Study of the Fates and Effects of the *Exxon Valdez* Oil Spill on Benthic Sediments in Two Bays in Prince William Sound, Alaska. 1. Study Design, Chemistry, and Source Fingerprinting

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This study was conducted to assess the subtidal effects of the *Exxon Valdez* oil spill in a large embayment in Prince William Sound, AK. A stratified random-sampling design was used to compare stations in an oiled bay, the Bay of Isles, with stations in Drier Bay, a bay that received little impact from the spill. The study included sediment chemistry, benthic ecology, and bioaccumulation elements. Only the results on chemistry of the oil in the bottom sediments are reported here. Analyses of sediment samples revealed four types of polycyclic aromatic hydrocarbons (PAH) in the two bays: (1) Alaska North Slope (ANS) crude oil attributable to the spill, (2) natural oil seep-derived background, (3) pyrogenic, and (4) diagenetic. The Bay of Isles subtidal sediments contained significantly higher levels of weathered ANS-PAH attributable to the spill than did Drier Bay. However, the levels of ANS-PAH in the Bay of Isles were generally lower than those of the petrogenic background PAH naturally present in the subtidal sediments of the sound. This natural petrogenic background PAH component increased in concentration with increasing depth zone (and increasing sediment clay content) for each bay. Drier Bay, a location of past cannery and mining activity, had significantly greater concentrations of pyrogenic PAH than did the Bay of Isles. All sediment PAH concentrations were well below the effects range-low (ER-L) sediment toxicity threshold value of 4000 ng/g for total PAH. The highest sediment total PAH concentration (1500 ng/g) occurred in Drier Bay, and the highest sediment ANS (spill)-PAH concentration (201 ng/g) occurred in the Bay of Isles. There is no evidence for large-scale offshore transport of *Exxon Valdez* crude to the subtidal sediments.

Introduction

On March 24, 1989, the *Exxon Valdez* ran aground on Bligh Reef in Prince William Sound (PWS), AK (Figure 1), spilling

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258 000 barrels of Alaska North Slope (ANS) crude oil into the marine environment (*1*). About 40% of the original volume spilled affected shorelines within PWS (*2*). However, both an extensive cleanup effort and the action of winter storms rapidly removed the oil from the shorelines. In 1989, about 780 km (16%) of the nearly 4800 km of PWS shoreline was impacted to varying degrees by the spill, but by 1991 the oil that remained on the shorelines consisted mainly of isolated patches of oiled sediment, and little fluid material remained. Shoreline surveys in 1991 found only 96 km of oiled PWS shoreline, an 88% reduction in 2 yr (*3*). However because of the rapid removal of oil from the shorelines, there was concern that oil residues had been transported offshore to deeper subtidal areas within the sound, possibly injuring benthic biota, particularly in sheltered nearshore subtidal areas in protected bays (*4−6*). As a result, a number of subtidal studies conducted in PWS focused on the collection and chemical and biological analysis of subtidal samples from water depths ranging from 0 to over 250 m (*5, 7−17*).

PWS is a large enclosed body of water with many islands and a mainland with a complex coastline formed by passages, fjord-like indentations, and irregular bays. Because of their sheltered nature and biological productivity, embayments presented a special case for the study of subtidal spill effects.

Numerous sources of natural and anthropogenic hydrocarbons in PWS sediments have been documented in PWS (*10, 16*). There are three major hydrocarbon types: (1) *petrogenic*, which is related to petroleum, including crude oil and its refined products; (2) *biogenic*, which is generated by biologic processes or in the early stages of diagenesis in marine sediments; (3) *pyrogenic*, which is generated in the high temperature processing or combustion of fossil fuels (coal and oil) and recent organic material such as wood. Natural and anthropogenic petrogenic PAHs have been identified in PWS sediments; the dominant source is seep-derived petrogenic hydrocarbons carried into PWS from the eastern Gulf of Alaska by the suspended sediment (*16, 18−20*). Chemical analyses of nearshore and offshore subtidal sediment samples taken from PWS in 1989 and 1991 identified two major types of petrogenic sources: (1) natural oil-seep petroleum with a low alkyl dibenzothiophene content; (2) *Exxon Valdez* (ANS) petroleum with a high alkyl dibenzothiophene content. Although PWS is not an industrialized area, it has a history of mining, fishing, and logging activities (*21*). Consequently, there are sites in PWS where human activity has caused localized inputs of pyrogenic and petrogenic hydrocarbons to nearshore marine sediments (*10, 16, 22, 23*).

In addition to differences in the PAH distribution, oil seep-derived natural background petroleum contains 18a(*H*)-oleanane ($C_{30}H_{52}$), a specific saturate biomarker for petroleum that has a post-latest Cretaceous or younger terrigenous source (*16, 18, 24, 25*). The ANS crude oils are derived from marine shale from an earlier geologic period (*26*). These crude oils, including the cargo oil of the *Exxon Valdez*, contain no oleanane (*10, 19, 27*).

Cannery operations and other activities in Drier Bay continued at this site into the 1940s (*21*). Although the cannery site is now in ruins, runoff from the remains of coal-fired steam boilers, various petroleum-fueled power plants, and other sources have caused elevated concentrations of pyrogenic PAH in the Port Audrey subtidal sediments.

The west arm of the Bay of Isles has a sill at its mouth and a deep depression in the middle that serves as a depositional area for marine- and land-derived organic matter. Bacterial action in the organically rich subtidal sediments (*28*) in this
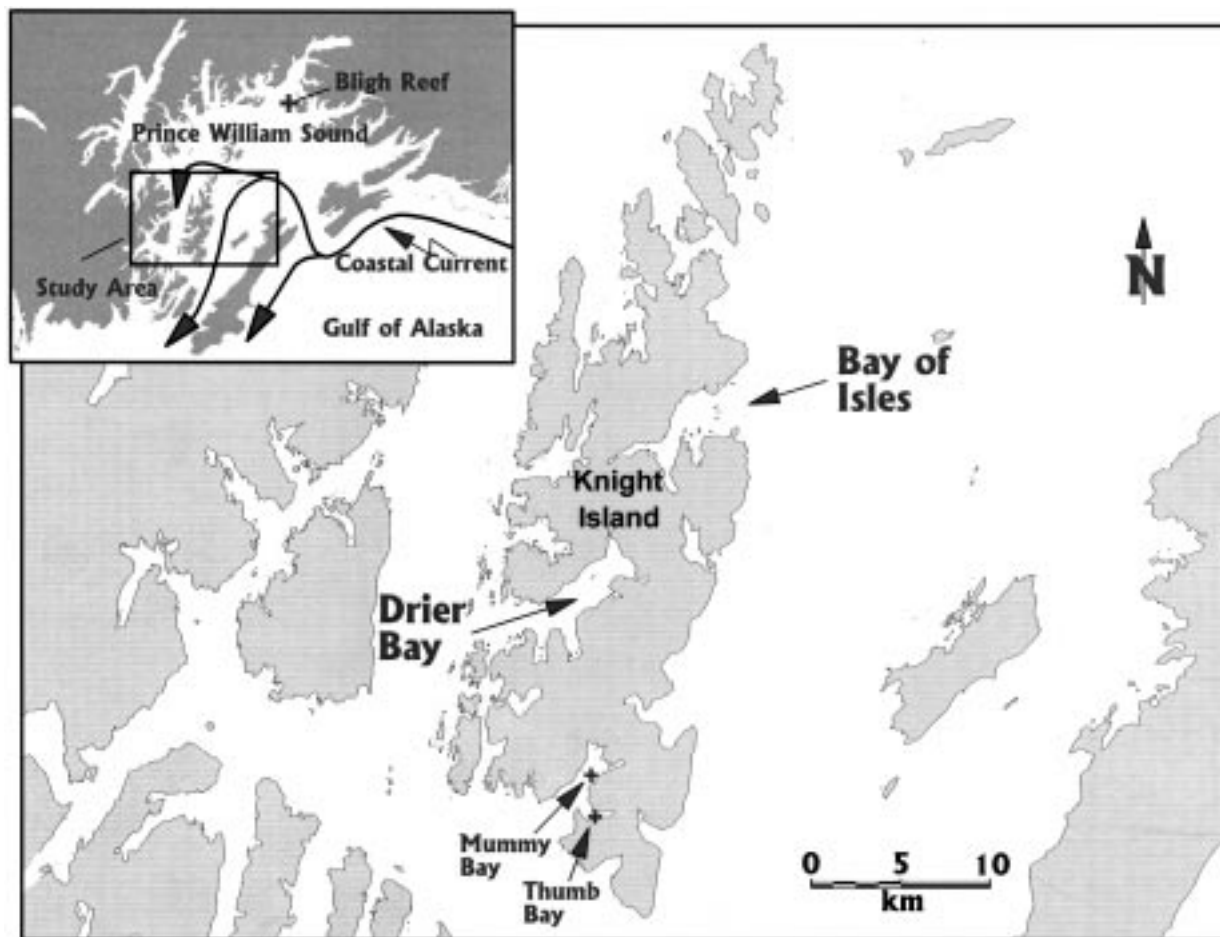
FIGURE 1. Prince William Sound showing detail of Knight Island and the locations of the Bay of Isles and Drier Bay.

depositional area has caused the formation of high concentrations of the diagenetic PAH perylene.

The goal of this study was to characterize and compare the subtidal-sediment hydrocarbon chemistry and its effects on infaunal biological communities in the Bay of Isles, a heavily oiled bay, and in Drier Bay, an unoiled (reference) bay. The results of the hydrocarbon chemistry of the bottom sediments are reported here.

Materials and Methods

Study Design. Figure 1 shows the locations of the two bays studied on Knight Island, the largest island in the PWS spill zone, with a total shoreline length of 459 km. The Bay of Isles (including islands) has a total shoreline length of 42.2 km and a total water area of 15.1 km². It is on the northeast part of Knight Island; because the shoreline faces east, parts of it were heavily oiled. Drier Bay, located on the southwest part of Knight Island, has a total shoreline length (including islands) of 52.7 km and a total water area of 18.6 km². Because its shoreline faces west, it was only lightly oiled and has been used as a reference bay in other studies (13).

The study was designed to collect surface sediment samples in an unbiased manner in order to (1) characterize sediments from three water depths in the study areas, with respect to the distribution of any petroleum residues present, and (2) characterize any remaining ecological effects of the spill at the time of sampling. This latter aspect is addressed in Gilfillan et al. (29). We used a stratified random-sampling design, analogous to the stratified random-sampling study of shoreline recovery in PWS described elsewhere (14−16). The random sampling design in both bays was stratified over the three depth zones to permit the comparison of the oiled and control bays by using information obtained from a limited number of randomly chosen sediment-sampling stations. In addition, 12 non-randomly chosen (fixed) stations of special interest or concern were sampled, seven in Drier Bay and five in the Bay of Isles. Fifteen stations were chosen in the 10−50-m depth range; 10 stations in the 50−100-m range and 10 stations in the 100−150-m range.

Station Selection. Prior to the selection of random and non-random ("fixed") stations, the shoreline and benthic topographic features of the two study bays were projected onto a planar Global Information System (GIS) database. Bathymetric charts and topographic maps were scanned, digitized at 10 m depth intervals using AutoCad software, and scaled by using field-verified benchmarks from existing National Ocean Survey (NOS) and National Geodetic Survey (NGS) data. All latitude/longitude information was converted to the Alaska State Plane Coordinate system. The bathymetric data were used to computer-map the depth contours at intervals of 10−50, 50−100, and 100−150 m. A 50 × 50 m grid was then projected over each depth-contour map, and the grids were aligned with the Alaska State Plane Coordinate system to facilitate navigation during sampling. Finally, candidate stations were randomly chosen by a computer among the points of intersection of the grid lines for each depth zone, resulting in a randomly ordered list of candidate stations for each depth zone. The total numbers of candidate stations for each bay and depth zone were as follows: Bay of Isles: (10−50 m) 2845 stations, (50−100 m) 2077 stations (100−150 m) 409 stations; Drier Bay: (10−50 m) 3323 stations, (50−100 m) 2161 stations, (100−150 m) 1892 stations. The coordinates of the candidate stations were recorded in Alaska State Plane Coordinates for use in the field. In practice, the

final station depths ranged from 8 to 170 m because of variations in the bathymetric data. Stations were randomly selected to eliminate bias in selecting sediment sampling stations.

To ensure that sediment samples were obtained from subtidal areas off heavily oiled shoreline locations in the Bay of Isles and near locations of known past anthropogenic activity in Drier Bay, a number of fixed stations were selected according to the coordinates of grid intersections in each of the depth zones in each bay.

Field Methods. *Station Location.* Navigation and station location within each embayment was achieved to within ±5 m accuracy by using a Motorola Mini-Ranger Mark IV Navigation System, and existing navigational controls were located with maps and other records. A minimum of three shore-based transmitters were placed at pre-determined surveyed points or at existing NOS and NGS control points (benchmarks) to provide sufficient coverage within each bay in the specific area being sampled. A ship-based directional receiver was used with standard methods of triangulation to bring the vessel to the coordinates of each sampling station. Before and immediately after sample collection, the navigational equipment was calibrated over a known range to verify the accuracy of the systems. Trilateration was used to survey control positions and for all navigational instrument calibrations.

Once the shore-based navigation network was in place, the sampling vessel was maneuvered onto the first station position in the list of candidate stations for a given depth zone. The depth of the station was verified and corrected for tide. If the depth did not meet the range criteria for that station or if obstructions were present that did not allow safe vessel operation, the vessel moved to the next random sediment station on the candidate list.

Subtidal-sediment samples were obtained with a modified (0.5 × 0.5 m) Van-Veen sampler. A minimum of five attempts was made to deploy the grab to retrieve any one sample. A grab was deemed suitable for chemical and biological sample collection if a sediment depth of at least 10 cm was collected and if the surface layer of the sediment was undisturbed. Sampling at a given station was discontinued if a suitable sample could not be obtained within a 100-m radius of the initially selected station coordinates. At certain shallow-water stations, safe vessel operation required that samples be collected by divers after the stations had been located and marked according to the procedure described above. If a suitable sample could not be obtained at a given station, the vessel moved to the next randomly chosen station on the candidate list.

After collection, a sediment sample for infaunal biology was obtained by inserting a core tube with a 10-cm diameter in the sediment to a depth of 10 cm. Treatment and storage of the biology samples is described elsewhere (29). Sediment chemistry samples were then collected by removing the top 0−2-cm sediment layer around the biology core with a calibrated scoop. A minimum of 200 mL of sediment was collected at each station. Sediment samples for chemical analysis were frozen at −20 °C until they could be analyzed.

Analytical Methods. The analytical approach involved compound-specific measurements for alkanes within the saturated hydrocarbon fraction (SHC), PAHs (Table 1), and saturate biomarker compounds (diterpanes, triterpanes, and steranes). In addition, sediment grain-size distribution and total organic carbon (TOC) content were measured and used as concomitant variables in the statistical analysis. Quality assurance for analytical chemistry included written standard operating procedures, laboratory work plans, and internal data auditing. Quality-control consisted of using blanks, standard reference materials (SRMs), check samples, spiking, and rigorous data quality objectives concerning surrogate recovery ranges and SRM accuracy limitations. Details of the analytical methods, the analytical targets, and the data quality objectives are described in detail elsewhere (16).

Interpretive Methods and Data Analysis. *Estimating the Amount of Background versus Spill Petroleum in a Subtidal-Sediment Sample.* The primary means used for source discrimination was the analysis of the distributions of PAH analytes, because PAHs are more resistant to weathering than the alkane compounds within the aliphatic fraction (30) and because the distribution of PAHs in many sources is diagnostic of those sources. Using PAH distributions to distinguish petrogenic, biogenic, and pyrogenic PAH sources is summarized below and is discussed in more detail by Page et al. (16).

An important feature of the environmental fate of ANS crude is the relative constancy of the ratio of C2D/C2P (C2-dibenzothiophene/C2-phenanthrene) over a wide range of concentrations and degrees of weathering, where the degradation rate of the phenanthrenes and dibenzothiophenes is nearly the same (16, 19). Data from the 1991 shoreline ecology program in the Bay of Isles (14) were used to define the composition of weathered *Exxon Valdez* crude (EVC) as it existed in the subtidal zone immediately adjacent to a heavily oiled shoreline known to contain spill oil as of 1991. These data gave a C2D/C2P ratio of 1.04 ± 0.15, which represents the characteristics of the petroleum available for transport to nearshore subtidal locations in the Bay of Isles. The PWS prespill background measured in sediment layers greater than 10 cm below the sediment surface in deep subtidal cores taken in 1991 (16,19) has a ratio of C2D/C2P = 0.16 ± 0.02, which is close to that of Katalla crude oil and of subtidal sediments collected off Yakataga Peninsula and Katalla in the Gulf of Alaska (16). The values of C2D/C2P for natural petrogenic background and ANS (see ref 16) are significantly different ($p < 0.0001$). The differences in the PAH distributions (16) of prespill petrogenic background and ANS petroleum permit the calculation of the amounts of these two hydrocarbon sources in a sediment sample containing both.

The key assumption in this allocation process is that the petrogenic PAH component in a subtidal sediment sample from PWS is a mixture of petrogenic PAH from two sources: natural seep-derived petroleum background and ANS petroleum. The amounts of ANS-derived petrogenic PAH for the subtidal sediment samples in this study were calculated from the PAH data using the approach presetned in ref 16. The formula used was

$$ PAH_{ANS\ Petro} = \frac{C2P_{Sample}}{0.082}\left[1 - \left[\frac{1.04 - \left(\frac{C2D}{C2P}\right)_{Sample}}{0.88}\right]\right] \quad (1) $$

The concentration of background petrogenic PAH is calculated by subtracting the result of eq 1 from the total measured petrogenic PAH. Equation 1 differs slightly from an earlier version (see ref 16) because the mixing-model parameters relate specifically to the embayments in this study rather than to the entire PWS area.

Uncertainties in the reference and ANS C2D/C2P values govern the ability to significantly detect the addition of ANS-PAH to petrogenic background PAH. The precision and accuracy of the data are reflected in the values of the 95% confidence intervals. For the data in the present study, the values with the 95% confidence intervals for the ANS and petrogenic background C2D/C2P ratios are 1.04 ± 0.028 and 0.16 ± 0.015, respectively. An overall 95%-confidence range of ± 10% is obtained for a sample that has 100% petrogenic background PAH when these 95% confidence limits are incorporated into the numerator and denominator of eq 1.

TABLE 1. Aromatic Compounds Quantified in Samples from Bay of Isles and Drier Bay and the Number Designations Used in Figure 2

designation	compound	designation	compound
1	naphthalene	20	C2 dibenzothiophenes
2	C1 naphthalenes	21	C3 dibenzothiophenes
3	C2 naphthalenes	22	fluoranthene
4	C3 naphthalenes	23	pyrene
5	C4 naphthalenes	24	C1 fluorantheenes/Pyrenes
6	acenaphthylene	25	benz[*a*]anthracene
7	acenaphthene	26	chrysene
8	fluorene	27	C1 chrysene
9	C1 fluorene	28	C2 chrysene
10	C2 fluorene	29	C3 chrysene
11	C3 fluorene	30	C4 chrysene
12	anthracene	31	benzo[*b*]fluoranthene
13	phenanthrene	32	benzo[*k*]fluoranthene
14	C1 phenanthrenes/anthracenes	33	benzo[*e*]pyrene
15	C2 phenanthrenes/anthracenes	34	benzo[*a*]pyrene
16	C3 phenanthrenes/anthracenes	35	perylene
17	C4 phenanthrenes/anthracenes	36	indeno[1,2,3-*cd*]pyrene
18	dibenzothiophene	37	dibenz[*a,h*]anthracene
19	C1 dibenzothiophenes	38	benzo[*g,h,i*]perylene

Comparisons between Bays. Statistical comparison of the random stations in each depth zone of the two bays could be extrapolated to the bays as a whole. The geometric means of PAH analyte concentrations were used as the basis of the statistical tests. The analytes tested were the following sums of alkyl PAH that are generally associated with petroleum sources: (C1+C2+C3+C4)-naphthalenes (C14N); (C1+C2+C3+C4)-phenanthrenes (C14P); (C1+C2+C3) dibenzothiophenes (C13D); and (C1+C2+C3+C4)-chrysenes (C14C); pyrogenic PAH (calculated as the sum of three-, four-, five-, and six-ring parent PAH analytes, equivalent to the sum of analytes **6**, **7**, **12**, **13**, **22**, **23**, **25**, **26**, **31**, **32**, **34**, **36**, **37**, **38** in Table 1) and total petrogenic PAH (calculated as the total resolved PAH minus perylene minus pyrogenic PAH). The bays were compared directly and with the ANS component removed from the PAH distributions.

The ANS component was removed from the PAH distribution of a given sample by subtracting the ANS contribution from the original data for each PAH analyte. First, the overall ANS contribution for a given sediment sample was estimated by using the mixing-model calculation described above. Then, using the Bay of Isles 1991 heavily oiled shoreline standard as a reference for weathered EVC, the PAH distribution of this ANS standard, in proportion to the fraction of ANS in the sample, was subtracted from the PAH distribution of the sample on an analyte by analyte basis (see Figure 2). These "spill-free" data were then used to compare the depth zones between the bays to help elucidate any inherent physiographic differences present in the bays.

The chemistry data were first transformed as log10 ($x +$ 1), where x represents the analyte concentration (as ng/g). Log transformation is often applied to inherently nonnegative positively skewed data so that they can be analyzed by using normal error theory. One-way analysis of covariance (SuperANOVA; Abacus Software) was carried out with "control vs oiled" as the factor related to the spill. The effect of concomitant variables (i.e., natural station-specific factors) were fit before testing for oiling effect. Removing the effect of these variables eliminated some of the natural differences between oiled and reference bays. These included percentage of gravel, percentage of clay, TOC, and the concentration of perylene, a diagnostic quantity for depositional character. In addition to testing for an overall oiling effect, a Student's *t*-test (without covariates) was performed in SuperANOVA (Abacus Software, Inc.) to compare oiled-bay analyte geometric means with reference for each depth zone.

Results

Sediment Chemistry. The concentrations of key PAH analytes for the randomly selected stations (R stations in table) and fixed (F stations in table) for the Bay of Isles (oiled bay) and Drier Bay (reference bay) are summarized in Table 2. The results of the application of the mixing-model calculation (eq 1 above) to the data in Table 2 are also given as calculated ANS and background PAH. Where present in Bay of Isles sediment samples, ANS residues were an increment to the natural petrogenic background in 1991. This is shown by the Bay of Isles C2D/C2P values (Table 2) that lie between those of prespill background (0.16) and weathered EVC (1.04). The addition of ANS residues to background is indicated by an elevation in the C2D/C2P ratio because of the mixing of the higher sulfur spill-oil residues with lower sulfur petrogenic background. Because ANS has about eight times the amount of dibenzothiophene as background (seep) petroleum, the addition of a small increment of ANS to background results in a disproportionately large increase in the C2D/C2P ratio.

The data in Table 2 confirm that diagenetic, unsubstituted pyrogenic, and petrogenic PAH sources are present in both bays. The concentration of perylene at the Bay of Isles West Arm station F011 (480 ng/g) comprised over 70% of the TPAH in this highly anoxic, organic-rich (TOC = 7.1%) sediment sample.

The four subtidal-sediment stations closest to the cannery ruins at Port Audrey in Drier Bay had the high concentrations of unsubstituted pyrogenic PAH, which comprised between 56% and 73% of the TPAH present. If the fraction of alkyl PAH present in pyrogenic sources were also included in the calculation of the pyrogenic PAH for these samples, the actual fraction of pyrogenic PAH present would be greater than 90%. The two sediment stations with the highest TPAH for both bays were stations F071 and R031 in Port Audrey, Drier Bay. The Bay of Isles, which has no record of similar industrial activity, had lower average sediment concentrations of unsubstituted pyrogenic PAH for the randomly chosen stations for all three depth zones.

The data in Table 2 indicate that there are two petrogenic PAH sources in both bays, ANS and seep-derived background PAH. The average concentrations of the ANS total petrogenic PAH in the randomly chosen stations in the Bay of Isles ranged from 55 to 57 ng/g for all three depth zones. For Drier Bay, the average concentrations of total petrogenic PAH attributable to an ANS source ranged from 4 to 9 ng/g. These are
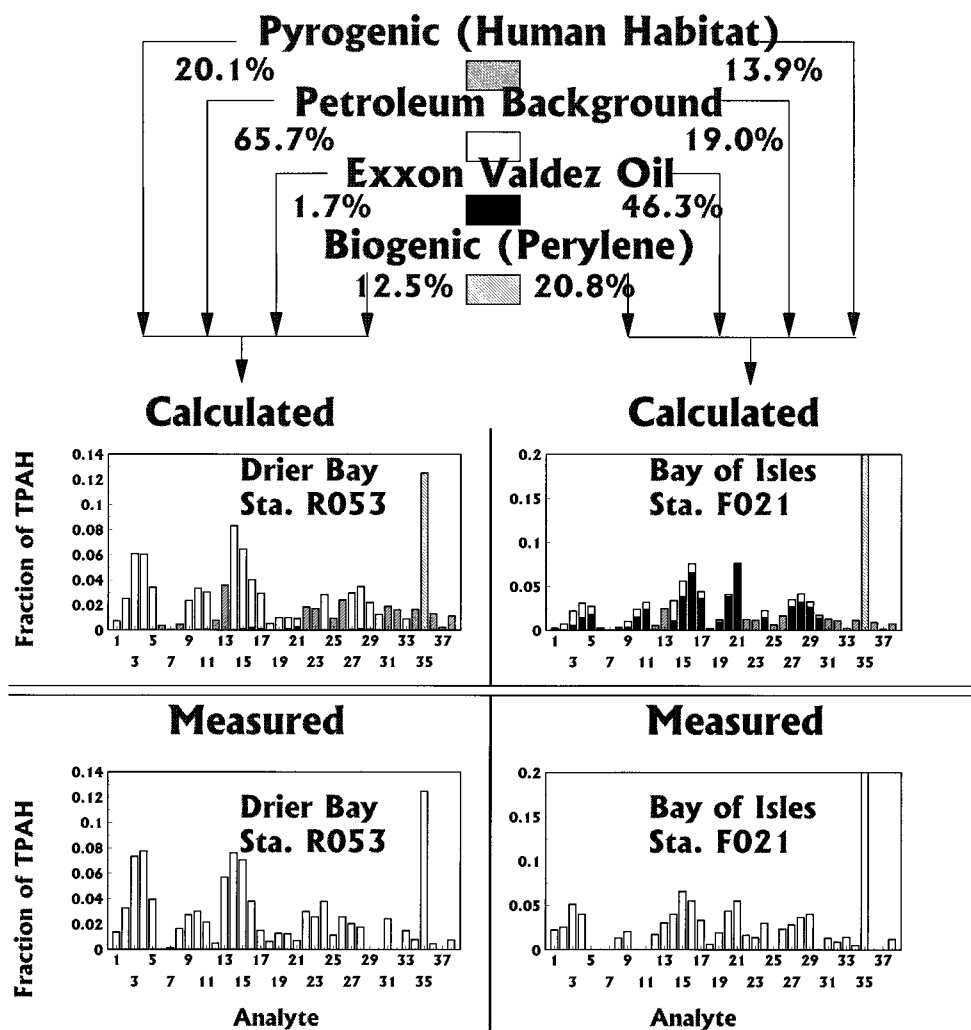
FIGURE 2. Allocation of PAH sources in two sediment samples: Drier Bay Station R053 and Bay of Isles Station F021. The percentage contribution for each of the four PAH sources were estimated by the mixing-model calculation described in the text. The relative contributions of the reference PAH distributions in the calculated PAH profiles are differentiated by different patterns in the stacked histograms.

very low levels of petrogenic PAH and are from 70–1000 times lower than the effects range-low (ER-L) sediment threshold of effect value of 4000 ng/g (*31*). The sediment concentration of background petrogenic PAH increased with depth for both bays. For the Bay of Isles, the average concentrations of background petrogenic PAH ranged from 77 ng/g for 10–50-m random stations to 443 ng/g for the 100–150-m random stations. For Drier Bay, the averages ranged from 120 ng/g for 10–50-m random stations to 368 ng/g for 100–150-m random stations.

A linear regression of the percentage of clay vs (ng/g of petrogenic PAH) for all Bay of Isles and Drier Bay samples gave the regression equation:

$$(\text{ng/g of petrogenic PAH}) = 5.9 \times (\% \text{ clay}) + 87.5$$
$$r^2 = 0.65$$

and for the seep-derived background PAH component:

$$(\text{ng/g of background petrogenic PAH}) = 5.2 \times$$
$$(\% \text{ clay}) + 76.4 \qquad r^2 = 0.61$$

The averages for the percentage of clay in the Bay of Isles samples were greater than those for Drier Bay for all depth zones; the average clay percentage for the Bay of Isles 50–100-m depth (46.7%) zone was significantly greater ($p < 0.05$)

than that from the corresponding Drier Bay depth zone (16.2%). The close relationship between background petrogenic PAH and clay percentage is consistent with the transport and sedimentation of background PAH in association with the clay fraction of suspended sediment from sources to the east of PWS (*16, 19, 20*).

The results of the one-way analysis of variance and comparison of geometric means (*t*-test) for the data in Table 2 are presented in Table 3. The results also include the data with the ANS component subtracted from each analyte before statistical analysis.

The ratio of the pentacyclic triterpane hydrocarbons [18a-(*H*)-oleanane ($C_{30}H_{52}$) to 17a(*H*),21b(*H*)-hopane ($C_{30}H_{52}$)] is used to demonstrate either the presence or the absence of oleanane. Oleanane was detected in all field samples analyzed, indicating the presence of background petroleum. The ratio ranged from 0.09 to 0.14 in Bay of Isles and from 0.16 to 0.27 in Drier Bay. Reference samples of EVC (ratio = 0.0) and Katalla (seep) crude oil (ratio = 0.17) indicate the absence of oleanane in the EVC sample and its presence in the Katalla sample. The rest of the saturate fraction of the sediment samples consisted largely of biogenic components (*n*-C15, *n*-C17, pristane, and terrestrial plant waxes). The lack of a petrogenic saturate hydrocarbon distribution indicates that any petrogenic residues in alkane fraction were heavily biodegraded (*30*).

TABLE 2. Concentrations of Measured and Calculated Sediment PAH Values for Bay of Isles (BOI) and Drier Bay (DB)

	measured										calculated	
station	C14N[b]	C14P[c]	C13D[d]	C14C[e]	Per[f]	Pyro[g]	TPAH[h]	Petro[i]	D2/P2[j]	C2P[k]	ANS[l]	Bkgrnd[m]
						BOI (10−50 m)						
F011	47	38	ND[n]	7	480	52	673	140	0.00	22	ND	14
F021	32	53	32	29	57	38	273	178	0.67	18	126	5
F031	31	38	12	17	29	91	248	128	0.46	11	46	8
R011	18	24	10	23	24	20	144	100	0.39	8	26	7
R021	52	65	25	53	72	52	381	257	0.44	22	84	17
R031	16	32	13	28	29	26	171	117	0.44	11	42	7
R041	35	72	43	76	46	38	346	262	0.73	22	173	8
R051	25	31	11	21	16	24	151	111	0.37	10	29	8
R061	56	42	12	21	20	30	237	187	0.33	15	36	15
R071	19	25	7	20	28	22	141	91	0.31	9	17	7
R081	23	29	11	15	16	21	135	98	0.47	9	39	5
R091	8	10	7	10	8	7	54	39	0.80	3	22	1
R101	ND	ND	ND	ND	5	2	9	3		ND	ND	ND
R111	9	18	9	8	7	20	83	56	0.62	6	37	1
R121	4	7	3	4	1	4	28	23	0.53	2	10	1
R131	43	74	38	37	77	50	394	267	0.50	28	132	13
R141	51	102	54	96	98	86	568	385	0.68	28	201	18
R151	3	4	1	2	1	4	20	15	0.34	2	4	1
						DB (10−50 m)						
F021	22	29	5	8	85	73	249	92	0.25	10	12	8
F041	28	52	7	22	41	293	510	176	0.19	16	(8)[o]	16
F051	10	7	ND	3	12	6	43	25	0.00	4	ND	2
F061	31	32	5	8	74	29	205	102	0.23	11	10	9
F071	48	112	10	82	120	843	1364	401	0.13	35	ND	40
R011	57	50	3	21	24	124	340	192	0.00	20	ND	19
R021	32	31	3	9	25	33	161	102	0.17	11	(2)	10
R031	46	126	17	70	130	939	1497	429	0.20	35	19	40
R041	40	36	2	10	16	27	159	116	0.00	13	ND	11
R051	16	17	2	5	19	39	114	56	0.17	6	(1)	5
R061	11	15	1	8	23	42	112	47	0.00	4	ND	4
R071	27	35	4	16	39	82	231	110	0.15	13	ND	11
R081	25	53	3	15	27	477	656	152	0.09	13	ND	15
R091	30	46	3	25	66	289	514	160	0.12	15	ND	16
R101	11	12	ND	4	10	14	58	34	0.00	5	ND	3
R111	14	18	ND	6	21	45	115	49	0.00	6	ND	4
R121	17	17	3	5	21	49	129	60	0.23	6	6	5
R131	26	32	4	8	34	53	182	94	0.18	10	(2)	92
R141	29	24	ND	3	31	23	123	69	0.00	10	ND	69
R151	51	49	8	17	15	32	218	171	0.29	18	33	153
						BOI (50−100 m)						
F042	177	170	46	81	50	121	802	631	0.28	58	93	538
F052	128	119	41	58	59	91	605	455	0.37	38	110	346
R012	50	63	17	46	20	63	312	230	0.30	20	39	191
R022	118	106	24	65	22	79	511	409	0.26	35	47	362
R032	101	106	30	53	26	70	469	374	0.31	35	75	299
R042	89	87	28	62	30	71	41	339	0.32	29	66	273
R052	37	50	19	33	15	32	226	179	0.36	16	43	135
R062	89	117	33	75	100	93	614	421	0.31	39	80	341
R072	72	72	22	45	41	53	386	292	0.33	24	56	235
R082	80	82	25	48	70	61	448	318	0.33	30	72	246
R092	60	53	12	25	9	39	243	195	0.27	18	27	169
R102	161	172	34	105	62	124	802	615	0.22	55	(44)	571
						DB (50−100 m)						
R012	37	33	6	10	25	40	187	122	0.20	11	(6)	116
R022	63	59	8	18	38	66	308	204	0.18	19	(5)	199
R032	77	89	10	27	140	222	644	282	0.13	32	ND	282
R042	46	60	7	20	53	64	294	177	0.00	21	ND	177
R052	116	101	10	17	28	89	453	336	0.15	35	ND	336
R062	47	49	8	19	43	74	288	171	0.20	17	(9)	161
R072	124	97	15	23	23	87	466	355	0.17	35	(3)	352
R082	89	97	15	35	54	112	495	329	0.18	32	(11)	318
R092	26	27	2	9	21	52	160	87	0.00	9	ND	87
R102	85	70	9	15	28	77	349	244	0.18	25	(7)	237
						BOI (100−150 m)						
R013	151	173	43	90	55	115	770	600	0.28	58	93	507
R023	171	159	28	88	45	119	750	585	0.21	53	35	550
R033	132	120	28	53	28	82	546	436	0.24	41	48	388
R043	134	135	34	66	26	85	599	487	0.26	47	62	425
R053	94	80	19	45	13	55	378	310	0.24	29	33	278
R063	179	175	38	93	44	120	803	639	0.24	58	65	574
R073	147	130	30	68	14	84	587	489	0.27	41	61	427
R083	67	63	17	48	19	43	330	267	0.27	20	29	238
R093	202	175	41	83	49	115	828	664	0.26	58	80	584
R103	159	141	29	61	25	99	634	510	0.23	47	(48)	462

TABLE 2 (Continued)

station	C14N[b]	C14P[c]	C13D[d]	C14C[e]	Per[f]	Pyro[g]	TPAH[h]	Petro[i]	D2/P2[j]	C2P[k]	ANS[l]	Bkgrnd[m]
							measured				calculated	
						DB (100–150-m)						
F013	91	52	8	4	9	44	264	210	0.18	20	(6)	205
F033	115	83	3	13	23	61	375	291	0.00	28	ND	291
R013	171	170	25	65	72	166	815	577	0.18	55	(17)	561
R023	152	156	20	52	100	177	800	524	0.18	55	(11)	512
R033	69	66	11	18	29	56	304	219	0.18	22	(5)	214
R043	160	134	16	24	62	134	647	451	0.15	43	ND	451
R053	164	147	24	28	92	148	736	496	0.18	52	(12)	484
R063	116	73	4	8	18	67	357	272	0.00	28	ND	272
R073	112	102	13	30	36	119	516	361	0.19	35	(14)	347
R083	143	132	19	32	73	124	645	448	0.19	44	(16)	432
R093	34	30	3	9	10	20	136	106	0.17	12	(1)	105
R103	96	93	14	31	74	94	482	314	0.19	32	(14)	300

[a] PAH concentrations are in ng/g dry weight of sediment (ppb). [b] C14N, sum of C1–C4 naphthalene isomers. [c] C14P, sum of C1–C4 phenanthrene isomers. [d] C13D, sum of C1–C3 dibenzothiophene isomers. [e] C14C, sum of C1–C4 chrysene isomers. [f] Per, perylene (diagnetic). [g] Pyro (pyrogenic), sum of three-, four-, and five-ring parent analytes; equivalent to the sum of the following numbered analytes in Table 1: **6, 7, 12, 13, 22, 23, 25, 26, 31, 32, 34,** and **36–38**. [h] TPAH, sum of all PAH analytes. [i] Petro (petrogenic), TPAH-Pyro-Per. [j] D2/P2, ratio of C2 dibenzothiophene/C2 phenanthrenes. [k] C2P, concentration of C2 phenanthrene. [l] ANS, ANS from any source component present calculated by the mixing model. [m] Bkgrnd, natural petrogenic component calculated by the mixing model. [n] ND, not detected. [o] ANS-PAH values in parentheses comprise less than 10% of the petrogenic PAH and are considered to be not significantly different from zero.

TABLE 3. Statistical Results[a] of ANOVA Model To Test Oiling Effect on Sediment Chemistry

analyte group	model with all measured PAH data						model with ANS component subtracted					
			Mean[d]						mean[d]			
	impact[b]	t-test[c]	BOI[e]	DB	% Diff[e]	% det diff[f]	impact	t-test	BOI	DB	% diff	% det diff
					10–50 M							
C14 N	S	S	16	25	−39	32	S	S	14	25	−46	31
C14 P	NS	S	22	31	−29	35	S	S	12	30	−61	30
C13 D	S	S	10	3	278	48	NS	NS	2	2	−17	35
C14 C	S	S	16	10	50	35	NS	NS	8	10	−20	35
Pyro	S	S	19	67	−73	46	S	S	19	67	−73	45
Petro	NS	NS	81	99	−19	35	S	S	45	96	−54	44
					50–100 M							
C14 N	NS	S	79	64	24	21	S	NS	75	63	19	22
C14 P	NS	S	85	62	36	19	S	NS	66	61	9	20
C13 D	NS	S	23	8	197	26	S	NS	8	7	22	23
C14 C	NS	S	52	18	189	16	S	S	38	17	127	18
Pyro	S	S	64	79	−19	21	S	S	64	79	−19	21
Petro	S	S	316	193	50	19	NS	S	261	207	26	19
					100–150 M							
C14 N	NS	S	138	111	24	14	NS	S	134	111	21	15
C14 P	S	S	129	99	30	13	NS	S	111	97	15	13
C13 D	S	S	29	13	138	22	S	S	15	11	37	19
C14 C	S	S	67	25	174	26	S	S	55	23	133	26
Pyro	NS	NS	88	96	−8	16	NS	NS	88	96	−8	16
Petro	NS	S	481	342	41	12	S	S	427	334	28	11

[a] Tests were conducted for random stations only and for individual depth zone ranges. The data were tested directly and tested with the ANS component subtracted out from each PAH analyte. [b] Significance (at $p < 0.05$) of ANOVA model (over stations) with covariates = log(TOC), log(perylene), arcsin (%clay). [c] t-test result: One-tailed mean > or < reference; S, significantly different from reference; NS, not significantly different; tested at $p < 0.05$. [d] geometric mean of analyte groups in ng/g (ppb). DB, Drier Bay; BOI, Bay of Isles. [e] % difference from reference (Drier Bay) for the analysis of actual geometric means. [f] % difference in the model-adjusted geometric means tht could have been detected. For the analysis of log-transformed values, % detectable difference, = (exp 10 (log critical difference) − 1) × 100.

Discussion

There are four fundamental components of this and any oil spill study: (1) hydrocarbon source must be identified; (2) the distribution and concentration of residues of spill oil in the study area must be determined; (3) the hydrocarbon chemistry of the study area must be compared to that of an unoiled control area. As we found in this study, it is often the case that petroleum from the oil spill is not the only significant hydrocarbon source in areas where spills have occurred (see also refs 19 and 32). The distribution of analytes detected in a given sediment sample will be a composite of all contributing sources.

Sources of Hydrocarbons. Seep-derived petrogenic background PAH was identified in all sediment samples that had sufficient PAH present to enable the detection of alkyl phenanthrenes and alkyl dibenzothiophenes. The detection of background petrogenic PAH in samples from all depth zones is consistent with the results of other studies (*16, 19, 20*) and with the detection of oleanane, a specific marker for petrogenic background in all sediment samples analyzed. The ANS-derived residues, characterized by a high sulfur PAH signature, were detected in subtidal sediments from specific areas associated with heavily oiled shorelines. In all cases from these areas, the petrogenic PAH fraction was composed of varying proportions of material from both sources. Only 6 of the 82 sediment samples analyzed had more than 50% of the petrogenic PAH fraction that could be attributed to the spill. Moreover, these were all in the shallow
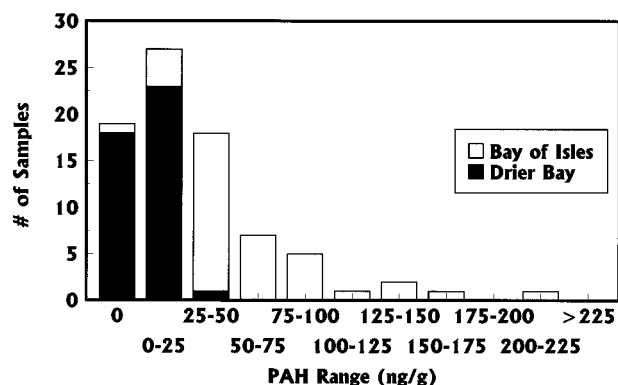
FIGURE 3. Frequency distribution of ANS percentage in total PAH for all random and fixed embayment study sediment samples.

upper arms of the Bay of Isles and were generally near the heavily oiled peat bog noted in the Bay of Isles.

Unsubstituted PAH from pyrogenic sources are present in all of the sediment samples. Pyrogenic PAHs form a major part of TPAH in samples from the subtidal areas near Port Audrey, the site of a former cannery in Drier Bay. For Drier Bay sediment samples (F071 and R031) most closely associated with the putative pyrogenic sources at Port Audrey, the average concentration of fluoranthene is 185 ng/g; that of pyrene is 150 ng/g; and that of TPAH is 1430 ng/g. These concentrations are in the same order of magnitude of the ER-L threshold values (31) in sediment: fluoranthene is 600 ng/g; pyrene is 350 ng/g; and TPAH is 4000 ng/g.

PAH in sediments can be allocated to a given source on the basis of the results of the mixing-model that estimates the proportions of ANS-PAH and background PAH present. This process is illustrated in Figure 2 for a Bay of Isles shallow-water sediment sample and a Drier Bay deep-sediment sample. The reference PAH distribution for each source was scaled by the overall percentage contribution of the PAH source in a given sample. The resulting PAH profiles were then added to give the "calculated" PAH profiles in Figure 3. The calculated distributions show the contribution from

each source and are compared with the actual measured PAH distributions in Figure 2. Given the effects of weathering and variations in local pyrogenic PAH sources, the agreement between the calculated distributions and the measured distributions is quite good. Although some analytes in the measured PAH distributions were not detected in the sample, they may have been present in low amounts.

EVC Residues in Subtidal Sediments. The data in Table 2 show that the sediment concentrations of ANS residues in the randomly chosen stations in the Bay of Isles 10−50-m depth zones vary considerably from station to station. The highest concentrations of ANS residues were found in sediment stations associated with shorelines that were heavily oiled in 1989, in particular those shorelines at the western end of the Bay of Isles. The highest ANS-PAH sediment concentration was 201 ng/g at Bay of Isles station R141, which is 20 times smaller than the conservative ER-L sediment toxicity threshold value of 4000 ng/g for TPAH (31). Figure 3 shows that few sediment samples have elevated concentrations of ANS-PAH. For this study, about 90% of the samples had less than 30% of the TPAH attributable to an ANS source.

The average ANS-PAH sediment concentrations for the Bay of Isles random stations over the three depth zones is remarkably constant at 55−57 ng/g (Figure 4). This suggests that petrogenic material from the spill was dispersed within the Bay of Isles rather than moving from shoreline to benthos. Such a dispersal was fairly uniform in a semi-enclosed body of water such as an embayment. Fine-grain sediments can act as a vehicle for the transport and dispersal of petroleum in the marine environment as shown by studies of previous spills (33−35), for the *Exxon Valdez* oil spill (36), and for the long-range transport of seep-derived background petrogenic hydrocarbon from sources in the eastern Gulf of Alaska into Prince William Sound (16, 19). For the same Bay of Isles random stations, the average concentrations of petrogenic background PAH increases from 77 ng/g in the shallowest depth zone to 282 ng/g for the middle depth zone and 443 ng/g for the deepest zone (Figure 4). This parallels increasing clay content in the sediment and suggests that the background PAHs are transported into the sound with the
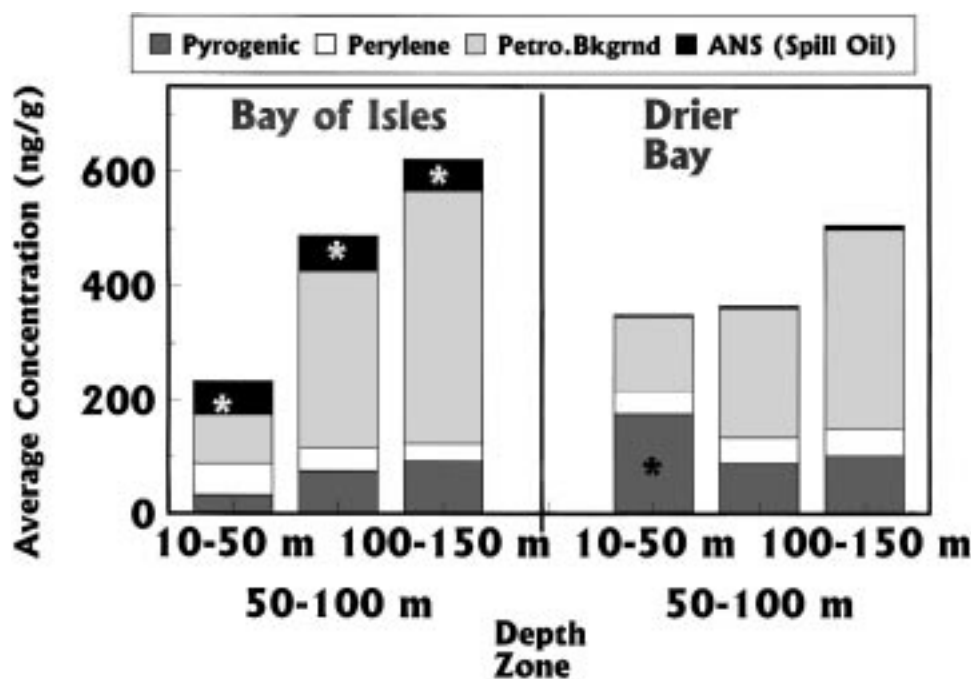

FIGURE 4. Mean PAH concentrations of the random stations for the three depth-zones of Drier Bay (control) and Bay of Isles (oiled). PAH concentrations are separated into ANS, petroleum background, perylene (biogenic), and pyrogenic sources. An asterisk (*) designates differences that are significant at $p = 0.05$ (simple t-test).

suspended sediment imported from seep/sediment sources to the east (*16, 19*).

Because of its orientation, it would be expected that Drier Bay would receive less suspended sediment and associated petrogenic background than the Bay of Isles. This is the case for the random stations in the two deepest depth zones in Drier Bay where the average sediment petrogenic background PAH concentrations are around 80% of those for the Bay of Isles (Figure 4). Although ANS-derived PAHs are reported for the Drier Bay stations, the concentrations are very low and probably not significantly different from background. The average ANS-PAH concentrations derived from the application of the mixing-model calculations to the Drier Bay random stations range from 4 to 9 ng/g over the three depth zones. For many samples, the nanograms per gram of alkyl dibenzothiophene analytes were close to the detection limit of approximately 1 ng/g. Drier Bay station (R151), near the mouth of the bay, probably has ANS residues from the spill amounting to 20% of the petrogenic PAH present.

Comparison of the Bay of Isles and Drier Bay. The present study was designed to assess the effects of an oil spill in a large embayment using a limited number of sampling stations. The number of stations had to be small enough to meet the practical constraints of a sampling and analytical program, but large enough to detect important spill effects. The stratified random selection of 35 sampling stations over three depth zones in both the oiled and the reference bays enabled the results to be generalized to the bays as a whole. The study design included the measurement of covariates, such as sediment grain size, and sediment organic carbon content. The data analysis plan was successfully used to quantify positive and negative differences in the chemical parameters measured in the two bays.

Because PAHs are associated with the toxicity of petroleum, the statistical comparisons between the oiled and the reference bay were based on key PAH analyte groups, as indicated in Table 2. The ability of the stratified random-study design to detect differences between analyte groups for the two bays varied with depth zone. In the shallowest depth zone, the percentage of detectable difference ranged from 32% to 48% for the 15 randomly chosen replicate stations in each bay, reflecting the patchy character of sediment and PAH deposition from spill and natural sources in shallow water. For the 10 replicate stations in the deeper zones (50–100 and 100–150 m) in each bay, the power to detect differences increased because of the greater uniformity of sediment character and geochemistry with increasing depth (detectable differences decreasing to 12–26% of mean; Table 3).

Statistical analyses were conducted on both measured PAH data as well as the data with the ANS component subtracted from the measured data (spill-free data). This allows comparisons of the bays as if the spill had not occurred, thereby identifying the inherent differences in the bays. The results of the statistical comparisons of the PAH chemistry for the random stations in the three depth zones of the two bays are summarized in Figure 5. The bars represent the difference in the geometric means of the analyte groups between the oiled bay and reference bay. The length of each bar represents percent difference between the oiled (Bay of Isles) and reference (Drier Bay) means. For example, the greatest difference of 278% is for the measured C1–C3 dibenzothiophenes (D on Figure 5) in the 10–50-m depth zone, which represents a difference between rounded-off means of 10 ng/g for the Bay of Isles and 3 ng/g for Drier Bay. These are close to the method detection limits of 1–10 ng/g (*16*) for alkyl PAH in this study and demonstrate the value that sensitive and accurate analytical methods have in detecting differences between dilute samples. All depth
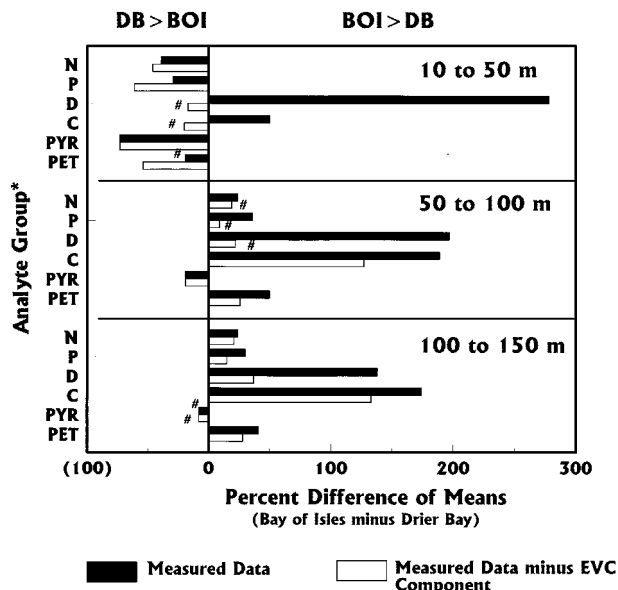

FIGURE 5. Summary of statistical comparisons of the Bay of Isles (BOI) and Drier Bay (DB). The bars represent the percent difference between the geometric means of the analyte groups as given in Table 2. Analyte groups are abbreviated as follows: N, the sum of C1–C4 naphthalenes; P, the sum of C1–C4 phenanthrenes; D, the sum of C1–C3 dibenzothiophenes; C, the sum of C1–C4 chrysenes; PYR, pyrogenic PAH; PET, petrogenic PAH. A number sign (#) designates difference that are *not* significant at $p = 0.05$ (simple *t*-test).

zones of Drier Bay have greater mean concentrations of pyrogenic PAH than the Bay of Isles, which is consistent with the prior cannery and mining activity in Drier Bay and the absence of such activities in the Bay of Isles (*21*). The shallow depth zone of Drier Bay also has a significantly higher mean concentration of petrogenic background PAH than the Bay of Isles, as indicated in the DB > BOI columns for that depth zone in Figure 5. However, the higher petrogenic content of the shallow-depth sediments in Drier Bay is likely an artifact of not including alkylated PAH in the pyrogenic component (see Materials and Methods).

The mean concentrations of the dibenzothiophenes (D) and chrysenes (C) are significantly greater in the Bay of Isles than in Drier Bay in all depth zones because of the high sulfur character and enrichment in alkyl chrysenes due to weathering (*16*) of ANS (spill) residues. The mean concentrations of petrogenic PAH (PET in Figure 5) in the two deeper Bay of Isles depth zones are significantly greater than Drier Bay whether or not ANS is included. This indicates that the petrogenic background from transported seep oil is significantly greater in the deeper zones of the Bay of Isles. This is consistent with the position the Bay of Isles relative to the flow of water and suspended sediment into PWS (Figure 1) and the greater percentage of clay present in the deep subtidal sediments.

The mean concentrations for each analyte group with and without the ANS contribution subtracted out (Table 2) show that the addition of ANS residues to petrogenic background increases the ratio of dibenzothiophenes to phenanthrenes (C13D/C14P; Table 2) because of the mixing of the high sulfur ANS residues with a low sulfur petrogenic background. Data on the ratios of C13D/C14P of the Bay of Isles shows a decrease with increasing depth [0.45 (10–50 m); 0.27 (50–100 m); 0.22 (100–150 m)], and the ratios are greater than the corresponding ratios for Drier Bay (0.10, 0.13, and 0.13, respectively). This trend is caused by the addition of small amounts of ANS residues to a much greater petrogenic background in the Bay of Isles that increases in

concentration with increasing water depth (clay content of sediments). With the ANS component subtracted out of the Bay of Isles, the resulting ratio is nearly identical in each bay (0.09–0.12 in Bay of Isles; 0.07–0.10 in Drier Bay).

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