Orimulsion® Bitumen Penetration and Retention in Coarse Sediment Shorelines

Orimulsion® Shoreline Studies Program

Canadian Coast Guard

PDVSA BITOR

Environment Canada Environnement Canada

Orimulsion® Bitumen Penetration and Retention in Coarse Sediment Shorelines

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Preface:
This study is a component of the Orimulsion® Shorelines Studies Program, a long-term globalized plan of studies for spill preparedness and spill response in the coastal environment. The study reported herein was funded by the Canadian Coast Guard, PDVSA Bitor and Environment Canada.

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SUMMARY

Orimulsion® is used as a fuel for power generation and in the heavy industry sector. It is transported to power stations around the world, including eastern Canada, where delivery is made by marine tanker from Venezuela. Orimulsion® is a (70%) bitumen -in- (30%) water emulsion that is stabilized with a small quantity (<0.2%) of a surfactant package. In the event of an accidental spill of Orimulsion®, studies have shown that two generic types of bitumen mixtures may occur: a ***dispersed bitumen*** mixture, where bitumen remains in the water column as a relatively low concentration of bitumen particles; and a ***coalesced bitumen*** mixture, where bitumen particles coalesce into positively buoyant lumps and/or patches. In event of contact with the shore, the two forms of bitumen could contact coarse sediment shorelines, common on Canadian coastlines. These experiments simulated initial stranding of bitumen on coarse-sediments.

Dispersed bitumen could reach the shoreline under certain conditions and penetration could be significant. Our tests showed >30 cm penetration and calculations suggest 2m penetration is theoretically possible in the absence of a ground-water table. However, retention of *dispersed* bitumen in coarse sediments is likely to be extremely low, typically in the range of 10 - 30 mg of bitumen per kilogram of sediment (i.e., 10 -30 ppm).

Coalesced bitumen is extremely adhesive and sticky. Special handling procedures, including the use of ice molds, were required for conducting *coalesced* bitumen experiments. Although most of our experiments simulated stranding under low-energy, quiescent conditions, limited observations of *coalesced* bitumen patties in the swash zone showed that the patties did not pick up sediment particles and did not adhere to pebble-cobble surfaces when stranded.
Under quiescent stranding conditions, initial penetration (0-tidal cycles) of *coalesced* bitumen is highly sediment-size-sensitive and temperature-sensitive. Under average temperature conditions, granules are basically impermeable (<1 cm penetration), pebbles are only slightly permeable (<5 cm except under hot conditions) and cobbles are moderately permeable (<10 cm except under hot conditions). Under cold (<5° C) temperatures, even cobbles become impermeable (<3 cm of penetration). Under warm conditions (>25° C) *coalesced* bitumen can penetrate to depths of greater than 30 cm in cobbles and to about 10 cm in pebbles within three hours. *Coalesced* bitumen will continue to migrate within sediments after initial stranding due to "tidal cycling" and is likely to continue penetrating until reaching the ground-water table (up to 30 cm penetration in cobbles after 4 tidal cycles at 13° C). Our tests did not show any release of *coalesced* bitumen once it had penetrated below the surface, indicating that normal tidal cycling results in a net downward movement of *coalesced* bitumen, creating a type of "bitumen conglomerate" in the subsurface.

Our experiments indicate that hydraulic washing is unlikely to be an effective countermeasure - warm water will only result in deeper penetration of the coalesced bitumen. Manual or mechanical recovery of bitumen-contaminated sediments is likely to be the principal cleanup technique.

While these studies provide helpful guidelines as to stranding of Orimulsion® derivatives under quiescent conditions, it is recommended that additional studies be conducted of (a) the weathering processes that will control coalesced bitumen morphologies and (b) stranding processes under wave action and a variety of temperatures.

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1.1 Statement of the Problem

Orimulsion® is a fuel product that is comprised of 70% bitumen, 30% water and <0.2% surfactant, which keeps the bitumen from coalescing. Orimulsion® is used as a fuel in a variety of industrial applications around the world, including electrical power generation plants in eastern Canada. It is shipped via double-hulled tankers from Venezuela.

Bitumen from an accidental spill of Orimulsion® could contact shorelines in the form of a *dispersed bitumen* plume or as weathered *coalesced* bitumen. *Dispersed* bitumen plumes are low concentration dispersions of bitumen particles suspended in the water column. These plumes could contact shorelines and penetrate beach sediments as a result of nearshore spills. Coalesced bitumen is a very viscous, high-concentration mixture of bitumen and water. It originates from the coalescence of dispersed bitumen at sea. *Coalesced* bitumen would likely strand on the shoreline in the form of either tar balls, patties or mats.

Studies of bitumen coating and removal from rock surfaces have recently been addressed by Harper *et al* (2002a). However, there has been very little testing of Orimulsion® in sediments and no evaluation of Orimulsion® penetration and retention in coarse sediments. Interaction of Orimulsion® derived bitumen with coarse sediments, which are a common type of shoreline sediment on Canadian coastlines, is therefore a potential concern. Moreover, there was no standardized protocol for application of the bitumen to sediments (i.e., a reproducible method to simulate the contact of bitumen with the shoreline). The previous studies by Harper and Kory (1997) on Orimulsion® sediment interactions were conducted in small-scale tests with much finer sediments and were only of a preliminary nature.

1.2 Project Objectives

The overall goal of this project is to improve our understanding of Orimulsion® bitumen interaction with coarse sediments through the use of moderate-scale experiments. The specific objectives of the experiments were to:

- develop a standardized method to apply *dispersed* and *coalesced* bitumen to the coarse grained sediment test substrates and to estimate the quantity of bitumen retained on and in the substrate.
- evaluate how the two forms of bitumen interact with coarse sediments, particularly in terms of penetration and retention characteristics.
- evaluate how various environmental factors such as tides and temperature affect penetration and retention in coarse sediments.
- interpret the results in terms of potential response options and cleanup options for coarse sediment shorelines.

A series of meso-scale, bench top experiments were conducted at the University of Victoria's Marine Technology Centre in Sidney, BC to address these objectives. The general approach for all the experiments was to place a known volume or weight of bitumen on clean sediments, apply the experimental treatments and then measure the retention of bitumen in the sediments.

2.1 General Appr●ach

The objectives of these experiments are specifically focused on determining the variables that affect initial and ultimate penetration and retention of bitumen derived from Orimulsion® in coarse-grained coastal sediments. The natural process of contamination involves the floating forms ofoils or bitumen stranding on the shoreline as the tide falls. If the pore space in the sediments is large enough and the contaminant is fluid enough, it will drain into the sediments and be trapped within the sediment pore space. Movement of the sediments by wave action and pumping of pore waters by tidal and wave action promotes the removal of the contaminant but often this process is very slow.

Our experiments were set-up to mimic the natural stranding of bitumen derived from Orimulsion® on shorelines. The basic procedure was to fill a container with sediment, raise the water level to the top of the sediment, introduce a known amount of either *coalesced* or *dispersed* bitumen, and then lower the water levels to simulate a falling tide. In some cases, the containers were sampled after a single tide to evaluate initial bitumen retention, and in other cases the containers were sampled after several tides to evaluate bitumen retention over several tides. Because there was no existing protocol to simulate the initial stranding process, the development of a standardized method was required. For this reason, the following methodology includes some results of preliminary range-finding investigations, as they provide rationale for selection of appropriate procedures and direction for the final experimental approach.

The following treatments were evaluated during the experiments:

- the effect of *bitumen type* (*dispersed* or *coalesced)* on penetration and retention
- the effect of *sediment size* on bitumen penetration and retention
- the effect of *intertidal elevation* (e.g., upper and lower intertidal zones) on bitumen penetration and retention
- the effect of *tidal cycles* or time on the bitumen penetration and retention
- the effect of *temperature* on bitumen penetration and retention.

The results provide a framework for understanding what might happen to shorelines in the event of an accidental spill of Orimulsion® in the marine environment.

2.2 Containers

The testing containers had to be wide enough to minimize any edge effects, deep enough to simulate typical surface sediment layers that might be contaminated in a spill, and preferably inexpensive enough to be disposable. Polyethylene pails (20 L nominal volume) were selected to meet these test criteria. All measurements were initially made using the bottom of the pail as the reference point and then converted to depth below the surface of the sediment.

Additional details are contained in Appendix A. The surface of the sediment was set up to be 30.3 cm above the base of the pail.

Pails were fitted with standpipes and reference rulers to allow the precise measurement of water levels within the pail (Fig. 1). The pails were also fitted with a drain, centered in the base of the bucket, which was attached to a valve. Tidal changes were simulated by (a) opening the base valve to simulate an ebb tide and (b) closing the base valve and filling from the surface to simulate a rising tide. Elevation levels of the pore water were monitored using the standpipe and fill/drain rates adjusted to approximate tidal rise and fall rates of St. Andrews, New Brunswick.

2.3 Sediments

Coarse sediments are typical in the upper intertidal zone of much of Canada's maritime coastline. The high permeability of these coarse sediments is of particular concern because of the penetration potential and the high reservoir capacity.

Three sizes of uniformly sorted coarse sediment were selected for testing: granules, small pebbles and very large pebbles (Table 1; Fig. 2); the very large pebbles are referred to as "cobbles" within this report. Sediment specifications are detailed in Appendix B. Although most natural sediments on beaches are not uniformly sorted, we chose well sorted-sediment to aid in the consistency from experiment to experiment, particularly in terms of sediment porosity and permeability. Natural sediments are often a mixture of different clast sizes, but the permeability of the mixture will be determined by the smallest clast size. Additional reasons for working with uniformly-sorted sediments include: the number of clasts per unit volume is known, the surface area of the clasts per unit volume is known, and the number of grain-to-grain contacts can be estimated (see Harper and Kory 1995; Appendix B).

Table 1 Size Specifications of Unimodal Test Sediment

Sediment	Mean Diameter (mm)	Bottom Sieve (mm)	Top Sieve (mm)	Mineral Density (g/cm^3)	Target Porosity (%)	Bulk Density (g/cm^3)	Sphericity (%)
Granules	3.4	2.38	5.00	2.66	35	1.729	61
Pebbles	14.5	10.0	20.0	2.91	40	1.746	64
Cobbles*	43.0	30.0	75.0	2.44	40	1.464	63

*Note: our "cobble"-sized sediment is technically "very large pebble".

All sediments were screened, fresh-water washed, and dried prior to container loading. Bulk densities of each sediment type were used to calculate the weight of sediment required to fill a pre-set volume to a known porosity. The original target of 40% porosity within the sample containers was achieved for cobbles and pebbles. Sediment characteristics of the granules caused unwanted compaction of 40% porosity volumes during routine handling procedures in initial range-finding investigations; all further tests with granules were conducted at 35% porosity.

Figure 1 Photograph of pail showing the valve system at the base, the standpipe and the standpipe rule.

Figure 2. Photo of the three sediment types used in the experiment: cobbles (left), pebbles (centre) and granules (right).

2.4 Orimulsion® and Bitumen Types

Orimulsion® consists of bitumen (70%), water (30%) and a surfactant (<0.2%). Figure 3 shows densities of the Orimulsion® and constituent bitumen (Masciangioli and Chirinos 2001). Cerro Negro bitumen has an API gravity range from 8 to 8.5, its viscosity varies from 8×10^3 to 5×10^4 cP, at 35 °C, its specific gravity (60/60) is 1.0107, its pour point is 26.7 °C, and its flash point is 133 °C. Previous experiments have shown that there are two generic types of bitumen that might reach the shore:

- *weathered coalesced bitumen* formed when the individual dispersed bitumen particles collide, agglomerate and coalesce on the water surface. Coalesced bitumen is very viscous, cohesive and sticky and would likely strand in the form of lumps, tar balls, patties or matts.
- *dispersed bitumen*, which is similar to the stock Orimulsion® but where bitumen particles are in a dilute low concentration dispersion-suspension plumes within the water column.

2.4.1 *Coalesced* Bitumen

Coalesced bitumen was created by adding Orimulsion® to artificial seawater (Instant Ocean®) according to the procedure of Fieldhouse and Sergy 2001, with the addition of air to enhance mixing. The process causes bitumen to coalesce on the water surface, where it is then harvested (Figure 4). The volumes of harvested bitumen were essentially the same as predicted in the protocol of Fieldhouse and Sergy (2001). Several batches of *coalesced* bitumen were made and harvested. The different batches were composited, stirred to homogenize, and stored under refrigeration for subsequent use. This provided a uniform bulk stock of bitumen for all experiments. A detailed description is in Appendix C.

Table 2 Measured Density of *Coalesced* Bitumen (at 18°C)

Experiment	Pre Experiment Bitumen Density (g/cm^3)
	Mean
1a, 2a, 2b	0.964
3a, 3b	0.972
4a, 6a, 6b	1.028
5a, 5b	1.055
7a, 8a, 8b	0.955
9axx, 9bxx	1.059
10a, 10b	1.016
11a,11b	1.055
12a,12b	0.904
Overall Mean:	**1.001**

A sample of the coalesced bitumen was analyzed for physical properties (Masciangioli and Chirinos 2001). The bitumen sample, resulted in a water-in-oil emulsion with 16 % of water content, and an apparent viscosity (estimated at a shear rate of 25 s^{-1}) about three times that of the pure bitumen evaluated at the same temperature. Water content of the coalesced bitumen determined at the Environment Canada laboratory averaged 18.3% (Fingas, 2002, pers. comm.).

A number of measurements of density (by displacement) of the coalesced bitumen are summarized in Table 2. The variation is due to air and seawater incorporated during preparation. These measurements show that the coalesced bitumen is generally buoyant in seawater. Our tests with both surface and submerged sorbent pads showed that even weathered coalesced bitumen coatings that were washed off rock or cobble surfaces remained buoyant in normal seawater.

The action of stirring the bulk stock coalesced bitumen typically caused a certain amount of de-watering. We postulated that this de-watering might occur during the natural coating of pebble, cobble and bedrock surfaces. To test this theory, 50 g of coalesced bitumen was deposited onto a steeply inclined plastic planar surface. As gravity "smeared" the mass of bitumen, the water that was released was collected at the base of the inclined surface (Figure 5).

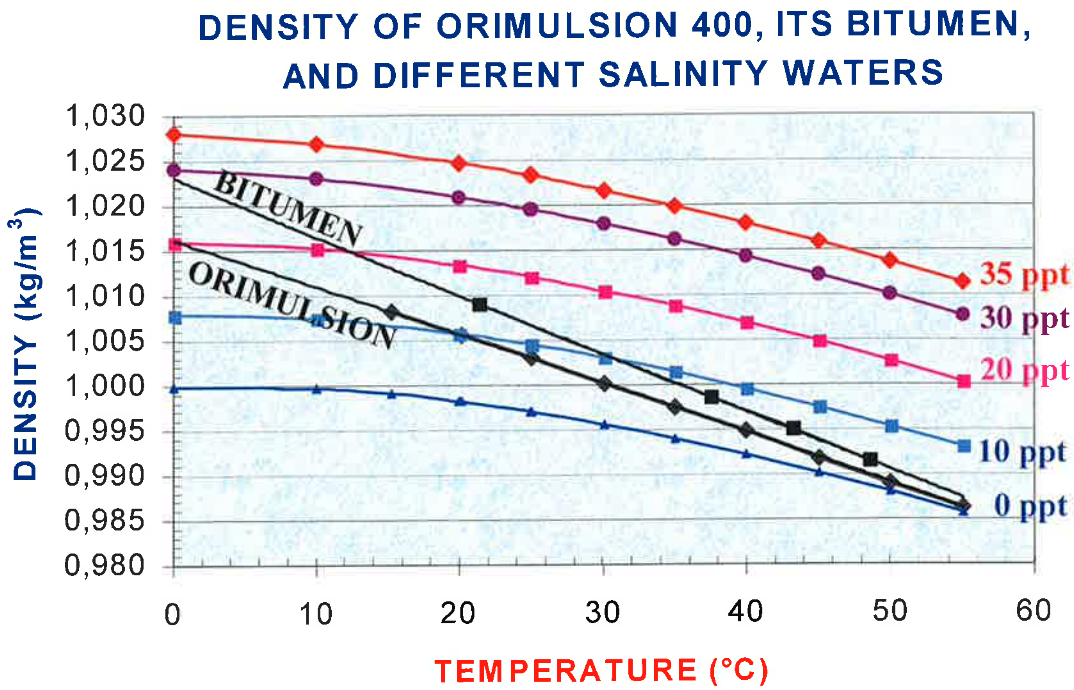


Figure 3 Densities of Orimulsion® and its constituent bitumen as a function of temperature (from Masciangioli and Chirinos 2001).

Figure 4 Surface of mixing tank showing the accumulated coalesced bitumen.

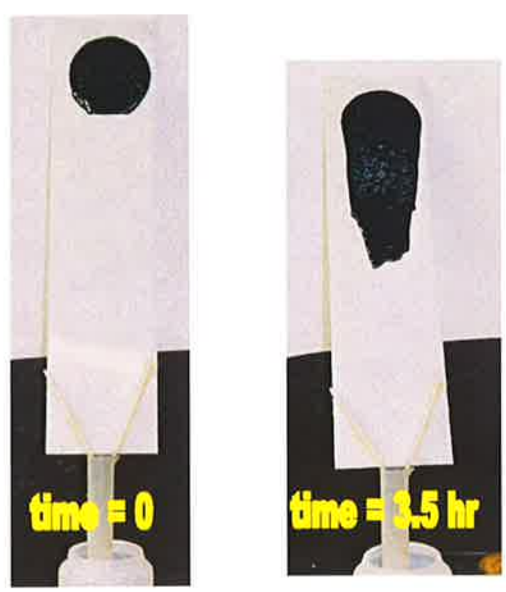


Figure 5 A smear test of 50g of bitumen on an inclined surface. Approximately 4.5 g of water was collected after 3.5 hours.

The water collected was 4.5 g, suggesting initial water content of at least 9% in the stock bitumen. This is consistent with the observations of properties Masciangioli and Chirinos (2001) and suggests that de-watering does occur during the coating process.

2.4.2 *Dispersed* Bitumen

We simulated a dispersed bitumen sediment contact by exposing the coarse sediment columns with a standard concentration of dispersed bitumen, then extracting the retained bitumen using a DCM extraction technique. *Dispersed* bitumen mixtures were made according to procedures developed by Fieldhouse and Sergy (2001) except that non-iodized NaCl was used as the salt to create simulated seawater (of 33 ppt). The stock Orimulsion® enabled preparation of dispersed bitumen with adequate stability. Our target *dispersed* bitumen concentration was 700 ppm, a 1:1,000 dilution of well-mixed Orimulsion® stock. Typical concentrations of stock *dispersed* bitumen, prior to application on sediments, as measured through DCM extraction (Appendix D) were ~650 ppm. The difference between target and measured concentrations was due to coalescence of the bitumen as thin films on the surface of the dispersion and adhesion to preparation apparatus.

A new shipment of Orimulsion was received and used in the experimentation. During the range finding phase of the study, it was observed that Orimulsion dispersions made in Instant Ocean and natural Pacific Ocean seawater proved to be less stable than previously observed. The greatly increased rate of coalescence in these media made it very difficult to maintain the bitumen dispersion needed to expose the tiles and create the desired bitumen coating. Even dispersions in iodized salt water (NaCl) displayed what appeared to be somewhat increased rates of coalescence than non-iodized NaCl saltwater mixtures.

At the time of writing there is no explanation as to the cause of the increased rate of coalescence observed in this study and from this Orimulsion. Several possibilities were considered (biodegradation of the surfactant, freezing, contamination or handling practices of the drums containing the emulsion), but nothing conclusive was proven. It is clear that the effect was both real and repeatable, however, no similar observations have been made in other previous or subsequent studies.

2.5 Treatments

Three environmental "process' effects were of interest in the Orimulsion®-sediment interaction tests: (1) the effect of *tidal submergence and emergence*, which is determined by the position of the stranding within the intertidal zone, (2) the effect of *tidal cycling* (i.e., the repeated draining and filling of pore space with seawater and (3) the effect of *temperature* due to surface heating from solar radiation.

2.5.1 Tides

The power plant of St. John's, New Brunswick is scheduled for conversion to an Orimulsion® fuel source. We therefore chose to use tidal curves for nearby St. Andrews, New Brunswick as the basis for our tidal simulations. In that we are only simulating a very small portion of the "beach" system, there are only two components of the tidal curve of interest: the rate of rise and fall of tides and the amount of time a given portion of the intertidal zone is submerged. Typical tidal curves that were used to choose these components are shown in Figure 6.

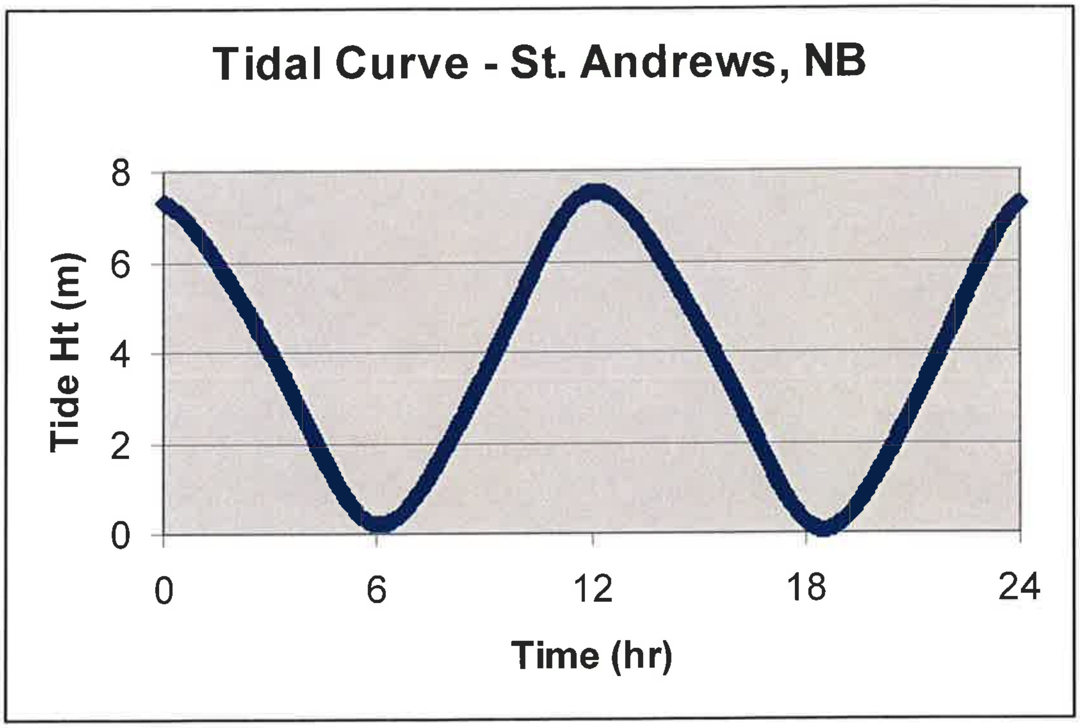


Figure 6. Tidal Curve for St. Andrews, New Brunswick.

A typical rate of rise and fall of the tide, except at the very top or bottom of the curves, is in the range of 2.5 cm/minute and this was used in the experiments. Valves at the base of the containers (Fig. 1) were used to manually control the drain/tidal fall rate. External standpipes and rules on the experimental buckets allowed direct observation of the water level height within each container as it drained or filled.

Tidal Submergence and Emergence Periods

An upper and lower intertidal zone position were used to determine the effect of tidal elevation of the stranded Orimulsion® on retention. The emergence/submergence characteristics for the tidal curve (Figure 6) are summarized in Table 3.

Table 3 Submergence/Emergence Characteristics

Intertidal Zone Position	Emergence per 12 hr Tidal Cycle (hr)	Submergence per 12hr Tidal Cycle (hr)
Upper Intertidal (+6 m above datum)	9.5	2.5
Lower Intertidal (+2 m above datum)	2.5	9.5

Tidal Cycles

The effect of time on retention and penetration was evaluated by using a simulated tidal cycling: draining and filling the test containers with artificial seawater. Zero time is the time of initial stranding and all sampling took place 3 hours after stranding (Fig. 7) or three hours after completion of the last tidal cycle (Fig. 8). Sampling after four tidal cycles simulates a two-day window and approximates how much time might be required in a typical spill response.

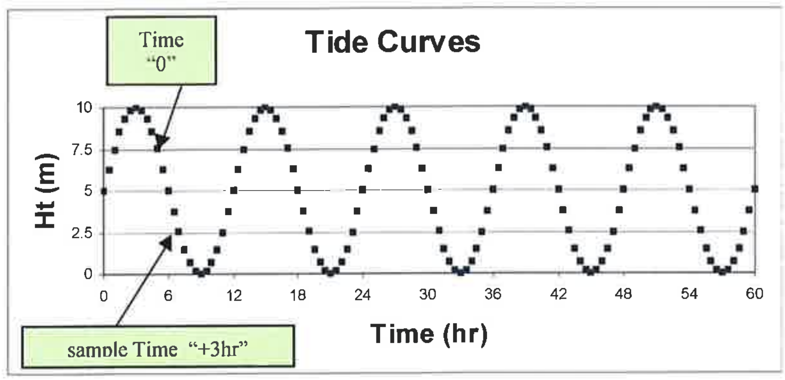


Figure 7 Extended tidal curve showing the initial stranding time for upper intertidal zone tests.

2.5.2 Temperature

Most of the experiments were conducted at ~13° C air temperature, the standard temperature of the experimental facility. This average is in the range of annual air temperatures occurring on southern Canadian east and west coast shorelines. To investigate the effect of temperature on penetration and retention of bitumen in sediments, some experiments involved higher or lower temperature as an additional parameter.

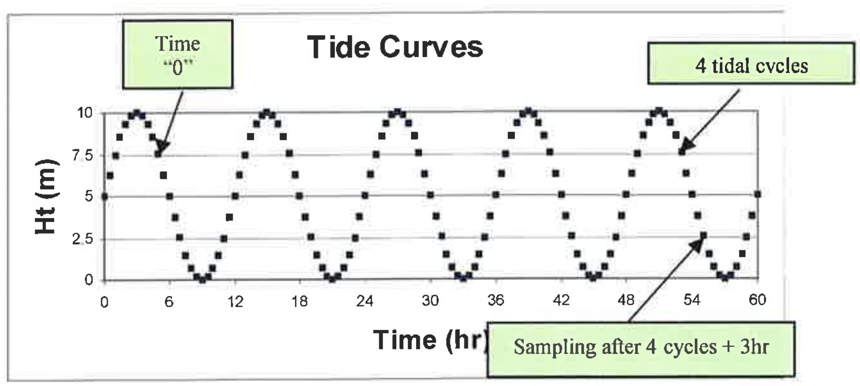


Figure 8. Sampling interval after four tidal cycles.

The higher surface temperature of 35° C was simulated by using heat lamps to elevate surface temperatures of sediment buckets. The lower temperature tests were conducted using a 5° C water, which was controlled with an ice-water bath. The temperatures of air and sediments were monitored during the experiments.

2.6 Experimental Matrix

The following treatments were evaluated: bitumen type, sediment size, tidal zone position, tidal cycle duration, and temperature. The full test matrix called for 36 separate experiments to be run in duplicate. Table 4 summarizes the test matrix, conducted for each of the two bitumen types: *coalesced* and *dispersed (*detailed experimental matrix in Table 5 and 8).

Table 4 Summary of Treatment Parameters

Treatments	Classes	Description
Bitumen Type	*Coalesced* Bitumen *Dispersed* Bitumen	*coalesced* bitumen is a highly viscous, sticky hig-concentration of bitumen particles *dispersed* bitumen is a dilute, low-concentration dispersion of bitumen particles
Sediment	Granules Pebbles Cobbles	unimodal sediments; pre-washed; standard porosity (cobbles and pebbles = 40% porosity; granules = 35% porosity)
Tidal Elevation	upper intertidal lower intertidal	*upper intertidal zone* (UITZ) for a 12-hr tide cycle was 9.5hr of emergence and 2.5 hr of submergence; *lower intertidal zone* (LITZ) was 9.5 hr of submergence and 2.5 hr of emergence.
Tidal Cycles	0 4	1 tidal-cycle = 12 hr (i.e. 4 cycles = 48 hr)
Temperature	5° C 13° C 35° C	5° C experiments were achieved using a controlled water bath; 13° C was the standard room temperature; 35° C was achieved by using surface heat lamps

Preliminary range-finding tests with *coalesced* bitumen (Appendix C) indicated that very little penetration (<0.5 cm) occurred in the granule-size sediment. Detailed measurement of penetration and retention was not warranted, and tests on granules were run without replication.

Preliminary range-finding tests with *dispersed* bitumen (Appendix D) showed extremely high penetration and very low retention in all sediments. Based on these results cobbles were eliminated from further dispersed bitumen tests. Dispersed bitumen tests using pebbles and granules were run in duplicate.

2.7 Testing, Sampling and Measurement Procedures

The general procedure was to fill a test container with sediment, raise the water level to the top of the sediment, introduce the bitumen mixture (either *dispersed* or *coalesced* bitumen) and then lower the water level to simulate a falling tide. Each test had a specific set of the experimental parameters (sediment size, bitumen type, tidal zone position, tidal cycle duration, and temperature). At the conclusion of each test treatment scheme, the test container contents were either sampled or measured directly to determine penetration and retention, depending on the form of bitumen introduced. The distinctly different bitumen forms required substantially different protocols and each is described separately. Documentation of the experiments was supplemented by digital photography (Appendix E).

2.7.1 *Coalesced* Bitumen

Stranding

The experiments were designed to simulate the stranding of *coalesced* bitumen on shoreline sediments under relatively quiescent conditions. The bitumen that is likely to be encountered is in the form of a "patty" – generally defined as a discrete accumulation of oil >10 cm diameter. In order to conduct reproducible tests, uniform masses and shapes of *coalesced* bitumen had to be generated and placed on the surface sediments. The challenge was that the *coalesced* bitumen is extremely adhesive and sticks readily to most surfaces, including handling instruments and containers, including Teflon coated containers. Previous work did show that *coalesced* bitumen was much less likely to adhere to thoroughly water-wetted surfaces. This led to the development of an improved bitumen handling technique using ice molds. This system proved to be excellent for handling the *coalesced* bitumen and placing uniform volumes and shapes of bitumen in the test containers.

A standard ice mold was created, using artificial seawater, with a dish-shaped cavity (Fig. 9). The mold was placed on a triple-beam balance and tared. Warmed (40° C) *coalesced* bitumen was added until the target weight of 500g of *coalesced* bitumen was achieved. This mold produced a standard pancake-shaped bitumen patty 20 cm in diameter and 1.6 cm in thickness. The ice mold was then inverted onto the sediments (Fig. 10) and within a few minutes the ice mold could be removed, depositing a standard *coalesced* bitumen patty on the surface sediments (Fig. 11). When the patty was placed on the sediment surface, the water level was initially at the surface of the sediment and then slowly lowered (about 2.5 cm/minute) simulating the natural fall of the tide.

Experimental Tests

Table 5 shows the full test matrix for *coalesced* bitumen treatments. Artificial seawater, created from commercially available aquarium salt mixture (InstantOcean®) was used to fill the test containers to the sediment surface prior to bitumen stranding and for any subsequent tidal cycling.

Coalesced Bitumen Retention Measurements

Initial plans to measure the penetration and retention of *coalesced* bitumen involved sub-sampling the test sediments, followed by DCM extraction. Extraction by dichloromethane (CH_2Cl_2; usually referred to as DCM) is a standard procedure for extraction of bitumen from sediment. However, extremely large volumes of DCM would have been required to extract the 500g of coalesced bitumen from our containers and would have been costly, labour-intensive, and created large amounts of chlorinated hydrocarbon wastes. During the course of preliminary range-finding work, an innovative alternative method was developed.

Preliminary range-finding work with the *coalesced* bitumen, specifically on pebbles, yielded cohesive bitumen-sediment conglomerate masses or "plugs", at the test temperatures of ~13° C. Chilling these plugs (2-4° C) facilitated observation and measurement of penetration depths. As well, a number of the preliminary plugs were sub-sampled, and DCM extractions were conducted to estimate bitumen retention in designated layers of the sediment column.

Figure 9 An ice mold prior to filling with *coalesced* bitumen.

Figure 10 Ice mold and bitumen in inverted position on top of a test column.

Figure 11. Close up of "puck" of *coalesced* bitumen on cobbles after the ice mould has been removed.

Table 5 Experimental Matrix – Coalesced Bitumen

Exp No	Code	Bitumen Type		Sediment Type			Tidal Cycles		Temperature Profile			Tidal Elevation	
		D	C	G	P	C	0	4	cold	cool	hot	Upper	Lower
1a	CG0CU_1		•	•			•			•		n/a	n/a
2a	CP0CU_1		•		•		•			•		n/a	n/a
2b	CP0CU_2		•		•		•			•		n/a	n/a
3a	CC0CU_1		•			•	•			•		n/a	n/a
3b	CC0CU_2		•			•	•			•		n/a	n/a
4a	CG4CU_1		•	•				•		•		•	
5a	CP4CU_1		•		•			•		•		•	
5b	CP4CU_2		•		•			•		•		•	
6a	CC4CU_1		•			•		•		•		•	
6b	CC4CU_2		•			•		•		•		•	
7a	CG4CL_1		•	•				•		•			•
8a	CP4CL_1		•		•			•		•			•
8b	CP4CL_2		•		•			•		•			•
9a	CC4CL_1		•			•		•		•			•
9b	CC4CL_2		•			•		•		•			•
10a	CG0HU_1		•	•			•				•	n/a	n/a
10b	CG0HU_2		•	•			•				•	n/a	n/a
11a	CP0HU_1		•		•		•				•	n/a	n/a
11b	CP0HU_2		•		•		•				•	n/a	n/a
12a	CC0HU_1		•			•	•				•	n/a	n/a
12b	CC0HU_1		•			•	•				•	n/a	n/a
28a	CG0CU_1		•	•			•		•			n/a	n/a
27a	CP0CU_1		•		•		•		•			n/a	n/a
27b	CP0CU_2		•		•		•		•			n/a	n/a
26a	CC0CU_1		•			•	•		•			n/a	n/a
26b	CC0CU_2		•			•	•		•			n/a	n/a

Estimations of oiled sediment volumes based on "plug" dimensions were made. In attempts to validate these estimated volumes, plugs were placed in plastic bags and immersed in water to determine volume by displacement. Extension of this concept led to a simple *in situ* water displacement technique to estimate the volumes of coalesced bitumen retained in the sediment.

Dry sediments were carefully packed in the containers to a predetermined porosity, and the following procedure was used to record the pore volume for each 1 cm layer of the test column.

> Standard volumes of water added to the sediment test column and the water level on an external standpipe recorded after each volume addition. The entire test column was filled to approximately 5 cm above the sediment surface. Using this procedure, pore-space volumes of various layers within the sediment could be accurately determined (to ±25 mL for a 5 cm layer). This procedure was repeated three times for each test column prior to oiling (Table 6) with a total processing time of about 0.5 hr.

There are potential problems with the technique including capillary water retention at the grain-to-grain contacts, the occurrence of capillary water tables and potential compaction due to handling during the experiment. However, for the relatively coarse sediments that we tested, these problems appeared minimal.

Table 6 summarizes typical replicate volume measurements for test sediment (pebble), prior to bitumen application. The standard deviation of the measurements was typically less than 2% for the replicate determinations of pore volume, except for the surface layer, which showed larger variance because of the open-framework of the pores; however, measurement error was still less than 5% even for this layer.

Table 6 Pore Volume Measurements by the Displacement Method (Exp. 2a)

Depth (cm)	Vol_*1* (mL)	Vol_*2* (mL)	Vol_*3* (mL)	Mean (mL)	s.d (mL)	s.d./ mean
0-5	1,456	1,374	1,374	1,401	47.7	3%
5-10	1,142	1,104	1,093	1,113	25.9	2%
10-15	1,106	1,066	1,084	1,085	20.0	2%
15-20	1,085	1,063	1,055	1,068	15.6	1%
20-25	993	1,029	1,030	1,017	20.8	2%

Following the bitumen application, the displacement measurements were repeated, to re-measure the pore volumes, which would then be partially filled with *coalesced* bitumen. Figure 12 and Table 7 show the results of pre- and post-treatment measurements for Experiment 2a (pebble sediment, 0-tidal cycles, 13° C test temperature). The total volume of measured displacement was 518 mL, which agrees well with the 500g mass of bitumen (density ~1.004) initially applied. This technique was found to provide a rapid, low-cost, reasonable picture of the retained coalesced bitumen within the coarse sediments.

Coalesced Bitumen Penetration Measurements

In addition to the displacement measurements to estimate bitumen volume, another innovative approach was used to document the penetration of *coalesced* bitumen into the sediment. Following the displacement measurements, the entire container of sediment was frozen. The sediment mass was then extracted from the container. In most cases the non-oiled sediment "sloughed -off", leaving the bitumen-sediment conglomerate intact as a frozen plug (see Fig. 13). In its frozen state, the conglomerate plug kept its original form, which facilitated observations and measurements of penetration depth. Typically a few "fingers" of *coalesced* bitumen extended beyond the main penetration front. We recorded the *maximum finger depth* of penetration as well as an estimate of the *penetration front depth* for each coalesced bitumen-sediment plug. Plugs were also photographed on a grid to illustrate dimensions (Fig. 13).

2.7.2 Dispersed Bitumen

Stranding

These experiments were designed to simulate the stranding of *dispersed* bitumen on shoreline sediments under relatively quiescent conditions. Sediment containers were set-up in the same way as that outlined for the *coalesced* bitumen tests, with dry sediment packed to a pre-determined porosity. The container was then filled with seawater (InstantOcean®) to the sediment surface. Three litres of dispersed bitumen mixture, 1:1,000 dilution of Orimulsion® stock in 33ppt non-iodized NaCl saltwater, was very gently poured onto the water/sediment surface to simulate a dilute mixture of Orimulsion® stranding on the shore. Preparation details are contained in Appendix D. This volume of ~700 ppm bitumen contains ~2.1 g of bitumen. The water level of the container was then lowered at a typical tide-rate fall (~2.5 cm/min) to simulate stranding during a falling tide. As the water table approached the bottom of the container (<10 cm above the base), a 250 mL sample of the effluent was collected. Analysis of

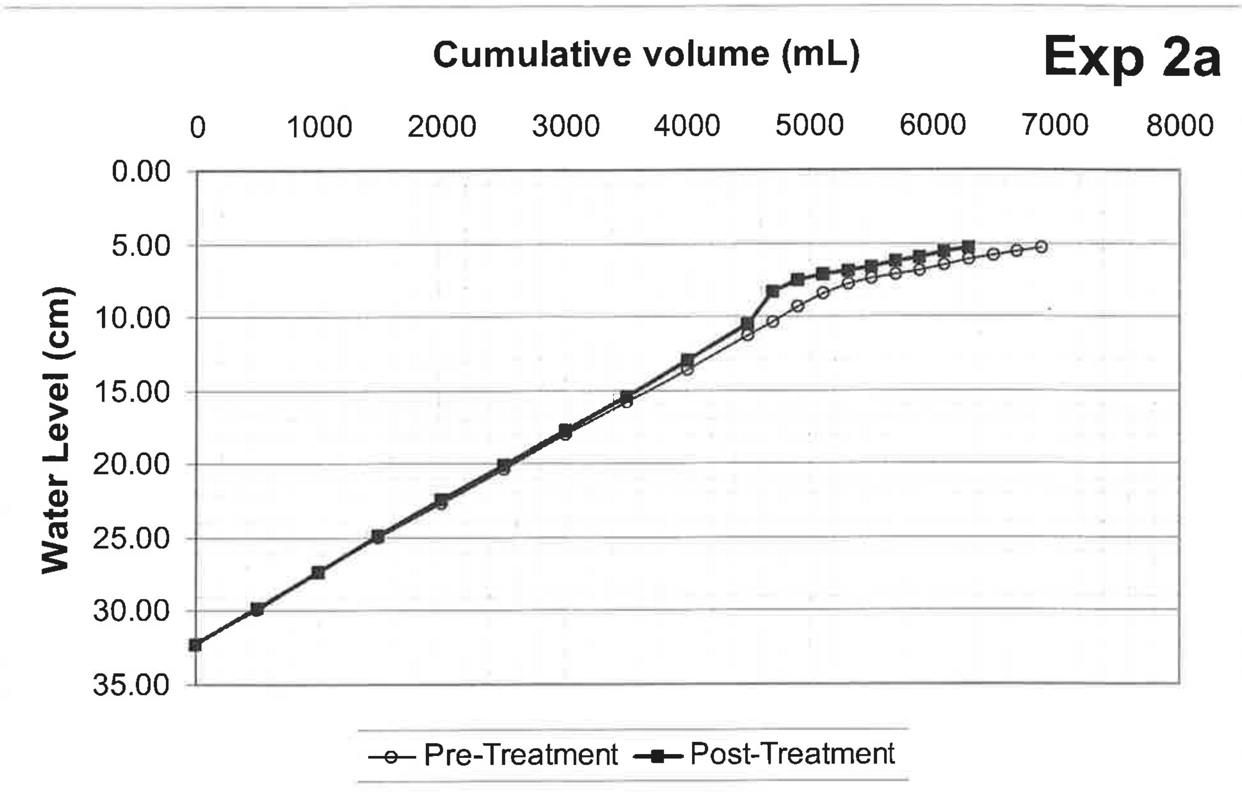


Figure 12 An example of the displacement filling data showing the volume of the pore space as a function of the height above the bottom of the pail. The pre-treatment curve indicates the pore volume in the absence of any *coalesced* bitumen. The post-treatment curve indicates the volume of the pore space after the treatment. The difference between the two curves is attributed to volume of *coalesced* bitumen retained in the pore space.

Table 7 Pre and Post Oiling Displacement Measurements

Layer	Pre Oil Vol (mL)	Post Oil Vol (mL)	Bitumen Vol (mL)
0-5cm	1,401	1,033	367
5-10cm	1,113	1,037	75
10-15cm	1,085	1,056	29
15-20cm	1,068	1,036	31
20-25cm	1,017	1,002	15
		Total:	**518**

this effluent provided an index of the dispersed bitumen concentration that was reaching the base of the column (Fig. 14). Effluent concentrations were generally 200-300 mg/kg (200-300 ppm) indicating about half the bitumen (~1 g) was retained in the sediment column.

Experimental Tests

In general the dispersed bitumen treatment matrix (Table 8) followed that of the coalesced bitumen experiments (Table 5) with sediments, intertidal position, number of tidal cycles and temperatures all considered important environmental variables to be evaluated. We eliminated the most of the cobble-sized experiments (except Exp 15a) because the pebble-size tests appeared to provide a reasonable approximation of the cobble results.

Table 8 Experimental Matrix – Dispersed Bitumen

Exp No	Code	Bitumen Type		Sediment Type			Tidal Cycles		Temperature Profile		Tidal Elevation	
		D	C	G	P	C	0	4	cool	hot	upper	lower
13a	DG0CU_1	•		•			•		•		n/a	n/a
13b	DG0CU_1	•		•			•		•		n/a	n/a
14a	DP0CU_1	•			•		•		•		n/a	n/a
14b	DP0CU_2	•			•		•		•		n/a	n/a
15a	DC0CU_1	•				•	•		•		n/a	n/a
16a	DG4CU_1	•		•				•	•		•	
16b	DG4CU_1	•		•				•	•		•	
17a	DP4CU_1	•			•			•	•		•	
17b	DP4CU_2	•			•			•	•		•	
19a	DG4CL_1	•		•				•	•			•
19b	DG4CL_1	•		•				•	•			•
20a	DP4CL_1	•			•			•	•			•
20b	DP4CL_2	•			•			•	•			•
22a	DG0HU_1	•		•			•			•	n/a	n/a
22b	DG0HU_2	•		•			•			•	n/a	n/a
23a	DP0HU_1	•			•		•			•	n/a	n/a
23b	DP0HU_2	•			•		•			•	n/a	n/a

Figure 13 A side-view photo of frozen plug of *coalesced* bitumen in pebbles. The sediment surface is at the top of the photo and the base or maximum penetration depth at the bottom of the photo. The grid is 5-cm square.

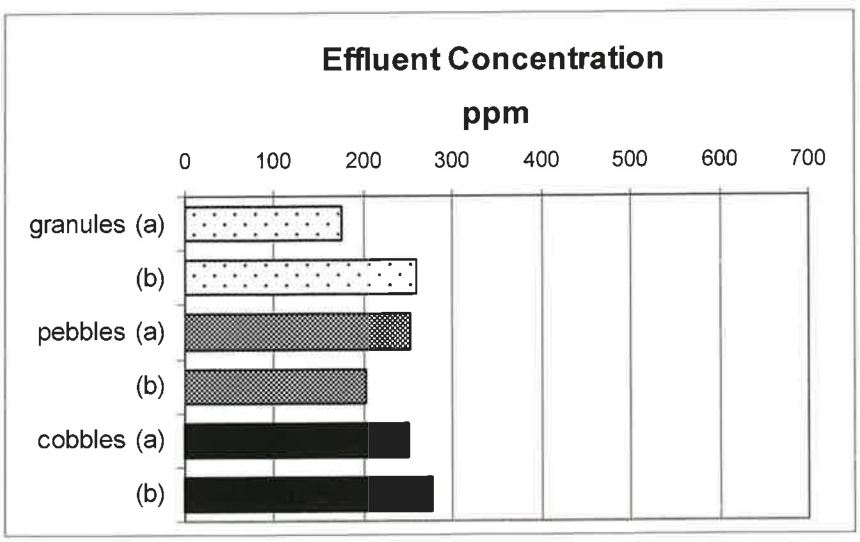


Figure 14 Dispersed bitumen effluent concentrations from various tests. Loading concentrations averaged about 650 - 700 mg/kg (ppm).

Penetration and Retention Measurements

Following the application of treatments, containers were frozen to immobilize the dispersion, then destructively sampled for DCM extraction analysis. Samples were collected from three layers within the sediment column:

- 0 to 5 cm (2.5 cm reference depth),
- 12.5 to 17.5 cm (15 cm reference depth) and
- 20 to 25 cm (22.5 cm reference depth).

Replicate samples (~1 kg granules or pebbles, ~2 kg cobbles) were collected for processing. The DCM analysis entailed extracting the sediment with successive small aliquots of DCM, combining the volumes, then evaporating the solvent to yield a bitumen residue for gravimetric determination. The absolute detection limit of bitumen using this technique was 3.0 mg, which translates to 1.5 ppm bitumen on a 2.0 kg sample. Data are expressed in terms of weight of bitumen per unit weight of wet sediment, and penetration/retention profiles were constructed from the data.

3.0 RESULTS

This section provides a summary of the data collected from the experiments designed to evaluate the effects of:

- *bitumen type* on penetration and retention
- *sediment size* on bitumen penetration and retention
- *position within the tidal zone* (e.g., upper and lower intertidal zones) on bitumen penetration and retention
- *tidal cycles* or time on the bitumen penetration and retention
- *temperature* on bitumen penetration and retention

Behaviour of the two Orimulsion® derivative forms of bitumen are substantially different, so results have been separated for *bitumen type.* Raw data is collated in Appendices C and D respectively for *coalesced* and *dispersed* bitumen types.

3.1 Coalesced Bitumen Tests

Both penetration and retention data were collected for the *coalesced* bitumen tests (Appendix C). The penetration data provides a simple, representative index of Orimulsion® retention. The bitumen retention information, as determined through our displacement measurement technique, presents a more detailed profile

3.1.1 Penetration Data

> *How does sediment size affect coalesced bitumen penetration?*

Sediment-Size Treatments – in the tests with no tidal cycling, *coalesced* bitumen was allowed settle for three hours into the sediments, prior to the initiation of the displacement tests and freezing. This procedure simulates an initial oiling scenario (Fig. 15). This simplest treatment combination at ambient temperature of 13° C with no tidal cycles and no differentiation of intertidal position allows assessment of the effect of sediment size. Virtually no penetration occurred in the granules (e.g., the granules are impermeable to coalesced bitumen at the 13° C test temperatures), minor penetration occurred in the pebbles (3.5 cm) and moderate penetration occurred in the cobbles (9 cm).

> *How does tidal zone elevation affect coalesced bitumen*

Tidal Zone Elevation Treatments - Upper intertidal zone (UITZ) sediments were submerged for 2.5 hr and emerged for 9.5 hr per tidal cycle, and lower intertidal zone (LITZ) sediments were submerged for 9.5 hr and emerged for 2.5 hr per tidal cycle. The penetration of *coalesced* bitumen in granule sediments was negligible, and intertidal position appears to have a very limited effect. For larger clast sizes, the *coalesced* bitumen penetration data was not substantially different between the upper and lower intertidal simulations, with *coalesced* bitumen penetrating to >30 cm in cobble sediment in both treatments (Fig. 16). For pebble sediments, the effect of intertidal position appears slight, and is obscured by the high variability of average penetration front depth.

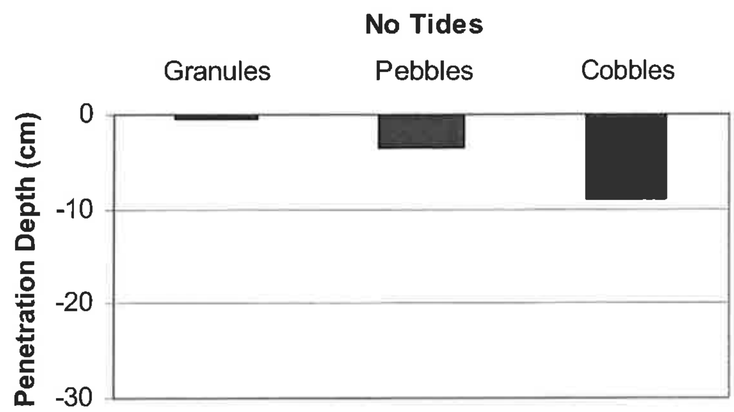


Figure 15 Initial *coalesced* bitumen penetration depths (no tides) for different sediments (penetration depths were determined from measurements of the main *penetration front* of the frozen plugs; replicates were averaged).

How does tidal zone elevation affect coalesced bitumen penetration?

Tidal Cycling Treatments - an additional treatment involved testing the effect of tidal cycling on bitumen movement within the sediments. In as little as 4-tidal cycles, *coalesced* bitumen was worked to depths of greater than 30 cm in the cobbles, three times the no-tide penetration depth (Fig. 16). The results suggest that *coalesced* bitumen is relatively mobile within cobbles, and that tidal flushing facilitates the movement of bitumen (as compared to the no-tide treatment, where penetration was limited to 9 cm in the cobbles).

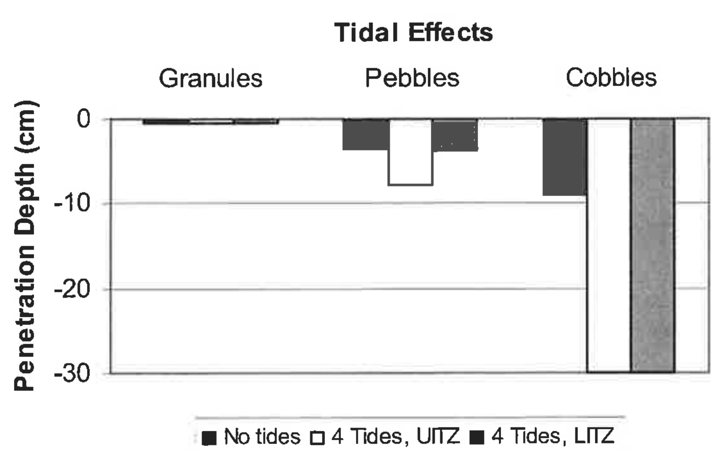


Figure 16 Penetration depths for different sediments and intertidal zone positions.

Plots of the average penetration depths do not provide the overall picture of the coalesced bitumen within the container. The depth of the *concentration maximum* was plotted for each of the experiments and provides a different perspective of the coalesced bitumen movement (Fig. 17).

While the penetration depth data suggests there is not much difference between the UITZ and LITZ treatments (Fig. 16), the concentration maxima data show that there *is* significantly more downward movement in the UITZ treatments than in the LITZ treatments (Fi.g 17). The concentration maxima is more than double the depth in the UITZ treatment versus the LITZ treatment. It is important to note that the actually "dry" time varied significantly among the three treatments. The total drying time for (a) the no-tide treatment was 3 hr, (b) for the upper intertidal zone treatments was actually 41 hr ([9.5 hr x 4] + 3 hr), and (c) for the lower intertidal zone was 13 hr ([2.5 hr x 4] + 3 hr). As such, the difference in depths of concentration maxima may be mostly related to total drying time with gravity pulling the *coalesced* bitumen downward. The data show that *coalesced* bitumen continues to be downwardly mobile at least until a groundwater table is encountered that limits additional penetration.

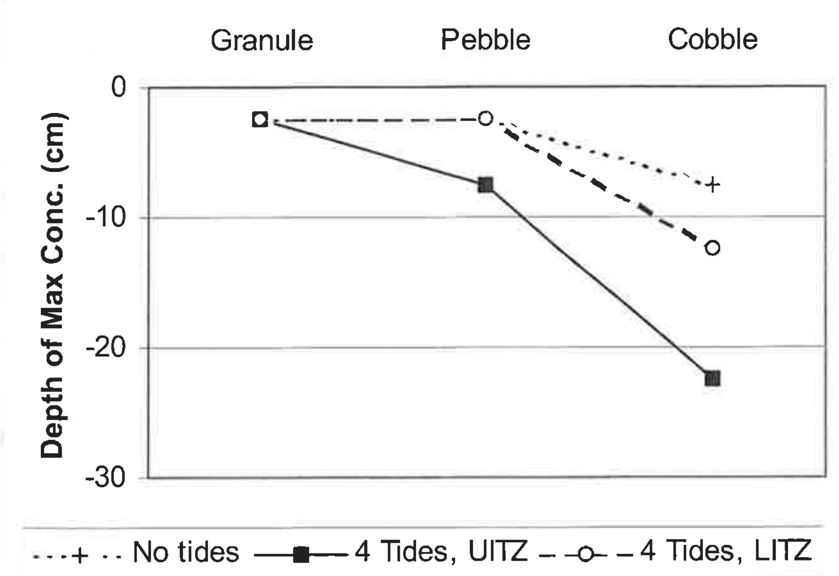


Figure 17. Summary of maximum *coalesced* bitumen concentration depths, based on displacement measurements. All tests conducted at ~13° C (the total sediment column was 30 cm in depth; UITZ = upper intertidal zone; LITZ = lower intertidal zone).

> *How does temperature affect coalesced bitumen penetration?*

<u>Temperature Treatments</u> – experiments were conducted with three different temperatures to test temperature effects on penetration with zero tidal cycles and no intertidal zone position. In the case of the "hot" treatment, heat lamps were used to increase surface sediment temperatures (surface temperatures to ~ 35° C), similar to that which would occur as a result of solar radiation. The "cold" treatment used a controlled temperature bath (5° C) to simulate a "cold-beach initial stranding". The "cool" treatment was performed at a room temperature of ~13° C. The

penetration data (Fig. 18) provide a graphic illustration of temperature effects on the bitumen sediment permeability. The temperature effects are most pronounced for the highly permeable cobble sediments and only moderately pronounced for pebble-sized sediment.

A simple experiment was also conducted to see if hot water flushing would significantly reduce the viscosity of the coalesced bitumen and increase penetration into the granules. Ten litres of 40° C water were poured over a test patty, and displacement tests conducted on the resulting frozen plug. The "hot-water" flush did not significantly increase penetration of bitumen into the granules (average penetration depth of two replicates were 1.4 cm) and observations suggest that little penetration into granules occurred under any circumstances (Fig. 15, 16, 18).

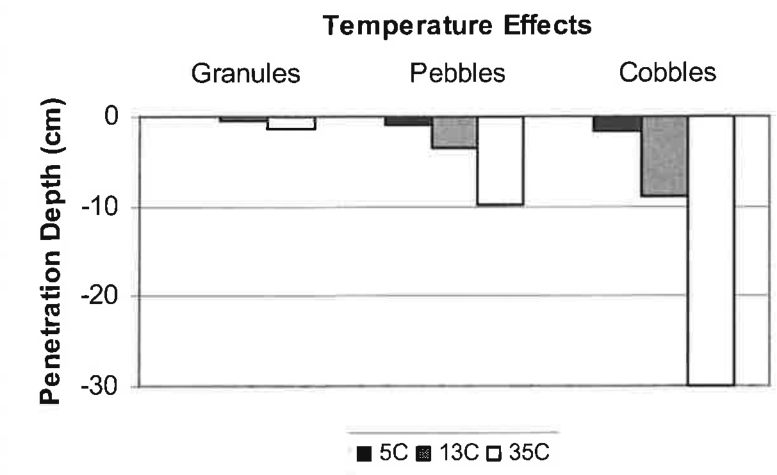


Figure 18 Temperature treatments for the three sediments are summarized (penetration depths were determined from measurements of the main penetration front of the frozen plugs; replicates were averaged).

3.1.2 Retention of Coalesced Bitumen in Subsurface Sediments

Estimates of the volume of coalesced bitumen were made by measuring the difference in pore space volume before and after each treatment (see Section 2.7.1). Treatments involving sediment, tidal cycling and temperature were tested.

> *How does sediment size affect coalesced bitumen retention ?*

Sediment-Size Treatments – a series of tests were run with standard sediment sizes at ~ 13°C but no tidal cycling to test the effect of sediment size on retention. The *coalesced* bitumen was applied using the ice-molds and 3 hours after the application, the displacement measurements were conducted. The *coalesced* bitumen retention values are schematically illustrated in Figure 19. Measurements are not very accurate for displacements less than 50mL per layer and should be used *in conjunction with* the penetration observations that are described in the previous section (Section 3.1.1). The granules data show that all coalesced bitumen was retained in the surface layer and in fact the penetration observations indicate that maximum penetration was less than 1 cm (Fig. 15). *Coalesced* bitumen penetrated to 4 cm in the pebbles (Fig. 15), which is consistent with the volumetric retention

estimates that showed almost all of the retained bitumen in the 0-5 cm layer (Fig. 19). The penetration front in the cobbles was estimated at 9 cm (Fig. 15) and most of the coalesced bitumen was retained in the 5-10 cm layer of the cobbles (Fig. 19); a few of the coalesced fingers which extend below the main penetration front probably account for the apparent coalesced volume below 10 cm.

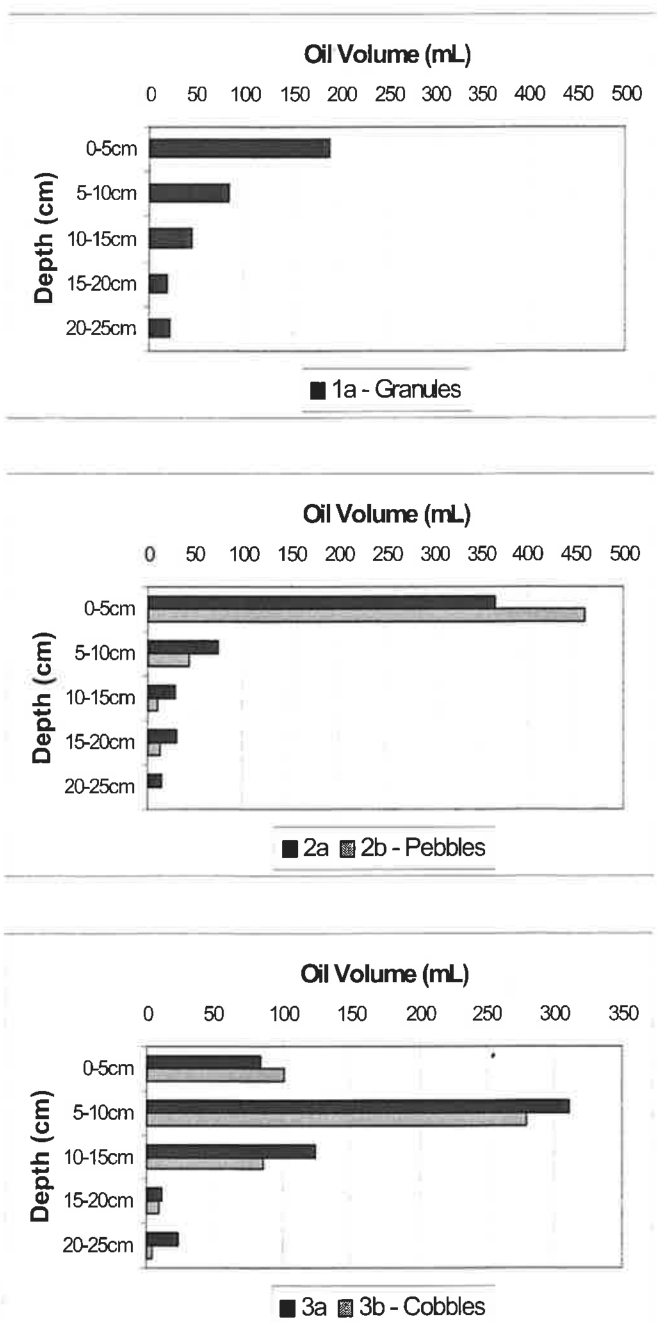


Figure 19 Coalesced bitumen retention as determined by pore-space displacement measurements 3hr after oiling. The retention is expressed as the volume of bitumen per 5-cm thick layer. Only one test was run for granules but the two replicates are shown for the pebbles and cobbles.

> *How does tidal zone elevation and tidal cycling affect coalesced bitumen retention ?*

Tidal Elevation and Tidal Cycle Treatments – a series of tests were run with standard sediment sizes at ~13°C with four tidal cycles at two tidal elevations to test tidal cycling effects. There was no penetration of the coalesced bitumen into the granules so only the pebble and cobble information is presented (Fig. 20). For the upper intertidal zone (UITZ) tests (Fig. 20), the penetration front for pebbles was estimated at 8 cm (Fig. 16) with the maximum concentration noted in the 5-10 cm layer (Fig. 17); some fingers penetrated below the 10 cm depth. With the cobbles, the *coalesced* bitumen penetrated to the bottom of the sediments (30 cm; Fig. 16) and retention increased with depth such that the maximum concentration was in the 20-25 cm layer (Fig. 17 & 20). When the data are compared to the zero tide tests (Fig. 19), it is clear that the tidal cycling has a significant effect on the movement of coalesced bitumen in pebble and cobbles sediments. The treatment design does not allow us to distinguish the effect of time (there are 9.5 hr/cycle x 4 cycles + 3 hr = 41 hr of emergence or drying) versus the effect of water movement within the pore spaces.

The lower intertidal zone (LITZ) tests are summarized in Figure 21; there was no penetration in the granules (Fig. 16) and no retention data are presented. For the pebbles, the penetration front was estimated at 4 cm although some coalesced bitumen fingers penetrated to at least 6.5 cm; most of the *coalesced* bitumen was retained in the top 5 cm (Fig. 21). In these lower intertidal zone tests, the concentration maximum occurred in the 0-5 cm layer as compared to the upper intertidal zone tests (Fig. 20) where the concentration maximum occurred in the 5-10 cm layer. The comparative data suggest that the emergence time (13 hr for the LITZ tests versus 41 hr for the UITZ tests) is more important in affecting bitumen movement than pore water flushing.

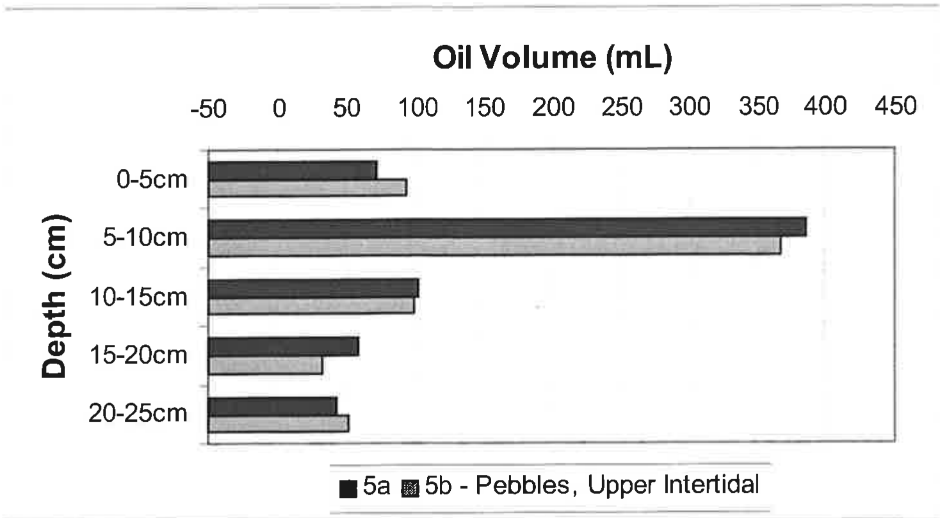
The LITZ cobble tests showed a fairly uniform retention within the test column with oil retention volumes in all layers of 100 to 150 mL except for the bottom layer (20-25 cm) which was around 75 cm (Fig. 21). There is no distinctive concentration maximum. The comparison between the UITZ (Fig. 20) and LITZ (Fig. 21) suggest that coalesced bitumen moved deeper in the UITZ tests, below the bottom of our test column (>25 cm).

> *How does tidal zone elevation and tidal cycling affect coalesced bitumen retention ?*

Temperature Treatments – the temperature treatment tests involved standard sediment sizes, without tidal cycling (sampling three hours after initial stranding) at three different temperatures. For the cold, 5° C, tests, the maximum *coalesced* bitumen penetration during the initial oiling was < 2cm for all test sediments, including the cobbles (Fig. 16); the retention data (Fig. 22) show that virtually all the bitumen is retained above the 5 cm depth.

The 13°C temperature data (Fig. 19) show a concentration maximum in the 0 - 5 cm layer for pebbles and in the 5-10 cm layer for the cobbles. The granule retention data (Fig. 19) suggests some penetration but the actual penetration depths were less than 1 cm.

The hot tests, where the surface was warmed by a heat lamp and achieved a surface temperature of ~35°C showed the greatest retention values, especially for the pebbles and cobbles. In the pebbles, where the penetration front was observed at 10 cm, the concentration maximum occurred in the 5-10 cm layer (Fig. 23). In the cobbles, a 30 cm penetration front was observed, and the concentration maximum was near the bottom of the test column after three hours (Fig. 23).



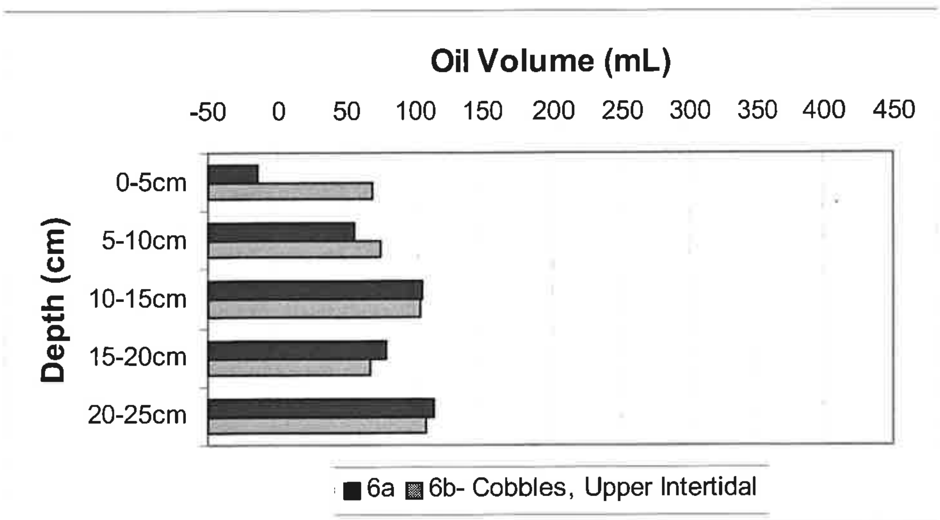
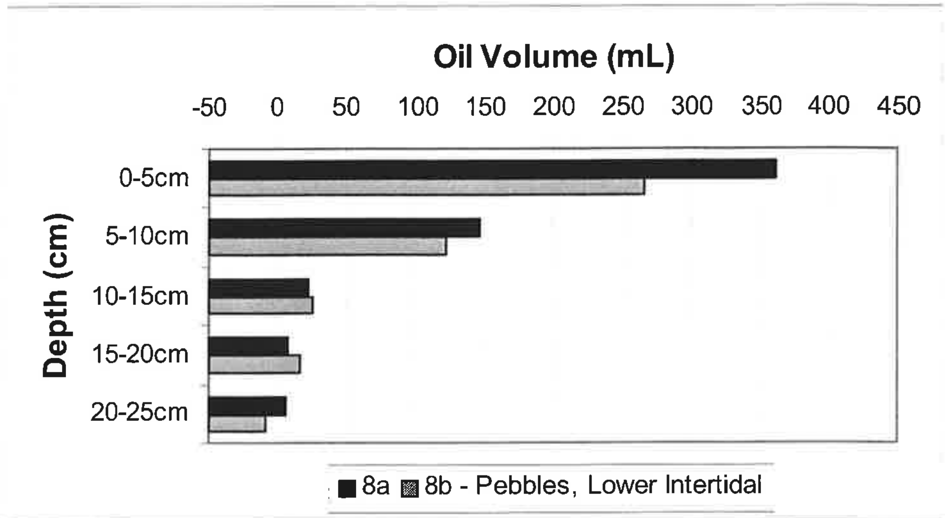


Figure 20 Coalesced bitumen retention after 4-tidal cycles, upper intertidal zone (9.5 h of emergence and 2.5 hr submergence per 12-hr tidal cycle). Displacement measurements made 3 hr after the last tidal cycle was completed.



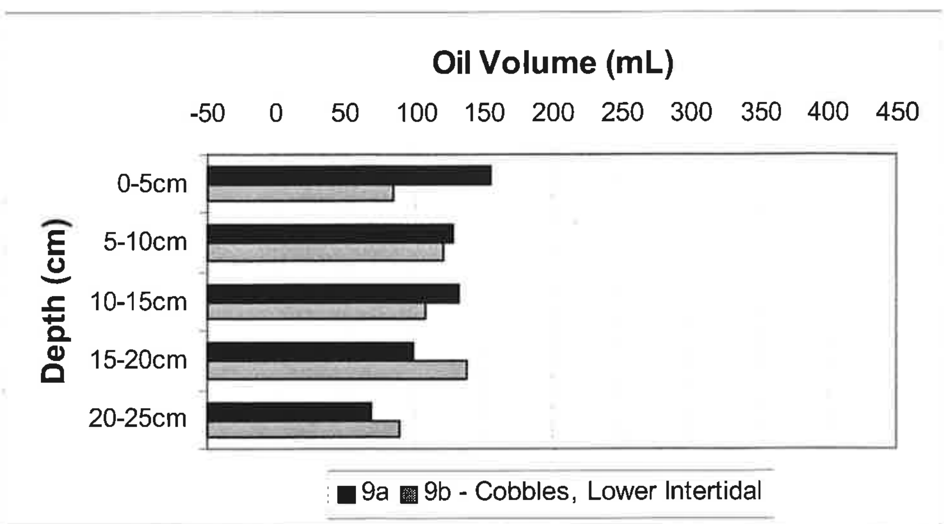
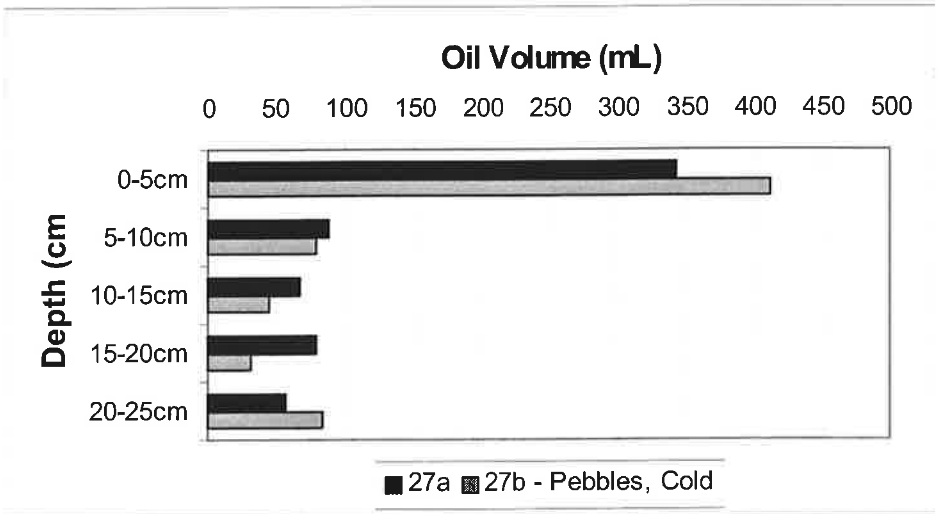


Figure 21 Coalesced bitumen retention after 4-tidal cycles, lower intertidal zone (2.5 h of emergence and 9.5 hr submergence per 12-hr tidal cycle). Displacement measurements were made 3 hr after the last tidal cycle was completed.



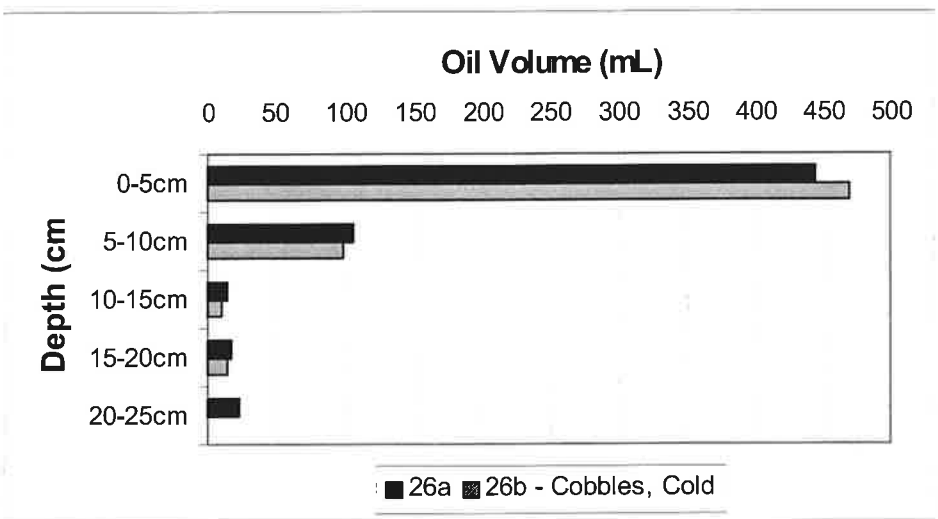
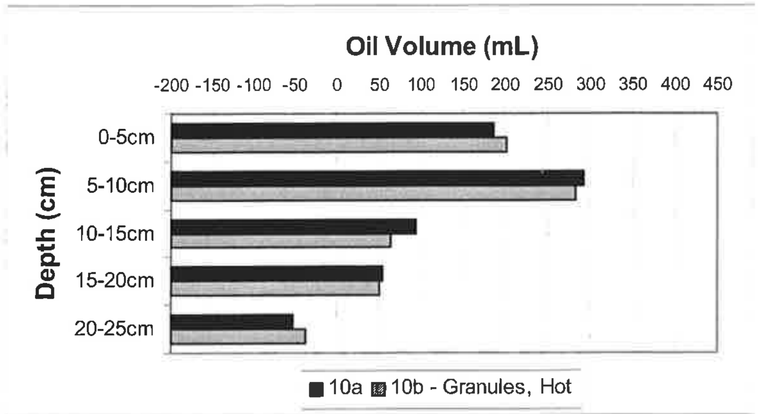
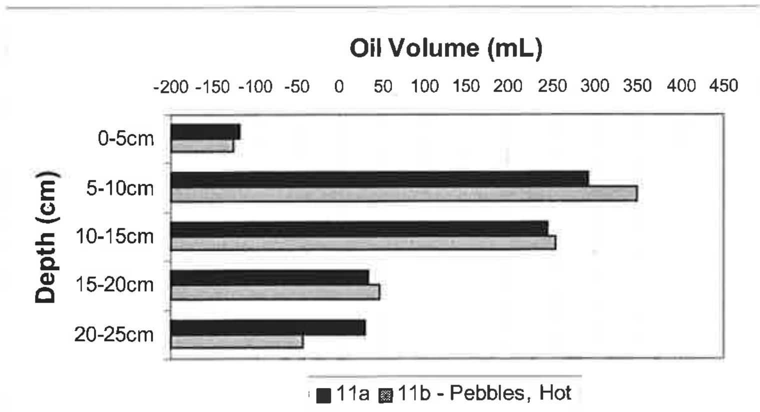


Figure 22 Coalesced bitumen retention with the test column cooled to 5°C using an ice bath. Displacement measurements were made 3 hr after initial stranding.





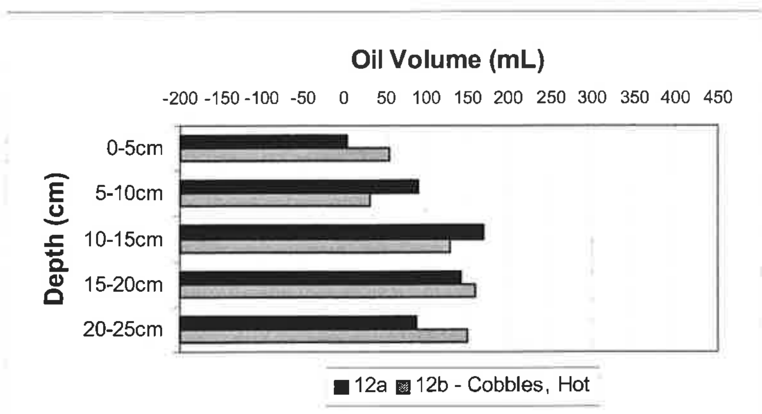


Figure 23 Coalesced bitumen retention with surface heating to ~35C using heat lamps. Displacement measurements were made 3 hr after initial stranding.

3.1.3 Large-Scale Swash Box Tests

Several tests of coalesced bitumen "patties" were observed in a swash box to examine how *coalesced* bitumen masses might strand on the beach under wave action. In these tests, a bitumen patty was placed in the "swash zone" and the interaction with sediment observed. The water temperature at the time of the tests was low (6°C) and may have contributed to the poor adhesion properties of the bitumen. We had speculated that the highly adhesive nature of the *coalesced* bitumen would pick up sediment particles so that the "patty" eventually would become coated and negatively buoyant. This adhesion process was not observed; the thoroughly wetted bitumen did not pick up sediment. "Patty deformation and molding" to clasts: occurred when the patty eventually stranded (Fig. 24 and 25), but was not highly adhesive in nature.

Figure 24 Image capture from video of a *coalesced* bitumen patty (~20cm in diameter) stranding on pebbles within the swash zone. This patty was not washed off by subsequent swash.

Figure 25 Image capture from video of the same *coalesced* bitumen patty as shown at left after being peeled off from the pebbles. The patty did *not* adhere the surface of the pebbles but the pebble casts are clearly visible, indicating that the *coalesced* bitumen was slowly (~7 minute interval) flowing into the pore spaces of the pebbles.

Two processes of significance to response planning were noted during the swash experiments: (1) sediment particles did not adhere to the surface skin of the *coalesced* bitumen patty, at least during the 6° C tests that we observed and (2) when the patty finally stranded, it was not the adhesive nature of the bitumen that attached the patty to the sediment but rather the oozing of the *coalesced* bitumen over the pebble-cobble surface, creating a "cast" of the sediment surface and preventing the patty from lifting off by the swash. Also of significance is that the coalesced bitumen patty remained positively buoyant throughout the > 1 hr tests.

3.2 *Dispersed* Bitumen Tests

Three litres of *dispersed* bitumen of 700 ppm bitumen (1:1,000 dilution of the Orimulsion®)was applied in each treatment, and this volume contained ~2.1 g of bitumen in suspension. By capturing the bitumen-in-water effluent that ran through the container and by extracting the bitumen that was retained in the sediments, a picture of bitumen retention in coarse sediments was obtained.

3.2.1 Penetration of Dispersed Bitumen

> *What is the limit of dispersed bitumen penetration, assuming a surface loading of 700 ppm of bitumen ?*

The *dispersed* bitumen penetrated to the base of the sediment column in all of the tests and we collected effluent from a variety of tests that showed that bitumen concentrations were in the range of 200 to 300 ppm (Fig. 14). That is, about half the bitumen was retained in the first 30cm of penetration (i.e., 1 g of bitumen). The data suggest that about 2% of the bitumen is removed per centimeter of penetration and using this removal rate, the maximum depth of penetration can be estimated (Fig. 26).

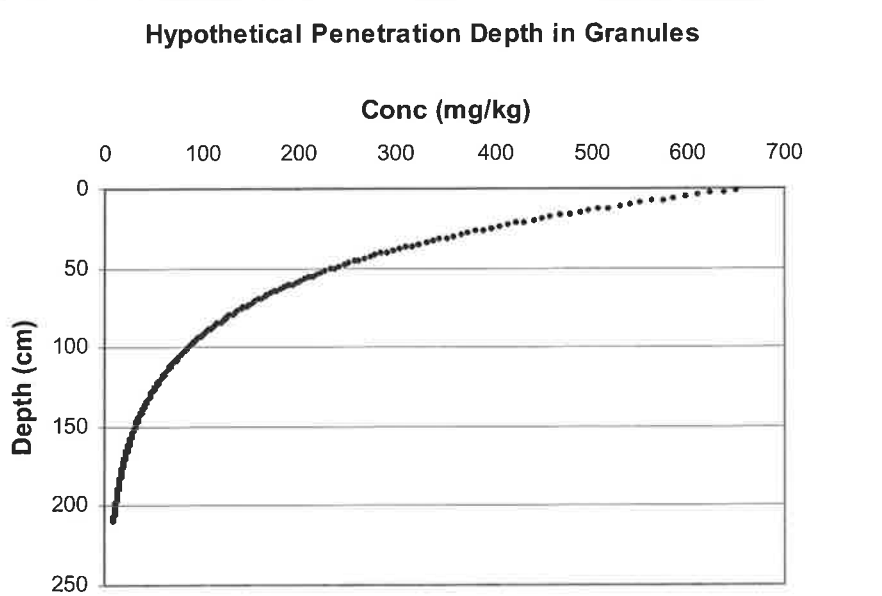


Figure 26 Hypothetical estimates of *dispersed* bitumen concentration with depth, based on our experimental data for 0 to 30 cm. The estimates suggest that bitumen could penetrate to 2m, although the concentrations are very low (<50 mg/kg)

These estimates assume that there is no water table that might limit penetration of the *dispersed* bitumen.

3.2.1 *Dispersed* Bitumen Retention

How does sediment size affect dispersed bitumen retention ?

Sediment Size Treatments – the "initial stranding" tests were conducted with no tides, where the *dispersed* bitumen (~700 ppm concentration) was drained immediately through the sediments and then allowed to "dry" for three hours; these tests were conducted at ~13°C. The sediment columns were destructively sampled after three hours and retention for different layers determined by DCM extraction techniques for each of three 5-cm thick sediment layers.

General retention of the *dispersed* bitumen (Fig. 27) was in the range of 10-40 mg of bitumen per kilogram of wet sediment. The granules treatment showed no significant gradient with depth but both pebbles and cobbles showed significantly higher retention of bitumen in the surface layer. Retention was extremely low. Results might vary with differing loading concentrations of bitumen.

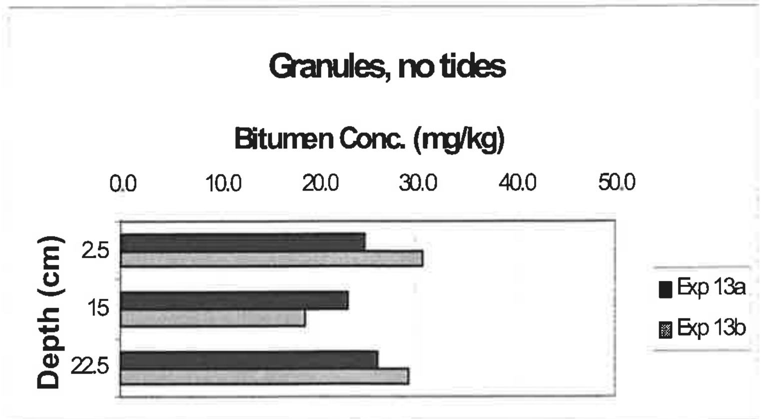
How does tidal zone elevation and tidal cycling affect dispersed bitumen retention ?

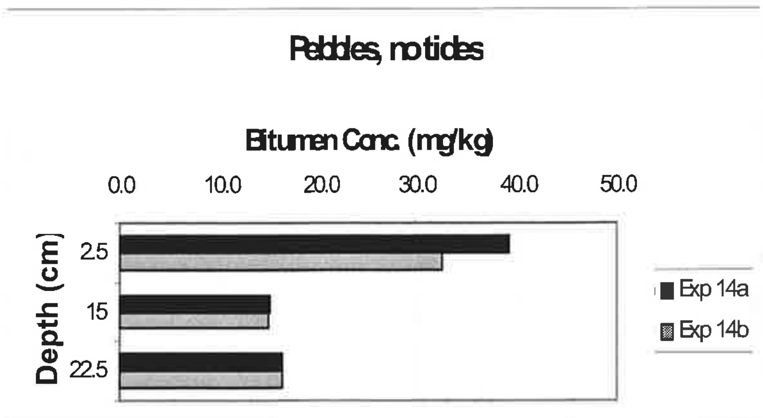
Tidal Zone Position and Tidal Cycling Treatments – this treatment tested the effect of tidal cycling on bitumen retention within the sediments. Cobble sediments were not tested because of the extremely low concentration in the initial experiments (Fig. 27). For the upper intertidal zone (UITZ), where sediments were alternatively dried for 9.5hr and submerged for 2.5 hr, most concentrations were in the 10 - 40 mg/kg range (Fig. 28). For the lower intertidal zone (LITZ), where sediments were alternatively submerged for 9.5hr and dry for 2.5 hr, most concentrations were also in the 10 - 40 mg/kg range (Fig. 29). For both zones, there was some variation in depth with highest concentrations near the surface. We interpret this trend as surface "skimming" effect where thin films of coalesced bitumen that form on the water surface from the dispersion and strand on the surface sediments. The within-treatment variability obscured any measurable effect of intertidal zone position.

Following four tidal cycles, there appeared to be no effect of tidal cycling on granule sediments, and little effect on pebble sediments. There was little variation of bitumen with depth in the granules, similar to the no-tide treatment (Fig. 27). The pebble treatment showed very low concentrations and slightly less retention than the no tide treatment. The data is not conclusive with respect to the effect of pore-water tidal pumping on bitumen retention.

How does temperature affect dispersed bitumen retention ?

Temperature Treatment – these experiments used standard sediments with no tides at a variety of temperatures to test for temperature effects on *dispersed* bitumen retention. Replicates of sediment columns were tested with initial 3 L loading of a dispersed bitumen mixture followed by a surface heating using heat lamps to simulate heating by solar radiation. Overall the concentration profiles (Fig. 30) were not substantially dissimilar to the no-tide, no heating experiments (Fig. 27), although the bitumen concentrations in the granules-heating treatment were about 25% higher. The mechanisms that might produce this result are not clear, and the data may simply reflect high replicate variance that is evident throughout all the *dispersed* bitumen treatment tests, particularly in surface samples.





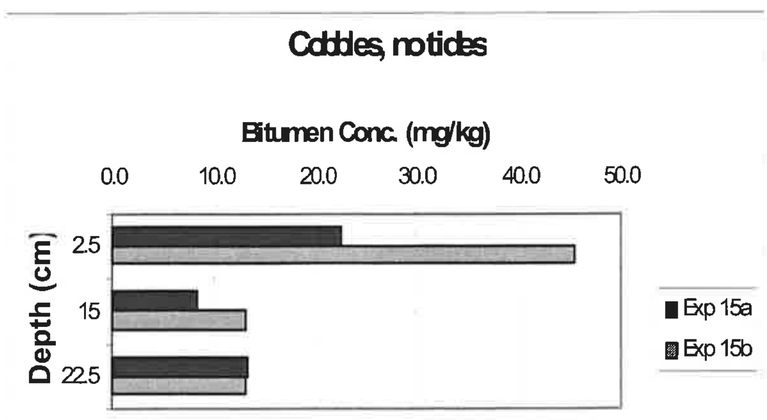


Figure 27. Dispersed bitumen retention in subsurface sediments as determined from DCM extraction Higher retention in surface sediments (pebbles and cobbles) is attributable to surface "skims" of coalesced bitumen that formed during the handling process. Two replicates are shown for each treatment.

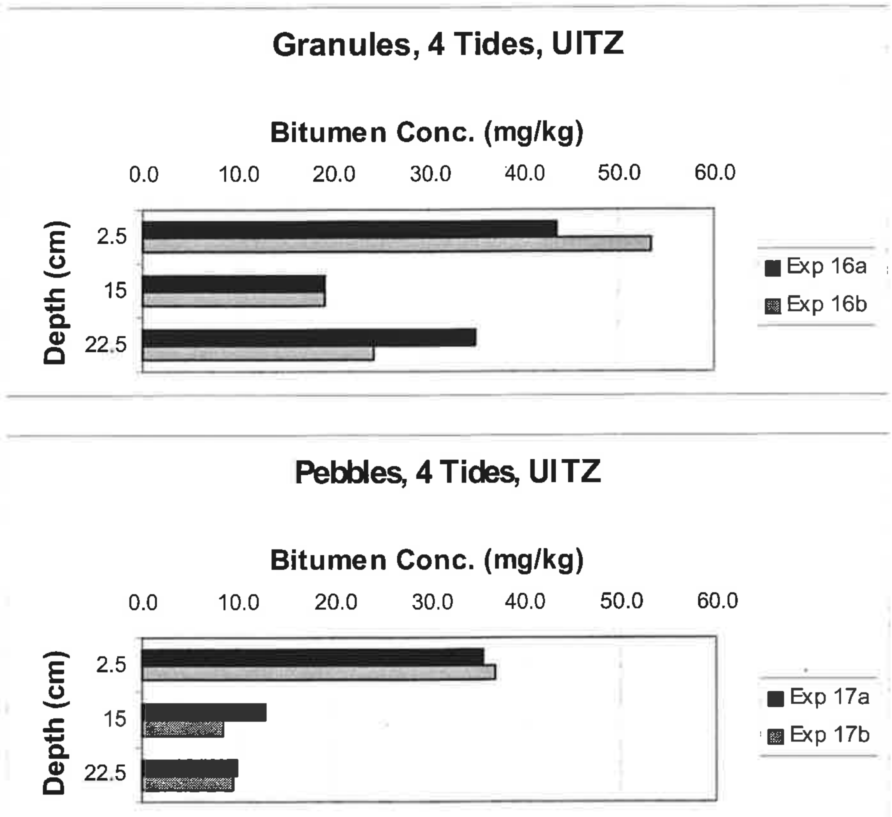
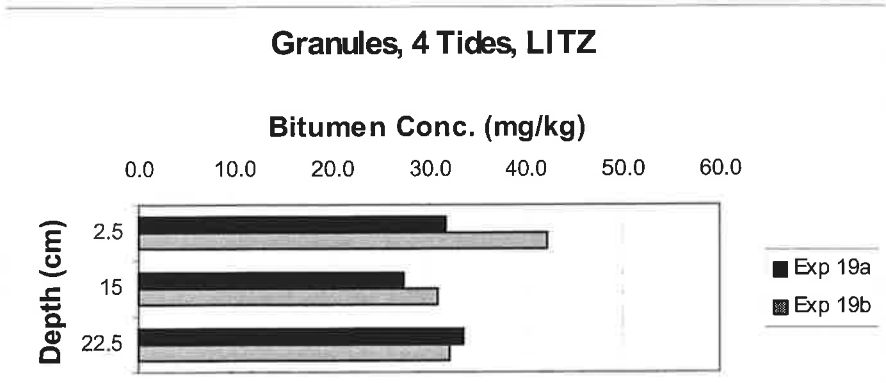


Figure 28 *Dispersed* bitumen concentration profiles after four tidal cycles, upper intertidal zone (UITZ). Two replicate were run for each treatment.



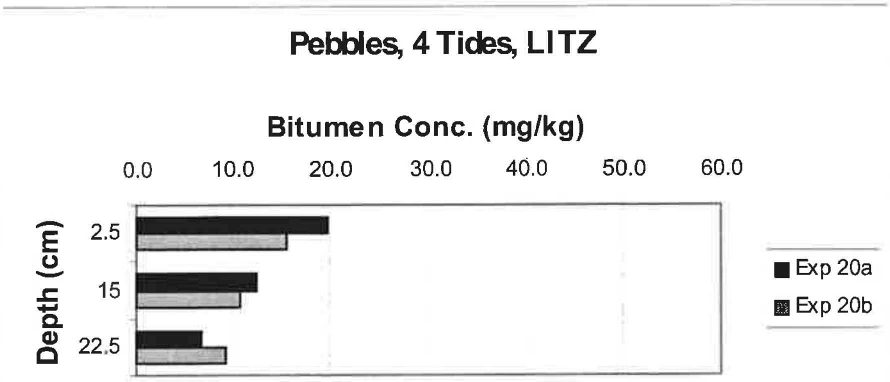
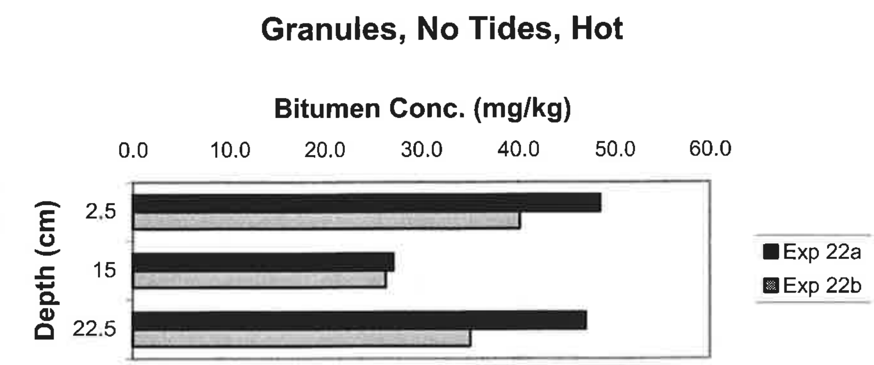


Figure 29 *Dispersed* bitumen concentration profiles for the 4-tides, lower intertidal zone treatment. Two replicate treatments were conducted for each treatment.



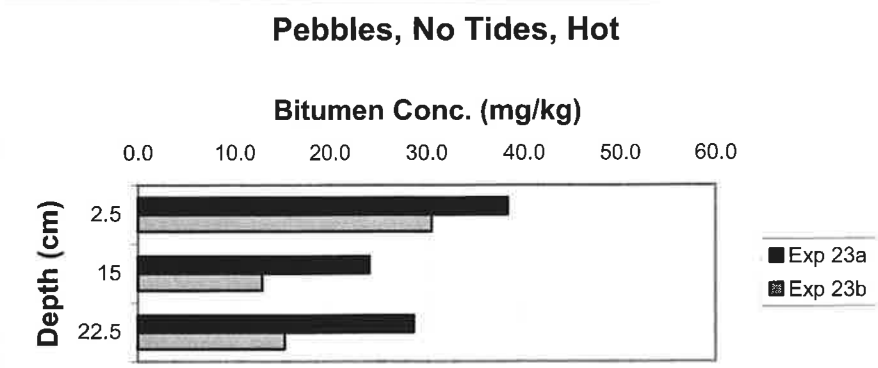


Figure 30 *Dispersed* bitumen concentration profiles for the "no tides" "hot" temperature treatment. Two replicate treatments were conducted for each treatment.

4.0 DISCUSSION OF RESULTS

The various experiments were designed to address questions that might be useful for response planning in the event of an accidental Orimulsion® spill.

4.1 Experimental Handling Procedures

A number of lessons were learned in terms of handling the Orimulsion® and resulting bitumen mixtures. The protocols developed by Fieldhouse and Sergy (2001) provide some consistency in terms of handling but we identified additional protocol issues.

4.1.1 Dispersed and Coalesced Bitumen Formulation

We found this coalescence process sensitive to the salt-types in the seawater, where InstantOcean® and natural seawater resulted in relatively rapid coalescence and non-iodized NaCl resulted in a much lower coalescence rate. Even using iodized NaCl caused a significant increase in coalescence. It is presently uncertain if this is a result of an anomalous Orimulsion® stock used in this experiment. Future Orimulsion® studies should be sensitive to this issue and the protocols of Fieldhouse and Sergy (2001) may ultimately require modification.

4.1.2 Coalesced Bitumen Handling

Coalesced bitumen is an extremely adhesive substance, making it difficult to measure out pre-determined volumes or weights of coalesced bitumen. The only material that it did not stick to readily was water. We found the use of ice-coating for molds and instruments was the only way we could effectively handle the coalesced bitumen.

4.1.3 Coalesced Bitumen Retention Measurement

We developed a water displacement test procedure for documenting *coalesced* bitumen retention in the subsurface of our test columns. Our initial tests of this procedure were very encouraging and we used three sets of measurements to document pre-treatment pore volumes of the sediments and three sets of measurements for post-treatment pore volumes. Our three replicate measurements were almost always very close and standard deviations (typically less than 0.1 mL standard deviation per layer). However, some of the measurements , particularly in granules, indicated *coalesced* bitumen penetration into the subsurface but subsequent freezing and excavation showed that actual penetration was limited to less than 1 cm. We believe that the apparent pore space reduction was due to settlement of the sediment during the handling process; small vibrations or shocks probably caused the settlement as the container was (a) set-up in the test apparatus, (b) was removed from the test apparatus and (c) was subjected to a second set of displacement measurements; The containers were handled 2-3 times after the initial displacement measurements, providing scope for vibrations, shocks and settlements. The replicate estimates for *coalesced* bitumen retention in pebbles and cobbles were generally very close (Fig. 19 to 23) and suggest that the technique was appropriate for these coarser sediments where settlement potential is less.

An additional potential source of error is at the "surface" of coarse sediment. The target porosity of 40% was documented in the subsurface (>5cm depth) but near the surface the porosity increases to 100% in the "theoretical" layer just above the sediment surface. The sediment clasts near the surface are an open framework becoming more porous towards the maximum elevation of the surface. The sensitivity of the displacement measurement technique is poorer in these larger poor volumes because the *coalesced* bitumen fills only a small portion of this open framework volume. We later determined that the *coalesced* bitumen did not spread laterally within the sediments and we probably could have used larger diameter and larger volume test pucks of *coalesced* bitumen to reduce variability of the measurements.

4.2 Discussion of Experimental Results

In the event of an Orimulsion® spill two forms of bitumen might reach the shore: *coalesced* or *dispersed* bitumen. Our tests provide some insight into the processes that will occur should each of these bitumen forms strand on a coarse-sediment beach.

4.2.1 Dispersed Bitumen Stranding

It is possible that dilute mixtures of *dispersed* bitumen could reach the shoreline, should a spill occur in close proximity to the shore. *Dispersed* bitumen will readily penetrate all coarse substrates. At the dispersed bitumen concentrations we tested (nominal 700ppm) the retention concentrations are extremely low - in all cases less than 60 mg of bitumen per kilogram sediment and generally less than 30 mg/kg. The retained bitumen is not visible on the clast surfaces but produce a faint smear on fingers when handled. Our theoretical calculations of bitumen penetration suggest that *dispersed* bitumen, of 700 ppm concentrention plume, could penetrate to depths of 2 m if there were no limiting ground water table, although the concentrations at this depth would be extremely low (<5 ppm).

The previous experimental work by Harper and Kory (1997) is not directly comparable to the current study in that loading levels involved undiluted Orimulsion (750,000 ppm) compared to our loading levels of 700 ppm (three orders of magnitude different). Corresponding retention in granules and pebbles were in the range of 6,000 to 50,000 mg/kg sediment compared to our measured retention of 10 to 60 mg/kg of sediment (three orders of magnitude different). Consistent trends between the two experiments are: (a) temperature does not appear to have a strong affect on dispersed bitumen retention and (b) dispersed bitumen appears to remain mobile on wetted surfaces and may be flushed or "diluted" by tidal pumping.

The *dispersed* bitumen tests did not indicate any significant trends between treatments or within layers. There is typically a higher surface concentration of bitumen (Fig. 27), which we interpret as an artifact of the coating procedure where coalesced bitumen films or "skims" that form on the surface of the water are deposited on the surface sediments as the tidal-level falls.

Our tests were not conclusive in identifying how mobile the *dispersed* bitumen is following initial stranding. There is some indication that dispersed bitumen concentrations in both the granules and pebbles are *less* after 4 tidal cycles (Fig. 28 & 29) than after the initial stranding levels (Fig. 27), suggesting mobility and gradual dispersion of the bitumen; this trend is not strong however, or statistically significant.

Studies of *dispersed* bitumen coatings on rock surfaces (Harper and Ward 2002; Harper *et al* 2002a) suggest that if sediments are kept wet, the bitumen will remain mobile. A deluge-type flushing *may* be effective in removing the extremely low concentrations of subsurface bitumen.

4.2.2 Coalesced Bitumen

We speculated that *coalesced* bitumen might pick-up small sediment particles during the stranding process and become negatively buoyant. Observations of *coalesced* bitumen patties in the swash zone showed that the patties *did not* pickup sediment particles on the surface of the patty, as expected. It appears that the coalesced bitumen is not as adhesive or sticky to the wetted sediment particles as we expected (although these tests were run at 6° C temperatures – slightly cooler than most of our tests). When the patty finally stranded on the cobble-pebble sediment (Fig. 24), it was easily peeled off. The patty did ooze down into the pebble-cobble matrix, creating a cast of the clasts, so that the patty attached to the sediment by "form-fitting" (Fig. 25) rather than simple adhesion. The observation is important in identifying a lack of adhesion to surfaces that remain wet and that may have bio-films on the surface.

Several smaller swash box experiments were conducted with both floating and submerged sorbents to ascertain if negatively buoyant bitumen might occur under breaking wave and swash conditions – our submerged sorbents did not capture any bitumen particles suggesting that our speculation about negatively buoyant coalesced bitumen was incorrect.

For granule or pebble sized sediment matrices, initial penetration of *coalesced* bitumen will be *extremely limited* (<10 cm), even under relatively hot summer conditions. Initial penetration on cobble beaches can be significant (>30 cm) under "hot" conditions, however. Under cold conditions (<5° C) it unlikely that *coalesced* bitumen will penetrate deeply into cobble-sized sediments (<5 cm).

Previous experimental work by Harper and Kory (1997) is consistent with the observations made in these experiments. Penetration of *coalesced* bitumen was very limited (<1cm) in sediments finer than pebbles (granules and coarse sand). Even for coarser sediments (pebbles) penetration was very limited (<1cm) except at high temperatures (25°C) where 4.5 cm of penetration occurred (Harper and Kory 1997, Table 6). Experimental data from our tests showed penetration of 2.5 cm at 15°C and 9.5cm at 35°C, as such bracketing the previous experimental data.

The position of stranding on the intertidal zone appears to be a significant factor in penetration and retention. Upper intertidal stranding, where there are long periods of emergence allows significantly greater penetration than lower intertidal stranding, where submergence and associated buoyancy forces counteract the downward migration of *coalesced* bitumen. The *coalesced* bitumen concentration maximum for UITZ tests was approximately double that of the LITZ treatments (Fig. 17). Our tests did not allow separation of tidal zone position effects and tidal pumping effects. That is, we can not determine if the emergence time was more of factor in *coalesced* bitumen movement than water movement through the pore space. Because the water movement is relatively slow, we *assume* that the emergence/submergence ratio or intertidal zone stranding position is more significant than tidal cycling but do not have data to support that assumption.

Temperature of the *coalesced* bitumen and sediments has a significant effect on penetration. Under *cold* conditions (5°C), initial penetration was limited to less than <3 cm in all sediments,

including cobbles. Under *cool* conditions (~13°C) penetrations depths doubled over the *cold* conditions and under *hot* conditions (35°C surface heating), penetration tripled over the *cool* conditions (Fig. 18). In stranding under hot or sunny conditions there is the potential for substantial penetration over a few tidal cycles, whereas under cold conditions, sediments are essentially impermeable and penetration is limited.

Hot flushing of *coalesced* bitumen stranded on granules did not sufficiently decrease the viscosity to cause penetration into the sediments. It may be that hot-water washing on adjacent rock surfaces, seawalls or large boulders would not cause *coalesced* bitumen to penetrate into granule-sized or finer sediments. However, this projection would require verification.

4.3 Implications to Countermeasure Planning

Our experiments address issues about what type of response is most appropriate *should stranding on a shoreline occur.*

4.3.1 Dispersed Bitumen Treatments

If a dispersed bitumen mixture comes in contact with the shoreline, concentrations are likely to be low and retention in sediments in the range of 10-30 mg of bitumen per kg of sediment (ppm). Keeping sediments wet will minimize the potential of the bitumen to adhere to sediment surfaces. However, normal hydraulic washing that create a downward flow of water through the sediment may increase the penetration. A deluge type flooding of the beach surface that produces a net outflow of groundwater from the beachface is likely to limit penetration and will probably remove mobile bitumen. Given the complexity of setting up deluge systems (usually set up for hundreds of metres of beach) and the anticipated low retention concentrations (<30 ppm), this technique may be feasible only on local scale.

It is also not certain if the bitumen washed from the subsurface would float so that it could be recovered.

4.3.2 Coalesced Bitumen Treatments

If widely coalesced bitumen patties were to strand on a shoreline, immediate manual pickup of the patties is likely to be the simplest way to prevent penetration into the intertidal sediments. In situations where beach sediment temperature could be elevated (e.g., warm ambient air temperatures or sunny conditions), expedient removal of the bitumen will be required to minimize the penetration, which can be up to >30cm in cobble-sized sediments under *hot* conditions during a single tide. Manual pick-up efforts should be strategized to treat coarse beaches (boulder-cobble) first, working towards finer sediments. Submergence and associated buoyancy effects reduces penetration potential in the lower intertidal zone so upper intertidal zones should receive treatment priority.

We considered the use of hydraulic washing techniques as a strategy but any washing technique is likely to move bitumen *down* into the sediments. While the use of a deluge system to create an outward groundwater flow might be useful in limited applications, manual recovery of the *coalesced* bitumen would probably be preferred over hydraulic washing techniques. We were concerned about negatively buoyant *coalesced* bitumen that might result from hydraulic washing and conducted a few simple tests in swash boxes. *Coalesced* bitumen that was washed with a

spray washer did not adhere to submerged sorbent pads, suggesting negatively buoyant *coalesced* bitumen may not be a significant issue.

We could not see any benefit in using heated water in coalesced bitumen treatment – elevated water temperatures will increase permeability and facilitate *downward* migration of the coalesced bitumen causing larger volumes of subsurface sediment to be contaminated.

5.1 Conclusions

1. *Coalesced* bitumen is extremely adhesive and sticky when handling in air but less so when handling with wetted surfaces. Special handling procedures, including the use of ice molds, were required for conducting *coalesced* bitumen experiments. However, *coalesced bitumen* patties in the swash zone did not pick up sediment particles and did not adhere to pebble-cobble surfaces when stranded.

2. Initial penetration (0-tidal cycles) of *coalesced* bitumen is highly sediment-size-sensitive. Under average temperature conditions ~15°C, granules are basically impermeable (<1 cm penetration), pebbles are only slightly permeable (<5 cm except under hot conditions) and cobbles are moderately permeable (<10 cm except under hot conditions).

3. Penetration of *coalesced* bitumen into coarse sediments is also highly temperature sensitive. Under cold (<5° C) temperatures, even cobbles become impermeable (<3 cm of penetration). Under warm conditions (>25° C) *coalesced* bitumen can penetrate to depths of greater than 30 cm in cobbles and to about 10 cm in pebbles within three hours.

4. *Coalesced* bitumen will continue to migrate within sediments after initial stranding due to "tidal cycling" and is likely to continue penetrating until reaching the ground-water table (up to 30cm penetration in cobbles after 4 tidal cycles). Our tests did not show any release of *coalesced* bitumen once it had penetrated below the surface, indicating that normal tidal cycling results in a net downward movement of *coalesced* bitumen, creating a type of "bitumen conglomerate".

5. In limited testing of hot-water flushing of *coalesced* bitumen on granules, there was no significant increase of penetration due to the flushing. Based on results from warm temperature conditions (Conclusion 3), it is likely that any hot-water hydraulic treatment would tend to increase penetration of bitumen into the subsurface sediments.

6. *Dispersed* bitumen may reach the shoreline under certain conditions. Penetration could be significant in coarse sediments – our tests showed >30 cm of penetration and calculations suggest 2m penetration is theoretically possible in the absence of ground water tables. However, retention of *dispersed* bitumen in coarse sediments is likely to be extremely low, typically in the range of 10 - 30 mg of bitumen per kilogram of sediment at our initial loading concentration of ~700 ppm of bitumen.

5.2 Recommendations

1. These experiments provide a first approximation of the stranding process of Orimulsion® forms on shorelines. There is little information, however, on the weathering process of Orimulsion® prior to stranding. That is, the rate at which bitumen coalesces following a spill and

the types of *coalesced* bitumen masses that may form (e.g., balls, patties or mats of coalesced bitumen). It is expected that the coalescence process is likely to be sensitive to water quality differences and temperature. Some large-scale (e.g., wave tanks) or open-ocean experiment spill would be extremely useful in documenting the rate of coalescence and resulting morphologic forms of the *coalesced* bitumen.

2. We have little understanding of the actual stranding process under more energetic conditions. Limited observations of *coalesced* bitumen stranding in swash suggest that *coalesced* bitumen does not adhere easily to wetted sediments under cold conditions. It is not certain, however, what type of interaction might occur under warmer conditions. Again, some larger-scale experiments such as those that might be conducted in a wave tank under controlled conditions would be very useful. Even very small experiments involving a few 500g *coalesced* bitumen patties in the swash zone will be very helpful in resolving issues such as "frosting" of the bitumen patties with sediment, temperature sensitivity of the process, etc.

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Harper, J.R. and M. Kory 1995. Stranded Oil in Coarse Sediment Experiments (SOCSEXII). Contract Report by Coastal & Ocean Resources Inc. of Sidney, BC for the Emergencies Science Division, Environment Canada. 60 pp.

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Harper, J.R., S. Ward, G. Sergy, T. Brown and M. Dempsey 2002b. Orimulsion® Penetration and Retention in Coarse Sediments. *Proceedings* of the 25th Arctic Marine Oil Spill Project (AMOP) Technical Seminar, Environment Canada, Ottawa.

Masciangioli, P and M. Chirinos 2001. Rheology of Cerro Negro bitumen and bitumen recovered from a simulated Orimulsion® spill. Internal Report by Bitor Corp, Departmento de Ecología y Ambiente, October 2001, 7p.

Masciangioli, P, E. Abreu and B. Angulo 2001. ORIMULSION® 400 Phase IIR Dispersion/Coalescence Tests. Internal Report by Bitor Corp, Departmento de Ecología y Ambiente, Decmeber, 8p.

Appendix A

Container Specifications

The containers for Orimulsion® - sediment interaction tests were standard polyethylene 20 litre pails, roughly 38 cm high and 28 cm in diameter. Two batches of pails, black and white, with slight differences in overall dimensions were obtained. Detailed measurements of dimensions were conducted (Tables A-1 and A-2; electronic files bucket.xls and buckets2.xls), and internal volume profiles were constructed (Figure A-1). This enabled calculation of sediment weights that were required to fill the buckets to a height of 32.5 cm, at a specific sediment porosity.

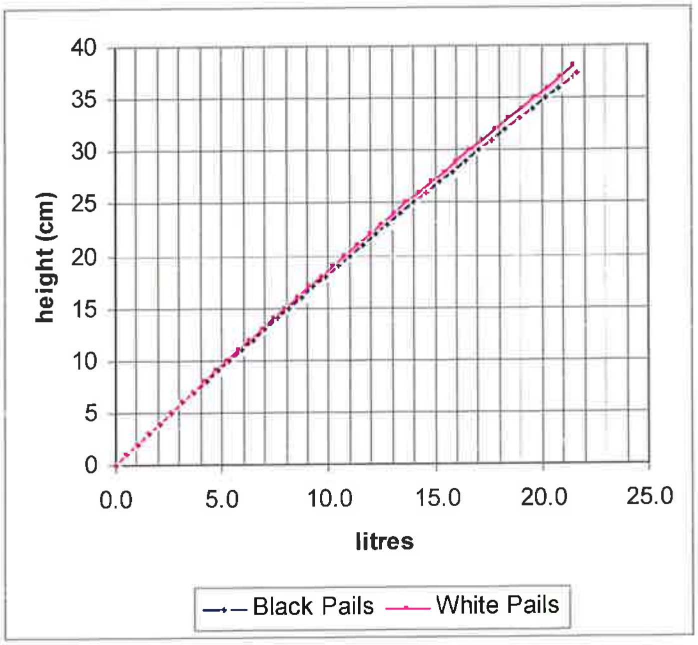

Figure A-1 Volume versus water level height for containers.

Buckets were modified for the sediment tests (Fig. A-2; photo 0093a.jpg). Buckets were tapped at two levels, just below the rim and just above the base, and fitted with inlet and outlet tubes. These tubes were commercially available PVC plumbing items. Simple, cost-effective seals were made on these fittings using thermoplastic "hot-glue" guns. A standard plumbing ball valve was attached to the lower outlet tube.

Buckets were also tapped at the same levels, and smaller PVC elbows were installed. A 35 cm length of clear, vinyl tubing connected the elbows to create a transparent standpipe. An inexpensive polystyrene ruler was affixed adjacent to the standpipe to allow measurement of water level in the container. Lengths of flexible clear vinyl tubing provided extension of the fill and drain fittings.

Fig. A-2 Photo of test container.

Table A-1 Black Bucket Measurements

CALCULATED BUCKET VOLUMES

height (cm) total	bottom I.D. (cm)	top I.D. (cm)	bottom radius B/2 (cm)	top radius C/2 (cm)	volume pi/2(dxd + exe)*h (cubic cm = mL)	h = 1 cm
37.3000	25.7000	28.7000	radius increment	0.04021448		
						5 cm layer
0.0		25.7000				0
1.0	25.7000	25.7804	12.8500	12.8902	520.3732	0.5
2.0	25.7804	25.8600	12.8902	12.9300	523.6125	1.044
3.0	25.8600	25.9395	12.9300	12.9698	526.8443	1.571
4.0	25.9395	26.0191	12.9698	13.0096	530.0860	2.101
5.0	26.0191	26.0987	13.0096	13.0493	533.3377	2.634
6.0	26.0987	26.1782	13.0493	13.0891	536.5993	3.171
7.0	26.1782	26.2578	13.0891	13.1289	539.8709	3.711
8.0	26.2578	26.3373	13.1289	13.1687	543.1524	4.254
9.0	26.3373	26.4169	13.1687	13.2085	546.4438	4.800
10.0	26.4169	26.4965	13.2085	13.2482	549.7452	5.350
11.0	26.4965	26.5760	13.2482	13.2880	553.0565	5.903
12.0	26.5760	26.6556	13.2880	13.3278	556.3778	6.459
13.0	26.6556	26.7351	13.3278	13.3676	559.7090	7.019
14.0	26.7351	26.8147	13.3676	13.4074	563.0502	7.582
15.0	26.8147	26.8943	13.4074	13.4471	566.4013	8.149
16.0	26.8943	26.9738	13.4471	13.4869	569.7623	8.718
17.0	26.9738	27.0534	13.4869	13.5267	573.1333	9.292
18.0	27.0534	27.1329	13.5267	13.5665	576.5142	9.868
19.0	27.1329	27.2125	13.5665	13.6063	579.9051	10.448
20.0	27.2125	27.2921	13.6063	13.6460	583.3059	11.031
21.0	27.2921	27.3716	13.6460	13.6858	586.7167	11.618
22.0	27.3716	27.4512	13.6858	13.7256	590.1374	12.208
23.0	27.4512	27.5307	13.7256	13.7654	593.5680	12.802
24.0	27.5307	27.6103	13.7654	13.8052	597.0086	13.399
25.0	27.6103	27.6899	13.8052	13.8449	600.4591	13.999
26.0	27.6899	27.7694	13.8449	13.8847	603.9196	14.603
27.0	27.7694	27.8490	13.8847	13.9245	607.3900	15.210
28.0	27.8490	27.9285	13.9245	13.9643	610.8704	15.821
29.0	27.9285	28.0081	13.9643	14.0041	614.3607	16.436
30.0	28.0081	28.0877	14.0041	14.0438	617.8609	17.054
31.0	28.0877	28.1672	14.0438	14.0836	621.3711	17.675
32.0	28.1672	28.2468	14.0836	14.1234	624.8912	18.300
33.0	28.2468	28.3263	14.1234	14.1632	628.4213	18.928
34.0	28.3263	28.4059	14.1632	14.2030	631.9613	19.560
35.0	28.4059	28.4855	14.2030	14.2427	635.5113	20.196
36.0	28.4855	28.5650	14.2427	14.2825	639.0712	20.835
37.0	28.5650	28.6446	14.2825	14.3223	642.6410	21.477
37.3	28.6446	28.7000	14.3223	14.3500	193.7029	21.671
						0.3 CM
			TOTAL VOLUME		21671.1434	

Table A-2 White Bucket Measurements

CALCULATED BUCKET VOLUMES

height (cm) total	bottom I.D. (cm)	top I.D. (cm)	bottom radius B/2 (cm)	top radius C/2 (cm)	volume pi/2(dxd + exe)*h (cubic cm = mL)	h = 1 cm
38.0000	25.5000	28.2000	radius increment	0.03552632		
						5 cm layer
0		25.5000				0.000
1	25.5000	25.5711	12.7500	12.7855	512.1297	0.512
2	25.5711	25.6421	12.7855	12.8211	514.9837	1.027
3	25.6421	25.7132	12.8211	12.8566	517.8456	1.545
4	25.7132	25.7842	12.8566	12.8921	520.7154	2.066
5	25.7842	25.8553	12.8921	12.9276	523.5932	2.589
6	25.8553	25.9263	12.9276	12.9632	526.4788	3.116
7	25.9263	25.9974	12.9632	12.9987	529.3725	3.645
8	25.9974	26.0684	12.9987	13.0342	532.2740	4.177
9	26.0684	26.1395	13.0342	13.0697	535.1835	4.713
10	26.1395	26.2105	13.0697	13.1053	538.1009	5.251
11	26.2105	26.2816	13.1053	13.1408	541.0262	5.792
12	26.2816	26.3526	13.1408	13.1763	543.9595	6.336
13	26.3526	26.4237	13.1763	13.2118	546.9007	6.883
14	26.4237	26.4947	13.2118	13.2474	549.8498	7.432
15	26.4947	26.5658	13.2474	13.2829	552.8068	7.985
16	26.5658	26.6368	13.2829	13.3184	555.7718	8.541
17	26.6368	26.7079	13.3184	13.3539	558.7447	9.100
18	26.7079	26.7789	13.3539	13.3895	561.7256	9.661
19	26.7789	26.8500	13.3895	13.4250	564.7144	10.226
20	26.8500	26.9211	13.4250	13.4605	567.7111	10.794
21	26.9211	26.9921	13.4605	13.4961	570.7157	11.365
22	26.9921	27.0632	13.4961	13.5316	573.7283	11.938
23	27.0632	27.1342	13.5316	13.5671	576.7488	12.515
24	27.1342	27.2053	13.5671	13.6026	579.7772	13.095
25	27.2053	27.2763	13.6026	13.6382	582.8135	13.678
26	27.2763	27.3474	13.6382	13.6737	585.8578	14.264
27	27.3474	27.4184	13.6737	13.7092	588.9101	14.852
28	27.4184	27.4895	13.7092	13.7447	591.9702	15.444
29	27.4895	27.5605	13.7447	13.7803	595.0383	16.039
30	27.5605	27.6316	13.7803	13.8158	598.1143	16.638
31	27.6316	27.7026	13.8158	13.8513	601.1982	17.239
32	27.7026	27.7737	13.8513	13.8868	604.2901	17.843
33	27.7737	27.8447	13.8868	13.9224	607.3899	18.450
34	27.8447	27.9158	13.9224	13.9579	610.4976	19.061
35	27.9158	27.9868	13.9579	13.9934	613.6133	19.675
36	27.9868	28.0579	13.9934	14.0289	616.7369	20.291
37	28.0579	28.1289	14.0289	14.0645	619.8684	20.911
38	28.1289	28.2000	14.0645	14.1000	623.0078	21.534
			TOTAL VOLUME		21534.1640	

Appendix B

Sediment Specifications

B1.0 Sediment Preparation

Three sediment size classes were determined as appropriate for the Orimulsion®-sediment interaction studies. Planning specifications called for uniformly sorted coarse sediments: granules, small pebbles and very large pebbles (termed cobbles in this experiment), to simulate a range of sediment sizes commonly occurring on Canadian coastlines. Due to facility capabilities and handling requirements for meso-scale experiments, clast sizes larger than cobbles were considered unsuitable for our purposes. It was postulated that information obtained using the lower-end small cobble size, less permeable sediment, could be reasonably extrapolated to the larger clast sizes.

Bulk volumes of gravel (construction aggregates) were obtained. The commercially available "drain rock" was very close to our original requirements for cobble sized clasts (~7.5 cm) and only required a fresh-water wash and air-drying prior to use.

The pebble-sized category (nominal size 2 cm) required sorting to bring the sediment into a uni-modal distribution size class. Steel screens were obtained, and bulk sediment was manually wet-screened using fresh water, to select the desired pebble size class. An initial pass over a standard bottom screen (nominal opening size 10.0 mm) to remove smaller clasts was sufficient.

The granule-sized category of fines required substantial processing. Manual wet-screening with fresh water through top screen nominal opening 5.0 mm, and bottom screen nominal opening 8-mesh/2.38 mm retained approximately 10% of the original mixed sediment volume as the selected granule-size fraction.

The washed sediments were air-dried prior to use. Overall mineral densities were determined by displacement techniques: submergence of a known dry sediment weight in a known volume of water contained in a large graduated cylinder. Samples of each sediment were submitted to Thurber Engineering, Ltd. for sieve analysis; results are shown in Table B-1. Grain shape and mineralogy analysis was conducted in-house on samples of each sediment size, of a minimum of 100 clasts, Table B-2 (electronic file MSExcel97 grain-size analysis.xls).

Table B-1 Sieve Analysis

Large pebbles

Sieve size (mm)	Weight retained (g)	% retained
75	0	0
50	5399.5	25.7
37.5	14041.7	66.9
25	1535.2	7.3
pan	0	0

Pebbles

Sieve size (mm)	Weight retained (g)	% retained
25	0	0
19	771.9	15.1
16	1746.1	34.2
12.5	1707.7	33.4
9.5	849.2	16.6
4.75	36.4	0.7
pan	1.2	0

Granules

Sieve size (mm)	Weight retained (g)	% retained
9.5	0	0
4.75	15.5	1.5
2.36	977.3	94.8
1.18	36.3	3.5
pan	1.9	0.2

Table B-2 Mineralogy

Summary Statistics

	Cobbles	Pebbles	Granules
Angularity			
angular	7	7	22
subangular	27	21	24
subrounded	28	44	35
rounded	28	23	19
well rounded	10	5	0
Total	100	100	100
Mineralogy			
epidote	2	1	0
quartzite	11	7	11
metasediment	3	14	9
granite	22	8	19
gabbro	7	7	11
metabasalt	8	0	2
basalt	47	63	48
Total	100	100	100
% Sphericity			
average	62.8	64.2	60.8
median	70	70	70
mode	70	70	70
min	20	30	30
max	90	90	90

B2.0 Sediment Loading Procedures

Weights of sediments required to pack a known volume to a specific porosity were calculated (Table B-3) based on the sediment characteristics. For each test container, a "filter" layer of mixed fine gravel and sand was packed, 35% porosity, to a height of 5 cm in the base of the bucket. A piece of plastic mesh was used to exclude sediment from the outlet drain pipe fitting. The test sediments were packed on top of this filter layer to a depth of 25 cm, using the required weight to fill the slightly tapered cylindrical volume to the target porosity: 40% for cobbles and pebbles, 35% for granules. Packing to target porosity was achieved through shaking and repetitive impact ("thumping"). Attempts to maintain a 40% porosity using granules were not successful. Even careful handling of loaded test containers caused packing below 40% porosity.

Previous experiments (Harper and Kory 1995) evaluated sediment attributes that could be important in oil retention in subsurface sediments, including number of clasts per units volume, surface area of clast per unit volume and number of grain-to-grain contacts per unit volume (Table B 4).

Table B-3 Computed Dry Weights for Packing Container to Pre-Determined Porosity

Bucket Layers				Granules			Pebbles			Cobbles		
Ht (cm)	Thickness (cm)	Volume (L)	Porosity	Mineral Density (g/cm3)	Bulk Density (g/cm3)	Granules Weight (kg/layer)	Mineral Density (g/cm3)	Bulk Density (g/cm3)	Granules Weight (kg/layer)	Mineral Density (g/cm3)	Bulk Density (g/cm3)	Granules Weight (kg/layer)
25-30cm	5	3.054	0.35	2.660	1.729	5.280	2.91	1.8915	5.777	2.44	1.586	4.844
15-25cm	10	5.850	0.35	2.660	1.729	10.115	2.91	1.8915	11.065	2.44	1.586	9.278
5-15cm	10	5.431	0.35	2.660	1.729	9.390	2.91	1.8915	10.273	2.44	1.586	8.614
0-5cm	5	2.634	0.35		***Total:***	***24.785***		***Total:***	***27.115***		***Total:***	***22.735***

Table B 4 Summary of Clast Surface Area and Grain-to-Grain Contact Data (after Harper and Kory 1995)

Sediment Type	Mean Diameter (mm)	Number of Clasts per cubic metre (x1,000)	Mean Surface Clast Area (cm^2)	Surface Area per Unit Volume (m^2/m^3)	Grain-to-Grain Contacts ($\#/m^3 x10^6$)
granules	3.4	34,850	0.408	1,420	209
pebbles	14.5	219	8.63	189	1.03
cobbles (v. large pebbles)	43	12.1	64.8	78.2	0.057

Appendix C

Coalesced Bitumen

C1.0 Coalesced Bitumen Preparation

The procedures developed by Fieldhouse and Sergy (2001) were followed for the production of coalesced bitumen.

The Orimulsion® stock was shipped to our warehouse facility from Bathurst, New Brunswick in a 45-gallon polyethylene drum. The contents of the drum were mixed by manually rolling the drum for ~500 revolutions at a rate of ~ 12 revolutions per minute, with direction of revolution reversed at 12 second intervals. The mixing process was carried out prior to any sub-sampling of the stock Orimulsion®. A commercially available molasses gate was installed on the drum to facilitate withdrawal of Orimulsion®.

Artificial seawater was prepared from Instant Ocean, a commercially available formulation for saltwater aquarium systems, and was mixed to 33 ppt weight/volume. Resulting solutions were not 34 ppt salinity as measured through conductivity, more typically in the range of 26 ppt. Seawater in the locale of the warehouse facility, from Patricia Bay, was measured at 25.5 ppt at 8° C. It is speculated that the Instant Ocean formulation contains non-dissociative components.

Coalesced bitumen was prepared in a batch process. The artificial seawater was prepared *in situ,* 8.25 kg Instant Ocean added to 250 L water in a 1200 L capacity polyethylene tank, and mixed both manually with a steel rod and using compressed air for 2 hours. 1.25 litres of well-mixed Orimulsion® stock was added to the seawater, again using compressed air to assist mixing for 20 minutes. The bitumen was allowed to coalesce overnight, forming a layer on the surface. The bitumen was then harvested by collecting masses of the bitumen on the end of a steel rod, and transferring to a clean, 20 L polyethylene pail. The tank contents were allowed to stand, and further coalesced bitumen was collected twice more, at two hour intervals. Projected weights of bitumen were 0.875 kg, based on the initial volume of Orimulsion®. Actual harvest weights from all batches were typically ~1.0 kg, indicating a proportion of seawater, roughly 12%, is entrained in the coalescence/ harvesting process. A bulk stock of ~20 kg of coalesced bitumen was collected from successive batches, stirred to mix, and stored covered at 4° C prior to use.

Following bitumen harvesting, the seawater- Orimulsion® mixture was bubbled for a further 2 hours to coalesce as much remaining bitumen (~25 g) as possible. The floating waste bitumen was removed using sorbent pads, and as much residue as possible on the interior of the tank was removed using a steel scraper. The wastewater was pumped into a 1,500 L capacity oily-water separator to remove more waste particulate bitumen. The water from the oily-water separator was pumped into another settling tank, and further polished by circulating through a fine sand filter (commercially available pool filter system). Discharge of the treated water into the municipal drain was permitted only after hydrocarbon levels were determined to be within allowable limits. Typical hydrocarbon levels were ~0.1 ppm TEH, as determined by Cavendish Labs.

C2.0 Coalesced Bitumen Properties

Coalesced bitumen is a black, cohesive, highly viscous and adhesive substance. Water (and air) entrained during the preparation procedure forms a water-in-oil emulsion with the bitumen. Rheology of the coalesced bitumen is complex. Samples of the coalesced bitumen stock were sent to PDVSA Intevep for viscosity measurements (electronic file viscosity~.doc) and to Environment Canada River Road laboratory for water content determination.

C3.0 Retention and Penetration Measurements

Data is contained in electronic files:

Penetration depths.xls
Displacement1.xls
Series1.xls
Series2.xls
Series3.xls
Series4.xls
Series4Temperatures.xls
Series5.xls
Pre-post_density.xls

Appendix D

Dispersed Bitumen

D1.0 Dispersed Bitumen Preparation

The basic procedures developed by Fieldhouse and Sergy (2001) were followed for the production of dispersed bitumen.

The Orimulsion® stock was shipped to our warehouse facility from Bathurst, New Brunswick in a 45-gallon polyethylene drum. The contents of the drum were mixed by manually rolling the drum for ~500 revolutions at a rate of ~ 12 revolutions per minute, with direction of revolution reversed at 12 second intervals. The mixing process was carried out prior to any sub-sampling of the stock Orimulsion®. A commercially available molasses gate was installed on the drum to facilitate withdrawal of Orimulsion®.

Artificial seawater was prepared from Instant Ocean, a commercially available formulation for saltwater aquarium systems, and was mixed to 34 ppt weight/volume. Resulting solutions were not 34 ppt salinity as measured through conductivity, more typically in the range of 26 ppt. Seawater in the locale of the warehouse facility, from Patricia Bay, was measured at 25.5 ppt at 8 C. It is speculated that the Instant Ocean formulation contains non-dissociative components.

Previous work (Harper *et al* 2002) involving the production of Orimulsion® dispersions noted some trends of the behaviour of dispersed bitumen. Dispersions in water alone are reasonably stable, with the majority of bitumen remaining in suspension for several days. Dispersions in 33 ppt weight/volume non-iodized NaCl solution are also fairly stable, with coalescence of the majority of suspended bitumen into thin films on the surface occurring over a period of several days. Dispersions in iodized NaCl solutions appeared to be slightly less stable. Dispersions in 33 ppt weight/volume Instant Ocean solutions were more difficult to produce, with even minor mixing energy required to disperse the Orimulsion® causing coalescence of bitumen particles into globules and thread-like strings that readily formed viscous, adhesive masses on the surface.

It was postulated that the artificial seawater formulation contained a component that directly interfered with the surfactant used in the Orimulsion® oil-in-water emulsion. However, attempts to produce dispersions in natural seawater (Patricia Bay) yielded similar results. The possibility of contamination or degradation of the original Orimulsion® supplied was investigated. It was theorized that bio-degradation would result in measurable changes in pH. A sample submitted to Cavendish Labs had a pH of 9.89. Environment Canada confirmed that this was a typical reading and no biodegradation of the formulation had occurred. It was concluded that the behaviour of Orimulsion® dispersions in seawater was influenced by several factors, and further investigation was outside the scope of this project. Although it was desirable to investigate the behaviour of Orimulsion® or bitumen under conditions simulating the marine environment as closely as possible, the variable nature and instability of the artificial and nature seawater dispersions suggested greater consistency could be achieved using non-iodized NaCl solutions to approximate seawater.

Small batches of 1:1,000 dilution of Orimulsion® were prepared in a 20 L container, (fitted with a standpipe, ruler, drain tube and ball valve) immediately prior to use. Saltwater was prepared by dissolving 660 g of non-iodized NaCl in 20 L of water, and aerating using compressed air for 2 hours. 20 mL of well-mixed Orimulsion® stock were delivered from a 50 mL syringe, manually stirring with an aluminum rod, with minimal mixing energy. A 100 mL sample was withdrawn from this initial dispersion, for bitumen concentration determination via DCM extraction.

D2.0 Dispersed Bitumen Application/Loading Procedure

Test containers were loaded with selected sediment. The sediment was wetted, to simulate stranding on a falling tide, by filling the container from the top with Instant Ocean artificial seawater, to just above (~ 1 mm) the highest point of sediment. The 20 L container of the freshly-prepared 1:1,000 dispersion was positioned above the test bucket to permit gravity feed of the stock dispersion onto the test sediment surface layer. 3.0 L of the dispersion was applied at a flow rate of ~50 mL/sec so as not to disturb the surface layer of sediment. Samples (100 mL volume) of stock dispersion were taken between the application procedure on pairs of test containers, and following the last application, as well.

Immediately after the application of the dispersion, the ball valves at the base of the test bucket were opened to allow the dispersion to drain through the sediment at ~2.5 cm depth/min to simulate tidal fall rates. The fall rate was monitored using the transparent standpipe and ruler, and the ball valve adjusted to control the flow if necessary. When the level of seawater-dispersion mixture in the container had dropped to ~15 cm above the base of the bucket, a 250 mL sample of effluent was collected.

Following completion of the treatment scheme, test containers were frozen, sediment plugs were removed from the buckets, and selected layers within the sediment column were sub-sampled, to be analyzed for bitumen retention. Sample weights collected were in the range of ~1kg for granules and pebbles, and ~2 kg for cobbles.

D3.0 Bitumen Concentration Determination

Levels of bitumen were determined , by gravimetric methods using a solvent extraction technique for both aqueous mixtures and oiled sediments. Dichloromethane (DCM) extraction was the recommended procedure. Spectrophotometric/pesticide residue analysis grade DCM was used for the extractions. Extractions were carried out in a fume hood, and standard precautions (e.g. polyethylene gloves used instead of the more permeable latex or vinyl ones) were used to ensure safe handling and absolute minimal exposure to the toxic chlorinated hydrocarbon solvent or extracts.

D3.1 Aqueous Dispersed Bitumen Suspensions

A known weight or volume (typically 100-250 mL) of aqueous sample was transferred to a clean, solvent-rinsed 250-mL separatory funnel, using small rinses (3x3mL) to transfer any traces of bitumen adhering to the sample collection beaker. The contents of the separatory funnel were washed with successive aliquots (5x10 mL) of DCM, with shaking, and careful venting to

prevent loss of contents. The DCM extract volumes were drained from the funnel and collected in a clean, solvent-rinsed 100 mL beaker. The fifth aliquot of DCM was usually clear and colourless, occasionally with a very faint straw colour, indicating virtually complete extraction of bitumen. The remaining aqueous portion of the sample was poured into a glass waste container with polyethylene fiber/felt oil-and-grease sorbent pads to remove traces of DCM prior to disposal. The DCM extract was transferred to a clean separatory funnel, and back-washed with clean, fresh water to remove concomitant salt. The washed extract was transferred to a labeled, pre-weighed (to 0.1 mg) aluminum evaporating dish. Evaporation of the DCM solvent was assisted by very gentle warming, placing the evaporating dishes on a tray above a hot-water (~40 C) bath. The dishes, with bitumen residues were dried overnight (15 hours) at 70 C. The aluminum dishes were re-weighed to determine the weight (to 0.1 mg) of bitumen residue.

A 250-mL sample of 33 ppt weight/volume non-iodized NaCl solution was used as a blank control. Extraction by the method described above, but without back-washing the DCM extract with fresh water, resulted in 0.3 mg of solvent -extractable materials (NaCl). This translates to 1.2 ppm as the threshold of detection for bitumen by this method, actual limit is slightly lower, as concomitant salt is removed from extracts through back-washing. Presence of trace amounts of bitumen, <1.0 ppm, could be easily determined visually in the DCM extract, as a pale straw colour.

D3.2 Oiled Sediment Samples

Sediments from the test containers were collected in labeled, pre-weighed, heavy-duty, re-sealable (zip-loc) polyethylene storage bags; bag and contents re-weighed (to 0.05 g) to calculate a wet sediment weight. It proved convenient and effective to extract the sediments directly, as contained within the bags. This simple version of the extraction procedure, as modified from the procedure recommended by the scientific authority, did not require specialized equipment or complex laboratory apparatus, and reduced sample handling.

Aliquots (15-25 mL) of DCM were poured directly into the sample bags, which were then sealed, pressing to remove air. Removal of air at this stage allowed for expansion of the bag in the next step, due to the high vapor pressure of DCM. The sediment -solvent mixture was mixed by manually rolling (directionally random, "bean-bag style") for 1 minute. The sample bags were then carefully opened and the DCM extract was drained into a clean, solvent-rinsed 100 mL beaker. This process was repeated until the DCM extract was colourless; five aliquots were usually sufficient for the bitumen levels (<50 mg/kg) encountered in this experiment. Unused, empty sample bags were also "extracted" to give a blank. Preliminary work used unoiled, dry granule sediment as a reference blank.

The DCM-bitumen extract was transferred to a labeled, pre-weighed (to 0.1 mg) aluminum evaporating dish. Evaporation of the DCM solvent was assisted by very gentle warming, placing the evaporating dishes on a tray above a hot-water (~40° C) bath. The dishes, with bitumen residues were dried overnight (15 hours) at 70° C. The aluminum dishes were re-weighed to determine the weight (to 0.1 mg) of bitumen residue. Blank sample bags yielded on average 2.8 mg of solvent-extractable materials. Blank dry sediments yielded on average 4.1 mg on ~0.5 kg sample, fine particulates visible.

According to the recommended procedure, the combined DCM extract normally would be filtered to remove particulates. These fines may be pre-existing, or generated through the sample manipulation (especially cobble clasts). Preliminary range-finding showed that thoroughly wet sediments (drained, not dripping) treated with this procedure produced negligible (<2 mg) particulates. This was determined by extracting clean sediment wetted with artificial seawater, and evaporating the unfiltered DCM extract. Extraction of dry cobble sediments, however, typically produced ~10 mg of particulates. This difference may be due to preferential aqueous wetting of sediment and fines; fines held in the aqueous phase are less likely to transfer to the organic phase. Previous work (Harper *et al* 2002) with DCM-bitumen extracts that involved filtering was found to introduce appreciable, variable losses of bitumen on filters and associated apparatus. These losses were due to capillary action/"wicking" of the extract to the upper edge of the filter, and the frequent formation of DCM "frost" which exacerbates upward movement of bitumen. For this project, a compromise was devised: minimize fines transfer by extracting wet sediments, minimize bitumen losses by not filtering, and accept a slightly higher limit of bitumen detection due to small amount of concomitant particulates.

The threshold of bitumen determination using this method is ~3 mg by weight, which translates as 1.5 ppm on a 2 kg sample.

D4.0 Retention and Penetration

Preliminary range-finding showed very high penetration levels even on the least permeable granule sediment. Bitumen dispersion was clearly evident in the effluent from the test buckets (3 L of 1:1,000 dispersion initially applied). Bitumen concentration of the effluent, as determined by DCM extraction, ranged from ~100 - 300 ppm, after passing through a sediment depth of 30 cm, including a 5-cm thick sand filter.

General trends for retention of bitumen on granule sediment were investigated, by applying 3 L of 1:1,000 dispersion to sediment surface at water level, then allowing the water level to fall at a typical rate, completely draining the test container. Representative sub-samples in triplicate of 500-800 g, were taken from layers at specific depths below the sediment surface. These layers were designated as surface, shallow subsurface, deep subsurface, and filter sand. Bitumen retention was gravimetrically determined through the DCM extraction procedure. Figure D-1 shows the results for a preliminary test using NaCl solution as the tide water.

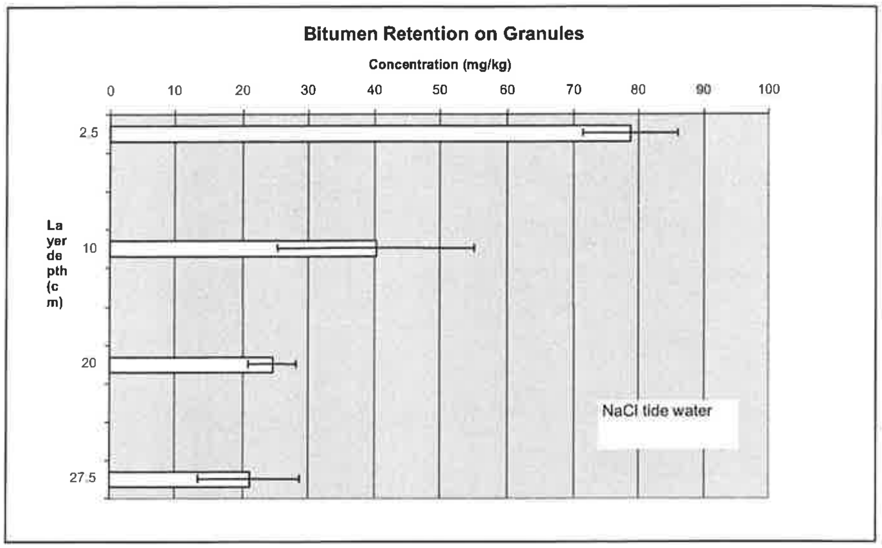

Figure D-1 Plot of dispersed bitumen retention at various levels within the test column.

Results for the treatments are presented in Section 3.2.

Appendix E

Electronic Files

FOLDER	FILE	FORMAT	DESCRIPTION
report	OreSedRpt9.doc	MSWord97	Full Report
Appendix A	Buckets2.xls	MSExcel97	Raw data + charts
Appendix B	Grainsize.xls	"	
	Layers.xls	"	Sediment specs
Appendix C	Viscosity.doc	MSWord97	Masciolangi report
	PH_tests.xls	MSExcel97	
	Pre_postdensity	"	
	Displacment1	"	
	Penetration	"	
	Series1	"	0tide
	Series2	"	4tideupper
	Series3	"	4tidelower
	Series4	"	0tidehot
	Series4temp	"	Layer temp.
	Series5	"	0tidecold
Appendix D	Dispersed.xls	"	Data+charts
Photos	xxx.jpg	Image file	Digital photos
	Photlog1.mdb	MSAccess97	database
Figures	xxx.jpg	Image files	Pictures imbedded as figures in the report.