

*Exxon Valdez* Oil Spill  
State/Federal Natural Resource Damage Assessment Final Report

**Nearshore Transport of Hydrocarbons and Sediments  
Following the *Exxon Valdez* Oil Spill**

Subtidal Study Number 3B  
Final Report

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**Study History:** In 1989 and 1990, this project was part of Air and Water Study #3 (Geographic and Temporal Distribution of Dissolved and Particulate Petroleum Hydrocarbons in the Water Column), consisting of water column sampling, deployment of mussel cages for uptake of hydrocarbons over time (NOAA), and the focus of this report, deployment of sediment traps, for which the ADEC acted as lead agency. In 1991, the mussels and sediment traps were continued as Subtidal Study #3 (Bio-availability and Transport of Hydrocarbons). Preliminary hydrocarbon and sedimentological results were presented at the *Exxon Valdez* Oil Spill Symposium in Anchorage, AK in February 1993 (published in the Symposium Abstracts). A version of this report is in press for publication [Short, J. W., D. M. Sale, J. C. Gibeaut. 1995. Nearshore transport of hydrocarbons and sediments following the *Exxon Valdez*, in Rice, S.D., R.B. Spies, D.A. Wolfe and B.A. Wright (Eds). 1995. *Exxon Valdez* Oil Spill Symposium Proceedings. American Fisheries Society Symposium Number 18 (In press)].

**Abstract:** Following the *Exxon Valdez* oil spill, sediment traps were deployed in nearshore subtidal areas of Prince William Sound, Alaska (PWS) to monitor particulate chemistry and mineralogy. Complemented by benthic sediment chemistry and core sample stratigraphy at the study sites, results were compared to historical trends and data from other *Exxon Valdez* studies. These results clearly indicate the transport of oil-laden sediments from oiled shorelines to adjacent subtidal sediments. The composition of hydrocarbons adsorbed to settling particulates at sites adjacent to oiled shorelines matched the PAH pattern of weathered *Exxon Valdez* crude oil. The highest total PAH concentrations were found near more heavily oiled shorelines and exhibited a declining trend over time. Oil-laden sediments were only slightly incorporated into nearshore benthic sediments, except where uneven bathymetry impedes the transport of sediments from nearshore depositional areas. Hydrocarbon patterns and clay mineralogy show that hydrocarbon contributions from PAH-laden sediments carried into PWS through Hinchinbrook Entrance infrequently exceeded 400 ng/g in the shallow subtidal (< 20 m depth) at sites within or near the path of the spill.

**Key Words:**

cores, clay mineralogy, *Exxon Valdez*, PAH, particulates, Prince William Sound, sediment transport, sediment traps, oil spills

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Nearshore Transport of Hydrocarbons and Sediments  
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**EXECUTIVE SUMMARY**

The *Exxon Valdez* oil spill of March 24, 1989 in Prince William Sound (PWS), Alaska, resulted in extensive intertidal oiling of shorelines along the path of the oil. Of the approximately 41,400 m<sup>3</sup> of crude oil thought to have spilled initially, it was estimated that by mid-April 1989 about 40-45% had beached within PWS. Previous studies have shown that oiled shorelines may provide reservoirs of oil for persistent contamination of adjacent seawater and subtidal sediments.

The sediment traps deployed for this study were designed to capture sediments falling out of suspension, in order to evaluate the transport of oil-laden sediments from contaminated shorelines to adjacent shallow subtidal sediments. Traps were deployed in 10 m seawater depths at 4 oiled stations and 1 reference station in Prince William Sound in November 1989. Sediments collected by these traps during 6 collection intervals between November 1989 and March 1992 were analyzed for hydrocarbon chemistry, and for sedimentological and mineralogical characteristics, including grain size distribution and mineral composition.

Sediment traps were deployed at 9 additional locations during one of these deployment intervals (August 1990 to March 1991) to evaluate oiled-sediment transport under a greater variety of shoreline oiling and energy conditions. Sediment traps were deployed at 10, 15 and 20 m seawater depths at 6 stations during deployment intervals following June 1991, to evaluate migration of oil-contaminated sediments into deeper subtidal areas, following reports that contamination of benthic sediments and hydrocarbon-degrading microbial activity were evident at seawater depths below 20 m. In addition, benthic surface sediments were collected within 1 m of the traps at all of the stations where traps were deployed, and benthic sediment core samples were collected at 7 of the sediment trap stations. The benthic surface and core sediment samples were also analyzed for hydrocarbons and for sedimentological characteristics, and compared with similar results for trapped sediments.

Results of the hydrocarbon analyses were compared with corresponding results for weathered *Exxon Valdez* oil collected from the sea surface 11 days after the spill to corroborate the likely origin of the hydrocarbons found. Sediment grain size and mineralogy of trapped sediments provided evidence of the origin and transport mechanisms, and comparable results for adjacent benthic sediments provided additional indications of the sedimentary environment of the sediment trap sites, as well as the likely origin of these benthic sediments.



Results of the hydrocarbon analyses of the trapped sediments clearly indicate the transport of *Exxon Valdez* oil from oiled beaches to adjacent shallow subtidal sediments. The composition of hydrocarbons found in sediments trapped from all 4 of the oiled locations during the first deployment interval were consistent with the composition of weathered *Exxon Valdez* oil. Total polycyclic aromatic hydrocarbon (PAH) concentrations of trapped sediments were highest at the east arm of Northwest Bay during the first trap deployment (November, 1989 to June, 1990), where these concentrations exceeded 75,000 ng/g (dry weight basis). Total PAH concentrations of sediments trapped at the other 3 oiled locations ranged from 8,660 to 28,400 ng/g.

Total PAH concentrations of trapped sediments at all 4 oiled stations established in 1989 generally declined with time to between 700 ng/g and 6,280 ng/g for sediments trapped during the March 1991 to June 1991 deployment interval. Sediments trapped during subsequent deployment intervals are thought to have been contaminated during collection by combustion hydrocarbons, and the data from these trapped sediments were excluded from interpretation in this report (the raw data is included in the data appendices).

Hydrocarbon analysis of sediments trapped from other stations indicated relatively low concentrations of PAH's, and the composition of these PAH's was consistent with *Exxon Valdez* oil only at Bay of Isles, Chenega Island, and Disk Island (also adjacent to initially heavily oiled shorelines), where total PAH concentrations ranged up to 3,500 ng/g. Total PAH concentrations in sediment trapped at the reference station in Port Fidalgo ranged from 317 - 1,880 ng/g, and were compositionally distinct from *Exxon Valdez* oil.

Results of hydrocarbon analyses for sediments collected in traps deployed at deeper seawater depths (15 and 20 m) corroborate results for traps deployed at 10 m depths at corresponding stations, and indicate relatively widespread dispersion of oiled, suspended sediments.

*Exxon Valdez* oil-laden suspended sediments were only slightly incorporated into adjacent benthic surface sediments at the study sites. Comparison of PAH concentrations and patterns, and sediment grain size distributions, of suspended and benthic sediments, indicates that oil-laden suspended sediments are finer-grained than adjacent benthic sediments, and are continuously transported to deeper basins in protected bays, or to open areas of PWS. This scenario is supported by sediment grain size distributions of benthic sediment cores collected from 7 of the locations, which indicate the intensity of subtidal currents at corresponding locations. Total PAH concentrations derived from *Exxon Valdez* oil were less than 2,500 ng/g in shallow (10 - 20 m) benthic surface sediments at oiled locations, and approached this value only in the east arm of Northwest Bay. The shorelines of this north-facing bay were heavily oiled and exposed to higher energy wave action, but the uneven bathymetry of bedrock formations and benches forms subtidal areas protected from tidal and wave energy, impeding the transport of benthic sediments. We anticipate that similar contamination levels probably

occurred at other locations in PWS where these conditions are present. Benthic sediment PAH concentrations were much lower (generally well below 500 ng/g) in subtidal sediments of other oiled locations studied such as Disk Island, Snug Harbor, or Sleepy Bay, where one or more of the environmental conditions causing accumulation in benthic sediments at Northwest Bay were absent.

The PAH concentrations and patterns of trapped and shallow (< 20 m) benthic sediments analysed during this study show that contributions from sources other than the *Exxon Valdez* oil spill are generally well below 400 ng/g at locations within or near the path of the spill through the Sound. The clay mineralogy of trapped sediments supports the conclusion that oil spilled from the *Exxon Valdez* is the dominant source of hydrocarbons found in nearshore sediments. The illite/chlorite clay mineral ratio of sediments trapped at sites adjacent to shorelines contaminated by the *Exxon Valdez* is closer to that of clay-sized minerals originating from the adjacent littoral zone, rather than to the illite-rich sediments originating from outside Prince William Sound.

This investigation into nearshore sediment contamination suggests that fine-grained intertidal sediments from shorelines oiled by the *Exxon Valdez* spill were transported to adjacent shallow subtidal areas by waves associated with winter storms and shoreline treatment activities. The residence time in shallow subtidal benthic sediments of the oil-contaminated sediments depends primarily on the energy available to transport these sediments to deeper, lower energy sites. Oiled shorelines prone to sediment transport from storms or treatment activities, and low-energy subtidal conditions caused by low current velocities, low wave energy, or uneven bathymetry that forms pockets protected from tidal and wave energy, promote accumulation of oil-contaminated sediments in the shallow subtidal adjacent to the oiled beaches. Although benthic sediment contamination at 20 m and shallower depths was low compared to suspended sediment concentrations, it is likely that higher levels of benthic sediment contamination are present in deeper, lower energy, fine-grained sedimentation sites within oiled embayments. There is both hydrocarbon chemistry and mineralogical evidence that other sources of PAH's, such as PAH-laden sediments from outside Prince William Sound, provide a relatively small contribution of PAH's to shallow, subtidal sediments of the western Sound within or near the path of the *Exxon Valdez* oil spill.

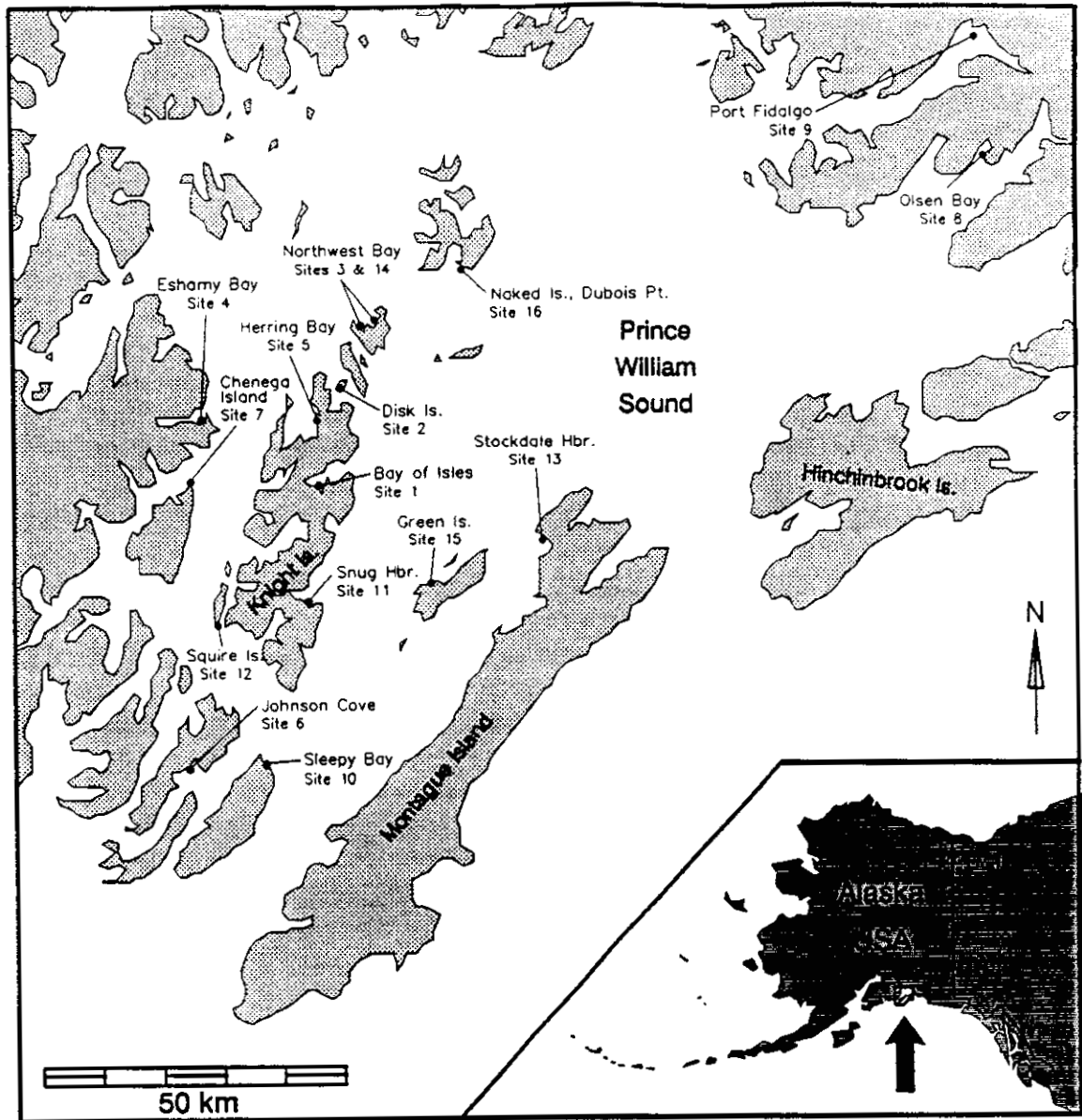


Fig. 1. Map of Prince William Sound, Alaska, showing the locations of sampling stations. Each station is identified by a number which corresponds with those in tables 1 and 2.

## Nearshore Transport of Hydrocarbons and Sediments Following the *Exxon Valdez* Oil Spill

### INTRODUCTION

The *Exxon Valdez* oil spill of March 24, 1989 in Prince William Sound (PWS), Alaska, resulted in extensive intertidal oiling of shorelines along the path of the oil. Of the approximately 41,400 m<sup>3</sup> of crude oil thought to have spilled initially, Wolfe et al. (1994) estimate that by mid-April 1989 about 40-45% had beached within PWS. These oiled shorelines may provide reservoirs of oil for persistent contamination of adjacent seawater and subtidal sediments.

Some of the beached oil and oil-contaminated sediments may be transported to subtidal areas following reintroduction into nearshore waters by wave and tidal processes and leaching by ground water flowing through the intertidal zone from the backshore (Owens et al. 1987, Boehm et al. 1987). Shoreline cleanup activities following the *Exxon Valdez* oil spill contributed to subtidal deposition as oil and sediments escaped from containment booms during mechanical treatment operations (primarily in 1989 and 1990), subsequent to berm-relocation efforts (1990) and excavation (1989-1991) that exposed subsurface oil to winter storm activity. Bulk oil re-dispersed into the nearshore seawater column may be adsorbed onto inorganic particulate matter (Meyers and Quinn 1973, Bassin and Ichiye 1977), or be ingested by zooplankton and incorporated into feces that settle onto benthic surface sediments (Clark and MacLeod 1977, Conover 1971). The settling velocities of particles removed from the shorelines may be low enough that the oiled sediments are carried far from nearshore areas before settling; or, alternatively, these particles may settle in the nearshore benthos, and then be resuspended into the water column for further transport. Oiled particulates settling onto the benthic surface may be incorporated into bottom sediments by further accumulation of sediments or through bioturbation.

The primary objective of this study was to examine the transport of *Exxon Valdez* crude oil from oiled shorelines through adjacent seawater to subtidal sediments. Specifically, we sought to determine if sediments settling out of the water column in nearshore subtidal environments contained adsorbed petroleum hydrocarbons derived from *Exxon Valdez* crude oil, and to determine the mechanism of transport. To accomplish these objectives, sediment traps, used after other oil spills to monitor settling particulates for oil contamination [Johansson et al. 1980 (moored traps), Michel et al. 1993 (base-mounted traps)], were deployed to collect settling organic and mineral particulate matter offshore of oiled and unoled shorelines. At some of these stations and during some deployment periods, we also collected benthic surface sediments and sediment core samples adjacent to the deployed sediment traps. The deployment stations included

locations adjacent to heavily oiled shorelines, and reference locations remote from the path of the spilled oil through the Sound.

Sedimentological data sharpens the picture of transport processes at work near shorelines impacted by the *Exxon Valdez* oil spill. Sediment grain size distributions and the statistical moments (mean, standard deviation, skewness, and kurtosis) provide data to uncover relationships between sediment properties and geomorphological processes and settings (Lewis, 1984). Stratigraphic analysis of benthic cores provides a picture of the processes that resulted in deposition or erosion of sediments. Through hydrocarbon sampling at various depths within the cores, we evaluated the pattern and concentration of hydrocarbons in the benthic sediment column. Additionally, much work has been done on the minerology of Prince William Sound sediments (Molnia and Hein 1982, Naidu and Mowatt 1983, Klein 1983), and relating this work to the clay minerology of trapped sediments assists in determining their likely origin.

### **OBJECTIVES**

- A) To determine if sediments settling out of the water column in nearshore environments contain adsorbed hydrocarbons.
- B) To decipher subtidal oiled sediment transport mechanisms through analysis of benthic sediments, and stratigraphic analysis of bottom cores.

### **STUDY AREA**

#### **I. Sampling Station Locations and Sampling Periods**

The locations of the sediment trap study sites are depicted in figure 1. From November 1989 to August 1990, five suites of 3 sediment traps each were deployed at 10 meters below MLLW at four oiled locations (Snug Harbor, Knight Island; Sleepy Bay, Latouche Island; both arms of Northwest Bay, Eleanor Island) and a reference site in Port Fidalgo. In August 1990, additional traps were deployed at 10 m to include fifteen sites. During this period traps were redeployed at Snug Harbor, Sleepy Bay, both arms of NW Bay and at Port Fidalgo, and new deployments were made at Stockdale Harbor on Montague Island, Green Island, Bay of Isles and Herring Bay on Knight Island, Johnson Cove on Evans Island, Squire Island, north Chenega Island, in Eshamy Bay, Disk Island and off Dubois Pt. on Naked Island. Sediment traps placed off the northwest tip of Green Island and off Dubois Point on Naked Island were not found after initial deployment in 1990, and no new traps were deployed there. (The sediment trap in Herring Bay was not found until August 1991, and then redeployed at 10 m). In March 1991, the traps were limited to six sites to allow sampling at several depths (Sleepy Bay; Snug Harbor, Bay of Isles on Knight Island; Disk Island; Northwest Bay, Eleanor Island; and a new reference site at Olsen Bay in Port Gravina). At each site, divers placed a suite of 3 traps at 10, 15 and 20 meters below MLLW, except at Bay of Isles and Northwest Bay, where steep

subtidal slopes limited trap placement to 10 and 20 meters, and at Olsen Bay, where a 20 meter trap was deployed. All but two of the study sites were located in western Prince William Sound, within or along the perimeter of the main path of oiling.

Table 1 shows the samples taken at each study site for each deployment period. The sediment traps were initially deployed in November 1989, retrieved in June 1990 and redeployed for retrieval in August 1990. The traps were left for the second winter period and retrieved in March 1991, when another placement of traps occurred. Retrieval and deployments were repeated in June and September 1991, and March 1992.

Sediment samples obtained from the traps and from adjacent benthic sediments were analyzed chemically and sedimentologically (table 1). Particulates retrieved from the sediment traps were analysed for hydrocarbons, and from March 1991 to March 1992, selected trap samples were analysed for grain size, organic carbon and nitrogen, and clay mineralogy. Sediment samples from the upper 2 cm of the benthic surface around the traps were analysed for hydrocarbons, and selected samples after March 1991 were analysed for grain size. Sediment core samples were taken in June and September of 1991 for stratigraphic, grain size and hydrocarbon analyses.

## II. Physical Characterization of Sampling Stations

Table 2 lists the physical characteristics and oiling conditions for shorelines adjacent to each study site and benthic sediments near the trap locations. The environmental sensitivity index (ESI) is a measure of the sensitivity of intertidal shorelines to oiling, with regard to oil residence time and treatment difficulty (Michel and Hayes, 1991). Shoreline segments adjacent to sediment trap sites are mixed sand and gravel beaches (ESI 6), gravel beaches (ESI 7), or sheltered rocky coasts (ESI 8), categories that make up 71% of the shoreline in Prince William Sound (Michel and Hayes 1991). Sediment traps were located within 75 to 400 meters of the supratidal zone of these shorelines. The sixteen sediment trap sites included a range of wave energy conditions: seven of the trap sites were in embayments such as the Bay of Isles and Eshamy Bay, protected from wind-generated waves, while the other sites are moderate to high energy environments exposed to waves from various directions and fetch distances. Sleepy Bay and Snug Harbor are considered high energy locations, evidenced by sorting and movement of sediments on the beach faces (Michel and Hayes, 1991; Pavia, 1991), sorting of benthic sediments, and the presence of wave ripples on the shallow subtidal benthic surface between 10 and 15 m depth at Snug Harbor (Sale and Gibeaut, 1995).

While the residence time of oil varied dependent on site energy, substrate and treatment, a steady decline in shoreline oiling contamination is apparent at all study sites. Six of the study sites were initially heavily oiled, 5 were lightly to moderately oiled and no oiling was reported at 3 sites, including both reference locations. Shoreline oil contamination remained adjacent to 4 study sites in Spring 1992 (Table 2). Detailed oiling and treatment histories for each site can be found in Sale and Gibeaut (1995).

Table 1. Sampling stations, locations, seawater depths and sample types collected during each deployment period. Sample replicates used for various analyses are noted (see key below). Station numbers correspond with those of Table 2 and Figure 1.

KEY TO SAMPLE TYPES:

T Sediment trap sample for hydrocarbon analysis

TG Sediment trap sample for grain size analysis

TGM Sediment trap sample for grain size, organic carbon/nitrogen, clay mineralogy

B Sample from upper 2 cm of benthic surface for hydrocarbon analysis

BG Sample from upper 2 cm of benthic surface for grain size analysis

C Core sample for stratigraphic analysis, subsampled for hydrocarbon chemistry

STATION	LOCATION	DEPTH (m)	LONGITUDE (Deg min sec)	LATITUDE (Deg min sec)	SAMPLES TAKEN AT EACH DEPLOYMENT PERIOD <sup>1</sup>					
					Nov 89 - Jun-90	Jun 90 - Aug.90	Aug 90 - Mar-91	March 91 - Jun-91	June 91 - Sept. 91	Sept. 91 - Mar-92
1	BAY OF ISLES	20	147 42 21	60 22 43				T,B	T,TG,B,C	T,TGM,BG
1	BAY OF ISLES	10	147 42 24	60 22 42		B		B	T,TG,B,C	T,TGM,BG
2	DISK ISL.	20	147 39 37	60 29 57			B,BG	T,TGM,B,C	T,TG,B	T,TGM,BG
2	DISK ISL.	15	147 39 35	60 29 57			B,BG	T,TGM,B	T,TG,B,C	T,TGM,BG
2	DISK ISL.	10	147 39 37	60 29 53		B	T,B,BG	T,TGM,B,C	T,TG,B	T,TGM,BG
3	EAST NW BAY	20	147 34 43	60 33 09				T,TGM,B	T,TG,B,C	T,TGM,BG
3	EAST NW BAY	10	147 34 41	60 33 06	T,B	T,B	T,B,BG	T,TGM,B,C	T,TG,B	T,TGM
4	ESHAMY BAY	10	147 58 07	60 27 43		B	T			
5	HERRING BAY	10	147 42 48	60 28 16		B			T,TG,B,C	T,TGM
6	JOHNSON COVE	10	147 58 27	60 03 58		B	T			
7	N CHENEGA ISL	10	148 00 14	60 22 45		B	T			
8	OLSEN BAY	20	146 12 57	60 44 31					B,C	
8	OLSEN BAY	10	146 12 57	60 44 37					B	T,TGM,BG
9	PORT FIDALGO	10	146 17 11	60 50 21	T,B	T,B	T,B,BG			
10	SLEEPY BAY	20	147 50 09	60 04 02			B,BG	T,TGM,B,C	T,TG,B	T,TGM,BG
10	SLEEPY BAY	15	147 50 09	60 04 02			B,BG	T,TGM,B	T,TG,B,C	T,TGM,BG
10	SLEEPY BAY	10	147 50 12	60 03 58	T,B	T,B	T,B,BG	T,TGM,B,C	T,TG,B	T,TGM,BG
11	SNUG HARBOR	20	147 43 34	60 14 24			B,BG	T,TGM,B,C	T,TG,B	T,TGM,BG
11	SNUG HARBOR	15	147 43 34	60 14 20			B,BG	T,TGM,B	T,TG,B,C	T,TGM,BG
11	SNUG HARBOR	10	147 43 43	60 14 15	T,B	T,B	T,B,BG	T,TGM,B,C	T,TG,B	T,TGM,BG
12	SQUIRE ISL.	10	147 56 27	60 14 34		B	T			
13	STOCKDALE HRBR.	10	147 11 40	60 19 32		B	T,B			
14	WEST NW BAY	12	147 36 08	60 32 44	T	T,B	T			
15	GREEN ISL.	10	147 29 04	60 16 04		B				
16	NAKED ISL.	10	147 22 05	60 37 32		B				

Note 1. First date is deployment of traps, second is retrieval. Samples taken at end of each period.

Table 2. Physical characteristics, oiling and treatment for intertidal shorelines adjacent to sediment trap stations for 1989-1992. Oiling conditions are initial for the year, reflecting previous years treatment and winter storms. Naked and Green Island data not presented due to elimination as study sites in 1990. Station numbers correspond to those in Table 1 and Figure 1.

STATION	LOCATION	ESI CLASS	WAVE ENERGY	BENTHIC SEDIMENTS <sup>4</sup> (Top 2 cm: 10 - 20 m depth)	Initial 1989			Spring 90			Spring 91			Spring 92		
					Surf <sup>1</sup>	Sub <sup>2</sup>	Tx <sup>3</sup>	Surf <sup>1</sup>	Sub <sup>2</sup>	Tx <sup>3</sup>	Surf <sup>1</sup>	Sub <sup>2</sup>	Tx <sup>3</sup>	Surf <sup>1</sup>	Sub <sup>2</sup>	Tx <sup>3</sup>
1	BAY OF ISLES	8	Low	Coarse silt - muddy sands	H	OP	Me	M-L	OP(berm)	Ma	M-L	OR	Ma	L	OR	Ma
2	DISK ISL	8,6	Mod. - High	Coarse sand-muddy sand	H	OP	Me	M	OR	Ma	M-L	OR-OF	Ma	L	NO	Ma
3	EAST NW BAY	8,6	Moderate	Coarse - muddy sand	H	OP	Me	M(berm)	OP-OR	Ma	L-NO	OP-OR	Ma	NO	OP-OR	NONE
4	ESHAMY BAY	8,6	Low		L-NO	NO	Me	L-NO	NO	NONE	L-NO	NO	NONE	NE	NE	NONE
5	HERRING BAY	8	Low	Muddy, sandy gravel (10 m)	H	OP-OR	Me	H-M	OR	Ma	M-L	OR	Ma	NE	NE	NONE
6	JOHNSON COVE	8	Low		L	NO	NONE	L	NO	NONE	L	NO	NONE	NE	NE	NONE
7	N CHENEGA ISL	8,7	Moderate		H	OP-OR	Me	L	OR-OF	Ma	L	OR	Ma	NE	NE	NONE
8	OLSEN BAY	8,6	Low	Coarse sandy mud (10 m)	NO	NO	NONE									
9	PORT FIDALGO	8,6	Low	Very coarse - silty sand	NO	NO	NONE									
10	SLEEPY BAY	6	Mod. - High	Very coarse - muddy sand	H-M	OP	Me	M	OP	BR,Me	M-L	OP-OR	BR-Me	L	OR	Ma
11	SNUG HARBOR	6	Mod. -High	Fine - very fine sand	H-M	OP,OR	Me	M-L	OP	BR	L-NO	NO	NONE	NE	NE	NONE
12	SQUIRE ISL	8	Low		L-NO	NO	Me	NO	NO	NONE	NE	NE	NONE			
13	STOCKDALE	8,7	Moderate		NO	NO	NONE									
14	WEST NW BAY	8,6	Mod. - High		H	OP-OR	Me	L	OP-OR	Me,Ma	NO	NO	NONE	NE	NE	NONE

1. Surface oiling condition noted represents average condition of shoreline segments adjacent to trap station. Original 1989 classification system used for consistency.
2. Subsurface oiling condition noted represents condition of worst subsurface oiling lens in adjacent intertidal segments.
3. Tx (Treatment) represents the most intrusive method used for that treatment season.
4. Benthic sediment textural descriptions for sediments around traps are shown only for sites where grain size analysis was available (BG samples in Table 1).

Sources: Michel and Hayes, 1991, for ESI, oiling and some treatment information;  
 Joint agency/Exxon shoreline assessment team (SCAT, SSAT, ASAP, MAYSAP, FINSAP) reports for oiling conditions  
 Pavia 1991, for oiling conditions and berm relocation  
 ADEC Daily Shoreline Assessment Reports (DSA) for treatment information

Environmental Sensitivity Index (ESI)

- 1 Exposed rocky coast
- 2 Exposed wave-cut platforms
- 3 Fine-grained sand beaches
- 4 Coarse-grained sand beaches
- 5 Exposed tidal flats
- 6 Mixed sand and gravel beaches
- 7 Gravel beaches
- 8 Sheltered rocky coasts
- 9 Sheltered tidal flats
- 10 Salt marshes

Key to TREATMENT (Tx)

- Me Mechanical  
 High/low pressure, cold/hot water/steam washing  
 Heavy equipment removing beach sediments
- BR Berm Relocation using heavy equipment
- Ma Manual  
 Pickup of debris by hand and with shovels  
 Raking and hand tilling  
 Absorption pads and hand washing  
 Bioremediation

Key to SURF(ACE) OILING CONDITIONS:

- H Heavy  
 M Medium  
 L Light  
 NO no oil  
 NE not evaluated

Key to SUB(SURFACE) OILING CONDITIONS

- OP Oil fills pore spaces  
 OR Oil residue on sediments  
 OF Oil film on sediments  
 NO No oil



## METHODS

### I. Sediment Trap Apparatus

The sediment traps were designed to capture sediments and particulates falling out of suspension. Sediment traps have been used to determine sedimentation rates in embayments (Lund-Hansen, 1991) and the open ocean (Woods Hole, 1989), and after oil spills to monitor settling particulates for oil contamination (*Tsesis* spill in 1977, Johansson et al., 1980; Gulf War spill, Michel et al. 1993). The sediment trap design for this study incorporated guidelines developed from previous sediment trap work with open-ocean moored traps and laboratory flume studies (Woods Hole, 1989). Based on the lack of data regarding currents in the embayments of PWS, the traps were designed so that the aspect ratio, symmetry, and spacing would be adequate for a variety of conditions. The trapping cylinders were constructed of Schedule 40 PVC, 15 cm. I.D. and 1.2 meters tall. A baffle of 1.0 cm. square grid, 1.0 cm. deep fit flush with the top of each trap to limit the formation of turbulent eddies that could resuspend captured particulates. A trap suite consisted of three cylinders mounted on a 60 x 60 cm concrete base by pipe clamps to rebar set in the concrete. A rebar hook was set in the center of the base for attachment of winch lines. The trap cylinders were placed on the base in a triangular configuration to allow orientation to wave-induced shore-normal currents, spaced at 46 cm centers and aligned to reduce chances any cylinder would be downstream of another. Each cylinder had an 8:1 aspect ratio ( $A=H/D$ , where H is the height and D is the inside diameter) to minimize eddies, reduce in-trap flow, and allow for a tranquil layer within the trap (Woods Hole, 1989). The 1.2 meter height of the trap cylinders was intended to minimize capture of resuspended benthic sediments. Cylinders were leveled to maintain orientation to currents and the water column.

### II. Sample Collection

#### A. Sediment Trap Samples

The sediment traps were deployed and recovered by divers using the winch and crab block on the support vessel. Trap cylinders (and all sampling and filtration gear) were precleaned and decontaminated by washing with Alconox and hot water, rinsing with acetone, and wiping with hexane. The cylinders were clamped onto the base, and 230 g of precombusted (at 450 °C) sodium chloride was added to the bottom of each cylinder. The salt created a density gradient that suppressed resuspension of captured sediments (Woods Hole, 1989). The trap suite was lowered over the side of the vessel until the tops of the cylinders were just above the waterline. They were then filled with seawater by filtration through 0.5 mm nylon mesh to exclude organisms and sediments. Precautions were taken to assure no oil or diesel sheen was on the water near the traps. The traps were lowered to the bottom using a crab block and a line with attached buoy, and an additional permanent marker buoy was deployed from the opposite side of the vessel as the traps settled on the bottom. We attempted to place the traps in

approximately the same location each deployment, and all trap deployments at a particular depth are estimated to have been within a circle of 30 meters radius. Divers detached the line from the traps to avoid disturbance of particulate settling patterns, leaving the permanent marker buoys approximately 6 m from the traps.

After retrieval, trap contents were allowed to settle on deck for a minimum of one hour. A 1.3 meter pipette and refractometer were used to measure the salinity gradient within the sediment trap cylinders (see Sale and Gibeaut, 1995, for salinity data).<sup>1</sup> The top 2/3 of the water was decanted off, and the remaining water in the cylinder (approximately 4-5 liters) was poured through a cleaned sieve to remove small crustaceans, algae, and other organisms. The water was then filtered through pre-combusted 9 mm glassfiber filters in a 3 Buchner funnel array on board the vessel. As a filter became covered with sediment, it was removed and placed in a labelled I-Chem sample jar that indicated the depth, station and trap cylinder number (1, 2 or 3), and a new filter was placed in the array until all the water from that cylinder had been filtered. The filtration apparatus was then decontaminated as noted above before processing the next cylinder. Filter blanks and procedural blanks (deionized water run through new filters in the array) were taken periodically and frozen in I-Chem jars.

#### B. Benthic Surface Sediments

During retrieval of selected traps, divers filled two, 250 ml I-Chem sample jars with sediment from the upper benthic layer (0-2 cm) in a 1 meter radius around the trap base. Each sample was a composite from two sides of the trap; other benthic samples for grain size analysis were taken along the transect line between the traps deployed at different seawater depths. Samples taken by hand were collected using a stainless steel cup, spoon, or trowel. All implements were decontaminated before each trap retrieval. Samples were frozen immediately after collection (benthic samples and cores) or filtration (trap samples).

#### C. Benthic Sediment Core Samples

During trap retrievals in June and September 1991, benthic sediment cores were collected around the base of the sediment traps to provide data on background hydrocarbon levels, evaluate core stratigraphy and determine if *Exxon Valdez* crude oil was present in benthic sediments below the 2 cm surface layers sampled by other studies. The benthic sediment core samples were collected by divers during trap retrieval using a precleaned stainless steel coring tube, 15 cm long with a diameter of 10 cm. Water was siphoned off the top of the core tube after settling, and the sediments were frozen in the tube. The outside of the coring tube was gently heated, releasing the still-frozen core

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<sup>1</sup> The salinity gradient varied from 26 ppt in the top third of the traps and 102 ppt in the brine layer when 4.55 kg of salt were added to the traps, to 24 ppt and 41 ppt respectively when 0.23 kg were used. The lower quantity of salt was used after March 1991 to counter potential problems with undissolved salt in the bottom of the cylinders during late 1990 retrievals.

into a plastic container. The samples were stored frozen under custody, and shipped to the laboratory with specific instructions on sampling protocols for removing subsamples for HC chemistry.

#### D. Surface Mousse Oil Samples

Samples of mousse oil were collected from the sea surface inside PWS at Snug Harbor, Bay of Isles, and Smith Island, 11 days following the grounding of the *T/V Exxon Valdez*. These collections were all within 100 m of very heavily oiled beaches. The mousse oil was collected off the sea surface by using a plate of glass on which oil adhered, and then scraping the oil into a clean sample collection jar.

### III. Sample Storage

After filtration, the filtrate and trapped sediments were frozen in custody-sealed I-Chem sample jars on board the vessel. The samples were kept frozen until ready for analysis. Benthic sediment samples were also custody-sealed and frozen for analysis. Surface mousse oil samples were stored at 5 C for 3 days, then frozen at -20 C until analysis.

### IV. Sample Labelling and Chain of Custody

Sample labels included site name, type of sample, Julian date of sampling, sample depth (if applicable), and replicate number. The record of each person who had custody of samples, the date, time, and location of custodial transfer; and signatures of transferring parties are on file at the Auke Bay Laboratory. Shipping containers were cross-wrapped with custody tape signed and dated by the person shipping the containers.

### V. Hydrocarbon Analysis

Approximately 1 mg aliquots of each of the mousse oil samples were analyzed by the same procedures described below for sediment samples. Results of these analyses are presented in Table II-1, Appendix II, and in fig. 9a.

#### A. Preparation of Sediments for Hydrocarbon Analysis

Sediments were prepared and analyzed following procedures presented in detail by Larsen et al. (1992). About 10 to 20 g of wet sediments from the benthic surface or core sample sediments, or 0.13 to 15 g of sediment from the sediment traps, was added to 80 g anhydrous sodium sulfate for dehydration, and spiked with 500  $\mu$ L hexane solution containing 5 alkane and 6 aromatic deuterated surrogate hydrocarbon standards (listed in Table I-1, Appendix I).

Hydrocarbons were extracted from sediments by prolonged room temperature agitation with dichloromethane following a procedure developed by Brown et al. (1980). The

mixture of sediment, sodium sulfate, and surrogate standards was agitated mechanically for 3 successive periods of 16, 6, and 16 hours with each of 3 successive 100 mL aliquots of dichloromethane. The dichloromethane was separated by filtration after each agitation period. The combined dichloromethane extracts (ca. 300 mL) were reduced in volume over steam and exchanged with hexane to a final volume of ca. 1 mL.

Extracted alkane and aromatic hydrocarbons were separated by silica gel-alumina column chromatography. The chromatographic column consisted of 20 g silica gel (deactivated with 5% water) above 10 g alumina and 20 g elemental copper (for sulfur removal) in a 20 mm id glass column filled with pentane. The alkane hydrocarbons eluted with 50 mL pentane, followed by the aromatic hydrocarbons that eluted with 250 mL 1:1 pentane:dichloromethane (by volume). The pentane solutions containing the alkane hydrocarbons from the samples were each reduced in volume over steam and exchanged with hexane to a final volume of ca. 1 mL, spiked with 50  $\mu$ L hexane internal standard containing 42 ng/ $\mu$ L dodecylcyclohexane (DCH) for estimating recoveries of the deuterated alkane hydrocarbon surrogate standards added initially, and stored for analysis by gas chromatography. The pentane:dichloromethane solutions containing the aromatic hydrocarbons were reduced in volume over steam to a final volume of ca. 0.5 mL, and stored for further purification before analysis by gas chromatography/mass spectrometry.

Aromatic hydrocarbons from the sample extracts were further purified by gel-permeation high performance liquid chromatography (HPLC). The injection volume was 0.5 mL into dichloromethane flowing at 7 mL/min through 2 size-exclusion gel columns (Phenomenex, phenogel, 22.5 mm x 250 mm, 100 Å pore size) connected sequentially. The initial 110 mL eluate was discarded, and the following 53 mL was concentrated over steam and exchanged with hexane to a final volume of ca. 1 mL, then spiked with 25  $\mu$ L hexane containing 80 ng/ $\mu$ L hexamethylbenzene (HMB) as an internal standard for estimating recoveries of the deuterated aromatic hydrocarbon surrogate standards added initially.

## B. Polynuclear Aromatic Hydrocarbon (PAH) Analysis

### 1. Instrumental Method

PAH's in samples and in standards were separated and analyzed using a Hewlett-Packard 5890 series II gas chromatograph equipped with a 5970B mass selective detector (MSD). The injection volume was 2  $\mu$ L into a splitless injection port at 300°C. The initial oven temperature was 60°C, increasing at 10°C per minute immediately following injection to a final temperature of 300°C which was maintained for 25 minutes. The chromatographic column was a 25 m fused silica capillary (0.20 mm ID) coated with a 0.33  $\mu$ m thick film of 5% phenyl methyl silicone. The helium carrier gas was maintained at 70 kPa inlet pressure.

The chromatographic column eluted into the 70 eV electron impact MSD through a 300°C transfer line. The ionizer temperature and pressure were 240°C and  $10^{-5}$  torr, respectively. The mass detector was operated in the selected ion monitoring (SIM) mode, and the specific ions and retention time windows of the SIM Table were chosen to detect all the calibrated aromatic hydrocarbons, the surrogate standards, and the 200 most prominent peaks found on the total ion chromatogram of an aliquot of crude oil from the hold of the *T/V Exxon Valdez* analyzed as a sample, with the MSD operating in the scan mode. The MSD was tuned using mass 69, 102, and 512 fragments of perfluorotributylamine prior to each batch of samples analyzed.

## 2. PAH Identification

### a. Calibrated PAH's

Calibrated PAH's were identified on the basis of (1) retention time and (2) the ratio of two mass fragment ions characteristic of each hydrocarbon. Calibrated PAH's are listed in Table I-2, Appendix I, and include dibenzothiophene and the aromatic hydrocarbons in Standard Reference Material (SRM) 1491 supplied by the National Institute of Standards and Technology (NIST). Also listed in Table I-2 are the mass of the quantification ion, the mass of the confirmation ion, and the mean ratio of these two ions in the calibration standards. Chromatographic peaks were identified as a calibrated aromatic hydrocarbon if both ions were co-detected at retention times within  $\pm 0.15$  minutes of the mean retention time of the hydrocarbon in the calibration standards, and if the ratio of the confirmation ion to the quantification ion was within  $\pm 30\%$  of the expected ratio.

### b. Uncalibrated PAH's

Uncalibrated aromatic hydrocarbons include the alkyl-substituted isomers of naphthalene, fluorene, dibenzothiophene, phenanthrene, fluoranthene, and chrysene listed in Table I-3, Appendix I. Uncalibrated aromatic hydrocarbons were identified by the presence, within a relatively wide retention time window, of a single mass fragment ion that is characteristic of the uncalibrated aromatic hydrocarbon sought. Table I-3 lists the mass of the fragment ions used for both identification and measurement, and the retention time windows used. Note that the retention time windows for uncalibrated aromatic hydrocarbons are much wider than those for calibrated aromatic hydrocarbons. Mass fragments of uncalibrated aromatic hydrocarbons that eluted outside the windows listed in Table I-3 would not have been detected.

### 3. PAH Measurement

#### a. Calibrated PAH's

Concentrations of calibrated PAH's in the sample extracts were estimated using a multiple internal standard method employing a 5-point calibration curve for each calibrated aromatic hydrocarbon. The deuterated surrogate standards that were initially spiked into each sample are treated as internal standards, where each surrogate compound is associated with one or more calibrated PAH's (see Tables I-1 and I-2, Appendix I). A calibration curve for each calibrated PAH and batch of samples analyzed is based on 5 different hexane dilutions of dibenzothiophene and NIST SRM 1491, where 1 mL of each dilution contained the same amount of deuterated surrogate standard as was initially spiked into the samples. Each calibration curve is derived from linear regression of the ratio of MSD/SIM quantification ion response of the calibrated PAH and the associated deuterated surrogate standard as the ordinate, and the ratio of the amount of calibrated PAH and the amount of deuterated surrogate in 1 mL of each of 5 calibration standards as the abscissa. The highest calibration standard is 25 times more concentrated than the lowest standard, and PAH concentrations in the lowest standard correspond with PAH concentrations in a 20 g sample of sediment ranging from 1.8 to 4.2 ng/g (or 1.44 to 10.5 times the PAH concentrations that would have resulted from samples containing PAH's at the method detection limits, see below).

The amount of a calibrated PAH in the dichloromethane extract of a sediment sample was calculated as the product of the inverse of the calibration curve regression line slope, the ratio of MSD/SIM quantification ion response to the calibrated PAH and the associated deuterated surrogate standard for the sample extract, and the amount of the deuterated surrogate standard associated with the PAH. The concentration of a calibrated PAH in the sediment sample was calculated as the ratio of the amount of the hydrocarbon in the dichloromethane extract and the calculated dry weight of the sediment. Note that this procedure compensates for losses of calibrated PAH's during sample preparation.

#### b. Uncalibrated PAH's

Concentrations of uncalibrated PAH's in the sediment samples were determined using calibration curves and procedures for the most similar calibrated PAH. The MSD/SIM response to the quantification ion of each uncalibrated PAH identified, bearing the same number of carbon atoms in the alkyl- substituents, and derived from the same unsubstituted PAH, were summed; this sum was used in place of the most similar calibrated PAH response in the procedure described above for calculating concentrations of calibrated PAH's. For example, the fluorene calibration curve and procedure was used for all the alkyl-substituted fluorenes identified, but the 1-methylphenanthrene calibration curve and procedure was used for all the alkyl-substituted phenanthrenes.

#### 4. Detection Limits

##### a. Calibrated PAH's

Method detection limits (MDL's) were estimated for each calibrated PAH analyte following the procedure described in Appendix B, 40 CFR Part 136. Detection limit masses for each calibrated PAH are listed in Appendix II, table II-8; detection limits for each sample were determined as the ratio of the experimentally estimated MDL expressed as a mass, and the sample dry weight.

##### b. Uncalibrated PAH's

Method detection limits for uncalibrated PAH's were not experimentally determined. Consequently, detection limits for these analytes are arbitrarily assumed as the MDL of the most closely related calibrated PAH analyte, and were determined for each sample similarly.

#### 5. Quality Assurance

##### a. String Structure and Quality Control Samples

Samples were analyzed in batches consisting of 12 samples, which together with 5 calibration curve standards, and 6 quality control samples arranged in a specific sequence, are denoted as strings. The 6 quality control samples included 2 mid-level calibration standards, 2 reference samples, and 2 method blanks, one of which was spiked with hydrocarbon standards (denoted as "spiked blank"). One each of the mid-level calibration standards and of the reference samples, and the method blank were analyzed in the middle of each string, and the remaining three quality control samples were analyzed at the end of each string.

The mid-level calibration standards were analyzed to assess calibration accuracy and to verify instrument stability during analysis of the string; the results are summarized in Table III-2, Appendix III. Note that this assessment of accuracy is directly related to NIST standards for all calibrated PAH's except dibenzothiophene. The reference samples were 1 g aliquots of a material prepared by NIST (denoted as QC-SED-1), and were analyzed to assess analytical precision within and among strings for calibrated PAH analytes. The results of the reference sample analyses are summarized in Table III-1, Appendix III.

Method blanks were analyzed to assess contaminants introduced during processing and analysis. Sediment samples and method blank samples were processed and analyzed identically, except the method blanks contained no sediment. Also, additional method blanks were spiked with an amount of NIST SRM 1491 and dibenzothiophene equivalent to amounts that would be present from 10 g sample aliquots at sample concentrations of

3.2 to 112 ng PAH/g. These spiked blank samples were analyzed to assess overall method accuracy. The results of the spiked method blank sample analyses are summarized in Table III-3, Appendix III.

b. Calibration Curve Linearity and Surrogate Standard Recoveries

Calibration curve linearity, expressed as the square of the correlation coefficient of regression ( $r^2$ ), was greater than 0.99 for more than 95% of the PAH calibration curves. Recoveries of the deuterated surrogate standards that were initially added to each sample, were estimated by comparing the ratio of deuterated surrogate response and the HMB internal standard of a sample with the mean of the same ratio derived from the calibration standards of the sample string (1 mL of each calibration standard contains the same amounts of these standards as was added to each sample, and each sample was concentrated to about 1 mL for instrumental analysis). PAH's that are associated with deuterated surrogate standard recoveries of less than 30%, or more than 150%, are treated as missing, affecting 2.2% of the PAH data.

c. Analytical Precision and Accuracy

The precision of the analytical procedure for selected PAH analytes, expressed as the coefficient of variation (CV's, i.e., the ratio of the standard deviation and the mean of the calibrated PAH's found in the reference samples, expressed as percent) calculated from the results of the 29 strings analyzed, ranged from 6.7% to 40.2% (median 15.7%; Table III-1, Appendix III). Mean accuracy, determined as the ratio (expressed as percent) of the mean amount of calibrated PAH found in the NIST calibration check samples of the 29 strings analyzed for this study and the amount added, ranged from 94.9% to 100.9% (median 98.6%); corresponding coefficients of variation ranged from 2.0% to 22.2% (median 4.4%; Table III-2, Appendix III). Mean accuracy based on the spiked blank samples ranged from 83.0% to 116.0% (median 96.9%); corresponding coefficients of variation ranged from 4.9% to 17.0% (median 10.5%; Table III-3, Appendix III).

d. Contaminants in Method Blanks

Calibrated PAH's were detected above respective MDL's only once in the analysis of 25 calibrated PAH's in each of 29 method blanks (i.e., detection frequency =  $1/(25 \times 29)$ ). Uncalibrated PAH's were detected above estimated MDL's twice in the analysis of 18 uncalibrated PAH's in each of the 29 method blanks.



## C. Alkane Hydrocarbon Analysis

### 1. Instrumental Method

Alkanes in samples and in standards were separated and analyzed using a Hewlett-Packard 5890 series II gas chromatograph equipped with a flame ionization detector (FID). The injection volume was 1  $\mu$ L into a splitless injection port at 300°C. The 60°C initial oven temperature was maintained for 1 minute, then increased at 6°C per minute to a final temperature of 300°C which was maintained for 26 minutes. The chromatographic column was a 25 m fused silica capillary (0.20 mm ID) coated with a 0.33  $\mu$ m thick film of 5% phenyl methyl silicone. The helium carrier gas flow rate was 0.80 mL per minute, and the column effluent was combined with 34 mL per minute nitrogen make-up gas before entering the FID. The FID was operated using hydrogen and air flowing at 33 and 410 mL per minute, respectively.

### 2. Alkane Hydrocarbon Identification

Alkane hydrocarbons were identified on the basis of their retention times. Any peak detected above the integrator threshold within  $\pm 0.25\%$  of the mean retention time of an alkane in the calibration standards was identified and quantified as that alkane. The calibration standards were prepared at our Laboratory, and contained the normal alkanes from decane through triacontane, dotriacontane, tetratriacontane, and 2,6,10,14-tetramethylpentadecane (pristane).

### 3. Alkane Hydrocarbon Measurement

Concentrations of calibrated alkanes in sediments were estimated using an internal standard method employing a 5-point calibration curve for each calibrated alkane hydrocarbon. The deuterated surrogate standards that were initially spiked into each sample were treated as internal standards, where each surrogate compound is associated with a group of related calibrated alkanes (see Tables I-1 and I-4, Appendix I). A calibration curve for each calibrated alkane and batch of samples analyzed is based on 5 different hexane dilutions of the concentrated alkane standard prepared at our Laboratory, where 1 mL of each dilution contained the same amount of deuterated surrogate standard as was initially spiked into the samples. Each calibration curve is derived from linear regression of the ratio of FID response of the calibrated alkane and the associated deuterated surrogate standard as the ordinate, and the ratio of the amount of calibrated alkane and the amount of deuterated surrogate in 1 mL of each of 5 calibration standards as the abscissa. The highest calibration standard is 50 times more concentrated than the lowest standard, and alkane concentrations in the lowest standard correspond with alkane concentrations in a 20 g sample of sediment ranging from 21 to 64 ng/g (or 2.4 to 23.6 times the alkane concentrations that would have resulted from samples containing alkanes at the method detection limits, see below).

Concentrations of 2,6,10,14-tetramethylhexadecane (phytane) were also estimated as the mean of results derived from the calibrations curves for octadecane and nonadecane, because a suitable standard for this alkane was not available. The accuracy of this procedure was evaluated by comparison with NIST-derived standards (see below).

Amounts of uncalibrated alkane hydrocarbons and the cumulative amount of hydrocarbons in the unresolved complex mixture (UCM) were calculated using respective detector responses and the calibration curve for hexadecane. Flame ionization detector response due to the UCM was determined as the difference of the total FID response and the response due to distinguishable peaks.

#### 4. Detection Limits

Method detection limits (MDL's) were estimated for each calibrated alkane analyte following the procedure described in Appendix B, 40 CFR Part 136. Detection limit masses for each calibrated alkane are listed in Appendix II, table II-8; detection limits for each sample were determined as the ratio of the experimentally estimated MDL expressed as a mass, and the sample dry weight.

#### 5. Quality Assurance

##### a. String Structure and Quality Control Samples

Samples were analyzed in strings comprising 12 samples, 5 calibration curve standards, and 7 quality control samples arranged in a specific sequence. The 7 quality control samples included 2 mid-level calibration standards, 2 reference samples, a method blank, and a NIST-derived alkane standard. One each of the mid-level calibration standards and of the reference samples, and the method blank were analyzed in the middle of each string, and the remaining 4 quality control samples were analyzed at the end of each string.

The mid-level calibration standards were analyzed to verify instrument stability during analysis of the string; the results are summarized in Table III-4, Appendix III. The reference samples were 1 g aliquots of a material prepared by NIST (denoted as QC-SED-1), and were analyzed to assess analytical precision within and among strings for the calibrated alkane analytes. The results of the reference sample analyses are summarized in Table III-5, Appendix III.

Method blanks were analyzed to assess contaminants introduced during processing and analysis. Sediment samples and method blank samples were processed and analyzed identically, except the method blanks contained no sediment. Method blanks spiked with an amount of Laboratory prepared standards equivalent to amounts that would be present from sample concentrations of 4,110 to 12,800 ng alkane/g (assuming a 1 g sample aliquot), were analyzed to assess overall method accuracy. The results of the

spiked method blank sample analyses are summarized in Table III-6, Appendix III. Also, a NIST-derived alkane standard (denoted as QA-CH-2) was analyzed with each string to relate accuracy assessments of alkanes with NIST standards; results of these analyses are summarized in Table III-7, Appendix III.

#### b. Calibration Curve Linearity and Surrogate Standard Recoveries

Calibration curve linearity, expressed as the square of the correlation coefficient of regression ( $r^2$ ), was greater than 0.99 for more than 95% of the alkane calibration curves. Recoveries of the deuterated surrogate standards that were initially added to each sample, were estimated by comparing the ratio of deuterated surrogate response and the DCH internal standard of a sample with the mean of the same ratio derived from the calibration standards of the sample string (1 mL of each calibration standard contains the same amounts of these standards as was added to each sample, and each sample was concentrated to about 1 mL for instrumental analysis). Alkanes that are associated with deuterated surrogate standard recoveries of less than 30%, or more than 150%, are treated as missing, affecting 0.35% of the alkane data.

#### c. Analytical Precision and Accuracy

The precision of the analytical procedure is evaluated on the basis of the results of the two reference samples analyzed with each string. Alkane CV's in the NIST QC-SED-1 reference samples ranged from 5.6% to 33.3% (median 12.4%; Table III-5, Appendix III). Mean accuracy, determined as the ratio (expressed as percent) of the mean amount of calibrated alkane found in the calibration check samples and the amount added, ranged from 98.5% to 101.8% (median 99.5%); corresponding coefficients of variation ranged from 1.1% to 20.0% (median 1.5%; Table III-5, Appendix III). Mean accuracy based on the spiked blank samples ranged from 92.2% to 108.0% (median 99.7%); corresponding coefficients of variation ranged from 3.5% to 14.5% (median 4.9%; Table III-6, Appendix III). Mean accuracy based on the NIST QA-CH-2 standards ranged from 84.8% to 130.6% (median 94.1%); corresponding coefficients of variation ranged from 3.6% to 51.3% (median 4.7%; Table III-7, Appendix III).

#### d. Contaminants in Method Blanks

Calibrated alkanes were never detected above respective MDL's in the analysis of 25 calibrated alkanes in each of 29 method blanks.

#### D. Dry Weight Determination

Ratios of sediment wet and dry weights were measured by dehydrating 1 g of wet sediment for 24 h at 60°C and weighing the mass remaining.

## VI. Geochemical and Geological Methods

### A. Sediment Trap and Benthic Surface Samples

A variety of analyses were performed on the sediment trap and benthic surface sediments. Grain size and hydrocarbon analyses were completed on most samples. Hydrocarbon analysis methods were described above.

#### 1. Grain Size Analysis

Grain size distributions of samples were analyzed at the University of Alaska at Fairbanks using the general method of Folk (1974). Raw final data from the grain size analysis are presented in Sale and Gibeaut (1995). A subsample of the original sediment was taken for analysis, the weight of the subsample dependent on the nature of the original sample. Granulometric analysis was carried out by the combined sieve-pipette technique. The analysis resulted in grain size distributions in 1/2 phi size intervals, with the exception of the sediment trap samples, where small weights of trapped sediments would allow resolution only to 1 phi intervals.

A representative subsample of sediment was taken into a 250 ml beaker, and, after adding 50 ml of distilled water, was placed into an ultrasonic bath to help disaggregate particle flocs. Any large size wood or shell fragments were hand-picked and discarded. The remaining sediment was transferred to a blender, and with 400 ml of distilled water was lightly blended for 5 min. to further disperse particles. This slurry of sediment was wet-sieved through a 230-mesh sieve into a petri dish to separate the  $<62 \mu\text{m}$  fraction consisting of the silt and clay (mud) size particles from the larger sand and gravel size classes. The mud fraction was transferred to a 1 L measuring jar for pipette analysis, while the coarse fraction was dried in an oven and put aside for dry sieving.

Grain size analysis of the mud fraction by pipette technique, taking into account Stokes settling time-velocities for particles, followed Krumbein and Pettijohn (1938) and Folk (1980), modified to correspond to laboratory ambient temperature. Prior to the analysis, an aliquot of 2 g of sodium hexametaphosphate was added to the 1 L mud suspension to further deflocculate the fine particles. Pipette analysis was carried out to  $1 \mu\text{m}$  size, and individual pipette fraction was weighed to 5 decimal places in a Mettler precision balance.

Sieve analysis of the coarse fraction  $>62 \mu\text{m}$  fraction used a nest of sieves at 1/2 phi intervals for at least ten minutes in a ROTAP unit, and particles in each size grade were weighed to 3 decimal places.

Results of the sieve and pipette analysis were combined and the weights of the individual size fractions estimated according to the steps outlined in Folk (1980). Weight percents and cumulative weight percents were calculated and cumulative frequency curves hand-

drawn on log probability paper. From these, selected percentiles were obtained and used to calculate conventional grain size statistical parameters, using the University of Washington SEDAN program on the University of Alaska computer system.

## 2. Organic Carbon/Nitrogen and Clay Mineralogy

In addition to hydrocarbon and grain size analyses, trap samples collected over the spring of 1991 and the winter of 1991/92 were analyzed for concentrations by weight of organic carbon and nitrogen, and percentages of illite and chlorite clay minerals at the University of Alaska, Fairbanks. Organic carbon (OC) and nitrogen (N) of selected trap samples were analyzed according to the method outlined in Naidu (1985). A 5-10 g split of the sediment was treated with 10% HCl to remove carbonate, and the carbonate-free sample was pulverized using an agate mortar and pestle. A known aliquot by weight of the powder was analysed for OC and N using a PE Model 240B CHN analyzer.

Clay minerals in the  $< 2 \mu\text{m}$  sediment fraction were analysed by X-ray diffraction following Naidu and Mowat (1983) and Biscaye (1965). The method included separation of the  $< 2 \mu\text{m}$  fraction from suspension by settling or centrifugation. This fraction was then treated with  $\text{H}_2\text{O}_2$  to oxidize organic matter. A slurry of the organic free sediment was smeared on a glass slide to obtain basal-oriented (001) grains, glycolated and subject to X-ray analysis. Clay minerals were identified based on the presence of characteristic basal (001) crystal reflections. Semi-quantitative estimates of the various clay minerals followed methods in Biscaye (1965).

Portions of the same samples were also qualitatively inspected for grain characteristics using a 30x binocular microscope.

## B. Sediment Cores

Core analyses were performed at the University of South Florida in the following order.

### 1. X-radiographs

Before splitting and while still frozen each core was removed from its plastic container and X-rayed. The X-radiographs were obtained at the University of South Florida's Medical Clinic. Various settings were tried for each core to obtain the best image.

### 2. Splitting Cores and Sampling for Hydrocarbon Analyses

While still frozen, each core was split and sampled at various stratigraphic intervals for hydrocarbon and grain size analyses. The splitting and sampling procedure prevented contamination from outside sources and between sediment layers in the cores. Tools included a coping saw, razor blades, glass beakers, gloves, and a glass plate. Prior to the splitting of each core, all tools were washed with warm water and Alconox, rinsed with

hot water, and allowed to air dry. After drying, each tool was rinsed first with acetone and then hexane.

When all tools were cleaned and ready for splitting, the core to be split and sampled was removed from the freezer and placed on the glass plate. The frozen core was split along its length with the coping saw. Coping saw movements were limited to strokes of less than 2 to 3 cm along the length of the core to prevent smearing the sediments. Once the core was split, it was inspected for discrete layers, and one half was set aside for later analysis. Inspection of the X-radiographs at this point was very helpful.

When horizons for hydrocarbon samples were determined, a thin layer of sediment on the surface of the split face was removed, and the samples were excavated from the interior of the sample half of the core using a razor blade. Sediment was placed in a pre-weighed beaker sitting on an electronic scale. Sediment was added to the beaker until at least 30 grams were obtained. The sample was transferred to a pre-cleaned I-Chem jar, labeled, secured with evidence tape, and immediately frozen. A corresponding sample for grain size analysis was obtained from the same horizon and from the remaining exterior part of the core. The razor blade, beaker, and gloves were exchanged for clean tools before the next sample was taken from the core. Before sampling the next core, all equipment was cleaned as described above.

Hydrocarbon samples were kept frozen and were shipped overnight in coolers with dry ice to the Alaska Department of Environmental Conservation's Oil Spill Response Center in Anchorage, Alaska. The samples were then transferred frozen to the NOAA/NMFS Auke Bay Fisheries Laboratory in Juneau, Alaska. Chain of custody was maintained throughout the procedure.

### 3. Core Descriptions

The half of the core that was not sampled was placed in an aluminum jacket to prevent disruption and allowed to thaw. After thawing, the core was carefully scraped to reveal sedimentary structure and lithology. A 30x binocular microscope aided in core descriptions. A sketch was made of each core detailing observations to the nearest millimeter. Standard visual-aid diagrams were used for sediment descriptions (figs. 2 through 5). Lithology was described using the classification scheme of Folk et. al (1970) (fig. 6) and the Udden-Wentworth grain-size scale (Lewis 1984) (fig. 7). Overall sediment color was determined by using a rock color chart following the Munsell color system. Initial qualitative classifications were modified as appropriate after considering quantitative grain size analyses.

### 4. Photographs

Each core was photographed in natural sunlight using a 35 mm camera with a macro lens and Kodachrome 64 film (see Gibeaut, 1993, for photographs).

## 5. Grain Size Analysis

Grain size analyses generally followed the methods already described for the sediment trap and benthic surface samples. Samples were first rinsed with distilled water, allowed to settle for several days, and then the excess water decanted. Samples were wet sieved through a 4 phi screen to separate the mud fraction. Sediment caught on the 4 phi screen were dried. After drying of the coarse fraction, organic debris was manually removed and weighed separately. The coarse fraction was dry sieved at 1 phi intervals. The mud fraction was separated into clay and silt fractions by pipette analysis (Folk, 1980). Small sample sizes required the use of 1 phi intervals.

## VII. Observations and Underwater Photography

During retrieval and deployment of the sediment traps, divers made visual observations of the topography, bedforms, sediment types, and flora and fauna of the benthic surface and in the surrounding water column at each site. These observations were written down immediately after the dives on a standard form that allowed for easy data entry and comparison between sites. The observations, as well as copies of the forms, are included in *Study Site Descriptions, Oiling and Treatment Histories and Data Report*, a companion volume in the final report of this study to the State of Alaska, Department of Environmental Conservation (Sale and Gibeaut, 1995).

During cruises in March 1991 and March 1992, before the spring plankton bloom when water visibility in Prince William Sound is at a maximum, underwater photographs of the sediment traps in situ, and of the benthic surface near the sediment traps, were taken by J. Lincoln Freese of NOAA/NMFS Auke Bay Fisheries Laboratory. Some of these photos are also included in Sale and Gibeaut (1995).

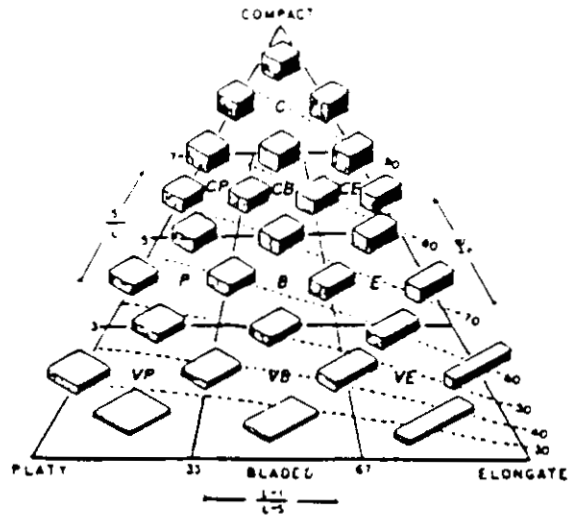


Fig. 2. Form triangle used to estimate the shapes of sediment particles in the cores (after Zingg 1935).

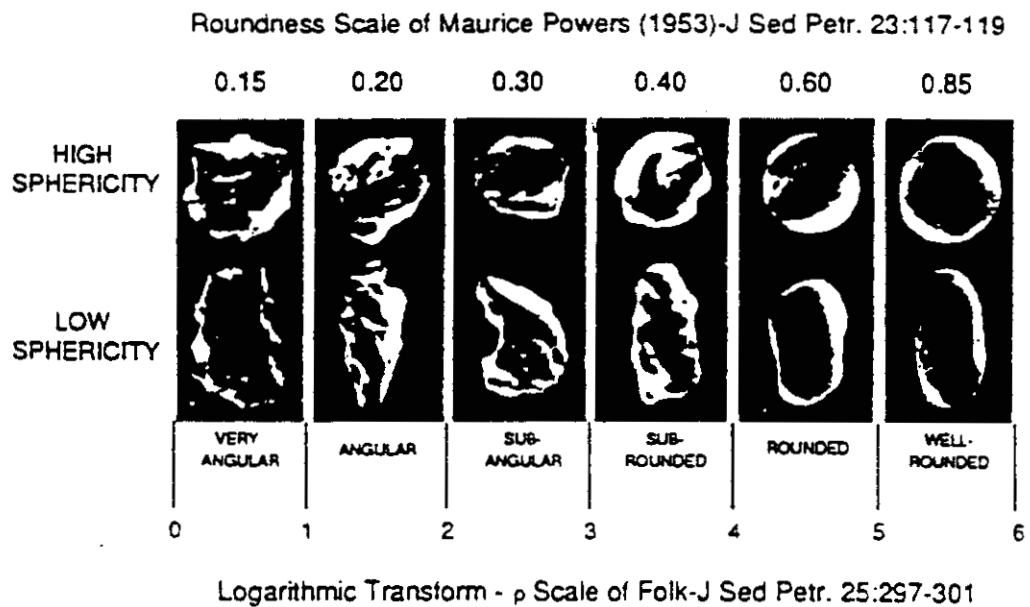
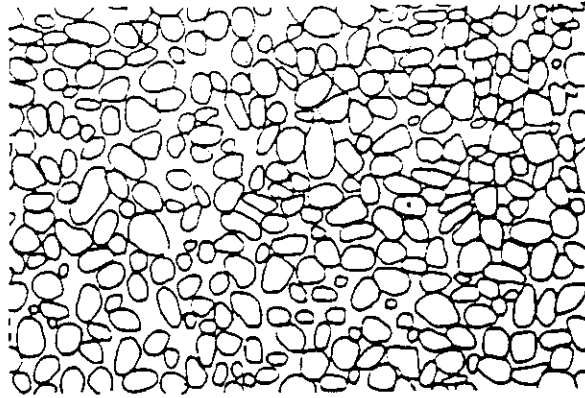
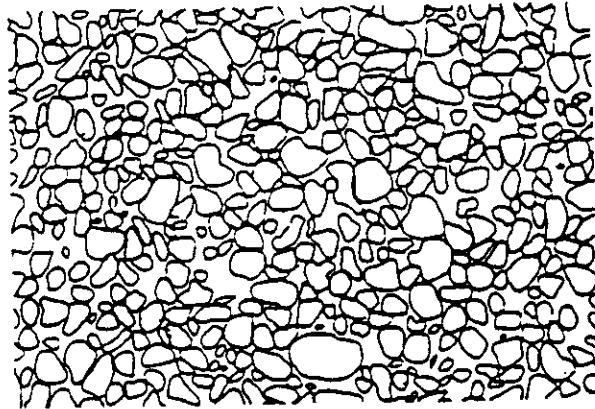


Fig. 3. Chart for estimating roundness of sediment particles.

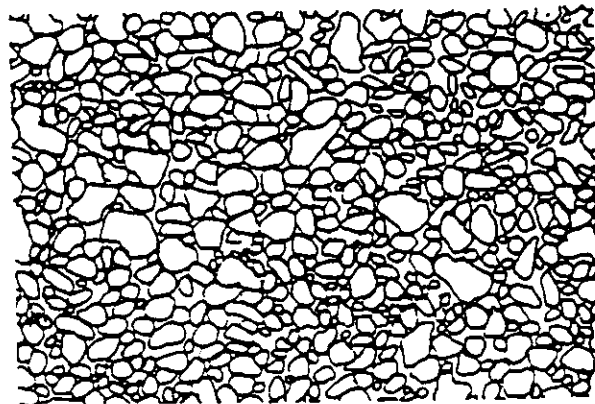
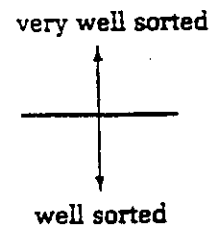




$\sigma_1 = 0.0$  very well sorted



$\sigma_1 = 0.35$



$\sigma_1 = 0.5$

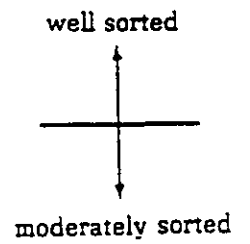


Fig. 4. Diagram for visual estimates of sorting of sediments in the cores (from Lewis 1984).

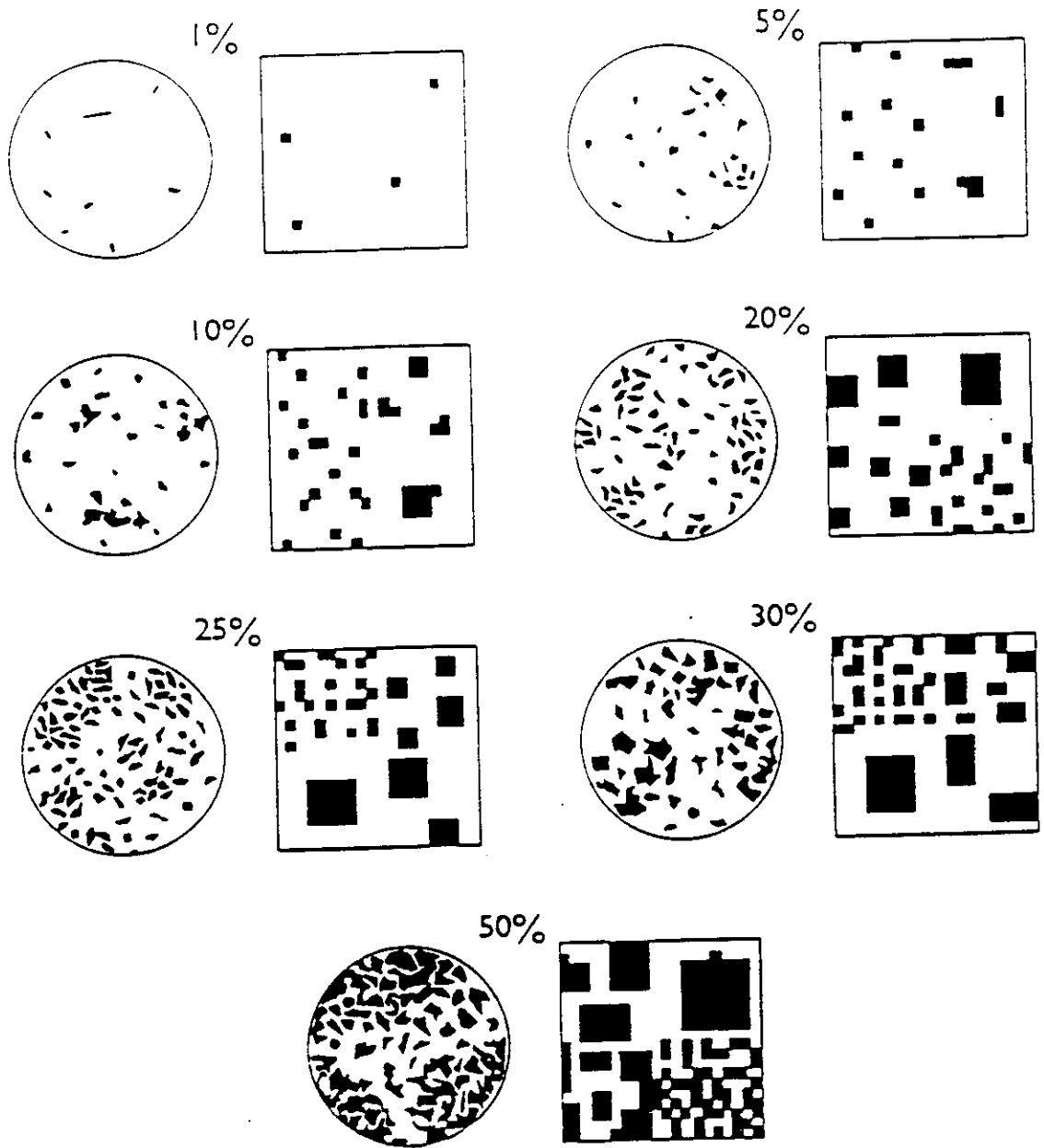
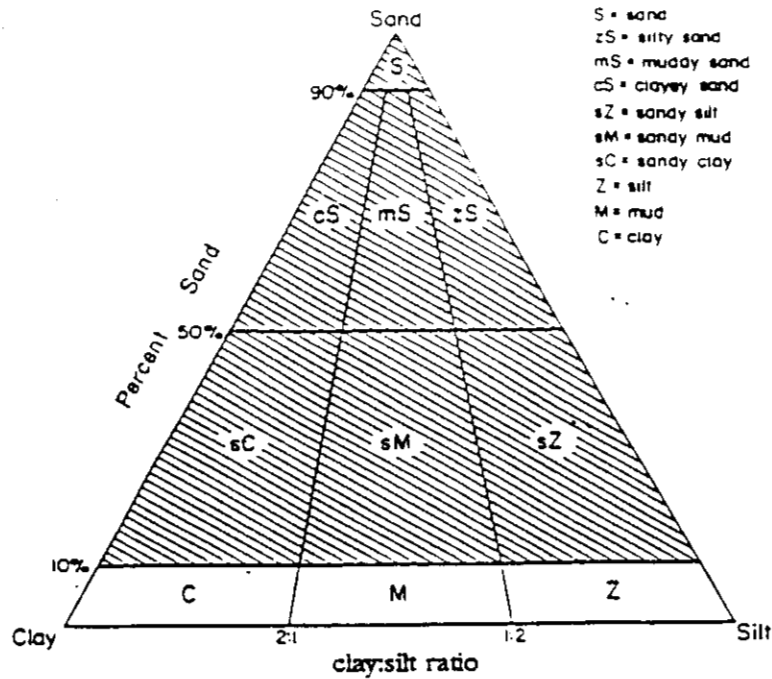


Fig. 5. Percentage estimation comparison charts (Folk et al. 1970 as presented in Lewis 1984).

A.



B.

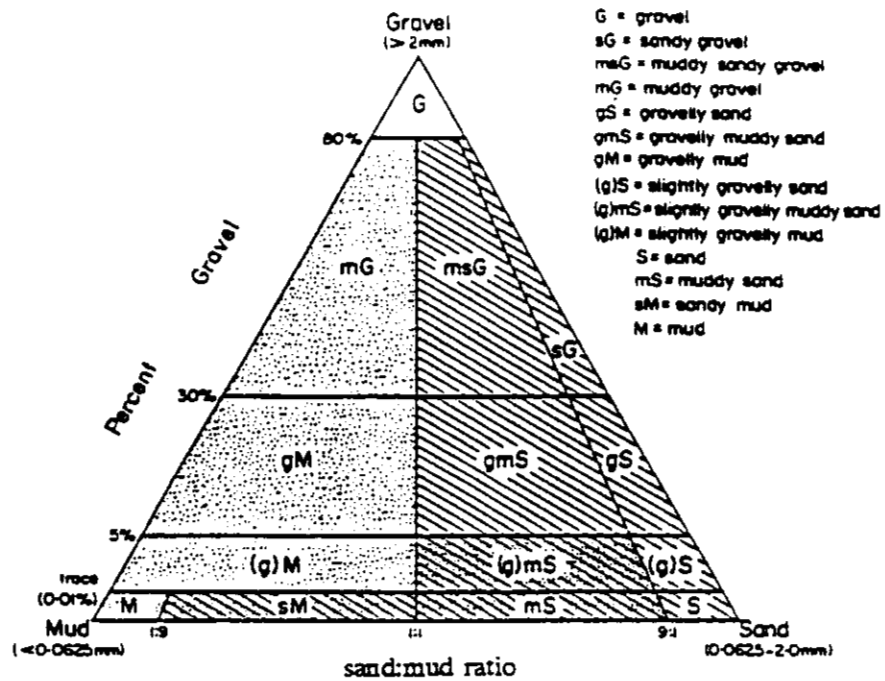


Fig. 6. Textural classification schemes of Folk et al. (1970). Diagrams are modified from Lewis (1984). A.- Classification for sediments with no gravel. B.- Classification for sediments with gravel.

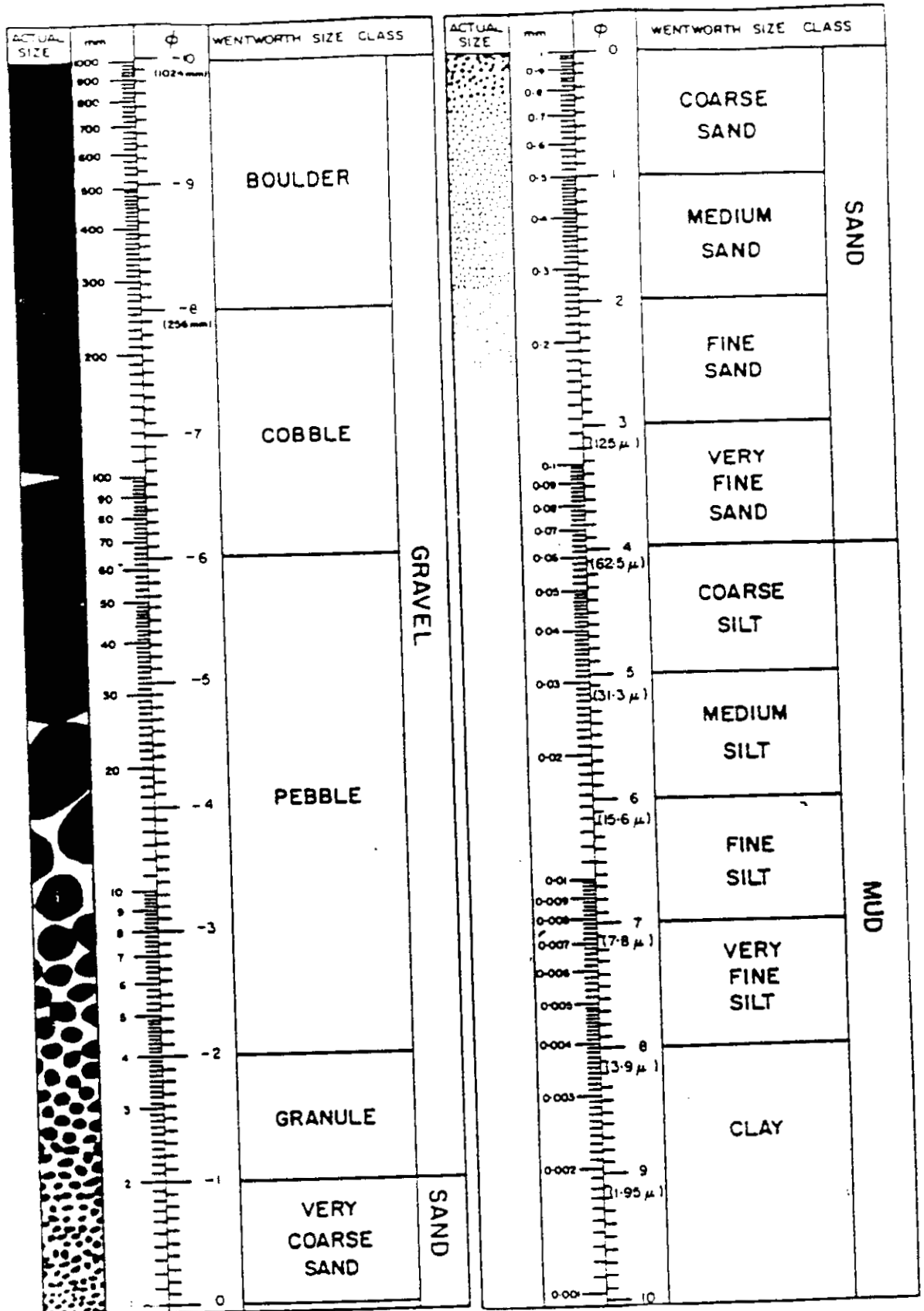


Fig. 7. Udden-Wentworth grain-size scale including phi and millimeter scales used in this study. Diagram from Lewis (1984).

## VIII. Data Analysis

### A. Hydrocarbon Data

#### 1. Hydrocarbon Data Excluded from Comparisons

Hydrocarbon data were not used for comparative purposes in the results section of this report in the following 3 cases: (1) the sample weights of 12 samples were not accurately measured, so hydrocarbon concentrations for these samples are only approximate; (2) the sample aliquot wet weight of 16 sediment trap samples was less than 0.5 g, resulting in high sample detection limits for these samples compared with the higher-mass sample aliquots; and (3) the surrogate standard recoveries were less than 30% or greater than 150% for any of the PAH surrogate standards except benzo[a]pyrene-d<sub>12</sub> and perylene-d<sub>12</sub>.

The hydrocarbon data that were not used for comparisons in the results section are listed in Appendix II, tables II-5 through II-7. This excluded data generally corroborates data compared in the results section, when proper allowance is made for the defects noted above.

#### 2. Presentation of Hydrocarbon Composition

The relative concentrations of PAH's and of phytane in hydrocarbon samples is consistently presented in this report as proportions of the mean total PAH concentration of the sample. This permits comparison of hydrocarbon composition among samples from sediment traps, the epibenthos, and benthic core samples, and among samples of widely different total PAH concentrations.

#### 3. Calculation of Total PAH

Total PAH is calculated as the sum of all the PAH's listed in Tables I-2 and I-3, Appendix I, except the 4 calibrated PAH compounds that are included in corresponding uncalibrated PAH measurements (1- and 2-methylnaphthalene, 2,6-dimethylnaphthalene, and 1-methylphenanthrene), and except for perylene, a naturally occurring PAH in Prince William Sound marine sediments. Variability about mean total PAH is given as  $\pm$  standard error (i.e., the ratio of the standard deviation and the square root of the number of sample replicates).

## B. Geochemical and Geological Data

### 1. Grain Size Data

The four moment measures were calculated using the graphical method of Folk and Ward (1957) and the entire grain size distribution for each sample. The graphical method was found to be the most appropriate because of "open tails" in the size distributions. In addition, the four moments of just the sand fraction were calculated using the method of moments (Lewis 1984).

### 2. Correlations between Sedimentology, Oil Spill Events, and Hydrocarbon Pollution

All geological data including grain size and composition as well as physical setting and energy conditions occurring during trap deployment periods were considered to explain observed levels of oil pollution. Initial oiling, cleanup activities, and nature of persistent oiling of the adjacent shorelines were also considered. The type and amount of this data and its site-specific nature allowed only qualitative correlations.

## RESULTS

### I. Hydrocarbon Results

The concentrations of the hydrocarbons determined in this study are tabulated in Appendix II, in Tables II-1 through II-7. Hydrocarbon concentrations are given on a dry weight basis. Following is a summary and interpretation of the results in those tables.

#### A. Sediment trap samples

##### 1. Initial Deployment - November 1989 to June 1990

###### *Stations Adjacent to Oiled Beaches - 10 m Seawater Trap Deployment Depths*

Sediment trap concentrations of PAH's derived from *Exxon Valdez* crude oil were highest in the traps deployed adjacent to 4 heavily oiled beaches during the first deployment period (November 1989 to June 1990). Of the 4 heavily-oiled sites, mean total PAH concentrations were highest at Northwest Bay-East arm ( $75,500 \pm 2,040$  ng PAH/g sediment,  $n = 2$ ) and Sleepy Bay ( $28,400 \pm 1,980$  ng/g,  $n = 3$ ), and were lowest at Northwest Bay-West arm ( $7,190 \pm 1,390$  ng/g,  $n = 3$ ; fig. 8). Subsequent PAH concentrations in sediments trapped at these stations were consistently lower.

The abundance of individual PAH's and of phytane relative to the total PAH in sediments collected during the initial deployment of the traps at the 4 stations adjacent to oiled beaches is consistent with that of highly weathered *Exxon Valdez* crude oil. The most abundant PAH's measured in these sediments generally correspond with the most abundant PAH's in the mousse samples collected 11 days following the initial spill (compare fig. 8 and fig. 9a), except the sediment trap PAH's show increasing preferential losses of lower molecular weight and of less substituted PAH's. The pattern of these preferential losses is very consistent among sediment trap replicates and among the 4 deployment stations (compare figs. 8a through 8d). In addition, note that (1) the high molecular weight and un-substituted PAH's that are not abundant in the mousse samples are also not abundant in the trapped sediments, and (2) phytane, abundant in the weathered mousse, is also consistently abundant in these trapped sediments. Finally, the normal alkanes with molecular weights greater than n-eicosane were present at concentrations that were approximately as high as the alkyl-substituted PAH homologues in these samples, and that the UCM was substantial (i.e. present at concentrations approaching  $10^6$  ng/g in some samples).

###### *Port Fidalgo Control Station*

At the Port Fidalgo control station, the concentrations of trapped sediment PAH's were substantially lower, and were distributed differently, than at the 4 stations adjacent to heavily oiled beaches during the first deployment period. The mean total PAH

concentration of sediments trapped at Port Fidalgo during the first deployment period was  $1,880 \pm 245$  ng PAH/g ( $n = 3$ ), or less than 30% of the lowest station adjacent to an oiled beach during this period. In addition to the alkyl-substituted PAH homologues characteristic of petroleum sources, several un-substituted homologues including 4 and 5 ring PAH's were relatively abundant in the trapped sediments at Port Fidalgo during the initial trap deployment (fig. 9b). Also, phytane was not detected in the sediments trapped during the initial deployment interval at Port Fidalgo.

## 2. Temporal Trends

### *Stations Adjacent to Oiled Beaches - 10 m Seawater Trap Deployment Depths*

Total PAH concentrations of sediments trapped at stations adjacent to oiled beaches generally declined in sediments trapped subsequent to the first deployment interval. Mean total PAH concentrations in sediments trapped during the June 1990 to August 1990 deployment interval ranged from  $1,820 \pm 989$  ng/g ( $n = 2$ ) to  $14,500 \pm 178$  ng/g ( $n = 2$ ), a range from 4% (at Northwest Bay-East arm) to 88% (at Northwest Bay-West arm) of values during the previous winter deployment at corresponding stations (fig. 10). PAH concentrations of sediments trapped during the August 1990 to March 1991 deployment interval were comparable with those of corresponding stations collected during the June 1990 to August 1990 deployment interval, except at Northwest Bay-East arm, where the total PAH concentration increased from  $3,120$  ng/g ( $n = 1$ ) to  $11,200$  ng/g ( $n = 1$ ; fig. 10). Mean total PAH concentrations of sediments trapped during the March 1991 to June 1991 deployment interval declined further at Sleepy Bay and Snug Harbor, to  $5,780 \pm 586$  ng/g ( $n = 3$ ) and  $787 \pm 147$  ng/g ( $n = 3$ ). However, at Northwest Bay-East arm, the mean total PAH concentration of sediment trapped during the March 1991 to June 1991 deployment interval remained higher than that of the June 1990 to August 1990 deployment interval, at  $6,280 \pm 1,240$  ng/g ( $n = 2$ ; fig. 10).

The abundance of individual PAH's and of phytane relative to the total PAH's in sediments trapped during the initial and the subsequent deployment intervals are very similar (fig. 11). As noted above, this pattern of relative PAH abundances is broadly consistent with highly weathered *Exxon Valdez* crude oil. However, the pattern of relative PAH abundances for sediments trapped during the June 1990 through August 1990 deployment interval and the other deployment intervals differ in three respects: (1) from June to August 1990, the abundance of naphthalenes is relatively higher; (2) the abundance of the chrysenes is relatively lower; and (3) the most abundant homologues of dibenzothiophene and phenanthrene tend to be the dimethyl- rather than the trimethyl-homologues. These differences are consistent with *Exxon Valdez* crude oil that is somewhat less weathered (compare figs. 9a and 11).



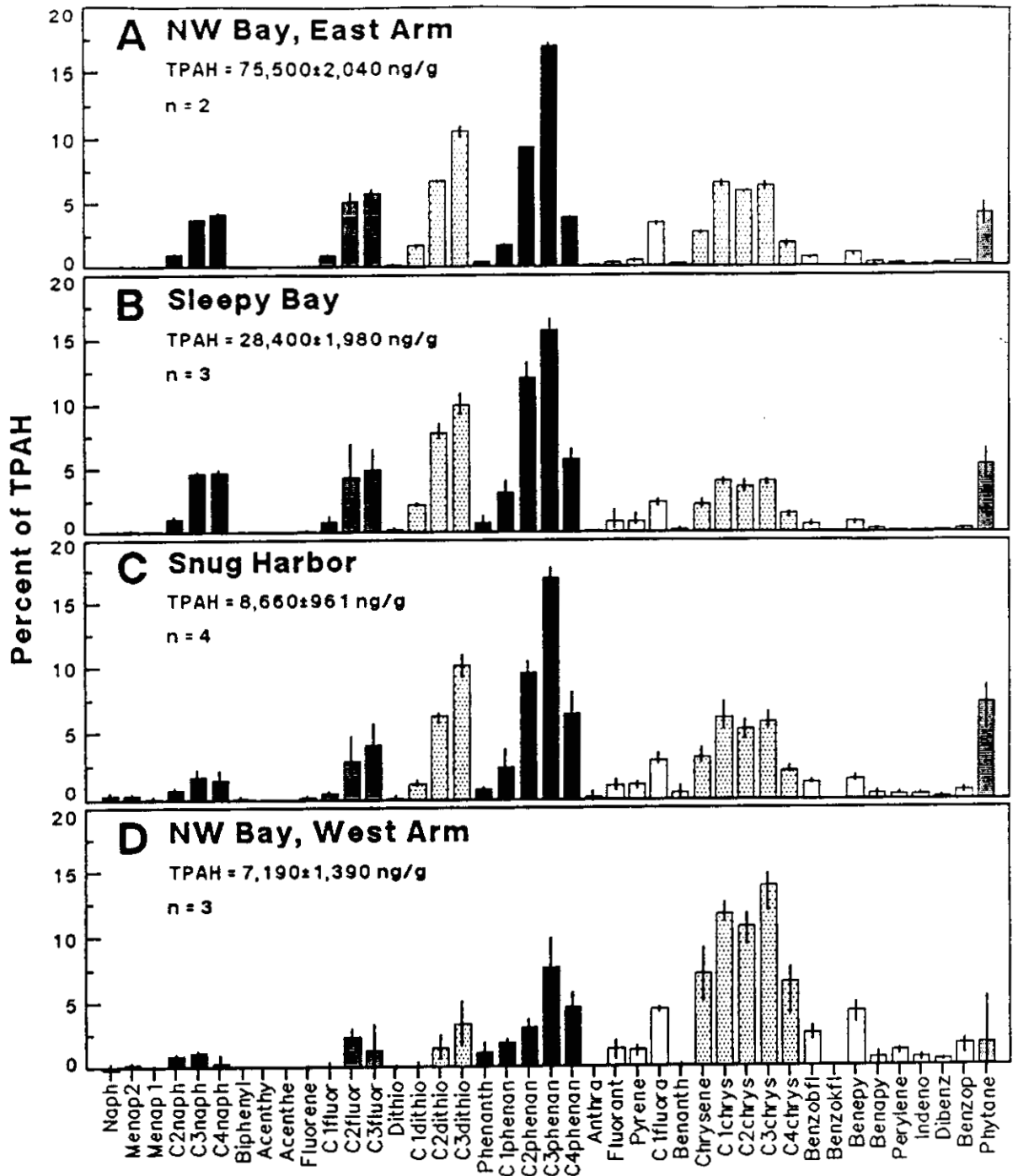


Fig. 8 (a - d). Relative abundance of PAH and phytane in sediments collected in 10 m depth traps deployed from November, 1989, to June, 1990, at stations adjacent to heavily oiled beaches. Heavy bars indicate the proportion of the total PAH due to the corresponding hydrocarbon indicated on the abscissa, and the associated vertical lines indicate the range of n replicated analyses. The mean total PAH concentration is also listed as ng PAH/g dry sediment weight.

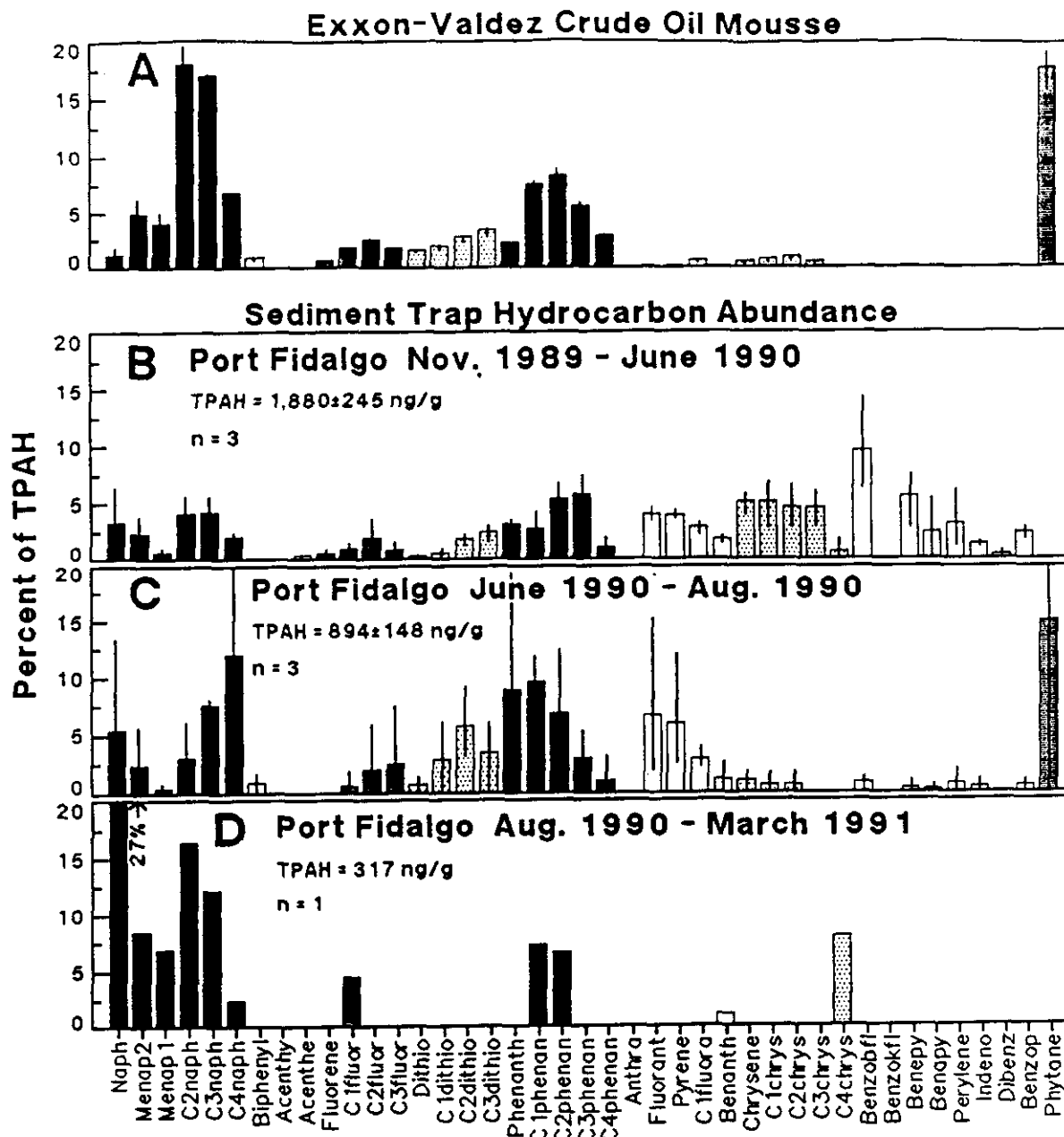


Fig. 9 (a - d). (a) Relative abundance of PAH and phytane in petroleum mousse collected near Snug Harbor, Bay of Isles, and Smith Island 11 days following the grounding of the T/V Exxon Valdez (PAH and phytane proportions from these 3 stations are composited for presentation in this figure); (b - d) relative abundance PAH and phytane in sediments collected in 10 m depth traps deployed from November, 1989, to June, 1990, at the Port Fidalgo control station. Heavy bars indicate the proportion of the total PAH due to the corresponding hydrocarbon indicated on the abscissa, and the associated vertical lines indicate the range of n replicated analyses. The mean total PAH concentration is also listed as ng PAH/g dry sediment weight in b - d.

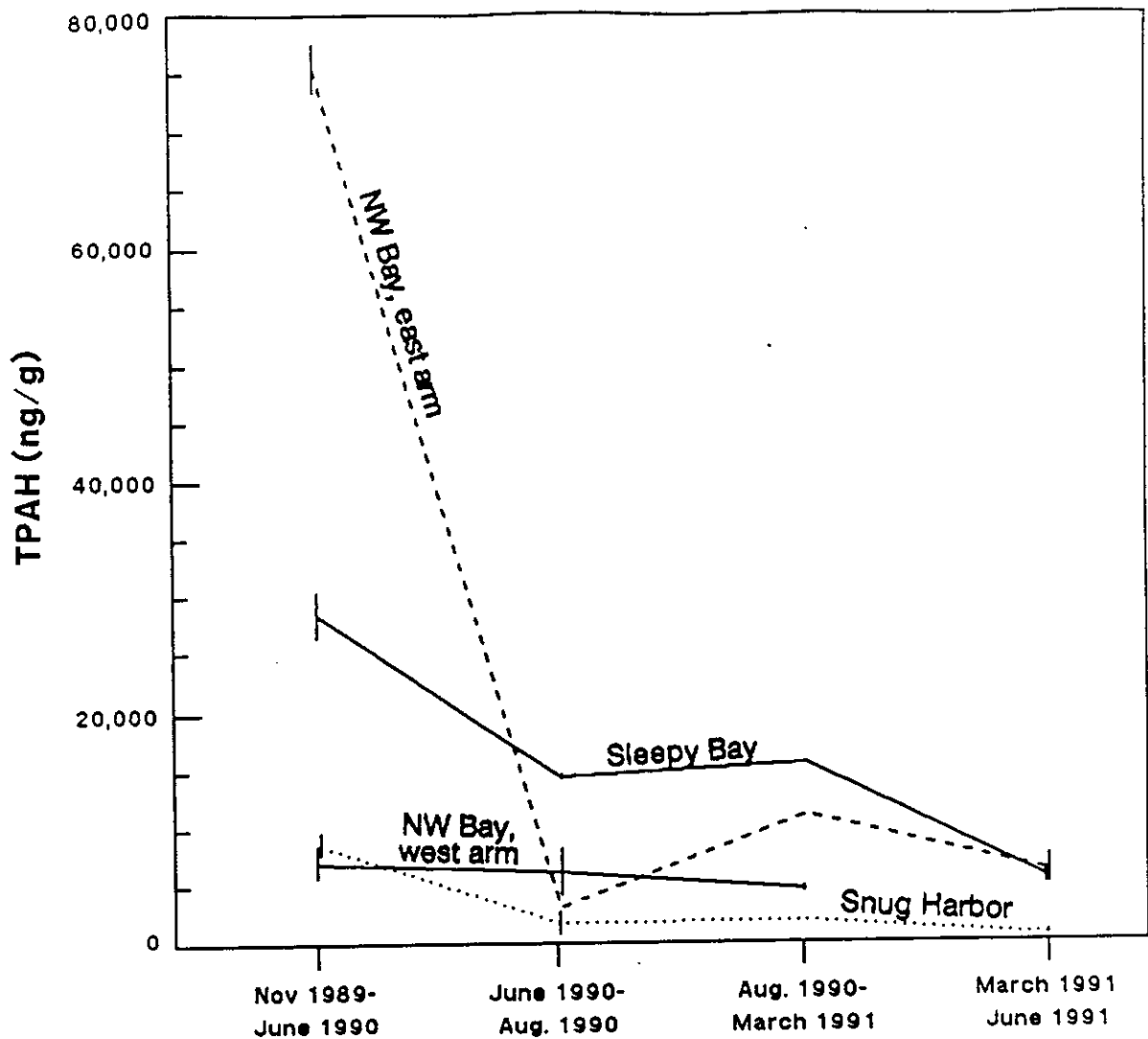


Fig 10. Concentrations of total PAH in sediment traps deployed during 4 sequential deployment intervals at stations adjacent to heavily oiled beaches following the Exxon Valdez oil spill of March 24, 1989, in Prince William Sound, Alaska. The deployment intervals were: (1) November 1989 to June 1990, (2) June 1990 to August 1990, (3) August 1990 to March 1991, and (4) March 1991 to June 1991. TPAH units are ng/g dry sediment weight.

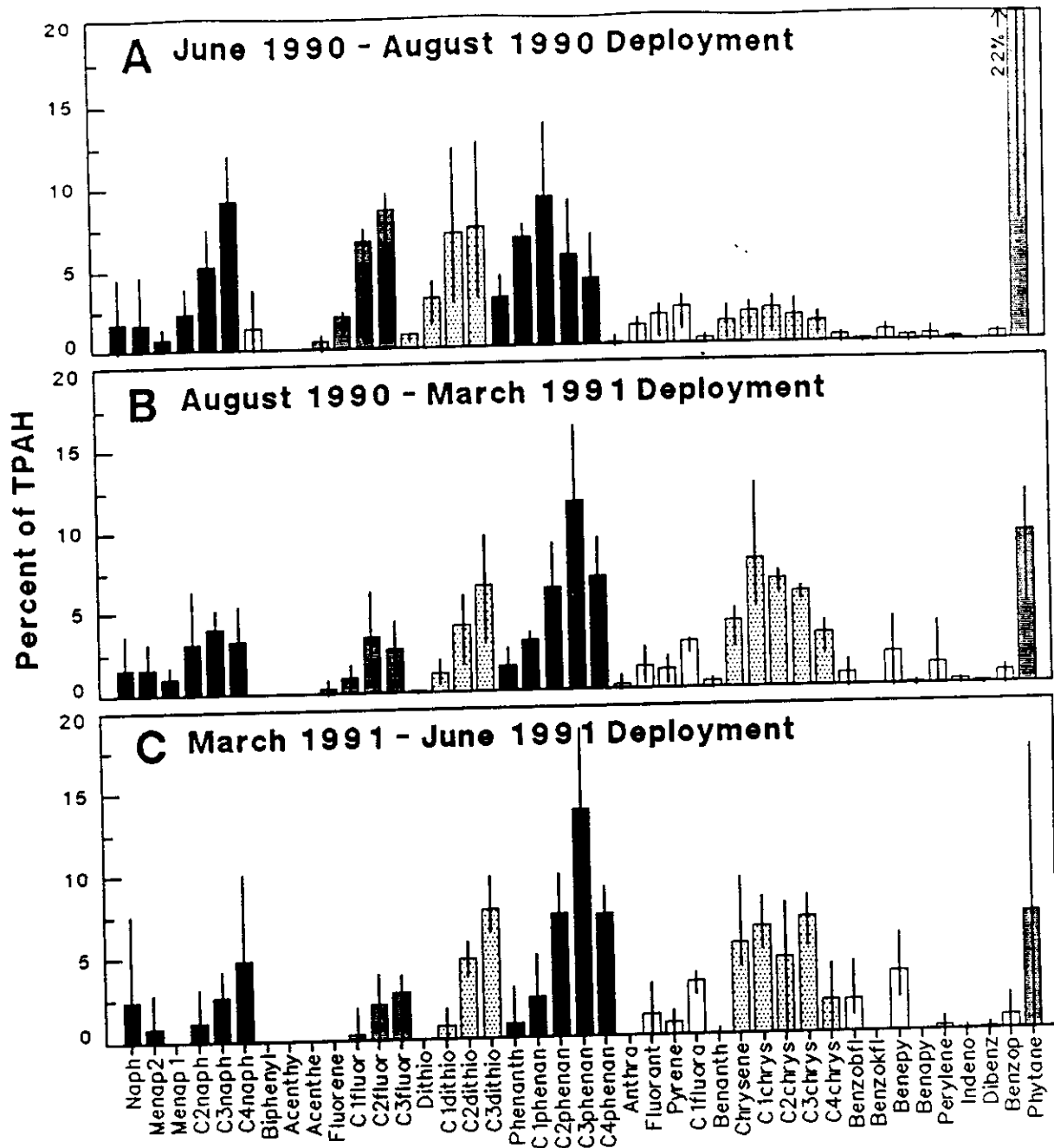


Fig. 11 (a - c). Range of relative PAH and phytane abundances in sediments collected in 10 m depth traps deployed at 4 stations adjacent to heavily oiled beaches from (a) June 1990 to August 1990; (b) August 1990 to March 1991; and (c) March 1991 to June 1991. These ranges comprise all sediment trap replicates for all 4 stations.

## Port Fidalgo Control Station

Compared with the initial deployment interval, PAH concentrations of sediments trapped at the Port Fidalgo control station were even lower during subsequent trap deployment intervals. The total PAH concentration in sediments trapped during the deployment intervals June 1990 to August 1990 and August 1990 to March 1991 were  $894 \pm 148$  ng/g ( $n = 3$ ) and 317 ng/g ( $n = 1$ ), respectively, and consisted primarily of naphthalenes, phenanthrenes and fluoranthene/pyrenes, or else just naphthalenes (fig. 9c,d). Also, phytane was detected sporadically in these sediments at concentrations near detection limits.

### *Seasonal Variation of Pristane, n-Pentadecane, and n-Heptadecane*

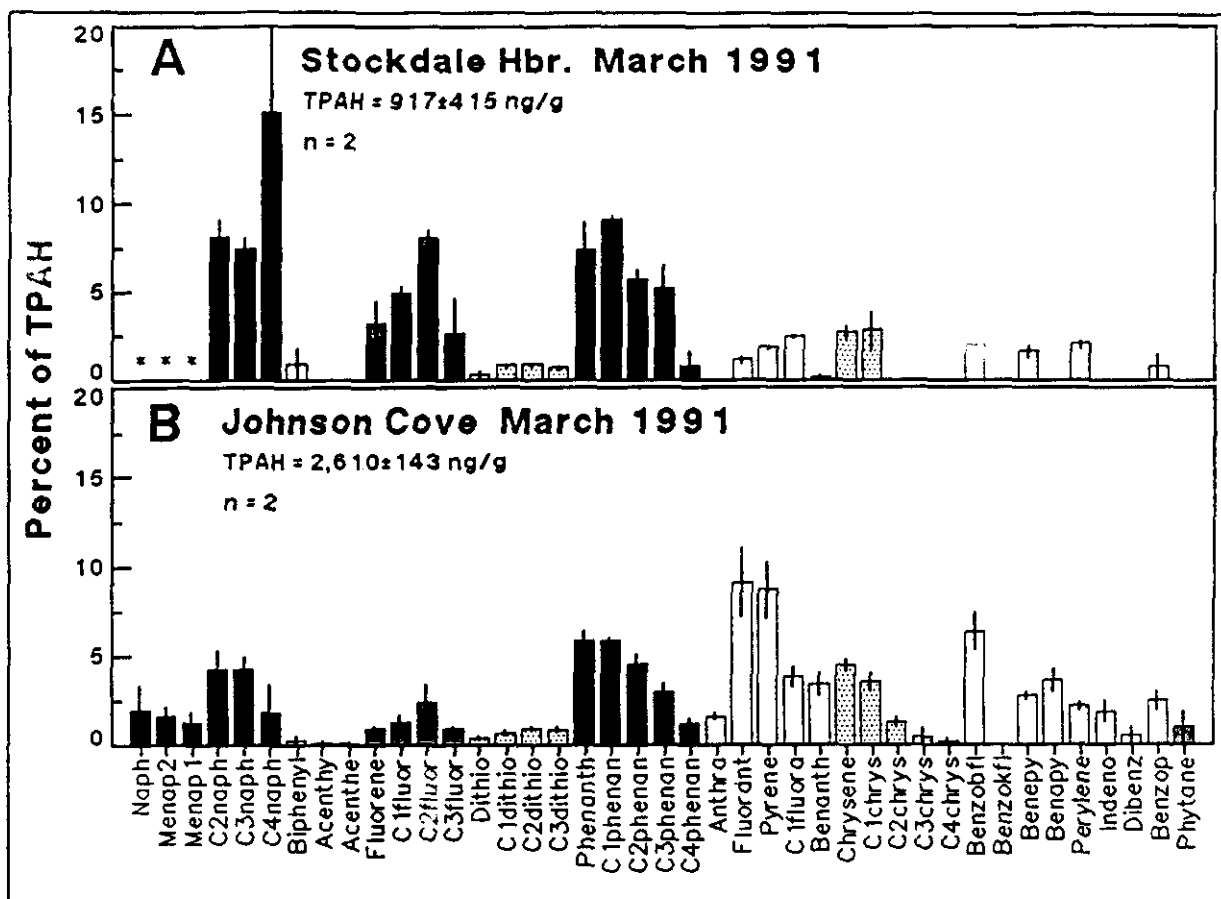
Concentrations of pristane increased dramatically in sediments that were trapped during deployment intervals that included the Spring season. With one exception, pristane concentrations consistently increased in the sediments of traps deployed during Spring, often by several orders of magnitude. The exception was at Northwest Bay-East arm, during the November 1989 to June 1990 deployment interval. Also, marked increases of n-pentadecane and n-heptadecane occurred in trap deployments that included late Summer.

### 3. Geographic Distribution - 10 m Seawater Deployment Depths

Sediment traps were deployed at 9 additional stations during the August 1990 to March 1991 deployment interval to determine the hydrocarbon content and composition of sediments trapped at additional stations, including additional stations that were not adjacent to heavily oiled beaches (7 of the 9 were subsequently found). Mean total PAH concentrations and patterns consistent with weathered *Exxon Valdez* crude oil were evident at Disk Island and less clearly at Chenega Island, where total PAH concentrations of  $3,500 \pm 873$  ng/g ( $n = 2$ ) and 1,140 ng/g ( $n = 1$ ) were measured. The Disk Island station is adjacent to a shoreline that was heavily oiled in 1989 and where oiling remained at least light through Spring 1992, whereas initial heavy oiling at the Chenega Island station was reduced to sporadic patches of light oiling within the first year (1989-90)(see Table 2).

PAH's in sediments trapped at Stockdale Harbor, a site east of the spill path, display an important alternative pattern of relative PAH abundance. The mean total PAH concentration in these sediments was at least  $917 \pm 415$  ng/g ( $n = 2$ ; the naphthalenes and methylnaphthalenes were not accurately measured due to unacceptable surrogate standard recoveries). The distribution of the relative PAH abundances indicate (1) dibenzothiophene homologue concentrations about one tenth those of corresponding phenanthrene homologue concentration, (2) substantial abundances of phenanthrene and chrysene, with monomethyl homologues of these the most abundant of each series, and abundances of more substituted homologues that decrease with degree of substitution,

and (3) relatively low abundances of 4- and 5-ring unsubstituted PAH's (fig. 12). This distribution of relative PAH abundances is not consistent with weathered *Exxon Valdez* crude oil. However, it is similar to a regional background of PAH's in Prince William Sound that is most clearly evident in the deeper basins of the Sound, and at shallower subtidal locations near Hinchinbrook Entrance (see Discussion below).



\* = Data excluded due to unacceptable surrogate recoveries

Figure 12 (a - b). Relative abundance of PAH in sediments collected in 10 m depth traps deployed from August 1990 to March 1991 at (a) Stockdale Harbor and at (b) Johnson Cove. Heavy bars indicate the proportion of the total PAH due to the corresponding hydrocarbon indicated on the abscissa, and the associated vertical lines indicate the range of n replicated analyses. TPAH units are ng/g dry sediment weight.

Sediments trapped at the Johnson Cove station during the August 1990 to March 1991 deployment interval contained elevated PAH concentrations with almost the same distribution as at Stockdale Harbor. The mean total PAH concentration was 2,610 ± 143 ng/g (n = 2), and although the unsubstituted 4- and 5- ring PAH's were relatively more abundant at Johnson Cove than at Stockdale Harbor, the PAH's were otherwise distributed similarly.

At 2 other stations, Eshamy Bay and Squire Island, mean total PAH concentrations were low (740 ng/g and  $334 \pm 23.7$  ng/g) and although the individual PAH's were detected less frequently, the overall distribution of PAH's was most similar to that at Stockdale Harbor.

During the March 1991 to June 1991 deployment interval, sediments trapped at Disk Island exhibited mean total PAH concentrations of  $1,400 \pm 192$  ng/g ( $n = 2$ ). These were substantially lower than those observed during the previous August 1990 to March 1991 deployment interval, and consisted primarily of naphthalenes and phenanthrenes (also, phytane was not detected in these sediments). Sediment traps deployed in the Bay of Isles in August 1990 were found in June 1991, and the total PAH concentration was  $2,130 \pm 750$  ng/g ( $n = 3$ ). The Bay of Isles station was adjacent to a beach that was heavily oiled, and the distribution of relative PAH abundances in the traps was consistent with weathered *Exxon Valdez* crude oil.

#### 4. Variation of PAH Concentration and Composition with Depth

Sediment traps were deployed at additional deployment depths during the March 1991 to June 1991 deployment interval to determine the variation of PAH concentrations in trapped sediments with trap deployment depth. At Northwest Bay-East arm and at Sleepy Bay, where total PAH's above 5,000 ng/g were found in sediments trapped at 10 m seawater depths, PAH and phytane concentrations in sediments trapped at 15 m or 20 m seawater depths were nearly identical with the 10 m depth results, and all were similar to weathered *Exxon Valdez* crude oil. However, at Bay of Isles, Disk Island, and Snug Harbor, where total PAH concentrations in sediments trapped at 10 m seawater depths were less than about 2,200 ng/g, the PAH concentrations of sediments trapped at deeper depths were as little as 28% those at corresponding 10 m depths. Also, the distribution of relative PAH abundances in sediments trapped at 10 m was similar to that of weathered *Exxon Valdez* crude oil at Bay of Isles and Snug Harbor stations, but the PAH's in sediments trapped at the deeper depths of these stations consisted primarily of naphthalenes or of naphthalenes and phenanthrenes.

#### 5. Combustion PAH Contamination of September 1991 and March 1992 Samples

Sediments trapped during the June 1991 to September 1991 and the September 1991 to March 1992 deployment intervals were apparently contaminated by PAH's characteristic of combustion sources. These sediments often contained high and variable concentrations of unsubstituted PAH's (see Tables II-2 and II-5, Appendix II), which we believe are derived from diesel exhaust that contaminated these samples during initial retrieval of the sediment traps. We have therefore excluded these samples from further consideration.

## B. Benthic surface sediments

Concentrations of individual PAH's in benthic surface sediments were often near or below detection limits, which usually precluded interpretation of relative PAH abundance patterns in these cases. Sediments with higher concentrations of total PAH's also contained greater numbers of PAH analytes measured above detection limits, and where comparisons were possible, these samples usually had patterns of relative PAH abundances very similar to those of trapped sediments at corresponding stations.

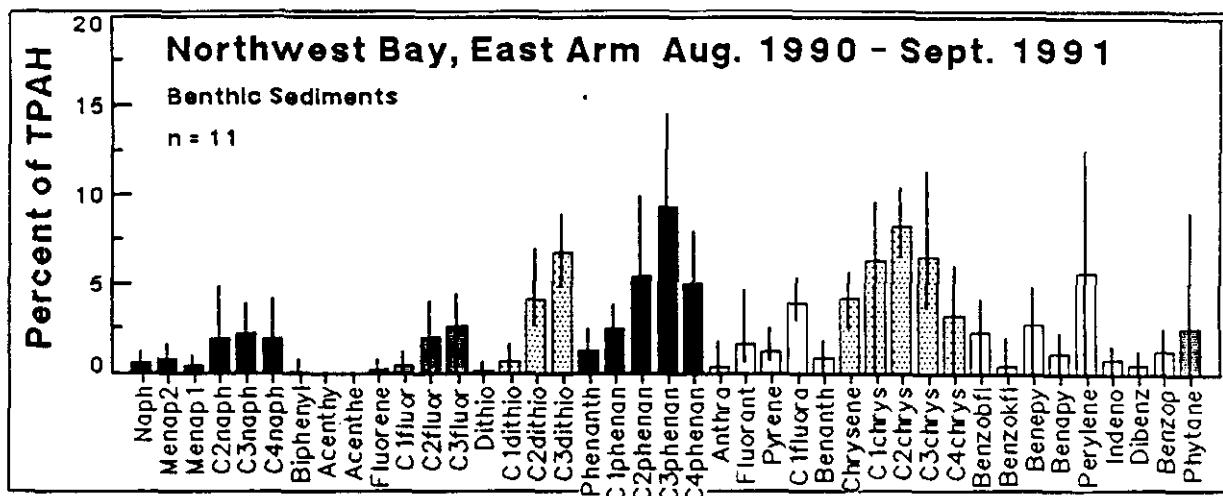


Fig. 13. Relative abundance of PAH and phytane in benthic surface sediments collected at Northwest bay-East arm at seawater depths ranging from 10 m to 20 m, from June 1990 through September 1991. Heavy bars indicate the proportion of the total PAH due to the corresponding hydrocarbon indicated on the abscissa, and the associated vertical lines indicate the range of the 11 analyses included in this composite presentation.

### *Northwest Bay-East arm*

Mean concentrations of total PAH's in benthic surface sediments were highest at Northwest Bay-East arm, and the PAH composition was similar to that of PAH's in trapped sediments there. Mean total PAH concentrations at 10 m seawater depth increased from at least 426 ng/g (n = 1) in June 1990, to 2,080 ng/g (n = 1) in June 1991, and were above 1,200 ng/g in September 1991 (Table II-3 and II-6, Appendix II here and following). Mean total PAH concentrations were generally similar on corresponding dates at 15 m and 20 m seawater depths, although at 20 m depth the concentration declined from over 1,890 ng/g (n = 1) in March 1991 to 295-351 ng/g in June-September 1991. The pattern of relative PAH abundances in the benthic sediments at this station was consistently similar to that observed in the trapped sediments there, and is similar to weathered *Exxon Valdez* crude oil (compare figs. 8a, 9a, & 13).



### *Bay of Isles, Northwest Bay-West arm, and Disk Island*

Concentrations of total PAH's consistent with weathered Exxon Valdez crude oil were lower and less clearly evident in benthic surface sediments at Bay of Isles, Northwest Bay-West arm, and Disk Island (see Table II-3, Appendix II). At Bay of Isles, mean total PAH concentrations of benthic sediments ranged from 39.9 ng/g ( $n = 1$ ) to  $269 \pm 144$  ng/g ( $n = 4$ ) at 10 m seawater depths, and ranged from 403 ng/g to 429 ng/g at 20 m seawater depths; also, the pattern of relative PAH abundances of the higher-concentration samples is similar to that of weathered *Exxon Valdez* crude oil. While the 10 m benthic sediments at Bay of Isles show a decrease in mean total PAH from August 1990 to June 1991, an increase is apparent from June 1991 to September 1991, coinciding with a period of excavation when a very oily trench was opened on the adjacent shoreline (the same pattern is evident at Disk Island, coinciding with excavation there). The pattern of relative PAH abundances is also apparent at Northwest Bay-West arm, although the mean total PAH concentration observed in benthic sediments there was low,  $223 \pm 66.7$  ng/g ( $n = 4$ ). At Disk Island, mean total PAH concentrations at all depths were consistently less than 100 ng/g except for one observation of 931 ng/g at 20 m seawater depth in September 1991. The pattern of relative PAH abundances in the anomalously high sample is similar to that of weathered *Exxon Valdez* crude oil, but in the remaining samples the concentrations of individual PAH's were too frequently below detection limits to discern PAH distribution patterns.

### *Johnson Cove, Stockdale Harbor, and Sleepy Bay*

The mean total PAH concentration measured in Johnson Cove benthic sediments was  $483 \pm 102$  ng/g ( $n = 3$ ), and the pattern of relative PAH abundances was similar to the sediments trapped there. Likewise at Stockdale Harbor, where benthic sediment PAH concentrations were measured at  $245 \pm 21.8$  ng/g ( $n = 3$ ) and 302 ng/g ( $n = 1$ ). At Sleepy Bay, mean total PAH concentrations ranged from  $58.3 \pm 26.4$  ng/g ( $n = 4$ ) to 357 ng/g ( $n = 1$ ), and the higher-concentration samples had patterns of relative PAH abundances that were either similar to that at Stockdale Harbor, or else to Northwest Bay.

### *Other Stations*

Concentrations of total PAH's at the remaining stations sampled for benthic surface sediments were too low to discern PAH distribution patterns. At the Port Fidalgo control station, most PAH's were below detection limits, and mean total PAH concentrations were consistently less than 25 ng/g. Similarly, at Chenega Island, Eshamy Bay, Green Island, Herring Bay, Naked Island, and Snug Harbor, individual PAH's were frequently below detection limits, and mean total PAH concentrations were less than 125 ng/g (Table II-3, Appendix II). At Olsen Bay, a single observation in September 1991 contained 267 ng/g total PAH's.

### *Seasonal Variation of Pristane in Benthic Surface Sediments*

As in trapped sediments, pristane concentrations increased markedly in benthic surface sediments collected in the Spring. Spring concentrations of pristane were usually lower by a factor of about 100 in the benthic surface sediment samples compared with concentrations in corresponding trapped sediments except at Sleepy Bay, where the factor was closer to 1,000.

#### C. Benthic Sediment Core Samples

Concentrations of individual PAH's in benthic sediment core samples were usually near or below detection limits. Sediment core samples that contained the higher concentrations of total PAH's also contained greater numbers of PAH analytes measured above detection limits, and where comparisons were possible, the uppermost segment of cores usually had patterns of relative PAH abundances very similar to those of corresponding benthic surface sediments. However, the only PAH abundance pattern evident in the deeper segments of the cores was that typified by sediments trapped at Stockdale Harbor.

#### *Northwest Bay-East arm and Bay of Isles*

In the uppermost segments of benthic sediment cores from Northwest Bay-East arm and Bay of Isles, the relative PAH abundance patterns resembled that of weathered *Exxon Valdez* crude oil. In the 1 - 4 cm sediment depth segments of cores collected from 10 and 20 m seawater depths at Northwest Bay-East arm, concentrations of total PAH's were 500 and at least 218 ng/g, respectively, and the pattern of relative PAH abundance is similar to that of the benthic surface sediments there (Tables II-4 and II-7, Appendix II here and following). The same pattern is also evident in 0 - 5 cm core segments from Bay of Isles, where total PAH concentrations ranged from 379 ng/g to 475 ng/g.

In the lower segments of benthic sediment cores from Northwest Bay-East arm and Bay of Isles, when enough PAH's were measured above detection limits, the PAH distribution patterns resembled those of sediments trapped at Stockdale Harbor. PAH's in the lower segments of cores collected from the 10 m seawater depth at Northwest Bay-East arm decreased with segment depth to a total PAH concentration of 86.5 ng/g in the 9.5 - 12 cm segment. In contrast, total PAH concentrations ranged from 145 ng/g to 223 ng/g in core segments from 4 to 12 cm in the 20 m seawater depth core at this station, and the pattern of relative PAH abundance resembled the Stockdale Harbor pattern. In the lower segments of cores from Bay of Isles, PAH concentrations ranged from 190 ng/g to 473 ng/g, and distribution patterns also resembled the Stockdale Harbor pattern.

### *Sleepy Bay*

At Sleepy Bay, the highest total PAH concentrations were measured in the uppermost segments of cores collected at seawater depths of 10 m and 15 m, and the pattern of relative PAH abundance in these segments resembled the Stockdale Harbor pattern, but with enhanced abundances of 4- and 5- ring unsubstituted PAH's. Total PAH concentrations were 292 ng/g to 429 ng/g at 10 m and 15 m seawater depths. PAH concentrations were markedly lower in the deeper core segments at these seawater depths. However, results for the 20 m seawater depth cores were not consistent with those for the 10 m and 15 m cores. At 20 m seawater depth, total PAH's increased with core depth from 123 ng/g in the 1 - 3 cm segment to 280 ng/g in the 3 - 8 cm segment, and in both segments the pattern of relative PAH abundance was unique.

### *Other Stations*

With one exception, total PAH concentrations at the remaining stations were less than about 150 ng/g, and consequently too low to discern patterns of relative PAH abundances. The exception is in the 5 - 8 cm segment of a core collected at 15 m seawater depth at Snug Harbor, where the total PAH concentration was 223 ng/g, and the PAH distribution most closely resembled that of *Exxon Valdez* crude oil.

### *Seasonal Variation of Pristane*

The seasonal variation of pristane in benthic surface sediments and in benthic sediment core samples is similar. When detected in benthic sediment cores, pristane concentrations were consistently highest in samples collected in Spring, and always decreased with sediment core depth.

## II. Sedimentological Results

### A. Suspended and Benthic Sediment Grain Size

The sediment traps were designed to capture particulates falling out of suspension and to exclude resuspended benthic sediments. This was accomplished by having the opening of the traps 1.2 m above the bottom. The presence of numerous benthic foraminifera and echinoderm spines in the core samples, but only a few benthic foraminifera and no echinoderm spines in the trap samples, indicates that at least very fine-grained sand and coarser material was generally not resuspended and deposited in the traps. Mud-sized grains, however, probably were captured by the traps as resuspended material. The proportion of resuspended sediments to total sediments captured cannot be determined.

Figure 14 displays the mean-grain size of sediments captured in the traps. All samples had a mean-grain size of fine sand or finer, although there is some variability among sites and through time. The high-energy site at Snug Harbor had the coarsest sediments

falling out of suspension and ranged from fine sand to medium silt. Traps set in Herring Bay in the summer and winter, eastern Northwest Bay in the winter at 20 m depth, and Disk Island in the summer at 10 m depth captured particularly fine sediments. Only the site in eastern Northwest Bay appeared to have a systematic trend in mean-grain size with depth. Here the sediments from 20 m were consistently finer-grained than sediments from 10 m.

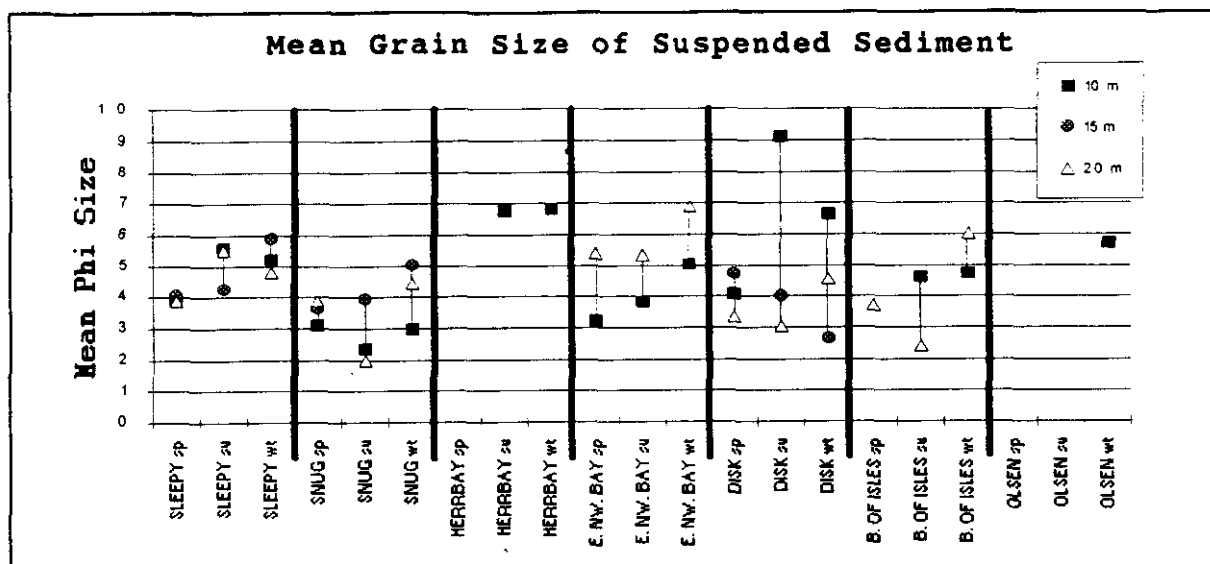


Fig. 14. Mean grain size of suspended sediment in Phi units by location and season: sp= spring deployment from March, 1991 to June, 1991; su= summer deployment from June, 1991 to September, 1991; wt= winter deployment from September 1991 to March, 1992. Phi is the negative base 2 logarithm of the sediment size in millimeters ( $-\log_2(\text{size, in mm})$ ). Larger Phi values indicate finer-grained sediments.

At Sleepy Bay, Snug Harbor, eastern Northwest Bay, and the Bay of Isles sediments collected over the spring of 1991 were generally coarser-grained than sediments collected over the winter of 1991/92. At the Disk Island site this is also the case for sediments from 10 and 20 m depth but not from 15 m depth. A qualitative inspection of the trapped sediments indicates that this temporal pattern is caused by the relative abundance of diatoms in spring sediments compared to winter sediments. Diatom tests are discoidal in shape and are the size of coarse silt to very fine sand.

The relative amount of clay-sized grains in suspended sediments is shown in figure 15. Clay content ranged from 0% over the summer in the Bay of Isles at 20 m depth to over 60% collected during the summer at Disk Island at 10 m depth. The only clear pattern among stations is that Snug Harbor, a high-energy site, consistently had low clay amounts of less than 15%, and, even though the data are sparse, it appears that suspended sediments at the Herring Bay station contain a relatively large amount of clay. The deep, 20 m trap at Northwest Bay consistently collected more clay-sized grains than the shallower 10 m trap, but at Disk Island the opposite was true. The other stations showed

no depth-related patterns. Clay-sized sediment content is higher during the winter than during the spring and follows the pattern expected from the mean grain size parameter described above.

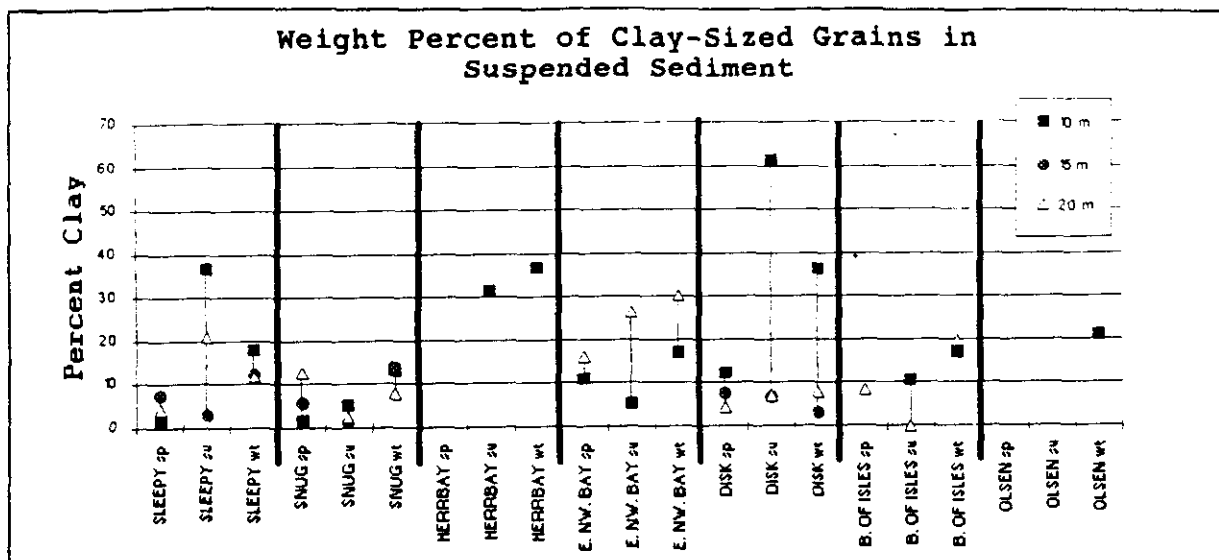


Fig. 15. Weight percent of clay-sized grains in suspended sediment by location and season: sp = spring deployment from March, 1991 to June, 1991; su = summer deployment from June, 1991 to September, 1991; wt = winter deployment from September 1991 to March, 1992.

The mean-grain size for bottom sediments taken adjacent to the traps in March and April, 1991 and 1992 ranged from pebble- to silt-sized (Table 3). Figure 16 displays mean grain size data. There is no indication of a temporal shift in mean grain size at Sleepy Bay, Snug Harbor or Disk Island, but sediments in the east arm of NW Bay became finer grained. The higher energy sites at Sleepy Bay and Snug Harbor tend to have finer sediments than those at the relatively lower energy sites of eastern NW Bay and the Bay of Isles. Sleepy Bay shows a trend of decreasing grain size from shallow to deeper water, but Northwest Bay, Disk Island, and the Bay of Isles show the opposite trend. Snug Harbor shows no trend either way.

Table 3 compares suspended sediments collected over the winter of 1991/92 with benthic sediments collected at the end of the winter. In every case, benthic sediments are coarser grained than suspended sediments, usually by more than one phi unit. All areas except Snug Harbor have significant amounts of gravel material on the bottom (10% or more). Benthic sediments at Bay of Isles, Disk Island, east arm of Northwest Bay, and Olsen Bay are very poorly sorted to extremely poorly sorted, whereas sediments from the relatively high-energy locations of Sleepy Bay and Snug Harbor are significantly better sorted (moderately well-sorted to poorly sorted). Gravel content is less at the better sorted, high-energy sites. Suspended sediments are also significantly better sorted at the two high-energy sites, but the suspended sediments are significantly less sorted than the

benthic sediments there. At the lower energy sites, suspended sediments are very poorly to extremely poorly sorted, the same as the benthic sediments.

Table 3. Mean grain size and sorting comparisons of benthic and suspended sediments. Larger phi values for mean grain size indicate finer-grained sediment, whereas smaller phi values indicate coarser grained sediment. High sorting values indicate a large range in grain size, and these sediments are considered poorly sorted.

Location	Depth (m)	Mean grain size (Phi)		Sorting (Phi)	
		Benthic	Suspended	Benthic	Suspended
Bay of Isles, Site 1	10	0.63	4.73	3.30	3.53
Disk Island, Site 2	20	-0.48	4.56	2.90	2.22
Disk Island, Site 2	15	0.47	2.67	3.81	2.65
Disk Island, Site 2	10	0.97	6.60	0.89	4.35
east NW Bay, Site 3	20	0.87	6.90	4.48	4.69
east NW Bay, Site 3	10	4.47	5.04	3.37	2.86
Olsen Bay, Site 8	10	5.15	5.70	3.97	2.91
Sleepy Bay, Site 10	20	3.19	4.82	0.64	1.33
Sleepy Bay, Site 10	15	3.27	5.87	0.96	1.93
Sleepy Bay, Site 10	10	2.08	5.20	1.44	2.53
Snug Harbor, Site 11	20	3.43	4.46	0.57	2.05
Snug Harbor, Site 11	15	3.28	5.02	0.63	1.92

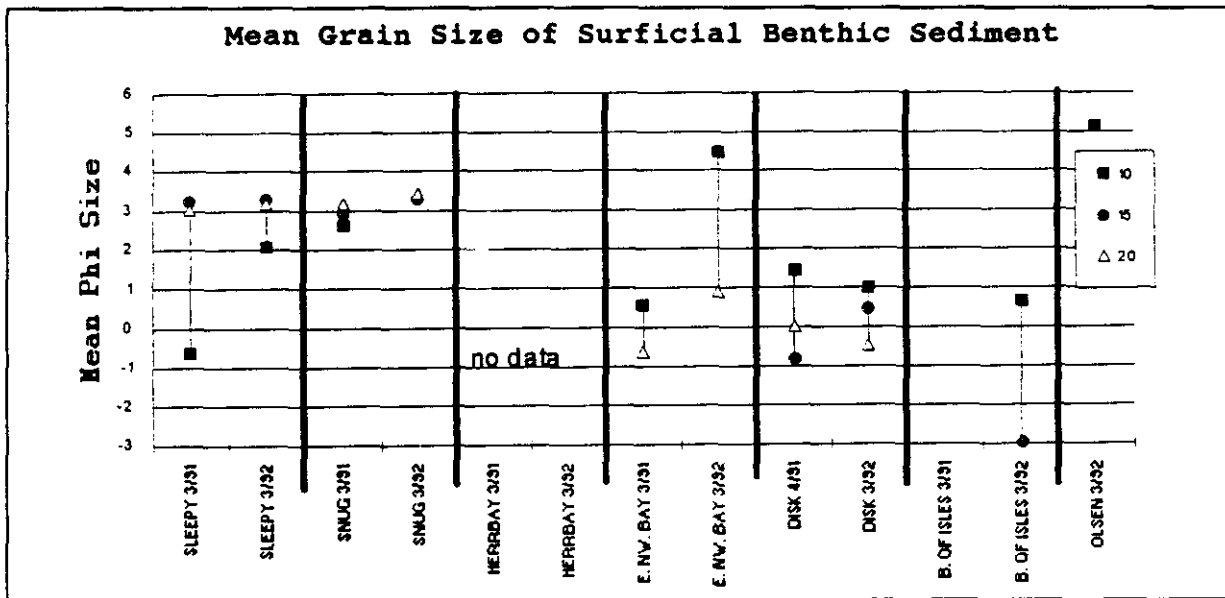


Fig. 16. Mean grain size of surficial bottom (benthic) sediment in Phi units by location and season: sp= spring deployment from March, 1991 to June, 1991; su= summer deployment from June, 1991 to September, 1991; wt= winter deployment from September 1991 to March, 1992. Sediments were taken from 0 to 2 cm of the sediment column.

## B. Organic carbon content of suspended sediments

Percent of organic carbon by weight in suspended sediments ranged from 2.5% to 9% for the spring and winter sediments (fig. 17). Northwest Bay tended to have the greatest amount of carbon; Snug Harbor and Sleepy Bay during the winter had the least. The data are sparse, but there is an indication that for the 20 m samples, organic carbon decreased by about 2% during the winter compared to the spring. There are no other temporal or spatial patterns apparent in the data.

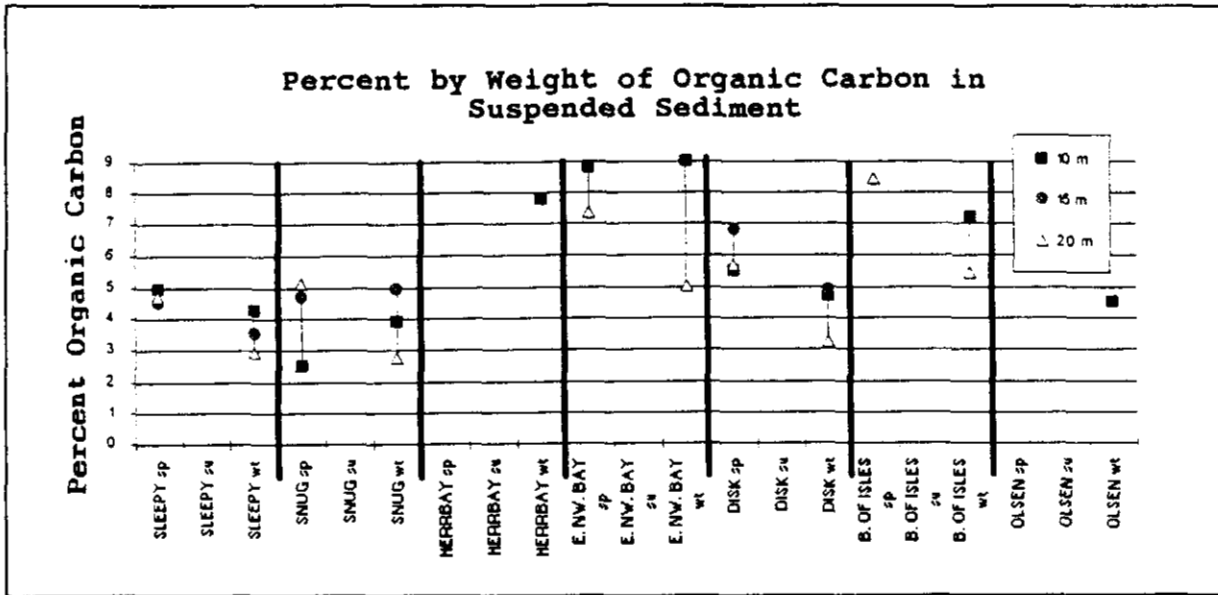


Fig. 17. Percent by weight of organic carbon in suspended sediment by location and season: sp= spring deployment from March, 1991 to June, 1991; su= summer deployment from June, 1991 to September, 1991; wt= winter deployment from September 1991 to March, 1992.

## C. Clay mineral content of suspended sediments.

The relative amounts of two clay minerals were determined for the suspended sediments. The abundance ratio of chlorite to illite is shown in figure 18 and table 4. This ratio ranged from 0.64 measured at the 10 m depth in Olsen Bay over the winter of 1991/92 to 1.56 measured at the 10 m depth in Sleepy Bay over the spring of 1991. Most of the samples fell between 0.8 and 1.3 with no spatial or temporal patterns. Most of the samples had ratios greater than one, and every site, except Olsen Bay, had at least one sample greater than one.

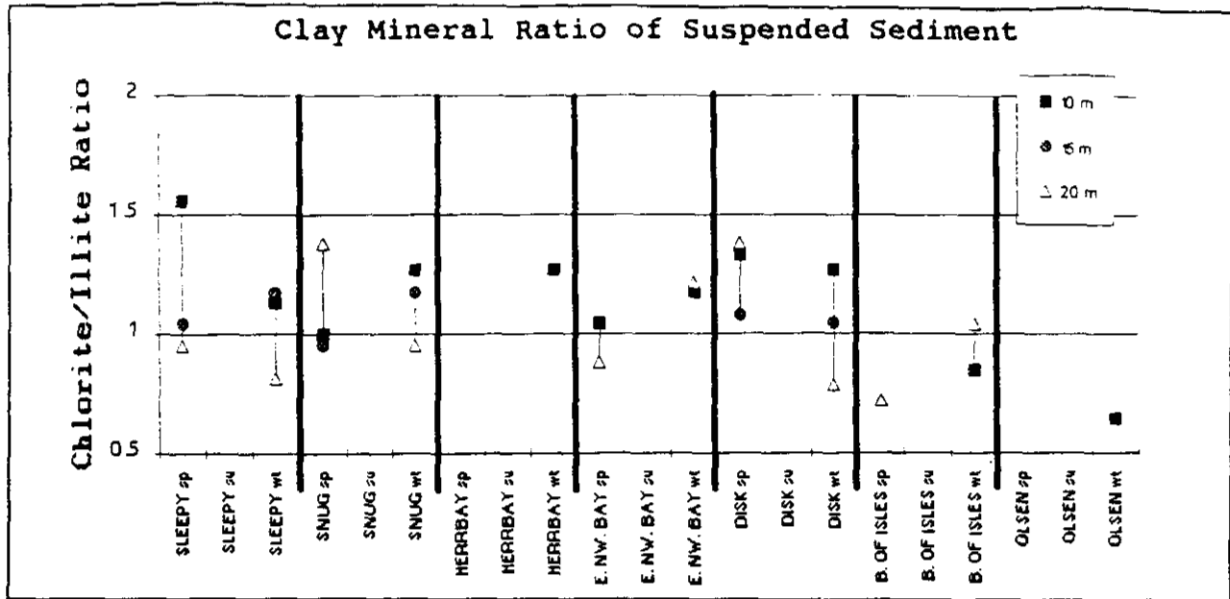


Fig. 18. Chlorite to illite clay mineral abundance ratio of suspended sediments by location and season: sp = spring deployment from March, 1991 to June, 1991; su = summer deployment from June, 1991 to September, 1991; wt = winter deployment from September 1991 to March, 1992. Dominant chlorite content indicates that clay sediments are predominantly derived from adjacent shorelines and not from outside of Prince William Sound.

#### D. Core Stratigraphy

Following is a summary of the stratigraphy for the 7 study sites where short sediment cores were obtained. Detailed core logs, photographs, x-radiographs, and sediment analyses are presented in Gibeaut (1993), and summarized in Sale and Gibeaut (1995).

##### *Sleepy Bay*

Three cores from Sleepy Bay at 10, 15, and 20 m depths are 135, 85, and 150 mm long, respectively. Sediments retrieved in the cores are poorly to very poorly sorted gravelly and slightly gravelly muddy sands. In the 10 m core, the sand fraction is fine-grained and makes up 63 to 72 percent of the sediment whereas in the 15 and 20 m cores, the sand fraction is very fine-grained and makes up 78 to 86 percent of the sediment. The 10 m core contains about 6 percent mud compared to the 12 percent in the deeper cores. Gravel content is higher in the 10 m core at about 25 percent compared to less than 10 percent in the 15 and 20 m cores. The above relationships indicate a subtle fining of sediment in the offshore direction with a jump in fining between 10 and 15 m water depths. The fining is due to an increase in mud, a decrease in gravel, and a fining in the sand range. Even at the 20 m depth, however, pebble-sized rocks up to 50 mm in diameter, whole shells, and shell fragments are present.



Sediments in all the cores are dominantly darkly colored rock fragments with a few percent of shell material. All three cores contain a small amount of organic debris. In the 20 m core, organic debris, which includes wood fragments, is concentrated in a subsurface layer associated with granule and very coarse sand sized shell fragments. Also in the 20 m core is an articulated bivalve. Worm tubes are present in the 10 and 15 m cores.

Crude bedding is present and consists of interbedded gravelly sand and silty sand and shelly, gravelly sand. This interbedding is best developed in the 10 m core where four distinct layers are apparent. In all the cores, the surface layers are relatively fine-grained. Bottom photographs and diver observations at Sleepy Bay reveal sparse macro brown algae (*Hedophyllum sp.*, *Agarum sp.*, *Laminaria sp.*) at 10 and 15 m depths, less at 20 m. A sediment mound probably caused by a burrowing polychaete worm is present in the bottom photograph from 20 m as well as a single *Pycnopodia Helianthoides*. All the photographs display what appears to be organic debris on the sediment surface (Sale and Gibeaut, 1995).

These cores are interpreted to be from an area where sediment erosion and deposition occurs quite often and where combined wave and tide induced currents reach velocities of at least 50 cm/s. The presence of barnacle fragments in the 10 and 15 m cores indicates sediment transport from the adjacent shoreline.

#### *Disk Island*

A 125 mm core from 10 m, a 130 mm core from 15 m, and a 100 mm core from 20 m water depths were obtained from the Disk Island location. All the cores are over 90 percent sand with only 0 to 2 percent gravel and about 5 percent mud. Sediments fine in an offshore direction, particularly when only the sand fraction is considered. Sediments go from medium and coarse sand at 10 m to fine sand at 15 m to fine and very fine sand at 20 m water depth. Shell content is slightly higher at 10 m where a granule-sized fraction of shell fragments makes up a few percent of the sediment. One pebble is present in the 20 m core. Overall, the sediments are dominantly rock fragments with a few percent of shell fragments and small amounts of organic debris including sea grass blades in the 20 m core.

Some structures are apparent in the cores. The 10 m core is normally graded and some obscure cross-stratification is present. The 15 m core also contains what appears to be cross-stratification, and the 20 m core is normally graded. All cores show isolated traces of burrowing and rooting.

Bottom photographs and diver observations at Disk Island recorded scattered cobbles and large and small shell fragments at all depths but a greater abundance of large shells at the deeper depths. At 15 and 20 meter depths, macro brown algae (of same genera as

noted at Sleepy Bay) covered three to ten percent of the bottom. At 10 meters, however, the bottom was devoid of vegetation (Sale and Gibeaut, 1995).

Grain size, sedimentary structures, and bottom photographs suggest that the sediments retrieved in these cores are from a relatively energetic environment with current velocities well above 20 cm/s. The 10 meter depth is significantly more energetic than the deeper depths as evidenced by coarser grain size, graded and stratified deposits, and lack of vegetation in the soft sediments.

### *Snug Harbor*

Three cores were obtained from Snug Harbor. Cores from 10 m and 15 m water depths are 120 mm long, and a core from 20 m depth is 135 mm long. Sediments are poorly to moderately sorted and consist of dark colored platy rock fragments with scattered shells. Sediments are 75 to 97 percent fine to very fine sand, with the remaining fraction being mostly silt. Sediments become finer grained from 10 to 15 m depth but are very similar between 15 and 20 m depths. Offshore fining is due to a decrease in the size of the sand-sized fraction from fine to very fine sand and an increase in the amount of mud from 3 to 15 percent.

Layering is evident in the cores. The 10 m core has an upper section of fine sand with scattered whole and fragmented shells including an articulated bivalve and an echinoderm piece with spines intact. This upper unit has only a few percent mud but overlies a silty sand with about 15 percent mud. This silty sand in the bottom of the 10 m core corresponds to the silty sand found throughout the 15 and 20 m cores. The 15 and 20 m cores have more organic debris than the 10 m core and have distinct organic debris layers including wood fragments, spruce needles, and sea grass blades in the middles of the cores. Both the 15 and 20 m cores have articulated bivalves with one in situ bivalve in the 20 m core. Also found in the deeper cores are agglutinated worm tubes. Distinct burrows are apparent in all the cores.

Bottom photographs and diver observations at Snug Harbor reveal the bottom at all three depths to contain sediment mounds created by burrowing organisms, probably polychaete worms. An extensive eelgrass bed (*Zostera marina*) is found along the transect at approximately 3 meters depth, and very sparse clumps are growing at the 15 and 20 m depths. Five *Pycnopodia helianthoides* appear on the sediment traps in the photograph from the 10 m depth. A diatom mat and/or organic debris layer on the sediment surface is apparent in all the photographs, though less so in the 20 m photograph (Sale and Gibeaut, 1995). The diatom mat adds moderate cohesion to the benthic surface sediments.

Cores and observations from Snug Harbor reveal that sediments at depths of 10 to 30 m are probably deposited during relatively high-energy events and that conditions between events are moderate to low energy. During periods between storms or extreme tidal

current events, organic debris may settle on the surface and burrowing activity may proceed to depths of at least 100 mm. Currents, however, remain sufficiently competent to prevent the accumulation of significant amounts of mud settling from suspension. Energy levels remain significantly higher at the 10 m depth than the deeper depths. It is hypothesized that during storms, sand is moved from shallower to deeper depths and covers and incorporates the organic debris layer and diatom mat deposited during low-energy conditions.

#### *Northwest Bay, East Arm*

Two cores were obtained from the east arm of Northwest Bay. A core from 10 m depth measured 130 mm long and a core from 20 m depth measured 120 mm in length. The sediments in these cores are muddy, sandy, gravel. Both cores contain about 50 percent medium-grained sand, 30 percent pebble gravel, and 20 percent mud with slightly more silt than clay. The gravel fraction consists of shell fragments and rock pebbles. Most pebbles are subangular and platy in shape and some were rotated in the cores during the coring process. The sand fraction is also shelly with shell fragments coarser than other sand grains. Organic debris makes up a few percent by weight of the sediments. Overall, there is no textural difference between the two cores.

A number of discernable layers are apparent in the cores. Layers with relatively large amounts of organic debris are interbedded with layers of shell hash and layers with large flat pebbles. In the 10 meter core, a bottom layer with much organic material is overlain by shell hash with obscure stratification. This shell hash layer is overlain by large flat pebbles. The large flat pebbles reside about 10 mm below the surface and are overlain by a relatively fine-grained surface layer with abundant organic debris including spruce needles. The 20 meter core has a distinct shell hash layer with abundant organic debris and sharp upper and lower contacts. The surface layer in the 20 m core is an organic-rich shell hash.

The 20 m core contains a bivalve in life position a few millimeters below the surface, and an articulated bivalve shell is apparent in the X-radiograph of the 10 m core. Whole gastropod shells are also present in the cores. Other than the presence of these shells, however, there is no evidence for bioturbation; physical sedimentary processes apparently overcome any effects left by organisms.

Diver observations note the bottom topography of Northwest Bay east arm to be highly variable, with benches and pockets of accumulated sediments interspersed among bedrock outcrops. Bottom photographs taken by divers reveal the bottom at 10 m depth to be muddy and sparsely covered by macro brown algae similar to that found at Sleepy Bay. At 20 m depth no vegetation is present and cobbles and shell fragments form an apparent lag deposit on the surface. The photographs confirm the textural differences observed in the surface layers of the cores and demonstrate varying sedimentological

processes between 10 and 20 m depths for some time prior to the photographs in March, 1992 (Sale and Gibeaut, 1995).

It is difficult to determine the nature of sedimentation in this bay from just the two cores and bottom photographs. It is apparent, however, that coarse-grained sediments are transported during relatively high-energy events and that relatively fine-grained organic-rich sedimentation occurs during low energy times. Varying tidal current velocities with depth may cause the lag deposit at 20 m depth and allow finer grained organic-rich sedimentation at 10 m depth. Wave energy is likely higher at 10 m depth than at 20 m, and thus alone would not create the observed conditions.

### *Bay of Isles*

Two cores were obtained from the Bay of Isles. A core from 10 m depth measured 105 mm in length and a core from 20 m depth measured 70 mm in length. The shallow core is a gravelly mud and contains more than 50 percent mud with silt and clay occurring in equal portions. The gravel content is less than 10 percent and includes pebble-sized shell fragments and platy rocks as well as granule-sized shell fragments. The sand fraction in the 10 m core is medium- to fine-grained sand and makes up about 30 percent of the core. The 20 m core is coarser-grained than the 10 m core and is classified as a muddy, sandy, gravel with about 30 percent gravel sized material in the form of platy, elongate rock pebbles and shell fragments. This deeper core contains only 15 percent mud and 56 percent medium-grained sand. All sediments retrieved in the cores are poorly to very poorly sorted and contain over 5 percent of organic debris, which is a large amount compared to the other cores studied.

Three layers are readily apparent in the photograph and x-radiograph of the 10 m core. A slightly gravelly mud layer containing articulated bivalves and very fragile pellets is sandwiched between layers of gravelly mud. The upper layer has a very distinct lower contact that is probably erosional. The upper layer contains over 10 percent organic debris including spruce needles concentrated in the bottom of the unit. Large shells in the top unit tend to be horizontal, and this unit also contains abundant small gastropods (periwinkles). The lower gravelly mud has a slight fining upward trend apparent in the gravel fraction.

The 20 m core contains four layers, but they are not as well defined as in the 10 m core. The top unit of this deeper core is a very thin, less than 1 mm, mud layer that settled during low-energy conditions or possibly after the core was taken. The next three layers of the core consist of a relatively fine-grained muddy sand sandwiched by an upper gravelly sand and a lower sandy gravel.

No distinct burrows are evident in either of the cores. It should be noted that benthic foraminifera are abundant in both cores and that rock pebbles have a dark coating that

can be scratched off. The composition of the dark coating is unknown. No photographs of the bottom were available for the Bay of Isles.

These short cores indicate that low-energy sedimentation of fine sediments falling out of suspension is punctuated by times of high-energy when resuspension and deposition occurs. High-energy events concentrate layers of coarse shelly sand and gravel and also incorporate mud that was deposited during low-energy conditions but resuspended during the high-energy events. During low-energy times mollusc, foraminifera, and echinoderms inhabit the bottom and thoroughly bioturbate the sediment to at least 50 mm depth. Much organic debris, shell, and rocks are derived from the adjacent shoreline.

### *Herring Bay*

Divers obtained one core from Herring Bay at a depth of 10 m. This core is 115 mm long and is classified as a muddy, sandy, gravel. The sediments in this core are distinctly bimodal with modes of silt and pebbles. Overall, sediments coarsen upward due to an increase in gravel and a decrease in mud. The gravel percent increases from 18 percent in the lower part to 58 percent in the upper part. The gravel fraction is predominantly subangular, pebble-sized, rock fragments with some shell. Mud content decreases upward from 38 to 13 percent, and the sand content is relatively stable between 29 and 44 percent.

There are two units clearly discernable in this core. The lower unit from 65 to 115 mm is a gravelly, muddy, medium-grained sand with scattered 5 mm bivalve shells. No bioturbation or physical sedimentary structures are apparent in this lower unit. The upper unit is coarser and is a muddy, sandy, gravel. This upper unit has a distinct lower contact and is normally graded. It is capped by a gravelly layer which contains fragments of macro algae. This upper unit displays no evidence for bioturbation and is interpreted as a storm deposit having been deposited during the waning stage of a high-energy event. No bottom photographs of Herring Bay were available for this report.

### *Olsen Bay*

One core from 19 m water depth was obtained by divers in Olsen Bay. This core is 75 mm long and contains muddy gravel. Sediments are very distinctly bimodal with modes of pebble and silt. Gravel content is 39 percent, silt content is 31 percent, and clay content is 22 percent. Only 8 percent of the sediment is sand sized. Pebbles include subangular rock fragments and large shell fragments. Organic material includes sea grass blades and disseminated black organic matter. No organic or physical structures are apparent in this core, and photographs of the bottom were not available for this report. This core is distinct from the other cores because of its high percentage of mud and low sand content.

## DISCUSSION

### Benthic Sediment Contamination by *Exxon Valdez* Oil

Our results indicate that benthic surface sediments at Northwest Bay-East arm were contaminated to seawater depths as deep as 20 m by weathered crude oil from the Exxon Valdez oil spill, and that the contaminating crude oil was associated with particulate matter mobilized off adjacent oiled beaches. Crude oil spilled from the *T/V Exxon Valdez* is indicated as the proximate source of the PAH's that contaminated benthic surface sediments at Northwest Bay-East arm for several reasons:

- (1) a close correspondence of hydrocarbon analytes in the petroleum mousse collected from the seafloor 11 days after the spill, and the analytes in the sediments trapped during the initial deployment interval there;
- (2) temporal association of the highest PAH concentrations in the trapped sediments during the first trap deployment interval succeeding the spill, followed by generally lower subsequent concentrations;
- (3) the similar patterns of relative PAH abundance's in initially trapped sediments and in benthic surface sediments subsequently;
- (4) the substantially lower concentrations and markedly different patterns of relative abundance's of these PAH's in the deeper segments of sediment core samples, thereby obviating other background sources for the higher PAH concentrations of the benthic surface sediments.

The relatively high PAH concentrations found in the benthic sediments in the east arm of Northwest Bay further corroborate the *Exxon Valdez* oil source. Although the benthic surface sediments in the east arm of Northwest Bay are contaminated with EVOS oil, the concentration of PAH's is much less than that discovered in the sediment traps. There are two reasons for this discrepancy. The first involves the expressing of total PAH concentration as percent by weight of sediment. Benthic sediments are much coarser-grained than the suspended sediments caught in the traps (Figures 14 and 16; Table 3). Thus, the level of contamination of the fine-grained fraction of the benthic surface sediments, where preferential adsorption of hydrocarbons occurs, is diluted by the coarse-grained fraction, which may or may not carry PAH's.

The second reason is that wave or tide energy levels are high enough, and fine-grained sediment supply low enough, that the more highly contaminated mud-sized sediment mostly bypasses the site. This is the reason for the relatively coarse-grained and often gravelly benthic sediments in the first place. Cores reveal a very poorly sorted, muddy, sandy, gravel in the upper 10 cm of the sediment column at the east arm of NW Bay. Crudely stratified shell hash interbedded with muddy, organic rich layers, and organic debris that includes spruce needles and wood fragments indicates that periods of relatively high energy such as winter storms have been important in depositing the sediments recovered in the short cores. During the waning stages of storms and between storms, relatively fine-grained sediments may be deposited, but normal energy levels

from waves or tides are apparently high enough to remove fine-grained, surface layers and form pebble lag deposits. Some mud is incorporated into storm deposits, particularly the upper portion that is deposited during waning storm periods, and all mud deposited between storms may not be removed before or during a subsequent, high-energy event. Organisms, such as the whole clam recovered in life position in the 20 m core may also work fine-grained sediment into the bottom. Much of the fine-grained sediment caught in the traps, however, ultimately bypasses the site and is either exported out of the Bay or deposited in deeper, lower-energy sites within the Bay.

The failure to consistently detect *Exxon Valdez* oil-derived PAH's in benthic surface sediments at the other locations where results from the sediment traps indicated an input of these PAH's is explained by higher-energy subtidal conditions. Along with variations in benthic topography, higher energy promotes the export of the finer-grained, oil-laden sediments either into open Prince William Sound, or to deeper, lower-energy sites near these locations. Thus, the relatively high-energy subtidal conditions indicated at e.g. Disk Island and Sleepy Bay lead to relatively short residence times in shallow subtidal sediments for oil-laden sediments mobilized from the oiled upper-intertidal shorelines at these locations. Even where less energetic subtidal conditions are indicated, such as at the Bay of Isles and Herring Bay, sediment movement is still sufficient to prevent substantial accumulations of oil-contaminated sediment in the shallow subtidal sites sampled at these locations.

#### **Transport Mechanism of *Exxon Valdez* Oil Contaminated Sediments**

The nearly identical pattern of relative PAH abundance's found in the sediment traps deployed initially at stations adjacent to oiled beaches, and which persisted in these trapped sediments at least until June 1991, indicates *Exxon Valdez* crude oil was mobilized into the water column at these stations. The observation that concentrations of PAH's evidently derived from *Exxon Valdez* crude oil in trapped sediments at these stations generally decline with time after the spill, together with the proximity of persistent reservoirs of this oil on nearby adjacent beaches, suggests mobilization of oil from these reservoirs, either by fall and winter storms, or by beach treatment activities. Suspended sediments collected during the winter, however, generally have higher weight percents of clay-sized grains than spring and summer sediments (fig. 15). A qualitative inspection of the suspended sediments revealed that sand-sized, planktonic, diatom tests are abundant in spring and summer sediments relative to winter sediments. Thus the oil concentrations observed during the spring and summer may be depressed by the diluting effect of clean, newly produced biological sediment.

Jahns et al. (1991) concluded that the primary process for natural removal of shoreline oil by waves and tidal flushing is through the formation of an emulsion of micron-sized mineral particles, polar components of oil residue, and seawater that impeded the adhesion of oil to the larger rocks on the shorelines. Since these emulsion floc particles were composed mainly of seawater and fine-grained sediments, Stokes Law of settling

velocities for individual grains suggest that the flocs could be transported great distances before settling and be widely dispersed. Other physical processes may however act to trap fine sediments in estuarine embayments (Drake, 1976): physicochemical flocculation with other particles in the water column, for example, can produce flocculent settling rates an order of magnitude greater than the individual grains (Kranck, 1975). The results of the sediment trap hydrocarbon chemistry suggest that at least a portion of the shoreline oil was settling onto nearshore benthic sediments between 10 and 20 meters below MLLW, depths which were generally within 75 to 400 meters from the supratidal zone.

Beach treatment activities provided a secondary mechanism for mobilizing oil from beach reservoirs into adjacent seawater. This may account for the relatively less-weathered *Exxon Valdez* crude oil found in the sediment traps during the summer of 1990. During the 1990 cleanup season, adjacent beaches were tilled or raked exposing subsurface oil. In some cases, oiled sediment was removed (although incompletely) or the beach was left "open" for oil removal by wave and tide energy. Sheens were commonly observed emanating from freshly tilled beaches. Only moderate weathering of subsurface oil, often as concentrated layers of oiled sediment, had occurred by 1991 (Michel and Hayes, 1993). Such layers were present on beaches adjacent to a number of the trap sites.

#### **Sources of PAH's in Subtidal Sediments of Prince William Sound**

There are two primary sources of petroleum PAH's in subtidal sediments of Prince William Sound. One source is natural PAH-laden sediments from outside the Sound, and the other is from shoreline sediments contaminated with oil from the *T/V Exxon Valdez*. The pattern of relative PAH abundance typified by Stockdale Harbor sediments closely matches the description given by Page et al. (1993) of sediment-borne PAH's that originates outside Prince William Sound. Page et al. (1993) speculate that this suite of PAH's originate as terrestrial or marine oil seeps that enter the Alaska coastal current east of the Sound, and are carried into the Sound through Hinchinbrook entrance where current velocities drop resulting in deposition of these naturally oiled sediments. The pattern of relative PAH abundance's that characterizes this source has also been observed in deeper sediments of the Sound by O'Clair et al. (1993), and in low intertidal sediments at Constantine Harbor (near Hinchinbrook entrance) by Short et al. (1993). The PAH's we observed in sediments trapped at Stockdale Harbor are almost certainly derived from this source as are the other trapped and benthic sediments we found with similar PAH distributions.

Molnia and Hein (1982) and Naidu and Mowatt (1983) both concluded that the Copper River via the central Gulf of Alaska to the east of Prince William Sound is the dominant source of clay-sized sediment to the Sound. Both teams showed that suspended sediments in the lower Copper River have high illite concentrations (average more than 50%) when compared to other coastal and shelf sediment sources in the northern Gulf



of Alaska. Molnia and Hein (1982) interpreted the presence of illite-dominated sediments in Prince William Sound as indicating sediment influx from the Copper River. Naidu and Mowatt (1983) discovered small amounts of expandable clay-sized minerals in central Prince William Sound but an absence of these minerals in glacially derived coastal sediments of the Sound. Expandable minerals are present in Copper River sediments and in sediments outside the Sound; therefore, they also concluded an outside influx of sediment to the central Sound. LANDSAT images (Molnia and Hein, 1982; Burbank, 1974) show that sediment plumes of the Copper River enter Prince William Sound through Hinchinbrook Entrance to the west. Furthermore, Royer (1981) showed that the freshwater driven coastal current provides a mechanism for suspended sediment transport from the Copper River into Prince William Sound.

It is clear from the studies cited above and from this study that the deep, central areas, and, to a lesser extent, shallower areas throughout Prince William Sound receive illite-rich sediments from the Copper River that may contain PAH's from natural sources outside the Sound. The proportion of sediment from outside Prince William Sound versus sediment from within Prince William Sound, however, is unknown. A study by Klein (1983) does indicate that illite is relatively more abundant in the deep (more than 300 m) parts of the Sound just northwest of Hinchinbrook Entrance than in the shallower areas adjacent to Islands to the southwest (i.e. Knight, Eleanor, Latouche, Elrington Islands etc.). A remapping of Klein's data in terms of chlorite to illite ratios shows that this ratio is generally less than 0.6 in the central and northeastern Sound northwest of Hinchinbrook Entrance but increases to the southwest along the east coast of Knight Island to more than 0.9. Higher ratios also occur around Eleanor and Ingot Islands and are above 0.68. These trends indicate a decrease in the relative amounts of Copper River sediments away from the central Sound northwest of Hinchinbrook Entrance and toward the Sound's oiled Islands.

Clay mineralogy of the suspended sediments collected during this study at 10 to 20 m depths strongly indicates a source from the adjacent littoral zone. This evidence is independent of hydrocarbon chemistry discussed above. Chlorite to illite ratios of trapped sediments in this study are well above the values in the central Sound and generally higher than any of the samples from Klein's study. The lowest ratio of the six oiled locations was 0.72, and most samples had values greater than 1.0 (Table 4, fig. 18). Klein's samples were deeper than 40 m. Thus the suspended sediments analyzed for our study are shallower and closer to shore than for Klein's study. The higher chlorite to illite ratios, therefore, indicate that the shorelines are the dominant source for clay-sized suspended sediments found in our traps.

Table 4. Chlorite and Illite clay mineral content in suspended sediments by location and season: sp= spring deployment from March, 1991 to June, 1991; su= summer deployment from June, 1991 to September, 1991; wt= winter deployment from September 1991 to March, 1992. Depth refers to water depth (referenced to mean lower low water, MLLW). nd = no data available for that site and deployment period.

Location	Depth (m)	Illite %		Chlorite %		Chlorite/ Illite ratio	
		sp 91	wt 91/92	sp 91	wt 91/92	sp 91	wt 91/92
Bay of Isles, Site 1	20	58	49	42	51	0.72	1.04
Bay of Isles, Site 1	10	nd	54	nd	46	nd	0.85
Disk Island, Site 2	20	42	56	58	44	1.38	0.79
Disk Island, Site 2	15	48	49	52	51	1.08	1.04
Disk Island, Site 2	10	43	44	57	56	1.33	1.27
east NW Bay, Site 3	18	53	45	47	55	0.89	1.22
east NW Bay, Site 3	10	49	46	51	54	1.04	1.17
Herring Bay, Site 5	10	nd	44	nd	56	nd	1.27
Olsen Bay, Site 8	10	nd	61	nd	39	nd	0.64
Sleepy Bay, Site 10	20	51	55	49	45	0.96	0.82
Sleepy Bay, Site 10	15	49	46	51	54	1.04	1.17
Sleepy Bay, Site 10	10	39	47	61	53	1.56	1.13
Snug Harbor, Site 11	20	42	51	58	49	1.38	0.96
Snug Harbor, Site 11	15	51	46	49	54	0.96	1.17
Snug Harbor, Site 11	10	50	44	50	56	1.00	1.27

The PAH concentrations we observed in benthic surface samples at Stockdale Harbor, where PAH's are apparently derived primarily from natural sources external to the Sound, together with concentrations we observed in sediment core samples of similar PAH distribution, suggests that total PAH concentrations derived from these natural sources infrequently exceeds 400 ng/g in benthic sediments at 10 to 20 m seawater depth, at least at locations along the spill path through the Sound. Total PAH concentrations in benthic surface sediments at Stockdale Harbor remained below this value, where the input was demonstrated by the sediment trap results. Also, total PAH concentrations in the deeper segments of sediment cores were usually well below this value.

## CONCLUSIONS

1. Finer-grained intertidal sediments contaminated by *Exxon Valdez* oil were transported to adjacent shallow subtidal areas by waves associated with winter storms, and by beach treatment activities. Oiled-sediment concentrations in the traps generally declined during the period November 1989 through June 1991.
2. Residence times of *Exxon Valdez* oil-contaminated sediments in the shallow subtidal adjacent to oiled beaches depends primarily on the energy available to transport these sediments to deeper, lower-energy sites within the embayments or to the open areas of Prince William Sound. At most sites where *Exxon Valdez* oil contaminated sediment transport was observed, these residence times are probably less than 1 year. However, in the east arm of Northwest Bay, the residence time may be somewhat longer than 1 year.
3. Several conditions promote accumulation of oil-contaminated sediments in the shallow subtidal adjacent to oiled intertidal beaches: (a) where beaches are prone to sediment transport caused by winter storms or shoreline treatment, and (b) low-energy subtidal conditions caused by low tidal current velocities, low wave energy or uneven bathymetry that forms pockets protected from tidal or wave action.
4. Although benthic sediment contamination at 20 m and shallower depths was low compared to suspended sediment concentrations, it is likely that higher levels of benthic sediment contamination are present in deeper, lower energy fine-grained sedimentation sites within oiled embayments such as NW Bay and Bay of Isles.
5. Other sources of PAH's in shallow (to 20 m) subtidal sediments along the spill path through Prince William Sound, including local anthropogenic sources and natural sources external to the Sound, rarely exceed 400 ng/g total PAH. The relatively small contribution of PAH-laden sediments originating outside the Sound to shallow subtidal sediments of the western Sound is indicated by both hydrocarbon and mineralogical evidence.

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## APPENDIX I

### SURROGATE STANDARDS FOR DETERMINATION OF ALKANES AND PAH'S AND CALIBRATED AND UNCALIBRATED PAH'S AND CALIBRATED ALKANES DETERMINED IN SEDIMENT AND TRAP SAMPLES

Table I-1.--Deuterated surrogate hydrocarbon standards used for determination of alkanes and PAH's in benthic sediments and sediments collected in traps deployed along and adjacent to the path of spilled oil following the grounding of the *Exxon Valdez* in Prince William Sound.

Table I-2.--Calibrated PAH's determined in benthic sediments and sediments collected in traps deployed along and adjacent to the path of spilled oil following the grounding of the *Exxon Valdez* in Prince William Sound, Alaska.

Table I-3.--Uncalibrated PAH's determined in benthic sediments and sediments collected in traps deployed along and adjacent to the path of spilled oil following the grounding of the *Exxon Valdez* in Prince William Sound, Alaska.

Table I-4.--Calibrated alkane hydrocarbons determined in benthic sediments and sediments collected in traps deployed along and adjacent to the path of spilled oil following the grounding of the *Exxon Valdez* in Prince William Sound, Alaska.



Table I-1.--Deuterated surrogate hydrocarbon standards used for determination of alkanes and PAH's in benthic sediments and sediments collected in traps deployed along and adjacent to the path of spilled oil following the grounding of the *Exxon Valdez* in Prince William Sound. The deuterated surrogate hydrocarbon standards, each identified by a number in the left-hand column, are listed below, together with the quantification ion mass of the PAH's, and the concentration in hexane of each of the standards in the sample spiking solution. A 500  $\mu$ l aliquot of this solution was spiked into each environmental or quality control sample analyzed. The numbers in the left-hand column are used to relate the calibrated hydrocarbon analytes listed in Tables I-2 and I-4 below with the deuterated standards listed here.

I.D. #	Name	Mass of quantification ion	Concentration in spike solution (ng/ml)
1	Naphthalene - d <sub>8</sub>	136	2.5
2	Acenaphthene - d <sub>10</sub>	164	2.5
3	Phenanthrene - d <sub>10</sub>	188	2.00
4	Chrysene - d <sub>12</sub>	240	2.00
5	Benzo[a]pyrene - d <sub>12</sub>	264	2.50
6	Perylene - d <sub>12</sub>	264	2.50
7	n-Dodecane - d <sub>26</sub>	n/a	10.50
8	n-Hexadecane - d <sub>34</sub>	n/a	9.79
9	n-Eicosane - d <sub>42</sub>	n/a	10.40
10	n-Tetracosane - d <sub>50</sub>	n/a	9.89
11	n-Triacontane - d <sub>62</sub>	n/a	10.00

Table I-2.--Calibrated PAH's determined in benthic sediments and sediments collected in traps deployed along and adjacent to the path of spilled oil following the grounding of the *Exxon Valdez* in Prince William Sound, Alaska. The calibrated aromatic hydrocarbons, and standardized abbreviations for them, are listed below, together with the number of the associated surrogate standard (see Table I-1 above), quantification ion mass, confirmation ion mass, and the mean ratio of these two ions in the calibration standards, of which the latter three are used for identification.

PAH	Abbreviation	Quantification ion mass	Confirmation ion mass	Expected ion ratio	I.D. number of surrogate std. used
Naphthalene	Naph	128	127	15	1
2-Methylnaphthalene	Menap2	142	141	88	1
1-Methylnaphthalene	Menap1	142	141	88	1
2,6 Dimethylnaphthalene	Dimeth	156	141	67	2
2,3,5 Trimethylnaphthalene	Trimeth	170	155	90	2
Biphenyl	Biphenyl	154	152	28	1
Acenaphthylene	Acenthy	152	153	13	2
Acenaphthene	Acenthe	154	153	99	2
Fluorene	Fluorene	166	165	92	2
Dibenzothiophene	Dithio	184	152	15	3
Phenanthrene	Phenanth	178	176	19	3
Anthracene	Anthra	178	176	18	3
1-Methylphenanthrene	Mephen1	192	191	57	3
Fluoranthrene	Fluorant	202	101	15	3
Pyrene	Pyrene	202	101	19	3
Chrysene	Chrysene	228	226	25	4
Benz-a-anthracene	Benanth	228	226	28	4
Benzo-b-fluoranthene	Benzobfl	252	253	22	5
Benzo-k-fluoranthene	Benzokfl	252	253	22	5
Benzo-e-pyrene	Benepy	252	253	23	5
Benzo-a-pyrene	Benapy	252	253	24	5
Perylene	Perylene	252	253	25	6
Ideno-1,2,3 cd-pyrene	Indeno	276	277	24	5
Dibenzo-a,h-anthracene	Dibenz	278	279	22	5
Benzo-g,h,i-perylene	Benzop	276	277	23	5

Table I-3.--Uncalibrated PAH's determined in benthic sediments and sediments collected in traps deployed along and adjacent to the path of spilled oil following the grounding of the *Exxon Valdez* in Prince William Sound, Alaska. The uncalibrated aromatic hydrocarbons, and standardized abbreviations for them, are listed below, together with the quantification ion mass and retention time windows used for identification.

Name	Abbreviation	Quantification ion mass	Retention time window (min)
C2 - Naphthalenes	C2naph	156	11.0 - 14.5
C3 - Naphthalenes	C3naph	170	12.5 - 16.5
C4 - Naphthalenes	C4naph	184	14.0 - 18.5
C1 - Fluorenes	C1fluor	180	15.0 - 18.0
C2 - Fluorenes	C2fluor	194	16.5 - 20.0
C3 - Fluorenes	C3fluor	208	18.0 - 21.5
C1 - Dibenzothiophenes	C1dithio	198	17.0 - 21.0
C2 - Dibenzothiophenes	C2dithio	212	18.0 - 23.0
C3 - Dibenzothiophenes	C3dithio	226	19.5 - 26.0
C1 - Phenanthrenes/Anthracenes	C1phenan	192	17.5 - 20.5
C2 - Phenanthrenes/Anthracenes	C2phenan	206	19.0 - 22.5
C3 - Phenanthrenes/Anthracenes	C3phenan	220	20.0 - 23.5
C4 - Phenanthrenes/Anthracenes	C4phenan	234	21.0 - 25.0
C1 - Fluoranthenes/Pyrenes	C1fluora	216	20.0 - 28.0
C1 - Chrysenes	C1chrys	242	24.5 - 27.5
C2 - Chrysenes	C2chrys	256	26.0 - 29.0
C3 - Chrysenes	C3chrys	270	27.0 - 31.0
C4 - Chrysenes	C4chrys	284	28.0 - 33.0

Table I-4.--Calibrated alkane hydrocarbons determined in benthic sediments and sediments collected in traps deployed along and adjacent to the path of spilled oil following the grounding of the *Exxon Valdez* in Prince William Sound, Alaska. The calibrated alkane hydrocarbons, and standardized abbreviations for them, are listed below, together with the number of the associated surrogate standard (see Table I-1 above).

Name	Abbreviation	I.D. of Surrogate Standard
n-Decane	C-10	7
n-Undecane	C-11	7
n-Dodecane	C-12	7
n-Tridecane	C-13	7
n-Tetradecane	C-14	8
n-Pentadecane	C-15	8
n-Hexadecane	C-16	8
n-Heptadecane	C-17	8
Pristane	Pris	8
n-Octadecane	C-18	9
n-Nonadecane	C-19	9
n-Eicosane	C-20	9
n-Heneicosane	C-21	9
n-Docosane	C-22	10
n-Tricosane	C-23	10
n-Tetracosane	C-24	10
n-Pentacosane	C-25	10
n-Hexacosane	C-26	10
n-Heptacosane	C-27	11
n-Octacosane	C-28	11
n-Nonacosane	C-29	11
n-Triacontane	C-30	11
n-Dotriacontane	C-32	11
n-Tetratriacontane	C-34	11

## APPENDIX II

### SEDIMENT TRAP, BENTHIC SEDIMENT AND BENTHIC CORE SAMPLE HYDROCARBON CHEMISTRY DATA

Table II-1. Alkane and PAH hydrocarbon concentrations of floating mousse oil collected from the searface at Snug Harbor, Bay of Isles, and Smith Island, 11 days following the *Exxon Valdez* oil spill of March 24, 1989.

Table II-2. Mean Alkane and PAH hydrocarbon concentrations of sediments collected from sediment traps deployed at stations in Prince William Sound, Alaska, during the period November 1989 through March 1992, following the *Exxon Valdez* oil spill of March 24, 1989.

Table II-3. Alkane and PAH hydrocarbon concentrations of benthic sediments collected near deployed sediment traps at stations in Prince William Sound, Alaska, during the period June 1990 through September 1991, following the *Exxon Valdez* oil spill of March 24, 1989.

Table II-4. Alkane and PAH hydrocarbon concentrations of sediment core samples collected near deployed sediment traps at stations in Prince William Sound, Alaska, during the period June 1991 through September 1991, following the *Exxon Valdez* oil spill of March 24, 1989.

Table II-5. Alkane and PAH hydrocarbon analysis results of sediments collected in sediment traps that were excluded from Table II-2 due to extreme surrogate recoveries (denoted by \*), sample wet weights less than 0.5 g (denoted by \*\*), and sample wet weights that were unreliably measured (denoted by \*\*\*).

Table II-6. Alkane and PAH hydrocarbon analysis results of benthic sediments that were excluded from Table II-3 due to extreme surrogate recoveries.

Table II-7. Alkane and PAH hydrocarbon analysis results of sediment core samples that were excluded from Table II-4 due to extreme surrogate recoveries (denoted by \*).

Table II-8. Method detection limits for PAH and alkane analytes for this study.

Table II-1 Hydrocarbon Analysis of 'Exxon Valdez' Mousse Oil

Station Name	Bay of Isles	Smith Island	Snug Harbor
Sample weight (mg)	4.7	4.5	4.1
PAH's(ng/g)			
Naph	314000	77800	128000
Menap2	1100000	450000	648000
Menap1	892000	377000	538000
Dimeth	833000	448000	613000
C2naph	3440000	1870000	2580000
Trimeth	496000	308000	436000
C3naph	2950000	1810000	2530000
C4naph	1140000	753000	1049000
Biphenyl	192000	98200	137000
Acenthy	-	-	-
Acenthe	-	-	-
Fluorene	109000	65200	93500
C1fluor	292000	193000	280000
C2fluor	407000	284000	403000
C3fluor	272000	197000	268000
Dithio	268000	168000	239000
C1dithio	297000	217000	317000
C2dithio	427000	329000	468000
C3dithio	515000	398000	551000
Phenanth	375000	248000	356000
Mephen1	285000	201000	283000
C1phenan	1170000	850000	1190000
C2phenan	1320000	977000	1280000
C3phenan	922000	652000	857000
C4phenan	468000	335000	444000
Anthra	9960	7570	10300
Fluorant	16900	13100	18500
Pyrene	28100	19400	27800
C1fluora	102000	78600	111000
Benanth	8600	8180	12700
Chrysene	77000	71700	104000
C1chrys	97200	93500	130000
C2chrys	131000	111000	155000
C3chrys	79500	66800	78900
C4chrys	18300	2780	8380
Benzofl	9840	9840	13800
Benzokfl	-	-	-
Benapy	19300	20100	26400
Benapy	-	-	-
Perylene	-	-	-
Indeno	-	-	-
Dibenz	278	472	-
Benzop	4980	2010	4850
Total Aromatics (w/o Perylene)	17500000	10800000	15100000
Alkanes(ng/g)			
C10alk	456000	31600	132000
C11alk	1220000	238000	548000
C12alk	2620000	983000	1320000
C13alk	3900000	1910000	2600000
C14alk	8280000	2240000	6500000
C15alk	9020000	2650000	8070000
C16alk	8370000	2580000	7680000
C17alk	8600000	2770000	8010000
Prstane	6270000	2080000	5740000
C18alk	5730000	3880000	4680000
Phytane	3140000	2100000	2440000
C19alk	6040000	4240000	5280000
C20alk	5150000	3550000	4310000
C21alk	4440000	3080000	3480000
C22alk	2350000	1780000	2980000
C23alk	1970000	1530000	2570000
C24alk	1980000	1530000	2580000
C25alk	1680000	1310000	2170000
C26alk	1730000	1180000	1810000
C27alk	1110000	864000	1440000
C28alk	1070000	817000	1220000
C29alk	884000	687000	938000
C30alk	773000	582000	769000
C32alk	540000	380000	531000
C34alk	679000	521000	647000
ALKANES	141000000	73800000	119000000
UCM	385000000	244000000	310000000

Table II-1. Alkane and PAH hydrocarbon concentrations of floating mousse oil collected from the seasurface at Snug Harbor, Bay of Isles, and Smith Island, 11 days following the Exxon Valdez oil spill of March 24, 1989. Analyte concentrations are given as ng analyte/g mousse oil. Alkanes refers to the sum of all resolvable alkanes observed, which includes the specific alkane analytes listed. The UCM is the estimate of the unresolved complex mixture.

Table II-2. Mean Alkane and PAH hydrocarbon concentrations of sediments collected from sediment traps deployed at stations in Prince William Sound, Alaska, during the period November 1989 through March 1992, following the Exxon Valdez oil spill of March 24, 1989. Also listed are station names followed by station numbers in parentheses, where the station numbers correspond with those of fig. 1 and table 1 (see text); the water column depth in meters of the sediment trap; the mean sample analysis aliquot wet and dry weights; and the number (N) of replicates included in the means. Units are ng analyte/g dry sediment weight. Hyphens indicate analysis results below method detection limits adjusted for the sample analysis aliquot dry weight. Total aromatics refers to the sum of the means of each PAH analyte listed, excluding perylene. Variability of mean total aromatics is indicated by  $\pm 1$  standard error. Alkanes refers to the sum of all resolvable alkanes observed, which includes the specific alkane analytes listed. The UCM is the estimate of the unresolved complex mixture. Samples that did not meet the criteria for PAH surrogate standard recovery or minimum sample aliquot wet weight described in the Methods section (see text) were excluded from this table, but are presented in Table II-5 below.











Table II-2 Sediment Traps

Station Name (#)	Snug Harbor (11)	Snug Harbor (11)	Squire Island (12)	West NW Bay (14)	West NW Bay (14)	West NW Bay (14)
Date collected	March 92	March 92	March 91	June 90	August 90	March 91
Depth (m)	15	20	10	10	10	10
Mean wet wt. (g)	1.56	1.33	2.62	2.09	5.64	1.07
Mean dry wt. (g)	0.94	0.74	1.43	0.76	1.67	0.56
N	2	2	2	3	2	2
<b>Mean PAH's (ng/g)</b>						
Naph	44.1	23.2	35.4	11.9	60.2	149
Menap2	28.2	74.3	28.0	19.9	58.6	140
Menap1	11.2	46.9	19.8	8.20	32.7	85.5
Dimedr	-	37.8	-	8.34	45.8	68.9
C2naph	55.7	117	50.8	68.1	132	238
Trimeth	15.5	25.8	9.58	11.8	93.4	44.7
C3naph	66.0	119	42.7	86.4	415	227
C4naph	106	179	5.71	35.2	684	112
Biphenyl	-	-	-	-	34.2	-
Acenthy	-	-	-	-	-	-
Acenthe	65.0	166	-	-	-	-
Fluorene	85.2	315	8.14	6.74	26.1	22.8
C1fluor	16.7	89.3	7.98	14.3	140	70.1
C2fluor	53.5	173	15.7	184	448	221
C3fluor	48.4	125	-	125	531	75.1
Dithio	29.9	75.7	-	3.32	50.2	-
C1dithio	15.5	31.0	-	15.4	246	29.3
C2dithio	29.6	30.6	7.57	127	610	95.9
C3dithio	38.1	28.2	10.9	271	599	172
Phenanth	813	1760	18.4	77.9	185	113
Mephen1	69.8	107	-	11.8	91.3	-
C1phenan	190	409	23.6	132	443	162
C2phenan	106	193	9.69	235	567	156
C3phenan	98.2	101	-	593	274	354
C4phenan	39.7	65.6	-	332	154	217
Anthra	124	347	-	-	-	-
Fluorant	983	1820	4.18	95.2	66.3	65.8
Pyrene	734	1400	4.84	88.9	125	63.9
C1fluora	194	391	3.46	329	91.3	135
Benanth	300	514	1.48	9.62	10.3	13.2
Chrysene	395	698	-	492	35.1	231
C1chrysa	159	269	-	868	54.4	543
C2chrysa	37.9	59.7	-	770	56.8	313
C3chrysa	60.8	22.1	13.5	991	38.9	264
C4chrysa	31.7	-	22.5	442	43.5	186
Benzofl	371	1120	-	188	16.9	33.3
Benzokf	-	-	-	-	-	-
Benepyl	237	447	-	306	20.8	168
Benapy	244	520	-	58.4	10.6	-
Perylene	92.8	175	-	92.6	38.4	133
Indeno	128	351	-	47.1	6.27	9.41
Dibenz	61.8	170	-	40.3	-	-
Benzop	179	402	-	115	20.7	52.4
Mean						
Total Aromatics (w/o Perylene)	6380±1700	12600±843	334±23.7	7190±1390	6290±2010	4720±185
<b>Mean Alkanes (ng/g)</b>						
C10alk	-	-	-	24.5	-	96.8
C11alk	-	-	-	55.3	-	50.0
C12alk	-	-	-	32.4	42.8	55.6
C13alk	-	-	-	826	45.2	223
C14alk	39.7	134	82.1	30.3	79.8	298
C15alk	1410	2680	272	184	853	1790
C16alk	97.8	227	30.8	109	87.7	314
C17alk	630	486	642	1620	1800	1680
Pristane	709	811	426	78500	1660	5710
C18alk	-	-	-	54.6	565	-
Phytane	-	-	-	181	1050	485
C19alk	191	164	47.8	256	718	384
C20alk	-	60.2	-	365	654	410
C21alk	125	62.2	-	504	947	475
C22alk	118	186	70.0	711	388	415
C23alk	133	-	-	1990	356	791
C24alk	-	-	-	4270	572	1040
C25alk	399	377	43.6	6380	649	1330
C26alk	-	209	-	5950	1040	599
C27alk	1160	879	320	7080	1270	3110
C28alk	245	-	-	6170	778	609
C29alk	407	478	130	5340	1090	1320
C30alk	-	222	-	3850	1840	951
C31alk	-	-	-	-	1740	-
C32alk	550	173	-	4310	2150	1800
C33alk	-	-	-	-	1120	-
C34alk	866	381	288	4200	792	2100
ALKANES	13900	15100	4520	210000	22200	64800
UCM	99200	33800	29600	977000	470000	575000

Table II-3. Alkane and PAH hydrocarbon concentrations of benthic sediments collected near deployed sediment traps at stations in Prince William Sound, Alaska, during the period June 1990 through September 1991, following the *Exxon Valdez* oil spill of March 24, 1989. Also listed are station names followed by station numbers in parentheses, where the station numbers correspond with those of fig. 1 and Table 1 (see text); the water column depth in meters of the collected benthic sediment sample; the mean sample analysis aliquot wet and dry weights; and the number (N) of replicates included in the means. Units are ng analyte/g dry sediment weight. Hyphens indicate analysis results below method detection limits adjusted for the sample analysis aliquot dry weight. Total aromatics refers to the sum of the means of each PAH analyte listed, excluding perylene. Variability of mean total aromatics is indicated by  $\pm 1$  standard error. Alkanes refers to the sum of all resolvable alkanes observed, which includes the specific alkane analytes listed. The UCM is the estimate of the unresolved complex mixture. Samples that did not meet the criteria for PAH surrogate standard recovery or minimum sample aliquot wet weight described in the Methods section (see text) were excluded from this table, but are presented in Table II-6 below.









Table II-3 Benthic Sediments

Station Name (#)	Snug Harbor (11)	Snug Harbor (11)	Squire Island (12)	Stockdale Harbor (13)	Stockdale Harbor (13)	West NW Bay (14)	Green Island (15)	Naked Island (16)
Date collected	Sept 91	Sept 91	August 90	August 90	March 91	August 90	August 90	August 90
Depth (m)	15	20	10	10	10	10	10	10
Mean wet wt. (g)	20.1	20.1	16.3	15.4	20.0	16.7	16.1	14.9
Mean dry wt. (g)	13.4	13.7	10.4	10.4	13.6	9.24	10.3	10.6
N	1	1	3	3	1	4	3	3
Mean PAH's (ng/g)								
Napn	1.81	1.41	1.82	7.30	7.36	2.66	4.76	2.53
Menap2	1.65	1.49	2.63	9.03	11.2	2.74	3.25	1.73
Menap1	-	-	1.90	3.91	3.96	2.01	2.22	1.34
Dimeth	2.16	1.82	4.04	8.38	7.50	3.00	5.31	-
C2napn	5.60	4.31	6.99	10.5	15.7	3.00	7.30	-
Trmeth	0.96	0.91	0.84	-	1.63	-	1.55	-
C3napn	4.25	3.71	3.31	4.47	8.13	5.03	7.48	5.43
C4napn	1.56	1.46	2.21	-	3.46	8.77	7.41	5.69
Biphenyl	-	-	-	7.52	7.95	-	-	-
Acenthy	-	-	-	-	-	-	-	-
Acenthe	-	-	-	-	-	-	-	-
Fluorene	1.95	1.39	0.89	11.3	13.4	-	-	-
C1fluor	1.93	-	-	11.5	12.8	-	-	-
C2fluor	1.75	-	-	8.60	12.4	6.96	3.99	-
C3fluor	-	-	-	1.73	3.62	10.8	5.28	3.31
Dithio	-	-	-	1.59	2.00	-	-	-
C1dithio	0.73	-	-	-	2.31	-	-	-
C2dithio	1.12	1.11	-	-	1.63	9.77	5.19	3.24
C3dithio	1.26	1.49	-	-	1.38	17.9	5.76	3.22
Phenanth	8.21	2.21	6.17	39.3	44.3	5.51	4.35	4.01
Mephent	2.62	-	1.76	4.15	3.59	2.65	1.96	1.01
C1phenan	6.65	3.73	8.35	27.2	34.7	10.9	7.81	2.88
C2phenan	4.49	3.43	6.06	11.1	15.4	16.0	8.52	2.65
C3phenan	6.42	2.89	-	-	6.29	17.3	3.63	-
C4phenan	-	-	-	-	-	15.3	-	-
Anthra	-	-	-	-	-	-	-	-
Fluorant	4.67	1.39	5.85	6.12	7.36	7.21	1.02	3.13
Pyrene	4.36	1.22	4.78	6.79	10.4	5.77	0.97	-
C1fluora	2.37	1.17	3.29	13.9	11.7	5.47	-	-
Benanth	0.93	-	1.85	0.96	2.65	1.22	-	-
Chrysene	-	-	3.89	11.9	11.3	9.13	2.03	0.62
C1chrys	-	-	-	3.28	10.3	12.2	-	-
C2chrys	-	-	-	2.69	3.62	17.5	-	-
C3chrys	-	-	-	1.03	-	7.19	-	-
C4chrys	-	-	-	-	-	7.21	-	-
Benzofl	1.72	-	1.84	8.76	16.4	1.96	-	-
Benzokfl	-	-	2.16	8.54	-	1.40	-	-
Benepy	1.20	0.95	1.79	8.41	7.50	5.43	-	-
Benapy	-	-	2.51	1.85	3.76	1.00	-	-
Perylene	4.37	4.14	36.8	29.0	11.2	34.9	7.90	-
Indeno	-	-	1.30	4.10	2.36	1.26	-	-
Dibenz	-	-	-	2.13	1.77	-	-	-
Benzop	-	-	2.05	9.11	5.32	4.40	2.93	-
Mean								
Total Aromatics (w/o Perylene)	64.6	33.4	71.7±42.2	245±21.8	302	223±66.7	83.9±38.1	39.8±18.7
Mean Alkanes (ng/g)								
C10alk	-	-	-	-	-	-	-	-
C11alk	-	-	4.52	11.1	-	-	4.70	-
C12alk	-	-	3.78	6.98	-	1.20	5.83	-
C13alk	-	-	8.91	8.30	-	2.99	6.05	-
C14alk	16.2	-	-	3.18	-	-	-	-
C15alk	41.3	17.7	12.6	28.1	-	23.3	17.5	12.1
C16alk	9.16	-	46.6	17.9	-	74.9	19.2	8.57
C17alk	13.9	16.6	130	30.0	27.5	148	34.7	18.1
Prstane	-	-	12.7	46.0	15.8	114	19.0	18.2
C18alk	-	-	6.32	8.70	-	11.2	7.47	5.82
Phytane	-	-	-	4.28	-	28.8	6.81	6.83
C19alk	4.85	5.87	10.0	38.4	16.8	28.5	6.60	6.74
C20alk	-	-	9.12	7.01	-	17.6	6.80	4.79
C21alk	-	8.01	15.1	13.8	11.1	40.0	9.09	-
C22alk	-	-	16.5	12.8	-	19.6	3.29	-
C23alk	-	-	21.9	11.6	-	42.7	4.27	4.45
C24alk	-	-	13.0	7.91	-	26.0	4.90	-
C25alk	12.0	13.3	20.1	10.2	-	44.5	5.88	-
C26alk	-	-	31.9	14.0	-	34.8	6.04	-
C27alk	23.7	29.8	97.9	69.8	43.3	207	16.8	5.23
C28alk	-	-	24.5	5.78	-	50.4	4.62	-
C29alk	20.2	18.1	53.1	61.8	27.9	169	13.2	-
C30alk	-	-	15.4	3.62	-	75.3	8.31	-
C31alk	-	-	119	36.7	-	232	20.2	4.01
C32alk	-	-	49.0	6.87	-	107	16.4	-
C33alk	-	-	66.2	17.1	-	151	8.95	-
C34alk	12.0	10.8	29.2	4.08	-	97.8	9.03	-
ALKANES	321	337	817	486	429	1750	266	90.8
UCM	2820	3230	5520	7480	1820	64700	5980	429

Table II-4. Alkane and PAH hydrocarbon concentrations of sediment core samples collected near deployed sediment traps at stations in Prince William Sound, Alaska, during the period June 1991 through September 1991, following the Exxon Valdez oil spill of March 24, 1989. Also listed are station names followed by station numbers in parentheses, where the station numbers correspond with those of fig. 1 and Table 1 (see text); the water column depth in meters where the sediment core sample was collected; the depth interval in cm of the sediment core analyzed; the mean sample analysis aliquot wet and dry weights. Units are ng analyte/g dry sediment weight. Hyphens indicate analysis results below method detection limits adjusted for the sample analysis aliquot dry weight. Total aromatics refers to the sum of the means of each PAH analyte listed, excluding perylene. Alkanes refers to the sum of all resolvable alkanes observed, which includes the specific alkane analytes listed. The UCM is the estimate of the unresolved complex mixture. Samples that did not meet the criteria for PAH surrogate standard recovery or minimum sample aliquot wet weight described in the Methods section (see text) were excluded from this table, but are presented in Table II-7 below.





Table II-4 Sediment Cores

Station	Snug	Snug	Snug	Snug	Snug	Snug	Snug	Snug
Name (#)	Harbor (11)	Harbor (11)	Harbor (11)	Harbor (11)	Harbor (11)	Harbor (11)	Harbor (11)	Harbor (11)
Date collected	June 91	June 91	June 91	June 91	June 91	Sept 91	Sept 91	Sept 91
Depth (m)	10	20	20	20	20	15	15	15
Core Depth (cm)	8.0 - 11.0	1.0 - 3.0	4.5 - 6.5	7.0 - 9.0	10.5 - 12.5	2.0 - 4.0	5.0 - 8.0	8.0 - 11.0
Mean wet wt. (g)	9.98	10.2	10.2	10.1	9.95	10.2	10.2	10.1
Mean dry wt. (g)	7.82	7.00	7.05	7.27	7.35	7.05	7.21	7.31
Mean PAH's (ng/g)								
Naph	-	10.6	25.5	5.04	16.0	5.99	4.11	5.12
Menap2	-	2.71	8.76	2.01	6.06	4.88	2.25	2.22
Menap1	-	-	4.94	-	3.25	-	-	-
Dimeth	-	-	-	-	-	3.98	3.14	-
C2naph	-	4.68	7.44	4.77	7.34	10.2	7.40	3.12
Trimeth	-	-	1.41	-	-	1.40	-	-
C3naph	1.86	2.83	5.42	3.79	4.96	8.34	7.02	3.27
C4naph	-	1.87	2.88	1.58	2.46	2.65	4.87	1.68
Biphenyl	-	-	7.57	-	-	-	-	-
Acenthy	-	-	-	-	-	-	-	-
Acenthe	-	-	-	-	-	-	-	-
Fluorene	-	2.68	3.59	-	3.17	-	-	2.73
C1fluor	-	-	8.57	-	3.38	3.75	-	-
C2fluor	-	-	7.25	-	7.72	3.91	7.97	-
C3fluor	-	3.12	3.53	-	-	-	13.0	-
Dithio	-	-	-	-	-	-	-	-
C1dithio	-	-	-	-	-	-	3.48	-
C2dithio	-	-	-	-	-	1.80	19.6	1.94
C3dithio	-	-	1.70	-	-	1.98	22.7	2.66
Phenanth	-	-	20.7	3.11	10.3	15.3	4.67	3.63
Mephen1	-	-	-	-	-	-	-	-
C1phenan	-	-	7.52	4.32	4.60	9.58	7.93	-
C2phenan	-	-	3.86	-	-	6.00	24.9	-
C3phenan	-	-	-	-	5.28	4.66	32.9	4.32
C4phenan	-	-	3.93	-	-	4.24	15.4	-
Anthra	-	-	-	-	-	-	-	-
Fluorant	-	1.59	4.21	2.52	2.88	2.93	8.95	4.11
Pyrene	-	1.64	3.50	2.14	2.63	2.77	5.97	4.18
C1fluora	-	-	2.18	1.34	-	2.15	5.15	1.89
Benanth	-	0.67	1.10	1.33	1.10	-	1.82	2.23
Chrysene	-	-	7.32	-	-	10.6	6.33	-
C1chrys	-	-	-	-	-	-	5.73	-
C2chrys	-	-	-	-	-	-	-	-
C3chrys	-	-	-	-	-	-	3.76	-
C4chrys	-	-	-	-	-	-	-	-
Benzokfl	-	-	5.65	3.60	3.79	4.34	3.65	3.70
Benzokfl	-	-	-	-	-	-	-	-
Benepy	-	-	4.58	2.20	3.93	7.28	3.79	2.39
Benapy	-	-	-	-	-	-	-	-
Perylene	-	10.7	8.55	9.15	8.45	8.41	7.35	6.96
Indeno	-	-	-	-	-	1.43	-	-
Dibenz	-	0.78	0.71	-	-	-	-	-
Benzop	-	-	-	-	5.05	10.2	-	-
Mean								
Total Aromatics (w/o Perylene)	1.86	33.2	152	37.8	93.9	125	223	49.2
Mean Alkanes (ng/g)								
C10alk	-	-	8.92	-	-	-	-	-
C11alk	-	-	-	-	-	-	-	-
C12alk	-	-	-	-	-	-	-	-
C13alk	-	-	-	-	-	-	-	-
C14alk	-	-	12.6	-	7.92	-	-	7.50
C15alk	-	-	-	-	-	-	-	-
C16alk	-	-	-	-	-	-	-	-
C17alk	-	28.4	50.1	34.0	30.5	28.6	27.3	29.1
Pristane	-	84.8	-	-	-	-	-	-
C18alk	-	-	-	-	-	-	-	-
Phytane	-	-	-	-	-	-	-	-
C19alk	-	8.16	19.9	7.68	9.86	11.3	8.55	10.4
C20alk	-	-	-	-	-	-	-	-
C21alk	-	-	-	-	-	-	-	-
C22alk	-	-	10.4	-	-	-	-	-
C23alk	-	-	-	-	-	-	-	-
C24alk	-	-	-	-	-	-	-	-
C25alk	-	31.8	44.0	-	25.8	-	-	-
C26alk	-	-	-	-	-	-	-	-
C27alk	-	48.5	80.7	32.2	43.3	35.7	-	40.0
C28alk	-	-	-	-	-	-	-	-
C29alk	-	26.9	73.6	-	22.3	-	-	-
C30alk	-	-	-	-	-	-	-	-
C31alk	-	-	-	-	-	-	-	-
C32alk	-	-	-	-	-	-	-	-
C33alk	-	-	-	-	-	-	-	-
C34alk	-	-	-	-	-	-	33.0	-
ALKANES	2670	707	842	184	378	305	94.2	481
UCM	-	-	-	-	-	-	9.93	-

Table II-5. Alkane and PAH hydrocarbon analysis results of sediments collected in sediment traps that were excluded from Table II-2 due to extreme surrogate recoveries (denoted by \*), sample wet weights less than 0.5 g (denoted by \*\*), and sample wet weights that were unreliably measured (denoted by \*\*\*). Dry weights were not determined for italicized samples, so concentrations are reported on wet weight basis for these samples. See Table II-2 legend for further explanation of symbols and conventions.









Table II-6 Compromised Benthic Surface

Station Name (#)	East NW Bay (3)	Sleepy Bay (10)	Sleepy Bay (10)	Snug Harbor (11)
Date collected	June 90	June 90	June 91	June 90
Depth (m)	10	10	15	10
Mean wet wt. (g)	20.0	20.1	20.1	20.1
Mean dry wt. (g)	8.56	13.4	13.8	14.3
Recovery	-	-	-	-

Mean PAH's(ng/g)

Naph	1.76	2.21	-	1.29
Menap2	3.61	2.06	1.58	1.11
Menap1	-	2.55	-	-
Dimeth	2.69	-	-	-
C2naph	8.08	6.20	4.34	1.37
Trimeth	1.97	2.76	1.64	-
C3naph	9.30	7.80	5.73	1.42
C4naph	8.57	2.64	3.19	-
Biphenyl	-	-	-	-
Acanthy	-	-	-	-
Acenthy	-	2.97	-	-
Fluorene	2.60	6.32	-	-
C1fluor	-	-	-	-
C2fluor	8.97	-	1.71	-
C3fluor	18.1	-	-	-
Dithio	1.59	1.22	-	-
C1dithio	5.67	-	1.90	-
C2dithio	30.8	1.61	6.50	-
C3dithio	59.0	1.61	7.72	-
Phenanth	14.5	47.7	3.82	-
Mephen1	9.04	3.72	4.24	-
C1phenan	20.4	13.3	7.97	-
C2phenan	43.7	9.03	13.2	-
C3phenan	77.7	5.61	18.2	-
C4phenan	32.7	2.42	6.57	-
Anthra	7.59	7.73	-	-
Fluorant	19.6	46.8	3.86	-
Pyrene	17.3	44.7	3.82	-
C1fluora	35.3	14.0	8.13	-
Benanth	A	A	A	A
Chrysene	A	A	A	A
C1chrys	A	A	A	A
C2chrys	A	A	A	A
C3chrys	A	A	A	A
C4chrys	A	A	A	A
Benzobfl	A	A	A	-
Benzokfl	A	A	A	-
Benepy	A	A	A	-
Benapy	A	A	A	-
Perylene	A	A	A	-
Indeno	A	A	A	-
Dibenz	A	A	A	-
Benzop	A	A	A	-

Mean Total Aromatics (w/o Perylene)	426	228	98.3	5.19
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Mean Alkanes(ng/g)

C10alk	-	-	-	-
C11alk	-	-	-	-
C12alk	-	-	-	-
C13alk	-	-	-	-
C14alk	11.4	7.89	6.72	-
C15alk	43.5	18.4	15.6	-
C16alk	14.8	6.83	6.59	-
C17alk	95.4	18.4	27.3	8.54
Pristane	190	34.6	376	136
C18alk	-	-	-	-
Phytane	-	-	-	-
C19alk	24.2	5.07	8.40	-
C20alk	20.3	-	-	-
C21alk	27.2	8.79	8.72	-
C22alk	53.8	9.75	9.48	-
C23alk	-	-	-	-
C24alk	-	-	35.3	-
C25alk	90.8	16.4	27.1	5.71
C26alk	30.8	-	20.0	-
C27alk	232	19.8	36.0	-
C28alk	48.0	14.8	14.9	-
C29alk	143	24.4	35.6	-
C30alk	113	36.1	40.5	-
C31alk	-	-	-	-
C32alk	129	52.0	72.2	-
C33alk	-	-	-	-
C34alk	165	62.0	81.3	10.2
ALKANES	5240	1420	2380	779
UCM	53.5	16.8	21.7	3.53

Key: - = bad surrogates

Table II-6. Alkane and PAH hydrocarbon analysis results of benthic sediments that were excluded from Table II-3 due to extreme surrogate recoveries (denoted by \*). See Table II-3 legend for further explanation of symbols and conventions.

Table II-7. Alkane and PAH hydrocarbon analysis results of sediment core samples that were excluded from Table II-4 due to extreme surrogate recoveries (denoted by \*). See Table II-4 legend for further explanation of symbols and conventions.

Table II-8. Method detection limits for PAH and alkane analytes for this study. Method detection limits (MDL's) were estimated for each analyte following the procedure described in Appendix B, 40 CFR Part 136. Detection limits are expressed as absolute mass, and sample-specific detection limits were calculated as the ratio of these masses and the sample dry weight.

Table II-7 Compromised Sediment Cores

Station	Bay of	East NW	Snug
Name (#)	Isles (1)	Bay (3)	Harbor (11)
Date collected	Sept 91	June 91	June 91
Depth (m)	10	20	10
Core Depth (cm)	8.5 - 10.5	1.0 - 4.0	1.0 - 5.0
Mean wet wt. (g)	10.2	10.0	10.0
Mean dry wt. (g)	4.50	5.39	7.41
Recovery	-	-	-

Mean PAH's(ng/g)

Naph	10.4	-	3.99
Menap2	12.1	2.98	1.28
Menap1	8.06	-	-
Dimeth	11.9	4.53	-
C2naph	32.5	12.3	-
Trimeth	7.07	1.94	-
C3naph	34.2	11.3	-
C4naph	13.9	5.10	-
Biphenyl	-	-	-
Acenthy	-	-	-
Acenrhe	-	-	-
Fluorene	8.36	-	-
C1fluor	13.7	-	-
C2fluor	18.1	5.64	-
C3fluor	7.45	3.61	-
Dithio	-	-	-
C1dithio	2.65	2.33	-
C2dithio	2.88	6.72	-
C3dithio	2.20	11.2	-
Phenanth	8.24	5.63	1.82
Mephen1	-	-	-
C1phenan	27.0	12.4	-
C2phenan	21.7	13.5	-
C3phenan	14.7	23.1	-
C4phenan	-	14.6	-
Anthra	-	-	-
Fluorant	4.85	7.04	-
Pyrene	4.21	4.51	-
C1fluora	8.29	10.0	-
Benanth	A	A	-
Chrysene	A	A	-
C1chrys	A	A	-
C2chrys	A	A	-
C3chrys	A	A	-
C4chrys	A	A	-
Benzobfl	8.99	20.1	A
Benzokfl	-	-	A
Benepy	6.57	20.6	A
Benapy	-	8.96	A
Perylene	106	63.7	A
Indeno	-	4.53	A
Dibenz	1.31	2.78	A
Benzop	3.74	8.51	A

Mean  
Total Aromatics 276 218 7.09  
(w/o Perylene)

Mean Alkanes(ng/g)

C10alk	18.6	-	-
C11alk	16.3	-	-
C12alk	16.3	-	-
C13alk	21.9	-	-
C14alk	30.1	-	-
C15alk	-	42.4	-
C16alk	37.5	-	-
C17alk	132	123	-
Pristane	-	1060	51.2
C18alk	-	-	-
Phytane	-	-	-
C19alk	39.2	18.9	-
C20alk	-	-	-
C21alk	40.5	20.2	-
C22alk	-	16.0	-
C23alk	82.3	-	-
C24alk	-	-	-
C25alk	536	-	-
C26alk	-	-	-
C27alk	381	161	-
C28alk	42.4	-	-
C29alk	294	94.1	-
C30alk	69.2	79.6	-
C31alk	-	-	-
C32alk	-	88.5	-
C33alk	-	-	-
C34alk	-	145	-
ALKANES	4590	4060	A
UCM	-	34.8	8.12

Key: \* = bad surrogates

Table II-8 Method Detection Limits - ABL Sediment (ng)

Naph	10.1
Menap2	9.44
Menap1	20.6
C1naph	30.0
Dimeth	19.5
C2naph	19.5
Trimeth	9.48
C3naph	9.46
C4naph	9.48
Biphenyl	43.0
Acenthy	25.0
Acenrhe	12.1
Fluorene	18.3
C1fluor	18.3
C2fluor	18.3
C3fluor	18.3
Dithio	9.64
C1dithio	9.64
C2dithio	9.64
C3dithio	9.64
Phenanth	13.3
Mephen1	27.2
C1phenan	27.2
C2phenan	27.2
C3phenan	27.2
C4phenan	27.2
Anthra	33.2
Fluorant	9.12
Pyrene	10.4
C1fluora	9.12
Benanth	3.34
Chrysene	26.4
C1chrys	26.4
C2chrys	26.4
C3chrys	26.4
C4chrys	26.4
Benzobfl	12.2
Benzokfl	7.96
Benepy	12.1
Benapy	32.2
Perylene	11.7
Indeno	6.80
Dibenz	4.94
Benzop	9.34

Alkanes(ng)

C10alk	61.8
C11alk	44.8
C12alk	67.0
C13alk	57.6
C14alk	45.0
C15alk	202
C16alk	88.4
C17alk	114
Pristane	210
C18alk	242
Phytane	242
C19alk	55.0
C20alk	108
C21alk	4.20
C22alk	62.6
C23alk	222
C24alk	350
C25alk	75.4
C26alk	212
C27alk	170
C28alk	141
C29alk	152
C30alk	186
C31alk	186
C32alk	242
C33alk	242
C34alk	145

**APPENDIX III**  
**QUALITY ASSURANCE DATA**

Table III-1.--Summary of calibrated PAH concentrations measured in reference samples.

Table III-2.--Summary of calibrated PAH concentrations measured in calibration stability samples.

Table III-3.--Summary of calibrated PAH concentrations measured in spiked method blank samples.

Table III-4.--Summary of alkane concentrations measured in calibration stability samples.

Table III-5.--Summary of alkane concentrations measured in reference samples.

Table III-6.--Summary of alkane concentrations measured in spiked blank accuracy evaluation standards.

Table III-7.--Summary of alkane concentrations measured in NIST-derived accuracy evaluation standards (QA-CH-2).

Table III-1.--Summary of calibrated PAH concentrations measured in reference samples. Two reference samples were processed and analyzed with each batch of 12 sediment samples. Listed below for each calibrated PAH is (1) the mean measured concentration, calculated from all the reference samples analyzed; (2) the standard deviation associated with (1); (3) the coefficient of variation (CV), calculated as 100 times the ratio of (2) and (1), and the number, n, of reference samples included for these calculations. A total of 29 batches were analyzed; n is less than twice this number due to unacceptable recovery of associated deuterated surrogate standards. Except for dibenzothiophene, which was purchased commercially, the PAH's in these reference samples were derived from Standard Reference Material 1491, supplied by NIST. The concentrations reported are ng PAH/g.

Aromatic Hydrocarbon	(1) Mean	(2) SD	(3) CV (%)	n
Naph	909	68.99	7.6	51
Menap2	1122	82.42	7.3	51
Menap1	731	53.28	7.3	51
Dimeth	481	76.18	15.8	56
Trimeth	254	17.01	6.7	56
Biphenyl*	211	17.48	8.3	39
Acenthy	32	3.59	11.3	56
Acenthe	31	4.89	15.6	56
Fluorene	114	23.69	20.9	56
Dithio	136	19.77	14.6	56
Phenanth	668	76.52	11.5	56
Mephen1	222	78.20	35.3	56
Anthra	102	21.32	20.9	56
Fluorant	507	53.88	10.6	56
Pyrene	452	51.56	11.4	56
Benanth	192	24.95	13.0	54
Chrysene	319	63.26	19.8	54
Benzobfl	657	120.2	18.3	54
Benzokfl**				54
Benepy	289	58.27	20.2	54
Benapy	142	27.88	19.6	54
Perylene	260	43.32	16.6	54
Indeno	143	29.80	20.9	54
Dibenz	44	17.49	40.2	54
Benzop	138	22.29	16.2	54

\* Excluding results from 1 batch of reference material that was consistently elevated by a factor of about 9.

\*\* Below MDL in the reference samples

Table III-2.--Summary of calibrated PAH concentrations measured in calibration stability samples. A mid-level calibration standard (prepared from NIST standards) was analyzed in the middle and near the end of each batch of 12 sediment samples, to verify the accuracy and stability of the calibration curve determined initially for the batch. Listed below for each calibrated PAH is (1) the mean measured concentration, calculated from all the verification standards analyzed; (2) the standard deviation associated with (1); (3) the coefficient of variation (CV), calculated as 100 times the ratio of (2) and (1); (4) the nominal concentration of the standard; (5) the percent accuracy, calculated as 100 times the ratio of (1) and (4); and (6) the number, n, of verification standards included for these calculations. A total of 29 batches were analyzed; n may be less than twice this number due to unacceptable recovery of associated deuterated surrogate standards (see Methods section). Concentrations are ng PAH/g, assuming a sample aliquot of 1 g.

Aromatic Hydrocarbon	Mean	SD	CV (%)	Expected Value	Percent Accuracy	n
Naph	344.6	7.48	2.2	345	99.9	58
Menap2	396.0	9.63	2.4	395	100.2	58
Menap1	415.2	8.49	2.0	415	100.0	58
Dimeth	358.2	10.3	2.9	360	99.5	58
Trimeth	326.8	8.28	2.5	330	99.0	58
Biphenyl	347.3	11.9	3.4	350	99.2	58
Acenthy	340.4	15.1	4.4	348	97.8	58
Acenthe	367.4	10.4	2.8	364	100.9	58
Fluorene	365.2	11.9	3.3	364	100.3	58
Dithio	386.9	15.4	4.0	400	96.7	58
Phenanth	348.6	11.2	3.2	351	99.3	58
Mephen1	344.1	11.7	3.4	350	98.3	58
Anthra	393.6	15.6	4.0	391	100.7	58
Fluorant	288.8	15.2	5.2	296	97.6	58
Pyrene	288.4	14.3	4.9	295	97.8	58
Benanth	180.0	20.2	11.2	180	100.0	56
Chrysene	341.6	75.8	22.2	352	97.0	56
Benzobfl	249.8	24.2	9.7	263	95.0	55
Benzokfl	271.4	22.6	8.3	279	97.3	55
Benepy	266.6	31.4	11.8	281	94.9	55
Benapy	329.9	20.3	6.1	340	97.3	55
Perylene	351.0	23.4	6.7	356	98.6	55
Indeno	304.1	29.7	9.8	314	96.8	55
Dibenz	256.5	34.4	13.3	259	99.0	55
Benzop	251.1	20.0	8.0	265	95.1	55

Table III-3.--Summary of calibrated PAH concentrations measured in spiked method blank samples. A method blank sample spiked with a NIST PAH standard was analyzed with each batch of 12 sediment samples, to assess method accuracy. Listed below for each calibrated PAH is (1) the mean measured concentration, calculated from all the verification standards analyzed; (2) the standard deviation associated with (1); (3) the coefficient of variation (CV), calculated as 100 times the ratio of (2) and (1); (4) the nominal concentration of the standard; (5) the percent accuracy, calculated as 100 times the ratio of (1) and (4); and (6) the number, n, of verification standards included for these calculations. A total of 29 batches were analyzed; n is less than this number due to unacceptable recovery of associated deuterated surrogate standards (see Methods section). Concentrations are ng PAH/g, assuming a sample aliquot of 1 g.

Aromatic Hydrocarbon	Mean	SD	CV (%)	Expected Value	Percent Accuracy	n
Naph	385	43.5	11.3	413	93.1	28
Menap2	478	31.6	6.6	473	101.1	28
Menap1	509	29.7	5.8	498	102.2	28
Dimeth	361	58.7	16.2	432	83.6	28
Trimeth	392	19.2	4.9	396	99.1	28
Biphenyl	410	27.1	6.6	360	114.0	28
Acenthy	398	36.7	9.2	418	95.1	28
Acenthe	429	23.0	5.4	437	98.1	28
Fluorene	480	81.4	17.0	436	110.1	28
Dibenzo	398	57.1	14.3	480	83.0	28
Phenanth	404	42.9	10.6	421	96.1	28
Mephen1	407	42.8	10.5	420	96.9	28
Anthra	429	44.4	10.4	469	91.4	28
Fluorant	340	37.3	11.0	355	95.7	28
Pyrene	338	38.7	11.4	353	95.8	28
Benanth	200	19.8	9.9	215	93.0	27
Chrysene	413	57.2	13.8	422	97.8	27
Benzobfl	352	36.8	10.5	315	111.8	27
Benzokfl	364	31.0	8.5	334	109.0	27
Benepy	391	41.3	10.6	337	116.0	27
Benapy	396	32.1	8.1	407	97.2	27
Perylene	406	38.6	9.5	427	95.2	28
Indeno	364	47.6	13.1	377	96.5	27
Dibenz	296	46.0	15.5	311	95.2	27
Benzop	317	34.5	10.9	317	100.1	27



Table III-4.--Summary of alkane concentrations measured in calibration stability samples. A mid-level calibration standard was analyzed in the middle and near the end of each batch of 12 sediment samples to verify the stability of the calibration curve determined initially for the batch. Listed below for each alkane is (1) the mean measured concentration, calculated from all the verification standards analyzed; (2) the standard deviation associated with (1); (3) the coefficient of variation (CV), calculated as 100 times the ratio of (2) and (1); (4) the nominal concentration of the standard; (5) the percent accuracy, calculated as 100 times the ratio of (1) and (4); and (6) the number, n, of calibration stability standards analyzed. Concentrations are ng alkane/g, assuming a sample aliquot of 1 g.

Alkane	Mean	SD	CV (%)	Spike Amount	Percent Accuracy	n
C10	12544	194.3	1.5	12740	98.5	58
C11	12014	131.8	1.1	12120	99.1	58
C12	12864	145.4	1.1	12890	99.8	58
C13	13361	172.2	1.3	13260	100.8	58
C14	12748	178.6	1.4	12740	100.1	58
C15	12027	132.8	1.1	11980	100.4	58
C16	13279	153.0	1.2	13180	101.8	58
C17	14649	627.3	4.3	14470	101.2	58
Pristane	13796	331.7	2.4	13550	101.8	58
C18	15255	242.8	1.6	15410	99.0	58
C19	13365	172.4	1.3	13490	99.1	58
C20	11956	173.7	1.5	12080	99.0	58
C21	11594	220.7	1.9	11750	98.7	58
C22	13357	200.4	1.5	13370	99.9	58
C23	11952	159.0	1.3	11980	99.8	58
C24	12430	164.5	1.3	12470	99.7	58
C25	11710	163.9	1.4	11760	99.6	58
C26	11614	222.3	1.9	11680	99.4	58
C27	4901	120.9	2.5	4930	99.4	58
C28	12915	492.0	3.8	13010	99.3	58
C29	11558	305.5	2.6	11650	99.2	58
C30	12190	297.7	2.4	12300	99.1	58
C32	11527	1187.0	10.3	11640	99.0	58
C34	11860	2374.7	20.0	11920	99.5	58

Table III-5.--Summary of alkane concentrations measured in reference samples. Two reference samples were processed and analyzed with each batch of 12 sediment samples. Listed below for each alkane is (1) the mean measured concentration, calculated from all the reference samples analyzed; (2) the standard deviation associated with (1); (3) the coefficient of variation (CV), calculated as 100 times the ratio of (2) and (1); and (4) the number, n, of reference samples included for these calculations. The reference spikes were prepared from commercially purchased alkanes. The concentrations reported are ng alkane/g.

Alkane	Mean	SD	CV (%)	n
C10	1010	362.5	33.0	58
C11	1338	231.4	17.3	58
C12	1713	145.6	8.5	58
C13	1969	211.2	10.7	58
C14	1879	233.3	11.9	58
C15	2355	371.9	15.8	58
C16	1790	104.7	5.8	58
C17	2199	299.9	13.6	58
Pristane	1197	158.3	13.2	58
C18	1435	105.0	7.3	58
Phytane	795	98.7	12.4	58
C19	1344	92.4	6.9	58
C20	1351	75.3	5.6	58
C21	1319	82.9	6.3	58
C22	1318	73.4	5.6	58
C23	1391	91.9	6.6	58
C24	1210	164.2	13.6	58
C25	1578	177.6	11.3	58
C26	1098	203.4	18.5	58
C27	1723	363.3	21.1	58
C28	825	274.7	33.3	58
C29	1764	170.8	9.7	58
C30	661	109.6	16.6	58
C32	477	82.8	17.4	58
C34	439	95.6	21.8	58

Table III-6.--Summary of alkane concentrations measured in spiked blank accuracy evaluation standards. One of these standards was analyzed at the end of each batch of 12 sediments to verify the accuracy of alkane determinations. Listed below for each alkane is (1) the mean measured concentration, calculated from all the verification standards analyzed; (2) the standard deviation associated with (1); (3) the coefficient of variation (CV), calculated as 100 times the ratio of (2) and (1); (4) the nominal concentration of the standard; (5) the percent accuracy, calculated as 100 times the ratio of (1) and (4); and (6) the number, n, of spiked blank samples analyzed. The concentrations reported are ng alkane/g, assuming a sample aliquot of 1 g.

Alkane	Mean	SD	CV (%)	Spike Amount	Percent Accuracy	n
C10	9789	831	8.5	10620	92.2	29
C11	10036	356	3.5	10100	99.4	29
C12	10962	400	3.6	10740	102.1	29
C13	11515	488	4.2	11050	104.2	29
C14	10590	534	5.0	10620	99.7	29
C15	10255	531	5.2	9980	102.8	29
C16	11403	530	4.7	10980	103.9	29
C17	12836	1867	14.5	12060	106.4	29
Pristane	12198	791	6.5	11290	108.0	29
C18	12655	625	4.9	12840	98.6	29
C19	11146	545	4.9	11240	99.2	29
C20	9979	520	5.2	10070	99.1	29
C21	9645	563	5.8	9790	98.5	29
C22	11415	448	3.9	11140	102.5	29
C23	10148	383	3.8	9980	101.7	29
C24	10477	409	3.9	10390	100.8	29
C25	9773	400	4.1	9800	99.7	29
C26	9620	430	4.5	9730	98.9	29
C27	4033	203	5.0	4110	98.1	29
C28	11073	583	5.3	10840	102.1	29
C29	9831	446	4.5	9710	101.2	29
C30	10271	441	4.3	10250	100.2	29
C32	9530	623	6.5	9700	98.3	29
C34	9575	910	9.5	9930	96.4	29

Table III-7.--Summary of alkane concentrations measured in NIST-derived accuracy evaluation standards (QA-CH-2). One of these standards was analyzed at the end of each batch of 12 sediments to verify the accuracy of alkane determinations. Listed below for each alkane is (1) the mean measured concentration, calculated from all the evaluation standards analyzed; (2) the standard deviation associated with (1); (3) the coefficient of variation (CV), calculated as 100 times the ratio of (2) and (1); (4) the nominal concentration of the standard, as determined by the National Institute of Standards and Technology; (5) the percent accuracy, calculated as 100 times the ratio of (1) and (4); and (6) the number, n, of NIST-derived accuracy evaluation samples analyzed. Concentrations are ng alkane/g, assuming a sample aliquot of 1 g.

Alkane	Mean	SD	CV (%)	Spike Amount	Percent Accuracy	n
C10	8586	431	5.0	9300	92.3	29
C11	8971	413	4.6	10580	84.8	29
C12	8711	375	4.3	9300	93.7	29
C13	8232	366	4.4	8700	94.6	29
C14	8105	294	3.6	8630	93.9	29
C15	7973	302	3.8	8480	94.0	29
C16	6961	259	3.7	7400	94.1	29
C17	6583	291	4.4	6830	96.4	29
Pristane	4003	258	6.4	4340	92.2	29
C18	5907	346	5.9	6410	92.2	29
Phytane	544	201	36.9	450	120.9	29
C19	5052	302	6.0	5480	92.2	29
C20	4912	296	6.0	5270	93.2	29
C22	4014	191	4.8	4280	93.8	29
C24	3011	142	4.7	3210	93.8	29
C26	2263	149	6.6	2360	95.9	29
C28	1450	137	9.4	1610	90.1	29
C30	1091	127	11.6	1160	94.1	29
C32	964	290	30.1	940	98.4	29
C34	1045	536	51.3	800	130.6	29