

LONG-TERM FATE OF DISPERSED AND UNDISPERSED CRUDE OIL IN TWO NEARSHORE TEST SPILLS

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ABSTRACT: The fate and effects of two nearshore discharges of Murban crude oil at Long Cove, Searsport, Maine in August 1981 were studied following a one-year, pre-spill baseline study of the test areas. An upper and a lower intertidal sampling area within a 60 × 100 meter test plot were exposed to dispersed oil in water resulting from the discharge of 250 gallons of oil pre-mixed with 25 gallons of Corexit 9527 dispersant. Release of treated oil was around high-water slack tide on the surface of the water, with added mixing energy provided by mixing gates deployed by small boats. The maximum water depth over the test areas was 3.5 meters. Untreated crude oil (250 gallons) was released on an ebbing tide within a separate, boomed-off 60 × 100 meter test plot. A third test plot served as an oil-free reference plot.

Water samples taken near the surface and near the bottom during and after discharge showed that chemically dispersed oil loses lower boiling hydrocarbons in both the aliphatic and aromatic fractions below n-C₁₇ as the droplets diffuse downward. Data are given for sediment samples taken from the test plots 11 months pre-spill and 10 months post-spill. Hydrocarbon analyses of the sediment samples show little incorporation of dispersed oil into the sediments of the treated oil plot relative to the sediments exposed to undispersed oil.

To gain quantitative information concerning the risks to the near-shore benthos of dispersant use, a controlled oil spill experiment was conducted in Long Cove, Searsport, Maine, on August 19, 1981. In this project, the environmental fate and effects of a spill of Murban crude oil pre-mixed with an oil spill dispersant, Corexit 9527 (Exxon) was compared with the effects of a spill of an untreated Murban crude oil. The study areas were analyzed both chemically and biologically for a one-year, pre-spill baseline period and for more than one year post spill. In addition, analysis of dispersed oil in water was performed during the discharge phase of the experiment. The spill site was chosen on the basis of several criteria including: the presence of intertidal animal communities and beach sediment types representative of New England coastal habitats; the lack of any recreational use in the study area; the lack of commercial shell-fishing in the area, in this case due to sporadic, low-level coliform inputs; and an orientation of the study area to permit an onshore southwest wind during the summer when prevailing winds are from that quarter.

Three intertidal study plots, each 60 × 100 meters, were established at the head of Long Cove. In addition, five subtidal sampling stations were established. Figure 1 shows these plots in relationship to the rest of Long Cove. Each plot has an upper and lower intertidal sampling area, each set up in a 6 × 6 meter sampling grid at one meter intervals. At each sampling date, each area was sampled for benthic infaunal analysis and sediment hydrocarbon chemistry.

One test plot served as an untreated reference plot and was up-stream from the other plots in terms of the prevailing wind and tide-

driven water flow in Long Cove. The second test plot was exposed to 250 gallons of Murban crude oil. The oil was released on an ebbing tide over a one-hour period within double containment booms running along the margins of the plot. Three kilograms of hexadecane (n-C₁₆) was added to the untreated oil to provide a distinctive n-alkane distribution for purposes of identifying the oil post spill. The

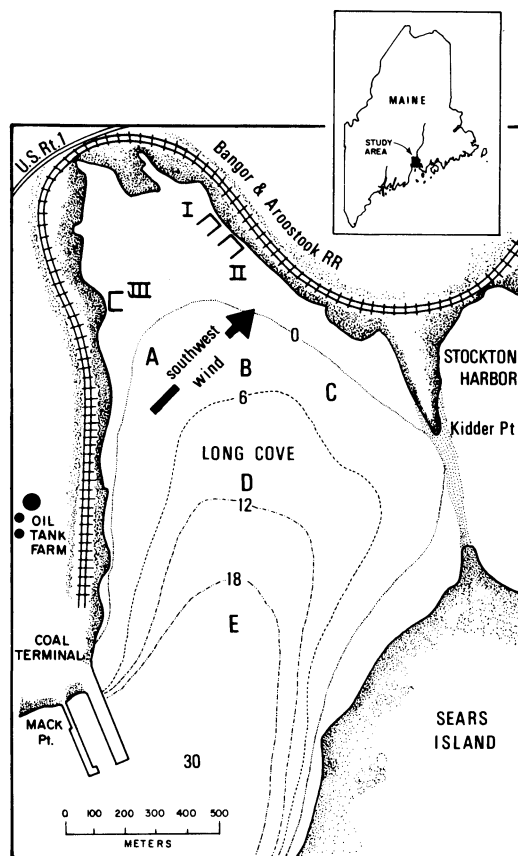


Figure 1. Map of Long Cove, Searsport, Maine—The locations of the intertidal test plots and subtidal (A, B, C, D, E) sampling stations are shown. Test plot III was exposed to oil plus dispersant, Test plot II was the unoiiled reference plot, and test plot I was exposed to untreated oil.

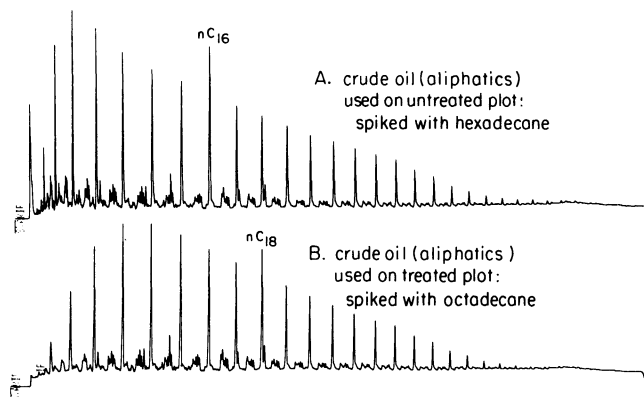


Figure 2. Gas chromatograms of the aliphatic fraction of the untreated Murban crude oil and of the Murban crude oil pre-mixed with dispersant—The figure shows the effect of adding excess $n\text{-C}_{16}$ as a marker to the untreated oil and excess $n\text{-C}_{18}$ as a marker to the treated oil.

untreated oil remained within the boomed plot for 24 hours (two tidal cycles) and then was cleaned up using conventional methods as if it were an actual nearshore spill.

The third test plot was exposed to a spill of 250 gallons of crude oil pre-mixed with 25 gallons of Corexit 9527. The treated oil was identified using a spike of octadecane ($n\text{-C}_{18}$) to permit post-spill identification of dispersed oil. Figure 2 shows gas chromatograms of the treated and untreated oil aliphatic fractions showing the result of the added n -alkane in each. The oil and dispersant was released on the surface of the water during two-hours around high-water slack tide when the water was relatively still.

The upper and lower intertidal sampling areas were exposed simultaneously by pumping oil and dispersant to a five-meter-long discharge manifold with perforations every 15 cm and mounted on a floating diffuser board. Each discharge manifold was deployed over each sampling area and supplied equally with oil-dispersant from a barge anchored between the two sampling areas. The oil and dispersant mixture formed an emulsion in seawater almost immediately on contact with the water. Additional vertical and horizontal mixing energy was provided by mixing gates mounted on small boats over each sampling/dischARGE area during discharge.

The dispersant-treated oil was released over an area smaller than that which the untreated oil impacted. This means that the actual exposure of the benthos to dispersed oil corresponded to the 100 percent dispersal of an oil slick of greater volume/area than the sampling areas exposed to the untreated oil.

The object of the dispersed oil discharge was to provide the nearshore benthic communities in the study area with as realistic a worst-case exposure as possible. The dispersant-treated oil was released on the water surface rather than by other modes because oil spills normally are treated with chemical dispersants while on the water surface. Subsurface oil-plus-dispersant release was considered inappropriate because it would have been inconsistent with the known chemical and physical behavior of dispersed oil.

For example, the American Petroleum Institute offshore oil spill studies demonstrate that dispersed oil rapidly loses volatile low boiling hydrocarbon fractions near the surface and that its downward diffusion is limited.^{5,7,8} Limited downward diffusion of dispersed oil in controlled field experiments also was observed by Buckley, *et al.*¹ These studies indicate that a loss of lower molecular weight oil fractions by volatilization and dissolution near the water surface may lower the acute toxicity of those fractions of chemically dispersed oil that, through downward diffusion, may interact with the bottom. Subsurface oil discharge or direct application of oil and dispersant mixtures to intertidal areas at low tide, therefore, would obviate an important weathering mechanism occurring in chemically dispersed oil in a real spill situation.

The preliminary results of the analytical program for this project covering the period from one week before the discharges ($D-1$) to one week after ($D+1$) have been presented elsewhere.^{10,4} The data presented dealt with the following topics.

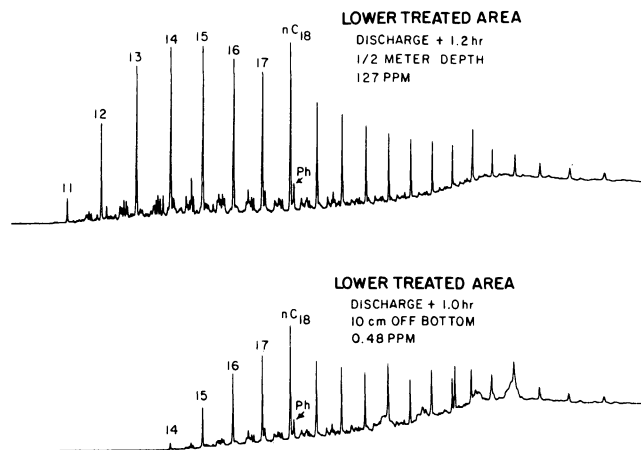


Figure 3. Gas chromatograms of the total extractables in water samples taken 0.5 meter subsurface (upper GC) and 10 cm off the bottom (lower GC)—When these samples were taken, the water depth was three meters and the dispersant-treated oil had been released for about one hour.

- Field fluorometry during the discharge phase gave a total integrated exposure of dispersed oil at the bottom in the study areas of 30-to-40 parts per million (ppm) per hour. No dispersed oil in water was detected after two tidal cycles.
- Gas chromatographic analysis of water samples taken at 0.5 meter depth and at 10 cm off the bottom during and after discharge showed that dispersed oil reaching the bottom had lost a significant fraction of low boiling hydrocarbons. This is illustrated for a set of representative gas chromatograms in Figure 3 for total CH_2Cl_2 extractables from two water samples taken from the same site at the same time but at different water depths. The chromatograms show that virtually all the material (aromatics and aliphatics) boiling below $n\text{-C}_{15}$ has been lost by the dispersed oil that had diffused downward to a depth of approximately three meters. The $n\text{-C}_{18}$ spike used to tag the dispersed oil also is clearly evident in Figure 3.
- Gas chromatographic and gas chromatographic/mass spectrometric (GC/MS) data were presented comparing the relative amounts of mono(C_1)- and di(C_2)-methyl dibenzothiophene (DBT) isomers in the $D-1$ week and $D+1$ week sediment samples. These sulfur heteroaromatics provided a useful means of distinguishing oil inputs from coal-derived hydrocarbon inputs at the study areas. In the clam and mussel tissues analyzed, the C_1 - and C_2 -DBTs provided a sensitive means of following uptake and release of oil.⁴ Clams and mussels exposed to untreated oil took up more oil over time than animals exposed to dispersed oil. This also was observed for the intertidal sediments. In the subtidal stations, a transient three-fold increase in C_1 - and C_2 -DBTs was observed in the unconsolidated surface (nephroid) layer only at the subtidal station (A) nearest the dispersed oil plot.

Methods

Before the discharge of oil, the test plots were sampled at $D-12$ months, $D-11$ months, $D-2$ months, $D-1$ month, and $D-1$ week. On each sampling date, pentuplicate sediment cores were taken for hydrocarbon chemistry and for benthic infaunal analysis. Subtidal stations were sampled at $D-11$ months, $D-5$ weeks, $D-3$ weeks, and $D-1$ week. After discharge, the sampling program continued as before at intervals of $D+1$ week, $D+2$ weeks, $D+5$ weeks, $D+10$ weeks, $D+44$ weeks, $D+11$ months, and $D+12$ months.

During dispersed oil discharge, two six-meter boats sampled water at time intervals at depths of 0.5 meter subsurface and 0.1 meter off the bottom in each of the sampling areas exposed to dispersed oil. (Details of the water sampling program and the preliminary results have been reported elsewhere.¹⁰ Sampling was performed using 12

volt submersible pumps at each depth. Water was pumped at five gallons per minute through linear polyethylene tubing through the flow cell of a Turner Designs model 10 series field fluorometer and then to a sampling manifold where five sample bottles could be filled simultaneously. All water samples were poisoned with mercuric chloride to prevent bacterial contamination of the sample. The smallest concentration of dispersed oil in water detectable in the field was 0.05 ppm. Water samples (two liters) for GC analysis were extracted with three 75-milliliter portions of methylene chloride, dried over Na₂SO₄ and concentrated to a residue. The residue was weighed and analyzed by capillary gas chromatography (see below).

Sediment samples were taken in pentuplicate from randomly chosen coordinates within each sampling area using a 7 cm, all-aluminum, solvent-rinsed coring tool. Subtidal sediments were sampled using a PONAR grab deployed from a boat. Before analysis, all sediment samples were passed through a 7 mm mesh screen to remove gravel and large detritus. Pentuplicate samples were either pooled and homogenized before analysis or analyzed individually. For the *D* - 11 month, *D* - 1 week, and *D* + 1 week samples, all five replicates were analyzed individually for all intertidal areas to gain an estimate of variability. In addition, the upper sampling area of the untreated oil plot at *D* + 44 weeks was analyzed for both the 0-to-2.5 cm and 2.5-to-15 cm strata individually. The 0-to-2.5 cm and 2.5-to-15 cm layers were sampled and analyzed individually at all plots for *D* - 1 week, *D* + 1 week, and *D* + 10 weeks.

Wet sediment samples were Soxhlet extracted for 24 hours with methanol followed by a 24-hour extraction with methylene chloride. The methanol extract was extracted three times with n-pentane. The pentane and methylene chloride extracts were washed with salt water, dried with Na₂SO₄, combined, evaporated to a residue, and weighed on a microbalance. All or part of the total extractable residue was separated into fractions by liquid chromatography using a silica/alumina (activity I) column with a layer of activated copper to remove sulfur. The hexane eluate contains the aliphatic fraction. Elution with 50/50 hexane/methylene chloride yields an "aromatic" (polar) fraction of hydrocarbons containing any aromatic hydrocarbons present plus other substances that behave as aromatics in the liquid chromatography procedure.

Each fraction was quantitated gravimetrically and analyzed by gas chromatography. The pre-spill aliphatics were analyzed using an all-glass, 30-meter SE-30 SCOT column in a Perkin-Elmer 3920B gas chromatograph with an MS-41 capsule injection accessory and helium carrier gas. The post-spill samples were analyzed as above using a SE-30 0.3 mm ID, fused silica, 15-meter WCOT column. The aromatics were analyzed using a 15-meter, 0.3 mm ID, SE-52 fused silica column in a Perkin-Elmer Sigma 3B gas chromatograph with a capsule injector, as above. In both cases, the capsule injector was used to enhance reproducibility and to prevent column degradation by high boiling residues.

Results

The data in this paper will deal primarily with an interpretation of data for the sediment aliphatic hydrocarbons from the pre- and post-spill sampling periods. These data are reasonably complete at the time this paper was written and permit conclusions to be made concerning the long-term (greater than one week) behavior of sediment hydro-

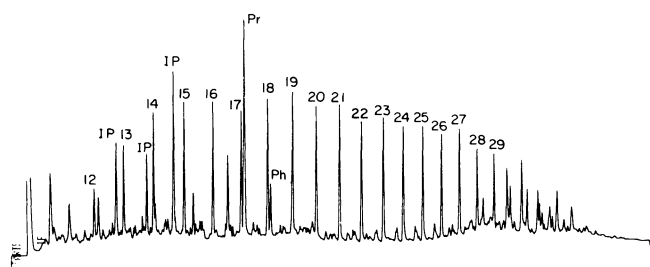


Figure 4. Gas chromatogram of the aliphatics fraction of hydrocarbons extracted from unburned coal lumps collected in Long Cove

carbons in the study areas. Moreover, the aliphatics comprise a greater percentage of the whole crude oil (50.6 percent by weight) than the aromatics (19.5 percent by weight) and thus would be a more sensitive overall indicator of oil uptake by sediments.

Complicating the data interpretation was the presence of extractable aliphatics and aromatics in sediment samples derived from unburned coal originating from a coal dock at the mouth of the cove, one mile away from the study areas. The degree of coal input increased in going from reference area (II) to untreated oil area (I) to treated oil area (III). Figure 4 shows a GC of the aliphatic hydrocarbons extracted from coal collected from the beach area south of area III. The distribution of hydrocarbons in Figure 4 is quite different from that of

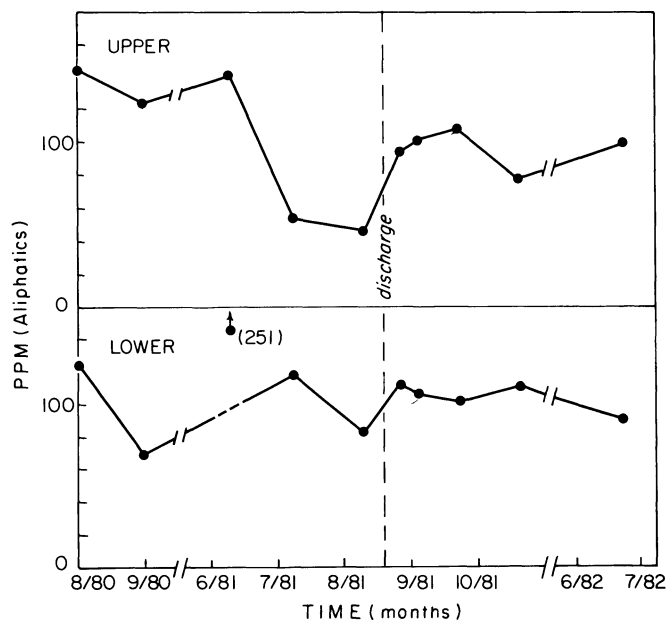


Figure 5. Variation in the concentration of sediment aliphatic hydrocarbons with time at the test plot exposed to untreated oil—All points represent 0-to-15 cm core samples.

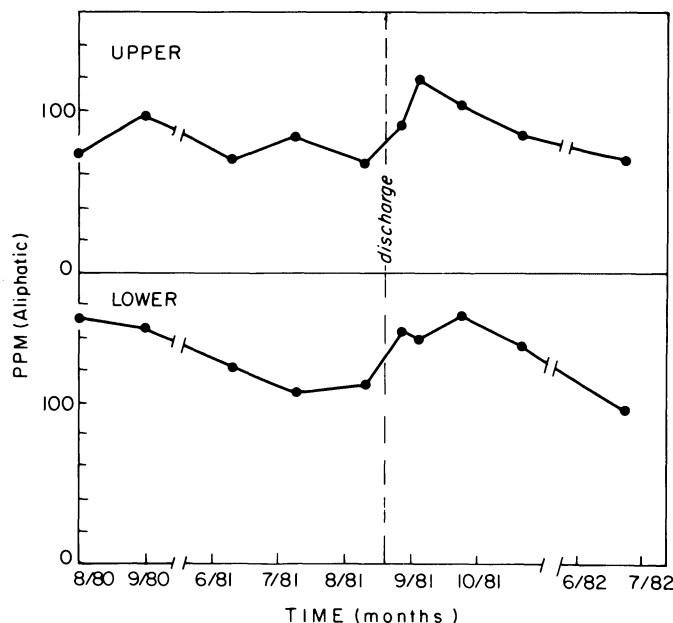


Figure 6. Variation in the concentration of sediment aliphatic hydrocarbons with time at the test plot exposed to oil plus dispersant for 0-to-15 cm cores

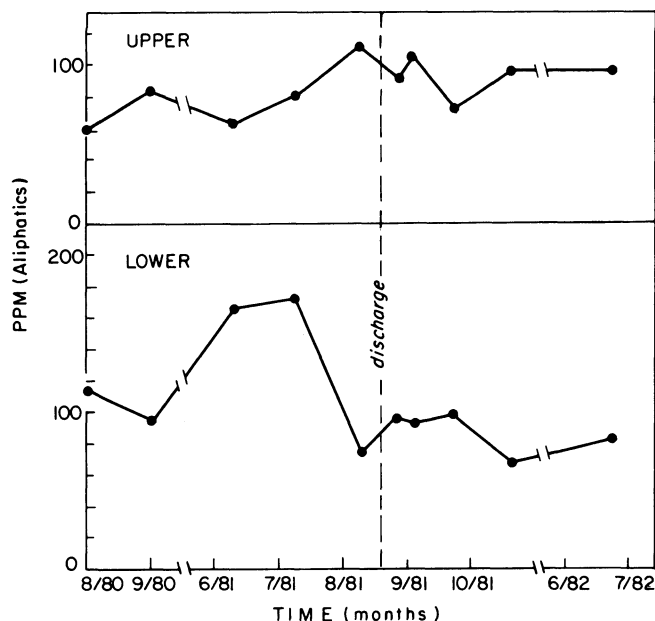


Figure 7. Variation in the concentration of sediment aliphatics with time at the unoiled reference plot for 0-to-15 cm cores

the crude oil used (Figure 2). The Murban crude, being a light crude, has only a small fraction of high boiling material; this is not the case for the coal hydrocarbons. In addition, the fraction of isoprenoid hydrocarbons appears greater in the coal sample. These observations are similar to those reported by Tripp, *et al.*¹² As coal use increases, this source of extractable marine hydrocarbons could become a complicating factor in future oil spill studies.

Table 1 gives the gravimetric results of sediment hydrocarbon analyses for samples taken during the pre- and post-spill periods. Because many of the sampling dates were analyzed as pooled 0-to-15 cm samples, all of the data obtained as stratified cores, replicate or pooled, are expressed as weighted 0-to-15 cm averages to permit comparison between dates. The data in Table 1 are summarized in Figure 5-7. In each of these figures, the date of oil discharge is clearly noted.

Figures 5-7 show that seasonal variations in sediment aliphatics are responsible for most or all of the variation in all areas except the upper untreated oil area (Figure 5), where there is a clear increase in sediment aliphatics after discharge. Many of the sites exhibited increases in sediment aliphatics attributable to late-spring/early-summer algae blooms.

Table 2 and Figure 8 give the gravimetric results for sediment hydrocarbon analyses of the 0-to-2.5 cm strata only. Any inputs of petroleum hydrocarbons would be expected to cause the greatest changes in this upper sediment layer, particularly when comparing $D - 1$ week and $D + 1$ week data. For those replicates analyzed individually, the results are given as averages plus or minus the sample standard deviation(s). These standard deviation values express a combination of variability within the analytical methodology and the natural intra-site variability in the field. A reasonable working estimate of analytical precision in the analytical methods used is ± 10 percent or better based on replicate analyses of standard samples. Looking at the data in Table 2 and taking the natural and analytical variabilities into account, no real change in the reference area and the treated oil area took place between $D - 1$ and $D + 1$ week. There is a significant increase in the 0-to-2.5 cm layer from $D - 1$ to $D + 1$ week at the upper area exposed to undispersed oil.

The gas chromatographic and gravimetric data were analyzed further to amplify differences between treated and untreated oil inputs at each area for the various sampling dates. The basis for this data treatment is illustrated by Figures 9 and 10. Figure 9 shows a representative set of gas chromatograms for the aliphatics extracted from the untreated oil upper sampling area at $D - 1$ and $D + 1$ week. The pre-spill chromatogram shows an alkane distribution that is primarily biogenic in origin with little material boiling below $n-C_{17}$. The

Table 1. Gravimetric results of hydrocarbon analyses as a function of time—The dates marked (*) are 0-to-15 cm weighted averages of 0-to-2.5 cm and 2.5-to-15 cm stratified cores. All values are given as ppm on a dry weight of sediment basis. D signifies discharge date.

Plot	Date	Upper Area			Lower Area		
		Aliphatics	Aromatics	Total	Aliphatics	Aromatics	Total
Treated oil	8/80	73	63	136	153	82	235
	9/80	97	64	161	145	75	220
	6/81	70	58	129	121	78	199
	7/81	80	45	129	106	86	192
	$D - 1$ wk*	69	74	143	111	98	209
	$D + 1$ wk*	92	72	164	144	120	264
	$D + 2$ wk	120	126	246	140	101	241
	$D + 5$ wk	104	62	166	154	97	251
	$D + 10$ wk*	86	62	148	136	85	216
	$D + 44$ wk*	70	73	143	97	128	225
Untreated oil (mid-plot, upper area)	8/80	144	60	205	124	93	217
	9/80	123	47	170	70	91	161
	6/81	141	30	171	251	74	325
	7/81	53	32	85	118	161	279
	$D - 1$ wk*	48	27	75	84	103	187
	$D + 1$ wk*	95	40	135	112	93	205
	$D + 2$ wk	102	43	145	107	79	186
	$D + 5$ wk	109	45	154	101	77	178
	$D + 10$ wk*	78	49	127	111	103	214
	$D + 44$ wk*	101	74	175	91	not yet complete	
Unoiled reference	8/80	59	35	94	114	52	166
	9/80	83	36	119	94	49	143
	6/81	63	33	95	166	60	226
	7/81	80	86	165	172	54	227
	$D - 1$ wk	111	45	166	74	51	125
	$D + 1$ wk	92	54	146	95	72	167
	$D + 2$ wk	105	50	155	92	60	152
	$D + 5$ wk	72	51	123	97	84	181
	$D + 10$ wk	95	48	143	67	54	121
	$D + 44$ wk	95	not yet complete		82	not yet complete	

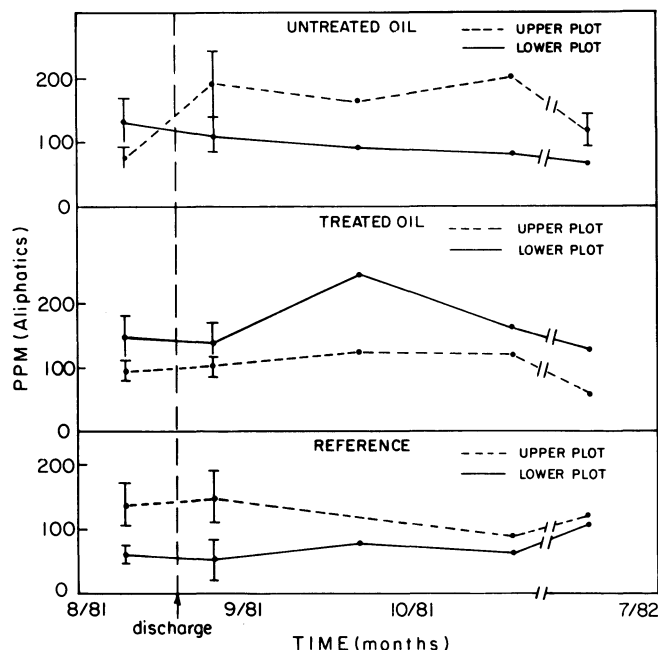


Figure 8. Variation in the concentration of aliphatic hydrocarbons in the 0-to-2.5 cm strata of sediment samples taken from all three test plots as a function of time—Error bars given with those data done in pentuplicate represent the sample standard deviation above the mean value.

post-spill GC clearly shows a major petroleum contribution to the sediment aliphatics from the untreated oil, as evidenced by the clearly enhanced *n*-C₁₆ peak.

The relative contribution of the lower boiling alkanes (*n*-C₁₅ + *n*-C₁₆), characteristic of the Murban crude n-alkane distribution and absent from the pre-spill samples, was determined from the GC data and compared with the (biogenic) *n*-C₂₉ contribution in the pre-spill sediments. This ratio $R = (C_{15} + C_{16})/C_{29}$ reflects the relative amount of untreated oil in the sediments at area I and was determined from the GC data for each sediment sample analyzed. This ratio for each sample, multiplied by the corresponding aliphatic ppm value, yielded a corrected set of internally consistent aliphatic values proportional to the relative amount of untreated oil in the samples. This was done for all strata and for all replicates analyzed. The results were expressed for the 0-to-15 cm overall core depth as in Table 1.

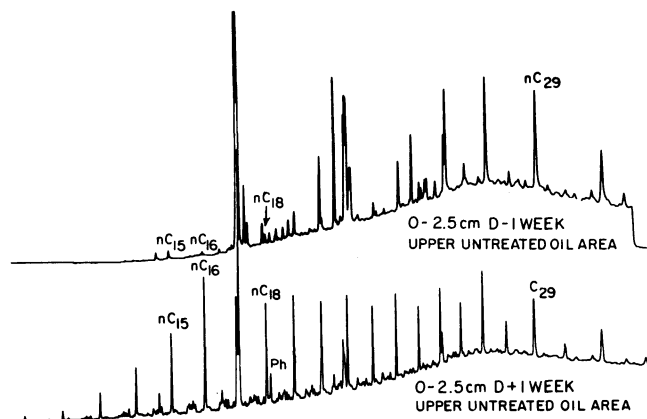


Figure 9. Gas chromatograms of the aliphatic fraction of hydrocarbons extracted from the 0-to-2.5 cm sediment layer for samples taken from the upper untreated oil area one week before discharge (*D* - 1, upper GC) and at *D* + 1 week (lower GC)—The *n*-C₁₆ spike clearly shows in the lower gas chromatogram.

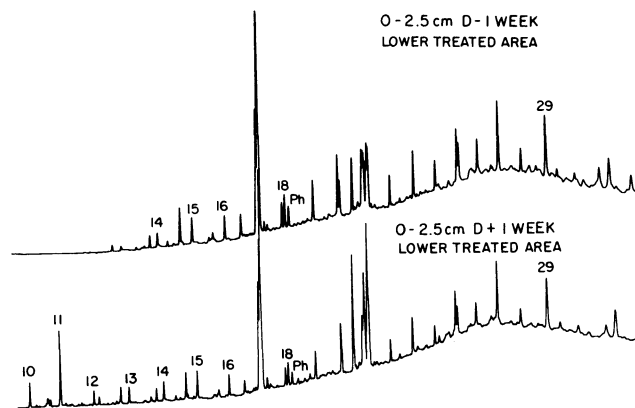


Figure 10. Gas chromatograms of the aliphatic fraction of hydrocarbons extracted from the 0-to-2.5 cm layer of sediment samples taken from the lower dispersed-oil-exposed area at *D* - 1 week (upper GC) and at *D* + 1 week (lower GC)—Little uptake of oil-derived aliphatics over the coal-derived aliphatic background is evident.

Table 2. Gravimetric results for sediment hydrocarbon analyses of the 0-to-2.5 cm strata only—Samples analyzed in pentuplicate are given as averages ± the standard deviation. All values are given as ppm or a dry weight of sediment basis. Dates are given relative to oil discharge (*D*).

Plot	Date	Aliphatics	Upper Area Aromatics	Total	Aliphatics	Lower Area Aromatics	Total
Treated oil	<i>D</i> - 1 week	94 ± 17	93 ± 24	186 ± 31	149 ± 33	136 ± 14	272 ± 25
	<i>D</i> + 1	102 ± 15	88 ± 20	190 ± 34	142 ± 30	109 ± 35	251 ± 65
	<i>D</i> + 5	128	63	191	247	170	417
	<i>D</i> + 10	124	98	222	163	129	292
	<i>D</i> + 44	62	59	121	131	183	315
Untreated oil (mid-plot, upper area)	<i>D</i> - 1	78 ± 16	43 ± 15	121 ± 31	131 ± 39	72 ± 13	203 ± 48
	<i>D</i> + 1	192 ± 52	67 ± 15	259 ± 61	108 ± 23	89 ± 20	197 ± 42
	<i>D</i> + 5	165	39	204	94	79	172
	<i>D</i> + 10	204	87	292	85	93	177
	<i>D</i> + 44	122 ± 24	120 ± 30	240 ± 54	72	not yet complete	
Unooled reference	<i>D</i> - 1	137 ± 32	52 ± 2	189 ± 33	61 ± 11	62 ± 22	123 ± 32
	<i>D</i> + 1	149 ± 41	90 ± 8	238 ± 44	52 ± 25	63 ± 7	115 ± 30
	<i>D</i> + 5		sample contaminated		80	95	175
	<i>D</i> + 10	92	60	152	63	65	128
	<i>D</i> + 44	120	not yet complete			not yet complete	

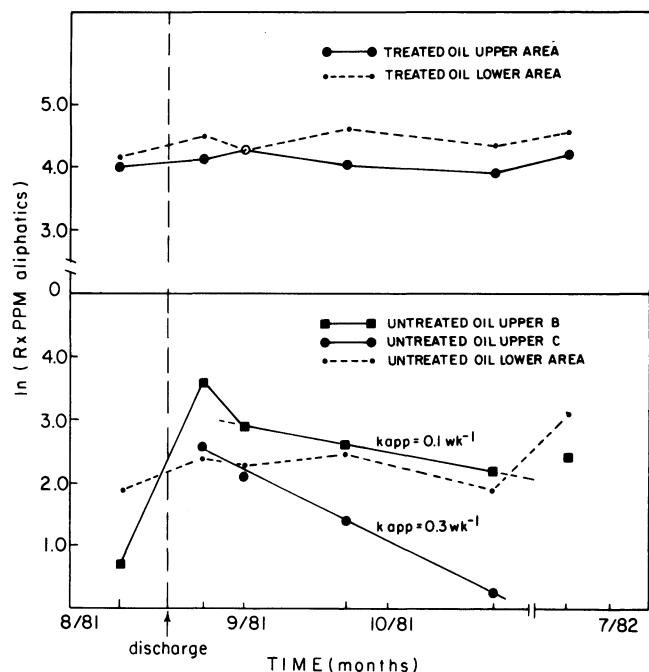


Figure 11. Graphs of \ln (corrected sediment aliphatic ppm) versus time for the untreated-oil-exposed and dispersed-oil-exposed areas—For the untreated-oil data, the slopes of the linear segments of the graphs yield the pseudo first order rate constants given on the figure. The half-life for oil decay at each area is given by $0.693/k_{app}$.

Figure 10 shows representative pre- and post-spill gas chromatograms of the aliphatic fractions of hydrocarbons extracted from the 0-to-2.5 cm layer at the lower treated-oil sampling area. Both the pre- and post-spill GCs, when compared with the coal aliphatics shown in Figure 4, demonstrate that unburned coal matter is a significant source of background aliphatics in this area. For the dispersant-treated oil, n -C₁₈ was added before discharge as a marker to augment that naturally present (Figure 2). There is no evidence in Figure 10 that the post-spill aliphatics are augmented in n -C₁₈ as was observed in Figure 9 for the untreated oil.

Using the approach discussed above, the ratio $R = (n\text{-C}_{15} + n\text{-C}_{18})/n\text{-C}_{29}$ was determined from the GC data for each sample analyzed. Addition of dispersed crude oil to the sediments would have increased this ratio over the baseline value. Gravimetric ppm values were corrected in the same manner as for the untreated oil by multiplying the $(n\text{-C}_{15} + n\text{-C}_{18})/n\text{-C}_{29}$ ratio times the ppm value for each sediment sample analyzed from the dispersed oil plot. No uptake of dispersed oil by the sediments in this plot would yield no change in these corrected values over time beyond any seasonal variations.

The corrected aliphatic ppm values for the treated and untreated oil-exposed plots are given in Table 3. Figure 11 plots these data as $\ln(R \times \text{ppm})$ vs time. The linear segments for this log plot for the two upper untreated oil sites (see discussion below) show that the undispersed oil residues in the sediments are degrading by rate processes that are pseudo first order in oil concentration. For the more heavily impacted area B, this oil breakdown had an apparent rate constant of $k_{app} = 0.1$ per week, yielding a half-life of oil in the sediments of seven weeks. The less heavily impacted area C had a $k_{app} = 0.3$ per week and a half-life of 2.3 weeks. The lower untreated oil area showed no observable changes. The areas exposed to dispersed oil showed no changes that could be related to the oil discharge.

Discussion

Analysis of the water samples by GC¹⁰ shows that dispersed oil that has lost sufficient buoyancy to permit downward diffusion from the surface has a smaller proportion of hydrocarbons boiling below n -C₁₇

Table 3. Gravimetric results for the aliphatic fraction of sediment hydrocarbons corrected for non-petroleum inputs—The values given are determined for 0-to-15 cm, as in Table 1.

Plot	Date	Upper		Lower	
		Ratio (R) × ppm ₁	Ratio (R) × ppm ₁	Ratio (R) × ppm ₁	Ratio (R) × ppm ₁
Treated oil	D - 1 week	56		64	
	D + 1	63		92	
	D + 2	73		72	
	D + 5	60		100	
	D + 10	51		80	
	D + 44	67		98	
Untreated oil ₂	D - 1	(B) 2	(C) —	(D) —	7
	D + 1	37	13	26	11
	D + 2	18	8.3	5.6	10
	D + 5	13	4	11	12
	D + 10	9	1.3	16	7
	D + 44	11	—	2	22

1. For each set of gas chromatographic data, the ratio $(C_{15} + C_{16})/C_{29}$ was determined for the untreated-oil plot samples and the ratio $(C_{15} + C_{18})/C_{29}$ for the treated-oil plot samples. The ratio times the corresponding aliphatic ppm value represents a corrected ppm value for which the contribution of the light Murban crude oil used in the experiment is amplified.

2. For the upper untreated-oil plot, results are given for the mid-plot (B) sampling area and for two secondary upper sampling areas (C and D) displaced laterally with respect to the upper mid-plot area.

than dispersed oil near the surface (Figure 2). This observed change with water depth in hydrocarbon distribution in chemically dispersed oil is consistent with measurements of C₁-C₁₀ hydrocarbons in chemically dispersed oil obtained during the API offshore oil spill experiments.^{5,7,8} Furthermore, this effect was anticipated by Canevari² in studies dealing with the droplet size effects of oil dispersed with "self-mixing" dispersants. Rapid attenuation of oil concentration with depth was observed in this study and confirms the observations of other field studies with oil spill dispersants.^{10,1,8}

The lower boiling fractions lost during the downward diffusion of dispersed oil from the surface include the more acutely toxic fractions containing one and two-ring aromatics such as mono-, di-, and trimethyl naphthalenes. This means that chemically dispersed oil interacting with the nearshore benthos, even in relatively shallow water (less than 4 m) as in the present experiment, undergoes a significant alteration in acute toxicity. Thus, while steady-state exposure of animals to dispersed oil in the laboratory might adequately estimate toxicity to animals living in the upper 1-to-2 meters of the water column, such experimental regimes may not yield realistic information about benthic effects.

The data given in Table 1 and summarized in Figure 5-7 show that seasonal variation must be taken into account in interpreting changes observed over time at an oil spill site. In the upper untreated area, considerable uptake of oil in the 0-to-2.5 cm layer was observed (Table 2), as well as a correspondingly smaller increase in the amount of oil in the 2.5-to-15 cm layer (compare values in Table 1 with Table 2 as well as Page, *et al.*¹⁰). This is consistent with the relatively slow downward mixing of oil in sediments observed in tank studies by Wade and Quinn.¹³

For the lower untreated-oil area, the small initial oil uptake observed may be due partly to the relatively small size of the untreated oil spill. This poor uptake of oil also may be related to the finer grain size in the lower untreated area than the upper areas. Poor oil uptake by fine grain, water-logged intertidal sediments also was observed in a test spill experiment by Rowland, *et al.*¹¹ The behavior of the sediments exposed to dispersed oil (Figure 6) shows that any uptake of aliphatics by the sediments is small compared with the background variation, as shown in Figure 7.

The data for the upper 0-to-2.5 cm strata (Table 2) show the oil uptake pattern more clearly. Unfortunately, stratified core samples were not taken during much of the baseline period so the analysis of seasonal variation in the 0-to-2.5 cm layer covers only the period D - 1 week to D + 44 weeks. The data in Figure 8 show that only in the upper area exposed to undispersed oil was there a detectable uptake of oil. That no oil uptake was detected in the dispersed-oil-exposed plot is consistent with the fact that clams and mussels taken

from the treated-oil plot exhibited a five to eight fold lower uptake of C_1 and C_2 -dibenzothiophenes than clams and mussels exposed to the untreated oil¹⁰

The treatment of the data to produce the results shown in Figure 11 was based on combining the GC data and the gravimetric data for each sample to amplify changes in the sediment aliphatics related to the uptake of oil from the experiment. For the sediment data analyzed in this way for the dispersed-oil-exposed plot, no change is observed from pre- to post-spill. This is in agreement with the data in Tables 1 and 2. The same is true for the lower intertidal area exposed to untreated oil, except for the $D + 44$ week value which probably reflects an increased input of unburned coal over the winter of 1981–1982.

The post-spill behavior of the sediment aliphatics at the upper untreated-oil plots (Figure 11) clearly shows a pseudo first order decay process for two of the three upper areas (B and C) analyzed post spill. The third area (D), showed significant oil uptake but a less regular loss of oil. This most likely is due to the depositional nature of area D compared with the other two areas. Upper area D, therefore, would receive more oil after discharge via suspended particulate matter than the other upper areas, thus producing an irregular oil weathering curve.

It is noteworthy that the more heavily oiled upper area B exhibited a slower loss of oil over time ($t_{1/2} = 7$ weeks) than area C ($t_{1/2} = 2.3$ weeks) which was less heavily oiled. This result is related to earlier studies in Long Cove on a 1971 spill of JP-4 and No. 2 fuel oil that heavily impacted an intertidal beach area 0.5 mile south of area III (Figure 1). Sediment samples from the spill impact area^{6,3,9} showed that for those areas of beach most heavily impacted by the 1971 spill, no weathering of the oil was observed over the course of eight years. It was proposed that a strong physical-chemical interaction between the beach clay fraction and the petroleum hydrocarbons prevented normal oil weathering processes.⁶ That the oil in the area initially impacted more heavily in the present study degraded at a slower rate is consistent with these earlier studies in Long Cove. While each oil spill situation is unique, the half-lives for oil in the present study are in the same range as other quantitative studies over time. For example, data given by Wade and Quinn¹³ for controlled ecosystem studies with No. 2 fuel oil showed an oil (aliphatic) decay half-life of approximately two weeks.

Conclusions

This experiment involved the comparison of the fate and effects of two test oil spills. One was a 275-gallon spill of oil plus dispersant released on the water surface over a total water surface area initially about 300 m². The other test spill of 250 gallons of untreated oil was released within a 6,000 m² boomed area. In terms of volume per unit area, the dispersed-oil release corresponded to the 100 percent dispersion of a spill of about 2,000 gallons/acre (2×10^4 liters/hectare). The important conclusion of this work is that for an oil discharge consistent with a real spill treatment scenario, incorporation of dispersed oil into the intertidal (shallow water) benthos is small compared with conventional shoreline oil impact followed by conventional cleanup procedures.

Because the release of dispersed oil in the present study took place in shallow water (less than 4 m deep), any adverse effect would be expected to be magnified relative to oil dispersal in a larger, deeper body of water. In comparing the effects of nearshore chemical dispersal of an oil spill versus the option of shoreline impact and subsequent cleanup, a mitigating factor is that in a field situation dispersed oil that has lost sufficient buoyancy to diffuse downward, even in relatively shallow water, has lost most of the lower boiling petroleum fractions normally associated with acute toxic effects.

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