Aspects of the Exxon Valdez oil spill—a forensic study and a toxics controversy

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ABSTRACT

After the *Exxon Valdez* oil spill in Prince William Sound in March, 1989, much work has been done to track the spilled oil and study its fate and its affect on the environment. Our studies involved developing and applying methods to identify and track the spilled *Exxon Valdez* oil (EVO) as it weathered, as well as to differentiate it from other petrogenic hydrocarbon input sources in PWS. Application of these methods to the study area has yielded two important findings. First, it was discovered that not all the oil or tar on the beaches was EVO. Instead, tarry residues of oil from the Monterey Formation, Southern California, also were prominent on some of the Prince William Sound beaches along with EVO. Monterey Formation oil was used in the early development of Alaska, before the discovery of North Slope Crude, and most likely was disbursed throughout the Sound from the port of Old Valdez in the Great Alaskan Earthquake of 1964. The second study also involves differentiating petrogenic sources. A third petroleum input source to PWS, namely natural oil seeps in the Gulf of Alaska, has been claimed by others to contribute a substantial, and potentially toxic, polycyclic aromatic hydrocarbon (PAH) background to the Prince William Sound benthic sediments. If this claim is true, it would have the effect of mitigating the long-term effects of the oil spill. Our studies and cooperative work with NOAA provide evidence that it is coal and not oil that contributes this PAH background. Unlike the case with oil, PAHs in coal would not be bioavailable and thus would be considered contaminants but not pollutants capable of causing adverse effects on exposed biota. Resolution of the source of the PAHs is, therefore, an important environmental issue.

This work in identifying petroleum sources, both natural and anthropogenic, has a great deal of transfer value to other estuarine systems. The geochemical information obtained in Prince William Sound can be extrapolated and applied to the study of oil residues on the California coastline and in San Francisco Bay. Current studies are attempting to correlate or differentiate spills in these two areas and sort out the origin of the petroleum input sources.

INTRODUCTION

On 24 March 1989, the T/V *Exxon Valdez* grounded on Bligh Reef in Prince William Sound (PWS), Alaska (Fig. 1), causing the largest oil spill in U.S. history. About 41 million liters (11 million gals = 258,000 bbls) of North Slope crude oil spilled into the water and eventually reached about 16% (500 km) of the shorelines of the sound. The oil spill was an environmental and visual disaster as crude oil spread throughout the sound and washed up on the pristine beaches. Massive efforts were undertaken to clean up the oil-contaminated beaches and remove oil from the water. Over the years many studies have been undertaken to document the effects of the spill.

Some studies analyzed the biological effects (for example, Maki, 1991, and Rice and others, 1996); others focused on tracking the spilled oil and studying its distribution and fate in the environment (for example, Page and others, 1995; Bence and others, 1996; O'Clair and others, 1996; Short and others, 1996; Short and Heintz, 1997). Starting two months after the spill and continuing through 1997, the U.S. Geological Survey conducted a series of investigations to look at the geological fate of the spilled oil (Kvenvolden and others, 1993; Hostettler and Kvenvolden, 1994; Carlson and others, 1997). Various aspects of the oil spill aftermath have been pursued, with the focus particularly on two areas: a forensic study to determine the source of

oil(s) present on the PWS beaches, and a study to help determine the source of background hydrocarbons, particularly polycyclic aromatic hydrocarbons (PAHs), many
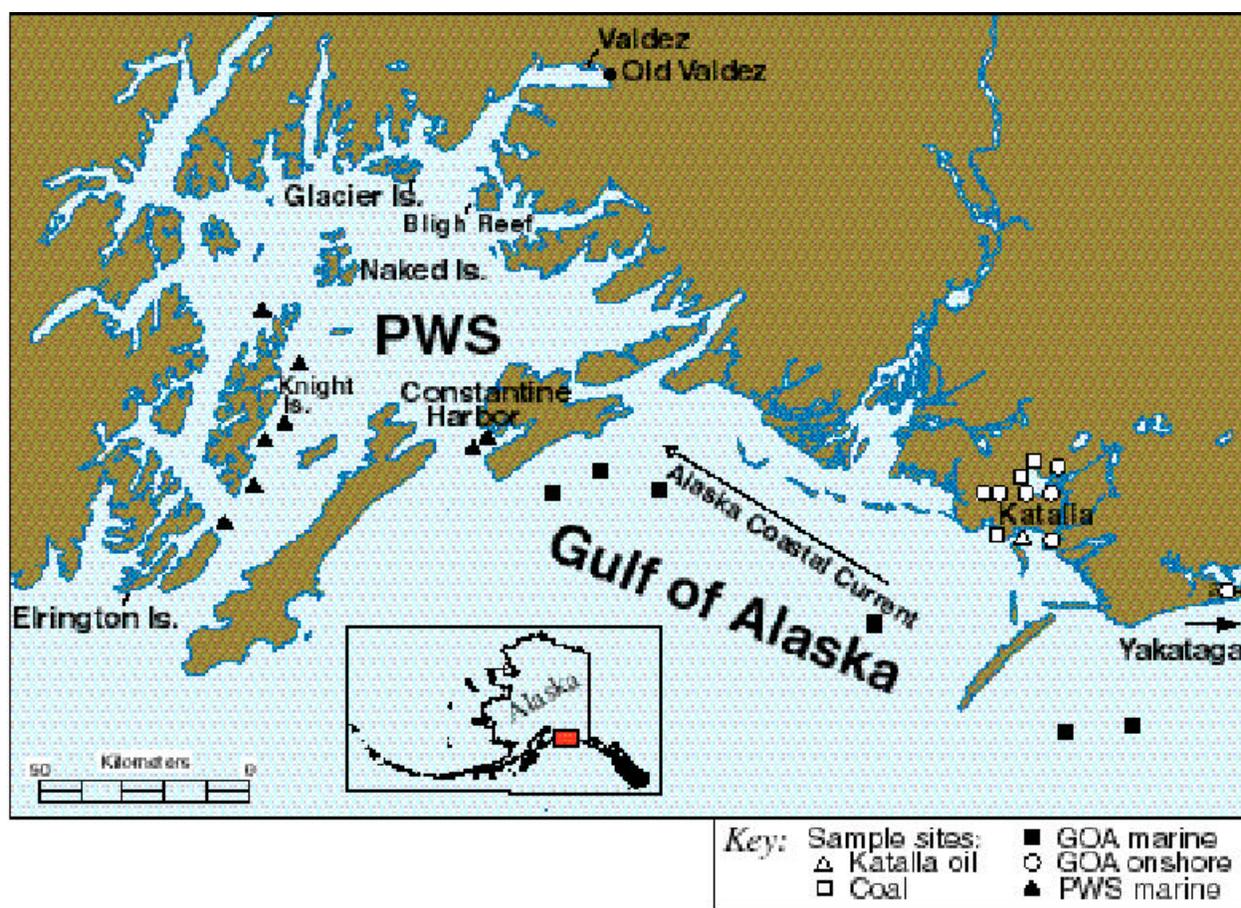
Figure 1. Map of Prince William Sound and Gulf of Alaska (GOA) study area.

of which are toxic, in the benthic sediments of PWS. This paper summarizes these two efforts.

The forensic study was undertaken after it was discovered that not all of the oil and tar residues on the beaches of PWS were attributable to *Exxon Valdez* oil (EVO) (Kvenvolden and others, 1993). Any tar or oil prominent in the recent geologic record of PWS would be relevant as the responsibilities and repercussions of the oil spill were sorted out.

The second focus of our work has been to investigate the source(s) of the background hydrocarbons in the benthic sediments of PWS. In general, these sediments, especially deeper water sediments, have been shown not to contain any residual EVO (Bence and others, 1996). However, the sediments have been shown to contain somewhat elevated levels of PAHs relative to the eastern reach of the Gulf of Alaska (Short and others, 1999). Many of these PAH are potentially toxic to native biota. These PAHs

have been attributed to petrogenic sources (the term "petrogenic" is used here in its generic sense, meaning organic matter originally sourced from rocks; as such, then, it can refer to oil, coal, and sediments containing oil and/or coal constituents). The PAHs are assumed to have originated in the Gulf of Alaska and to have been transported into PWS by the Alaska Coastal Current. There is a significant dispute as to which petrogenic source is responsible for the PAHs. A large body of work by Exxon (for example, Page and others, 1997, Bence and others, 1996) has claimed that the PAHs are from natural oil seeps in the Gulf of Alaska, particularly at Katalla and Yakataga (see Fig. 1). In contrast, this study and a previous study by Short and others (1999) presents evidence that the source of the PAHs is coal from the same region. Whether the PAHs are from oil or coal is an extremely relevant environmental issue in PWS. Even though oil and coal contain many of the same

PAH constituents, PAHs from oil are bioavailable and capable of causing adverse effects to exposed biota, whereas PAHs from coal are very tightly bound within the coal matrix and generally not bioavailable (Chapman and others, 1996). If oil from natural seeps were a chronic PAH source to PWS, then biota in the marine ecosystem would have already adapted to these hydrocarbons. Long-term effects of an oil spill would, therefore, be mitigated, and once the catastrophic impacts immediately after the spill had passed, there would be no further impact attributable to the spill oil. On the other hand, if the PAH are derived from coal, there is no adaptive benefit to biota with respect to PAH input from anthropogenic sources, and long-term environmental effects of the oil spill can be more readily evaluated.

In both of these studies, the identification and differentiation of sources of hydrocarbons in a sedimentary environment is critical. A variety of molecular and isotopic techniques can be applied. For individual oils from a single source, carbon isotopic analysis of the whole oil can be a defining characteristic, even when the oil is in a weathered state. Another analytical approach is individual component analysis. Oils, tars, and sediments are very complex mixtures that may contain a wide variety of organic constituents. This paper will focus on petrogenic hydrocarbons. In sediments these organic compounds can derive from very diverse sources, both natural and anthropogenic. In addition, there is broad overlap among specific compounds that might originate from any of these sources. Finally, the sedimentary system is generally dynamic, in that its components are subject to change through the processes of diagenesis and weathering.

Weathering adds a further dimension to the problem of identifying hydrocarbon input in the environment. Weathering can involve water-washing, chemical degradation (e.g., photo-oxidation), microbial degradation, solubilization, evaporation, mechanical redistribution, and other such processes (Hunt, 1996). Thus, in addition to the high degree of complexity of sedimentary constituents, the system is in a constant state of flux because these components are continually exposed to weathering. Furthermore, weathering effects can vary. Petroleum PAHs, for example, have been noted to be more subject to weathering than those in coal (Short and others, 1999) and

those from pyrogenic sources (Bouloubassi and Saliot, 1993) due to differences in matrix effects and particle associations. Weathering of PAH in petroleum has been shown to follow a progression in the number of rings, in which compounds like naphthalene with two fused aromatic rings are degraded faster than three-ring compounds such as phenanthrene, with the rate of degradation being 2>3>4>5 aromatic rings. In addition, parent PAHs degrade faster than their alkylated homologs, and C1>C2>C3>C4 (Volkman and others, 1984).

There are several approaches to identifying sources of hydrocarbons that are subject to weathering. The first approach, referred to here as _weathering invariant_, involves identifying a specific analyte or group of analytes, either not subject to weathering or not yet weathered, which is known to come from a given source. The use of ratios of aliphatic hopane and sterane biomarkers to differentiate specific crude oils in PWS, Alaska, is one example of this approach (Kvenvolden and others, 1995). Biomarkers, which are molecular fossils, are highly refractory and have been shown to resist postdepositional alteration in the environment until extreme weathering has occurred (Volkman and others, 1984). A second approach, _weathering variant_, considers the weathered system and mathematically extrapolates backward from the current levels of constituents to the original concentrations of the pure source material at the time of deposition. This approach was used by Short and Heintz (1997) in their work in following EVO as it weathered in the environment. A third approach, _weathering covariant_, utilizes ratios of analytes assumed to weather at the same rate. This approach has been used by Page and others (1995) and Douglas and others (1996) who utilized ratios of alkyl dibenzothiophenes to alkyl phenanthrenes in tracking EVO in PWS and differentiating it from background aromatic hydrocarbons. All three approaches provide powerful tools for establishing hydrocarbon sources. However, of the three approaches, _weathering invariant_ may be the most robust, because it utilizes constituents that have not yet been altered in the environment and hence carry the chemical signature of the original source most reliably.

Our study also introduced a new parameter, the PAH refractory index (RI), to apply to correlations of petrogenic systems. The RI is a ratio of specific members of two classes of the most refractory PAH compounds present in crude oils, namely triaromatic steranes (T) and monomethyl chrysenes (C) (T/C, see Fig. 2 and Table 1). Triaromatic steranes are perhaps the most refractory components of oil; they are present even when almost no traces of other PAHs are resolvable through analysis by gas chromatography-mass spectrometry (GC/MS) (for example, Hostettler and Kvenvolden, 1994). They also persist in sediments as some of the last of the resolvable PAH components of weathered petroleum contamination (Killops and Howell, 1988; Hostettler and others, 1992). In general, however, triaromatic steranes are either absent or less common in coal than in oil, (Lu and Kaplan, 1992) due to differences in formation pathways between crude oil and coal. Chrysene and its alkylated homologs are also highly refractory. As the highest molecular weight PAH family typically present in an analytical profile of petroleum (for example, Page and others, 1995), the chrysenes are, therefore, among the most refractory of the regular PAHs. Alkylated chrysenes are common in both crude oils and coals (Barrick and others, 1984). Monomethyl chrysene, rather than chrysene, was chosen for the refractory index because chrysene can have a combustion as well as a petroleum source. The refractory index, then, falls into the _weathering invariant_ category, like hopane and sterane biomarkers, and, as such, should be a useful parameter for source correlation. It has been shown to work well in differentiating specific oil families in PWS, specifically EVO, California (Monterey) oil, and Katalla seep oil, but to give values close to 0 for several Alaska coals (Hostettler and others, 1999).

METHODS

Sample collection. Samples and sampling procedures are described in Carlson and others (1997) and Short and others (1999). Samples for this study include EVO and other oils and tars from PWS beaches, a composite sample of unweathered Katalla oil, a surface seep sample of exposed Katalla oil, offshore sediments from the northern Gulf of Alaska and PWS, and terrestrial riparian sediment samples from the Duktoth, Copper, and Bering Rivers. Coal samples were collected from outcrops in the Bering River coal field and from the beach at Katalla.

Sample analysis. Bulk carbon isotopic analysis was done on the tars and oils from the beaches as described in Carlson and others (1997). Individual component analysis on all samples also is described in the same reference. Briefly, this analysis consisted of air drying the sediment samples and grinding to pass a 32 mesh screen, or, in the case of the tars, weighing out an aliquot, extracting with or dissolving in dichloromethane, treating with HCl-activated copper to remove sulfur, and fractionating by alumina/silica gel column chromatography into a hexane fraction, containing aliphatic hydrocarbons, and a 30% benzene- or dichloromethane-in-hexane fraction containing PAHs and other aromatic compounds. These fractions were then analyzed by GC/MS in the full-scan and selected-ion-monitoring (SIM) modes. Biomarker parameters used in the identification of the various petrogenic sources were calculated and are discussed elsewhere (Kvenvolden and others, 1993, 1995; Carlson and others, 1997). Full-scan GC/MS analysis of the aromatic fraction was used for calculation of the refractory index and a semi-quantitative comparison of naphthalenes, phenanthrenes, dibenzothiophenes, chrysenes, and triaromatic steranes. The refractory index was calculated
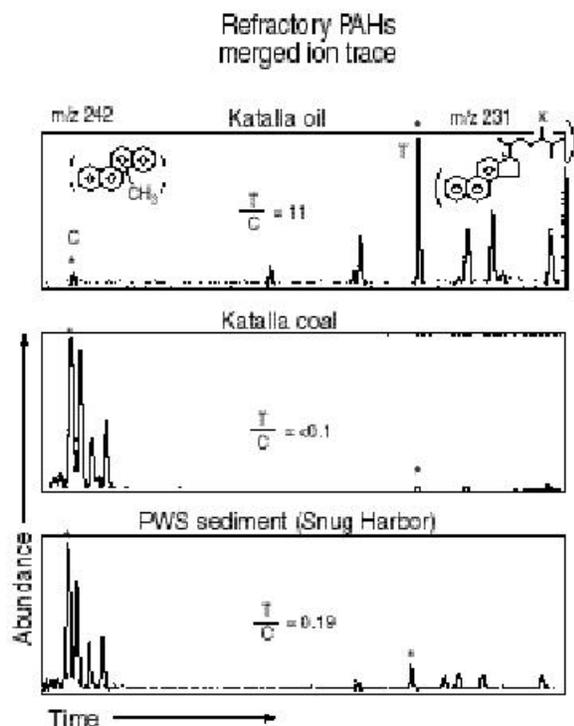
Figure 2. Refractory index ratio: GC/MS extracted ion profiles from the aromatic fraction of Katalla seep oil, Katalla coal, and a typical PWS benthic sediment. The merged trace utilizes m/z 231 for the suite of C_{26}-C_{28} triaromatic steranes (X = H, CH_3, C_2H_5) and m/z 242 for methyl chrysenes. The major peak (*) for each suite was used to calculate the refractory index.

from the ratio of the peak heights of the major peak of the C_{26} to C_{28} triaromatic sterane suite (m/z 231 extracted ion chromatogram, peak identified as consisting of the $C_{26}R$ and $C_{27}S$ epimers) to the major peak of the monomethyl chrysene suite (m/z 242 extracted ion chromatogram, first and dominant peak), as shown in Figure 2. Values for calculated parameters are given in Table 1.
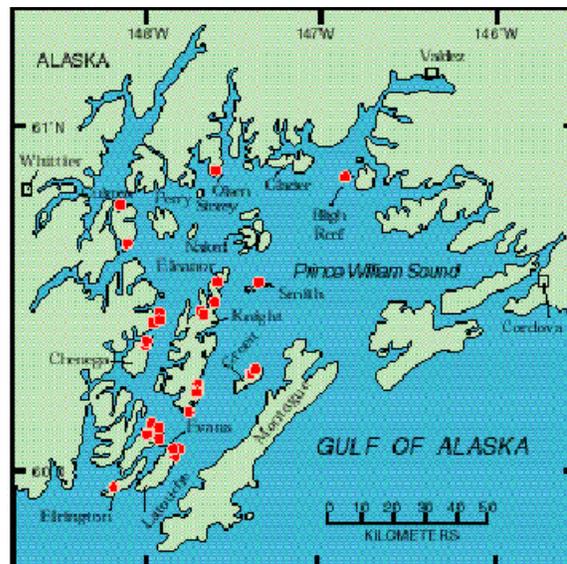
A.   Prince William Sound showing locations where residues of *Exxon Valdez* oil have been found.
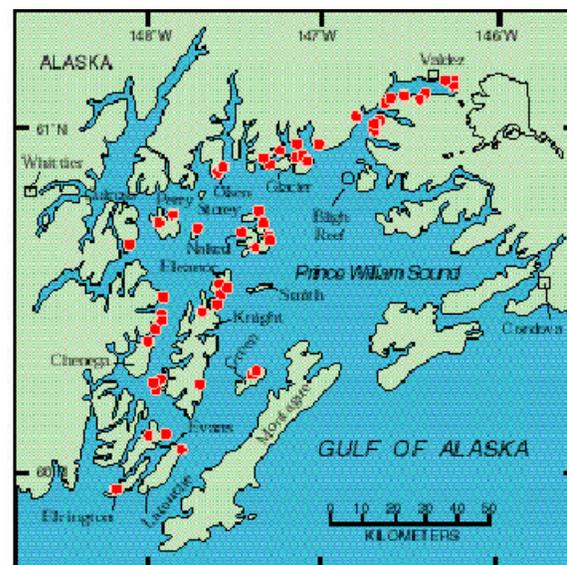
B.   Prince William Sound showing locations of tar balls related to Monterey Formation (Miocene) source rocks of California.

Figure 3. Locations of oil and tar balls.

RESULTS AND DISCUSSION

Forensic study: In the analysis of tar ball and oil samples found on the beaches of PWS it was found that the beached oils and tarballs had two distinctly different chemical signatures. Figure 3 shows the distribution of the two different families of tarry residues of these oils in our sample sets. The parameters that best identified

and correlated these tars and oil residues were carbon isotope compositions ($\delta^{13}C_{PDB}$) of the whole-oil samples and selected terpene biomarker ratios. Of particular value is the biomarker ratio [C_{26}-tricyclic terpane (S?+R?)]/C_{24}-tetracyclic terpane, called the Triplet (T) because of how it appears on m/z 191 mass chromatograms (Fig. 4). This parameter was first noticed in an earlier study of North Slope
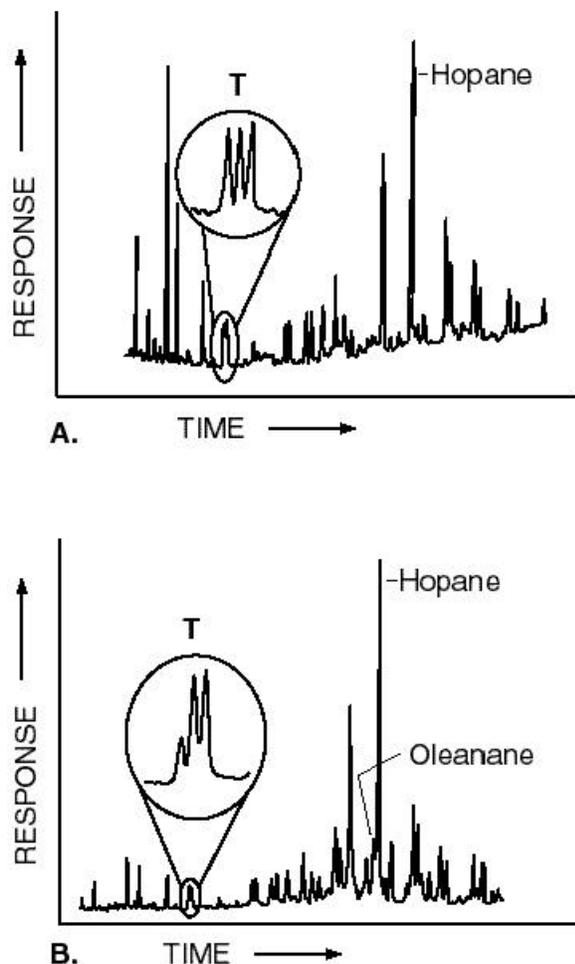
Figure 4. m/z 191 mass chromatograms showing the peaks used for the Triplet ratio and those used for the Oleanane index.

crude oils (Kvenvolden and others, 1985). Studies on PWS show that T = 2.0 ±0.1 in 25 samples of EVO (n=1) and residues (n=24) (Fig. 5A); the $\delta^{13}C$ values for 28 samples of EVO (n=1) and residues (n=27) are –29.4 ±0.1 ‰ (Fig. 5B). These parameters clearly correlate the EVO and its residues. In contrast, T = 5.1 ±0.5 in 39 samples of tar balls (Fig. 5A), and the $\delta^{13}C$ values

for 61 samples of tar balls are –23.7 ±-0.2 ‰ (Fig. 5B). These values, particularly the distinctively heavy $\delta^{13}C$, are within the range of oil products sourced from the Monterey Formation of southern California (Curiale and others, 1985).
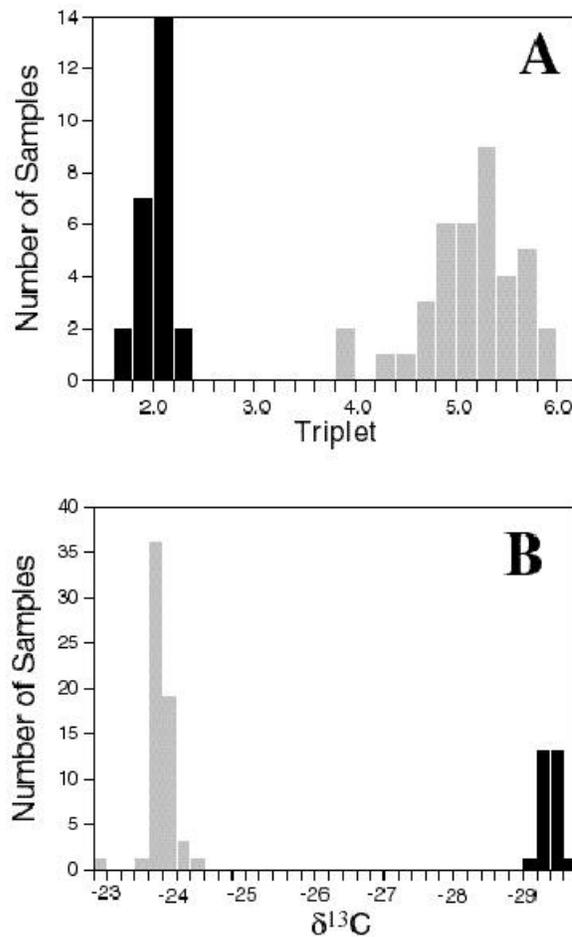
Figure 5. Triplet biomarker and stable carbon isotope value distributions for oils and tars found on PWS beaches.

In addition to compiling evidence that the original source of the second oil was indeed the Monterey Formation in southern California, a plausible explanation for its widespread distribution in PWS was necessary. The waters of PWS flow counterclockwise through the sound and out to the southwest, driven by the Alaska Coastal Current. Therefore, Valdez, the northernmost point in PWS, is an obvious possible origination point for these oils (Fig 3B). In 1964, 25 years before the EVO spill and also on Good Friday, the Great Alaskan Earthquake

occurred. Huge storage tanks of Monterey Formation California oil, which was used in the development of Alaska before North Slope Crude or Cook Inlet oil was discovered, located in the port of Old Valdez, were ruptured and destroyed in this earthquake. However, in the aftermath of the chaos caused by the 9.1 magnitude earthquake, the fate of the California oil was not documented. Kvenvolden and others (1995) and Carlson and others (1997) have suggested that this oil was disbursed throughout PWS after the earthquake and that it is the tarry residues of this oil that is retained in the recent geological record, often in the same locations as the EVO.

Background hydrocarbons in benthic sediments. Several approaches have been used to address the question of the source of the PAH background to the PWS sediments. Some of the geochemical parameters are listed in Table 1 and discussed below. Exxon's long-held claim that natural oil seeps from the Katalla/Yakataga region of the Gulf of Alaska contribute this background is based on three major geochemical correlations: the correspondance of the ratios of C2D/C2P (D = dibenzothiophene and P = phenanthrene), the

presence of oleanane, a C_{30} biomarker commonly found in oils of the late Cretaceous or Tertiary and not present in EVO, and the similarity of PAH fingerprints given by the background PAH in benthic sediments and the water/suspended sediment PAH from seep streams (Bence and others, 1996). Coal is discounted as a potential source primarily due to a reported lack of coal deposits in the drainage areas of streams east of the Bering River.

An alternate source suggested by Short and others (1999) acknowledges the above-mentioned similarities, but shows that the alkylated Db/Ph ratios as well as the presence of oleanane (shown in Table 1 as an oleane/hopane index) fall within the same range for coal as well as seep oil and benthic sediment samples. These ratios are therefore inadequate discriminants. As for the purported dearth of coal sources in the area, references in Short and others (1999) show that the literature details extensive coal deposits along this reach of the Gulf of Alaska coast.

Table 1. Ranges of parameter values. See text for parameter definitions.

Parameters	PWS Background	-------------------------- Gulf of Alaska --------------------------			
	Marine sediment (n = 6 - 10)	Marine sediment (n = 6)	Coal (n = 3)	Onshore (n = 8)	Seep Oil f = fresh; w = weathered
C2D/C2P[a]	0.11 - 0.21	0.22 – 0.25	0.17 – 0.59	0.07 – 0.31	0.18(f,w)
Oleanane Index[a]	0.19 – 0.37	0.13 – 0.14	0.08 – 0.12	0.01 – 0.22	0.12(f,w)
MSE (Kat)[b]	1.68 – 4.41	1.55 – 1.82	3.25 – 7.20	2.07 – 8.46	0.05(w)
MSE (CH)[b]	0.19 – 0.54	0.20 – 0.30	0.60 – 1.14	0.86 – 1.77	1.21(w) 2.68 (f)
RI (T/C)[b]	0 – 0.2	Š 0.1	0 - 0.02	0(most)–0.3	11(w), 13(f)

[a] Parameter used by Bence and others (1996) as evidence of naturally occurring oil seep contribution to benthic sediments

[b] Parameter used by Short and others (1999) as evidence of coal contribution to benthic sediments

Whereas Bence and others (1996) claim that there are numerous natural oil seeps in the same region and assume these seeps have sufficient outflow to deliver at least 360 to 1200 tons of petroleum per year in order to account for the loadings of PAH in PWS, Short and others (1999) claim that the seeps are small, with low productivity, and limited accessibility to Gulf of Alaska waters (for example, no oil slicks documented from these seeps into the Gulf waters, and no published reports of offshore seeps). However, coal particles eroded by natural processes would be widespread and accessible to transport to PWS. Indeed, finely divided coal particles can be seen in the intertidal area and all along the beach at Katalla. Short and others (1999) then examined other geochemical parameters. They also considered the PAH fingerprints of the oils, coals, and sediments and looked more closely at the weathering characteristics of the PAH in the seep oil and in benthic sediments. Using pattern similarity analysis, they calculated two parameters of the mean square error (MSE) of logarithmically transformed proportions of the 14 most persistent PAHs in the respective samples (Table 1). The first parameter, MSE(CH), compared patterns in samples with patterns characteristic of intertidal sediments at Constantine Harbor (CH), PWS. This site was chosen as a reference because PAH concentrations in CH sediments have remained unchanged since 1977 and are representative of deeper subtidal sediments elsewhere in PWS (Short and Heintz, 1997). The second parameter, MSE(Kat), compared the patterns of relative PAH concentrations with those in fresh Katalla seep oil, but in this case, corrected for weathering losses in the samples. Both parameters are natural log functions, with smaller numbers indicating greater similarity and larger numbers indicating less similarity. The value 0.05 of MSE(Kat) for the weathered Katalla seep oil indicates how well the weathering model accounts for weathering losses. Table 1 shows that the PAH fingerprints in PWS and Gulf of Alaska benthic sediments are very similar (MSE = 0.54) to that at CH; coal is also close (e.g., 0.60 for coal at Katalla Beach), whereas Katalla seep oil, both fresh and weathered, are very dissimilar (MSE(CH) = 2.68 and 1.21, respectively). The PAH fingerprints of the PWS benthic sediments are quite dissimilar to those of Katalla seep oil

(MSE(Kat) = 1.68-4.41), even accounting for weathering.

The last parameter utilized is the refractory index. Katalla seep oil has a RI of 11 and 13. However, the benthic sediments and coal all give very low values and differ from the RI of Katalla oil by one to two orders of magnitude. The lack of a substantial presence of triaromatic steranes in the GOA and PWS benthic sediments, as reflected in the RI, is another contraindication for substantial oil input in PWS, particularly oil related to seep oil from Katalla.

One last factor considered by Short and others (1999) was the bioavailability of the PAHs in the respective potential sources. Juvenile coho salmon, collected 100 m downstream from an oil seep, were found to contain significant levels of petrogenic PAHs. However, in a comparable study, mussels further down stream and very near particulate coal outcrops had none of the petrogenic PAHs, indicating that the coal PAHs were not bioavailable and also that the oil productivity upstream was so small, or the weathering so complete, that the PAHs did not reach biota this distance away.

CONCLUSIONS

Geochemical parameters described in this study have enabled us to differentiate petroleum input sources to the recent geologic record in PWS, Alaska. First, it was found that oil washed up on the beaches in the Sound comes from two different sources—EVO from the oil spill of March 1989, and Monterey Formation, California, oil from the aftermath of the Great Earthquake of 1964. Second, evidence is contributed to the ongoing controversy as to which of two petrogenic sources of PAH is responsible for the PAH background in the benthic sediments of PWS, natural oil seeps from the coastline of the Gulf of Alaska or coal from the same area. Our studies, and cooperative work with NOAA, provide evidence that coal is the more likely source. This evidence includes a geographic and geologic framework for the coal origin and transport, geochemical parameters including weathering extrapolations and ratios of refractory constituents of the petrogenic PAH, and bioavailability experiments, all of which correlate better with a coal-sourced PAH background in the benthic sediments of PWS.

In addition to contributing to the body of information after the *Exxon Valdez* oil spill, the geochemical information and procedures obtained in these studies have implications and applications that can be carried over to other estuarine systems. For example, EVO is representative of a mixture of North Slope crude oils, and the Monterey tar balls are representative of crude oils produced from the Monterey Formation source rocks of California. Both of these types of oils are commonly transported along coastal California and into San Francisco Bay. Application of the work in PWS can help differentiate or correlate these oils and tars from spills and natural outcrops, as well as answer questions as to whether they have natural or anthropogenic origins.

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