



NOAA Technical Memorandum NOS ORCA 126

Evaluation of the Condition of Prince William Sound Shorelines Following the Exxon Valdez Oil Spill and **Subsequent Shoreline Treatment**

1997 Geomorphological Monitoring Survey

Seattle, Washington March 1998



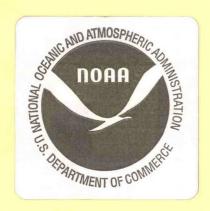
Office of Ocean Resources Conservation and Assessment National Ocean Service National Oceanic and Atmospheric Administration U.S. Department of Commerce

The Office of Ocean Resources Conservation and Assessment (ORCA) provides decisionmakers comprehensive, scientific information on characteristics of the oceans, coastal areas, and estuaries of the United States of America. The information ranges from strategic, national assessments of coastal and estuarine environmental quality to real-time information for navigation or hazardous materials spill response. Through its National Status and Trends (NS&T) Program, ORCA uses uniform techniques to monitor toxic chemical contamination of bottom-feeding fish, mussels and oysters, and sediments at about 300 locations throughout the United States. A related NS&T Program of directed research examines the relationships between contaminant exposure and indicators of biological responses in fish and shellfish.

ORCA provides critical scientific support to the U.S. Coast Guard during spills of oil or hazardous materials into marine or estuarine environments. This support includes spill trajectory predictions, chemical hazard analyses, and assessments of the sensitivity of marine and estuarine environments to spills. The program provides similar support to the U.S. Environmental Protection Agency's Superfund Program during emergency responses at, and for the cleanup of, abandoned hazardous waste sites in coastal areas. To fulfill the responsibilities of the Secretary of Commerce as a trustee for living marine resources, ORCA conducts comprehensive assessments of damages to coastal and marine resources from discharges of oil and hazardous materials.

ORCA collects, synthesizes, and distributes information on the use of the coastal and oceanic resources of the United States to identify compatibilities and conflicts and to determine research needs and priorities. It conducts comprehensive, strategic assessments of multiple resource uses in coastal, estuarine, and oceanic areas for decisionmaking by NOAA, other Federal agencies, state agencies, Congress, industry, and public interest groups. It publishes a series of thematic data atlases on major regions of the U.S. Exclusive Economic Zone and on selected characteristics of major U.S. estuaries.

ORCA implements NOAA responsibilities under Title II of the Marine Protection, Research, and Sanctuaries Act of 1972; Section 6 of the National Ocean Pollution Planning Act of 1978; the Oil Pollution Act of 1990; the National Coastal Monitoring Act of 1992; and other Federal laws. It has four major line organizations: Coastal Monitoring and Bioeffects Assessment Division, Hazardous Materials Response and Assessment Division, Strategic Environmental Assessment Division, and the Damage Assessment Center.



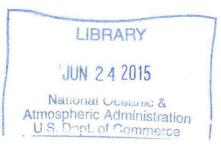
NOAA Technical Memorandum NOS ORCA 126

Evaluation of the Condition of Prince William Sound Shorelines Following the Exxon Valdez Oil Spill and Subsequent Shoreline Treatment

1997 Geomorphological Monitoring Survey

57 NG NO.126

Miles O. Hayes and Jacqueline Michel Research Planning, Inc. Post Office Box 328 Columbia, South Carolina 29202



Edited By:

Gary Shigenaka NOAA Hazardous Materials Response and Assessment Division 7600 Sand Point Way Northeast Seattle, Washington 98115



Seattle, Washington

United States Department of Commerce William Daley Secretary National Oceanic and Atmospheric Administration D. James Baker Under Secretary for Oceans and Atmosphere National Ocean Service W. Stanley Wilson Assistant Administrator for Ocean Services and Coastal Zone Management Hazardous Materials Response and Assessment Division Office of Ocean Resources Conservation and Assessment National Ocean Service National Oceanic and Atmospheric Administration U.S. Department of Commerce Silver Spring, Maryland

NOTICE

This report has been reviewed by the National Ocean Service of the National Oceanic and Atmospheric Administration (NOAA) and approved for publication. Such approval does not signify that the contents of this report necessarily represent the official position of NOAA or of the Government of the United States, nor does mention of trade names or commercial products constitute endorsement or recommendation for their use.

ACKNOWLEDGMENTS

This study is part of the continuing monitoring survey sponsored by the Hazardous Materials Response and Assessment Division of NOAA, David M. Kennedy, Division Chief, Robert Pavia, Contracting Officer Technical Representative, and Gary Shigenaka Project Technical Manager. The chemical analyses were carried out at the Environmental Studies Institute, Louisiana State University (LSU), under the supervision of Charles E. Henry, Jr., Paulene O. Roberts of LSU assisted the authors with the field work during the July 1997 survey, and she conducted the chemical analysis of the samples. Others who contributed significantly to the field work include Ed Levine, NOAA Scientific Support Coordinator; Scott Zengel, RPI biologist; and Eiji Imamura, Marine Research Specialists Graphic; and other technical support were provided by Joe Holmes, Dot Zaino, and Becky Cox of the RPI Staff.

CONTENTS

CHAPTER	PAGE
1	INTRODUCTION1-1
2	METHODS OF STUDY 2-1
3	RESULTS OF JULY 1997 SURVEY 3-1
	Introduction
	Cobble/Boulder Platforms with Berms 3-1
	Introduction
	Station N-1 (Point Helen)
	Station N-3 (Smith Island)
	Station N-4 (Smith Island)
	Station N-7 (Knight Island)
	Station N-15 (Latouche Island) 3-38
	Bayhead Beaches 3-48
	Introduction
	Station N-18 (Sleepy Bay)
	Station N-14 (Northwest Bay) 3-53
	Pebble Beach/Tidal Flats
	Introduction
	Station N-9 (Block Island) 3-54
	Sheltered Rocky Coasts
	Rocky Rubble Slopes
	Introduction
	Station N-13 (Herring Bay)
	The Exposure Index at Bass Harbor 3-66

CONTENTS continued

4	OIL WEATHERING CHARACTERISTICS	4-1
	Analytical Issues	4-1
	Weathering Patterns	4-1
5	SUMMARY OF OBSERVATIONS EIGHT YEARS AFTER THE SPILL	5-1
	Surface Oil Removal Rates and Mechanisms	5-1
	Subsurface Oil Persistence in Gravel Beaches	5-2
	Effectiveness of Berm Relocation and Sediment Reworking	5-9
	Persistence of Oil on Sheltered Rocky Shores	5-10
	Importance of a Stable Armor on Gravel Beaches	5-14
	Other Remaining Questions	5-14
Glossary		G-1
References		R-1
APPENDIX I	CONCENTRATIONS OF TARGETED	
	POLYNUCLEAR AROMATIC HYDROCARBONS	
	IN SAMPLES COLLECTED IN JULY 1997	A-I-1

LIST OF FIGURES

Figure	1-1.	Location of permanent stations surveyed as part of NOAA's geomorphology/chemistry monitoring program during the July 1997 survey	1-2
Figure	3-1	Station N-1 (Point Helen; Knight Island)	3-3
Figure		Field sketches of station N-1 (Point Helen)	3-6
_			
Figure		Changes at station N-1 (Point Helen)	3-8
Figure	3-4.	Distribution of surface sediments within the intertidal zone of station N-1 (Point Helen)	3-9
Figure	3-5.	Topographic beach profile changes at station N-1 (Point Helen)	3-11
Figure	3-6.	Time-series plot of the interval and degree of subsurface oil at station N-1 (Point Helen)	3-14
Figure	3-7.	Descriptions for two trenches dug at station N-1 (Point Helen) on 22 July 1997	3-15
Figure	3-8.	HOR at the bottom of the two trenches dug on profile N-1 (Point Helen) on 22 July 1997	3-16
Figure	3-9.	Station N-3 (Smith Island) on 21 July 1997	3-19
Figure	3-10.	Topographic changes at station N-3 (Smith Island)	3-20
Figure	3-11.	Station N-3 (Smith Island) on 22 July 1997	3-21
Figure	3-12.	Time-series plot of the interval and degree of subsurface oil at station N-3 (Smith Island)	3-23
Figure	3-13.	Description of trenches A and B at station N-3 (Smith Island) on 21 July 1997	3-24
Figure	3-14.	HOR in sediments in bottom of trench B at station N-3 (Smith Island)	3-25
Figure	3-15.	Field sketches of station N-4 (Smith Island) on 24 July 1994 and 21 July 1997	3-27
Figure	3-16.	Profile changes at station N-4 (Smith Island)	3-28
Figure	3-17.	Station N-4 (Smith Island) on 21 July 1997	3-30
Figure	3-18.	Distribution of surface sediments within the intertidal zone of station N-4 (Smith Island)	3-31
Figure	3-19.	Station N-7 (Knight Island)	3-32
Figure	3-20.	Erosion at station N-7 (Knight Island)	3-33

List of Figures continued

Figure 3-21.	Possible explanation for the removal of oil from the upper platform at station N-7 (Knight Island)	3-34
Figure 3-22.	Time-series plot of the interval and degree of sub- surface oiling at station N-7 (Knight Island)	3-36
Figure 3-23.	Station N-15 (Latouche Island)	3-39
Figure 3-24.	Station N-15 (Latouche Island)	3-40
Figure 3-25.	Comparison beach profile plots for station N-15 (Latouche Island)	3-43
Figure 3-26.	Comparison of July 1997 survey with earlier survey at station N-15 (Latouche Island)	s 3-44
Figure 3-27.	Time-series plot of the interval and degree of sub- surface oiling at station N-15 (Latouche Island)	3-45
Figure 3-28.	Trenches at station N-15 (Latouche Island)	3-46
Figure 3-29.	Trench descriptions for station N-15 (Latouche Island) on 22 July 1997	3-47
Figure 3-30.	Station N-18 at the head of Sleepy Bay	3-49
Figure 3-31.	Station N-18 at the head of Sleepy Bay	3-51
Figure 3-32.	Comparison of surface sediment distribution patterns for station N-18 (Sleepy Bay)	3-52
Figure 3-33.	Station N-9 (Block Island) on 20 July 1997	3-55
Figure 3-34.	Photographs of station N-9 (Block Island) on 20 July 1997	3-56
Figure 3-35.	Oiled area near station N-9 (Block Island)	3-58
Figure 3-36.	Photographs of station N-6 (Bay of Isles) on 21 July 1997	3-60
Figure 3-37.	Pebble beach just north of station N-10 (Herring Bay)	3-62
Figure 3-38.	Photographs of station N-13 (Herring Bay) on 23 July 1997	3-64
Figure 3-39.	Cobble/boulder beach at the head of Bass Harbor	3-67
Figure 3-40.	Model of amplification of wave heights at head of Bass Harbor as a result of reflection of refracted swell	3-68

List of Figur	es continuea	
Figure 4-1.	Double-ratio plots for all the 1997 samples	4-4
Figure 4-2.	PAH histogram plots for the twelve 1997 samples from NOAA stations	4-7
Figure 5-1.	Schematic model of the behavior and persistence of oil from the initial stranding to the summer of 1997 at station N-3 (Smith Island)	5-3
Figure 5-2.	Schematic model of the behavior and persistence of oil at station N-1 (Point Helen) for the period 1990-1997	5-6
Figure 5-3.	Schematic model of the behavior and persistence of oil from the initial stranding to the end of 1997 on cobble/boulder platforms with berms	5-7
Figure 5-4.	Return of sediment to the beach just west of profile N-14 (Northwest Bay) in a sequence of landward-migrating, mixed sediment swash bars	5-11
Figure 5-5.	Model for the persistence of oil on sheltered rocky rubble slopes	5-12
Figure 5-6.	Model for the persistence of oil on sheltered rocky shores with a thin sediment veneer	5-13
Figure 5-7.	Subsurface oil under coarse gravel armor	5-15
	LIST OF TABLES	
Table 2-1.	Listing of the survey dates and stations visited during the NOAA geomorphological/chemical monitoring program	2-2
Table 2-2.	Results of chemical analyses of sediment samples collected during the July 1997 survey	2-4
Table 3-1.	Maximum surface oiling observed on gravel beach profiles	3-12
Table 3-2.	Historical summary of the interval and degree of subsurface oil at station N-1 (Point Helen)	3-13
Table 3-3.	TEO and PAH concentrations in sediments from the bottom of trenches dug in the upper platform at Point Helen (N-1) over time	3-17
Table 3-4.	Historical summary of the interval and degree of subsurface oil at station N-3 (Smith Island)	3-22

List of Tables continued

Table 3-5.	TEO and PAH concentrations in sediments from the bottom of trenches dug in the upper platform at Smith Island (N-3) over time	3-26
Table 3-6.	TEO and PAH concentrations in sediments from the bottom of trenches dug in the upper platform at Knight Island (N-7) over time	3-37
Table 3-7.	TEO and PAH concentrations in sediments from the bottom of trenches dug in the upper platform at Herring Bay (N-13) over time	3-65
Table 4-1.	Key for the abbreviations used on the PAH histogram plots	4-2
Table 4-2.	Weathering stages for all 20 samples collected in 1997	4-2

CHAPTER 1 INTRODUCTION

Since September 1989, the Hazardous Materials Response and Assessment Division of NOAA has sponsored surveys of the geomorphological changes and oil distribution at 18 stations throughout Prince William Sound, Alaska. This work originally was designed to provide the scientific basis for decision-making by the U.S. Coast Guard, as the Federal On-Scene Coordinator of the *Exxon Valdez* oil spill, on shoreline treatment in 1990 and beyond. Other objectives evolved as the study progressed, including: 1) providing a physical and chemical framework for sites included in NOAA's biological monitoring program; 2) monitoring the effectiveness of certain countermeasures, such as berm relocation; and 3) gaining a better understanding of the processes of natural cleansing of gravel beaches.

Three of the original stations, N-5, N-6, and N-13, were at locations that had been set-aside (not treated) for research on comparisons of the environmental effects and oil persistence on untreated shorelines with those that had been treated. The intertidal zones of the other stations were treated with one or more of the following techniques: hot-water flushing; nutrient addition; manual removal; berm relocation; and sediment tilling.

The shoreline surveys have been repeated up to fourteen times over the period September 1989 to July 1997. Results based on the surveys conducted through July 1994 have been presented elsewhere (Michel et al. 1990, Michel and Hayes 1991, Michel et al. 1991, Michel and Hayes 1993a, 1993b, and 1993c, and Michel and Hayes 1996). This report synthesizes the data collected during the survey of July 1997 with the earlier results.

Whereas Prince William Sound is a relatively sheltered area, at least in comparison with the open north Pacific Ocean, only the more exposed sites are subject to significant wave action during the passage of frequent extratropical cyclones. There are also many areas in Prince William Sound that are completely sheltered from significant wave action. The study sites were chosen to represent the spectrum of hydrodynamic energy levels that exist throughout the Sound. Shoreline environments studied include: exposed cobble/boulder platforms with berms; bayhead beaches with mobile fine gravel; pebble beach/tidal flat areas; sheltered rubble slopes; and sheltered bedrock. All of these shoreline types were heavily oiled during the spill. Figure 1-1 shows the location of stations surveyed in July 1997. General observations were made during the July 1997 survey at two sites near the NOAA stations on Latouche Island where PES-51, a shoreline cleaning agent, was being used to aid removal of residual oil in areas important to the people of Chenega Village.

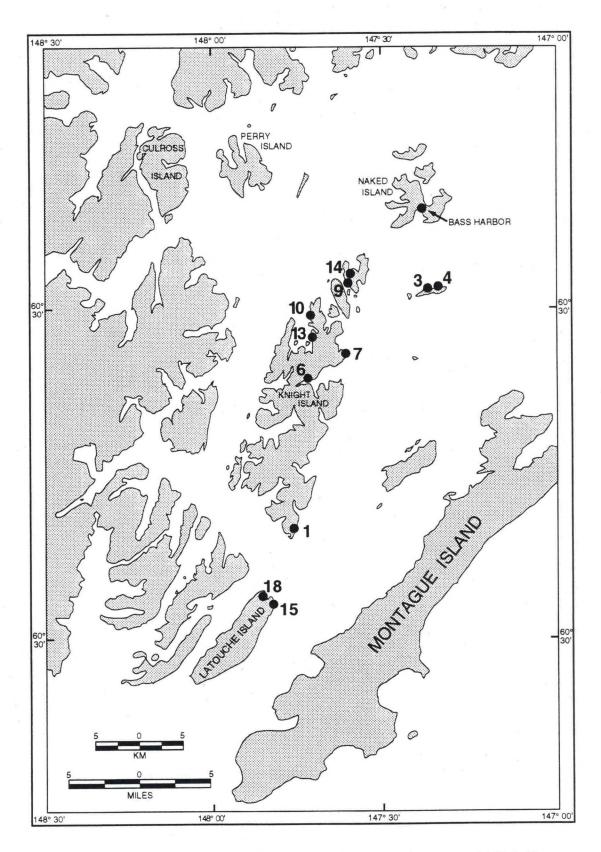


Figure 1-1. Location of permanent stations (dots) surveyed as part of NOAA's geomorphology/chemistry monitoring program during the July 1997 survey.

CHAPTER 2 METHODS OF STUDY

A detailed description of the methods of study used on this project is given in Michel and Hayes (1991). The field area has been visited 14 times to date during the project, the first time in September 1989 and the last in July 1997. Table 2-1 lists the stations monitored during each survey.

Field visits to the study sites were planned to coincide with maximum spring low tides. All field surveys were conducted within the window of 2.5 hours on either side of low tide. During each site visit, a topographic profile was run perpendicular to the beach, and details of the morphology, sediments, and surface oil distribution patterns were noted at each survey interval. The station was photographed and sketched in detail, highlighting the distribution of oil, if present, and the effects of cleanup. Trenches were dug at intervals along the profile to determine the depth of oil penetration and collect samples. Each trench was described and photographed in detail.

Twenty (20) samples of both surface and subsurface oiled sediments were collected during the July 1997 survey. Surface samples were collected from the top 2 centimeters (cm). Subsurface samples were collected from discrete intervals, frequently from the bottom of the oiled sediments in the trench. Other intervals were collected as appropriate, such as six samples of mousse and oiled sediments from two of the PES-51 treatment sites on Latouche Island. No samples were composited; all samples were grab samples.

To date, over 840 samples have been analyzed for total extractable organics (TEO). Over 140 samples have been characterized chemically by gas chromatography/mass spectroscopy (GC/MS) to track weathering patterns in the persistence of polynuclear aromatic hydrocarbons (PAHs). Chemical analyses were carried out by the Environmental Studies Institute at Louisiana State University. From 1989 to 1994, TEO was reported as "total petroleum hydrocarbons", or TPH, and was determined gravimetrically after solvent extraction with freon (Standard Method 503). For the July 1997 samples, this method is now referred to as TEO. The July 1997 samples were also analyzed by GC using a Flame Ionization Detector (GC-FID) and the results reported as TPH. For the typically heavily contaminated samples collected, TEO is a good indicator of bulk oil contamination. TPH by GC-FID provides a more quantitative measure of mid-range hydrocarbons and a chromatographic picture which provides more information on the source of hydrocarbons and the degree of weathering. Henry et al. (1997) summarized these changes as follows: "Why the

Table 2-1. Listing of the survey dates and stations visited during the NOAA geomorphological/chemical monitoring program.

		19	89					19	990			19	991	1992	1994	1997
Station Number	16-20 Sept.	17-23 Oct.	3-9 Nov.	3-8 Dec.	Ja		30 Jan 3 Feb.	28 Feb 5 Mar.	23-31 May	22-23 June	1-8 Sept.	19-25 Jan.	25-29 Aug.	10-16 Aug.	21-26 July	19-24 July
N-1	Х	X	X	X	1 >	(Χ		X		X	X	X	X	X	X
N-2	X	X	X)	(X		X		X					
N-3	X	X		X)	(X	X	X		X	X	X	X	Х	X
N-4	X	X		X)	(X	X	X		X	X	X		Х	X
N-5	X	X		X)	(X		X		X		X		Х	
N-6	X	X)	(X		X		X	X	Х	X
N-7	X	X		X)	(X		X		X	X	X	X	Х	X
N-8	X	X	X	X)	X	X	X								
N-9	X	X	X)	X	X	X		X	X	X		X	X	X
N-10	X	X	X	X)	X	X	X	X		X	X	X	X	X	X
N-11	X	X	X)	X	X	X	X		X	X	X	X	Х	
N-12	X	X	X)	X	X	X	X		X	X	X	X	X	1
N-13	X	X	X	X)	X	X	X	X		X	X	X	X	X	X
N-14	X	X		X			X		X		X	X		X	Х	X
N-15	X	X	X	X	3	X	X		X	X	X	X	X	X	X	X
N-16	X		X	X			X			X						
N-16Y										X						
N-17	X		X	X			X				X	X	X	X	X	
N-18	X	X	X	X		X	X		X		X	X	X	X	X	X
Shelter	Bay											X				
Crab B	ay										X			1		
Sheep I	Bay											X				
Bass H	arbor										X					X
ELI-1 (Elringt	on Isla	nd)									*			Х	
Mussel	Beach													X		
Outside	e Prince	e Willia	am Sou	nd												
PD-1									X							
US-5									X						1	
YG-2									X							
PB-1									X							

TPH name change? The gravimetric analytical procedure used was a modified Oil and Grease method. The samples submitted for analysis were coarse gravel saturated with oil. Clearly, the oil and grease extractables were derived entirely from residual petroleum contamination. For clearity, the results were reported simply as TPH. Over time, the concentration and chemical nature of persistent oil contamination in the intertidal beaches

of Prince William Sound has changed. In addition, the use of the same analytical technique for high organic substrates such as marsh sediments clearly highlighted the lack of specificity inherent in the gravimetric method. By reporting the gravimetric results as TEO, the chemistry information contained within that value is better defined. TEO is the sum of the solvent soluble fraction after filtration. If no other extractable organics are present, the TEO value is the best estimation of bulk oil concentration. In contrast, TPH is only a selected portion of the bulk oil. TPH sample preparation includes a fractionation step to exclude the more polar TEO constituents such as biogenic lipids and, in the case of crude oil, the polar constituents and asphaltenes. TPH results will always be less than the TEO from the same sample extract. In addition, when GC-FID is used to quantify the TPH fraction, only the semivolatile hydrocarbons applicable to gas chromatography will be detected."

All sample extracts were also analyzed by GC/MS, targeting 40 PAHs known to characterize petroleum hydrocarbons. Hopanes and steranes were also measured. A detailed discussion of the analytical methods is provided in Henry et al. (1997). The results for individual PAHs, hopanes, and steranes are listed in Appendix I. Table 2-2 lists the samples collected, the visual descriptions of oiling as recorded in the field, and the TEO, TPH, and total targeted PAH results in milligrams of oil per kilogram of sediment (mg/kg), dry weight.

Throughout the text of this report, the terminology and definitions used are those established during the 1991 interagency shoreline surveys of the oiled regions (MAYSAP). Surface oil was described using the following terms:

Asphalt pavement (AP): Heavily oiled sediments held cohesively together.

Coat (CT): Oil which ranges between 0.1 and 1.0 millimeter (mm) thick (can be easily scratched off with fingernail).

Stain (ST): Oil less than 0.1 mm thick (cannot be easily scratched off with fingernail).

Film (FL): Transparent or translucent film or sheen.

Subsurface oil was described using the following terms:

Heavy oil residue (HOR): Pore spaces partially filled with oil; oil usually not flowing out of sediments. For the July 1997 survey, three sediment samples were described as HOR, and the actual TPH concentrations were 9,600-19,000 mg/kg.

Medium oil residue (MOR): Sediments heavily coated with oil; pore spaces are not filled with oil; pore spaces may be filled with water. Only one sample was described as MOR, and the actual TPH concentration was 8,900 mg/kg.

Table 2-2. Results of chemical analyses of sediment samples collected during the July 1997

survey.

	survey.					
Station N	o./Zone ¹	Depth (cm)	Visual Oil ² Description	TEO (mg/kg)	TPH (mg/kg)	Total PAH (mg/kg)
Point He	len					
N-1-1	Tr. A, Upper platform	50-55	HOR	32,000	19,000	570
N-1-2	Tr. B, Upper platform	40-45	HOR	21,000	9,600	490
Smith Isl						
N-3-1	Tr. A, Upper platform	28-35	HOR	27,000	17,000	450
N-3-2	Tr. B, Upper platform	10-15	MOR	17,000	8,900	450
Bay of Is	<u>sles</u>					
N-6-1	Tr. A, Upper rocky	0-5	AP	19,000	6,700	150
N-6-2	Tr. B, Upper rocky	0-5	AP	44,000	14,000	340
NE Knig	ht Island					
N-7-1	Tr. B, Upper platform	35-40	LOR	6,500	3,700	6.8
N-7-2	Tr. C, Upper platform	50-60	LOR	4,200	1,500	13
Block Isl				2.12	770	0.0
N-9-1	Off Profile, Tidal flat	2-10	LOR	840	770	23
N-9-2	Off Profile, Upper rocky	0-2	AP	13,000	5,400	210
Herring	Bay					
N-10-	1 Tr. A, Pebble beach	65-75	LOR	2,300	340	8.4
Herring	Bay				100	0.0
N-13-	1 Tr. A, Upper rubble	15-20	LOR	400	130	2.3
Northwe	•				4.1	
	1 Mid beachface	5-10	clean	-	4.5	trace
Latouch			OF	1 (00	EEO	7.5
N-15-	1 Tr. B, Upper platform	12-15	OF	1,600	550	7.3
	<u>atment Sites – Sleepy Bay</u>				0.000	200
	Untreated area - surface			26,000	9,800	200
	Untreated area - asphalt		AP	33,000	6,900	170
	Treated area - surface			3,700	1,400	25
	Treated area - asphalt & mouss		21,000	5,800	110	
	atment Area – NE Latouche (I			44.000	10.000	F7 0
	Treated site - oiled sediment &			46,000	18,000	570
P-6	Treated site - surface mousse or	n boulders	3	480,000	200,000	4,800

Zones refer to geomorphology of the beach profile, as described in the text. Tr = trench.

² HOR = heavy oil residue; MOR = medium oil residue; LOR = light oil residue; OF = oil film; AP = asphalt pavement.

Light oil residue (LOR): Sediments lightly coated with oil. Four sediment samples were described as LOR, and the actual TPH concentrations were 130-1,500 mg/kg.

Oil film (OF): Continuous layer of sheen or film on sediments; water may bead on sediments. Only one sediment sample was described as OF, and the actual TPH concentration was 550 mg/kg.

The sediments of the beaches studied are composed primarily of gravel, which means the sediments have an average diameter greater than 2 mm. Gravel is subdivided into four classes on the basis of size:

<u>class</u>		size range
granule		2-4 mm
pebble	_	4-64 mm
cobble	_	64-256 mm
boulder	_	greater than 256 mm

On the figures throughout this report showing trench descriptions, histograms are used to represent field estimates of grain-size distributions in the various sedimentary units. Abbreviations used in these histograms are boulders (B), cobbles (C), pebbles (P), granules (G), and sand (S).

CHAPTER 3 RESULTS OF JULY 1997 SURVEY

INTRODUCTION

The field survey portion of this study was carried out between 19-24 July 1997, using the vessel *Outer Limits* and a skiff as transportation to the field sites. The primary goal of the project was to observe physical persistence and chemical weathering of oil residues along the different shoreline types in Prince William Sound after eight years. Three years had passed since the last survey, which was conducted in July 1994.

Eleven stations were surveyed during the July 1997 study, each of which is discussed in some detail in this report. In addition, trends observed in other surveys and the most important points from previous reports are reviewed. Although this report is complete in and of itself, we recommend that the reader be familiar with four previous reports, which completely characterize each of the original sites for the period September 1989 to January 1991 (Michel and Hayes 1991), and present the most significant changes observed during the August 1991 survey (Michel and Hayes 1993a), the August 1992 survey (Michel and Hayes 1993c), and the July 1994 survey (Michel and Hayes 1996).

COBBLE/BOULDER PLATFORMS WITH BERMS

Introduction

Five of the stations surveyed during the July 1997 field study were classified in the category cobble/boulder platforms with berms. A more general term for this category would be intermittently exposed gravel beaches. These are the most exposed beaches (to wave action) occurring in Prince William Sound, as well as the coarsest-grained. As gravel beaches go, their morphology is somewhat unique, primarily because they were uplifted during the Good Friday earthquake of 1964, and do not appear to have yet achieved equilibrium with respect to beach-forming processes. The typical morphology of these beaches is illustrated by the topographic profile in Figure 3-1.

On gravel beaches, the coarser gravel fractions are moved landward during storms, forming a peaked mound of coarse gravel at the most landward part of the beach called the storm berm. This pattern is in contrast to sand beaches, where the sediment is moved off-

shore during storms. Accordingly, the most landward part of the cobble/boulder platforms with berms usually contains an elevated storm berm, which has lower-level spring-tide and neap-tide berms superimposed on its relatively steep seaward side. Most of the gravel beaches in this class are underlain by what appear to be uplifted wave-cut rock platforms, which are usually steeper on the landward half (upper platform; Figure 3-1A). As discussed earlier (Michel and Hayes 1991, 1993a, 1993c, and 1996), the gravel that overlies the bedrock platform has a veneer, or armor, of well-sorted cobbles and boulders as a result of the finer clasts having been winnowed away by storm-wave-generated currents. The sediment under the armor is considerably finer-grained than the armor itself, even containing sand and granules with depth. When these beaches were covered with oil during the spill, some of the oil penetrated through the overlying armor and into the protected finer-grained sediments below. The subsurface oil thus secured under the surface armor of coarse gravel was one of the more difficult issues dealt with during the spill cleanup. One of the primary goals of this survey was to determine the quantity and chemical makeup of any oil remaining under the armor after eight years of exposure to the natural processes of chemical weathering, tidal flushing, and sediment erosion.

Station N-1 (Point Helen)

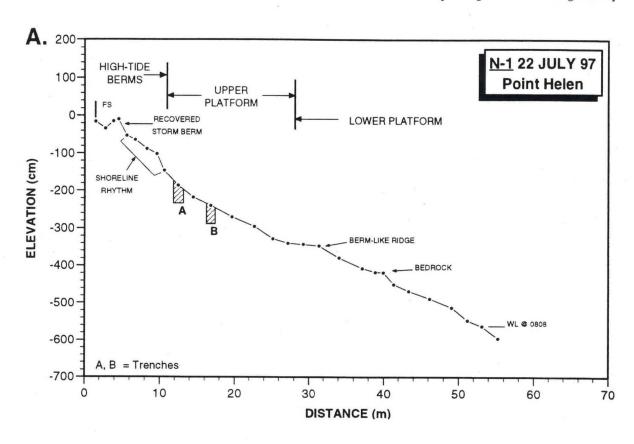
<u>Introduction</u>. Station N-1 is located a little over 1.5 kilometers (km) north of the southern tip of Knight Island at Point Helen (Figure 1-1). The permanent beach profile at station N-1 is located 150 meters (m) north of a prominent raised sea stack that is located in the middle of the intertidal zone. This part of Knight Island was uplifted 2.5 m during the Good Friday earthquake of 1964.

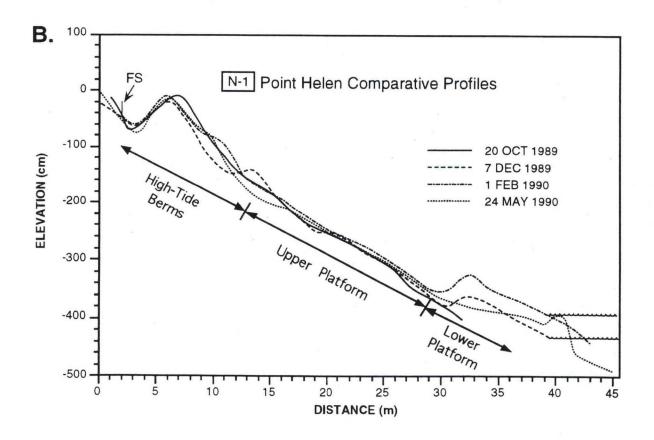
This station is one of the more exposed (to wave action) of our study sites, with an effective fetch of 15 to 20 km to the east and 45 to 50 km to the north-northeast. Wind data collected by NOAA at three stations in the Sound for the storm season of 1989/1990 show

Figure 3-1. (Facing Page) Station N-1 (Point Helen; Knight Island).

A. Topographic profile surveyed on 22 July 1997 showing morphological subdivisions and location of trenches dug on that date.

B. Changes in the beach profile between September 1989 and May 1990. Note the erosional/depositional patterns at the high-tide berms, the relative stability of the upper platform, and the presence of migrating swash bars on the lower platform. (From Michel et al. 1991; Figure 4.)





that storm winds in the Sound blow overwhelmingly out of the north and northeast (discussed by Michel and Hayes 1991).

Morphology and sediments. The morphology of this station on 22 July 1997 is illustrated by the beach profile plot shown at a 5:1 vertical exaggeration in Figure 3-1A. This beach has a very strong north-to-south longshore sediment transport rate, as evidenced by:

1) abundance of intertidal swash bars, particularly in the lower intertidal zone, which have a strongly oblique orientation to the beach and slip faces that slope to the south;

2) strikingly asymmetrical high-tide berms in the form of rhythmic topography moving south; and 3) clear grain-size trends from coarse to fine in a north to south direction.

Despite the fact that this gravel beach is anchored to a raised, wave-cut rock platform, it has undergone remarkable changes over time, which are clearly illustrated by the sequential beach profile plots for the surveys carried out in 1989 and 1990 given in Figure 3-1B. The offshore face of the storm berm showed numerous short-term changes caused primarily by the migration of rhythmically spaced neap- and spring-tide berms. The plot also illustrates the frequent occurrence of migrating gravel swash bars on the lower platform. The field sketch for the 1994 survey given in Figure 3-2C illustrates the presence of both high-tide rhythmic topography and lower intertidal gravel swash bars during that survey.

On this and all other beaches in the exposed cobble-boulder beach class, the sediment grain size increases in an offshore direction, with pebbles being most common in the high-tide berm area and boulders being most common on the lower platform. Examination of 32 trenches dug at this site show that a surface armor had developed over the underlying sediments of the upper and lower platforms. In places, the mean size of the sediment that makes up the surface armor may be four times as great as that of the underlying sediment. Most of the gravel fragments are rounded as a result of abrasion during transport by wavegenerated currents and by impacts resulting from movement of the individual clasts by breaking waves. Rounded gravel is further evidence of the relatively high degree of wave energy at this site.

As late as the summer of 1991, some zones of persistent subsurface oil remained under the extensive storm berm at Point Helen, including the area of the station N-1 study site. To deal with this oil, a 2000-m long segment of the storm berm was planed-off flat, exposing the oiled sediments. Some of the heavily oiled sediment was removed, but most of the remaining excavated sediment was pushed onto the upper platform, so it could be reworked and cleaned by wave action. The field sketch in Figure 3-2A and photograph in Figure 3-3B show the area on 27 August 1991, a short time after the berm relocation project was

completed. The original, relatively prominent storm berm present at the site before the relocation project was carried out is shown in Figure 3-3A.

The history of the changes of the morphology and sediments at station N-1 since the major berm relocation project of 1991 is illustrated by the field sketches in Figure 3-2, the photographs in Figure 3-3, the grain size data in Figure 3-4, and the beach profile plots in Figure 3-5. The sketch in Figure 3-2A, drawn immediately after the relocation project, and the photograph in Figure 3-3B, show the planed-off storm berm. As seen in the photograph in Figure 3-3B, the numerous logs on the storm berm were pushed into chaotic piles back of the beach. Comparison plots of the grain size trends before (on 24 May 1990) and immediately after the berm relocation given in Figure 3-4A and 3-4B show that the pebbles of the original high-tide berms were redistributed down slope over the cobble/boulder surface of the upper and lower platforms during the relocation process.

One year later, on 13 August 1992, a large shoreline rhythm had reformed in the vicinity of the former high-tide berms. The morphology of these rhythms, depicted by the sketch in Figure 3-2B and the photograph in Figure 3-3C, indicates that there was a considerable amount of sediment moving from north to south along the profile in the vicinity of the high-tide line. The grain-size plot in Figure 3-4C and the field sketch in Figure 3-2B show that a high percentage of pebbles were still on the surface of the upper platform (around 50 percent of the total sediment cover), unlike before the berm relocation, when the sediments on the surface of the upper platform averaged about 70 percent cobbles and 30 percent boulders.

Three years later, on 23 July 1994, a new storm berm had formed, which was further seaward and considerably smaller than the original storm berm was before the relocation project. The new storm berm is clearly seen in the photograph in Figure 3-3D and the profile plot in Figure 3-5A. The comparative beach profile plots in Figure 3-5A show that approximately 75 cm to over a meter of the gravel present in the high-tide shoreline rhythm and on the upper and lower platforms in August 1992 had been eroded away at the time of the 23 July 1994 survey. The grain-size plot in Figure 3-4D shows that most of the pebbles on the upper platform had been removed and that the high-tide berm area was predominantly pebbles, at least on the surface.

Six years after the berm relocation project was carried out, on 22 July 1997, a storm berm near the size of the original berm before the relocation project had been reestablished about 2 m landward of its original position in 1990 (see Figures 3-1A, 3-2D, and 3-5A, B).

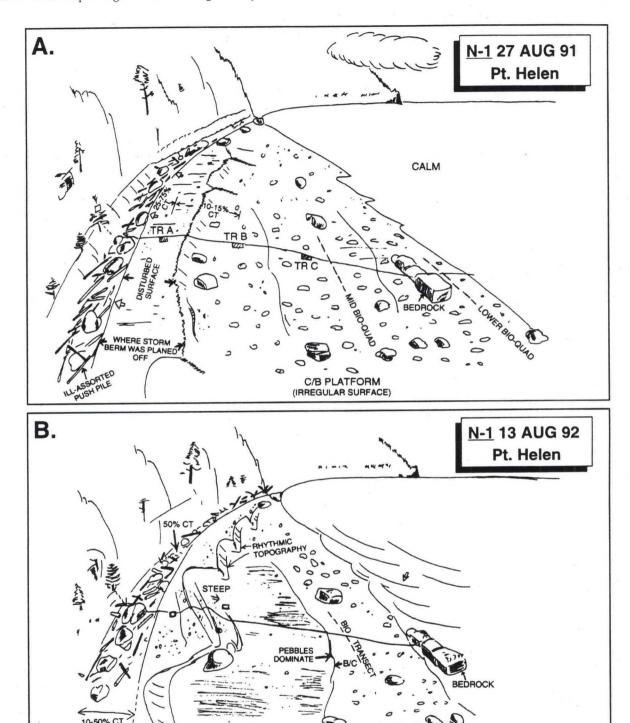
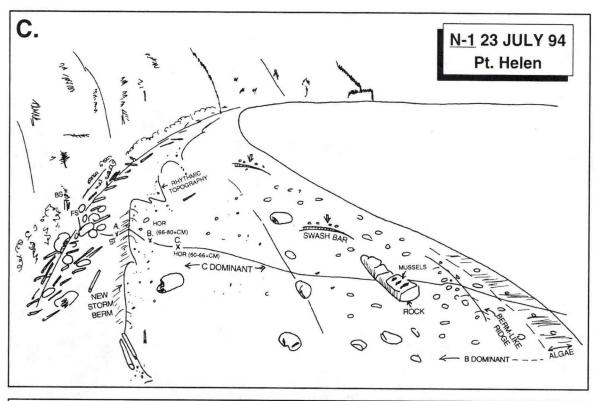


Figure 3-2. (Above and Facing Page) Field sketches of station N-1 (Point Helen). Compare with photographs in Figure 3-3.

- **A.** 27 August 1991. Note planed-off nature of the storm-berm area resulting from the berm-relocation project.
- **B.** 13 August 1992. Note the asymmetrical high-tide berms and rhythmic topography along high-tide line adjacent to the planed-off area.



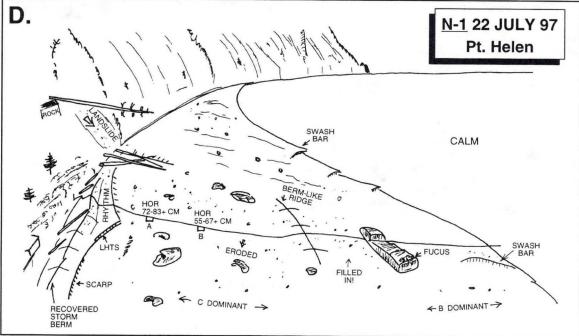


Figure 3-2. (Continued) Field sketches of station N-1 (Point Helen). Compare with photographs in Figure 3-3.

- C. 23 July 1994. A new storm berm had begun to form. Note rhythmic topography at high-tide line and southerly migrating swash bars on the lower intertidal zone.
- D. 22 July 1997. The storm berm had recovered to near its original configuration. A new berm-like ridge had formed in middle of profile, filling in area on landward side of exposed bedrock.

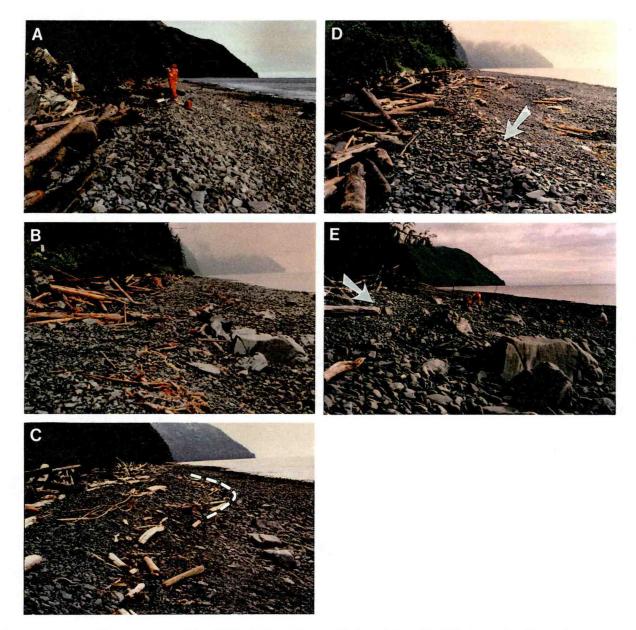
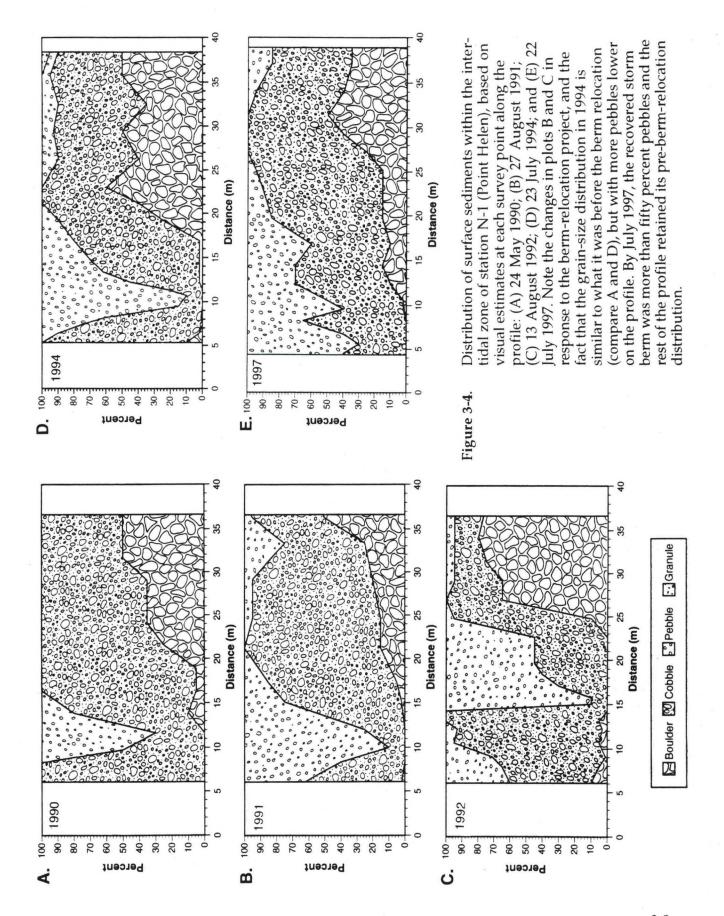


Figure 3-3. Changes at station N-1 (Point Helen; Knight Island). All views look north.

- **A.** 20 October 1989. Person is standing on crest of storm berm which had been recently activated by storm-generated waves. Photograph by D. Hall.
- **B.** 27 August 1991. Area of former storm berm that had been planed-off during the berm-relocation project carried out earlier in the summer. Compare with photograph in A and field sketch in Figure 3-2A.
- C. 13 August 1992. The new high-tide berm developed on the offshore side of the planed-off area is outlined by a dashed line (compare with field sketch in Figure 3-2B).
- **D.** 23 July 1994. A small storm berm (arrow) has begun to form in the old planed-off area.
- E. 22 July 1997. Arrow points to fully recovered storm berm. Area in foreground was highly erosional at this time.



At the time of the July 1997 survey, another shoreline rhythm in the form of a neap berm was present near the mean high-tide line and the formation of a berm-like ridge on the lower platform had caused considerable accretion in that area (Figure 3-5D). The beach several meters south of the profile was highly erosional (Figures 3-2D and 3-3E). The grain-size distribution pattern (Figure 3-4E) was similar to the pattern observed in July 1994 (Figure 3-4D), but the high-tide berm and upper platform areas were considerably finer-grained than they had been before the relocation project (Figure 3-4A). Six years later, the chaotic piling of logs and large boulders left behind the beach during the relocation project had changed little (see photographs 3-3B and 3-3E).

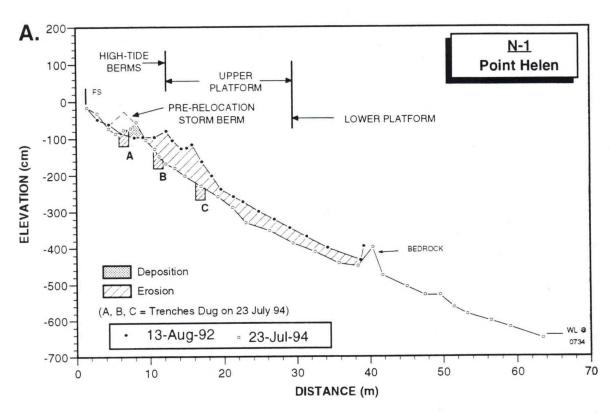
These observations indicate that for a major berm location project, such as the one carried at station N-1, in a setting with a similar wave climate, it will take between three and six years for the removed storm berm to return to its original size and position. Though there are some similarities in the patterns, it will take more than six years for the grain size distribution pattern to completely resume its original makeup. The armoring on the upper platform had already been re-formed by the time of the August 1992 survey, but we do not know exactly how long it took.

Surface oil. By the time of the August 1992 survey, all of the NOAA stations in the cobble/boulder platforms with berms class were essentially free of surface oil, except for station N-1, which still had a maximum reading of 50 percent CT on the clasts in the planed-off storm berm area (see Table 3-1). Beginning with the May 1990 survey, during which a maximum reading of 100 percent oiling was recorded, this station always had the highest amount of surface oil of any of the exposed gravel beaches. The early high readings were the result of oily debris being pushed over the top of the storm berm during a mid-October 1989 storm. The high readings from 1991 forward were the result of the excavation

Figure 3-5. (Facing Page) Topographic beach profile changes at station N-1 (Point Helen) that illustrate the following:

A. Changes between 13 August 1992 and 23 July 1994. Much of the sediment that had accumulated on the platform as a result of the berm relocation (summer 1991) and the migration of a major shoreline rhythm onto the profile (summer 1992) had been eroded away and a relatively small storm berm had formed.

B. Comparison between 23 July 1994 and 22 July 1997 surveys. By 1997, the area landward of the bedrock outcrops had filled in with gravel in the form of a berm-like ridge and the storm berm had reformed about 2 m landward of its original position.



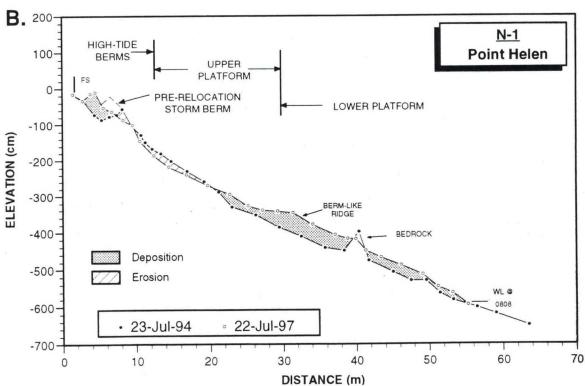


Table 3-1.	Maximum surface oiling	g observed on grave	el beach profiles (i	n percent).
------------	------------------------	---------------------	----------------------	-------------

Station	September 1989	May 1990	August 1991	August 1992	July 1994	July 1997
N-1	95	100	75*	50	5	Тисло
N-3	100	20	5	0	0	Trace 0
N-4	75	0	0	, ,	0	0
N-7	80	5	0	0	0	0
N-14	90	5	-	0	0	0
N-15	100	15	60*	1	0	0
N-17	70	0	0	0	0	0
N-18	100	5	50*	0	0	0

^{*} Site of major berm relocation/excavation project.

of the oiled subsurface gravel during the berm relocation project and its being placed along the highest portion of the profile, out of the zone of wave reworking. A maximum reading of five percent CT was made in the storm berm area during the July 1994 survey, with only a trace being found during the July 1997 study.

<u>Subsurface oil</u>. Table 3-2 and Figure 3-6 illustrate subsurface oiling observed in trenches dug at station N-1 since September 1989. Several conventions are used in these summaries, which are explained below:

- 1) The trench data are grouped by geomorphological zone. Figure 3-1 shows the boundaries of the three zones at N-1. The exact location of trenches in each zone varied somewhat during each survey. When two different trenches were dug within the same zone, they are shown on the same line and separated by a slash. In contrast, different degrees of oiling within a trench are listed on different lines. For example, in December 1989, the trench in the high-tide berms had LOR from 0-15 cm and MOR from 15-54+ cm.
- 2) The depths are recorded as relative to the mean sediment surface, which does not include the parts of cobbles and boulders that protrude above the surface. The reported depths do not include the surface armor.
- 3) A plus symbol (+) is used to indicate that clean sediments were not reached at the bottom of the trench. Many times water filled the trenches, making it difficult to determine degree of oiling of the sediments below the water table. Where these data are plotted, such as in Figure 3-6, the bottom of the oiling may be inferred from other trenches, which is indicated by dashed lines.
- 4) Degree-of-oiling categories were assigned based on field observations, correlated with TPH as measured for selected intervals. The vertical contact between oiling

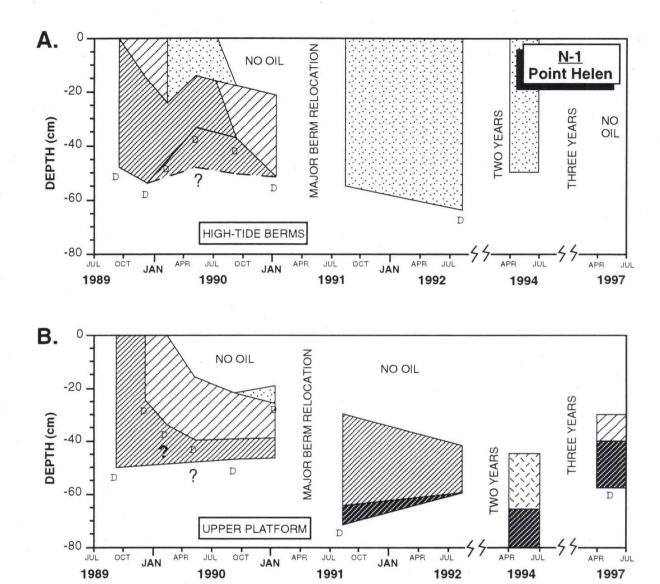
Table 3-2. Historical summary of the interval and degree of subsurface oil at station N-1 (Point Helen). Depths are reported in centimeters below the surface armor.

Survey Date	High-tide Berms	Upper Platform Lower Platform	
Oct. 1989	0-48+ (MOR)	0-50+ (MOR)	
Dec. 1989	0-15 (LOR) 15-54+ (MOR)	0-25+ (LOR)	
Feb. 1990	0-25 (ST) 25-45+ (MOR)	0-34+ (LOR)	
May 1990	0-14 (ST) 14-34+ (MOR)	16-40+ (LOR)	
Sept. 1990	18-38+ (LOR)	22-38 (LOR) 38-48+ (MOR)	
Jan. 1991	22-52+ (LOR)	20-26+ (ST)/0-40 (No oil)	
Major berm-relocation	n project—summer 1991		
Aug. 1991	0-55 (OF)	30-65 (MOR)/35-75+ (LOR) 65-72+ (HOR)	
Aug. 1992	19-64+ (OF)	42-60 (MOR/HOR)	
July 1994	0-50+ (ST)	45-66 (OF) 66-80+ (HOR) 60-65+ (HOR)	
July 1997		30-40 (LOR) 40-52+ (HOR)/47-58+ (HOR)	

degrees was drawn as a sharp break, although it is realized that, in many cases, changes in degree of oil contamination are gradual, especially for the early surveys. Over time, reworking of sediments did produce sharper contacts between degrees of oiling. Temporal changes in oiling are also connected, drawn as straight lines between two points with no effort made to change the slope, show a gradual change, or indicate a sudden change related to a storm event. Because of the multi-year intervals for the 1992, 1994, and 1997 surveys, no lines are used to connect these data.

5) Only the oiled intervals are shown in each table. That is, if the top 25 cm in a trench were clean, with sediments containing light oil residue below, and clean sediments were not reached at the bottom of the trench at 40 cm, then the data for that month would be listed as 25-40+ (LOR).

The berm relocation project of the summer of 1991 had a major impact on the subsurface oil in the area of the high-tide berms. Surveys carried out after the relocation project showed only oil film and stain on the subsurface sediments, though the oiled zone extended to depths of 50 cm as late as the July 1994 survey. No subsurface oil was observed in the high-tide berm area during the July 1997 survey.



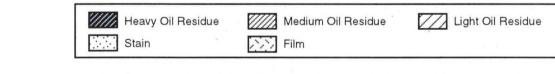


Figure 3-6. Time series plot of the interval and degree of subsurface oil at station N-1 (Point Helen). See text for explanation of conventions used.

Such was not the case for the subsurface sediments of the upper platform (Figure 3-6 and Table 3-2), where either MOR or HOR remained present throughout the survey period. As the trench descriptions of Figure 3-7 show, the trenches at positions A and B had HOR starting at depths of 47 cm and 40 cm, respectively, and extending beyond the bottom of the trenches. The HOR zone was about 25 cm shallower in 1997 compared to 1994, because about 25 cm of sediment were eroded from the upper platform between the two surveys (note the erosion in Figure 3-5B). Thus, there has been no change in the absolute elevation of

N-1 POINT HELEN, 21 JULY 1997

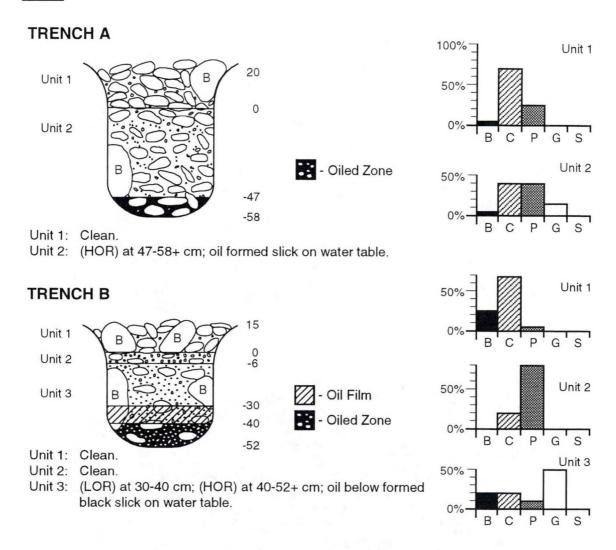


Figure 3-7. Descriptions for two trenches (A and B) dug at station N-1 (Point Helen) on 22 July 1997 (see Figure 3-1A for location of trenches). Note heavy oil at depth in both trenches. The histograms on the right side are grain-size distributions from boulder (B) to granule (G) for the units delineated in the trench.

the oiled layer since 1994. Photographs of the oiled sediments in both trenches are given in Figure 3-8.

There has been a surprising lack of change in the oil content and degree of weathering in the HOR remaining at Point Helen. Table 3-3 lists TEO and total PAHs for sediment samples collected from the bottom of trenches dug in the upper platform since 1991. Considering the heterogeneity of samples of oiled gravel, the TEO levels are relatively consistent. The TEO/PAH ratio is also consistent.





Figure 3-8. HOR at the bottom of the two trenches dug on profile N-1 (Point Helen) on 22 July 1997. See Figure 3-1A for location of trenches. This oil was the least weathered of all 1997 samples.

- A. Trench A. The HOR began at 47 cm below the armor.
- B. Trench B. The HOR began at 40 cm below the armor.

50

56

Survey Date	TEO (mg/kg)	PAH (mg/kg)	TEO/PAH*
1991	12,580	N/A	_
1992	13,960	109	128

360

570

Table 3-3. TEO and PAH concentrations in sediments from the bottom of trenches dug in the upper platform at Point Helen (N-1) over time.

18,000

32,000

The TEO/PAH ratio in fresh North Slope Crude oil, as measured over the period 1991-1997, ranges between 50-73, thus the deeply buried oil in Point Helen beaches has not undergone significant weathering as indicated by the loss of PAHs. The GC-FID chromatographic traces also indicated only moderate weathering, with alkane peaks present in the range of n-C15-30. These samples have consistently been among the least weathered of all samples collected during each survey (see discussion in Chapter 5). It appears that, for the gravel beach at Point Helen, natural removal by tidal flushing loses its effectiveness at depths of about 40 cm below the armor. After two years, the oil had weathered to the point that it was strongly adhered to the sediments.

Station N-3 (Smith Island)

1994

1997

Introduction. This station is located on the northwestern end of Smith Island (Figure 1-1) and has a straight-line fetch to the northeast that extends 45-50 km over open water in the Sound, making this one of the most exposed gravel beaches in the study area. The profile, which has been surveyed 13 times, is located just east of a natural groin of bedrock where the island takes an abrupt turn to the southwest. Consequently, the study site is an area of natural accumulation of gravel, creating a rather thick layer of gravel over the underlying bedrock platform, which was uplifted 1.5 m during the 1964 earthquake.

Morphology and sediments. Station N-3 is characterized by a large, high storm berm and relatively flat upper and lower platforms that slope 4.5 and 4 degrees, respectively (see field sketch and profile plot in Figure 3-9). An erosional event that occurred between 30 January and 4 March 1990 lowered the whole profile about 40 cm. However, as shown by the comparison plots of the beach profiles run in August 1992 and July 1994 in Figure 3-10A,

^{*} TEO/PAH in fresh North Slope Crude is 50-73.

this is typically a very stable beach, showing few changes between summer surveys. At some time between the July 1994 and July 1997 surveys, this beach was again impacted by at least one severe storm, which eroded the upper platform and high-tide berms 20-40 cm and elevated and pushed back the storm berm. This change can be seen in the comparison profile plots of the 1994 and 1997 surveys given in Figure 3-10B. Most of the other stations surveyed in July 1997 also showed evidence of some erosion, presumably as a result of the same storm or group of storms.

This station typically contains two or three shore-parallel gravel ridges located on the upper and lower platforms. We have termed these features <u>berm-like ridges</u>, because of their similarity to intertidal sand ridges that typically occur on sand beaches with a large tidal range. They have only been observed by us in Prince William Sound. These ridges are thought to form near the lower three of the four mean levels of stillstand during the tidal cycle, which is marked by a strong diurnal inequality in the Sound: 1) low-high tide; 2) high-low tide; and 3) low-low tide. Three of these ridges occurred along the profile during the 21 July 1997 survey (see field sketch in Figure 3-9A).

Like all the other stations in the <u>cobble/boulder platforms with berms</u> class, sediments along the profile increase in grain-size in an offshore direction, with cobbles and pebbles making up most of the upper profile and cobbles and boulders dominating the lower half of the profile. The surface of the upper and lower platforms, pictured in Figure 3-11A, has a well-developed coarse gravel armor of well-rounded cobbles and boulders. As discussed in earlier reports, this armor is thought to have formed as the result of storms winnowing out the finer material and leaving the coarser, abraded sediment behind. The armor overlies finer, more poorly sorted material, and moves a significant amount only during major storms.

<u>Surface oil</u>. The last time surface oil was observed at this station was during the August 1991 survey, when the highest reading was 5 percent stain.

<u>Subsurface oil</u>. The subsurface oiling history at this site, which has retained the greatest amount of subsurface oil of any of the NOAA sites studied, is outlined in Table 3-4, and the time-series plot in Figure 3-12. The descriptions of trenches A and B given in Figure 3-13 show the character of the subsurface oil at the time of the 21 July 1997 survey.

The heavy and medium oil residues in the subsurface sediments of the high-tide berm present before the berm relocation project of July 1990 were almost gone by the time of the August 1991 survey, attesting to the success of that project which only addressed the oil in the high-tide berm area. The major storm that occurred during the January/March 1990

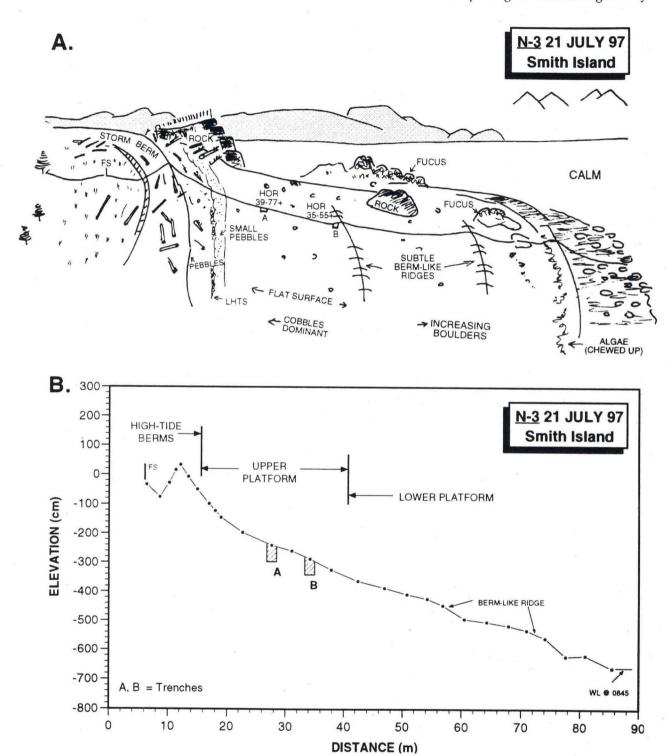


Figure 3-9. Station N-3 (Smith Island) on 21 July 1997.

- A. Field sketch. Note presence of three berm-like ridges.
- B. Topographic profile. Note steep, eroded face of the storm berm.

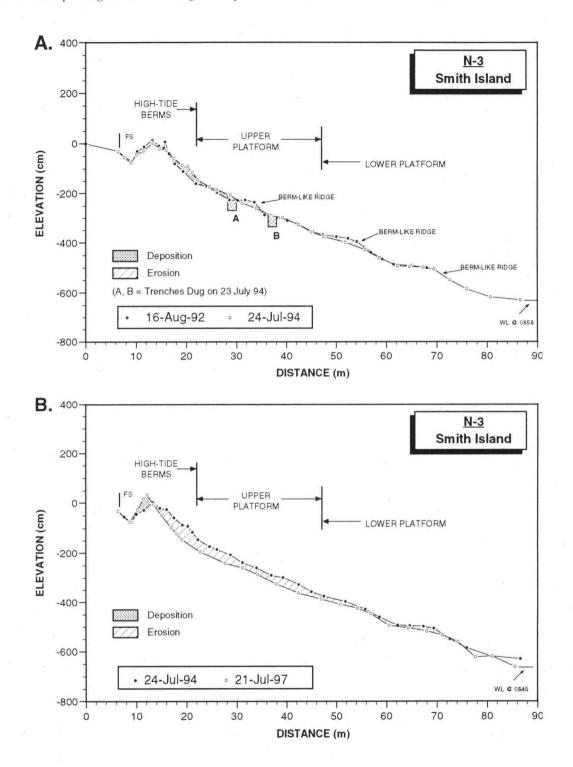


Figure 3-10. Topographic changes at station N-3 (Smith Island).

- **A.** Topographic profiles run on 16 August 1992 and 24 July 1994, showing very little change between surveys, which is typical of this site.
- **B.** Topographic profiles run on 24 July 1994 and 22 July 1997, showing erosion along much of the profile at the time of the 1997 survey.

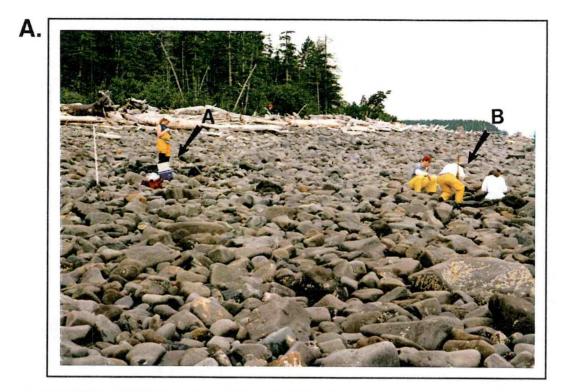




Figure 3-11. Station N-3 (Smith Island) on 22 July 1997.

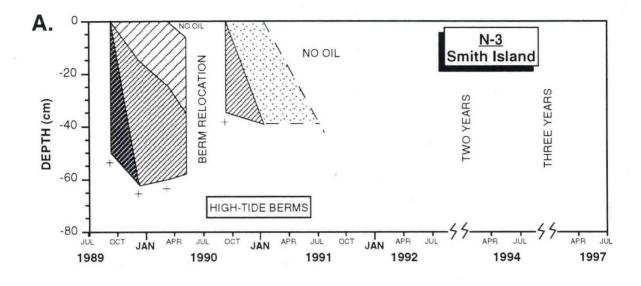
- **A.** The armored surface of the upper platform. Arrows point to trenches A and B.
- **B.** Oil in sediments (HOR) and on water table at bottom of trench A, 52 cm below the armor and 72 cm below the beach surface. The sediments at 28-35 cm below the armor contained 27,000 mg/kg TEO and 450 mg/kg PAH.

Table 3-4. Historical summary of the interval and degree of subsurface oil at station N-3 (Smith Island). Depths are reported in centimeters below the armor.

Survey Date	High-tide Berms	Upper Platform	Lower Platform	
Sept. 1989	0-50+ (HOR)	0-60+ (HOR)	0-25 (HOR)	
Dec. 1989	0-15 (LOR) 15-62+ (MOR)	0-52+ (HOR)	0-30+ (HOR)	
Mar. 1990	0-25 (LOR) 25-60+ (MOR)	0-32+ (HOR)	No oil	
May 1990	7-35 (LOR)	5-25+ (HOR)	No oil	
Berm-relocation proje	ect – July 1990			
Sept. 1990	0-35+ (MOR)	0-44+ (ST)/0-38+	0-44+ (ST)/0-38+ (HOR)	
Jan. 1991	0-40 (ST)	0-42+ (HOR)	0-35 (LOR)	
Aug. 1991	No oil	22-32 (MOR)/0-10 (OF) 32-45 + (HOR)/10-60+ (HOR)		
Aug. 1992	No oil	14-42+ (MOR)/3-32+ (MOR)		
July 1994	No oil	14-47+ (HOR)/4-40+ (HOR)		
July 1997	No oil	14-52+ (HOR)/10-30+ (HOR/MOR)		

period removed the subsurface oil that previously occurred in the lower platform area. However, heavy oil residues have persisted in the subsurface sediments of the upper platform throughout the survey period. During the 21 July 1997 survey, trench A had HOR sediments from 14-52+ cm below the well-developed surface armor and trench B had HOR/MOR sediments from 10-30+ cm. The heavily oiled sediments and oiled water table at the bottom of the two trenches are shown in Figures 3-11B (trench A) and 3-14B (trench B). The photographs of trench B in Figure 3-14 show that the physical appearance of the oil in that area had changed little between the surveys of 14 July 1994 and 21 July 1997.

Table 3-5 lists the chemical results for sediment samples collected mostly from the bottom of trenches dug into the upper platform at station N-3 on Smith Island. The sampling depth was usually between 10 and 35 cm below the armor, shallower than at Point Helen. Yet the residual oil at station N-3 was very similar to Point Helen in terms of the consistently high oil concentration and moderate degree of weathering. The alkanes were more degraded at N-3, as indicated on the GC-FID trace as fewer peaks on a "hump" of an unresolved complex mixture.



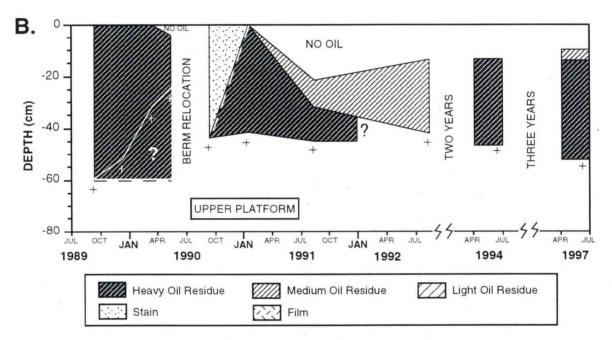
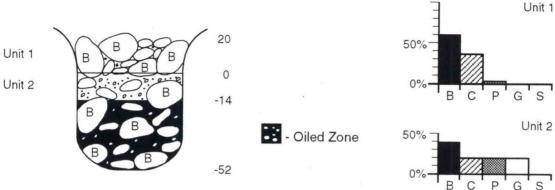


Figure 3-12. Time-series plot of the interval and degree of subsurface oil at station N-3 (Smith Island), based on trench descriptions and chemical analyses, for the (A) high-tide berms and (B) upper platform.

It is important to note that the second sample listed for the 1991-1997 surveys was from trench B on the upper platform, collected between 10-25 cm below the armor, a relatively shallow depth. The surface armor is 20 cm thick, densely packed, and of uniform-sized boulders. Over the period 1990-1994, this part of the beach profile was very stable and did not show any evidence of sediment erosion or deposition, or oil removal. In 1997, the beach surface at trench B was lowered about 15 cm, perhaps eroding some of the oil and exposing some of the deeply penetrated oil.

N-3 SMITH ISLAND, 21 JULY 1997

TRENCH A



Unit 1: Surface armor of boulders and cobbles.

Unit 2: Heavily oiled (HOR) 14-52 cm, not clean below 52 cm; boulders with heavily oiled sediments packed between.

TRENCH B

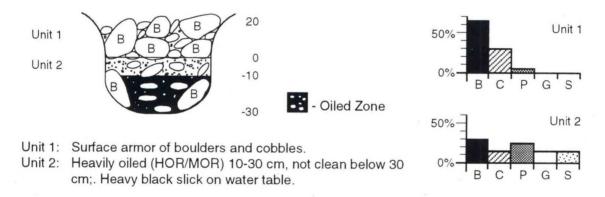


Figure 3-13. Description of trenches A and B at station N-3 (Smith Island) on 21 July 1997, showing presence of heavy subsurface oil under conspicuous surface armor. See Figure 3-9 for location of trenches.

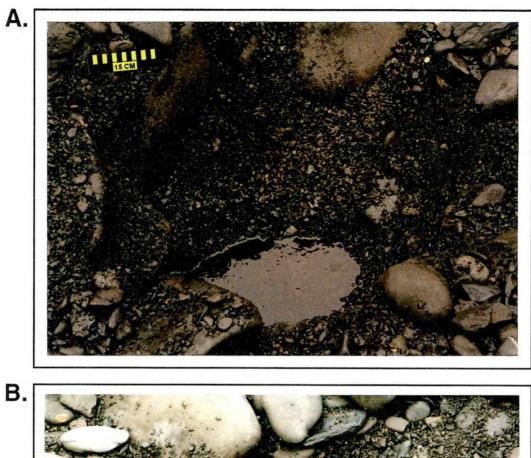




Figure 3-14. HOR in sediments in bottom of trench B at station N-3 (Smith Island), five years (A; 24 July 1994) and eight years (B; 21 July 1997) after the *Exxon Valdez* oil spill. Samples from the bottom of each trench contained 17,000 mg/kg TEO, or nearly two percent oil by weight. PAH concentrations were 250 mg/kg in 1994 and 450 mg/kg in 1997.

Table 3-5.	TEO and PAH concentrations in sediments collected from the bottom of
	trenches dug in the upper platform at Smith Island (N-3) over time.

Survey Date	TEO (mg/kg)	PAH (mg/kg)	TEO/PAH*
1989	43,500	N/A	-
1990	10,120	N/A	_
1991	4,670	116	40
	9,210	895	10
1992	8,150	11	740
	12,420	25	500
1994	16,000	300	53
	17,000	250	68
1997	27,000	450	60
	17,000	450	38

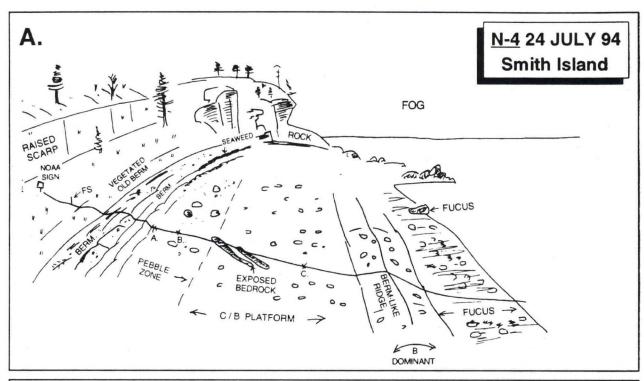
^{*} TEO/PAH in fresh North Slope Crude oil is 50-73.

Station N-4 (Smith Island)

<u>Introduction</u>. This station is located one-third of the way from the east end of Smith Island (Figure 1-1). It has a similar physical setting to station N-3, with a fetch of 40-45 km in a northeasterly direction. The 1997 survey was the twelfth time the beach had been studied.

Morphology and sediments. This beach is primarily an uplifted rock platform (raised 1.5 m during the 1964 earthquake) that is usually covered with a relatively thin veneer of gravel. As the sketches in Figure 3-15 show, the beach does not contain a major storm berm and it is backed by a raised vertical scarp, which attests to its overall erosional character. However, there was enough sediment in the high-tide berms area to retain subsurface oil for months after the spill and a berm relocation project was carried out during the summer of 1990.

The beach profile plot in Figure 3-16A shows that immediately after the berm relocation project, the relocated sediment was piled on the lower part of the high-tide berms and over the upper platform. This material had been removed by the time of the 26 August 1991 survey, apparently being deposited mostly at the far west end of the beach. The erosional process continued, and by 24 July 1994, none of the relocated sediment was present along



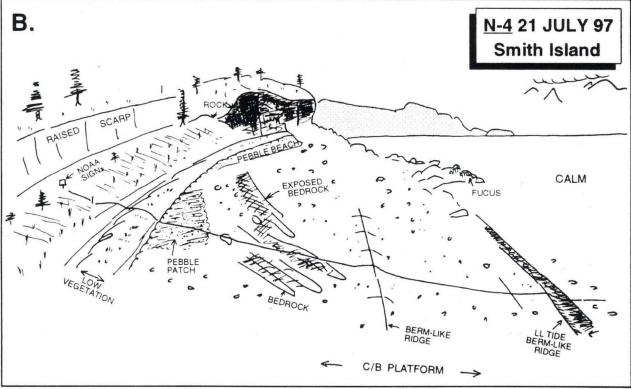
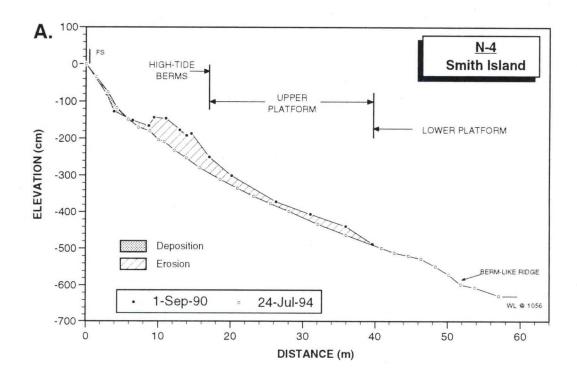


Figure 3-15. Field sketches of station N-4 (Smith Island) on 24 July 1994 (A) and 21 July 1997 (B). The 1997 survey was the first time such a large mass of exposed bedrock was observed in the intertidal zone.



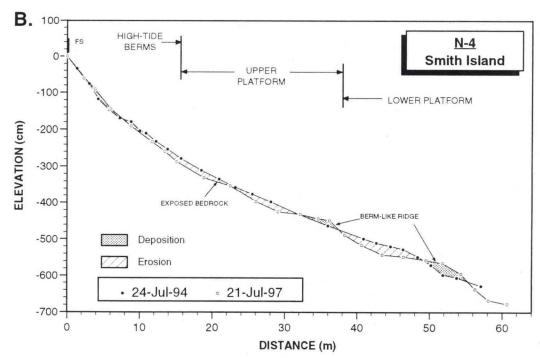


Figure 3-16. Profile changes at station N-4 (Smith Island).

- **A.** The profile run on 1 September 1990 shows a large pile of sediment on the upper half of the profile that was excavated during the berm relocation project in late summer 1990. This sediment had been eroded away by the time of the 24 July 1994 survey.
- **B.** The 21 July 1997 survey shows even more erosion of the profile down to the bedrock platform.

the profile (Figure 3-16A). Between 1994 and 1997, the beach along the profile continued to erode, as the comparison plot in Figure 3-16B shows. At the time of the July 1997 survey, the profile was the most erosional it had been at any time during the study, with a large exposure of bedrock occurring in the mid-tide area (illustrated by sketch and photos in Figures 3-15B and 3-17B), and buildup of a large pebble beach to the west of the profile.

The surface sediment distribution pattern at this station has always been highly variable, as the comparison grain-size plots of Figure 3-18 show. The mobility of the surface sediment is aided by the fact that this is the finest-grained of all the <u>cobble/boulder platform with berms</u> stations. As the photograph in Figure 3-17A shows, pebbles are especially common on the upper reaches of the profile. The abundance of finer, more mobile gravel is probably a contributing factor to the relatively rapid natural removal of oil at this station, which was very heavily oiled during the spill.

Surface and subsurface oil. All surface oil at this site was removed by the storms that occurred during thefirst nonsummer months after the spill (1989/1990). The subsurface oil in the high-tide berm area was gone by the time of our August 1991 survey, presumably aided by the berm relocation project. What appeared to be patchy subsurface oil was present as MOR in the sediments on the upper platform during the August 1991 survey, but it was absent during the July 1994 survey. Station N-4 was not visited during the 1992 survey. The rapid disappearance of the subsurface oil in the platform area at this site is thought to be the result of the combined steep slope of the upper platform (6 degrees), which enhances drainage at low tide, and the thinness of the sediment cover over the bedrock.

Station N-7 (Knight Island)

<u>Introduction</u>. Although this station contains a very large storm berm (Figures 3-19 and 3-20A), it appears to be more sheltered than the other stations in this class from all but major storms. The fetch perpendicular to the beach is only 8 km, but open effective fetches of 15 to 20 km to the northeast (40 degrees to beach) and 60 km to the east-northeast (60 degrees to beach) allow for significant wave activity during major storms. The 20 July 1997 survey marked the twelfth time this station had been studied.

As discussed in earlier reports, this beach was one of the sites selected in 1990 for monitoring the effectiveness of bioremediation on subsurface oil. Our profile line was the boundary between the area fertilized with Customblen (a slow-release pellet formulation)

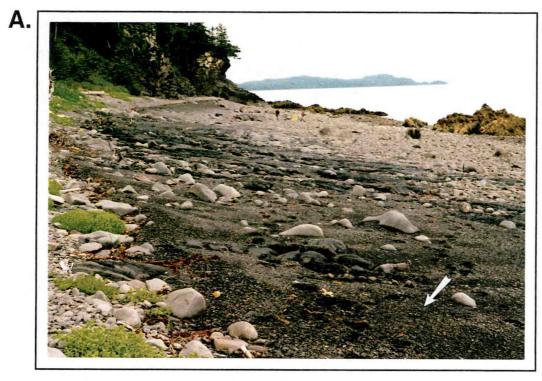




Figure 3-17. Station N-4 (Smith Island) on 21 July 1997.

- **A.** View looking west from high-tide line. Arrow points to veneer of pebbles on bedrock platform. Compare with sketch in Figure 3-15B.
- **B.** Exposed bedrock in mid-tide zone. This was the largest exposure of bedrock observed at this site since 1989.

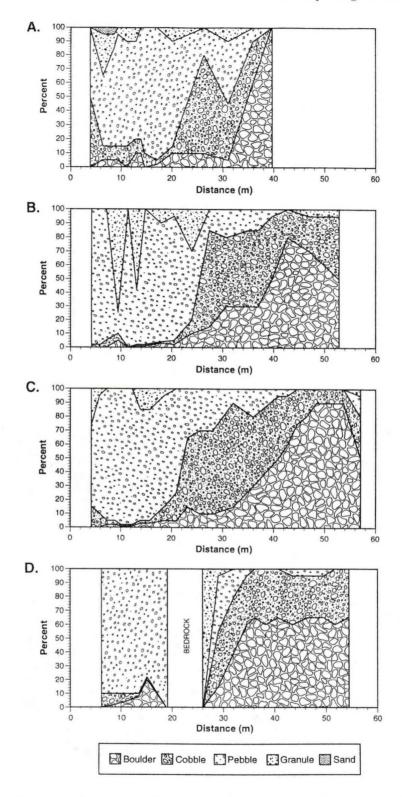
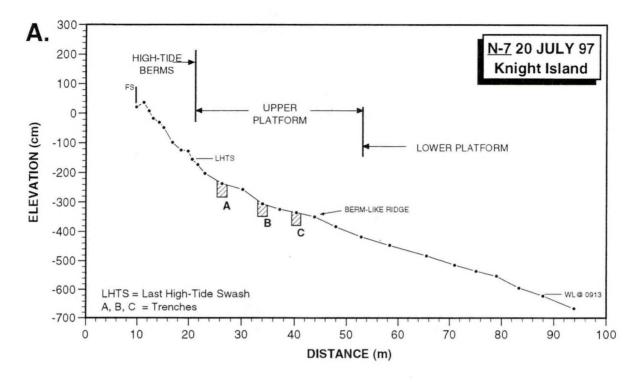


Figure 3-18. Distribution of surface sediments within the intertidal zone of station N-4 (Smith Island), based on visual estimates at each survey point along the profile:
(A) 1 September 1990; (B) 26 August 1991; (C) 24 July 1994; and (D) 21 July 1997. The plot in A was measured shortly after the berm-relocation project of the summer of 1990. Bedrock was exposed for seven meters along the mid-tide zone at the time of the 1997 survey.



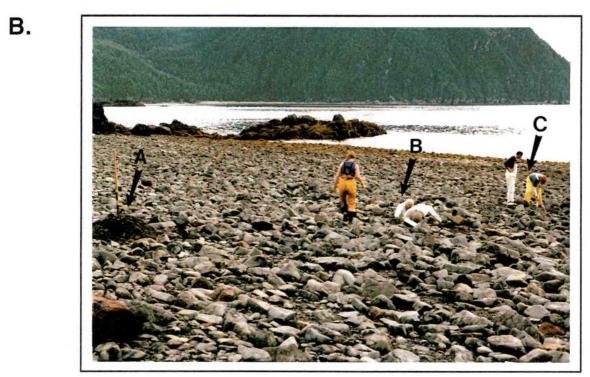
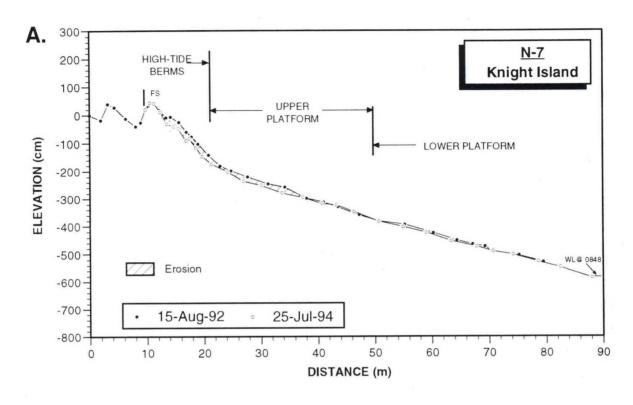


Figure 3-19. Station N-7 (Knight Island).

- A. Topographic profile surveyed on 20 July 1997.
- **B.** Surface of upper platform. Arrows indicate location of the three trenches dug along the profile (see also locations in A). Note open spacing between boulders on the beach surface.



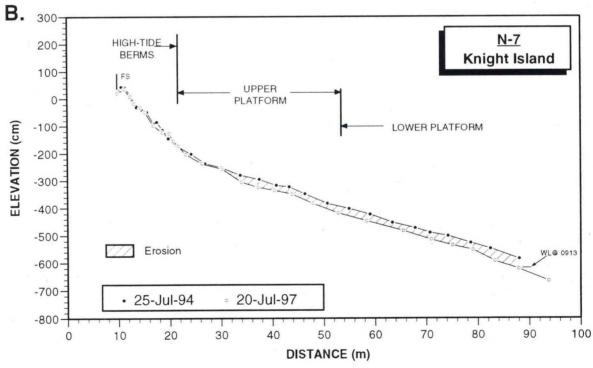


Figure 3-20. Erosion at station N-7 (Knight Island). Between August 1992 and July 1994, there was erosion along the high-tide berms and upper platform. Between July 1994 and July 1997, there was further erosion lower down the profile.

and that not fertilized. At the end of the test, on 8 September 1990, the entire beach was treated on an experimental basis with the oleophilic fertilizer Inipol.

Morphology and sediments. The upper and lower platforms, which slope seaward at 5 and 3 degrees respectively, are the flattest of all the stations in this class. As the comparison plot of the 1992 and 1994 surveys in Figure 3-20A show, the upper platform and high-tide berms areas are typically subject to considerable change. However, historically, the lower part of the upper platform and the lower platform remained remarkably stable throughout the study except for the 1997 survey, when the surface of the lower platform was eroded as much as 50 cm (Figures 3-20B and 3-21) since the survey three years earlier. Thus, another of the stations appears to have been impacted by a major storm, or storms, in the interim between the 1994 and 1997 surveys.

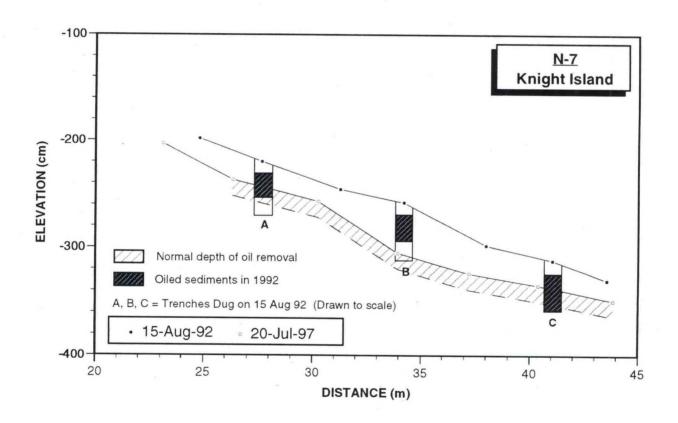


Figure 3-21. Possible explanation for the removal of oil from the upper platform at station N-7 (Knight Island). The oil in trenches A and B was apparently either eroded away (as in trench B), or was partially eroded away as the surface of the beach was lowered and partially as a result of being in the upper ~15 cm of sediments, the normal depth of oil removal over a period of a couple of years (as in trench A). The oil below the removal zone in trench C was still present as a surface film on the trench sediments during the July 1997 survey.

The surface sediments at this station, pictured in Figure 3-19B, coarsen in a seaward direction, are relatively poorly sorted, and contain some subangular clasts. Boulders make up 40 to 50 percent of the surface sediments of the lower platform. Although the sediments of both the upper and lower platforms are heavily armored, the surface armor itself is not as well sorted or densely packed as at the other sites in this class, and in places there are spaces between the coarse sediments of the surface layer. This armor does not appear to be as much a barrier to the lower subsurface oil as does the armor at the other <u>cobble/boulder platform with berms</u> stations.

<u>Surface oil</u>. No surface oil was observed at this station after the storm season of 1989/1990 (see Table 3-1).

<u>Subsurface oil</u>. The subsurface oiling history of station N-7 is depicted in Figure 3-22. Even though berm relocation was not carried out at this site, the subsurface oil in the high-tide berms area was cleaned by natural processes by the summer of 1991.

The subsurface oiling of the upper and lower platform areas has a much more complex history than that of the high-tide berms. There was subsurface oil in the lower platform area through the January 1991 survey, but none found on the lower platform during the August 1991 survey. As shown in Figure 3-22B, HOR remained in the sediments of the upper platform through the July 1994 survey period. However, from the August 1991 survey forward, the upper 15-30 cm of the sediments below the armor were clean, suggesting that natural processes were removing the oil from the uppermost sediments. Also, by 1992, the heavily oiled sediments of the upper platform were the most intensely weathered of the samples taken during the survey of that year. By 1994, the heavy oiling was still present, though considerably deeper, and the oil was at an advanced to extreme weathering stage. By 1997, even though TEO concentrations were 4,200 and 6,500 mg/kg, the GC-FID traces showed no discernable peaks and only a very slight hump. The oil residue in the gravel beach at station N-7 were, again in 1997, the most weathered of all stations. Table 3-6 lists the TEO and PAH results for sediments collected from the bottom of trenches in the upper platform, showing that after 1991, even at high levels of total oil, the PAHs were mostly degraded.

The puzzling weathering pattern observed at this station was discussed as follows by Michel and Hayes (1996): "One possibility is that the higher chemical weathering and physical removal at this site are related to the application of fertilizer during the 1990 test with Customblen and Inipol. However, both types of fertilizers were applied to other beaches. Application rates at N-7 were within the guidelines for widescale application (Prince et al. 1990). This station was the only gravel beach in our monitoring program

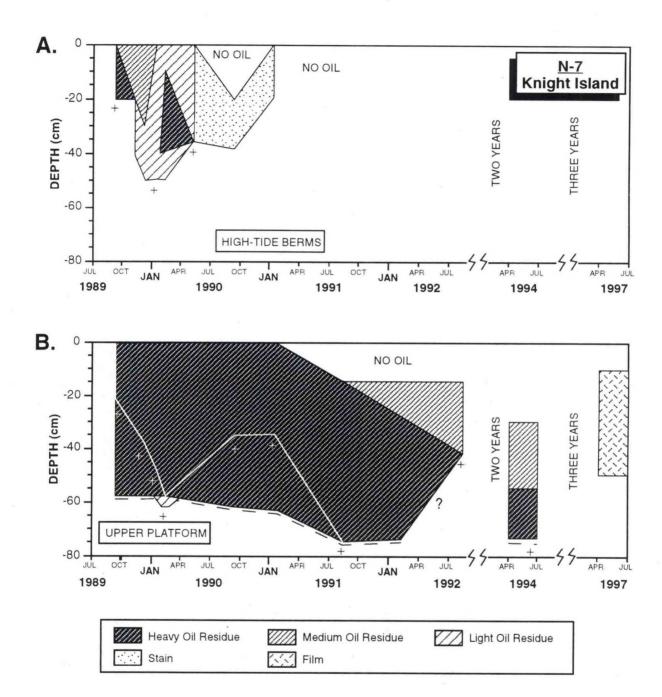


Figure 3-22. Time-series plot of the interval and degree of subsurface oiling at station N-7 (Knight Island), based on trench descriptions and chemical analyses, for (A) high-tide berms, and (B) upper platform. Note the near-complete removal of subsurface oil from the high-tide berms after the first storm season, and the persistence of oil in the subsurface sediments of the upper platform through July 1994. By July 1997, however, only a thin film of oil was left on the sediments in trench C.

Table 3-6.	TEO and PAH concentrations in sediments collected from the bottom of
	trenches dug in the upper platform at Knight Island (N-7) over time.

Survey Date	TEO (mg/kg)	PAH (mg/kg)	TEO/PAH*
1990	8,430	_	_
1991	6,480	121	53
1992	18,710 15,870	36 36	520 440
1994	7,700	17	450
1997	4,200	13	320

^{*} TEO/PAH in fresh North Slope Crude oil is 50-73.

that received two applications of Customblen in 1990. Even for samples collected as early as August 1991, station N-7 samples were more extensively weathered than other gravel beaches (Michel and Hayes 1993a). There does not appear to be any geomorphic or hydrologic difference between N-7 and other gravel beaches to explain the higher degree of weathering of the subsurface oil." Upon further consideration, perhaps the more open nature of the surface armor at station N-7 is part of the explanation.

During the survey on 20 July 1997, we found no visible subsurface oil in trenches A and B (Figure 3-21) and only an oil film at depths of 10-50 cm in trench C. A possible explanation for this disappearance of the oil, other than the bioremediation project just discussed, is that it was eroded away by the large storm, or group of storms, that clearly occurred in the study area some time during the three years between the 1994 and 1997 surveys. An enlargement of the comparison plots of the profiles run in 1992 and 1997 is given in Figure 3-21. Taking into account the standard 15 cm of natural removal of oil from the surface downward (Michel et al. 1991), the zones of oil described in trenches A and B during the 1992 survey are both above the bottom of the 15 cm removal zone on the 1997 plot. The plot also indicates that only trench C should have had oil still preserved below the natural removal zone in July 1997. Presumably, this is the oil that remained as the oil film described in trench C (Figure 3-22B).

If the hypothesis presented in Figure 3-21 is correct, this is only the second documented case for a major erosional event removing oil from the platform area of these <u>cobble/boulder platforms with berms</u>. The other example occurred during the late winter storm of 1990, which apparently removed heavy subsurface oil from the lower platform of station N-3.

Station N-15 (Latouche Island)

<u>Introduction</u>. The profile site for station N-15 is located near the center of a northwest-southeast oriented pocket beach on the northeast corner of Latouche Island (Figure 1-1). The average fetch distance is approximately 50 km; therefore, this station is subject to considerable wave action. The beach was uplifted 3.5 m during the 1964 earthquake, the maximum for any of our study sites. Because the present beach area is uplifted sea bottom rather that a rock platform, the gravel veneer is underlain by a reddish, finegrained sediment.

Morphology and sediments. The morphology of this station at the time of the 22 July 1997 survey (fourteenth time since 1989) is illustrated by the field sketch and beach profile given in Figure 3-23. This wide and relatively flat gravel beach, at which the upper and lower platforms slope seaward at angles of 6 and 4 degrees respectively, contained a well-defined storm berm and two berm-like ridges at the time of the 1997 survey. The surface of the beach has a superbly formed armor composed primarily of rounded and well-rounded cobbles relatively uniform in size (see photographs in Figure 3-24). This beach almost always has berm-like ridges, with distinct grain-size trends related to the ridges. The crest of the ridge is always coarser-grained, commonly containing at least a few boulders, and the swales are considerably finer-grained, containing some pebbles.

Berm relocation. The second largest berm relocation project we studied was carried out at this beach, being surpassed by only the large project discussed above at Point Helen (station N-1). Our field team observed the relocation project in progress on 5 September 1990 (described in detail by Michel and Hayes 1991), during which the sediments from a large linear excavation pit were placed on the upper platform in a zone about 25 m wide. This pile of sediment is clearly shown on the profile plot measured on 5 September 1990 (Figure 3-25A). The berm relocation project was very successful in the removal of the subsurface oil at this station, but the recovery of the profile to its original morphology has been quite slow. The plot in Figure 3-25A compares the 23 July 1994 survey with the 5 September 1990 survey, showing that there was a loss of sediment from the profile during that interval. Several lines of evidence discussed in Michel and Hayes (1991) indicate that there is a predominant longshore sediment transport from northwest to southeast along this beach, thus the sediment lost from the profile was probably moved toward the southeast end of the pocket beach. The comparison of the July 1994 survey with the 26 May 1990 survey, carried out before the berm relocation project, also shows a net loss of sediment at the profile site during that period.

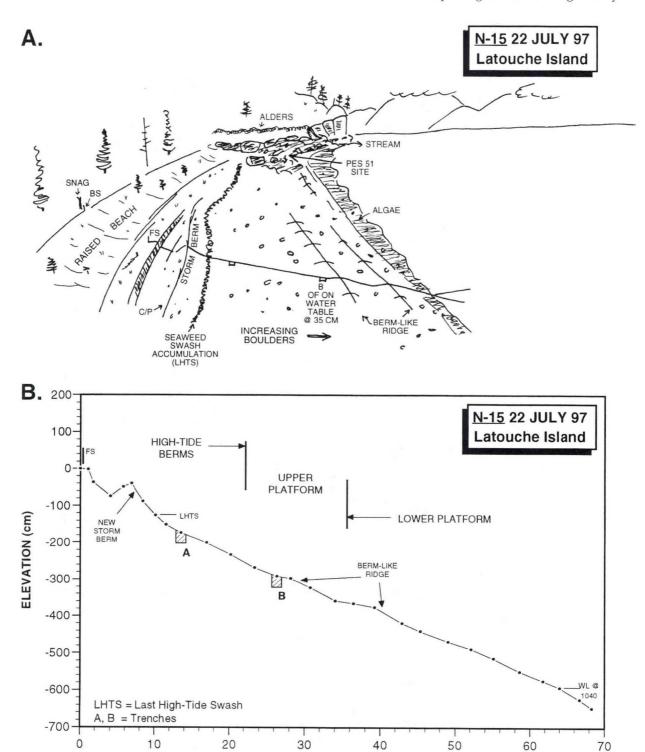


Figure 3-23. Station N-15 (Latouche Island).

- **A.** Field sketch on 22 July 1997. Storm berm had returned to near its original position before the berm relocation project of September 1990.
- **B.** Topographic profile of beach on 22 July 1997. Plotted at 5:1 vertical exaggeration.





Figure 3-24. Station N-15 (Latouche Island) (22 July 1997).

- ${\bf A.}\;$ View looking north from the last high-tide swash line (LHTS). Arrow points to trench ${\bf A.}\;$
- **B.** Rounded cobbles on beach surface near trench A. Note that the armor is densely packed and relatively uniform in size.

The profile measured during the 22 July 1997 survey is compared with three earlier surveys in Figure 3-26. The most striking feature of the 1997 profile is what appears to be a completely recovered storm berm. Figure 3-26A compares the 1997 profile with the one measured during the berm relocation project, on 5 September 1990. Note that the new storm berm in 1997 occupies the position of the excavation pit in 1990. The comparison of the 1997 plot with the 23 July 1994 profile in Figure 3-26B shows that the storm berm was still quite small in 1994. Figure 3-26C compares the 1997 profile with the one surveyed before the berm relocation project (26 May 1990), indicating that the relative volumes of sediment were about the same but that the 1997 storm berm is two or three meters seaward of the one present before the berm relocation.

In summary, the grain-size distribution and armoring along this profile had recovered by the time of the 1994 survey (Michel and Hayes 1996), and the storm berm had come close to recovery by the time of the 1997 survey. Thus, we can conclude that it takes around six or seven years for a beach to completely recover its morphology and sediment distribution pattern after berm relocation projects of the same magnitude as the one carried at station N-15 on beaches with a similar grain size and wave climate.

<u>Surface oil</u>. No surface oil has been observed at this beach since the August 1992 survey (Table 3-1). An anonymously high reading of 60 percent was made during the August 1991 survey, which was a direct result of the berm relocation project of September 1990. These surface sediments were cleaned of oil on this high energy beach during the non-summer stormy months of 1991/1992.

<u>Subsurface oil</u>. Most of the subsurface oil in the high-tide berms was gone by the end of the first storm season (Michel and Hayes 1996). As shown by the plot in Figure 3-27, the subsurface oil on the upper platform at this site was greatly decreased after the berm relocation project. The last time oil residue was observed in the subsurface sediments of the upper platform was during the August 1992 survey. Oil film was observed below 20 cm depths in trench B during both the July 1994 and July 1997 surveys.

The nature of the subsurface sediments in trenches A and B is illustrated by the photographs in Figure 3-28 and the trench descriptions in Figure 3-29. An oil film on the ground water at the base of trench B is clearly seen in Figure 3-28B. Also note the fine-grained nature of the sediments under the cobble armor.

For the one sediment sample collected from 12-15 cm in trench B, the TEO was 1,600 mg/kg, TPH was 550 mg/kg, and PAH was 7.5 mg/kg. All of these values are close to

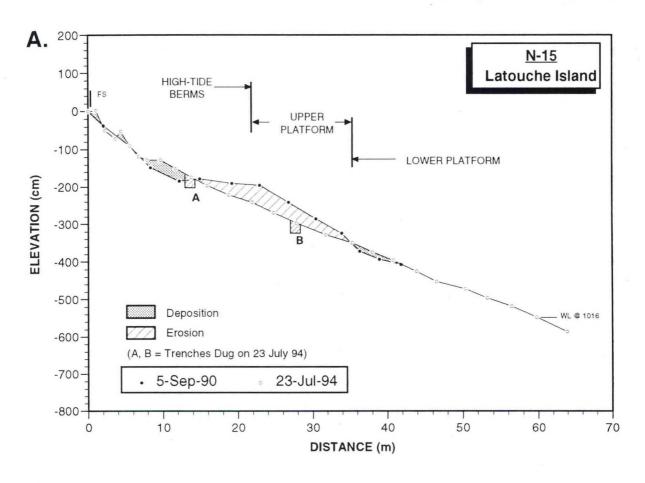
background for the Sound. However, just north of the station, there was an extensive treatment of oil residues using PES-51 with air knife injection, which re-mobilized oil. The treatment crews had completed work just a few days prior to our survey, and were removing the last of the equipment the day before our survey. We observed bands of oil coating the shoreline at the high-tide line, and patches of mousse and pavements in boulder and bedrock crevices. A sample of the mousse contained 480,000 mg/kg TEO (or nearly 50 percent oil), 200,000 mg/kg TPH, and 4,800 mg/kg PAH (Table 2-2).

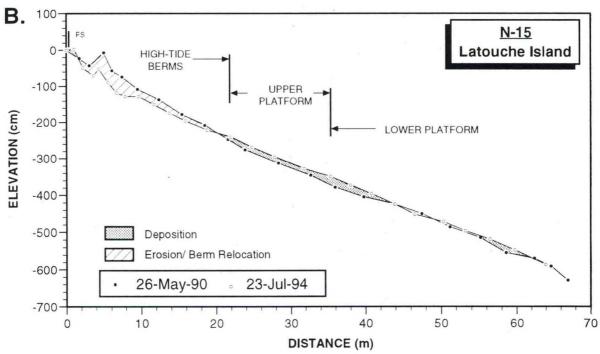
A sample of oiled sediment and mousse was similar in oil characterization but at onetenth the concentrations of the mousse. It is not likely that this re-mobilized oil will be deposited in the gravel beach sediments; the volume of oil is so low that it only coated the surface sediments.

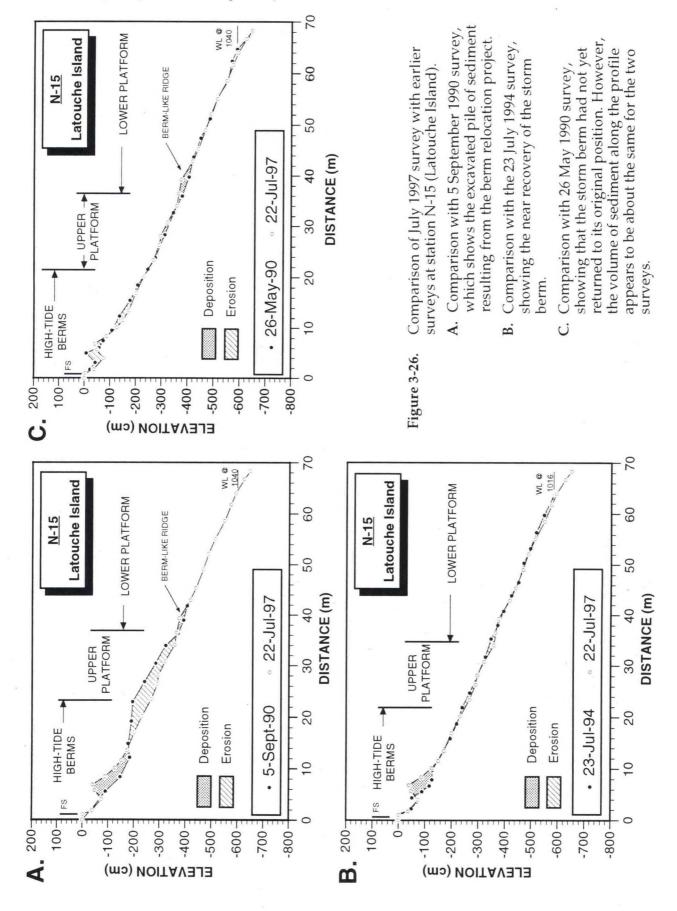
Figure 3-25. (Facing Page) Comparison beach profile plots for station N-15 (Latouche Island) plotted at a 5:1 vertical exaggeration.

A. Surveys on 5 September 1990, taken just after the berm relocation, and the survey of 23 July 1994, illustrating the ultimate loss of much of the sediment excavated during the berm-relocation project during the intervening four years.

B. Surveys on 26 May 1990 (prior to berm relocation) and 23 July 1994, which shows a net loss of sediment in the high-tide berm area, and gain on the platforms over the four-year period.







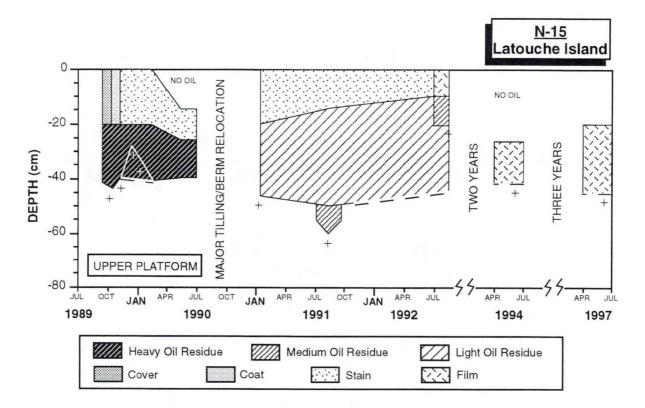


Figure 3-27. Time-series plot of the interval and degree of subsurface oiling at station N-15 (Latouche Island), for the period September 1989 through July 1994. The major tilling/excavation in September 1990 greatly reduced the oil concentration in the upper platform. Without this physical removal and breakup of the heavy oil layer below the armor, it is likely that an asphalt pavement would have formed and persisted for a very long time.



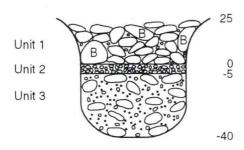


Figure 3-28. Trenches at station N-15 (Latouche Island) (22 July 1997).

- **A.** Trench A in the area of high-tide berms, which was relocated in 1990, contained no oil.
- **B.** Oil film on surface of ground water at the base of trench B located on the upper platform where the relocated sediments were piled in 1990.

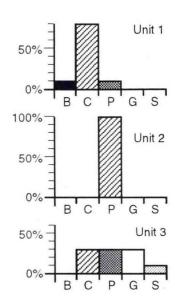
N-15 LATOUCHE ISLAND, 22 JULY 1997

TRENCH A

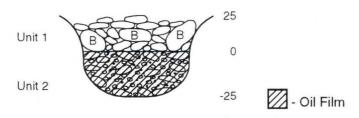


- Unit 1: No oil; well-developed cobble armor.
- Unit 2: No oil; all pebbles.
- Unit 3: Sediments were reddish brown, clay-rich soil mixed with

gravel.



TRENCH B



Unit 1: No oil; well-developed cobble armor.

Unit 2: Oil film; thin silver sheens on the water table at base of trench.





Figure 3-29. Trench descriptions for station N-15 (Latouche Island) on 22 July 1997. Oiled sediments only occurred in trench B. Note excellent armoring of the surface sediments in trench B. See Figure 3-23 for location of trenches.

BAYHEAD BEACHES

Introduction

Two of the stations studied, N-18 (Sleepy Bay) and N-14 (Northwest Bay), are classified here as bayhead gravel beaches. Both of these stations are located at the apex of moderately large bays (Figure 1.1), are considerably more sheltered than the cobble/boulder platforms with berms, and have streams that flow across the beach near the permanent profile. The switching of the stream mouths has had a major influence on the long-term changes of the beaches. As was pointed out by Michel and Hayes (1991), these gravel beaches differ from those classified as cobble (1991), these gravel beaches differ from those classified as cobble in the following ways: 1) the grain size of the gravel is smaller, being composed mostly of pebbles and small cobbles; 2) they do not have shore platforms with armored cobbles and boulders on the surface; 3) they are not exposed to direct wave attack generated over a long fetch in relatively deep water; and 4) they contain streams which have formed minor deltas on the beach near the profile. Interestingly, even though these beaches are more sheltered than the exposed gravel beaches, both stations are free of oil at the present time, unlike the more exposed beaches just discussed.

Station N-18 (Sleepy Bay)

<u>Introduction</u>. Located at the very south end of Sleepy Bay (Figure 1.1), this station is the site of occasionally significant wave action, as evidenced by the way the beach has changed during the thirteen surveys we have carried out at this site. The large waves that do occasionally impact the beach are presumably the result of its northerly orientation and a northeasterly fetch of 25 km. The stream at the head of the bay is the site of a run of pink salmon.

As noted by Michel and Hayes (1993a and 1996), Sleepy Bay was one of the most heavily oiled areas of Prince William Sound during the spill, probably because once the oil entered the semi-enclosed bay, it was difficult for it to escape. Large amounts of oil penetrated the pebble berms and the stream banks to the east of the profile to depths ranging from 50 to 125 cm. Consequently, this beach became an area of considerable concern during the spill response, particularly with the pink salmon spawning beds being nearby.

Morphology and sediments. The physical condition of this station at the time of the 19 July 1997 survey is illustrated by the field sketch and beach profile in Figure 3-30. The morphology has been greatly influenced by the switching of the stream mouth. As pointed

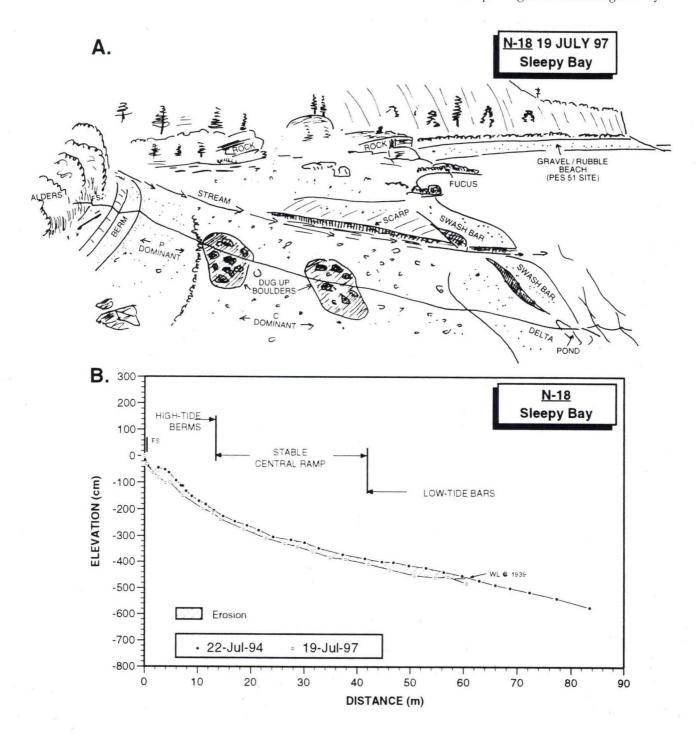


Figure 3-30. Station N-18 at the head of Sleepy Bay.

- A. Field sketch on 19 July 1997, showing two residual patches of boulder-sized rubble that were excavated from the underlying slope during the beach-excavation project of the summer of 1991. Stream appears to have switched recently to a straighter course across the top of the swash bar.
- **B.** Comparison of July 1994 and July 1997 surveys, showing evidence of erosion all along the profile.

out in the earlier reports, during periods of low runoff, the stream mouth is diverted to the east by the build up of a gravel bar in front of the stream as a result of west-to-east sediment transport. During periods of high runoff, the stream cuts straight across the bar, as had been the case some time before the July 1997 survey. The field sketch in Figure 3-30A shows the stream cutting through the middle of a swash bar that had formerly diverted the stream mouth to the east.

Like most of the other stations surveyed in July 1997, this one had also undergone significant erosion in the interim between the 1994 and the 1997 surveys. The comparison plot of the two surveys given in Figure 3-30B shows erosion of 20-50 cm all along the profile. This kind of change is not unusual for this profile. Similar erosion observed during the January 1991 survey had exposed a large zone of formerly subsurface oil in the central ramp area.

Oiling history. This was a very heavily oiled area and a troublesome one because of penetration of the oil into the porous sediments deposited by the stream. During the January 1991 survey, all five trenches dug on the profile contained heavy amounts of subsurface oil, and the oiled sediments were exposed on the surface in places. A sample collected from a depth of 30 cm from about mid-tide level contained 34,000 mg/kg oil (Michel and Hayes 1993a). In response to this persistent problem, the entire subsurface oil zone east of the stream was excavated during the summer of 1991. In the process of excavating the oil, two piles of large boulder-sized rubble were left along the profile. The beach had returned to its original configuration by the time of the August 1992 survey, but the coarse rubble was still visible during the 19 July 1997 survey (see field sketch in Figure 3-30A and photographs in Figure 3-31). The sediment distribution plots given in Figure 3-32 also show that the coarse rubble dug up during the 1991 excavation was still present in 1997.

Clean-up at nearby PES-51 site. No surface or subsurface oil has been observed along the profile at station N-18 since the summer of 1991, after the excavation project was completed. However, the rocky rubble shoreline a few hundred meters west of the site retained a considerable amount of oil and thus was one of the segments where PES-51 was used to remove residual oil from sites important to the people of Chenega Village in the summer of 1997. Paulene Roberts of LSU visited the treated area on 19 July 1997 and collected two samples of surface sediments and oil pavements in both treated and untreated areas (results are listed in Table 2-2).





Figure 3-31. Station N-18 at the head of Sleepy Bay (19 July 1997).

- **A.** View looking west across the eroded middle portion of the profile (compare with Figure 3-30A). Note boulder rubble on beach surface.
- **B.** Close-up of boulder rubble excavated during cleanup in the summer of 1991 and still present on the surface in 1997.

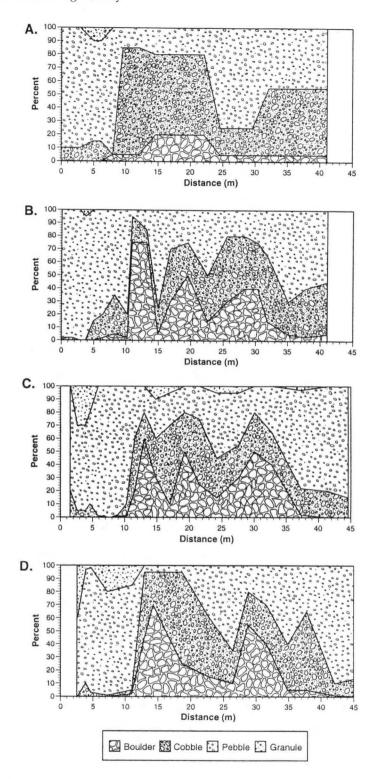


Figure 3-32. Comparison of surface sediment distribution patterns for station N-18 (Sleepy Bay) on: (A) 26 May 1990; (B) 14 August 1992; (C) 22 July 1994; and (D) 19 July 1997. The increase in the boulder content in the middle of the profile in the surveys from 1992 onward was the result of a major beach excavation project carried out on this beach in the summer of 1991. Obviously, waves at this site do not generate currents with sufficient competency to transport these large boulders.

Station N-14 (Northwest Bay)

This station, which has been surveyed ten times to date, is located at the head of the west arm of Northwest Bay on Eleanor Island (Figure 1-1). Wave action is probably low-to-moderate during storms because of the narrow entrance and long length of the bay. How-ever, even moderate waves can generate currents strong enough to move the relatively fine gravel of this beach (more than 50 percent pebbles with a considerable granule fraction).

This beach has been of interest to us because of the way it was treated thoroughly during the 1989 cleanup effort. As noted by Michel and Hayes (1996; p. 3-58), "there was extensive flushing of oiled sediment into the lower intertidal and subtidal zone during the 1989 washing activities. Whereas the hydraulic flushing was an efficient way to clean this fine-grained and relatively hard-packed beach, the biological monitoring studies being conducted by NOAA at this site suggest that the hydraulic flushing had the following negative effects on the biota: 1) direct mortality of organisms; 2) reduced growth rates; and 3) slowed recolonization of nearshore infauna because of the loss of fines and organics in the translocated sediments, direct burial, and elevated levels of oil contamination (Houghton et al. 1992)".

Our observations over time have shown a slow, but continued return of sediments to the beach since the hydraulic flushing occurred. During the 21 July 1994 survey, we observed swash bars composed of fine gravel moving back up the profile. At the time of the 23 July 1997 survey, the beach appeared to have recovered to its original configuration. A sediment sample from an area where asphalt pavements persisted through 1992 had no TEO or PAH above detection levels, and only 4.5 mg/kg TPH.

It is interesting that the two bayhead gravel beaches, N-18 and N-14, though more sheltered than the exposed gravel beaches, have no remaining oil yet the stations like N-1 and N-3 still do. This is at least partly due to the facts that: 1) the coarse gravel armoring of the exposed beaches shields the subsurface oil from exposure to reworking by waves; and 2) the bayhead beaches were cleaned up more aggressively (i.e., the oiled subsurface sediments were removed), partly because of their proximity to salmon streams. More aggressive cleaning might be conducted on fine-gravel beaches because the smaller sediments are more readily reworked by waves and they recover more quickly than coarse-gravel beaches under similar conditions. However, as exemplified by the studies at this site, it is important not to flush or push the sediments too far down the beachface.

PEBBLE BEACH/TIDAL FLATS

Introduction

Exposed tidal flats are rare in Prince William Sound, comprising only 0.1 percent (2.6 km) of the shoreline, and they are even rarer in the part of the Sound affected by the *Exxon Valdez* oil spill. The flats are composed of sand to small pebbles, and they are typically backed by a pebble beach, indicating exposure to some wave action. There is usually peat below the shallow sediments. These habitats can host a rich biological community. Only one of the flats, station N-9 on Block Island, was surveyed during the July 1997 study.

Station N-9 (Block Island)

Morphology and sediments. This key site for the NOAA biological monitoring program is illustrated by the field sketch and topographic profile in Figure 3-33 and the photograph in Figure 3-34. There have been no significant changes in either the morphology or the sediment distribution pattern at this station during any of the twelve times that the station has been surveyed. The flat appears to have been formed on a raised rock bedrock depression, and rock outcrops surround it on three sides, including the seaward edge. The water table is very close to the surface, being perched on top of a peat layer covered with fine gravel, coarse sand and abundant shell fragments.

Oiling history. This flat was heavily oiled during the spill and it and adjoining rock outcrops were intensively treated with high-pressure, hot-water flushing techniques in 1989; manual removal and nutrient addition were conducted in 1990. No visible surface oil has been observed along this profile since June 1990. However, the heavy oil loading caused patchy oil penetration and contamination of subsurface sediments in adjacent areas. In particular, the sediments just east of the profile, close to the bedrock outcrop, have remained heavily oiled, and are the site of various clam transplant and uptake experiments by the biological study team. At the time of the 20 July 1997 survey, sheens on the ground water in trenches B and C were still visible, as well as in other puddles scattered over the flat. A photograph of the sheens in trench C is given in Figure 3-34B. No sediment samples were collected along the profile in 1997, because previous samples with similar visual oiling contained extremely low levels of TEO and PAH. These sheens behave as expected for being petroleum-sourced, that is, they swirl in continuous lines rather than break with jagged edges as typical for natural sheens in organic sediments. However, it is difficult to discern the presence of very low levels of contamination.

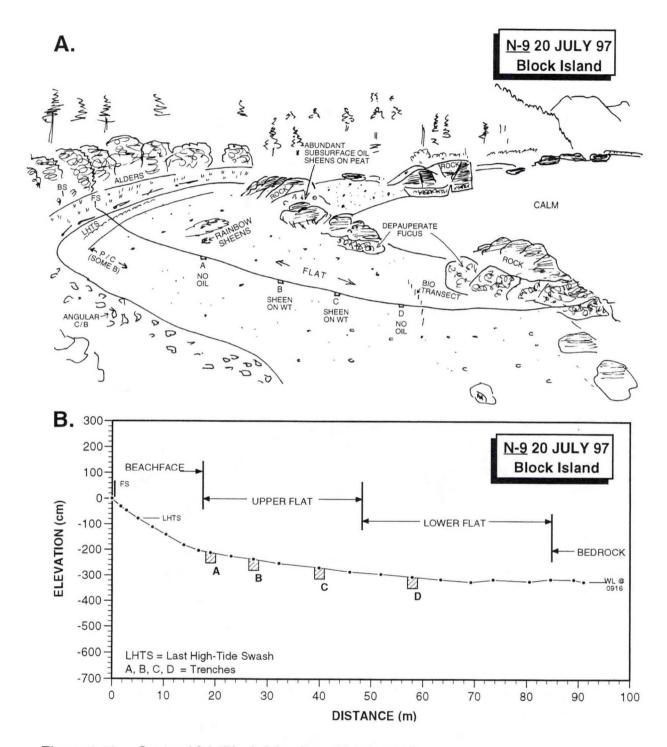


Figure 3-33. Station N-9 (Block Island) on 20 July 1997.

- **A.** Field sketch. Note location of trenches and sheens on water table (WT). The oiled rubble area illustrated by the photographs in Figure 3-35 occurs around the rock outcrop in the middle distance.
- **B.** Topographic profile of the tidal flat. Light sheens were seen on the water table in trench C (Figure 3-34C) and a trace of dull sheen in trench B. No oil was observed in trenches A and D.

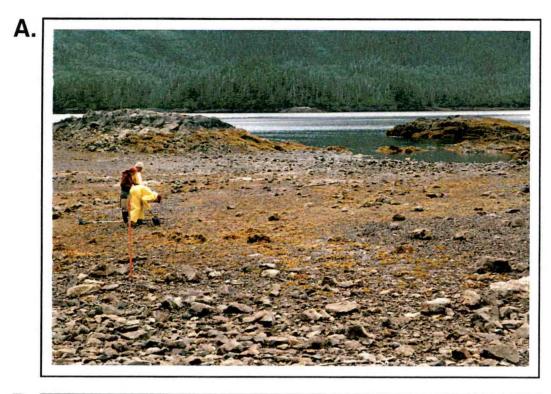




Figure 3-34. Photographs of station N-9 (Block Island) on 20 July 1997.

- **A.** View down profile from near high-tide line. The survey team is examining trench B.
- **B.** Sheens on water table at trench C.

A sample of tidal flat sediments was collected from the area of the biology clam transplant experiment (No. N-9-1; Table 2-2). This sample had a TEO of 840 mg/kg, TPH of 770 mg/kg, and PAH of 23 mg/kg. The GC-FID trace indicated that the n-alkanes were highly weathered. There was only a slight hump and no individual peaks. The PAH concentrations and pattern indicated that the PAHs had undergone significant weathering, although more than half (14 mg/kg) of the PAHs remaining were two- and three-ring PAHs (see page A-I-2 in the appendix). Eight years after the spill, these sediments still contain enough low-molecular-weight PAHs in the top 10 cm to cause chronic toxicity.

As part of this survey, a reconnaissance study was made of the rock outcrops and rubble adjacent to the profile, where asphalt pavement residues had been noted previously. In fact, the asphalt pavements had been broken up and/or removed as part of the 1991 cleanup efforts. Figure 3-35 shows a series of photographs of this area, which consists of an irregular bedrock surface covered by angular gravel and sand. In the deeper depressions in the bedrock, there is a layer of peat. The oil was concentrated in the depressions below the gravel and in the peat, forming a soft pavement. When disturbed, the oil formed sheens and brown oil droplets on the water table in shallow trenches. A sample of the asphalt pavement had a TEO concentration of 13,000 mg/kg and 210 mg/kg PAH. The GC-FID trace showed a large hump but no individual peaks, indicating near complete degradation of the n-alkanes. But, the PAH pattern was similar to the oil from deep in the gravel beaches at Point Helen and Smith Island, having undergone only moderate PAH weathering. In fact, this pavement was the least weathered (in terms of its PAH pattern) of five asphalt pavement samples collected in 1997, even though it had the lowest oil content (see Table 2-2).

SHELTERED ROCKY COASTS

As pointed out by Michel and Hayes (1991), many parts of Prince William Sound affected by the *Exxon Valdez* oil spill are characterized as sheltered rocky coasts, that is, a narrow bedrock cliff or ledge that contains little or no surface sediments. Oil heavily coated the entire bedrock surface initially, but persisted mostly on the upper intertidal zone, above the heavy *Fucus* cover. Over the first year, at least 50 percent of the surface oil was removed (Michel et al. 1991). By two years later, only trace amounts of oil remained on bedrock surfaces. However, sheltered rocky coasts had three persistent types of oil residues: 1) oil associated with sediment accumulations on the bedrock, such as tombolos; 2) oil trapped in

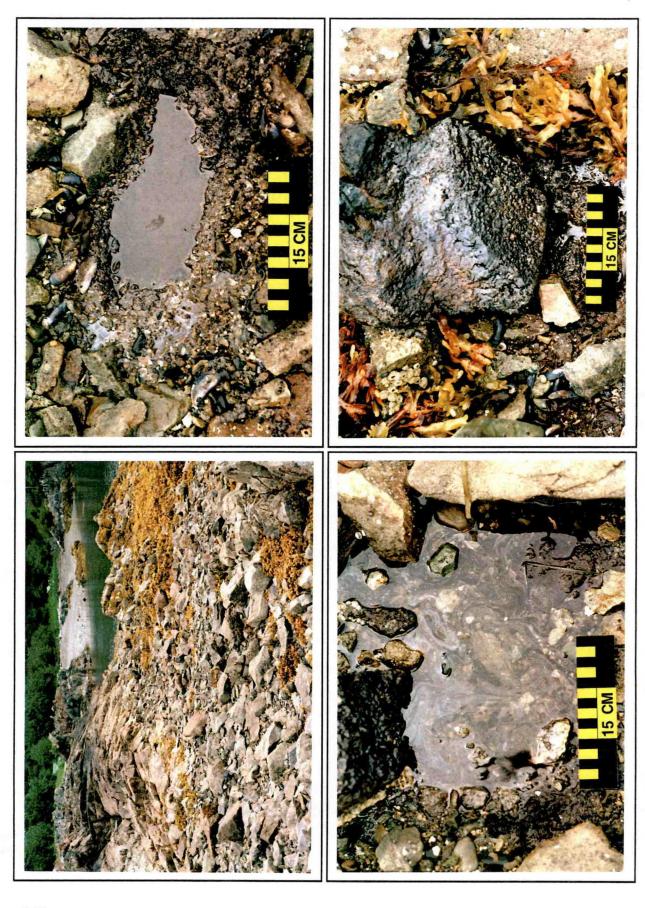


Figure 3-33). Photo in upper left is overview of area and the other three show individual shallow trenches in the oiled Oiled area near N-9 (Block Island) on 20 July 1997 (see location labeled as abundant subsurface oil in field sketch in rubble. Figure 3-35.

crevices and under a thin sediment veneer on the rock surface; and 3) very patchy coating of oil remaining on the sides and undersides of large rock outcrops.

Station N-6 in Bay of Isles (Figure 1-1) is a typical sheltered rocky shore, with a thin veneer of sediment formed by in-place weathering of the bedrock (Figure 3-36A). The station is located on the eastern end of a set-aside segment, thus no cleanup was conducted in 1989.

During the survey on 21 July 1997, oil residues in the form of asphalt pavements covered 2-5 percent of the surface over a width of about 10 m of the upper intertidal zone. The oil penetrated the more permeable surface sediments, to a depth of about 10 cm, to where the substrate become silty and impermeable (see photograph in Figure 3-36B). Two asphalt pavement samples were collected at depths of 0-5 cm: 6-1 was from the upper part of the oiled zone and was a hard pavement throughout; 6-2 was from the lower part of the oiled zone and had a hardened surface but the oil below was soft and mousse-like. The hard pavement had 19,000 mg/kg TEO, 6,500 mg/kg TPH, and 150 mg/kg PAH (Table 2-2). However, the oil was highly degraded; the GC-FID trace was featureless, and nearly all of the two- and three-ringed PAHs were below detection levels. This sample was one of the most weathered collected in 1997.

In contrast, the second sample from this site had about double the concentrations of all "total" parameters, and was much less weathered. The GC-FID trace had a large hump and even a few peaks. Over half of the 340 mg/kg PAH were two- and three-ringed PAHs. This high variability in weathering conditions in two samples of surface pavements collected just a few meters apart exemplifies the difficulty of making general statements on the fate of Exxon Valdez oil after eight years.

Michel and Hayes (1996) noted that these "scattered patches of pavement at station N-6 are expected to persist for tens of years. However, the oil is extremely immobile and not likely to be released to the environment. Continued weathering and hardening of the surface crust are expected to decrease the likelihood of release". This opinion still appears to be valid, based on the observations made three years later during this survey.

Another sheltered rocky coast, station N-10 in Herring Bay (Figure 1-1) was visited for the fourteenth time on 23 July 1997. This profile, which runs down a gully between two massive bedrock outcrops, still contained a trace of surface oil—a small patch of oil coat on the side of a sheltered rock ledge. Such patches could be found scattered around similar settings, indicating the importance of exposure to sunlight as a factor which increases oil

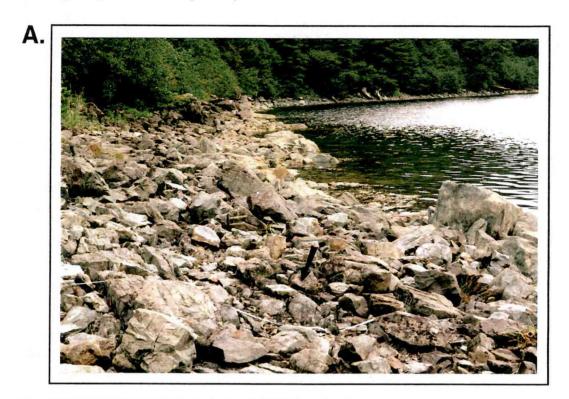




Figure 3-36. Photographs of station N-6 (Bay of Isles) on 21 July 1997.

- **A.** View across the profile showing the surface covered with sediments derived from in-place weathering of bedrock. The arrow points to the location of trench B.
- **B.** Trench B. This asphalt pavement was hard on the surface, but mousse-like and soft below. Sample N-6-2 was collected from this site.

weathering. We did not see oil coats on any bedrock surfaces exposed to direct sunlight, only on the undersides and shadowed surfaces.

The well-developed pebble beach located just north of profile N-10 is shown in the photograph in Figure 3-37A. In May 1990, our team discovered a deeply buried oil layer in this pebble beach about 50 m north of the profile. This layer, which continued to sheen profusely as late as the time of the July 1994 survey, was of interest for several reasons, which are given in the following discussion from Michel and Hayes (1996):

"In July 1994, the depth to the oiled layer in a trench located in the lower intertidal zone was 26 cm (compared to 22 cm in 1992), and clean sediments were reached at a depth of 63 cm, thus the oiled layer was 37 cm thick Chemical analysis of a sample from 35-52 cm showed the sediments contained 470 mg/kg TPH and 13 mg/kg PAHs The TPH level was relatively low because the oil occurred as a thin coating on individual clasts rather than filling the pore spaces. In a trench at the high-tide line, the oiled sediments began at 42 cm and clean sediments were reached at 86 cm The oil formed a thick brown sheen when the trench was flooded by the rising tide, appearing unchanged from that observed in 1992 and shown in Figure 3-38 in Michel and Hayes (1993). The oil at this site was among the least weathered of all samples collected in 1994 This deep oil layer most likely represents the remains of oil which originally penetrated to these depths and has not yet been removed by natural processes. It is surprising that the oil had persisted more than five years, because the well-rounded and well-sorted pebbles are readily reworked by storm waves and high flushing rates would be expected in such well-sorted and permeable sediments. However, it is obvious that the sediments are not reworked to depths greater than 26-42 cm because of the persistence of the oil and the organic clay coating on the clasts. This site may be unique in that the deeply penetrated oil is still present in the lower intertidal zone."

At the time of the 23 July 1997 survey, a 10-cm zone of LOR was found in trench A at 65 cm below the surface (highest trench in Figure 3-37A). The oiled band is shown in Figure 3-37B at the very bottom of the picture. Note the lack of gravel coarser than pebbles for the entire thickness of the beach. The pebbles in the oiled zone were also coated with a soft, gray clay; the pebbles above this zone did not have the clay coating, suggesting that they had been cleaned by reworking. A sample from the oiled zone had 2,300 mg/kg TEO, 340 mg/kg TPH, and 8.4 mg/kg PAH. The GC-FID trace was flat and featureless, indicating that the n-alkanes had been completely degraded. The PAH pattern indicated advanced weathering, with about 40 percent of the PAH being two- and three-ringed PAHs. The

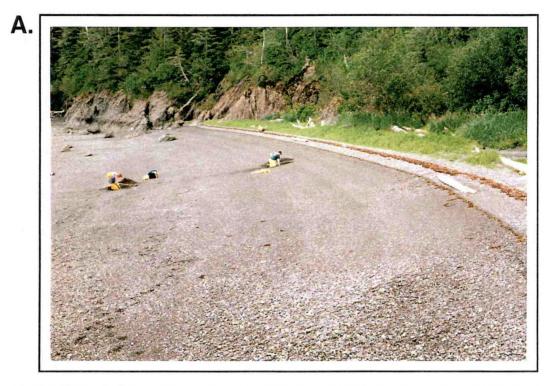




Figure 3-37. Pebble beach just north of station N-10 (Herring Bay).

- **A.** View of beach looking north from station N-10. Person at right is digging trench A.
- $\boldsymbol{B.}\;\;$ Trench A. The oiled zone is at the very bottom of the photo.

physical persistence and intermediate degree of weathering of the oil in this pebble beach was not expected after eight years. Though of limited impact because of its depth, this oil has a very slow natural removal rate, also because of its great depth. In semi-exposed areas, even pebble beaches are not readily reworked to depths of 65 cm or more.

ROCKY RUBBLE SLOPES

Introduction

The typical rocky rubble slope shoreline is composed of a rocky rubble upper intertidal zone and a zone of finer sediments in the lower intertidal zone, interpreted to be a raised bay bottom (uplifted during the 1964 earthquake). The rocky rubble slopes themselves are bedrock, which is overlain by a poorly sorted mix of angular gravel clasts up to large boulders in size which have accumulated there under the influence of gravity. There is little to no wave action at these sites, and the topographic profiles do not change over time. Therefore, natural removal processes are limited to tidal flushing, biodegradation, and photo-oxidation. The rubble sediments range widely in their degree of permeability, as does the depth to which oil penetrated the substrate.

Station N-13 (Herring Bay)

This typical rocky rubble slope is pictured in Figure 3-38A. Angular boulders and cobbles overly a poorly sorted substrate, as is shown in the trench in Figure 3-38B.

This site was a set-aside, thus there was no cleaning conducted. Oil initially formed a heavy coat on the upper 10 m of the rocky rubble. This oil coat slowly dried, cracked, and flaked-off like peeling paint from the exposed rock faces. The most persistent oil coat was on the sides and undersides sheltered from direct sunlight. No surface oil as such has been observed at this station since January 1991, so the heavy surface oil coat had been naturally removed in less than two years. There is essentially no wave action at this site, so physical removal processes were not significant. The oil coating on rocky substrates rapidly dried out and so adherence of fine-grained sediments (e.g., oil/fines interaction of Owens et al. 1993) was probably not significant. Desiccation and flaking off appear to be the primary processes of natural removal of heavy oil coating on rocky substrates. Thinner stains may, in some cases, be more persistent because they do not crack and peel.

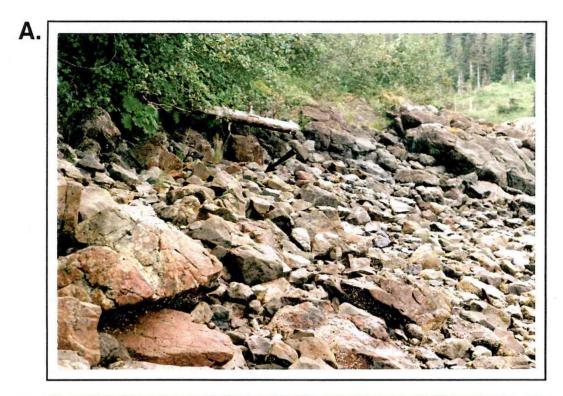




Figure 3-38. Photographs of station N-13 (Herring Bay) on 23 July 1997.

- **A.** View of the upper intertidal zone showing the rocky rubble slope. The profile begins where the log extends from the vegetation. Note the coarseness of the surface rubble, compared to the sediment substrate below the rubble, shown in the lower photograph. Arrow points to trench A.
- **B.** Trench A. A sediment sample collected at 15-20 cm contained low levels of extremely weathered oil.

The subsurface oiling pattern at this site has been very complex. The substrate is a very poorly sorted mix of angular gravel packed in a fine-grained matrix of granules and fine sand. Oil penetrated the more permeable zones or voids, and so TEO concentrations varied widely over short spaces and time (9/89-3/90), from <10 to 47,000 mg/kg. Table 3-7 lists TEO and PAH results for samples collected during the last four summer surveys. As recently as 1994, black oil droplets formed on the water table in both trenches in the rubble slope, and the PAH pattern reflected only intermediate weathering. By 1997, subsurface oil was only visible in the upper trench, where black oil droplets again formed on the water table. A soft, organic-looking material was present, and an iridescent sheen covered the sediments at 10-30 cm below the surface rubble (which was 20 cm thick). However, a sample from this zone contained very low, essentially background, levels of TEO, TPH, and PAH. A second trench on the lower edge of the rubble was free of visible oil. The persistence of free black oil in the substrate for eight years is even more surprising because of the amount of ground water flowing through the rubble when trenches are dug. Oil loading on this site was very high, and without any cleanup, the oil obviously penetrated deeply and persisted. Because natural removal is so slow, these kinds of shorelines should have priority for protection and cleanup.

Table 3-7. TEO and PAH concentrations in sediments collected from the bottom of trenches dug in the upper platform at Herring Bay (N-13) over time.

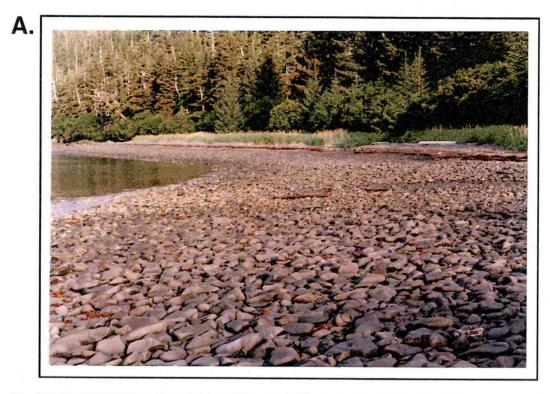
Survey Date	TEO (mg/kg)	PAH (mg/kg)	TEO/PAH*
1991	5,500	51	108
1992	7,720	15	515
1994	4,700	120	39
1997	400	2.3	174

^{*} TEO/PAH in fresh North Slope Crude oil is 50-73.

THE EXPOSURE INDEX AT BASS HARBOR

As an addendum to our report on the 1994 survey, Michel and Hayes (1996) proposed an exposure index for oiled shorelines (also presented in Hayes 1996). This concept, which was tested on the oiled shorelines of Prince William Sound, can be used to predict potential cleansing by wave action. Wind gauge data correlated with three effective fetch distances measured perpendicular to and at 45 degrees to the shoreline are used to calculate the exposure index. In Prince William Sound, both geomorphological and biological criteria for exposure to waves agreed with the readings calculated for the index, with one notable exception, the biology station in Bass Harbor (Figure 1.1). The Bass Harbor site, which is illustrated by the photographs in Figure 3-39, was classified in the biology program as exposed boulder/cobble. Note that the gravel is rounded and has a well-sorted armor, suggesting exposure to and reworking by waves. However, the exposure index reading calculated for Bass Harbor was only 176, which placed it in the moderately exposed class.

As shown by the sketch in Figure 3-40, Bass Harbor is located at the head of a narrow arm of the Sound that projects north into an indention in Naked Island. The exposure index calculations are based on both fetch distance and wind direction. The fetch distance to the south of Bass Harbor is considerable, but the wind data that was used in the calculations showed almost no readings out of the south. The exposure index does not take swell effects into account, because they are generally not very significant in enclosed embayments such as Prince William Sound. However, in the case of Bass Harbor, it is conceivable that easterly and southeasterly swell generated during big storms are refracted into the Bass Harbor arm in the manner depicted in Figure 3-40. In addition, when we were at the Bass Harbor station on 24 July 1997, we observed waves reflecting from the side walls of the arm and being amplified as they approached the biology station area in the manner shown on the inset drawing in Figure 3-40. Waves that obliquely impact a hard surface such as a rock cliff or concrete seawall are reflected off at a 90 degree angle. This refraction/reflection process may produce waves with the potential to sort and round the cobble/boulders found at the biology station in Bass Harbor.



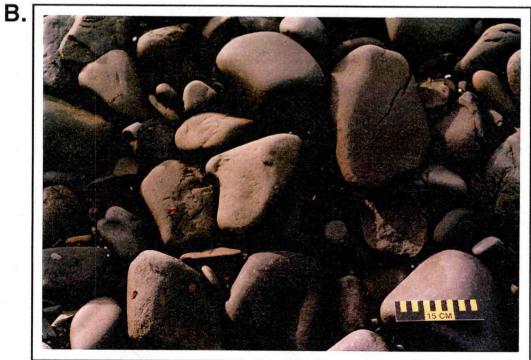


Figure 3-39. Cobble/boulder beach at the head of Bass Harbor on 24 July 1997.

- **B.** Subrounded cobbles and boulders on beach surface near mid-tide line.

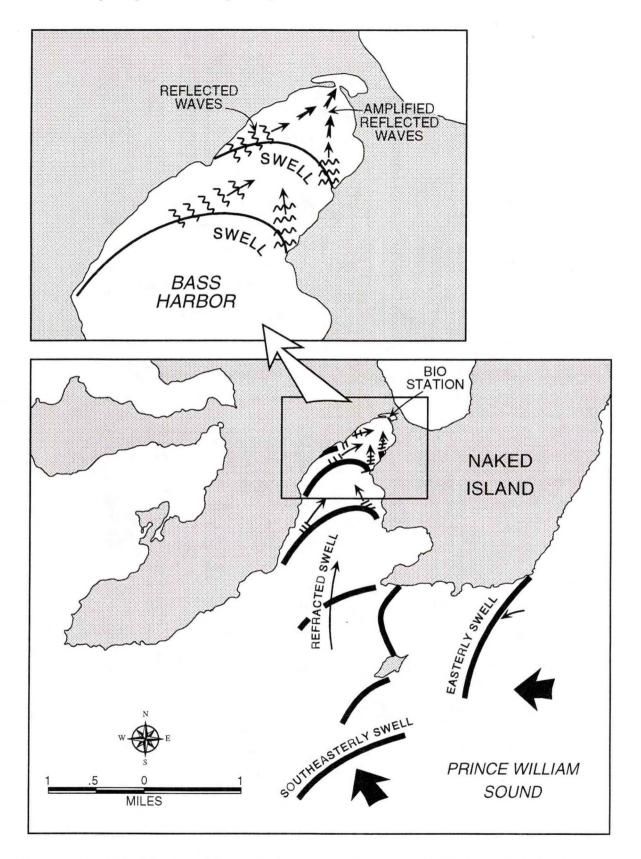


Figure 3-40. Model of amplification of wave heights at head of Bass Harbor as a result of reflection of refracted swell.

CHAPTER 4 OIL WEATHERING CHARACTERISTICS

ANALYTICAL ISSUES

The analytical procedure used for the 1997 sediment samples provided by the Institute for Environmental Studies, Louisiana State University changed somewhat from those used in the past. First, a more selective estimate of TPH was determined by GC-FID, in addition to the usual gravimetric analysis, which is now referred to as total extractable organics (TEO). Second, the list of targeted analytes was expanded to include the PAH homologues of C_4 -phenanthrene, C_3 - and C_4 -pyrene, and C_3 - and C_4 -chrysene, and the hopanes and steranes were quantified. Hopanes are highly resistant to biodegradation, thus can be used as an internal standard for normalizing PAH concentrations among samples with widely varying levels of petroleum. In previous reports, PAH concentrations were normalized using C_2 chrysene, which is not as stable.

WEATHERING PATTERNS

The chemical results are presented using two formats. First, diagnostic double-ratio plots were generated, using the C_2 - and C_3 -homologues of the PAH groups of phenanthrene and dibenzothiophene. These PAH groups are both three-ringed PAHs which undergo preferential removal by degradation of the lighter homologues. As the oil weathers, the ratios shift toward zero, allowing comparison of the degree of weathering among samples.

The second format is a histogram plot of the concentrations of individual targeted PAH alkyl homologues, normalized to hopane. The PAH pattern is traditionally used to characterize oils, for fingerprinting, weathering, and toxicity assessment. Table 4-1 lists the abbreviations used on the PAH histogram plots. The plots can be compared against the plot for the original source oil to characterize the weathering stage of the oil in each sample. Comparisons of the weathering stages of the 1997 samples can be made using a scheme proposed by Sauer et al. (1993), as described below and listed in Table 4-2:

<u>Stage I</u> (Initial Weathering) indicates oil in which evaporation has been the dominant process for the loss of PAH compounds. A small amount of loss may also have occurred from dissolution. Stage I is characterized by loss of the parent compounds of the di-aromatic hydrocarbons. Stage I oil would have been removed from natural

Table 4-1. Key for the abbreviations used on the PAH histogram plots.

Abbreviation	PAH Name	
NAPH	Naphthalene	
FLU	Fluorene	
DBT	Dibenzothiophene	
PHEN	Phenanthrene	
ANT	Anthracene	
NBT	Naphthobenzothiophene	
FLANT	Fluoranthene	
PYR	Pyrene	
B(a)ANT	Benz(a)Anthracene	
CHRY	Chrysene	
$B(b+k)F^*$	Benzo(b,k)Fluoranthene	
B(e)P	Benzo(e)Pyrene	
B(a)P	Benzo(a)Pyrene	
PERYL	Perylene	
INDPYR	Indeno(1,2,3-c,d)pyrene	
BENZP	Benzo(g.h.i)perylene	
DIBENZ	Dibenz(a,h)anthracene	

Table 4-2. Weathering stages for all 20 samples collected in 1997. See text for discussion. See Figure 5-2 for PAH patterns.

Sample Number	Weathering Stage	
N-1-1	I	
N-1-2	П	
N-3-1	- II	
N-3-2	П	
N-6-1	IV	
N-6-2		
N-7-1	IV	
N-7-2	IV	
N-9-1	Ш	
N-9-2	II	
N-10-1	Ш	
N-13-1	IV .	
N-14-1	IV	
N-15-1	IV	
P-1		
P-2	Ш	
P-3	Ш	
P-4	IV	
P-5		
P-6	Ш	

weathering processes once the oil stranded onshore. No sediment samples collected in either 1994 or 1997 from Prince William Sound were characterized as being at Stage I weathering.

Stage II (Moderate Weathering) indicates oil in which the C_0 - C_1 -, and C_2 -alkyl groups of the two- and three-ringed PAH compounds have been progressively reduced. Total naphthalenes have been reduced so that they are about equal to total phenanthrenes, compared to the original oil where the naphthalenes are about three times more abundant than total phenanthrenes. These oil residues have been exposed to biodegradation and photo-oxidation over the last eight years, though at reduced rates. Five of the twenty samples collected in 1997 were classified as at Stage II weathering.

Stage III (Advanced Weathering) indicates oil in which the PAH pattern shows continued losses of the naphthalene, fluorene, and phenanthrene alkyl homologues. Because they are more resistant to weathering, the naphthobenzothiophenes have increased in relative abundance and can even be the dominant PAH group in the pattern. Eight of the 1997 samples were classified as at Stage III weathering.

Stage IV (Extreme Weathering) indicates oil which has undergone extensive transformation. The PAH pattern is nearly devoid of the two- and three-ringed PAH compounds. Naphthobenzothiophenes are the dominant PAH group, and chrysenes have increased in relative abundance. However, the hydrocarbons are still considered to be of a petrogenic, rather than a pyrogenic origin because of the presence of naphthobenzothiophenes and the dominance of the alkyl homologues of pyrene and chrysene over the parent compounds. Seven of the 1997 samples were classified as at Stage IV.

Figure 4-1 shows the double-ratio plot for all samples collected in 1997, compared with the 1997 measurement for NSC. Figure 4-1A shows the fourteen samples from the NOAA stations; Figure 4-1B shows the six samples collected from the PES-51 treatment sites. Most of the samples fall along a line from the upper right, where the NSC source oil is plotted, toward the origin. The two samples which plot farthest from this line (14-1 and 15-1) contained very low levels of PAHs, probably at background. The samples which are clustered close to the source oil contained the highest PAH concentrations, at 340-570 mg/kg. Four out of the five samples which plot near the source oil represent the deeply penetrated oil in the beaches at Point Helen and Smith Island. They were moderately weathered (Stage II), and the least weathered of all samples collected in 1997.

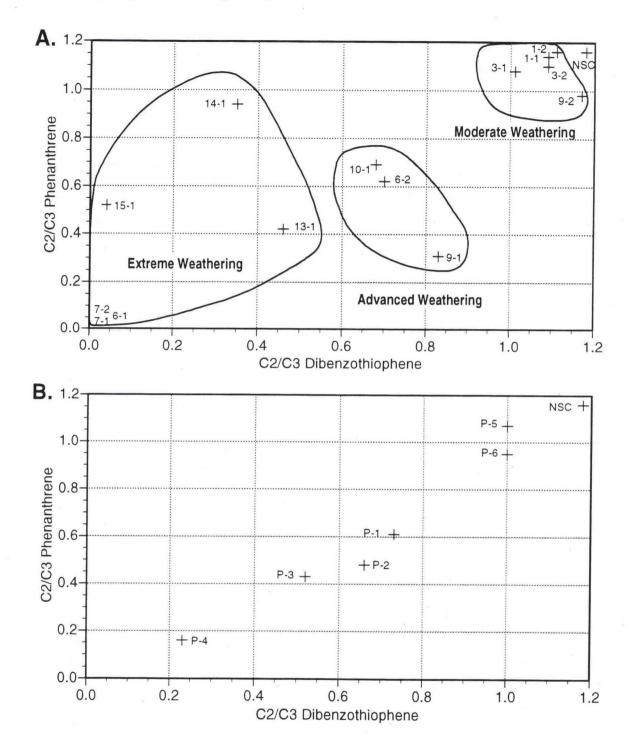


Figure 4-1. Double-ratio plot for all the 1997 samples: (A) from NOAA stations; and (B) PES-51 treatment sites. NSC is the source oil from the *Exxon Valdez*. Weathering preferentially degrades the C₂-homologues, shifting the points toward the origin. See Table 2-2 for sample descriptions.

In contrast, the sediment samples from the gravel beach at N-7 had PAH patterns which were extremely weathered (Stage IV) and the most weathered of all samples collected in 1997. Even though the TEO levels were 4,200 and 6,500 mg/kg, they had the highest ratio of TEO/PAH of any sample. The PAHs had been almost completely degraded. These samples have been the most weathered for each period since 1992. As discussed in Chapter 3, several factors are suggested as the cause of this high degree of degradation: 1) special application of Customblen and Inipol in 1990 when the beach was used as a nutrient test site; 2) the open nature of the surface armor; and 3) erosion during episodic storms which lowered the beach profile by tens of centimeters.

The PAHs in the sediment sample from the tidal flat at N-9 on Block Island indicated advanced weathering, and a significant increase in weathering compared to 1994. The oil deeply buried in the pebble beach at N-10 also underwent a significant increase in weathering between 1994 and 1997, and is now considered to be at Stage III weathering.

The least weathered cluster in Figure 4-1A includes the asphalt pavement collected from the peaty sediments in depressions on the rocky outcrop at N-9 on Block Island. This pavement was much less weathered, compared to pavements on bedrock collected at N-6 and the PES-51 treatment areas in Sleepy Bay (P-2 and P-4) which contained much more oil. Asphalt pavements have undergone a wide range of weathering, and it is not clear which factors are most important in controlling the rate of degradation.

Oil loading is obviously an important factor influencing PAH weathering rates, but not the only one. Henry et al. (1997), using the nC-18/phytane ratio as an indicator of the degree of biodegradation, suggest that there is a reduction in the degradation rate above 20,000 mg/kg TEO, 10,000 mg/kg TPH, and 250 mg/kg PAH. That is, samples with concentrations above these threshold levels eight years after the spill still had some nalkanes present. Since n-alkanes are the most readily degraded compounds in oil, their persistence for eight years indicates that these oil residues are still only moderately weathered. PAHs are more resistant to biodegradation than n-alkanes, as well as the major contributors to oil's toxicity, so they are valuable indicators of the potential for on-going impacts from residual oil.

It is interesting to note that the oil/sediment samples collected at the PES-51 treatment sites, shown in Figure 4-1B, also span a full range of PAH weathering degrees. The least weathered were the two samples from the treatment area just north of N-15 on Latouche Island (P-5 and P-6). This shoreline segment (LA-15C) is a composed of exposed bedrock with a thin veneer of boulders and patches of finer gravel. Patches of mousse and oiled

sediments persisted in wave shadows under and behind the larger boulders. We visited the segment shortly after cleanup with PES-51 was terminated. There was a high-tide band of oil coat throughout the treatment area. Obviously, the treatment had mobilized a significant amount of oil. This persistent oil had undergone moderate-to-intermediate weathering of the PAHs. The GC-FID traces showed moderate weathering of the n-alkanes, with only a slight hump and peaks for compounds in the range of C15. Sample P-6 was a mousse which contained 480,000 mg/kg TEO, or nearly 50 percent oil. Emulsified oil weathers very slowly, particularly where the deposit is thick.

Four sediment samples were collected by Paulene Roberts of LSU from the PES-51 treatment areas inside Sleepy Bay (LA-19A and LA-20B), two from an untreated area (P-1 and P-2), and two from a treated area (P-3 and P-4). The GC-FID trace for all four samples showed advanced weathering of the n-alkanes. The PAHs were most weathered in the two samples from the treated area, though this is not likely to be related to the recent PES-51 treatment, since PES-51 only increases the efficacy of removing oil from substrates. It is more likely that the oil in the treated area was more weathered before treatment. The time between treatment and our sampling was only a few days, and not enough time for post-treatment weathering differences to occur, particularly for heavily oiled sediments.

Figure 4-2 shows histograms of the PAHs in each sample from the NOAA stations, normalized to hopane. The determination of weathering stage shown in Table 4-2 was based primarily on the pattern of PAHs as shown in these histograms. The samples are listed in Figure 4-2, grouped by station type, with the NSC reference oil shown on the bottom of each page for comparison.

The first four samples shown in Figure 4-2 are of the deeply buried oil in the gravel beaches at Point Helen (N-1) and Smith Island (N-3). Total PAHs in these samples were very high, 450-570 mg/kg. These samples were at Stage II weathering, as indicated by the reduction in total naphthalenes so that they are about equal to total phenanthrenes, compared to the original oil where the naphthalenes are about three times more abundant than total phenanthrenes. The C_0 - C_1 -, and C_2 -alkyl groups of the two- and three-ringed PAH compounds have been progressively reduced, compared to the fresh oil. Note how similar the patterns of the four- and five-ringed PAH compounds in these gravel beach samples are to the fresh oil; they are essentially unchanged. In comparison, the next two samples shown in Figure 4-2 are from the gravel beach at N-7, where the oil has undergone extreme weathering. The only PAHs remaining are the four- and five-ringed compounds, and they total only 6.8 and 13 mg/kg. This oil was at Stage IV weathering. However, the hydrocarbons are still considered to be of a petrogenic, rather than a pyrogenic, origin

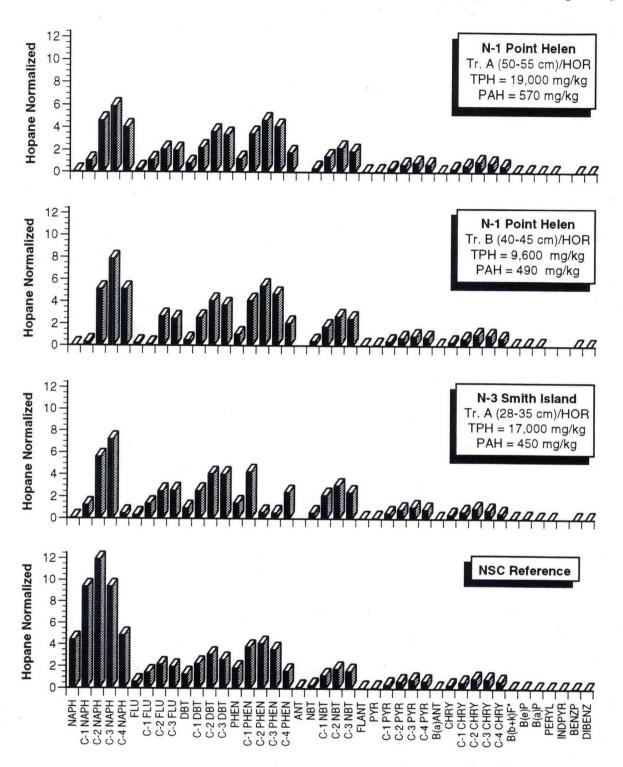


Figure 4-2. PAH histogram plots for the twelve 1997 samples from NOAA stations, normalized to hopane.

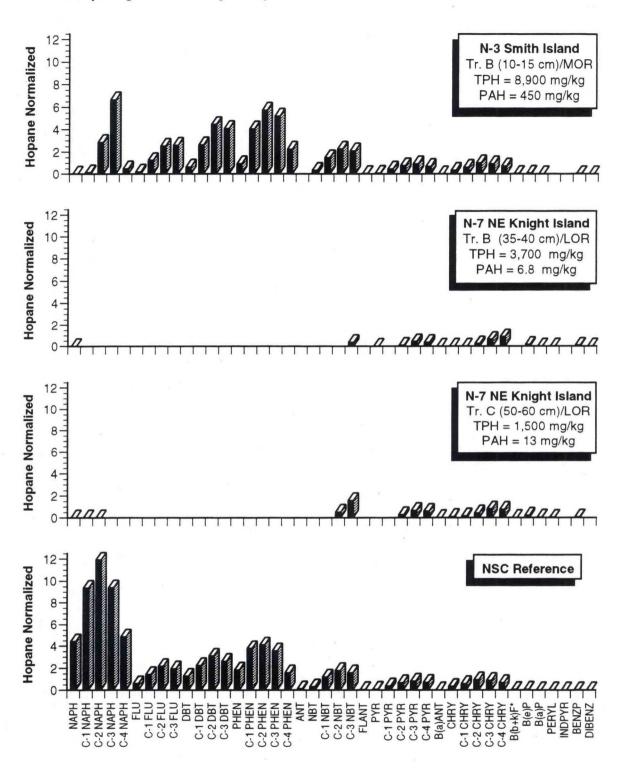


Figure 4-2. Continued.

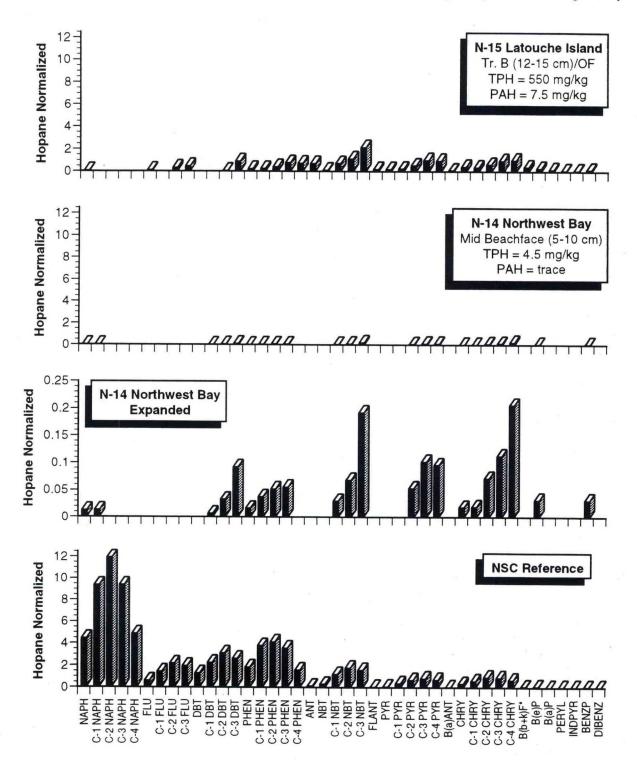


Figure 4-2. Continued.

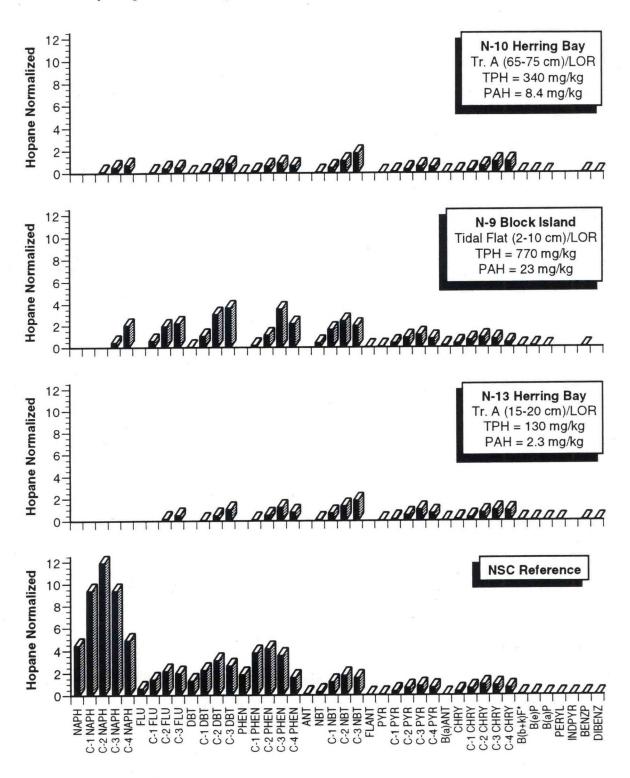


Figure 4-2. Continued.

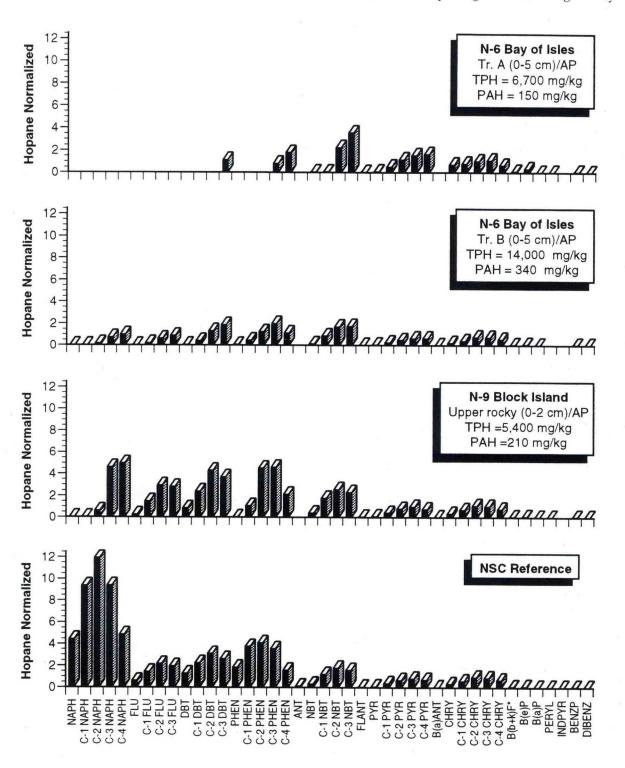


Figure 4-2. Continued.

because of the presence of naphthobenzothiophenes and the dominance of the alkyl homologues of pyrene and chrysene over the parent compounds. Since these samples were collected from deep within gravel beaches heavily oiled during the *Exxon Valdez* spill, it is likely that the oil residues are from the spill, rather than from other sources of chronic oil pollution. Fuels used by vessels in the Sound are primarily diesel which would not contain the four- and five-ringed PAH compounds.

The sample from the gravel beach at N-15 on Latouche Island contained very low PAH levels (7.5 mg/kg), but also had a petrogenic (crude oil) PAH pattern at Stage IV weathering (same as in 1994). The samples from the PES-51 treatment area just to the north of our study site contained significant amounts of naphthalenes and fluorenes, which are absent in the N-15 sample, indicating that there was no contamination by oil remobilized from the adjacent treated site.

The next sample shown in Figure 4-2 is from the pebble beach in Northwest Arm (N-14), which contained only 0.02 mg/kg total PAH. The PAH histogram is shown at the same scale as the other samples, and also expanded to show the PAH pattern. Even though the levels are extremely low, the PAH pattern still resembled a crude oil petrogenic source, although there may be some diesel fuel contamination, which is likely because Northwest Arm is a popular anchorage site. The sample from 65-75 cm deep in the pebble beach at N-10, in Herring Bay, contained hydrocarbons which were clearly of crude oil source and at Stage III weathering. Note that the naphthobenzothiophenes had increased in relative abundance to the point that they are the dominant PAH group in the pattern, yet the two-and three-ringed PAHs were still present. In 1994, a sample from a trench lower on the beachface was at Stage II weathering.

The sediment sample from the tidal flat on Block Island (N-9-1) contained PAHs at Stage III weathering, since the two- and three-ringed PAHs were still dominant. The nalkanes in this sample had completely degraded. In 1994, the sample from the tidal flat was at Stage III weathering.

The next sample, N-13-1, is from the set-aside rocky rubble shore in Herring Bay. Total PAHs were only 2.3 mg/kg, and the pattern indicates Stage IV weathering. Yet, black oil droplets and sheens were still observed on the water table in the trench from which the sample was collected. Two samples collected in 1994 were at Stage II+ and III, indicating that weathering has continued at this site.

The next three samples (on the fifth page of PAH histograms in Fig. 4-2) are of asphalt pavements collected from Bay of Isles (N-6) and Block Island (N-9). Note that they range in PAH weathering from Stage II to Stage IV. The least weathered is from Block Island, which contained the lowest oil content. The two samples from the set-aside rocky shore in Bay of Isles were collected only a few meters apart. The most weathered pavement (N-6-1) was at the higher tidal elevation and hard throughout, whereas N-6-2 was collected about mid-tide and had a soft, mousse-like interior. In 1994, the upper sample from N-6 was classified as at Stage III weathering, and the lower sample at Stage II+, so it appears that weathering of these pavements has progressed since 1994.

As noted in previous reports, there is relatively good agreement between the two approaches to characterize the degree of weathering among the 1997 sample set. All of the samples with a PAH pattern indicative of Stage II weathering plotted in the upper right corner of Figure 4-1. The three samples at Stage III PAH weathering plotted in a middle grouping. The Stage IV samples plotted in a larger area than the other groups, primarily because the total PAHs were very low, close to background. The double-ratio plot method starts to vary when PAH levels approach the detection level.

In summary, eight years after the spill, oil residues in Prince William Sound ranged from moderately to extremely weathered. The least weathered residues (at Stage II) were found in samples collected from gravel beaches with well-established armor. There had been little to no change in weathering stage for the oil from these sites since 1994. There was evidence of some physical erosion, but little chemical change of this deeply penetrated oil. In contrast, most other oil residues have increased in weathering, compared to 1994. Only one asphalt pavement was at Stage II weathering. All other samples contained hydrocarbons which were at Stage III and IV.

CHAPTER 5 SUMMARY OF OBSERVATIONS EIGHT YEARS AFTER THE SPILL

Fourteen geomorphological field surveys covering a period of eight years following the *Exxon Valdez* oil spill have provided observational data at eighteen field sites within Prince William Sound. Over time, surveys at seven of the sites were discontinued, with eleven sites being resurveyed during the July 1997 study. Some of the most important observations derived from the eight-year investigation are summarized below.

SURFACE OIL REMOVAL RATES AND MECHANISMS

Most of the surface oil at all of the gravel beach sites was removed by wave action during the storms of the nonsummer months of 1989/1990, with a large percentage of the removal occurring by the end of December 1989. Maximum readings of 50-100 percent surface oiling were made during the August 1991 survey at stations N-1 (Point Helen), N-15 (Latouche Island), and N-18 (Sleepy Bay), all of which were sites of major berm relocation/excavation projects. By July 1994, only station N-1 retained any surface oil, a maximum reading of 5 percent, and none was observed at any gravel beach site during the July 1997 survey.

The rates of surface oil removal at the sheltered sites were significantly slower, with about half of the surface oil coverage existing through March 1990. The most persistent surface oil was oil coat on the sides of rock surfaces and asphalt pavements in crevices and wave shadows at the base of boulders. The thickness of the surface oil was much greater on sheltered shorelines, with coat and pavements, compared to the stain persisting on exposed gravel beaches. Removal of the thicker oil coating on sheltered shorelines appeared to occur by desiccation, photo-oxidation, cracking, and peeling, rather than by abrasion of sediment movement. The asphalt pavements in sheltered habitats have been very persistent, particularly where they are thick. The surface had dried into a hardened crust within the first two years. However, eight years later they commonly contained a soft, mousse-like interior which was only moderately weathered.

According to James C. Gibeaut (personal communication), a survey carried out for all the oiled areas in Prince William Sound in the summer of 1993, four years after the spill (sponsored by the *Exxon Valdez* Oil Spill Trustee Council), showed that about 5 km of the shore-

line still retained surface oil, which resided mostly between "mid- to upper-intertidal boulders and in bedrock fractures". During the 1997 survey, we observed surface oil of this type near stations N-6 (Bay of Isles), N-9 (Block Island), N-15 (Latouche Island), and N-18 (Sleepy Bay). We also observed work in progress by cleanup crews who had applied the chemical agent PES-51 to remove the surface oil at sites important to the people of Chenega Village.

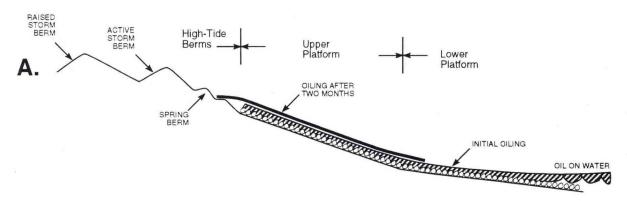
SUBSURFACE OIL PERSISTENCE IN GRAVEL BEACHES

Probably the most significant observation made during the later years of this study was of the amount and modes of preservation of the oil still present in subsurface sediments, particularly in gravel beaches. Four years after the spill, Gibeaut and co-workers found subsurface oil along about 7 km of the shoreline of the Sound, in 109 distinct locations. Furthermore, our study shows that subsurface oil still remains at or in the near vicinity of eight of the eleven stations we resurveyed in July 1997 in amounts that exceeded 25,000 mg/kg TEO (2.5 percent oil by weight) at two of the sites, eight years after the spill.

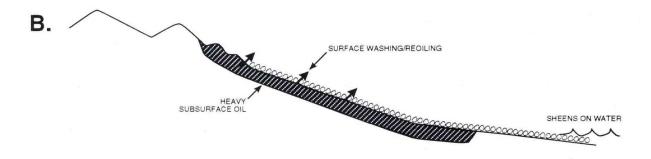
The largest amount and the least weathered subsurface oil we found after eight years was in the intermittently exposed, coarse-grained gravel beaches, in particular at stations N-1 (Point Helen) and N-3 (Smith Island). In the report on the August 1992 survey, Michel and Hayes (1993a) placed these two beaches into Subclass I of the group termed cobble/boulder platforms with berms, namely those that have a well-established coarse-grained armor, are relatively flat, and contain a thick veneer of sediments over the rock platform.

A schematic model for the behavior and persistence of the subsurface oil at station N-3 (Smith Island) is given in Figure 5-1. The oil at depth in the high-tide berms and beneath the surface armor on the upper platform was apparently changed little during the nonsummer storm season of 1989/90. However, subsurface oil on the lower platform was removed sometime between January and March 1990, presumably during one or more major storms. The surface of the lower platform was lowered about 50 cm during that erosional episode. The face of the storm berm was excavated and the exhumed gravel was placed on the surface of the upper platform as part of a berm relocation project carried out during the summer of 1990. By the time of the August 1991 survey, the high-tide berms had resumed their original configuration, with a maximum reading of 5 percent surface oil cover in that area. The subsurface oil was gone from the high-tide berms, but the subsurface oil under the

INITIAL OILING (1st Few Weeks)



FIRST SPRING/SUMMER (1989)



FIRST STORM SEASON (1989/90)

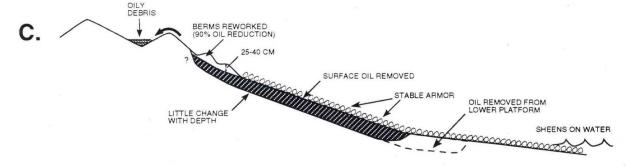
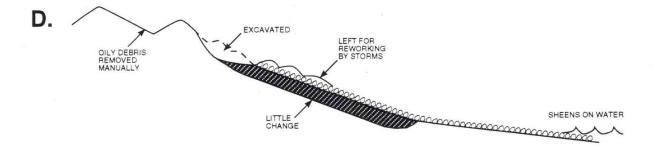
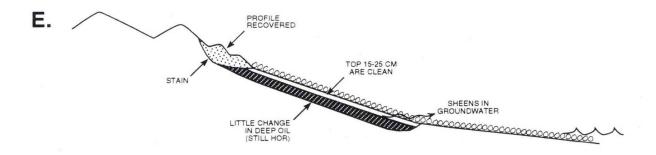


Figure 5-1. Schematic model of the behavior and persistence of oil from the initial stranding to the summer of 1997 at station N-3 (Smith Island), an example of Subclass I of the cobble/boulder platform with berms—those with a well-established coarse-grained armor on the upper and lower platforms, relatively flat slope, and relatively thick veneer of sediments over the underlying bedrock.

SECOND SUMMER (1990 Berm Relocation)



THIRD SUMMER (1991)



FOURTH SUMMER (1992); SIXTH SUMMER (1994); NINTH SUMMER (1997)

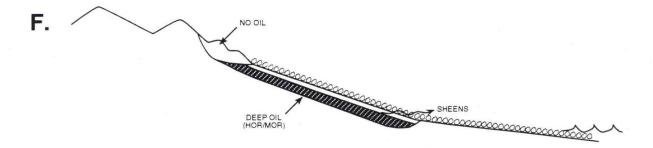


Figure 5-1. Continued.

armor of the upper platform had changed little in August 1992. This subsurface oil at N-3 showed almost no change in visual appearance, oil loading, or degree of weathering over the next five years.

The subsurface oiling history at station N-1 is similar to that of N-3 through the storm season of 1990/1991 (shown by diagrams A-C in Figure 5-1). However, a berm relocation project was not carried out at this site until the summer of 1991, when the entire storm berm was removed and placed on the upper platform. The result of this process is illustrated by the depiction of the summer 1991 survey, which was conducted shortly after completion of the project (Figure 5-2E). Before the relocation project, the subsurface oil was located below 15-25 cm of clean sediments under the original surface armor. The 15-25 cm thick zone of clean sediment was created by wave action and flushing over the first two years. This type of cleaning had occurred at all the cobble/boulder beaches by the summer of 1991. At the time of the August 1992 survey, there was still a cover of sediment over the original upper platform surface, but this was sediment moving alongshore from north to south in the form of rhythmically spaced high-tide berms. Therefore, the deeper subsurface oil had been buried under a thick layer of sediments for at least a year. By July 1997, the surface of the upper platform was near its original position, and a well-developed surface armor was present (Figure 5-2G). The subsurface oil was still HOR, containing up to 32,000 mg/kg TEO.

The lack of weathering of this deeply penetrated oil at stations N-1 and N-3 was particularly interesting. The oil residues from these gravel beaches were the least weathered of all samples collected in both 1994 and 1997, with no significant changes occuring during that three-year period. Sheens were still observed in 1997 draining from the undisturbed beach at Smith Island on the falling tide. It appears that the presence of a large, dense surface armor can cause very long-term persistence and very slow weathering of oil which has penetrated deeply into gravel beaches.

Two of the stations classified as cobble/boulder platforms with berms, stations N-4 (Smith Island) and N-17 (Perry Island) were placed in Subclass II by Michel and Hayes (1993a). These beaches contain highly mobile sediments, have a relatively steep slope, compared to the other beaches in the cobble/boulder platform group, and have a thin veneer of sediments on the rock platform. A schematic model of the behavior and persistence of oil at these two sites is given in Figure 5-3. Berm relocation projects were carried out at both of these beaches during the summer of 1990, during which oiled sediments in the high-tide berm areas (offshore face of storm berm) were excavated and placed on the upper platform. In August 1991, the beach profile had recovered to its original configuration and only light

SECOND SUMMER (1990)

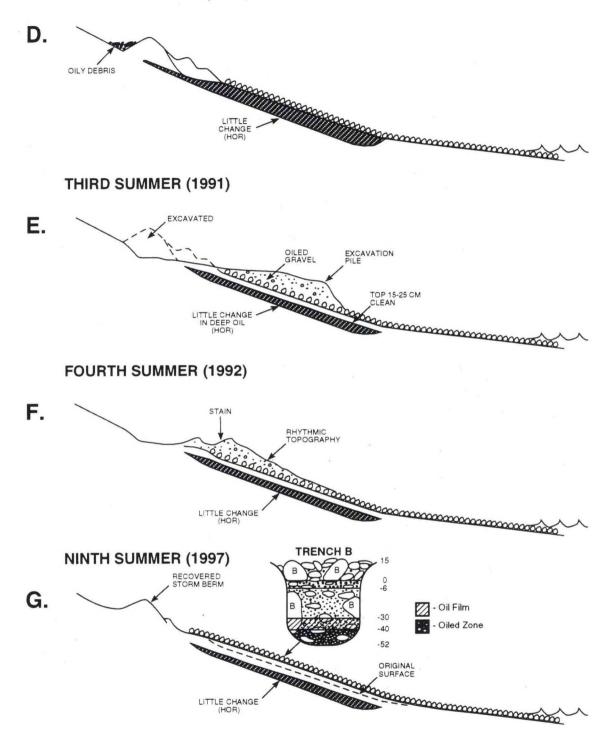
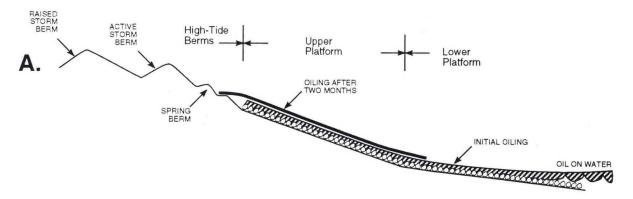
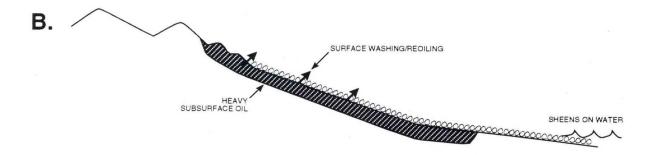


Figure 5-2. Schematic model of the behavior and persistence of oil at station N-1 (Point Helen) for the period 1990-1997. The character of the oil from initial oiling through the first storm season was essentially the same as that shown for station N-3 (Smith Island) in diagrams A, B, and C in Figure 5-1.

INITIAL OILING (1st Few Weeks)



FIRST SPRING/SUMMER (1989)



FIRST STORM SEASON (1989/90)

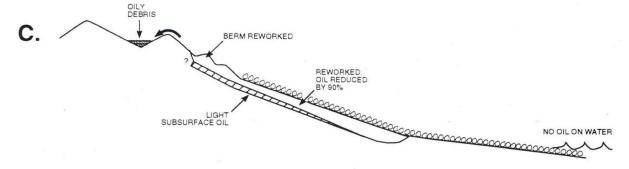
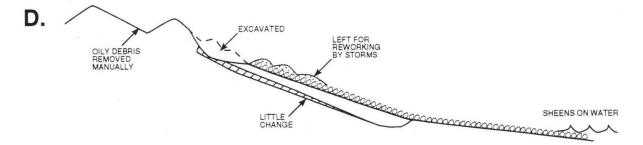
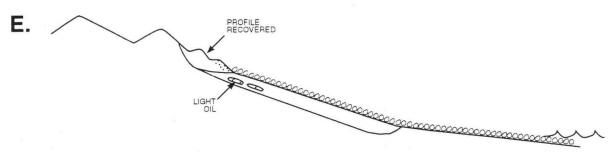


Figure 5-3. Schematic model of the behavior and persistence of oil from the initial stranding to the end of 1997 on cobble/boulder platforms with berms, Subclass II—those with highly mobile sediments, relatively steep slope of the upper and lower platforms, and relatively thin veneer of sediments on the underlying bedrock. Stations N-4 (Smith Island) and N-17 (Perry Island).

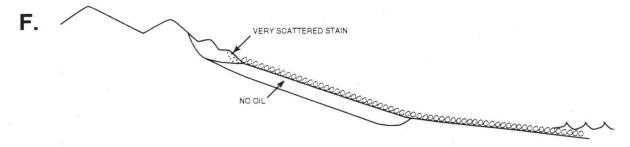
SECOND SUMMER (1990 Berm Relocation)



THIRD SUMMER (1991)



FOURTH SUMMER (1992)



NINTH SUMMER (1997) - AT STATION N-4 (SMITH ISLAND)

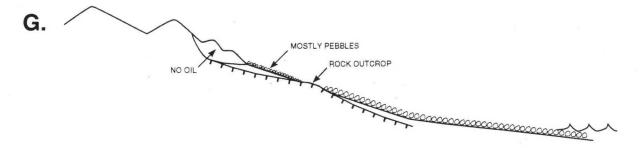


Figure 5-3. Continued.

oiling was observed in the subsurface sediments. By August 1992, there was no subsurface oil left at either site. As shown by Figure 5-3G, station N-4 was eroded down to bedrock in the mid-tide zone in July 1997. We believe the removal of the subsurface oil at these two stations is the result of their relatively steep slopes and thin veneer of sediment over the uplifted bedrock platform, which enhanced removal by both ground water flushing and erosion by wave action.

Two additional stations in the cobble/boulder platforms with berms class, N-7 (Knight Island) and N-15 (Latouche Island), were essentially free of subsurface oil eight years after the spill. The major difference between station N-7 and stations N-1 and N-3 is the lack of a closely packed, thick armor. The spaces between subangular cobbles and boulders of the surface armor at N-7 may have permitted better flushing of the deeper, finer-grained oiled sediments. Also, added fertilization at this site may have enhanced the biodegradation of the oil. The significant erosion at this beach between years five and eight probably completed the removal of most of the subsurface oil. Two factors probably contributed to the earlier removal of the subsurface oil at station N-15: 1) the major berm relocation project carried out there in September 1990 allowed much of the originally subsurface oil to be removed by wave action; and 2) the gravel cover is relatively thin, being underlain by an impermeable muddy sediment formerly deposited on the sea floor (before uplift during 1964 earthquake).

EFFECTIVENESS OF BERM RELOCATION AND SEDIMENT REWORKING

Berm relocation was carried out at an unprecedented scale at the *Exxon Valdez* spill site during the summers of 1990 and 1991. Five of the six NOAA stations in the cobble/boulder platforms with berms class were subject to relocation projects of differing degrees, and all of these projects were successful in removing the subsurface oil in the high-tide berms area. Ironically, the subsurface oil was also removed naturally within the same time frame from the high-tide berms at station N-7 (Knight Island), where no berm relocation was carried out. Stations where only the face of the storm berm (high-tide berms area) was removed, the beach returned to its original configuration both in terms of its morphology and sediment distribution pattern after the first storm season. However, at station N-1 (Point Helen), where the entire storm berm was removed in the summer of 1991, it took between three and six years for the storm berm to completely recover, and as of July 1997, six years after the project, the grain-size distribution had not completely returned to its original configuration.

At station N-15 (Latouche Island), where the entire storm berm was also removed and a linear trench was dug along the upper platform, the grain-size distribution and armoring had recovered by August, 1994 and the storm berm had come close to recovery by July 1997. In conclusion, we believe berm relocation is a useful and effective method of removing subsurface oil; however, if there is a desire for the beach to return to its natural configuration within months, then a site-specific understanding of the beach cycle is of critical importance to the success of the project.

Extensive sediment excavation and reworking was conducted at Sleepy Bay in 1991. The fine-gravel berms recovered very quickly. However, in July 1997, the remnants of two piles of boulder-sized rubble still remained on the central ramp. Thus, if it is important that the beach return to its natural configuration, the size of the sediments exposed at a site should be limited to those that can be readily re-worked by the normal storm waves.

At station N-14, the extensive washing of the mixed fine-gravel, granule, and sand sediments during the 1989 cleanup very effectively removed the subsurface oil, for the most part. However, NOAA's biological monitoring studies of this site suggested that the hydraulic flushing seriously impacted the infauna because of the loss of fines and organics in the translocated sediments, direct burial, and elevated levels of oil contamination (Houghton et al. 1992). Accordingly, it was of interest to determine if the sediment washed downslope during the cleanup would eventually be returned back up to the intertidal beach by natural processes. As the diagram in Figure 5-4 shows, a major intertidal bar had formed just west of our profile in May 1990 and it slowly migrated up the beach, approaching the high-tide line by July 1994. By August 1997, the beach appeared to have been fully recovered to its original sedimentary makeup.

PERSISTENCE OF OIL ON SHELTERED ROCKY SHORES

Oil has persisted on two types of sheltered rocky shores in Prince William Sound: rocky rubble slopes and rocky shores with thin sediment veneers. Figure 5-5 shows a model on the fate of oil on sheltered rocky rubble slopes, such as at station N-13. Surface oil persisted for over two years, primarily as oil coat on the sides of the surface rubble and asphalt in crevices. Because of the permeability of the rubble, oil penetrated at the high-tide zone to depths and concentrations unexpected for a rocky shore. This subsurface oil persisted for a very long time and weathered slowly, through 1994. After eight years, there was a significant decrease in the oil loading and the residual oil was highly weathered. The rate of subsurface oil removal was faster for the lower part of the rubble. By 1997, this lower zone

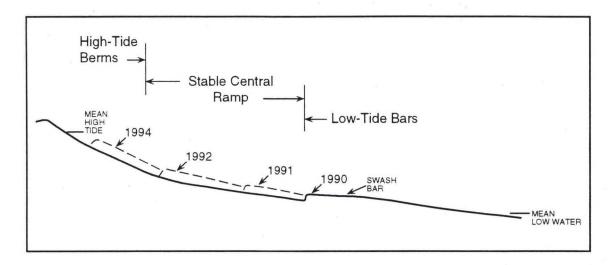


Figure 5-4. Return of sediment to the beach just west of profile N-14 (Northwest Bay) in a sequence of landward-migrating, mixed sediment swash bars.

was free of oil, whereas black oil droplets were still visible in trenches near the high-tide level. Because of the long-term persistence of oil in this shoreline type, we have modified the shoreline classification system to differentiate between permeable versus impermeable rocky shores. Removal of oil from permeable rocky shores should be of high priority, particularly if the oil is initially on the surface, to prevent its penetration and persistence.

On rocky shores with thin sediment veneers, modeled in Figure 5-6, the oil tended to form thick, persistent pavements rather than penetrate the poorly sorted substrate. After four years, oil coat and pavements were still visible on the surface. With little to no mechanism for physical removal by wave action or groundwater flow, the oil residues weathered in place. Where the pavements were exposed to air and sunlight longer, they hardened throughout. However, where they were protected in deep crevices or lower in the intertidal zone, after eight years they formed only a hardened surface with soft, mousse-like interiors. It was the persistence of these patches of pavement and mousse-like oil which led to the use of PES-51 to remove them from selected areas in 1997. Since the oil deposits with the greatest persistence were in areas of high oil concentrations, the concept of oil removal to some threshold level as a first cleanup objective might be appropriate. Often further removal involves highly intrusive methods. The objective should be to leave the rocky surfaces in a condition where natural processes will be most effective.

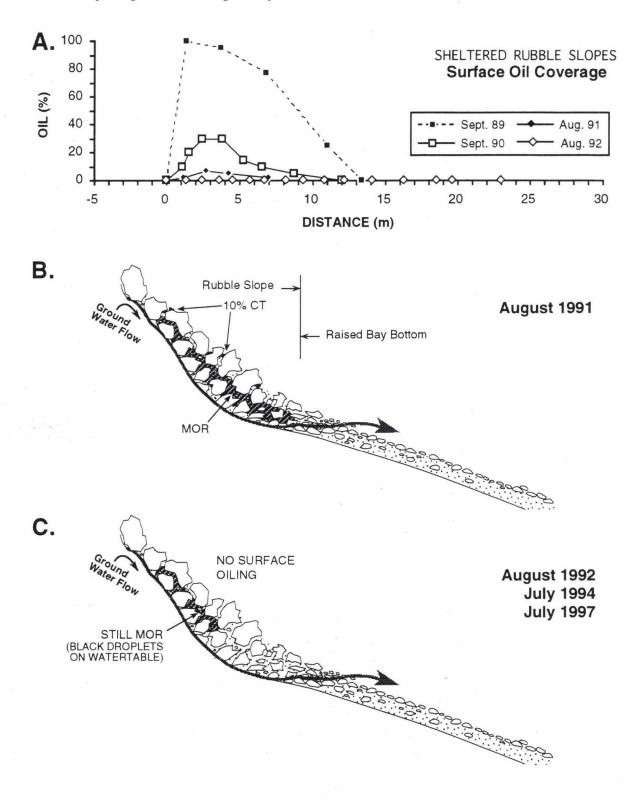


Figure 5-5. Model for the persistence of oil on sheltered rocky rubble slopes.

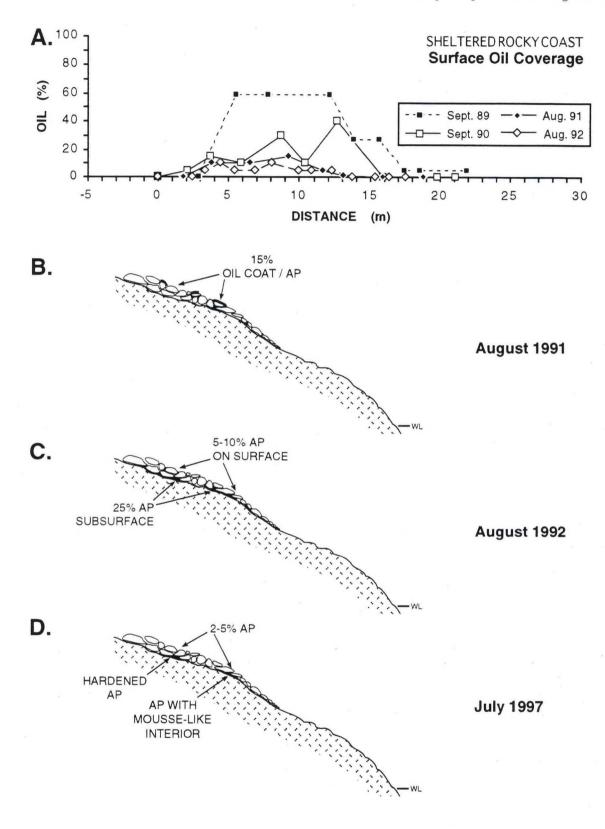


Figure 5-6. Model for the persistence of oil on sheltered rocky shores with a thin sediment veneer.

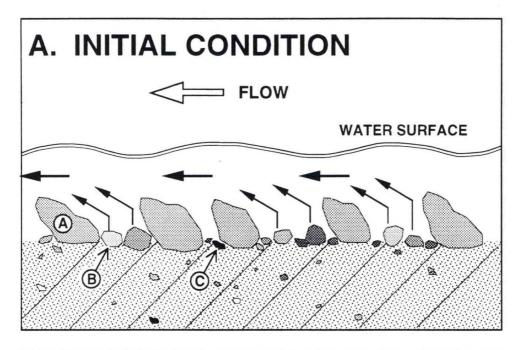
IMPORTANCE OF A STABLE ARMOR ON GRAVEL BEACHES

One of the more significant discoveries of this study is the importance of the stable armor that had developed over the upper and lower platforms of the more exposed, coarser-grained gravel beaches in the Sound. The stability of the armor and its ability to protect the subsurface oil from erosion even during a major storm is the primary reason there was still HOR in the subsurface sediments of these types of beaches eight years after the spill. As pointed out by Michel and Hayes (1991), the process of armor formation is well studied on gravel bars in rivers, but this work is the first to examine the phenomenon of armoring on beaches in any detail. Armoring appears to develop on gravel beaches that have a wide range of gravel sizes. Because of variations in wave conditions, beaches typically have constantly changing current velocities. Therefore, the threshold and maximum transport conditions for the particles of different sizes within the gravel can be achieved at different times. Also, in the process of sediment transport, smaller particles are sometimes shielded by larger particles. These factors combine to allow intermediate-sized gravel and fine gravel not shielded by the larger particles to be removed from that part of the beach at velocities too low to transport the largest gravel. Therefore, a coarse armor develops on top of the finer particles, as is shown in Figure 5-7A and B. Armoring does not occur in the high-tide berms where the gravel is repeatedly turned over and moved around by waves at high tide during storms. It only occurs on the flatter portions of the profile from the base of the berms to the low-tide line. Once the armoring is achieved, the surface of the beach is strengthened to the extent that extreme erosional events are required to mobilize the coarse armor. Hence, the oil in the finer sediments under the armor is protected from removal for an extended period of time, obviously for at least as much as eight years at stations N-1 and N-3. Sketches of trenches that revealed the presence of subsurface oil under armor at two of our stations, N-3 and N-7, are given in Figure 5-7C-F. How to effectively remove subsurface oil from under the armor on gravel beaches is a question deserving further consideration.

OTHER REMAINING QUESTIONS

In addition to the difficult issue of how to effectively remove subsurface oil from armored gravel beaches, several other questions have been raised by this investigation that are worthy of further study:

1. What would be the result of moving the armor aside and physically removing the subsurface oil?



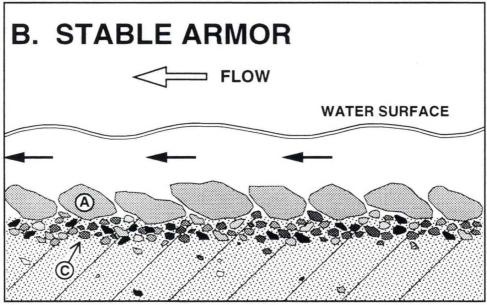


Figure 5-7. Subsurface oil under coarse gravel armor. A and B: Process involved in the development of an armored surface of coarse material on a gravel beach. The particles of size A are too large to be removed by prevailing currents, those of size B are readily transportable, and some of those of size C are sheltered by the larger particles and are not picked up by the current. The C particles are on the order of 1.5 to 5 times smaller than the A particles.

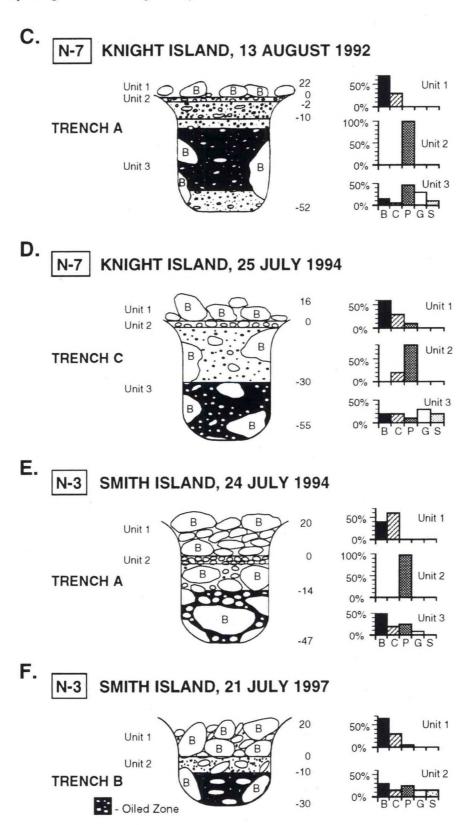


Figure 5-7. Continued. C, D, E, and F: Examples of trenches dug at station N-7 (Knight Island); C, D) and N-3 (Smith Island; E, F) showing oiled subsurface sediments under boulder/cobble armor.

It is our understanding that this was not done in 1991 because of concerns over potential impacts to the biota as well as destabilization of the beach itself. The threshold conditions required for armor to form, and hence return to its original configuration, are poorly understood at best. Would this be a worthwhile experiment at a wave tank facility such as the Coastal Oil Spill System (COSS) in Corpus Christi, Texas? A field experiment to disrupt the armor and remove the oil at a specific locality such as station N-3 is another possibility.

2. Would an exceptional storm, caused by extraordinary atmospheric conditions such as El Nino, mobilize the armor and remove the oil?

A detailed understanding of the beach cycle in Prince William Sound, which is poorly understood at the present time, would be the first step in answering this question. Field surveys would have to be timed to measure the effects of individual extratropical cyclones. Wave tank experiments on current velocities required to move such large gravel would also be helpful.

3. Why was the deeply penetrated oil not flushed out during the repeated tidal inundations over the past eight years?

Oil/fine particles interaction was first hypothesized based on experiments conducted with oiled sediments contaminated with oil from the Exxon Valdez from Prince William Sound by Bragg and Yang (1995). Owens and Sergy (1997) argue that the only conditions under which these processes are not effective in the breakdown and removal of all residual stranded oil are: 1) where oil is above the high water line; and 2) when the oil has an asphalt skin which prevents the oil/fines particles from breaking away from the oil surface. Neither of these exceptions apply to deeply penetrated oil in the gravel beaches in Prince William Sound. The oil in these beaches is liquid enough to form a slick on the water table in trenches, so it seems that it would be susceptible to flushing, particularly if oil/fine particles interactions were occurring. A first step may be to examine oiled subsurface sediments we have collected over time under a microscope to detect the presence and relative abundance of fine particles, any temporal changes, and differences among sites with oil at different weathering stage and total oil content. We would have to determine whether long-term freezing affects the ability to observe the oil/fine particles effect. In addition, it may be appropriate to develop a detailed sampling plan to collect fresh samples from a range of sites to test the influence of oil/fine particles interaction on oil persistence in Prince William Sound.

Another mechanism for the persistence of moderately weathered, liquid oil in the gravel beaches may be related to the adhesiveness of North Slope Crude oil, which would, in turn,

be related to its chemical composition. With a high asphaltene content, is NSC more likely to persist once in contact with subsurface sediments? Do we expect other crude oils with different compositions to behave differently?

4. Why was the oil at station N-7 (Knight Island) weathered so intensely?

Was it because of the additional nutrient application, or greater armor permeability? We collected samples only from the vicinity of our profile (taking care to avoid the sites of previous trenches). A systematic sampling of the beach, perhaps repeating the samples collected during the nutrient experiment, may provide further information on the role of nutrients.

5. What affects the relative weathering rates of the asphalt pavements?

We observed a very wide range in the degree of weathering of the oil in persistence asphalt pavements. A study plan could be developed to identify the types of pavements still present in the Sound, describe their physical setting, and chemically and physically characterize them.

GLOSSARY

AP asphalt pavement

B boulders

C cobble amcentimeter CT coat

CV cover

G granules

GC and flame ionization detection GC-FID

GC/MS gas chromatography/mass spectroscopy

EI Exposure Index

HOR heavy oil residue

km kilometer

LOR light oil residue

LSU Louisiana State University

millimeter m

milligram per kilogram mg/kg

mm millimeter

MOR medium oil residue

nanogram

ng NOAA National Oceanic and Atmospheric Administration

OF oil film

P pebbles

PAHs polynuclear aromatic hydrocarbons

RPI Research Planning, Inc.

S sand ST stain

TEO total extractable organics **TPHs** total petroleum hydrocarbons

TR trench 1997 Geomorphological Monitoring Survey

REFERENCES

Bragg, J.R. and S.H. Yang. 1995. Clay-oil flocculation and its effects on the rate of natural cleansing in Prince William Sound following the *Exxon Valdez* oil spill. I: *Exxon Valdez Oil Spill-Fate and Effects in Alaskan Waters* Eds: P.G. Wells, J.N. Butler, and J.S. Hughes. ASTM STP 1219. Philadelphia, Pennsylvania: American Society for Testing and Materials, pp 178-214.

Hayes, M.O. 1996. An exposure index for oiled shorelines. *Spill Science & Technology Bulletin, Vol. 3*, No. 3, pp 139-147.

Henry, C.B., Jr., P.O. Roberts, E.B. Overton, M. Frederick, R. LeBlanc, and R. East. 1997. Summary of chemical results: 1991 Prince William Sound Geology cruise. Baton Rouge: Institute for Environmental Studies, Louisiana State University. 25 pp plus appendices.

Houghton, J.P., D.C. Lees, T.A. Ebert, and W.B. Driskell. 1992. Evaluation of the 1991 condition of Prince William Sound shorelines following the *Exxon Valdez* oil spill and subsequent shoreline treatment. Volume II. 1991 Biological Monitoring Survey. NOAA TM NOS ORCA 67. Seattle: Hazardous Materials Response and Assessment Division, NOAA. 201 pp.

Michel, J., C.B. Henry, Jr., W.J. Sexton, and M.O. Hayes. 1990. The *Exxon Valdez* winter monitoring program results. *Proceedings, Conference on Oil Spills; Management and Legislative Implications*, May 15-18, 1990, Newport, Rhode Island. Eds: M.C. Spaulding and M. Reed. New York: American Society of Civil Engineers. pp 396-407.

Michel, J., M.O. Hayes, W.J. Sexton, J.C. Gibeaut, and C.B. Henry, Jr. 1991. Trends in natural removal of the *Exxon Valdez* oil spill in Prince William Sound from September 1989 to May 1990: *Proceedings*, 1991 International Oil Spill Conference: Prevention, Behavior, Control, Cleanup. March 4-7, 1991, San Diego, California. Washington, D.C.: American Petroleum Institute. pp 181-187.

Michel, J. and M.O. Hayes. 1991. Geomorphological controls on the persistence of shoreline contamination from the *Exxon Valdez* oil spill. Report HMRAD 91-2. Seattle: Hazardous Materials Response and Assessment Division, NOAA. 306 pp plus appendix.

Michel, J. and M.O. Hayes. 1993a. Evaluation of the condition of Prince William Sound shorelines following the *Exxon Valdez* oil spill and subsequent shoreline treatment. Volume I. 1991 Geomorphological Shoreline Monitoring Survey. NOAA TM NOS ORCA 67. Seattle: Hazardous Materials Response and Assessment Division, National Oceanic and Atmospheric Administration. 94 pp.

Michel, J. and M.O. Hayes. 1993b. Persistence and weathering of *Exxon Valdez* oil in the intertidal zone—3.5 years later. *Proceedings*, 1993 International Oil Spill Conference, *Prevention, Behavior, Control, Cleanup*. 29 March-1 April 1992, Tampa, Florida, Washington, D.C.: American Petroleum Institute. pp 279-286.

Michel, J. and M.O. Hayes. 1993c. Evaluation of the condition of Prince William Sound shorelines following the *Exxon Valdez* oil spill and subsequent shoreline treatment. Volume I. Summary of the Results—Geomorphological Shoreline Monitoring Survey of the *Exxon Valdez* Spill Site, Prince William Sound, Alaska, September 1989-July 1992. NOAA TM NOS ORCA 73. Seattle: Hazardous Materials Response and Assessment Division, National Oceanic and Atmospheric Administration. 102 pp plus appendix.

Michel, J. and M.O. Hayes. 1996. Evaluation of the condition of Prince William Sound shorelines following the *Exxon Valdez* oil spill and subsequent shoreline treatment. Volume II. 1994 Geomorphological Monitoring Survey, July 1994. NOAA TM NOS ORCA 91. Seattle: Hazardous Materials Response and Assessment Division, NOAA. 120 pp plus appendix.

Owens, E. H. and G.A. Sergy. 1997. Application of recent technical advances to the decision process for shoreline treatment. *Proceedings of the 1997 International Oil Spill Conference, Improving Environmental Protection—Progress, Challenges, Responsibilities* 7-10 April 1997, Ft. Lauderdale, Florida. Washington, D.C.: American Petroleum Institute. pp 289-295.

Owens, E.H., G.A. Sergy, B.E. McGuire, and B. Humphrey. 1993. The 1970 Arrow oil spill: What remains on the shoreline 22 years later? *Proceedings of the 16th Arctic and Marine Oil Spill Program Technical Seminar*, 7-9 June 1993, Calgary, Alberta: Ottowa, Ontario: Environment Canada. pp 1149-1167.

Prince, R.C., J.R. Clark, and J.E. Lindstrom. 1990. Bioremediation Monitoring Program, September 1990 Update. Annandale, New Jersey: Exxon Research and Engineering Co. 78 pp.

Sauer, T.C., J.S. Brown, P.D. Boehm, D.V. Aurand, J. Michel, and M.O. Hayes. 1993. Hydrocarbon source identification and weathering characterizations of intertidal and subtidal sediments along the Saudi Arabian coast after the Gulf War oil spill. *Marine Pollution Bulletin*, Vol. 27:117-134.

APPENDIX

Concentrations of Targeted Polynuclear Aromatic Hydrocarbons in Samples Collected in July 1997

Concentrations of Targeted PAHs in Samples Collected in July 1997

Field ID:	N-1-1	N-1-2	N-3-1	N-3-2	N-6-1	N-6-2	N-7-1
	ng/mg (wet)	ng/mg (wet)	ng/mg (wet)	ng/mg (wet)	ng/mg (wet)	ng/mg (wet)	ng/mg (wet)
NAPH	0.21	0.11	0.41	0.06	nd	0.01	0.0009
C-1 NAPH	10.29	2.20	9.41	0.90	nd	0.06	nd
C-2 NAPH	45.89	38.09	43.92	21.41	nd	2.57	nd
C-3 NAPH	58.30	58.59	56.46	50.18	nd	11.57	nd
C-4 NAPH	39.87	38.09	3.76	3.68	nd	15.75	nd
FLU	2.66	1.70	2.55	1.46	nd	0.23	nd
C-1 FLU	10.89	1.06	10.47	9.22	nd	2.84	nd
C-2 FLU	20.27	19.83	19.57	18.92	nd	9.79	nd
C-2 FLU	19.21	18.42	20.02	19.41	nd	13.99	nd
DBT	7.71	3.74	7.31	4.73	nd	0.65	nd
C-1 DBT	21.56	18.92	19.72	19.71	nd	6.10	nd
C-1 DB1	35.98	30.38	31.80	33.51	nd	20.81	nd
C-2 DBT	33.12	27.39	31.48	30.75	8.69	29.78	nd
	11.70	7.62	11.12	6.89	nd	0.86	nd
PHEN	-			30.59	nd	7.06	nd
C-1 PHEN	34.16 46.18	30.47 40.27	33.36 45.17	43.08	nd	19.60	nd
C-2 PHEN			41.70	39.20	6.13	31.76	nd
C-3 PHEN	40.56 17.38	34.83 15.24	18.76	16.80	13.81	18.04	nd
C-4 PHEN	17.38 nd	13.24 nd	nd	nd	nd	nd	nd
ANT	3.18	2.99	4.13	2.44	0.33	2.15	nd
NBT C-1 NBT	13.93	12.95	16.85	11.04	0.39	13.64	nd
	21.64	19.92	23.53	16.95	17.38	26.91	nd
C-2 NBT C-3 NBT	18.79	18.43	18.76	15.77	27.64	27.99	0.777
FLANT	0.30	0.25	0.28	0.28	0.03	0.03	nd
PYR	0.58	0.23	0.50	0.28	0.49	0.61	0.003
C-1 PYR	3.66	2.81	4.04	3.32	3.98	3.81	nd
C-1 P 1 R C-2 PYR	6.70	5.37	6.68	5.70	8.85	7.40	0.180
	8.47	6.65	8.38	6.88	11.95	9.94	0.906
C-3 PYR		5.63	6.68	5.22	12.83	10.15	0.755
C-4 PYR	6.99		0.08	0.13	12.83		0.733
B(a)ANT	0.14	0.11	2.96	2.45	5.46	3.50	0.014
CHRY	3.08	2.44		4.53	6.19	6.19	0.023
C-1 CHRY	5.85	4.88	5.14		7.88	11.83	0.022
C-2 CHRY	9.31	7.81	7.51 6.32	7.55 6.94	8.44	11.63	1.342
C-3 CHRY	8.22	7.16			4.95	8.61	1.834
C-4 CHRY	5.70				0.78	0.46	nd
B(b+k)F*	0.52	0.26	0.80		2.53	1.12	0.323
B(e)P	0.77	0.47			0.11	0.09	0.002
B(a)P	0.02			0.12			
PERYL	0.03		0.06		0.05	nd	0.002
INDPYR	nd				nd	nd	nd
BENZP	0.18	0.13			0.33	0.35	0.166
DIBENZ	0.07				0.06	0.09	0.012
ТТАН:	574.05			446.85	149.28	338.01	6.845
HOPANE**	9.97				7.77	16.11	2.102
Total Naph	154.56	137.07	113.96	76.23	0.00	29.97	0.00
Total Phen	149.98	128.42	150.11	136.57	19.94	77.32	0.00
Ratio N/P	1.03	1.07	0.76	0.56	0.00	0.39	#DIV/0!

Concentrations of Targeted PAHs in Samples Collected in July 1997

Field ID:	N-7-2	N-9-1	N-9-2	N-10-1	N-13-1	N-14-1	N-15-1
	ng/mg (wet)						
NAPH	0.0077	nd	0.008	nd	nd	0.000	0.019
C-1 NAPH	0.0119	nd	0.060	nd	nd	0.000	nd
C-2 NAPH	0.0161	nd	2.250	0.077	nd	nd	nd
C-3 NAPH	nd	0.28	17.580	0.307	nd	nd	nd
C-4 NAPH	nd	1.29	18.986	0.416	nd	nd	nd
FLU	nd	nd	0.918	nd	nd	nd	0.046
C-1 FLU	nd	0.39	5.610	0.061	nd	nd	nd
C-2 FLU	nd	1.25	11.220	0.001	0.030	nd	0.140
C-2 FLU	nd	1.43	10.710	0.281	0.030	nd	0.204
DBT	nd	0.02	3.220	0.281	nd	nd	
C-1 DBT	nd	0.66	9.058	0.080	0.009	0.000	nd
C-1 DB 1	nd	1.97	16.438	0.080	0.009	0.000	nd
						0.001	0.017
C-3 DBT	nd	2.37	14.090	0.483	0.161		0.402
PHEN	nd	nd	0.077	0.022	nd	0.000	0.098
C-1 PHEN	nd	0.12	4.032	0.109	0.016	0.001	0.103
C-2 PHEN	nd	0.72	17.228	0.347	0.079	0.001	0.178
C-3 PHEN	nd	2.30	17.595	0.500	0.188	0.001	0.344
C-4 PHEN	nd	1.42	8.064	0.388	0.119	nd	0.325
ANT	nd	nd	nd	nd	nd	nd	0.309
NBT	nd	0.26	1.510	0.031	0.015	nd	0.045
C-1 NBT	nd	1.05	6.709	0.274	0.108	0.001	0.315
C-2 NBT	1.072	1.58	9.728	0.626	0.207	0.001	0.507
C-3 NBT	3.275	1.28	8.722	1.025	0.287	0.004	0.980
FLANT	nd	0.02	0.134	nd	nd	nd	0.081
PYR	nd	0.05	0.280	0.011	0.005	nd	0.081
C-1 PYR	nd		1.550	0.070	0.026	nd	0.104
C-2 PYR	0.580	0.56	2.988	0.179	0.079	0.001	0.236
C-3 PYR	1.385	0.74	3.735	0.340	0.157	0.002	0.454
C-4 PYR	1.212	0.52	2.801	0.303	0.107	0.002	0.426
B(a)ANT	0.014	0.11	0.060	0.023	0.004	nd	0.038
CHRY	0.198	0.24	1.283	0.067	0.025	0.000	0.192
C-1 CHRY	0.341	0.42	2.614	0.161	0.048	0.000	0.168
C-2 CHRY	0.859	0.57	4.04	0.359	0.109	0.001	0.277
C-3 CHRY	1.652	0.47	3.80	0.568	0.146	0.002	0.433
C-4 CHRY	1.542	0.27	2.85	0.582	0.136	0.004	0.457
B(b+k)F*	0.038	0.05	0.18	0.012	0.010	nd	0.177
B(e)P	0.433	0.08	0.28	0.036	0.007	0.001	0.123
B(a)P	0.055	0.01	0.03	0.003	0.004	nd	0.072
PERYL	0.045	nd	0.02	nd	0.003	nd	0.028
INDPYR	nd	nd	nd	nd	nd	nd	0.028
BENZP	0.103	0.01	0.09	0.034	0.011	0.001	0.063
DIBENZ	nd	nd	0.03	0.003	0.004	nd	nd
ТТАН:	12.841	22.76	210.57	8.359	2.252	0.028	7.475
HOPANE**	2.109	0.65	3.83	0.578	0.158	0.021	0.456
Total Naph	0.04	1.58	38.88	0.80	0.00	0.00	0.02
Total Phen	0.00			1.37	0.40	0.00	1.05
Ratio N/P	#DIV/0!	0.35		0.59	0.00	0.16	0.02

Concentrations of Targeted PAHs in Samples Collected in July 1997

Field ID:	P-1	P-2	P-3	P-4	P-5	P-6	NSC Mean
	ng/mg (wet)	ng/mg (wet)	ng/mg (wet)	ng/mg (wet)	ng/mg (wet)	ng/mg (wet)	ng/mg (wet)
NAPH	0.0043	0.0072	0.0009	0.008	0.07	0.28	751.99
C-1 NAPH	0.0468	0.0380	0.0035	0.019	2.45	2.36	1592.55
C-2 NAPH	1.3667	0.3979	0.0099	0.034	22.55	99.23	2026.44
C-3 NAPH	9.3508	4.1581	0.1938	0.292	4.90	299.28	1594.87
C-4 NAPH	12.9472	8.9421	0.8918	1.441	3.92	283.53	824.63
FLU	0.1409	0.0519	nd	nd	1.52	5.48	98.52
C-1 FLU	1.8781	0.9728	0.0973	nd	9.96	68.55	237.95
C-2 FLU	6.7819	4.9290	0.5446	0.904	24.18	185.07	366.35
C-2 FLU	9.9121	8.4312	1.1538	3.785	26.55	207.92	329.42
DBT	0.2808	0.0635	nd	0.025	6.03	16.45	215.69
C-1 DBT	2.9499	11.1065	0.0928	0.029	25.72	197.36	380.88
C-1 DBT	12.4392	8.3299	1.0725	1.613	48.23	328.94	525.70
C-2 DBT	17.0594	12.6932	2.0437	7.167	48.23	328.94	444.42
PHEN	0.0621	0.0693	2.0437 nd	0.007	9.66	23.36	307.90
C-1 PHEN	3.0291	1.2136	0.1867	0.007	40.84	179.71	639.73
C-1 PHEN	11.6503	6.5014	0.8053	0.901	65.87	377.39	697.31
C-2 PHEN	19.0289	13.4362	1.8738	5.482	61.48	395.37	601.75
C-4 PHEN	10.4853	8.6685	1.3527	7.832	26.79	197.68	265.03
ANT	nd	nd	1.3327 nd	nd	20.79	nd	19.06
NBT	1.5638	0.8330	0.1142	0.111	3.82	24.67	48.61
C-1 NBT	9.2405	6.7433	0.8432	4.300	20.90	115.13	198.13
C-1 NBT	17.4148	14.6765	2.1554	14.693	32.55	213.81	297.67
C-2 NBT	15.9932	16.2631	2.5610	17.560	29.34	246.70	263.09
FLANT	0.1399	0.0976	0.0140	0.030	0.40	4.73	5.24
PYR	0.1395	0.3685	0.0647	0.404	0.78	11.61	9.96
C-1 PYR	1.9030	1.9653	0.3243	1.697	5.67	62.51	60.79
C-1 P T R	4.3768	4.4219	0.7531	3.636	9.73	105.67	109.93
C-2 P T R	6.0895	6.3872	1.2170	6.059	12.43	135.44	135.99
C-4 PYR	5.3283	5.6502	1.0421	6.261	10.81	111.62	113.68
	0.0561		0.0033		0.17	1.39	2.07
B(a)ANT CHRY	1.8883	nd 2.1251	0.0033	nd 1.876	5.16	58.69	53.58
		3.7501		2.569	9.62	88.99	96.59
C-1 CHRY	3.6313		0.6230		15.81	134.43	
C-2 CHRY	5.81	6.56 6.56	1.17	5.14	13.75	134.43	156.11 143.99
C-3 CHRY	5.33		1.35	6.68	10.31	106.03	
C-4 CHRY	3.63	5.31	1.29	4.63	0.87	8.03	109.00 8.47
B(b+k)F*	0.38	0.33	0.06	0.37	1.23	16.56	12.47
B(e)P	0.70	0.84	0.18	0.81			
B(a)P	0.14	0.13	0.01	0.13	nd	1.99	2.15
PERYL	0.08	0.10	nd	0.10	nd	1.46	1.46
INDPYR	nd	nd	nd	nd	nd	nd	0.69
BENZP	0.13	0.15	0.07	0.13	0.33	5.60	3.62
DIBENZ	0.04	0.05	0.01	0.03	0.10	1.21	1.23
TTAH:	203.61	173.33	24.54	106.76	569.33	4791.37	13754.69
HOPANE**	7.56	6.61	2.01	8.63	15.69	223.60	170.24
Total Naph	23.72	13.54	1.10	1.79	33.90	684.69	6790.47
Total Phen	44.26	29.89	4.22	14.22	204.65	1173.52	2511.73
Ratio N/P	0.54	0.45	0.26	0.13	0.17	0.58	2.70