Exxon Valdez Oil Spill Restoration Project Final Report

Recovery of Sediments in the Lower Intertidal and Subtidal Environment

Restoration Project 93047-1
Final Report

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Study History: This study began as NRDA Air/Water Study Number 2 "Petroleum Hydrocarbon-Induced Injury to Subtidal Marine Sediment Resources" in 1989. Status reports under this study number were submitted in 1989 and 1990. In 1991, the number of the study was changed to Subtidal Study Number 1. The title remained the same. A status report under the new number was submitted in November 1991. The final report for Subtidal Study Number 1 was submitted in September 1994. No field work was performed in 1992. In 1993, Restoration Study Number 93047 "*Exxon Valdez* Restoration Project: Subtidal Monitoring" was initiated. The final report for Restoration Study Number 93047 was submitted in July 1995. Peer review comments were received on 25 October 1995. A paper titled "Contamination of Subtidal Sediments by Oil from the *Exxon Valdez* in Prince William Sound, Alaska" will appear in The *Exxon Valdez* Oil Spill Symposium Proceedings.

Abstract: Sediments were collected at ten locations in Prince William Sound in July 1993 to determine the geographical and bathymetric distribution of oil from the *Exxon Valdez* oil spill in the low intertidal zone and subtidal region. We sampled sediments at mean lower low water (0 m) and at five subtidal depths from 3 to 100 m. No *Exxon Valdez* oil was found in sediments at 0 m where the greatest mean intertidal concentration of total polynuclear aromatic hydrocarbons excluding perylene (54 ng/g) was observed at Moose Lips Bay. Subtidal sediments showed polynuclear aromatic hydrocarbon composition patterns similar to *Exxon Valdez* oil at three sites, Herring Bay, Northwest Bay and Sleepy Bay. Contamination of sediments by *Exxon Valdez* oil reached a depth of 20 m at Northwest Bay and Sleepy Bay. The greatest mean concentration of total polynuclear aromatic hydrocarbons excluding perylene in benthic sediments (1,231 ng/g) occurred at 20 m at Northwest Bay. In deep sediments (≥40 m) we found no evidence of weathered *Exxon Valdez* oil. The hydrocarbon concentrations in sediments at these depths were similar at reference and assessment locations. Petroleum hydrocarbons at the 100 m depth were chiefly from the Katalla source.

Key Words: *Exxon Valdez*, hydrocarbon concentrations, Prince William Sound, recovery, subtidal sediments

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TABLE OF CONTENTS

LIST OF TABLES

EXECUTIVE SUMMARY

In 1993, four years after the *Exxon Valdez* oil spill, we sampled subtidal sediments at ten locations in Prince William Sound to determine the geographical and bathymetric distribution of oil from the Spill in the sediments. We sampled sediments in July near mean lower low water and at five subtidal depths in the 3-100 m range.

Sediments at mean lower low water (0 m) at both assessment and reference sites showed no evidence of *Exxon Valdez* oil. The greatest mean concentration of total polynuclear aromatic hydrocarbons found in intertidal sediments in 1993 was at Moose Lips Bay (54 ng/g).

Subtidal sediments showed polynuclear aromatic hydrocarbon composition patterns similar to *Exxon Valdez* oil at three sites where oil had come ashore in 1989: Herring Bay, Northwest Bay and Sleepy Bay. Contamination of subtidal sediments by *Exxon Valdez* oil at oiled locations reached a depth of 20 m only at Northwest Bay and Sleepy Bay. In subtidal sediments the greatest concentration of *Exxon Valdez* oil was at the 20 m depth. The highest mean total polynuclear aromatic hydrocarbon concentration, where the *Exxon Valdez* oil-polynuclear aromatic hydrocarbon composition pattern was evident, was 1,231 ng/g in sediment collected at 20 m at Northwest Bay.

In deep sediments ($\geq$40 m) we found little evidence of *Exxon Valdez* oil. The total polynuclear aromatic hydrocarbon concentrations in sediments at these depths were similar at oiled and reference locations. The polynuclear aromatic hydrocarbon composition pattern characteristic of weathered *Exxon Valdez* oil was absent at these depths. The total polynuclear aromatic hydrocarbon concentration in the deepest sediments ($\geq$100 m) usually exceeded that at 40 m. Petroleum hydrocarbons at the 100 m depth were chiefly from the Katalla source.

LIST OF FIGURES

INTRODUCTION

In the months following the *Exxon Valdez* oil spill (EVOS) petroleum hydrocarbons attributable to *Exxon Valdez* oil (EVO) were observed in subtidal sediments in a number of locations over a broad geographical range in Prince William Sound (PWS). Patterns in the distribution of the concentration of individual polynuclear aromatic hydrocarbon (PAH) analytes in subtidal sediments were similar to the PAH composition pattern found in EVO (EVO-PAH) at 80% of the locations where oil had come ashore in 1989 (O'Clair et al., 1996). This result indicated that detectable quantities of EVO were transported to the subtidal region at a large proportion of those locations where oil had become stranded on shore after the Spill. It is possible that oil was transported to the subtidal region at the remaining 20% of the locations where oil had come ashore in 1989, but that the oil was either not present subtidally in detectable quantities or was missed by our sampling methodology. The greatest concentration of total polynuclear aromatic hydrocarbons (TPAH, excluding perylene) in subtidal sediments exhibiting the EVO-PAH composition pattern averaged 1,486 ng/g in sediments collected at the 3-m depth at Northwest Bay in July 1989. Subtidal EVO contamination was largely confined to shallow depths (3-20 m) adjacent to shorelines where moderate to heavy oiling occurred. Between 1989 and 1991, concentrations of petroleum hydrocarbons derived from EVO decreased and became more patchily distributed in subtidal sediments, and sediment hydrocarbons became more difficult to match with EVO. By 1991, the EVO-PAH pattern was consistently present in subtidal sediments only at Northwest Bay; although, the EVO-PAH pattern occurred sporadically in the subtidal sediments of three other moderately to heavily oiled locations. Wolfe et al. (1994) estimated that about 13% of the spilled oil was transported to the subtidal region and remained there as of October 1992. Although most of the oil transported subtidally is thought to occur in the Gulf of Alaska (Wolfe et al. 1994), a substantial amount may have remained in the subtidal sediments of PWS in 1993.

The purpose of this report is to describe the geographical and bathymetric distribution of petroleum hydrocarbons from the EVOS in subtidal sediments in PWS four years after the Spill. Measurements of the chemical composition of the hydrocarbons were used to distinguish EVO from other sources of petroleum hydrocarbons. We report here the extent to which EVO has persisted in low intertidal and subtidal sediments between 1989 and 1993; thereby, providing information on the natural recovery of the subtidal sediments from EVO contamination. Because Karinen et al. (1993) measured background petroleum hydrocarbon concentrations in intertidal sediments before the EVOS, we can report the degree of recovery of low intertidal sediments to prespill concentrations.

OBJECTIVES

A. Determine the composition and concentration of petroleum hydrocarbons from the EVOS in intertidal and subtidal sediments (0-100 m) in PWS by gas chromatography/mass spectrometry.

1. Determine the concentrations of TPAHs and *n*-alkanes in subtidal sediments and compare with concentrations in intertidal sediments and in subtidal sediments in previous years after the EVOS.

B. Determine the distribution of EVO with bathymetric depth and compare with bathymetric distribution of EVO in previous years.

C. Determine persistence of EVO in subtidal sediments over time.

D. Compare the distribution of EVO in subtidal sediments with those of hydrocarbons from other sources.

METHODS

Study Sites

The geographical nomenclature in this report follows O'Clair et al. (1996). Geographical position is described by three terms: location, site, and station. Location refers to a general area where one or more sampling sites were established (e.g., Northwest Bay). Site refers to a relatively small geographical area containing the bathymetric transect used to sample various bottom depths for sediments. Only one site was sampled at each location in 1993. The origin of the bathymetric transect (where it intersected the shore) is shown as the geographical position of each site in Table 1 and Figure 1. Station refers a specific spot along a bathymetric transect where sediment samples were collected (e.g., the 20 m depth station). Assessment locations are those where EVO was reported to have come ashore. Reference locations are those where no oil came ashore. Sediments were sampled at ten sites (five reference sites and five assessment sites; Table 1, Fig. 1) in PWS in 1993. Dates of sampling in 1993 were 8-16 July (Table 1).

Sediment Collection

Standard operating procedures were adopted for the collection of all sediments (Appendix I). Intertidal collections were made at about mean lower low water (MLLW, 0 m); actual sampling elevation was within the range of +0.5 to -1 m depending on the distribution of fine sediments. Depending on the tide stage, intertidal sediments were collected by beach teams or by divers. Subtidal sediment sample collections were made at depths of 3, 6, 20, 40, and 100 m below MLLW. Collections at 3, 6, and 20 m were made by divers on transects laid along the appropriate isobath. Three samples, each a composite of eight subsamples collected randomly along a 30 m transect laid along the appropriate isobath, were taken at each of the shallow stations (0-20 m).

Table 1.--Location of sites and date stations were sampled at each site where intertidal and subtidal sediments were collected in 1993 in PWS. Six stations were sampled at each site. Depths sampled were 0, 3, 6, 20, 40, and 100 m.

Site		North Latitude	West Longitude	
No.[1]	Name	o ' "	o ' "	Date
Reference Sites				
10	Drier Bay	60 19 12	147 44 00	11 July
26	Lower Herring Bay	60 24 12	147 47 48	10 July
28	Moose Lips Bay	60 12 30	147 18 06	13 July
32	Olsen Bay	60 45 05	146 11 13	16 July
45	Zaikof Bay	60 16 53	147 02 19	13 July
Assessment Sites				
5	Bay of Isles	60 23 00	147 44 54	15 July
20	Herring Bay	60 25 51	147 47 06	9 July
31	Northwest Bay	60 33 07	147 34 36	8 July
38	Sleepy Bay	60 04 01	147 50 11	12 July
40	Snug Harbor 25	60 14 13	147 43 58	14 July

[1] Site numbers follow O'Clair et al. (1996).

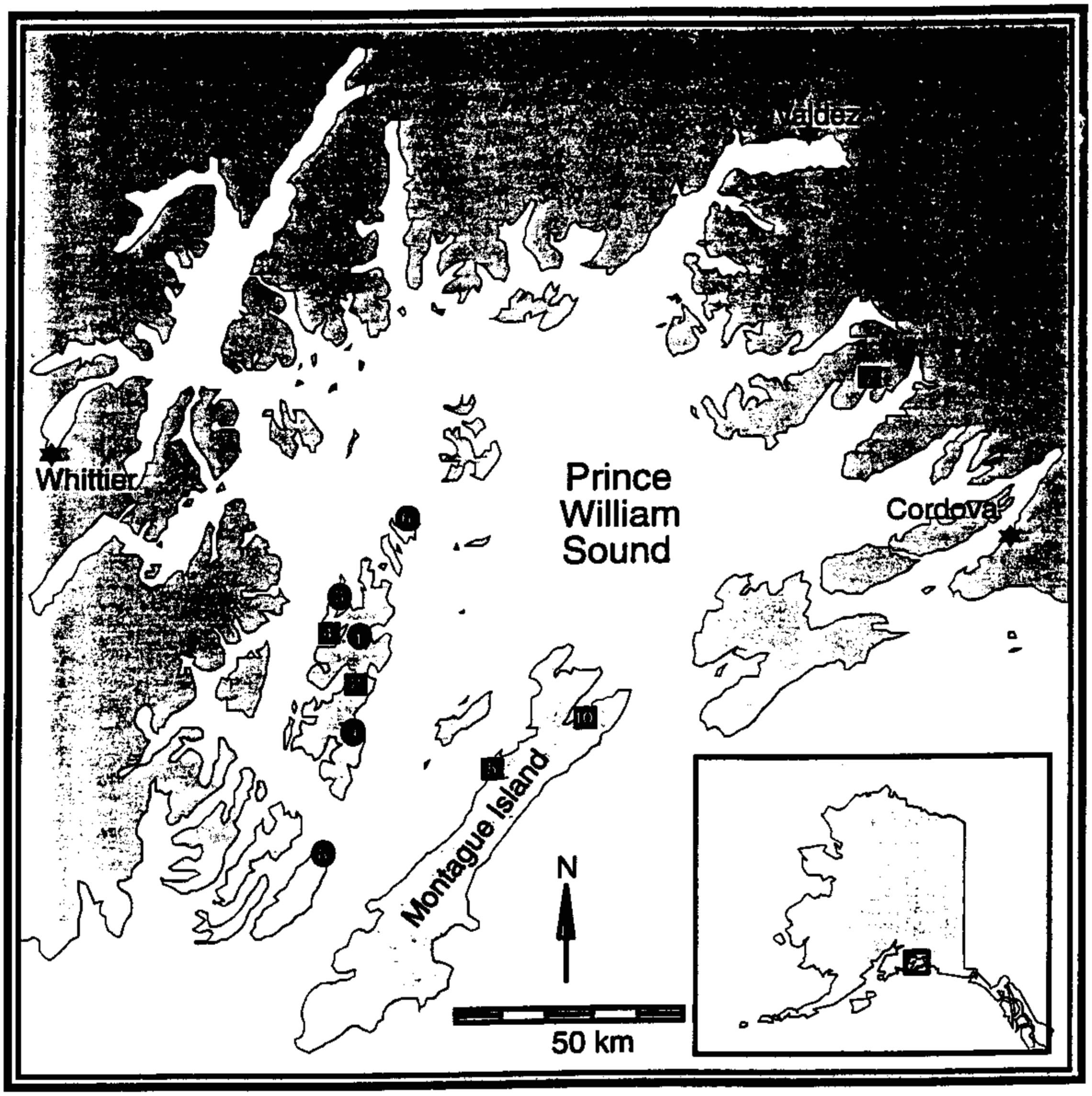

Figure 1.--Distribution of assessment (circles) and reference (squares) sites sampled in 1993 in PWS. See Table 1 for the geographical coordinates of each site. Numbered sites are: 1) Bay of Isles; 2) Drier Bay; 3) Herring Bay; 4) Lower Herring Bay; 5) Moose Lips Bay; 6) Northwest Bay; 7) Olsen Bay; 8) Sleepy Bay; 9) Snug Harbor 25; 10) Zaikof Bay.

A stainless-steel Smith-McIntyre grab was used to collect sediments at 40 and 100 m depths. Remote sampling with a grab included three grabs taken at each station. Four cores were removed from randomly selected points on the surface of the sediment contained in each grab. The subsamples were combined to form one sample per grab.

All samples collected by hand (including those removed by hand from the grab) were taken from the surface (top 0-2 cm) of the sediment column. Samples taken by hand in the intertidal region or by divers were collected with a stainless-steel core tube or spoon. Each subsample was transferred to a sample jar by a spatula. The core tube and the spatula were washed, dried, and rinsed with methylene chloride between sampling periods. Sample jars certified hydrocarbon-clean according to Environmental Protection Agency standards were used to store sediments. Samples were kept cool after collection and frozen within a few hours. Appropriate blanks were collected at each site.

Chain-of-custody procedures were followed after sample collection. The samples were packed in boxes which were sealed with custody tape. Boxes of samples were placed in coolers with enough blue ice to keep the samples frozen while in transit from the field to the Laboratory. All samples were accompanied by chain-of-custody forms from the field to the Auke Bay Laboratory for temporary storage in a locked freezer before shipment to the analytical facility. At least one field worker traveled with the samples from the field to the Laboratory. At the Auke Bay Laboratory, custody of the samples was signed over to a representative of Technical Services Study Number 1, Hydrocarbon Analytical Support Services and Analysis of Distribution and Weathering of Spilled Oil.

Hydrocarbon and Data Analysis

Sediment samples were analyzed for petroleum hydrocarbons by means of gas chromatography/mass spectrometry at the Auke Bay Laboratory. Short et al. (In press (a)) summarize the analytes, methods, detection limits, and the accuracy and precision of the methods used in the chemical analysis. For a detailed description of the analytical methods used in this study see Short et al. (In press(a)) and the references therein.

Results of the chemical analysis were screened on the basis of surrogate recoveries and minimum detection limits (MDLs). Individual analytes and the summary statistics affected by them [e.g., total polynuclear aromatic hydrocarbons including perylene (∑PAH), TPAH, total normal alkanes (TNA, i.e the sum of the normal alkanes), and total hydrocarbons] were excluded from the analysis if the recoveries of corresponding analyte surrogates fell outside the range 30-150%. Concentrations of individual analytes reported below MDLs were replaced by "0's" for our analyses. The MDL for aromatic hydrocarbons was 1 ng/g, and for aliphatic hydrocarbons was 10 ng/g. These are conservative MDL concentrations. All concentrations above the MDLs were considered to have the same accuracy and precision. Hydrocarbon concentrations are reported on a dry weight basis to three significant figures when concentrations exceeded 10 ng/g, and to two significant figures for lower concentrations. A total of 180 sediment samples was analyzed for hydrocarbons from the ten sites sampled.

The high sulfur content of EVO helped to distinguish it from other PAH sources. In particular, concentrations of alkyl-dibenzothiophenes that reach at least 20% of the concentrations of alkyl-phenanthrenes are characteristic of higher-sulfur oils such as EVO, and the presence of alkyl-chrysenes (at concentrations 3% or more of those of alkyl-phenanthrenes) distinguishes EVO from products refined from it (Short et al., In press (b)). Accordingly, we used the following criteria to compare hydrocarbon concentrations in sediments in individual composite samples with those in EVO. The pattern of PAH concentrations in the sediment samples was judged similar to EVO if it consistently met each of three criteria in all replicated samples: (1) the ratio of alkyl dibenzothiophenes (summed) to alkyl phenanthrenes (summed) exceeded 0.20; (2) the ratio of alkyl chrysenes (summed) to alkyl phenanthrenes (summed) exceeded 0.03; and (3) the concentration of alkyl phenanthrenes (summed) exceeded 20 ng/g. This latter criterion was necessary to insure that chrysenes would be detected if present. Although these criteria for distinguishing the EVO source are not unique to this paper (e.g. see O'Clair et al., 1996; and Babcock and Short, 1996) they have not been used widely and should be considered *ad hoc*.

The carbon preference index (CPI; Farrington and Tripp 1977) was used to distinguished oiled from non-oiled sediments. The index has the form:

$$CPI=\frac{2(n\text{-}C_{27}+n\text{-}C_{29})}{n\text{-}C_{26}+2n\text{-}C_{28}+n\text{-}C_{30}}$$

where $n\text{-}C_i$ is the concentration (ng/g) of the *n*-alkane of carbon number I. The CPI is near 1 for oiled sediments. Values from 5 to 7 indicate unoiled sediment.

Concentrations shown in the text are given as mean concentration ● the standard error of the mean. Unless otherwise noted means are the average of three replicates. Coefficients of variation shown in Tables 2 and 3 are corrected for bias (Sokal and Rohlf 1981). The unbiased estimator is:

$$V*=(1+\tfrac{1}{4n})V$$

Table 2.--Concentration (ng/g) of TPAH in sediments from all stations in PWS, Alaska sampled in 1993. Numbers in the body of the table are mean TPAH and coefficient of variation (in parentheses). Numbers are preceded by an asterisk where the PAH composition pattern matched weathered EVO in at least one replicate. Unless otherwise noted the number of replicates is three. ND indicates that all TPAH analytes were below detection limits.

Site			Depth					
No.	Name	Date	0 m	3 m	6 m	20 m	40 m	100 m
Reference Sites								
10	Drier Bay	11 Jul	0.36 (93.9)	2.67(103.7)	38.8 (44.0)	138 (41.2)	214 (93.8)	931 (9.3)
26	Lower Herring Bay	10 Jul	2.13 (74.4)	1.80 (34.6)	0.84 (118.0)	9.82 (62.2)	50.1 (55.2)	520 (16.0)
28	Moose Lips Bay	13 Jul[a]	54.0 (59.7)	106 (36.0)	108 (26.4)	155 (67.0)	280 (13.2)	449 (45.7)
32	Olsen Bay	16 Jul[b]	7.72 (50.5)	25.0 (16.7)	97.7 (34.3)	167 (41.4)	172 (54.2)	469 (12.0)
44	Zaikof Bay	13 Jul	8.28 (14.2)	88.4 (3.7)	121 (27.3)	178 (11.9)[c]	290 (19.5)	377 (48.2)
Assessment Sites								
5	Bay of Isles	15 Jul	ND	1.06 (15.0)	74.3 (143.8)	393 (34.0)	181 (41.8)	686 (20.3)
20	Herring Bay	9 Jul	18.2 (97.1)	* 320 (59.0)	* 58.2 (55.5)	97.5 (85.6)	64.0 (70.2)	351 (54.5)
31	Northwest Bay	8 Jul	24.5 (47.6)	* 140 (105.9)	* 524 (68.1)	* 1231 (53.8)	151 (8.6)	687 (6.0)
38	Sleepy Bay	12 Jul[d]	9.98 (35.4)	13.5 (71.4)	8.14 (65.4)	* 963 (44)[c]	134 (39.4)	550 (13.8)
40	Snug Harbor 25	14 Jul	10.0 (26.2)	5.06 (63.2)	27.0 (168.4)	35.1 (13.3)	184 (28.2)	724 (3.0)

a. Stations at 40 and 100 m at Moose Lips Bay sampled on 12 July.

b. Stations at 40 and 100 m at Olsen Bay sampled on 15 July.

c. $n = 2$

d. Stations at 40 and 100 m at Sleepy Bay sampled on 11 July.

Table 3.--Concentration of TNA in sediments from all stations in PWS, Alaska sampled in 1993. Numbers in the body of the table are mean TNA (ng/g) and coefficient of variation (in parentheses). Unless otherwise noted the number of replicates is three.

Site			Depth					
No.	Name	Date	0 m	3 m	6 m	20 m	40 m	100 m
Reference Sites								
10	Drier Bay	11 Jul	30.9 (110)	79.8(62.4)	732 (42.8)	1042 (24.3)	597 (83.3)	1708 (15)
26	Lower Herring Bay	10 Jul	40.3 (42.7)	15.4 (126.2)	5.32 (187.6)	62.6 (47.9)	204 (40.1)	1271 (9.1)
28	Moose Lips Bay	13 Jul[a]	76.4 (88.4)	116 (34.9)	167 (30.6)	106 (29.5)	321 (25.3)	535 (44.4)
32	Olsen Bay	16 Jul[b]	413 (47.5)	912 (42.2)	1462 (64.1)	1136 (20)	394 (53.4)	823 (2.9)
44	Zaikof Bay	13 Jul	27.1 (68.3)	198 (33.6)	254 (30.3)	242 (46.8)[c]	427 (32.2)	865 (106.7)
Assessment Sites								
5	Bay of Isles	15 Jul	11.1(98.7)	45.4 (24.6)	1392 (123)	2806 (26.5)	734 (46.8)	1211 (14.2)
20	Herring Bay	9 Jul	184 (36.6)	1089 (33)	453 (31.6)	285 (39)[c]	162 (90)	701 (65)
31	Northwest Bay	8 Jul	981 (80.4)	357 (51.9)	762 (13.3)	3288 (55.2)	379 (6.8)	1171 (19.4)
38	Sleepy Bay	12 Jul[d]	53.4 (34.7)	39 (14.2)	73.6 (67)	837 (81.7)[c]	108 (59.7)	633 (3.4)
40	Snug Harbor 25	14 Jul	7.6 (187.6)	15.4 (63.1)	289 (180)	94.4 (22)	684 (19)	1176 (9.3)

a. Stations at 40 and 100 m at Moose Lips Bay sampled on 12 July.

b. Stations at 40 and 100 m at Olsen Bay sampled on 15 July.

c. $n = 2$

d. Stations at 40 and 100 m at Sleepy Bay sampled on 11 July.

RESULTS

Assessment Sites

Five assessment locations were sampled in 1993; four (Herring Bay, Northwest Bay, Sleepy Bay, and Snug Harbor) were heavily oiled in the upper intertidal zone during the EVOS. The fifth, Bay of Isles, is a protected bay on the eastern side of Knight Island that was sporadically oiled during the Spill.

Intertidal Stations

We found relatively low aromatic hydrocarbon concentrations in intertidal sediments (0 m station) at the five assessment sites sampled in 1993 (Table 2). This station was located at a tidal height of about MLLW. Most of the EVO was stranded at higher elevations on the shore (about mean high water). The highest mean TPAH concentration found at the 0 m station of assessment locations sampled in 1993 was 24.5 ± 6.2 ng TPAH/g dry sediment weight. This concentration was found at Northwest Bay, and it was markedly less than that found in intertidal sediments at Northwest Bay in July 1989 (Table 2, Fig. 2). At three of the other assessment sites sampled in July 1993, the mean TPAH concentrations were 18.2 ± 9.4, 10 ± 1.9, and 10 ± 1.4 ng TPAH/g sediment in 0 m sediments from Herring Bay, Sleepy Bay and Snug Harbor 25, respectively. All PAH analytes in intertidal sediments collected at Bay of Isles were below detection limits (Table 2). The TPAH concentration never exceeded 36 ng TPAH/g sediment in 0 m sediment samples from assessment locations in 1993. The PAH concentrations in sediments at intertidal stations at the five assessment locations were too low to permit the discrimination of a PAH composition pattern consistent with weathered EVO.

The TNA concentration in intertidal sediments at those assessment sites sampled in 1993 was relatively low. We found the highest mean TNA concentration (981 ± 420 ng/g) at Northwest Bay where the highest assessment site TPAH was found (Tables 2 and 3). This mean TNA concentration was more than twice as high as the highest mean TNA concentration at any reference station. The ratio of mean TNA to mean TPAH at assessment sites ranged greatly from 0.76 (Snug Harbor) to 40 (Northwest Bay).

The CPI values for intertidal sediments generally could not be calculated because the concentrations of alkanes C_{26}, C_{28} and/or C_{30} were below detection limits. Only those from Northwest Bay could be calculated. There, a mean CPI of 1.1 indicated the presence of oil. However, the PAH concentrations in the Northwest Bay sediments were too low to permit us to conclude that the oil was weathered EVO.

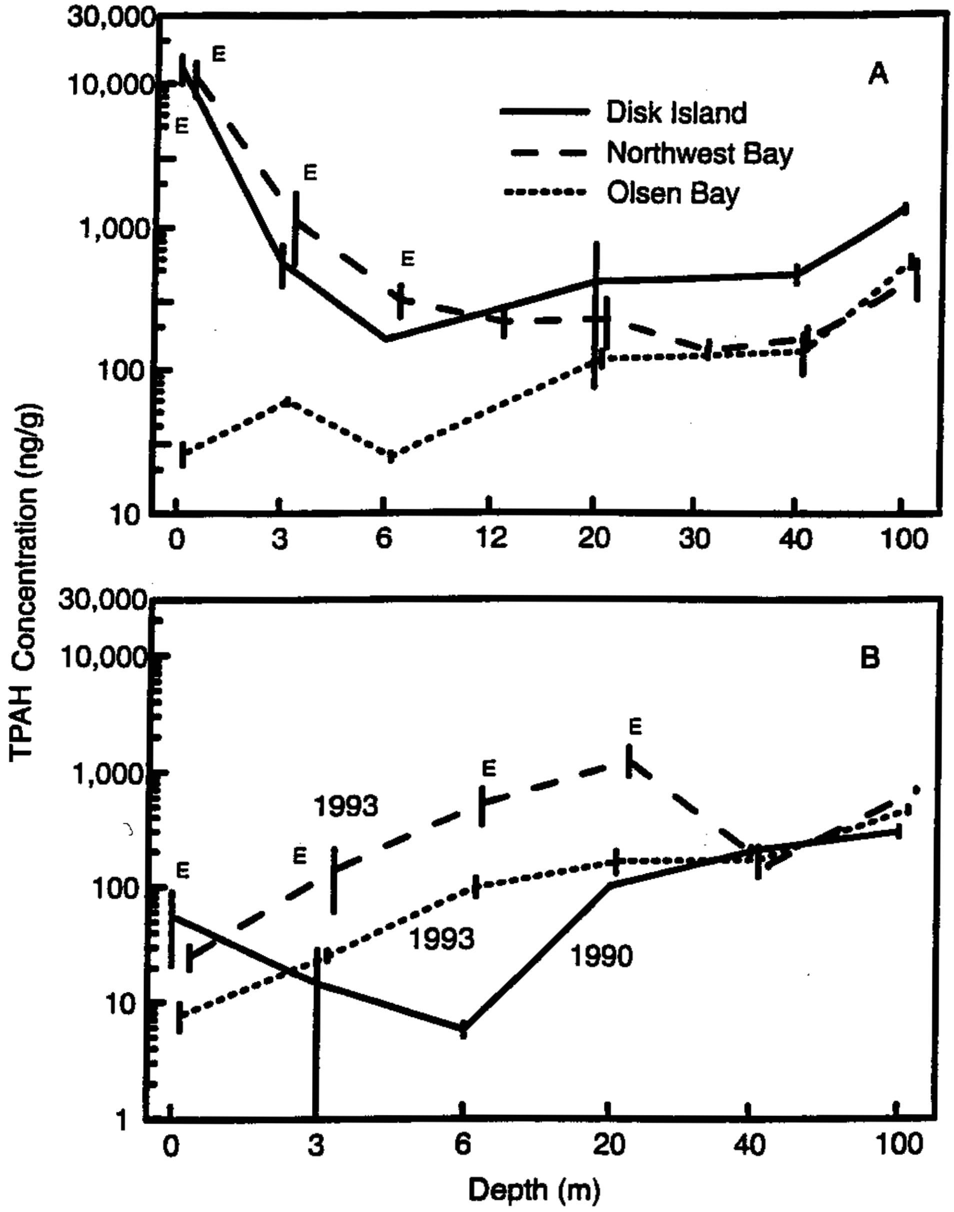

Figure 2.--Depth distribution of mean concentrations of TPAHs at Disk Island, Northwest Bay and Olsen Bay in July 1989 (A) and from 1 to 4 years later (B). Disk Island was not sampled after 1990 because of low hydrocarbon concentrations in intertidal and shallow subtidal sediments there in July 1990. Error bars are ± one standard error of the mean. An "E" identifies those sediments that exhibited a PAH analyte pattern characteristic of EVO.

Shallow Subtidal Stations

Concentrations of EVO hydrocarbons in shallow subtidal sediments (3-20 m) at assessment sites were usually greater than those in intertidal sediments at those sites. Shallow subtidal sediment samples were collected at all locations where intertidal samples had been collected. At the two locations (Northwest Bay and Herring Bay) where we found the highest mean TPAH concentrations in intertidal sediments; we found substantially higher mean TPAH concentrations in shallow subtidal sediments. This increase was more pronounced at Northwest Bay than at Herring Bay (Table 2). At the three other assessment sites TPAH concentrations in shallow subtidal sediments were generally about the same as or greater than TPAH concentrations in intertidal sediments.

We found a PAH composition pattern consistent with weathered EVO in subtidal sediments in three (Northwest Bay, Herring Bay and Sleepy Bay) of the five assessment sites sampled in 1993. At Northwest Bay, the EVO-PAH pattern was consistently present in subtidal sediments from 3 m to 20 m (Fig. 2). The mean TPAH concentration in these sediments ranged from 140 ± 79.1 ng/g at the 3 m depth to 1231 ± 353 ng/g at the 20 m depth (Table 2).

At Herring Bay, the EVO-PAH pattern was found in all three samples collected at the 3 m depth. The mean TPAH concentration in these samples was 320 ± 100 ng/g (Table 2). One of three samples collected at the 6 m depth at Herring Bay showed the EVO-PAH pattern. The TPAH concentration in that sample was 87.1 ng/g. The second of the three samples from 6 m exhibited a PAH pattern indicating contamination by diesel oil because: (1) alkyl chrysenes were absent [Reference to a PAH in the plural (e.g. chrysenes) denotes the unsubstituted PAH together with the alkyl-substituted homologues collectively as a group]; (2) alkyl phenanthrenes (summed) exceeded 20 ng/g; and (3) the ratio of alkyl dibenzothiophenes (summed) to alkyl phenanthrenes (summed) exceeded 0.20. The concentrations of PAH analytes (especially alkyl phenanthrenes which were present in the aggregate at a concentration below 20 ng/g) in the third sample from 6 m at Herring Bay were too low to discern a petroleum hydrocarbon pattern. Mean TPAH concentrations were less than 320 ng/g in shallow subtidal sediments from depths greater than 3 m at Herring Bay (Table 2).

The EVO-PAH pattern was found in one sample from Sleepy Bay. The sample was collected at the 20 m depth, and it contained a TPAH concentration of 697 ng/g. The other two samples from the 20 m depth exhibited a PAH pattern characterized by: (1) a ratio of alkyl dibenzothiophenes to alkyl phenanthrenes less than 0.20; (2) a ratio of alkyl chrysenes to alkyl phenanthrenes that exceeded 0.03; and (3) a concentration of alkyl phenanthrenes that exceeded 20 ng/g. This pattern is indicative of petroleum hydrocarbons from the Katalla oil seep identified by Page et al. (1994); although, another possible source for the Katalla hydrocarbons may be coal (O'Clair et al., 1996 and Short et al., In press(a)).

As with TPAH, the TNA concentration in shallow subtidal sediments at assessment sites tended to exceed the intertidal TNA concentration. A notable exception was Northwest Bay where the intertidal TNA concentration exceeded that at the 3 and 6 m depths (Table 3). The greatest mean TNA concentration (3288 ± 968 ng/g) found in subtidal sediments in 1993 occurred in sediments exhibiting the EVO-PAH pattern from the 20 m depth at Northwest Bay. Sediments from this station also exhibited the greatest mean TPAH concentration observed in 1993 (Table 2). The mean TNA concentration at other stations where sediments showed the EVO-PAH pattern ranged from 357 ± 98.7 ng/g (Northwest Bay, 3 m station) to 1089 ± 192 ng/g (Herring Bay, 3 m station) (Table 3).

The ratio of mean TNA to mean TPAH in the shallow subtidal region at assessment sites ranged from 0.9 (Sleepy Bay, 20 m station) to 43 (Bay of Isles, 3 m station). The range in this ratio was comparable to that observed in intertidal sediments at assessment sites. The range was markedly narrower (0.9 to 7.8) for sediments from shallow subtidal stations where the EVO-PAH pattern was observed.

The CPI values could be calculated for two-thirds of the shallow subtidal stations at assessment sites. Values for the remainder of the stations could not be calculated because the concentrations of alkanes C_{26}, C_{28} and/or C_{30} were below detection limits. The CPI values for these stations reflected alkane distributions that were not strongly indicative of oiled sediments. The lowest mean CPI values were observed at the 6 m (CPI = 4.6) and 20 m (CPI = 3.4) stations at Northwest Bay. The PAH concentrations at these stations showed the EVO-PAH pattern. Mean CPI values for other shallow subtidal assessment stations where the EVO-PAH pattern was found ranged from 8.8 to 16.8. (At the 6 m depth at Herring Bay the one replicate for which a CPI could be calculated had a value of 21.)

Deep Subtidal Stations

The TPAH concentration and the PAH composition pattern in sediments at depths ≥40 m at assessment sites were similar to those at reference sites (Fig. 2, see below). The EVO-PAH pattern was absent from all sediment samples collected at deep subtidal stations (Table 2). When the concentration of PAH analytes was great enough to discern a hydrocarbon source, the PAH composition pattern differed from that of weathered EVO such that the concentrations of dibenzothiophenes were relatively low. The ratio of alkyl dibenzothiophenes to alkyl phenanthrenes was less than 0.20 in those deep subtidal samples. The TPAH concentration in sediments at depths of 40 m and 100 m was often higher than in sediments in the 3 m to 20 m depth range.

At the 40 m depth, the concentration of PAH analytes was too low to distinguish a hydrocarbon source in a third of the replicates from assessment locations. In 47% of the replicates from assessment locations, the PAH composition pattern showed a ratio of alkyl dibenzothiophenes to alkyl phenanthrenes less than 0.20, an absence of alkyl chrysenes, and a concentration of alkyl phenanthrenes that exceeded 20 ng/g. This pattern was characteristic of an unknown hydrocarbon source, possibly diesel oil. The remaining replicates (20%) showed a PAH composition pattern indicative of the Katalla source. The median TPAH concentration in replicates from 40 m at assessment sites was 146 ng/g (range, 26-238 ng/g; Fig. 3).

At the 100 m depth at assessment sites, all of the replicates showed a PAH composition pattern indicative of the Katalla source. The median concentration was 643 ng/g (range, 204-763 ng/g; Fig. 3).

The TNA concentration in deep subtidal sediments at assessment sites tended to vary from station to station and showed no consistent pattern of change relative to shallower sediments, although values usually exceeded intertidal TNA concentrations. The only exception was Northwest Bay where the intertidal TNA concentration exceeded that at the 40 m depth (Table 3). The greatest mean TNA concentration (1211 ± 91 ng/g) found in deep subtidal sediments at assessment sites in 1993 occurred in sediments from the 100 m depth at Bay of Isles. Sediments from this station also exhibited a mean TPAH concentration among the highest observed in deep sediments in 1993 (Table 2).

The ratio of mean TNA to mean TPAH in the deep subtidal region at assessment sites ranged from 0.8 (Sleepy Bay, 40 m station) to 4 (Bay of Isles, 40 m station). The range in this ratio was much narrower than that observed in intertidal and shallow subtidal sediments at assessment sites. The range at 100 m (1.2 to 2) was narrower than that for sediments from 40 m.

The CPI values could be calculated for all but one (Sleepy Bay, 40 m station) of the deep subtidal stations at assessment sites. The CPI values for the 40 m stations reflected alkane distributions that were not strongly indicative of oiled sediments. The lowest mean CPI value (4.2) at this depth at assessment stations was observed at Northwest Bay. The mean CPI values for the 100 m depth were lower than those for the 40 m depth at all assessment sites. The lowest values (2.4-2.6) for sediments at 100 m were found at Northwest Bay, Sleepy Bay and Snug Harbor 25. These values approached that (CPI $\approx$ 1) considered to be indicative of oiled sediments (Table 4).

Reference Sites

Intertidal Stations

The EVO-PAH pattern was not found at intertidal stations at the five reference sites sampled in 1993. All replicate sediment samples contained concentrations of PAH analytes too low to distinguish a hydrocarbon source. The highest mean TPAH concentration found, at the 0 m station of the reference sites sampled in 1993, was 54 ± 17.2 ng TPAH/g dry sediment weight. This concentration was found at Moose Lips Bay (Table 2). At the other four reference sites sampled in July 1993, the mean TPAH concentrations were 0.36 ± 0.18, 2.1 ± 0.84, 7.7 ± 2.1, and 8.3 ± 0.63 ng TPAH/g sediment in 0 m sediments from Drier Bay, Lower Herring Bay, Olsen Bay and Zaikof Bay, respectively. The mean TPAH concentration at these stations was generally

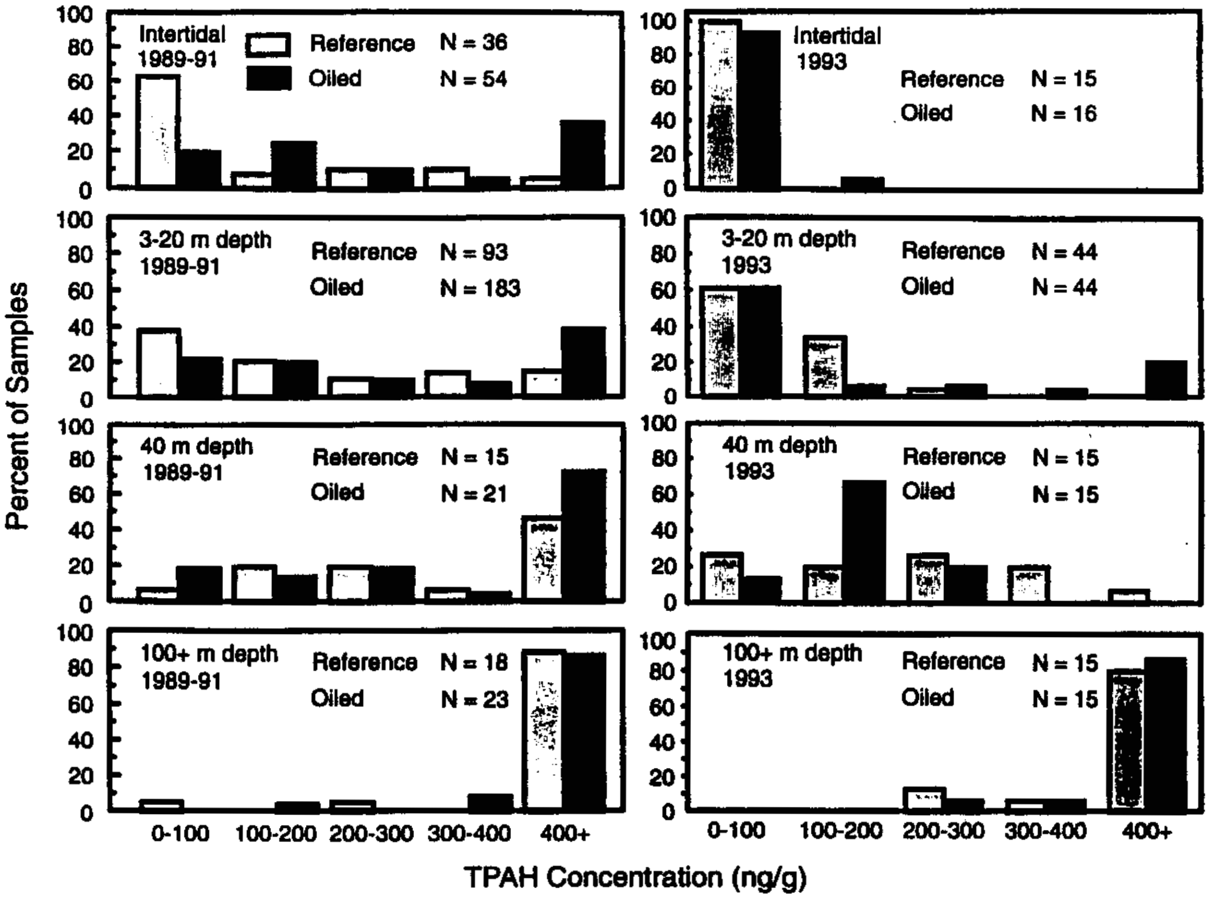

Figure 3.--Percentage of sediment samples in five concentration ranges of TPAH in sediments from the intertidal region (0 m) and the subtidal region at bathymetric depths of 3 m to 20 m, 40 m and 100 m at reference stations and heavily oiled stations from 1989 to 1991 and 1993.

Table 4.--Mean CPI for sediments from all stations in PWS, Alaska sampled in 1993. Superscripts indicate sample size where *n* is not equal to three. NA indicates that CPI could not be calculated.

Site			Depth					
No.	Name	Date	0 m	3 m	6 m	20 m	40 m	100 m
Reference Sites								
10	Drier Bay	11 Jul	NA	NA	19.3^{2}	22.1	13.3	5.72
26	Lower Herring Bay	10 Jul	NA	NA	NA	NA	11.1^{1}	10.3
28	Moose Lips Bay	13 Jul[a]	NA	NA	NA	NA	9.0^{1}	2.9^{2}
32	Olsen Bay	16 Jul[b]	NA	15.4	19.2	22.4^{2}	14.0^{1}	6.0^{2}
44	Zaikof Bay	13 Jul	NA	7.6^{1}	5.1^{1}	NA	7.1^{2}	5.8
Assessment Sites								
5	Bay of Isles	15 Jul	NA	NA	64.7^{1}	10.7^{2}	8.0	5.3
20	Herring Bay	9 Jul	NA	16.8	21^{1}	21.1^{1}	7.0^{1}	3.6
31	Northwest Bay	8 Jul	1.1	8.8	4.6	3.4	4.2	2.4
38	Sleepy Bay	12 Jul[c]	NA	NA	NA	9.3	NA	2.6
40	Snug Harbor 25	14 Jul	NA	NA	0	NA	12.9	2.6

a. Stations at 40 and 100 m at Moose Lips Bay sampled on 12 July.

b. Stations at 40 and 100 m at Olsen Bay sampled on 15 July.

c. Stations at 40 and 100 m at Sleepy Bay sampled on 11 July.

similar in magnitude to that found at assessment sites (Fig. 2). The median TPAH concentration at reference intertidal stations was 7 ng/g (range, 0-87.5; Fig. 3). The TPAH concentration was consistently below the median in intertidal sediments from Lower Herring Bay and Drier Bay.

The TNA concentration in intertidal sediments at reference sites was relatively low, averaging somewhat lower than that in intertidal sediments from assessment sites. The highest mean TNA concentration (413 ± 104 ng/g) at reference sites occurred at Olsen Bay (Table 3). This mean TNA concentration was more than five times higher than the highest mean TNA concentration at any of the other reference stations. The ratio of mean TNA to mean TPAH at intertidal reference stations showed a greater range (1.4 to 86) than at assessment sites (0.76 to 40). No CPI values could be calculated for the intertidal sediments collected at reference sites because the concentrations of alkanes C_{26}, C_{28} and/or C_{30} were below detection limits.

Shallow Subtidal Stations

As at assessment sites the concentration of TPAH in shallow subtidal sediments (3-20 m) at reference sites was usually markedly greater than those in intertidal sediments at those sites (Table 2). The TPAH concentrations tended to increase with increasing depth in the shallow subtidal zone at reference sites. The exception to this trend occurred at Lower Herring Bay where the mean TPAH concentration at the intertidal station exceeded that at the 3 and 6 m stations.

No evidence of the EVO-PAH pattern was found in shallow subtidal sediments at the reference sites sampled in 1993. Most of the sediment samples from shallow subtidal stations at reference sites contained concentrations of PAH analytes too low to distinguish a hydrocarbon source. However, in one replicate sediment sample each at the 20 m station at Olsen Bay, Moose Lips Bay and Zaikof Bay, and at the 6 m station at Zaikof Bay, the PAH composition pattern was characteristic of an unknown hydrocarbon source, possibly diesel oil. The remaining replicate from the 20 m station at Zaikof Bay (just two replicates were analyzed from the 20 m station at Zaikof Bay) had a PAH composition pattern consistent with the Katalla source.

The highest mean TPAH concentration found at shallow subtidal stations at the reference sites was 178 ± 13.3 ng TPAH/g dry sediment weight at 20 m at Zaikof Bay (Table 2). The TPAH concentration in sediments that showed a PAH composition pattern indicative of the unknown hydrocarbon source ranged from 156 ng/g (Zaikof Bay, 6 m) to 265 ng/g (Moose Lips Bay, 20 m). The TPAH concentration in the replicate from the 20 m station at Zaikof Bay that showed the Katalla pattern was 192 ng/g. At those shallow subtidal reference stations where no replicate samples were found, that exhibited one of these two PAH patterns, the mean TPAH concentration never exceeded 138 ng/g. The mean TPAH concentration varied greatly between sites within both the group of reference sites and the group of assessment sites such that only at 20 m did the TPAH concentration tend to differ between groups. At 20 m, the TPAH concentration at assessment sites tended to exceed that at reference sites.

As with TPAH, the TNA concentration in shallow subtidal sediments at reference sites tended to exceed the intertidal TNA concentration. The sole exception to this trend was Lower Herring Bay where the mean intertidal TNA concentration exceeded that at the 3 and 6 m depths (Table 3). The greatest mean TNA concentration (1462 ± 499 ng/g) found in subtidal sediments at reference sites occurred in sediments from the 6 m depth at Olsen Bay. By contrast, the mean TPAH concentration at the 6 m depth at Olsen Bay was substantially lower than the greatest mean TPAH concentration found in the shallow subtidal zone at reference sites. The mean TPAH concentration at the 6 m depth at Olsen Bay (98 ± 17.9 ng/g) was the median of the mean TPAH concentrations at the reference sites. The opposite relationship held for the station showing the greatest mean TPAH concentration in shallow subtidal reference sediments (Zaikof Bay, 20 m). The mean TNA concentration at the 20 m station at Zaikof Bay (242 ± 71 ng/g) was slightly above the median of the mean TNA concentrations at the reference sites.

The ratio of mean TNA to mean TPAH in the shallow subtidal region at reference sites ranged from 0.7 (Moose Lips Bay, 20 m station) to 36.4 (Olsen Bay, 3 m station). The range in this ratio was comparable to that observed in shallow subtidal sediments at assessment sites.

The CPI values could be calculated for less than half (47%) of the shallow subtidal stations at reference sites. Values for the remainder of the stations could not be calculated because the concentrations of alkanes C_{26}, C_{28} and/or C_{30} were below detection limits. The CPI values for these stations reflected alkane distributions indicative of unoiled sediments. The lowest CPI value recorded for shallow subtidal sediments at reference sites was 5.1 in one replicate from the 6 m depth at Zaikof Bay (Table 4).

Deep Subtidal Stations

As stated above, the TPAH concentration and the PAH composition pattern in sediments at depths ≥40 m at reference sites were similar to those at assessment sites. The EVO-PAH pattern was absent from all sediment samples collected at deep subtidal stations (Table 2). When the concentration of PAH analytes was great enough to discern a hydrocarbon source, the PAH composition pattern differed from that of weathered EVO such that the concentrations of dibenzothiophenes were relatively low. The ratio of alkyl dibenzothiophenes to alkyl phenanthrenes was less than 0.20 in those deep subtidal samples. The mean TPAH concentration in sediments at depths of 40 m and 100 m at reference sites was often higher than in sediments at shallower reference depths (Fig. 2), and on average somewhat higher at 40 m but not 100 m than the mean TPAH concentration at these depths at assessment sites.

At the 40 m depth, the concentration of PAH analytes was too low to distinguish a hydrocarbon source in a third of the replicates from reference sites. In 40% of the replicates from reference sites the PAH composition pattern was characteristic of the unknown (possibly diesel oil) hydrocarbon source. The remaining replicates (27%) showed a PAH composition pattern indicative of the Katalla source. The highest mean TPAH concentration found at the 40 m depth at the reference sites was 290 ± 30 ng TPAH/g dry sediment weight at Zaikof Bay (Table 2).

Two replicates from the 40 m depth at Zaikof Bay exhibited the PAH composition pattern characteristic of the unknown hydrocarbon source, and the third replicate showed the Katalla pattern. The mean TPAH concentration in those replicates for which a hydrocarbon source could not be distinguished was 73 ± 16 ng/g. The mean TPAH concentration in those replicates with the PAH composition pattern characteristic of the unknown hydrocarbon source was 248 ± 48 ng/g. Finally, the mean TPAH concentration in those replicates showing the Katalla pattern was 292 ± 18 ng/g.

At the 100 m depth at reference sites all but one of the replicates showed a PAH composition pattern indicative of the Katalla source. The one replicate that did not show the Katalla pattern was collected at Olsen Bay. The PAH composition pattern of that replicate was characteristic of the unknown (possibly diesel oil) hydrocarbon source. The TPAH concentration in that replicate was 444 ng/g. The mean TPAH concentration in the rest of the replicates was 557 ± 63 ng/g. The greatest mean TPAH concentration found at the 100 m depth at the reference sites was 931 ± 46 ng/g at Drier Bay (Table 2)

The TNA concentration in deep subtidal sediments at reference sites tended to vary from station to station, and although values did not show a consistent pattern of change relative to shallower sediments, they often exceeded intertidal and shallow subtidal TNA concentrations. The greatest mean TNA concentration (1708 ± 136 ng/g) found in deep subtidal sediments at reference sites occurred at the 100 m depth at Drier Bay, the same station that showed the greatest mean TPAH (Tables 2 and 3).

The ratio of mean TNA to mean TPAH in the deep subtidal region at reference sites ranged from 1.1 (Moose Lips Bay, 40 m station) to 4.1 (Lower Herring Bay, 40 m station). The range in this ratio was much narrower than that observed in intertidal and shallow subtidal sediments at reference sites, and about the same as that observed in the deep subtidal region at assessment sites. As at assessment sites, the range of the ratio of mean TNA to mean TPAH at the 100 m depth (1.2 to 2.4) at the reference sites was narrower than that for reference sediments from the 40 m depth (1.1 to 4.1).

The CPI values could be calculated for all deep subtidal stations at reference sites. The mean CPI values for both the 40 m stations and the 100 m stations reflected alkane distributions that were indicative of unoiled sediments (Table 4). The only exception may have been the 100 m station at Moose Lips Bay where the mean CPI value (2.9) approached that expected to indicate oiled sediment. As at the assessment sites, the mean CPI values for the 100 m depth were lower than those for the 40 m depth at all reference sites.

DISCUSSION

Assessment Sites

Intertidal sediments

The EVOS clearly contaminated lower intertidal sediments (near MLLW) at some locations with crude oil (O'Clair et al., 1996). The highest mean concentration of TPAH observed in the lower intertidal zone was 12,729 ng/g at Disk Island in July 1989. Very high concentrations of TPAH were also found at Northwest Bay (mean TPAH, 11,686 ng/g) and Herring Bay (mean TPAH, 1,837) in July 1989. By July 1991 the mean concentration of TPAH in sediments from the 0 m station at Northwest Bay had dropped to 584 ng/g. However, at the 0 m station at Herring Bay in June 1991 the concentration of TPAH remained high (mean TPAH, 2,346 ng/g); although the distribution of PAHs did not indicate EVO as the source (O'Clair et al., 1996). The present study found further reductions in the concentration of TPAH at the 0 m station at Northwest Bay (mean TPAH, 24 ng/g) and Herring Bay (mean TPAH, 18 ng/g) by July 1993.

Lower-intertidal sediments were also contaminated by EVO in 1989 at other locations such as Bay of Isles (mean TPAH, 243 ng/g, September 1989) and Sleepy Bay (mean TPAH, 335 ng/g, September 1989). [The 0 m station at Snug Harbor 25 was not sampled until June 1990. EVO contamination appeared in sediments from that station in July 1990 (mean TPAH, 2,551 ng/g).] The EVO in lower-intertidal sediments at these sites was present at a lower TPAH concentration than initially found at Disk Island or Northwest Bay. The PAHs in the intertidal sediments at these sites were qualitatively similar to PAHs at Disk Island and at Northwest Bay in 1989. Moderate to heavy oiling was observed in the upper intertidal zone at all of the locations (O'Clair et al., 1996). By July 1993 the mean TPAH in lower-intertidal sediments had decreased to 10 ng/g or less at Bay of Isles, Sleepy Bay and Snug Harbor.

EVO was indicated as the source of the PAHs in lower-intertidal sediments at Disk Island, Northwest Bay, Herring Bay and other heavily oiled locations in 1989-91 by: (1) the close similarity between relative PAH abundances in the intertidal sediments and those in floating mousse collected 11 days after the Spill; (2) high concentration of *n*-alkanes and CPI near 1 indicating a petrogenic source of the alkanes; and (3) the proximity of the intertidal station to the heavily-oiled upper intertidal shoreline where oil was visually apparent in spring 1989 (indicating oil concentrations near percent levels; O'Clair et al., 1996). Characteristics of the hydrocarbons in sediments that indicated weathered EVO in 1993 were: (1) a the ratio of alkyl dibenzothiophenes to alkyl phenanthrenes that exceeded 0.20; (2) a ratio of alkyl chrysenes to alkyl phenanthrenes that exceeded 0.03; and (3) a concentration of alkyl phenanthrenes that exceeded 20 ng/g. In 1989 Bay of Isles, Block Island, Foxfarm, Herring Bay, Northwest Bay, Sleepy Bay and Snug Harbor showed PAH distributions indicative of EVO contamination in sediments from the 0 m station. By 1991, EVO was indicated in lower-intertidal sediments at Herring Bay (April), Northwest Bay (June), Sleepy Bay (June) and Snug Harbor 25 (June;

O'Clair et al., 1996). In 1993, PAH concentrations in lower-intertidal sediments were too low to discriminate among the known possible sources of petroleum hydrocarbons in PWS.

Prior to the EVOS Karinen et al. (1993) monitored a suite of PAHs in intertidal sediments in eastern PWS near the oil tanker route in case of an oil spill. Their study began in 1977 (when the Trans Alaska Pipeline Terminal at Valdez began operations) and continued until 1980. The analytical methods used in their study were the same as those used in the present study. After the EVOS, the concentrations of individual aromatic analytes in sediment samples collected in 1989 from the 0 m station at such heavily-oiled sites as Disk Island usually averaged one to three orders of magnitude greater than the baseline concentrations of those same analytes reported by Karinen et al. (1993). Individual aromatic analytes in sediment samples from the 0 m station at Northwest Bay and Herring Bay in 1989 averaged up to two orders of magnitude greater than the concentrations of individual aromatic analytes reported by Karinen et al. (1993) depending on the analyte (O'Clair et al., 1996). Concentrations of individual aromatic analytes in intertidal sediments at Northwest Bay and Herring Bay in 1993 decreased to levels well within the range of those reported by Karinen et al. (1993), never exceeding 4 ng/g.

In 1989, EVO contamination of many of the intertidal sediments at heavily-oiled sites was supported by an associated high *n*-alkane concentration and a low CPI at stations where the TPAH concentration was also high. At stations where the TPAH concentration was lower, the magnitude and distribution of *n*-alkane concentrations were often confounded by alkanes from terrigenous sources indicated by higher CPI values. TNA concentrations ranging to over 1,000 ng/g derived, in large part, from terrestrial plant waxes (Kolattukudy 1976; Eglinton and Hamilton 1967; Eglinton et al. 1962) and from marine bacteria (Oro et al. 1967), blue-green algae (Winters et al. 1969), and planktonic and macrophytic algae (Clark and Blumer 1967; Blumer 1971) were widespread in intertidal sediments at reference stations and at assessment stations where oiling in the upper intertidal zone was low or absent (O'Clair et al., 1996). The concentrations of *n*-alkanes in lower-intertidal sediments at most sites in 1989 and at those sites studied in 1993 were similar to *n*-alkane concentrations in pre-EVOS intertidal sediments in PWS (Karinen et al. 1993). The greatest mean TNA found in lower-intertidal sediments in 1993 was 981 ng/g at Northwest Bay. The CPI of those sediments (1.1) indicated a petroleum source. A CPI could not be calculated for the 0 m station at other assessment sites in 1993 because the concentrations of alkanes C_{26}, C_{28} and/or C_{30} were below detection limits.

Subtidal Sediments

O'Clair et al. (1996) concluded that detectable contamination of subtidal sediments by EVO in 1989 was "not widespread throughout the Spill path, but rather was restricted to those relatively few locations where conditions favored subtidal accumulation". Those conditions included shorelines that were: (1) heavily oiled; (2) exposed to wave action or cleaned; and (3) were adjacent to shallow-subtidal sediment deposits on low-gradient slopes. Those conditions prevailed at Herring Bay and Northwest Bay where good evidence of EVO contamination in shallow subtidal sediments in 1989 was consistently found. The mean TPAH concentration in shallow subtidal sediments that exhibited the EVO-PAH pattern at Herring Bay and Northwest Bay in 1989 ranged from 239 to 921 ng/g and from 517 to 1,486 ng/g, respectively (O'Clair et al., 1996). Contamination by EVO of shallow subtidal sediments at Herring Bay and Northwest Bay persisted to July 1993. At these two sites in July 1993, the PAH composition pattern indicative of weathered EVO was found at 3 m and 6 m depths at Herring Bay and at 3-20 m depths at Northwest Bay. The mean TPAH concentration in shallow subtidal sediments showing the EVO-PAH composition pattern at Herring Bay and Northwest Bay in 1993 ranged from 58 to 320 ng/g and from 140 to 1,231 ng/g, respectively.

The EVO-PAH pattern was frequently found at depths to 20 m but rarely deeper in 1989, presumably because there was adequate energy available from waves or currents to transport contaminated sediments to the 20 m depth, but not to depths as great as 40 m or 100 m and/or the quantity of contaminated sediments transported to greater depths was not great enough to permit the detection of EVO-PAHs above the hydrocarbon background (O'Clair et al., 1996). By 1993 the EVO-PAH pattern was found in sediments at the 20 m depth only at Northwest Bay and Sleepy Bay (see below).

At some moderately to heavily oiled sites environmental conditions were less favorable for transport of EVO-contaminated intertidal sediments to subtidal depths. These sites included Bay of Isles and Snug Harbor 25 which were more sheltered from wave action than Herring Bay and Northwest Bay or had shorelines that were less heavily oiled initially than those of Herring Bay and Northwest Bay. Conversely, at sites such as Sleepy Bay, shorelines were heavily oiled, but intertidal and shallow subtidal sediments were probably exposed to wave action that was heavier than that experienced by intertidal and shallow subtidal sediments at Herring Bay and Northwest Bay. These conditions may have precluded long sediment residence times in shallow subtidal sediments at least as deep as 6 m. Evidence for EVO contamination of subtidal sediments at these sites was less consistent, and the TPAH concentration was generally lower than at Herring Bay and Northwest Bay (O'Clair et al., 1996). In July 1993 we found no evidence for EVO contamination of shallow subtidal sediments at these sites except at Sleepy Bay where the EVO-PAH composition pattern was found in sediments from the 20 m depth. The mean TPAH concentration in these sediments was 963 ng/g.

In the first three years following the EVOS, the EVO-PAH composition pattern was rarely found at assessment sites in sediments from subtidal depths below the 20 m depth. The EVO-PAH pattern was found in sediments below the 20 m depth on two occasions only during the time period 1989-91— at the 40 m depth at Bay of Isles and Northwest Bay in June 1991 (O'Clair et al., 1996). In 1993, the EVO-PAH pattern was never observed below the 20 m depth at assessment sites.

Reference Sites

Intertidal sediments

Lower-intertidal sediments at reference sites were clearly not contaminated by EVO in 1989. The TPAH concentration at these sites was usually less than 100 ng/g, and where comparable, selected PAH concentrations were similar to those in intertidal sediments sampled by Karinen et al. (1993) during the period 1977 to 1980 in eastern PWS (O'Clair et al., 1996). We found no evidence of EVO contamination of lower-intertidal sediments at reference sites in 1993. The TPAH concentration of lower-intertidal sediments at all reference sites in 1993 was less than 55 ng/g. Individual PAH concentrations in these sediments were similar to those reported by Karinen et al. (1993), where comparable.

Subtidal Sediments

The PAH composition pattern resembled that of weathered EVO in shallow subtidal sediments at reference sites on only a few occasions during the first years following the EVOS (1989-91). Where the EVO-PAH pattern was observed at these sites it was present in one replicate only, and probably reflected a mixture of PAHs from other sources. The TPAH concentration at those shallow subtidal reference stations, where the EVO-PAH pattern was found, ranged from 303 to 800 ng/g (O'Clair et al., 1996). In 1993, no evidence of the EVO-PAH composition pattern was found in shallow subtidal reference sediments. The mean TPAH concentration in these sediments ranged from 0.84 to 178 ng/g.

As at assessment sites, the EVO-PAH composition pattern was rarely found in deep subtidal sediments in the first three years after the EVOS. The EVO-PAH pattern was found in sediments at the 100 m depth at Olsen Bay in July 1989 and at the 100 m depth at Lower Herring Bay in July 1990. As with those instances when the EVO-PAH composition pattern was found in shallow subtidal sediments at reference sites, these observations indicating the presence of EVO in deep subtidal reference sediments were probably spurious, reflecting a mixture of PAHs from other sources. The mean TPAH concentration at those deep subtidal reference stations where the EVO-PAH pattern was found ranged from 574 to 1,702 ng/g (O'Clair et al., 1996). In 1993, the EVO-PAH pattern was never observed in deep subtidal sediments at reference sites. The mean TPAH concentration in these sediments ranged from 50 to 931 ng/g.

Geographic distribution of EVO

O'Clair et al. (1996) found EVO in lower intertidal and subtidal sediments over a broad geographic range in PWS in 1989. The area over which EVO contamination of these sediments was found ranged from Northwest Bay at the north end of Eleanor Island to Foxfarm (intertidal sediments only) at the southern end of Elrington Island; although, EVO contamination was geographically patchy depending on where large quantities of oil came ashore. Subtidal sediments contained EVO at eight locations where oil had come ashore (oiled locations) in 1989.

Contamination of subtidal sediments by EVO at oiled locations reached a depth of at least 20 m at five locations in 1989. By 1991, the distribution of EVO contaminated subtidal sediments was restricted to four locations on Eleanor Island (Northwest Bay) and Knight Island (Bay of Isles, Herring Bay and Snug Harbor). EVO contamination was also found in intertidal but not subtidal sediments at Sleepy Bay on Latouche Island. By 1991, contamination of subtidal sediments by EVO at oiled locations was found to reach a depth of 20 m at only two sites, Northwest Bay and Snug Harbor 25 (O'Clair et al., 1996).

By 1993, EVO contaminated subtidal sediments were further restricted in geographical distribution. The EVO-PAH composition pattern was found in shallow subtidal sediments at only three locations: Herring Bay, Northwest Bay and Sleepy Bay. EVO contamination in 1993 reached a depth of 20 m at just two sites, Northwest Bay and Sleepy Bay.

Other sources of hydrocarbon contamination

O'Clair et al. (1996) reported that the TPAH concentration of sources of petroleum hydrocarbons other than EVO in lower- intertidal sediments was usually below 30 ng/g and rarely exceeded 200 ng/g in the first three years after the EVOS. They concluded that intertidal sediments in PWS not affected by the EVOS remained substantially free of petrogenic hydrocarbons for the most part. They found mainly three patterns of PAH composition in intertidal samples: (1) predominantly 2-ring PAHs of unknown source found most frequently in intertidal sediments collected in 1989; (2) a pattern consistent with diesel oil derived from North Slope crude oil in which the PAH composition pattern was nearly identical to that of EVO except for the general absence of chrysenes (Page et al. 1994); and (3) a pattern characteristic of a pyrolytic source composed predominantly of unsubstituted PAHs, sometimes found in conjunction with concentrations of alkyl-substituted PAHs that decreased with the degree of alkyl substitution. O'Clair et al. (1996) suggested that the probable sources of PAHs in intertidal sediments where EVO was absent included diesel oil and products of pyrolysis associated with small (and often temporary) human settlements, and forest fires. Residues of asphalt spilled from storage tanks at Valdez during the Great Alaska Earthquake of 1964 were found by Kvenvolden et al. (1993a and 1993b) in intertidal sediments PWS. Although they do not indicate at which tidal level their samples were taken, Kvenvolden et al. (1993a and 1993b) residues probably came from upper tidal levels; our sediments were collected at MLLW. We did not analyze our sediments using Kvenvolden et al. (1993a and 1993b) methods for these California asphalt residues (O'Clair et al. 1996). In 1993, no evidence of hydrocarbons from any petrogenic source was found in sediments from the lower intertidal zone. The concentration of PAHs in intertidal sediments was too low to discriminate a petrogenic source.

As with intertidal sediments, O'Clair et al. (1996) occasionally found a mean TPAH concentration greater than 100 ng/g in shallow subtidal sediments where EVO was not indicated. The probable sources of these PAHs were the same as for PAHs in intertidal sediments. In 1993, we found three patterns of PAH composition in subtidal sediments indicative of hydrocarbon sources other than EVO. The first pattern indicated diesel oil and was characterized by: (1) alkyl chrysenes absent, (2) a concentration of alkyl phenanthrenes (summed) that exceeded 20 ng/g; and (3) a ratio of alkyl dibenzothiophenes (summed) to alkyl phenanthrenes (summed) that exceeded 0.20. The second pattern indicated oil (or coal?) from the Katalla source that was characterized by: (1) a ratio of alkyl chrysenes to alkyl phenanthrenes that exceeded 0.03; (2) a concentration of alkyl phenanthrenes that exceeded 20 ng/g; and (3) a ratio of alkyl dibenzothiophenes to alkyl phenanthrenes less than 0.20. The final pattern indicated an unknown petrogenic source, perhaps diesel that was characterized by: (1) alkyl chrysenes absent; (2) a concentration of alkyl phenanthrenes that exceeded 20 ng/g; and (3) a ratio of alkyl dibenzothiophenes to alkyl phenanthrenes less than 0.20.

The majority of sediment samples collected in the shallow subtidal region at reference sites and assessment sites in 1993, not exhibiting the EVO-PAH composition pattern, contained PAH concentrations too low to distinguish a petrogenic source from them. The percentage of samples not exhibiting the EVO-PAH pattern that contained these low PAH concentrations ranged from 55% (20 m depth) to 100% (3 m depth) at assessment sites and from 71% (20 m depth) to 100% (3 m depth) at reference sites.

Only one sample collected at 6 m at Herring Bay showed a PAH pattern indicative of diesel oil. Two samples (20 m depth, Sleepy Bay) exhibited the Katalla pattern at assessment sites, and one sample (20 m depth, Zaikof Bay) showed the Katalla pattern at reference sites. The number of samples exhibiting the unknown (possibly diesel) PAH pattern ranged from one (6 m depth) to three (20 m depth) at both the assessment and the reference sites.

O'Clair et al. (1996) found that deep subtidal sediments were uniformly contaminated by PAHs derived from marine oil seeps or some other natural source of PAHs. The PAH composition pattern characteristic of this source was similar to that of weathered EVO, except for substantially lower relative abundances of dibenzothiophenes. Page et al. (1994) attributed this PAH composition pattern to marine oil seeps near Katalla Island. The present study also found the Katalla PAH pattern to be common in deep subtidal sediments, especially at 100 m. At the 40 m depth, the Katalla pattern was observed in 20% of the sediment samples from the assessment sites and 27% of the samples from the reference sites. At the 100 m depth, the Katalla pattern was observed in 100% of the sediment samples from the assessment sites and 93% of the samples from the reference sites.

CONCLUSIONS

Although oil from the EVOS contaminated shores over a broad geographic range in PWS in 1989, by 1993 the distribution of EVO in shallow subtidal sediments was much more restricted and no low intertidal sediments were found to be contaminated. Contamination of subtidal sediments was restricted to three sites within the trajectory of the oil spill: Herring Bay, Northwest Bay and Sleepy Bay. The bathymetric distribution of oil at contaminated sites in 1993 showed the greatest concentration of petroleum hydrocarbons at the 20 m depth. In the subtidal region, petroleum hydrocarbons exhibiting a concentration pattern consistent with EVO were restricted to shallow depths (3-20 m). Petroleum hydrocarbons at depths ≥40 m were found to be from sources other than EVO. At the 100 m depth petroleum hydrocarbons were chiefly from the Katalla source.

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APPENDIX I

Standard operating procedures for sampling benthic sediments.

INTERTIDAL SEDIMENTS

1. Choose an area of intertidal beach having a substrate as homogeneous as possible with particle sizes of 2 mm or less. The area must be large enough to accommodate a 30 m transect. Lay the transect parallel to the water's edge within the designated area.

2. Choose eight random distances along the transect from a random number table or pocket calculator.

3. Three samples of substrate will be collected at each station (= transect). Each sample will represent a composite of eight subsamples, each subsample having been taken at one of the eight randomly selected points. Using a metal core tube and spatula or metal scoop, remove approximately 10 g of sediment from the upper 2 cm of substrate at one of the eight randomly selected points on the transect and place in a properly cleaned 4 oz jar. Repeat the procedure for two more jars, collecting 10 g of sediment from adjacent patches of substrate and placing it in each of the two additional jars.

4. Repeat the procedure described in 3 for the seven remaining points on the transect.

5. At one station per site, a sample blank (handled in the same way as the sediment samples except without receiving any sediment) will be taken.

6. Label, seal (with custody control seal), and freeze sediment samples and blank as soon as possible after collection.

7. Proper cleaning procedure for sampling implements and jars.

Sampling implements - All sampling implements will be washed with soap and water, rinsed, dried, rinsed with methylene chloride, and if not used immediately, wrapped in clean aluminum foil that has been rinsed with methylene chloride. The cleaning procedure will be performed before each transect is sampled.

Jars - If sample jars have not come from the supplier cleaned to Environmental Protection Agency specifications, they will be baked for 4 hours at 440°C or rinsed with methylene chloride. Sample jars will have teflon-lined lids rinsed with methylene chloride or will be capped with aluminum foil rinsed with methylene chloride before the lid is replaced after sample collection.

SUBTIDAL SEDIMENTS

Diver collected

Sampling will be conducted as described above for intertidal sediments, with the following modifications.

1. Lids will be closed on sample jars on the surface before divers descend to the bottom to prevent contamination by petroleum hydrocarbons floating on the surface of the water.

2. Care must be taken to avoid contamination of dive mitts/gloves with petroleum hydrocarbons.

Remote sampling by van Veen grab or Smith-McIntyre grab.

1. The interior surfaces of the grab must be clean prior to deployment. The grab will be lowered to the bottom and activated to enclose a sample of substrate and then retrieved. The surface of the water will be checked visually for sign of contamination by petroleum hydrocarbons (such as an oil sheen) before the grab is lowered or retrieved through it. If any indication of oil is observed, the vessel will be moved to a visually clean area.

2. When the grab is brought to the surface and placed on deck, care must be taken to avoid contamination of the surface of the grab sample with lubricants from the grab sampling equipment and vessel exhaust. The grab sample will be subsampled with a stainless-steel core tube and spatula. The location of the subsamples will be determined randomly. Four subsamples will be taken from each sample and placed in a properly cleaned 4 oz jar. Three samples will be taken at each station. Subsamples of different grabs will be placed in separate jars. Samples will be labeled, sealed, and frozen as soon as possible after being collected.

3. Sampling implements and jars will be cleaned as described in the section on intertidal sediments above.