

Exxon Valdez Oil Spill
Restoration Project Annual Report

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

Restoration Project 94285
Annual Report

This annual report has been prepared for peer review as part of the *Exxon Valdez* Oil Spill Trustee Council restoration program for the purpose of assessing project progress. Peer review comments have not been addressed in this annual 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 or 1993. 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. Hydrocarbon analysis of the sediment samples collected for this project was completed in September 1995. Data analysis is currently in progress. FY 94 was the last field season for this project which will be closed out with a Final Report prepared in FY 96.

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. We sampled two additional locations in Prince William Sound for comparison. Sediments were sampled near mean lower low water and at three subtidal depths in the 3-20 m range. Hydrocarbon analysis using gas chromatography/mass spectrometry has just been completed. Data analysis and final report writing is currently in progress.

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 oil from the spill in the sediments there. For comparison we also sampled sediments at two locations (one which had been heavily oiled in 1989 and another which was a reference location) in Prince William Sound. Sediments were sampled in July near mean lower low water and at three subtidal depths in the 3-20 m range. Hydrocarbon analysis was completed in September 1995. Hydrocarbon analysis was performed using gas chromatography and mass spectrometry. Data analysis and final report writing is currently in progress. The final report will be completed by March 1996. This deadline is consistent with the Detailed Project Description for this study which projected a final report completion date six months after completion of the hydrocarbon analysis.

INTRODUCTION

In the first year after the *Exxon Valdez* oil spill (EVOS) O'Clair et al. (In prep.) found subtidal sediments to be contaminated by petroleum hydrocarbons from the EVOS 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) 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). O'Clair et al. (In prep.) is currently being rewritten in response to reviewer's comments. 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).

The purpose of this report is to review our progress in determining the geographical and bathymetric distribution of petroleum hydrocarbons from the EVOS in subtidal sediments in NGOA five years after the spill and the extent to which EVO has persisted in low intertidal and subtidal sediments between 1989 and 1994, thereby providing information on the natural recovery of the subtidal sediments from EVO contamination in the NGOA.

OBJECTIVES

- A. Determine the composition and concentration of petroleum hydrocarbons from the EVOS in intertidal and subtidal sediments (0-20 m) in the NGOA 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. Compare concentrations of hydrocarbons in subtidal sediments in the NGOA with concentrations at comparable depths in Prince William Sound (PWS).
- C. Determine the distribution of EVO with bathymetric depth and compare with bathymetric distribution of EVO in the NGOA in 1989.
- D. Determine persistence of EVO in subtidal sediments in the NGOA over time.
- E. Compare the distribution of EVO in subtidal sediments in the NGOA with those of hydrocarbons from other sources.

METHODS

Study Sites

The geographical nomenclature in this report follows O'Clair et al. (In prep.). 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 paired bathymetric transects used to sample various bottom depths 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 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 (O'Clair et al., In prep.). Reference locations are those where no EVO was detected in 1989.

Sediments were sampled at a total of 10 locations using the same methods employed during the NRDA study. Eight locations were sampled in the NGOA (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 herein to have been assessment sites (Table 1, Figure 1). Black Bay and Tonsina Bay were reference sites. Two sites were sampled in PWS (Northwest Bay and Olsen Bay). Northwest Bay was a contaminated site, Olsen Bay was a reference site. Northwest Bay and Olsen Bay were sampled on 25 June 1994. Dates of sampling for the NGOA sites 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). Intertidal collections were made at about 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 and 20 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 station (0-20 m).

All samples 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 EPA standards were used to store

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

Site ¹		North Latitude	West Longitude	Number of Stations
No.	Name	o ' "	o ' "	
<u>Northern Gulf of Alaska</u>				
47	Black Bay	59 32 07	150 12 17	8
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
	Tonsina Bay	59 18 42	150 55 00	8
53	Windy Bay	59 13 50	151 31 00	8
<u>Prince William Sound</u>				
31	Northwest Bay	60 33 07	147 34 36	8
32	Olsen Bay	60 45 05	146 11 13	8

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

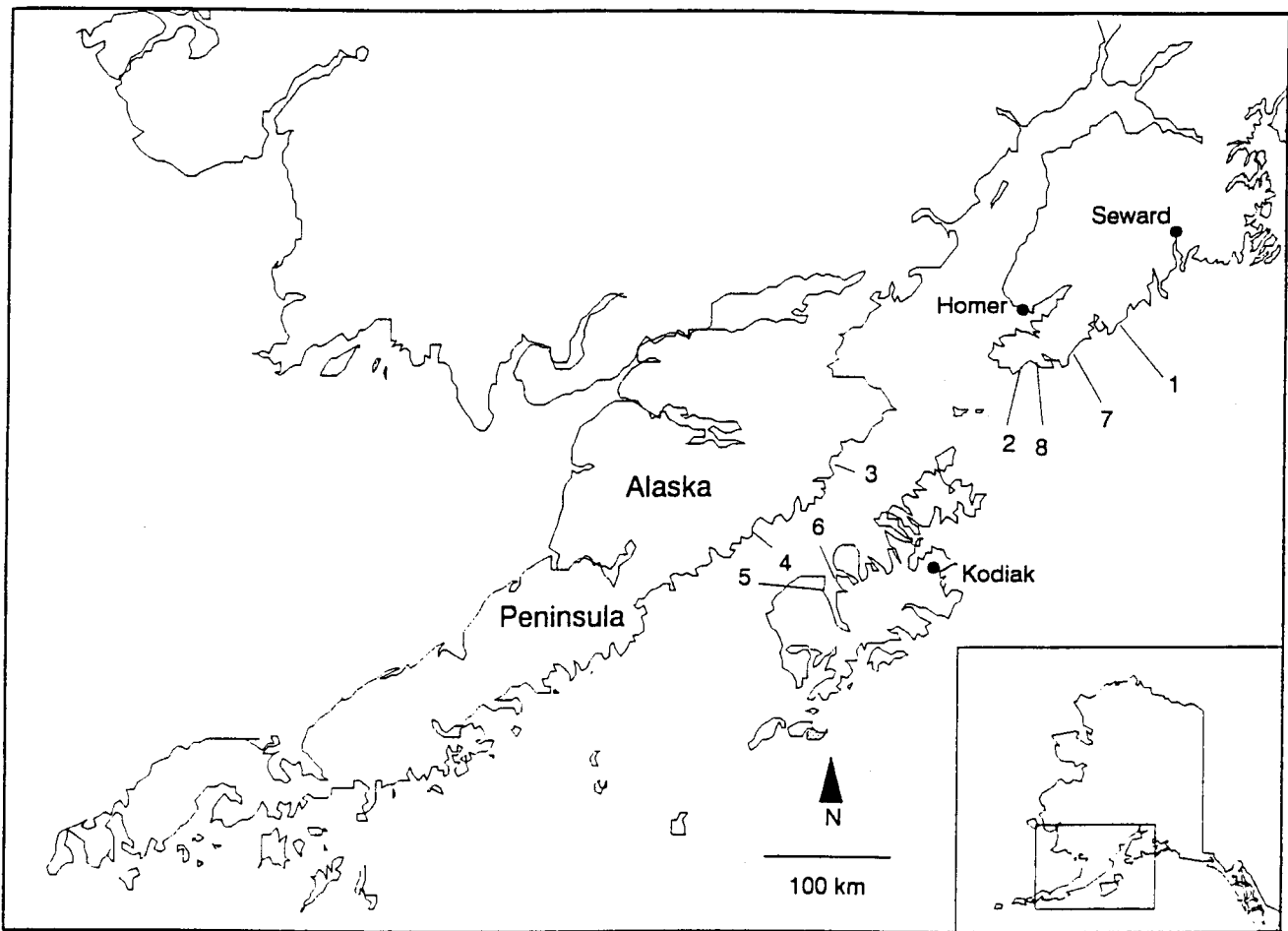


Figure 1. Distribution of sites sampled in 1994 in the NGOA. See Table 1 for the geographical coordinates of each site. Numbered sites are: 1) Black Bay; 2) Chugach Bay; 3) Hallo Bay; 4) Katmai Bay; 5) Larson Bay; 6) Spiridon Bay; 7) Tonsina Bay; 8) Windy Bay.

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 travelled 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.

Hydrocarbon and Data Analysis

Sediment samples were analyzed for petroleum hydrocarbons by means of gas chromatography/mass spectrometry at the Auke Bay Laboratory. 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, TPAH, total normal alkanes (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 MDL were replaced by "0's" for our analyses. The MDL for aromatic hydrocarbons was 1 ng/g; that for aliphatic hydrocarbons was 10 ng/g. Hydrocarbon concentrations will be reported in the final report on a dry weight basis to 3 significant figures when concentrations exceed 10 ng/g, and to 2 significant figures for lower concentrations. A total of 216 sediment samples was analyzed for hydrocarbons from the 10 sites sampled.

The high sulfur content of EVO helps 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). Accordingly, we will use the following criteria to compare hydrocarbon concentrations in sediments with those in EVO. The pattern of PAH concentrations in the sediment samples will be judged similar to EVO if it consistently meets each of three criteria in all replicated samples: (1) the ratio of alkyl dibenzothiophenes (summed) to alkyl phenanthrenes (summed) exceeds 0.20; (2) the ratio of alkyl chrysenes (summed) to alkyl phenanthrenes (summed) exceeds 0.03; and (3) the concentration of alkyl phenanthrenes (summed) exceeds 20 ng/g. This latter criterion is necessary to insure that chrysenes will be detected if present.

The carbon preference index (CPI; Farrington and Tripp 1977) will be used to distinguish oiled from non-oiled sediments. 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 indicate unoiled sediment.

Concentrations shown in the text of the final report will be given as mean concentration \pm the standard error of the mean (SE). Unless otherwise noted means will be the average of three replicates. Coefficients of variation (V) that will be tabulated in the final report will be corrected for bias (Sokal and Rohlf 1981). The unbiased estimator is:

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

RESULTS

Sediment hydrocarbon analysis for this study has been completed. Quantitative (resulting in tabular and graphical outputs) analysis is in progress. Final report preparation has begun. The final report will be completed by March 1996. This deadline is consistent with the Detailed Project Description for this study which projected a final report completion date six months after completion of the hydrocarbon analysis.

DISCUSSION

O'Clair et al. (In prep.) found little evidence of subtidal sediment contamination by EVO in NGOA. This result was, in part, attributable to the limited number of samples that were analyzed from the NGOA, but it probably also reflected the relatively small proportion of the spilled oil that exited the Sound and subsequently spread over the much larger area of the NGOA. 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. (In prep.) 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 O'Clair et al. (In prep.) were substantially less confident of the source of the hydrocarbons in the samples. They conclude that because of the relatively small percentage of the spilled oil that exited PWS and 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.

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., In prep.).

In our upcoming final report we will use a much more extensive set of hydrocarbon data on sediments collected in NGOA in 1994 to determine: 1) the composition and concentration of petroleum hydrocarbons from the EVOS in intertidal and subtidal sediments (0-20 m) in the NGOA, 2) how concentrations of hydrocarbons in subtidal sediments in the NGOA compare with concentrations in sediments at comparable depths in PWS, 3) the persistence of EVO in subtidal sediments in the NGOA over time, and 4) the distribution of EVO in subtidal sediments in the NGOA compared with that of hydrocarbons from other sources.

CONCLUSIONS

This study represents the final assessment of the extent to which subtidal sediments in NGOA were contaminated by the EVOS. Because our study draws on a more extensive set of sediment samples than did that of O'Clair et al. (In prep.) we expect that our final report which will be available for peer review by March 1996 will provide a more comprehensive view of persistent contamination by EVO of subtidal sediments in NGOA in 1994 than has been reported for freshly contaminated sediments in NGOA in 1989.

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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.

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 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.