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Persistence of oiling in mussel beds after the *Exxon Valdez* oil spill

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Abstract

Persistence and weathering of *Exxon Valdez* oil in intertidal mussel (*Mytilus trossulus*) beds in Prince William Sound (PWS) and along the Gulf of Alaska was monitored from 1992 to 1995. Beds with significant contamination included most previously oiled areas in PWS, particularly within the Knight Island group and the Kenai Peninsula. In sediments, yearly mean concentrations of total petroleum hydrocarbons ranged from <60 μg/g in reference beds to 62,258 μg/g wet wt., or approximately 0 to 523 μg/g dry wt. total polynuclear aromatic hydrocarbons (TPAHs). In mussels, mean TPAH concentrations ranged up to 8.1 μg/g dry wt. Hydrocarbon concentrations declined significantly with time in some, but not all mussels and sediments, and should reach background levels within three decades of the spill in most beds. In 1995, mean hydrocarbon concentration was greater than twice background concentration in sediments from 27 of 34 sites, and in mussels from 18 of 31 sites.

Keywords: Mussels; *Mytilus trossulus*; Prince William Sound; Gulf of Alaska; *Exxon Valdez*; Petroleum hydrocarbons; Oil spills; Monitoring

1. Introduction

Large quantities of crude oil spilled from the *Exxon Valdez* in 1989 were deposited intertidally on beaches in Prince William Sound (PWS) and along the Gulf of

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Alaska (GOA). Post-spill cleanup efforts to remove oil stranded in intertidal areas involved extensive use of hydraulic treatment methods on some beaches. Approximately one-third of all shoreline segments in western PWS were washed with high-pressure hot water; much of the marine life so treated perished (Houghton, Lees, Driskell, Lindstrom & Mearns, 1996; Mearns, 1996). Because aggressive cleanup was often devastating, most dense, oiled mussel (*Mytilus trossulus*) beds on finer, unconsolidated substrates were not cleaned. These important communities provide food and habitat for other organisms and physically stabilize intertidal areas. The general assumption was that natural processes would clean the beds in a reasonable time.

Natural rates of hydrocarbon loss were slower than anticipated, and substantial quantities of *Exxon Valdez* oil remained trapped in sediments underlying dense mussel beds in 1991 (Babcock, Rounds, Brodersen & Rice, 1994). Thus, contaminated mussels were a potential source of chronic hydrocarbon exposure for consumers and other species dependent on them, including humans. Studies suggested consumption of oiled mussels by vertebrate predators had negative impacts (Duffy, Bowyer, Testa & Faro, 1996; Sharp, Cody & Turner, 1996), although this has been contested by others (Hertung, 1995; Stubblefield, Hancock, Ford, Prince & Ringer, 1995).

Our primary objectives were to determine the geographic extent and intensity of oiling in contaminated mussel beds in PWS and along the GOA, and to monitor annual hydrocarbon changes in mussels and sediments of selected beds. We also investigated mechanisms of oil transfer from sediment to mussel, the influence of storm activity on hydrocarbon concentrations, and rates of oil weathering in PWS and the GOA. Continued monitoring is advisable, because hydrocarbon concentrations in both sediments and mussels exceeded background concentrations, in the majority of sites sampled during the last year of study (1995).

2. Materials and methods

2.1. Site selection and description

To determine the geographic extent of mussel bed contamination by *Exxon Valdez* oil, extensive surveys were conducted in PWS and along the Kenai and Alaska Peninsulas (Fig. 1). Hereafter, we refer to the two peninsulas as the GOA (Gulf of Alaska). Initial samples were collected only where significant oiling was observed by the: (1) Alaska Department of Environmental Conservation (Shoreline Assessment records); (2) Alaska Department of Fish and Game (S.M. Patten, unpublished data, Alaska Department of Fish and Game); and (3) US Fish and Wildlife Service (Sharp et al., 1996). Primary criteria for site selection were the presence of moderately to densely packed mussel beds on relatively fine sediments (i.e. <1 cm diameter), and detection of crude oil by visual or olfactory means. For comparison, samples were also collected from two reference sites with little or no oil contamination (Fig. 1) (Short & Babcock, 1996). Although our research describes the geographic extent of

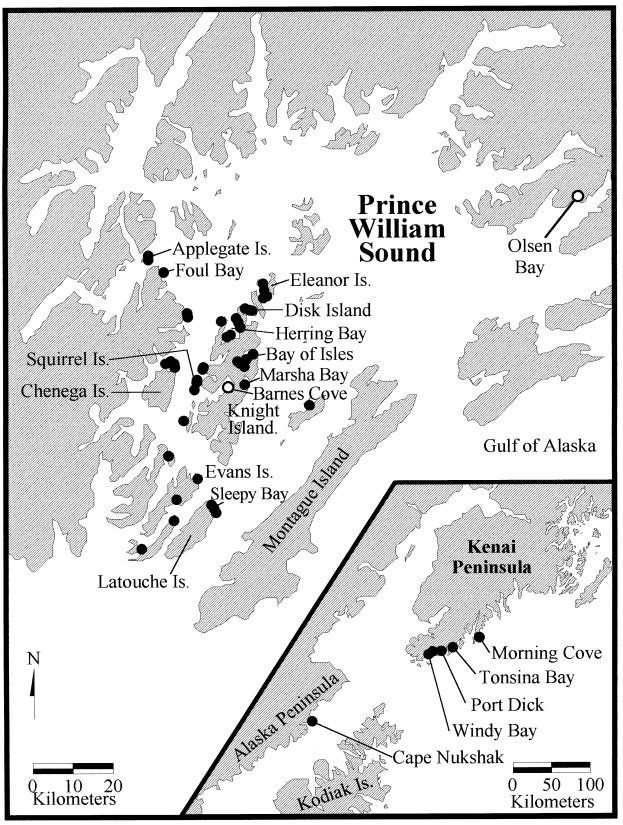

Fig. 1. Location of mussel beds sampled for petroleum hydrocarbons in Prince William Sound and along the Gulf of Alaska. The shaded area indicates the extent of floating *Exxon Valdez* oil. All beds were located in the spill impact area except the Olsen Bay reference site. Reference sites are indicated by open circles; solid circles indicate contaminated sites.

significant mussel and sediment contamination, sampling was not random, thus we could not estimate the percentage of significantly contaminated beds from the universe of all beds. Our conclusions were further constrained to description of the most oiled portions of beds, and do not detail within-bed variability as a function of elevation or other factors because sample transects were located medially through the most oiled portions of these beds, parallel to the shoreline. A total of 98 beds were sampled. [Detailed site information not included in this paper, are reported by Babcock, Harris, Carls, Brodersen and Rice (1998) and Irvine and Cusick (1995).]

Identified sites were first sampled in 1992, circa 3 years after the spill. Sites with measurable oil were generally resampled to determine inter-annual change in hydrocarbon concentration (Table 1). Nine sites that had oil in 1992 were dropped from further study in following years because no visual or olfactory evidence of oil remained. A few previously unknown sites were added in 1993 and 1995 after

Table 1
Number of mussel beds sampled by year, from 1992 through 1995 in Prince William Sound (PWS) and along the Gulf of Alaska (GOA)

Year	Number sampled	
	PWS	GOA
1992	65	13
1993	32[a]	16[a]
1994	29[b]	0
1995	24[c]	10

[a] Includes five previously unidentified sites.
[b] Includes six previously unidentified sites.
[c] Includes four previously unidentified sites.

contamination was discovered. Sites were sampled at least once a year except those along the GOA were not sampled in 1994.

In PWS, mussel bed size ranged from approximately 20 m^2 (a small bed on Disk Island) to 700 m^2 (the large bed on the tombolo adjacent to Eleanor Island). Density of mussels ranged from thinly interspersed (288 mussels/m^2 at Aguliak Island) to multiple layers (5000 mussels/m^2 at Eleanor Island). Most beds were situated on mixed sand and gravel substrates, and the mussels were usually relatively evenly dispersed throughout the sampling area. However, the presence of large cobbles and boulders created heterogeneity in many beds.

In the GOA, mussel bed size ranged from approximately 20 to 800 m^2, and the substrate ranged from mud to boulders and bedrock. The largest bed was at Pikes Point in the west arm of Port Dick. Mussel density was not measured in GOA beds.

2.2. Sampling procedures

A transect was placed parallel to the waterline through the middle of each mussel bed (as topography allowed) or the obviously oiled portion of the bed using modified methods of Babcock et al. (1994) and Karinen, Babcock, Brown, Macleod, Ramos and Short (1993). The length of the transect line, usually 30 m, varied according to bed size and topography and ranged from 10 m at one Disk Island site to 50 m at Foul Bay. Triplicate, pooled subsamples of surface sediment (59 ml minimum) were randomly collected from the upper 2 cm at eight to 10 spots within 1 m of the transect line in PWS. Collection spoons and glass storage jars were hydrocarbon free. (Equipment used for hydrocarbon sampling was prewashed with soap and hot water, rinsed, dried, and rinsed with dichloromethane or certified as hydrocarbon free by the manufacturer.) Triplicate, pooled samples of 20 to 25 mussels were similarly collected; mussel length ranged from 25 to 40 cm. (Sampling procedures differed slightly in the GOA; samples were pooled within three sample zones parallel to the transects. Distances between the transect line and upper and lower zones ranged up to 2 m. These procedural differences were minor and did not require special analysis.) Air blanks were collected for quality control purposes at

most sites. All samples were cooled immediately and frozen within 2–4 h. Data from samples collected from several beds in PWS after they were manually cleaned in 1994 (Babcock et al., 1998) were not included in the analysis.

2.3. Chemical analysis

All sediment samples were analyzed by an ultraviolet fluorescence fast-screening technique adapted from Krahn, Ylitalo, Joss and Chan (1991) and Krahn et al. (1993). Sediments were extracted twice with methylene chloride. Extracts were separated with a high-performance liquid chromatograph, and quantified with a fluorescence detector (260 nm excitation, 380 nm emission). Emission output was centered at maximum phenanthrene output. A standard curve based on the amount of phenanthrene in *Exxon Valdez* oil was used to estimate total petroleum hydrocarbon (THC) concentration. Mean THC concentration is reported in μg/g wet weight; $n = 3$ unless otherwise noted. The method detection limit for THC was 50 μg/g.

All mussels from the GOA were analyzed by gas chromatography/mass spectroscopy (GC/MS), but mussels from PWS were analyzed only when THC concentration in underlying sediments was significant. A subset (69 of 776 samples) of sediments with elevated THC were selected for analysis by GC (Short, Jackson, Larson & Wade, 1996) to confirm polynuclear aromatic hydrocarbon (PAH) composition. Experimentally determined method detection limits depended on sample weights, and generally were 1 ppb in tissue, and < 2 ppb in sediment. Concentrations of individual PAH below method detection limits were treated as zero. Tissue concentrations are reported in μg/g dry weight; wet to dry weight ratios were measured by dehydrating 1 g wet samples for 24 h at 60°C and weighing the remaining mass. The accuracy of the hydrocarbon analyses was about ±15% based on comparison with National Institute of Standards and Technology values, and precision expressed as coefficient of variation was usually less than approximately 20%, depending on the PAH. Total PAH (TPAH) concentrations were calculated by summing concentrations of individual PAH except perylene. Perylene was excluded because there are contemporary natural biological sources. Relative PAH concentrations were calculated as the ratio of PAH concentration to TPAH concentration.

The ultraviolet fluorescence estimates were reliable predictors of TPAH content in sediment. Correlation between THC concentration and TPAH concentration was good [$r^2 = 0.68$, $P < 0.001$, $n = 70$, $F_o/F_{crit} = 38$ (see following paragraph for explanation of F_o/F_{crit})].

2.4. Data analysis

To predict the time when concentrations in sediments and mussels would reach background levels, concentrations were regressed against time. Regressions were limited to oiled beds with data spanning 3 or more years to ensure that short-term variation in THC concentration did not yield spurious predictions. Models considered for time series data were ladder of powers (x-transformations from linear

through $-1/x^3$), exponential, and power. No single model fit all data adequately. The predictive usefulness of regression models was judged by correlation, probability, and F_o/F_{crit}, where F_o = observed F-ratio and $F_{crit} = F(v_m, v_r, 1-\alpha)$, where v_m = regression degrees of freedom, v_r = residual degrees of freedom, and $\alpha = 0.05$. The F_o/F_{crit} criterion is designed to determine how useful the regression is, as distinct from significant, and is the more conservative measure of importance. Outcomes where $F_o/F_{crit} \geqslant 4$ were considered to be useful (Draper & Smith, 1981). Sediment regressions were based on THC, and mussel regressions were based on TPAH. Times when concentrations in sediments and mussels would reach background concentrations were estimated from these models. For sediments, background concentrations at the two reference sites (Barnes Cove and Olsen Bay) were essentially synonymous with method detection limits, and only one background value (52 μg/g) exceeded them. Background TPAH concentration in tissue, 0.09 μg/g, was estimated empirically from the entire mussel data set. Below this concentration it became difficult to discern the oil signal in PAH composition fingerprints. This estimated background concentration for mussels was the same as mean reference concentration in mussels at Barnes Cove and Olsen Bay (0.09 ± 0.03 μg/g, $n = 16$).

Oil weathering in mussels was estimated in two ways, and the source of oil in bed sediments and mussels was confirmed with a model developed by Short and Heintz (1997) designed to determine if PAH composition was consistent with that in weathered *Exxon Valdez* oil. The model, which was successfully validated by comparison with thousands of samples from the study area, uses experimentally determined first-order loss-rate constants for 14 PAHs to calculate an index of weathering (w) that summarizes exposure history. [$w = 0$ in unweathered samples and increases with weathering. For all environmental samples recorded in the Natural Resource Damage Assessment database (Short, Nelson et al., 1996), w ranges up to 11.3 for sediment and 9.9 for mussels. For this paper we use the following definitions: unweathered ($w = 0$), slightly weathered ($0 < w \leqslant 2$), moderately weathered ($2 < w \leqslant 8$), and highly weathered ($w > 8$).] Bootstrapped error distributions from experimental and environmental samples provided the basis for testing the null hypothesis that the composition of PAH in a sample was consistent with that of weathered *Exxon Valdez* oil (Short & Heintz, 1997). However, w could only be estimated when 14 of the more persistent PAHs were present in the sample, and was calculable for only 27% of the data. Weathering was also estimated by regressing percent phenanthrenes (sum phenanthrenes/TPAH) against time; typically percentages of phenanthrenes increase prominently and percentages of naphthalenes decrease as oil weathers (Short & Heintz, 1997). To avoid samples where oil was no longer detectable, records where sum phenanthrenes was less than method detection limits were excluded.

To examine regional trends in hydrocarbon concentration and weathering, raw data were first summarized as a single mean for each unique sample time at each site to avoid pseudo-replication. These reduced data sets were then regressed as previously described.

Hydrocarbon concentrations in sediments and mussels in the last year of study (1995) were considered significantly elevated if the lower 95% confidence bound of the sample mean was twice the estimated background concentration.

Total PAH to total hydrocarbon ratios were calculated for sediment and mussel samples as a means of investigating the mechanism of oil transfer from sediment to mussel. Ratios were calculated for all sediment and mussel GC/MS data. Equal ratios in the two matrices indicated that mussels accumulated particulate oil when filter feeding. Alternatively, the ratio should be greater in mussels than in sediment if mussels were exposed to hydrocarbons in solution because alkanes are much less soluble than PAH. Sample location was not considered in these comparisons, but data were restricted to concentrations that were >2 times the background concentration (i.e. $THC_{sediment} > 100$ μg/g, and $TPAH_{mussel} > 0.18$ μg/g). Ratio distributions were inspected for each matrix, and normality was tested with the D'Agostino *D*-test. Ratio data were arc-sin transformed before single-factor analysis of variance to compare values in sediment and mussels.

3. Results

Sediments and mussels from some visibly oiled intertidal areas in PWS and the GOA remained contaminated through 1995, and *Exxon Valdez* oil was identified as the source of contamination. Contaminated sediments were visibly oiled and odorous, and the oil was easily detected. Oil sheens on pools of water were often visible without any manual disturbance. Composition of PAH in mussels and sediments was consistent with the composition of *Exxon Valdez* oil (Short & Heintz, 1997). Of 738 mussel samples, *w* was estimable in 196, and *Exxon Valdez* oil was identified in 186 of these ($2.6 \leqslant w \leqslant 9.2$; moderately to highly weathered) (Short & Heintz, 1997). Of 72 sediment samples, *w* was estimable in 42, and *Exxon Valdez* oil was identified in 39 of these ($0 \leqslant w \leqslant 10.7$; unweathered to highly weathered) (Short & Heintz, 1997).

Sediments and mussels in the two reference areas (Olsen Bay and Barnes Cove) were not contaminated by oil in any year (1992–1995). THC concentration in reference sediment never significantly exceeded background concentration (52 μg/g maximum), was frequently not detectable (in 16 of 25 samples), and averaged 4 ± 2 μg/g. Total PAH concentration in reference mussels ranged from 0 to 0.43 μg/g and averaged 0.09 ± 0.03 μg/g ($n = 16$). Composition of PAH at reference sites was unlike PAH composition in *Exxon Valdez* oil (Fig. 2).

3.1. Geographic extent and intensity of oil in sediment and mussels

In PWS sediment, annual mean THC concentrations were greater than 7000 μg/g wet wt. in 35 of 83 mussel beds in one or more observation years (Fig. 3). The highest mean THC concentrations occurred in 1992, and ranged up to 62,258 μg/g at Foul Bay. Highly contaminated sediments (5000–7000 μg/g) were observed in seven other PWS mussel beds, and moderately contaminated sediments (1000–5000 μg/g) were documented in another 13 beds. The highest mean concentrations in sediments were generally observed in 1992 (24 of 28 samples; seven additional sites were not sampled in 1992) (Fig. 3). However, the highest concentrations at a site did

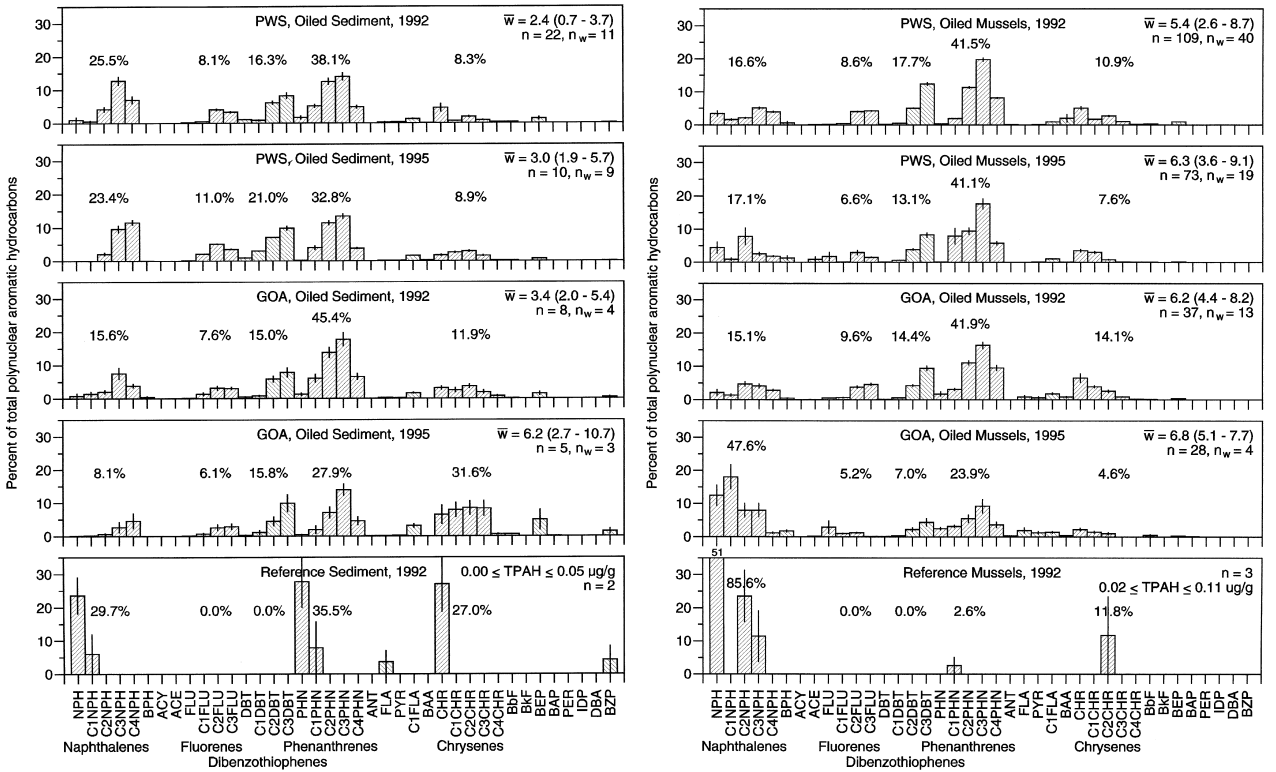

Fig. 2. Polynuclear aromatic hydrocarbon composition in oiled mussels and sediment from Prince William Sound (PWS) and the Gulf of Alaska (GOA) at earliest (1992) and latest (1995) sample dates. Hydrocarbon composition in reference samples is included for comparison. Percentages printed inside the graphs are total percentages of the following homologous chemical groups (left to right): naphthalenes, fluorenes, dibenzothiophenes, phenanthrenes, and chrysenes. Mean weathering ($\bar{w}$) and range of w are reported for each group of samples; n = total number of samples, n_w = number of samples where w was estimable.

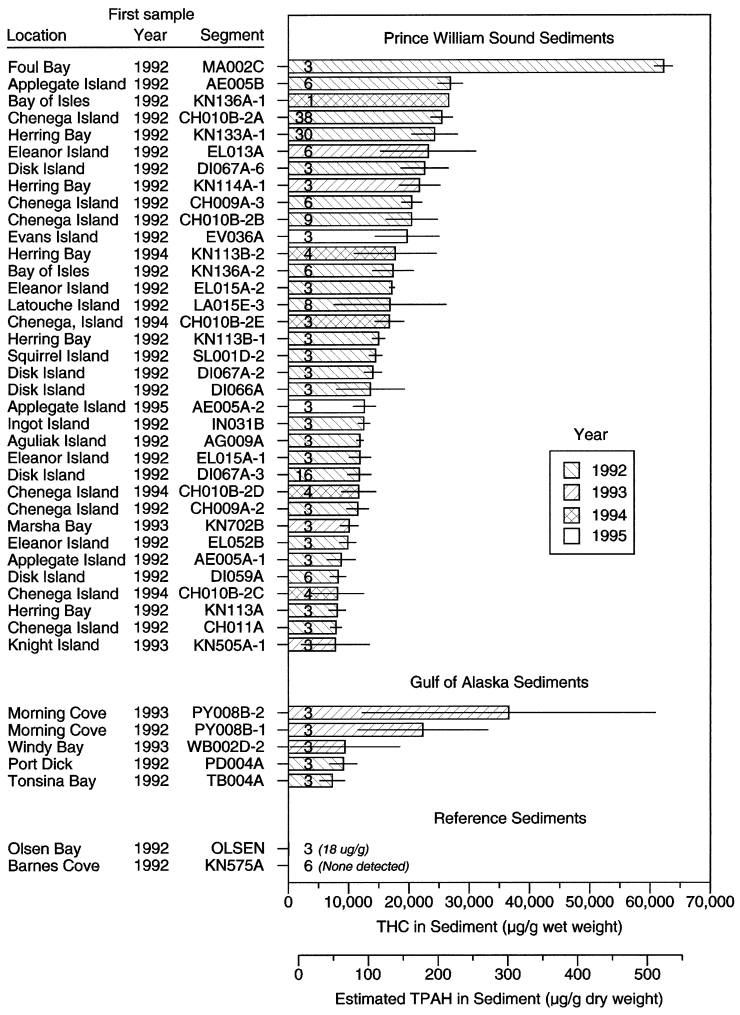

Fig. 3. Annual mean concentrations of total petroleum hydrocarbons (THC) in mussel bed sediments from 1992 through 1995 where concentration exceeded 7000 µg/g wet wt. Only the maximum annual mean (±S.E.) is reported for each site, and the corresponding observation year is indicated. The number of observations is indicated on each bar.

not always occur in the first year of observation, demonstrating the persistence and patchiness of contamination and possibly the mobility of subsurface oil.

In GOA sediment, the annual mean THC concentration in at least one observation year was greater than 7000 µg/g wet wt. in five of 18 mussel beds (Fig. 3). The highest annual mean THC concentrations occurred in 1993, and ranged up to 36,538 µg/g in Morning Cove. Moderately contaminated sediments (1000–5000 µg/g) were documented in 10 additional mussel beds along the GOA. The only oiled mussel bed

identified on the Alaska Peninsula was at Cape Nukshak (4639 μg/g). Although the highest mean concentrations in sediments in the GOA were generally observed in 1993 (three of five samples), two of these sites were not sampled until 1993 (Fig. 3).

In mussels, annual mean TPAH concentration from 21 beds in PWS and six beds along the GOA was greater than 1.0 μg/g dry wt. in at least one observation year (Fig. 4). In PWS mussels, the highest mean TPAH concentrations ranged up to 8.1 μg/g at Foul Bay, and concentrations greater than 3.0 μg/g were observed at five additional sites. The highest mean concentrations in PWS mussels were generally observed in 1992 (14 of 16 samples; five additional sites were not sampled in 1992) (Fig. 4). Along the GOA, TPAH concentrations in mussels ranged up to 5.0 μg/g at Morning Cove in 1995, and half the highest mean concentrations were in 1995, demonstrating persistent contamination over the study period.

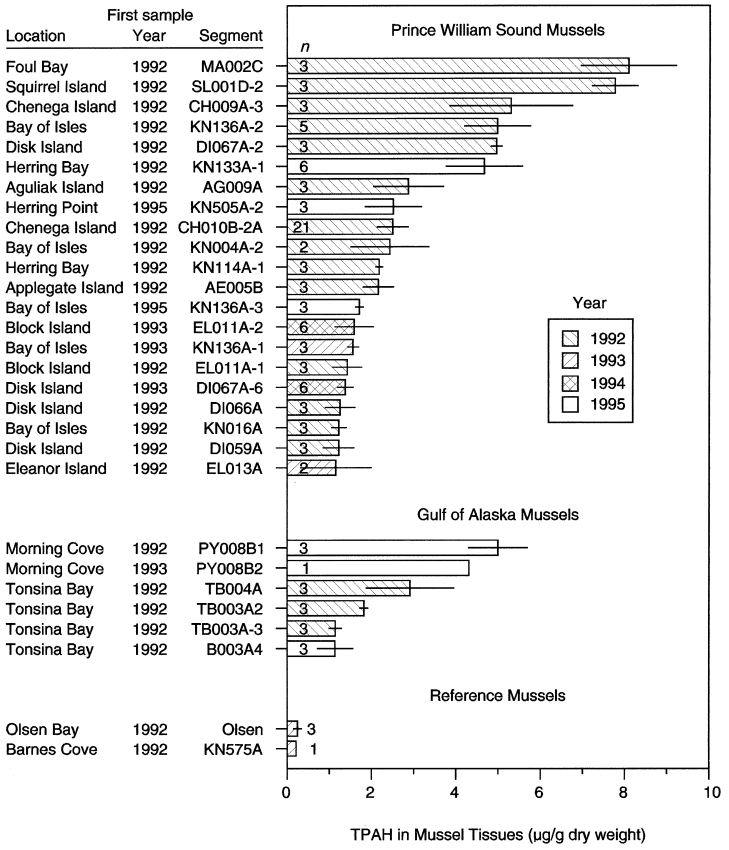

Fig. 4. Annual mean concentrations of total polynuclear aromatic hydrocarbons (TPAH) in mussels from 1992 through 1995 where concentration exceeded 1.0 μg/g dry wt. Only the maximum annual mean (±S.E.) is reported for each site, and the corresponding observation year is indicated. The number of observations is indicated on each bar. Beaches are identified by name and segment number.

The relationship between TPAH and alkane concentrations in sediments and mussels were roughly equal in both matrices, suggesting mussels were contaminated by whole oil, but the TPAH/total hydrocarbon ratio was strongly skewed in mussels, suggesting additional exposure to dissolved PAH. Arc-sin-transformed mean ratios did not differ significantly between sediments and mussels ($P = 0.663$). Distribution of the TPAH/total hydrocarbon ratio in sediments was approximately normal; mean = 2.3%±0.2, median = 2.1%, skew = 0.9, kurtosis = 1.2, range 0.2–6.4%. However, the ratio was strongly skewed in mussels; mean = 5.0%±0.7, median = 1.0%, skew = 4.6, kurtosis = 21.8, range 0.1–100%.

3.2. Temporal changes in petroleum hydrocarbon content of sediments and mussels

In sediment, THC concentration declined significantly without human intervention in some, but not all beds (Table 2, Fig. 5). Under the time restrictions imposed (observations spanning 3 or more years at accepted sites), THC concentration at 24 sites was regressed to determine natural rates of hydrocarbon decline. Declines of THC in sediment were significant at 18 of these sites ($P \leqslant 0.042$), but scatter was high in some cases ($0.12 \leqslant r^2 \leqslant 0.91$) (at sites where declines were not significant, correlation was generally poor $0.08 \leqslant r^2 \leqslant 0.39$). Although significant increases in THC concentration were not observed, there was no evidence of hydrocarbon loss in sediment from two beds (i.e. where the lower 95% confidence band was above background concentration and the slope was positive — Table 2). During the observation period, estimated lower confidence bands at 13 sites remained above twice the background concentration ($2 \times 50 = 100$ μg/g), dropped below 50 μg/g at nine sites, and dropped below 100 μg/g at the two remaining sites (Fig. 5). Predicted dates by which THC concentration in sediment would decline to background concentration (50 μg/g) ranged from late 1993 to 2016 (i.e. roughly 5–32 years after the spill).

The frequency of sediments containing high oil concentrations declined with time in PWS, corroborating regression predictions of oil decline. The number of beds with sediment concentration greater than 1000 μg/g was 40 of 54 in 1992, and 14 of 24 in 1995 [data from beds experimentally restored in 1994 (Babcock et al., 1998) were not included in these comparisons]. Concentration declines were similarly obvious along the GOA.

In mussels, TPAH concentration declined significantly with time in nine of 23 beds ($P \leqslant 0.043$; $0.08 \leqslant r^2 \leqslant 0.94$), but did not return to background in 10 beds (Table 3, Fig. 6). Considering only data with significant regressions, predicted dates by which TPAH concentration in tissue would decline to background concentration (0.09 μg/g) ranged from mid 1992 to mid 1994 (i.e. 3–5 years after the spill). However, TPAH concentrations in mussels remained significantly above background at 10 sites, and substantive TPAH concentrations remained in at least two additional sites (Foul Bay and Tonsina Bay), but their distribution was patchy. There were no significant increases in concentration ($P_{\text{regression}} \geqslant 0.116$), and there was no evidence of hydrocarbon loss in mussels from at least four beds (i.e. cases where the lower 95% confidence band was above background and the slope was positive — Table 3). Three of

Table 2
Predicted dates when total petroleum hydrocarbon concentration in sediment will reach background level[a]

Name	Segment	Obs. range	n	Model	Slope	r^2	P	Predicted background date
Applegate Island	AE005B	92–95	15	$-1/x^2$	-1.19×10^{4}	0.91	**< 0.001**	04/30/94
Bay of Isles	KN136A-1	92–95	8	Exponential	-7.60×10^{-1}	0.39	0.100	08/19/2000
Bay of Isles	KN136A-2	92–95	15	Log	-6.62×10^{3}	0.47	0.005	11/13/97
Chenega Island	CH009A-3	92–95	15	$-1/x$	-1.33×10^{4}	0.83	**< 0.001**	09/07/2012
Chenega Island	CH010B-2A	92–94	77	Exponential	-2.59×10^{-1}	0.12	0.002	03/01/2016
Chenega Island	CH010B-2B	92–94	16	$-1/x^3$	-6.85×10^{2}	0.17	0.114	Remains > background (1)
Disk Island	DI066A	92–94	9	Power	-2.56×10^{0}	0.81	**0.001**	01/14/97
Disk Island	DI067A-2	92–94	9	$-1/x^3$	-3.64×10^{2}	0.31	0.118	Remains > background (1)
Disk Island	DI067A-6	92–95	18	Exponential	-6.26×10^{-1}	0.70	**< 0.001**	06/09/2002
Eleanor Island	EL013A	92–95	33	Exponential	-7.68×10^{-1}	0.27	0.002	07/27/98
Evans Island	EV036A	92–95	9	Exponential	2.03×10^{-1}	0.27	0.156	Positive slope (1)
Foul Bay	MA002C	92–95	12	$-1/x^3$	-1.50×10^{4}	0.86	**< 0.001**	Remains > background (1)
Latouche Island	LA015E-2	92–95	26	Exponential	-4.15×10^{-1}	0.18	0.032	01/19/2000
Herring Bay	KN119A	92–95	9	$-1/x^3$	4.87×10^{2}	0.19	0.243	Positive slope (1)
Herring Bay	KN133A-1	92–95	57	Linear	-6.69×10^{3}	0.13	0.006	04/30/96
Marsha Bay	KN702B	93–95	9	Exponential	-2.40×10^{0}	0.92	**< 0.001**	11/03/95
Sleepy Bay	LA018A	92–95	9	Exponential	-9.39×10^{-1}	0.83	**0.001**	01/16/94
Squirrel Island	SL001D-2	92–94	7	Power	-2.24×10^{-1}	0.09	0.508	Remains > background (1)
Morning Cove, GOA	PY008B-1	92–95	9	Exponential	-1.10×10^{0}	0.47	0.042	03/20/97
Port Dick, GOA	PD004A	92–95	9	Exponential	-1.16×10^{0}	0.68	0.007	11/10/96
Tonsina Bay, GOA	TB003A-1	92–95	9	Exponential	-7.12×10^{-1}	0.87	**< 0.001**	07/08/97
Tonsina Bay, GOA	TB003A-2	92–95	9	Exponential	-1.22×10^{0}	0.78	**0.002**	11/11/95
Tonsina Bay, GOA	TB003A-4	92–95	9	Exponential	-5.55×10^{-1}	0.54	0.023	09/25/98
Windy Bay, GOA	WB009A	92–95	9	Power	-1.40×10^{0}	0.70	0.005	11/28/98

[a] Regressions were limited to beaches where data were collected in 3 or more years. Beaches are identified by name and segment number. Observations ranged (obs. range) from 1992 through 1995; n = number of observations, r^2 is squared correlation coefficient, P is probability of significant regression, $F_o/F_{crit} \geqslant 4$ where P is printed in bold type. Predicted background date was estimated using the best-fit model (see text); estimates were not valid where concentration (and slope) increased. Background concentration was estimated empirically from reference sites as 50 μg/g; (1), lower 95% confidence band was greater than background concentration during the observation period. Sites from the Gulf of Alaska (GOA) are marked; all others are from Prince William Sound.

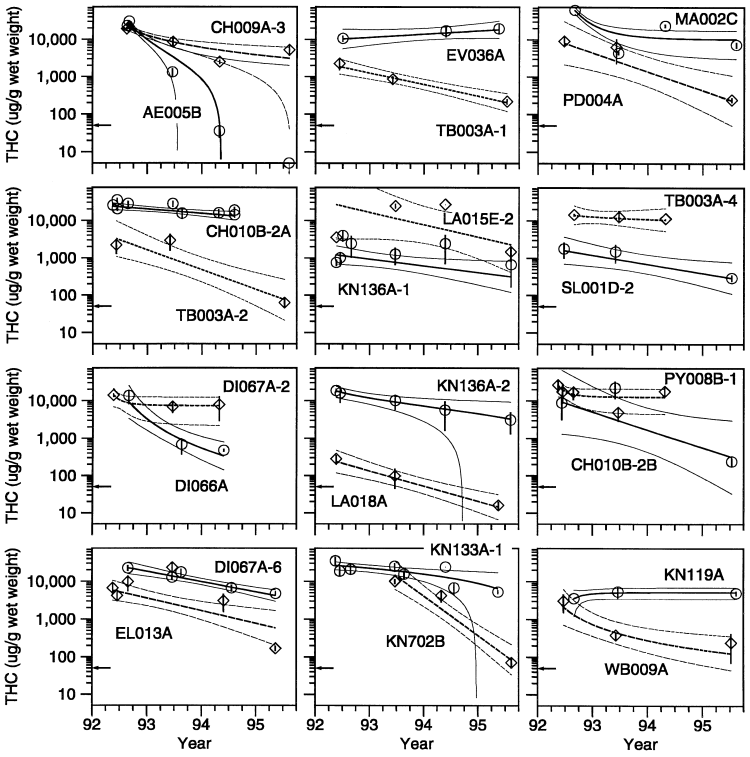

Fig. 5. Change in total petroleum hydrocarbon (THC) concentrations in sediment from sites sampled in 3 or more years. Bold lines are regression fits, and thin lines are 95% confidence bands. The estimated background THC concentration, 50 μg/g, is indicated with arrows.

the beds with significant remaining TPAH were subsequently restored (Babcock et al., 1998).

Correlation between hydrocarbon concentration and time was generally poor when estimated regionally, but there were generally downward trends in concentration (Fig. 7). Hydrocarbon concentration declines in GOA sediment were significant ($r^2 = 0.64$, $P < 0.001$, $F_o/F_{crit} = 6.4$). Hydrocarbon concentration in PWS sediment and mussels tended to decline, but correlation was poor ($r^2 = 0.12$, $P = 0.006$, $F_o/F_{crit} = 2.1$, and $r^2 = 0.14$, $P = 0.021$, $F_o/F_{crit} = 1.4$, respectively). There was no evidence of TPAH concentration declines in GOA mussels between 1992 and 1995 ($r^2 = 0.00$, $P = 0.653$).

3.3. Relationship between sediment and mussel contamination

Predicted changes in hydrocarbon concentration in sediments and mussels at specific sites were generally similar (compare Figs. 5 and 6). Although there were some discrepancies, there were no cases where concentration increased significantly in one matrix and decreased significantly in the other matrix. Some minor discrepancies

Table 3
Predicted dates when total polynuclear aromatic hydrocarbon (TPAH) concentration in mussels will reach background level[a]

Name	Segment	Obs. range	n	Model	Slope	r^2	P	Predicted background date
Applegate Island	AE005B	92–95	11	$-1/x^3$	-6.28×10^{2}	0.92	**< 0.001**	12/17/93
Bay of Isles	KN136A-1	92–95	7	$-1/x^3$	-3.01×10^{3}	0.82	0.005	Remains > background (1)
Bay of Isles	KN136A-2	93–95	14	$-1/x^2$	5.02×10^{2}	0.69	**< 0.001**	Remains > background (1)
Chenega Island	CH009A-3	92–95	10	$-1/x^2$	-2.45×10^{3}	0.81	**< 0.001**	06/14/94
Chenega Island	CH010B-2A	92–94	49	$-1/x^{0.5}$	-1.07×10^{3}	0.08	0.047	Remains > background (1)
Chenega Island	CH010B-2B	92–94	9	$-1/x^3$	-1.14×10^{1}	0.16	0.282	Remains > background (1)
Disk Island	DI066A	92–94	8	Exponential	-2.24×10^{0}	0.94	**< 0.001**	10/03/93
Disk Island	DI067A-6	93–95	17	$-1/x^3$	1.20×10^{3}	0.07	0.291	Positive slope (1)
Eleanor Island	EL013A	92–95	13	Exponential	2.77×10^{-1}	0.15	0.189	Positive slope (1)
Evans Island	EV036A	92–95	12	$-1/x^3$	-6.04×10^{0}	0.07	0.399	Remains > background (1)
Foul Bay	MA002C	92–95	12	$-1/x^1$	-5.04×10^{3}	0.62	0.002	Remains > background (2)
Herring Bay	KN119A	92–95	9	Exponential	-3.68×10^{0}	0.96	**< 0.001**	03/28/93
Herring Bay	KN133A-1	92–95	35	Linear	5.22×10^{2}	0.06	0.154	Positive slope (1)
Latouche Island	LA015E-2	92–95	15	Linear	5.15×10^{1}	0.03	0.552	Positive slope (2)
Marsha Bay	KN702B	93–95	8	Exponential	-3.47×10^{0}	0.52	0.045	01/11/94
Sleepy Bay	LA018A	92–95	8	$-1/x^3$	6.12×10^{0}	0.19	0.285	06/29/92 (3)
Squirrel Island	SL001D-2	92–94	9	$-1/x^3$	-9.80×10^{2}	0.80	**0.001**	Remains > background (1)
Morning Cove, GOA	PY008B1	92–95	9	Exponential	1.32×10^{-1}	0.17	0.272	Positive slope (1)
Mars Cove, GOA	PD004A	92–95	8	Linear	8.05×10^{1}	0.05	0.601	Positive slope (2)
Tonsina Bay, GOA	TB003A-1	92–95	9	Linear	8.87×10^{1}	0.14	0.330	Positive slope (4)
Tonsina Bay, GOA	TB003A-2	92–95	9	$-1/x^3$	-9.45×10^{1}	0.39	0.073	Remains > background (2)
Tonsina Bay, GOA	TB003A-4	92–95	9	Linear	2.25×10^{2}	0.32	0.116	Positive slope (4)
Windy Bay, GOA	WB009A	92–95	8	$-1/x^{0.5}$	-1.40×10^{2}	0.40	0.090	03/31/93

[a] Regressions were limited to beaches where data were collected in 3 or more years. Beaches are identified by name and segment number. Observations ranged (obs. range) from 1992 through 1995; n = number of observations, r^2 is squared correlation coefficient, P is probability of significant regression, $F_o/F_{crit} \geqslant 4$ where P is printed in bold type. Predicted background date was estimated using the best-fit model; estimates were not valid where concentration (and slope) increased. Background concentration was estimated empirically from the entire mussel tissue data set as 0.09 μg/g; (1), lower 95% confidence band was greater than background concentration; (2), lower 95% confidence band overlaped background concentration; (3), confidence bands bracketed background concentration; and (4), lower 95% confidence band overlapped background concentration in early observations, but not at all times. Sites from the Gulf of Alaska (GOA) are marked; all others are from Prince William Sound.

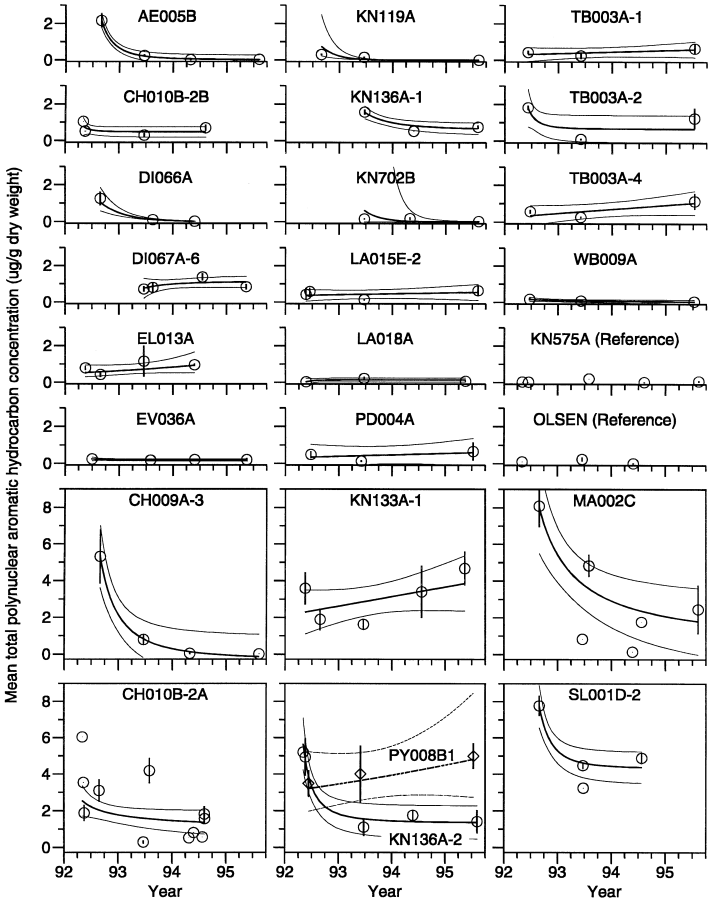

Fig. 6. Change in total polynuclear aromatic hydrocarbon (TPAH) concentrations in mussels from sites sampled in 3 or more years. Bold lines are regression fits, and thin lines are 95% confidence bands.

might be explained by differences in the time spanned by the data: e.g. sediment data were collected from 1992 to 1995 at DI067A-6, but mussel data ranged from 1993 to 1995. The most obvious model discrepancy was in Herring Bay (KN133A-1), where THC concentration in sediment declined significantly ($P = 0.006$), but TPAH in mussels appeared to increase ($P = 0.154$). Scatter in both matrices at KN133A-1 was high, and we infer hydrocarbon concentrations were patchy. Additional data surveys, scheduled in 1999, may resolve some of these differences.

For all sites combined, TPAH concentration in mussels was significantly related to THC concentration in sediments ($P < 0.001$, $F_o/F_{crit} = 14$), but scatter was very high ($r^2 = 0.31$) (Fig. 8). The most extreme point observed, where THC > 60,000 μg/g, appeared to be a leverage point, but the regression was also significant and positive without this point ($P < 0.001$, $F_o/F_{crit} = 7$). There were generally too few

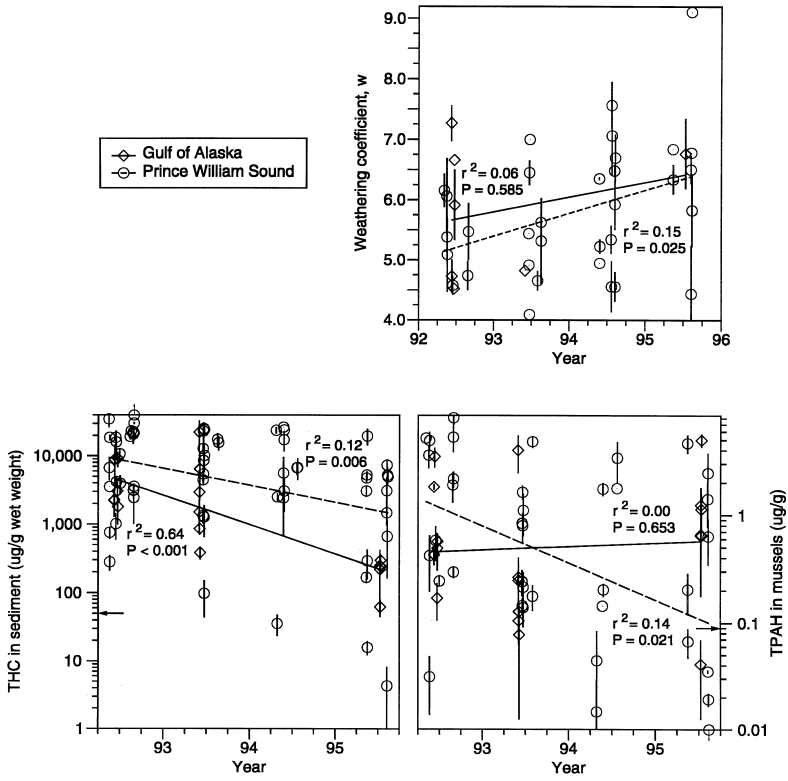

Fig. 7. Regional trends in hydrocarbon concentration and weathering. Each plotted mean±S.E. is a concentration or weathering coefficient for a unique sample time at each site.

data pairs for adequate regression statistics at individual beds (generally $n=3$; maximum $n=6$).

3.4. PAH composition and weathering in sediments and mussels

Composition of PAH in mussels and sediments at oiled sites was consistent with that of weathered *Exxon Valdez* oil in PWS and the GOA (Fig. 2). In both regions, naphthalenes through chrysenes were generally present; occasionally heavier compounds, such as benzo(e)pyrene, were also detected. Fewer naphthalenes were present than would be expected in fresh oil, and phenanthrenes generally dominated. Composition of alkylated compounds in homologous PAH families was characteristic of typical weathering (Short & Heintz, 1997).

Weathering of PAH tended to increase between 1992 and 1995, as estimated from mussel samples, although re-exposure of less weathered oil was observed at some sites. Correlation between w and time was poor when estimated regionally, but was occasionally strong at specific sites. Regionally, correlation between w and time were negligible (but positive) in the GOA ($r^2=0.06$, $P=0.585$, $F_o/F_{crit}=0.1$) and in PWS

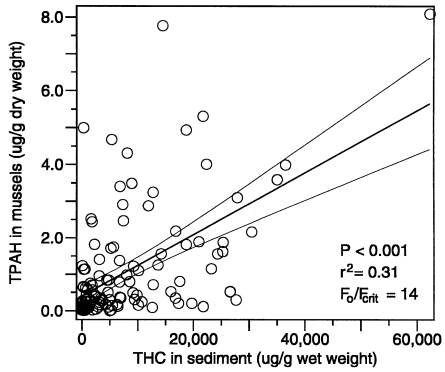

Fig. 8. Relationship between total polynuclear aromatic hydrocarbon (TPAH) concentration in mussels and total hydrocarbon (THC) concentration in sediment. All Prince William Sound and Gulf of Alaska sites with paired TPAH and THC data are included.

($r^2 = 0.15$, $P = 0.025$, $F_o/F_{crit} = 1.3$) (Fig. 7). Regressions of w in mussels versus time were possible at only six of 26 sites, and only two of these regressions were significant ($0.003 \leqslant P \leqslant 0.044$). Both significant slopes were positive, suggesting increased weathering; correlation was moderate to strong ($0.59 \leqslant r^2 \leqslant 0.91$). Percent phenanthrene regressions were estimable for 20 of 35 sites; increased weathering was significant at five sites, but decreased weathering was significant at two Tonsina Bay (GOA) sites.

Oil from the GOA was, on the average, more weathered than oil from PWS, but there was broad data overlap. Estimated from mussel tissue with analysis of covariance (where year was the covariate), mean adjusted weathering (w) was greater in the GOA (6.4±0.3) than in PWS (5.7±0.1) ($P = 0.037$), but there was broad data overlap in each year (1992, 1993, 1995). Weathering was also greater in GOA sediment (4.1±1.1, range 0.8–10.7) than in PWS sediment (2.6±0.2, range 0.6–6.2), estimated with analysis of variance ($P = 0.042$).

3.5. Effects of storm activity on mussel bed structure, hydrocarbon concentration, and composition

Vigorous winter storm activity over the winter of 1992–1993 removed approximately 40% of the mussel layer from the Eleanor Island (EL013A) bed. This bed, which was located on a tombolo on the southwest side of the island, originally had the highest density of mussels in our study (> 5000 individuals/m^2). Oil sheens were observed on the entire upper portion of the bed in June 1993, and underlying sediments were visibly redistributed. After winter, THC concentrations in surface sediments (23,206 μg/g in 1993) were significantly greater than in 1992 (3098 μg/g) ($P = 0.031$) (Fig. 5), and the oil appeared to be less weathered in both matrices. By 1994, the THC concentration in surface sediments had returned to about the 1992 level (3056 μg/g), and in 1995 a further reduction was evident (169 μg/g) (Fig. 5). Hydrocarbon concentrations in mussels also tended to increase after the storm, but

pre- and post-storm differences were not significant (Fig. 6). By 1995, the last year of the study, approximately 95% of the mussels were gone.

3.6. Concentrations in sediments and mussels at the end of study (1995)

Hydrocarbon concentrations in sediments and mussels at the majority of sites sampled in the last year of study were greater than background concentrations, indicating continued contamination. Mean THC concentration sediments from 27 of 34 sites (79%) in the last year of study was >100 μg/g (two times background concentration), and was significantly greater than background concentration in 14 of these samples (41%). Mean TPAH concentration in mussels from 18 of 31 sites (58%) in the last year of study was >1.8 μg/g (two times background concentration) and was significantly greater than background concentration in six of these samples (15%). [Sites manually restored in 1994 (Babcock et al., 1998) were not included in this end-of-study analysis.]

In the last year of study, three- and four-ring PAH were present in the majority of mussels where TPAH concentration was greater than background. Phenanthrenes were detected in 100 of 107 samples (93%), and chrysenes were detected in 93 of 107 samples (87%), demonstrating their persistence in the environment. Phenanthrenes accounted for 40%±2 of the TPAH in 1995 samples where TPAH was greater than background, and chrysenes accounted for 11%±1 of the TPAH in these samples.

4. Discussion

The original assumption that natural weathering would cause residual *Exxon Valdez* oil concentrations in sediments underlying all mussel beds to decline rapidly was incorrect. Although cleanup of sensitive mussel beds was avoided in 1989 and 1990 to protect these beds, significant long-term contamination persisted, raising concerns for mussel health and reproduction, and entry of petroleum hydrocarbons into species that prey on mussels. Our surveys document high concentrations of oil 3–6 years after the *Exxon Valdez* spill, and these surveys were used to recommend and guide post-spill cleanup efforts in 1994 (Babcock et al., 1998). General regional trends toward decreased hydrocarbon concentration in sediment and mussels were evident, but were not significant within the observation period (1992–1995).

The hydrocarbon concentrations observed in this survey greatly exceeded background and historical levels. In sediments, a THC concentration greater than 62,000 μg/g wet wt. was found at one site, and TPAH concentrations greater than 8 μg/g dry wt. were documented in mussels. In contrast, concentrations in sediments of reference beds were less than 60 μg/g THC and less than 0.5 μg/g TPAH in mussels. Historically (1977–1980), sediments and mussels collected from established stations along the shipping lane through PWS, and collected in 1989 from these and additional stations in the oil impact area before landfall of the oil, indicated little or no presence of contaminating petroleum hydrocarbons (Babcock, Irvine, Harris, Cusik & Rice, 1996; Karinen et al., 1993; Short & Babcock, 1996).

The geographic distribution of mussel beds with significant oil contamination after 1991 included most areas originally impacted by the spill in PWS and along the Kenai Peninsula. Most of the contaminated mussel beds in PWS were located within the Knight Island group, an area particularly impacted by the spill. Most of the oiled beds in the GOA were along the southwestern portion of the Kenai Peninsula, but oil also persisted in at least one bed on the Alaska Peninsula (Cape Nukshak). The primary source of PAH was *Exxon Valdez* oil (Short & Heintz, 1997), but other sources were also apparent in some cases. Pyrolytic sources of PAH were evident in some mussels collected in 1993 along the Kenai Peninsula, e.g. in Morning Cove. However, only *Exxon Valdez* oil had been evident in samples collected in 1992 along the Kenai Peninsula.

The volume of stranded oil may be the principal reason why most long-term contamination was observed within PWS rather than along the GOA. A large volume of oil (approximately 41% of the total spilled) was stranded in PWS. Less oil was stranded over a larger area outside PWS — about 5% of the total volume along the Kenai Peninsula and 2% along the Alaska Peninsula (Wolfe et al., 1994).

The most reasonable source of oil in mussels is oil trapped in sediment. However, the high variability between TPAH concentration in mussels and sediments suggests the linkage between them is indirect. Similar conclusions were reached by Boehm et al. (1996), and Harris, Rice, Babcock and Brodersen (1996) who found that correlation of TPAH concentration in mussels and sediment at specific sampling points was low. All three studies are in agreement that TPAH concentrations in sediment were much greater than in mussels. Although the range of mean TPAH concentrations observed in mussels in 1993 were very similar between our study and that by Boehm et al. (1996) (0.03–4.8 and 0.02–4.0 μg/g, respectively), we observed much higher mean TPAH concentrations in sediments (0.0–301 μg/g) than Boehm et al. (1996, 0.02–6 μg/g). Discrepancies in TPAH concentration in sediment may have resulted from differences in sampling procedures or locations, and other uncontrolled factors.

Transfer of hydrocarbon contamination from underlying sediment to mussels is likely mediated by water. Oil in particulate form may enter surrounding water from contaminated sediment and later be consumed by filter-feeding mussels. Similarity of TPAH/total hydrocarbon ratios in sediment and mussels support this mechanism as the primary route of mussel contamination. Boehm et al. (1996) also suggest ingestion of small droplets or tarry particles may explain the hydrocarbon transfer. However, unlike in sediments, where the distribution of the TPAH/total hydrocarbon ratio was normal, the distribution was highly skewed in mussels, and ranged up to 100% TPAH. The observed skew could not be explained simply by differences in method detection limits, or by removing samples where TPAH < 2 times background concentration. This suggests that mussels may also have been exposed to PAH in solution, but this route of exposure was likely secondary. Baumard et al. (1999) report that the PAH fractions accumulated by mussels is influenced by turbidity; lighter, dissolved fractions (including phenanthrenes) are accumulated from water, whereas accumulation of heavier fractions (penta- and hexa-aromatics) is associated with suspended sediment.

Serious long-term contamination of sediments and mussels was evident, but there are indications that natural environmental processes are reducing hydrocarbon concentrations, and that much of the remaining oil will gradually dissipate without human intervention. Evidence of decreasing oil concentration was based on general regional trends, visual and olfactory observation, site-specific regression predictions, and on concentration data from sites sampled too infrequently for regression analysis. Some sites were dropped from the survey because little or no oil remained. Significant natural reductions in hydrocarbon concentration were observed in approximately one-half of the beds, and concentrations should reach background levels within three decades of the spill in most beds. However, rates of hydrocarbon loss among beach sediments were quite variable, and in a minority of cases there was no evidence of loss. Beaches that lost oil most slowly were either sheltered or were armored by cobble or boulders, thus reducing wave-induced sediment movement and remobilization of buried oil. Eight years after the spill, Hayes and Michel (1999) also found cobble/boulder armoring resulted in retention of oil.

Dense layers of mussels apparently protected underlying sediment from the weathering processes that naturally degrade oil. The lack of weathering was indicated by observation of low oil viscosity, aromatic odors, and visible slicks on site, and by similarity of PAH composition to that in moderately weathered oil. Weathering proved to be difficult to estimate; few mussels samples (27%) had all PAH required for rigorous first-order kinetic loss rate modeling (Short & Heintz, 1997) and results were not clear. Consequently, the change in percent phenanthrenes was used as a less rigorous estimation of weathering. Again results were equivocal; increased weathering was apparent at some sites, but decreased weathering was also observed.

In some cases, storm activity had obvious and dramatic impacts on bed structure and sediment movement, and likely influenced hydrocarbon concentrations. For example, about 40% of the mussels from the Eleanor Island tombolo (EL013A) disappeared after vigorous storm activity in the winter of 1992–1993, and the underlying sediments were redistributed. Apparently this disruption remobilized oil trapped in sediment, and accounted for the marked increases in TPAH concentrations in surface sediments observed in 1993. Disturbances of this nature and lack of information on volume and composition of oil buried deeper than 2 cm for all survey beds limit the usefulness of the regression models used to predict long-term oil concentrations.

Unlike surveys reported by Boehm et al. (1996), we were unable to estimate the percentage of significantly contaminated mussel beds in PWS and the GOA from our data set because our sample locations were not chosen randomly. Thus we can neither support nor refute the conclusion of Boehm et al. (1996) that the percentage of mussels associated with residual oil in PWS was less than 3% in 1993. We do concur, however, that the percentage of significantly oiled mussels is decreasing with time but find that it may take three decades or more before PAH concentrations in all mussel bed sediments reach background levels.

Oil remaining in PWS and the GOA at the time of this study should be considered toxic. Although weathering was more advanced in the GOA than in PWS, sediment and mussels from both regions contained PAH with known toxicity, including two-,

three-, and four-ring compounds. There is now strong evidence that PAH in weathered oil are toxic to at least $w = 4.9$ (pink salmon eggs, Heintz, Short & Rice, 1999), and yearly mean ws in sediment did not exceed this value until 1995 (GOA only). Thus, the oil had not lost most or all of its toxicity in either area, as suggested by some authors (Boehm et al., 1996; Gilfillan, Page, Harner & Boehm, 1995; Page, Boehm, Douglas, Bence, Burns & Mankiewicz, 1998). Rather, weathered oil is actually considerably more toxic per unit mass than unweathered oil because the most toxic compounds are also the most refractory, as demonstrated in controlled laboratory trials with Pacific herring eggs (Carls, Hose & Rice, 1999) and pink salmon eggs (Heintz et al., 1999). Long-term exposure of PWS mussels to weathered oil reduced fitness 7 years after the spill; oil-exposed mussels had significantly lower air survival times than reference mussels $\overline{w} = 7.0 \pm 0.4$ (range 3.2–8.5 at oiled sites and $0.6 \leqslant \text{TPAH} \leqslant 2.0$ μg/g) (Thomas, Harris & Rice, 1999). Because toxicity of PAH increases both with ring number and alkylation (Black, Birge, Westerman & Francis, 1983; Rice, 1985; Rice, Short & Karinen, 1977) and phenanthrenes and chrysenes frequently accounted for a significant fraction of the PAH in mussel tissues in 1995, contaminated mussels may continue to pose a significant toxic threat to the health of predatory species. Barrow's Goldeneyes, Harlequin ducks, river otters, and sea otters may still be encountering oil in areas impacted by the spill because cytochrome P450 induction is significantly greater in tissues of animals captured in oiled areas than in those from reference areas (Holland-Bartels et al., 1998).

Although oil-contaminated mussel beds were broadly distributed throughout the spill-impact region, and the intensity of contamination was high, the total area of contamination has become rather small. This raises a question. Should we be concerned about small physical areas? If there were disproportionate consumption by top predators, including humans, there would be obvious concern. Disproportionate consumption is possible because areas with high mussel density may be more attractive to predators than areas with less density, and may generally be more sheltered from wave activity, further increasing attractiveness. Because contamination has not been completely eliminated by 6 years of natural weathering, some beds will likely continue to be sources of oil for a rather long time. Residual oil may continue to affect the biota, even though we may not fully understand these effects. Although Hartung (1995) and Stubblefield et al. (1995) conclude that long-term sublethal toxic effects of *Exxon Valdez* oil on wildlife are unlikely, we contend proof that measurably contaminated food does not affect predators is very difficult in a highly variable natural ecosystem. Thus, we recommend that contaminated beds should be monitored until *Exxon Valdez* oil concentrations in mussels and underlying sediments are at background levels, and that predators that utilize these resources be similarly monitored.

5. Conclusions

Sediments and mussels over a wide geographic area remained contaminated with petroleum hydrocarbons 6 years after the *Exxon Valdez* oil spill, and are a potential

chronic source of contamination for predatory species that consume mussels. Although the general trend was decreasing contamination, significant contamination may persist at some sites for several decades. However, storm disturbances and paucity of information on volume and composition of oil buried deeper than 2 cm limit the predictability of residual contamination levels. Composition of PAH in mussels and sediments was consistent with *Exxon Valdez* oil as the source. The geographic distribution of beds with significant contamination included most previously oiled areas in PWS, particularly within the Knight Island group, and the Kenai Peninsula. Long-term contamination is worse in PWS than along the GOA.

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