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Estimate of Oil Persisting on the Beaches of Prince William Sound 12 Years after the *Exxon Valdez* Oil Spill

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We estimated the amount of oil remaining in Prince William Sound, Alaska, 12 yr after the 1989 *Exxon Valdez* spill to assess its importance as a long-term reservoir of toxic hydrocarbons. We found oil on 78 of 91 beaches randomly selected according to their oiling history. Surface oiling was recorded for randomly placed quadrats, which were then excavated and examined for subsurface oil. The cumulative area of beach contaminated by surface or subsurface oil was estimated at 11.3 ha. Surface oil varied little with tide height, but subsurface oil was more prevalent at the middle tide heights. The mass of remaining subsurface oil is conservatively estimated at 55 600 kg. Analysis of terpanes indicated that over 90% of the surface oil and all of the subsurface oil was from the *Exxon Valdez* and that Monterey Formation oil deposited after the 1964 Alaska earthquake accounted for the remaining surface oil. These results indicate that oil from the *Exxon Valdez* remains by far the largest reservoir of biologically available polycyclic aromatic hydrocarbons on beaches impacted by the spill and that biota dependent on these beaches risk continued exposure.

Introduction

Shorelines polluted by oil spills require practical methods for monitoring impacts. The extent of oiling must be monitored to effectively allocate beach protection and clean up resources, to determine persistence, and to assess damages. These determinations must be done quickly, reliably, and inexpensively, often in an atmosphere of crisis. The method usually used relies on shoreline cleanup assessment teams (SCAT), who comprehensively inspect beaches following standardized procedures, hereafter termed the SCAT method (*1*−*4*). Excavations to monitor subsurface oil, especially at longer time intervals following an incident when subsurface oil may not be obvious, may augment these visual assessments. The SCAT method produces a point estimate of the oiled area and a qualitative indication of oiling intensity; these tend to be underestimates because some subsurface oil may escape detection.

The SCAT method, used extensively for 4 yr following the 1989 *Exxon Valdez* oil spill in Prince William Sound (PWS), provided the basis for defining the initial extent of oiled beaches and for monitoring oil persistence by both government- and industry-supported teams (*5*, *6*). According to a 1992 SCAT survey, the extent of oiled shoreline had decreased from 783 to 10 km (*6*), with most of the oil, including subsurface oil, in the upper intertidal or supratidal zones. On the basis of excavations of thousands of pits from 1990 to 1992, the cumulative area of beach contaminated by subsurface oil had diminished to an estimated 12 000 m^2 (*6*). These trends suggested that oil remaining after 1992 would soon disperse to negligible amounts (*5*−*9*).

At some locations, *Exxon Valdez* oil seemed more persistent than expected based on the 1990−1992 SCAT surveys. A survey conducted in 1993 suggested that remaining oil might persist because it was no longer disturbed by cleanup efforts (*5*). Where oil was protected from dispersion by cobble-boulder surface armor (*10*, *11*) or by mussel beds (*12*), subsurface oil was often encountered through the late 1990s. A beach cleaning effort at Sleepy Bay in 1997 encountered substantial deposits of subsurface oil (*13*), which raised questions regarding oil persistence elsewhere. Public concerns regarding the extent of remaining oil led the Exxon Valdez Trustee Council, a consortium of Federal and State of Alaska agencies, to support the study we report here, conducted during the summer of 2001.

We used methods based primarily on random sampling instead of the comprehensive assessment approach of the SCAT method to provide a quantitative, probability-based estimate of the amount of oil remaining (i.e., an interval estimate as well as a point estimate). We were not confident that the surface oil remaining in 2001 would be a reliable indicator of subsurface oil, which also indicated randomization of sampling effort. A SCAT survey of surface oil was conducted on each of our randomly selected beaches so that results from our randomly placed quadrats could be compared. Our objectives were to provide estimates and confidence intervals for the total area of beach that remained contaminated in PWS and for the mass of oil remaining.

We employed two compatible random sampling designs for estimating oiled areas on individual beach segments: stratified random sampling (SRS) and stratified random adaptive sampling (SRAS). These involved a large-scale sampling effort with excavation of nearly 9000 pits. The SRAS design gives more precise estimates when sampling something that is rare and highly aggregated and was included in case the detection frequency of oil was very low. We report here results from the SRS design only. Because oil was frequently detected, both designs produced similar estimates, and the increased precision of the SRAS design was negligible. The SRAS results are available from the authors on request.

Methods

Our study area included all the shorelines in the western PWS impacted by the *Exxon Valdez* spill (Figure 1). We sampled three mutually exclusive categories of beaches defined by the persistence of visually evident oil during SCAT surveys conducted from 1989 through 1993 (*5*, *14*). These categories included discrete segments of beaches described as heavily (category I) or moderately (category II) oiled at any time during the period from 1990 to 1993 and beaches described as heavily oiled during 1989 but that had only light to no oil impact during subsequent years (category III). Category III beaches were not expected to have significant amounts of oil, but surveys after 1989 were scant for this category. The total length of all the segments is 116.6 km,

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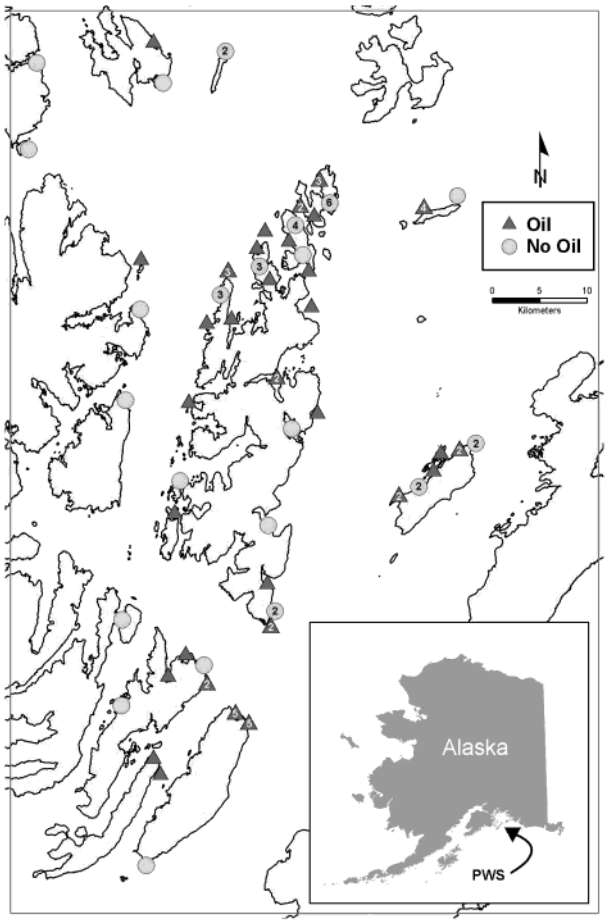

FIGURE 1. Map of the study area in Prince William Sound, Alaska. Symbols indicate stations where oil was detected (triangles) or not (circles) in our randomly placed quadrats. Numbers inside symbols indicate stations too close to resolve at this scale.

comprising lengths of 24.4, 49.1, and 43.1 km in categories I, II, and III, respectively.

Sampling Design. Our field crew was able to sample one 100-m length of beach during one low tide interval, so our basic sampling unit for beaches is segments of 100 m or less. Shorter segments resulted from shorter beach lengths described during the earlier surveys or from the remainders of long beach segments after partitioning into 100-m segments. This resulted in two classes of beach segments (i.e., 100 m and <100 m) and six sampling strata, the product of the three sampling categories and two segment classes. Beach segments in each category were selected by simple random sampling without replacement if 100 m in length or by probability proportional to length (PPL) if less than 100 m. The PPL sampling requires sampling with replacement. A total of 7.9 km of shoreline, comprising 91 distinct segments (Figure 1), was selected and sampled along with 5.3 km from category I where most remaining oil was anticipated. Cumulative lengths of categories II and III were 1.9 and 0.75 km, respectively. The proportion of available beach that was selected within the <100- and 100-m classes were respectively 26.6% and 20.1% in category I, 7.6% and 2.8% in category II, and 2.2% and 1.6% in category III.

The selected beach segments were located by global positioning system (GPS) after reconciliation with known landmarks and maps of previous surveys (*14*). Tidal elevation was determined by an infrared laser-level beam, the height of which was determined by survey reference to observed tide height and predicted tide heights for Cordova, AK, corrected for the nearest tidal monitoring station. We estimate

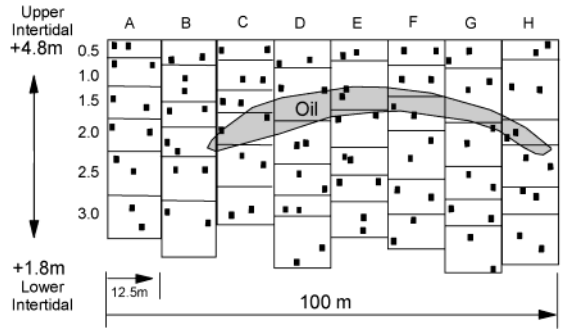

FIGURE 2. Diagram of a typical random sampling grid on a 100-m beach segment. The letters across the top denote 12.5-m columns, and the left-hand number column denotes 0.5-m vertical tidal drops from the upper margin of the sampling grid. The 96 black squares, two per 0.5 m vertical drop·column block, denote a typical random placement of quadrats within the sampling grid, and the gray-shaded area indicates a hypothetical oil patch. Random quadrat placements were made independently for each block and sampling grid. Sampled beach segments shorter than 100 m had fewer columns and randomly placed quadrats.

errors associated with planar coordinates as about ±2 m, based mainly on GPS uncertainty, and with vertical elevations as about ±0.25 m because we did not correct observed tide heights for atmospheric pressure.

We established a sampling grid between +1.8 m and +4.8 m above tidal datum on each beach segment (Figure 2). Each 100-m beach section length was divided into eight columns, each 12.5 m wide. Shorter beach segments were divided into fewer columns. A meter tape laid alongshore on the beach and other meter tapes laid perpendicular along the column boundaries delineated the grid boundaries. Beaches were searched visually for evidence of surface oil within the grid following the SCAT protocols. Leaders of previous SCAT surveys in PWS provided training in the proper identification of the SCAT oiling classifications (*5*). The areal extent of surface oil was estimated as proportions of beach area covered by reference to the meter tapes, and each surface oil patch was classified according to type: asphalt pavements/mousse (AP/MS, classes combined here), surface oil residue (SOR), tar balls (TB), coat (CT), or oil film (OF) (*5*).

The grids were sampled by SRS concurrently with the SCAT surveys. The sampling grid columns were partitioned into rectangular blocks by six 0.5-m vertical tidal elevation intervals, resulting in 48 blocks on a 100-m beach (Figure 2). Two 0.25-m^2 quadrats were randomly placed within each block, based on randomly selected distances along the meter tapes. Each quadrat was evaluated for the presence of surface and subsurface oil. Oil visually evident within the uppermost 5 cm of a beach surface was considered surface oil. The presence of subsurface oil was evaluated by digging a test pit within each quadrat to a depth of 0.5 m or until boulders or bedrock intervened and examining the pit for evidence of oil by sight and smell. Subsurface classifications included no oil (NO), oil film (OF), and light, medium, or heavy oil residue (LOR, MOR, and HOR, respectively) as defined in ref *5*. A total of 7484 random quadrats were drawn, of which 6775 were excavated, with the remainder located on surface boulders, bedrock, or cliffs. We occasionally dug pits deeper than 0.5 m or at intertidal elevations below the lower grid boundary of +1.8 m to evaluate whether oil occurred outside of our sampling design boundaries.

Estimation of Oiled Beach Areas. The estimated total area of beach covered by oil discovered during our SCAT surveys is simply the product of the measured oiled area multiplied by the ratio of available and selected beach lengths for each of our six beach-sampling strata. Results within categories are summed for presentation here (cf. Table 1).

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TABLE 1. Estimated Beach Area (ha) Covered by Surface Oil within Prince William Sound 12 yr following the *Exxon Valdez* Oil Spill, Based on SCAT Surveys of Randomly Selected Beaches[a]

	category I	category II	category III	combined categories
100 m beach segments	0.542	0.096	0.070	
<100 m beach segments	0.162	0.078	nd	
combined segments	0.704	0.174	0.070	0.948

[a] nd, not detected.

The oiled area A_j for the jth sampled beach segment, based on the randomly placed quadrats, is estimated as

$$\hat{A}_j = \sum_{i=1}^{K} N_i \bar{y}_i \tag{1}$$

where K is the number of blocks in the entire segment, N_i is the ratio of the area of block i and the area of the quadrat (0.25 m^2), and $\bar{y}_i$ is the average number of oiled quadrats found in block i (either 0, 0.5, or 1).

The two classes of beach segments (i.e., 100- and <100-m lengths) had different estimators of oiled area. The total oiled area $T_{s,100\mathrm{m}}$ for each of the three 100-m categories is estimated as

$$\hat{T}_{s,100\mathrm{m}} = \frac{N_{100\mathrm{m}}}{n_{100\mathrm{m}}} \sum_{j=1}^{n_{100\mathrm{m}}} \hat{A}_j \quad s = 1, 2, 3 \tag{2}$$

where $N_{100\mathrm{m}}$ is the total number of beach segments in each category (s) within the 100-m oiling category and $n_{100\mathrm{m}}$ is the sampled number of beach segments.

The total oiled area $T_{s,<100\mathrm{m}}$ for each of the three <100-m categories is estimated as

$$\hat{T}_{s,<100\mathrm{m}} = \frac{L_{<100\mathrm{m}}}{n_{<100\mathrm{m}}} \sum_{j=1}^{n_{<100\mathrm{m}}} \frac{\hat{A}_j}{L_j} \quad s = 1, 2, 3 \tag{3}$$

where $L_{<100\mathrm{m}}$ is the total length of beach segments in each category (s) within the <100-m oiling category, $n_{<100\mathrm{m}}$ is the sampled number of beach segments, and L_j is the length of the jth beach segment.

The total oiled area in Prince William Sound (T_{PWS}) is the sum of the six oiled area estimates:

$$T_{\mathrm{PWS}} = \sum_{s=1}^{3} (\hat{T}_{s,100\mathrm{m}} + \hat{T}_{s,<100\mathrm{m}}) \tag{4}$$

Surface and subsurface oiled areas were estimated separately in this fashion.

Gravimetric Analysis of Oil. Oil was extracted from typical samples of each subsurface oil classification and weighed to establish a basis for estimating the mass of oil remaining in PWS. A total of 97 test pits (15 HOR, 26 MOR, 45 LOR, and 11 NO) each $(0.5\ \mathrm{m})^3$ were selected, and the distribution of these samples across beaches was approximately proportional to the distribution of subsurface oil occurrences for each visual oiling category. Oil was scraped from particles larger than 6 cm and added to the remaining contents of the pit, which were weighed and thoroughly mixed, after which a 2-kg subsample was extracted twice, with each extraction using 1 L of dichloromethane for 2 h. The dichloromethane of the combined aliquots was distilled over steam, and the residual material was weighed. Results are expressed as kg oil m^{-2} beach surface area, where the oil mass is determined as the product of the oil mass per kilogram in the 2-kg subsample and the mass of the homogenized test pit contents.

Estimation of Subsurface Oil Mass. To estimate the mass of oil in each beach segment, we calculated the proportion of oiled area belonging to each of the three visual oiling categories (HOR, MOR, and LOR) and then multiplied the proportion by the average weight of oil in that category. The mass of the NO category was assumed to be zero. The total oil mass estimate for an individual beach segment is the sum of the oil masses for the three visual oiling categories.

The total mass of oil in each of the three categories of the 100-m beach segment class is denoted as $W_{s,100\mathrm{m}}$, estimated as

$$\hat{W}_{s,100\mathrm{m}} = \frac{N_{100\mathrm{m}}}{n_{100\mathrm{m}}} \sum_{j=1}^{n_{100\mathrm{m}}} \sum_{m=1}^{3} \hat{A}_j \hat{p}_{jm} \bar{w}_m \quad s = 1, 2, 3 \tag{5}$$

where, $\hat{p}_{jm}$ is the proportion of oiled quadrats belonging to visual oiling category m within beach segment j, and $\bar{w}_m$ is the average mass of oil in visual oiling category m estimated from gravimetric samples.

The total mass of oil in each of the three categories of the <100-m beach segment category is denoted as $W_{s,<100\mathrm{m}}$, estimated as

$$\hat{W}_{s,<100\mathrm{m}} = \frac{L_{<100\mathrm{m}}}{n_{<100\mathrm{m}}} \sum_{j=1}^{n_{<100\mathrm{m}}} \sum_{m=1}^{3} \frac{\hat{A}_j}{L_j} \hat{p}_{jm} \bar{w}_m \quad s = 1, 2, 3 \tag{6}$$

The total mass of oil in all of Prince William Sound (W_{PWS}) is estimated as

$$\hat{W}_{\mathrm{PWS}} = \sum_{s=1}^{3} (\hat{W}_{s,100\mathrm{m}} + \hat{W}_{s,<100\mathrm{m}}) \tag{7}$$

We used bootstrap-generated distributions from 1000 resamplings of masses or areas to estimate standard errors and 95% confidence intervals (95% CI) per stratum. Resampling with replacement was used for the strata with <100-m segments and resampling without replacement for the 100-m segment strata. Precision of total oiled areas and masses across strata was determined similarly from 1000 totals of estimates per stratum.

Qualitative Analysis of Oil. Typical samples of surface ($n = 27$) and subsurface ($n = 38$) oil deposits along with seven samples of unoiled (control) sediments were analyzed by gas chromatography/mass spectrometry (GC/MS) to evaluate oil sources and weathering. The surface oil samples included 15 AP/MS samples, 3 SOR samples, and 9 tarball samples. The subsurface oil samples included 6 HOR samples, 13 MOR samples, 18 LOR samples, and 1 OF sample. Bulk tarballs and asphalt pavement samples (1−100 mg) were dissolved in dichloromethane. Sediment samples (0.1−7 g) were extracted with dichloromethane at 100 °C and 2000 psi for 10 min in a Dionex ASE 200 accelerated solvent extractor. The dichloromethane solutions were exchanged with hexane over steam and separated into aliphatic and aromatic fractions by column chromatography (10 g of 2% deactivated alumina over 20 g of 5% deactivated silica gel). Aliphatics eluting with 50 mL of pentane were analyzed by GC/MS at m/z 191 for terpanes (*15*) following concentration to ~1 mL of hexane over steam. Polycyclic aromatic hydrocarbons (PAHs) eluting with 50 mL of 1:1 (v/v) pentane:dichloromethane were exchanged into ~1 mL of hexane over steam and further purified by size-exclusion high-performance liquid chromatography. Purified PAH were measured by GC/MS operated in the selected ion monitoring mode (*16*).

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TABLE 2. Estimated Mean, Coefficient of Variation (%), and 95% Confidence Interval of Beach Area (ha) Covered by Surface Oil within Prince William Sound 12 yr following the *Exxon Valdez* Oil Spill, Based on Stratified Random Sampling[a]

	category I	category II	category III	combined categories
100 m beach segments	1.21 (27.1%) 0.627−1.90	1.90 (65.7%) 0.158−4.65	nd	
<100 m beach segments	0.755 (32.4%) 0.327−1.27	0.264 (38.7%) 0.0829−0.478	nd	
combined segments	1.97 (21.2%) 1.19−2.81	2.16 (57.9%) 0.386−4.94	nd	4.13 (32.0%) 2.07−7.71

[a] nd, not detected.

Analyzed PAH include parent and alkyl-substituted naphthalenes, fluorenes, dibenzothiophenes, phenanthrenes, and chrysenes.

Oil source identification is by comparison with reference chromatograms of terpanes for *Exxon Valdez* oil and for asphalt originating from the Monterey Formation in California, which contaminated PWS following release from storage tanks during the 1964 Alaska earthquake (*15*). *Exxon Valdez* oil was identified on the basis of the joint absence of 17α(*H*),18α(*H*),21β(*H*)-28,30-bisnorhopane and of 18(α+β)-(*H*)-oleanane, and ratios near 2 of Triplet (C_{26}-tricyclic terpane (*S*?) + C_{26}-tricyclic terpane (*R*?))/C_{24}-tetracyclic terpane (*17*). Oil derived from the Monterey Formation contained bisnorhopane and oleanane and had ratios near 4 of Triplet (*17*). The weathering state of *Exxon Valdez* oil is indicated by an index, *w*, of PAH weathering losses (*18*). Slightly weathered oil is indicated by $0 < w < 2$, moderate weathering by $2 < w < 6$, and heavy weathering by $w > 6$.

Results

Proportion of Beaches Still Oiled. The distribution of detected oil among sampled beaches was highly variable. We found oil in randomly placed quadrats on 53 of the 91 selected beach segments. Eleven had only surface oil, 14 had only subsurface oil, and 28 had both. The oil detection frequency ranged from 0% on 38 segments to over 30% on 6 others. The most heavily oiled segments are within sheltered embayments that received the brunt of the initial oil landfall. Other geomorphologic associations with oil detection frequency were less evident, although persistent oil was found on beaches with boulder/cobble surface armoring, nearly level slopes of the middle intertidal, or a thick sediment veneer over a bedrock platform as reported previously (*11*).

Oil was also present on 25 of the 38 beaches where oil was not found in our randomly placed quadrats. This oil was present as small (<10 m^2) surface asphalt pavements or as tarballs in the upper intertidal discovered by our SCAT surveys (on 24 beaches), or as a large patch of subsurface oil discovered by our opportunistic sampling (1 beach). We found no evidence of oil at 13 beaches, 7 of which were from category III. Hence, we found some form of oil at 86% of the beaches we visited and on 93% of the combined beaches of categories I and II.

Surface Oil Estimates. The beach area covered by surface oil found by the SCAT surveys was just under 1 ha (Table 1). Oil was found in all three beach categories, with about 70% on the category I beaches. The 100-m segments accounted for 71% of the oil detected. Overall, this oil was mainly present as AP/MS (55%) and SOR (39%), followed by TB (2.9%), CT (2.0%), and OF (0.66%).

The SRS estimate of surface oiled beach area is 4.13 ha (95% CI: 2.07− 7.05 ha; Table 2), which is significantly larger than the SCAT-based estimate. This area is nearly evenly divided between category I and category II beaches, and more oil was found in the 100-m segments than the <100-m segments. Surface oil was not detected within the randomly placed quadrats on any of the category III beaches sampled, in contrast with the SCAT survey results.

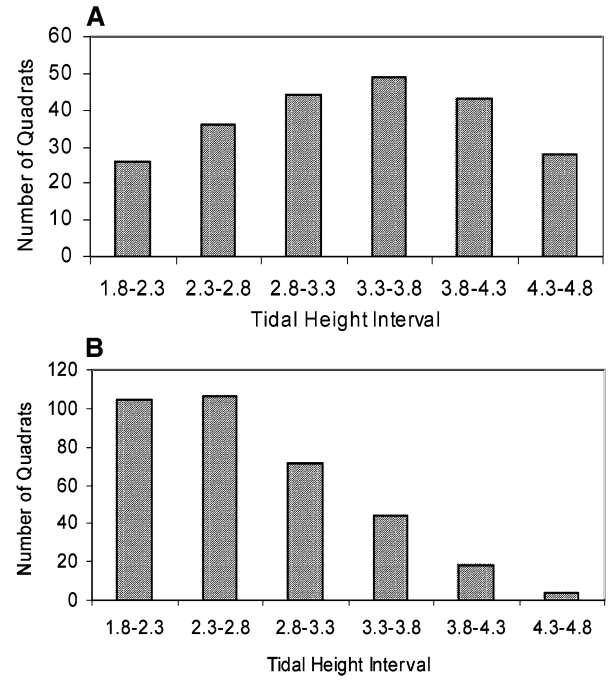

FIGURE 3. Distribution of surface (A) and subsurface (B) oil quadrats vs tidal height.

The 100-m segments of category II account for 91% of variance for the total area estimate, a consequence of the lower proportions of area sampled as compared with the other selection classes of categories I and II. The SCAT-based estimates fall just under the lower bounds of the respective 95% CIs for the 100-m and the <100-m segments of categories I and II (compare Tables 1 and 2). The close scrutiny of the randomly placed SRS quadrats revealed surface oil not found during the SCAT surveys on 13 beaches as compared with the 24 beaches where surface oil was found by the SCAT surveys but was not within the SRS quadrats.

The surface oil was distributed throughout the upper half of the intertidal. Surface oil was most often detected within the +3.3 m to +3.8 m tidal elevation stratum, but was also frequently detected near the upper and lower boundaries of our sampling grid (Figure 3A).

Subsurface Oil Estimates. The SRS estimate of beach area contaminated by subsurface oil was 7.80 ha (95% CI: 4.06−12.7 ha; Table 3). As with the SRS estimates of surface oil, the subsurface oiled area is nearly evenly divided between category I and category II beaches, with less than 10% in category III beaches. Most variance (78%) is from the 100-m segments of category II. Subsurface oil was most often encountered as LOR (62%), followed by MOR (21%), OF (11%), and HOR (6%).

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TABLE 3. Estimated Mean, Coefficient of Variation (%), and 95% Confidence Interval of Beach Area (ha) Containing Subsurface Oil within Prince William Sound 12 yr following the *Exxon Valdez* Oil Spill, Based on Stratified Random Sampling[a]

	category I	category II	category III	combined categories
100 m beach segments	2.27 (28.6%) 1.14−3.67	2.90 (70.3%) 0.238−7.14	nd	
<100 m beach segments	1.29 (35.8%) 0.490−2.33	0.709 (59.3%) 0.0913−1.66	0.640 (97.7%) 0−1.99	
combined segments	3.56 (22.5%) 2.12−5.32	3.61 (57.7%) 0.696−8.17	0.640 (97.7%) 0−1.99	7.80 (29.2%) 4.06−12.7

[a] nd, not detected.

TABLE 4. Estimated Mean, Coefficient of Variation (%), and 95% Confidence Interval of Subsurface Oil Mass (t) within Prince William Sound 12 yr following the *Exxon Valdez* Oil Spill, Based on Stratified Random Sampling[a]

	category I	category II	category III	combined categories
100 m beach segments	18.6 (28.6%) 6.73−36.6	17.5 (77.8%) 0.462−48.8	nd	
<100 m beach segments	7.53 (36.0%) 3.01−13.8	4.93 (66.2%) 0.305−12.4	7.01 (100.2%) 0−24.1	
combined segments	26.2 (31.6%) 12.7−46.6	22.4 (62.8%) 3.00−55.1	7.01 (100.2%) 0−24.1	55.6 (32.2%) 26.1−94.4

[a] nd, not detected.

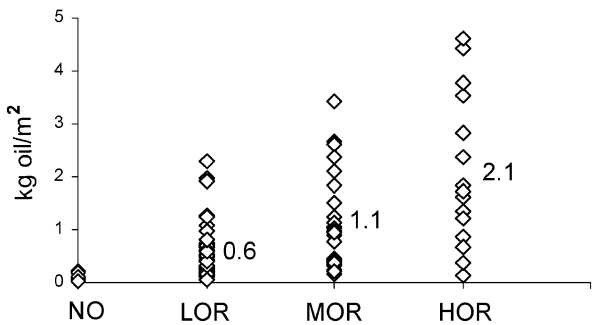

FIGURE 4. Oil mass per unit area for oil classification categories LOR, MOR, and HOR, which indicate light, medium, and heavy oil residue, respectively (see Methods). Numbers plotted are category means.

Subsurface oil was more often detected in the lower tidal elevations of our sampling grid (Figure 3B). This suggests that oil may often be found in the lower intertidal, corroborated by our discovery of subsurface oil at tidal elevations below our sampling grid, often extending to 0 m tidal elevation, on 18 beaches during our opportunistic sampling.

Our SRS estimate of beach surface area contaminated by either surface or subsurface oil is 11.3 ha (95% CI: 6.78−17.2 ha). Because these areas intersect, this estimate is not simply the sum of surface and subsurface area estimates. Overall, the intersection is estimated as 15.7% of the surface oiled area and is lower for category I beaches (10.8%) than for category II beaches (20.2%).

Oil Mass. The mass of oil per unit surface area in the gravimetric samples was variable, but the means roughly double between categories in ascending the oil classifications (Figure 4). The mean mass of oil per unit area of beach ranged from 0.59 kg m^{-2} for LOR to 2.1 kg m^{-2} for HOR. Incorporation of these results into eqs 5−7 led to an estimate of 55 600 kg (95% CI: 26 100−94 400 kg; Table 4). Oil mass variability estimates are consistently somewhat greater than those for corresponding subsurface oiled areas (compare Tables 2−4) but follow similar trends.

Oil Sources and Weathering. All of the surface oil samples analyzed were either *Exxon Valdez* oil or Monterey Formation asphalt. All nine of the tarball samples were derived from the Monterey Formation, with oleanane and bisnorhopane clearly evident and Triplet ratios from 2.7 to 4.5. All but 2 of the 14 AP/MS samples were *Exxon Valdez* oil, with oleanane and bisnorhopane absent and Triplet ratios from 0.83 to 2.20. The two AP/MS samples from the Monterey Formation were small (<0.25 m^2) tar mats collected from the upper intertidal. Two of the *Exxon Valdez* AP/MS samples were slightly weathered, three were moderately weathered, and the rest were heavily weathered with $w > 10$ for six of the samples. All three SOR samples were moderately weathered *Exxon Valdez* oil.

All of the 38 subsurface oil samples had Triplet ratios from 1.04 to 2.18 and lacked bisnorhopane and oleanane, consistent with *Exxon Valdez* oil. The oil in these samples was usually less weathered than the surface oil samples, with the median $w = 3.3$ (range 0.94−12.1).

The sum of the PAH concentrations in the seven control samples and the OF sample range from 19 to 100 ng/g as compared with concentrations ranging from 355 ng/g to 14.7 mg/g (median 68.6 μg/g) in other sediment and oil samples.

Discussion

Oil Sources. Surface oil in the sampled region came from the *Exxon Valdez* spill or from storage tanks of asphalt and other Monterey Formation petroleum products that ruptured during the 1964 earthquake (*15*). Monterey Formation oil was usually found above +3 m tide height and typically occurs as flattened tarballs firmly adhered to cobbles and boulders and infrequently as small (<0.25 m^2) tar mats (*15*, this study). This distribution suggests that tarballs were stranded by high tides and softened sufficiently during periods of high insolation to dry and adhere to rocks. This stranding mechanism would limit the size of tarballs because large tarballs, less likely to absorb enough heat to adhere, would be more susceptible to further waterborne transport and ultimately would exit into the Gulf of Alaska. Oil from the *Exxon Valdez* was much less viscous than commercial asphalt and initially came ashore under high-energy wave conditions throughout the range of tidal excursion, leading to extensive oil patches throughout the intertidal area. This led to greater variety in the occurrences of persistent *Exxon Valdez* oil,

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including subsurface oil, extensive asphalt pavements, sheening surface oil residues, and possibly tarballs that may be difficult to distinguish from Monterey Formation tarballs in the field (*15*).

We were unable to chemically characterize each of the hundreds of oil occurrences we encountered during this project, so instead we collected type samples based on visual appearance. All of the tarballs and two small asphalt pavement samples were from the Monterey Formation source, but the larger asphalt pavement samples (>0.25 m^2) we encountered were *Exxon Valdez* oil. Because the tarballs as a whole account for <3% of the surface oil encountered in our SCAT survey, we conclude that petroleum derived from the Monterey Formation probably accounts for less than 10% of the surface oil we discovered. Because all of the subsurface oil is *Exxon Valdez* oil, Monterey Formation oil remains a minor source of hydrocarbons on the beaches most heavily impacted by the *Exxon Valdez* spill. Other recent anthropogenic sources have been suggested as important based on anecdotal information (*19*), but we did not encounter evidence for these sources on any of our 91 beaches.

Accuracy, Precision, and Bias of Estimates. Our sampling underestimated the area of oil-contaminated beach in PWS because it excluded (i) tidal elevations lower than +1.8 m, (ii) beaches described as lightly or moderately oiled in 1989 but not thereafter, (iii) pit depths deeper than 0.5 m, and (iv) oil not evident visually or by odor. Of these, failure to sample the lower intertidal probably caused the greatest bias. The increasing frequency of subsurface oil from the upper (+4.8 m) to the mid-tidal (+1.8 m) elevation grid limits (Figure 3A) along with the results of our opportunistic sampling of the lower intertidal suggest that subsurface oil may be encountered within the lower intertidal nearly as often as in the upper intertidal. The lower limit of the initial oil impact was about +0.5 m, based on the lowest low tide during the period of initial landfall after the spill, so the proportion of the initially oiled tidal elevation (+0.5 to +4.8 m) below our sampling grid is about 30%, suggesting an underestimate of oiled beach of similar magnitude. In contrast, the small estimated contribution from category III beaches suggests that oiled beach areas in the unsampled portions of PWS are probably negligible, as are contributions from oil present at depths more than 0.5 m below the beach surface based on infrequent detection of oil in pits we occasionally dug to depths of 1 m. Considering these sources of bias, we believe it very unlikely that more than 25 ha of the intertidal remained contaminated with surface or subsurface oil by summer 2001.

Our estimate of oil mass is directly affected by underestimation of the oiled area and also by exclusion of surface oil. Assuming a mean surface oil thickness of 1 mm (and some asphalt pavements were 3 cm thick), an oiled area of 4 ha implies 40 000 L or about 38 400 kg of surface oil. The amount of oil that remained is therefore probably greater than our estimate of 55 600 kg, perhaps by as much as a factor of 2 (accounting for both the subsurface oil in the lower intertidal as well as the surface oil).

Our estimates would have been more precise if we had allocated more sampling effort to the category II, 100-m beach segments at the expense of our adaptive sampling effort. Our estimates of oiled areas on individual beaches contributed almost negligible variance as compared to variance associated with expanding these estimates to the whole of the respective sampling classes. The greatest uncertainty arose from the category II, 100-m sampling class, where we sampled only 2.8% of the class and where substantial oil was occasionally encountered.

Comparison of 2001 SCAT and Random Sampling Methods. The consistently larger estimates of beach area contaminated by surface oil derived from the SRS as compared with the SCAT method is primarily due to two factors. First, the definition of surface oil used for the SRS method includes oil within the upper 5 cm of beach sediments, and this was not always evident without disturbing the surface material. Second, surface oil was often obscured by weathering or epiflora from casual observation. The SRS method involved closer scrutiny of small (0.25 m^2) portions of beach, so less obvious surface oil was more likely to be observed.

The detection of some surface oil in the category III, 100-m class by the SCAT method, but not by the SRS method, is a stochastic result of the random allocation of the SRS sampling quadrats. Oil detected during the SCAT surveys was not detected within the SRS quadrats on 10 other beaches as well, and the possibility of not finding oil within the SRS quadrats when oil patches are in fact present within the sampling grid contributes to the variance of the estimates of total oiled areas.

Oil Persistence. Although the volume of oil has declined considerably, our study suggests the area of oiled beach has probably changed little since 1992. Comparison of subsurface oiling intensities found during our study (mainly LOR) with intensities reported for the previous studies (mainly MOR and HOR; *5*, *6*) suggests that dispersion after 1992 may not have reduced the oiling intensity enough to reduce the area of visibly oiled beach. Our 2001 estimates of surface and subsurface oil are higher than the highest results reported for 1992 (*6*) or 1993 (*5*) by factors of 2 or more. The methods used for the earlier studies underestimated the extent of oiled beach because some oiled beaches were not sampled and because sampling effort was directed mainly toward the upper intertidal where oil was incorrectly thought to be most persistent. However, to conclude that the area of oiled beach significantly diminished from 1993 to 2001, the earlier survey results would require adjustment upward by a factor of 3 or more before exceeding the upper bounds of our confidence intervals, and we believe an adjustment of this magnitude is unrealistic in view of the large sampling effort of the previous surveys.

Although the oil remaining is only about 0.14−0.28% of the volume originally beached, the decline was most rapid during the first few years. About 2% of the original spill volume of *Exxon Valdez* oil was estimated to remain on PWS beaches by fall 1992 (*20*), implying losses of about 58% per year during the first 3.5 yr. Assuming a density of 0.96 for weathered oil (*21*), this volume is equivalent to about 806 000 kg. Comparison with our 2001 estimate of 55 600 kg, possibly an underestimate by a factor of 2, implies an annual loss rate of 20− 26%, substantially slower than anticipated (*9*).

The persistence of subsurface oil in the mid- and lower-intertidal area was unexpected. Previous work emphasized the prevalence of persistent oil in the upper intertidal (*5*, *6*, *10*, *11*, *22*), based on the conjecture that oil would adhere better in the drier upper intertidal (*3*). Subsequent sampling focused on the upper intertidal (*5*, *6*), producing results that appeared to confirm the conjecture. Although surface oil may very well have persisted mainly in the upper intertidal, our study indicates the same is not true for subsurface oil. In addition, the middle and especially the lower intertidal are intrinsically less accessible, and sampling there is more dangerous because the often extensive epiflora can be extremely slippery to traverse. We therefore suspect that subsurface oil in the middle and lower intertidal often escaped detection during previous surveys because of inadequate sampling effort.

The distributions of surface oil and of subsurface oil were clearly different by 2001, but the processes causing this divergence are not clear. The criteria used for the SCAT surveys of 1989−1993 did not differentiate among a wide range of oiling intensities that were lumped as "heavy", which

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might include oiled sediment lenses ranging from 1 cm to 1 m in thickness. Hence, the distribution of extremely oiled sediments was not well-documented, and the distribution of the persistently oiled sediments we found during 2001 may reflect the initial distribution of extremely oiled sediments.

The unexpected persistence of subsurface *Exxon Valdez* oil, often only moderately weathered and extending into the more biologically productive middle and lower intertidal, confirms the potential for long-term biological effects after 1992 on beaches most heavily impacted by the spill. While adequate for allocating oil spill response measures, our study indicates that the usual SCAT method may not be adequate for quantitatively monitoring the long-term persistence of oil, at least in cases such as the *Exxon Valdez* where a considerable proportion of beached oil may not be obvious after a few months.

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