NOAA Technical Memorandum NOS OR&R 2

PAVEMENT IN PATAGONIA, ASPHALT IN ALASKA:

Case Studies in Oil Spill Pavement Formation, Fate, and Effects

Seattle, Washington

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NOTICE

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Plate iii. Panoramic view of Punta Espora backbeach showing extent of asphalt pavement from the *Metula* spill. Digital composite of photographs by G. Shigenaka.

INTRODUCTION

Large oil spills are not necessarily the long-term environmental disasters that initial images from affected areas may suggest. However, they typically cause substantial short-term damage and certainly can impact living resources such as wildlife in significant and visceral ways. As a result, there are strong pressures to clean up as much spilled oil as practical or affordable. Rarely is a large spill left in place to degrade naturally.

On August 9, 1974, the very large crude carrier (VLCC) *Metula* grounded inside the First Narrows in the Strait of Magellan, Chile. The ship was carrying a cargo of ~1.4 million barrels (bbl) of Light Iranian Crude Oil, as well as a lesser amount of Bunker C oil. Between August and October 1974, an estimated 415,000 bbl of oil (400,000 bbl crude and 15,000 bbl Bunker C) were spilled into the Strait of Magellan (Owens and Robson 1987, NOAA 1992). There were no attempts to contain or disperse the released oil, and no organized shoreline cleanup operations took place. As such, this incident represents a rare opportunity to study the fate and effects of a large petroleum release into the environment without the interpretive complications contributed by cleanup effects.

At the opposite end of the response spectrum was the *Exxon Valdez* spill in Prince William Sound, Alaska. On March 24, 1989, the fully loaded T/V *Exxon Valdez* grounded on Bligh Reef outbound from the Alyeska Terminal facility in Valdez. The vessel released an estimated 10.8 million gallons (~260,000 bbl) of North Slope crude oil into a remote and biologically rich environment. The spill was the largest in U.S. waters, and subsequently resulted in the largest, most expensive cleanup operation ever mounted.

These two incidents were starkly different and yet shared common attributes. The similarities and differences provide some lessons for future spill response and for understanding the long-term behavior of oil in the subarctic marine environment. The Hazardous Materials Response and Assessment Division (HAZMAT) of the National Oceanic and Atmospheric Administration (NOAA) has closely monitored conditions in Prince William Sound in the aftermath of the *Exxon Valdez* spill. However, for obvious reasons of geographic distance and remoteness, the *Metula*-affected region has not been extensively studied by spill researchers in the Northern Hemisphere.

The Punta Espora region along the Strait of Magellan in Patagonia was visited by a member of the NOAA *Exxon Valdez* monitoring team on February 11, 1995. This area had been identified by many previous researchers as the most heavily impacted portion of the shoreline oiled by the *Metula* spill. Variously designated as "station MT-" by Blount (1978), and "Puerto Espora" by Owens and Robson (1987) and Baker et al. (1993), the Punta Espora area (Figure 1) encompasses several shoreline and habitat types, including a highly impacted coastal marsh. An original objective of the 1995 revisit was to document conditions at at least two different habitat types. Unfortunately, unforeseen logistical complications precluded assessment of conditions in the marsh area of Punta Espora and the revisit described here focused only on that part of the shoreline called the "backbeach" area by Owens and Robson (1987) and Owens et al. (1987). This section of shoreline is a gravel beach very protected from direct exposure to the Strait of Magellan by a spit. Large amounts of oil initially stranded on the beach, and over time formed a highly persistent asphalt "pavement".

NOAA/HAZMAT has traditionally supported revisiting the sites of previous oil spills to assess long-term consequences, and this was the reason for the trip to Punta Espora. Goals for the revisit included:

- Comparison of 1995 conditions with those previously documented between 1975 and 1993.
- Repetition of 1977 and 1987 photographs taken by Owens and Robson (1987).
- Collection of Global Positioning System data for the Punta Espora site.
- Collection of residual oil samples to be analyzed by GC/MS and interpreted within the framework of long-term weathering trends and comparisons to oil residues from other spills.
- Comparison of observed conditions at the *Metula* spill site with those in the region affected by *Exxon Valdez*.

The area in Prince William Sound, Alaska, chosen for comparison to Punta Espora was located at the head of an embayment on the southeastern side of Knight Island, a region of heavy initial impact. The embayment—Snug Harbor—contained three sections of shoreline designated as "set-aside" sites (oiled areas where virtually no cleanup activity was sanctioned). One of these set-aside shorelines was highly protected from wave exposure and included a gravel beach where oil stranded high in the intertidal zone, forming a pavement of oil and sediment. This location (Figure 2) has been visited regularly by NOAA scientists since 1990.

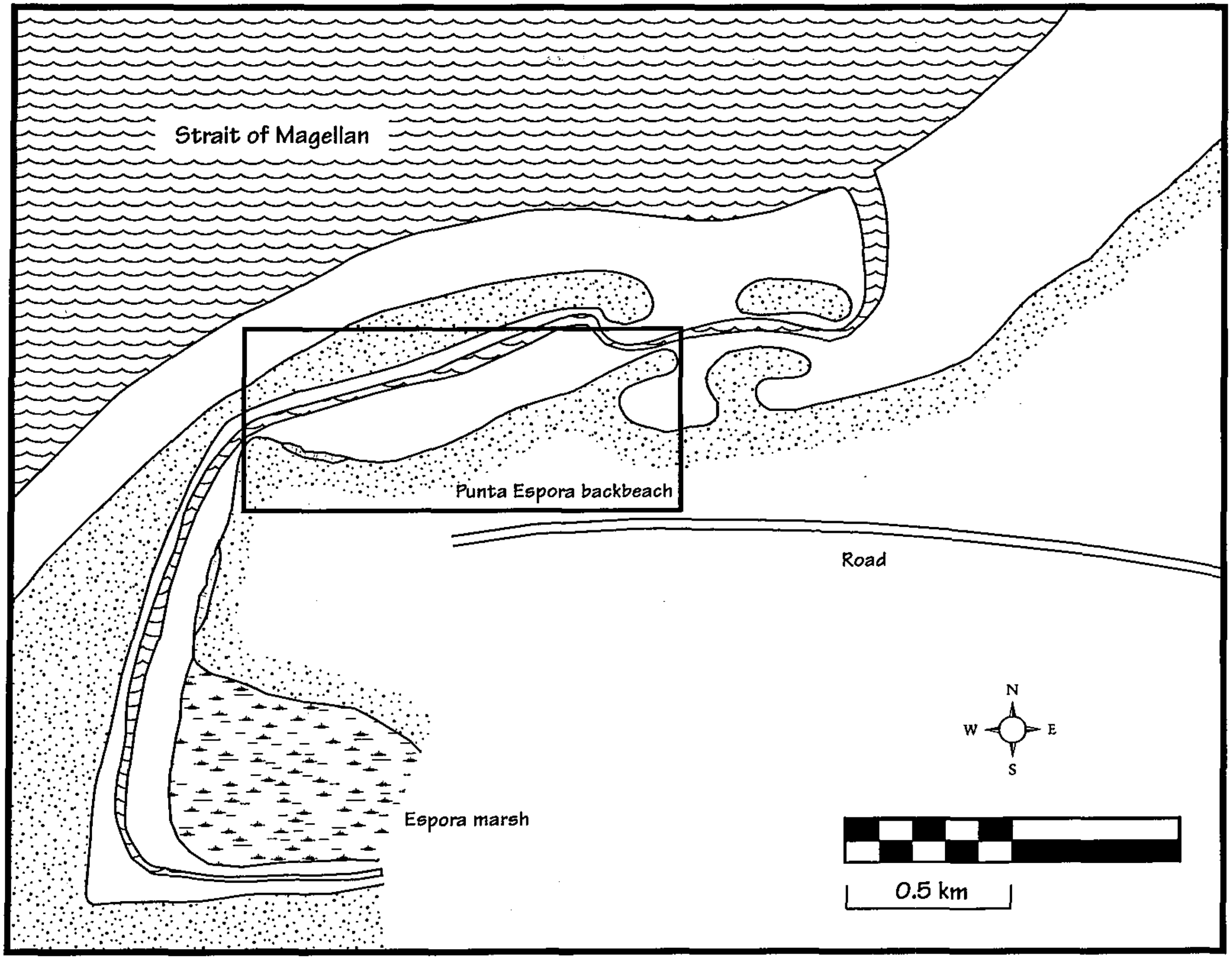


Figure 1. The *Metula* Punta Espora study area. Enclosed portion shows "backbeach" documented in text and photographs and enlarged as Figure 2. Adapted from diagram by Owens and Robson (1987).

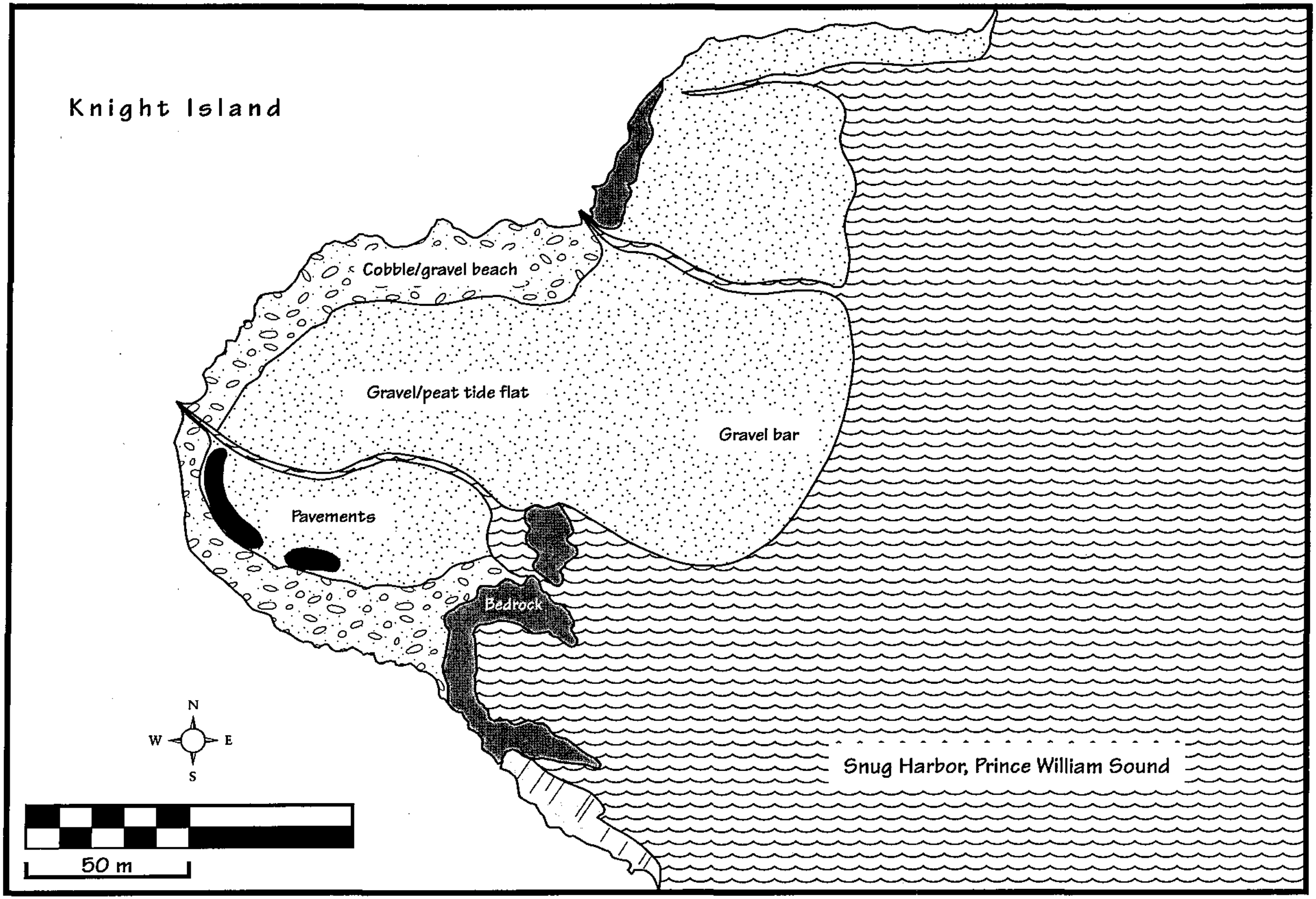


Figure 2. The *Exxon Valdez* Snug Harbor study area, showing approximate location of asphalt pavements during August 1990, shoreline survey. Based on original sketch map by D. Orvis dated August 19, 1990.

The site of the *Metula* spill was studied by a number of researchers, especially in the first 3 years following the incident. Both the physical impacts as well as biological effects were documented in some detail. However, as might be obvious or expected, the level of research scrutiny for this spill did not begin to approach that for the *Exxon Valdez*. Nonetheless, the reports of investigators provide excellent documentation of conditions. See, for example, Blount (1978), Straughan (1981), Baker et al. (1976), and Owens and Robson (1987).

The details of the *Exxon Valdez* spill and its impacts have been described in sometimes excruciating detail, and will not be elaborated here except to provide background information and introduce relevant specifics. In general, it is sufficient to say that the scale of the spill and the area affected were unprecedented, and the response and subsequent cleanup activities were extraordinarily complex and frequently beset by practical and bureaucratic inefficiencies. Retrospective "final report" by the state and federal government agencies most extensively involved in the *Exxon Valdez* reflect the complexity and scale of operations: The State report (Piper 1993) is 184 pages long while the federal report (U.S. Coast Guard [USCG] 1993) is a comparative two-volume behemoth of nearly 1600 pages.

METULA: Initial Impacts

Because the initial release occurred quite close to the shoreline of the Strait of Magellan (~2–3 kilometers [km] offshore), it beached quickly—within 2 to 4 hours. According to Hann (1977), a layer of oil/water emulsion covered nearly 75 km of shoreline. The oiled areas measured 15 to 25 meters (m) across with oil (emulsion) depths of 2 to 4 centimeters (cm). Initial biological impacts were characterized by Hann as smothering of some organisms, oiling of waterfowl, and substrate changes that made the intertidal environment uninhabitable by biota such as limpets. Some of the oil was eventually refloated and carried away by the tide, and some was buried or incorporated into beach sediments.

There was virtually no effort to recover the spilled product. Hann (1977) noted that the rationale for the lack of organized effort was based on the presumption that most of the oil would be carried out to the open ocean by currents and that the remote location of the spill makes the costs of response there prohibitive. Blount (1978) elaborated and expanded the list of reasons:

No attempt was made to control or clean up the oil on the water or the beaches for several reasons: 1) there was some question as to who was legally and financially responsible for such an operation, 2) the amount and lateral extent of the pollution, as well as potential environmental damage caused by the spill, were not immediately known, 3) cleanup equipment and skilled manpower were not readily available in such a remote location, and 4) strong winds, tidal currents and wave activity plus shoreline inaccessibility would have made cleanup operations a logistical nightmare.

EXXON VALDEZ: Initial Impacts

The grounding of the *Exxon Valdez* on March 24, 1989, was followed by the rapid release of ~258,000 bbl of crude oil into Prince William Sound. An additional 1 million bbl were lightered from the crippled tanker. Although mobilization for response and cleanup began almost immediately, the remote location of the spill and a shortage of locally available equipment hampered early efforts at containment and recovery. On March 26, severe storms spread the spilled oil over a much greater geographic area as noted in the US CG Federal On-Scene Coordinator's (FOSC) report (USCG 1993):

> The storm that began on 26 March for all purposes closed the "window of opportunity" for an efficient and effective floating oil cleanup operation. The changes in characteristics of the oil after the storm were profound. What had been a somewhat cohesive slick of fresh oil became widely dispersed patches of mousse and sheen.

By March 30, the leading edge of the oil had advanced through and out of Prince William Sound and into the Gulf of Alaska. By mid-May, shorelines nearly 900 km to the southwest from the grounding site were impacted. At the peak of cleanup activity in the summer of 1989, more than 11,000 workers, 1400 vessels, and 80 aircraft were involved (USCG 1993).

METHODS

Punta Espora site permit

Permission to visit the Punta Espora site and collect samples was obtained through the Hydrographic and Oceanographic Service of the Chilean Navy in Valparaiso.

Position information

Global Positioning System (GPS) information was collected using a Garmin GPS 45 MultiTrac8 receiver. Position accuracy for this unit is nominally rated at 100 m with signal degradation under the U.S. Department of Defense Selective Availability Program.

Photography

Photographs were taken using an Olympus OM-4 35-millimeter (mm) camera in aperture-priority auto mode and Kodak Ektachrome 400 film. Zuiko lenses (50mm f1.4, 50mm f3.5, and 21mm f3.5) were used.

Chemistry collections

Samples of asphalt were collected on both east and west sides of a large concrete block that defined the approximate midpoint of a large, contiguous asphalt patch. Collections were made within 5 m of the block by breaking off pieces on the leading (landward) edge, wrapping in solvent-cleaned aluminum foil, and bagging in ziplock-type plastic bags. Surgical gloves were worn during sampling. Once the samples had been returned to the United States, they were stored frozen until analyzed by GC/MS and gravimetric total petroleum hydrocarbon (TPH).

In Prince William Sound, samples of pavement were collected along the seaward edge of the northern end of the patch. Samples were packaged in the same manner as described above for the *Metula* site and stored frozen until analyzed.

Sample Analysis

All pavement samples were analyzed by the Institute for Environmental Studies at Louisiana State University using the methods of Henry and Overton (1993) summarized in Appendix A. Table 1 identifies the target compounds. Quantification was accomplished by an internal standard method using naphthalene-d8, anthracene-d10, chrysene-d12, and perylene-d12. All parent (nonalkylated aromatic) hydrocarbons, except naphthobenzothiophenes, were quantified using authentic standards. Naphthobenzothiophenes were quantified using a response factor derived from dibenzothiophene, and the absolute values reported should be interpreted as only semiquantative. All alkylated aromatic hydrocarbon homologues were quantified using response factors derived from their nonalkylated parent compounds.

Table 1. Target hydrocarbon compounds quantified by GC/MS in the pavement study.

Compound	Abbreviation in Figures	Ion Mass
alkanes* (nC-10 through nC-31)		85
decalin*		138
C-1 decalin*		152
C-2 decalin*		166
C-3 decalin*		180
naphthalene	NAPHTHALENE	128
C-1 naphthalenes	C-1 NAPH	142
C-2 naphthalenes	C-2 NAPH	156
C-3 naphthalenes	C-3 NAPH	170
C-4 naphthalenes	C-4NAPH	184
fluorene	FLUORENE	166
C-1 fluorenes	C-1 FLU	180
C-2 fluorenes	C-2 FLU	194
C-3 fluorenes	C-3 FLU	208
dibenzothiophene	DIBENZOTHIOPHENE	184
C-1 dibenzothiophenes	C-1 DBT	198
C-2 dibenzothiophenes	C-2 DBT	212
C-3 dibenzothiophenes	C-3 DBT	226
phenanthrene	PHENANTHRENE	178
C-1 phenanthrenes	C-1 PHEN	192
C-2 phenanthrenes	C-2 PHEN	206
C-3 phenanthrenes	C-3 PHEN	220
naphthobenzothiophene	NAPHTHOBENZOTHIOPHENE	234
C-1 naphthobenzothiophenes	C-1 NBTP	248
C-2 naphthobenzothiophenes	C-2 NBTP	262
C-3 naphthobenzothiophenes	C-3 NBTP	276
fluoranthrene	FLUORANTHENE	202
pyrene	PYRENE	202
C-1 pyrenes	C-1 PYR	216
C-2 pyrenes	C-2 PYR	230
chrysene	CHRYSENE	228
C-1 chrysenes	C-1 CHRY	242
C-2 chrysenes	C-2 CHRY	256
benzo(b)fluoranthene	BENZO(b)FLUORANTHENE*	252
benzo(k)fluoranthene	(BENZO(b)FLUORANTHENE*)	252
benzo(e)pyrene	BENZO(e)PYRENE	252
benzo(a)pyrene	BENZO(a)PYRENE	252
perylene	PERYLENE	252
indeno(1,2,3-cd)pyrene	INDENO(1,2,3-cd)PYRENE	276
dibenzo(a,h)anthracene	DIBENZO(a,h)ANTHRACENE	278
benzo(g,h,i)perylene	BENZO(g,h,i)PERYLENE	276

*benzo(k)fluoranthene quantified with benzo(b)fluoranthene.

Grain-Size Analysis

Approximately 0.5 kilograms (kg) of sediment was serially extracted to remove all oil. Filters were used to ensure that no sediment fines were lost in transfer of the solvent extract. The extract was discarded and the sample substrate was dried. Grain-size was determined by a serial sieving method. Each sieved fraction was weighed and the values normalized to percentages.

OBSERVATIONS AND RESULTS

Site locations

Metula Punta Espora

Selected GPS latitude and longitude data for the surveyed area as follows (refer to Figures 1 and 3):

Waypoint A: West end of asphalted area
59° 28.83' S
69° 28.71' W

Waypoint B: At large concrete block, approximate midpoint of asphalted area
59° 28.79' S
69° 28.50' W

Waypoint C: East end of asphalted area
59° 28.71' S
69° 28.34' W

GPS data verified that the large concrete block (waypoint B) was located approximately midway between the east and west edges of the contiguous asphalted area. The distance between points A and B, and between points B and C, was 240 m. Because the distance between points A and C defines the length of the contiguous asphalt patch on the beach, this was estimated to be ~0.5 km. The width of the asphalted area was difficult to determine because its lower margin was not well defined and graded into muddier substrate at the edge of the stream. For much of the asphalt, width was estimated at ~5 m.

The pavement itself was nearly impervious and was difficult to collect using standard oil sampling methods. Collection of core samples was not possible with the equipment available due to the substrate hardness.

Exxon Valdez, Snug Harbor

Exxon documents (Silbert and Maki 1989) list the latitude and longitude of the Snug Harbor study site as 60° 15′ 52.19″ N, 147° 45′ 28.51″ W. An existing NOAA monitoring site close to the beach in question and located ~0.5 km away from the silbert and Maki site has been documented by GPS at 60° 15′ 43″ N, 147° 45′ 57″ W.

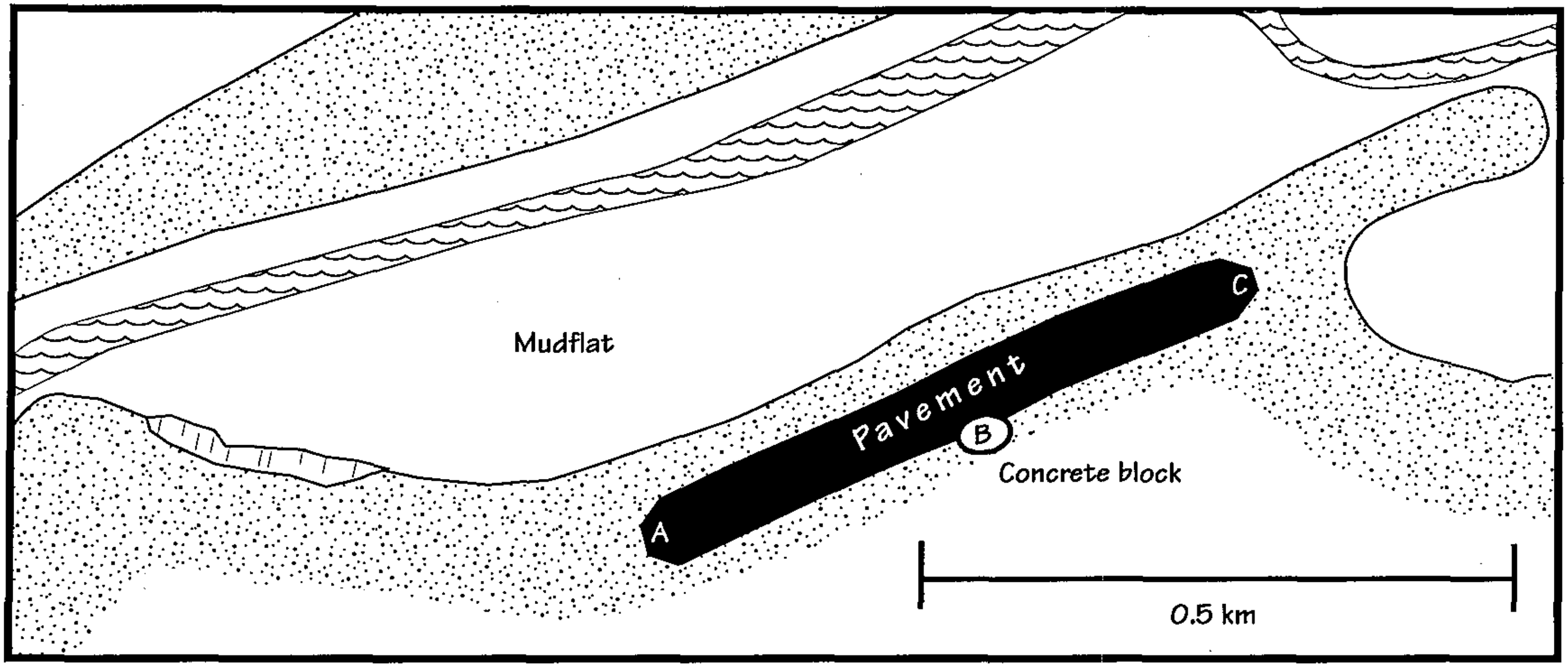


Figure 3. Detail of *Metula* Punta Espora study site, showing approximate location of pavement and GPS waypoints discussed in text.

Biological observations

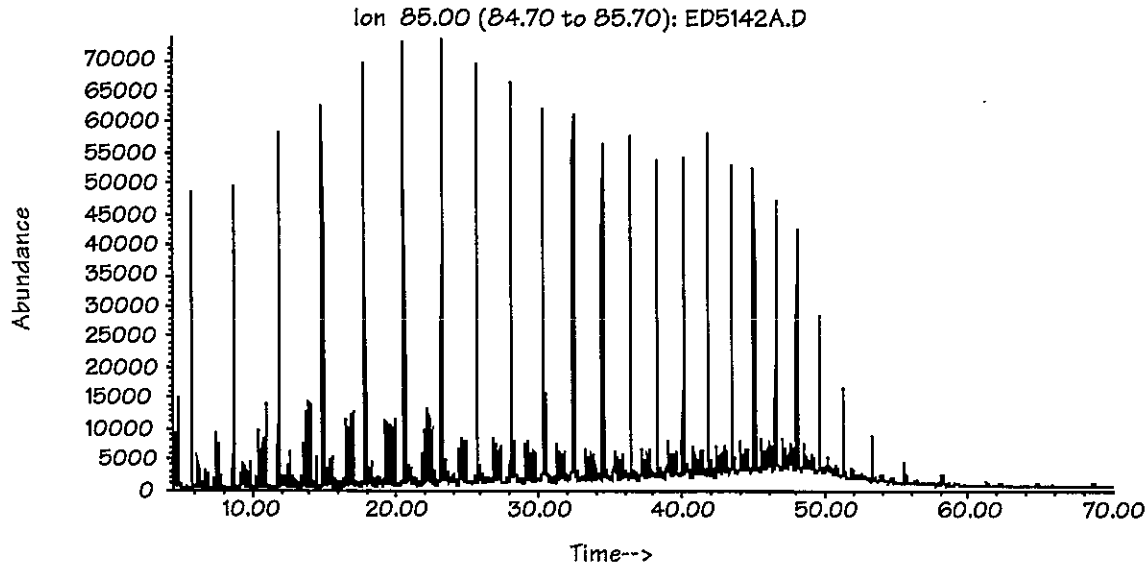
In both study areas, biological communities in the immediate vicinity of the pavements were sparse, probably due to the high elevation in the intertidal for both occurrences. Algal communities were the most prevalent in the upper intertidal/supratidal portion of the Punta Espora backbeach studied. The dominant plant in the area affected by the pavement was the pickleweed or glasswort, (*Salicornia ambigua*).Lower in the intertidal, on the adjacent mudflat, the green alga *Ulothrix flacca* was very much in evidence. No epifauna or other attached macrobiota were observed on the pavement itself.

The pavement in Snug Harbor bordered the supratidal, and the upper edge of the material lies at the upper edge of the beach. As such, there were few intertidal macrobiota. American dunegrass, *Elymus mollis*, was found immediately above the pavement and to some extent (as discussed below) growing into its leading edge.

Chemistry and grain-size results

Figure 4 compares the alkane chromatographic profiles (m/z 85) of an Arabian Light crude oil and the *Metula* hexane extract. The *Metula* samples reflected extensive alteration by physical and biological processes of degradation: The GC trace of the heavily weathered pavement exhibited little or no alkane profile remaining and only trace levels of aromatic hydrocarbons.

Figure 5 compares the relative concentration of asphaltenes with total extractable petroleum hydrocarbons. The two pavements from the *Metula* site (Espora 1 and Espora 2) are significantly lower in percent oil than the samples collected at the *Exxon Valdez* site (Snug 1 and Snug 2). The average concentration of extractable petroleum hydrocarbons in the *Metula* pavements was only 1.6%, compared with a mean of 31% at the *Exxon Valdez* site. The percent asphaltenes follow a similar trend 0.36% compared with 7.3%. The *Exxon Valdez* pavement contained 20 times the oil extracted from the *Metula* pavement samples.



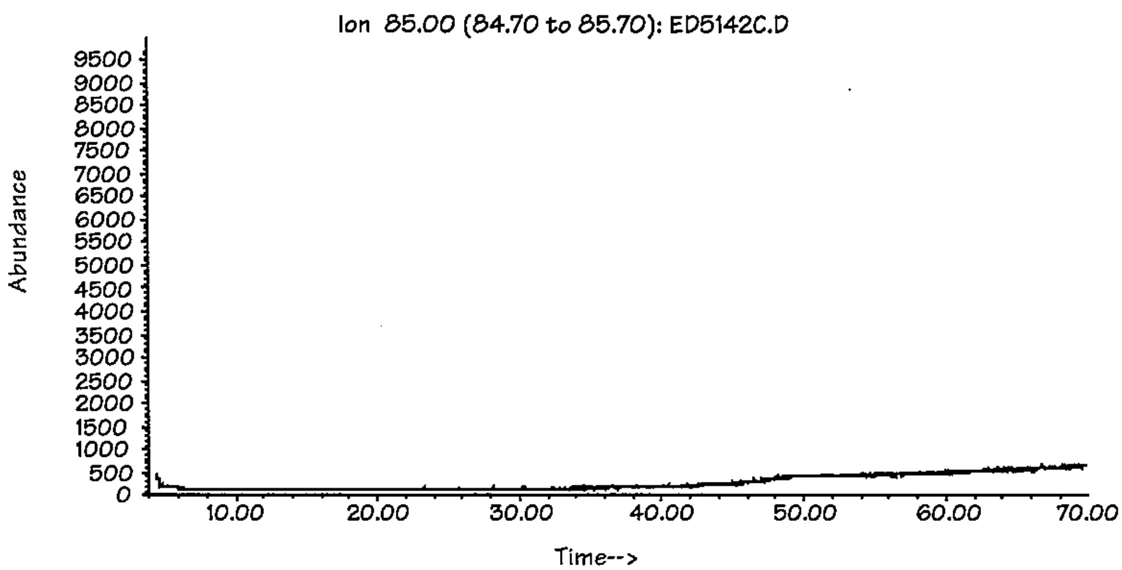


Figure 4. Comparison of the alkane chromatographic profile (m/e 85) for unweathered Arabian Light crude oil (top) and a pavement sample collected at the *Metula* Punta Espora spill site (bottom).

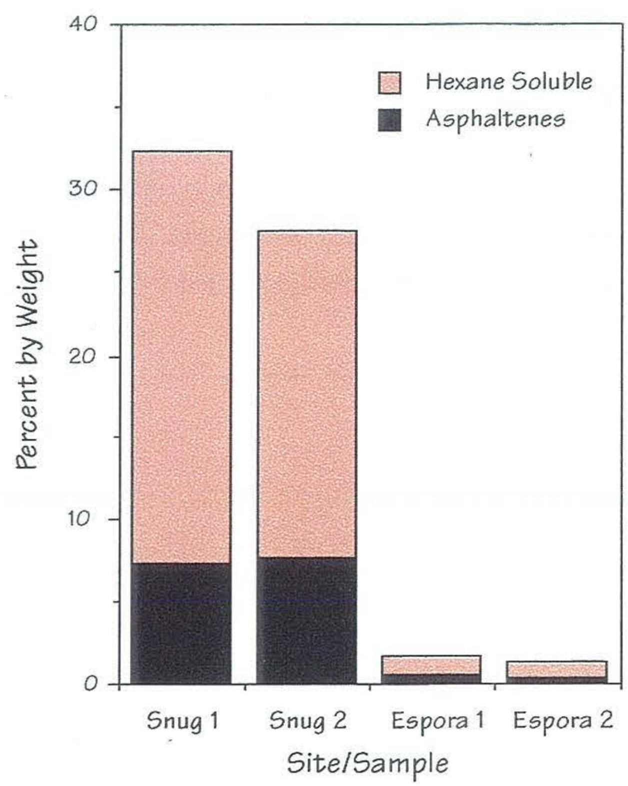


Figure 5. Relative concentration of percent asphaltenes to total extractable petroleum hydrocarbons in pavement samples from Snug Harbor and Punta Espora.

Grain-size characteristics of the incorporated sediment in pavement samples may in part explain the differences in oil concentrations. Figure 6 shows the distribution of grain sizes in the pavement samples evaluated. The most significant difference between the *Metula* and the *Exxon Valdez* pavements is the lack of fine-grained material at the Snug Harbor site. The mean concentration of beach material <0.5 mm in size is only 1.5% for the *Exxon Valdez* pavement collected at Snug Harbor, while the *Metula* pavements contained a much greater proportion of this size fraction, 19%. The Snug Harbor sample was significantly more tar-like, even pliable, while the *Metula* pavement samples were hard and crumbly.

Figure 7 profiles the aromatic hydrocarbons in the type of crude oil spilled from the *Metula* and in one of the Punta Espora pavements. The dominant aromatic hydrocarbons still present at time of sampling at Punta Espora were the C-3 alkylated naphthobenzothiophenes. The hopane and sterane constituents portrayed in the GC/MS profile (Figure 8) were far too degraded to allow source-fingerprint confirmation or hopane normalization techniques.

The *Exxon Valdez* pavement sample was more recent (5 years old), yet the GC/MS profile exhibited a highly weathered oil profile, completely degraded of any resolvable normal alkanes or isoprenoid hydrocarbons (Figures 8 and 9). The aromatic hydrocarbon profile of the Snug Harbor sample presented in Figure 10 is representative of a highly degraded oil, but not to the same extent as the *Metula* pavements. One might expect the profile to continue to degrade along the same trend as identified in the older pavement samples over the next decade.

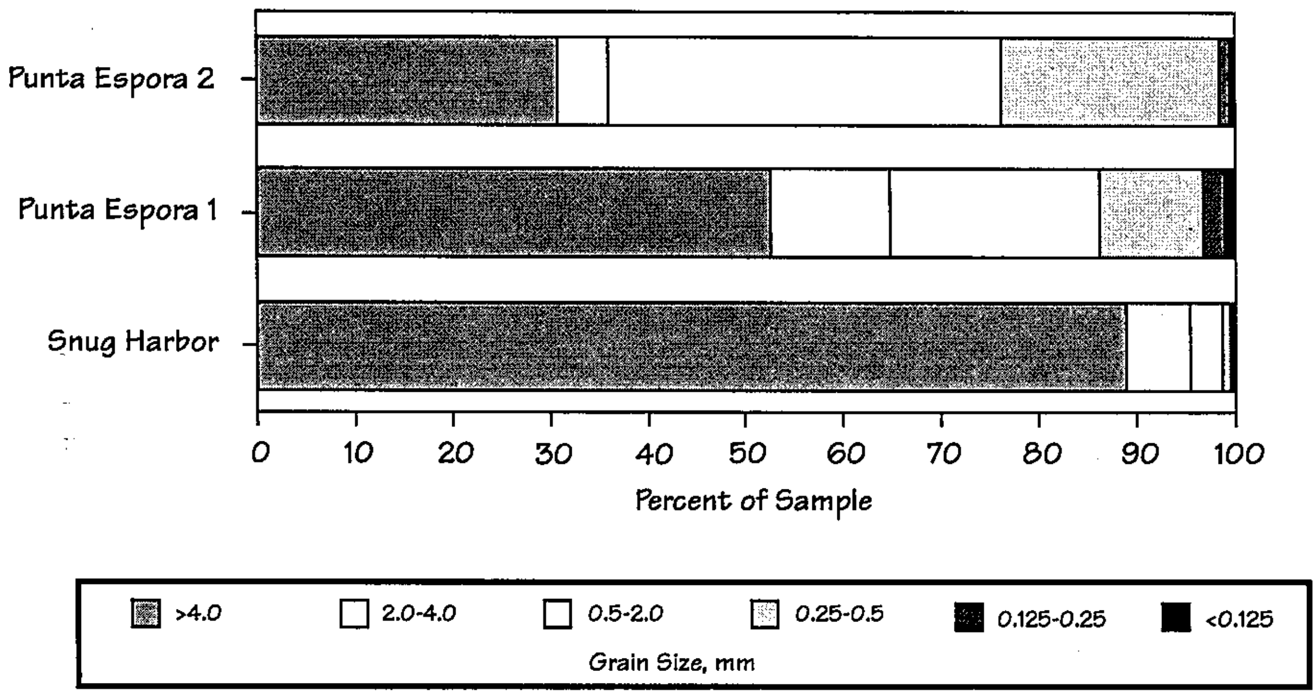


Figure 6. Grain-size analyses of pavement samples collected at Punta Espora and Snug Harbor.

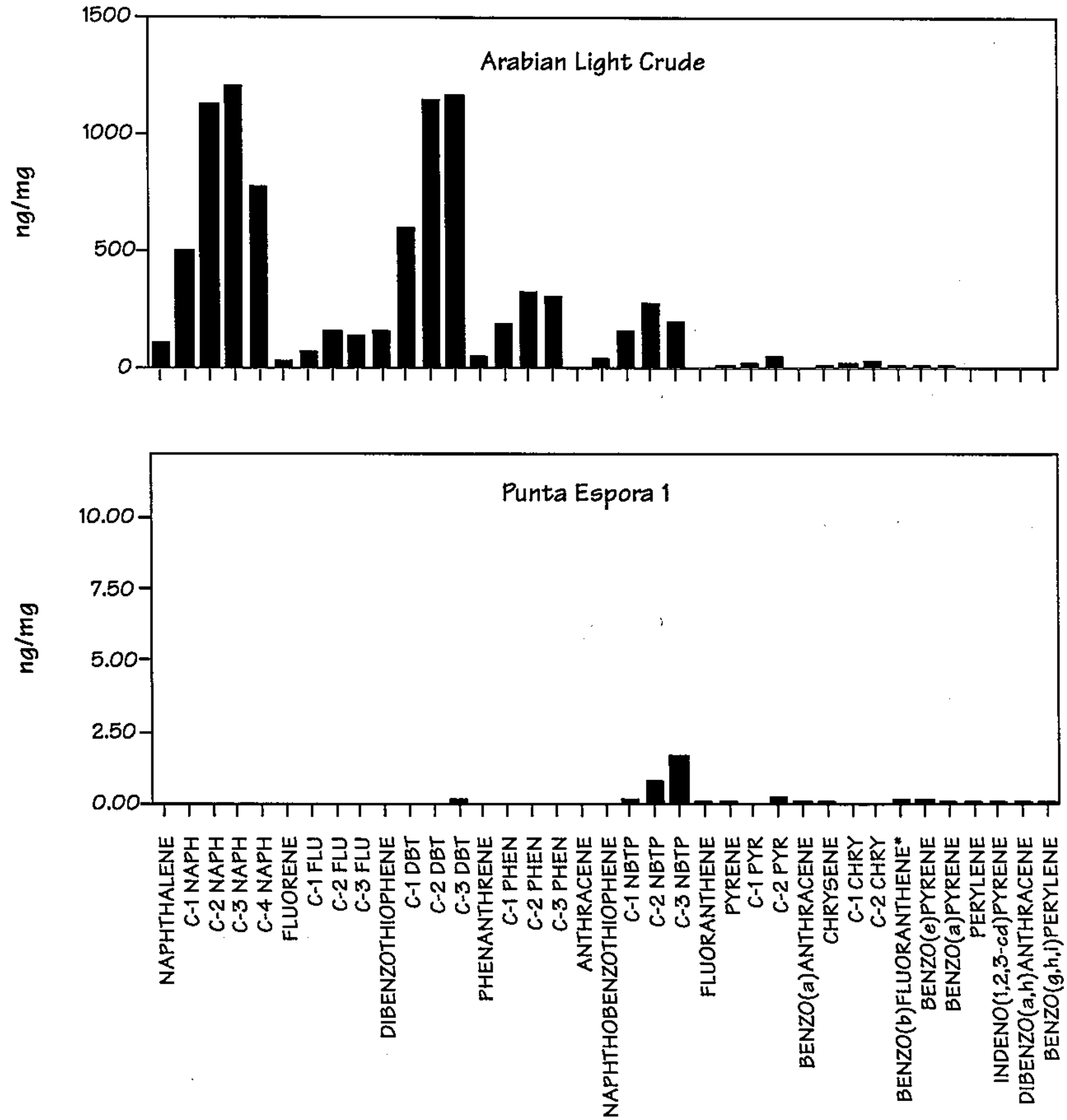


Figure 7. Concentration and distribution of selected aromatic hydrocarbons detected in unweathered Arabian Light crude oil and a pavement sample collected at the Punta Espora spill site.

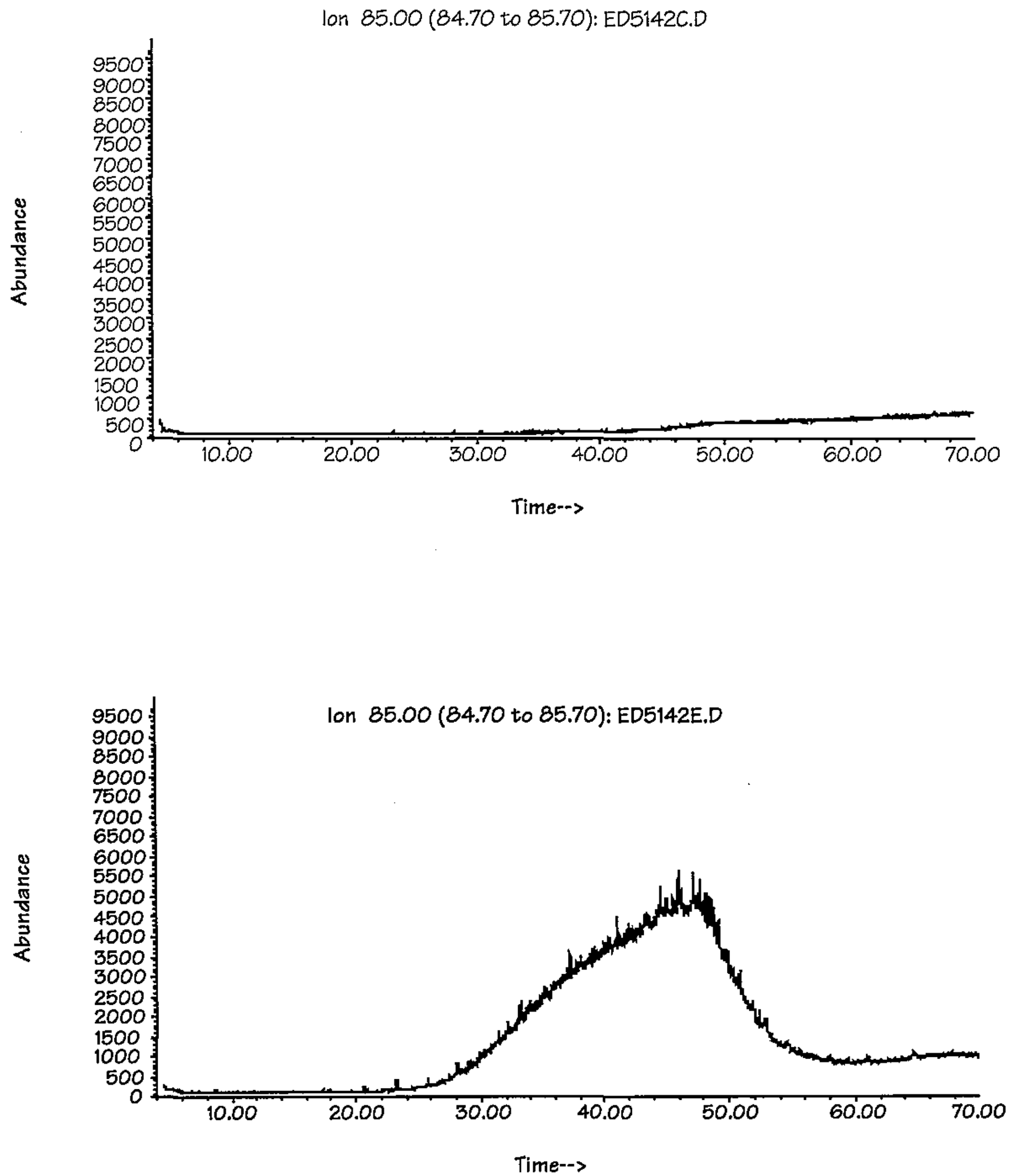


Figure 8. Comparison of the alkane chromatographic profile (m/e 85) of a Punta Espora pavement sample (top) and a pavement sample collected at the Snug Harbor site (bottom).The y-axes on both are expanded to highlight what little alkane signature is present.

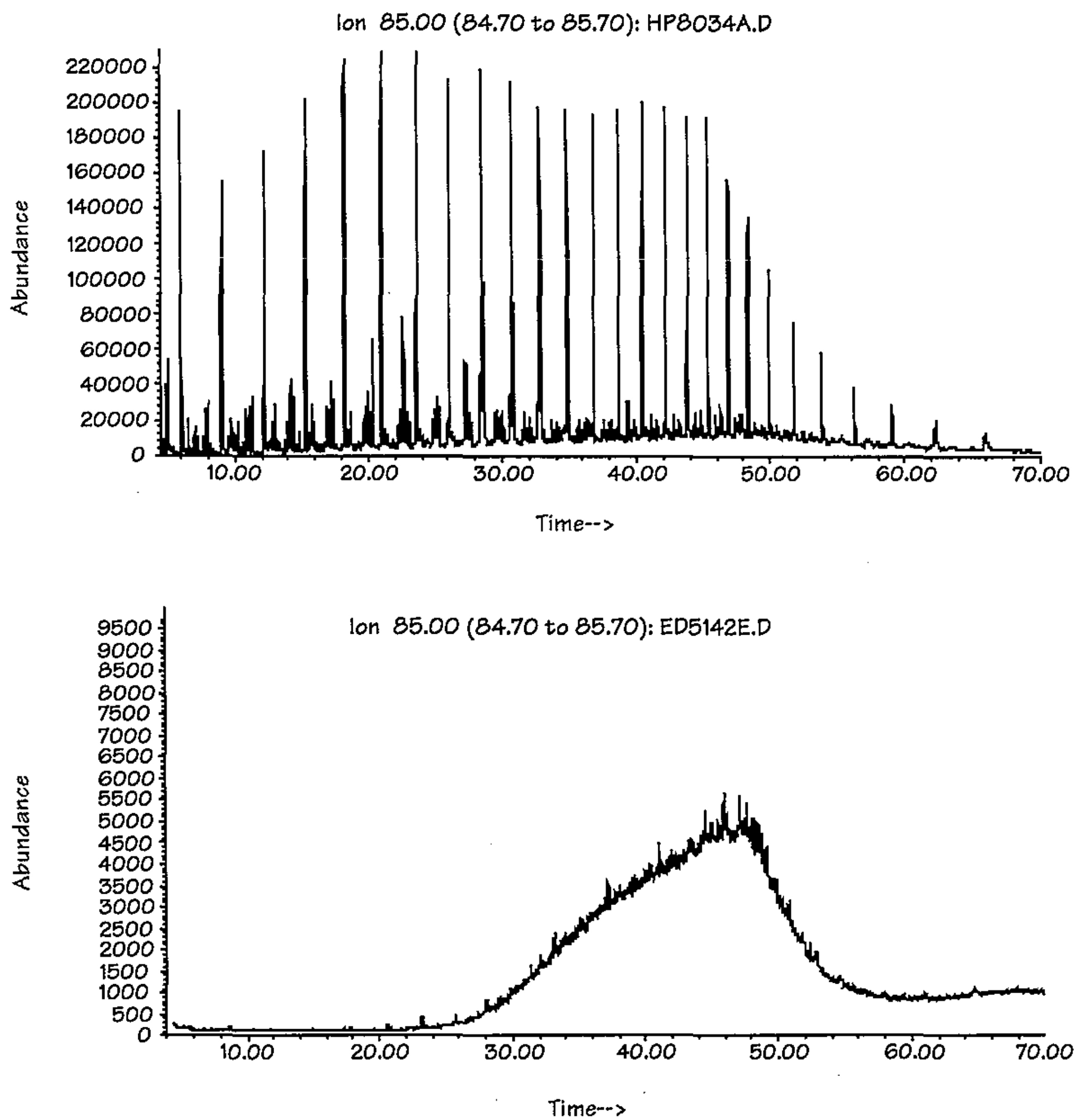


Figure 9. Comparison of the alkane chromatographic profile (m/e 85) for slightly weathered *Exxon Valdez* reference oil (top) and a pavement sample collected at the Snug Harbor study site (bottom)

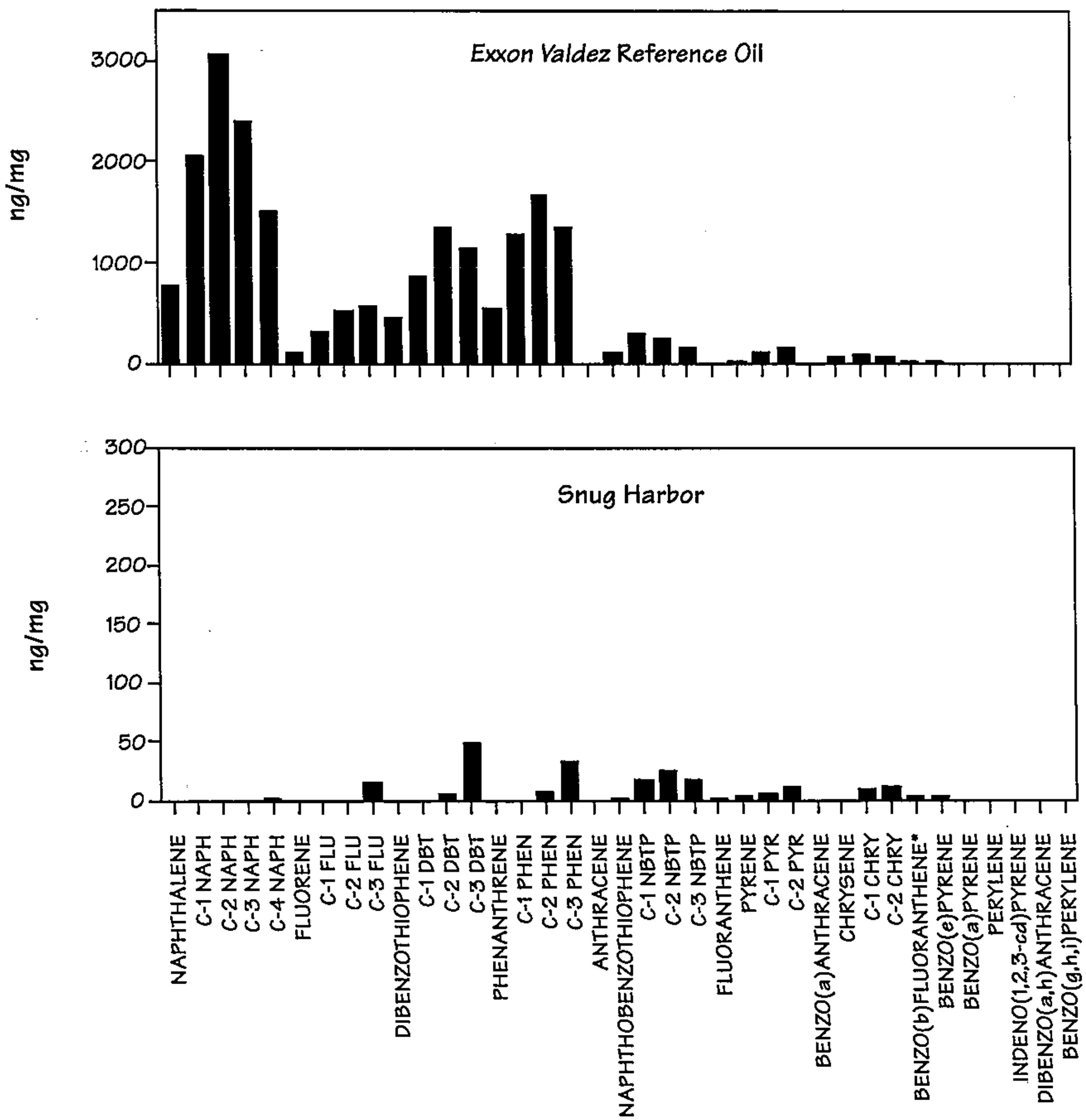


Figure 10. Concentration and distribution of selected aromatic hydrocarbons detected in *Exxon Valdez* reference crude oil and a pavement sample collected at the Snug Harbor *Exxon Valdez* study site

DISCUSSION

Spill responders have at their disposal a range of techniques for the cleanup of large oil spills. The exact combination of methods is determined by the nature of the spilled product, location, environmental sensitivities, aesthetics, and political considerations, among others. Spill cleanup strategies relying on some of the more environmentally aggressive or intrusive cleanup techniques (e.g., *Torrey Canyon, Exxon Valdez*) have been described in some detail; however, discussions of the long-term consequences of approaches at the other end of the response spectrum—essentially "doing nothing"—are much less frequently found in the literature, gray or otherwise. There is a perception that *doing nothing* in a major spill is environmentally ill-advised, and veterans of spill response are very familiar with the resultant pressures to *do something* when an oil catastrophe occurs. This is despite evidence that in specific instances no response can in itself represent a viable and even preferred alternative.

This is not to suggest that "doing nothing" is the recommended approach in all situations. Some of the early media and agency reports from the NOAA monitoring program that tracked recovery from the *Exxon Valdez* spill and cleanup, left the impression that the cleanup "did more harm than good". While this was to some extent true, it was an oversimplification that ignored the context of the science and did little to provide meaningful guidance to spill responders. The real value of the monitoring program in Prince William Sound has been to document the biological effects of aggressive shoreline cleanup so that true environmental tradeoffs inherent in using such techniques are known. In this way, the decisionmakers whose job it is to craft a response strategy can evaluate the pros and cons of the potential cleanup methods in an informed and scientifically supported (as opposed to anecdotal) way.

Given this background, the area affected by the *Metula* spill over 20 years ago provides a relevant and unique basis for comparing long-term effects among other spill sites. Barring other compelling circumstances (such as an ongoing armed conflict), it seems unlikely that oil spills in the future will be left in place to weather and degrade naturally.

Contrasting the Metula and Exxon Valdez

Although similarities exist between the *Metula* and the *Exxon Valdez* spills, there are also a number of obvious differences. The most significant among the latter include the spilled oil type, the degree of cleanup that took place, and the nature of the physical environment.

Spilled oil type

Although both the primary products spilled in the two incidents were crude oils, the Iranian Light crude and North Slope crude oils are physically and chemically different. As the name implies, the Iranian product is a lighter oil, with an API density of 33.2 and a kinematic viscosity of 25.2 cSt at 60°F. This contrasts with North Slope crude, with an API density of 26.8 and kinematic viscosity of 58.4 cSt (NOAA 1993). The products, however, are similar in density characteristics (0.86 g/cc at 60°F for Iranian, vs. 0.89 g/cc for North Slope). In both spills, extensive formation of emulsions occurred.

Degree of cleanup

As previously noted, there was no cleanup of the oiled shorelines during the *Metula* spill. In stark contrast, the most extensive cleanup operations ever mounted for an oil spill took place during the *Exxon Valdez* incident. However—as we have noted—during the *Exxon Valdez* spill and cleanup, a handful of oiled sites were reserved and no significant cleanup activities took place there. These so-called "set-aside sites" were established so that oiling effects could be distinguished from treatment effects during assessment of shoreline impact. It is almost certain that without such an agreement and site designation, the pavement in Snug Harbor that we are comparing to that from Punta Espora would have been removed by cleanup crews.

Physical environment

The climate in Patagonia and along the Strait of Magellan is generally similar to that in Prince William Sound in that they are both high-latitude areas with strong maritime influences. Baker et al. (1976) referenced the following climatic information for Patagonia:

Mean annual maximum temperature 6.7°C
Coldest month July, with mean temperature 2.5°C
Warmest month January, with mean temperature 11.7°C
Annual precipitation 350–450 mm.

This compares with Valdez in Prince William Sound (Alaska Climatic Atlas ref):

Mean annual maximum temperature 6.7°C
Coldest month January, with mean temperature –5.3°C
Warmest month July, with mean temperature 13.1°C
Annual precipitation 1440 mm.

The most noticeable climatic differences are the colder winters and the greater rainfall in Alaska. Prevailing winds, which can be significant in both locations, peak in different seasons in the two areas. In Prince William Sound, high winds accompany fall and winter storms; in the Strait of Magellan, consistent strong winds blow from west to east primarily during the summer.

The range of tides in both locations can be extreme, and this was a determinant of the location of oil stranding in the intertidal as well as the degree to which it refloated. In the Punta Espora region of the Strait of Magellan, the range is greater than 6 m (Blount 1978); in Prince William Sound (Port Valdez), it is 5.3 m (Hameedi 1988).

Prince William Sound shorelines are characteristically rocky: bedrock, boulder/cobble, or gravel, with a strong glacial influence still at work shaping the surrounding mountainous landscape. Shorelines along the Strait of Magellan are not nearly as rocky, and the surrounding land consists largely of relatively flat plains and low hills. The coastal environment includes both high-energy, coarse-grained beaches (similar to those found in Prince William Sound) and low-energy, fine-grained estuaries (Blount 1978).

Pavements at Punta Espora and Snug Harbor

There has been surprisingly little change in the character or extent of the asphalt pavement on the Espora backbeach between 1977 and 1995. Three years after the spill, Hann (1977) described the area as "...paved like an airport ramp with oil 2 to 10 inches deep in the sediment." He estimated that between 1974 and 1977, about 10% of the pavement had eroded. At that time (1977), Hann predicted that the asphalt pavement would remain for 7 to 10 years. However, in the 10-year period (1977–87) following this prediction, Owens and Robson (1987) noted that only 1 to 2 m had eroded along the landward margin of the pavement. Comparison of Plates 12 and 13 indicates that erosion between 1987 and 1995 has been equally as slow, with probably less than a 1- to 2-m reduction in band width.

In Snug Harbor, Prince William Sound, an August 1989 Exxon memorandum (Silbert and Maki 1989) described the extent of contamination at the site of interest in the following manner: "The site is heavily oiled in the upper intertidal to supra intertidal zone, a tar-like consistency. The area of the protected shoreline, within the intertidal, is approximately 3000 m^2 (30m x 100m). Light to moderate oil exists in the mid to low intertidal. This moderately to heavily oiled beach will unlikely release oil to contaminate adjacent coasts. Wave levels are so low in the almost completely enclosed bay that the oil will most likely degrade in place."

An interagency survey team described the pavement in 1993 in the following way: "Asphalt pavement is well-defined, dry, and hard. The pavement is friable after being broken and chipped with a shovel portions (are) buried under 1 to 3 cm of pebbles." Photographs of the pavement in 1993 estimated by the survey team to measure 3 m x 50 m, are shown in Plate 16. Plate 18 shows a closeup of a piece of the pavement in June 1993. The material shows little or no signs of diminishing (except for the periodic sample collection by monitoring scientists, which over several decades may result in removal of the entire patch). Plates 17 and 19 basically repeat Plates 16 and 18 in 1997, 4 years after the first photos and 8 years after the spill.

In both cases, the pavements are located so high in the intertidal zone that submergence occurs only during tidal extremes. Both pavements are highly sheltered from regular wave exposure. As a result, the most important mechanisms of degradation would be expected to be those associated with temperature, light, wind, and rain. Blount (1978) had suggested that short-period waves might be the most significant erosional influence on the Punta Espora pavement, but it appears that the total of all such forces has been minimal.

Biological Observations

At the Snug Harbor site affected by the *Exxon Valdez* and the Punta Espora backbeach "paved" by the *Metula*, the physical alteration of beach substrate has most noticeably influenced high intertidal and supratidal plant growth. That is, the impenetrable surface caused by the asphalt formation in both locations has restricted the distribution of plant species normally expected to occur there. This is illustrated in Plates 13 and 20. Plate 20 shows a tall marsh-type grass, *Elymus mollis*, at the upper edge of the Snug Harbor site constrained from further incursion toward the water by the asphalt. Figure 13 depicts a similar (though lower intertidal) situation at Punta Espora in which *Salicornia ambigua* is limited from seaward expansion down the beach by the presence of the asphalt pavement. In the Snug Harbor example, the *Elymus mollis* grass would likely not extend much lower into the intertidal, as its preferred habitat is upper intertidal and supratidal. At Punta Espora, the *Salicornia* probably would cover much of the upper intertidal zone presently covered by asphalt. At Snug Harbor, there was some evidence that the marsh grass at the margin of the asphalt pavement could push its root/rhizome system into the edge of the asphalt (Plate 21); at Punta Espora, there was no sign that *Salicornia ambigua* could incorporate, accommodate, or penetrate the pavement there.

There was no evidence that in either case the asphalt pavements provided usable additional substrate for epibiotic organisms. That is, the presence of attached biota utilizing the hard, stabilized pavement surface was not observed. This was probably due to the location of both pavements at the upper margins of the upper intertidal, where few epibiota occur.

Chemistry and Physical Characteristics of the Pavements

Examination of the chemistry results provides perhaps the most revealing contrasts between the Snug Harbor/ *Exxon Valdez* pavement and the Punta Espora/ *Metula* pavement. In terms of oil content and chemical composition, they are very different. The *Metula* pavement contained <2% extractable petroleum hydrocarbons, compared with >30% in the *Exxon Valdez* pavement. While some of this difference can be attributed to the difference in time elapsed since the spills (>20 years vs. <10 years, respectively), other contrasting characteristics may drive a divergence in the chemical fate of these pavements after comparable periods of time in the environment. For example, analysis of grain size of the non-petroleum material incorporated into the pavements reveals that the *Metula* asphalt contained a much greater proportion of fine-grained (<0.5 mm) sediment (~20%) than did the *Exxon Valdez* sample (~2%).

The role of characteristics such as grain size in determining the ultimate fate of oil left to weather naturally in protected settings is not completely clear, but a certain percentage of fine-grained material may represent a necessary component for the formation of the extremely hard and persistent pavement found at Punta Espora. Grain-size analyses from the backbeach area at Punta Espora reported by Blount (1978) show a substantial contribution of smaller grain-size fractions both on the upper beach (1.18 ø size average) and in the adjacent tidal flat area (3.03 ø size average)[1]. Although not analyzed in a directly comparable manner, grain-size analyses in 1995 and 1996 adjacent to the Snug Harbor set-aside site (Houghton et al. 1997) reflect a size structure much more heavily weighted toward large fraction material than Punta Espora: the grain size for six samples averaged only 15.2 ± 5.1% ≤ ø size 1. Spilled oil cements the beach substrate to form a hard matrix analogous to road pavement. The Snug Harbor site lacked fine sediments and was composed of a coarser substrate dominated by pebble-sized material.

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[1]In the standard definition of grain-size phi (Folk 1974), a value of −2 = 4.0 mm; 0 = 1.0 mm; 1=0.5 mm; and 3 = 0.125 mm.

Preliminary work by members of our chemistry team strengthens this supposition of the importance of grain size in shaping at least some pavement characteristics. Other examples of hard pavement, from such disparate sources as a parking lot of human origin and a piece of pavement from the *Amoco Cadiz* oil spill, have also been found to contain little oil and a significant component of fine-grained sediment. This leads us to suggest that lack of a fine-grained component may result in a much more pliable and biologically degradable material that ultimately never reaches the extreme represented by *Metula* samples.

Despite the apparent differences in pavement character, it seems clear that stranded oil on a highly sheltered depositional (sand/gravel) beach will produce a persistent material that may remain on the shoreline for years or decades. This material is likely to be of low inherent toxicity, but may significantly alter the characteristics of the physical substrate and shift the nature of biological communities expected at the unimpacted beach.

Relevance to Spill Response

Are these observations and extrapolations relevant in the "real world" of oil spill response and cleanup? Beyond providing more general information about the long-term consequences of oil spills, the *Metula-Exxon Valdez* examples suggest that physical features of environment play important roles in influencing the fate of oil remaining in the environment. Understanding the relationship between substrate grain size and stranded oil will help to flag the conditions in which persistent pavements can occur and aid in establishing priorities (and levels) for shoreline cleanup. For example, given that the presence of fine-grained beach material facilitates the formation of highly persistent pavements, then spill-response decisionmakers may be inclined to establish more rigorous cleanup standards for oil removal in areas where these conditions are found.

This study is a preliminary examination of the causal link between oil-spill response and cleanup and the persistence of pavements. Additional data collection and a more focused investigation would help define the conditions under which pavements persist. This, in turn, would provide useful information about the "what-if" of leaving oil untreated and the environmental trade-offs associated with that action, ultimately helping to answer the "how clean is clean?" question regularly encountered at the end of an oil spill cleanup.

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ACRONYMS

bbl	barrel(s)
cm	centimeter(s)
DCM	dichloromethane
g	grams
g/cc	
GC/MS	gas chromatography-mass spectrometry
GPS	Global Positioning System
g-TPH	gravimetric total petroleum hydrocarbon
HAZMAT	Hazardous Materials Response and Assessment Division (NOAA)
kg	kilogram(s)
km	kilometer(s)
mL	milliliter
mm	millimeter(s)
NOAA	National Oceanic and Atmospheric Administration
TPH	total petroleum hydrocarbons
USCG	United States Coast Guard
VLCC	very large crude carrier

APPENDIX

DETAILS OF CHEMICAL METHODOLOGIES

Sample extraction

A subsample of each pavement was weighed into a 40-milliliter (mL) vial along with ~5 grams (g) of anhydrous sodium sulfate. The samples were extracted with 20 mL of hexane enhanced by sonication. Each sample weighed ~10 g with 4 mL of extract removed and reserved for GC/MS analysis. An additional 10 mL were removed for gravimetric total petroleum hydrocarbon (g-TPH) determination of the hexane soluble fraction. The sample was twice more extracted with hexane and the extracts discarded (these final hexane extracts served, primarily, to effectively separate the remaining hexane-soluble hydrocarbons from the remaining asphaltene-type residues). The sample was then extracted with 20 mL dichloromethane (DCM). Again, 10 mL was subsampled and subjected to g-TPH to assess the asphaltene concentration. The hexane extract was filtered through 0.45-micron Teflon™ filters prior to gravimetric analysis. The asphaltene extract was not filtered but centrifuged prior to g-TPH analysis. The hexane extract was not fractionated and injected directly into the GC/MS.

GC/MS analysis

GC/MS is an effective means of separating oil constituents, and is a sensitive and highly selective tool for characterizing spilled oil samples. GC/MS is widely accepted for scientific investigations and has been used for oil-spill response activities, oil fate and effects studies, and baseline pollution monitoring (Overton et al. 1981; Boehm and Farrington 1984; Michel et al. 1991; Sauer and Boehm 1991; Sauer et al. 1993). The hexane-soluble fraction of each pavement sample was analyzed by GC/MS for target alkane and aromatic hydrocarbons by methods previously detailed (Henry and Overton 1993, Roques et al. 1994). All GC/MS analyses were conducted on a Hewlett Packard 5890 GC directly interfaced to Hewlett Packard 5971 MSD. The GC separation was performed on a 30-m DB-5 type capillary column with a 0.25-mm internal diameter and 0.25- micron film thickness (J&W Scientific, Folsom, CA). The GC flow rate and temperature program were optimized such that phytane and n-C18 were baseline resolved and pristane and n-C17 were near baseline resolved. The GC temperature program follows: initial column temperature of 55°C for 3 minutes then increased to 290°C at a rate of 5°C/minutes and held at the upper temperature for 15 minutes The injection temperature is set to 250°C and only high-temperature, low-thermal bleed septa are used. The interface to the MS was maintained at 290°C. All gasses were ultrahigh purity.

PLATES

Plate 1

1977

Plate 2

1987

Plate 3

1995

Plates 1-3. Punta Espora backbeach site in 1977 (Plate 1), 1987 (Plate 2), and 1995 (Plate 3). Photos by E. Owens (1&2) and G. Shigenaka (3).

Plate 4

1987

Plate 5

1995

Plates 4-5 Punta Espora backbeach site in 1987 (Plate 4) and 1995 (Plate 5). Photos by E. Owens (4) and G. Shigenaka (5).

Plate 6  1987

Plate 7  1995

Plates 6-7. Closeup of leading edge of Punta Espora pavement in 1987 (Plate 6) and 1995 (Plate 7). Photos by E. Owens (6) and G. Shigenaka (7).

Plate 8

1987

Plate 9

1995

Plates 8-9. View of Punta Espora pavement surface in 1987 (Plate 8) and 1995 (Plate 9). Photos by E. Owens (8) and G. Shigenaka (9).

Plate 10  1987

Plate 11  1995

Plates 10-11. Punta Espora backbeach site in 1987 (Plate 10) and 1995 (Plate 11). Photos by E. Owens (10) and G. Shigenaka (11).

Plate 12

1987

Plate 13

1995

Plates 12-13. Punta Espora backbeach site in 1987 (Plate 12) and 1995 (Plate 13). Note *Salicornia ambigua* on landward (left) side of pavement. Photos by E. Owens (12) and G. Shigenaka (13).

Plate 14 Closeup of *Salicornia ambigua* stand at Punta Espora, 1995. Photo by G. Shigenaka.

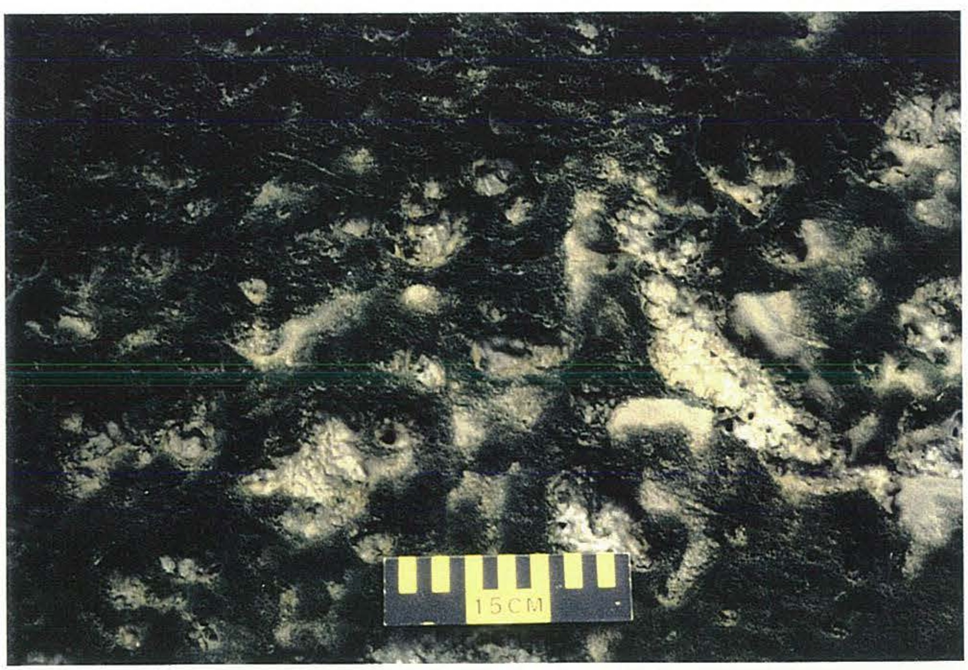


Plate 15. Closeup of mudflat surface, showing *Ulothrix flacca* at Punta Espora, 1995. Photo by G. Shigenaka.

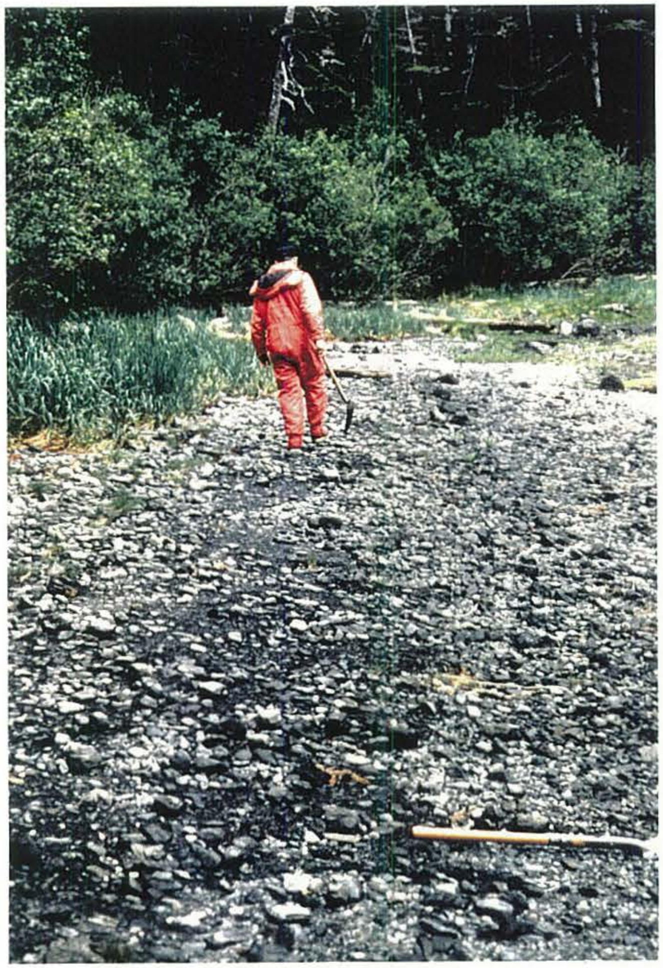


Plate 16

1993

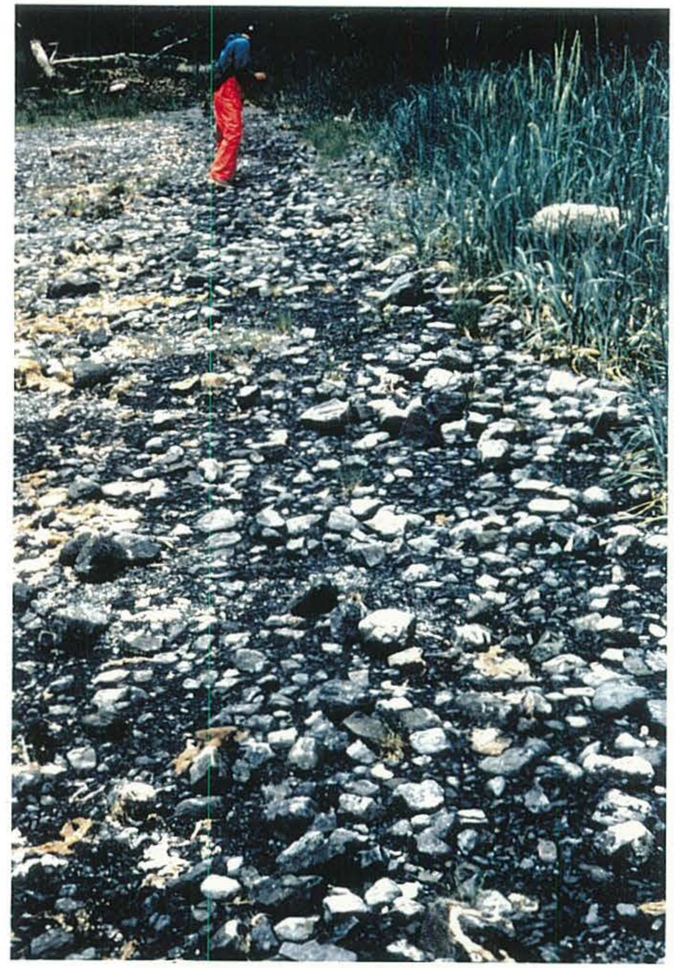


Plate 17

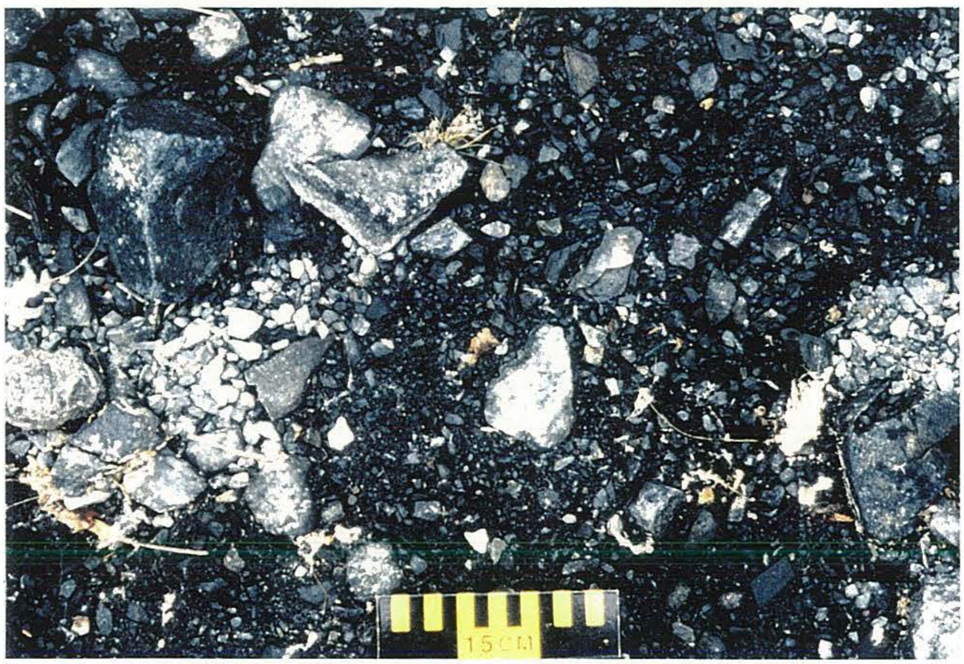
1997

Plates 16-17. Snug Harbor setaside site, showing pavement at edge of intertidal in 1993, facing north (Plate 16), and 1997, facing south (Plate 17). Photos by G. Shigenaka.

Plate 18

1993

Plate 19



1997

Plates 18-19. Closeup of surface of Snug Harbor pavement in 1993 (Plate 18) and 1997 (Plate 19). Photos by G. Shigenaka.

Plate 20

1997

Plate 21

1996

Plates 20-21 Upper edge of pavement at Snug Harbor showing adjacent *Elymus mollis* dunegrass in 1997 (Plate 20) and 1996 (Plate 21). Note growth of roots/rhizhomes into pavement in Plate 21. Photos by G. Shigenaka.