# 15 Advances in Forensic Techniques for Petroleum Hydrocarbons: The *Exxon Valdez* Experience

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## 15.1 Introduction

The March 25, 1989, *Exxon Valdez* oil spill (EVOS) in Prince William Sound (PWS), Alaska, is the most extensively studied spill in history. In the years immediately following the spill and continuing today, PWS and the adjacent Gulf of Alaska (GOA) have proven to be natural laboratories for the development and testing of new chemical forensic techniques for oil spill impact studies.

EVOS released approximately 258,000 barrels of a total cargo of 1.26 million barrels of Alaska North Slope (ANS) crude oil. It is estimated that ~40% of that oil was stranded along 783 km of shorelines in southwestern PWS (Jahns et al., 1991; Owens, 1991; Wolfe et al., 1993). By the summer of 1990, ~55% of the oil was removed due to cleanup efforts and to the effects of winter storms (Michel et al., 1991) and other natural weathering processes. By 1992, the length of oiled shoreline had been reduced by ~90%. A 2001 NOAA study (Short et al., 2004) estimated that 55.6 mT (~336 barrels) of *Exxon Valdez* crude (EVC) residues remained, with the majority of that oil classified as light and buried in the middle- and upper-intertidal zones on boulder-cobble beaches. Furthermore, that study, using a first-order kinetics model, estimated that the residues were being removed at a rate of 20–26% per year. If the assumptions in the model are correct, by the end of 2005, less than 100 barrels of oil, or <0.05% of the volume originally spilled, remain. By comparison, it is estimated that 0.016% of the oil spilled from the *Florida* (1969), and ~0.2% of the *Arrow* spill (1970) remain after more than 35 years (Peacock et al., 2005; Ed Owens, personal communication, 2006).

As oiling levels decreased, the significance of prespill hydrocarbon sources, both natural and anthropogenic, became increasingly important. This early finding that multiple hydrocarbon sources contributed to the PWS marine environment underscored the need for tools that could quantitatively resolve them in order to properly assess the potential long-term environmental impact from the spill. Of particular interest was the discovery that the prespill benthic sediments in the sound contained a substantial background of petrogenic hydrocarbons derived from Tertiary hydrocarbon systems consisting of petroliferous shales,

oil seeps, and coals, located in the eastern GOA. It has been suggested that 10–12 years after the spill, polycyclic aromatic hydrocarbons (PAH) from those residues were bioavailable at levels sufficient to impact populations of fish and wildlife (e.g., Bodkin et al., 2002; Trust et al., 2000). Consequently, identification and quantification of degraded spill remnants in the potential exposure pathways, i.e., water column, food chain, and benthic sediments, were required. New forensic environmental geochemistry tools were developed to address hydrocarbon source resolution in sediments and tissues and concentrations of spill hydrocarbons in the potential exposure pathways.

An oil spill in U.S. waters initiates a sequence of scientific events under the injury assessment phase of the U.S. federal natural resource damage assessment (NRDA) process. The Federal NRDA regulations under The Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA) defines recovery period as the "length of time required to return the services of the injured resource to their baseline condition," where baseline services "should reflect conditions that would have been expected at the assessment area had the discharge of oil not occurred, taking into account both natural processes and those that are the result of human activities" (U.S. Code of Federal Regulations, 2001). Therefore, the application of chemical forensics to the identification and quantification of all hydrocarbon sources in a spill zone is an essential part of the injury assessment process. Injury assessment has to be based upon well-defined dose-response relationships linking measured biological effects to clearly defined PAH sources.

## 15.2 Identification of Hydrocarbon Sources in PWS

### *15.2.1 Multiple Sources of Hydrocarbons*

Multiple hydrocarbon inputs at oil spill sites are well-documented, and an objective forensic approach should consider the possibility other hydrocarbon sources, both anthropogenic and natural (e.g., Boehm et al., 1997; Neff et al., 2005), may exist. Examples of spills in which there are hydrocarbon inputs from sources other than the primary spill include the *Metula* spill site in the Straits of Magellan (Baker et al., 1975), the Antarctic *Bahia Paraiso* spill (Kennicutt et al., 1992), and the 1978 *Amoco Cadiz* spill on the Brittany coast (Gundlach et al., 1981; Page et al., 1988). This earlier experience underscored the importance of considering multiple sources of petroleum in designing postspill injury assessment studies of the *Exxon Valdez* oil spill in PWS and the Gulf of Alaska (GOA).

Numerous studies of the fate and effects of EVOS show that the impacted area has many sources of hydrocarbons other than EVC (e.g., Kvenvolden et al., 1995; Bence et al., 1996; Page et al., 1995, 1996, 1999, 2002a; Boehm et al., 1997, 2001; Van Kooten et al., 2002). PWS has a long history of human activity, and there are numerous sites of both present and past human activity that provide localized inputs to the marine environment of hydrocarbons derived from fossil fuel use (Page et al., 1999, 2002a; Wooley, 2002). These localized hydrocarbon sources are superimposed on a regional background consisting of natural petroleum hydrocarbons derived from petroleum hydrocarbon systems in the eastern GOA (Page et al., 1996; Bence et al., 1996; Boehm et al., 2001) and globally sourced combustion products. The application of advanced fingerprinting and geochemical forensic methods to chemistry data for intertidal and subtidal sediment samples identified and quantitatively resolved a number of hydrocarbon sources that contribute to the PWS marine environment:

1. Petrogenic hydrocarbons
   a. Weathered EVC petroleum residues
   b. Petroleum and refined products from the Miocene Monterey Formation (CA)
   c. Hydrocarbons derived from eroding organic sediments and oil seep sources east of PWS
   d. Refined petroleum products, such as marine diesel and heavy fuel oils

released during commercial and recreational boating activities
2. Pyrogenic hydrocarbons derived from the burning of petroleum products and wood
   a. Global and regional atmospheric sources
   b. Point sources at active and historical sites of human activity
3. Biogenic hydrocarbons generated by natural biologic or diagenetic processes

Each of these hydrocarbon sources was identified through the application of chemical fingerprinting methods that focused on the distributions of the polycyclic aromatic hydrocarbons (PAH) and the saturate and aromatic biomarkers (steranes, triterpanes, and triaromatic steroids).

Because comparable PAH data have been available through sampling and analytical studies beginning in 1989, and because the PAH distributions are highly diagnostic of many of the hydrocarbon sources in the region, the use of PAH analyte distributions to distinguish hydrocarbon sources has been the most important fingerprinting tool. PAH profiles for examples of the major hydrocarbon sources in PWS are shown in Figure 15-1. Analysis of the distributions of PAH analytes is a useful means for source discrimination because some PAH are more resistant to weathering than the aliphatic fraction (NRC, 1985) and their distributions vary among sources. However, in situations where the samples are extremely degraded, loss of diagnostic PAH may preclude source identification. In those cases, the more refractory saturate and aromatic biomarkers are used. The chemical criteria used to distinguish petrogenic, biogenic, and pyrogenic sources are discussed in detail elsewhere (Page et al., 1995; Bence et al., 1996; Burns et al., 1997, 2006) and are briefly reviewed here.

### *15.2.2 Petrogenic Hydrocarbons*

These include crude oil and its refined products and are characterized by homologous families of related 2- to 4-ring PAH (naphthalenes, fluorenes, phenanthrenes, dibenzothiophenes, and chrysenes), where the unsubstituted parent PAH for each family is less abundant than the alkylated homologues. In many crude oils and middle distillates, the PAH composition is dominated by the light, 2- to 3-ring compounds. With the exception of the alkyl chrysenes, 4- to 6-ring PAH are usually at levels below their limits of detection in oil. Sources of petrogenic PAH to the PWS marine environment include weathered and unweathered EVOS crude, an Alaska North Slope (ANS) pipeline crude oil released in the 1989 spill (Figures 15-1A and B); diesel fuel refined from ANS crude oil (Figure 15-1C); natural oil and gas seeps in the eastern Gulf of Alaska (GOA); heavy fuel oils and asphalts brought in from other parts of the world, including Cook Inlet, southern California (Figure 15-1E), the Far East, etc.; and kerogens derived from eroding Tertiary shales and coals in the eastern GOA and brought into the sound as suspended sediments by the counterclockwise circulation of the Alaskan Coastal Current (Royer et al., 1990). The regional petrogenic background in the benthic sediments of PWS (Figure 15-1D) is formed through the deposition of these suspended particulates.

Diesel refined from ANS and other crude oils is a periodic contaminant to PWS due to ongoing marine incidents. The diesel PAH fingerprint is similar to that of ANS crude oil but lacks the 4–6 ring PAH (i.e., alkyl chrysenes) that are removed in the refining process. Refining also removes the majority of the saturate and aromatic biomarkers.

Prior to the onset of oil production from the Cook Inlet (1958) and North Slope fields (1977), petroleum and petroleum products were imported from the lower 48 states. Major components of those shipments were crude oil and refined products, including asphalt for highway and airport runway construction, produced from the Miocene Monterey Formation in California (Lethcoe and Lethcoe, 2001). Remnants from those shipments are found at numerous locations throughout Prince William Sound. In the early 1990s, Kvenvolden et al. (1993, 1995) reported widely distributed tar deposits on shorelines in northern and western

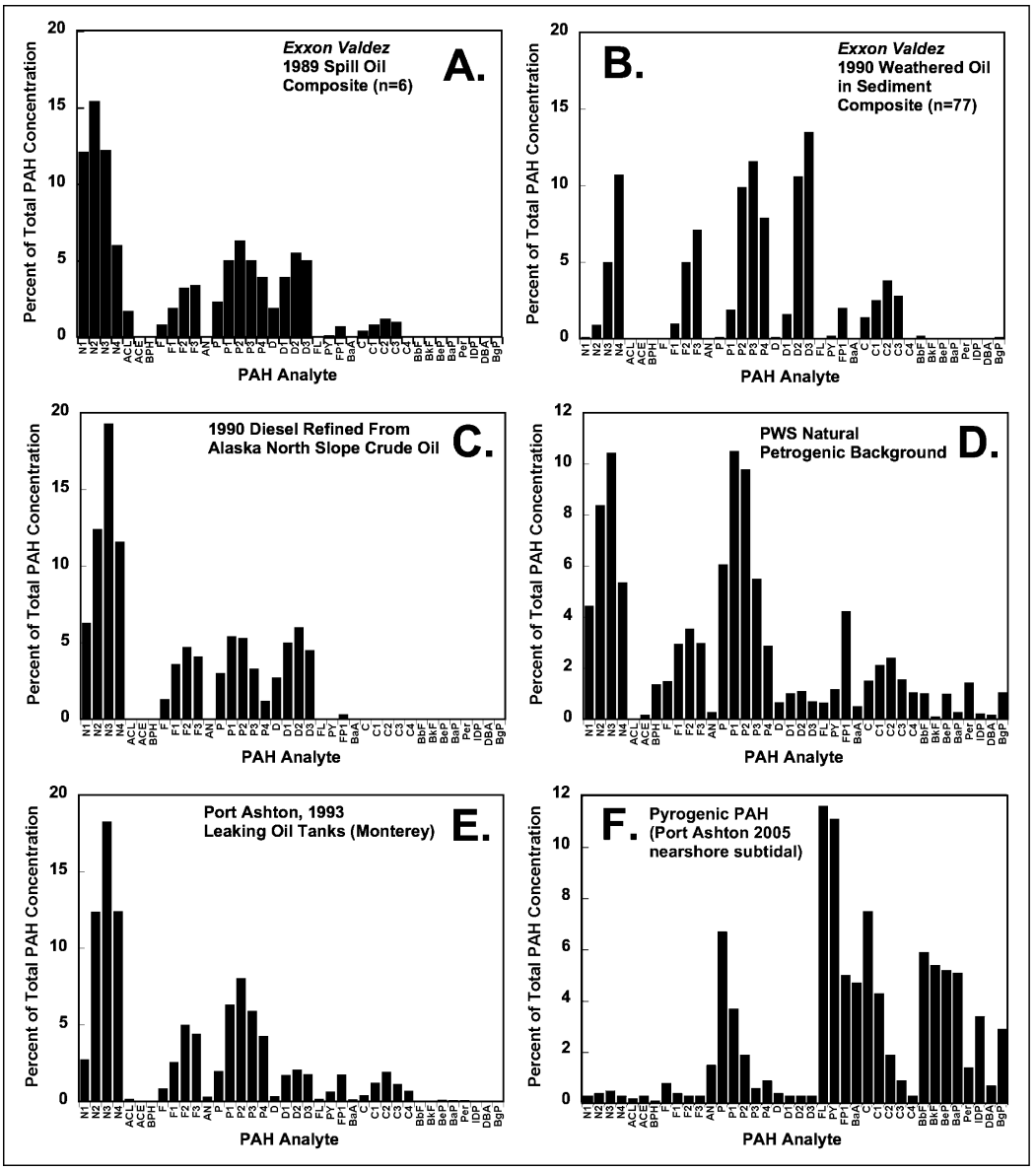


**Figure 15-1** PAH compositions of major hydrocarbon source inputs to the marine environment of PWS. A PAH analyte may be a single compound, such as $C_0$-phenanthrene, or the sum of a group of isomers, such as $C_1$-phenanthrene, which has four isomers. N1, N2, N3, N4 = $C_1$, $C_2$, $C_3$, $C_4$-naphthalenes; ACL = acenaphthylene; ACE = acenaphthene; BPH = biphenyl; F, F2, F2, F3 = $C_0$, $C_1$, $C_2$, $C_3$-fluorenes; P, P1, P2, P3, P4 = $C_0$, $C_1$, $C_2$, $C_3$, $C_4$-phenanthrenes/anthracenes; D, D1, D2, D3 = $C_0$, $C_1$, $C_2$, $C_3$-dibenzothiophenes; FL = fluoranthene; PY = pyrene; FP1 = $C_1$-fluoranthenes/pyrenes; BaA = benzo(*a*)anthracene; C, C1, C2, C3, C4 = $C_0$, $C_1$, $C_2$, $C_3$, $C_4$-chrysenes; BbF = benzo(*b*)fluoranthene; BkF = benzo(*k*)fluoranthene; BeP = benzo(*e*)pyrene; BaP = benzo(*a*)pyrene; Per = perylene; IDP = indeno(1,2,3-cd)pyrene; DBA = dibenzo(*a*,*h*)anthracene; BgP = benzo(*g*,*h*,*i*) perylene.

parts of PWS having a $^{13}C$-enriched carbon isotope composition (~–24 per mil as compared to the EVOS value of ~–29 per mil) that was consistent with Monterey oils. It is hypothesized that the 1964 Alaskan earthquake released some of this material from storage tanks that ruptured at Valdez and at other locations throughout PWS (Kvenvolden et al., 1995). In addition to their distinctive carbon isotopic composition, these products are readily identified on the basis of their saturate biomarker (primarily the triterpanes) and PAH (Figure 15-1E) compositions.

### 15.2.3 Biogenic Hydrocarbons

Biogenic hydrocarbons are generated by biologic processes or in the early stages of diagenesis in marine sediments (e.g., perylene, a 4-ring unsubstituted PAH). Perylene can be seen as an addition to the predominantly petrogenic PAH profile in Figure 15-1D and is present in most subtidal sediment samples. Retene, a conifer-derived alkyl-substituted phenanthrene, is of considerable interest because it is abundant in the PWS marine environment and it has been known to induce cytochrome P4501A (CYP1A) activity in rainbow trout (Fragaso et al., 1998; Hawkins et al., 2003). Retene is also produced through the thermal alteration of diterpenoids in conifer wood (Rogge et al., 1998). Thus, it is a common product in wood smoke, and regional atmospheric inputs from forest fires are a likely source of retene to PWS. The pentacyclic triterpane 17 beta(H),21 beta(H)-hop-22(29)-ene (diplotene) is a bacterially derived biomarker that is formed in soils.

### 15.2.4 Pyrogenic Hydrocarbons

These are generated by the combustion of fossil fuels, such as coal, oil, and diesel fuel, and of recent organic material such as wood. Pyrogenic sources have a PAH distribution dominated by the 4- to 6-ring PAH, e.g., fluoranthene, pyrene, and benzo(a)pyrene, and by the parent compounds of the 3-, 4-, and 5-ring PAH, with decreasing abundances of alkyl homologs in each group (Figure 15-1F). They are of particular concern in PWS because some, e.g., chrysene, benzo(a)pyrene, and benzo(a)anthracene, are strong inducers of CYP 1A in fish (e.g., Lee and Anderson, 2005). Inputs of pyrogenic PAH to the PWS marine environment include atmospheric fallout of particulates from both global and regional sources, point source inputs at both active and historic population and industrial centers, and the ubiquitous inputs from fuel consumption by commercial and pleasure boats.

## 15.3 Composition of *Exxon Valdez* Crude and Its Weathering Products

### 15.3.1 Bulk Composition and Trace Chemistry

The *Exxon Valdez* crude (EVC) was a 1989 Alaskan pipeline crude consisting of a mixture of oils from the Alaskan North Slope fields. In 1989, that mixture was in the approximate proportions of 76% Prudhoe Bay, 17% Kuparuk, 5% Endicott, and 2% Lisburne (Bence and Burns, 1995). In the years since the spill, the composition of the pipeline crude has changed as production from some fields declined and production from newly discovered fields was brought on line.

EVC is a medium sulfur crude (~1.3–1.4% S) consisting of, in approximate weight proportions, $C_{1–10}$ volatiles (20%), $>C_{10}$ saturated hydrocarbons (30%), aromatic and naphthenoaromatic hydrocarbons (30%), and asphaltenes (resins and nitrogen, sulfur, and oxygen compounds) (20%) (Figure 15-2A). In the first few days following the spill, most of the volatile fraction was lost due to evaporation (Wolfe et al., 1993). The PAHs, including the heterocyclic sulfur-containing dibenzothiophenes, comprise approximately 12,000–14,000 ppm (1.2–1.4 wt.%).

EVC and its weathering products are readily distinguishable from other natural and anthropogenic hydrocarbon sources occurring in the region (e.g., Cook Inlet, Yakataga, Katalla, and Monterey (CA) oils, refined products,

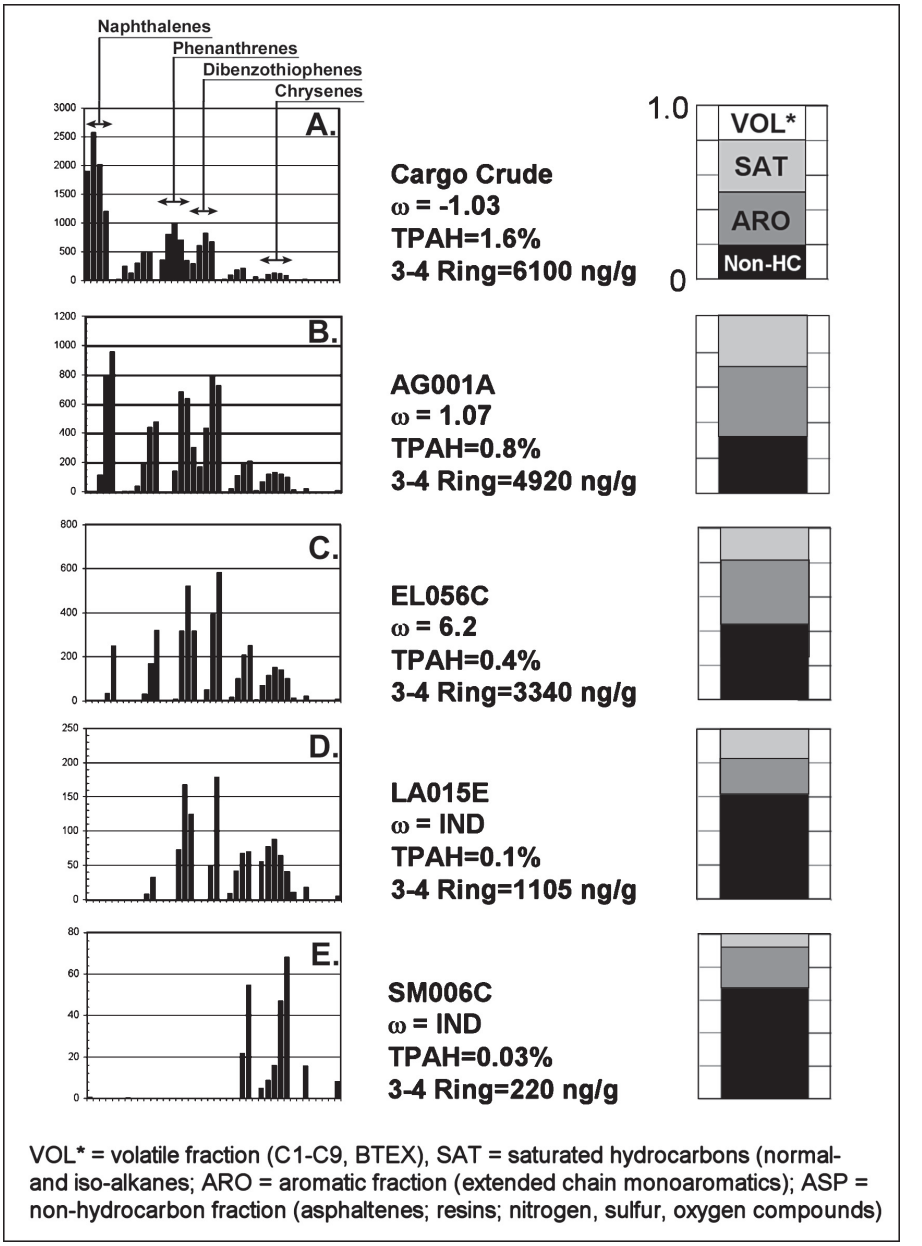


**Figure 15-2** PAH distributions, TPAH and 3–4-ring PAH concentrations, major fraction compositions, and weathering parameters for EVC and four variably weathered PWS shoreline oil samples. The weathering parameter, ω, calculated from the distributions of 14 PAH analytes (Short and Heintz, 1997) becomes indeterminate (IND) at advanced weathering states when one or more analytes are not detected.

kerogens from eastern Gulf of Alaska Tertiary sediments, and combustion products) on the basis of their PAH and saturate and aromatic biomarker compositions (e.g., Kvenvolden et al., 1993; Page et al., 1995; Bence et al., 1996; Short et al., 1996; Van Kooten et al., 2002). The primary distinguishing feature of the PAH fingerprint of EVC is the approximately equal abundances of the phenanthrene and dibenzothiophene analytes—a consequence of its higher sulfur content compared to other petrogenic hydrocarbon sources in the region—which is reflected in the $C_2$-Db/$C_2$-Ph ratio (Table 15-1A). Moderate weathering of EVC in the shoreline regime does not significantly alter this relationship (Figure 15-1B). Consequently, this has been a useful parameter in the quantitative deconvolution of mixtures of hydrocarbon sources in shoreline and benthic sediment samples (Burns et al., 1997). However, because there are differences in the relative proportions of the alkylated PAH groups reported for EVC among laboratories, deconvolution of sources in mixed samples analyzed at different laboratories may not be possible.

**Table 15-1A** Major Hydrocarbon Fractions, TOC, and PAH Characteristics of EVC, Weathered EVC, PWS Prespill Benthic Sediments, Oil Residues at Historical Human Activity (HA) Sites, and Potential Background Sources

| *Hydrocarbon Source Type* | *Sat : Aro : NSO* | *TOC (%)* | *TPAH/TOC (µg/g OC)* | *TPAH (% of oil or extract)* | *LPAH/ TPAH* | *$C_2$-Db/ $C_2$-Ph* | *$C_2$-Ch/ $C_2$-Ph* | *Pyrogenic Index FP/(FP + C 24Ph)* |
|---|---|---|---|---|---|---|---|---|
| EVC ($N$ = 25) ($\omega$ = −1.0) | 38 : 38 : 24* | 85 | 15,300 | 1.3 ± 0.1 | 0.94 ± 0.01 | 0.86 ± 0.06 | 0.13 ± 0.01 | 0.01 ± 0.002 |
| Moderately weathered EVC EL056C ($\omega$ = 6.2) | 18 : 38 : 43 | ND | ND | 0.4 | 0.71 | 1.23 | 0.48 | 0.01 |
| Heavily weathered EVC LA015E ($\omega$ = IND) | 8 : 25 : 67 | ND | ND | 0.03 | 0.00 | Undefined | ∞ | Undefined |
| HA site oil residues | | | | | | | | |
| Unakwik | 29 : 35 : 36 | ND | — | 0.30 | 0.72 | 0.48 | 0.35 | 0.02 |
| Port Audrey | 1 : 60 : 39 | ND | — | | 0.67 | 0.06 | 0.42 | 0.79 |
| Latouche Town site | 27 : 36 : 37 | ND | — | 0.55 | 0.64 | 0.53 | 0.53 | 0.10 |
| Pt. Ashton | ND | ND | — | 1.12 | 0.89 | 0.27 | 0.20 | 0.06 |
| Katalla wellhead oil | | 84.9 | 6,240 | 0.53 | 0.95 | 0.13 | 0.07 | 0.01 |
| Johnson Crk seep | | 79.2 | 30,800 | 2.44 | 0.77 | 0.14 | 0.18 | 0.02 |
| Munday Crk seep | | 76.6 | 8,000 | 0.61 | 0.50 | 0.08 | 1.45 | 0.03 |
| Yakataga FM shale ($N$ = 6) | ND | 0.38 ± 0.1 | 13,170 ± 13,250 | 4.16 ± 3.4 | 0.85 ± 0.09 | 0.20 ± 0.12 | 0.15 ± 0.14 | 0.15 ± 0.08 |
| Kulthieth FM coal ($N$ = 7) | 8 : 23 : 69 | 58.6 ± 9.8 | 600 ± 300 | 4.43 ± 2.89 | 0.78 ± 0.04 | 0.04 ± 0.04 | 0.29 ± 0.08 | 0.06 ± 0.03 |
| Bering River coal (low volatile bituminous) | ND | 85.5 | 242 | 0.42 | 0.78 | 0.34 | 0.40 | 0.11 |
| PWS prespill benthic sediments ($N$ = 4) | ND | 0.64 ± 0.22 | 1780 ± 240 | 0.41 ± 0.14 | 0.74 ± 0.01 | 0.13 ± 0.02 | 0.23 ± 0.02 | 0.10 ± 0.01 |

*Excluding volatile fraction.

**Table 15-1B** Saturate and Aromatic Biomarker Indices for EVC, Weathered EVC, PWS Prespill Benthic Sediments, Oil Residues at Historical Human Activity (HA) Sites, and Potential Background Sources

| *Hydrocarbon Source Type* | *$C_{30}$-Hopane (μg/g)* | *Trisnorhopane Index TS/(TS + TM)* | *Oleanane Index Ol/(Ol + $C_{30}$-hopane)* | *$C_{24}Tt/(C_{24}Tet+C_{26}Tri(S+R))$* | *$C_{27}:C_{28}:C_{29}$ (ααα) (20S + 20R)* | *$C_{29}$ααα (20S)/(20S + 20R))* | *TAS Index $C_{20-21}/(C_{20-21}+C_{26-28})$* |
|---|---|---|---|---|---|---|---|
| EVC ($N$ = 25) (ω = −1.0) | 120 ± 13 | 0.42 ± 0.02 | 0.00 | 0.31 ± 0.02 | 0.47 : 0.24 : 0.29 | 0.51 ± 0.04 | 0.18 ± 0.01 |
| Moderately weathered EVC EL056C (ω = 6.2) | 224.7 | 0.44 | 0.00 | 0.36 | 0.47 : 0.27 : 0.27 | 0.42 | 0.20 |
| Heavily weathered EVC LA015E (ω = IND) | 252.8 | 0.44 | 0.00 | 0.33 | 0.47 : 0.25 : 0.29 | 0.48 | 0.13 |
| HA site oil residues | | | | | | | |
| Unakwik | 216.7 | 0.35 | 0.19 | 0.44 | 0.42 : 0.35 : 0.23 | 0.31 | 0.09 |
| Port Audrey | 17.3 | 0.04 | 0.07 | 0.20 | 0.40 : 0.31 : 0.29 | 0.39 | 0.70 |
| Latouche town site | 201.3 | 0.33 | 0.19 | 0.45 | 0.42 : 0.35 : 0.24 | 0.32 | 0.09 |
| Pt. Ashton | 132.2 | 0.29 | 0.18 | 0.20 | 0.42 : 0.34 : 0.24 | 0.32 | 0.20 |
| Katalla wellhead | 514 | 0.48 | 0.10 | 0.28 | 0.40 : 0.25 : 0.35 | 0.57 | 0.12 |
| Johnson Creek seep | 463 | 0.20 | 0.25 | 0.98 | 0.04 : 0.19 : 0.77 | 0.55 | 0.33 |
| Munday Ck seep | 556 | 0.19 | 0.24 | 0.95 | 0.04 : 0.20 : 0.76 | 0.57 | 0.29 |
| Yakataga FM ($N$ = 6) | 0.014 ± 0.008 | 0.16 ± 0.11 | 0.16 ± 0.08 | 0.61 ± 0.20 | 0.22 : 0.22 : 0.56 | 0.05 ± 0.03 | 0.11 ± 0.12 |
| Kulthieth FM coal ($N$ = 7) | 4.9 ± 4.1 | 0.17 ± 0.05 | 0.10 ± 0.03 | 1.00 | 0.28 : 0.20 : 0.52 | 0.51 ± 0.02 | 0.40 ± 0.08 |
| Bering River Coal (low-volatile bituminous) | 0.0 | Undefined | Undefined | Undefined | Undefined | Undefined | Undefined |
| PWS prespill benthic sediments ($N$ = 4) | 0.007 ± 0.003 | 0.26 ± 0.03 | 0.21 ± 0.01 | 0.60 ± 0.03 | 0.32 : 0.28 : 0.40 | 0.29 ± 0.04 | 0.13 ± 0.16 |

ND = not determined.

EVC also has saturate and aromatic biomarker (steranes, triterpanes, and triaromatic steroids) compositions that can be used to distinguish it and its weathered equivalents from other hydrocarbon sources in the region. In the petroleum industry, these biomarkers are used to identify depositional environments of petroleum source rocks, to constrain the thermal histories of those source rocks, and to evaluate the extent of biodegradation of oils. The greater stability of these compounds relative to many of the PAHs make them useful for quantitative source allocations (e.g., Burns et al., 1997; see also Chapter 8 herein). Specific distinguishing characteristics of the triterpanes in EVC (Table 15-1) include the absence of the source indicator 18α(H)-oleanane ($C_{30}H_{52}$), extended pentacyclics, TS/(TS + TM) = 0.4, $C_{24}$ tetracyclics/($C_{24}$ tetracyclics + $C_{26}$ tricyclics) = 0.3 (e.g., Bence et al., 1996; Kvenvolden et al., 1993). The absence of oleanane and $C_{24}:C_{26}$ serves to discriminate EVC and its weathering products from Monterey (CA) tars and residual fuel oils and from natural seep oils, the organic shales from which the seeps were sourced, and low-to-high thermal maturity coals associated with the Tertiary sedimentary province in the eastern Gulf of Alaska (e.g., Bence et al., 1996; Kvenvolden et al., 1995; Van Kooten et al., 2002). Specific features of the steranes include the relative proportions of the source indicator $C_{27}:C_{28}:C_{29}$(ααα)(20S + 20R) and the thermal maturity indicator $C_{29}$ααα(20S/(20S + 20R)). These discriminate EVC from Monterey (CA) tars and oils and low-thermal maturity Kuskutz coals from the Kulthieth Formation (Table 15-1B). The triaromatic steroid (TAS) index $(C_{20+21})/((C_{20-21}) + (C_{26-28}))$ is useful in distinguishing EVC from various Monterey tars and

oils, from the prespill benthic background, and from low-thermal maturity Koskutz coals (Table 15-1B). It further discriminates the Koskutz coals from the prespill benthic sediment background.

### 15.3.2 Weathering Trends

#### 15.3.2.1 Data Sources

Oil stranded on the shorelines was subjected to variably intense physical and chemical weathering depending upon the extent of sequestration (i.e., buried beneath a boulder-cobble veneer, trapped in the wave shadow behind protective outcrops, etc.). Residual oil suites collected from both surface and subsurface regimes define the EVOS natural weathering trends. Laboratory studies, conducted both by NOAA (Heintz et al., 1999; Carls et al., 1999) and the University of Idaho (Brannon et al., 2006), involving water circulation through oiled gravel columns, reveal the compositional changes that occur under controlled conditions.

#### 15.3.2.2 Major Fraction Trends

In the first few days following the spill, the volatile fraction, comprising approximately 20% of the oil by weight, was lost (Wolfe et al., 1993). Over the years, oil stranded on the shoreline underwent chemical, biological, and mechanical weathering at varying rates dependent upon the degree of exposure to environmental conditions. Changes in the major oil fraction include loss of the saturate and aromatic fractions accompanied by a concomitant increase in the nonhydrocarbon component (asphaltenes and resins) (Figure 15-2). At the most extreme stages of weathering, the nonhydrocarbon component comprises 70% or more of the residual oil.

#### 15.3.2.3 PAH Trends

With natural weathering on PWS shorelines the EVC PAHs, as a group, are removed from the oil. In the most extreme cases, TPAH is reduced to less than 0.05 wt.% of the residual oil (Table 15-1A, Figure 15-2). Weathering produces predictable changes in the PAH distributions based upon the relative solubilities of the individual compounds. This is evident in the progression of the calculated values of the Short and Heintz (1997) weathering parameter, ω, which increases with increasing degree of weathering (Figure 15-2) and becomes indeterminate at higher weathering states when one or more of the PAH analytes used in the calculation are no longer detected. The 2- and 3-ring PAH (light PAH) are removed more quickly than the 4-ring PAH (heavy PAH or HPAH). Consequently, the relative concentration of the HPAH fraction (fluoranthenes/pyrenes and chrysenes) in the total PAH fraction increases and LPAH/TPAH decreases with degree of weathering. However, the concentration of HPAH as a fraction of the residual oil decreases (Figure 15-2; Table 15-1A). Consequently, weathered oil does not become increasingly toxic due to buildup of 3- and 4-ring PAH, as has been suggested (Bue et al., 1996; Heintz et al., 1999).

The relative rate of removal of the PAH groups as the oil weathers is naphthalenes > fluorenes > phenanthrenes ≅ dibenzothiophenes ≅ fluoranthenes/pyrenes > chrysenes. Within each PAH group, the preferential removal is parent > C1 > C2 > C3.

The PAH pyrogenic index (fluoranthene + pyrene)/(fluoranthene + pyrene + $C_{2-4}$ phenanthrene) or (FP)/(FP + C24Ph) was used to discriminate combustion products (fluoranthene and pyrene) from EVC and its weathering products (Neff et al., 2006). This ratio in the cargo crude is 0.01 (Table 15-1A). With both natural weathering on the shoreline and artificial weathering in the laboratory, that ratio increases gradually to a maximum of ~0.05 (Figure 15-3). Fluoranthene, pyrene, and $C_4$ phenanthrene (the most stable of the alkylated phenanthrenes) are removed from the oil at essentially the same rate such that when mass loss approaches 60%, the ratio is undefined. A conservative upper limit of 0.20 was selected by Neff et al. (2006). Samples having TPAH >100 ng/g and (FP)/(FP + C24Ph) values

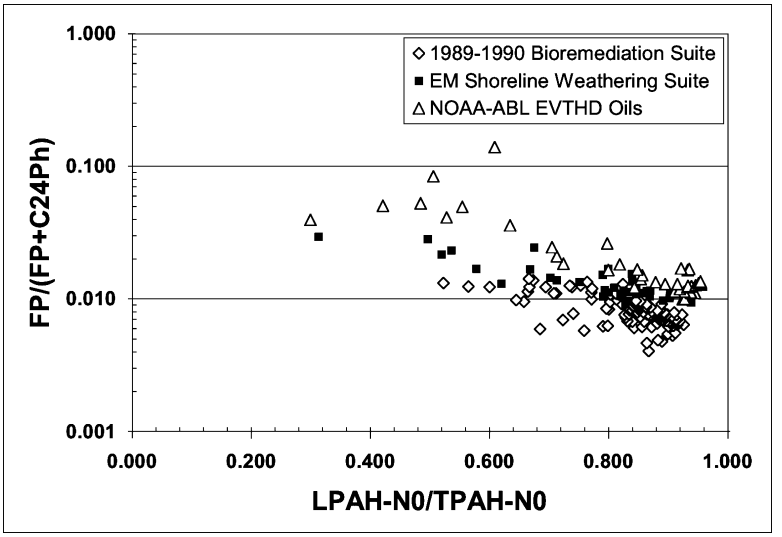


**Figure 15-3** Pyrogenic index FP/(FP + C24Ph) vs. the ratio of low-molecular-weight (2–3-ring PAH) to total PAH, LPAH/TPAH, for naturally and artificially weathered shoreline oils. LPAH/TPAH decreases with increased weathering. 1989–1990 bioremediation suite oils are from Prince et al. (1994). EM shoreline oil weathering suite from samples collected in 2001–2002. NOAA EVTHD oils from the 2003 version of *Exxon Valdez* Trustees Oil Database on NOAA-NMFS, Auke Bay Laboratory webpage (www.afsc.noaa.gov/abl/oilspill). These include oils that were weathered in the laboratory.

>0.20 were interpreted to contain combustion products.

#### *15.2.3.4 Mass Loss during Weathering*

Utilizing the methodology of Douglas et al. (1996), which assumes conservation of $C_{30}$-hopane during weathering, a conservative estimate of the minimum mass loss can be made using the following equation: percent oil depletion = [1 − Ho/Hs] × 100%, where Ho is the concentration of $C_{30}$-hopane in EVC and Hs is the concentration of $C_{30}$-hopane in the weathered oil sample. When applied to the two weathered samples of EVC reported in Table 15-1B, minimum mass losses of 39% (sample EL056C) and 46% (sample LA015E) are calculated. Shoreline oil samples collected in 2001–2002 have minimum mass losses of up to 60% of the oil. Inert asphaltenes and resins comprise the largest component of the heavily weathered oils (Figure 15-2). This method of calculating mass loss cannot be used when weathering is so severe that $C_{30}$-hopane is not conserved. Significant loss of $C_{30}$-hopane is observed in subsurface oil residues at a number of locations. Weathered oils collected at Point Helen (shoreline segment KN-405A) in 2005 have only 20 ppm $C_{30}$-hopane, 0.01% PAH (consisting only of $C_3$- and $C_4$-chrysenes), 13% saturates, 29% aromatics, and 57% NSOs.

## 15.4 Resolution of Inputs to the Natural Background

Studies conducted between 1989 and 1991 in PWS and the GOA involved the collection and chemical analysis of over 10,000 seafloor sediment samples taken from water depths ranging from 0 m to over 750 m (e.g., Rapp et al., 1990; Manen et al., 1993; Boehm et al., 1995; Sale and Short 1995; Page et al., 1995, 1996; Short et al., 1996). One of the objectives of these investigations was to determine if the rapidly diminishing shoreline oil residues were being transferred to subtidal sediments where, potentially, they could enter the food chain.

The result is a large body of chemical data on benthic sediments from stations both inside and outside the spill zone.

Three components were essential to the resolution of the natural background: (1) an analytical program that could differentiate similar petrogenic sources with high precision; (2) an extensive sampling program to collect seafloor and subseafloor benthic sediments and samples of the numerous potential hydrocarbon sources to the PWS marine environment; and (3) application of a quantitative statistical allocation technique. PAH, triaromatic steroids (TAS), triterpane, and sterane distributions for the PWS subsurface (prespill) petrogenic background and hydrocarbons sources that contribute to that background are shown in Figures 15-4 and 15-5.

The identification of 18α(H)-oleanane ($C_{30}H_{52}$) in deep seafloor sediment samples taken after the spill in 1989 (Rapp et al., 1990) was one of the earliest indications of nonspill origins of seafloor petrogenic hydrocarbons in PWS. Oleanane is a saturate biomarker for petroleum, having a post-latest Cretaceous terrigenous source and is not present in ANS crude oils (Bence et al., 1996; Peters et al., 2005).

Page et al. (1995, 1996) reported the results of sampling and analytical programs carried out in 1989, 1990, and 1991 whose goals were to detect EVC contributions to seafloor sediments, to quantify the amount of EVC present relative to the pre-existing petrogenic background, and to characterize historical inputs of petrogenic and nonpetrogenic hydrocarbons. Seven separate surveys sampled 649 subtidal locations in PWS and the GOA and collected more than 2300 samples that were subsequently analyzed for PAH, and for the 1991 samples, for saturate biomarkers as well. These stations ranged from near-shore locations (<100 m from the nearest shoreline), stations in protected bays, offshore stations (~100 to 1000 m offshore), to deep subtidal stations (>1000 m offshore). Chemistry data were obtained for seafloor surface (0–2 cm) sediments and from $^{210}$Pb age-dated sediment cores providing samples from depths of up to 32 cm below the seafloor. These lower sedimentary layers were deposited up to ~150 years prior to the 1989 spill (Page et al., 1995).

These studies showed that EVC and its residues were readily distinguishable from the regional background PAH by their very different $C_2$-Dbt/$C_2$-Ph ratios (Table 15-1A and Figure 15-6). However, identification of the individual components that made up the regional background was not possible. The 1991 study linked the regional background in PWS to hydrocarbon systems (petroleum source rocks and natural oil seeps) east of PWS along the GOA coast, an area of oil production in the early 1900s.

The observation that both benthic sediments and coals from the Katalla area of the GOA had low values for the refractive index (RI) (def., triaromatic steroids/1-methylchrysene) was used by Hostettler et al. (1999) to conclude that the source of the natural hydrocarbon background in the benthic sediments of the GOA and PWS was most likely due to coal (see, also, Short et al., 1999; Van Kooten et al., 2002). However, coal is only one of several possible explanations for the measured low RI values in PWS sediments (Bence et al., 2000), and other chemical constraints indicate that these coals cannot be important components of the PWS natural background (Tables 15-1A and 15-1B). For example, high maturity (Ro > 1.5) coals from the Bering River coal fields have high concentrations of total organic carbon (TOC) and low concentrations of saturate biomarkers. The very low TOC concentrations of PWS benthic sediments and relatively high concentrations of saturate biomarkers (e.g., hopane) preclude these high-maturity coals from being important components of the background (Table 15-1A; Figures 15-4 and 15-5). Inputs of low-maturity Koskutz coals from the Kulthieth formation (see Van Kooten et al., 2002) are constrained to relatively small amounts by low TPAH/TOC, $C_2$-Dbt/$C_2$-Ph, and oleanane indices and high TAS index (Table 15-1A, 15-1B; Figures 15-4K and 15-5K).

At those intertidal sites in PWS where residual subsurface oil remains, the spatial relationships of hydrocarbons introduced from

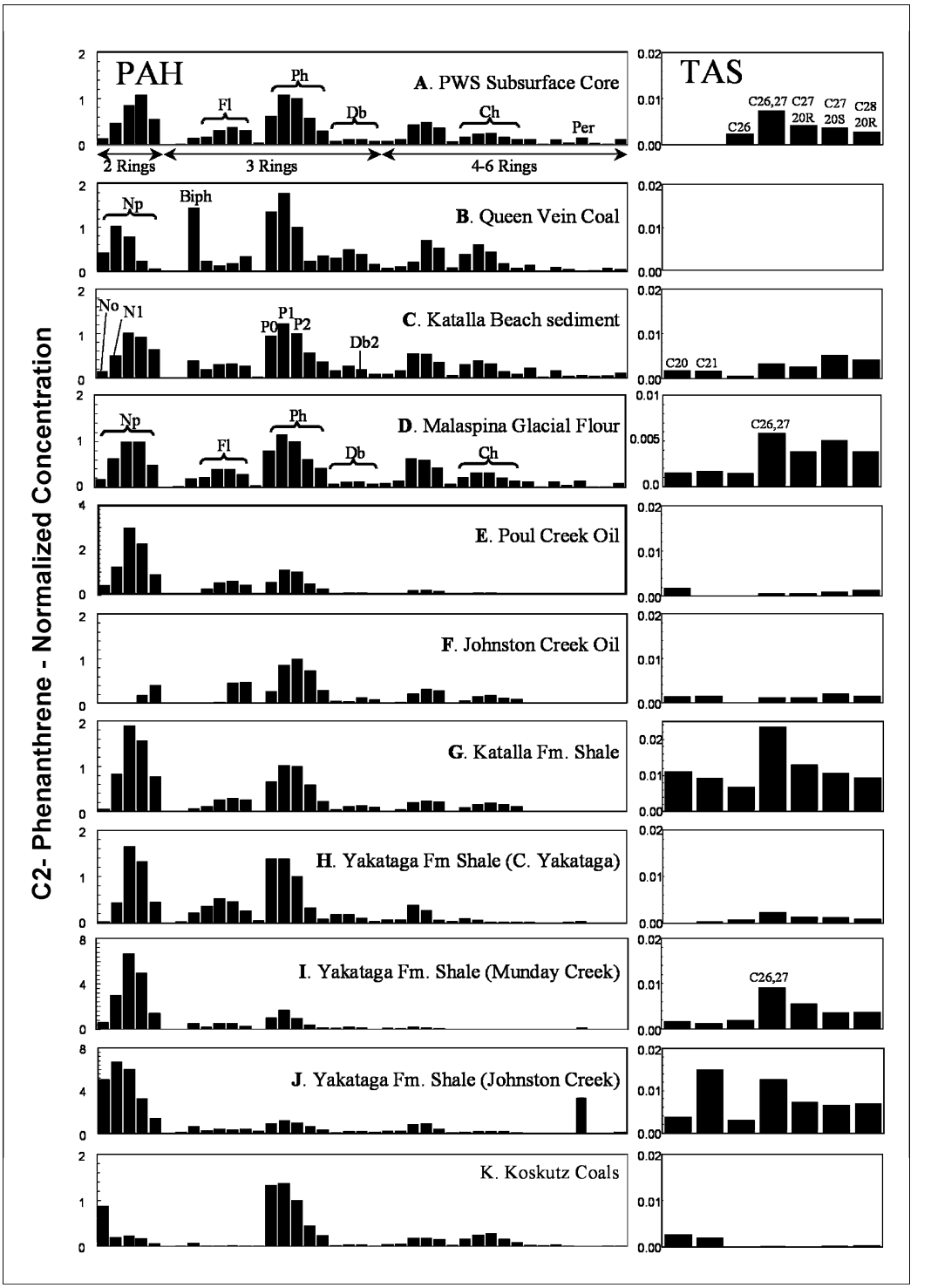


**Figure 15-4** PAH and triaromatic steroid (TAS) compositions ($C_2$-phenanthrene-normalized) for (A) PWS prespill segment of a benthic core, (B–J) potential source inputs to the natural background. Abbreviations: Np = naphthalenes, Fl = fluorenes, Ph = phenanthrenes, Db = dibenzothiophenes, Ch = chrysenes, Per = perylene, N0 = $C_0$-naphthalene, N1 = $C_1$-naphthalene, P0 = $C_0$-phenanthrene, P1 = $C_1$-phenanthrene, P2 = $C_2$-phenanthrene, Db2 = $C_2$-dibenzothiophene. Adapted with permission from Boehm et al. (2001). Copyright 2001, American Chemical Society.

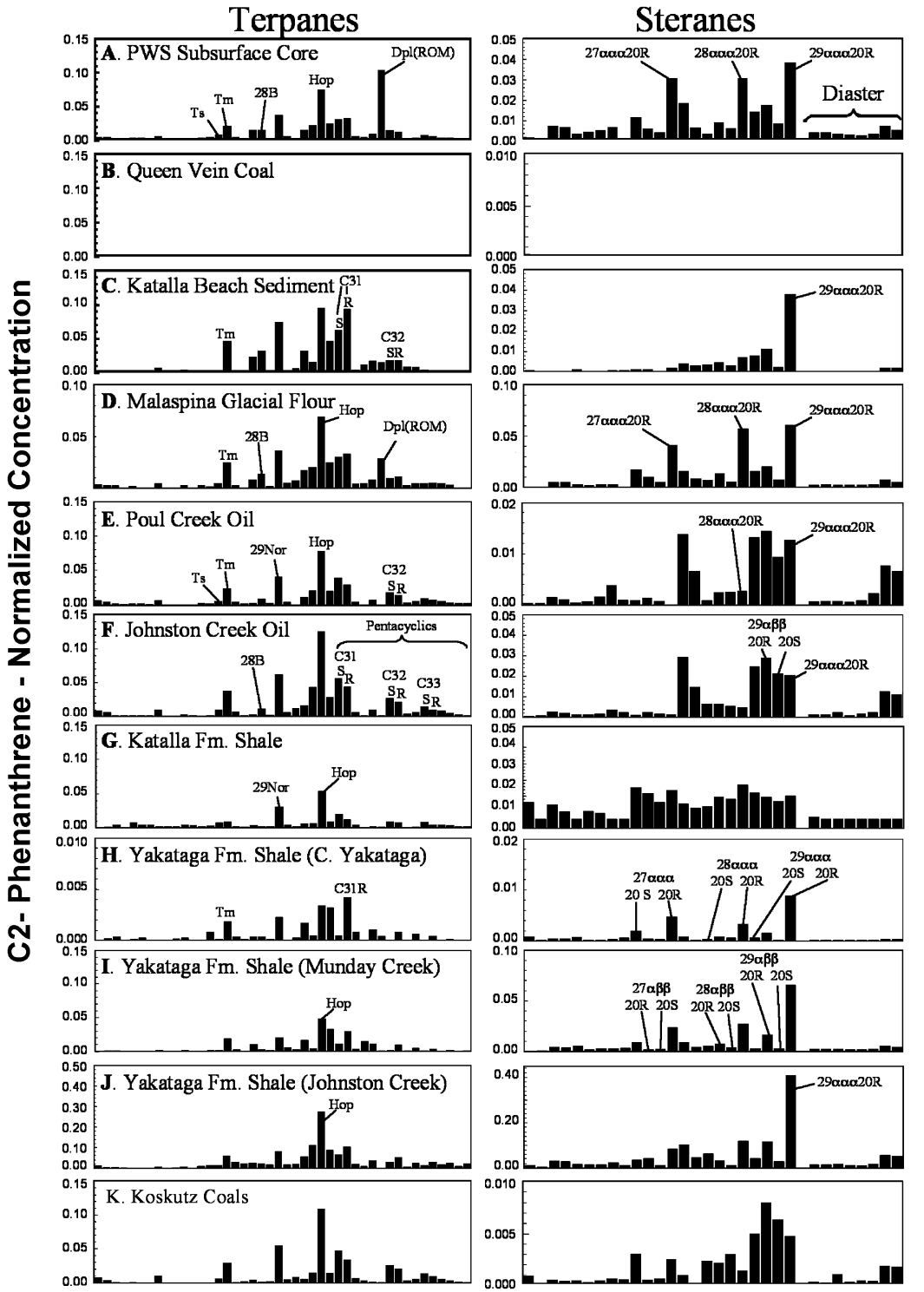


**Figure 15-5** Triterpane and sterane compositions (C2-phenanthrene-normalized) for (A) PWS benthic core, (B–J) potential source inputs to the natural background. Abbreviations: Ts = 17α(H)-22,29,30-trisnorhopane, Tm = 18α(H)-22,29,30-trisnorhopane, 28B = $C_{28,30}$-bisnorhopane, Dpl(ROM) = diplotene, recent organic matter (the Copper River is a major source), 29Nor = norhopane, Hop = $C_{30}$-hopane, Diaster = diasteranes. Adapted with permission from Boehm et al. (2001). Copyright 2001, American Chemical Society.

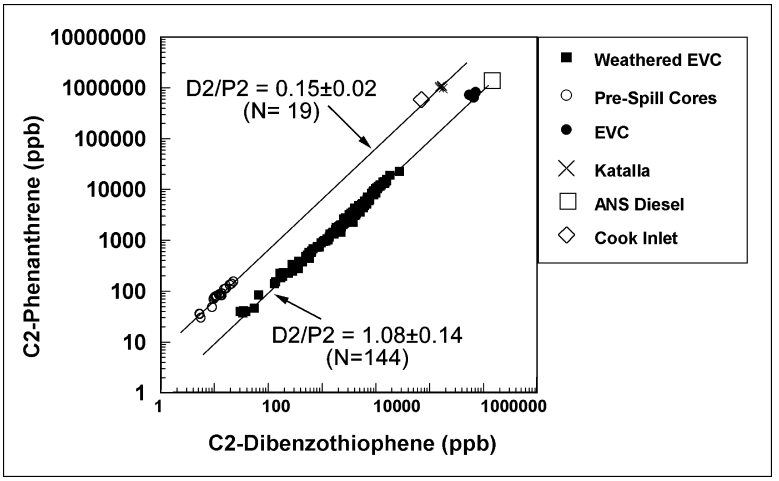


**Figure 15-6** $C_2$-Dibenzothiophenes *versus* $C_2$-phenanthrenes (D2/P2) relationship of weathered EVC, diesel refined from ANS crude feed stock at a Kenai Refinery, PWS regional background hydrocarbons from deep subtidal cores, and Katalla and Cook Inlet crude oils.

different sources to the intertidal, zero tide, to the near-shore shallow subtidal, and to offshore sediments are well documented in data collected during Exxon-supported and NOAA surveys. The PAH compositions, reported by NOAA in the PWSOIL database, of the seafloor sediments at various water depths for one of those sites sampled in 2001, Northwest Bay, Eleanor Island, are shown in Figure 15-7. Intertidal subsurface sediments in Figure 15-7 have a PAH distribution dominated by weathered EVC. At the zero tide level TPAH is markedly lowered, the heavily weathered EVC component is reduced to ppb levels, and the 4- to 6-ring PAHs of a pyrogenic component have increased. From 3–6-m water depths, the petrogenic component in seafloor sediments is further reduced and now contains a recognizable contribution from the petrogenic background (high naphthalenes/fluorenes ratio) and the 4- to 6-ring PAH pyrogenic component is enhanced. Heavily weathered EVC, indicated by the comparable concentrations of $C_3$-Ph and $C_3$-Db, is a minor component at low ppb levels. At 10 m, the pyrogenic (4- to 6-ring) component dominates. The regional background (low $C_2$-Db/$C_2$-Ph) is a minor component and no EVC is detected. At 20 and 60 m, regional background, pyrogenic PAH, and perylene dominate the fingerprints. At a water depth of 100 m, the regional petrogenic background signal dominates. The increase of TPAH with water depth in the subtidal sediments is due to the close association of the PAH with the fine-grained fraction (clay/mud) in the sediments.

## 15.5 Hydrocarbon Source Allocations

### *15.5.1 Source Allocation Models*

The techniques used for source identification and the quantitative allocation of hydrocarbon sources in mixtures have been developed and evolved in environmental studies and the petroleum industry largely over the last 20 years (Burns et al., 1997, 2006; Mudge, 2002). Methods to quantitatively allocate the multiple source components found in the PWS marine environment evolved as understanding of the complexity of hydrocarbon inputs improved. These methods included simple analyte-ratio mixing models, principal component analysis, and quantitative multivariate techniques such as partial least squares (PLS).

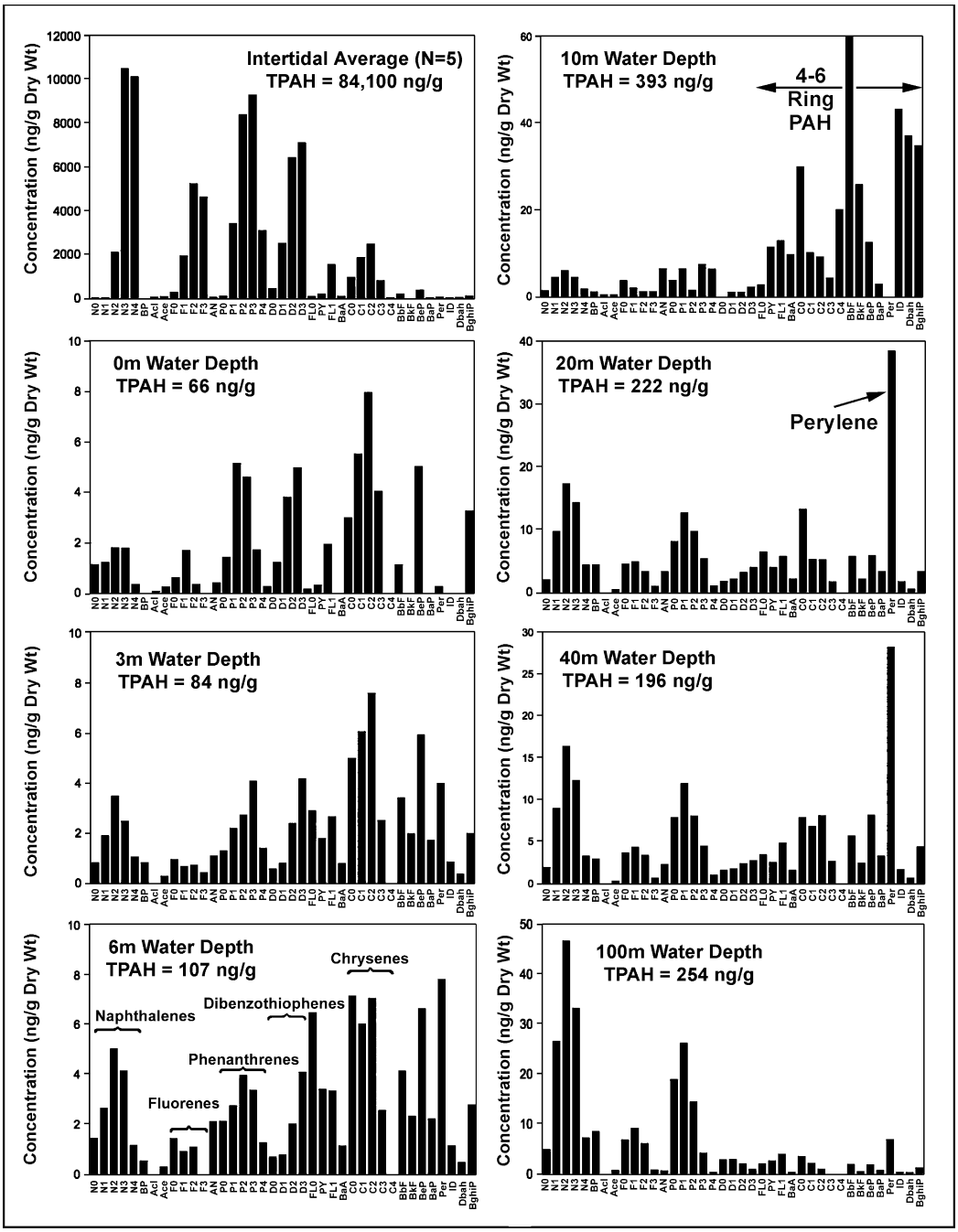


**Figure 15-7** Sediment PAH compositions for a profile from the mid-tide zone to 100-m water depths at a location containing buried EVC residues on the beach, Northwest Bay, Eleanor Island. (Data from S. Rice, personal communication, 2003).

### 15.5.2 Qualitative Allocation Models

Short and Heintz (1997) developed a first-order loss-rate kinetics weathering model, calibrated with the results of experiments on gravels coated with oil and washed in the laboratory for six months, to describe the extent of weathering of EVOS in a sample and to discriminate EVOS and the natural petrogenic background. The TPAH-normalized concentrations of 14 PAH analytes (13 alkylated PAH and unsubstituted chrysene) in a sample are compared to their concentrations in the unaltered cargo crude. A suite of 26 weathered oil samples containing all 14 analytes was used to describe the PAH analyte variability with extent of weathering. Discrepancies between the measured and model-predicted PAH concentrations in EVOS samples were compared with a probability distribution of these discrepancies derived from the experimentally weathered samples. The weathering parameter, ω, summarizes the exposure history of the volume of oil.

The model can be used with relatively fresh oils when all 14 analytes are present. However, if any of the 14 analytes is absent, the model fails. This could happen at any weathering condition for sediment samples having low PAH concentrations or for samples that contain sufficiently weathered oil. For EVC shoreline oil that condition is reached when the mass loss from the original oil approaches 50% and all of the alkylated naphthalenes have been removed (Figure 15-2).

The model is also used to determine the probability that a specific sediment sample contains EVOS PAH or PAH from the natural regional background. The background is defined by the normalized PAH distributions for the median value of 14 benthic sediment samples from Constantine Harbor. The error distribution for this pattern is obtained by comparing the other 13 patterns with the median pattern. The model then uses the error distributions determined for the weathering model (from the 26 samples in the weathering suite) and for the natural background model (from the 14 samples in the background suite) to determine the probability that a given benthic sediment sample contains PAH from one source or the other. The model cannot apportion those sources in mixed samples.

### 15.5.3 Quantitative Models

#### 15.5.3.1 PAH Ratios

The PAH-based fingerprinting and source-allocation method used by Page et al. (1995, 1996) was based on the observation that the regional background PAH had low ratios of alkyl dibenzothiophene to alkyl phenanthrene (e.g., $C_2$-Dbt/$C_2$-Phe) relative to the spill oil and its weathering products (Table 15-1A and Figure 15-6). Douglas et al. (1996) showed that the ratios for the respective isomers remain constant over a range of weathering states up to approximately 70% depletion of the total petroleum hydrocarbons present. Diesel fuel, refined from Alaska North Slope crude oil, has the same $C_2$-Dbt/$C_2$-Phe as EVC, but can readily be differentiated by the lack of PAH with 4 rings or greater ($C_2$-Ch/$C_2$-Phe = 0.0) and the lack of saturate and aromatic biomarkers, all having boiling points higher than the distillate fuel boiling-point range. The EVC TPAH contribution to a benthic sediment sample containing only two hydrocarbon components (petrogenic background and EVC) is determined from the following equation developed by Page et al. (1995). Subtracting this value from the total petrogenic PAH yields the total background-sourced petrogenic PAH.

$$\mathrm{TPAH}_{\mathrm{ANS}} = \frac{\mathrm{C_2-Phe}_{\mathrm{sample}}}{0.093}\left[1-\left[\frac{1.07-\left(\dfrac{\mathrm{C_2Dbt}}{\mathrm{C_2Phe}}\right)_{\mathrm{Sample}}}{0.92}\right]\right]$$

This source allocation model is based entirely on the 3-ring PAH. Consequently, it cannot distinguish ANS crude from ANS-derived diesel. Nor can it resolve the multiple petrogenic inputs that contribute to the natural hydrocarbon background. Due to variabilities in the distinguishing parameters, Page et al. (1996) concluded that low levels (less than

3 to 8%) of total petrogenic PAH having an ANS signature generally cannot be differentiated from the natural regional petrogenic background.

### *15.5.3.2 Statistical Models*

The use of a combination of principal components analysis (PCA) and partial least-squares (PLS) analysis was developed for specific use in apportioning the natural petrogenic background to its component sources. While there are some differences in the PAH compositions of the various sources (Table 15-1A and Figure 15-3), they alone cannot be used to resolve those sources. However, there are small, but important, differences in the saturated and TAS biomarkers among these sources (Table 15-1B and Figure 15-4). Consequently, statistical programs that use both the PAH and biomarkers can resolve them. Because some of the source inputs are distinguished by relatively small compositional differences at low concentration levels, highly precise analyses with lower method detection limits (MDLs) were required. Refinements to standard analytical methods including gas chromatography-mass spectrometry (GCMS) analysis in the selected-ion-monitoring mode (SIM), increased sample size, column cleanup of the extract, and decreased pre-injection volume (volume of final extract prior to injection into instrument) lowered MDLs by factors of 10 to 1000 (Douglas et al., 2004). In sediment samples, MDLs < 0.5 ng/g for the PAH, including the alkylated homologs, and biomarkers were achieved.

Principal components analysis (PCA) is a multivariate statistical technique where sets of data are subjected to statistical analysis to reveal underlying relationships between groups of parameters and hence groups of samples in which these parameters are measured. (See Chapter 9 herein.) Based upon extensive field sampling programs in PWS and the eastern GOA, Burns et al. (1997) selected 18 potential sources contributing to PWS shoreline and benthic sediments in the path of the spill. They included EVOS in various weathering states, diesel oil and diesel soot, creosote and other combustion sources, and the natural PAH background in PWS sourced in the Gulf of Alaska. PCA analysis (Figure 15-8) was used to categorize the samples

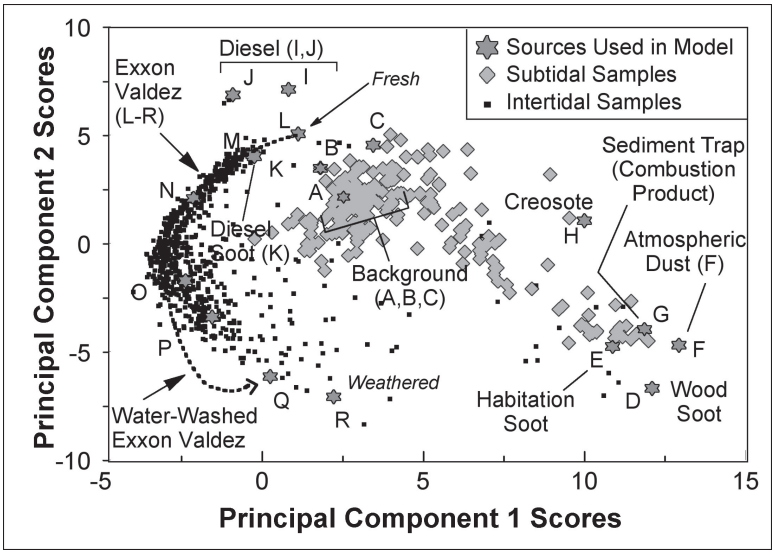


**Figure 15-8** Factor score plot resulting from the PCA analysis of PAH in shoreline and benthic sediments in PWS. Modified after Burns et al. (1997).

according to similarity of PAH composition and, by inference, source inputs.

The PCA results subsequently were used to determine the combination of PAH and biomarker analytes that best resolved the potential sources of hydrocarbons. Both in the earlier PWS studies (Burns et al., 1997) and in the later GOA studies (Boehm et al., 2001; Burns et al., 2000, 2006), the choice of analytes and numbers of sources were selected by PCA for use in the constrained least-squares analysis. PCA cannot on its own be used to quantify the various source components in a given sample. Furthermore, PCA can be highly influenced by outliers, samples with radically different source compositions that affect the analysis and the clustering of the samples on the PCA plots. A more quantitatively rigorous apportionment methodology was needed and a partial least-squares model was employed (Burns et al., 1997, 2006).

### *15.5.3.3 Statistical Models*

**15.5.3.3.1 Multivariate Methods — Constrained Least Squares** A constrained least-squares (CLS) model to allocate sources of PAH in PWS was used by Burns et al. (1997) in which iterative matching was used to determine the best fit of 36 PAH analytes in benthic sediment samples to 18 possible sources. For each sample, the model initially equalizes the contribution of total PAH from each source. Then the amount of total PAH from each source is varied using an iterative procedure that starts from the initial equalized contribution and systematically changes source contributions (the *xj* below) by small steps until the following expression is minimized:

$$\sum_{i=1}^{36}\left[\sum_{j=1}^{18}\left(S_{i,j}\,x_j/\mathrm{TPAH}_j\right)-d_i/\mathrm{TPAH}_{\mathrm{samp}}\right]^2$$

In this expression, *i* refers to the PAH analytes (1–36), *j* refers to the PAH sources (1–18), $s_{i,j}$ is the concentration of the *i*th analyte of source *j*, *xj* is the fraction of the sample's total PAH that is due to source *j*, TPAH*j* is the total PAH of source *j*, *di* is the concentration of the *i*th analyte of the sample, and TPAHsamp is the total PAH of the sample. The $s_{i,j}$ and TPAH*j* are described in Burns et al. (1997) for 18 possible sources. The procedure fits only the analytes that are detected in the analysis; analytes reported as nondetects are skipped so it is imperative that low detection limits (Douglas et al., 2004) be achieved on all samples. The least-squares algorithm always converges to the same results from different starting values. For each sample, the least-squares model calculates the contributions of each of the 18 sources and the goodness of fit. The contributions to a sample from any major source type (such as spill oil, diesel oil and diesel soot, natural background, or combustion products and creosote) can be determined by summing the contributions of appropriate sources and multiplying by the total PAH (TPAH) of the sample.

Burns et al. (2002, 2006), recognizing the limitations of using just the PAH analytes and the important additional chemical constraints provided by the saturate and aromatic biomarkers, incorporated them into the CLS model. They noted, however, that care must be taken to ensure that accurate and meaningful solutions are obtained. Results are affected by many factors including the selection of analytes and sources, the use of data from different labs and/or instruments, the presence of analytical noise in the data, and the need to be consistent with other sediment chemical constraints such as total organic carbon (TOC). For example, including too many low-concentration analytes, i.e., those well below the method detection limit (MDL), from a dataset containing concentration-dependent noise risks driving the solution in an incorrect direction. On the other hand, including too few can cause the solution to miss important contributing sources entirely. The use of data from different labs, even labs ostensibly following the same protocols, can result in incorrect source attributions due to different instrument sensitivities and differences in quantification procedures.

The expanded CLS model was used to quantitatively allocate sources in the prespill

benthic sediments of PWS and in the benthic sediments of the GOA east of PWS (Boehm et al., 2001, 2002). Based upon PCA results, 38 PAH analytes and biomarker compounds were selected and up to 18 GOA sources were identified. The constrained least-squares iterative method was then used to find the linear combination of analyte distributions from the 18 different sources that best matched the analyte distribution of the sample. The results of that analysis are shown in Figure 15-9. They show that the dominant contributors to both GOA and PWS sediments are the organic components (kerogens) of eroding shales and residues from the natural seeps. Seep contributions are particularly important in the GOA near the mouths of the streams, where seeps have been identified. Coal inputs are important

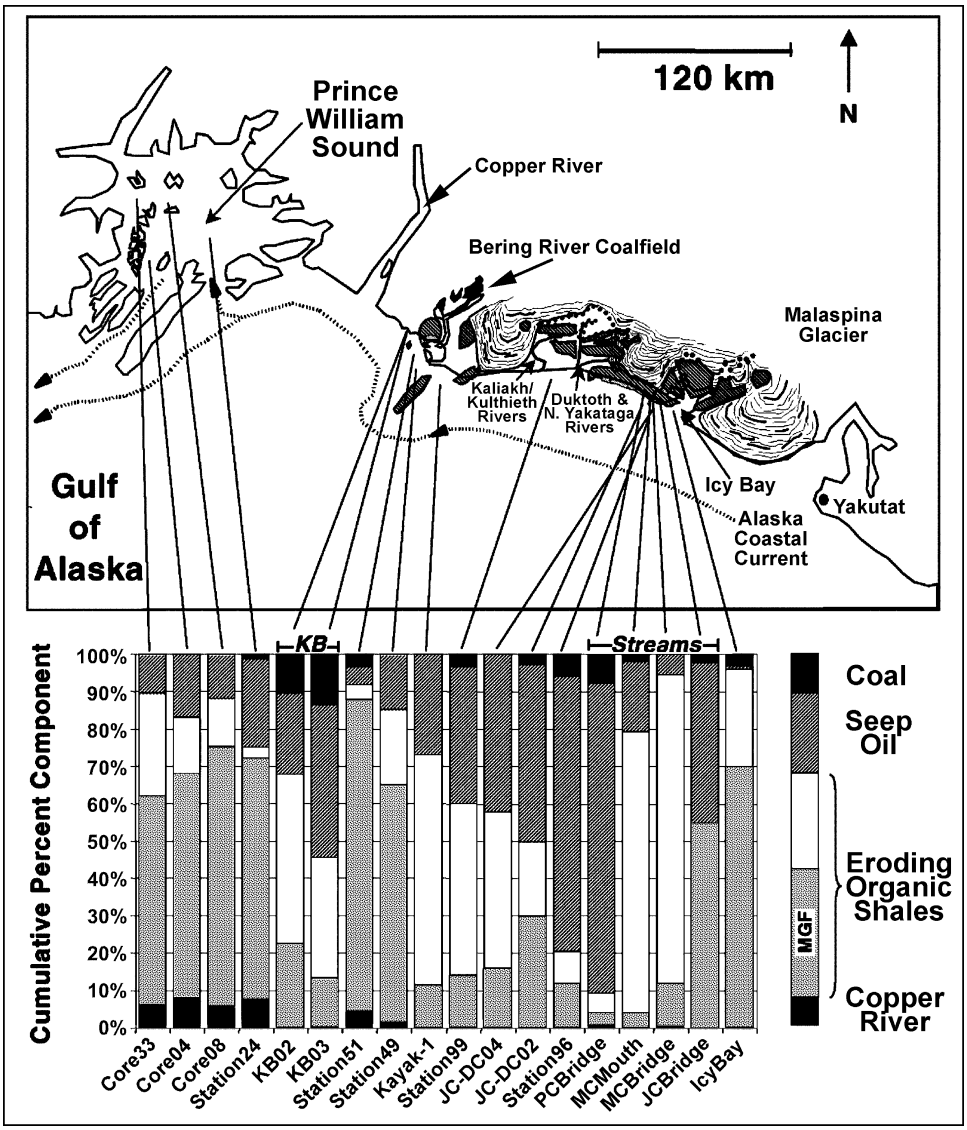


**Figure 15-9** Source apportionments for GOA and prespill PWS benthic sediments. KB = Katalla Beach; MGF = Malaspina Glacier Flour. Reprinted with permission from Boehm et al. (2001). Copyright 2001, American Chemical Society.

only at the mouths of streams whose drainage areas include coal seams. The important contributors to prespill benthic sediments in PWS are the shales and seep residues.

The current version of the CLS model includes 136 PAH and biomarker analytes and up to 30 sources (Burns et al., 2006).

**15.5.3.3.2 Multivariate Analysis — Partial Least Squares.** A partial least-squares (PLS) model was used by Mudge (2002) to assess the percentage contribution of coal, seep oil, shales, and rivers to the hydrocarbon loading of benthic sediments in the Gulf of Alaska. Previously published compositions of benthic sediment samples were analyzed using selected sites as sources in order to develop signatures. These signatures are based on the PAH and saturate biomarkers.

The principal components describing these sources are then fitted to the data for other sites around Prince William Sound (PWS) and Gulf of Alaska (GOA) to determine the proportion of the variability described by each source. A mixed source of coal, seep oil, eroding shales, and river sediments (two groups) described 13%, 18%, 24%, 26%, and 20%, respectively, of the variance in PWS and GOA benthic sediment data.

The procedure involves addition of a small constant to each analyte to permit log transformation of nondetected analytes. A principal components analysis (PCA) is conducted, followed by a PLS study. PCA identifies orthogonal data projections (principal components 1 and 2) that explain much of the variance in the data. The PCA results identified the five source types (oil, coal, shale, and river sediments groups 1 and 2). Source-type selection is based on the first two principal components, and some individual samples were excluded.

PLS is used to determine loadings factors for the source types and the amount of variance in target samples explained by each source-type loadings signature. If variance explained by the various source types totals more than 100%, variance explained is then normalized to 100%. To obtain percent contribution, CLS fits relative concentrations of all individual analytes rather than variance and is therefore more consistent with material balance constraints on individual analytes.

Different sources may explain the same amount of variance but have different degrees of fit to the relative concentrations. Consequently, PLS and CLS can yield different results for the same data set (Burns et al., 2006). The PLS model used by Mudge (2002) provides results for percent variance explained by the identified source types, not by individual source samples. By contrast, CLS determines the contributions of individual source samples, which can then be summed in various groupings to show contributions by source type. Source apportionment by both the CLS and PLS methods yield comparable results in that they both recognize that coal is not a major contributor to the background in benthic sediments of PWS. However, the 13% coal estimate produced by application of PLS to the data is certainly too high, given the high organic carbon content of coal (>50%) and the low total organic carbon in PWS benthic sediments (<1.0%), which is much lower than a 13% coal contribution would predict, as discussed in the next section.

### *15.5.3.4 Total Organic Carbon (TOC) Constraints on Source Allocations*

The application of multivariate statistical models to source allocation always provides a solution. But how realistic is that solution? It must be geologically reasonable, i.e., the source inputs to the model must actually be contributors given the geological setting. Furthermore, all potentially contributing sources must be included in the model. For some types of samples, the reasonableness of a solution can be checked independently using TOC mass-balance constraints. Those are samples in which the PAH and chemical biomarkers are in the TOC-contributing components (usually fossil forms of carbon such as kerogen, asphalt, oil) and are strongly correlated. For example, the results of the source allocations obtained by Boehm et al. (2001, 2002) were

checked using TOC as a constraint. The TOC content of all potential sources and the environmental samples are required for this check. The TOC contents and the relative amounts of the sources in the calculated best fit are used to calculate the TOC content of the mathematically reconstructed sample. This calculated value is then compared with the measured TOC content of the true sample. If recent organic matter (ROM) such as plant debris and animal remains is not an important component of the environmental sample, a close match between the calculated and measured values for TOC will indicate that the solution is permissible and may be correct. If the two do not agree within appropriate error limits, the source allocation cannot be correct. This mismatch could be due to the presence of ROM, which is a contributor of TOC but not of any of the analytes used in the source allocation, or it may indicate that all of the potential source inputs have not been considered. Mass-balance assessments of source input based on TOC, PAH, and chemical biomarkers are useful because sources having different thermal maturity levels and different organic facies, characteristics of the eastern GOA tertiary sedimentary section, can exhibit large differences in TOC-nomalized PAH and biomarker concentrations.

## 15.6 Allocation of Anthropogenic Sources of PAH

Prince William Sound has had an extensive history of human and industrial activity in PWS going back into the 1800s and earlier. Those activities, particularly ones involving fuel use, leave chemical signatures in near-shore and intertidal sediments (e.g., see Page et al., 1999, 2002a, 2004). Consequently, understanding the industrial and cultural history of the spill zone in an area like PWS is a key part of a comprehensive approach to environmental forensics. Pyrogenic and petrogenic hydrocarbons, unrelated to the 1989 spill, are present in the vast majority of the subtidal sediment samples analyzed (Page et al., 1995, 1996, 1999, 2002a, 2004; Bence et al., 1996). Localized shoreline sources of PAH that contribute to intertidal and near shore subtidal sediments are characterized by relatively high concentrations of 4- to 6-ring PAH (pyrogenic sources) or by their petroleum signatures (e.g., Monterey petroleum from unused fuel in derelict fuel tanks). These anthropogenic sources are located at villages, fish hatcheries, fish camps, recreational campsites as well as now-abandoned settlements, canneries, sawmills, and mines. Petroleum was the major energy source at these facilities.

The 1964 earthquake and the accompanying tsunami destroyed settlements and structures at sites throughout PWS (Lethcoe and Lethcoe, 2004). This destruction released significant quantities of petroleum products (Kvenvolden et al., 1995). Some entered the PWS marine environment from onshore locations and were dispersed into intertidal and near-shore subtidal areas. Because these chronically contaminated sites are located above the tide zone, hydrocarbon inputs have continued to the present time.

Field studies were conducted in 1999 and 2000 to characterize the near-shore subtidal sediments in embayments adjacent to sites of past industrial activity inside the *Exxon Valdez* spill zone in western PWS as well as bays that were heavily oiled in 1989 and an embayment outside the spill zone (Page et al., 2002a, 2004). Embayment locations are shown in Figure 15-10. Sediment samples were analyzed for saturate and aromatic biomarkers, PAH, total organic carbon (TOC), and grain size. Included were 36 2- to 6-ring PAH analytes, 44 $C_{19}$-$C_{35}$ tri-tetra- and pentacyclic triterpanes, demethylated hopanes (*m/z* 191), 14 $C_{21}$–$C_{29}$ regular steranes (*m/z* 217, 218), 8 $C_{27}$–$C_{29}$ diasteranes (*m/z* 259), and $C_{20}$–$C_{28}$ triaromatic steroids (*m/z* 231). Diagnostic patterns of PAH analytes and biomarker compounds were used to discriminate hydrocarbon sources in near-shore embayment sediments using an expanded version of the least-squares iterative methodology described by Burns et al. (1997). For this study, four categories of sources (weathered NSC, the prespill natural regional background,

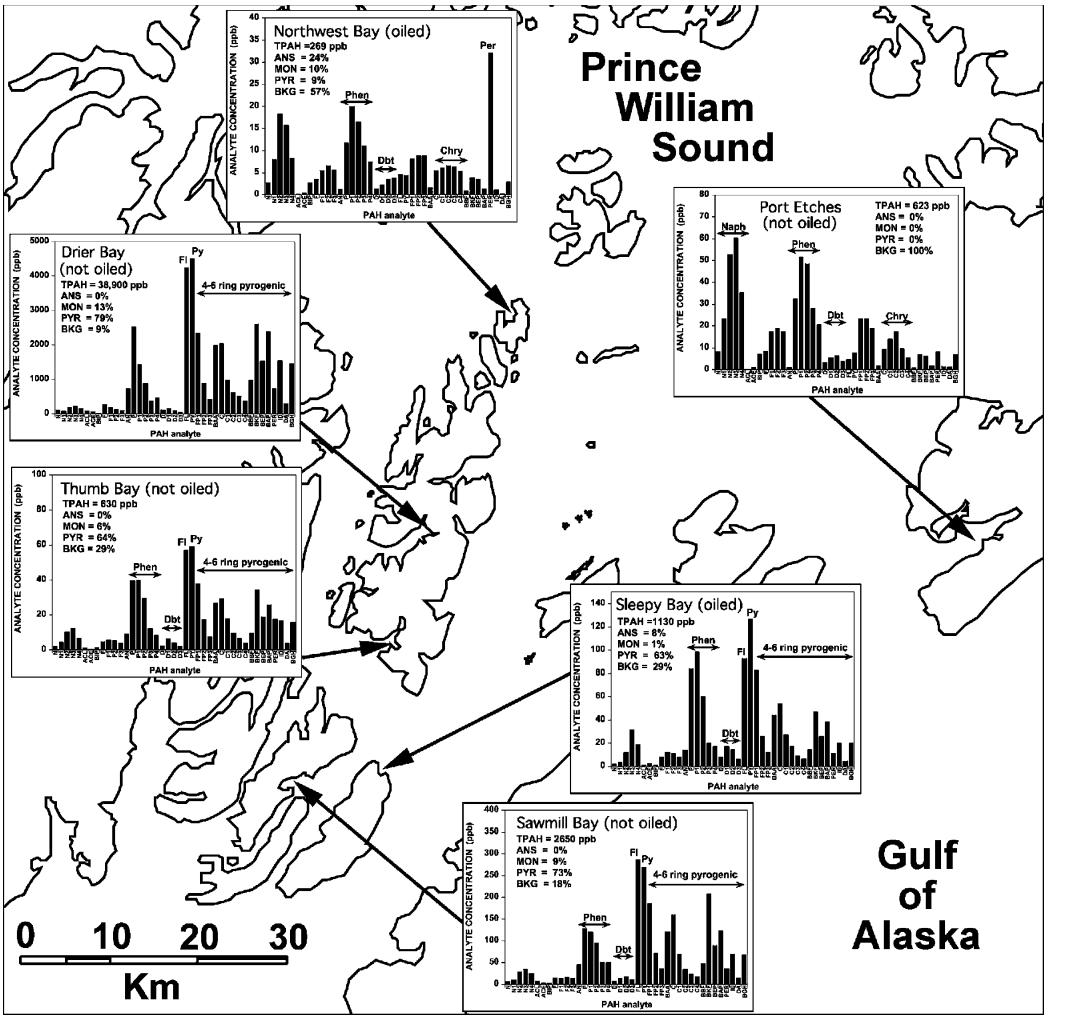


**Figure 15-10** 1999–2000 embayment benthic sediment sampling program with site locations, oiling category, representative sediment PAH profiles, and the results of the CLS source allocations, where ANS = Alaska North Slope oil, Mon = Monterey petroleum, PYR = pyrogenic PAH, and BKG = regional petrogenic background.

Monterey tars, and combustion products) were represented by 16 specific samples (see Page et al., 2002a) and 86 PAH and biomarker analytes were used to describe the hydrocarbon sources in the model.

The source allocation results of the CLS analysis are summarized in Table 15-2. They show that pyrogenic and regional petrogenic background hydrocarbons are the dominant sources, even in bays that were heavily oiled in 1989. In all cases, the relative amount of dibenzothiophenes is low, consistent with small or no inputs of ANS petroleum, either from the 1989 spill or other sources. Even at Sleepy Bay, which was heavily oiled in 1989, pyrogenic PAH, possibly from fuel use by fishing vessels known to anchor there, is the dominant source.

## 15.7 Identification of Hydrocarbons in Biological Samples

To assess the impact of the spill on the biological resources of the region, Bence and

**Table 15-2** Summary of Source Allocation Results for Subtidal Sediments Sampled in Six PWS Embayments in 1999 and 2000

| *Source Type* | *Sleepy Bay* | *Port Etches* | *Sawmill Bay* | *NW Bay* | *Drier Bay* | *Thumb Bay* |
|---|---|---|---|---|---|---|
| Spill path? | Yes | No | No | Yes | No | No |
| Industrial activity site? | No | No | Yes | No | Yes | Yes |
| Measured TOC (wt.%) | 0.37 | 0.49 | 0.49 | 0.98 | 10.85 | 1.75 |
| TPAH (ppb dry wt.) | 1130 | 623 | 2650 | 269 | 38,900 | 630 |
| ANS % | 8 | 0 | 0 | 24 | 0 | 0 |
| Monterey % | 1 | 0 | 9 | 10 | 13 | 6 |
| Pyrogenic % | 63 | 0 | 73 | 9 | 79 | 64 |
| Background % | 29 | 100 | 18 | 57 | 9 | 29 |

Burns (1995) used forensic chemistry to analyze tissue PAH data for more than 1500 tissue samples reported by the Oil Spill Health Task Force (OSHTF) and nearly 4700 tissue samples in PWSOIL, the government's damage-assessment database. OSHTF was formed shortly after the spill to assess subsistence food safety reported results for samples collected in 1989, 1990, and 1991. The November 1993 version of PWSOIL studied by Bence and Burns (1995) also reported data only for samples collected during the 1989–1991 period. Samples reported in that database were analyzed either at the NOAA-NMFS Auke Bay Laboratory (NOAA/ABL) or at the Geological and Environmental Research Group (GERG) of Texas A&M University. The public version of the government database EVTHD (*Exxon Valdez* Trustees' Hydrocarbon Database) was first released in 1996. The PWSOIL version became the general repository database for all samples, including those collected but not analyzed. Both continue to be maintained through funding support from the *Exxon Valdez* Trustee Council. In more recent years, studies by both *Exxon Valdez* Trustee- and Exxon-supported scientists have focused on the bioavailability of weathered EVOS residues to marine organisms. These have included analyses of intertidal biota at beaches where EVOS residues are buried beneath a boulder-cobble surface layer (Boehm et al., 2004; Neff et al., 2006) and of fish eggs and embryos that have been exposed to varying doses of oil in the laboratory (e.g., Heintz et al., 1999; Carls et al., 1999). The 2004 version of EVTHD, downloaded from the NOAA-NMFS-Auke Bay Lab website, contains additional chemical data for samples collected in the period 1991–1996 that were not evaluated by Bence and Burns (1995).

For their analysis of the OSHTF and PWSOIL (November 1993 version) databases, Bence and Burns (1995) developed a rigorous procedure for classifying the PAH signatures, where eight categories of PAH fingerprints were identified in the tissue databases.

1. EVC. *Exxon Valdez* crude and its weathering products (Figures 15-11A, 15-12).
2. WSF. Water-soluble fraction of EVC (Figure 15-14A) or of diesel (Figure 15-1).
3. DIESEL. EVC signature absent the alkylated chrysenes and usually confirmed by the truncated normal alkane distribution (Figures 15-11B, 15-12).
4. PETRO. Diesel signature, but alkylated chrysenes are below detection limits.
5. Non-ANS. Contains alkylated PAH, but no $C_2$-dibenzothiophene when $C_2$-phenanthrene > 10 ppb.
6. UNRESOLVED. Contains alkylated PAH, but concentrations are too low to be definitive.
7. ALKYL NAPH (ALKNP). Contains only alkylated naphthalenes.
8. PROCEDURAL ARTIFACT (PA). Consists solely of 25 required reporting

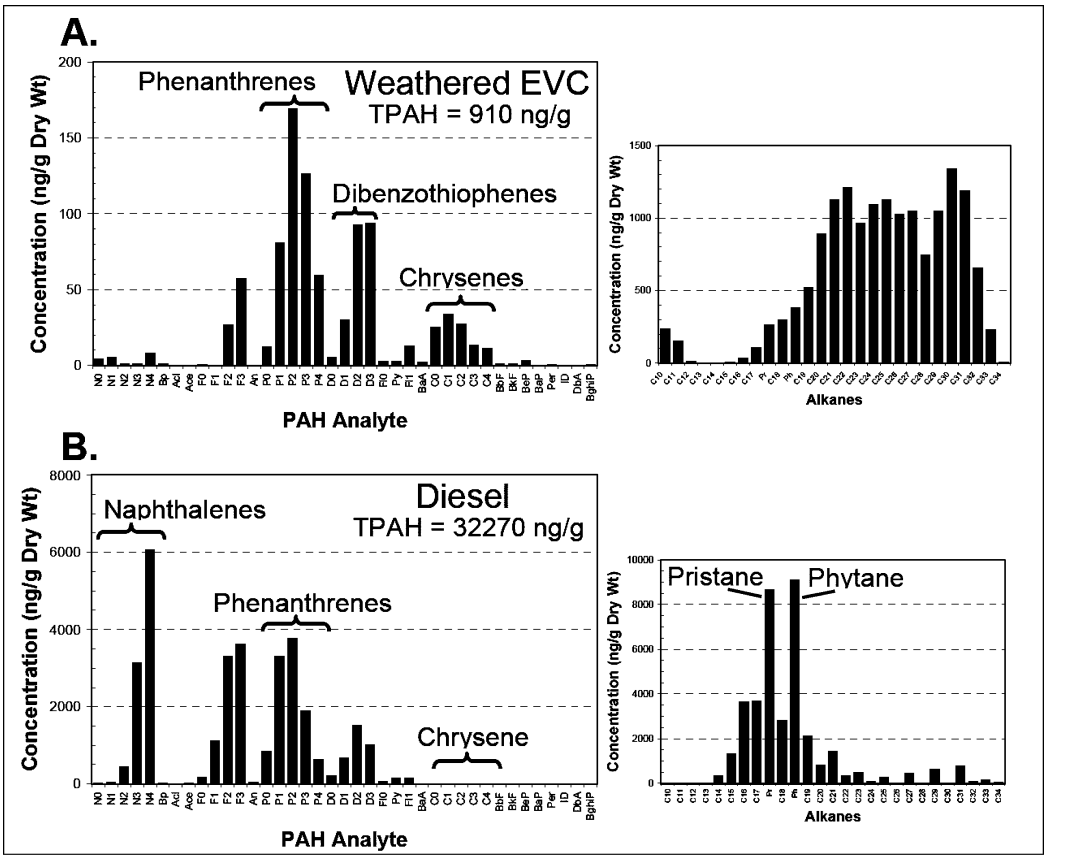


**Figure 15-11** PAH and alkane compositions of bald eagle eggshells. (A) Weathered EVC on eggshell collected at Italian Bay on June 8, 1989, EVTHD ID #23363. (B) Relatively fresh diesel on eggshell collected from Hells Hole in eastern PWS outside the spill zone on July 18, 1990, EVTHD ID #20029.

analytes including the two $C_1$-, one $C_2$-, and one $C_3$-naphthalene isomers, and 1-methylphenanthrene (Figures 15-12C, 15-13A, B). This PAH signature reflects an analytical protocol that required the reporting of an integrated signal for each of the 25 analytes when the signal was below the analyte MDL. No baseline correction was made. Consequently, it is integrated electronic noise. It is present in all analyses but is recognizable only in samples having PAH signals that are at their limits of detection.

All assignments of PAH classifications were made conservatively. That is, if a fingerprint contained a mixed signature, e.g., EVC and PETRO, it was classified as EVC.

When applied to the nearly 6200 analyses of tissues (excluding shellfish) in the two databases, Bence and Burns (1995) found the procedure to be highly diagnostic of EVC for samples of external surfaces, where selective uptake and metabolism were not issues and applicable for samples of the gastrointestinal tract. They found that, excluding shellfish, only a small fraction of the samples contained recognizable traces of EVC. Most of those samples were collected in 1989. Samples collected in 1990 rarely contained identifiable EVC. Samples reported to have been collected in 1991 never contained identifiable traces of

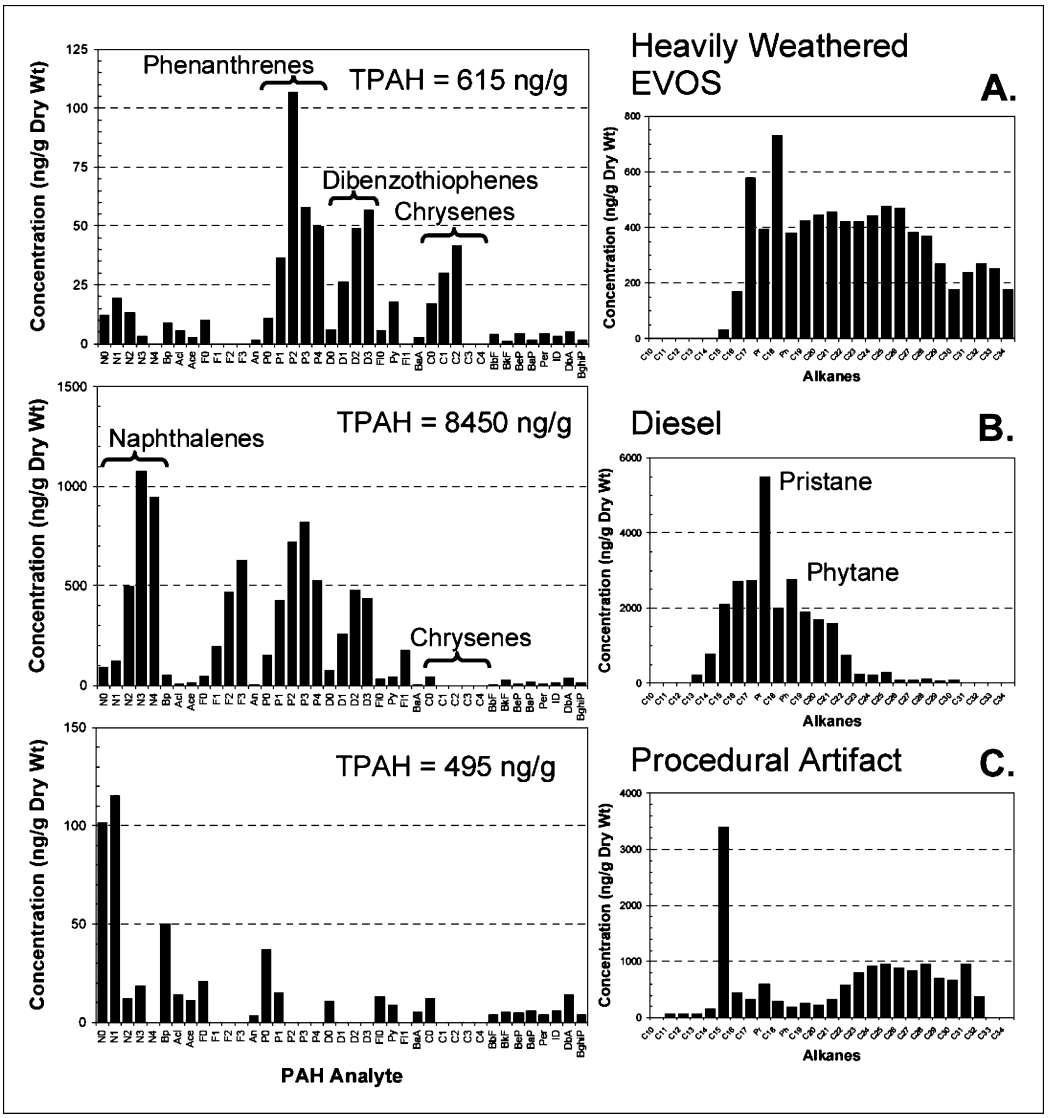


**Figure 15-12** PAH and alkane compositions for sea otter tissues. (A) Heavily weathered EVOS, sea otter skin collected April 12, 1989, EVTHD ID #27757, site not documented. (B) Relatively fresh diesel, sea otter fur collected August 1, 1990, site not documented, EVTHD ID #22851. (C) Procedural artifact, sea otter blood, Ogden Passage, SE Alaska, EVTHD ID #20044.

EVC. These results showed that subsistence foods were safe for human consumption shortly after the spill.

Procedural artifacts formed the dominant fingerprint in the EVTHD database. Diesel, presumably from field contamination, constituted the most common petroleum-sourced fingerprint.

The methodology developed by Bence and Burns was criticized by Carls et al. (2002) for failure to identify EVC in tissues of herring, including eggs, which had been exposed to EVC and its water-soluble fraction in laboratory experiments. However, those experiments were conducted after 1991 (Carls et al., 1999) and were not included in the 1993 version of

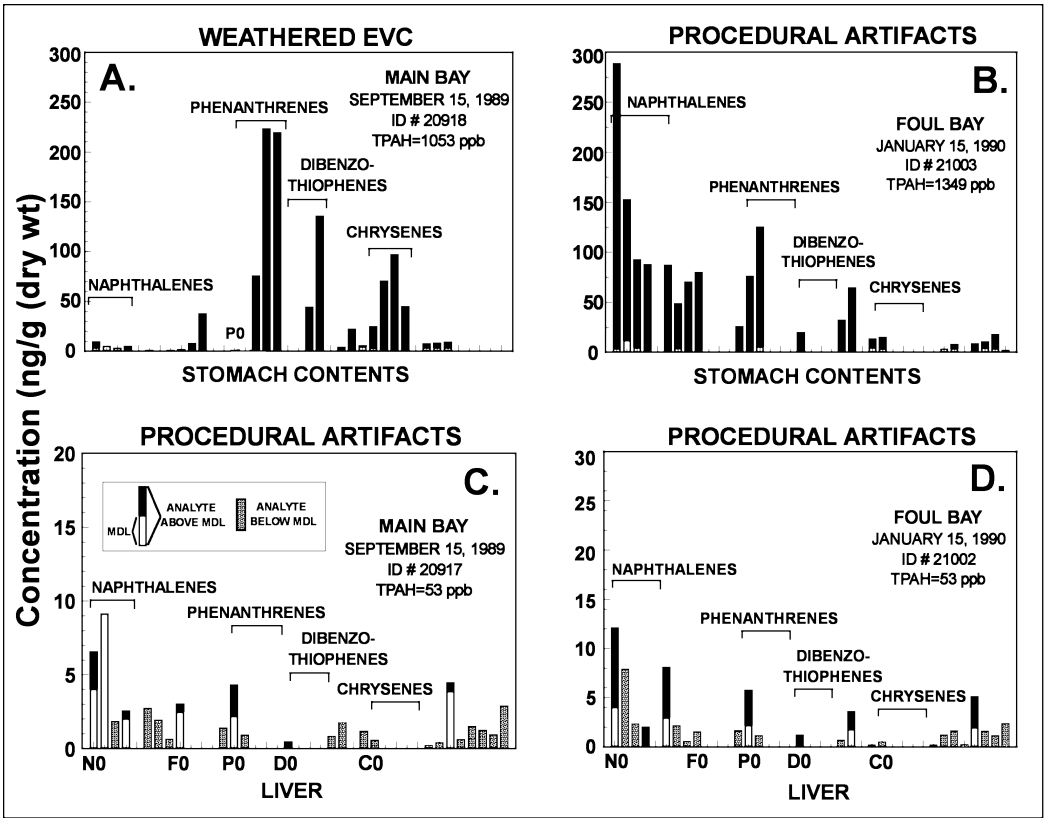


**Figure 15-13** PAH compositions for Harlequin duck stomach contents (A–B) and corresponding liver tissue (C–D) from the same bird collected by State of Alaska investigators. Adapted, with permission, from *STP 1219 Exxon Valdez Oil Spill: Fate and Effects in Alaskan Water*, copyright ASTM International, 100 Barr Harbor Drive, West Conshohocken, PA 19428.

PWSOIL that was evaluated by Bence and Burns (1995). Our subsequent analysis of the additional tissue data reported for 1991 through 1996 in the 2004 version of EVTHD is reported in Table 15-3. Results for field and laboratory-exposed samples are reported separately.

Because EVOS raised questions about the solubility of Alaska North Slope crude in water and the mechanisms by which fish and wildlife could be exposed to toxic components in the oil, a method was developed to discriminate an analysis of water that contained dispersed oil droplets from an analysis of the water-soluble fraction (WSF) of that oil. That method invoked the relative solubilities of the petrogenic PAH and their equilibrium octanol-water partition coefficients (Miller et al., 1985; Mackay et al., 1992) and was tested on the products of laboratory oil-exposure experiments. Briefly, an EVC-WSF designation is assigned when $C_2$-dibenzothiophene is present, $C_2$-phenanthrene > 1 ng/g, $C_0$-Db/$C_1$-Db > 1.0, $C_0$-Ph/$C_1$-Ph > 1.0, and $C_2$–$C_4$ chrysenes and other 4- to 6-ring combustion products, e.g., anthracene, benzo(*a*)pyrene, etc., are not detected. The presence of $C_2$–$C_4$ chrysenes at concentrations above their MDLs indicates that dispersed oil droplets, in addition to dissolved components, are present. ($C_0$/$C_1$-chrysene can be used to confirm the WSF designation when the methyl chrysenes are above their MDL.)

Laboratory exposure studies conducted by NOAA/ABL in the pink salmon and herring egg and embryo investigations involved direct exposure to artificially weathered EVC and to

**Table 15-3** Interpretations of Tissue (Excluding Shellfish) PAH Compositions Reported in the 2004 Version of EVTHD (See Text for Definition of EVTHD)

A. Laboratory-Exposure Samples

| *Year* | *Tissue (No. of Analyses)* | *EVC & EVC + WSF* | *WSF* | *DIESEL* | *PETRO* | *UNRES* | *ALK NP* | *PA* |
|---|---|---|---|---|---|---|---|---|
| 1991 | P. Salm. viscera (54) | 5 | | | | 45 | 4 | |
| | P. Salm. carcass (111) | 13 | | | | 85 | 13 | |
| 1992 | P. Salm. alevin (11) | 3 | 2 | | | 6 | | |
| | P. Salmon egg (4) | | 2 | | | 2 | | |
| 1993 | P. Salm. alevin (29) | 9 | | | | 20 | | |
| | P. Salm. egg (11) | 7 | 1 | | | 3 | | |
| | P. Salmon fry (3) | 2 | | | | 1 | | |
| 1994 | P. Salmon fry (14) | 3 | 11 | | | | | |
| | Herring egg (15) | | 14 | | | 1 | | |
| | Herr gonad (45) | | 18 | | | 27 | | |
| | Herr muscle (84) | 52 | | | | 32 | | |
| 1995 | P. Salmon (6) | 6 | | | | | | |
| | Herring egg (8) | 3 | | | | 5 | | |
| 1996 | P. Salmon (9) | 7 | | | | 2 | | |

B. Field-Exposure Samples

| *Year* | *Tissue (No. of Analyses)* | *EVC & EVC + WSF* | *WSF* | *DIESEL* | *PETRO* | *UNRES* | *ALK NP* | *PA* |
|---|---|---|---|---|---|---|---|---|
| 1991 | BLKI (1) | | | | 1 | | | |
| 1992 | None | | | | | | | |
| 1993 | HADU Fat (10) | | | | 2 | 8 | | |
| | HADU Gut (15) | | | 1 | 1 | 12 | | 1 |
| | HADU Liv (14) | | | | 3 | 9 | 2 | |
| 1994 | None | | | | | | | |

P. Salm. = pink salmon; BLKI = black kittiwake; HADU = harlequin duck.

naturally weathered EVC as well as to the water-soluble fractions (WSF) of the former. The chemistry data from those experiments are reported in EVTHD. Interpretations of the tissue analyses, following the decision-tree approach developed by Bence and Burns (1995), are reported in Table 15-3. A number of the samples designated as UNRES (UNRESOLVED) have some WSF characteristics, but the individual PAH analyte concentration levels are very close to their MDLs (ppb to sub-ppb in tissues) making their classification uncertain.

Many of the analyses classified as EVC also contain a WSF component as evidenced by $C_0$-Db/$C_1$-Db > 1.0 or $C_0$/$C_1$-chrysene > 1.0. Samples having these characteristics are placed in the EVC & (EVC+WSF) column of Table 15-3. A WSF fingerprint for pink salmon eggs exposed to weathered EVC in a 1994 NOAA/ABL experiment is shown in Figure 15-14A. It has the characteristic $C_0 > C_1 > C_2 > C_3$ pattern for the fluorenes, phenanthrenes, and dibenzothiophenes, and the chrysenes are at or below detection limits. A mixed EVC+WSF PAH composition for herring eggs exposed to artificially weathered EVC in NOAA/ABL 1993 laboratory experiments is shown in Figure 15-14B. These observations indicate that, for many of the laboratory exposure experiments conducted by NOAA/ABL in gravel column generators (Heintz et al., 1999; Carls et al., 1999), direct exposure to dispersed oil droplets in the water phase was the probable cause of observed harmful effects rather than exposure to low (≤1 ppb) total concentrations of water-soluble PAH. Brannon et al. (2006) used the same experimental design as

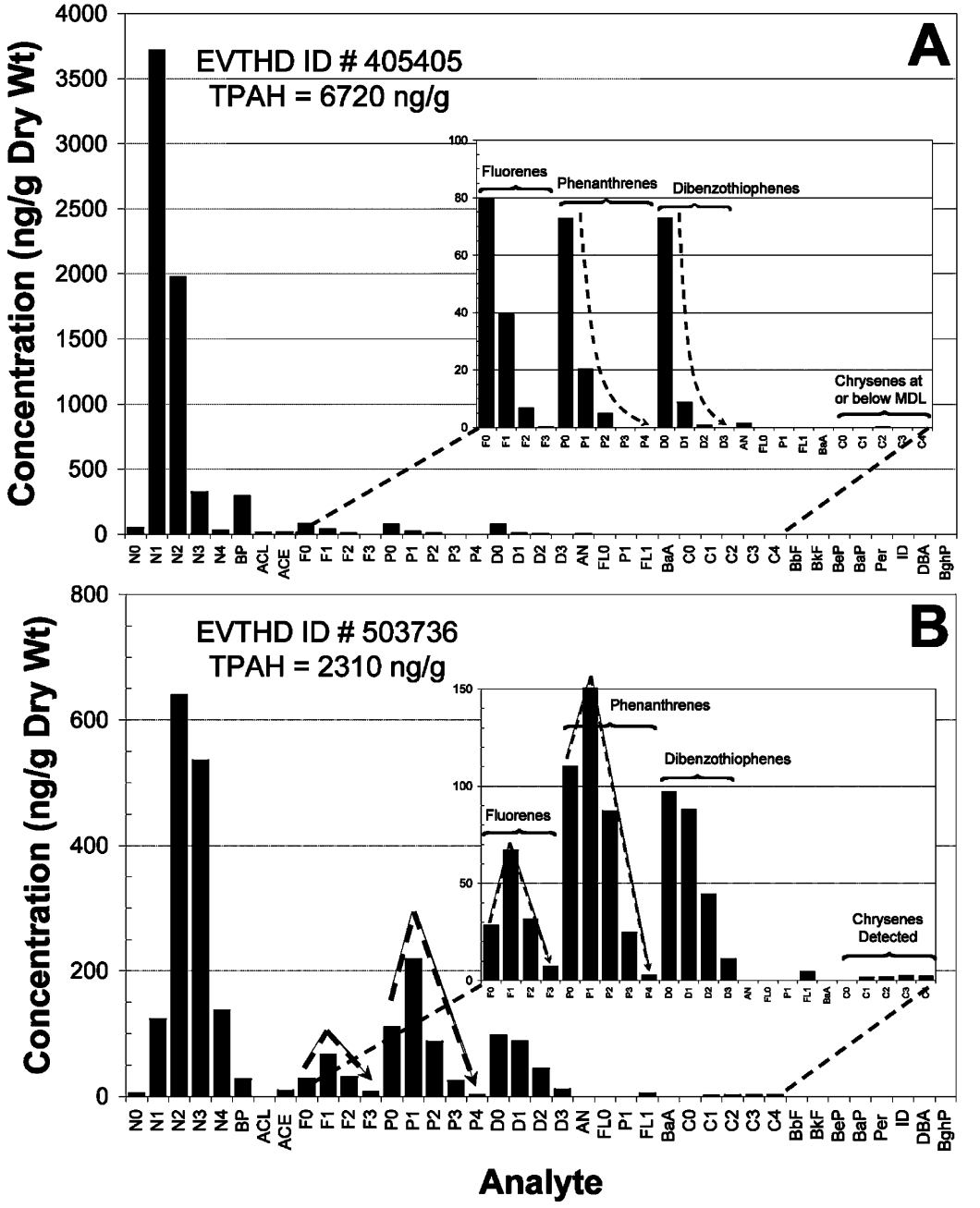


**Figure 15-14** PAH compositions of tissue exposed to weathered oil in column generator experiments conducted by NOAA/ABL, Juneau, AK. A. Pink salmon eggs after 36 days of exposure to artificially weathered EVC at a gravel loading of 281 ppm oil showing characteristic WSF composition. B. Herring eggs showing mixed oil + WSF composition.

used in the NOAA experiments to assess the toxicity of weathered EVC to pink salmon embryos. They observed that the experimental design of the generators did not exclude dispersed oil droplets from the aqueous phase and concluded that toxicity was not limited to the water-soluble fraction.

The results of the laboratory gravel generator experiments in which pink salmon embryos were exposed to very weathered oil (Heintz et al., 1999) formed the foundation of a changing paradigm in ecotoxicology proposed by Peterson et al. (2003). Those workers concluded that wildlife exposed to as little as 1 ppb TPAH dissolved in the aqueous phase can experience chronic sublethal effects, including population reductions and cascading indirect effects resulting in delayed population recovery. Because the source of the toxicity measured in those experiments was not due solely to the dissolved fraction, the experimental foundation upon which the changing paradigm is based is suspect and the experiments should be repeated with more rigorous controls to ensure that dispersed oil droplets are eliminated.

## 15.8 Applications of Forensic Methods to Assessments of Oil Bioavailability

### *15.8.1 PAH Uptake in Biota*

Measurements of petroleum fractions in sediments alone are insufficient to establish that there is a risk to wildlife because the spill remnants may be in forms and locations that are not available for uptake by biota. Therefore, the identification and quantification of tissue hydrocarbons, in conjunction with the analyses of the spill-contaminated sediments, is needed to establish the bioavailability of those spill remnants. Indicator species, such as bivalve molluscs, are often used to assess the bioavailability of petroleum residues present at a spill site because they concentrate bioavailable lipid-soluble material from the ambient water column. Consequently, when PAH levels in the water column are too low to measure using conventional methods, mussel PAH can be used to obtain an estimate of the PAH concentrations dissolved in the water. The method uses lipid-water partitioning coefficients to estimate the equilibrium water concentration of dissolved PAH (Neff and Burns, 1996). In addition, in those situations where PAH exposure to higher-life forms *via* the food chain is suspected, prey biota can be analyzed to assess exposure risk to foraging wildlife.

Because mussels are ubiquitous and integrate exposure over time, they are useful indicators of bioavailable hydrocarbon inputs and have served as the basis for many water-quality monitoring programs such as Musselwatch (O'Connor, 2002). Many studies of the *Exxon Valdez* spill have used the hydrocarbon chemistry of mussels and other biota to assess inputs of bioavailable hydrocarbons from residues of the spill, from sites of past and current industrial activity, and from natural petroleum hydrocarbon sources (e.g., see Babcock et al., 1996, 1998; Boehm et al., 1997, 2004; Carls et al., 2001, 2004; Neff et al., 2006; Page et al., 2005, 2006).

To assess the bioavailability of buried oil residues remaining on some beaches, a comprehensive mussel sampling program was conducted in 1998, 2000, 2001, and 2002 (Boehm et al., 2004). Using the fingerprinting methods described above to discriminate spill residues from other PAH sources, Boehm et al., (2004) found that petrogenic PAHs, attributable to the spill, were in low concentrations in mussels at sites where the underlying sediments have much higher concentrations of spill-related TPAH (Figure 15-15A, B, C, D). This illustrates the relative lack of bioavailability of the buried oil when the subsurface oil deposits are not disturbed. When the oil is disturbed, such as in the digging of pits for the deployment of SPMDs, mussels in the immediately adjacent area have elevated TPAH levels (Boehm et al., 2005). At sites having lower EVC-attributable concentrations in underlying sediments, low levels of pyrogenic compounds dominate the mussel PAH composition (Figure 15-15E, F, G, H).

Comparisons of TPAH levels in mussels at oiled sites with unoiled reference sites led

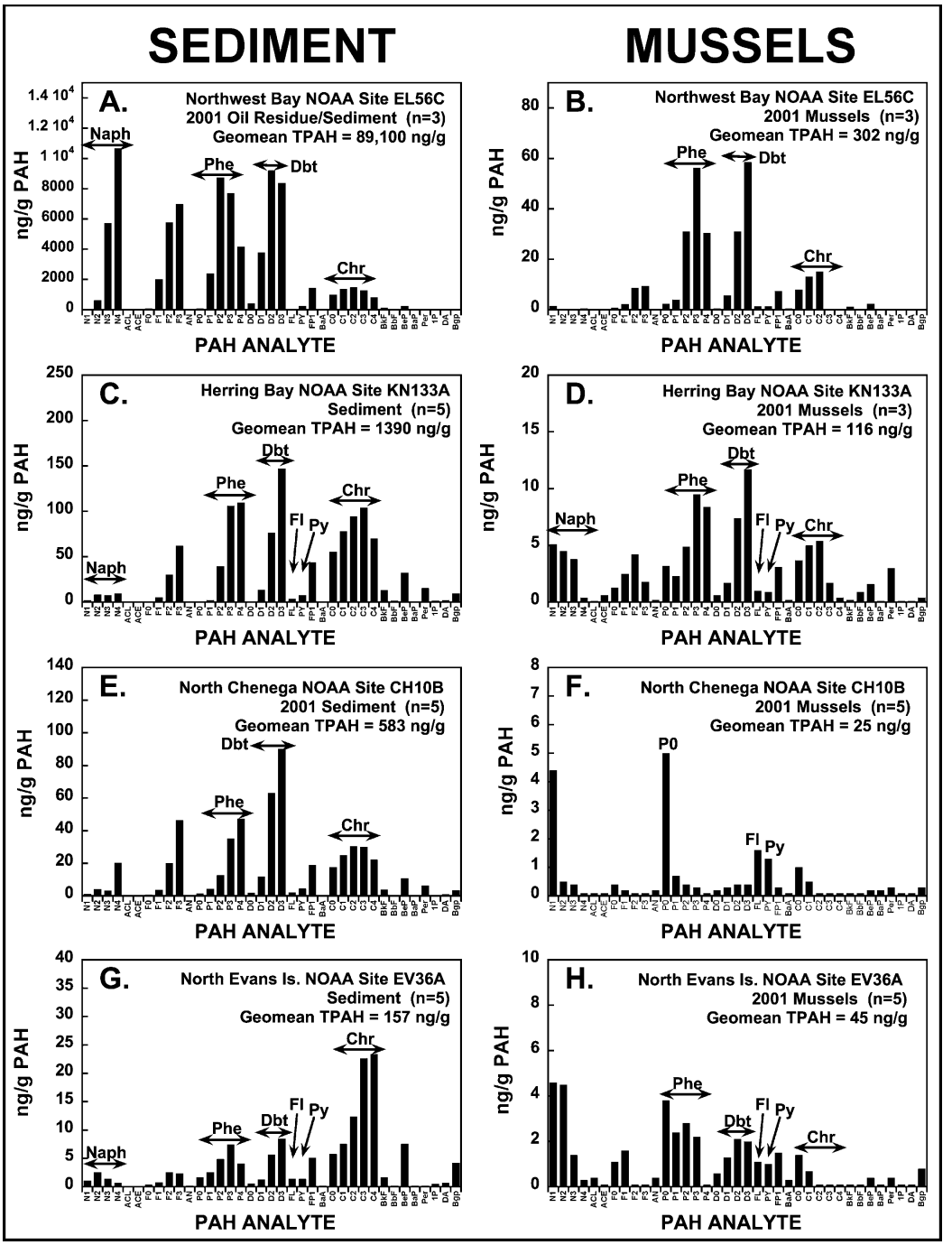


**Figure 15-15** Composition and concentration of PAH in mussel tissues from NOAA oiled mussel bed sites compared with the PAH composition and concentration of underlying sediments for samples collected in 2001. The data are presented as the geometric means of the analyte distributions of replicate samples at each site. Note that the mussel TPAH concentrations are factors of 3 to 300 lower than the TPAH concentrations in the corresponding sediments.

Boehm et al. (2004) to further conclude that bioavailable hydrocarbons in the *Exxon Valdez* oil spill zone in PWS were at or near background levels by 2002. This conclusion is in agreement with Carls et al. (2004), who reported that mussel beds that were heavily oiled in 1989 were at background levels by 1999. Page et al. (2005) repeatedly sampled and analyzed mussels from 11 oiled sites over the period 1990–2002 to quantify the changes in bioavailable PAH with time. From those time-series data, they concluded that the annual mean loss of bioaccumulated PAH in mussels was 25%.

In 2002, Neff et al. (2006) tested 7 species of intertidal biota at 16 sites having buried EVOS residues to determine if PAHs from those residues were sufficiently bioavailable to intertidal prey organisms that they might pose a health risk to populations of birds and wildlife that forage on the shore. Forensic fingerprinting methods were used to discriminate EVC PAH from other PAH sources. Mean tissue TPAH from all sources in clams, worms, and intertidal fish from oiled sites range from 24 to 36 ng/g dry weight; mean TPAH concentrations in sea lettuce, whelks, and hermit crabs, and intertidal range from 5 to 11 ng/g. Mean TPAHs in biota at unoiled reference sites and sites having a record of historical human and industrial activity (HA sites) range from 6 to 15 ng/g and 7 to 2200 ng/g, respectively. Oil residues at oiled sites are concentrated above +1.8 m in the middle- (upper half) and upper-intertidal zones, whereas the biota are located largely in the lower-tidal zone (below +1.3 m). Tide-zone averages for the mean sediment TPAH at the 16 oiled sites are 2500 ng/g upper-tidal zone, 1600 ng/g middle-tidal zone, and 70 ng/g lower-tidal zone. Figure 15-16 shows the TPAH levels in clams and sediments from the three categories of sites (oiled, reference, and HA).

A 2005 study analyzed clams collected from shallow subtidal and lower intertidal locations at sites that had been oiled in 1989 and where sea otters have actively foraged since. Results for two locations are shown in Figure 15-17. Combustion products (parent compounds dominant relative to the alkylated homologs; presence of 4- to 6-ring PAHs) dominate the PAH compositions of both. The Bay of Isles

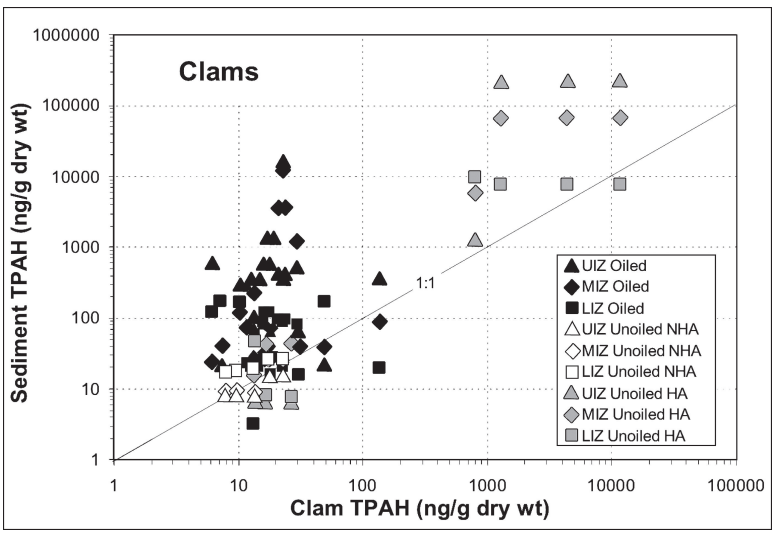


**Figure 15-16** Mean sediment TPAH versus composite clam TPAH for 16 oiled, 3 reference, and 4 HA sites in western PWS. UIZ = upper intertidal zone (+2 m mllw), MIZ = middle intertidal zone (+1–+2 m mllw), LIZ = lower intertidal zone (0–+1 m mllw).

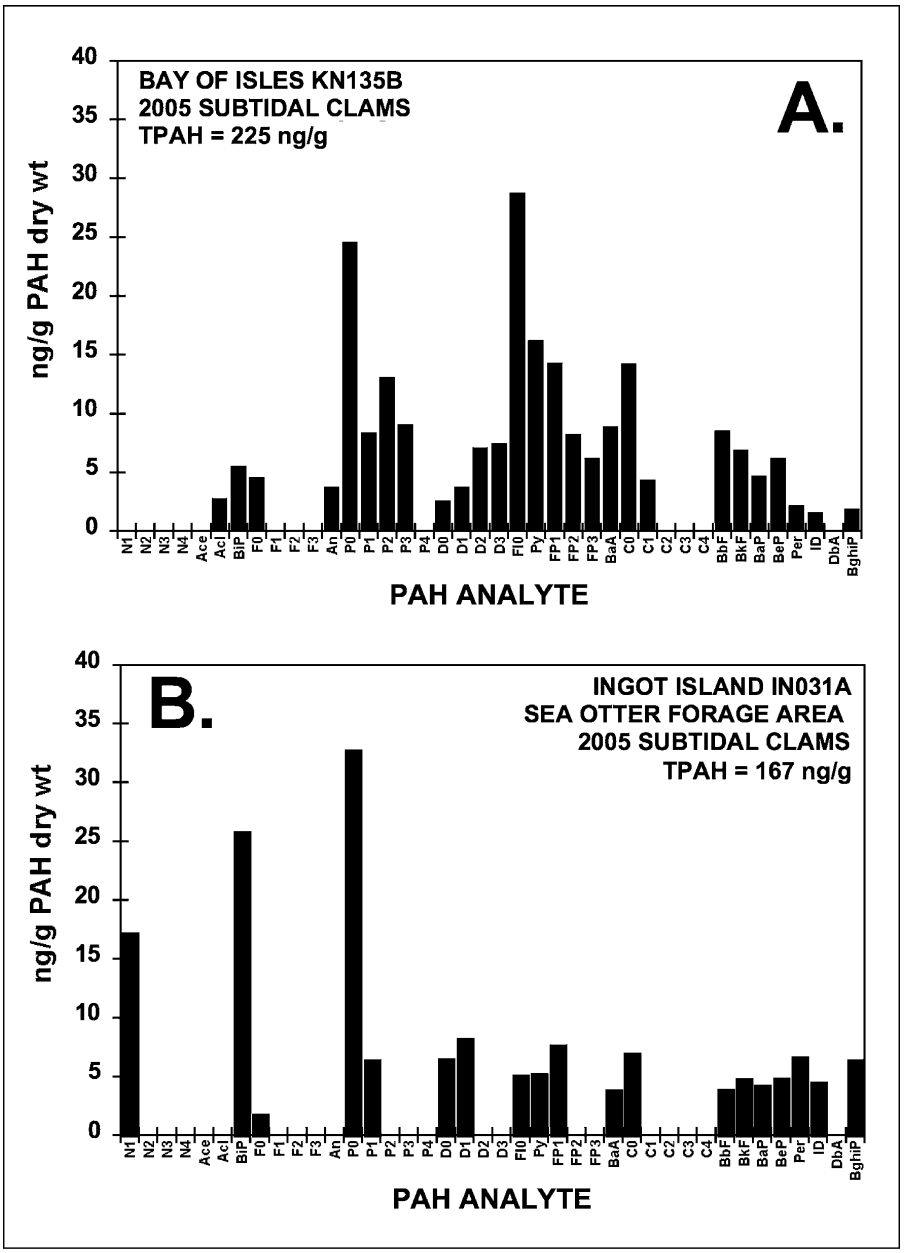


**Figure 15-17** PAH composition of composite clam tissues from two sea otter foraging sites that had been oiled in 1989.

sample (Figure 15-17A) also has a minor, heavily weathered, petrogenic component. The absence of alkylated chrysenes suggests that it is diesel. These results indicate that sea otters that feed on these clams probably would experience low levels of CYP 1A induction. However, that induction would be due to the presence of the strongly CYP 1A-inducing pyrogenic 4- to 6-ring PAHs present as part of the background and not to EVC residues.

### 15.8.2 Passive Sampling of PAH in Water

Passive samplers such as semipermeable membrane devices (SPMDs) and low-density polyethylene strips (LDPEs) are used as surrogates for mussels. They are stable, easily deployed and retrieved, moderately easy to process and analyze, and can be used to obtain water-quality data at locations where mussels cannot live. However, because they partition the PAH differently than mussels, results from these devices should be interpreted with caution. In a direct comparison of mussels and SPMDs as monitoring tools at a range of oiled and unoiled sites in PWS, Boehm et al. (2005) found that TPAH concentrations in mussels and in surface-deployed SPMDs were correlated, but that lower-molecular-weight PAHs were relatively more abundant in the SPMDs than in the mussels. At sites with buried oil, disruption of the beach substrate during deployment, such as placing the SPMDs in hand-dug pits, artificially enhances the bioavailability of the oil residues and results in anomalously high TPAH concentrations. The study concluded that when mussels are available, their collection and analysis are the recommended monitoring tools. This is especially true when the assessment involves estimations of risk to foraging wildlife, because the sampling of biota provides a more realistic evaluation of the composition and concentrations of PAH to which foragers might be exposed.

### 15.8.3 Biological Markers

Elevated biological markers (CYP 1A activity and bile fluorescent aromatic compounds) in fish and near-shore vertebrate predators sampled at some locations within the EVOS spill path have been cited as circumstantial evidence that PAHs in the residues of the spill are bioavailable to wildlife (Trust et al., 2000; Bodkin et al., 20002; Jewett et al., 2002). Those studies further concluded that this exposure has had harmful effects at the population level for some species. However, it should be pointed out that the levels of CYP 1A observed in those studies are generally low and are pervasive throughout the PWS region. For the study reported by Trust et al. (2000), the maximum values of CYP 1A, as measured by ethoxyresorufin *0*-deethylase (EROD) activity, in harlequin ducks from control sites (386 pmol/min/mg protein) were comparable to those from oiled sites (377 pmol/min/mg protein). Although certain PAH compounds such as benzo(*a*)pyrene and benzo(*k*)fluoranthene are strong inducers of CYP 1A (Lee and Anderson, 2005), they are either absent or at trace concentrations in EVC. Chrysene, present at ~50 ppm in EVC (Bence et al., 1996), is a weak to moderate inducer of CYP 1A activity. However, its solubility in water is so low ($\log K_{ow}$ ~6–8) (McKay et al., 1992; Neff et al., 1994; Neff and Burns, 1996) as to make exposure via the water column unlikely. Linking elevated biomarkers directly to a given source is problematic because there is no source specificity in the biomarker measurements. In PWS, this problem is compounded by the multiplicity of PAH sources that, potentially, could be the cause of elevated biomarkers in some wildlife species. For example, Huggett et al. (2003) conclusively demonstrated that sources other than EVOS spill residues are responsible for elevated CYP 1A and bile fluorescent aromatic contaminants (FAC) in five fish species collected in PWS and in the GOA at sites far-removed from the spill zone. The source of the biomarker induction is believed to be the regional background.

Elevated levels of CYP 1A and bile FAC were detected in some near-shore fish species caught at embayment locations in the spill zone in PWS that were also associated with past human and industrial activity (Huggett et al., 2003). Pyrogenic PAH comprise more than 50% of benthic sediment PAH in Drier Bay, Mummy/Thumb Bays, Sawmill Bay, and Sleepy Bay (Table 15-2), all sites of past or current industrial activity. Except for Sleepy Bay, these embayments were not oiled in 1989 (Page et al., 2002a, 2004). Subtidal sediments in Snug Harbor, an oiled bay, had ~12,000 ppb of pyrogenic PAH consistent with past fish

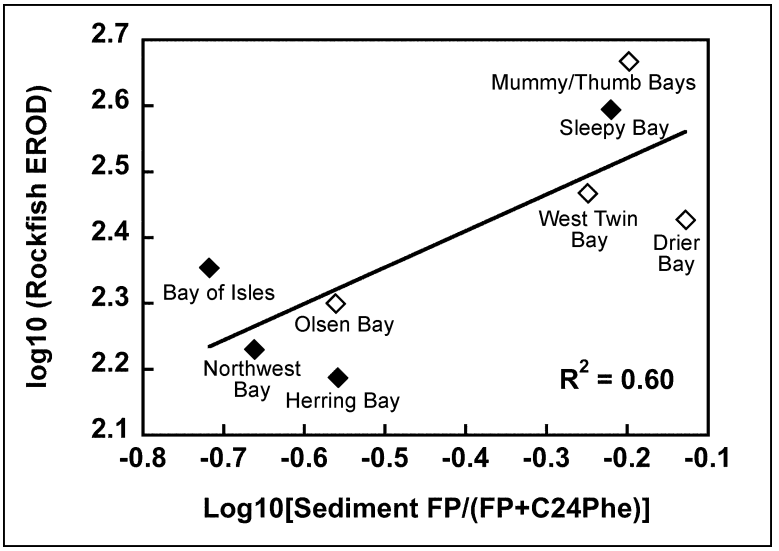


**Figure 15-18** Correlation of rockfish liver ethoxyresorufin *0*-deethylase (EROD) activity, a measure of the level of CYP 1A induction, with benthic sediment pyrogenic index (FP)/(FP + $C_{24}$Ph). Solid symbols = sites oiled in 1989. Open symbols = unoiled reference sites.

processing activity (Page et al., 1999). Pyrogenic PAHs with four or more rings are much more potent CYP 1A inducers than the 2–3-ring PAH that dominate most of the PAH fraction of EVC and its residues (Neff, 2001; Lee and Anderson, 2005). A positive correlation of the pyrogenic PAH indicator ratio (FP)/(FP + $C_2$ = $C_4$) in embayment benthic sediments with CYP 1A activities in rockfish at the same sites suggests that pyrogenic PAHs are the source of the induction (Huggett et al., 2003; Page et al., 2004) (Figure 15-18). There are no correlations of biomarker activity with 1989 oiling or with concentrations of EVC residues (Jewett et al., 2002; Page et al., 2004). Pyrogenic PAH from past and current industrial activities are the likely sources of CYP 1A induction in fish from the spill zone locations studied.

## 15.9 Summary

In the more than 16 years of research conducted to assess the environmental impact of the *Exxon Valdez* oil spill, forensic techniques have evolved and new ones have been developed to address a host of issues, some of which appear unique to this incident and the Prince William Sound environment. These advances include the development of analytical, interpretive, and statistical tools to quantitatively resolve the multiplicity of hydrocarbon source inputs to benthic and intertidal sediments. Analytical protocols were refined to be more precise at lower concentrations, and saturate and aromatic chemical biomarkers were merged with the PAH, making it possible to resolve distinct hydrocarbon sources having relatively small differences in composition. Mass balance of total organic carbon (TOC), that compared calculated with measured chemical compositions, was invoked to provide independent assessments of the reasonableness of a given source allocation. Results showed that the prespill benthic sediments in the sound contained a substantial background of petrogenic hydrocarbons derived from Tertiary hydrocarbons systems consisting of petroliferous shales, oil seeps, and coals located in the eastern GOA.

Methods were developed for the quantification of both total mass loss and the chemical changes that occur in various fractions of

shoreline oils as they weather. They confirmed that the inert asphaltenes and resin fractions make up an increasing fraction of the bulk oil as it weathers. Furthermore, they showed that all of the PAHs, including the 3- and 4-ring PAHs, are removed as weathering progresses, a feature of EVC not previously recognized. Although the alkylated chrysenes become an increasingly more important component of the PAH fraction, they decrease in the bulk oil as the total PAH fraction is removed during weathering. This is consistent with field observations that show oil toxicity decreases with weathering due to an overall decrease in toxic fractions with time.

A first-order kinetic model was developed to determine the rate of removal of subsurface oil residues. It showed that oil mass loss in 2001 was occurring at an annual rate of 20–26%, a rate similar to the annual mean loss of bioaccumulated PAH in mussels. If the assumptions made in that model are correct, at year-end 2005, less than 100 barrels of subsurface oil (<0.05% of the amount initially spilled) remain scattered along ~783 km of shoreline initially oiled. The proportion of these oil remnants to the amount initially released is comparable to those observed for the *Arrow* and *Florida* spills more than 35 years after those spills occurred.

Shortly after the spill, forensic fingerprinting tools were developed to identify sources of PAH in tissues of wildlife living in the spill zone and assess the suitability of those tissues for subsistence consumption. Those tools showed that most samples with identifiable EVC were samples of surfaces or the gastrointestinal tract collected in the first two years after the spill. Due to preferential uptake and differential metabolism, EVC was rarely recognized in internal tissues. PAH fingerprinting, when applied to tissues exposed to oil in laboratory experiments, revealed that in many cases the exposure was not solely to a water-soluble fraction of the oil as assumed but to dispersed oil microdroplets as well. Because the results of these experiments form the foundation of a proposed changing paradigm in ecotoxicology — that exposure to aqueous TPAH at ≤1 ppb concentrations can cause chronic sublethal effects in wildlife populations — they need to be repeated with more rigorous controls to ensure that a free oil phase in the form of microdroplets is not present.

Forensic fingerprinting tools facilitated correlations of biomarker (CYP 1A and FAC) levels in fish with the composition and amounts of PAH found in the region's natural hydrocarbon background showed that a component of the background was bioavailable. Slightly enhanced CYP 1A levels in sea otters and harlequin ducks that inhabit the spill zone of PWS are advanced as evidence for continuing exposure of wildlife to spill residues. However, low and variable levels of CYP 1A in those species are pervasive throughout the region that includes areas far beyond the area impacted by the spill. Natural and anthropogenic sources of PAH found throughout PWS and the GOA are likely responsible for this CYP 1A induction.

Concerns that PAH from the buried remnants of spill oil could be bioavailable to intertidal predators *via* the food chain at levels sufficient to have population-level impacts were addressed through the analysis of intertidal prey species at sites having buried oil residues. In this application of forensic techniques, it was shown that levels of PAH uptake in those prey species, including mussels, clams, worms, and intertidal fish, are far below levels known to cause harm to an individual intertidal forager, let alone entire populations. Furthermore, more than 99% of the shoreline in PWS now contains no oil residues. Consequently, claims of population-level impacts to wildlife in PWS seem implausible.

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