

Distribution and Weathering of Crude Oil Residues on Shorelines 18 Years After the Exxon Valdez Spill

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Received August 21, 2008. Revised manuscript received October 12, 2008. Accepted October 15, 2008.

In 2007, a systematic study was conducted to evaluate the form and location of residues of oil buried on Prince William Sound (PWS) shorelines, 18 years after the 1989 Exxon Valdez Oil Spill (EVOS). We took 678 sediment samples from 22 sites that were most heavily oiled in 1989 and known to contain the heaviest subsurface oil (SSO) deposits based on multiple studies conducted since 2001. An additional 66 samples were taken from two sites, both heavily oiled in 1989 and known to be active otter foraging sites. All samples were analyzed for total extractable hydrocarbons (TEH), and 25% were also analyzed for saturated and aromatic hydrocarbon weathering parameters. Over 90% of the samples from all sites contained light or no SSO at all. Of samples containing SSO, 81% showed total polycyclic aromatic hydrocarbon (TPAH) losses greater than 70%, relative to cargo oil, with most having >80% loss. Samples with SSO were observed in isolated patches sequestered by surface boulder and cobble armoring. Samples showing lowest TPAH loss correlated strongly with higher elevations in the intertidal zones. Of the 17 atypical, less-weathered samples having less than 70% loss of TPAH (>30% remaining), only two were found sequestered in the lower intertidal zone, both at a single site. Most of the EVOS oil in PWS has been eliminated due to natural weathering. Some isolated SSO residues remain because they are sequestered and only slowly affected by natural weathering processes that normally would bring about their rapid removal. Even where SSO patches remain, most are highly weathered, sporadically distributed at a small number of sites, and widely separated from biologically productive lower intertidal zones where most foraging by wildlife occurs.

Introduction

Subsurface oil (SSO) residues from the 1989 Exxon Valdez oil spill that remain on some PWS shorelines are the subject of continuing debate over their potential impact to wildlife that live and forage on the shoreline and to people that use the shoreline. While some studies (e.g., ref 1,) suggest that these residues remain relatively fresh and unweathered, others (e.g., ref 2,) found that the majority are extensively weathered.

As part of the natural processes that affect the fate of shoreline oil, burial, and/or sequestration of some of these residues as SSO occurs after the initial spill and the completion of cleanup (3, 4). SSO has been defined as oil that occurs beneath the top 5 cm in fine sediment under the boulder-cobble armor (5). Weathering processes on shorelines reduce the amount of surface oil and SSO, decrease the total extractable hydrocarbon (TEH) content in sediments, change the composition of hydrocarbon and nonhydrocarbon classes, and reduce the concentration of the toxicologically important compounds (i.e., the polycyclic aromatic hydrocarbons; PAH) (6). Previous studies on multiple spills have indicated that spilled oil may remain buried in patches on shorelines for many years but continues to undergo natural oil loss and weather over time (4, 6–8).

As a result of the *Exxon Valdez* grounding and spill in 1989, 258 000 barrels of Alaska North Slope crude oil was released into the marine environment (9). An estimated 40% of the original volume spilled affected shorelines in Prince William Sound (PWS) (10). About 783 km (16%) of the 4800 km of PWS, Alaska, and another 1300 km (13%) of the roughly 10 000 km of shoreline in the western Gulf of Alaska were oiled to varying degrees, as documented by the joint State, Federal, and Exxon Shoreline Cleanup Assessment Team (SCAT) surveys performed during the summer of 1989 (11). Subsequent shoreline surveys in 1991 and 1992 documented the locations of surface oil and SSO and found 96 and 10 linear km respectively of oiled shoreline in PWS. In more recent studies in PWS, SSO has been observed as a discontinuous, ~3 cm thick band, located under a 5–10 cm layer of surface sediment and/or boulder/cobble armor cover in the middle and upper tide zones (12). The extent of oiled shoreline and the amount of oil on a given shoreline continued to decrease after 1992 and the locations at which remaining SSO has been found since have been consistent with areas known to be oiled in 1992 (12).

In 2001, scientists from the National Oceanic and Atmospheric Administration (NOAA) measured the distribution and amounts of oil remaining on a statistically based selection of PWS shoreline segments (study sites) known to have been oiled in 1992 (13–17). They documented the amount of oil remaining as of 2001 and estimated a 20–25% per year decline from 1991–2001 in the amount of oil remaining on the shore. The NOAA survey (17) estimated that 55.6 t of SSO, mostly at light oiling levels, remained scattered along the 783 Km of shoreline originally oiled. This is equivalent to ~400 barrels of oil which represents ~0.4% of the amount of oil originally stranded. After 2001, the rates of decrease of SSO by natural processes slowed to about 4% per year as the remaining oil became more weathered and more sequestered (1). Patches of SSO residues persist on these shorelines and weather more slowly as they are incorporated in finer-grained sediments and isolated from weathering processes by surface armoring from boulders and cobbles and by underlying layers of impermeable bedrock and peat (3, 4, 18). By 2001, the remaining SSO residues were found in widely scattered patches in the intertidal zone, which were restricted almost

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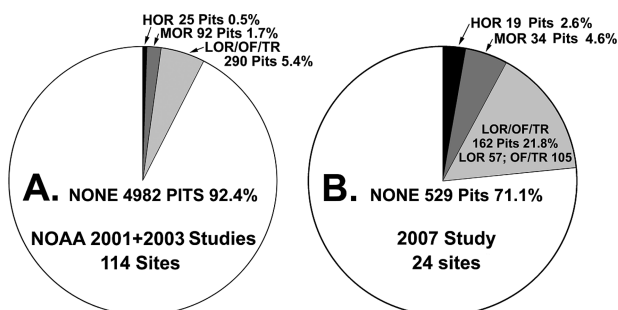


FIGURE 1. Distribution of number of pits corresponding to the visual oiling levels. (A) Data from NOAA surveys in 2001 and 2003 of 114 sites. Sites at which HOR and MOR-containing pits were found, along with 2005 NOAA survey data, were used to then select the 2007 study sites (Supporting Information Figures S1 and B). (B) 2007 data on oiling levels in dug pits from the 24 study sites. The data in Figure 2B represent an expanded study of those 2001/2003/2005 NOAA sites having HOR and MOR present (in Figure 2A). HOR = heavy oil residues; MOR = moderate oil residues; LOR = light oil residues; OF = oil film; TR = Trace sheen; NONE = no visible oil present.

exclusively to boulder/cobble/gravel-armored shorelines (3, 4, 12, 15, 18, 19).

Later surveys conducted by NOAA (2003, 2005) and by the authors (2002; 2004; 2007, the present study) documented and sampled remaining SSO residues. All of these survey results show that most SSO residues are confined to the middle and upper intertidal zones, with a few small SSO deposits reported at limited locations in the lower intertidal zone (12–14).

Several EVOS studies on the weathering of petroleum have documented the reductions in oil concentrations and changes in petroleum composition, including the reduction of PAHs in the oil residues (1, 2, 20, 21). The findings from these and other industry and government studies on the fate and weathering of the Exxon Valdez oil are consistent with those from other well-studied spills. In addition, there have been numerous studies on the bioavailability of the SSO residues. Published studies and reports documented the decreases of residual oil toxicity by the early to mid 1990s (22). By the late 1990s, decreases of PAH bioavailability back to background levels were observed through direct measurements of PAH in water (23), and intertidal biota (24–27). Indirect measures of bioavailability and exposure (i.e., induction of the cytochrome P4501A, or CYP1A, protein expression) have been studied and, while measurements in fish taken from shorelines show no evidence of exposure (28), other measurements made on wildlife have indicated that induction may still occur in general areas where SSO residues are found (26, 29).

The main objectives of the present study were (1) to determine the distributions, concentrations, and composition of SSO on a range of PWS beaches that had previously been identified in the statistically based NOAA shoreline studies conducted in 2001, 2003, and 2005 (1, 13–16) as having heavy or moderate SSO residues; (2) to examine the possible presence, form, and location of SSO residues at two known previously oiled otter foraging sites. Therefore, a study was conducted in 2007 to examine the nature of the locations where SSO residues are found and the extent of SSO weathering.

Methods and Materials

Site Selection. Twenty-two of the 24 study sites (Figure 1) sampled in 2007 were selected from among those sites previously surveyed in 2001, 2003, and/or 2005 by NOAA (1, 13–18). The 22 study sites included all 10 of the 2001/2003 NOAA sites known to contain heavy oil residues (HOR) and included 18 of 23 of the 2001/2003 sites known to contain

HOR and/or moderate oil residues (MOR), visual oiling terms previously defined in the literature (5, 11). As shown in Figure 1A the occurrences of HOR and/or MOR-containing pits at the sites surveyed by NOAA in 2001/2003 are uncommon (i.e., found only at 23 of 114 sites). Based on an analysis of NOAA's data (18), the selected 2007 sampling sites (Supporting Information Figure S1) were determined to contain 94% of all of the HOR and MOR mapped by NOAA in 2001 and 74% of all of the SSO mapped by NOAA, including the light oiling (LOR) categories. In addition to these 22 sites, two other sites heavily oiled in 1989 and previously identified as segments having extensive otter foraging activity (30)—Disc Island (DI067A-W) and Herring Bay (KN5000A)—were included. The importance of these latter sites is equal to or greater than the other sites; equal in that they were previously heavily oiled; greater in that they are sites where not only knowledge of distribution and weathering of oil is an issue, but also the possible encounters of this oil by wildlife are of importance.

Survey Methods. Sites were designated as primary (15 sites) or secondary (9 sites) depending on the sampling intensity planned. To accomplish the characterization and sampling at each site, two types of grids were established. Full grids were employed at all primary sites using four sampling transects parallel to the shoreline at four tidal elevations: +3.0 m (upper intertidal zone); +2.0 m (middle intertidal zone); +1.0 m (lower intertidal zone); +0.0 m, all relative to mean lower low water (MLLW). Partial grids were employed at all secondary sites using transects at the +3.0 m and +2.0 m tidal elevations only. The decision not to sample the lower intertidal zone at secondary sites was made on the basis of findings from prior surveys in which no SSO was found and also based on shoreline habitat (i.e., bedrock) at many of these locations. At most sites, each transect was 100 m long with grid points at each end and at 10 m intervals, establishing 11 sampling locations along each transect. Due to bedrock outcrops or cliffs, several sites were <100 m, resulting in shorter transects and fewer samples spaced at 10 m intervals.

Sampling and Data Collection Methods. Pits were dug at each grid point sometimes requiring the vigorous use of pry bars to remove boulders overlying beach sediment. Most pits were dug to 0.5 m depths, although in some cases the presence of underlying bedrock caused some to be shallower. These obstacles occurred most frequently at the Smith Island high-energy boulder-cobble veneer sites with significant shallow bedrock.

Each pit was analyzed visually by a trained oil geomorphologist, and the oiling level was recorded using standard SCAT designation of heavy, moderate, light, oil film/trace, and no oil residues (HOR, MOR, LOR Trace, and None, respectively) (5, 11). The depths and thicknesses of SSO layer(s) were recorded in those pits not filled by water. Photographs were taken of each pit. Sampling of the sediment substrate was conducted by representative subsampling of the entire mass of each pit excavation using a method similar to that of NOAA (15, 17). Samples were preserved via freezing for later chemical analysis. In total, oiling levels were recorded and samples of sediments obtained for chemical analyses from 744 pits from the 24 sites.

Chemical Analyses. All sediment samples were solvent-extracted and analyzed for total extractable hydrocarbons (TEH) by weighing the solvent-free residue (EPA method 1664, Rev A). TEH contains both hydrocarbons and non-hydrocarbon compounds. Twenty-five percent of the samples (181 of 744) were selected for additional, more detailed, analyses consisting of saturated hydrocarbons, including alkanes by GC-FID; and PAH and sterane/triterpane biomarker analyses by GC-MS SIM. These samples were selected using two criteria: those with high TEH, and/or visual oiling

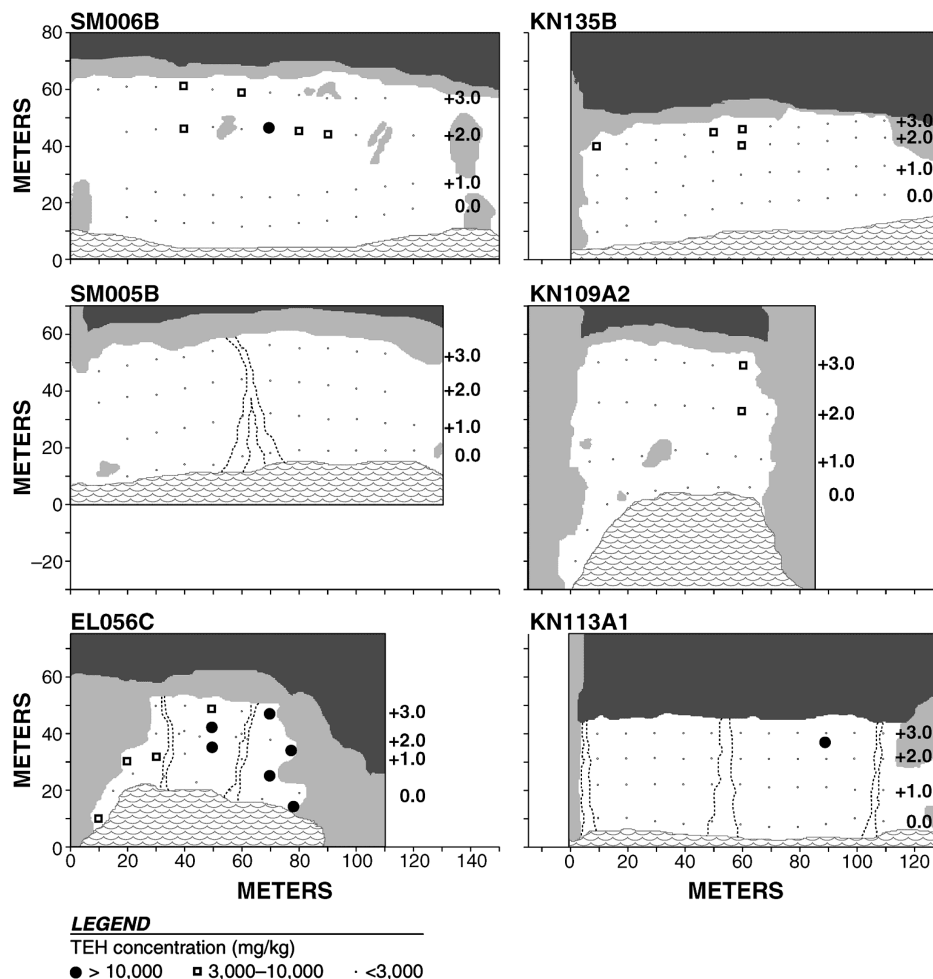


FIGURE 2. Site diagrams for six representative sites illustrating the number and location of pits with TEH concentrations greater than 10000 ppm (●); 3500 to 10 000 ppm (□); and <3500 ppm (●), corresponding to values >ER-M; values between ER-L and ER-M values; and less than ER-L, respectively. Each site diagram is oriented with the water at the bottom and the treeline at the top. Side shading represents rocky outcrops, bordering the sampling site.

levels and those associated with the 2 otter foraging sites. Samples selected included: 15 of the 19 pits designated as HOR; 20 of 32 MOR pits; 38 of 53 LOR pits; 42 of 108 OF/TR pits; and 66 of the 533 pits having no visible oil.

The analytical and quality assurance/quality control methods for TEH, stearamine/triterpane biomarkers, and PAH analyses of sediment samples have been published in detail elsewhere (31–33). The 41 target PAH analytes summed to determine the TPAH concentrations, include 2- through 6-ring parent PAH and the C₁ through C₃ or C₄ alkyl homologues of naphthalene, fluorene, phenanthrene, dibenzothiophene, chrysene, and fluoranthene/pyrene. Biomarkers (C₁₉–C₃₅ terpanes, C₂₁–C₃₀ steranes, C₂₁–C₂₂ diasteranes, C₂₇–C₂₉ diasteranes, and C₂₀–C₂₈ triaromatic steroids) were analyzed by GC/MS-SIM techniques described elsewhere (33). All analyte concentrations were calculated on a dry sample weight basis (ng/g sediment) to assess the sediment concentration and on an extract weight basis (μg/g extract) to calculate analyte losses relative to the original cargo crude oil. These analytical methods provide sediment method detection limits (MDLs) as follows: 0.015–0.12 ng/g dry wt for individual parent and alkylated PAH in sediments; 0.04 ng/g for hopane and individual biomarkers; 0.01–0.03 ng/g for individual alkanes.

Data Analysis Methods. To assess the weathering state of the petroleum PAH compounds, three data analysis methods were employed: (1) the PAH compositional profile as presented in PAH compound histograms; (2) the ratio of the total naphthalenes (C₁–4N) to total chrysenes (C₁–3C) (the

parent PAH compound plus alkyl-substituted C₁, C₂, C₃, and for alkylnaphthalenes C₄); and (3) the percent of TPAH remaining (TPAH_R). The %TPAH_R represents the percentage of PAH remaining in the sample extract (from 0 to 100%) compared to the PAH percentage in a fresh Exxon Valdez cargo oil standard that contains ~1.2 wt.% TPAH. The %TPAH_R represents the relative loss of TPAH through the combined processes of weathering. Computation of %TPAH_R was based on the conservative biomarker, stigmastane (21). Although hopane is a good conserved biomarker for short-term oil biodegradation studies, it has been found to degrade over longer periods and to be less stable than stigmastane (8, 21), which is why stigmastane was used in this study for determining the extent of weathering. Similarly, the percent of the normal alkanes remaining in residual SSO in the sediment extracts (% *n*-ALK_R) was compared to that in the cargo oil also using stigmastane as the conservative biomarker.

In the analysis of the data to determine PAH weathering, sediment samples with PAH concentrations greater than 500 ng/g were selected. This threshold concentration for data analysis is very low, but high enough to minimize the interference from background PAH (range ~10 to 300 ng/g; this study). The 500 ng/g threshold resulted in the exclusion of some samples with only trace (TR) or oil film (OF) visual oiling levels. Since the lowest TPAH found in any LOR-containing sample was 620 ng/g, all samples in the LOR category are included in the data analysis (see Table 1).

TABLE 1. TEH, TPAH Concentrations and PAH Weathering in Each Visual Oiling Category for 2007 Field Samples^a

visual oiling level	TEH($\mu\text{g/g}$ =ppm dry weight)		TPAH(ng/g =ppb dry weight)		%TPAH _R	
	medium	range	medium	range	medium	range
NO	110(<i>n</i> = 529)	2–25600	19(<i>n</i> = 67)	1–4440	N/A	N/A
OF/TR	754(<i>n</i> = 108)	32–69200	388(<i>n</i> = 42)	20–18700	9	1–34
LOR	3580(<i>n</i> = 57)	120–11600	7640(<i>n</i> = 38)	620–38000	14	2–36
MOR	8940(<i>n</i> = 34)	830–21200	25400(<i>n</i> = 20)	2290–62500	20	3–36
HOR	10700(<i>n</i> = 19)	3000–17400	65000(<i>n</i> = 15)	29200–88900	33	26–60

^a Visual oiling levels as defined in references (5, 11). NO = No oil observed; OF/TR = Oil film/Trace Residue; LOR = Light Oil Residue; MOR = Moderate Oil Residue; HOR = Heavy Oil Residue. %TPAH_R = percent of original TPAH remaining in sample; parameters defined in text. The TEH parameter measures all solvent-extractable lipids from all sources and can reflect high levels of biogenic material.

Results and Discussion

Overview of Oiling Levels. Of the 744 pits inspected visually in the field, 19 (2.6%) contained HOR and 34 (4.6%) contained MOR (Figure 1B). A large majority (529 or 70.8%) of pits in these 24 previously (1989) heavily oiled beaches contained no visible oil. An additional 162 pits (21.8%) contained only OF, TR, or LOR levels. As detailed below, the locations of heaviest SSO (i.e., HOR and MOR) were, with few exceptions, limited to the upper and middle intertidal zones. As previously mentioned, the occurrences of HOR and/or MOR-containing pits at the sites surveyed by NOAA in 2001/2003 were uncommon (Figure 1A), with most pits containing no SSO. Both the NOAA studies and our surveys found similar distributions of levels of SSO where it occurred, with LOR and lighter accounting for ~75% of the pits with SSO deposits.

At the two otter foraging sites, 2 of 66 pits surveyed contained traces of SSO. No SSO was found at either site at the lower intertidal zone, the primary location of clams and thus otter pit digging in PWS (26, 30). However, 1 of 22 pits surveyed at DI067A-West, contained a trace of sheen in one pit at +1.0 m, near the upper limit of the otter foraging zone (30). At the Herring Bay site (KN5000A), the most active otter foraging site studied on Northern Knight Island, an oil trace was found in one pit at the +3.0 tide elevation, well removed from the area of otter foraging activity.

TEH Concentrations. While each visual oiling level classification corresponds to a wide range of TEH and TPAH concentrations (Table 1), the gravimetric TEH concentrations in samples are quantitative. Thus TEH was used to evaluate SSO distributions at the study sites. Supporting Information Figure S2 illustrates the frequency distribution of TEH levels by tide zone. These results indicate that more samples with higher TEH levels are found in the upper and middle intertidal zones than in the lower intertidal zones. TEH concentrations are highest at the +3.0 m elevation. [TEH = 706 mg/kg (median); 610 mg/kg (geometric mean)]. The median TEH concentration decreases to 252 mg/kg in the middle intertidal zone. At mean low tide, 0.0 m MLLW, TEH levels are far lower and at or near background (86 mg/kg (median) and 110 mg/kg (geometric mean)). Background levels of TEH in sediments from the study sites ranged from about 50–150 mg/kg.

The highly variable observed TEH distributions between sites and the strong correspondence of the highest TEH levels with the highest tide zones are both significant. Because biological activity and intertidal infaunal abundance and diversity are much higher in the lower intertidal zones than in the middle and upper zones, the presence of sequestered SSO in the upper beaches is of far less ecological significance than SSO residues at the 0.0m and +1.0m elevations (34). The tidal range distributions shown in Supporting Information Figure S2 underscore the importance of understanding the within-site TEH variations and SSO occurrences at the study sites.

Analysis of the TEH and visual oiling distributions within each site confirms the extreme patchiness of the SSO. This patchiness can best be described by illustrating the locations of “important patches of SSO” on the study sites. To define the term “important patches of SSO” it is necessary to evaluate TEH concentrations in a toxicological context. This can be done by relating the TEH levels to the concentrations of TPAH in the sediments and, in turn, evaluating the TPAH concentrations against the NOAA sediment quality guideline values for TPAH (effects range - low (ER-L) = 4022 ng/g; and the effects range - median (ER-M) = 44 792 ng/g), which are useful indicators of potential harm due to chemical residues (22, 35). The ER-M is the concentration above which biological effects are likely; the ER-L is the concentration below which effects are unlikely. While these benchmarks were not designed specifically for use in intertidal sediments of PWS, they are well-established and are useful guidelines to assess chemical data from a toxicological viewpoint.

It was first necessary to describe the overall relationship of TEH to TPAH concentrations in sediment samples that were analyzed for both parameters. This information was, in turn, used to understand where the “important patches of SSO” are located at the sites (i.e., the subset of 744 grid points). Using the TEH and TPAH data from the subset of 181 samples, the relationship can be described as follows:

$$\text{LogTEH} = 1.44 + 0.548\text{LogTPAH} \quad (R^2 = 0.77)$$

This relationship was used to determine the TEH concentration equivalent to the TPAH values of the ER-L and the ER-M and their 95% confidence levels are ER-L = 2600 mg/kg (ppm) (95% confidence range 2200–3100 mg/kg); ER-M = 9760 mg/kg (95% confidence range is 7700 – 12300 mg/kg).

Small “important patches of SSO” (TEH > ~3000 mg/kg) were found at 18 of the 24 study sites. Of the 744 samples only 47 (6.3%) were above the ER-M (mg/kg) - single pits, all at the upper intertidal zone at 13 separate sites. Figure 2 shows the resultant “important patches of SSO” at six sites representing the range of sites shown previously (13–17) to contain SSO.

TEH concentrations within the entire 44-sample grid at each site were used in these plots and were compared to the above sediment quality guideline values. The sites shown in Figure 2 are typical of all study sites. Four of these six sites (SM006B; SM005B; KN109A2; EL056C) were among those containing the most SSO (55% of the HOR and MOR mapped in 2001) (18). As shown in Figure 2, the important SSO deposits are extremely patchy, and at most sites the isolation and patchiness of SSO corresponds closely to beach features (large boulders, wave shadows, armoring) that promote sequestration (3, 12, 19). The findings in this paper are consistent with those reported by Michel et al. (18), who also found the distribution of the residual oil in 2001 in PWS to be very patchy. Significantly, the SSO patches at most sites are found in the upper intertidal zones, far removed from the biologi-

cally productive zones. It is likely that such small isolated patches may be found on other PWS beaches where SSO was documented in early (1990–1992) SCAT surveys. It has been shown that such patchy SSO residues do not result in bioavailable PAH levels different from background (26, 27) unless the sediment was disturbed by sampling activities (36).

Another indication of the “patchiness” of the SSO buried in the various beaches is the thickness of the SSO deposits. For the sites illustrated in Figure 2, thickness of the visually observed SSO layers ranged from 1 to 25 cm in the excavated pits with a median thickness of 5 cm, similar to that previously reported (12). These data indicate the relative narrowness of the SSO band and the vertical patchiness within the beach sediment column.

A singular exception to these trends was noted at the Northwest Bay site (EL056C) (Figure 2). Here discontinuous SSO patches were found buried and sequestered in the boulder cobble areas at +0.0 m MMLW and +1.0 m MMLW tide zones along with the significant SSO patches found at the middle and upper zones as well. A close reconstruction of the cleanup history of Northwest Bay through cleanup records and photographs from 1989 indicates that the entire end of this Bay was used as an oil collection point (E. Gundlach, personal communications). Therefore the presence of persistent SSO deposits at this unique site may be explained, in part, by the 1989 site cleanup history.

PAH Concentrations. TPAH concentrations were determined in 181 of the 744 subsurface sediment samples collected. Concentrations varied widely among and within sites, as did visual oiling levels and TEH concentrations. TPAH concentrations ranged from background levels in the 10–300 ng/g range, often comprised of 50% or more of the single diagenetic (biogenic) PAH compound, perylene, to approximately 80 000 ng/g at the most heavily oiled SSO locations in the upper and middle intertidal zones at some sites.

Of the 181 samples analyzed for PAH, 35 are from pits with the heaviest visual oiling levels, HOR and MOR, and represent most of the HOR and MOR-containing pits. Concentration and compositional data for these individual samples along with summaries of LOR and OF/TR samples are summarized in Supporting Information Table S1. TPAH concentrations range from 3320 to 88900 ng/g in these HOR and MOR samples. Twenty-eight of these 35 samples (80%) were from the +3 m or +2 m tide zones; 6 of 35 (17%) from the +1.0 m zone; and 1 of 35 (3%) was from the low tide zone, at +0.0 m. The distribution of TPAH concentrations in subsurface sediments at the sites mimic both the visible oiling levels and TEH concentrations and confirm the patchiness of SSO shown in Figure 2. The sites shown in Figure 2 and the data in Supporting Information Table S1 demonstrate that SSO patches tend to predominate in the middle and upper intertidal zones at the rocky boulder-covered, exposed beaches in Northern Knight Island where SSO has been sequestered under the boulder/cobble-armored layers. The LOR and OF/TR sample summary results presented in Table 1 and Supporting Information Table S1 for these groups of samples illustrate that as oiling levels decrease, so do TEH and TPAH concentrations.

PAH Composition and SSO Weathering. Data presented in Supporting Information Table S1 are for samples with the highest levels of visual oil. As these samples might be expected to exhibit less weathering, they represent a good set of samples from which to examine the contention that relatively unweathered Exxon Valdez oil remains on the beaches of PWS.

The compositional parameters (Supporting Information Table S-1) are compared to those of the unweathered cargo oil to assess degree of weathering. The ratio of the naph-

thalenes to chrysenes (i.e., $C_{1-4}N/C_{1-3}C$) is very sensitive to weathering as the naphthalenes are lost preferentially due to volatilization, dissolution, and biodegradation (6). The highest value (i.e., least weathered sample) for this ratio in 2007 sediments is 5.23 compared to 17.2 in the cargo oil. The median values for $C_{1-4}N/C_{1-3}C$ in the highest visual oiling levels are 2.45 (HOR) and 1.5 (MOR) indicating substantial loss through weathering of the naphthalenes. Supporting Information Table S-1 shows that the TPAH in most of the high level samples are highly weathered. All 20 MOR samples have %TPAH_R < 36% with a median value of 20%. The degree of weathering was greater for the samples with the least visual oil (Supporting Information Table S-1). All LOR samples have less than 26% of TPAH remaining with a median value of 14%. Even during the latter stages of the cleanup in 1991/1992, NOAA and the U.S. Coast Guard concluded (37) that SSO levels of LOR and lighter did not pose risk and did not warrant further treatment. Only 17 samples in the entire collection of 181 (7.0%) (14 shown in Supporting Information Table S1; and three LOR samples at lower TPAH concentrations) have a %TPAH_R greater than 30%. All others are extensively weathered.

A review of the *n*-alkane weathering values in Supporting Information Table S1 indicates that the percent of *n*-alkanes remaining (%*n*-ALK_R) in 176 of the 181 samples is <1% relative to the cargo oil. Only one sample, from site ER020B, has any significant amount of *n*-alkanes remaining (%*n*-ALK_R = 20.1). This is an isolated sample of SSO sequestered by boulders at +3.0 m tide height at this site. These results suggest that the reports (1) of a significant amount of residual *n*-alkanes in beach sediments in PWS are extreme outliers rather than representative of the residual hydrocarbons in the SSO residues.

The sequence of weathering of the PAH assemblage in SSO is represented in Supporting Information Figure S3 using representative samples from the 2007 survey. The samples in Supporting Information Table S1 can be cross-referenced to these PAH compositions through the PAH parameters $C_{1-4}N/C_{1-3}C$ and %TPAH_R. Weathering of the PAH assemblage begins with the preferential loss of the more volatile, soluble, and biodegradable naphthalenes and continues with the slower degradation of PAH with three or more rings and with increasing degrees of alkylation. As all of the PAH compounds decrease in concentration, the fraction of TPAH represented by the chrysene homologous series increases with weathering. As the oil residues weather, their bulk composition changes as well. These changes can be evaluated by considering the %non-hydrocarbons (%Non-HC) present in the sample TEH concentrations (Supporting Information Table S1 and Figure S3). The percentage of these non-HCs, many of which are relatively resistant to weathering, increases from 20% in the cargo crude to >60% in the most weathered samples. These data demonstrate that PAH weathering in SSO remaining in beach sediments proceeded in a manner that is entirely consistent with weathering patterns of other oil spills (6).

Figure 3 summarizes the distribution by tide zone of %TPAH_R values for all sediment samples with TPAH >500 ng/g (*n* = 94). Almost all of the less weathered samples (i.e., those with %TPAH_R >30% of their TPAH remaining) were found in the upper intertidal zones. Fifteen of the 17 samples with TPAH_R >30% are in the middle and upper intertidal zones (Figure 3A, B). The other 2 are present at a single site, EL056C, previously discussed.

The 2007 survey of 22 sites where SSO residues were known to persist and of two previously oiled otter foraging sites shows that the weathering of the SSO remaining in PWS has progressed and continues to progress much as spilled oil has weathered at all other well-studied crude oil spills (e.g., refs 3, 7, 8). These findings are, in fact, supported by the existing

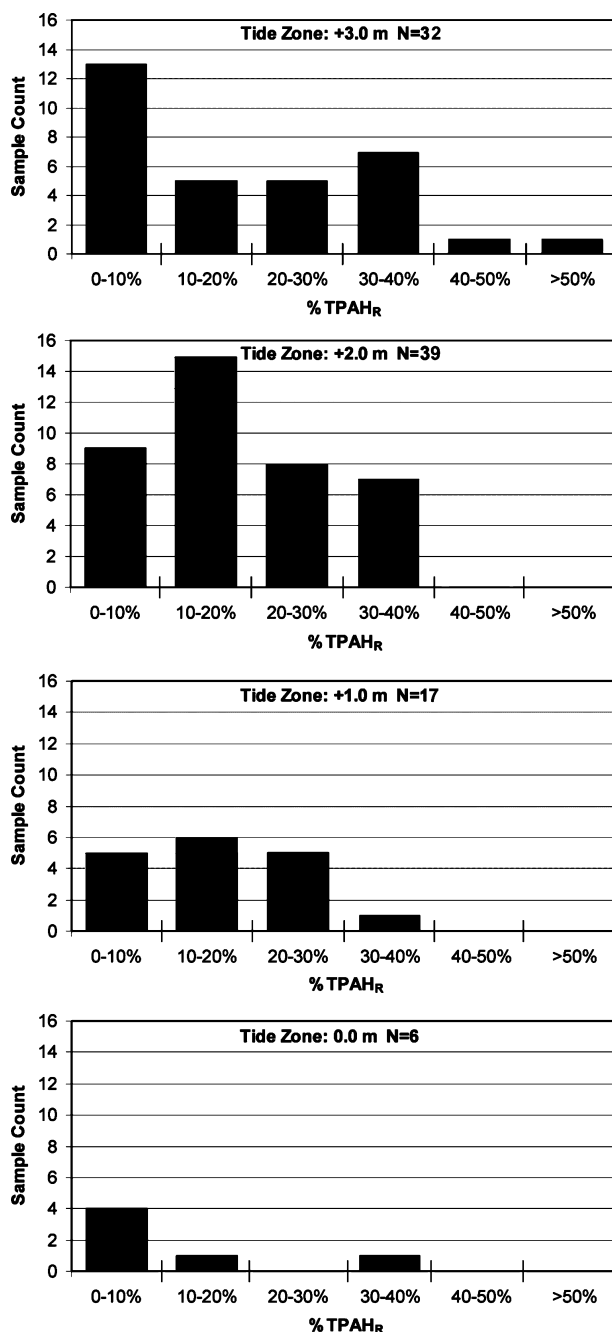


FIGURE 3. Frequency distribution of the number of samples with %TPAHR values in six ranges: 0–10%; 10–20%; 20–30%; 30–40%; 40–50%; >50%. Data are shown for each of four tide zones.

PWS data of Short et al. (Figure 3 in ref 1), which show that the PAH in those PWS samples are, with few exceptions, extensively weathered. Samples exhibiting lack of *n*-alkane weathering and the persistence of relatively unweathered oil, in general, alluded to in that paper (1) are in fact outliers, as evidenced by the more complete data set obtained and analyzed in the present work. Because most of the 2007 sites from the present study represent the majority of SSO mapped by NOAA in 2001/2003, there is no reason to conclude that any other sites with a similar oiling history would exhibit different characteristics with respect to form, location, patchiness, and weathering state than the SSO residues examined at the sites studied here. Additionally, previous studies have shown no significant bioavailability of PAH in these buried and sequestered residues (2–27). Important amounts of SSO are extremely patchy and are uncommon.

Residues of SSO that are not highly weathered are rare. Where they remain, they are largely confined to the upper intertidal zones, well-removed from areas of biological productivity. The findings at the otter foraging sites confirm previous studies showing that SSO does not occur at locations (sites and tide zones) where otters forage (30). These residues remain because they are sequestered and, as a result, are not bioavailable or released to the environment at levels that pose a risk to biota or humans using the shoreline.

Acknowledgments

This study was supported by the Exxon Mobil Corporation. We thank the field team: Douglas Reimer, EML Environmental Mapping Ltd.; Ben Amos, Linda Ziccardi, Waverly Thorsen, and Ian Ippolito, Exponent, Inc.; and the crew of the *M/V Rapture*; the data analysis assistance of Linda Cook of Exponent; and the analytical team led by Kerylynn Krahforst, Battelle Laboratories Duxbury, MA.

Supporting Information Available

One table and three figures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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ES8022623