5040	2.75	13900	**14300**	**3**
11	Big R. - mouth	539	1640	0.85	1400	**1940**	**28**
12	Johnston Cr. - upstream	145	579	0.33	193	**338**	**43**
14	Munday Cr. - upstream	135	514	3.49	1800	**1930**	**7**
Downstream from Documented Petroleum Seeps							
13	Johnston Cr. - mouth	1140	5130	0.54	2790	**3930**	**29**
17	Munday Cr. - seep tributary	2100	1020	0.33	337	**2440**	**86**
16	Munday Cr. - downstream from tributary	365	908	5.20	4720	**5090**	**7**
15	Munday Cr. - mouth	101	717	1.29	923	**1020**	**10**

* *defined as material that passes through a 0.7 μm glass fiber filter*

† *concentrations reported to three significant figures*

Table 3. Percentage of Hydrocarbons Associated with the Float Fraction (Coaly Material).

Station ID	Station Name	Mass, Sink (g)	Mass, Float (mg)	%TPAH, Float	%TNA, Float
Yakataga Forelands - Riparian Sediments					
10	Duktoth R. - mouth	262	104	**5.3**	**1.8**
11	Big R. - mouth	306	33.8	**14.0**	**4.0**
12	Johnston Cr. - upstream	278	293	**28.8**	**10.8**
13	Johnston Cr. - mouth	287	85.0	**10.7**	**4.5**
14	Munday Cr. - upstream	270	40.0	**8.0**	**4.0**
15	Munday Cr. - upstream	288	33.3	**4.5**	**1.7**
16	Munday Cr. - downstream from tributary	278	94.0	**20.2**	**7.7**
17	Munday Cr. - seep tributary	176	0.0	**0**	**0**
Gulf of Alaska - Benthic Sediments					
5	Icy Bay	235	18.5	**1.1**	**0.4**
6	East Yakataga	499	31.0	**2.8**	**1.2**
7	West Yakataga	228	37.4	**4.0**	**2.3**
9	Cape St. Elias	207	92.0	**6.1**	**1.8**

APPENDIX A. Polycyclic Aromatic Hydrocarbon Concentrations (ng PAH g^{-1} dry weight sample) in Bulk Sediment Samples and Prospective Hydrocarbon Sources.

Station ID	Station Name	TOC (wt.%)	TPAH	N0	N1	N2	N3	N4	bip	ace	acn	F0	F1	F2	F3	D0	D1	D2	D3
	Gulf of Alaska - Benthic Sediment Samples																		
1	south of Yakutat Bay	0.52	62	2	5	6	7	4	1	0	0	1	2	2	1	0	0	0	0
2	Yakutat Valley	0.62	580	12	41	59	51	17	9	0	1	19	31	36	12	3	4	3	1
3	Yakutat Bay	0.50	1720	58	214	193	155	53	32	0	3	48	60	48	14	9	9	6	2
4	Pt. Riou	0.41	2760	61	240	292	285	107	35	0	4	77	130	156	55	13	22	19	8
5	Icy Bay	0.48	5680	80	395	640	671	260	57	0	7	151	298	378	109	22	53	54	26
6	East Yakataga	0.19	1330	21	105	166	167	63	15	0	2	36	69	86	29	6	12	11	5
7	West Yakataga (Duktoth R.)	0.52	3230	66	266	342	351	140	38	0	5	89	158	198	60	14	27	24	11
8	W. Pamplona Spur	0.58	2510	54	220	292	271	98	34	1	4	64	109	132	43	13	21	18	8
9	Cape St. Elias	0.66	3010	63	266	341	339	129	35	0	4	78	140	176	56	13	25	21	9
	Yakataga Forelands - Riparian Sediment Samples																		
10	Duktoth River - mouth	0.20	2820	103	461	517	419	139	35	0	5	43	63	60	21	11	16	11	4
11	Big River - mouth	0.13	310	6	26	39	49	22	3	0	2	3	6	12	6	1	2	2	1
12	Johnston Creek - upstream	0.18	424	12	50	61	73	26	6	0	4	5	8	14	7	1	4	3	2
13	Johnston Creek - mouth	0.19	524	11	41	45	66	44	4	0	3	4	10	26	14	1	4	4	2
14	Munday Creek - upstream	0.17	206	4	17	21	33	16	2	0	2	2	4	7	4	1	2	1	1
15	Munday Creek - mouth	0.18	219	4	16	22	36	20	2	0	2	2	4	7	4	1	2	2	1
16	Munday Creek -downstream of tributary	0.16	230	4	18	24	39	21	2	0	2	3	5	9	5	1	2	2	1
17	Munday Creek - tributary	1.00	11300	43	263	584	616	353	27	0	3	19	53	164	154	9	34	29	61
	Prospective Hydrocarbon Sources																		
x	coal - KOS-8 15-10 µm	84.5	3930000	197000	618000	729000	610000	143000	76300	0	911	8500	30700	90200	31000	12100	25400	19700	7790
x	coal - Samovar Hills 15-10 µm	63.5	472000	15700	36700	53200	137000	97500	278	0	205	667	832	4950	3690	140	8200	1590	118
x	seep oil - Munday Creek	86.5	11200000	0	1370	12800	69600	65500	401	0	15	0	14100	63200	364000	0	12500	52300	137000
x	seep oil - Johnston Creek	85.7	6440000	546	5910	12100	70100	135000	553	379	4290	2930	85300	419000	443000	589	8860	74500	75700
x	shale - Kayak Island 15-10 µm	6.69	103000	1470	13700	21000	25900	14100	88	0	93	135	290	1580	773	401	1220	1340	787
x	siltstone - Marvitz Creek 15-10 µm	0.49	11700	326	2370	2620	1570	216	427	0	9	38	40	219	25	9	22	0	0

APPENDIX A. (cont'd) Polycyclic Aromatic Hydrocarbon Concentrations (ng PAH g^{-1} dry weight sample) in Bulk Sediment Samples and Prospective Hydrocarbon Sources.

Station ID	Station Name	P0	P1	P2	P3	P4	ant	flu	pyr	FP1	baa	C0	C1	C2	C3	C4	bbf	bkf	bep	bap	per	icp	dba	bgp
	Gulf of Alaska - Benthic Sediment Samples																							
1	south of Yakutat Bay	3	5	4	2	1	0	1	1	1	0	1	1	1	1	0	2	0	1	0	4	1	0	1
2	Yakutat Valley	37	67	48	24	6	1	5	8	18	2	9	13	9	2	1	7	0	5	2	6	2	1	7
3	Yakutat Bay	131	196	116	57	6	3	12	23	67	6	30	37	25	3	1	28	0	16	5	12	8	5	25
4	Pt. Riou	160	306	236	120	28	7	16	28	87	9	36	64	48	13	3	23	0	18	7	16	4	3	21
5	Icy Bay	250	606	564	290	98	8	20	43	129	13	61	127	116	32	5	31	0	27	10	15	5	4	26
6	East Yakataga	61	136	119	60	20	2	4	9	26	3	14	26	24	6	1	6	1	6	2	3	1	1	6
7	West Yakataga (Duktoth R.)	170	350	290	148	52	6	16	29	88	9	38	73	59	15	3	23	0	19	8	16	4	3	21
8	W. Pamplona Spur	148	285	144	116	41	7	16	26	80	8	34	62	47	12	2	20	18	16	6	14	4	4	20
9	Cape St. Elias	156	322	267	135	48	5	14	26	74	8	37	64	52	15	3	22	0	18	6	13	4	3	22
	Yakataga Forelands - Riparian Sediment Samples																							
10	Duktoth River - mouth	133	258	192	109	19	2	9	12	62	3	21	22	27	4	0	14	0	10	4	4	1	2	5
11	Big River - mouth	7	21	27	21	5	1	2	3	9	0	3	4	7	2	0	2	0	2	1	12	0	0	2
12	Johnston Creek - upstream	14	26	25	18	3	1	4	4	13	1	3	3	5	1	0	2	0	2	1	23	0	0	2
13	Johnston Creek - mouth	19	63	63	32	3	1	3	5	14	1	4	4	6	1	0	2	0	2	1	20	0	0	2
14	Munday Creek - upstream	6	12	12	9	1	1	2	3	7	0	2	2	3	1	0	2	0	2	1	17	0	0	3
15	Munday Creek - mouth	6	14	14	10	3	1	2	3	7	0	2	2	3	0	0	2	0	2	1	19	0	0	3
16	Munday Creek -downstream of tributary	7	14	14	11	1	1	2	3	8	0	2	2	3	0	0	2	0	2	1	18	0	0	2
17	Munday Creek - tributary	159	462	655	1250	1120	4	14	70	614	1	406	775	1940	698	37	170	0	241	54	84	0	58	71
	Prospective Hydrocarbon Sources																							
x	coal - KOS-8 15-10 µm	192000	394000	321000	152000	47300	1840	5800	8620	42100	7060	23100	51700	54000	14700	2050	3620	1200	4130	2900	166	171	1070	1630
x	coal - Samovar Hills 15-10 µm	2580	16400	21400	31600	17600	2010	974	862	3480	893	1230	3090	4530	928	347	25	88	109	492	2520	0	0	93
x	seep oil - Munday Creek	1090	231000	3250000	3630000	713000	5640	2730	138000	331000	72000	273000	548000	805000	205000	6170	80700	0	52200	11300	14050	2210	13800	7650
x	seep oil - Johnston Creek	60200	477000	1590000	1450000	226000	1930	13600	67000	251000	26900	101000	239000	268000	195000	12300	44900	0	40600	12000	4270	4450	6580	6470
x	shale - Kayak Island 15-10 µm	1510	4110	5540	4080	1700	10	34	112	143	22	173	442	1330	368	19	15	7	40	11	4	0	5	26
x	siltstone - Marvitz Creek 15-10 µm	991	1510	818	72	6	0	28	65	88	12	131	21	2	0	0	28	0	28	5	2	0	0	56

APPENDIX B. Aliphatic Hydrocarbon Concentrations (ng aliphatic g^{-1} dry weight sample) in Bulk Sediment Samples and Prospective Hydrocarbon Sources.

Station ID	Station Name	TOC (wt.%)	TNA	[UCM]	*n*C9	*n*C10	*n*C11	*n*C12	*n*C13	*n*C14	*n*C15	*n*C16	*n*C17	Pr	*n*C18	Ph	*n*C19	*n*C20	*n*C21
	Gulf of Alaska - Benthic Sediment Samples																		
1	south of Yakutat Bay	0.52	256		3	3	6	4	5	5	15	5	9	14	5	2	6	5	13
2	Yakutat Valley	0.62	632	1430	18	21	27	28	28	27	39	21	27	56	23	6	26	25	30
3	Yakutat Bay	0.50	1890	3890	71	71	93	95	94	83	129	79	88	139	70	18	70	67	72
4	Pt. Riou	0.41	2350	8000	75	87	123	123	117	112	153	103	106	221	102	38	105	106	108
5	Icy Bay	0.48	4690	23300	132	203	266	261	251	224	245	208	207	425	218	96	210	213	207
6	East Yakataga	0.19	1070	4450	37	42	58	57	41	48	75	43	45	98	40	17	42	43	43
7	West Yakataga (Duktoth R.)	0.52	2640	11800	86	100	147	145	141	128	188	120	118	256	119	50	119	119	120
8	W. Pamplona Spur	0.58	2320	8730	66	92	118	119	116	106	150	100	108	225	101	36	105	101	107
9	Cape St. Elias	0.66	2610	2270	107	84	133	133	131	121	179	118	118	288	116	56	114	112	114
	Yakataga Forelands - Riparian Sediment Samples																		
10	Duktoth River - mouth	0.20	4640	16100	127	144	174	161	185	142	173	156	172	505	205	99	216	223	230
11	Big River - mouth	0.13	614	6070	9	0	12	10	12	9	13	14	21	89	18	39	20	25	24
12	Johnston Creek - upstream	0.18	765	8230	13	13	17	18	16	24	23	19	22	114	23	62	24	26	28
13	Johnston Creek - mouth	0.19	755	7730	12	9	19	20	20	2	27	21	23	111	24	57	25	26	30
14	Munday Creek - upstream	0.17	479	5770	8	0	7	8	7	7	1	11	15	87	13	54	14	13	18
15	Munday Creek - mouth	0.18	511	4890	7	0	8	8	10	7	11	11	16	89	13	60	14	15	19
16	Munday Creek -downstream of tributary	0.16	498	5220	7	2	7	8	7	13	1	11	15	89	13	56	13	15	18
17	Munday Creek - tributary	1.00	4510	1210000	13	0	0	0	629	0	28	226	125	965	851	236	569	59	330
	Prospective Hydrocarbon Sources																		
x	coal - KOS-8 15-10 µm	84.5	706000	3280000	0	37100	76600	59700	50500	34900	51300	24300	24900	92200	30000	13600	30500	33600	33100
x	coal - Samovar Hills 15-10 µm	63.5	412000	2670000	0	2310	7640	5790	7340	4090	4340	7160	1130	163000	7390	11600	16800	17700	20800
x	seep oil - Munday Creek	86.5	3380000	247000000	7250	7070	0	0	0	386000	691000	316000	315000	625000	130000	12600	61500	127000	69400
x	seep oil - Johnston Creek	85.7	152000	43900000	246	2250	208	3040	3550	3960	5210	4420	8070	36400	3550	925	14500	1050	11300
x	shale - Kayak Island 15-10 µm	6.69	195000	1480000	3370	8610	12300	10700	12000	9850	12500	10700	10900	42000	10300	10700	9550	10800	9390
x	siltstone - Marvitz Creek 15-10 µm	0.49	9050	164000	134	150	640	219	275	338	186	136	433	1760	406	283	362	410	506

***BQL:** below quantitation limit*

***ND:** not detected*

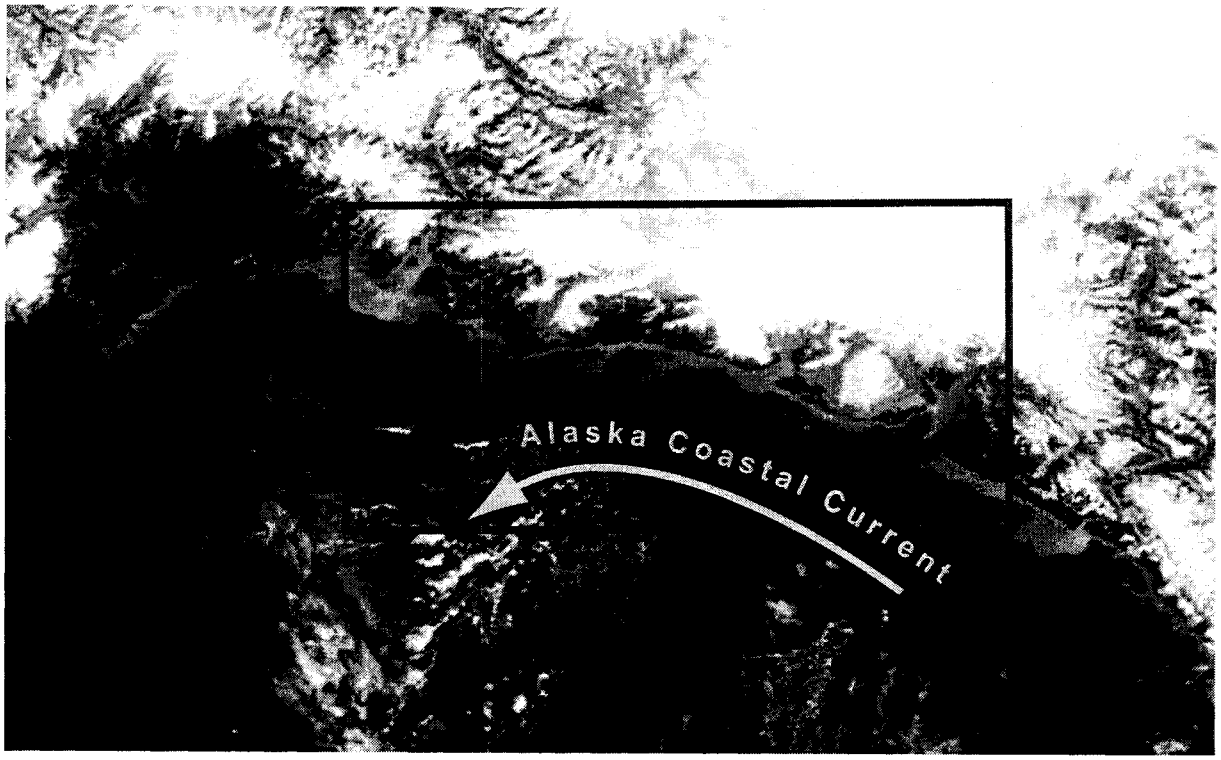
APPENDIX B. (cont'd) Aliphatic Hydrocarbon Concentrations (ng aliphatic g^{-1} dry weight sample) in Bulk Sediment Samples and Prospective Hydrocarbon Sources.

Station ID	Station Name	*n*C21	*n*C22	*n*C23	*n*C24	*n*C25	*n*C26	*n*C27	*n*C28	*n*C29	*n*C30	*n*C31	*n*C32	*n*C33	*n*C34	C27st	C28st	C29st	ol	hop
	Gulf of Alaska - Benthic Sediment Samples																			
1	south of Yakutat Bay	13	6	8	4	16	5	39	2	43	8	19	8	14	2	BQL	BQL	BQL	BQL	BQL
2	Yakutat Valley	30	19	24	21	31	19	39	13	46	13	30	7	24	4	1	BQL	1	1	3
3	Yakutat Bay	72	69	78	65	92	65	135	44	114	37	64	37	5	4	1	BQL	2	1	5
4	Pt. Riou	108	83	95	85	105	81	113	62	115	44	77	23	38	13	7	10	10	3	15
5	Icy Bay	207	168	186	169	196	161	213	139	204	97	149	54	72	35	14	16	20	13	31
6	East Yakataga	43	40	45	43	51	43	52	33	47	24	38	14	20	8	4	3	5	2	8
7	West Yakataga (Duktoth R.)	120	90	100	90	109	85	115	68	120	48	86	26	43	15	8	10	11	4	19
8	W. Pamplona Spur	107	81	92	84	104	81	115	59	123	45	73	23	36	11	7	8	9	3	15
9	Cape St. Elias	114	84	96	87	108	89	123	71	132	58	86	29	51	17	8	9	11	5	25
	Yakataga Forelands - Riparian Sediment Samples																			
10	Duktoth River - mouth	230	246	253	253	264	247	255	178	204	120	142	47	77	41	7	5	12	9	40
11	Big River - mouth	24	24	29	30	37	34	50	29	67	21	56	18	23	9	15	10	17	3	14
12	Johnston Creek - upstream	28	26	33	31	41	37	56	33	81	16	72	31	36	7	21	24	31	4	23
13	Johnston Creek - mouth	30	26	33	33	42	37	58	33	80	18	69	26	34	9	21	15	28	5	24
14	Munday Creek - upstream	18	16	21	20	25	22	47	20	69	10	60	16	25	5	23	18	33	3	20
15	Munday Creek - mouth	19	17	22	20	29	22	45	20	74	12	63	17	27	6	20	15	24	2	15
16	Munday Creek - downstream of tributary	18	16	22	20	25	24	44	22	73	12	62	14	26	7	22	14	28	3	17
17	Munday Creek - tributary	330	94	0	52	129	0	57	106	669	159	252	0	157	1	42	81	201	466	1630
	Prospective Hydrocarbon Sources																			
x	coal - KOS-8 15-10 µm	33100	28900	31700	30000	30400	24700	22500	15000	14200	9380	6930	4790	1120	0	ND	111	557	717	6580
x	coal - Samovar Hills 15-10 µm	20800	17700	26400	28700	36900	29300	39100	27200	41100	14100	10700	24000	8370	6010	197	509	2190	327	12100
x	seep oil - Munday Creek	69400	5350	12000	52800	13700	63500	32500	2560	87300	18700	171000	729000	52400	28800	15300	20500	74400	153000	621000
x	seep oil - Johnston Creek	11300	8360	2710	5410	10100	4330	2360	9750	6290	0	19200	5010	17600	0	12300	10700	70400	173000	685000
x	shale - Kayak Island 15-10 µm	9390	8390	7690	6340	6360	4790	4350	3190	5800	2770	4730	1570	3450	4240	1430	1100	1020	116	2500
x	siltstone - Marvitz Creek 15-10 µm	506	772	707	512	462	387	263	138	224	67	458	638	231	0	49	62	57	4	64

BQL: *below quantitation limit*

ND: *not detected*

A



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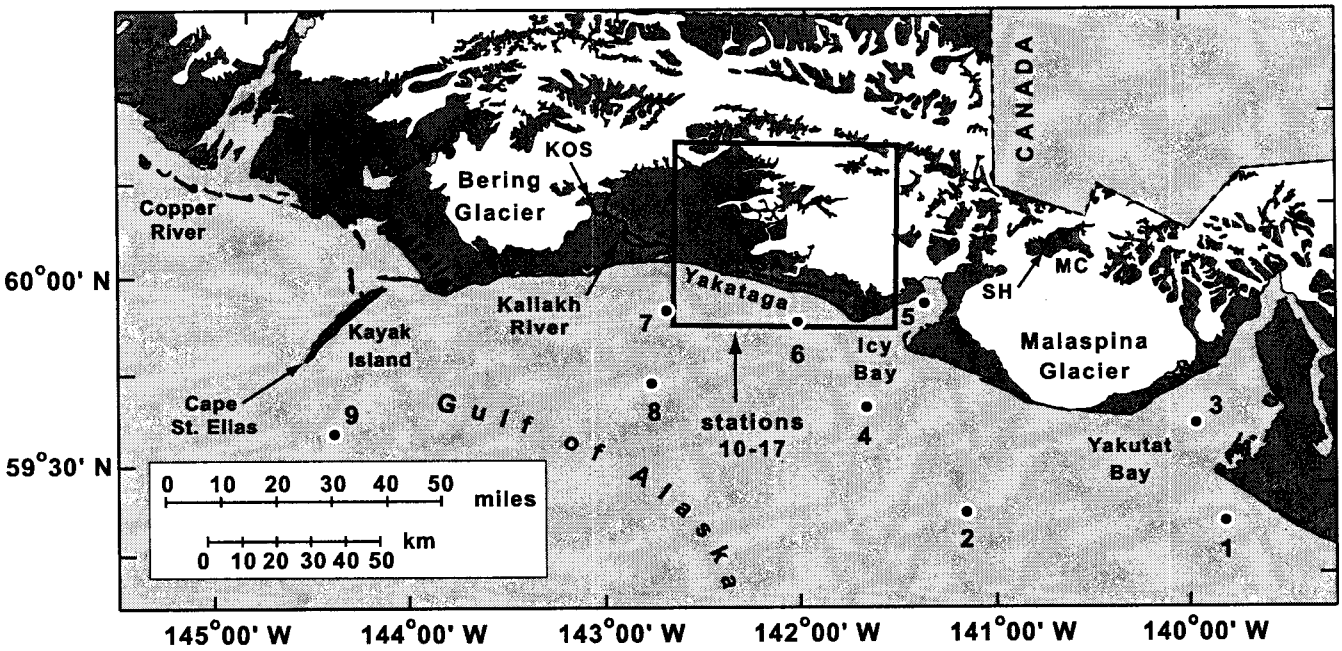


Figure 1 - Short et al. 2004

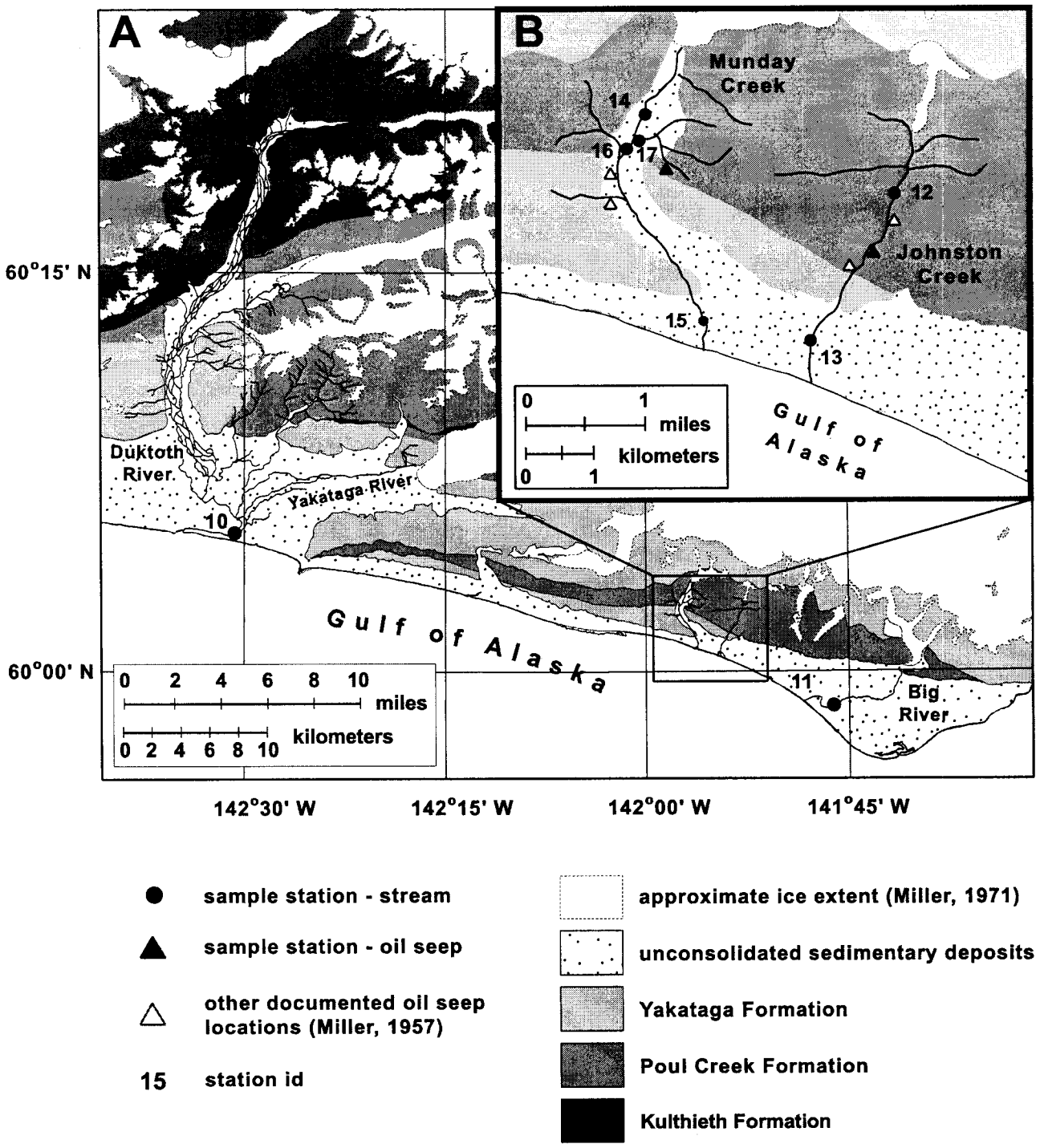
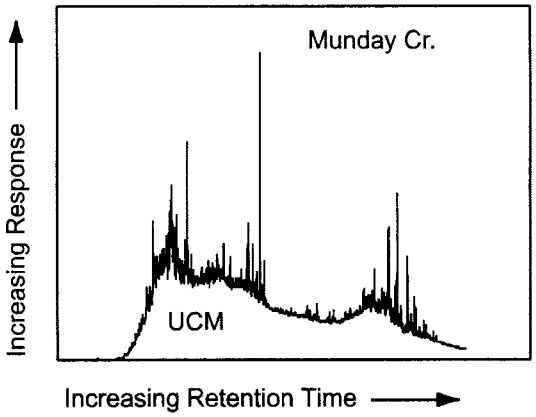


Figure 2 - Short et al. 2004

A



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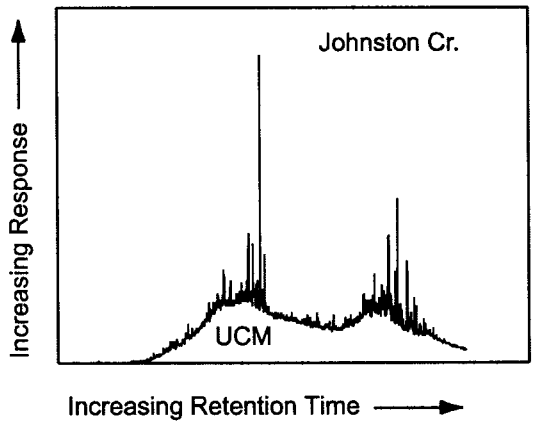
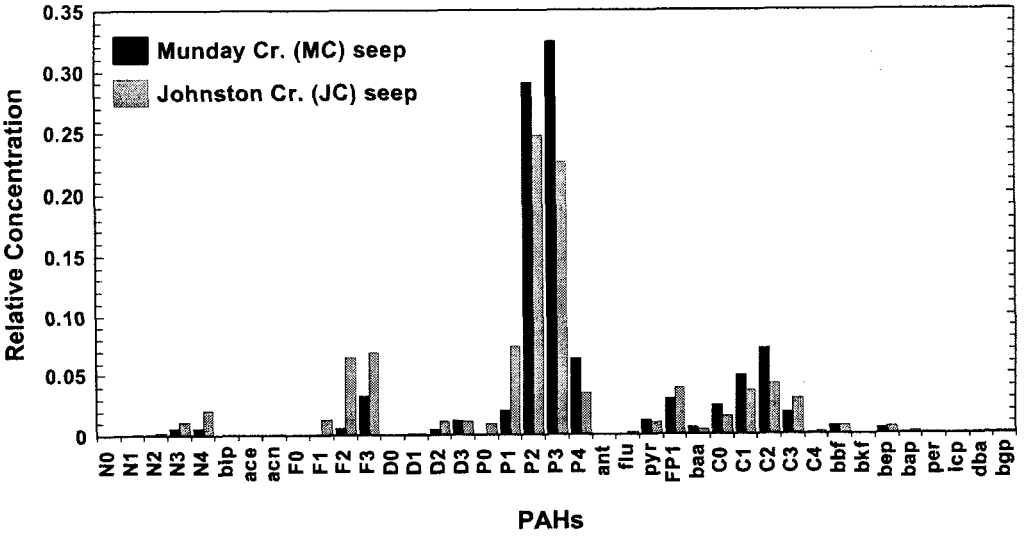


Figure 3 - Short et al. 2004

A



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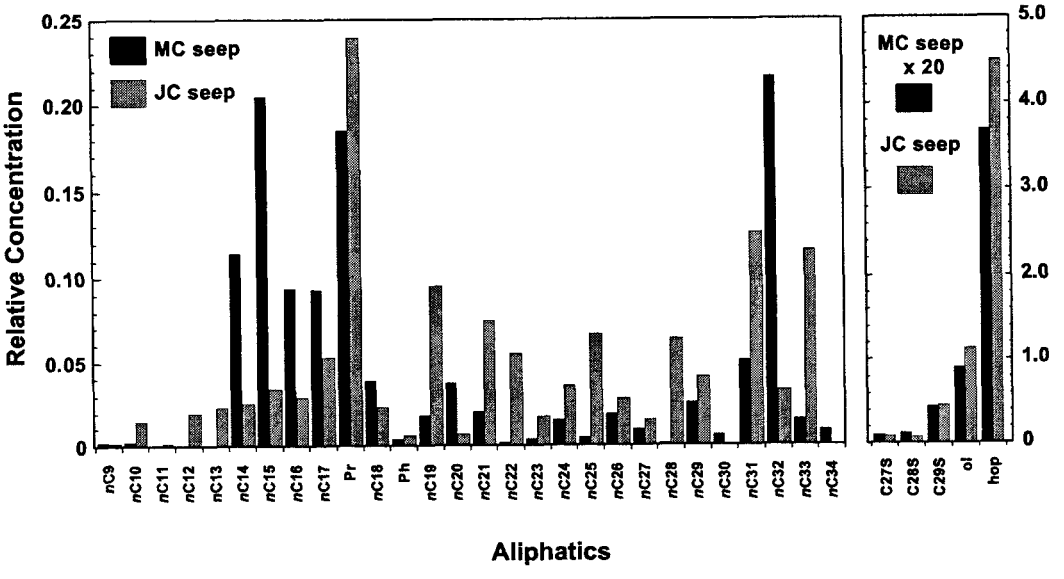


Figure 4 - Short et al. 2004

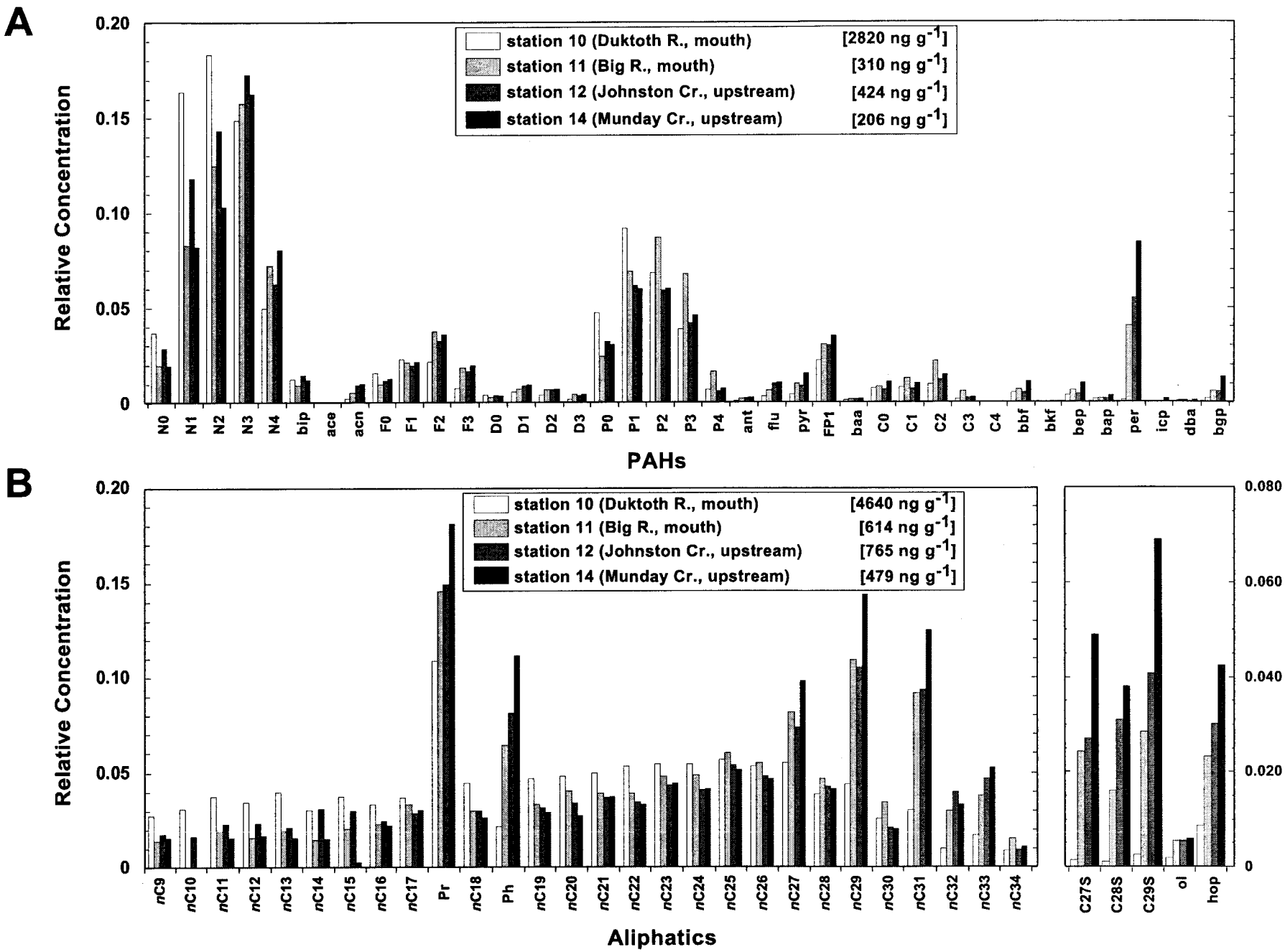


Figure 5 - Short et al. 2004

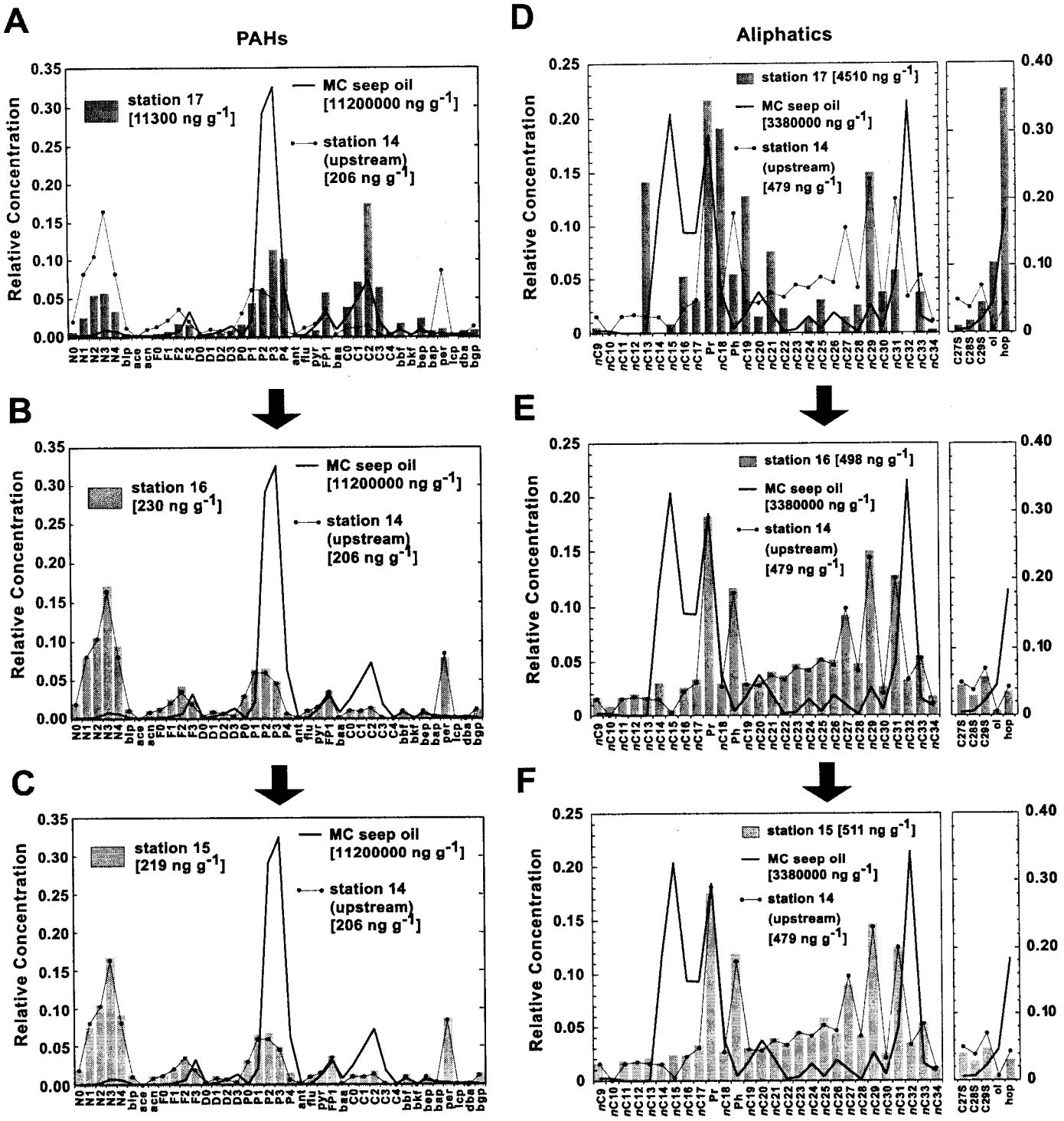
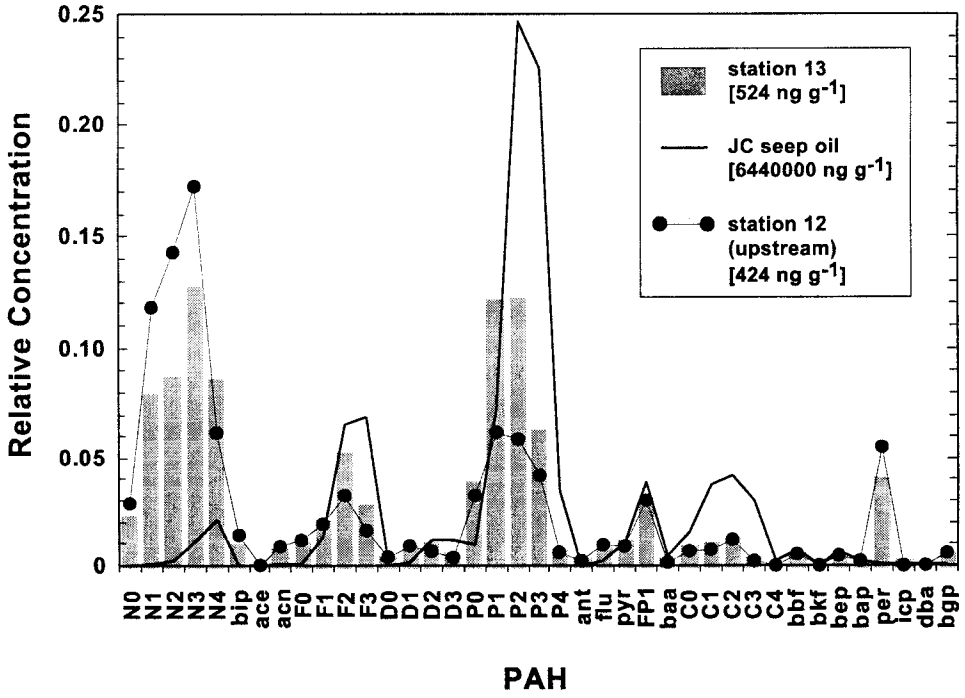


Figure 6 - Short et al. 2004

A



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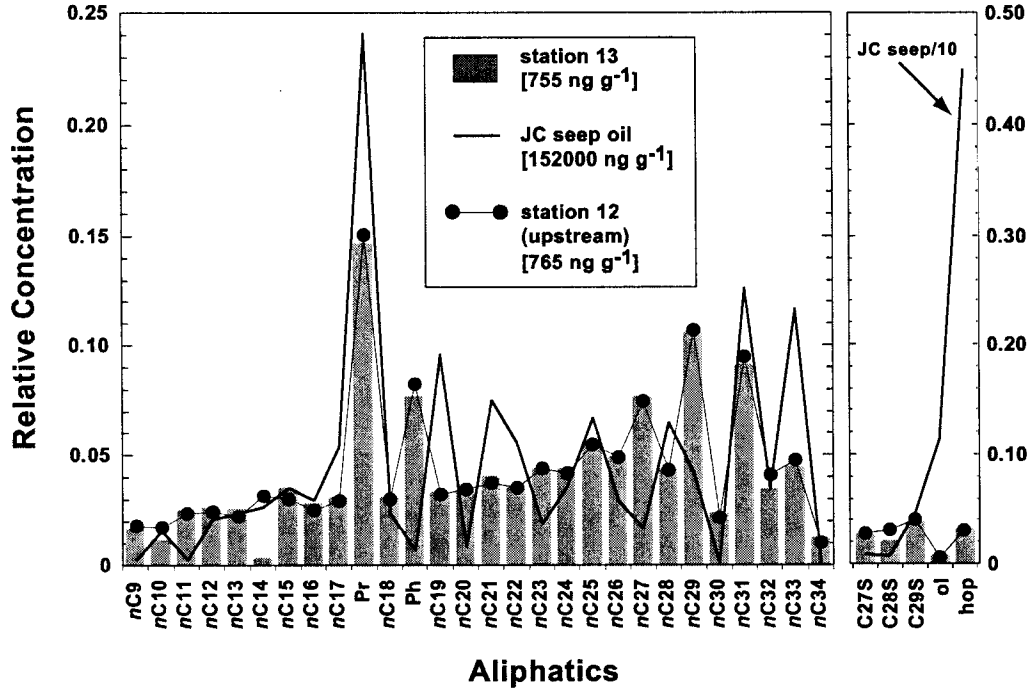


Figure 7 - Short et al. 2004

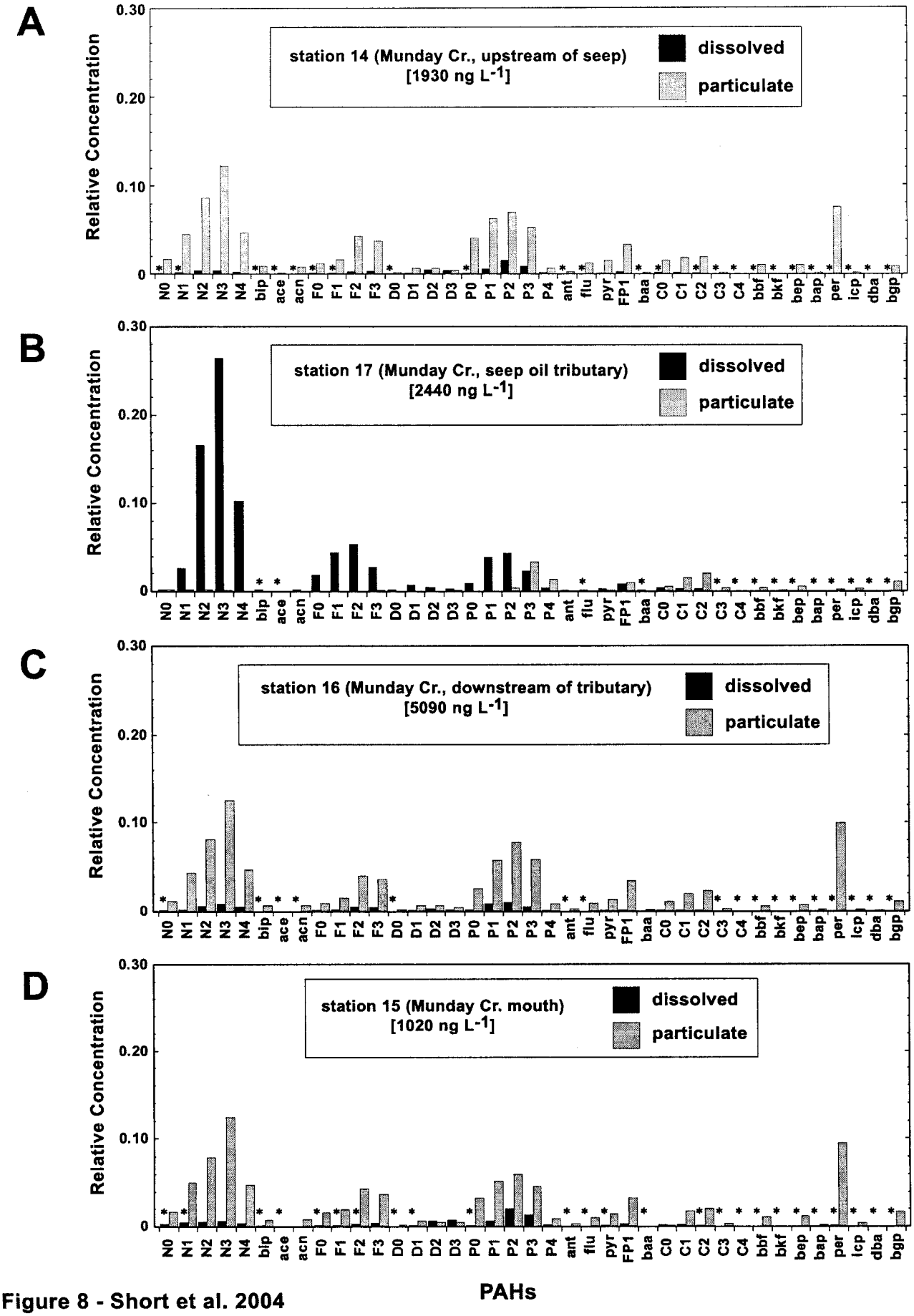


Figure 8 - Short et al. 2004

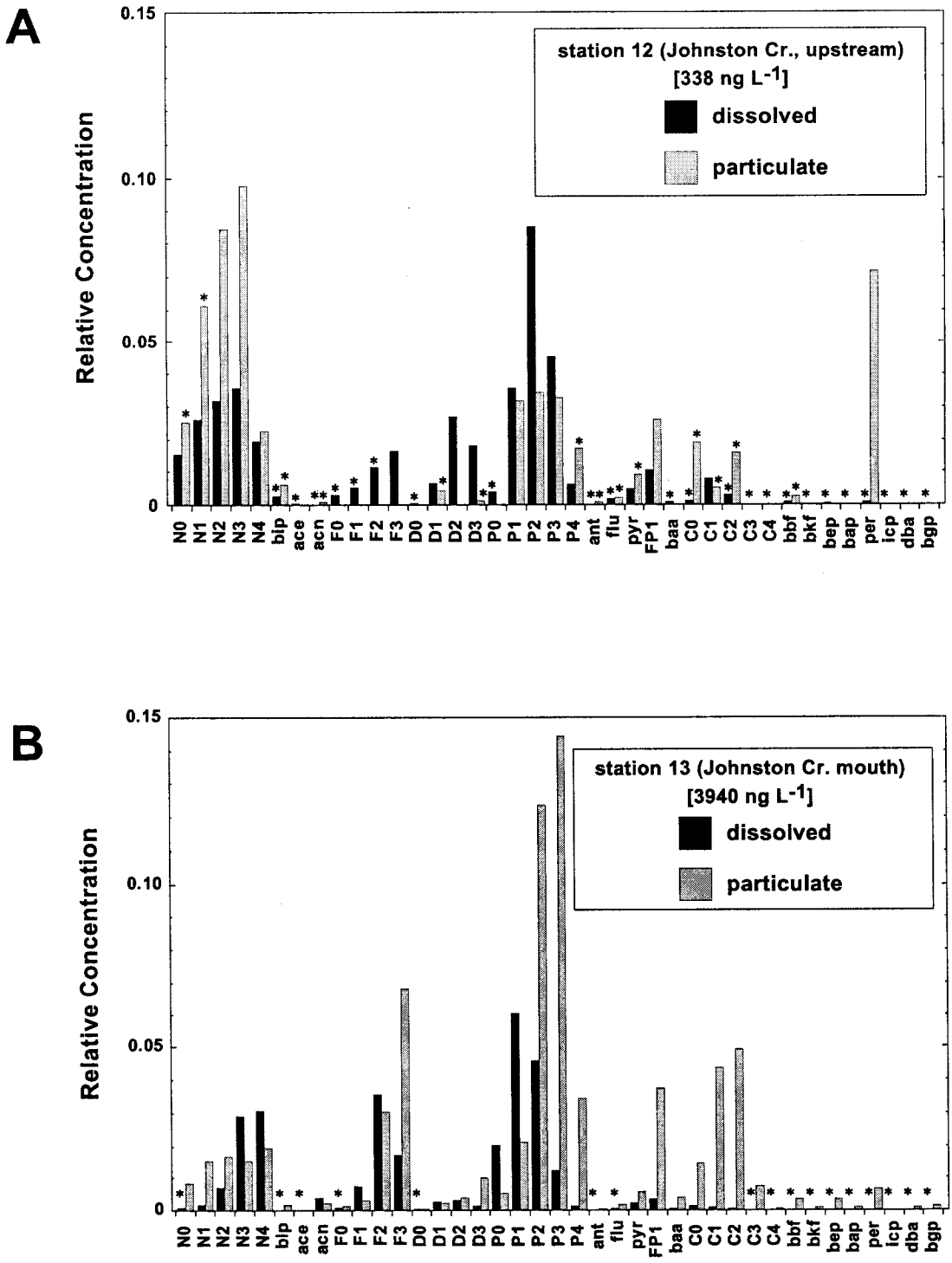
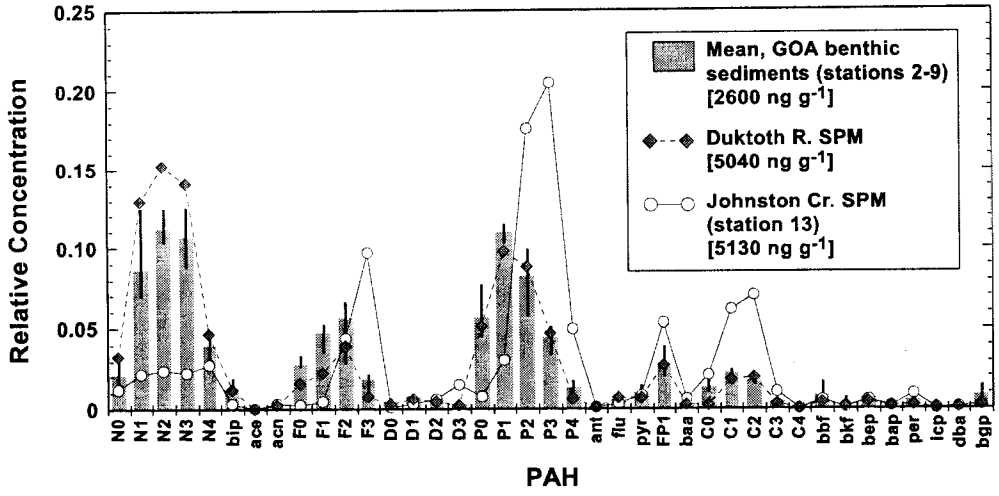


Figure 9 - Short et al. 2004

A



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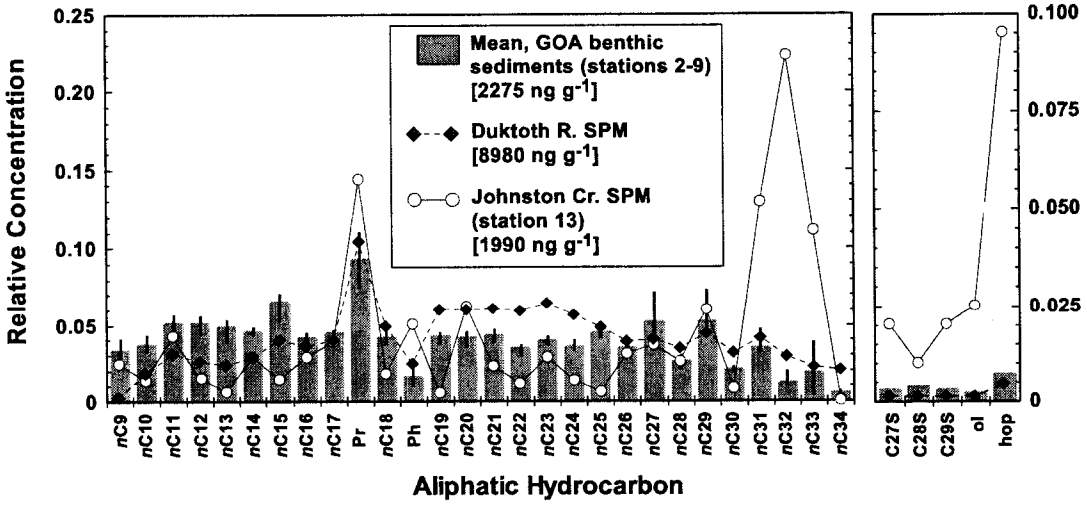


Figure 10 - Short et al. 2004

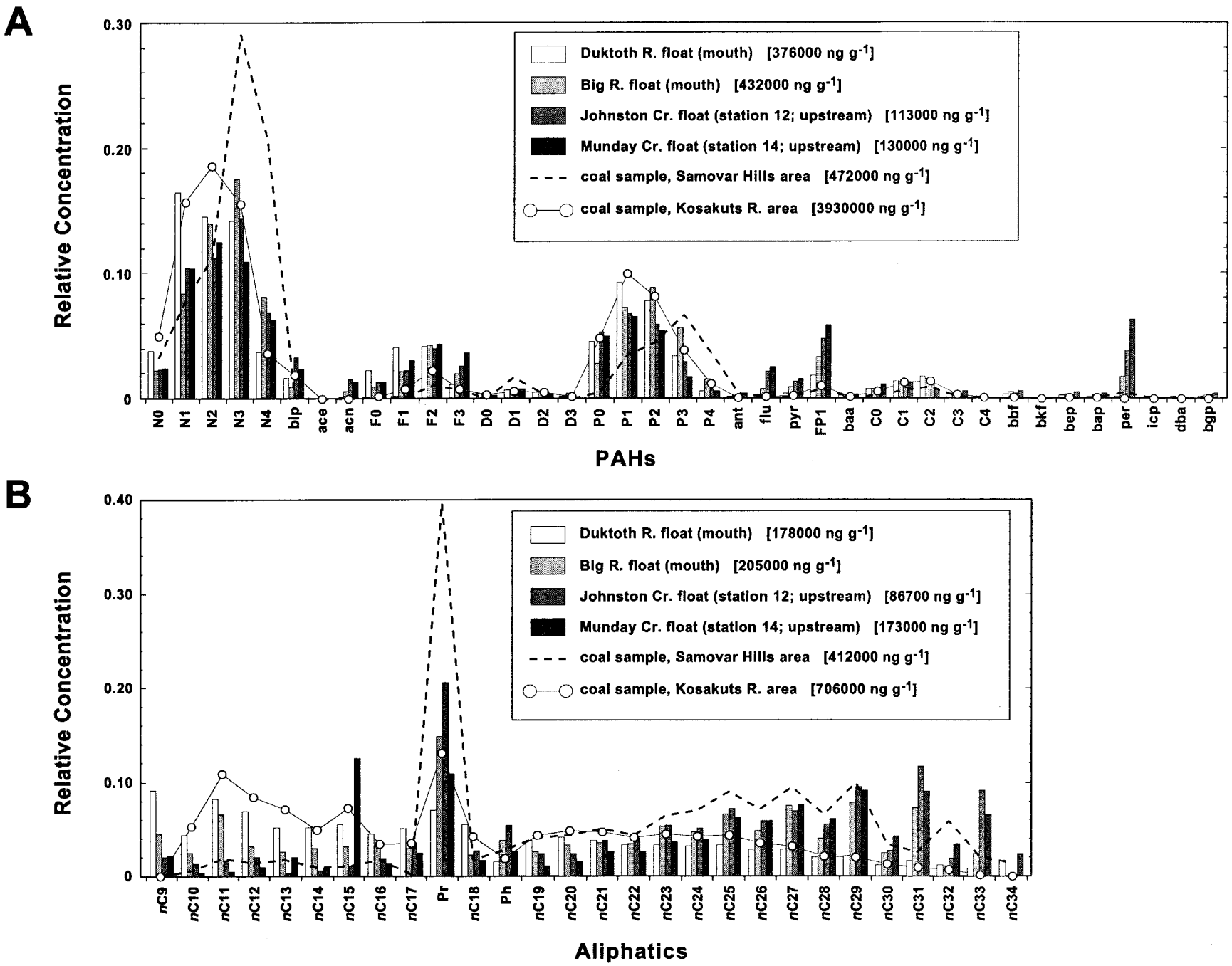
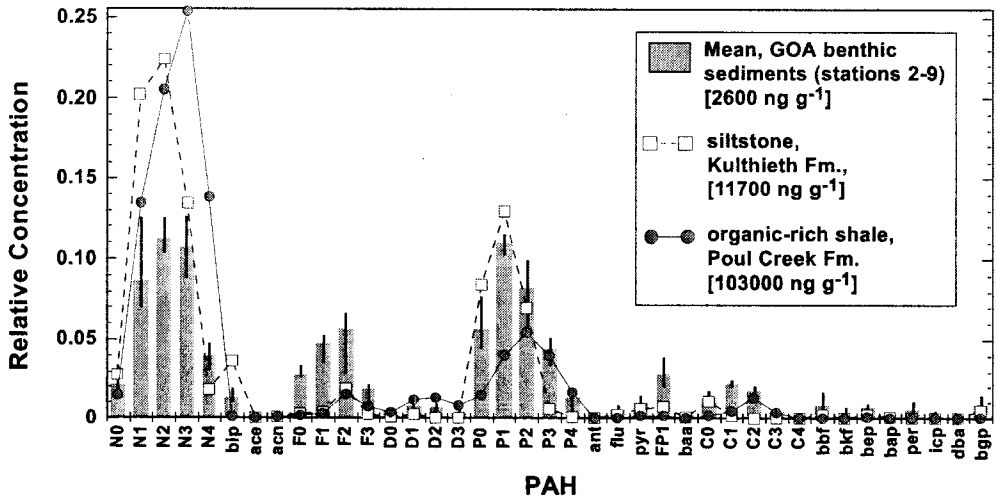


Figure 11 - Short et al. 2004

A



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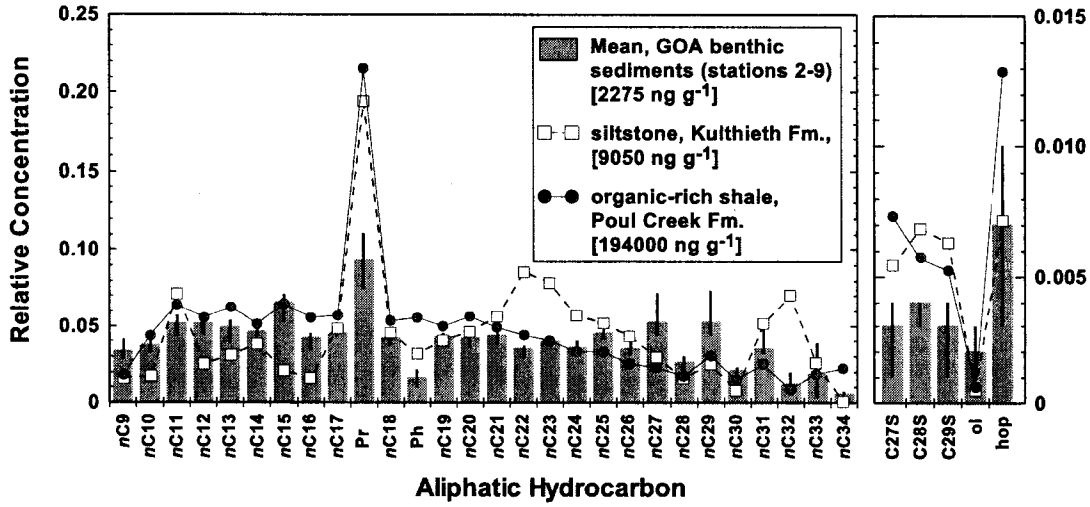

Figure 12 - Short et al. 2004