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031 Stranded Oil in Coastal Sediments: Permeation in Tidal Flats

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STRANDED OIL IN COASTAL SEDIMENTS: PERMEATION IN TIDAL FLATS

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SUMMARY

Physical/sedimentological parameters determining the retention and penetration of oil slicks in fine sediments were examined experimentally in natural and reconstituted cores, set up in a simulated tidal system. Thirty- five natural cores (1m long, 6.7 cm inside diameter) were collected from a tidal flat (Patricia Bay, Vancouver Island; mean grain size 153 (±29) microns; permeability 0.124 cm/min) and from a coarser sediment beach (Island View Beach, Vancouver Island; mean grain size 287 (±142) microns; 0.435 cm/min). Also 14 reconstituted cores were prepared from mixtures of Patricia Bay and Island View Beach sediments, with fine clay added, to yield a wider range of grain size (132-287 microns), mud content (0-4.7%), and permeability (0.0035-0.435 cm/min).

Known amounts of an experimentally weathered heavy oil (Alberta Sweet Mixed Blend) were layered onto the water columns over the sediment cores, and during the simulated ebb period were brought into contact with the core surfaces. Quantitative and qualitative measurements were made on gross oil fate, on permeation of oil into core sediments, and on biodegradation by a combination of infrared-spectroscopy and gas-chromatography. Also investigated were the influence of sediment grain size, percentage mud content, and time of tidal submersion.

Oil loading experiments with surface slicks of different thicknesses (0.5-10 mm) indicate increasing concentrations of hydrocarbons in the surface sediments with greater thicknesses of oil, but the bulk of the oil (96-100%) was found primarily in the top 2 cm with little penetration below 2 cm in fine sediment cores exposed to regular tidal incursions.

Penetration into the cores varied inversely with mud content as an index of fineness. Concentration of hydrocarbons in top 2 cm of sediments varied inversely with mud content, resulting in increased penetration and contamination in coarser sediments (>350 microns, <2% mud content).

Experiments with different tidal regimes indicated that penetration of hydrocarbons into sediments increased markedly in cores that were exposed to air for 60% or longer of the tidal cycle. Both penetration and sub-surface hydrocarbon concentrations were considerably higher in such exposed sediments than in sediments that were submerged during tidal floods for 60% or longer of the tidal cycle.

The data indicate that tidal flat sediments may be less vulnerable to oiling than previously thought, with greater than 95% of oiling restricted to the top 2 cm of homogeneous sediments. However, the penetration for hydrocarbons is sensitive to small increases in mud content and by the location of oiling sites relative to the mean water level.

RÉSUMÉ

Un système de marée simulé a été construit avec des carottes de sédiment naturel et reconstitué, afin de déterminer les mesures du rétention et pénétration des échappements d'huile dans les sédiments fins. Trente-cinq carottes de sédiment ont été utilisées (1 m longeur, 6.7 cm diamètre interne). Quelques carottes ont été recueillies sur un platier de marée (Baie Patricia, Ile de Vancouver; la granulométril des particules est de 153 (± 29 µm); la perméabilite de 0.124 cm/min. Quelques carottes ont été recueillies sur une plage avec des sédiments plus grossiers (Plage Island View, Ile de Vancouver; la granulométril des particules est de 287 (± 142 µm); la perméabilité de 0.435 cm/min. De plus, quatorze carottes reconstituées, ont été préparées à partir d'un mélange des sédiments de la Baie Patricia et de la plage Island View, et de boue fine, afin d'assurer une plus grande variabilité de la granulométril (132-287 µm); contenu en boue (0-4.7%); et de la perméabilité (0.0035-0.435 cm/min).

Des quantités d'huile lourde, qui a été altérée naturellement (Sweet Mixed Blend, d'Alberta) ont été placées sur l'eau du-dessus du sédiment. Lors de la simulation de la marée basse, l'huile recourrait le sédiment. Quelques mesures ont été prises, quantitatives et qualitatives, sur le destin d'huile; sur la pénétration de l'huile, dans le sédiment, et sur la biodégradation de l'huile, en employant le spectroscopie à rayon infra-rouge, et le chromatographie gazeuse. Aussi, l'influence de la granulométril des particules du sédiment, la quantité de boue, et le temps de submersion ont été étudiés.

Les essais nous ont indiqué que les concentrations des hydrocarbures à la surface du sédiment, ont augmenté avec l'augmentation de l'epaisseur de la couche d'huile (0.5-10 mm). La majure partie de l'huile (96-100%) a été trouvée dans les deux premiers cm sous la surface. Dans les carottes composées de sédiments fins, et exposées au cycle de marée ordinaire, on observe peu de pénétration sous les deux premiers cm.

La pénétration d'huile dans les carottes a augmenté inversement avec le contenu en boue. Dans les deux premiers cm de sédiment, la pénétration et contamination ont augmenté avec l'augmentation de la granulométril des particules (>350; <2% boue).

Des essais employant différents cycles de marée, nous ont montré que la pénétration d'huile a augmenté sensiblement dans les carottes qui étaient exposées à l'air pour 60% ou plus du cycle. La pénétration et contamination par l'huile dans les deux premiers cm du sédiment, étaient plus élevées dans ces carottes plutôt que dans celles qui étaient submergées pour 60% ou plus de cycle marée.

Les résultats nous indiquent que le platier de marée peut-être moins vunérable aux échappements d'huile qu'on avait pensé. Plus que 95% de la pénétration est restreinte aux deux premiers cm dans des sédiments homogènes. Cependant la pénétration est affectée par de feibles changements dan le contenu en boue, et par la localisation de l'echappement par rapport au niveau moyen de la mer.

INTRODUCTION

Low-energy coastal systems are considered among the most sensitive of marine ecosystems to oiling because of their vulnerability to oil stranding and the difficulty in their cleanup. This has been recognized repeatedly under real spill conditions in tidal flats and lagoons (Arrow, Anonymous 1970; Amoco Cadiz, Hess 1978), saltmarshes (Golden Robin, Vandermeulen and Ross 1977; Teal et al. 1978; Hampson and Moul 1978; Amoco Cadiz, Hess 1978; Vandermeulen et al. 1978; Metula, Gundlach et al. 1982) and mangrove systems (e.g., Page et al. 1979). It has been argued generally that a considerable risk to these ecosystems would come from the stranded oil penetrating into the sediment and consequently persisting for years or decades, degraded only by slow microbial degradation under anoxic conditions (e.g., Vandermeulen and Gordon 1976). Low-energy soft sediments such as temperate tidal flats and tropical mangrove swamps would be especially vulnerable to such oil-entrapment and persistence.

For intertidal sediments, such as are found in tidal flats, the problem is further magnified by the stranding and adherence of oil slicks directly onto the sediment surface. Thomas (1973, 1977) first described the sensitivity of different beach types and tidal levels to oiling in terms of wave-exposure and indicated the potential for long-term persistence of stranded oil in low-energy cobble-gravel-silt beaches of Chedabucto Bay, Nova Scotia, Canada. Subsequently, Vandermeulen and Gordon (1976) presented a first model of hydrocarbon remobilization from stranded oil in semi-porous sediments and described the routes of hydrocarbon movement through beach interstices.

Subsequent studies have identified substrate type (Michel et al., 1978; Gundlach and Hayes 1978) and sediment grain size (Owens 1978; Vandermeulen 1980) as determining the binding and entrapment of stranded oil. Of these, the mud content (terminology after Folk 1974, i.e., grain size <63 microns) has been found to correlate strongly with oil penetration in a detailed geomorphological study of an oiled estuarine beach of the Aber Benoit, France, eight years after the Amoco Cadiz. In a further analysis of oil/ sediment interaction, tidal pumping together with sediment permeability has been proposed as a major process in the penetration of oil into fine sediments (Owens 1977, 1978; Vandermeulen 1980). Based on these various observations and on field observations in Ile Grande saltmarsh (France), following the Amoco Cadiz supertanker spill, it was suggested that sediments with a mud content of greater than 1 to 2% would be relatively impervious to oil penetration (Vandermeulen et al., 1978). Meanwhile, observations at the experimental Baffin Island Oil Spill (BIOS) site indicated that oil stranded on a sheltered tidal flat was readily lifted off and transported elsewhere by tidal excursions (Owens et al. 1983).

In this paper, results from a series of three experiments to quantify one component of oil/sediment interaction - the permeation of oil and retention in muddy-sand sediments are described. A fourth experiment was conducted to evaluate the effect of organic substances on oil penetration and retention but results were questionable because permeability changed as a function of organic content. The three experimental series in particular involved the influence of (1) oil-loading, (2) tidal emergence-submergence, and (3) sediment grain size on oil permeation and retention. Using an experimental tidal system, aliquots of a weathered heavy crude oil were brought into contact with the upper surface of isolated natural sediment cores. Oil permeation and retention was then measured under a range of simulated tidal and sediment grain-size conditions. By choosing one natural sediment type, the authors controlled sediment type and the organic content as two possible competing variables in oil-binding and entrapment. Not included here are the potential contributions from dissolved water-accommodated hydrocarbons or from sedimentation by suspended sediment-bound hydrocarbons. Although natural sediments were used, the results obtained were consistent and indicate quantifiable relationships between sediment oiling and sediment parameters.

MATERIALS AND METHODS

EXPERIMENTAL SYSTEM

The experimental system consisted of 1-m sediment cores in 6.7 cm (inside diameter) acrylic core liners installed vertically in a simulated tidal system that was supplied from an overhead seawater-filled head-tank (Figure 1). For the flood portion of each tidal cycle, the columns were filled via the side and bottom inlets. To naturally simulate the ebb portion of the tidal cycle, the water column over the sediments was first lowered quickly with a suction pipette to within 1-2 cm of the sediment surface, after which the core was allowed to drain further through the bottom outlet.

The fill-and-drain curve (Figure 2), shows typical experimental "flood" and "ebb" phases of the water column above the sediment core surface as measured in a side-mounted standpipe manometer. Because of high water retention of the fine sediments, it was not possible to observe changes in level of the ground-water table within the cores.

Known aliquots of a crude oil were layered, at "high tide", onto the water over the sediment cores and were allowed to contact the sediment surface during the subsequent "ebb". By setting experimental cores at different heights relative to the head-tank, different conditions of tidal exposure, expressed as "%-emergence" were simulated (e.g., 0% emergence = subtidal; 50% emergence = mid-tide; 100% emergence = supratidal).

Prior to each experiment, newly installed sediment columns were first allowed to equilibrate through four tidal cycles (12 hrs each). Known amounts of the weathered test oil were then applied to the surface of the water column over each sediment core at "high tide", and a typical test duration then consisted of a further ten tidal excursions, twice daily.

TEST OIL

The oil used throughout was a heavy mixed crude oil (Alberta Sweet Mixed Blend - EPS Standard[1]) that had been artificially weathered by evaporation to 30-35% loss by weight (pour point 0°C, viscosity 88 CST at 20°C).

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[1] EPS Standard is a standard oil used by the Environmental Protection Service of Canada.

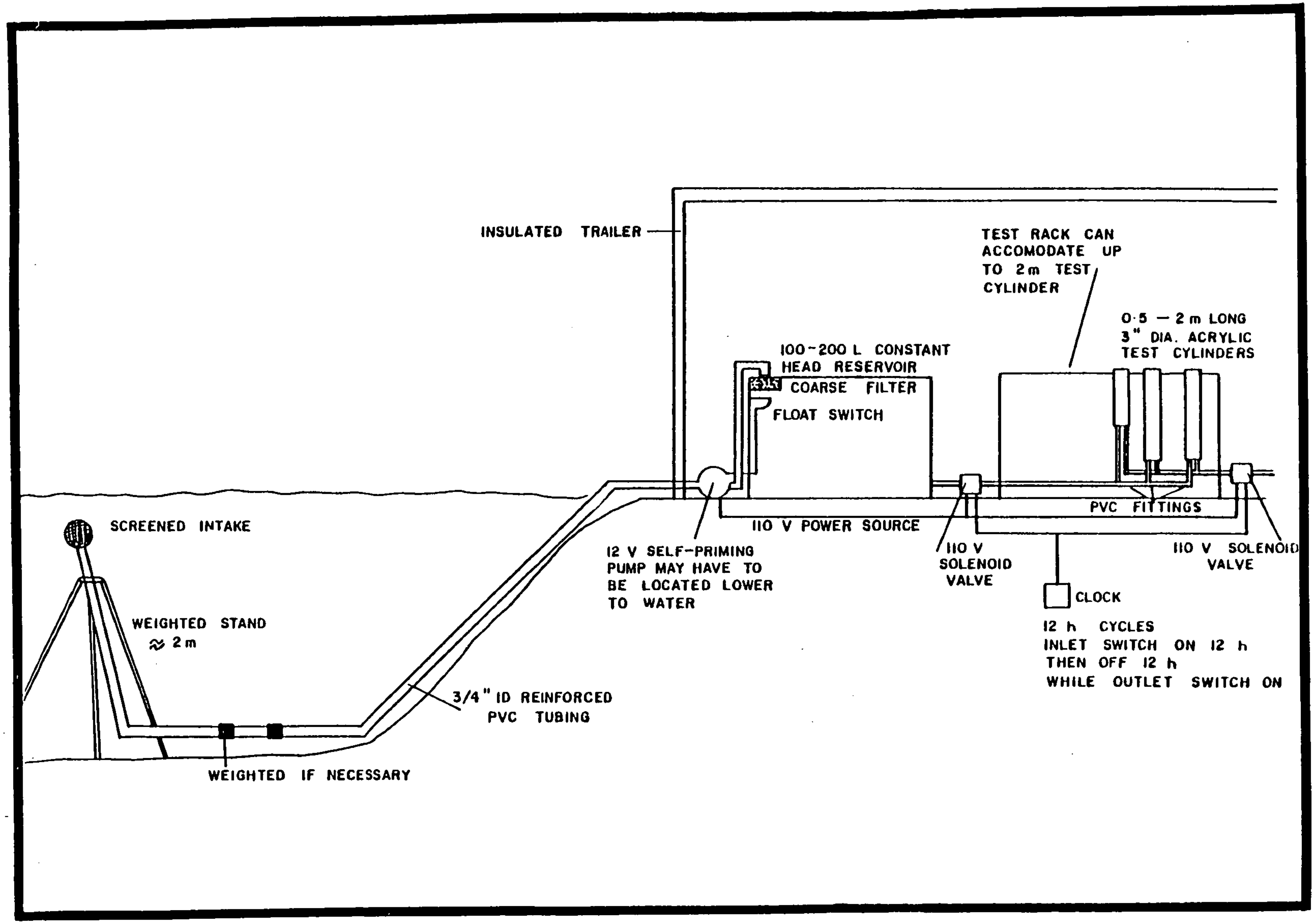

Figure 1. Experimental laboratory set-up of sediment cores in tidal seawater system.

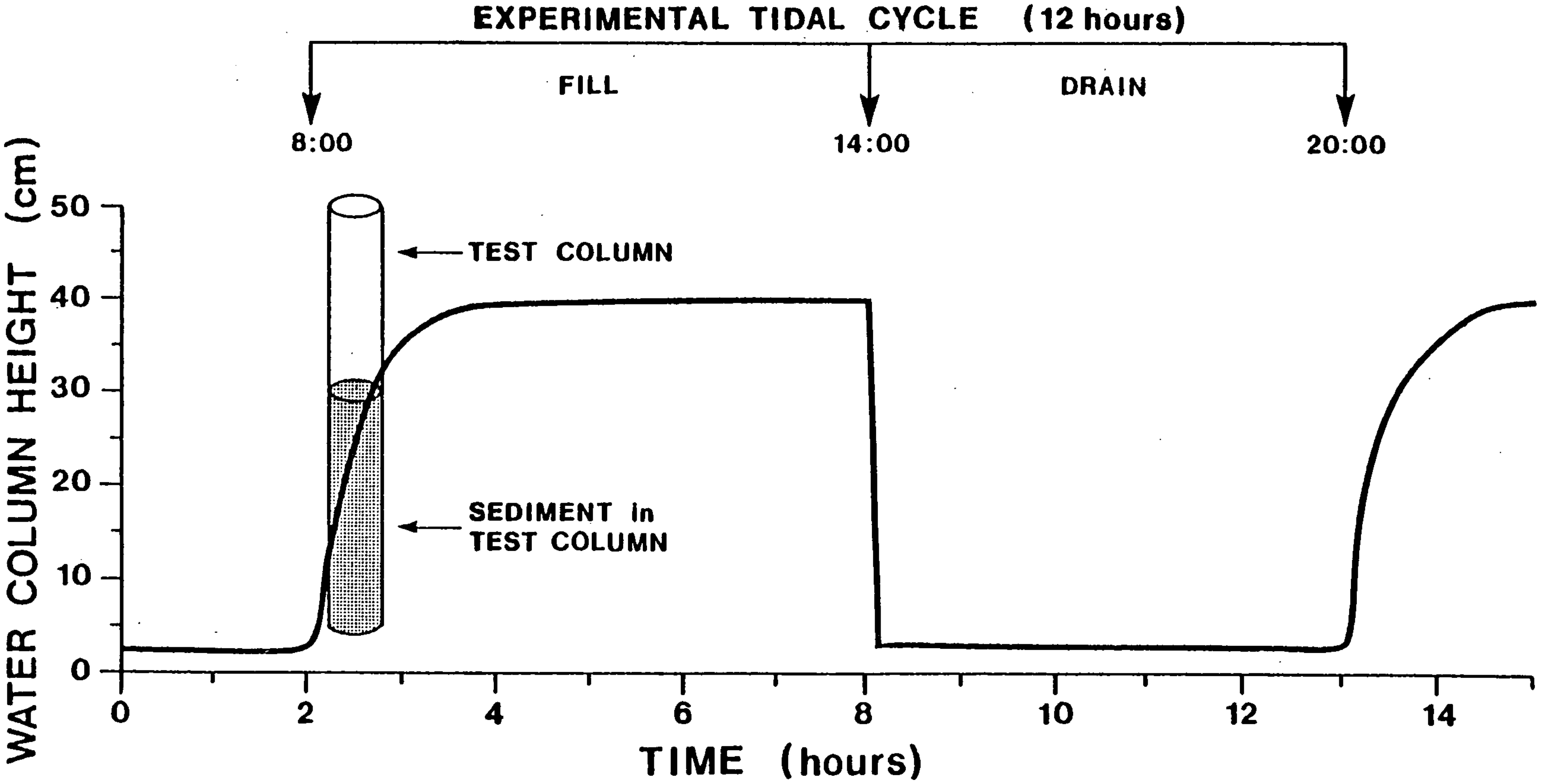

Figure 2. Experimental tidal cycle in isolated sediment cores.

SEDIMENT CORES

Undisturbed sediment cores collected from a nearby tidal flat (Patricia Bay, Sidney, British Columbia) served as the "standard" experimental cores. A series of cores taken from Island View Beach on Vancouver Island provided a slightly coarser sediment. Cores were transported intact to the experimental tidal system in the laboratory. Care was taken to avoid sediment cores containing animal burrows and other evidence of bioturbation. Once installed in the seawater system, ambient ocean water taken from the Patricia Bay was then cycled through the sediment columns as soon as possible so as to maintain the sediment cores in as near natural and undisturbed state as possible. Compaction and surface settling measurements were made throughout and indicated no detectable change in integrity of the sediment columns thus collected and maintained.

Differing sediment grain size compositions were obtained by mixing sediments from Patricia Bay with sediments taken either from Island View Beach or with commercially obtained potters clay. Such experimentally reconstituted sediment cores were equilibrated in the same manner as described for the natural sediment cores.

Experimental cores were run in duplicate. Sediment grain size, bulk density, and permeability were determined for all cores (Table 1). Inter-column variability was small. The mean sediment size of "standard" (Patricia Bay) sediments was 150 microns (range 140-160 microns) with a mean mud content of 1.5% (range 0.8-2.4%). Bulk density of standard sediments was 1.69 g/cm^3 (range 1.68-1.72 g/cm^3). Permeability, determined by the falling-head test (Spangler and Hardy 1973, p. 242), averaged 0.13 cm/min (range 0.089-0.18 cm/min). Preliminary examination of sediment cores exposed to seawater containing coloured dyes had shown no indication of abnormal drainage patterns within the cores under these conditions, and it was assumed that all cores drained homogeneously. A total of 35 natural cores and 14 reconstituted cores were tested in this way.

ANALYSIS

A complete budget on the disposition of the oil was determined by a combination of gravimetric and infrared-spectrophotometric (IR) techniques for each core. Oil quantities of various components of the system were estimated gravimetrically including: (a) all oil still floating on the water surface, (b) oil adhering to the walls of the core liners, (c) oil adhering on the surface (0 to 0.2 cm) of the sediments, and (d) any whole oil being drawn off during the simulated ebbing periods. Also, 2 cm sections of the sediment core were analysed by IR (Green et al. 1982). Recovery of oil for each experiment averaged 102% with a standard error of 5% and with a mean difference of 7.1% between replicates for all cores.

TABLE 1

Sediment parameters of selected Patricia Bay (PB), Island View Beach (IVB), and mixed sediment cores

Sediment parameters	PB	IVB	99.5% PB 0.5% clay	95% PB 5% clay	50% PB 50% IVB
mean grain size	150	280	150	130	210
(+ s.d.) (1)	30	120	40	60	80
mud content	1.27%	0%	1.5%	4.7%	1.14%
bulk density (2)					
- dry	1.69	2.08	1.41	1.54	1.32
- wet	2.07	2.54	1.71	1.91	1.53
permeability (3)	0.099	0.44	0.034	0.0035	.046
(range)	(.089-.12)				

(1) microns; (2) g/cm^3; (3) cm/min.

A particular concern at the beginning of the experiments was the potential migration of oil along the walls of the core liners, and the influence such an "edge-effect" might have on interpretation of results. Consequently, in a series of preliminary oil/sediment penetration experiments, the outer 0.5-cm ring of sediments lying immediately adjacent to the wall of the core liner were extracted separately and were analysed quantitatively. Results showed that, over the course of ten tidal cycles, between 2.3 and 3.4 times as much oil per gram of sediment became associated with the outer sediments as with the central sediment core. However, for all subsequent analyses, sampling was done separately on both the edge and the central section of each core so that edge effects could be monitored and an oil budget for each core established; results reported (Tables 2 to 5) are for the central portion of the core only. Cores were cooled and split during the sample analysis.

Penetration of oil into core sediments was determined quantitatively on 2 cm slices by IR and by quantitative and qualitative gas-chromatography (Green et al. 1982); 30-100 g sediment were extracted quantitatively by shaking (3 min) with 50 g reagent-grade carbon tetrachloride (CC14). CC14 extracts were analysed directly by gas-chromatography-mass spectrometry (Fowler and Hope 1984).

RESULTS

OIL-LOADING AND PENETRATION

The observed relationship between varying amounts of oil applied as surface slicks to the columns and its penetration by the "standard" Patricia Bay sediments is shown in Table 2. As the slick thickness increased from 0.5 to 5.0 mm, the concentration of oil in the top 2 cm of the sediment core increased in parallel fashion. There was no increase either in oil retained by the surface sediments or in sediment contamination when the slick thickness (amount applied) was increased from 5 to 10 mm. Visible penetration depths of oil into the sediment cores were consistently less than 1.0 cm, although this measure was subject to considerable variability, in part because of irregular "finger-like" penetration of the oil into the sediment cores, as was seen frequently in core cross-sections. This was confirmed by IR-analytical data of successive 2 cm slices, showing the presence of detectable hydrocarbons, although in markedly lower concentrations, down to 4 cm in several of the cores. Hydrocarbons were detected down to 6 cm in one of the two cores that received 10 mm of oil slick.

Characterization of sediment extracts by gas-chromatography and gas-chromatography-mass spectrometry generally confirmed these quantitative observations. Gas-chromatogram's of weathered, surface-bound oil, adhering to the surface of a Patricia Bay core after eight tidal cycles, showed the distribution of n-alkanes overlying a relatively small envelope of unresolved common material, no odd-even dominance, and C17: pristane and C18: phytane ratios <1.0 (Figure 3A) all considered characteristic features of a crude oil. This sample also displayed the loss of n-alkanes below C12, the result of the pre-test 30-40% weathering.

In contrast, extracts of sediments taken from the same core, but from the 10 to 12 cm sample showed no evidence of hydrocarbons with only the background gas-chromatogram typical for these sediments (Figure 3B).

Limit of hydrocarbon penetration was re-examined in a series of eight duplicate cores, loaded with 5 mm slicks. The results shown in Table 3 indicate that the bulk of the oil that penetrated into the sediments was found in the top 2 cm. Traces of oil were found at 2 to 4 cm, but for five out of the eight cores, only background levels of IR-detectable hydrocarbons were found below 4 cm. The concentration of hydrocarbons found in the surface sediments (0-2 cm) also was highly consistent, between 24,600 and 46,000 mg/kg, decreasing three orders of magnitude to between 110 and 880 mg/kg at the 2-4 cm depth.

TABLE 2

Oil loading and penetration

Oil loading (mm)	Core number	Visible oil limit (cm)	Oil concentration 0-2 cm (mg/kg)	Oil concentration 2-4 cm (mg/kg)	Oil concentration 4-6 cm (mg/kg)
0.5	21	0.4	810	170	14
0.5	22	0.9	2,800	18	20
1	23	0.6	3,700	110	12
1	24	0.6	3,900	27	12
5	25	0.7	27,900	190	61
5	26	0.8	29,700	120	11
5	30	0.2	26,200	110	39
5	31	0.3	28,700	880	440
5	48	0.7	24,600	240	258
5	49	0.8	31,500	168	300
10	27	0.5	27,500	1,100	290
10	28	1.0	18,900	160	45

NOTE: Penetration in experimental tidal flat cores of weathered Alberta Mixed Sweet Blend oil. Oil was applied as a surface on the water over the cores. Cores subject to eight tidal cycles with 57% emergence.

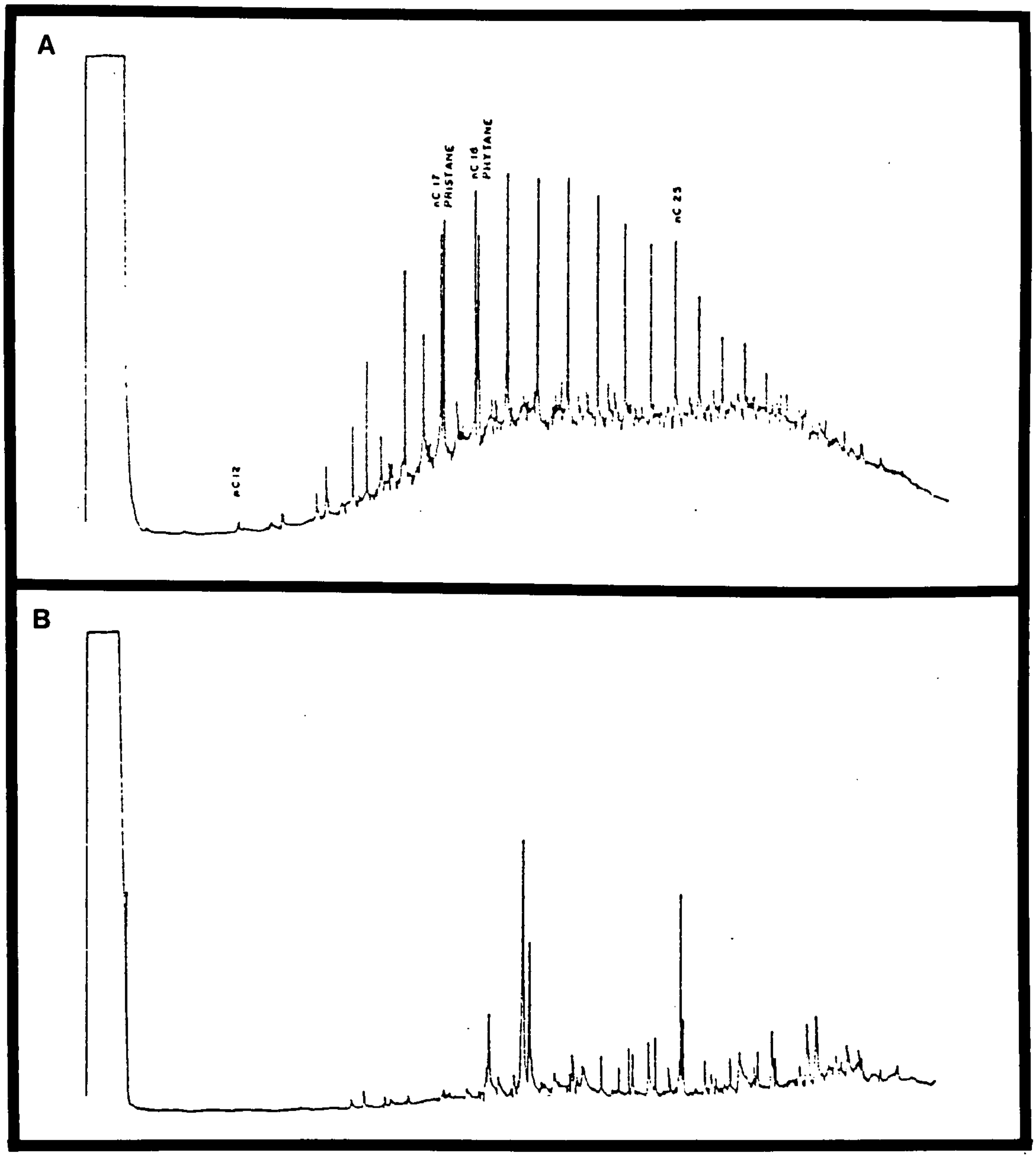

Figure 3. Gas-chromatograms (whole CCl4 extract of A) weathered test oil from the surface of a core after eight tidal cycles and B) sediments from the 10-12 cm depth of the core, indicating no oil at that depth.

TABLE 3

Standard Patricia Bay cores

Core Number	Oil recovery %	Visible oil limit (cm)	Oil concentration 0-2 cm (mg/kg)	2-4 cm (mg/kg)	4-6 cm (mg/kg)
13*	109	1.5	25,000	210	16
14*	99	2.5	46,000	280	8
25	92	0.7	27,900	190	61
26	93	0.8	29,700	120	11
30	97	0.2	26,200	110	39
31	93	0.3	28,700	880	440
48	91	0.7	24,600	240	250
49	98	0.8	31,500	160	300
Mean	97	0.9	30,050	270	140
S.D.	6	0.7	6,800	250	170

* 62.5% emerged

NOTE: Mean grain size: microns, s.d. microns, 1.27% mud content. Penetration in experimental tidal flat cores of weathered Alberta Mixed Sweet Blend oil. 5 mm of oil was applied on the water over the cores. Cores subject to eight tidal cycles with 57% emergence.

EFFECT OF EMERGENCE AND SUBMERGENCE

By placing a number of cores at different heights relative to the tidal head-tank, the effect of tidal exposure (expressed as % emergence) on oil adhesion was examined. Results indicated that, with the application of a constant 5.0 mm oil, both the amount of oil penetrating into the top 2 cm and the depth of penetration increased as the time of emergence increased from 0 to 15 hours emergence per day (Table 4). Beyond this, as the tidal emergence period increased from 15 to 24 hours per day emergence (i.e., permanently above tidal reach) there was no obvious further increase in either sediment contamination with hydrocarbon concentrations reaching a maximum. Visible oil penetration correlated weakly with increasing time of emergence. IR-detectable levels of hydrocarbons were found down to 6 cm depths in some cores with lengthy emergence time, but again there was only weak correlation between hydrocarbon penetration depths and time of emergence.

Qualitative GC-analytical results generally parallelled these quantitative crude oil chromatograms (Figure 3A); samples taken from the 6-8 cm interval of a 50% emerged core showed no evidence of hydrocarbons, and GC results were consistent with background sediment for these sediments-chromatograms (Figure 3B). However, a similar 6 to 8 cm interval sediment sample from a core that had been exposed to air only for eight tidal cycles (i.e., 100% emergent) showed the presence of highly degraded petroleum hydrocarbons, including loss of n-alkanes below C14, C17: pristane and C18: phytane ratios greater than 1.0 and an increased unresolved common materials.

SEDIMENT TYPE

The amount of concentration of oil hydrocarbons that penetrated into the sediments decreased as the mud content increased (Table 5). In fact, although there were two exceptions (cores #30, #31) as mud content increased, so penetration of hydrocarbons decreased; highest concentrations of hydrocarbons occurred in the Island View Beach sediment columns (i.e., the columns with the lowest mud content). The maximum amounts or concentrations were found in the top 0.2 cm section, but all cores also showed measurable concentrations of hydrocarbons at 2-4 cm. Traces of hydrocarbons were found at 4-6 cm in only some of the cores.

TABLE 4

Penetration and tidal emergence

Tidal emergence (h/24 h,%)	Core number	Visible oil limit (cm)	Oil concentration 0-2 cm (mg/kg)	Oil concentration 2-4 cm (mg/kg)	Oil concentration 4-6 cm (mg/kg)
0/24;0%					
	15	0.5	4,000	80	8
	16	0.5	1,400	62	25
12/24;50%					
	17	2.0	2,400	88	230
	18	2.0	1,900	190	95
13.6/24;57%					
	25	0.7	27,900	190	61
	26	0.8	29,700	120	11
	30	0.2	26,200	110	39
	31	0.3	28,700	880	440
	48	0.7	24,600	240	250
	49	0.8	31,500	160	300
15/24;62.5%					
	13	1.5	25,800	210	16
	14	2.5	46,000	280	8
22.5/24;91.5%					
	11	2.5	49,500	980	15
	12	3.0	52,600	4,500	16
24/24;100%					
	19	0.8-2.5	29,100	2,600	150
	110	1.5	44,300	1,700	140

NOTE: Penetration in experimental tidal flat cores of weathered Alberta Mixed Sweet Blend oil. 5 mm of oil was applied as a surface on the water over the cores. Cores were subject to eight tidal cycles.

TABLE 5

Penetration and grain size

Sediment type	Mud content (%)	Core number	Visible oil limit (cm)	Oil concentration 0-2 cm (mg/kg)	Oil concentration 2-4 cm (mg/kg)	Oil concentration 4-6 cm (mg/kg)
Island View Beach						
	0.35	32	3.0	70,600	5,200	41
	0.35	33	2.0-4.0	74,300	5,200	22
50% Island View/50% Patricia Bay						
	1.14	38	1.5	53,100	1,600	13
	1.14	39	1.5	61,400	1,800	31
Patricia Bay						
	1.27	25	0.7	27,900	190	61
	1.27	26	0.8	29,700	120	11
	1.27	30	0.2	26,200	110	39
	1.27	31	0.3	28,700	880	440
	1.27	48	0.7	24,600	240	250
	1.27	49	0.8	31,500	160	300
Patricia Bay +0.5% clay						
	1.53	34	0.8	20,700	180	16
	1.53	35	0.6	26,400	74	25
Patricia Bay +5% clay						
	4.69	36	0.2	650	610	210
	4.69	37	0.3	1,900	330	110

NOTE: Penetration in experimental tidal flat cores of weathered Alberta Mixed Sweet Blend oil. 5 mm of oil was applied as a surface on the water over the cores. Cores subject to eight tidal cycles with 57% emergence.

DISCUSSION

These observations indicate that at least in these experiments, which the authors believe provide a reasonable approximation of real world tidal flat conditions, not only will oil penetrate only slightly into fine or muddy (<250 microns) sediments, but also that this penetration of oil hydrocarbons increases with tidal exposure. It must be noted, however, that in drawing these general conclusions they have not included the potential influence of bioturbation and animal burrowing, tidal mixing and sediment reworking, and the process of deposition.

The simulated tidal system and the simple core system used here seem appropriate, considering the consistent results that were obtained (for example, Table 3). In fact, far greater variation had been expected in both overall trends in details of hydrocarbon penetration and oil retention knowing the very complex processes operating at the water-sediment interface and the influences of tidal mixing and sediment reworking. Also, in several instances the authors had to rely on small numbers of replicates. For these reasons, they believe that the experimental reduction of environmental variables from field to laboratory, as achieved here, was reasonable.

It would have been preferable to use cores with larger diameters (greater than 6.7 cm) for several reasons. The larger surface area would likely have reduced the edge effect on hydrocarbon penetration. Also, that the presence of the liner walls in the narrower core diameters may have influenced adhesion. However, there are considerable problems in obtaining undisturbed field cores with larger diameter core liners. Reconstituted sediments might have been used for larger diameter cores, but this would have introduced more unknowns. In fact, some of the observations obtained with reconstituted cores here (Table 5) were probably influenced by slight differences in permeabilities introduced by irregular or nonhomogeneous repacking of sediment columns. In hindsight, this effect could have been checked easily by comparing permeabilities and oil behaviour between a natural core of Patricia Bay sediment and a core of Patricia Bay that had been first disturbed and then reconstituted; this should form part of the experimental protocol in future studies. As it is, the results of hydrocarbons adhesion and penetration were within the range of the results obtained with the undisturbed natural cores.

The results obtained indicate that sediment permeability and water content, at least under these experimental conditions, are probably the most important factors that determine the penetration of hydrocarbons in these fine sediments. These, in turn, were dictated most strongly by the concentration of mud in the sediments. The relationship between mud content and hydrocarbon penetration retention (Figure 4) suggests a logarithmic linear function between these, with a transition in oil behaviour at about 1.5% mud. Undoubtedly this relationship will differ for different sediment types, and a broad range of calibrations are necessary

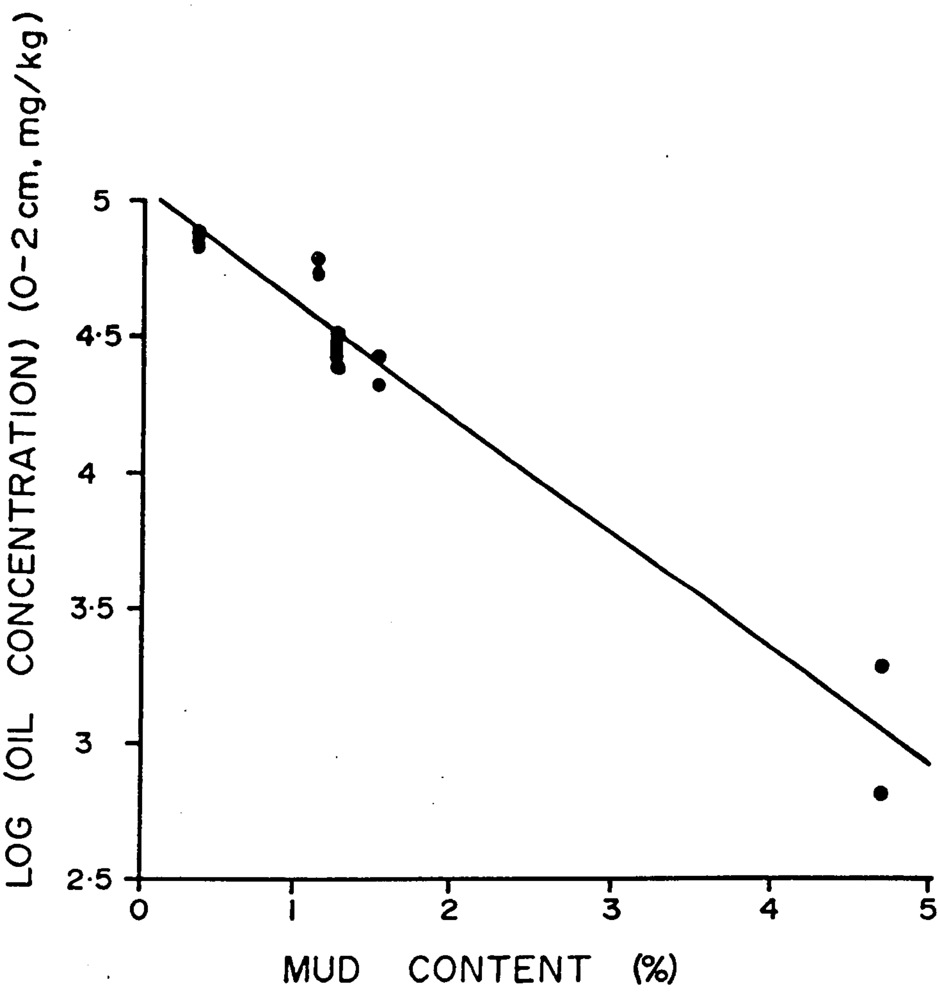

Figure 4. Relationship between mud contents and oil concentrations.

over a range of sediment types and mud content to clearly identify the dependence of oil behaviour on sediment parameters. However, these results indicate that such quantification is possible with environmentally realistic applications.

The various results showed an apparent upper limit to the amount of oil retained within the upper 2 cm of sediments in the loading experiments (for example, Table 2). The authors suggest that this apparent maximum sediment hydrocabon loading limit is a function of interstitial pore space size, rather than that the sediments were reaching total saturation with oil. In fact, simple calculations from the mass budgets showed that at the maximum loading limits observed, the sediments were in each case only 15 to 30% saturated with oil.

Particularly interesting is the influence of tidal exposure on altering hydrocarbon permeation in fine sediments, with greater subsurface hydrocarbon concentrations and permeation correlating with increasing emergence. For example, for the same sediment type (Patricia Bay tidal flat) an increase from 12 to 15 h emergence per 24 h period resulted in an order of magnitude increase in subsurface contamination (Table 4); undoubtedly this is because of the increased sediment draining with emergence and the longer drying out of the surface sediments. The environmental significance of this tidal emergence related phenomenon clearly is the potential for increased sediment contamination of those intertidal sediments located above mid-tide level, i.e., with longer than 12 h emergence per 24 h.

The authors have isolated the potential influence of organic content on hydrocarbon binding to the surface sediments by using cores with total organic content of <1% and cores taken from the same tidal flat. Little is known of such interaction, but the hydrophobic character of the bulk of petroleum hydrocarbons would suggest that such interaction is likely.

OBSERVATIONS

From an ecological and environmental point of view, probably the two most significant observations that arise out of this study are:

- In fine sediments with, mud-content greater than 1%, hydrocarbons permeate only the top 2 cm; and
- tidal emergence strongly influences hydrocarbon penetration, especially in sediments that emerge for more than 60% of the tidal cycle.

The implication of the first observation is that sediments in tidal flats may be much less vulnerable to oiling and long-term persistence of petroleum hydrocarbons following contact with stranded oilslicks than was thought formerly. The second observation emphasizes the sensitivity of fine-grained sediments (mean 250 microns) positioned along the upper intertidal zone, such as occur in estuaries. Although these might be relatively impervious to oil penetration if continuously waterlogged, their location along the upper intertidal zone and the resulting long periods of emergence (>60%) render them susceptible to oil penetration, and consequently make them long-term sinks for stranded spilled oil.

A third but less well defined observation is that hydrocarbon contamination appears to be sensitive to relatively small shifts in sediment grain size composition. For example, quite large differences in sediment contamination were observed among the experimentally reconstituted cores, although these cores were comprised of standard Patricia Bay sediment, and differed only slightly in overall grain size composition (Table 3).

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