

*Exxon Valdez* Oil Spill  
Restoration Project Final Report

Monitoring Lingering Oil from the *Exxon Valdez* Spill on Gulf of Alaska Armored Beaches and  
Mussel Beds Sixteen Years Post-Spill

Restoration Project 040708  
Final Report

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Study History: Project 040708 is the latest in several projects that have addressed the status and recovery of oiled shorelines along national park coastlines and oiled mussel beds outside of Prince William Sound, along Gulf of Alaska coasts that were initially contaminated by the 1989 *Exxon Valdez* spill. Projects that have included earlier sampling of these sites include: R103B (which later became 93090), 93036, 94090, 94266, 95090, 96090, 99459, 00459.

Abstract: Stranded *Exxon Valdez* oil has persisted for 16 years at boulder-armored beach sites along national park coastlines bordering the Gulf of Alaska. These sites are up to 640 km from the spill origin and were contaminated by oil mousse, a viscous water-in-oil emulsion. Although surface oil has continued to decline, subsurface oiling persists in patches. Especially striking is the general lack of weathering of stranded oil on armored beaches over the last 16 years. At three of the four sites where oil was sampled in 2005, the oil was compositionally similar to 11-day old *Exxon Valdez* oil, even after 16 years. The formation of mousse allowed less-weathered oil to be transported long distances. The sequestration of the oil beneath a boulder armor, coupled with the stability of the boulder armoring (investigated by examining movement of marked boulders), has contributed to the lengthy persistence of this stranded oil. Opportunistic sampling of several previously studied oiled mussel beds indicates continued contamination of at least one of the sites by not very weathered *Exxon Valdez* oil. Long-term persistence of oil in these habitats should cause reconsideration of response activities after spills, and may influence the Environmental Sensitivity Indices applied to these habitats.

Key Words: armored beaches, *Exxon Valdez*, Gulf of Alaska, monitoring, mussels, *Mytilus trossulus*, oil, oil mousse, oil spill, PAH, persistence, petroleum hydrocarbon, weathering

Project Data: The data collected by this project include: 1) description of oiling at selected shoreline sites in Kenai Fjords and Katmai National Parks; 2) quantitative percent cover estimates of persistent oiling within permanently marked quadrats; 3) bolt (boulder) movement data; 4) sampling of subsurface oiling via 'dip-stones'; 5) chemical analyses via gas-chromatography, mass-spectroscopy of oiled sediment samples collected by this project in 1992, 1994, 1999, and 2005; of mussel tissue samples and associated sediments collected in 1993, 1994, 1995, 1999, and 2005; and several oiled sediment samples collected by other entities in 1989. Descriptions of oiling and associated quantitative data are expressed fully in the text and tables of the report (data are descriptive and tabular; tabular data is in Excel spreadsheets); Gail Irvine is the custodian of these data (U.S.G.S., Alaska Science Center, 1011 East Tudor Road, Anchorage, Alaska 99503, phone 907/786-3653, fax 907/786-3636, E-mail [gail\\_irvine@usgs.gov](mailto:gail_irvine@usgs.gov)). The hydrocarbon data are held as part of a larger database, The Exxon

Valdez Oil Spill of 1989: State-Federal Trustee Council Hydrocarbon Database (EVTHD), 1989-2005. This database is housed at the Auke Bay Labs with Bonita Nelson as custodian (11305 Glacier Highway, Juneau, Alaska 99801-8626, phone 907/789-6071, fax 907/789-6094, E-mail bnelson@abl.afsc.noaa.gov). Data are available on diskette in multiple formats.

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Where a stable boulder armor protects gravel substrate from wave erosion, subsurface oil persists for years despite intermediate and high wave energies.

## Executive Summary

This study has focused on the nature of lingering oiling from the 1989 *Exxon Valdez* oil spill along Gulf of Alaska shorelines, outside of Prince William Sound. In particular, we have focused on investigating situations in which oil has persisted, analyzing why and how it persists, determining the rate of change in the chemical character of the oil, and the status of recovery of these oiled shorelines. A special impetus for this study was assessment of the injury to the wilderness character or services of the Katmai and Kenai Fjords National Park coasts that continued oiling represents. Although the focus of the 2005 research was an examination of residual oiling at a set of armored beaches located along national park coastlines that have been studied since 1992, we also opportunistically revisited a subset of previously sampled oiled mussel beds located on the outer Kenai Peninsula coast.

At the five armored beach sites revisited, we re-assessed both surface and subsurface oiling, evaluated the stability of the boulder armors, and took samples of oiled sediments for hydrocarbon analysis where feasible. The majority of these sites experience higher wave-energy than shorelines in Prince William Sound and all were oiled by mousse in 1989. Over the last five years, surface oil cover has continued to decline and is now at very low levels. However, oil mousse persists in the subsurface in amounts similar to what was there in 1999 at the sites where gravel deposits form the substrate below the boulder armor. Remarkably, chemical analyses indicate that this subsurface oil has experienced very little weathering since 1989. Most oiled sediment samples 16 years after the spill are compositionally similar to 11-day old *Exxon Valdez* oil. Subsurface oil at only one site, Cape Gull, has shown significant weathering over time. Analysis of movements in the boulder armors that cover the study beaches indicates only minor shifts in armor position. Since at least 1994, and probably since at least 1989, no episodes of deep wave scouring have occurred that were capable of exposing and physically dispersing subsurface oil deposited by the 1989 spill. The combination of oiling by mousse plus sequestration of the oil within a stable armor has allowed the long-term persistence of this only slightly- to moderately-weathered oil.

Also in 2005 four oiled mussel beds last sampled in 1999 were revisited and samples of mussels and underlying sediments were collected. Both chemical analyses and observations at the sites indicate that the areal extent and concentration of oil found in sediments has generally declined at most sites. However, at one of the Morning Cove sites on the outer Kenai coast, there has been little weathering of the *Exxon Valdez* oil. Comparisons of oiling of armored beaches and mussel beds along the Gulf of Alaska indicate that oil contamination of the armored beaches is more extensive and shows less overt change in the last 6 years than that in mussel beds. This may be due to differences in the elevation of the oiling, extent of armoring and substrate disturbance, or other factors.

## Introduction

When the T/V *Exxon Valdez* ran aground in March 1989, it was not anticipated that lingering oil contamination on non-sheltered coasts would persist for decades, especially given the rocky nature of much of the affected coastline. At that point, there were not many studies of long-term oil persistence following spills. However, studies from the *Exxon Valdez* oil spill (EVOS), as well as the increasing literature from other spills, have indicated that oil can persist for a decade or more (e.g., Owens et al., 1986; Teal et al., 1992; Baker et al., 1993; Vandermuelen and Singh, 1994; Irvine, 2000; Carls et al., 2001; Reddy et al., 2002; Irvine et al., 2002, 2006; Short et al., 2002, 2004) and that effects on biota can also be long-lasting (e.g., Hawkins and Southward, 1992; Klekowski et al., 1994; Dauvin, J.-C., 1998; Irvine, 2000; Bodkin et al., 2002; Esler et al., 2002; Peterson et al., 2003). In sheltered locations oil has been documented to persist for 15 to 30 years (e.g., Baker et al., 1993; Reddy et al., 2002). The persistence of oil in cobble- or boulder-armored beaches experiencing moderate to high wave energy, was recognized early on in studies of the *Exxon Valdez* spill (e.g., Michel and Hayes, 1993, 1996, 1999; Hayes and Michel, 1999; Irvine et al., 1997, 1999, 2002, 2006). Previously it was thought that oil would be rapidly removed from rocky shorelines subject to high wave energies (Vandermuelen, 1977; Irvine et al., 1999; Irvine, 2000). Consequently, rocky shores with high-energy wave regimes were given low Environmental Sensitivity Index ratings (Hayes et al., 1979), which are often used to determine response activities following spills.

Part of the reason why rocky shorelines defy predictions about oil persistence based on estimates of wave energy and wave exposure is that energy/exposure is highly modified by local conditions such as bedrock ledges and large boulders. Some rocky shorelines may experience extremely high wave energy at the scale of a kilometer-long section of shoreline, but oil stranded behind or under large boulders along this same stretch of shoreline may experience extremely low wave energies most of the time. The question becomes what "is most of the time"? We know that stranded oil persists longer on rocky shorelines than it would on sand beaches experiencing the same wave energy regime, but how much longer?

The primary focus of this investigation is on continued monitoring of the persistence and degradation of oil at boulder-armored Gulf of Alaska beaches that have been studied since 1992. These sites were resampled in 1994 and 1999. The continued contamination of these sites, arrayed along the Katmai and Kenai Fjords National Park coasts, compromises the scientific and recreational values, including wilderness characteristics of some of the most pristine wilderness-coast parklands in the world. These values and characteristics are clearly stated in both ANILCA (1980) and the Wilderness Act (1964). Lingering oil continues to degrade the special value of these protected lands, and the lack of weathering of much of the sequestered oil means that the oil, if released, could pose a risk to biota.

One might ask why these sites should be monitored in addition to sites within Prince William Sound. The patterns of oil persistence and degradation at Gulf of Alaska (GOA) sites differ in several important respects from Prince William Sound (Irvine et al., 1999). First, oil stranding in Prince William Sound (PWS) was often in a more fluid form (Payne et al., 1991) than the oil mousse that stranded on GOA coastlines outside PWS. Second, the geomorphic character of the Katmai or GOA shoreline is fundamentally different than in PWS, where wave energies are generally lower. We suggest that the results of studies of crude-oil weathering and persistence on shorelines inside Prince William Sound (Michel and Hayes, 1993, 1996, 1999; Hayes and Michel, 1999; Short et al., 2002, 2004) may not be directly transferable to GOA shorelines; analysis of differences may help us understand the dynamics producing the patterns (see Short et al., 2007).

As mentioned above, oil arrived on GOA shorelines in the form of mousse, which weathers differently than fluid oil. Mousse, a water-in-oil emulsion, weathers principally on its surface, leaving the interior portions of the mousse "patty" relatively unweathered (Payne et al., 1983;

Payne et al., 1991). Therefore, the formation of mousse allows long-distant transport of packages of less-weathered and thus relatively toxic oil (Patton et al., 1981; Irvine et al., 1999) and facilitates the long-term persistence of this less-weathered oil in sheltered situations on the shoreline (Baker et al., 1993; Irvine et al., 1999, 2006; Irvine, 2000). The three-dimensional structure of boulder-armored beaches allows this thick mousse to penetrate into finer sediments lying beneath stable, boulder lags. These surface armors attenuate wave energy and reduce wave re-working of the underlying substrates and the included oil. Additionally, oil on boulder-armored beaches is often stranded high in the intertidal zone, and is usually sheltered by the boulders from sun exposure.

We present data from our 2005 investigations of lingering oil at these GOA boulder-armored beaches as well as relevant data from earlier sampling. The persistence of both surface and subsurface oil, the chemical composition of the oil through time, and movement of the boulder armor have all been examined. In addition, we present data from our 2005 sampling of several oiled mussel beds located on the outer Kenai Peninsula coast. Previous studies have documented persistent oiling in mussel beds (Babcock et al., 1996, 1998; Carls et al., 2001) as recently as 1999 (Irvine et al., 2002; Carls et al., 2004), and there has been concern about the potential effect of such continued contamination on predators that feed on mussels (Trust et al., 2000; Bodkin et al., 2002; Esler et al., 2002; Peterson et al., 2003). The emphasis in this report is on changes observed from previous years compared to 2005. We conclude that for armored beach sites, surface oil cover has decreased significantly since 1994, but subsurface deposits of mousse remain, and the chemical weathering of this mousse remains surprisingly limited. Oiling within mussel beds has diminished considerably, but at one site sampled, hydrocarbon concentrations in sediments beneath the mussels are still high.

## **Objectives**

The 2005 objectives for this project were to:

- 1) Monitor surface and subsurface oil at 6 previously established sites (armored beaches) along the Gulf of Alaska coast.

- 2) Assess boulder movement at the sites in order to investigate the relationship of substrate stability to oil persistence.
- 3) Determine the chemical weathering of the oil.

Although not originally an objective of the study, we were able to opportunistically resample four Gulf of Alaska mussel bed sites that we have sampled historically.

## **Study Region**

### ***Outer Kenai Peninsula***

Along the Gulf of Alaska flank of the Kenai Mountains, active tectonism and glacial erosion have created an intricate, bedrock-dominated coastline. Glaciers have exploited fault systems and weaker rock types to carve deep fjords between these coastal mountains and the continental shelf. A large percentage of the total shoreline is contained within fjords. Rivers are short, steep, and relatively small; consequently they are unimportant generally as suppliers of sediments to this coastline. The coast of the Kenai Peninsula experiences a wider range of wave energies than does Prince William Sound, Kachemak Bay, or Cook Inlet. Consequently shorelines there show a wider range of geomorphic types than in southern PWS north of Montague Island. Shoreline terminology here and in the Katmai descriptions follows Michel et al. (1978), Domeracki et al. (1981), and Michel and Hayes (1996).

Exposed bedrock shorelines are abundant in the Kenai Fjords area. Wave-cut platforms are rare in the Kenai Fjords area although common in Shelikof Strait, Cook Inlet, and southern PWS. Sheltered bedrock shorelines occur along the western shore of Nuka Island and in sheltered embayments within the granitic plutons of the Pye Islands, Harris Peninsula, and southern Aialik Peninsula. Pocket beaches are common between bedrock headlands along both sheltered and exposed shorelines. On pocket beaches with high wave energy, the predominant sediments are rounded boulders and cobbles. Along sheltered shorelines, pocket beaches can

contain a wide variety of sediment types ranging from angular boulders to sands and even silts at depth. Commonly, a lag of boulders and cobbles armors finer sands and pebbles at depth on pocket beaches along sheltered shorelines.

### ***Katmai Coastline of Shelikof Strait***

The Katmai National Park and Preserve coast (Kashvik Bay to Cape Douglas) is one of the most geomorphically diverse coastlines in southern Alaska due to its intricate plan and the steep gradient in wave energies. Sandstone, conglomerate, greywacke, siltstone, and shale underlie most shorelines in Shelikof Strait (Detterman and Miller, 1985; Riehle et al., 1987). Glaciers have carved deep fjords between the near-coastal mountains and the strait. Explosive volcanic eruptions and active glacial erosion in the Aleutian Range have supplied unconsolidated sediments to adjacent shorelines, resulting in extensive sand and gravel beaches in some areas. Active tectonism associated with the Aleutian Trench created uplifted marine terraces in some areas and caused coastal submergence in others.

Northeast of Ninagiak Island (Figure 1, Site 4), the coastline is characterized by bedrock headlands and wave-cut bedrock platforms mantled with locally derived boulders. Headlands are separated by linear sand and gravel beaches fed by glacial outwash streams. Southwest of Ninagiak Island, the coast is formed by fjords containing large bayhead deltas.

Strong currents combined with large tides and directionally variable high winds create a rapidly changing, storm-wave environment along the Katmai coast. The Alaska Coastal Current (ACC) flows southwestward down Shelikof Strait (Royer et al., 1990). Current speeds range from 20 cm-sec<sup>-1</sup> in the early summer to 100 cm-sec<sup>-1</sup> in the autumn (Reed and Schumacher, 1986).

Tides in the northwestern Gulf of Alaska are semi-diurnal with a marked inequality between successive low waters. The mean diurnal range varies from 3.2 m at Seward to 4.2 m at Larsen Bay on western Kodiak Island (Wise and Searby, 1977). Maximum daily, high tide ranges are 2 to 6 m in Shelikof Strait (AEIDC, 1977). The Shelikof Strait is a storm-wave environment subject to strong winds originating from high-pressure cells over the continental interior and from passing cyclonic storms (Overland and Heister, 1980). Waves in western Shelikof Strait have a mean significant wave height (mean height of the highest 1/3 of all waves) between 3 and 4 m during the months October through March and decline to 1 to 2 m in the summer months. Maximum significant wave heights reach 7 to 9 m at these same stations (Wilson and Overland, 1986). Wave heights are >4 m for approximately 15% of the time between October and April (Brower et al., 1977).

## **Methods**

### ***Armored Beach Sites***

Survey methods employed in 2005 were similar to those used in 1994 and 1999. The six study sites (Figure 1) were selected in 1992 using shoreline-assessment data gathered by Exxon and the Alaska Department of Environmental Conservation between 1989 and 1991. At these sites, oil mousse had been consistently observed by oil-assessment teams after 1989 (Schoch, 1993). All sites are boulder-armored, gravel beaches, most with an underlying bedrock abrasion platform at shallow depth. Sites were accessed via skiffs from a larger (about 65') vessel that provided primary logistic support. Detailed site maps are presented in Irvine et al. (1997).

### **Surface and Subsurface Oiling**

Sampling methods used in 1992 were not useful for assessing changes in surface oil cover and did not address subsurface oiling, except for sediment samples taken for chemical analysis. Therefore, changes were made in 1994 to address these concerns. In August of 1994, a

series of permanent quadrats was established at each site in order to examine changes in surface oil cover through time. Individual quadrats, each 40 x 50 cm, were positioned over areas of the most extensive and persistent surface oiling. Three observers independently estimated percent oil cover. Results were compared and estimates modified until all observers agreed on oil coverage within 5%; an average of these values was then ascribed to the plot. Making these visual oil-cover estimates involved close scrutiny of the study quadrats both visually and manually. Surface wetness, shadowing, presence of the black lichen, *Verrucaria*, and partial covering by seaweed made careful, non-photographic assessment of oiling imperative. The position of each quadrat was marked permanently by placing two rock bolts at diagonal corners. Bolt locations were mapped to within  $\pm 2$  cm horizontal distance and  $\pm 1$  cm elevation using an automatic level, tape measure, and stadia rod from a temporary bench mark (tbn) marked by rock bolts on bedrock adjacent to the quadrat swarm.

The quadrat-marking bolts were placed in boulders, and less often in bedrock. Detailed leveling and horizontal mapping of the marker bolts allows quantification of boulder movements on the study beach during subsequent surveys.

Subsurface oiling was described by examining dip stones: naturally occurring stones that protruded from the substrate near but not within quadrats. These stones were loosened with a five-pound sledgehammer, then pulled out, and examined for oil clinging to their sides. After any oil along the dip stones was described and measured, the dip stones were then reinserted and tapped into place using the sledgehammer. The ideal dip stone was an elongate rock that extended vertically below the lowest subsurface oil, allowing the full depth of the oil lens at that location to be assessed.

Surface and subsurface oil were described in the following terms: 1) mousse -- thick emulsified oil, usually brown in color; 2) asphalt -- heavily oiled sediments held together cohesively in an oil matrix; 3) tar -- thick oil layer  $\geq 1$  mm thick, able to be scratched off; 4) coat -- oil that ranges from 0.1 to  $<1.0$  mm thick and that can be easily scratched off a stone with a fingernail; and 5) stain -- oil that is  $< 0.1$  mm thick that cannot be easily scratched off with a fingernail.

Two subsurface samples of oil-saturated sediments from each site were taken for chemical analysis. Each ca. 300 ml sample was collected using a stainless steel spoon. In many

cases, we were able to sample fairly sediment-free masses of mousse. The spoon was rinsed with dichloromethane prior to sampling or was heated for 24 hours at 225°C. Sampling jars were specially cleaned by the manufacturer. Oil samples were immediately placed in coolers with ice and were frozen within 2-4 hours of their collection.

In August 2005, we repeated the site description and sampling protocols used at these six sites in 1994 and 1999.

We described wave exposure at the study sites using methods detailed in Howes et al. (1994).  $F_{\max}$  is the maximum fetch distance in any direction that waves can approach a shore segment.  $F_{\text{em}}$  is effective modified fetch calculated at three different angles relative to the strike of the shoreline segment. These three angles are perpendicular to the general trend of the shore, 45° to the left of the shore-normal direction, and 45° to the right of it. Marked differences between  $F_{\max}$  and  $F_{\text{em}}$  indicate large directional differences in wave exposure and suggest the occurrence of vigorous long-shore drift. Very exposed sites have an  $F_{\max} > 1000$  km, and exposed sites have an  $F_{\max}$  between 500 and 1000 km. The semi-exposed category has an  $F_{\max}$  between 50 and 500 km. Exposure to an  $F_{\max}$  of 10-50 km yields a semi-protected exposure rating, and protected sites have an  $F_{\max}$  of <10km. Very protected sites have an  $F_{\max}$  of <1km.

### Boulder Stability Measurements

We assessed boulder movements by measuring changes in three parameters: 1) distance between bolts and the survey station at each site, 2) bearing relative to the bearing between the survey station and each bolt in 1994, and 3) the elevation of each bolt relative to its 1994 elevation. Some boulder movements are not detectable by these measurements. Because boulders can rotate in place, movements really refer to changes in bolt positions and not necessarily to lateral or vertical displacements of the entire boulder. The error bars assigned to boulder movements represent the range of values obtained when a representative bolt marker at each site was re-surveyed 5 times. Azimuth changes are the most insensitive measurement, because bolts are surveyed from only one datum. At site MR-1 in McArthur Pass, most of the bolts were affixed to bedrock outcrops and so are not of interest here. Boulders that are part of a beach's boulder armor can roll in place within the surrounding matrix of stones, or they can be displaced from it entirely. The distinction is important because a boulder rolling in place never

completely exposes the oil embedded in the smaller stones beneath it, while a displaced boulder leaves a chink in the armor that could result in local wave scour and removal of oiled sediments. In interpreting the positional monitoring data, we infer that a boulder rolled in place if the elevation or distance measurements change less than one meter, the typical long-axis diameter of boulders on these shorelines. A significant movement, one that could compromise the boulder armor is defined as one >1m change in distance or elevation (except at Cape Gull, with smaller boulders, see text below), and/or a >10 degree change in bearing. A bolt/boulder that is missing on a subsequent survey date is considered evidence for a breakdown in the boulder armor, except in cases where burial by sand or gravel obscures boulder positions.

### *Oiled Mussel Beds*

#### Sampling Procedures

At each site visited in 2005, photos were used to position a transect line parallel to the waterline in the location which had previously been sampled. Originally, these had been set through the middle of the obviously oiled portion of a mussel bed using modified methods of Karinen et al. (1993) and Babcock et al. (1994). The length of the transect line ranged from about 10 to 50 m, according to bed size and topography. A single pooled sample of surface sediment was taken at a site; each sample was a composite of 8 to 10 subsamples from the upper 2-5 cm, collected haphazardly along the transect line, usually within 1m of the line. 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. A single pooled sample of 20 to 25 mussels was similarly collected; mussel length ranged from ca. 20 to 40 mm. These techniques mirrored those used in 1999. Then, at sites where mussels were sparse, or where oiling was very slight or no longer observable, a single pooled mussel and single pooled sediment sample were collected. Air blanks were collected for quality control purposes at each site. These consisted of sample jars opened and set on the substrate while a sediment or mussel sample was taken, then closed at the completion of taking the other sample; no sample was placed in the jar. All samples were cooled immediately and frozen within 2-4 h.

## *Chemical analyses*

### Gas Chromatography/Mass Spectrometry Analysis

Polycyclic aromatic hydrocarbon (PAH) content of sediment samples was determined by gas-chromatography/mass-spectrometry (Short et al., 1996a). The analytes include unsubstituted and alkyl-substituted homologues of 2 to 4 ring PAH, and dibenzothiophene homologues (Table 1). PAH were extracted with dichloromethane, purified by alumina/silica gel column chromatography followed by size-exclusion high-performance liquid chromatography. Concentrations of PAH in the dichloromethane extracts were determined by the internal standard method based on a suite of deuterated-PAH standards. In 2005, aliquot weights of oil samples ranged from 2 – 15 mg, while sample aliquot weights of sediments and of mussels ranged from 7 – 9 g and from 0.47 g to 0.72 g dry weight, respectively. Method detection limits (MDLs) of PAH were experimentally determined (Glaser et al., 1981), and are reported elsewhere on a mass basis (Short et al., 1996a). The ratio of these mass-based MDLs and dry sample aliquot weights generally range from 500 to 10,000 ng/g for the oil samples, 1 to 6 ng/g for the other sediments, and 10 – 40 ng/g for the mussel tissues. Concentrations of individual PAH below method detection limits were treated as zero. Sediment and tissue concentrations are reported on a dry weight basis. Wet to dry weight ratios were determined by dehydrating 1 g wet samples for 24 h at 60 °C and weighing the remaining mass. Analytical accuracy is better than ±15% based on comparison with National Institute of Standards and Technology (NIST) values, and precision expressed as coefficient of variation usually ranged from 10 to 25%, depending on the PAH analyte. Total PAH (TPAH) concentrations were calculated by summing concentrations of individual PAH except perylene. Perylene was excluded because there are contemporary natural biological sources.

### Hydrocarbon Source Identification

The source of the PAH detected in the samples was evaluated by comparing the relative PAH distribution patterns with patterns derived from experimentally weathered *Exxon Valdez* oil (EVO) (Short and Heintz, 1997). Parameters of the EVO weathering model developed by Short and Heintz (1997) include the PAH proportions of unweathered EVO, relative first-order loss-rate constants for 14 selected PAH identified in Table 1, and a parameter  $w_i$  for the extent of

weathering of sample  $i$ , which can be used to compare degrees of weathering among samples. This latter parameter increases from near 0 for unweathered EVO to more positive values as weathering progresses.

The goodness-of-fit between the relative PAH distribution patterns of modeled vs. measured PAH in a sample is described by a mean-square-error (MSE) term, where MSE values of zero correspond to a perfect match, and increasingly positive values indicate progressively larger discrepancies between modeled vs. measured relative PAH abundances. An MSE value of 0.57 corresponds with a type I error of 0.05, indicating that a lack of fit between modeled and measured PAH of this magnitude occurs at a frequency of 5% from random effects when EVO actually is the sole source of the PAH. The median MSE value of samples known to contain EVO as the dominant hydrocarbon source is 0.1452 (Short and Heintz, 1997).

## Results

### *Armored Beaches*

#### Description of the Study Sites and Their Oiling Conditions in 1994, 1999, and 2005

##### *McArthur Pass: Site MR-1*

Located in a minor cove on the northern, mainland shore of McArthur Pass in Kenai Fjords National Park (Figure 1), the MR-1 site is protected in terms of wave exposure ( $F_{em} = 2$  km,  $F_{max} = 3$  km). This bedrock shoreline is only slightly modified by wave erosion and has a thin covering of poorly sorted, locally quarried, granitic cobbles and boulders (Figure 2). One to two meters of coseismic subsidence during the 1964 earthquake (Plafker, 1969) killed conifer trees along the seaward edge of the supratidal zone. This sudden drop in land level, which had similar effects as a rise in sea level, initiated bank erosion at the top of the shoreface in slope deposits of mixed soil and gravel. A stream mouth borders the site to the east, and this stream transports cobble-gravel sediments into the cove, but no significant longshore sediment transport is evident.

When first described in 1989, oiling at the MR-1 site consisted of “moderate” to “heavy” oiling (10% to > 50% cover) by mousse, soft asphalt, and tar (D.H. Mann, unpublished Exxon SCAT field notes, 1989). Oiling was mainly in the high intertidal zone, above the *Fucus* zone and consequently roughly above the level of mean high water (Plafker, 1969). In 1989,

subsurface oil penetration was limited to about 5 cm, mainly on account of the shallow bedrock. Abundant freshwater seepage on the shoreface may also have discouraged subsurface oiling. The relatively large size of surficial deposits on this shoreface and its relatively sheltered wave regime suggest that the risk of oil being buried by sediment accretion was low.

In 1994, we established 17 quadrats at the MR-1 site in areas of the heaviest remaining surface oil. Oil percent cover averaged 17% and consisted of coat, tar, and asphalt (Table 2). The majority of this oiling, including the coat, was on rock surfaces sheltered between the boulder armor. Appreciable amounts of surface oiling have been lost through the combined actions of wave abrasion and cleanup efforts. We had limited success assessing subsurface oiling at MR-1, due primarily to the thin mantle of cobbles and boulders on the bedrock platform. On one of the five dip stones examined, we found mousse extending to a depth of 2 cm below the surface. Some stones had near-surface bands of tar, others were clean (Tables 3, 4).

By 1999, 10 years after the spill, most of the once abundant surface oiling was gone at MR-1. Oil cover decreased significantly between 1994 and 1999 by an average of 45% ( $p \leq 0.01$ , Wilcoxon signed-rank test), (Figure 3, Table 2). Surface oil declined, again significantly, between 1999 and 2005 (Figure 4, Table 2), down to a mean percent cover of approximately 3 % (Figure 5).

The MR-1 site never had extensive subsurface oiling, partly because the bedrock lies close to the surface; however, the oil that was in the subsurface in 1989 probably remains. This conclusion is based on the continued occurrence of tar and asphalt at similar depths (most 2-4 cm; mean approx. 2 cm) on the dip stones we sampled in 1999 and 2005 (Tables 3, 4).

#### *Cape Douglas: Site CD-003A*

Located on the outside shoreline of the northern headland enclosing Sukoi Bay (Figure 1), the Cape Douglas site experiences high wave energies from the north, east, and obliquely from the south. Its overall wave exposure is classified as exposed based on a  $F_{em}$  of 453 km and a  $F_{max}$  of 880 km. The Cape Douglas area is extremely windy, evidenced by groves of prostrate alders and areas of stabilized sand dunes. The site (Figure 6) is located on the upper half of a sloping, wave-cut, bedrock platform. This platform is covered by a single layer of large boulders, 0.5 to 1.5 m in their longest dimensions, which have filled in the spaces between occasional, truncated bedrock stacks. Most of these boulders are subrounded with their corners

rounded off by battering against other stones, and they rest on the surface or are embedded to varying depths in a substrate of boulder gravel. Shoreward, the bedrock platform merges with a boulder-gravel and cobble-pebble ramp that rises steeply 5 m. On the crest and landward of this massive storm berm is a 5 to 10 m-wide band of drift logs. The upper cobble and pebble portion of the shoreface ramp is probably highly mobile; however, longshore movement of sediment is restricted by the bedrock headlands that interrupt this section of shoreline every 0.5-1 km.

Oiling in the study site was described as heavy in 1989. In 1990, the oil-impacted area was described as covering an area of 30 x 40 m. Oiling on the SCAT segment within which the CD-003A site resides was described as mousse in 1989 and as mousse, tar, coat, and stain in 1990 and 1991. An estimated 844 ft<sup>3</sup> of oil was removed from the larger segment in 1990 and bioremediation fertilizer was applied. Oiling descriptions, cleanup and bioremediation histories of the Katmai NP&P sites are detailed in Irvine et al. (1999).

During our visit to CD-003A in 1994, surface oiling was “very light” and consisted of scattered remnant patches of mousse, tar, coat, and stain plus subsurface mousse. We established 25 permanent quadrats at the CD-3 site in 1994. Oiling in these quadrats ranged from 4 to 45% in cover and consisted mainly of soft asphalt in the interstices of gravel sheltered under the boulder armor. The zone of persistent oiling is near the level of mean high water, inland of the bedrock platform and seaward of the cobble-pebble ramp.

We examined 19 dip stones from around the quadrats in 1994. Most of these revealed mousse persisting at depths greater than several centimeters (range 0 - 9 cm; mean 3.5cm; Table 3).

Between 1994 and 1999, surface oil cover declined significantly by an average of 74% (Figure 3), the most of any site. Surface oil cover did not decline significantly between 1999 and 2005 (Figure 4); the great decline in percent cover between 1994 and 1999 made it more difficult for changes in percent cover between 1999 and 2005 to be significant. Certainly the overall decline since 1994 is significant (Figure 5).

In contrast, subsurface oil has remained abundant as revealed by the examination of 20 dip stones in 2005 (Tables 3, 6). Mousse was found clinging to the sides of most of these stones after they were pulled from the substrate (Figure 7). The dip stones suggest that in 2005 mousse persisted widely in the substrate to depths of 2 to 10 cm, with an average depth of 4.6 cm (Tables 3, 6).

*Kiukpalik Island: Site SK-101.*

Lying offshore the Katmai coastline and exposed to the waves in Shelikof Strait, the Kiukpalik Island site (Figure 1) is classified as exposed due to long fetches to the northeast. The  $F_{\max}$  of this exposed site is 600 km, and the  $F_{\text{em}}$  is 500 km. The study site consists of a sloping bedrock platform quarried by waves out of granitic bedrock. The platform has been stripped of boulder cover along its seaward edge but is mantled under a ramp of boulders and cobbles starting near mean high water level and thickening inland. Large boulders, 1-2 m in long dimension, form a well-integrated armor over a substrate of small boulders, cobbles, and pebbles (Figure 8). Freshwater runs across this shoreface in several spots. The site is easily located by the lone grove of Sitka spruce trees growing behind it in the meadow.

In 1990, the area of the SK-101 site was described as having “medium” oiling within an area of 5 x 100 m. This oil was described as mousse, tar, coat, and stain. An estimated 1170 ft<sup>3</sup> were removed by cleanup efforts in 1990. In 1994, we described the persisting surface oiling as “very light” and covering an area of approximately 5 x 50 m.

We established 18 permanent quadrats at the Kiukpalik site in 1994. These quadrats cover the scattered areas of the worst, persistent oiling. All these pockets of remnant oil were located on the cobble-boulder-gravel substrate within and between the large-boulder armor. In 1994, surface oil cover percentages in these quadrats ranged from 12 to 38% (mean = 25%; Figure 3) and consisted mainly of coat, asphalt, and stain (Table 7). Surface oil cover declined significantly between 1994 and 1999 (Figures 3, 5). In 2005, due to infilling of much of the site with cobbles and boulders, surface oil in most quadrats could not reliably be assessed. Remaining oil observed was mainly coat and asphalt along with tar held in the interstices of surface stones.

In contrast to the declines in surface oil cover, subsurface oil continued to persist in a similar manner between 1994 and 1999. In 1994, we examined 15 dip stones for subsurface oiling. Many had bands of tar or asphalt near the surface with mousse at depths > 5 cm (mean depth, 4.5 cm; Table 3). Our impression was that heavy subsurface oiling persisted there in the form of only slightly weathered mousse in scattered pockets under the boulder armor. In 1999, examination of 18 dip stones at the Kiukpalik site revealed that extensive subsurface oil persisted there at similar depths (mean 5.7 cm; Tables 3, 8). The situation in 2005 was quite different.

We found that we could not sample subsurface oil because the site, or at least the areas between the boulders, had been infilled with smaller cobbles and boulders (Figure 9). Subsurface oil may remain beneath this newly enriched armor of cobbles and boulders (see results of boulder movements, and discussion presented later).

*Ninagiak Island: HB-050B*

Located in a small pocket beach on the south side of Ninagiak Island in Hallo Bay (Figure 1), the HB-050B site is classified as semi-exposed, based on a  $F_{em}$  of 75 km, and  $F_{max}$  of 120 km. The south side of Ninagiak Island consists of a high, relict wave-cut platform eroded by modern sea level to form a series of small pocket beaches <50 m wide and filled with a mixture of sand, pebbles, cobbles, and boulders. Boulders here tend to be smaller than at Cape Douglas or Kiukpalik, with long-dimensions from 30 to 80 cm. Unconsolidated sediments are locally derived from the eroding faces of bedrock cliffs.

At the HB-050B site, an armor of medium to large boulders covers a thin veneer of pebble to boulder gravel over a bedrock platform. The beach profile is relatively low angle, terminating inland at the foot of a 5-m high cliff. Freshwater seepage is evident in the upper intertidal zone. Following certain wave conditions, the sand and pebbles from the sea-arch beach to the west may encroach on the study site.

In 1990, oiling around the HB-050B site was described as “medium,” covering an area of approximately 5 x 10 m. Oiling was mousse, tar, and coat at that time. In 1994, we found the surface oil in the area of HB-050B to be “very light” and to consist of mousse, tar, coat, and stain.

We established 26 quadrats at the Ninagiak site in 1994. At that time surface oil cover averaged 24% (range 9-55%) in the quadrats and consisted mainly of asphalt (Figure 3, Table 9). Surface oil cover declined significantly between 1994 and 1999 (Figures 3 and 5). By 1999, the remaining surface oil was entirely asphalt, often containing sand, pebbles, and shell fragments. In 2005, much of the Ninagiak site had been infilled with gravel, primarily pebbles and small cobbles and 10 of the quadrat bolts could not be found, having been apparently buried (Figure 10). Of the 15 quadrats that could be laid out, substantial infilling of most of the quadrats meant they could not be assessed as previously for oil. Less than 5 were able to be assessed, and only 2

had any surface oil (Table 9). For these reasons, we did not include any figures for surface oil cover change at this site for 2005.

Subsurface oil in 1994, illuminated through dip stone sampling, revealed mousse present in the subsurface, often with an asphalt upper layer on top, with an average depth of the oil ‘lens’ of 3.5 cm (Tables 2, 8). Dip stones sampled in 1999 and 2005 had similar descriptors of subsurface oiling, and similar depths (Tables 2, 8, Figure 11), however, the number of dip stones sampled in 2005 was much smaller than earlier years due to the infilling of the site described above.

#### *Cape Gull: Site CG-001A.*

Located in a west-facing cove north of Cape Gull on the Katmai coast near Kafil Bay (Figure 1), the Cape Gull site experiences radically changing wave exposure with tide height. At low tide heights, the site adjoins a low-wave-energy lagoon floored by sands, pebbles, and shell fragments, and shielded by a bedrock islet. During high tides, the protecting islet is greatly reduced in area and the low-tide lagoon is drowned. Even during high tides, the wave exposure rating of the Cape Gull site is “protected”, with  $F_{\max} = 2.5$  km. The study site consists of a gently sloping, bedrock, wave-cut platform that is mantled thinly by sand-cobble gravel, which in turn is armored by small boulders (Figure 12). Inland, the shore platform terminates against a 3-4 m bedrock cliff and banks of soil and volcanic ash.

In 1989, the shoreline encompassing our study site was described as “heavily” oiled in an 12 x 100 m area. Oil at that time was described as mousse. Some 14,570 ft<sup>3</sup> were removed from the larger SCAT shoreline segment that includes the CG-001A site. In 1990, surface oiling here was still described as heavy and a further 41 ft<sup>3</sup> were removed. In 1994, we found the surface oiling to be “very light.” However, the portions of the CG-1 segment lying around the low-tide lagoon north of our quadrats may have been recently buried under a thin blanket of pebble gravel moving onshore and southwards onto the upper shoreface of the low-tide lagoon. The boulder-armored area where we established our permanent quadrats in 1994 was not affected by longshore transport of any kind.

In 1994 we could find only 12 patches of remnant surface oil suitable for establishment of monitoring quadrats. In these 12 quadrats, oil cover was asphalt and averaged 16.1 % cover (Figure 3, Table 11). Patches of persisting surface oiling were between the boulder armor on the

upper shoreface. By 1999 the surface oil coverage had declined to an average of 7.6% (Figure 3), and by 2005, surface oil cover had dropped to a mean of 1.46% (Figures 3, 4, 5, Table 11). As in 1994, the remnant surface oil at the Cape Gull site was entirely asphalt; we remarked in 2005 that much of the asphalt was embedded with shell hash (Table 11).

Subsurface oiling as described from the dip-stone sampling suggests little change in the depth of oil since sampling began in 1994 (Table 3), although the amount of subsurface oiling at this site was never as extensive as at the other study sites. In 2005 subsurface oil was described as mousse or asphalt with shell hash, or asphalt (Table 12). Forty percent of the dip stones examined in 2005 showed no evidence of subsurface oil (Table 3). In general, this site has had the highest proportion of “clean” or unoiled dip stones (Table 3). The aggregate of these observations suggest that oil occurs as widely scattered patches of mousse and asphalt in the armor-protected substrate.

#### *Kashvik Bay: Site KA-002.*

Located on the southern shoreline of outer Kashvik Bay, site KA-002 occupies the upper shoreface of a cobble-boulder beach (Figure 1). Locally quarried boulders rest in 0.5-1 m of gravel overlying bedrock (Figure 13). Shoreline configuration and wave exposure change markedly according to wave height with a large low-tide lagoon being exposed west of the site during spring tides. The bedrock platform underlying the intertidal zone is backed by a 5-10 m high vertical cliff in places and a steep earthen bank in others. The Kashvik site has a wave exposure rating of semi-exposed with an  $F_{\max}$  of 200 km and a  $F_{\text{em}}$  of 50 km. Wave fetch is markedly greater towards the southeast, which creates vigorous long-shore transport at the Kashvik Bay site from east to west. In 1989, oiling at the KA-002 site was described by a SCAT survey as moderate and covered an area estimated at 20 x 100 m. Cleanup in 1989, 1990, and 1991 removed an estimated 1489 ft<sup>3</sup> of oil. In 1989, oiling at the Kashvik Bay site was described as mousse. In 1990 it was described as mousse, coat, and stain. In 1994, we found the surface oiling at KA-002 to be very light across an area of 20 x 100 m and to consist of widely scattered traces of mousse.

During our 1994 visit to KA-002 we were unable to locate any spots for establishing permanent oil persistence quadrats. Comparing the near-vertical photographs taken along the transect lines in 1992 by National Park Service personnel (C. Schoch and J. Cusick), we noticed

that a large amount of sediment, cobble to small boulder in size, had been brought in by longshore drift from the east. While large boulders composing this beach's armor remained in their 1992 positions, the areas between them had been infilled with smaller sediments sometime between 1992 and 1994. This infilling of newly transported sediment had buried the remaining surface oiling under 20 to 40 cm of un-oiled material. Consequently, there was virtually no surface oiling remaining at KA-002, though we thought it likely that storm waves would sometime exhume the buried surface oil. Several pits dug through the newly deposited sediments at the Kashvik Bay site revealed mousse and tar still present beneath.

In 1999 we found that the cobble "sheet" that had buried the site in 1994 had moved further upslope and revealed patches of mousse and soft asphalt between and beneath boulders. The light brown color and apparently less weathered surface of the mousse suggest that it may have been uncovered in the last year. Fifteen dip stones from the Kashvik site (Tables 3, 13) demonstrated that mousse persisted in the subsurface throughout the site.

In 2005, we were unable to revisit this site due to weather.

### Stability of Boulder-Armored Beaches in the Gulf of Alaska

Information on the boulder movements at four of the six sites is presented below. At McArthur Pass, our marking bolts were placed in bedrock, so boulder movements are not being studied there. At Kashvik Bay, the boulder armor was largely covered by recently transported cobbles when we visited the site in 1994. Consequently, we did not mark boulders at that site.

#### *Cape Douglas*

Of the 25 bolts/boulders we monitored at this site, 44% shifted their positions in detectable ways during the 11- year study period (Figure 14). Two bolts (L and N) disappeared between 1999 and 2005, though it is possible that these two bolts are hidden under other stones or underneath boulders that have rolled over in place. A number of the boulders that moved did so by shifting one way between 1994 and 1999 and in the opposite direction between 1999 and 2005 (K, O, Q, W), or they showed only minor shifts in position (J, S, and V). These types of movements are consistent with boulders rolling and/or shifting in place within the overall boulder armor covering the beach. Only three bolts/boulders (A, I, and M) at Cape Douglas changed their positions by more than 1 m of distance. Coupled with the two missing

bolts/boulders, they represent significant movement by 20% of these marked boulders over the 11-year period of observation.

#### *Kiukpalik Island*

Between 1994 and 2005, 78% of the 18 marked boulders at this site underwent detectable position changes (Figure 15). Two of these (A and P) disappeared, though it is possible the bolts are hidden because the boulders have rolled over. Of the others that showed detectable changes, only bolt/boulder C changed its distance and elevation by more than 1m. The remaining changes in position were all <50 cm in distance, <35 cm in elevation, and <10 degrees in bearing. This is consistent with the large boulders that moved (many are > 1m in long diameter) simply shifting in place within the overall boulder armor.

#### *Ninagiak Island*

Of the 26 boulders we bolted at this site, ten of them (F, H, I, L, M, N, O, P, Q, and X) went missing between 1999 and 2005. Most of these probably were buried under a layer of pebbles that moved onto the site from the beach to the south sometime after 1999 (Figure 10). The small, negative-distance movements of bolts L, M, N, Q, R, S, and U between 1994 and 1999 (Figure 16) are probably artifacts of the deflection of the tape measure over or around a boulder that had moved near the survey station after 1994. Four bolts/boulders (C, J, O, and Z) shifted their positions by more than 50 cm in distance between 1994 and 2005, but no bolt moved more than 1 m in distance. Bolt/boulder J had returned to its starting location by 2005 (Figure 16). The large number of bolts that were buried after 1999 precludes meaningful estimates of the percentage of boulders that moved at this site.

#### *Cape Gull*

We placed 12 bolts at the Cape Gull site in 1994. In 2005, all were still accounted for. The most dramatic position change involved bolt K, which is attached to a boulder 25 cm in diameter. Between 1994 and 1999, bolt K moved about 55 cm closer to the survey station. After 1999, it moved 11.9 m from its 1994 position (Figure 17). Given the isolated location of this site, it is unlikely this clast was moved by a person, and bears seldom carry stones. Bolt K's elevation changed by about 20 cm between 1994 and 1999, and then by 40 cm between 1999 and 2005. Several other bolts/boulders made less dramatic movements. In summary, 33% of the

boulders at the Cape Gull site underwent detectable position changes between 1994 and 2005. One of these (I) had returned to its 1994 position by 2005. Only one boulder moved more than 50 cm.

#### PAH Composition of the Stranded Oil at Armored Beach Sites

Of the nine oiled sediment samples from armored beaches analyzed for PAHs in 2005, two samples, both from Cape Gull, could not be evaluated by the source identification model (Short and Heintz, 1997) because the samples were too weathered and the sample aliquots were too low. However, the detected PAH in one of the samples indicate that it is very weathered *Exxon Valdez* oil. The estimated  $w_i$  value for the sample that had detectable PAH indicates it is clearly the most weathered of the armored beach samples, except for the companion sample that was so weathered the PAH were below MDL. The PAH compositions of the other 7 oiled sediment samples are consistent with weathered *Exxon Valdez* oil (EVO) as the PAH source. The MSEs (mean square errors) of these samples ranged from 0.089 to 0.160, indicating matches that are consistent with analytical precision (Table 14, Figure 18).

The PAH concentrations of the samples analyzed confirms their relatively high oil content. Total PAH (TPAH) concentrations in 2005 samples (excluding Cape Gull) range from 0.505 to 3.37 mg TPAH/g sample (Table 14). Weathered EVO contains about 1.5% TPAH (Wang et al., 2003), so these TPAH concentrations are equivalent to oil concentrations that range from about 34 to 225 mg EVO/g sample. These concentrations are consistent with oil contamination that is obvious by sight or smell. Except at Cape Gull, concentrations of TPAHs appear to have changed little over time (Table 14).

Most of the samples from 2005 and previous years had weathered little beyond the initial evaporative weathering that occurred immediately following the T/V *Exxon Valdez* oil spill (Figure 18). Samples of EVO collected from the sea-surface of Prince William Sound 11 days following the oil spill (Short et al., 1996b) contain substantial proportions of naphthalenes and of the less-substituted alkyl-homologues of dibenzothiophene and other PAH, with values for the

weathering parameter ( $w_i$ ) that range from 0.229 to 0.884 (Table 14). Proportions of PAH in all of the armored beach samples except for the Cape Gull samples are similar, and have  $w_i$  values that range from -0.056 to 3.9 (Table 14). This indicates little additional weathering for these samples compared with the 11-day old sea-surface EVO samples. However, by 2005, the Cape Gull oil samples are so weathered that little of the initial complement of PAH is left, with the remaining PAH consisting mostly of 4-ring homologues.

### ***Oiled Mussel Beds***

#### General Oiling Observations and Hydrocarbon Analyses

The areal extent of oiling at the six sites revisited in 1999 (Figure 19) appeared visually to have decreased since the previous sampling in 1995. The site with the broadest apparent oiling in 1999 was Otter Beach in Tonsina Bay. Oil was visible in various locations across the site, sometimes first indicated by sheening.

The areal extent of oiling at the four sites revisited in 2005 (Figure 19) appeared visually to have decreased since 1999. Only one site had apparent oiling in 2005: Morning Cove-2. At all sites, only one composite sample of mussels and one composite sample of underlying sediments were taken due to the sparsity of apparent oiling (Camp Beach and Otter Beach) or sparsity of mussels and oil (e.g., the two Morning Cove sites).

Analysis of the PAHs in mussels and underlying sediments indicates that scant PAH from EVO are being accumulated by the mussels in 2005. Substantial PAH were present in sediments of only one of the beaches examined (Morning Cove-2), where the total PAH burden was 0.52 mg/g, and the  $w_i$  and MSE (mean square error) values clearly indicate this was not very weathered EVO (Table 15). Mussels exposed to these sediments accumulated an appreciable burden of PAH (856 ng/g), but the associated high MSE value indicates that PAH accumulation from other sources in addition to EVO was probably substantial. Inspection of the PAH distribution pattern of the mussel sample shows considerable contributions from combustion-derived PAH, indicated by the predominance of less-substituted homologues of 4- and 5-ring PAH. At the other three beaches, concentrations of PAH were consistently very low in mussels and sediments, the highest values being 120 ng/g in sediments from Morning Cove-1 (Table 15).

While the PAH distribution patterns of these samples are not inconsistent with EVO as a source, too few PAH were detected above MDL to confidently identify the source. Thus at only one mussel site of the four examined was there substantial contamination of not very weathered EVO.

## Discussion

### *The Oil Remaining at the Six Gulf of Alaska Armored Beach Sites*

Much of the *Exxon Valdez* oil that was present at our study sites in 1989 was removed either by manual cleanup or by wave action and other natural weathering processes; however, three of the five sites on the Kenai and Katmai National Park coastlines of the Gulf of Alaska that we revisited in 2005 still retain subsurface oil. Infilling of armors by finer sediments limited inspection or sampling at two sites, although oil was still visible in an unaffected part of the one site (Ninagiak). The persistence and retarded weathering of subsurface oil on these shorelines distant from the spill origin are due to a combination of factors that includes the arrival of the oil as mousse and its sequestration under boulder armor.

### Surface oil

Over the last five to eleven years, the extent of surface oiling has declined significantly at all five sites where quadrats to examine such change were established; note however, that in 2005 we were not able to re-assess surface oil coverage at Kiukpalik and Ninagiak due to infilling of much of the sites. The declines at three sites from 1994 to 2005 ranged from 81% - 91%. There is no clear relationship between loss of surface oil cover and wave energy, though the highest rate of decline in surface oil cover between 1994 and 1999 (74%) did occur at the site with the highest wave energy, Cape Douglas, with an  $F_{\max}$  of 880 km. The other sites, with highly varying wave energies, showed fairly similar rates of decline in surface oil cover. Additional monitoring sites would be needed to more accurately describe the relationship between wave exposure and the removal rate of surface oil.

Surface oil generally is restricted to protected boulder faces and to interstices between stones in the substrate protected by the boulder armor, or in the case of McArthur Pass, also to cracks in the bedrock. Since the quadrats were set up in 1994, five years after the *Exxon Valdez*

spill, we can assume that the surface oil was already declining through a combination of cleanup activities and natural processes of cleansing due to wave action. Surface oiling is now very low at these sites (means of 1-4%) and is expected to continue to decline.

### Subsurface oil

Subsurface oil is difficult to quantify, especially on these boulder-armored shores. We have used dip stones to assess the depth and nature of the oil still sequestered in these beaches. Since sampling of subsurface oil is not conducted in the same exact locations each year, we cannot describe how particular oil patches change with time. However, comparison of the 1994, 1999, and 2005 results indicates little change in the depth of subsurface oil. Subsurface oil still remains at these sites.

Chemical analysis of subsurface oil (mousse) samples has revealed remarkably little weathering of the oil at three of our four sites over the last 16 years; note that one additional site (Kashvik) that has had persistent oil could not be sampled in 2005. Oil at these sites is compositionally similar to eleven-day old *Exxon Valdez* oil. Why and how has this occurred? Both the boulder armoring of these beaches and the stranding of oil in the form of mousse have contributed to this, and these factors are discussed in greater detail below.

### ***Role of Boulder Armors in Protecting Oil Contamination***

Boulder-armors are common in the upper intertidal zones of bedrock platform shorelines bordering the Gulf of Alaska. These armors result from centuries to millennia of wave-induced, net erosion that selectively removes clasts smaller than boulders from the beach surface. The boulders that remain protect the underlying finer sediments from being disturbed by typically occurring wave impacts. Waves continually batter the boulders that compose the armor with logs and smaller boulders. Shifting boulders bump one another and cause further rounding off of sharp edges. Observations at the four sites where we tracked boulder movements suggest that even large boulders are rocked and rotated by waves, the process that sinters the boulders with neighboring boulders and with bedrock projections.

Over the last 13 years, since these sites were first established in 1992, there have been three instances where the large boulder armor has apparently remained stable while finer sediments have moved into (and in one case, also off) the sites, burying smaller substrates and

the underlying oil. At Kashvik Bay, large-scale transport of cobbles that buried the site between 1992 and 1994 prevented the establishment of permanent quadrats in 1994. By 1999 these cobbles had largely moved off the site, revealing an intact boulder armor that lay beneath, along with remnant *Exxon Valdez* oil. Between 1999 and 2005, both the Kiukpalik and Ninagiak sites were at least partially covered by cobbles and boulders (Kiukpalik) or pebbles (Ninagiak). At Kiukpalik, the marker bolts were able to be surveyed, while at Ninagiak, many of the bolts on boulders are presumed buried. These dynamics further illustrate the resistance of boulder armors to disturbance.

The boulder armor at the Cape Douglas site has been surprisingly stable over the last eleven years considering the exposed wave regime there. Between 1994 and 1999, only two (A and I) of the 25 marked boulders were displaced out of the boulder armor that covers this beach. Boulder A moved about 1.25 m and boulder I nearly 2 m up the beach (Figure 14). The fact that the marker bolt on boulder I maintained the same elevation despite its shift up the beach may be due to this boulder rolling as it moved. Neither boulder A nor I moved any further between 1999 and 2005. Only one additional boulder (M) is known with certainty to have been displaced out of the armor after 1999. It moved nearly 2 m nearer the survey station and altered its bearing by about 10 degrees. Two other bolts (L and N) disappeared between 1999 and 2005, perhaps because their boulders rolled enough to obscure the bolts or perhaps because their boulders moved out of the area. If we count L and N as displaced out of the armor, then by 2005 20% of the boulders marked at Cape Douglas had been displaced out of their positions in the 1994 armor. The boulder armor here has not rearranged itself significantly since 1994 and probably not since 1989 when the oil first arrived. We infer that the boulder armor that protects the oil stranded beneath it on this beach remained largely undisturbed over the study period.

At the Kiukpalik Island site, which also has an exposed wave regime, only one bolt/boulder changed its distance from the survey station by more than 1 m (Figure 15). Two other bolts disappeared, and if we assume their disappearance resulted from boulder movements exceeding 1 m, then 17% of the boulder armor at this site was disrupted between 1994 and 2005. We interpret the minor shifts in the positions of the 11 other bolts/boulders that changed their positions between 1994 and 2005 to be the result of boulders rolling or rotating within the intact armor.

The boulder armor of the Ninagiak beach apparently was not substantially disrupted over the 11-year survey period (Figure 16). However, in 2005 we could not locate 10 bolts, though it is likely they are buried under gravel that partly covered this site after 1999. This means that all statements made here involving 2005 data derive from incomplete data and are provisional. Four bolts/boulders (J, O, P, and Z) shifted their positions by more than 50 cm in distance between 1994 and 2005, but no bolt moved more than 1 m in distance. Four bolts/boulders (C, G, W, and Y) made detectable position changes between 1999 and 2005. We are reluctant to estimate a percentage of the armor that was disrupted until we know whether the 10 missing bolts were buried or displaced.

At Cape Gull, a site that has a protected wave regime, only one (K) of the 12 marked boulders changed its position by more than 1 m over the eleven year study period (Figure 17). Boulders on this beach are all <50 cm in maximum diameter, so they are smaller than boulders on the other study beaches. At Cape Gull, we infer that bolt/boulder A, which shifted its distance to the survey station by about 45 cm, in fact probably was displaced from the original boulder armor. Boulder I moved slightly, probably as the result of rolling or spinning in place. We estimate that only about 17% of the boulder armor at the Cape Gull site was disturbed between 1994 and 2005.

Observations of bolted boulder movements since 1994 indicate that the boulder armor at some sites has shifted only slightly. Most movements seem to result from individual boulders shifting within the space afforded them by neighboring clasts. At none of the sites did a complete re-ordering of a beach's boulder armor occur which would have permitted the scouring of oil-containing sub-boulder sediments. It appears that no storms capable of moving boulder armors and physically cleaning oil buried in the substrate beneath them have occurred in the past 16 years; at present, the occurrence frequency of such a storm is unknown.

### ***Interactions among Boulder Armoring and Oil Weathering and Persistence***

We suspect that the conjunction of initial oiling by mousse and boulder armors is responsible for the persistence of slightly weathered oil in medium- to high-energy wave environments for up to 16 years. The formation of mousse, a viscous water-in-oil emulsion containing up to 70% water (Payne et al., 1983), within the first few days following the *Exxon Valdez* spill, created a relatively stable form of oil that weathered principally on its exterior

surface, leaving the interior largely unchanged chemically. Rafts of mousse patties, each preserving a core of only slightly weathered oil, were carried great distances from the *Exxon Valdez* spill site.

The inverse relation between the concentration of oil in sediments and the degree of weathering noted for the armored beach samples in this study most likely reflects the effect of the relative surface area of the oil on weathering rate. High concentrations of oil imply larger particles or thicker films of oil in or on the sediments, with correspondingly smaller surface area per unit volume of oil. These smaller relative surface areas reduce evaporation and dissolution rates of PAH, and limit microbial access, leading to slower weathering rates (cf. Short and Heintz, 1997).

Without the three-dimensional nature and stability of the boulder-armored beaches, however, the oil would not have persisted for 16 years. The topographic complexity of the beaches allowed the oil to persist in more protected and moist crevices. The stability of the substrates on these beaches, demonstrated through examination of bolted boulders, has allowed persistence of subsurface oil while surface oil declined significantly (Table 3, Figure 5).

### ***Persistent Questions***

Our results document the persistence of slightly weathered oil within boulder-armored beaches. Several questions emerge from this observation. First, are the four study sites on the Katmai coast unusual for the stability of their armor? These particular sites were selected three years after the oil was stranded. Perhaps these sites represent unusually stable sites because they were the sites where oil still remained three years after stranding. To answer this methodological question, we would need to continue a similar investigation in Prince William Sound where a more complete record of oiled and un-oiled beaches exists and where we could quantify the possible correlation between the degree of armor development and oil persistence.

The second question concerns how boulder armors develop. We infer that these armors develop progressively in the face of repeated wave action. But if wave energy is too great relative to the size and fracture resistance of individual stone clasts, boulders lose the irregular shapes that are necessary to form a firmly integrated armor. They become rounded and hence more moveable, which makes the formation of a coherent armor impossible. Conversely, if wave energies are usually too small on a particular shoreline to effectively sinter the variously

shaped boulders into a coherent armor, no armor forms. Hence armor development may be the outcome of a regime of intermediate wave disturbance relative to the size and fracture resistance of the rocks.

Our results from the Katmai Coast suggest that oil persistence is positively correlated with the degree of boulder armor development on a beach. If this is true, and if armor development is maximal under intermediate wave-energy regimes, then an interesting hypothesis emerges. Namely, the shorelines most at risk for persistent oil contamination, given that oil stranding already has occurred there, are the well-armored beaches found where intermediate levels of wave action occur. Our observations along the Katmai Coast suggest that boulders 0.5 to 1.5 m in diameter can form well-integrated boulder armors capable of sheltering underlying oil in a poorly weathered state over decadal time scales. We hypothesize that similar results hold throughout the region of the *Exxon Valdez* spill where similar wave conditions, beach geology, and armoring exist.

### ***Mussel Beds***

We have discussed whether armoring of substrates by mussels may have contributed to the long-term persistence of oil in mussel (*Mytilus trossulus*) beds in the past (Irvine et al., 2002). Mussels attach to substrates by means of byssal threads, which trap fine sediments beneath the mussels. Following the *Exxon Valdez* oil spill, mussel beds were found to harbor high concentrations of residual oil (Babcock et al., 1996). Continued scrutiny of oiled mussel beds in Prince William Sound (Carls et al., 2001, 2004) and along the Gulf of Alaska has indicated that although the concentrations of oil are declining, a number of mussel beds remained contaminated 5-10 years post-spill (Irvine et al., 2002). By 2005, the number of contaminated beds and degree of oiling had declined for the subset of GOA beds revisited (Table 15), with only one of the revisited sites having high levels of relatively unweathered EVO in its sediments.

By comparison, oil contamination on armored beaches in the GOA has shown less overt change in the last 4-5, as well as 9-10 years than that in the GOA mussel beds. Although elevational differences (i.e., oiled mussel beds are lower in the intertidal than the persistent oiling we have observed at GOA armored beach sites) may contribute to the different trajectories of contamination, the finding of persistent oil low in the intertidal in PWS (Short et al., 2002, 2004) argues against elevation being the primary differentiating factor. Probably much more

significant is the relative stability of the different armors; there has probably been an almost complete turnover in mussels over the 16 years since the spill. Also, the geomorphology and oil persistence in mussel beds can not be considered to be independent. For example, the highest values obtained for oiled mussel beds in the Gulf of Alaska were obtained from mussels located in bedrock crevices or amongst large boulders where secondary sheltering or concentrating of the oil could have occurred. Thus it is not clear to what extent armoring by mussels has been responsible for the prolonged contamination of affected beds.

Within mussel beds, the underlying sediments often contain higher values of TPAHs than do the mussels themselves, as occurred also in 2005. The elevated cytochrome P450-1A values observed for several vertebrate predators of mussels in Prince William Sound suggest that contaminated mussels could be the source of the stress (Holland-Bartels, 1999; Trust et al., 2000; Bodkin et al., 2002; Esler et al., 2002). Residual oil from other sources, including armored beaches in Prince William Sound, could also be involved.

The bioavailability of PAH in oiled sediments to the mussels associated with them is limited, because of the low solubility of the PAH and because of the feeding habit of the mussels. As suspension feeders, mussels have two distinct modes of accumulating PAH, depending on the phase association of the PAH. If PAH are dissolved in true solution, mussels may absorb PAH through equilibrium partitioning. Alternatively, PAH may be associated with organic particulate material such as micro-droplets of crude oil. Because mussels feed by straining particulate material from the water column, their efficiency at accumulating hydrocarbons associated with particulates exceeds accumulation of dissolved hydrocarbons by a factor of nearly 100 (Short, 2005). Hence, low or undetectable concentrations of PAH in mussels indicate that the rate of oil micro-droplet formation is nearly negligible, as is the loss through dissolution of PAH from the bulk oil. Such slow dissolution rates are supported by the slow weathering of PAH in the oil, as indicated by the low values of the weathering parameter  $w_i$  a decade or more after the spill in these sediments (Tables 14 and 16). Thus the major source of PAH to predators more likely will come from ingestion of contaminated sediments rather than consumption of mussels.

## ***Implications***

As noted in Irvine et al. (1999), the persistence of subsurface oil beneath boulder armors on exposed beaches forces a reconsideration of the Environmental Sensitivity Indices previously applied to Gulf of Alaska shorelines. Vandermeulen (1977), Hayes (1980), Domeracki et al. (1981), and Gundlach et al. (1983) stated that exposed rocky headlands and wave-cut platforms were the shoreline types with the lowest ecological sensitivity to spilled oil due to the short residence time of oil stranded on these shorelines. Whereas this has been shown to be true for surface oil, our observations indicate that oil in the subsurface of boulder-armored beaches may be extremely persistent (Figure 18). The lack of weathering or retarded weathering of the subsurface oil, suggests an even greater concern.

Long-term persistence of oil can pose long-term threats to biota (e.g., Irvine, 2000), especially because the mousse sequestered beneath boulder armors has only slightly weathered and at most of our sites appears stable chemically over the last 16 years. The potential exists for the future release of still-toxic, slightly to moderately weathered oil from armored beach sites in the Gulf of Alaska, although the volume of oil sequestered is relatively small compared to the same shorelines in summer 1989, and to shorelines oiled inside Prince William Sound in 1989. If storm waves succeed in shifting the boulder armors and scouring the underlying substrates, a burst of liberated oil will occur. The rapid dispersion and dissolution of this oil could have locally deleterious effects; however, these are expected to be minimized by the very conditions that caused the oil's release.

Another aspect of this continued contamination concerns its effects on the wilderness values of these national park coasts. Surface oil is declining and soon will be quite minimal, however, it is the continued presence of subsurface oil (which can be visible amongst the boulders) that constitutes injury. This injury can be expressed as “contamination” or “soiling” of once pristine areas. Actual visitation to these areas is not necessary for the injury to be realized. Additionally, the continued potential for injury to naturally occurring biota also weighs in. The continued contamination of these sites in special wilderness areas argues for their continued monitoring through time, as does the need to understand the dynamics and full implications of such injury.

## Conclusions

Stranded *Exxon Valdez* oil has persisted for 16 years in at least four boulder-armored beaches and at least one mussel bed bordering the Gulf of Alaska. These sites are distant (280-640 km) from the spill origin, and were initially oiled by mousse. The armoring of the underlying substrates by boulders has fostered the persistence of stranded oil. The oil contamination on the armored beaches is more extensive and shows much less overt change in the last six years than that in the mussel beds. This is more likely due to higher disruption or turnover in the structure of the mussel beds through death of mussels, than to elevational differences between the settings.

In both habitats, the weathering of the oil has been slower than originally expected. Especially striking is the general lack of weathering of stranded oil on armored beaches over the last 16 years. Oil at three of the four armored-beach sites, 16 years after the spill, is compositionally similar to 11-day-old *Exxon Valdez* oil. This lack of weathering is due both to the condition of the oil stranding, mousse, with its low surface area to volume ratio, and the lack of disturbance of subsurface oil. Previously we postulated that the stability of the boulder armor protected the sequestered, stranded oil from disruption and breakdown. Current results confirm these ideas by showing that little movement in the boulder armor has occurred since our last visit, six years ago, or, indeed, over the 11-year period since boulder movement has been studied. Based on the observed persistence of oil at these sites since 1989, we postulate that little movement of the boulder armor has occurred over at least the last 16 years.

We did not find extensive oiling of mussel beds in the few beds we examined in 2005, however what oil remains could be a source of contamination for predators in the nearshore that feed on mussels. On armored beaches, sequestered oil has the potential for biological effects if it is released through disturbance of the armoring substrate, e.g., through unusually high-energy wave events, or if it proves attractive to inquisitive predators, such as brown bears, who feed in the intertidal along the Katmai coast (Smith and Partridge, 2004) and are known to be lipophilic and attracted to novel hydrocarbons (Smith pers. comm.). However, as mentioned above, the storm conditions that would release the oil would also minimize its biological effects. Long-term persistence of oil in these habitats should cause serious reconsideration of response activities after spills, and may influence the Environmental Sensitivity Indices applied to these habitats.

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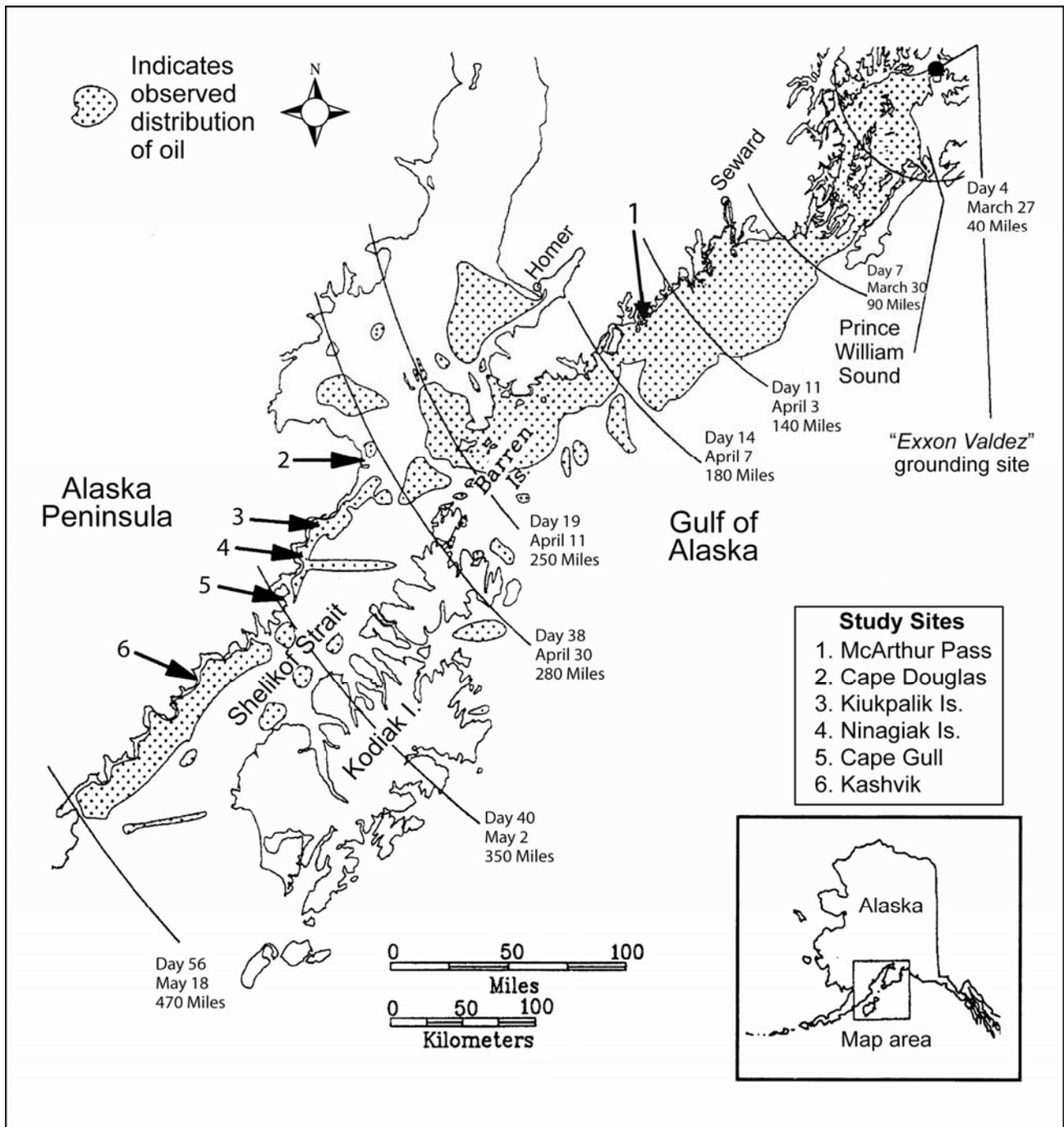


Figure 1. Map detailing location of armored beach study sites and the geographical distribution of oil through time following the 1989 *Exxon Valdez* spill. The oil distribution map is courtesy of the State of Alaska, Department of Environmental Conservation.



Figure 2. MR-1 (McArthur Pass site) in early May, 1994. Angular cobbles and boulders overlie granite bedrock at shallow depth.

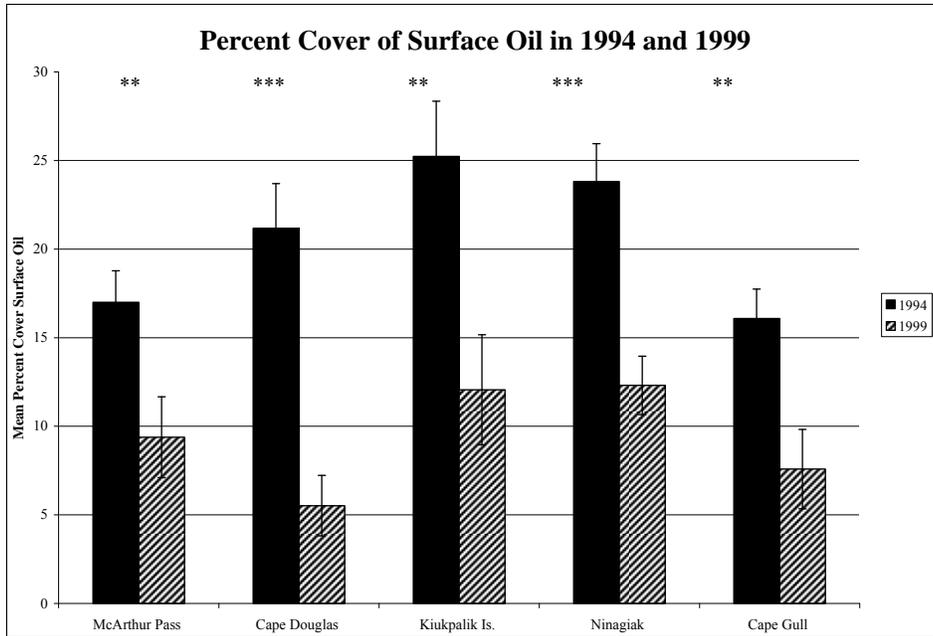


Figure 3. Changes in the mean percent cover surface oil at armored beach sites between 1994 and 1999. Error bars represent  $\pm 1$  standard error. All changes are significant (Wilcoxon signed-rank test), at  $p \leq 0.01$  (\*\*), or  $p \leq 0.001$  (\*\*\*)

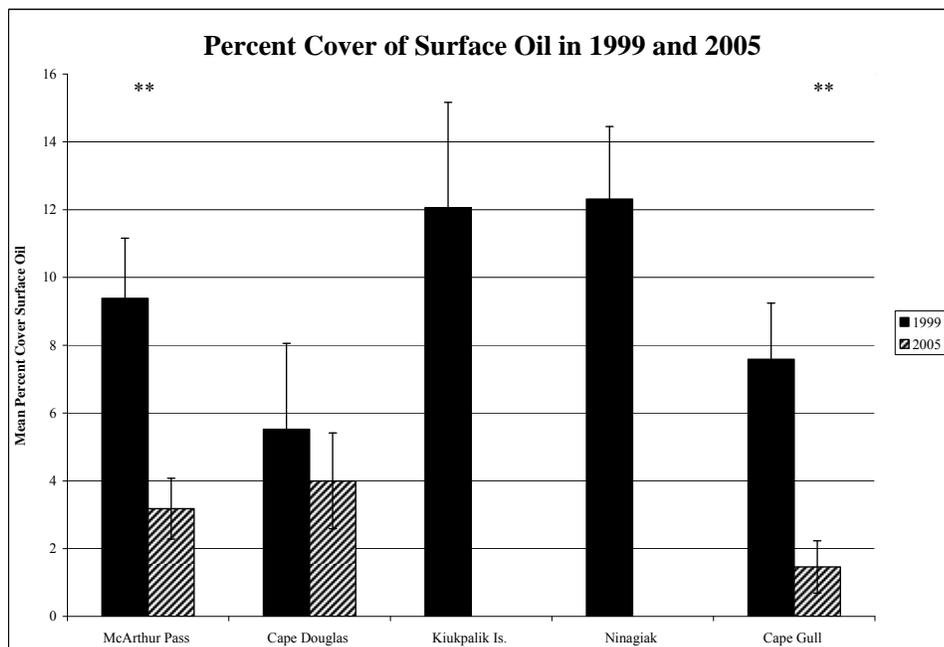


Figure 4. Changes in the mean percent cover surface oil at armored beach sites between 1999 and 2005. Error bars represent  $\pm 1$  standard error. McArthur Pass and Cape Gull show significant changes (Wilcoxon signed-rank test), at  $p \leq 0.01$  (\*\*), or  $p \leq 0.001$  (\*\*\*)

Most Kiukpalik and Ninagiak quadrats could not be assessed in 2005 due to infilling of quadrats by pebbles, cobbles or boulders.

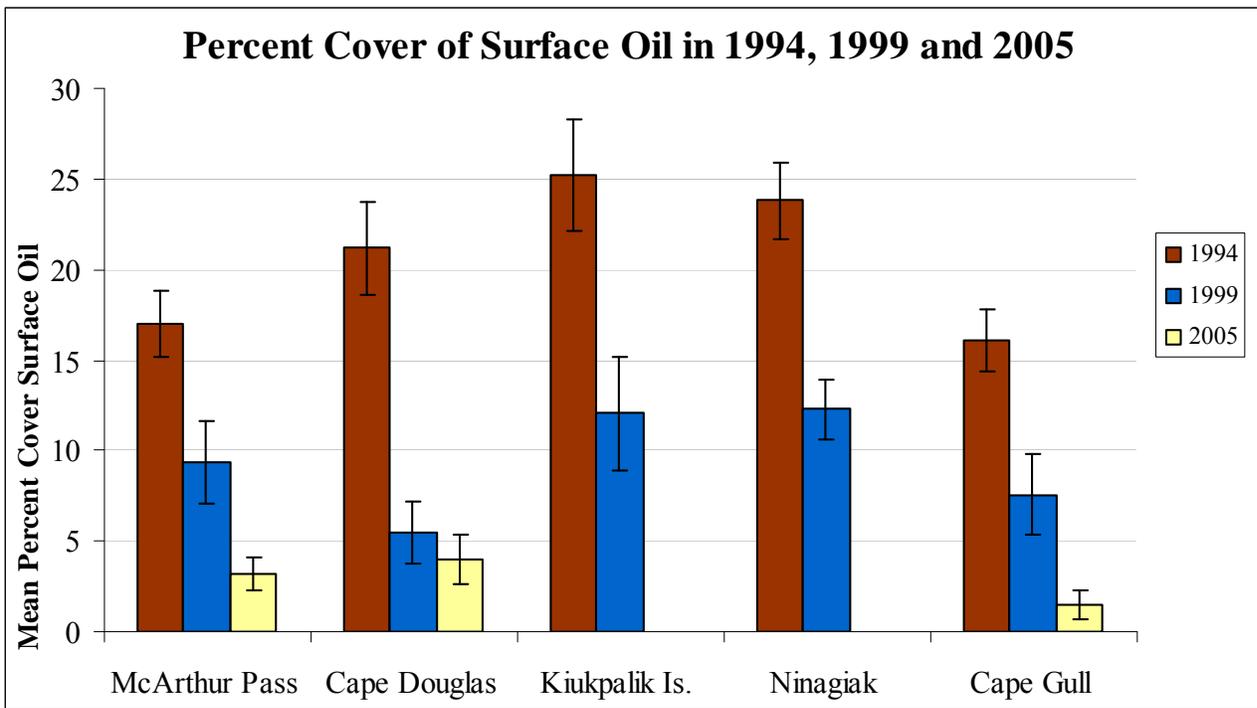


Figure 5. Mean percent cover surface oil at armored beach sites in 1994, 1999 and 2005. Error bars represent  $\pm 1$  standard error. No 2005 data for Kiukpalik and Ninagiak are presented since most quadrats could not be assessed.



Figure 6. Oil monitoring site at Cape Douglas in August 2005. Orange flagging temporarily marks the location of bolts on part of the site. In the foreground it is possible to see finer substrates that underlie the boulder armor.



Figure 7. Dip stones, which are part of the natural landscape, are dislodged from the substrate between boulders in order to measure the depth and state of subsurface oil. Image A shows dip stone 17 reinserted into the substrate from which it was dislodged at Cape Douglas in 2005. Note the superficial asphalt matrix in which a number of smaller stones are embedded. Image B shows the oiling on the exposed dip stone, which was measured as 1 cm of asphalt above >9 cm of mousse. An oil-water sheen formed on the disturbed oil below the dip stone.



Figure 8. View of the monitoring site on Kiukpalik Island in August 2005. At this and other sites, surface-oil-cover quadrats are marked by rock bolts placed into boulders.



Figure 9. Two sets of quadrat images showing the infilling of quadrats by cobble and boulders at Kiukpalik between 1994 and 2005. Images A and B show quadrat B in August 1994 (A) and August 2005 (B). Images C and D show quadrat F in August 1994 (C) and August 2005 (D). Quadrat dimensions are 40cm x 50cm.



Figure 10. Site photos of Ninagiak taken in 1994 (Image A) and 2005 (Image B). In 2005, much of the site was infilled by cobble and gravel, making the site difficult to sample.



Figure 11. Dip stone number 5 removed from the boulder matrix at Ninagiak in 2005. One cm of asphalt and over 2 cm of mousse were measured on this dip stone. Only when there is a clean area on the dip stone below the oil can the depth of oil at that specific location be determined.



Figure 12. Cape Gull site in August 2005. Dark patches on boulders are *Verrucaria* lichen. Several quadrat locations are indicated by yellow arrows.



Figure 13. An armor of cobbles and boulders at the Kashvik site. Note the fitted relationship of different shaped stones. Gravel underlies the armor.

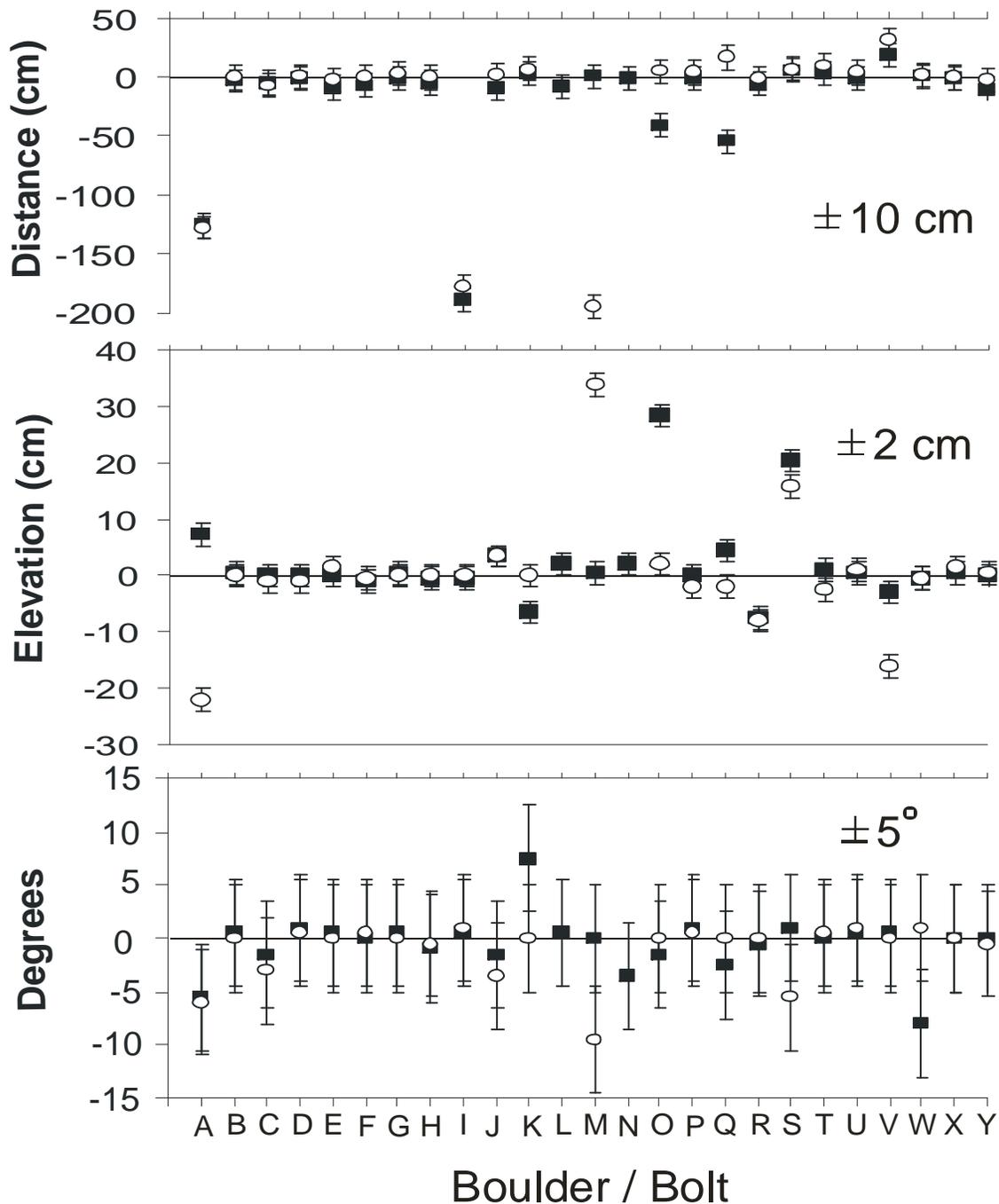


Figure 14. Movement of bolts set in boulders at the Cape Douglas site. Circles are 2005 data, filled squares are 1999 data. Both are relative to 1994 measurements. Distance changes are measured from a datum bolt, and negative values indicate bolt moved away from this datum. Positive values indicate bolt moved towards datum. Error in distance measurement is estimated at  $\pm 10$  cm and is mainly due to deflection of the tape around intervening boulders and to tape stretch. For elevation changes, negative values mean bolt is lower relative to its 1994 position. Positive values mean it rose in elevation relative to 1994. Elevation error is estimated at  $\pm 2$  cm. Error for the bearing measurements is estimated at  $\pm 5$  degrees.

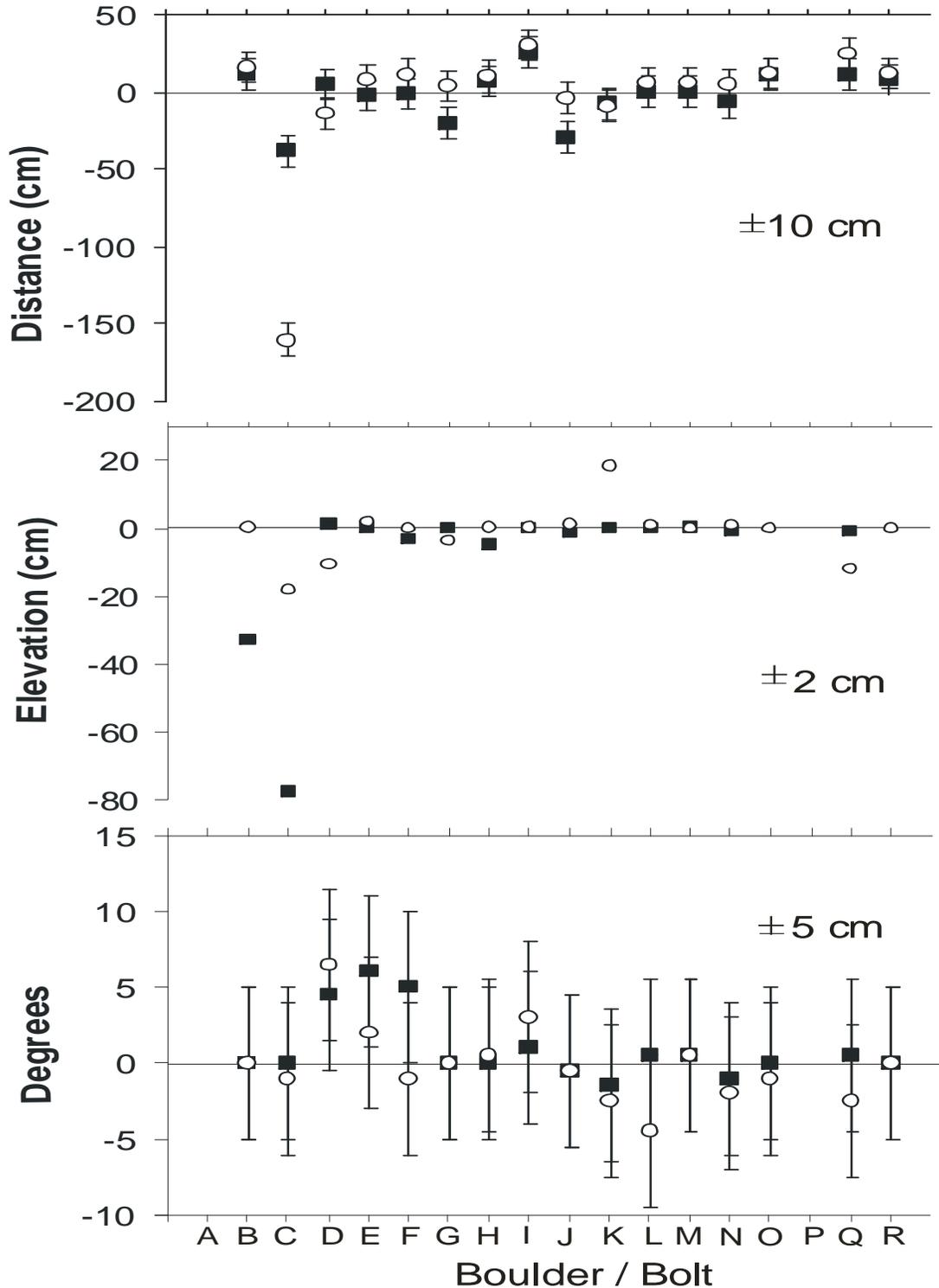


Figure 15. Movement of bolts set in boulders at the Kiukpalik Island site. Distance measurements were corrected to 1994 datum by adding 22 cm to 1999 and 2005 measurements. Filled squares = 1999 data; circles = 2005 data. Error for distance measurements =  $\pm 10$  cm. Errors for elevation measurements =  $\pm 2$  cm (error bars hidden behind symbols.) Errors in bearing estimates are  $\pm 5$  degrees.

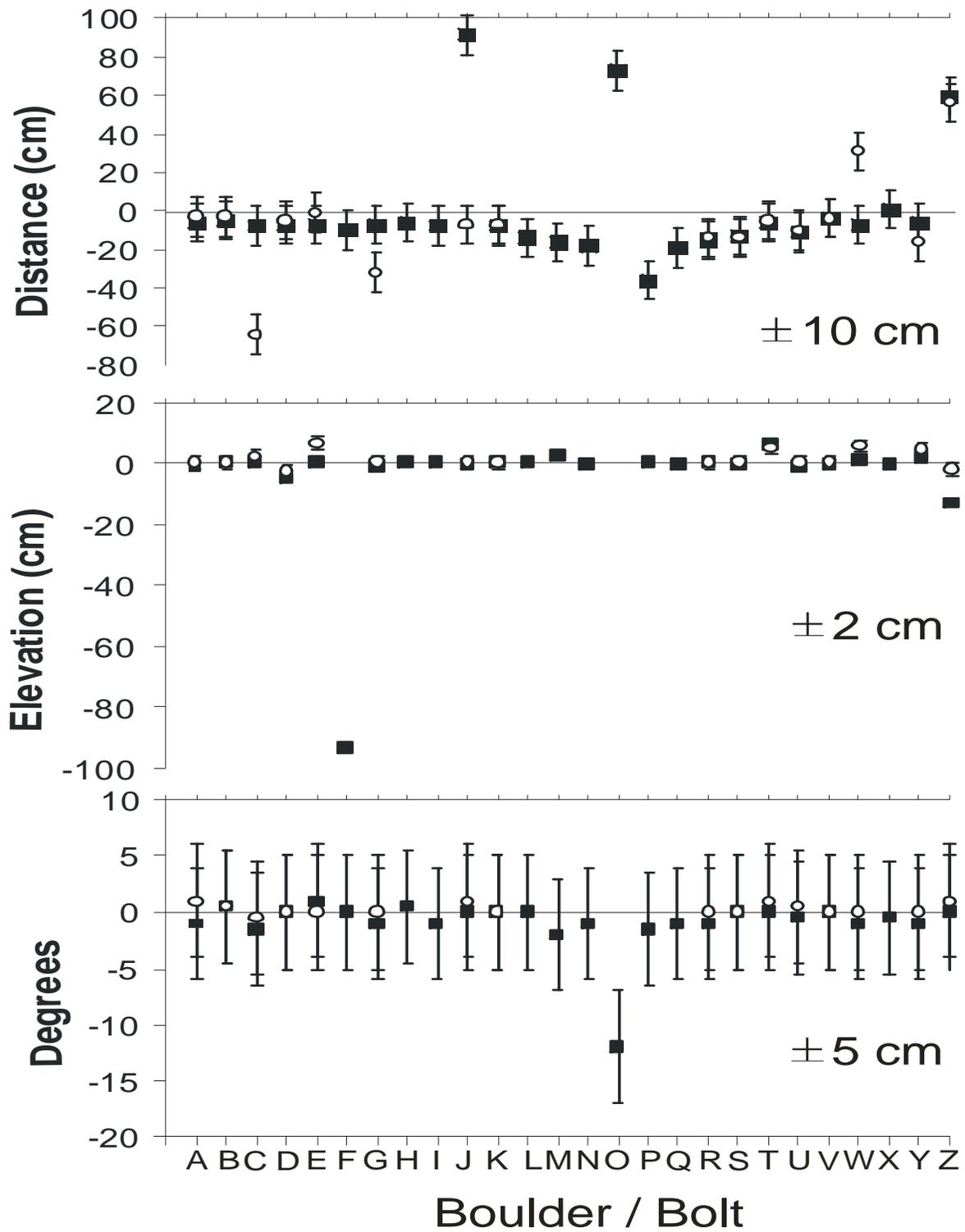


Figure 16. Movement of bolts set in boulders at the Ninagiak Island site. Filled squares = 1999 data; circles = 2005 data. Errors same as in Figure 1. Distance measurements are uncorrected.

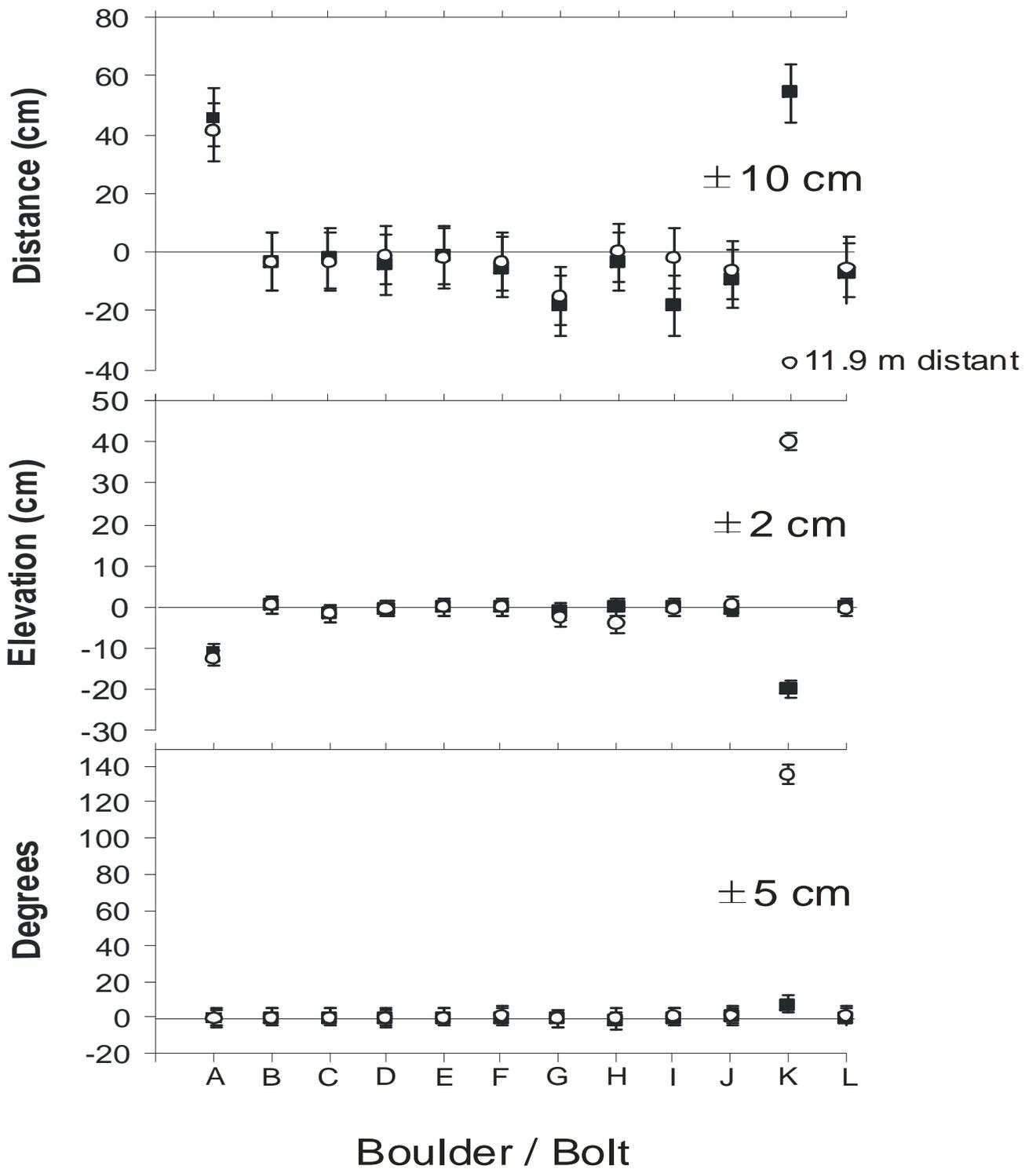


Figure 17. Movements of bolts at the Cape Gull site. Filled squares are 1999 data; open circles are 2005 data. Errors same as in Figure 14. Distance measurements are uncorrected.

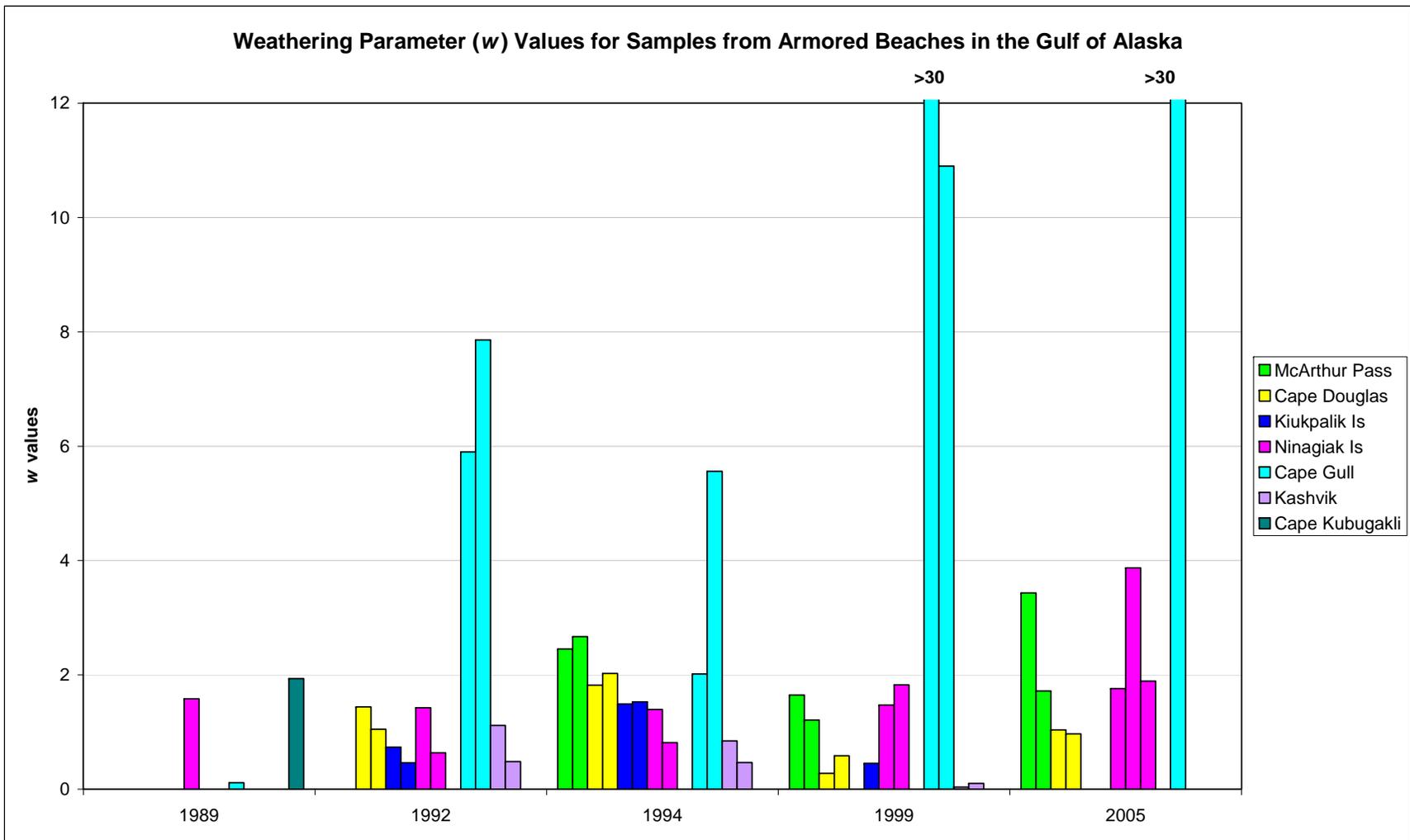


Figure 18. Weathering parameter values ( $w$ ) for subsurface oil samples from armored beaches in the Gulf of Alaska. The weathering parameter,  $w$ , is a dimensionless value that reflects the extent of first-order loss rates of PAH from the oil (Short and Heinz, 1997). Higher values reflect greater weathering along a linear scale. Samples of oil from all sites except Cape Gull demonstrate little weathering of the oil since 1989.

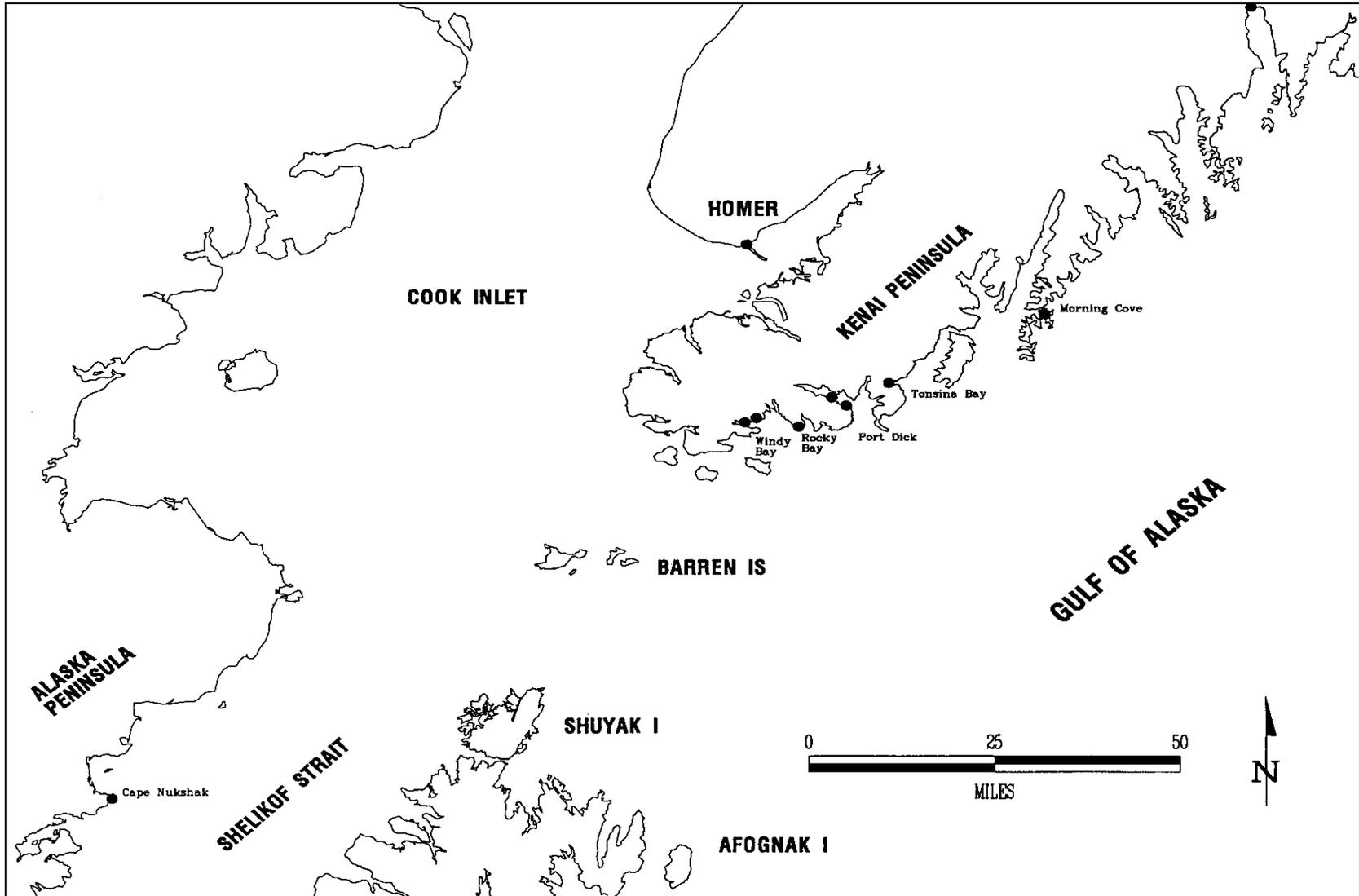


Figure 19. Mussel bed site locations in the Gulf of Alaska.

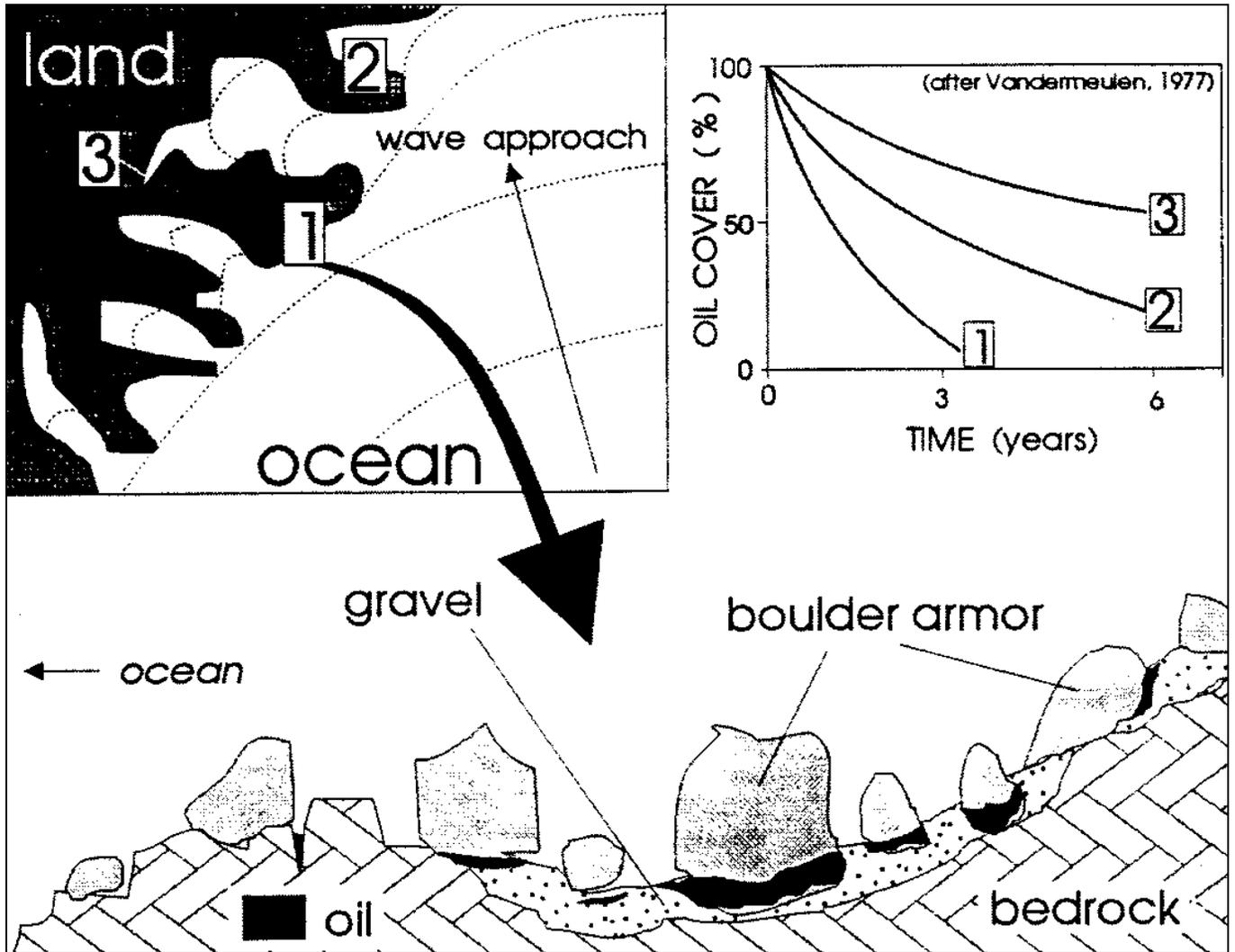


Figure 20. Surface oil persists longest on beaches with lower wave energies (upper two figures). However, results of the present study show that this may not be true for subsurface oil. Where a stable boulder armor protects gravel substrate from wave erosion, subsurface oil persists for years despite intermediate and high wave energies.

TABLE 1. Polycyclic aromatic hydrocarbons (PAHs) measured for this study.

PAHs	Abbreviation	PAHs	Abbreviation
Naphthalene	Naph	*C2 phenanthrene-anthracene	C2phenan
2-Methylnaphthalene	Menaph2	*C3 phenanthrene-anthracene	C3phenan
1-Methylnaphthalene	Menaph1	*C4 phenanthrene-anthracene	C4phenan
Biphenyl	Biphenyl	Fluoranthene	
C2 naphthalene	C2naph	Pyrene	
Acenaphthylene		C1 fluoranthene-pyrene	C1fluora
Acenaphthene		Benzo[ <i>a</i> ]anthracene	
*C3 naphthalene	C3naph	*Chrysene	Chrysene
*C4 naphthalene	C4naph	*C1 chrysene	C1chrys
Fluorene	Fluorene	*C2 chrysene	C2chrys
C1 fluorene	C1fluor	C3 chrysene	C3chrys
*C2 fluorene	C2fluor	C4 chrysene	C4chrys
*C3 fluorene	C3fluor	Benzo[ <i>b</i> ]fluoranthene	
Dibenzothiophene	Dithio	Benzo[ <i>k</i> ]fluoranthene	
*C1 dibenzothiophene	C1dithio	Benzo[ <i>e</i> ]pyrene	
*C2 dibenzothiophene	C2dithio	Benzo[ <i>a</i> ]pyrene	
*C3 dibenzothiophene	C3dithio	Perylene	
*Phenanthrene	Phenanth	Indeno[1,2,3- <i>cd</i> ]pyrene	
Anthracene	Anthra	Dibenzo[ <i>ah</i> ]anthracene	
*C1 phenanthrene-anthracene	C1phenan	Benzo[ <i>ghi</i> ]perylene	

Asterisk indicates PAHs used in the EVO weathering model (Short and Heintz, 1997) to evaluate EVO as the PAH source. Abbreviations are given for the most abundant of the analyzed PAH in weathered EVO.

TABLE 2. Surface oil cover and description of the oil in quadrats at McArthur Pass site (Segment MR-1) on 8/23/94, 7/28/99 and 8/22/05.

Quadrat	1994		1999		2005	
	%Oil Cover	Oil Description	% Oil Cover	Oil Description	% Oil Cover	Oil Description
A	25	coat with minor asphalt	2	coat with minor asphalt	0	
B	14	coat with minor interstitial asphalt	4	coat with minor interstitial asphalt	1	asphalt
C	13	coat, minor interstitial mousse	5	coat	0.5	asphalt
D	12	coat, interstitial asphalt	10	asphalt	8	
E	26	coat, minor interstitial mousse	3	asphalt	2	asphalt
F	13	coat	0.5	coat	0	
G	33	coat, asphalt	30	coat, asphalt	6	asphalt
H	17	coat, minor tar	16	coat, minor tar	6	asphalt
I	11	coat, interstitial tar	2	coat, interstitial tar	1.5	asphalt
J	12	interstitial tar, trace of coat	6	tar	0.5	
K	9	interstitial tar	5	interstitial tar, trace of coat	0	
L	12	coat, interstitial tar	6	interstitial tar, trace of coat	1	asphalt
M	22	interstitial tar, coat	4	interstitial tar, trace of coat	0.5	
N	30	interstitial tar	30	interstitial tar	8	
O	13	interstitial tar	2	interstitial tar	6	
P	12	interstitial tar	16	interstitial tar	1	asphalt
Q	15	coat, interstitial tar	18	interstitial tar, trace of coat	12	

TABLE 3. Subsurface oiling indicated by the depth of oil cover on dip stones in 1994, 1999 and 2005 on boulder-armored beaches.

Sites	Year	Max. oil depth (cm)	Mean depth (cm)	SE	n	%clean
McArthur Pass	1994	2	<b>1.4</b>	0.32	8	25
	1999	4	<b>2.4</b>	0.38	6	0
	2005	6	<b>2.1</b>	0.32	16	6
Cape Douglas	1994	9	<b>3.5</b>	0.71	19	26
	1999	>8	<b>3.7</b>	0.49	20	5
	2005	10	<b>4.6</b>	0.40	20	0
Kiukpalik Is.	1994	11	<b>4.5</b>	0.94	19	32
	1999	14	<b>5.7</b>	0.74	18	0
	2005					
Ninagiak Is.	1994	7	<b>3.5</b>	0.72	18	33
	1999	8	<b>2.1</b>	0.55	20	40
	2005	4.5	<b>3.8</b>	0.88	6	17
Cape Gull	1994	7	<b>1.6</b>	0.59	19	68
	1999	8	<b>2.3</b>	0.62	17	41
	2005	>3	<b>1.5</b>	0.41	10	40
Kashvik	1994					
	1999	8	<b>3.6</b>	0.41	15	0
	2005					

"Clean" refers to visual/olfactory absence of oil. Symbol ">" indicates that oiling condition extends below lowest part of dip stone. No sampling of Kashvik in 1994 and Kiukpalik in 2005 due to infill by sediments. Limited sampling at Ninagiak in 2005 due to infill of most of the site by sediments. Kashvik not sampled in 2005 due to severe weather constraints.

TABLE 4. Subsurface oiling described by dip stones at McArthur Pass (Segment MR-1) on 8/7/94, 7/28/99 and 8/22/05. "Clean" refers to absence of oil. List of conditions goes in stratigraphic sequence from surface downward. Symbol ">" indicates that oiling condition extends below lowest part of dip stone.

Stone Number	1994 Description of Oiling	Stone Number	1999 Description of Oiling	Stone Number	2005 Description of Oiling
94-1	clean	99-1	2 cm tar and mousse	05-1	6 cm asphalt, underlain by buried soil
94-2	1.5 cm clean, 1 cm tar, 1 cm mousse	99-2	1.5 cm tar	05-2	3 cm asphalt
94-3	>2 cm clean	99-3	3 cm tar	05-3	2 cm soft asphalt
94-4	1 cm tar	99-4	2 cm tar	05-4	2 cm soft asphalt
94-5	2 cm tar	99-5	4 cm tar	05-5	2 cm asphalt
94-6	2 cm tar	99-6	2 cm tar	05-6	1 cm asphalt
94-7	2 cm mousse			05-7	3 cm asphalt
94-8	2 cm tar			05-8	>12 cm clean
				05-9	1 cm asphalt
				05-10	2 cm asphalt
				05-11	>2 cm asphalt
				05-12	2 cm asphalt
				05-13	2 cm asphalt
				05-14	2 cm asphalt
				05-15	2 cm asphalt
				05-16	2 cm asphalt

TABLE 5. Surface oil cover, quadrat arrangement and description of oil at the Cape Douglas site (Segment CD003A) on 8/7/94, 8/8/99 and 8/16/05. Multiple values in 1999 are alternate quadrat positions necessitated by shifts in boulders/bolts. NA= Not Assessed; there may be multiple reasons why (e.g., bolt not found, boulders have moved and quadrat cannot be assessed, etc.).

Quadrat	1994		1999		2005	
	% Oil Cover	Oil Description	% Oil Cover	Oil Description	% Oil Cover	Oil Description
A	12	soft asphalt, rainbow and grey sheening	0		NA	
B	20	coat, stain, soft asphalt, grey sheen	0		0	
C	20	coat, soft asphalt, rainbow sheen	8, 2	hard asphalt	NA	
D	45	Interstitial mousse, soft asphalt, grey sheen	1	coat	18	asphalt
E	45	interstitial mousse, soft asphalt, grey sheen, coat, stain	<.05	coat	8	asphalt and gray sheen
F	20	interstitial mousse, soft asphalt, grey sheen	4	coat and asphalt	11	
G	15	coat, grey sheen	2, 5	coat	4	asphalt and gray sheen
H	45	interstitial asphalt, interstitial mousse	34	hard asphalt	16	trace of coat, hard asphalt
I	35	coat, thick interstitial mousse, soft asphalt, grey sheen	14	hard asphalt	0	
J	20	coat	0, 20	trace of coat, hard asphalt	14	trace of coat, hard asphalt
K	16	coat	3	trace of coat, hard asphalt	3	asphalt
L	40	interstitial asphalt, coat	0		NA	
M	40	coat, interstitial asphalt, rainbow sheen	22	asphalt	NA	
N	13	interstitial asphalt, coat	0		NA	
O	15	Interstitial asphalt, rainbow and grey sheen	0		0	
P	8	interstitial tar, coat	4	asphalt	2	asphalt
Q	19	coat, stain, interstitial tar, grey sheen, interstitial mousse	4	asphalt	NA	
R	12	coat, interstitial tar	3,1	coat and asphalt	0	
S	20	interstitial tar, coat, rainbow sheen, interstitial mousse	0		0	
T	16	interstitial mousse, rainbow sheen	1	coat and asphalt	0	
U	12	interstitial tar	10	coat and asphalt	0	
V	20	interstitial tar, coat	0		0	
W	9	interstitial mousse and tar	0		0	
X	8	coat	2, 4	coat	0	
Y	4	interstitial tar	0, 0.5	asphalt	0	

TABLE 6. Subsurface oiling described by dip stones at the Cape Douglas site (Segment CD003a) on 8/7/94, 8/8/99 and 8/16/05. “Clean” refers to absence of oil. List of conditions goes in stratigraphic sequence from surface downward. Symbol “>” indicates that oiling condition extends below lowest part of dip stone.

Stone Number	1994 Description of Oiling	Stone Number	1999 Description of Oiling	Stone Number	2005 Description of Oiling
94-1	2 cm mousse	99-1	4 cm mousse	05-1	>2 cm coat and mousse
94-2	3 cm mousse	99-2	2.5 cm mousse	05-2	6 cm coat and mousse
94-3	3 cm mousse	99-3	2 cm mousse	05-3	3 cm coat
94-4	3 cm mousse	99-4	1.5 cm mousse	05-4	>6 cm coat and asphalt
94-5	5 cm mousse	99-5	4.5 cm mousse	05-5	>4 cm asphalt and mousse
94-6	7 cm mousse	99-6	4 cm mousse	05-6	3 cm coat
94-7	>5 cm clean	99-7	>3 cm mousse	05-7	4 cm asphalt
94-8	>5 cm clean	99-8	2 cm mousse	05-8	>4 cm asphalt and mousse
94-9	>5 cm clean	99-9	8 cm mousse	05-9	>4 cm asphalt and mousse
94-10	>8 cm mousse	99-10	>5 cm mousse	05-10	>4 cm asphalt and mousse
94-11	>8 cm mousse	99-11	4.5 cm mousse	05-11	3 cm asphalt, 3 cm mousse
94-12	> 5 cm mousse	99-12	3.5 cm mousse	05-12	1 cm asphalt, 2 cm mousse
94-13	9 cm mousse	99-13	2 cm mousse	05-13	1 cm asphalt, >6cm mousse
94-14	>5 cm clean	99-14	5 cm mousse	05-14	1 cm asphalt, >2 cm mousse
94-15	1 cm mousse	99-15	3 cm mousse	05-15	1 cm asphalt, >3 cm mousse
94-16	2.5 cm mousse	99-16	3.5 cm mousse	05-16	2 cm asphalt, 3 cm mousse
94-17	>3 cm mousse	99-17	7 cm mousse	05-17	1 cm asphalt, >9cm mousse
94-18	7 cm mousse	99-18	>1 cm mousse	05-18	1 cm asphalt, >3 cm mousse
94-19	>5 cm clean	99-19	>8 cm mousse	05-19	1 cm asphalt, >4 cm mousse
		99-20	>5 cm clean	05-20	1 cm asphalt, >3 cm

TABLE 7. Surface oil cover and descriptions of the oil in quadrats at the Kiukpalik Island site (Segment SK-101) on 8/10/94, 8/9/99 and 8/18/05. In 2005 much of the site, including quadrats, was infilled with cobbles and boulders. NA= Not Assessed; there may be multiple reasons why (e.g., bolt not found, boulders have moved and quadrat cannot be assessed, etc.).

Quadrat	1994		1999		2005	
	% Oil Cover	Oil Description	% Oil Cover	Oil Description	% Oil Cover	Oil Description
A	28	coat	1	coat	0	
B	28	coat, interstitial tar	38	coat	NA	
C	20	stain, coat, interstitial tar, and mousse	8	stain, coat, interstitial tar, and mousse	NA	
D	38	stain, coat, interstitial tar	35	coat, asphalt	NA	coat
E	38	interstitial tar and mousse, stain, coat	2	coat	0	
F	30	stain, coat, interstitial tar	20	coat, tar	NA	
G	17	stain, coat, interstitial tar and mousse, grey sheen	33	minor coat, tar	NA	coat
H	58	coat, stain, interstitial mousse and tar	25	tar	NA	
I	36	stain, coat	4	coat, tar	NA	
J	<15		6	tar	NA	
K	14	coat, interstitial tar and mousse	6	tar	NA	
L	36	coat, interstitial tar and mousse	4	coat	NA	
M	<15		2	tar	NA	
N	12	coat, interstitial tar	6	tar	NA	
O	16	coat, interstitial tar and mousse	6	coat, tar	NA	coat
P	35	coat with spruce needles embedded	lost		NA	
Q	16	coat	8	coat	NA	
R	12	stain, coat,	1	coat	NA	

TABLE 8. Subsurface oiling described by dip stones at the Kiukpalik Island site (Segment SK- 101) on 8/8/94 and 8/9/99. In 2005, subsurface oil was not visible, hence no dip stones were sampled.

Stone Number	1994 Description of Oiling	Stone Number	1999 Description of Oiling
94-1	>10 cm clean	99-1	3 cm tar, 4 cm mousse
94-2	>10 cm clean	99-2	>2 cm mousse
94-3	>2 cm clean	99-3	3 cm tar, >5 cm mousse
94-4	>3 cm clean	99-4	2 cm tar, >6 cm mousse
94-5	> 5 cm clean	99-5	2 cm tar, >3 cm mousse
94-6	>7 cm mousse	99-6	>5 cm mousse
94-7	1 cm coat, 1 cm asphalt, >9 cm mousse	99-7	3 cm mousse
94-8	3 cm coat and mousse	99-8	2 cm tar, >8 cm mousse
94-9	1 cm of tar, >4 cm mousse	99-9	2 cm tar, >1 cm mousse
94-10	>5 cm clean	99-10	1 cm tar, >1 cm mousse
94-11	3 cm coat, 1 cm mousse	99-11	2 cm tar, >3 cm mousse
94-12	4 cm tar, >4 cm mousse	99-12	2 cm asphalt, 3 cm tar, >3 cm mousse
94-13	3 cm tar, >8 cm mousse	99-13	2 cm asphalt, 2 cm tar, 10 cm mousse
94-14	>2 cm asphalt	99-14	3 cm tar, >1 cm mousse
94-15	>2.5 cm asphalt	99-15	1 cm coat, 2 cm tar, >1 cm mousse
94-16	1 cm tar, >7 cm mousse	99-16	2 cm tar, >5 cm mousse
94-17	2 cm tar, >6 cm mousse	99-17	> 3 cm mousse
94-18	3 cm tar, >8 cm mousse	99-18	> 4 cm tar
94-19	1 cm tar, >4 cm mousse		

TABLE 9. Surface oil cover and description of the oil in quadrats at the Ninagiak Island site (Segment HB-050B) on 8/9/94, 8/10/99 and 8/19/05. NA= Not Assessed; there may be multiple reasons why (e.g., bolt not found, boulders have moved and quadrat cannot be assessed, etc.).

Quadrat	1994		1999		2005	
	% Oil Cover	Oil Description	% Oil Cover	Oil Description	% Oil Cover	Oil Description
A	37	asphalt	6	asphalt	0	
B	55	asphalt, brown mousse, rainbow sheen	10	asphalt	NA	
C	45	asphalt, brown mousse, rainbow sheen	40	asphalt	NA	
D	30	brown mousse, asphalt	8	asphalt	0	
E	28	asphalt	7	asphalt	NA	
F	21	asphalt	1	asphalt	NA	
G	12	asphalt	1	asphalt	NA	
H	27	asphalt	5	asphalt	NA	
I	28	asphalt	14	asphalt	0	
J	17	asphalt	2	asphalt	NA	
K	17	asphalt	12	asphalt	NA	
L	23	asphalt	12	asphalt	NA	
M	28	asphalt	20	asphalt	NA	
N	25	asphalt	25	asphalt	NA	
O	23	asphalt	16	asphalt	NA	
P	11	asphalt	18	asphalt	NA	
Q	13	asphalt	10	asphalt	NA	
R	37	asphalt	24	asphalt	NA	
S	23	asphalt	6	asphalt and tar	NA	
T	9	asphalt	8	asphalt	NA	
U	14	asphalt, rainbow sheen	10	asphalt	NA	
V	26	asphalt	14	asphalt	NA	
W	11	asphalt	14	asphalt	NA	
X	25	asphalt	14	asphalt	NA	
Y	18	asphalt	10	asphalt	0.5	asphalt
Z	16	asphalt	13	asphalt	13	asphalt

TABLE 10. Subsurface oiling described by dip stones at the Ninagiak Island site (Segment HB-050B) on 8/9/94, 8/10/99 and 8/19/05.

Stone Number	1994 Description of Oiling	Stone Number	1999 Description of Oiling	Stone Number	2005 Description of Oiling
94-1	>10 cm clean	99-1	>6 cm clean	05-1	0.5 cm asphalt, 4 cm mousse
94-2	3 cm clean, >1 cm mousse	99-2	>9 cm clean	05-2	1 cm asphalt, >3 cm mousse
94-3	2 cm coat, >5 cm mousse	99-3	>8 cm clean	05-3	2 cm asphalt, >2.5 cm mousse
94-4	>3 cm clean	99-4	9 cm clean, 5 cm coat, 3 cm mousse	05-4	1 cm asphalt, >2.5 cm mousse
94-5	1 cm asphalt, >5 cm mousse	99-5	>3 cm tar	05-5	1.5 cm asphalt, 5 cm mousse
94-6	4 cm tar, >3 cm mousse	99-6	1 cm clean, >2 cm mousse	05-6	12 cm clean
94-7	>3 cm mousse	99-7	>5 cm clean		
94-8	>2 - 7 cm mousse	99-8	>8 cm clean		
94-9	1 cm asphalt, 6 cm mousse	99-9	>5 cm clean		
94-10	>8 cm clean	99-10	>4 cm clean		
94-11	1 cm asphalt, >5 cm mousse	99-11	>2 cm asphalt		
94-12	>5 cm clean	99-12	>2 cm mousse		
94-13	>5 cm clean	99-13	12 cm clean, >2 cm mousse		
94-14	1 cm asphalt, 5 cm mousse	99-14	2 cm tar, 8 cm clean, >5 cm mousse		
94-15	1 cm clean, 1 cm asphalt, 2 cm mousse	99-15	2 cm clean, 2 cm coat, >4 cm mousse		
94-16	>3 cm mousse	99-16	2 cm asphalt, 2 cm mousse		
94-17	>11 cm clean	99-17	2 cm asphalt		
94-18	1 cm clean, 7 cm mousse	99-18	>5 cm clean		
		99-19	1 cm clean, >2 cm mousse		
		99-20	2 cm clean, 3 cm mousse		

TABLE 11. Surface oil cover and oil description in quadrats at the Cape Gull site (Segment K 0922-CG 001) on, 8/10/94, 8/10/99 and 8/21/05.

Quadrat	1994		1999		2005	
	% Oil Cover	Oil Description	% Oil Cover	Oil Description	% Oil Cover	Oil Description
A	11	asphalt	0	asphalt	0	
B	24	asphalt	1	asphalt	0	
C	11	asphalt	0	asphalt	0	
D	18	asphalt	0	asphalt	0	
E	12	asphalt	0	asphalt	0	
F	15	asphalt	20	asphalt	3	asphalt with shells
G	30	asphalt	19	asphalt	9	asphalt with shells
H	14	asphalt	6	asphalt	0	
I	12	asphalt	14	asphalt	0	
J	14	asphalt	15	asphalt	2	asphalt with shells
K	18	asphalt	10	asphalt	2	
L	14	asphalt	6	asphalt	0.5	asphalt with shells

TABLE 12. Subsurface oiling described by dip stones at the Cape Gull site (Segment K 0922-CG 001) on, 8/10/94, 8/10/99 and 8/21/05.

Stone Number	1994 Description of Oiling	Stone Number	1999 Description of Oiling	Stone Number	2005 Description of Oiling
94-1	>3 cm clean	99-1	>6 cm clean	05-1	>4cm clean
94-2	5 cm asphalt	99-2	>12 cm clean	05-2	>8 cm clean
94-3	>6 cm clean	99-3	>16 cm clean	05-3	>5 cm clean
94-4	7 cm mousse	99-4	>5 cm clean	05-4	2.5 cm shell mousse
94-5	>5 cm clean	99-5	6 cm asphalt	05-5	2 cm asphalt
94-6	>10 cm clean	99-6	1 cm tar, 8 cm asphalt	05-6	>2 cm shell mousse
94-7	>6 cm clean	99-7	2 cm tar	05-7	>2 cm shell mousse
94-8	>11 cm clean	99-8	2 cm mousse	05-8	>14 cm clean
94-9	>5 cm clean	99-9	>8 cm clean	05-9	3 cm shell asphalt
94-10	1 - 3 cm mousse	99-10	3.5 cm asphalt	05-10	> 3 cm shell asphalt
94-11	1 - 3 cm mousse	99-11	1 cm coat, 2.5 cm mousse		
94-12	0 - 1 cm clean, 3 - 9 cm mousse	99-12	>7 cm clean		
94-13	>4 cm clean	99-13	3 cm asphalt		
94-14	2 cm asphalt, 3 cm mousse	99-14	4 cm asphalt		
94-15	>4 cm clean	99-15	3 cm coat		
94-16	>3 cm clean	99-16	>3 cm coat		
94-17	>8 cm clean	99-17	>11 cm clean		
94-18	>2 cm clean				
94-19	>3 cm clean				

TABLE 13. Subsurface oiling described by dip stones at the Kashvik Bay site (Segment KA-002) on 8/12/99. Dip stones could not be sampled in 1994 due to infilling of the site with cobbles, and the site could not be sampled in 2005 due to storm systems.

Stone Number	1999 Description of Oiling
99-1	5 cm mousse
99-2	2 cm tar, 2 cm mousse
99-3	1 cm tar, 1 cm mousse
99-4	3 cm mousse
99-5	8 cm mousse
99-6	2 cm mousse
99-7	4 cm mousse
99-8	2 cm mousse
99-9	2 cm mousse
99-10	4 cm mousse
99-11	4 cm mousse
99-12	1 cm tar, 2 cm mousse
99-13	1 cm tar, 2 cm mousse
99-14	3 cm tar
99-15	5 cm mousse

TABLE 14. Total polycyclic aromatic hydrocarbon (TPAH) concentrations and weathering parameter (*w*) for sediment samples from Gulf of Alaska armored beaches. Concentrations for TPAH are given as mg TPAH/g dry sample weight. Weathering parameter values are dimensionless (Short and Heintz, 1997), with increasing values corresponding to greater weathering. Symbol “\*” indicates values that were estimated because extensive weathering caused the more volatile PAH to be below method detection limits, so weathering extent had to be estimated on the basis of the PAH that remained detectable. Two sediment samples generally were taken from each monitoring site during sampling events.

Location	#	1989			1992			1994			1999			2005		
		TPAH (mg/g)	<i>w</i>	MSE	TPAH (mg/g)	<i>w</i>	MSE	TPAH (mg/g)	<i>w</i>	MSE	TPAH (mg/g)	<i>w</i>	MSE	TPAH (mg/g)	<i>w</i>	MSE
McArthur Pass	A						0.513	<b>2.453</b>	0.136	0.312	<b>1.648</b>	0.246	0.506	<b>3.433</b>	0.160	
	B						1.993	<b>2.671</b>	0.350	1.230	<b>1.210</b>	0.106	0.505	<b>1.719</b>	0.139	
Cape Douglas	A				0.515	<b>1.442</b>	0.162	3.517	<b>1.819</b>	0.145	1.807	<b>0.277</b>	0.141	3.371	<b>1.039</b>	0.103
	B				0.832	<b>1.049</b>	0.149	3.430	<b>2.025</b>	0.161	0.311	<b>0.583</b>	0.235	2.501	<b>0.969</b>	0.091
Kiukpalik Is	A				1.237	<b>0.739</b>	0.137	2.838	<b>1.492</b>	0.130	1.697	<b>-0.056</b>	0.123			
	B				2.798	<b>0.464</b>	0.182	2.747	<b>1.527</b>	0.101	1.208	<b>0.453</b>	0.102			
Ninagiak Is	A	2.995	<b>1.583</b>	0.163	1.095	<b>1.424</b>	0.115	2.119	<b>1.393</b>	0.276	1.184	<b>1.473</b>	0.074	1.644	<b>1.761</b>	0.095
	C				2.211	<b>0.637</b>	0.204	2.371	<b>0.817</b>	0.167	0.395	<b>1.825</b>	0.129	1.031	<b>3.873</b>	0.089
	B													1.540	<b>1.890</b>	0.130
Cape Gull	A	3.199	<b>0.114</b>	0.230	0.260	<b>5.903</b>	0.296	0.341	<b>2.016</b>	0.061	0.009	<b>&gt;30.00*</b>		ND		
	B				0.291	<b>7.858</b>	0.454	0.364	<b>5.562</b>	0.071	0.075	<b>10.90*</b>		0.006	<b>&gt;30.00*</b>	
Kashvik	A				0.577	<b>1.117</b>	0.109	1.811	<b>0.844</b>	0.215	0.630	<b>0.036</b>	0.084			
	B				4.000	<b>0.486</b>	0.142	3.092	<b>0.468</b>	0.204	0.784	<b>0.103</b>	0.160			
Cape Kubugakli		2.831	<b>1.934</b>	0.334												
<b>Exxon Valdez oil collected in Prince William Sound, 11 days post spill</b>																
Smith Island		10.849	<b>0.870</b>	0.091												
Snug Harbor		15.064	<b>0.884</b>	0.086												
Bay of Isles		17.477	<b>0.229</b>	0.132												

Table 15. Total polycyclic aromatic hydrocarbon (TPAH) concentrations and weathering parameter ( $w$ ) for samples from oiled mussel beds taken in 1999 and 2005. Concentrations for TPAH are given in nanograms/gram and are computed on a dry weight basis. MSE: Mean Square Error of fit to weathered *Exxon Valdez* oil (cf. Short & Heintz, 1997). Sample wet and dry weight units are given in grams. Weathering parameter ( $w$ ) values are dimensionless (ibid.), with increasing values corresponding to greater weathering. TPAH values that are italicized are too low to determine  $w$  values; bold values are borderline fits for weathered *Exxon Valdez* oil caused by very low PAH concentrations [TPAH <55 ng/g], however they are almost certainly *Exxon Valdez* oil. Segment numbers refer to shoreline identification numbers assigned by the *Exxon Valdez* Interagency Shoreline Cleanup Committee.

Site-Sample	Segment Number	Sample Type	1999					2005				
			Dry Weight (g)	Wet Weight (g)	TPAH (ng/g)	MSE	$w$	Dry Weight (g)	Wet Weight (g)	TPAH (ng/g)	MSE	$w$
Morning Cove-1	PY008B-1	Mussel	0.98	9.28	67	0.325	6.634	0.66	8.42	<b>88</b>		
	PY008B-1	Sediment	0.9	1.26	4926	0.165	0.909	7.11	9.97	<i>120</i>		
Morning Cove-2	PY008B-2	Mussel	1.2	9.33	124	0.214	3.131	0.72	8.88	856	1.134	4.93
	PY008B-2	Sediment	0.74	1.05	5301	0.093	1.424	0.012	0.016	519000	0.097	1.87
Camp Beach	TB002A	Mussel	0.82	9.59	<i>4</i>			0.59	8.27	<i>0</i>		
	TB002A	Sediment	10.8	13.11	<b>42</b>	0.909	4.860	7.9	10.08	<i>0</i>		
Otter Beach	TB003A-4	Mussel	0.75	9.38	<i>2</i>			0.47	8.12	<i>34</i>		
	TB003A-4	Sediment	2.62	3.22	4857	0.221	2.347	7.82	9.62	<i>0</i>		
Windy Bay	WB002D-2	Mussel	1.66	10.09	<i>16</i>							
	WB002D-2	Sediment	12.24	14.89	<b>53</b>	1.254	8.087					
Port Dick	PD004A	Mussel	0.78	9.97	<i>1</i>							
	PD004A	Sediment	0.64	0.97	17925	0.090	2.652					