

Comparative Fate of Chemically Dispersed and Beached Crude Oil in Subtidal Sediments of the Arctic Nearshore

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ABSTRACT. A three-year investigation was conducted to examine the incorporation of petroleum hydrocarbons (PHC) into subtidal sediments following experimental releases of oil during the Baffin Island Oil Spill (BIOS) Project experiments. The concentrations of PHC were determined by synchronous scanning UV/Fluorescence spectroscopy, while the composition of residual saturated and aromatic hydrocarbons was determined by gas chromatography and gas chromatographic mass spectrometry.

A pre-spill sampling and four post-spill samplings (one day, two weeks, one year and two years after the releases) were conducted in each test bay. After the surface release and beaching of non-dispersant treated oil (Bay 11), accumulation of PHC at levels of 1-10 $\mu\text{g}\cdot\text{g}^{-1}$ was noted in subtidal sediments within two weeks. Concentrations steadily increased over the ensuing two years, so that two years after the release, up to 10% of the originally beached oil was present in subtidal sediments. Concentrations of up to 400 $\mu\text{g}\cdot\text{g}^{-1}$ were detected in the shallow offshore sediments. All oil residues in surface sediment appeared to be confined to the top 0-2 cm of the sediment column. The eroding oil from the Bay 11 beach was compositionally quite heterogeneous, with weathered, biodegraded oil, as well as relatively unweathered oil, found on the beach and in the offshore sediments. Biodegradation of oil appeared to be restricted to the beached oil, with no significant degradation apparently occurring subtidally. After two years, the offshore oil residues still contained low molecular weight alkanes as well as alkylated naphthalenes.

The situation in Bay 9, where chemically dispersed oil was discharged near the bottom, was quite different. In spite of a large water column exposure, the bottom sediments never contained more than 10 $\mu\text{g}\cdot\text{g}^{-1}$ of oil. Of this amount of oil, a significant fraction (20%) of the PHC was initially associated with the surface flocculent layer. Levels of oil in the Bay 9 sediments were on the order of 1-3 $\mu\text{g}\cdot\text{g}^{-1}$ one year after the release. Sediment PHC levels in the other less exposed bays (Bays 10 and 7) never exceeded 3 $\mu\text{g}\cdot\text{g}^{-1}$.

Key words: BIOS, experimental oil spill, petroleum hydrocarbons, arctic sediments, oil pollution

RÉSUMÉ. Une enquête s'étendant sur trois ans a été menée afin d'examiner la pénétration d'hydrocarbures pétroliers (HCP) dans les sédiments situés en dessous du niveau des marées, à la suite de déversements expérimentaux de pétrole durant les expériences du projet BIOS (projet de déversement de pétrole à l'île Baffin). Les concentrations de HCP ont été déterminées par spectrométrie de fluorescence aux U.V. synchrone à canal mobile, tandis que la composition des hydrocarbures résiduels saturés et aromatiques a été déterminée par chromatographie en phase gazeuse et par spectrométrie de masse chromatographique en phase gazeuse.

Dans chaque baie, on a prélevé un échantillon avant le déversement de pétrole et quatre par la suite (1 jour, 2 semaines, 1 année et 2 années après les déversements). Dans les deux semaines après que le pétrole traité non dispersable a été déversé et qu'il s'est échoué (baie 11), on a relevé des niveaux d'accumulation de HCP de 1 à 10 $\mu\text{g}\cdot\text{g}^{-1}$, dans les sédiments sous le niveau des marées. Les concentrations ont augmenté régulièrement au cours des 2 années suivantes, et, 2 ans après le déversement, jusqu'à 10% du pétrole échoué à l'origine sur les plages était présent dans les sédiments sous les marées. On a détecté des concentrations allant jusqu'à 400 $\mu\text{g}\cdot\text{g}^{-1}$ dans les sédiments situés en mer à faible profondeur. Tous les résidus du pétrole dans les sédiments de surface semblaient se concentrer dans les deux centimètres supérieurs de la colonne de sédiments. Le pétrole emporté par l'érosion de la plage de la baie 11 avait une composition assez hétérogène, avec du pétrole vieilli, biodécomposé, et aussi du pétrole relativement peu vieilli trouvé sur la plage et sur les sédiments au large. La biodécomposition du pétrole semblait être restreinte au pétrole échoué, celui situé en dessous du niveau des marées ne présentant pas de décomposition notable. Au bout de deux ans, les résidus du pétrole en mer contenaient toujours des alcanes de faible poids moléculaire et des naphthalènes alkylés.

Dans la baie 9, où on avait déversé du pétrole dispersé chimiquement près du fond, la situation était tout à fait différente. En dépit de l'exposition à une importante colonne d'eau, les sédiments du fond ne contenaient jamais plus de 10 $\mu\text{g}\cdot\text{g}^{-1}$ de pétrole. De cette quantité, une assez grande partie (20%) de HCP était associée à l'origine à la couche flocculeuse de surface. Un an après le déversement, les niveaux de pétrole dans les sédiments de la baie 9 étaient de l'ordre de 1 à 3 $\mu\text{g}\cdot\text{g}^{-1}$. Les niveaux de HCP dans les sédiments des autres baies moins exposées (les baies 10 et 7) n'ont jamais dépassé 3 $\mu\text{g}\cdot\text{g}^{-1}$.

Mots clés: BIOS, déversement de pétrole expérimental, hydrocarbures pétroliers, sédiments arctiques, pollution par le pétrole

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INTRODUCTION

This paper is one of a series in the *Arctic Supplement* on the Baffin Island Oil Spill (BIOS) Project. The BIOS Project, summarized by Sergy and Blackall (1987), conducted experimental oil releases in the arctic nearshore at Cape Hatt, N.W.T., in the summer of 1981. The release area was studied for two years after the releases.

The potential magnitude of long-term biological effects of spilled oil on marine communities is related to the concentrations and persistence of petroleum hydrocarbons (PHC) in subtidal sediments (NAS, 1985). One of the key goals of the BIOS Project was, therefore, to measure the concentrations of petro-

leum hydrocarbons and the trends in these concentrations in arctic subtidal sediments resulting from experimental releases of artificially weathered Lagomedio crude oil in two scenarios: release of chemically dispersed (Corexit 9527) oil beneath the sea surface and release of untreated oil on the surface.

While other oil spill research programs had investigated the fate and weathering of oil in sediments (e.g., Boehm *et al.*, 1981, 1982a; Keizer *et al.*, 1978; Teal *et al.*, 1978; see NAS, 1985 for other references), few have addressed the comparative fates of chemically dispersed and untreated oils (e.g., Page *et al.*, 1983). This type of comparative assessment is essential in providing a valid scientific basis for deciding when and if it is advisable to chemically disperse oil in arctic and other nearshore

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environments. In part, such a decision should be based on the expected extent of transport to and fate of oil in subtidal sediments.

This report presents a detailed summary of chemical studies carried out as part of the BIOS project for two years following the experimental releases of oil. Additional details of these chemical studies may be found in Boehm (1983), Boehm *et al.* (1981, 1982b, 1984b, 1985), Green *et al.* (1982) and Humphrey (1983). In this issue of *Arctic*, Cretney *et al.* (1987a,b,c) describe in detail the sampling and analytical methods used in the BIOS chemical studies and present data on the concentrations of hydrocarbons present in the water column, sediments and tissues before the oil releases. Humphrey *et al.* (1987a) describe the fate of released oil in the water column, Humphrey *et al.* (1987b) describe the uptake and release of oil by benthic animals and Owens *et al.* (1987) deal with the fate of oil stranded on the beaches.

METHODS AND MATERIALS

Physical Setting and Release Scenarios

The location of the experimental releases of crude oil is on the eastern shore of Ragged Channel in the Cape Hatt region of northern Baffin Island, N.W.T. (Fig. 1). The artificially weathered Lagomedio crude oil was released in Bay 11 on 19 August 1981. Of the 15 m³ of oil released on the ebbing tide in calm

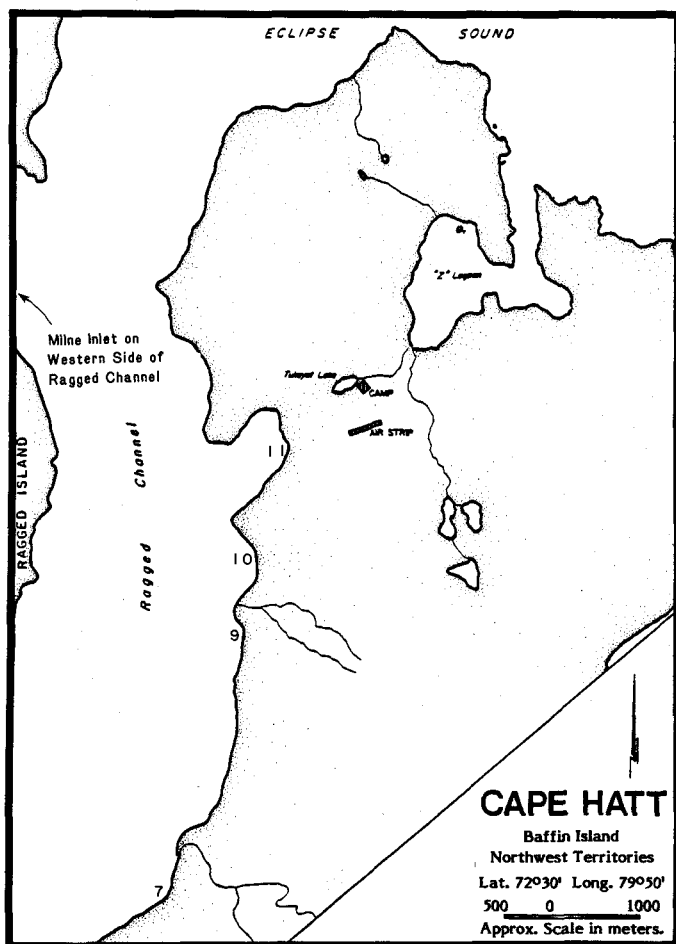


FIG. 1. Detail of test bay locations.

water over a 6 h period, approximately one-third remained stranded on the Bay 11 beach two days after its release (Owens *et al.*, 1987). The remainder was either recovered by surface oil skimmers or lost by evaporation or solution. The stranded oil was left on the beach face, and the changing mass of oil and its chemical characteristics were studied over the next two years (Owens *et al.*, 1987; Boehm *et al.*, 1984b).

The release of chemically dispersed oil occurred on 27 August 1981 in Bay 9 (Fig. 1). Premixed oil and dispersant (10:1) was mixed with seawater pumped through a diffuser pipe laid perpendicular to shore and 1 m off the bottom. The ratio of water to oil to dispersant was 50:10:1 and the application time was 6 h. This discharge represented a worst-case scenario of direct exposure of subtidal sediments to chemically dispersed oil, in that relatively unweathered oil with an abundance of toxic low molecular weight aromatic hydrocarbons was discharged at high concentrations very near the sediment-water interface. Details of these releases can be found in Dickins *et al.* (1987).

Sampling Strategy

Many scientific segments of the BIOS Project required information on the content and composition of PHC associated with subtidal sediments in the study bays. Thus, a number of sampling strategies were combined to yield the overall sediment sampling pattern (Cretney *et al.*, 1987; Snow *et al.*, 1987). Details of these sampling strategies and rationale are given in Boehm *et al.* (1982a), Green *et al.* (1982), Humphrey (1983) and Cretney *et al.* (1987). In general, subtidal sediment sampling in each bay focused mainly on two water depth strata (3 m and 7 m) oriented roughly parallel to the shoreline for a total distance of 150 m (Fig. 2). At each of the two depth strata, surface sediment samples from the upper 2 cm of sediment were collected at stations every 10 m along each of the three 50 m long benthic transects. Sediments were additionally collected from stations at five tissue plots located along each depth stratum and from two (i.e., "micro") stations located at the 10 m depth directly offshore from the ends of the 7 m depth stratum. These samplings were repeated as follows: pre-discharge; 1-3 days post-spill; 2-3 weeks post-spill; 1 year post-spill; 2 years post-spill. The 2-year post-spill sampling also included the detailed sampling of a Bay 11 offshore transect. In order to supplement the subtidal sediment information, samples of beach sediment were obtained from Bays 9 and 11 throughout the study. While additional sediment samples were obtained from Bays 10 and 7 as part of the study, this report focuses mainly on the results from Bays 9 and 11, the sites of the dispersed and untreated oil releases, respectively. The other study bays are discussed more extensively elsewhere (Boehm *et al.*, 1984b).

In addition to samples of surface sediment from the upper 2 cm of the sediment column, samples of surface sediment flocculent material (top 1-5 mm) were obtained during the immediate post-spill (1-3 days and 2 weeks post-spill) and 1-year post-spill sampling periods at certain locations to examine the recently deposited material most available to surface feeding animals.

Sampling Methods

Subtidal surface sediment (0-2 cm) was collected by divers skimming the top sediment layer into pre-cleaned solvent-rinsed glass jars. Surface floc was collected by divers using a device

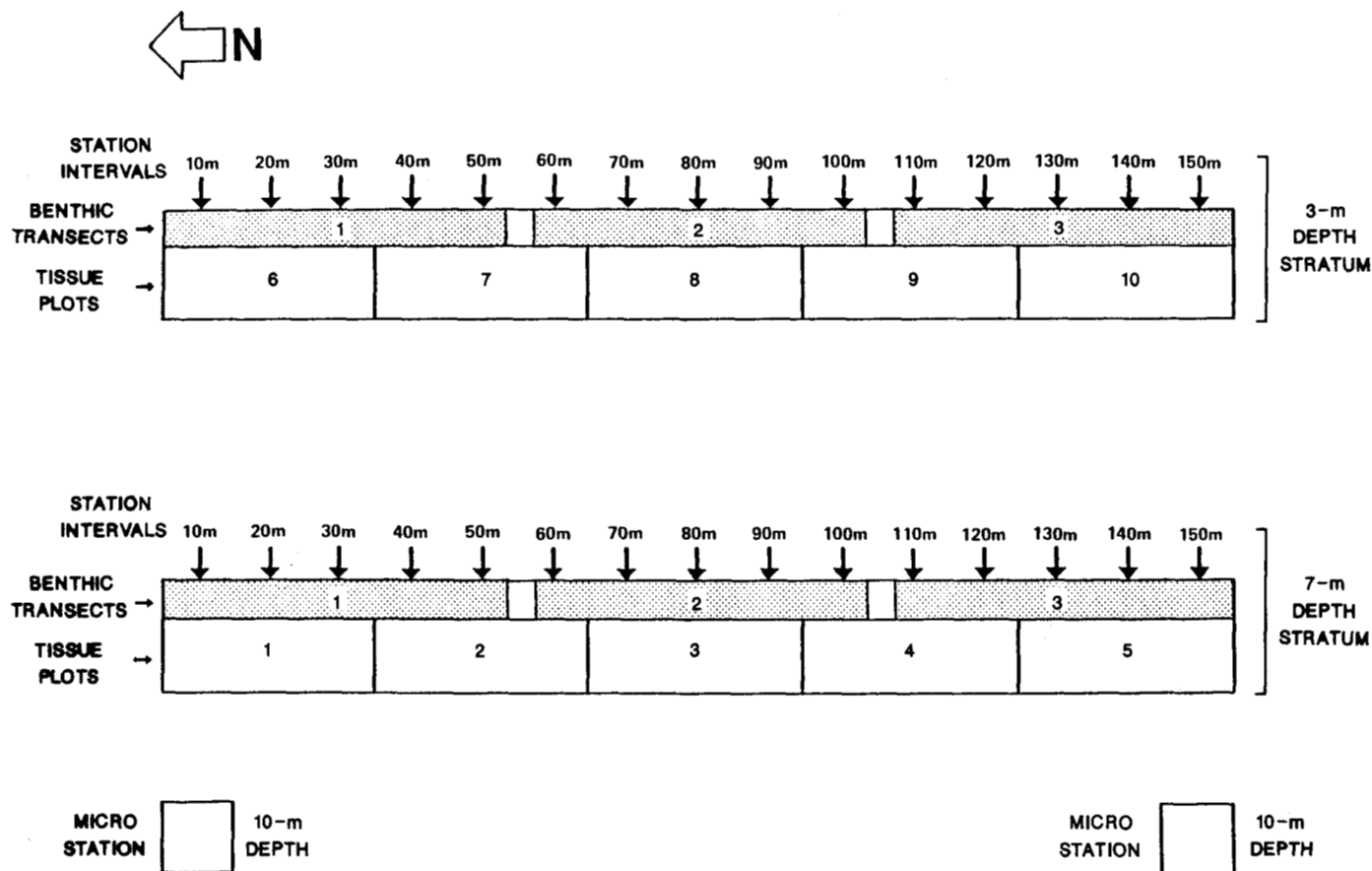


FIG. 2. Design of sampling transects and plots at which sediment samples were collected.

consisting of an inverted funnel and a pumping system, which "vacuumed" floc from the funnel placed over the sediment, through a precombusted Gelman AE glass fiber filter and through a stainless steel filter holder (see Cretney *et al.*, 1987a). Beach sediments were scooped from the top 5 cm into solvent-rinsed glass jars using a stainless steel trowel. Subsurface beach sediments (10-15 cm) were obtained as well. Samples were labelled, transported to the field laboratory and frozen for shipment to the analytical laboratory. As there was much potential for sampling contamination and cross-contamination, great care was taken to maintain the integrity of the samples by, for example, keeping sample jars closed when divers brought them through the air-sea interface.

Analytical Strategy

The general analytical strategy for all samples consisted of three levels of analysis (Fig. 3). In the first level, samples were solvent extracted and analyzed using synchronous ultraviolet spectrofluorometry (UV/F) to measure the content of petroleum relative to a Lagomedio crude oil standard. A subset of samples was analyzed at the second level using fused silica capillary gas chromatography with flame ionization detection (GC²-FID). This technique was used to quantify hydrocarbons, to distinguish petroleum from biogenic hydrocarbons and to evaluate the effect of weathering on the composition of the petroleum. Measurement of individual aromatic hydrocarbons was accomplished in the third level of analysis by computer-assisted capillary gas chromatographic mass spectrometry (GC²-MS).

Analytical Methods

The extraction, processing and analytical methods used have been extensively described elsewhere (Boehm *et al.*, 1982b; Cretney *et al.*, 1987a,b,c). The general analytical flow diagram is shown in Figure 4. Elements of analytical quality control, including analytical precision and accuracy, are addressed in Cretney *et al.* (1987a).

Data Interpretation Methods

PHC concentrations in sediments are presented in units of $\mu\text{g}\cdot\text{g}^{-1}$ dry weight. The data were treated according to methodologies outlined by Green (1979). The variance of the sample groups was found to be heterogeneous using Bartlett's test. Since a plot of $\ln S_i^2$ vs. $\ln X_i$ suggested a dependence of the variance (S_i) on the mean (X_i), the data were transformed using the log transformation

$$Z = \ln(X_i + 1)$$

Transformation removed most of the heterogeneity of variance. The 95% confidence intervals for each data set were calculated according to the following formula (Sokal and Rohlf, 1969):

$$95\% \text{ confidence interval} = \pm t_{0.05(n-1)} S/\sqrt{n}$$

The mean and confidence intervals were calculated using log transformed data and back-transformed to the original units for presentation. Data are reported in the following format: geometric mean (lower 95% confidence limit, upper 95% confidence limit).

The various concentrations of saturated hydrocarbons (e.g.,

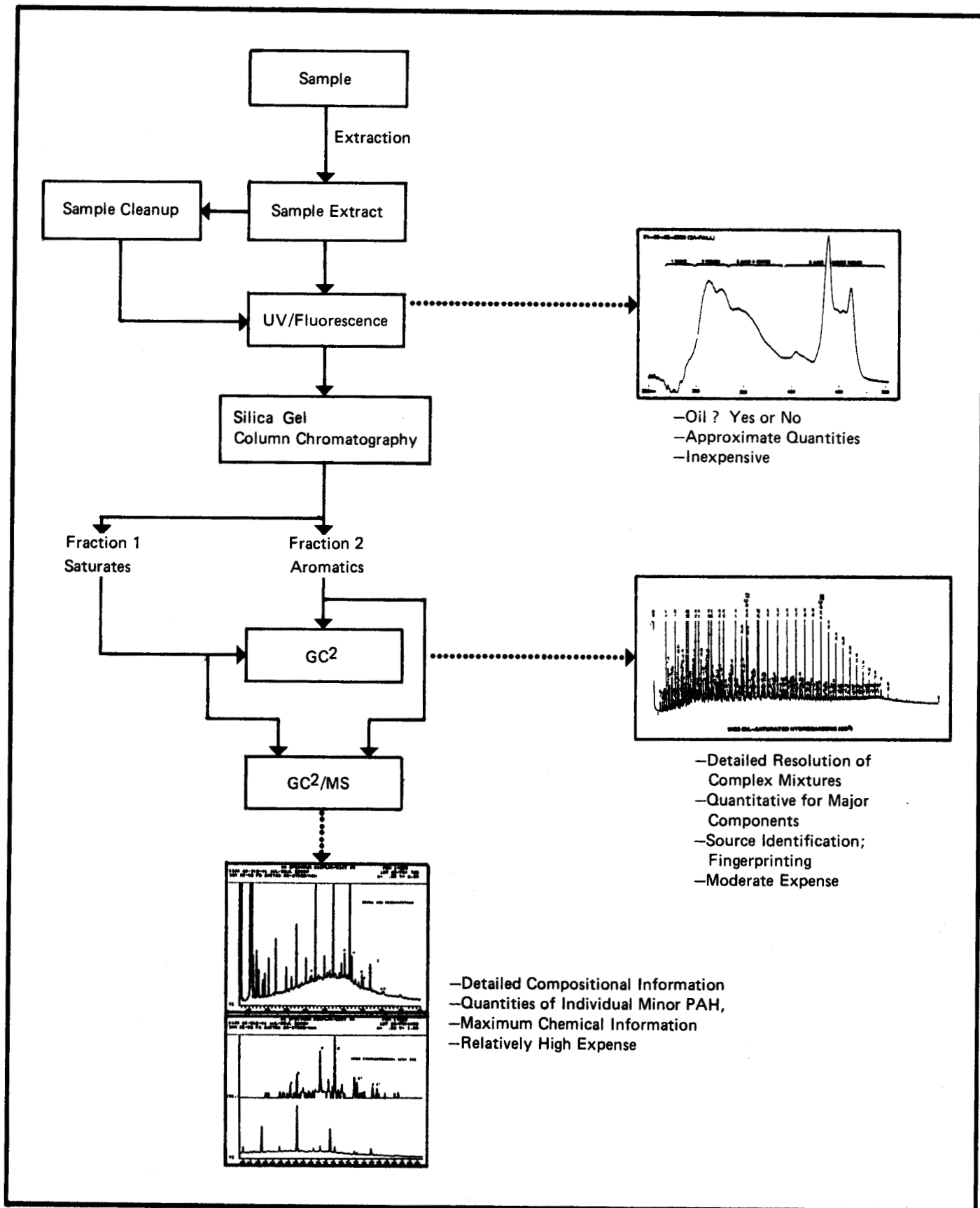


FIG. 3. Schematic of analytical strategy.

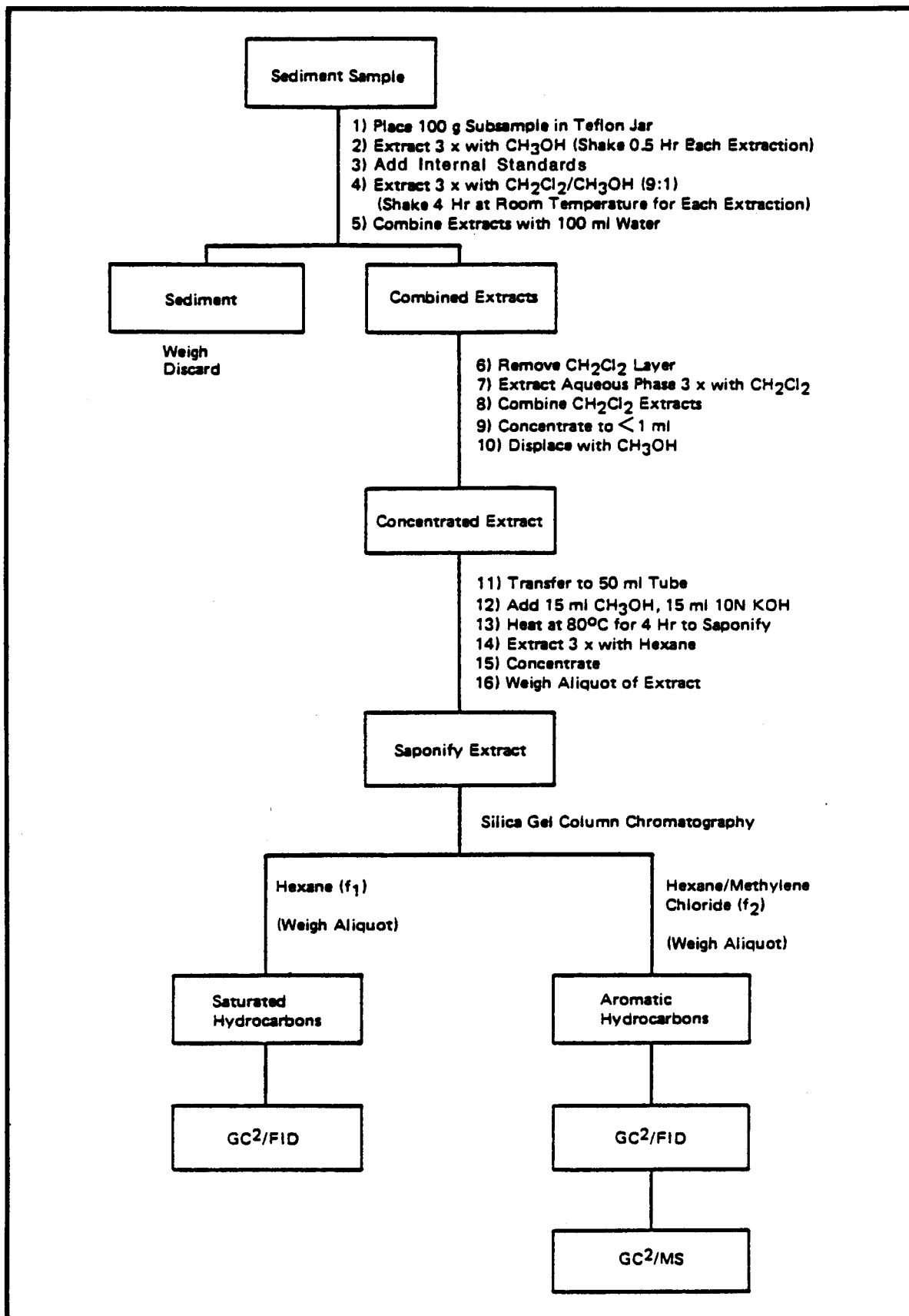


FIG. 4. Analytical scheme for hydrocarbon analysis of sediment samples (GC²-FID analysis).

n-alkanes, isoprenoid alkanes) derived from GC²-FID analysis and aromatic hydrocarbons derived from GC²/MS analysis were used to calculate a series of key diagnostic ratios (Table 1). These ratios are useful in establishing the composition of the residual petroleum, the relative importance of biogenic vs. petrogenic hydrocarbons and the degree to which the oil was weathered, compared with the released oil itself.

TABLE 1. Explanation of petroleum weathering and source ratios

1. The Biodegradation Ratio (Alkane/Isoprenoid) (Atlas <i>et al.</i> , 1981)	
$\text{ALK}_{14-18}/\text{ISO} = \frac{1400 + 1500 + 1600 + 1700 + 1800}{1380 + 1470 + 1650 + 1708 + 1810}$	
The ALK/ISO ratio approaches 0 as the n-alkanes are depleted. 1400, 1500 . . . are GC ² -FID retention indexes (Kovats and Keulemans, 1964).	
2. The n-C ₁₈ /Phytane Ratio (NAS, 1985)	
The C ₁₈ /Phy ratio also approaches 0 as n-C ₁₈ is preferentially depleted.	
3. The Pristane/Phytane Ratio (NAS, 1985)	
The Pris/Phy Ratio is equal to 0.7 in aged Lagomedio oil. As the amounts of the biogenic isoprenoid pristane increase to the petrogenic isoprenoid phytane, this ratio becomes large.	
4. The Saturated Hydrocarbon Weathering Ratio (SHWR)	
(Boehm <i>et al.</i> , 1984a)	
$\text{SHWR} = \frac{\text{sum of n-alkanes from n-C}_{10} \text{ to n-C}_{25}}{\text{sum of n-alkanes from n-C}_{17} \text{ to n-C}_{25}}$	
The SHWR approaches 1.0 as low-boiling saturated hydrocarbons (n-C ₁₀ to n-C ₁₇) are lost by evaporation.	
5. The Aromatic Weathering Ratio (AWR) (Boehm <i>et al.</i> , 1984a)	
$\text{AWR} = \frac{\text{Alkyl benzenes} + \text{naphthalenes} + \text{fluorenes} + \text{phenanthrenes} + \text{dibenzothiophenes}}{\text{Total phenanthrenes} + \text{dibenzothiophenes}}$	
The AWR approaches 1.0 as low-boiling aromatics are lost by evaporation and/or dissolution.	
6. Carbon Preference Index (CPI) (Farrington and Tripp, 1977)	
$\text{CPI} = \frac{2(\text{n-C}_{27} + \text{n-C}_{29})}{\text{n-C}_{26} + 2\text{n-C}_{28} + \text{n-C}_{30}}$	
The CPI is equal to 1.0 for petroleum and ranges from 3 to 6 for terrigenous plant waxes. The relative amounts of petroleum alkanes to terrigenous biogenics can be assessed through this ratio.	

RESULTS

Surface Oil Release — Bay 11

PHC Concentrations: The concentrations of PHC in Bay 11 subtidal sediments, expressed as Lagomedio crude oil equivalents, are presented in Table 2. Concentrations are presented as geometric means with lower and upper 95% confidence intervals in brackets. The time series data are summarized for sediments from the tissue plots and benthic transects and are graphically presented in Figure 5.

Oil concentrations began to increase in the subtidal sediment within two weeks of the oil release and subsequent beaching. After two weeks, concentrations were higher farther offshore at 7 m depth stations (1-5 μg·g⁻¹) than they were at 3 m (0.5-1 μg·g⁻¹). One year later, in 1982, concentrations of oil increased markedly at most stations. The highest concentrations were observed at the 3 m depth at the southern end of the sampling

line, similar to that observed in 1983, two years after the release. By 1983, oil concentrations had increased greatly, with concentrations greater than 100 μg·g⁻¹ and as high as 410 μg·g⁻¹ detected at the 3 m stations in transect 3. That oil was being transported to deeper areas of Bay 11 was evidenced by the elevated levels (5-10 μg·g⁻¹) above a background of approximately 0.2-0.5 μg·g⁻¹ in the region at the 35 m depth sampling stations.

A summary of the oil concentration data on the one offshore transect at the southern end of the Bay 11 sampling area is shown in Figure 6. Note that these concentrations were derived by GC²-FID results, in contrast to the other data, which were obtained by UV/F. GC²-FID results were observed to be systematically lower than the corresponding UV/F results from the same samples. Such systematic discrepancies result from the quantification of UV/F data using an oil standard, in this case a Lagomedio crude oil that was artificially weathered in the laboratory to a small degree. As spilled oil weathers naturally in the field with time, the compositional resemblance of the standard with the oil residues observed in actual samples diminishes. Quantification of oil residues in samples using the relatively unweathered samples thus results in an overestimate of actual oil concentrations. Such UV/F-determined concentrations are usually referred to as concentrations of "oil equivalents" based on a standard rather than absolute concentration of oil. Therefore, the differences between GC²-FID results and those obtained by the UV/F technique were expected. The data shown in Figure 6 indicated that the highest concentrations of PHC in the subtidal sediments of Bay 11 were found in shallow water of 2-4 m depth. This strongly indicated the establishment of an offshore gradient.

The results of PHC concentration determinations in the surface sediment (0-2 cm) and in the surface floc (Table 3) indicated that one day after the release and beaching of the untreated oil in Bay 11, PHCs had been transported to the subtidal sediments in small amounts. Floc concentrations of PHC indicated that an average of 3% of the PHC sediment content (range 1-30%) was associated with the top several mm (estimated at 1-5) of sediment in Bay 11. Floc-to-bulk sediment ratios as explained in Table 3, determined two weeks after the oil release, indicated that oil was apparently well mixed into the top 2 cm of sediment; the amount of PHC associated with the floc decreased to 0.4-0.5% of the total (Table 3).

Floc samples were obtained in 1982, one year after the oil release, to examine the hypothesis that erosional transport of oil off of the Bay 11 beach might contribute significant quantities of oil to the surface floc. Calculations of the ratio of PHC in floc vs. that in bulk sediments (0-2 cm) indicated that a very small percentage (0.2-0.9%) of the PHC was associated with the floc one year after the release (Table 3). While the quantity of PHC in floc increased one year later (1983, two years post-release), the relative percentage of oil in the floc compared to the bulk sediment decreased to 0.1-0.3%.

Samples of sediment from the Bay 11 beach were obtained to determine the mass budget of oil remaining on the beach (see Owens *et al.*, 1987) and to examine the beach sediment as source material to the subtidal sediments. While the PHC concentrations were extremely variable and patchy on the beach face, the residual concentration (determined by GC²-FID) of PHC decreased from a mean of 21 600 μg·g⁻¹ immediately following oil stranding (Boehm *et al.*, 1982b) to 10 100 μg·g⁻¹ one month later (September 1981). Mean concentrations

TABLE 2. Summary of Bay 11 sediment PHC concentrations ($\mu\text{g}\cdot\text{g}^{-1}$)^a

Station	Water depth (m)	1981			1982	1983
		Pre-release	1 day	2 weeks		
Tissue plots	3	0.21 (0.09,0.48) ^b	0.14(0.07,0.30)	0.62(0.32,1.2)	2.9(0.91,9.7)	22(11,46)
	7	0.51(0.19,1.4)	0.18(0.07,0.47)	1.0(0.59,1.9)	5.3(2.4,11.4)	13(9.8,16)
Transect 1	3	—	—	0.90(0.12,6.6)	4.0(0.94,17)	21(2.3,194)
	7	—	—	3.9(2.4,6.3)	6.6(4.3,10)	22(14,35)
Transect 2	3	—	—	0.46(0.18,1.2)	1.4(0.26,7.9)	14(0.95,207)
	7	—	—	4.7(1.8,12)	4.7(2.2,9.9)	12(9.3,15)
Transect 3	3	—	—	0.90(0.21,3.9)	10(0.70,153)	119(54,259)
	7	—	—	2.3(0.56,9.2)	4.0(0.98,16)	19(3.8,93)
Deep sediments	35	—	—	—	—	4.6(2.2,9.6)

^a Determined by UV/F analysis.

^b Concentrations presented as geometric means with lower and upper 95% confidence limits shown in parentheses.

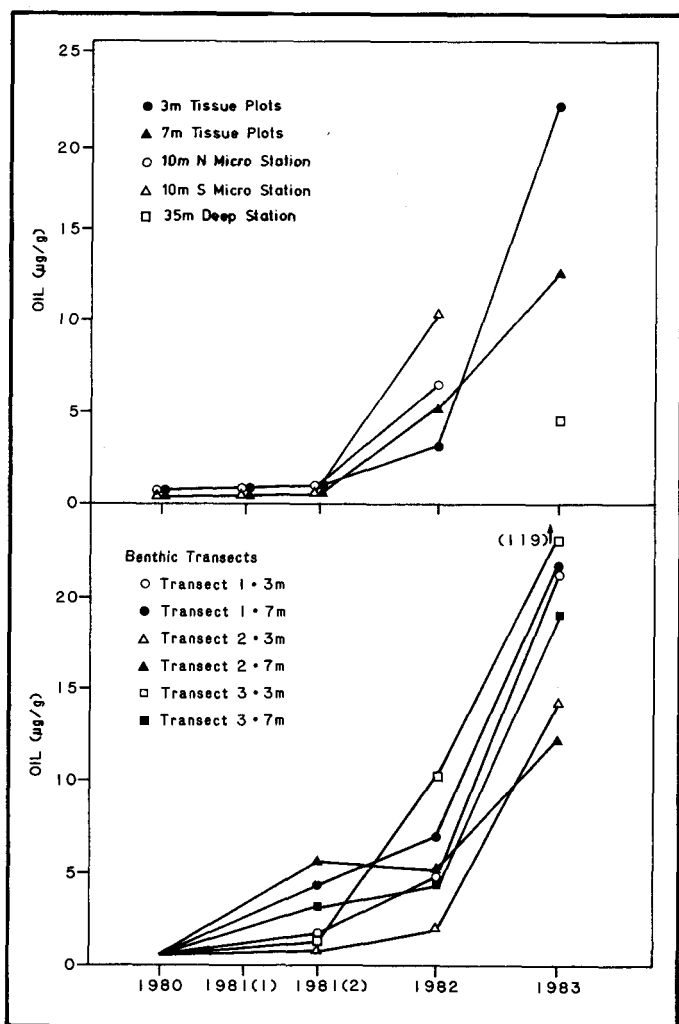


FIG. 5. Bay 11 sediment oil concentrations, 1980-83 ($\mu\text{g}\cdot\text{g}^{-1}$ by UV/F). Lines connecting symbols are intended only to show trends with time and should not be used for year-to-year interpolation.

observed in 1982 were $2560 \mu\text{g}\cdot\text{g}^{-1}$, indicating that oil was being removed from the beach face due to erosion during this period, as well as being decreased in mass due to further weathering. This decrease in mass has been extensively documented and studied by Owens *et al.* (1987).

PHC Composition: GC²-FID and GC²/MS analyses of the

saturated and aromatic PHC fractions respectively provided information on the PHC composition and, hence, its weathering state. The GC²-FID trace in Figure 7A is typical of the PHC composition of oiled sediments sampled within two weeks after the release. The unoiled sediments contained significant quantities of biogenic hydrocarbons associated with planktonic detritus (heptadecane or n-C₁₇, and pristane) and terrigenous plant materials (odd carbon chain, high molecular weight alkanes, n-C₂₅ through n-C₃₃) (Fig. 7B). Because the unoiled sediment contained negligible to very small quantities of the isoprenoid alkane phytane, concentrations of phytane above a prerelease background of $0.001 \mu\text{g}\cdot\text{g}^{-1}$ and the ratio of pristane to phytane (Pris/Phy) served as useful measures of the extent of PHC input, even two years after the spill when extensively weathered oil remained. In unoiled sediment, the background Pris/Phy ratios were generally greater than 20. As petrogenic phytane was added to the sediment the ratio decreased to a range of 1-3. Due to the very low abundance of phytane in baseline or unoiled sediments (generally less than $0.001 \mu\text{g}\cdot\text{g}^{-1}$), the presence of quantifiable levels of phytane signified the presence of oil. Because the ratio of phytane to oil was determined to be 1:150 in the Lagomedio oil, multiplying the determined amount of phytane by 150 could be used to estimate PHC concentrations. This conversion factor was helpful in converting GC²-FID data to PHC data where background levels of biogenic alkanes and other saturated hydrocarbons interfered with such calculations.

The Carbon Preference Index (CPI; see Table 1 for explanation) also served as a useful parameter in distinguishing oiled from non-oiled sediment. CPI values of unoiled sediment were consistently in the range of 5-7. Oil additions could be detected through an examination of this ratio, which decreased to a range of 1-3 when high levels of oil in the sediment were observed. The change in CPI was accompanied by a decrease in the Pris/Phy ratio. The CPI of Lagomedio crude oil was approximately 1.0. The rate of change of these ratio values from background values to oil values depends on several factors, including the relative ratios in oil vs. background sediments (i.e., end points); the concentration in background sediments of those components constituting the ratios; and the concentration of oil components relative to background levels of those components. Thus, the Pris/Phy ratio changed more rapidly than the CPI due to the very low background abundance of phytane in the sediment.

Two ratios of normal alkanes to isoprenoid alkanes were used to examine the state of biodegradation of the oil (see Table 1).

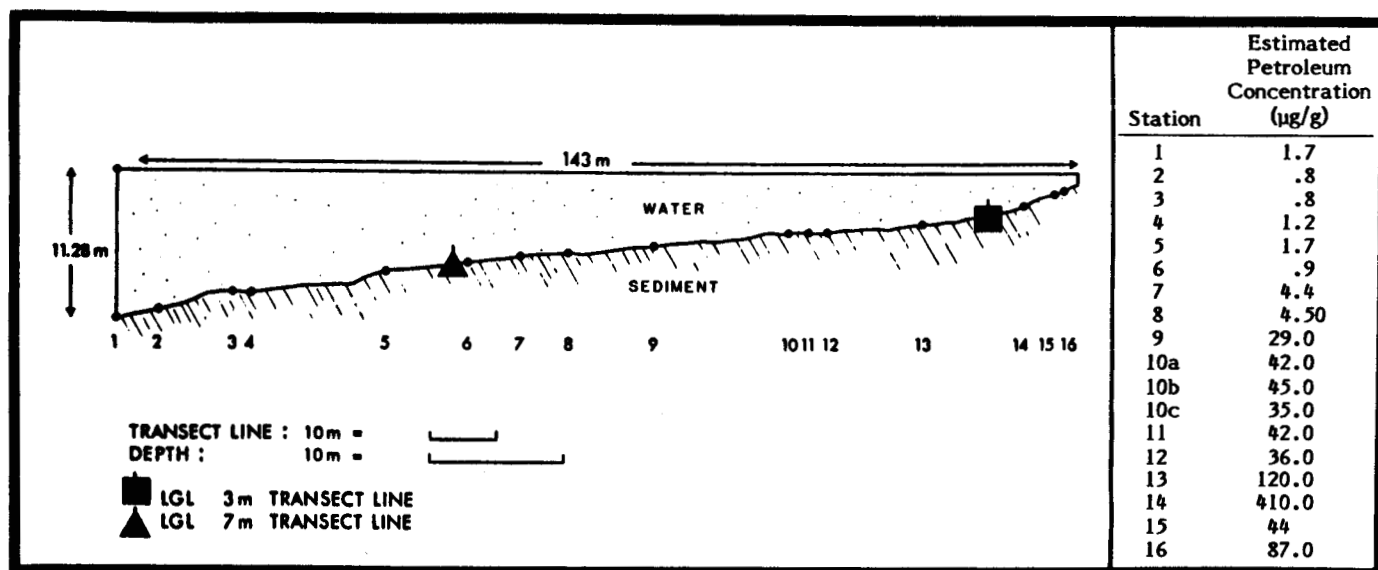


FIG. 6. Cross-sectional depth profile along Bay 11 microbiology sediment transect.

TABLE 3. Concentrations of Petroleum Hydrocarbons (PHC) in surface floc and sediment from Bay 11 tissue plots

Sampling	Water depth (m)	Concentration ^a				Ratio ^b PHC (floc):PHC (sediments)
		Floc (mg·m ⁻²)		Sediments (µg·g ⁻¹)		
		Range	Mean	Range	Mean	
Pre-release	3	0.05-0.12	ND	0.12-0.42	ND	ND
	7	<0.01-0.19	ND	0.22-0.99	ND	ND
1981 (1 day post-spill)	3	ND	ND	ND	ND	ND
	7	<0.01-0.40	0.09	0.07-0.54	0.15	0.03
1981 (2 weeks post-spill)	3	0.02-0.13	0.06	0.28-1.8	0.62	0.005
	7	0.03-0.24	0.09	0.52-1.7	1.0	0.004
1982 (1 year post-spill)	3	0.33-1.2	0.54	0.74-66	3.0	0.009
	7	0.16-0.33	0.22	1.3-50	5.3	0.002
1983 (2 years post-spill)	3	0.60-4.0	1.24	6.5-123	22	0.003
	7	0.23-0.39	0.29	8.1-21	13	0.001

^aDetermined by UV/F analysis.

^bWe wish to compare the amount of oil in the floc versus that in the sediment. Because floc weight was not measured, the concentrations of oil in the floc (expressed in mg·m⁻²) can be compared to concentrations of oil in the sediments (expressed in µg·g⁻¹ dry weight) using the following equation: Floc (mg·m⁻²) × 0.05 = Sediment (µg·g⁻¹). Derivation of this equation assumes the density of wet sediment is 2 g·cm⁻³; the water content of the sediment is 50%; and the sediment was sampled to a depth of 2 cm. Using these assumptions, 1 g of dry sediment is contained in the top 2 cm within a 0.5 cm² cross-sectional area.

1 µg oil·g⁻¹ dry sediment = 1 µg/0.5 cm² × 1 mg/10³ µg × 10⁴ cm²/m² = 20 mg·m⁻².

^cCretney *et al.*, 1987a.

ND = Not determined.

The ratio of *n*-C₁₈/Phy proved to be the more useful of the two in these sediments, due to the high background concentration of biogenic pristane, which affected the use of the ALK/ISO ratio. Typical ratios are presented in Table 4. The absolute concentrations of phytane are directly proportional to the PHC concentration. The *n*-C₁₈/Phy ratio generally decreased with time from an initial value similar to that of the oil (1.63) to a minimum mean value of 0.67 within the offshore transects in 1983. This change from 1.63 to 0.67 over two years does indicate that biodegradation had occurred because biodegradation preferentially removes *n*-C₁₈ and the other normal alkanes from the sediment. However, relatively undegraded oil was still present in the Bay 11 system, because several samples of sediment exhibited *n*-C₁₈/Phy values greater than 1.0.

The extent of weathering was quite variable, as shown in the GC²-FID traces in Figure 8. In general, the higher concentra-

tions of PHC were associated with less weathered oil. Figure 8B illustrates a saturated PHC fraction from a sample taken two years after the release. It has not only considerable quantities of *n*-alkanes remaining, but also a striking abundance of low-molecular weight *n*-alkanes (i.e., *n*-C₁₁ and *n*-C₁₂), which after two years should have disappeared from the sediment. Thus, a wide range of PHC compositions was observed two years after the Bay 11 oil release, as PHC concentrations continued to increase. The composition of PHC in Figure 8A is typical of a moderately weathered oil with evidence of biodegradation through the enhanced relative abundance of isoprenoid alkanes. A typical GC²-FID trace of the aromatic hydrocarbon fractions of a sediment with moderate to high oil levels is shown in Figure 8C. A weathered assemblage of aromatic hydrocarbons is indicated. Aromatic hydrocarbon compositions were examined by GC²/MS techniques. For quantitative results, graphical pre-

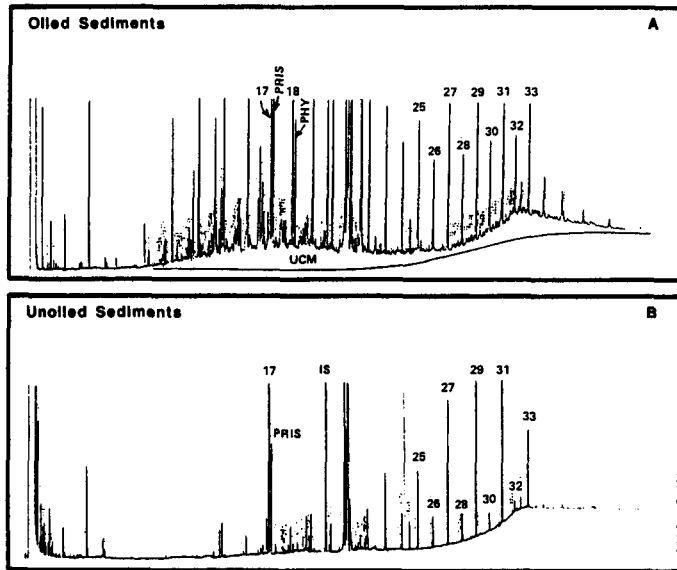


FIG. 7. Typical sediment GC² traces (saturates). "IS" indicates internal standard.

sentrations of analytical results from unoled sediment and typical 1982 and 1983 (one-year and two-year post-spill) samples are shown in Figure 9. The 1983, two-year post-spill samples exhibited a wide variety of aromatics. However, the composition of most samples was similar to that shown in Figure 9C. Loss of the more volatile and soluble alkylated naphthalenes (N) was the primary difference between the 1982 and 1983 (Fig. 9B and 9C) sample sets. After two years of environmental exposure, the aromatic hydrocarbon and heterocycle compositions were dominated by the alkylated phenanthrenes (P) and alkylated dibenzothiophenes (DBT), although quantities of alkylated naphthalenes were still present in the sediments.

Compositional determinations of oil from the Bay 11 beach were performed throughout the study. A broad spectrum of saturated and aromatic compositions was illustrated through these analyses. The GC²-FID trace in Figure 10A shows the original composition of the Lagomedio oil. This composition changed after deposition of the oil on the beach face. However, two years after stranding, "fresh," relatively unweathered oil was still found on the beach (Fig. 10B), along with highly

TABLE 4. Summary of typical compositional characteristics of PHC in Bay 11 subtidal sediments

Year	Water depth (m)	Phytane (μg·g ⁻¹)	Pris		n-C ₁₈	
			Phy	CPI	Phy	
Pre-release	all	0.001	20-100	5.0	ND	
1981 (2 weeks)	3	0.008	3.0	3.1	1.54	
	7	0.015	1.4	2.4	1.39	
1982 (1 year)	3	0.06	1.3	2.3	1.02	
	7	0.02	2.0	3.5	1.28	
1983 (2 years)	3	0.14	0.94	2.0	0.63	
	7	0.03	2.5	2.6	1.25	
	Offshore transect	—	—	2.0±1.1	0.67±.36	
Lagomedio crude oil ^a		6400 ^b	1.5	1.0	1.63	

^a Artificially weathered 8% by volume (Dickins *et al.*, 1987).

^b mg phytane·g⁻¹ crude oil.

ND = None detected.

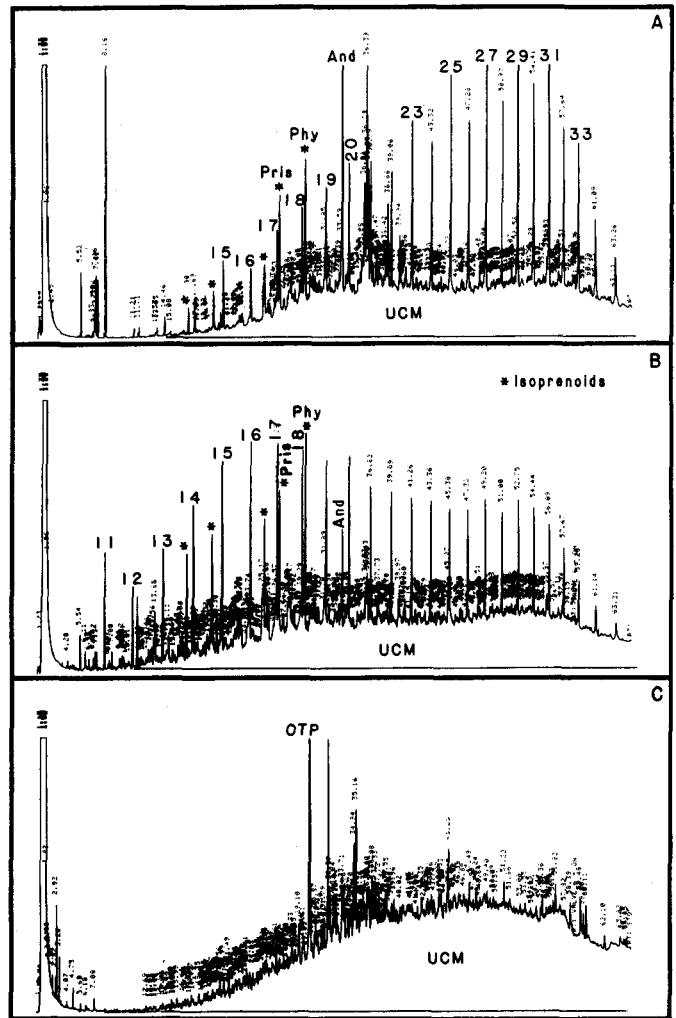


FIG. 8. GC² traces in Bay 11 microbiology plot sediment samples. A: Station 12 (saturates); B: Station 14 (saturates); C: Station 14 (aromatics). "And" peak on A and B indicates Androstane internal standard. Asterisks in A and B indicate isoprenoid alkanes.

weathered oil (Fig. 10C). The weathering states of the oil are summarized in Table 5. Owens *et al.* (1987) present more detailed data and a detailed discussion. The Saturated Hydrocarbon Weathering Ratio (SHWR) and the Aromatic Weathering Ratio (AWR) are used to quantitatively indicate the extent of weathering (see Table 1). Such ratios have been successfully applied to previous oil weathering studies (Boehm *et al.*, 1984a). Several important points were revealed. Although weathering occurred rapidly after deposition, two years after the stranding of oil relatively unweathered residues remained in

TABLE 5. Summary of weathering characteristics of residual oil on the Bay 11 beach face

Sampling	SHWR ^a	AWR ^a	ALK/ISO ^a
Lagomedio crude oil	2.5-2.9	2.5-3.0	2.5-2.8
1981 (1 day)	2.3-2.8	—	2.6-2.8
1981 (2 weeks)	1.1-1.9	—	1.8-2.8
1982 (1 year)	1.0-1.2	—	0.6-1.8
1983 (2 years)	1.0-2.0	1.0-3.5	0.2-2.5 0.3-2.5

^a See Table 1 for explanation of diagnostic ratios.

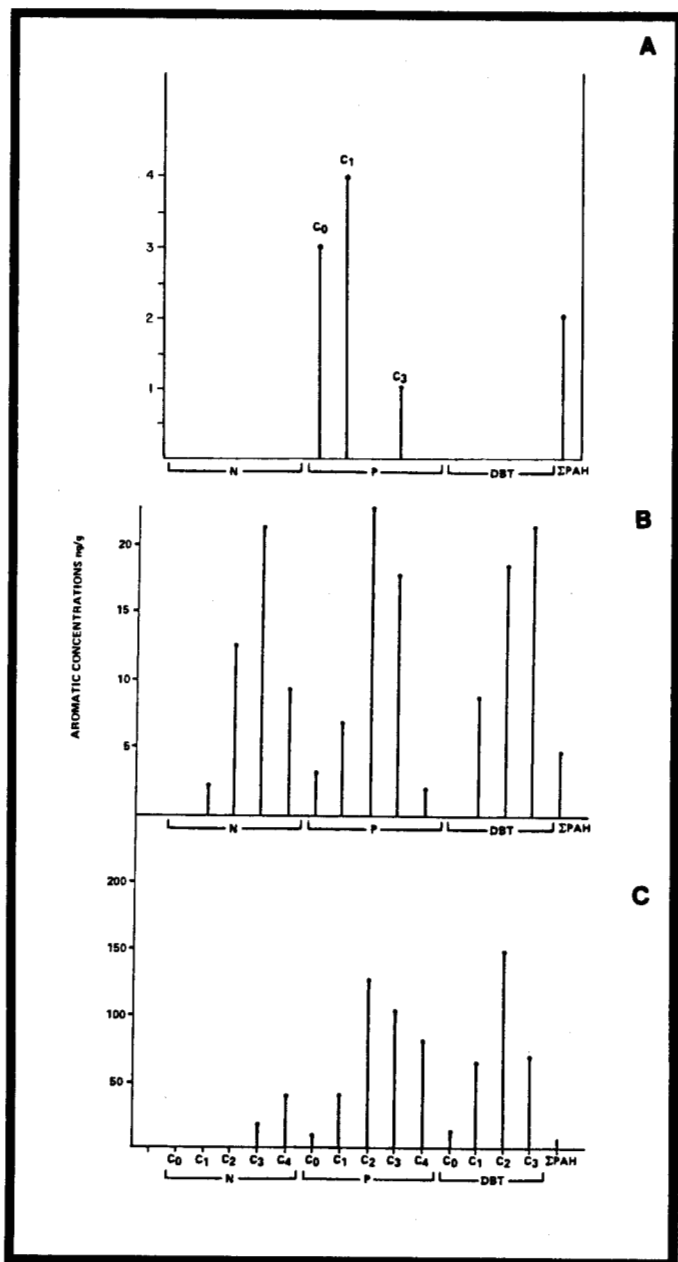


FIG. 9. Aromatic hydrocarbon profiles determined by GC²/MS. A: Milne Inlet sediment (background profile); B: Bay 11 tissue plot 8 (3 m) one year post-spill; C: Bay 11 tissue plot 10 (3 m) two years post-spill. N = naphthalenes; P = phenanthrenes; DBT = dibenzothiophenes; ΣPAH = total 2- to 5-ring PAH; C₀, C₁, C₂, C₃, C₄ refer to number of carbons on side chains.

isolated pockets on the beach. Biodegradation processes weathered the oil on the beach face so that ALK/ISO ratios decreased steadily to the point where one year after the release n-alkane depleted oil was found on the beach (ALK/ISO = 0.6). By 1983 degradation had proceeded further (ALK/ISO = 0.2). However, relatively undegraded oil was still found two years after the release in areas of the beach (ALK/ISO = 2.5), thus further supporting the finding that the chemical composition and weathering state on the beach face was extremely varied. Exposed oil characterized by a greater surface area (such as that coating rocks) was generally more highly weathered than pockets of oil protected by rocks or buried in the sediment (see Owens *et al.*, 1987).

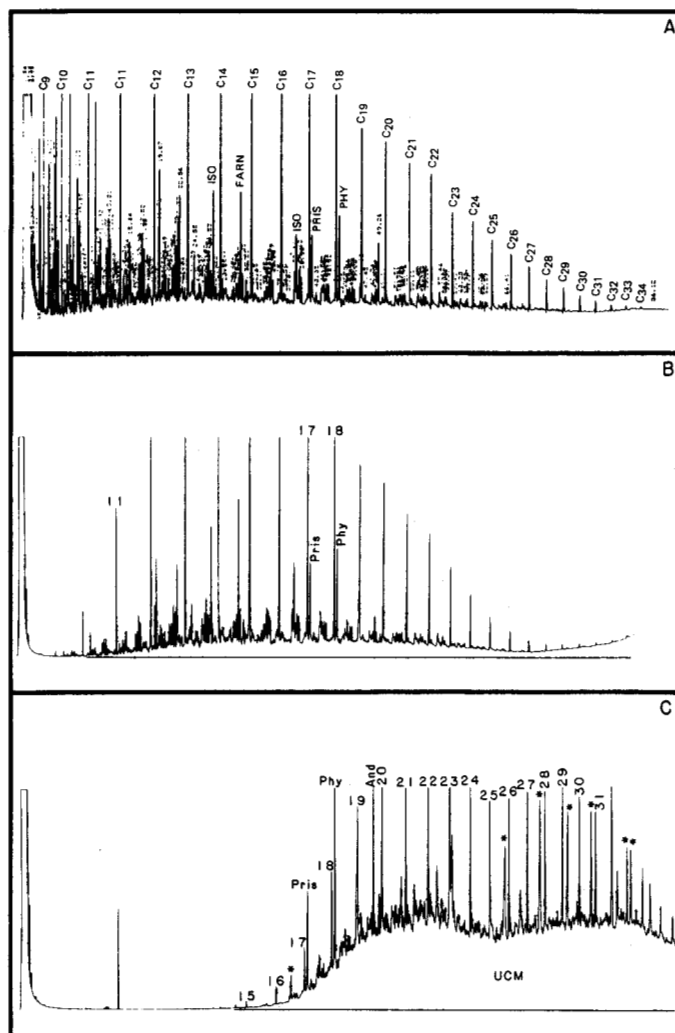


FIG. 10. GC² traces of Lagomedio crude oil and Bay 11 beach sediments. A: original Lagomedio crude oil; B: saturates S4146 (unweathered, undegraded); C: saturates S4139 (weathered and degraded); * = unidentified cyclic alkanes (terpenoids). "And" peak in C indicates Androstane internal standard.

Chemically Dispersed Oil — Bay 9

PHC Concentrations: PHC concentrations in Bay 9 subtidal sediments are summarized in Table 6. Concentrations are presented as geometric means and 95% confidence intervals. The data are also graphically presented in Figure 11. In spite of a very large exposure of the Bay 9 sediments to chemically dispersed oil, sediment concentrations were observed generally to be lower than 5 $\mu\text{g}\cdot\text{g}^{-1}$ one day after the discharge and to increase slightly to no more than 16 $\mu\text{g}\cdot\text{g}^{-1}$ when observed two weeks after the subsurface oil release. As described in other reports (Boehm *et al.*, 1982b; Humphrey *et al.*, 1987a), concentrations of dispersed oil in the Bay 9 water column were instantaneously as high as 160 $\text{mg}\cdot\text{l}^{-1}$ during the discharge. In contrast to the Bay 11 surface oil release, during which little oil was initially mixed in the water column, all of the Bay 9 released oil was discharged 1 m off the bottom and was theoretically available for sorption on sediments. Immediately after the discharge in Bay 9, sediment concentrations increased from a background value of approximately 0.4 $\mu\text{g}\cdot\text{g}^{-1}$ to 1-5 $\mu\text{g}\cdot\text{g}^{-1}$. At the time of the first sampling, one day after the discharge, large PHC concentrations were observed in the surface floc of the sediment (2-30 $\text{mg}\cdot\text{m}^{-2}$). As the data in Table 7 indicate, a

TABLE 6. Summary of Bay 9 subtidal sediment PHC concentrations ($\mu\text{g}\cdot\text{g}^{-1}$)^{a,b}

Station	Water depth (m)	1981			1982	1983
		Pre-release	1 day	2 weeks		
Tissue plots	3	0.33(0.18,0.60)	2.8(1.9,4.0)	5.2(2.5,11)	—	—
	7	0.18(0.05,0.73)	2.0(1.4,2.8)	7.8(4.3,14)	2.2(1.4,3.3)	7.6(5.7,10)
Transect 1	3	—	—	2.5(1.5,4.0) ^c	1.0(0.4,2.6)	1.0(0.28,3.1)
	7	—	—	3.7(2.6,5.4) ^c	—	—
Transect 2	3	—	—	—	0.52(0.21,1.3)	3.8(1.8,7.9)
	7	—	—	—	—	—
Transect 3	3	—	—	—	0.91(0.74,1.12)	5.2(3.5,7.8)
	7	—	—	—	—	—

^a Determined by UV/F in μg Lagomedio oil equivalents $\cdot\text{g}^{-1}$ dry sediment.

^b Concentrations reported as geometric means with lower and upper 95% confidence intervals shown in parentheses.

^c Summation of results from Transects 1, 2 and 3.

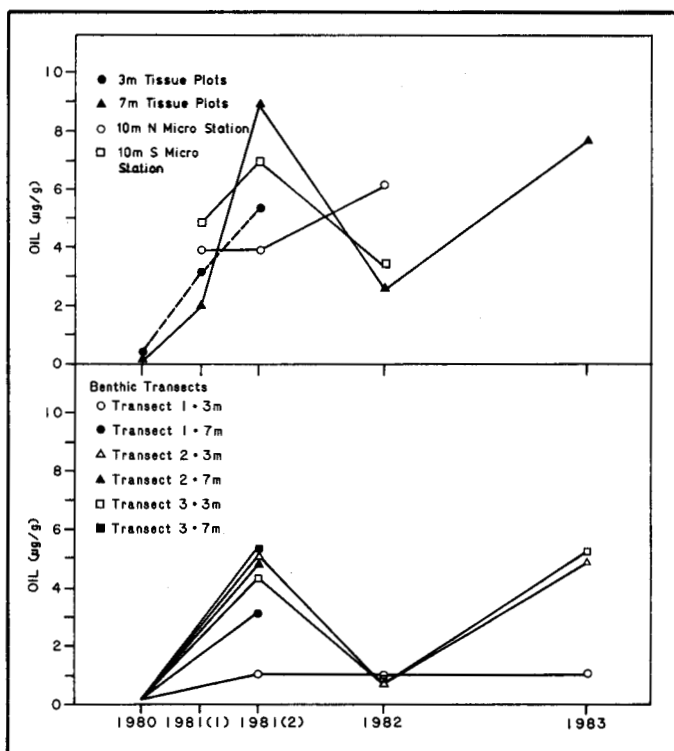


FIG. 11. Bay 9 sediment oil concentrations 1980-83 ($\mu\text{g}\cdot\text{g}^{-1}$ by UV/F). Lines connecting symbols are intended only to show trends with time and should not be used for year-to-year interpolation.

significant fraction (10-20%) of the sedimented oil in Bay 9 was initially (one day post-discharge) associated with this surface floc. After two weeks, in spite of increasing bulk sediment (0-2 cm) PHC content, the concentrations of PHC in the floc decreased to generally less than $0.2\text{ mg}\cdot\text{m}^{-2}$, indicating that the PHC in the sediments had been mixed beneath the top several mm and that the fraction of PHC associated with the floc was now less than 1%.

While PHC concentrations decreased during the year following the release (Table 6), an apparent increase in PHC concentrations was observed between 1982 and 1983, one and two years after discharge respectively. Analyses of Bay 9 beach sediments throughout the study revealed low but detectable quantities of PHC generally in the $1\text{-}2\text{ }\mu\text{g}\cdot\text{g}^{-1}$ range. These concentrations were similar to those in the subtidal sediments and, in contrast to the Bay 11 beach, indicated that the Bay 9

TABLE 7. Concentrations of PHC in surface floc from Bay 9 tissue plots

Sampling	Water depth (m)	Concentrations ($\text{mg}\cdot\text{m}^{-2}$) ^a		Ratio ^b PHC (floc): PHC (sediment)
		Mean	Range	
1981 (1 day)	3	4.1	1.7-7.8	0.07
	7	9.4	2.3-33	0.23
1981 (2 weeks)	3	0.10	0.07-0.17	<0.001
	7	0.09	0.04-0.25	<0.001
1982 (1 year)	3	ND	ND	ND
	7	ND	ND	ND
1983 (2 years)	3	ND	ND	ND
	7	ND	ND	ND

^a Determined by UV/F analysis.

^b Floc ($\text{mg}\cdot\text{m}^{-2}$) $\times 0.05 =$ Sediment ($\mu\text{g}\cdot\text{g}^{-1}$); see Table 3: footnote b for derivation of equation.
ND = Not determined.

beach could not have been a source of PHC to the offshore sediments. However, the transport of minor amounts of oil from Bay 11 to Bay 9 cannot be ruled out.

PHC Compositions: Initially (one day post-spill) the composition of PHC in Bay 9 sediments consisted of Lagomedio crude that had been depleted in volatile and soluble components of the saturated and aromatic fractions. As the water column chemical results indicated (Humphrey *et al.*, 1987a; Boehm *et al.*, 1982b), the dispersed oil was stripped of these components, leaving a soluble fraction of these components and a dispersed droplet plume of slightly weathered oil. Typical GC²-FID traces for the surface floc initially obtained in Bay 9 are shown in Figure 12. The GC²/MS-derived compositional profiles indicate that the alkylated benzenes and the more soluble naphthalene components were removed from the oil droplets before they were incorporated into the surface floc. One year after the discharge, although PHC concentrations had decreased, the residual PHC still retained significant n-alkane components (Fig. 13). The lack of depletion of these n-alkanes suggests that weathering of oil was quite slow and that subtidal biodegradation was not a significant process during the first year after sedimentation of oil. These normal alkanes were still present in small quantities in the PHC residue of the Bay 9 sediment two years after the release.

Reference Sites — Bays 7 and 10

Although Bays 7 and 10 were originally intended as reference

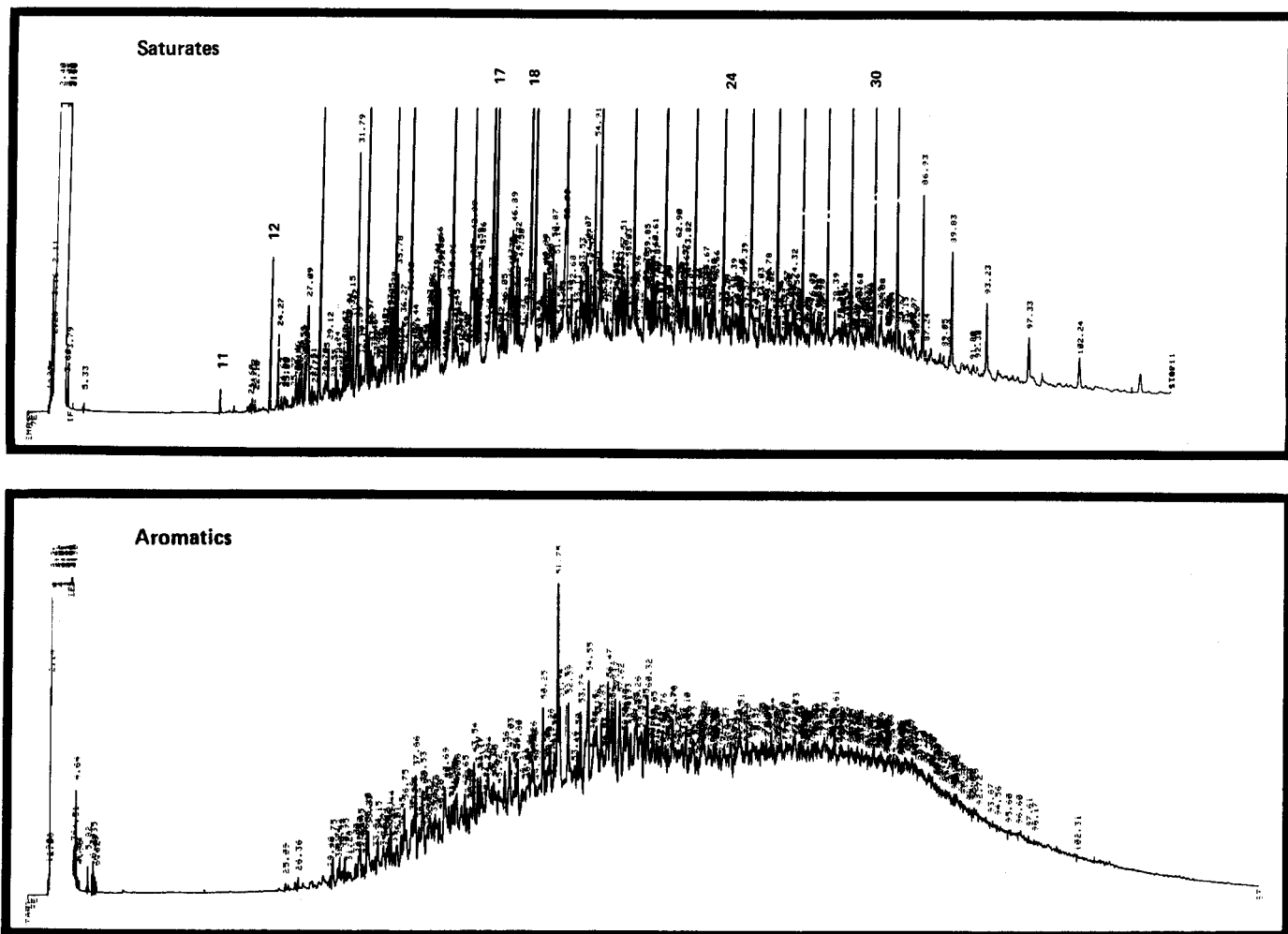


FIG. 12. GC² trace of surface floc from Bay 9, Station 2 (1st post-spill); A: saturated fraction, B: aromatic fraction.

sites, dispersed oil from the test spill at Bay 9 impacted Bay 10 and, to lesser degree, Bay 7.

A summary of the PHC concentrations in sediments of Bay 7 is presented in Table 8. No significant increases above baseline

were observed at the time of the first post-spill sampling and only slight elevations in sediment PHC levels were noted two weeks post-spill. Two years after the release, sediment PHC concentrations averaged 1.5-3 $\mu\text{g}\cdot\text{g}^{-1}$ or a five- to tenfold increase

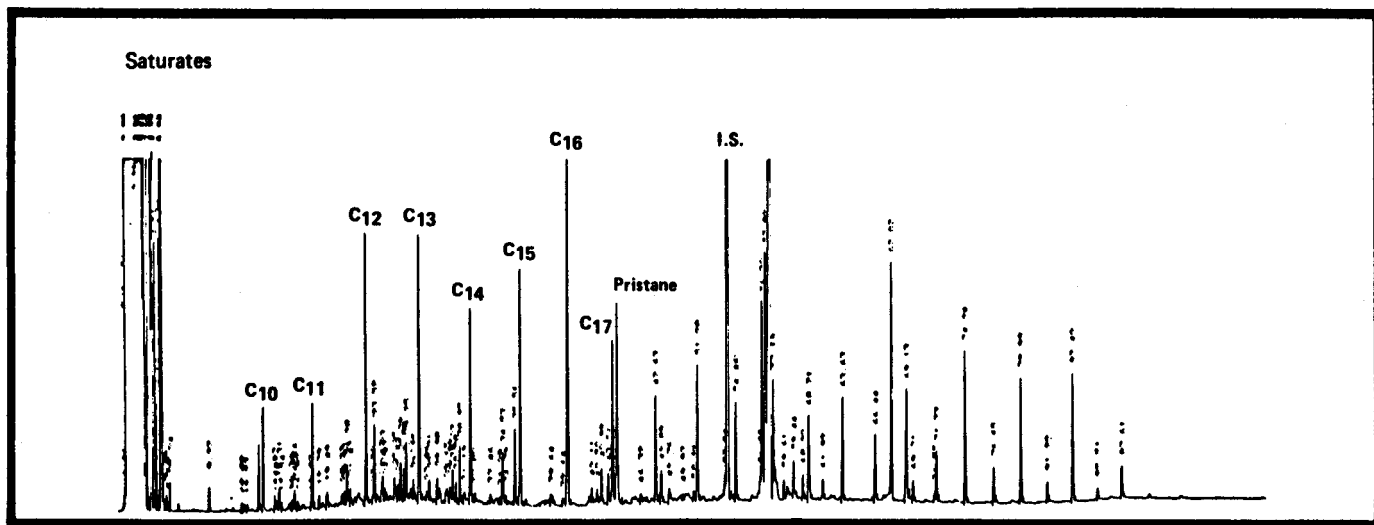


FIG. 13. GC² trace, benthic sediments of Bay 9, Transect 1 (3 m), one year after discharge. "I.S." indicates internal standard.

TABLE 8. Summary of Bay 7 sediment PHC concentrations ($\mu\text{g}\cdot\text{g}^{-1}$)^{a,b}

Station	Water depth (m)	1981			1982	1983
		Pre-release	1 day	2 weeks		
Tissue plots	3	0.33(0.12,0.91)	0.35(0.28,2.3)	0.37(0.15,0.93)	—	—
	7	0.47(0.26,0.85)	0.69(0.49,0.97)	0.93(0.58,1.5)	1.2(0.93,1.5)	3.2(1.1,9.1)
Transect 1	3	—	—	0.88(0.14,5.5)	—	2.0(1.5,2.7)
	7	—	—	0.99(0.33,2.9)	—	—
Transect 2	3	—	—	0.59(0.14,2.4)	—	1.5(0.52,4.5)
	7	—	—	0.99(0.35,2.8)	—	—
Transect 3	3	—	—	0.78(0.32,1.9)	—	1.0(0.22,4.7)
	7	—	—	1.2(0.18,8.4)	—	—

^a Determined by UV/F analysis.

^b Concentrations presented as geometric means with lower and upper 95% confidence limits shown in parentheses.

over baseline levels. The intrusion of low levels of chemically dispersed oil into Bay 7 is well documented (Green *et al.*, 1982).

Bay 10 sediment PHC concentrations are summarized in Table 9. Over the one-year period, hydrocarbon concentrations averaged generally less than $2\mu\text{g}\cdot\text{g}^{-1}$. Sediment levels two weeks after the release were comparable to those measured one year later and similar to the 1982 Bay 9 sediment PHC levels (less than $2\mu\text{g}\cdot\text{g}^{-1}$). High levels of water-borne oil in Bay 10 were observed during the chemically dispersed oil release (Green *et al.*, 1982).

DISCUSSION

The results of the sampling and analysis of subtidal sediments from the site of the surface oil release in Bay 11 and the site of the chemically dispersed subsurface oil release in Bay 9 indicate markedly different oil behavior. In Bay 11, only very small quantities of PHC were observed in the subtidal sediments during the first few weeks following the beaching of the oil. It appears clear that the beach served as a reservoir of oil that eroded over the ensuing two years and was deposited offshore in the subtidal sediments. Though the concentrations of PHC were greatest in the subtidal area shallower than 7 m, evidence indicates that PHCs were transported into the deeper areas of the bay as well. PHC concentrations had increased when last sampled in 1983, two years after the release, and were commonly in the $30\text{--}100\mu\text{g}\cdot\text{g}^{-1}$ range, with a single value observed to be $150\mu\text{g}\cdot\text{g}^{-1}$, although higher levels may have occurred outside of the immediate Bay 11 sampling stations. This oil was remarkably unweathered after two years; subtidal PHC compositions contained n-alkanes in the n-C₁₁ to n-C₁₆ range and alkylated

naphthalenes were still detected. The presence of similarly unweathered oil on the Bay 11 beach indicated that the beach certainly was a continuing source of oil to the offshore. It is estimated, using all available Bay 11 sediment data, that 0.2-2% of the original quantity of oil found on the beach five days after the release (5.3 m^3 ; Owens *et al.*, 1987) resided in the subtidal sediments one year after the release. This value increased to 1-10% at the time of the two-year post-release sampling.

These estimates are based on a large amount of data at 3 and 7 m depths, limited data at 10 and 35 m depths and data from one offshore transect. The oil continued to erode off the Bay 11 beach between August 1982 and August 1983, resulting in a sixfold increase in oil levels in the subtidal sediments. These data do not agree entirely with the beached oil mass budget of Owens *et al.* (1987). Owens *et al.* estimated, from detailed beach surveys, that 70% of the beached oil remained one year after the release and that 30% of the originally beached oil remained in August 1983, two years after the release. These decreases can be attributed to (1) erosion and offshore deposition, and (2) degradation and weathering on the beach face. Thus, even if one assumes that mechanism (2) is more important than (1), the estimate presented here of 10% transport offshore appears somewhat conservative. It is possible that greater PHC concentrations could have been found in unsampled areas beyond the southern extremity of our sampling stations.

Biodegradation of oil clearly occurred on the Bay 11 beach, as evidenced by decreases in the ALK/ISO ratio in the beached oil samples over time. This finding, coupled with that lack of apparent biodegradation of oil in subtidal sediment from Bay 9 and other bays not discussed here (see Bunch, 1987), suggests that biodegraded PHC residues were found in Bay 11 subtidal

TABLE 9. Summary of Bay 10 sediment PHC concentrations ($\mu\text{g}\cdot\text{g}^{-1}$)^{a,b}

Station	Water depth (m)	1981			1982	1983
		Pre-release	1 day	2 weeks		
Tissue plots	3	0.46(0.19,1.1)	1.4(1.0,1.8)	0.61(0.20,1.9)	—	—
	7	0.33(0.17,0.64)	0.88(0.52,1.5)	1.6(0.74,3.7)	1.7(1.3,2.1)	—
Transect 1	3	—	—	0.94(0.11,7.9)	0.83(0.38,1.8)	—
	7	—	—	1.1(0.52,2.3)	—	—
Transect 2	3	—	—	0.67(0.29,1.5)	0.68(0.64,0.72)	—
	7	—	—	1.7(0.78,3.9)	—	—
Transect 3	3	—	—	0.9(0.18,4.4)	0.65(0.07,5.8)	—
	7	—	—	1.7(0.65,4.2)	—	—

^a Determined by UV/F analysis.

^b Concentrations presented as geometric means with lower and upper 95% confidence limits shown in parentheses.

sediment as a result of the erosion of biodegraded residues from the beach face. Very slow biodegradation of oil in arctic sediments has been noted by Haines and Atlas (1982). The reason for the more extensive degradation of oil on the beach face is not clear but is probably related to a combination of available nutrients from rain-eroded tundra, along with seasonally elevated temperatures on the beach.

The Bay 9 dispersed oil scenario resulted in a markedly different subtidal sediment PHC situation. Here the source of oil was the 6 h initial discharge rather than a multi-year chronic input from the beach face. In spite of the large quantities of oil injected 1 m above the bottom during oil release, only a very small percentage was observed in the Bay 9 sediments and virtually no oil was transported to the beach. Initial concentrations of PHC in the sediment of 2-3 $\mu\text{g}\cdot\text{g}^{-1}$ increased to 4-10 $\mu\text{g}\cdot\text{g}^{-1}$ two weeks after the discharge. The surface floc initially accounted for approximately 20% of the sedimented oil, but two weeks later this floc had either been incorporated into the top 2 cm of sediment or had been transported out of the Bay 9 study area. The fact that much less than 0.1% of the discharged oil was found in the Bay 9 sediments indicates that chemically dispersed oil-sediment interactions were minimal, with sorption largely not occurring. In 1982, one year after the release, PHCs were still found in the Bay 9 sediments. PHC levels had decreased to 1-3 $\mu\text{g}\cdot\text{g}^{-1}$. The reason for the 1983 increase is unclear, but it may have been due to the northward movement of oil initially deposited near the diffuser pipe south of the Bay 9 study area or the unlikely intrusion of oil from Bay 11 into the Bay 9 area.

Chemically dispersed oil, released in Bay 9 and transported by currents, contaminated Bay 10 and, to a lesser degree, Bay 7. Initially intended as control sites, Bays 7 and 10 essentially became low-level dispersed oil exposure study areas for this investigation. Although sediments from these two bays generally exhibited lower overall PHC concentrations than Bay 9 sediments, the fate of the chemically dispersed oil was similar in all three bays and clearly different from the behavior of the untreated oil in Bay 11 sediments.

Sediments from the reference bays and from Bay 9 were minimally impacted by oil (PHC concentrations were always less than 10 $\mu\text{g}\cdot\text{g}^{-1}$ over the two-year study). In addition, GC² compositional determinations revealed no evidence of biodegradation of the treated oil in Bays 7, 9 or 10. In contrast, a steady increase in oil was associated with the sediments from Bay 11 for the duration of the study. These subtidal sediments appeared to be the main repository for stranded oil removed from the Bay 11 beach. Additional evidence for transport of beached oil to subtidal sediments came from the compositional makeup of the PHC, which revealed biodegraded residues resembling the composition found on the Bay 11 beach face (fewer n-alkanes relative to branched isoprenoids). Biodegradation of oil could not be confirmed in the subtidal sediments but was shown to occur in the intertidal or beach regions of Bay 11.

The results of this study and those of the companion studies (see Humphrey *et al.*, 1987a,b) are very significant because they illustrate some of the basic principles of the fate and weathering of spilled oil. The findings of this study also offer some definitive suggestions with regard to the relative short- and long-term fates of untreated vs. chemically dispersed oil in the Arctic. It seems clear that efficient chemical dispersion of oil results in the oil having little affinity for solid particles (i.e.,

sediments). In spite of the documented exposure of the benthic environment to large oil concentrations, as inferred from initial body burdens of benthic filter-feeding animals (Humphrey *et al.*, 1987b; Boehm, 1984), relatively little oil was observed in sediments sampled from Bays 9 and 10. A significant percentage of the small amounts of oil found in the Bay 9 and 10 sediments was associated with the sediment floc layer, which was apparently quickly eroded by near-bottom currents and removed from the study bays. While resident in the surface sediments, these small quantities of oil exhibited no evidence of biodegradation, a finding consistent with those of Haines and Atlas (1982) and Atlas *et al.* (1978). The untreated oil in Bay 11 was not sufficiently mixed into the water column during the initial spill event, so that virtually no oil was detected in the subtidal sediments until two weeks later, when oil originating on the beach was being deposited offshore.

In the year following the Bay 11 spill, oil concentrations increased in the subtidal sediments and at the termination of this study were still increasing. Levels of subtidal oil could be expected to increase in the subtidal sediments to much higher levels than reported here. This steady erosion of beached oil combined with the apparent lack of additional biodegradation in the subtidal sediments are evidence for a long-term buildup of PHC levels offshore, with the potential for bioaccumulation and, perhaps, other long-term biological effects. Because the physical weathering and biodegradation of oil on the beach resulted in the residual composition of subtidal oil being relatively enriched in alkylated two- and three-ringed polynuclear aromatic hydrocarbons (naphthalenes and phenanthrenes) and sulfur heterocyclic aromatics (dibenzothiophenes) (Boehm *et al.*, 1984b), these compounds can be expected to persist for longer periods in subtidal sediments until the oil is either physically transported farther offshore or physically dispersed by near-bottom currents.

These findings are entirely consistent with the weathering sequence of sediment-associated oil observed in other studies (e.g., Boehm *et al.*, 1981; Keizer *et al.*, 1978; Teal *et al.*, 1978; and other studies summarized in National Academy of Sciences, 1985) that indicate that subtidal sediment-associated oil in low-energy environments can persist for long periods of time, especially in arctic environments (Atlas *et al.*, 1978). Therefore, it appears that any decision that results in spilled oil not being chemically dispersed prior to a shoreline impact may result in a long-term chronic buildup of oil in the subtidal region.

SUMMARY OF CONCLUSIONS

The extensive study of PHC in subtidal sediments from the untreated surface oil release in Bay 11, where oil was allowed to impact the beach, and from the subsurface discharge of chemically dispersed oil in Bay 9 indicates the following:

1. Concentrations of PHC continued to increase in Bay 11 subtidal sediments for two years after the oil release and beaching. By the end of that period, erosion of oiled sediments had resulted in a large buildup of PHC in the subtidal sediments. Concentrations greater than 150 $\mu\text{g}\cdot\text{g}^{-1}$ were observed.

2. Biodegradation occurred on the Bay 11 beach face and the degraded residues were transported offshore. Following erosion from the beach, subtidal oil biodegradation was minimal.

3. Pockets of unweathered oil remained on the Bay 11 beach two years after release, allowing the transport of this oil offshore. Low molecular weight alkanes and alkylated naphtha-

lenes were still common features of some subtidal sediment PHC assemblage. Together with the homologous series of phenanthrenes and dibenzothiophenes, these compounds dominated the aromatic composition. Compositional heterogeneity of the oil on the beach has resulted in a similar heterogeneity offshore.

4. Due to beach sediment erosion, ice scour and other transport processes, at least 10% of the originally beached oil was transported to the Bay 11 subtidal sediment after two years. This suggests a continued buildup of oil in the subtidal sediments where spilled oil was untreated.

5. Sedimentation of oil in Bay 9, the site of the chemically dispersed oil release, was minimal, with PHC concentrations never exceeding $16 \mu\text{g}\cdot\text{g}^{-1}$. This observation was due to the lack of affinity of chemically dispersed oil for sediment particles. Any observed in Bay 9, 10 or 7 sediments was rapidly (within two weeks) decreased to very low levels.

6. The dispersed oil did not accumulate on the Bay 9 beach due to the effectiveness of the offshore dispersion of oil and the lack of a beach impingement in this bay.

7. A significant fraction of the sedimented oil in Bay 9 was initially associated with the surface floc, which was subsequently mixed into the sediment (0-2 cm) or transported out of the Bay 9 study area. After two years, oil was barely detectable in sediments from the site of the chemically dispersed oil.

8. Comparative assessment of the fates of chemically dispersed and untreated oil has provided new insight into the environmental effects of chemically dispersing an oil spill. Examination of subtidal sediment/oil interactions in the study bays suggests that in nearshore environments chemical dispersion can be an effective oil spill countermeasure to avoid long-term persistence of oil in the offshore sediment environment.

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