

Exxon Valdez Oil Spill
Restoration Project Final Report

Subtidal Monitoring: Recovery of sediments in the northern Gulf of Alaska

Restoration Project 95285
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 1A. A status report under the new number was submitted in November 1991. The final report for Subtidal Study Number 1A was published in 1996. No field work was performed in 1992. The final report on Restoration Study Number 93047 "*Exxon Valdez* Restoration Project, Subtidal Monitoring: Recovery of sediments in the subtidal environment," a recovery monitoring study conducted in Prince William Sound in 1993 was published in 1996. In 1994, Restoration Study Number 94285 "*Exxon Valdez* Restoration Project, Subtidal Monitoring: Recovery of sediments in the northwestern Gulf of Alaska" was initiated. Subtidal sampling in conjunction with this project was conducted in July 1994. The last field season for this series of projects was FY 94. This study will be closed out with this Final Report.

Abstract: We sampled subtidal and low intertidal sediments at eight locations in the northern Gulf of Alaska in July 1994 to determine the geographical and bathymetric distribution of oil from the *Exxon Valdez* oil spill in the subtidal region and compare oil concentrations with those in the low intertidal zone. Sediments were sampled near mean lower low water and at three subtidal depths in the 3-20 m range. The sediments were analyzed for hydrocarbons using gas chromatography/mass spectrometry. No *Exxon Valdez* oil was found in sediments from 0 m at assessment sites where the greatest mean intertidal concentration of total polynuclear aromatic hydrocarbons excluding perylene (79 ± 16.4 ng/g) was observed at Hallo Bay. One intertidal sediment sample from Tonsina Bay showed evidence of *Exxon Valdez* oil. A proportion (one half) of the subtidal sediment samples collected at one station (Windy Bay, 6-m depth) showed polynuclear aromatic hydrocarbon composition patterns similar to *Exxon Valdez* oil. The greatest mean concentration of total polynuclear aromatic hydrocarbons excluding perylene in benthic sediments (138 ± 28.8 ng/g) occurred at 6 m at Windy Bay. Petroleum hydrocarbons at the 20 m depth were chiefly (47% of all 20-m assessment samples) from the "Katalla" source.

Project Data: The data from this project is stored in the "*Exxon Valdez* oil spill of 1989: State Federal trustee council hydrocarbon database 1989-1995" (EVTHD). The EVTHD can be accessed on the Oil Spill Public Information Center webpage (<http://www.alaska.net/~ospic>), or by contacting the Hydrocarbon Data Analysis, Interpretation, and Database Maintenance project leader Ms. Bonita Nelson at (telephone) 907-789-6071 or e-mail bonita.nelson@noaa.gov.

Key words: *Exxon Valdez*, hydrocarbon concentrations, Gulf of Alaska, recovery, subtidal sediments

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EXECUTIVE SUMMARY

In 1994, five years after the *Exxon Valdez* oil spill, we sampled subtidal sediments at eight locations in the northern Gulf of Alaska to determine the geographical and bathymetric distribution of *Exxon Valdez* oil residues in intertidal and shallow subtidal sediments. Sediments were sampled in July near mean lower low water and at three subtidal depths in the 3-20 m range along paired bathymetric transects. Hydrocarbon analysis was performed using gas chromatography and mass spectrometry.

Sediments from mean lower low water (0 m) at assessment sites and reference sites showed no evidence of *Exxon Valdez* oil, except one sediment sample collected at Tonsina Bay (a reference site). Other sediment samples from the Tonsina Bay station showed contamination from the "Katalla" source and diesel oil. The greatest mean concentration of total polynuclear aromatic hydrocarbons (excluding perylene) found in intertidal sediments at assessment sites in 1994 was at Hallo Bay (79 ± 16.4 ng/g).

Subtidal sediments showed PAH composition patterns similar to *Exxon Valdez* oil in just three samples from one station (Windy Bay, 6-m depth). The greatest mean total polynuclear aromatic hydrocarbon concentration at a particular site usually occurred at the 20-m depth. The highest mean total polynuclear aromatic hydrocarbon concentration was 138 ± 28.8 ng/g in sediments collected from 6 m at Windy Bay, where the *Exxon Valdez* oil-polynuclear aromatic hydrocarbon composition pattern was found. In most sediment samples collected in northern Gulf of Alaska in 1994, polynuclear aromatic hydrocarbon analyte concentrations were too low to discriminate a source. When a source could be distinguished it was most frequently the "Katalla" source. The "Katalla" source was encountered most frequently at the 20-m depth. At that depth 47% of the assessment samples showed a polynuclear aromatic hydrocarbon composition pattern characteristic of the "Katalla" source when analyte concentrations were great enough to distinguish a source. Sediments in those samples were dominated by silt/clay.

INTRODUCTION

In the first year after the *Exxon Valdez* oil spill, O'Clair et al. (1996) found subtidal sediments to be contaminated by petroleum hydrocarbons from the spill at four locations (Chugach Bay, Hallo Bay, Katmai Bay, and Windy Bay) in the northern Gulf of Alaska (NGOA). The concentration of total polynuclear aromatic hydrocarbons excluding perylene (TPAH; see Methods for a list of those analytes included) was highest in intertidal sediments collected from Hallo Bay (348 ng/g) and Katmai Bay (339 ng/g). Weathered *Exxon Valdez* oil (EVO) also appeared in subtidal samples at 6 m and 20 m at Chugach Bay (TPAH = 80.6 ng/g and 362 ng/g) and at 3 m at Windy Bay (TPAH = 224 ng/g). 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. Most of that oil was transported to subtidal sediments in the Gulf of Alaska (Wolfe et al. 1994). Koons and Jahns (1992) concluded that most of the non-volatile portion of the spilled oil was transported out of Prince William Sound (PWS) into the Gulf of Alaska where it was dispersed into the open north Pacific Ocean by waves and currents. They argue that very little oil sedimented to the bottom.

The purpose of this report is to determine the extent to which EVO persisted in low intertidal and shallow subtidal sediments at formerly contaminated sites, and the geographic and bathymetric distribution of the remaining oil. Here we provide information on the recovery of the intertidal and subtidal sediments after EVO contamination in the NGOA.

OBJECTIVES

A. Determine the composition and concentration of petroleum hydrocarbons from the spill in intertidal and subtidal sediments (0-20 m) in the NGOA by gas chromatography/mass spectrometry.

1. Determine the concentrations of TPAH and n-alkanes in subtidal sediments and compare current concentrations in intertidal and subtidal sediments from previous years.

B. Determine the bathymetric distribution of EVO and compare with the EVO distribution in the NGOA in 1989.

C. Determine whether EVO in subtidal sediments in the NGOA persists.

D. Compare the distribution of EVO in subtidal sediments in the NGOA with that 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., Black Bay). Site refers to a relatively small geographical area containing paired bathymetric transects along which various bottom depths were sampled for sediments. Only one site was sampled at each location in 1994. The origin of the paired transects (where they intersected the shore) is shown as the geographical position of each site in Table 1 and Figure 1. Station refers to a specific spot along a bathymetric transect where sediment samples were collected (e.g., the 20-m-depth station). Assessment sites are those where EVO was reported to have contaminated low intertidal or subtidal sediments in 1989 (O'Clair et al. 1996). Reference locations are those where no EVO was reported in 1989.

Sediments were sampled at a total of eight locations using the same methods employed by O'Clair et al. (1996) with one modification; paired bathymetric transects were sampled at each site. O'Clair et al. (1996) sampled one bathymetric transect at each site. The locations were: Black Bay, Tonsina Bay, Windy Bay, Chugach Bay, Hallo Bay, Katmai Bay, Larson Bay and Spiridon Bay. Chugach Bay, Hallo Bay, Katmai Bay and Windy Bay were assessment sites. Larson Bay and Spiridon Bay were not sampled in 1989, but because oil came ashore in those bays they are considered oiled sites (Table 1, Fig. 1). Black Bay and Tonsina Bay were reference sites. The dates of sampling were 11-16 July 1994 (Table 1).

Sediment Collection

Standard operating procedures were adopted for the collection of all sediments (Appendix I). Sediments were collected at four depths along paired bathymetric transects (running perpendicular to shore from 0 to 20 m water depth). Intertidal sediments were collected at about mean lower low water (MLLW, 0 m); actual sampling location was within the range of +0.5 to - 1 m intertidal height, depending on the distribution of fine sediments. Depending on the tide stage, intertidal sediments were collected by beach teams or by divers on 30-m transects that paralleled shore. Subtidal sediment samples were collected at depths of 3, 6 and 20 m below MLLW. Collections at 3, 6, and 20 m were made by divers on 30-m transects along the appropriate isobath. Three samples, each a composite of eight subsamples were collected randomly (positions chosen using computer-generated random numbers) along each of the 30-m transects.

All samples were surficial (top 0-2 cm). 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 spatula. The core tube and the spatula were washed, dried, and rinsed with methylene chloride between stations. Sample jars certified hydrocarbon-clean according to EPA standards were used to store sediments. Samples were kept cool after

Table 1.--Location of sites in the NGOA and number of stations sampled at sites where intertidal and subtidal sediment samples were collected in July 1994.

Site ¹		North Latitude	West Longitude	Number of stations
No.	Name	o ' "	o ' "	
Reference Sites				
47	Black Bay	59 32 07	150 12 17	8
	Tonsina Bay	59 18 42	150 55 00	8
Assessment Sites				
49	Chugach Bay	59 11 12	151 37 48	8
50	Hallo Bay	58 27 29	154 00 14	8
52	Katmai Bay	57 54 30	155 40 30	8
	Larson Bay	57 33 02	153 58 50	8
	Spiridon Bay	57 42 15	153 53 05	8
53	Windy Bay	59 13 50	151 31 00	8

¹Site numbers follow O'Clair et al. (1996). Larson, Spiridon and Tonsina Bays were not covered in O'Clair et al. (1996), therefore no site numbers are shown.

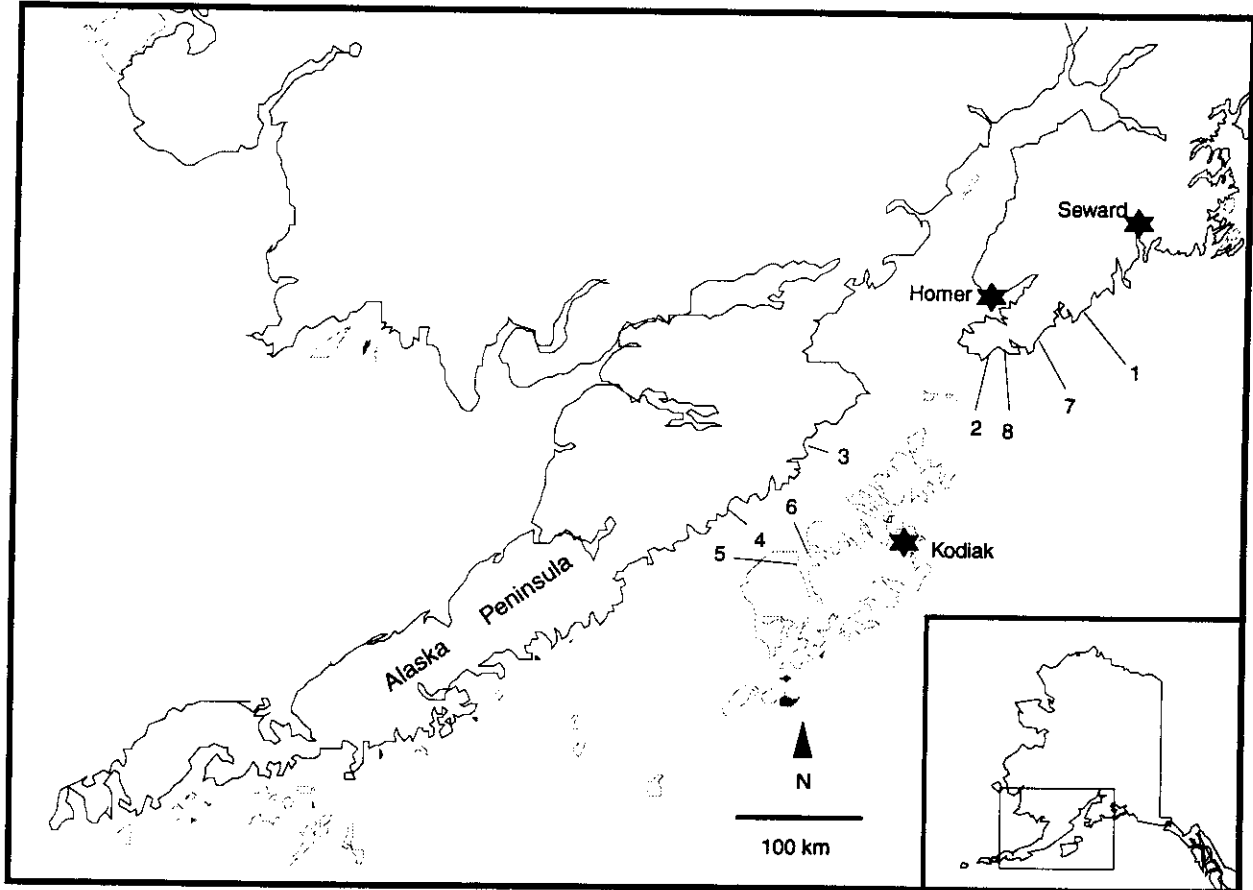


Figure 1.--Distribution of assessment (circles) and reference (squares) sites sampled in 1994 in the NGOA. See Table 1 for the geographical coordinates of each site. Numbered sites are: 1) Black Bay; 2) Chugach Bay; 3) Hallo Bay; 4) Katmai Bay; 5) Larson Bay; 6) Spiridon Bay; 7) Tonsina Bay; 8) Windy Bay.

collection and frozen (-20°C), usually within an hour, aboard a chartered support vessel. Appropriate field (air and water) 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 chain-of-custody tape. Boxes of samples were placed in coolers with enough blue ice to keep the samples frozen while in transit from the support vessel to the Auke Bay 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 the laboratory hydrocarbon database coordinator.

Grain Size, Hydrocarbon and Data Analysis

The size of the sediment particles in the hydrocarbon samples was determined visually following the Wentworth Grain Size Scale. The samples contained sediment particle sizes ranging from silt/clay to pebbles. The limiting diameters (smallest diameters) for the particles found in the NGOA samples were: silt/clay, <1/16 mm; sand, 1/16 mm; granules, 2 mm; pebbles, 4 mm. Particle sizes observed in each sample were recorded in order of decreasing abundance.

Sediment samples were analyzed for petroleum hydrocarbons by means of gas chromatography/mass spectrometry at the Auke Bay Laboratory. Results of the chemical analyses were screened on the basis of surrogate recoveries and minimum detection limits (MDL). Individual analytes and the summary statistics affected by them [e.g. TPAH and total normal alkanes (TNA, i.e. the sum of the normal alkanes)] were excluded from the analysis if the recoveries of corresponding analyte surrogates fell outside the range 30-150%. For example, if the surrogate of one polynuclear aromatic hydrocarbon (PAH) analyte fell outside the acceptable range, the TPAH concentration for that sample was excluded from the analysis. Concentrations of individual analytes reported below MDL 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. TPAH is the sum of those aromatic hydrocarbons listed in Table 2. TNA is the sum of those alkanes from C₁₀ to C₃₀ excluding pristane and phytane. Hydrocarbon concentrations are reported on a dry weight basis to three significant figures when concentrations exceed 10 ng/g, and to two significant figures for lower concentrations. A total of 164 sediment samples was analyzed for hydrocarbons from the eight sites sampled. TPAH could not be obtained for 24 samples and TNA could not be obtained for two samples because constituent analytes were outside the acceptable surrogate recovery range.

The high sulfur content of EVO helps to distinguish it from other PAH sources in the NGOA. 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. 1996). Accordingly, we used

Table 2.--PAH compounds summed to obtain TPAH.

Naphthalene	Anthracene
1-Methyl naphthalene	Fluoranthene
2-Methyl naphthalene	C ₁ -Fluoranthenes
C ₂ -Naphthalenes	Pyrene
C ₃ -Naphthalenes	Benzo[a]anthracene
C ₄ -Naphthalenes	Chrysene
Biphenyl	C ₁ -Chrysenes
Acenaphthylene	C ₂ -Chrysenes
Acenaphthene	C ₃ -Chrysenes
Fluorene	C ₄ -Chrysenes
C ₁ -Fluorenes	Benzo[b]fluoranthene
C ₂ -Fluorenes	Benzo[k]fluoranthene
C ₃ -Fluorenes	Benzo[e]pyrene
Dibenzothiophene	Benzo[a]pyrene
C ₁ -Dibenzothiophenes	Indeno[1,2,3-c,d]pyrene
C ₂ -Dibenzothiophenes	Dibenzo[a,h]anthracene
C ₃ -Dibenzothiophenes	Benzo[g,h,i]perylene
1-Methyl phenanthrene	Phenanthrene
C ₁ -Phenanthrenes	
C ₂ -Phenanthrenes	
C ₃ -Phenanthrenes	
C ₄ -Phenanthrenes	

the following criteria modified after O'Clair et al. (1996) to compare hydrocarbon concentrations in sediments 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 will be detected if present.

The carbon preference index (CPI; Farrington and Tripp 1977) was used to distinguish sediments contaminated by crude oil from those not contaminated by crude oil. The index has the form:

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

where $n-C_i$ 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 and greater indicate unoiled sediment.

Concentrations shown in the text are given as mean concentration \pm the standard error of the mean (SE). Coefficients of variation (V) were corrected for bias (Sokal and Rohlf 1981). The unbiased estimator is:

$$V^* = (1 + 1/4n)V$$

RESULTS

Assessment Sites

Six assessment locations were sampled in the NGOA in 1994. Intertidal sediments had been oiled during the spill at two of these locations (Hallo Bay and Katmai Bay). Subtidal sediments at two other locations (Chugach Bay and Windy Bay) showed evidence of oiling in 1989. The remaining two locations (Larson Bay and Spiridon Bay) were not sampled in 1989, but oil was reported to have come ashore at these locations.

Intertidal Stations

We found relatively low aromatic hydrocarbon concentrations in intertidal sediments (0 m station) at the six assessment sites sampled in 1994 (Table 3; Fig. 2). The 0-m station was

Table 3.--Concentration (ng/g) of TPAH in sediments from all stations in the NGOA, July 1994. Numbers in the body of the table are mean TPAH and, when n>1, number of replicates (superscripts) where the surrogate recoveries of all PAH analytes (except perylene) were within the acceptable range, and coefficient of variation (in parentheses).

Site			Depth (m)			
No.	Name	Date	0	3	6	20
Reference Sites						
47	Black Bay	7 July	40.1	21.4 ⁵ (117)	21.5 ⁵ (99.2)	25.9 ³ (88.7)
	Tonsina Bay	12 July	47.2 ⁵ (73.8)	7.3 ⁴ (80.1)	12.3 ⁶ (70.8)	36.9 ⁶ (96.8)
Assessment Sites						
49	Chugach Bay	13 July	3.1 ⁴ (158)	14.7 ⁶ (113)	11.0 ⁵ (106)	122 ⁶ (52.6)
50	Hallo Bay	14 July	79.0 ⁶ (52.9)	36.7 ⁶ (44.4)	62.6 ⁶ (57.9)	80.1 ⁶ (18.4)
52	Katmai Bay	15 July	0.4 ² (159)	13.3 ⁵ (154)	30.9 ⁶ (24.7)	60.7 ⁶ (33.0)
	Larson Bay	16 July	6.9 ² (68.9)	1.6	17.1 ² (70.8)	18.3 ² (42.4)
	Spiridon Bay	16 July	13.1 ² (132)	3.9 ³ (97.4)	2.2 ³ (93.9)	13.8 ² (137)
53	Windy Bay	12 July	5.3 ⁶ (106)	20.1 ⁶ (88.7)	138 ⁶ (53.4)	101 ⁶ (66.1)

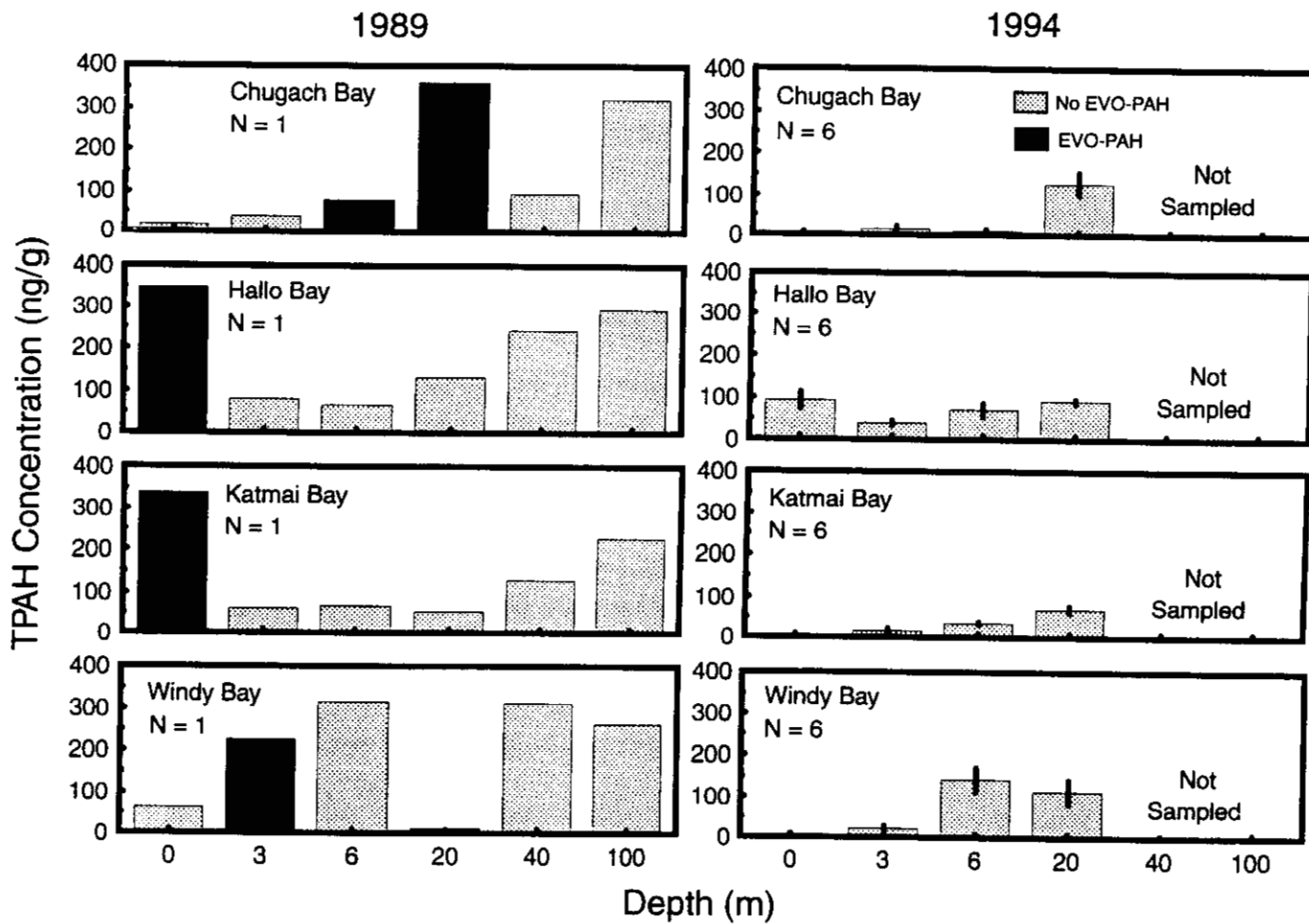


Figure 2.--Concentration of TPAH with depth at four assessment sites in the NGOA in 1989 and 1994. Error bars are one standard error of the mean.

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 in July 1994 was 79.0 ± 16.4 ng TPAH/g dry sediment weight (n=6) at Hallo Bay (Table 3; Fig. 2). Sediments at this station were dominated by sand and granule-sized particles. At the other assessment sites sampled in 1994, the mean TPAH concentration ranged from 0.4 ± 0.4 (Katmai Bay, n=2) to 13.1 ± 10.9 (Spiridon Bay, n=2).

None of the intertidal sediments from our assessment sites contained a PAH composition pattern consistent with weathered EVO (hereafter referred to as the "EVO-PAH pattern"). Half of the intertidal samples collected at Hallo Bay 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 a source identified by Page et al. (1995) as the Katalla oil seep, although another possible source for the "Katalla" hydrocarbons may be coal (O'Clair et al. 1996 and Short et al. 1996). The PAH concentrations in the remaining Hallo Bay intertidal samples and in sediments at intertidal stations at the remaining assessment locations were too low to permit the discrimination of the EVO-PAH pattern or of the composition pattern of any other source.

The TNA concentration in intertidal sediments at those assessment sites sampled in 1994 was relatively low. We found the highest mean TNA concentration (180 ± 101 ng/g, n=3) at Spiridon Bay. The second highest intertidal mean TNA concentration (173 ± 45.2 ng/g, n=6) occurred at Hallo Bay where the highest intertidal assessment station TPAH was found (Tables 3 and 4). The concentrations of all TNA analytes in intertidal samples from Katmai Bay and Larson Bay were below MDL. Where it could be calculated (for all sites except Katmai Bay and Larson Bay), the ratio of mean TNA to mean TPAH at assessment intertidal stations ranged from 2.2 (Hallo Bay) to 13.8 (Spiridon Bay).

The CPI for intertidal sediments at assessment sites generally could not be calculated because the concentrations of alkanes C_{26} , C_{28} and C_{30} were below detection limits. Only at Chugach Bay and Hallo Bay could a CPI be calculated (one sample at each site; Table 5). The CPI for Chugach Bay was based on the concentrations of alkanes C_{26} , C_{27} and C_{28} ; the concentrations of alkanes C_{29} and C_{30} were below detection limits. The CPI for Hallo Bay was based on the concentrations of alkanes C_{26} and C_{28} ; the concentrations of alkanes C_{27} , C_{29} and C_{30} were below detection limits. The PAH analyte distribution in these sediment samples (TPAH concentrations were 2.2 ng/g at Chugach Bay and 40.9 ng/g at Hallo Bay) did not indicate a crude oil source.

Shallow Subtidal Stations

Concentrations of aromatic hydrocarbons in shallow subtidal sediments (3-20 m) were usually (more than 72% of the time) greater than those in intertidal sediments at assessment sites.

Table 4.--Concentration (ng/g) of TNA in sediments from all stations in the NGOA, July 1994. Numbers in the body of the table are mean TNA and, when n>1, number of replicates (superscripts) where the surrogate recoveries of all n-alkane analytes were within the acceptable range, and coefficient of variation (in parentheses).

Site			Depth (m)			
No.	Name	Date	0	3	6	20
Reference Sites						
47	Black Bay	7 July	59.1 ³ (113)	37.8 ⁶ (127)	59.5 ⁶ (67.9)	103 ⁶ (49.9)
	Tonsina Bay	12 July	220 ⁶ (117)	37.9 ⁶ (94.6)	54.1 ⁵ (63.3)	117 ⁶ (58.8)
Assessment Sites						
49	Chugach Bay	13 July	17.3 ⁴ (255)	15.6 ⁶ (64.5)	18.8 ⁶ (63.2)	401 ⁶ (32.1)
50	Hallo Bay	14 July	173 ⁶ (66.9)	206 ⁶ (76.6)	208 ⁶ (24.8)	283 ⁶ (25.3)
52	Katmai Bay	15 July	0 ^{2,a}	30.2 ⁶ (95.4)	314 ⁶ (17.4)	591 ⁶ (11.8)
	Larson Bay	16 July	0 ^{3,a}	13.7 ³ (70.0)	41.3 ³ (36.8)	71.3 ³ (60.3)
	Spiridon Bay	16 July	180 ³ (106)	27.0 ³ (79.8)	32.1 ³ (30.9)	21.5 ³ (48.6)
53	Windy Bay	12 July	29.6 ⁶ (52.8)	49.8 ⁶ (44.0)	470 ⁶ (16.6)	660 ⁶ (34.2)

^aAll TNA analyte concentrations below MDL.

Table 5.--Mean CPI for sediments from all stations in the NGOA, July 1994. Numbers in the body of the table are mean CPI and, when n>1, number of replicates analyzed (superscripts). NC indicates that CPI could not be calculated because the concentrations of alkanes C₂₆, C₂₈ and C₃₀ were below detection limits.

Site			Depth (m)			
No.	Name	Date	0	3	6	20
Reference Sites						
47	Black Bay	7 July	1.62 ⁴	2.86 ²	3.74 ³	3.70 ³
	Tonsina Bay	12 July	1.10 ⁴	3.43 ²	1.90	8.20 ³
Assessment Sites						
49	Chugach Bay	13 July	0.68	NC	NC	20.7 ⁵
50	Hallo Bay	14 July	0	1.58	11.8 ²	10.3 ⁴
52	Katmai Bay	15 July	NC	NC	14.1 ⁶	9.10 ⁶
	Larson Bay	16 July	NC	NC	NC	NC
	Spiridon Bay	16 July	NC	NC	NC	NC
53	Windy Bay	12 July	NC	NC	20.0 ⁶	11.8 ⁶

Sediment particle sizes tended to be finer in samples from subtidal depths, especially at the 6 and 20 m depths, compared to those from the intertidal region. Shallow subtidal sediment samples were collected at all locations where intertidal samples had been collected. Occasionally, the mean TPAH concentration would decrease from 0 to 3 m in depth, but would increase at greater depths (Table 3). The highest mean TPAH concentration in the shallow subtidal region at assessment sites was 138 ± 28.8 ng/g at the 6-m station at Windy Bay (Table 3; Fig. 2). The sediment from this station was dominated by silt/clay and sand.

Our analyses detected a PAH pattern similar to that of EVO in subtidal sediments in three samples from the 6-m depth at Windy Bay. The mean TPAH concentration of these samples was 158 ± 38.2 ng/g. The sediment was silt/clay. Two of the remaining samples from that station showed the "Katalla" pattern. The mean TPAH concentration of these samples was 157 ± 48.6 ng/g. The last sample from the 6-m depth at Windy Bay contained PAH analyte concentrations too low to discriminate a petrogenic source. The "Katalla" pattern was also found at the 20-m stations of Windy Bay (67% of samples) and Chugach Bay (100% of samples) and at all subtidal stations at Hallo Bay (17% of 3-m samples, 67% of 6-m samples and 67% of 20-m samples). The PAH analyte concentrations in all of the remaining subtidal sediment samples from assessment sites were too low to discriminate a petrogenic source.

As with TPAH, the TNA concentration in shallow subtidal sediments at assessment sites tended to exceed the intertidal TNA concentration. The only exception was Spiridon Bay where the intertidal TNA concentration consistently exceeded that at subtidal depths (Table 4). The greatest mean TNA concentration (660 ± 88.5 ng/g) found in subtidal sediments in 1994 occurred in sediments from the 20-m depth at Windy Bay. Sediments from this station also exhibited the third highest mean TPAH concentration observed in 1994 (Table 3), and two-thirds of the samples from this station contained the "Katalla" PAH analyte pattern. Generally, the highest mean TNA concentrations tended to occur at stations where the EVO-PAH or "Katalla" PAH analyte patterns were found. The only exceptions were the 6-m and 20-m stations at Katmai Bay where a high mean TNA concentration was found (Table 4), but where the mean TPAH concentration was not particularly high (Table 3), and no petrogenic analyte pattern was found.

The ratio of mean TNA to mean TPAH in the shallow subtidal region at assessment sites ranged from 1.1 (Chugach Bay, 3 m station) to 10.2 (Katmai Bay, 6 m station). The range in this ratio was comparable to that observed in intertidal sediments at assessment sites. The range was markedly narrower (3.3 to 6.6) for sediments from shallow subtidal stations where the EVO-PAH or "Katalla" PAH pattern was observed.

The CPI values could be calculated for 44% 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 C_{30} were below detection limits. Where CPI values could be calculated, they reflected alkane distributions that were not indicative of sediments contaminated by crude oil, except at the 3-m station at Hallo Bay (mean CPI = 1.6; Table 5). Mean CPI values for the other shallow subtidal assessment stations ranged from 9.1 to 20.7 (Table 5).

Reference Sites

Intertidal Stations

The PAH analyte concentrations in most of the intertidal sediment samples from the two reference sites were too low to discriminate a petrogenic source. A PAH pattern similar to that of EVO was found in one sample at the intertidal station at Tonsina Bay. Another sample at that station exhibited the "Katalla" pattern. A third sample from the Tonsina Bay intertidal station showed a PAH analyte pattern indicative of diesel oil. The PAH analyte pattern of diesel oil was characterized by: (1) alkyl chrysenes absent, (2) alkyl phenanthrenes (summed) exceed 20 ng/g, and (3) the ratio of alkyl dibenzothiophenes (summed) to alkyl phenanthrenes (summed) exceeds 0.20. Only one sample from the intertidal station at Black Bay contained a PAH analyte concentration pattern of petrogenic origin. The PAH composition pattern of that sample exhibited 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 indicated an unknown hydrocarbon source, possibly diesel oil.

The highest mean TPAH concentration found at the 0 m station of the reference sites was 47.2 ± 14.8 ng TPAH/g dry sediment weight at Tonsina Bay (Table 3). The TPAH concentration could be calculated for only one sample from the intertidal station at Black Bay. In all other samples collected at that station at least one PAH analyte was excluded from the analysis because the surrogate recovery fell outside the acceptable range. The TPAH concentration of that sample was 40.1 ng TPAH/g sediment (Table 3). The TPAH concentration in most samples from Tonsina Bay, and the only sample from Black Bay for which a TPAH concentration could be calculated, exceeded the mean intertidal TPAH concentration at all assessment sites except Hallo Bay. As expected, the highest TPAH concentrations at Tonsina Bay were associated with samples in which a petrogenic source was identified. No petrogenic source could be identified in the sample from Black Bay with a TPAH concentration of 40.1 ng TPAH/g. Sediments in intertidal samples from Tonsina Bay were composed of pebbles, granules and sand. Those in Black Bay intertidal samples were composed of the same particle sizes as Tonsina Bay, but with sand rather than pebbles dominating.

The mean TNA concentration in intertidal sediments at reference sites was relatively high compared to that in intertidal sediments from assessment sites. The highest mean TNA concentration (220 ± 101 ng/g) at the two reference sites occurred at Tonsina Bay (Table 4). This mean TNA concentration was nearly four times greater than that at Black Bay and greater than the mean intertidal TNA concentration at all assessment sites. The ratio of mean TNA to mean TPAH at intertidal reference stations showed a narrower range (1.5 to 4.7) than at assessment sites (0 to 13.8).

The mean CPI values for the intertidal sediments at Black Bay and Tonsina Bay were 1.62 and 1.1, respectively, indicating the presence of petroleum. The CPI of that sample from Black Bay that contained a PAH concentration pattern indicative of an unknown petroleum hydrocarbon

source was 1.4. The CPI in those samples from Tonsina Bay that contained a PAH concentration pattern indicating one or the other of three petrogenic sources ranged from 1.02 to 1.2 (Table 5).

Shallow Subtidal Stations

Unlike at the assessment sites, the concentration of TPAH in shallow subtidal sediments (3-20 m) at reference sites consistently averaged less than those in intertidal sediments at those sites (Table 3). The mean TPAH concentration tended to increase with increasing depth from 3 to 20 m at Tonsina Bay, but remained less than that for the intertidal station. At Black Bay the mean TPAH concentration remained relatively constant in the 3 to 20-m depth range, and the mean subtidal TPAH concentrations were less than the intertidal TPAH concentration there (Table 3). The greatest mean subtidal TPAH concentration at the reference sites was 36.9 ± 14.0 ng/g at the 20-m station at Tonsina Bay. This value was less than 67% of the mean TPAH concentrations at the 20-m stations at assessment sites, and was a little over 25% of the greatest mean TPAH concentration found at assessment sites.

No evidence of the EVO-PAH pattern was found in shallow subtidal sediments at the reference sites. All of the sediment samples from shallow subtidal stations at reference sites contained concentrations of PAH analytes too low to distinguish a hydrocarbon source.

As with TPAH, the mean TNA concentration in shallow subtidal sediments at Tonsina Bay was less than the mean intertidal TNA concentration (Table 4). At Black Bay, only the mean TNA concentration at 3 m was less than the mean intertidal TNA concentration. Subtidal sediments were composed of finer particles than intertidal sediments at both Tonsina Bay and Black Bay, tending toward sand and silt/clay at Tonsina Bay and sand and granules at Black Bay. The greatest mean TNA concentration (117 ± 26.9 ng/g) found in subtidal sediments at the reference sites occurred in sediments from the 20-m station at Tonsina Bay, the station with the highest mean subtidal TPAH concentration for reference sites (Tables 3 and 4). Sediments at this station were silt/clay. The mean TNA concentration at the 20-m station at Tonsina Bay was exceeded by 67% of the mean TNA concentrations for the 20-m station at the assessment sites.

The ratio of mean TNA concentration to mean TPAH concentration in the shallow subtidal region at the reference sites ranged from 1.8 (Black Bay, 3-m station) to 5.2 (Tonsina Bay, 3-m station). The range in this ratio at the reference sites was a little more than one-third (37%) that observed in shallow subtidal sediments at assessment sites.

The CPI values could be calculated for all of the shallow subtidal stations at the reference sites. The mean CPI values for these stations reflected alkane distributions indicative of unoiled sediments, except perhaps at the 6-m depth at Tonsina Bay where the mean CPI was 1.9 (Table 5). Nevertheless, the PAH analyte concentrations at this station were too low to permit detection of a particular petrogenic source. The mean CPI values for all subtidal stations at Black Bay and for the 3-m station at Tonsina Bay fell near or within the range of 3 to 6 indicating terrigenous plant waxes (Farrington and Tripp 1977).

DISCUSSION

O'Clair et al. (1996) found little evidence of subtidal sediment contamination by EVO in the NGOA. This result was, in part, attributable to the limited number of samples that were analyzed from the NGOA, but it may also have been a function of the large area over which EVO spread after it exited PWS. Wolfe et al. (1994) estimated that between 7 and 11% of the total spilled oil ultimately became beached in the Kenai and Shelikof Strait areas combined. Although O'Clair et al. (1996) found some indication of EVO in intertidal sediments at Hallo Bay and Katmai Bay and in subtidal sediments at Chugach Bay and Windy Bay, only one of three replicates was analyzed at each station at these locations. The TPAH concentrations in these samples were low; therefore, they were substantially less confident of the source of the hydrocarbons in the samples. They concluded that because of the relatively small percentage of the spilled oil that exited PWS compared to the extensive length of coastline in the NGOA, oiling of the beaches there was patchy and there was less oil available on the beaches in the NGOA than in PWS for redistribution to subtidal sediments. Moreover, they concluded that probably only in localized areas were conditions favorable to the transport of beached oil to adjacent shallow subtidal sediments (i.e., heavy initial shoreline oiling, exposure to high-energy wave action, and conditions of minimal disturbance for subtidal sediments on slopes of shallow gradient). As a result, most subtidal sediments outside PWS probably were not detectably contaminated by EVO (O'Clair et al. 1996).

In this report, we use a more extensive set of hydrocarbon data on sediments collected in the NGOA in 1994 to determine: (1) the composition and concentration of petroleum hydrocarbons from the spill in intertidal and subtidal sediments (0-20 m) in the NGOA, (2) the persistence of EVO in subtidal sediments in the NGOA over time, and (3) the distribution of EVO in subtidal sediments in the NGOA compared with that of hydrocarbons from other sources.

Assessment Sites

Intertidal sediments

The spill contaminated lower intertidal sediments (near MLLW) with crude oil at two locations (Hallo Bay and Katmai Bay) in the NGOA (O'Clair et al. 1996). The highest concentration of TPAH observed in the lower intertidal zone was 348 ng/g at Hallo Bay in August 1989, and at Katmai Bay was 339 ng/g. In July 1994, the mean concentration of TPAH at the 0-m station at Hallo Bay was 79.0 ± 16.4 ng/g and at Katmai Bay was 0.4 ± 0.4 ng/g.

EVO was indicated as the source of the PAHs in lower-intertidal sediments at Hallo Bay and Katmai Bay in 1989 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 (O'Clair

et al. 1996). Characteristics of the hydrocarbons in sediments that indicated EVO in 1994 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 1994, PAH concentrations in lower-intertidal sediments at Katmai Bay and in three samples from Hallo Bay were too low to discriminate among the known possible sources of petroleum hydrocarbons in the NGOA. In the remaining three intertidal samples from Hallo Bay, the distribution of PAH concentrations most closely matched that of the "Katalla" source. PAH concentrations in lower-intertidal sediments at all other assessment sites in 1994 were too low to distinguish a petrogenic source.

In 1989, EVO contamination of the intertidal sediments at Hallo Bay and Katmai Bay was confirmed 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 distribution of n-alkane concentrations was often indicative of alkanes from terrigenous sources. TNA concentrations ranging to more than 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 et al. 1971) were widespread in intertidal sediments at reference stations and at assessment stations where oiling in the upper intertidal zone was low or absent; therefore, alkanes from these nonpetrogenic sources were not masked by oil (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 1994 were similar. The greatest mean TNA found in lower-intertidal sediments in 1994 was 180 ± 101 ng/g at Spiridon Bay. A CPI could not be calculated for those sediments because the concentrations of alkanes C_{26} , C_{28} and C_{30} were below detection limits. The next greatest mean intertidal TNA in 1994 was 173 ± 45.2 ng/g at Hallo Bay. The CPI for those sediments was 0; the concentrations of alkanes C_{27} , C_{29} and C_{30} were below detection limits.

Subtidal Sediments

O'Clair et al. (1996) found evidence of EVO contamination in shallow subtidal sediments at Chugach Bay and Windy Bay in 1989. The TPAH concentrations in shallow subtidal sediments that exhibited the EVO-PAH pattern at Chugach Bay in 1989 were 80.6 ng/g (6-m depth) and 362 ng/g (20-m depth). The PAH concentration at at Windy Bay was 224 ng/g (3-m depth; O'Clair et al. 1996). Contamination by EVO of shallow subtidal sediments at Windy Bay persisted to July 1994. At this site in July 1994, the PAH composition pattern indicative of weathered EVO was found in three samples at the 6-m depth. The mean TPAH concentration in sediments from the 6-m depth at Windy Bay was 138 ± 28.8 ng/g. The EVO-PAH pattern was found at depths to 20 m at Chugach Bay in 1989. By 1994, the EVO-PAH pattern was found no deeper than 6 m.

Reference Sites

Intertidal sediments

Sediment samples collected in the lower-intertidal zone at Black Bay were not contaminated by EVO in 1989. The TPAH concentration at this station was 9.75 ng/g. Sediment samples collected from Tonsina Bay in 1989 were not analyzed; however, there was no evidence of obvious oiling of the intertidal site in 1989. These sites were therefore considered to be reference sites in 1994. In 1994, one of six sediment samples from the lower-intertidal zone at Tonsina Bay had a PAH analyte distribution indicative of EVO. The EVO-PAH analyte distribution in that sample may have reflected a mixture of PAHs from other sources. Two other sediment samples from that station contained analyte distributions indicative of two other sources: one was diesel oil, the other was the "Katalla" source. The remaining three samples had PAH analyte distributions too low to discriminate a petrogenic source. Nevertheless, Tonsina Bay may have been an inappropriate choice for a reference site in 1994. The mean TPAH concentration of lower-intertidal sediments at Black Bay and Tonsina Bay in 1994 was less than 50 ng/g.

Subtidal Sediments

The EVO-PAH composition pattern was absent from shallow subtidal sediments at Black Bay in 1989. The TPAH concentration at the shallow subtidal stations there ranged from 11.3 to 15.1 ng/g (O'Clair et al. 1996). Moreover, in 1994 no evidence of the EVO-PAH composition pattern was found in shallow subtidal sediments from Black Bay or Tonsina Bay. The PAH analyte distributions in all subtidal samples from these sites were too low to discriminate a petrogenic source. The mean TPAH concentration in subtidal sediments from these sites ranged from 7.3 to 36.9 ng/g.

Geographic distribution of EVO

O'Clair et al. (1996) found EVO in lower intertidal or subtidal sediments over a broad geographic range in the NGOA in 1989. The area over which EVO contamination of these sediments was found ranged from Windy Bay (3-m depth) at the eastern end of the study area to Katmai Bay (intertidal sediments only) at the western end (although EVO contamination was geographically discontinuous depending on where large quantities of oil came ashore). Subtidal sediments contained EVO at two locations (Chugach Bay and Windy Bay) 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 one location (Chugach Bay) in 1989. By 1994, EVO contaminated subtidal sediments were restricted to one station (Windy Bay, 6-m depth).

Other sources of hydrocarbon contamination

We found three patterns of PAH composition in benthic 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 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. This PAH composition pattern was similar to that of weathered EVO, except for substantially lower relative abundances of dibenzothiophenes. Page et al. (1995) attributed this PAH composition pattern to marine oil seeps near Katalla Island (see also Page et al. 1996); another possibility may have been coal (O'Clair et al. 1996). 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 (82%) collected in the intertidal region at reference sites and assessment sites in 1994 contained PAH concentrations too low to determine the source. One intertidal sample each showed a PAH pattern indicative of diesel oil (Tonsina Bay) or the unknown petrogenic source (Black Bay). Three samples exhibited the "Katalla" pattern at one assessment site only (Hallo Bay), and one sample showed the "Katalla" pattern at one reference site only (Tonsina Bay). 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.

As with the intertidal samples, the majority of subtidal sediment samples from all sites sampled in 1994 contained PAH concentrations too low to distinguish a petrogenic source. The percentage of samples that contained these low PAH concentrations ranged from 53% (20-m depth) to 97% (3-m depth) at assessment sites and was 100% at all subtidal depths sampled at reference sites. The proportion of subtidal sediment samples from assessment sites that contained hydrocarbons from the "Katalla" source tended to increase with depth while sediment grain size decreased. At 3 m, only 3% of the samples were contaminated by the "Katalla" source. Those samples were composed of sand. At 6 m, the percentage increased to 20, and at 20 m, 47% of the sediment samples contained "Katalla" hydrocarbons. All samples collected at or below 6 m that contained "Katalla" hydrocarbons were composed of sediments dominated by silt/clay. Fifty-three percent of these samples contained silt/clay exclusively, whereas 47% contained a mixture of silt/clay and sand with silt/clay more abundant than sand. No subtidal samples from assessment sites showed evidence of hydrocarbons from diesel or the unknown petrogenic source.

CONCLUSIONS

Although oil from the spill contaminated shores over a broad geographic range in the NGOA in 1989, by 1994 the distribution of EVO in shallow subtidal sediments was restricted to half the samples (n=3) collected at one subtidal assessment station (Windy Bay, 6-m depth). One additional sample collected in the low intertidal zone at Tonsina Bay contained a PAH analyte distribution characteristic of weathered EVO. The most frequently represented source of

petroleum hydrocarbons, where a source could be distinguished, was the “Katalla” source which was found in nearly half of the sediment samples from the 20-m depth. Most of the samples that contained the “Katalla” source were dominated by sediments in the silt/clay range of particle sizes. This study represents the final assessment of the extent to which subtidal sediments in the NGOA were contaminated by the spill.

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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 EPA 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.