Dilbit Crude Oil Weathering on Brackish Water: Meso-scale Tests of Behavior and Spill Countermeasures

Elliott Taylor[1], Greg Challenger[1], Jose Rios[1], Jim Morris[2], M.W. McCarthy[3], Colin Brown[4]
[1]Polaris Applied Sciences, Inc., Bainbridge Island, WA, USA
(ETaylor@PolarisAppliedSciences.com)
[2]Witt-O'Brien's, Seattle, WA, USA
[3]Mac McCarthy, Inc., Edmonds, WA, USA
[4] Colpat Pipeline Consulting Inc., Sherwood Park, Alberta, Canada

Abstract

Oil weathering and countermeasures testing was conducted with Cold Lake Blend (CLB) and Access Western Blend (AWB) dilbits from May 13 through May 26, 2013 at the Kinder Morgan/TransMountain Pipeline pump station in Gainford, Alberta. Based on visual observations, both dilbits exhibited properties that one would expect of a heavy, "conventional" crude oil. In no instance was any oil observed to have sunk. Densities increased as oil weathered approaching and, in some cases, exceeded 1000 kg/m^3. Viscosities increased rapidly with weathering exceeding 10,000cP within 24 hours for both dilbits exposed to moderate agitation. Visual observations of the surface of the oil in the various tanks showed that a crust formed as the oil weathered. Chemical analyses of the weathered oils and water column showed that concentrations of BTEX diminished rapidly although TPH values in the water column were variable and dependent on the degree of surface agitation.

Countermeasures tested included dispersant application, burning, shoreline cleaners, and skimmers. Visual observations of the dispersant test revealed that Corexit 9500 was marginally effective on 6-hour weathered oil and not particularly effective for more weathered dilbit. The test burn on 6-hour weathered oil was effective with a sustained burn and an estimated 70% oil combusted. Estimates show that approximately 50% of 24-hour weathered oil was burned, but only after sustained effort to ignite. The 72-hour weathered oil was not successfully ignited. Cleaning tests showed that removal of oil that had weathered for five days on water and then remained on tiles and exposed to air for four days was still effective when washing substrate treated with Corexit 9580. The time oil weathered on water before being placed on the tile was less important than the time the weathered oil was exposed to air. The three brush skimmers tested effectively recovered dilbit throughout the oil weathering tests.

1. Introduction

The oil properties and behavior of diluted Alberta oil sands bitumen are of interest to spill modelers, transportation and handling operators, environmental scientists, and spill responders as proposed pipeline expansion programs are underway for delivery of these crude oils to export destinations. Oil sands bitumens are blended with diluents to meet pipeline export specifications. These blends (dilbits) meet specific oil export tariffs and must fall within a defined range of density (not to exceed 940 kg/m^3 and viscosity (not to exceed 350 centistokes (cSt)) at reference temperatures. The blend is a single-phase liquid with its own unique properties; dilbit crude oil is not bitumen in suspension, in emulsion, or a two-phase liquid.

Although dilbits have been transported via pipeline for the past 30 years, and their general properties are akin to other heavy oils, the specific characteristics and behaviors of these oils as they weather have been the subject of a limited number of published studies. Tests conducted by Brown and Nicholson (1991) and Brown et al. (1992) documented the evaporative loss of CLB for summer and winter blends and the evaporative loss from four types of shoreline material, ranging from approximately 1 to 9 percent of 24-hour weathered oil, respectively. SL Ross (2010) evaluated the physical properties of two dilbit products to generate the necessary parameters for marine oil spill modeling. The products tested were MacKay River Heavy Bitumen diluted with synthetic crude (Suncor Synthetic Light) and Cold Lake bitumen diluted with condensate. The 2010 report noted that test oils were placed in a wind tunnel to generate evaporated oil products under controlled conditions and to measure the changes in physical properties. Results showed that all oils, with the exception of the MacKay River blend, had densities less than one when evaporated. The MacKay River blend densities remained lighter than standard seawater throughout the evaporation tests. Subsequently, SL Ross (2011) undertook a series of meso-scale tests using a circulating loop (flume) to assess the behavior of CLB dilbit under more natural weathering conditions in freshwater. Weathered dilbit continued to float on the freshwater surface in the flume during the full 13 days of testing.

2. Study Objectives and Design

In 2013, Kinder Morgan Canada, Inc. (KMC) undertook an initiative to expand upon previous studies through larger, meso-scale tests of dilbit crude oil (Witt O'Briens et al., 2013). Larger tank tests allow for simulated conditions that may be more typical of the marine setting of Burrard Inlet, the export point for dilbit from the Trans Mountain Pipeline (TMPL).

The overall study goal was to better understand and assess oil behavior, weathering, and oil spill response (OSR) countermeasures for spilled dilbit crude in a controlled simulated condition similar to the potential receiving environment of Burrard Inlet. The objectives of the applied research were multifaceted. One objective was to better understand and characterize the changes in physical and chemical properties of dilbit in an estuarine simulated condition over a 10-day period. Tanks tests done shortly following this present study, using synthetically weathered dilbit, are reported in Environment Canada et al. (2013) for marine conditions (salinities of 20 to 30 ppt). Another objective of the meso-scale trials was to determine the efficiency and effectiveness of dispersant, in-situ burning, and shoreline cleaning agents as potential countermeasures for various stages of weathered oil. The third objective of the study was to test various types of oil spill response skimmers under similar weathering conditions and to assess their efficiencies over time.

A Cold Lake Winter Blend (CLWB) dilbit was selected to provide a "standard" dilbit, with the winter blend representing more diluent initially. The slightly higher diluent is expected to result in higher hydrocarbon flux to atmosphere and to the water column (dissolution of acutely toxic low molecular weight hydrocarbons). The summer blend has fewer lighter end hydrocarbons and hence a slightly higher initial density than CLWB. More research has been completed with CLB dilbit than other blends; thus, it was expected that results from these tests would provide a basis for comparison with a broader range of prior research.

Winter specification Access Western Blend (AWB), a dilbit from the Athabasca region south of Fort McMurray, Alberta, was the second oil tested for physical and chemical properties under similar weathering scenarios as the tests on CLWB.

3. Methods

The CLWB and AWB studies were conducted from May 13 through May 26, 2013 at the TMPL pump station in Gainford, Alberta. The Gainford site was divided into several distinct research areas:

- Scientific study for CLWB, located outdoors (Figures 1 and 2);
- Scientific study for AWB, located under cover;
- Equipment testing for CLWB, located outdoors (Figure 1); and
- In-situ burning test site located in a close but safe distance from the rest of the research areas.

3.1 Oil Weathering

The scientific study tanks were filled with water at a prepared salinity, using SolarSalt, of 20 ppt. Water temperature, pH, and salinity were monitored twice daily in all of the science tanks. During the first two days of weathering, all CLWB tanks were directly exposed to wind (carrying visible amounts of dust) and direct sunlight. The night of May 17 (after approximately 48 hours of weathering without cover), these tanks were covered with a tent (Figure 2) in preparation for forecasted windy and rainy weather.

Air monitoring was carried out, for occupational safety purposes, during field testing operations. Benzene levels were within tolerances for half-face (cartridge) respirators and were required for all personnel working with the oil indoors or working directly with the oil in tanks. The only alarm activation occurred when a worker stepped immediately downwind of the exhaust from a skimmer power pack.

Tanks S1 through S3 were used for AWB weathering. The CLWB weathering was conducted in an industrial tank, shown on the left picture in Figure 1, divided into three rectangular areas: S9A, S9B, and S9C. Tanks S9A and S9C were rectangular surface tanks (2.97 m^2) inside S9B (18.58 m^2). Tank S4, measuring 1 m by 1 m, was located outside, uncovered, and was used to weather CLWB for countermeasures testing. Table 1 summarizes the dimensions of these tanks and includes the volume of spilled oil and estimated initial oil thickness.

Table 1. Tanks and oil characteristics

Tank I.D.	Tank dimensions (shape)	Water depth	Type of Dilbit	Oil spill quantity (Liters)	Initial Oil Thickness (mm)	Imposed weathering conditions
S1	2.38 m^2 x 2.13 m (Cylinder)	1.9 m	AWB	25	10.68	Static
S2	2.35 m^2 x 2.13 m (Cylinder)	1.9 m	AWB	25	10.80	Mild
S3	2.38 m^2 x 2.13 m (Cylinder)	1.9 m	AWB	25	10.68	Moderate
S4	1.49 m^2 x 1.22 m (Cube)	1 m	CLWB	20	13.46	Mild (outside)
S9A	2.97 m^2 x 1.4 m (Rectangular)	1.2 m	CLWB	30	10.09	Moderate
S9B	55.02 m^2 x 1.4 m (Rectangular)	1.2 m	CLWB	148	11.71	Static
S9C	2.97 m^2 x 1.4 m (Rectangular)	1.2 m	CLWB	30	10.09	Mild

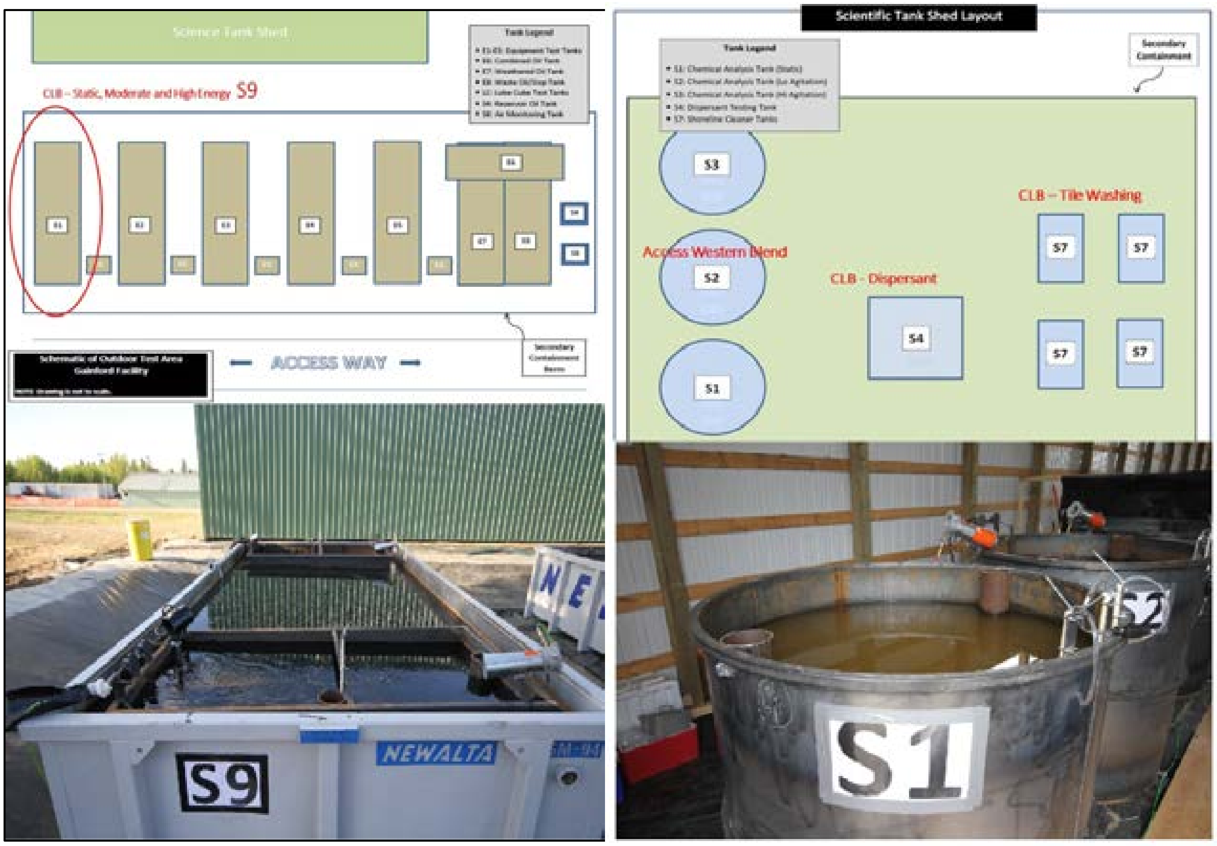

Figure 1. Tanks S9A, S9B, and S9C (left) and AWB tanks S1, S2, and S3 (right)

Figure 2. Tanks S9A, S9B, and S9C covered with tent

Each type of oil (CLWB and AWB) was exposed to three weathering conditions (wind and agitation) (Table 2):

- Static Conditions: No agitation induced. Wind exposure was minimized as far as was practical.
- Mild Agitation: Low imposed wind and wave conditions induced by simple mechanical means through intrinsically safe fans and a paddle mechanism.

- Moderate Agitation: Greater induced wind and wave agitation.

Table 2. Conditions imposed on each tank

Tank #	Dilbit Type	Agitation	Average T (Max and Min)	Average Salinity (Max and Min)	Average pH (Max and Min)
S1	AWB	Static – no agitation	15.9 (19 – 14)	20.6 (22 – 20)	7.5 (8.0 – 7.0)
S2	AWB	Mild – avg. wavelets height approx. 2 cm – 4 cm; avg. wind 5 mph (2.23 m/s)	14.3 (16 – 13)	21 (22 – 20)	7.5 (8.0 – 7.0)
S3	AWB	Moderate – avg. wavelets height approx. 5 cm – 7 cm; avg. wind 10 mph (4.5 m/s)	11.7 (16 – 10)	21.6 (23 – 20)	7.7 (9.0 – 7.0)
S4	CLWB	Mild – avg. wavelets height approx. 2 cm – 4 cm; avg. wind 5 mph (2.2 m/s)	16.1 (19 – 13)	22.5 (24 – 20)	7.6 (9.0 – 7.0)
S9A	CLWB	Moderate – avg. wavelets height approx. 5 cm – 7 cm; avg. wind 10 mph (4.5 m/s)	15.2 (23 – 9.3)	22.3 (24 – 20)	7.6 (8.5 – 7.0)
S9B	CLWB	Static – no agitation	14.9 (22 – 9)	21.2 (22 – 20)	7.5 (8.0 – 7.0)
S9C	CLWB	Mild – avg. wavelets height approx. 2 cm – 4 cm; avg. wind 5 mph (2.2 m/s)	15.1 (22 – 9.6)	21.7 (23 – 20)	7.5 (8.0 – 7.0)

Oil was applied to achieve approximately 1 cm slick thickness at the moment released (prior to evaporation or weathering processes). Containment by the tank configuration limited what would be the natural spread of oil in an unconfined condition, creating a thick slick similar to a confined spill, thus representing a case for slower evaporation rates with possible increased exposure to light ends, and potentially greater dissolution of hydrocarbons into the water column under some conditions at least initially.

Sampling was conducted throughout the 10-day weathering period for both whole oil (surface layer oil sample) and the water column of each tank at frequencies indicated in Table 3. Water column samples were drawn from 0.5, 1, and 1.5 m depths from each of the AWB test tanks (S1 to S3) and at 0.5 for the CLWB tanks. Physical tests for whole oil and chemical tests for water column samples were conducted by Maxxam Analytics Inc. in Edmonton and Calgary, with test protocols as defined in Tables 4 and 5. During the 10-day experimental period, several probes using a weighted sorbent drop and an oil snare on the end of a hand tool were employed to ascertain if any oil had sunken to the bottom of the tanks. No evidence of sunken oil was found from these probes. Absorbent pads were submerged during the 10-days period in the AWB test tanks, but no sunken AWB oil was observed at the conclusion of the tests. Visual inspections were conducted of both AWB and CLWB test tanks when they were emptied and no oil was observed on the bottom of the tanks.

Source oil extracted from the reservoir tank (S4) was taken to small tanks for dispersant and shoreline cleaner tests, and to an outdoor tank for in-situ burning (ISB). While sampling for physical and chemical properties of oil and water was done for both CLWB and AWB, countermeasure tests were conducted only on CLWB oil.

Table 3. Sampling frequency and testing protocols used for oil and water column studies

Elapsed Time	Oil Properties	Water Column HC	CLWB - Field Dispersant Effectiveness	CLWB - ISB	CLWB Shore Cleaner
0 hr	√	√			
2 hrs	√	√			
4 hrs	√	√			
6 hrs	√	√	√	√	
12 hrs	√	√			
1 day	√	√	√	√	√
2 days	√	√			
3 days				√	√
4 days	√	√			
5 days					√
6 days	√	√			
8 days	√	√			
9 days	√	√			
10 days	√	√			

Table 4. Test procedures used to measure physical properties of oil and/or oil-water emulsion

Property	Test Temperature °C	Technique/Instrumentation	Procedure (Lab SOP)
Density	15	Anton Paar Densitometer (DMA 4500)	ASTM D5002 (PTC SOP-00100)
Viscosity	Variable: 5 to 80 °C	Anton Paar Viscometer (SVM 3000 Stabinger)	ASTM D341, D7042 (PTC SOP-00267)
Interfacial Tension	15	CSC DuNouy Ring Tensiometer	ASTM D971-99a
Pour Point	N/A	ASTM Test Jars and Thermometers	ASTM D97/ASTM D5853 (PTC SOP-00068)
Flash Point	N/A	Closed Cup Flash Tester	ASTM D93 (PTC SOP-00082)
Water Content	N/A	Karl-Fischer Titration	ASTM D1123/ASTM D4377 (PTC SOP-000167)
Dispersant Effectiveness	20	Swirling Flask	ASTM F2059

Table 5. Chemical analyses

Analysis	Procedure (Lab SOP)	Medium	Samples
BTEX (benzene, toluene, ethylbenzene, and xylenes)	EPA 8260 -HS GC/MS (AB SOP-00039)	Water	3 each 40 mL
Alkylated PAH/SVOCs	ESTD-OR-20/EPA 8270D –GC/MS (AB SOP-000037; CAL SOP-00250)	Water	2 each 250 mL
HC Light Ends (C1-C7)	ASTM D5580	Water	2 each 250 mL
Total petroleum hydrocarbons (TPH)	EPA 3550C SM 5520CF - IR (CAL SOP-00096)	Water	1 each 500 mL
HC (C1 thru C29) + BTEX	Modified ASTM D2887	Oil	1 L

3.2 Chemical Dispersant

Tank SD, built to the same dimensions as S4, was located under cover and filled with water prepared to a salinity of 35 ppt to simulate more oceanic conditions for the dispersant tests. Salt water was chosen to represent the most likely location for dispersant application approval as opposed to a brackish (Burrard Inlet) condition. A measured volume of weathered CLWB oil previously collected from Tank S4 was applied to the water surface and allowed to spread on the static water surface. A water sample was drawn from 1 m below the surface before and at approximately 20 minutes following oil application for hydrocarbon analysis. Dispersant (Corexit EC 9500A) was then applied directly to the oil on water at a 1:20 ratio from a handheld spray bottle. The tank was then provided with mild agitation (3cm to 5cm chop) to aid in dispersant mixing and penetration into the oil.

Visual and photographic documentation were obtained of the dispersant application. A third water sample was collected from 1 m below the surface at approximately 20 minutes following dispersant application for hydrocarbon analysis. Sorbent pads were used to collect all oil remaining on the water surface and clinging to the tank walls following dispersant application. Sorbents were weighed to gauge how much oil remained after dispersant application. Tank SD was then drained and cleaned immediately after each test in preparation for the next test.

3.3 Controlled Burns

Two liters of oil were collected from Tank S4 at each of the following weathering intervals: 6 hours, 1 day, 3 days, and 5 days. Burns were conducted under a specific Safety Plan, with a waiver for the burn ban in place at the time, and with local fire department personnel and equipment on site. The outdoor burn basin consisted of an open top tank filled with freshwater, 3 m in diameter, and in which a 50 cm diameter steel ring was positioned on blocks such that the ring provided approximately 5 cm of freeboard above the water line. The 2 L weathered oil sample jars were weighed, then oil was slowly poured into the ring, and the empty containers with “clingage” were re-weighed.

Burn ignition was aided with diesel and a hand-held propane torch. More weathered oils (Day 1 and Day 3) required re-starts, for which additional diesel starter was added; an ISB test was not conducted on the Day 5 sample given the challenge of igniting the Day 3 sample. Data recorded during the burns included air temperature, water temperature, average wind speed (including peak gusts), and time of burn. Following the burn test, oil was collected using sorbents and weighed to provide an indication of the amount of oil remaining. A minor quantity of small (generally less than 3 mm) oil particulates and droplets were not recovered with sorbent pads.

3.4 Substrate Washing

A series of surface washing tests using shoreline cleaning agents were conducted on the rough surface of untreated granite tiles, oiled by hand with CLWB collected after 1 day, 3 days, and 5 days of weathering in Tank S4 (Figure 1, Tank S7). Shoreline cleaners, also known as surface washing agents or beach cleaners, are chemical agents applied to oil that are stranded on shoreline substrates, with the intent to lift oil off the substrate for subsequent containment and recovery. Weathered CLWB dilbit from Tank S4 was poured onto each of six 30.5 by 15.2 cm (12 in. by 6 in.), light colored, porous (not polished) granite tiles by hand such that the oil covered an entire side of the tile evenly with an oil coat (0.01 to 0.1 cm) as defined by Shoreline

Cleanup Assessment Technique (SCAT) standard terminology. Once oiled, tiles were allowed to stand in shade and/or sun, tilted at approximately 45 degrees, from 24 to 144 hours before treatment (Table 3). Oil thickness was estimated by running a thin piece of rigid waterproof paper through the oil and examining the oiled band on the paper against a graduated scale (Figure 4). This process was repeated with oil weathered on water for 72 hours (3 days) and 96 hours (5 days; Table 3). Air temperatures throughout the experiment ranged from 10°C at night to a maximum of 23°C during the day.

Tiles were treated with two agents: an off-the-shelf degreaser containing D-limonene, and Corexit 9580, a shoreline cleaning agent. Commercial D-Limonene was unavailable and the results should not be compared to other surface washing tests using commercial D-Limonene. The application rates used are those recommended by the US Environmental Protection Agency (EPA) for shoreline treatment with Corexit 9580. The application ratio tested was the recommended dosage of approximately 1 US gallon per 100 square feet (0.41 L/m^2) or 1.3 ounces (approximately 37 mL) per tile. The application volume was tested with the spray bottle to estimate the number of hand sprays that equals 1.3 ounces (≅37 mL).

A photograph of each tile was taken before and after treatment and compared to untreated wet tiles. For each test condition there was a reference tile with no shoreline cleaning agent and a tile with each of the cleaning agents.

The treatment consisted of ambient temperature freshwater run through a power washer adjusted to the lowest pressure available, and fitted with a fan tip to distribute the water to approximately 25 cm wide, or the width of the tile being cleaned. The tip was maintained by a governor at 22.5 cm from the tile surface (Figure 4). The pressure from the tip was consistent with a garden hose (0.21 – 0.31 megapascal (MPa); 30-45 pounds per square inch (psi)) and was safe for contact with human skin at 22.5 cm with no adverse effects. The treatment proceeded for 30 seconds (approximately 11 passes with the wand) and used approximately 3 L of water.

Observations included standard SCAT terminology for oil remaining on tile, oil removed in water, nature of oil removed in water (sinking, floating, color, character, adherence to sorbent materials), whether the cleaned tile produces sheen, and ease with which additional oil wiped off with casual contact and sorbent.

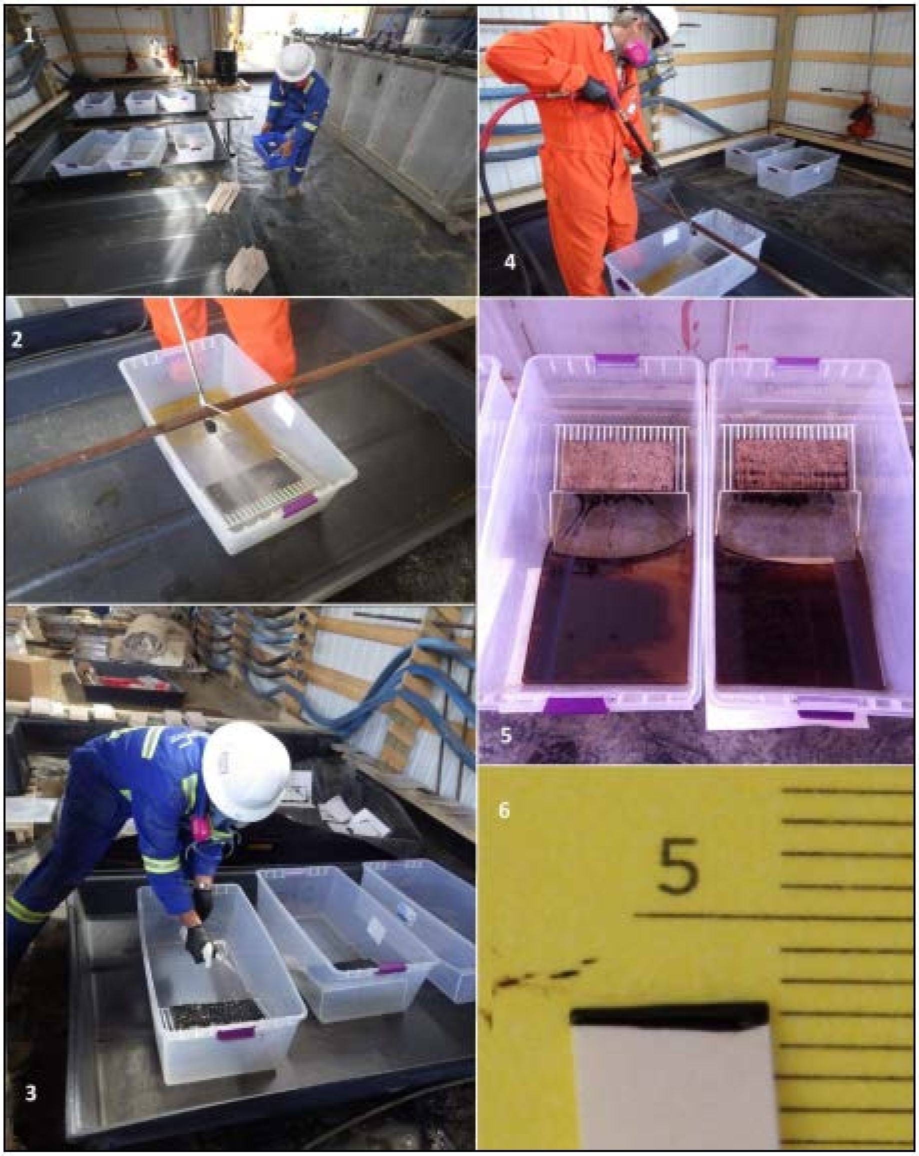

Figure 4. Surface washing test area; 2) Apparatus for consistent wash distance and pressure; 3) Applying Corexit 9580; 4) Washing; 5) Post-wash results on side pre-wet and pre-dry tiles; 6) Example measure of oil thickness on tile (lines are 1mm apart)

3.5 Equipment Testing

Skimmer manufacturers were offered the opportunity to test their equipment for dilbit recovery under consistent operating conditions and measurement procedures guided by ASTM standards:

- F-631:Standard Guide for Collecting Skimmer Performance Data in Controlled Environments
- F-2008:Standard Guide for Qualitative Observations of Skimmer Performance
- F2709-08: Standard Test Method for Determining Nameplate Recovery Rate of Stationary Oil Skimmer Systems

To allow vendors to correctly configure power units, check hose connections, and ensure operability prior to test commencement, vendors were given the opportunity to calibrate their equipment with the water of their respective tanks prior to the discharge of any oil.

Oil was discharged into the test tanks on May 13 and the subsequent tests followed the protocol as detailed below:

1. The oil was allowed to stand for 4 hours prior to skimmer testing to reduce the combustible gas and benzene levels.
2. Skimmer discharge lines were plumbed so that the recovered liquids could be diverted to either a calibration cube or to the common waste tank (E6). After achieving steady state operation in the discharged oil, the subject skimmer effluent was diverted from the common waste tank (E6) to the calibration cube for a specified time (initially 30 seconds but modified in later test periods to a full 4 minutes; see modification 1 below).
3. The product in the calibration cube was allowed to settle for approximately one day after which the total liquid volume was measured. The cube was then decanted of free water. Once the water was removed, the volume of the cube was again measured. An oil sample was then taken from the calibration cube sample tap and analyzed offsite for water content according to Karl-Fischer Titration procedures (ASTM D1123). The volumetric measurements were then used to determine the skimmer's recovery capacity and efficiency.
4. The fluids accumulated in the common waste tank (E6) were allowed to settle for approximately one day. Thereafter, the water was decanted, and the remaining emulsion was gravity fed in equal amounts back to the test tanks. This procedure provided each of the skimmers with a common starting point for the next test in the sequence (see modification 2 below).

In accordance with the plan, these procedures were repeated on Day 3 (~48 hours after the initial oil release); Day 5 (~96 hours); Day 7 (~144 hours); and Day 9 (~192 hours). On Day 10 (~240 hours), the last test day, a final test was conducted with skimmers exercised in tank E7, the weathered oil tank. The weathered oil tank (E7) was charged with 625 L (165 US gallons) of CLWB and left undisturbed for ten days. Originally, this last day test with 10 day weathered oil was to be a "Best in Show" exercise; however, this test was also modified (see modification 3 below) to better reflect evolving conditions.

3.5.1 Test Modifications Made During the Test Period:

Modification 1 - Discharge Time to the Calibration Cube: The initial plan called for all tests to be conducted for 30 seconds. This duration was based on ASTM guidance and the concern that the 1 m^3 calibration cube capacity would be exceeded. After the first day of testing concluded, it was determined that the calibration cubes had sufficient capacity and that the tests could be run for longer durations. On the second round of equipment tests (Day 3; ~48 hours), it was mutually agreed that the skimmers would run for 4 minutes after achieving steady state operation. This modification to the testing procedure remained consistent for the subsequent five tests.

Modification 2 - Common Waste Tank: After the first day of testing it was determined that diverting oil to the common waste tank, settling the liquids, and then redistributing that oil back to the test tanks was laborious and offered no benefit to the test. Therefore, a second protocol modification was made such that skimmer discharge – prior to its diversion to the calibration cube – would no longer be directed to E6, but would simply be recirculated back to the source tank.

Modification 3 - Last Test Day: The last test day was modified such that any vendor who wished to test their skimmer in tank E7 (10 day weathered CLWB) would be given that opportunity.

3.5.2 Equipment Used

The following skimmer systems were tested:

- The Aquaguard RBS Triton 60 DI3 - a brush skimmer driven by a diesel/hydraulic power pack.
- The Desmi DBD-5 system - a diesel/hydraulic powered skimmer fitted with an oleophilic brush-drum assembly.
- The Lamor MultiMax LAM 50/3C Brush Skimmer - a conveyor belt type oil skimmer with three stiff-brush-chains

4. Results

4.1 Oil Properties

Changes in the physical properties of AWB and CLWB dilbits were similar throughout the 10-day trials. Increased agitation (wave paddle and wind) yielded slightly faster weathering rates as revealed in oil densities (Figure 5). Initial oil densities of 921 kg/m^3 and 925 kg/m^3 of the AWB and CLWB dilbits, respectively, increased to greater than 980 kg/m^3 within approximately 24 to 48 hours of weathering in all cases in which agitation was applied. Relative densities continued to increase with further weathering albeit at a slower rate.

Oil and emulsion viscosities increased for both AWB and CLWB dilbits within the first 24 to 48 hours, factors that influence oil behavior on water and potentially affect oil skimming and pumping systems. AWB dilbit under moderate agitation showed the most pronounced initial increase in viscosity (Figure 6), increasing from an initial value of less than 1000 cSt to over 10,000 cSt within a 4- to 6-hour window. CLWB dilbit under moderate agitation reached 10,000 cSt at approximately 12 hours, whereas both dilbits, under mild agitation, required approximately 24 hours of weathering to achieve the same viscosity. Depending on the type of dilbit and agitation conditions, the viscosities of the emulsions continue to increase over time to the next order of magnitude, 100,000 cSt, after 4 to 8 days of weathering.

Tank S4 was used as a source of weathered oil for dispersant application, burning, and shore cleaning agent tests. With agitation conditions similar to Tank S2, the major difference between S2 and S4 was the location of S4 (exposed to sunlight and ambient atmospheric conditions). Absolute densities (at 15°C) exceeded 1000 kg/m^3 (freshwater) after weathering nine days, similar to Day 8 for the moderate agitation Tank S9A.

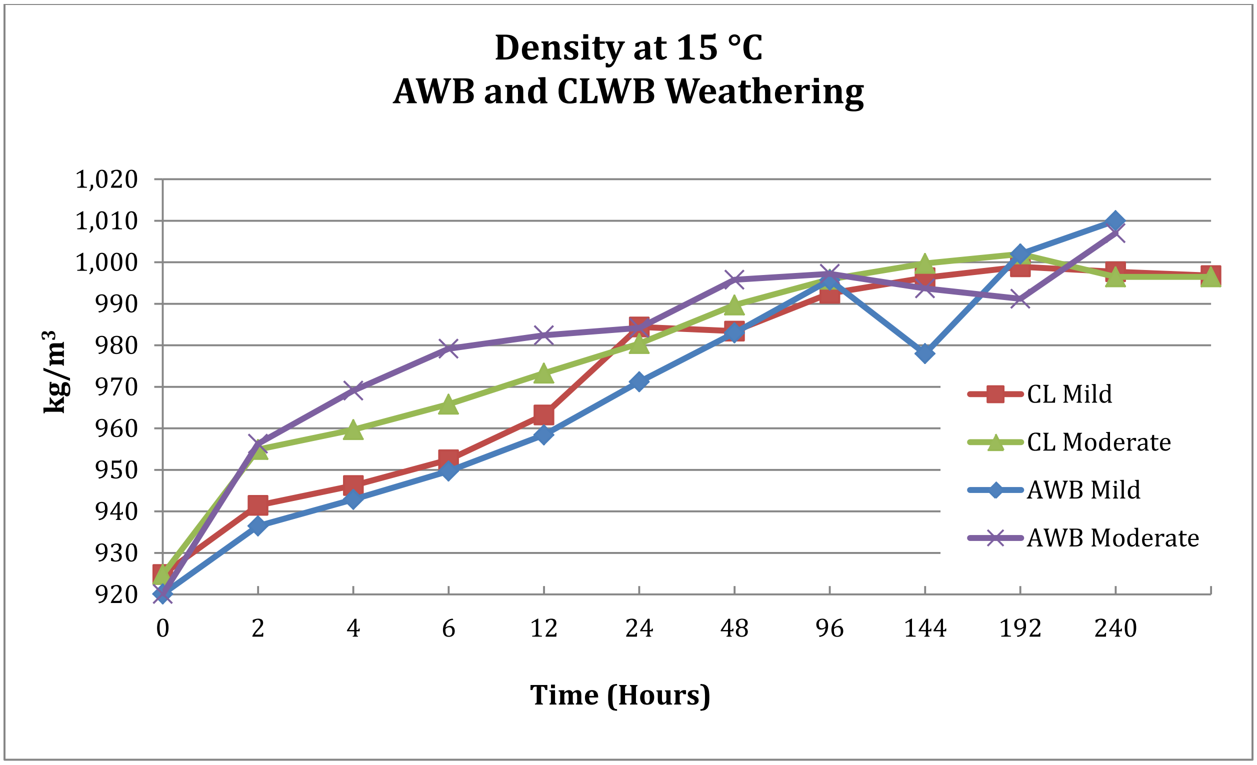

Figure 5. AWB and CLWB dilbit densities relative to degree of weathering

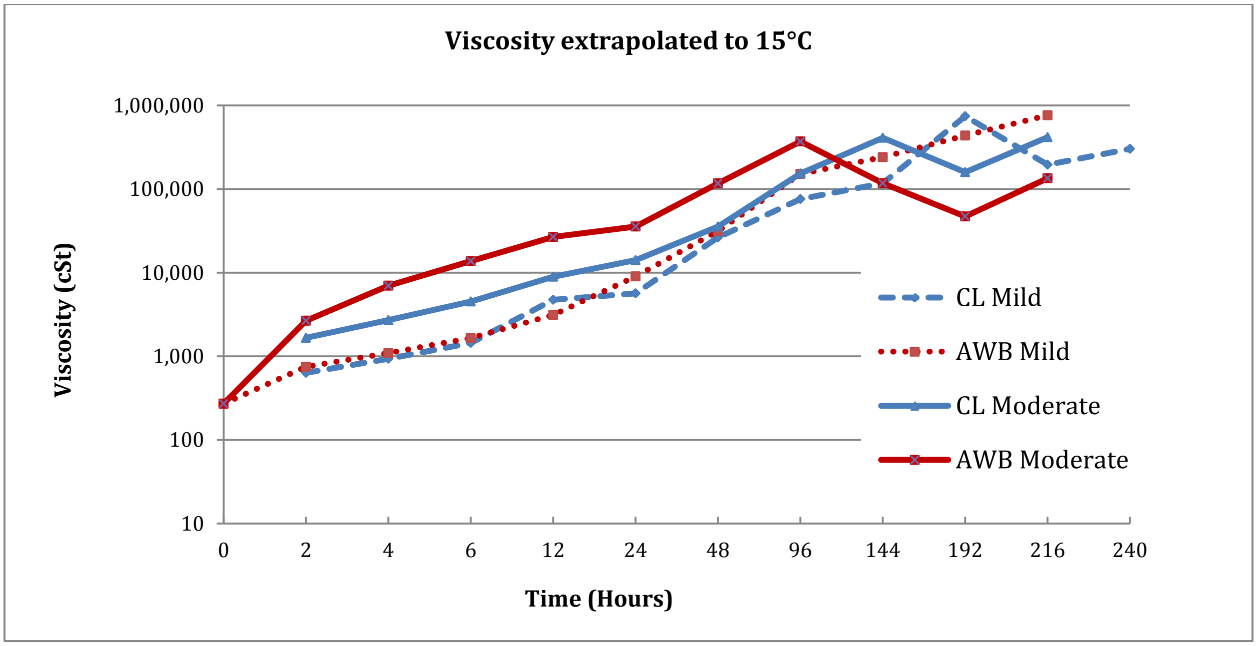

Figure 6. Viscosity of weathered AWB and CLWB dilbits under mild to moderate agitation

Both AWB and CLWB dilbits exhibited water uptake within the weathered oil matrix, although not as a stable, uniform emulsion but rather as a mechanically mixed and unstable oil-water combination. Water content analyses, conducted following procedures for whole oil, showed no systematic uptake or pattern for either oil during the weathering process. Given the unstable character of water in oil, sampling and sample processing may result in very different oil-water mixtures at the time of analyses; hence, no conclusions are drawn for those tests other than to note that the maximum water contents measured, above 40 percent, were noted on samples from three tanks (S3, S9A, and S4) with moderate and mild agitation, respectively, and after 1 to 3 days of weathering.

4.2 Oil and the Water Column

Oil distribution and partitioning into the water column are provided through TPH and BTEX analyses of water samples at specific depths below the water surface. The limited volume of water within each tank and the lack of any possible dilution, provides for very conservative measures of oil constituents in the water column relative to what may happen in open water conditions such as in Burrard Inlet. Total petroleum hydrocarbon (TPH) measured in the water columns of the AWB and CLWB dilbit tanks were in nearly all cases below detection thresholds (<2 mg/L) with the exception of tanks with moderate agitation (S3- AWB and S9A- CLWB). The highest TPH values measured were 120 mg/L at 1 m below the water surface from the CLWB dilbit and 60 mg/L at 50 cm below the water surface for AWB (Figure 7). By approximately 12 hours, all TPH values, regardless of depth in the water column or oil type, were near 10 mg/L in the tanks with moderate agitation.

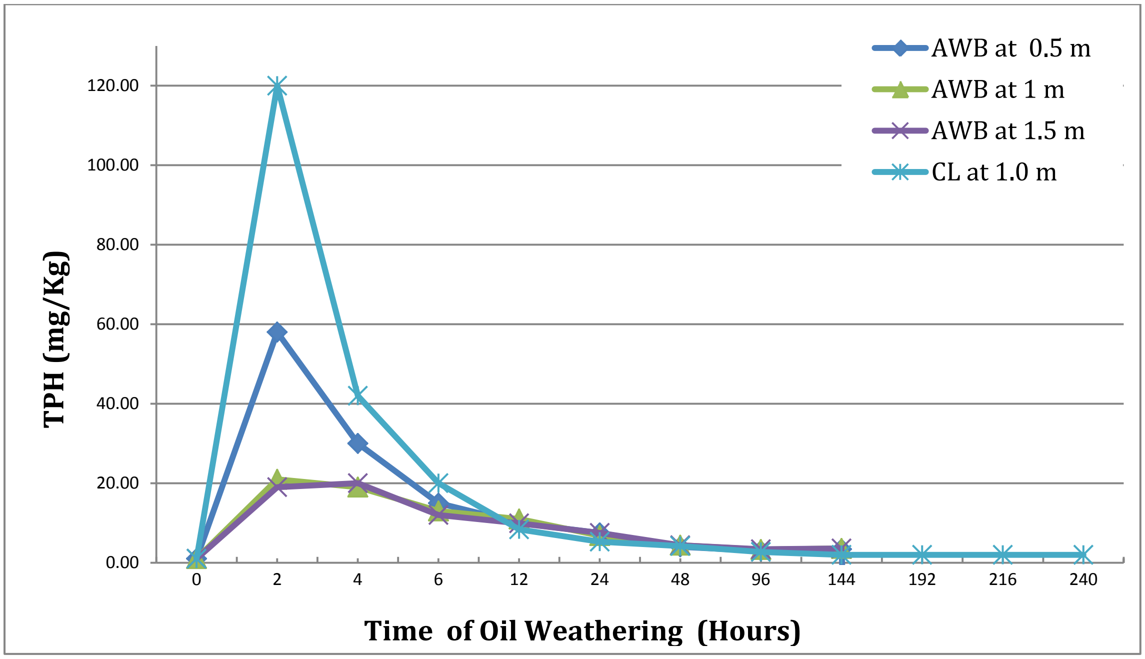

Figure 7. TPH in water column samples - AWB and CLWB weathering under moderate conditions

BTEX distribution into the water column was similar for both oils. In the static tests, dissolution of BTEX in the water column increased at 12 to 24 hours with maximum concentrations reaching approximately 900 micrograms per liter (µg/L) (∑ BTEX) at approximately 6 days. There was little evidence of a net loss of BTEX in the static water leading up to 10 days.

In mild wind and wave conditions, BTEX began to partition into the water column immediately reaching maximum ∑ BTEX concentrations of 1,200 µg/L (CLWB) to 1,500 µg/L (AWB) in 48 hours. Net loss of BTEX to volatilization was apparent at 48 hours with water concentrations dropping to less than 200 µg/L by 8 days.

In moderate wind and wave conditions, CLWB ∑BTEX reached 3,000 µg/L almost immediately followed by a net loss to <100 µg/L in 4 days. The AWB ∑BTEX reached maximum concentrations of approximately 1,700 µg/L after four hours followed by a slightly slower net loss to <200 µg/L after four days. It is possible that the CLWB tanks located outdoors resulted in more rapid net loss of BTEX compounds.

BTEX in the water column dissolves faster and is depleted in the water column with increased agitation (Figure 8 Tank S3 and Figure 9). These BTEX concentrations and the depletion rates shown are from the confined water in the tank below an artificially thick slick. Unconfined oil, mixing, and dilution would result in much faster depletion rates and lower concentrations.

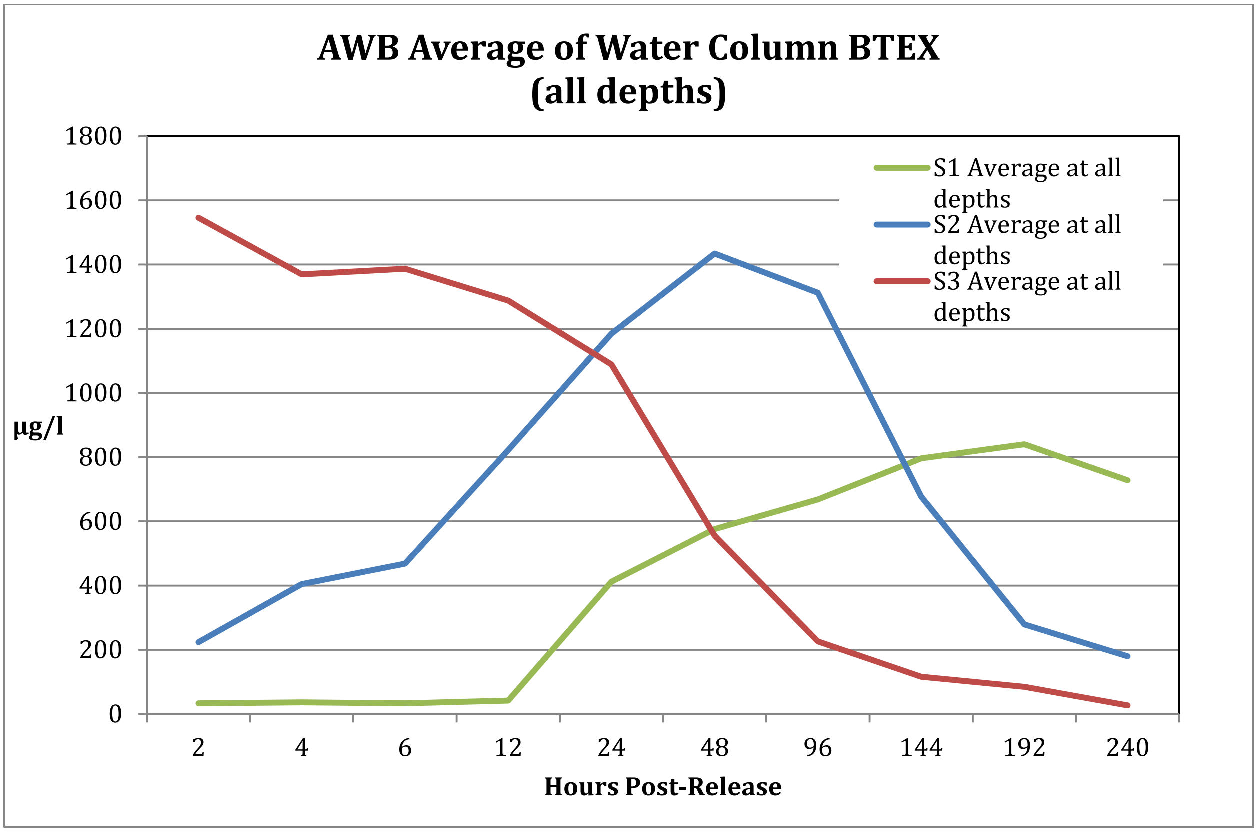

Figure 8. Average BTEX concentrations in water from 0.5, 1, and 1.5 m below AWB dilbit

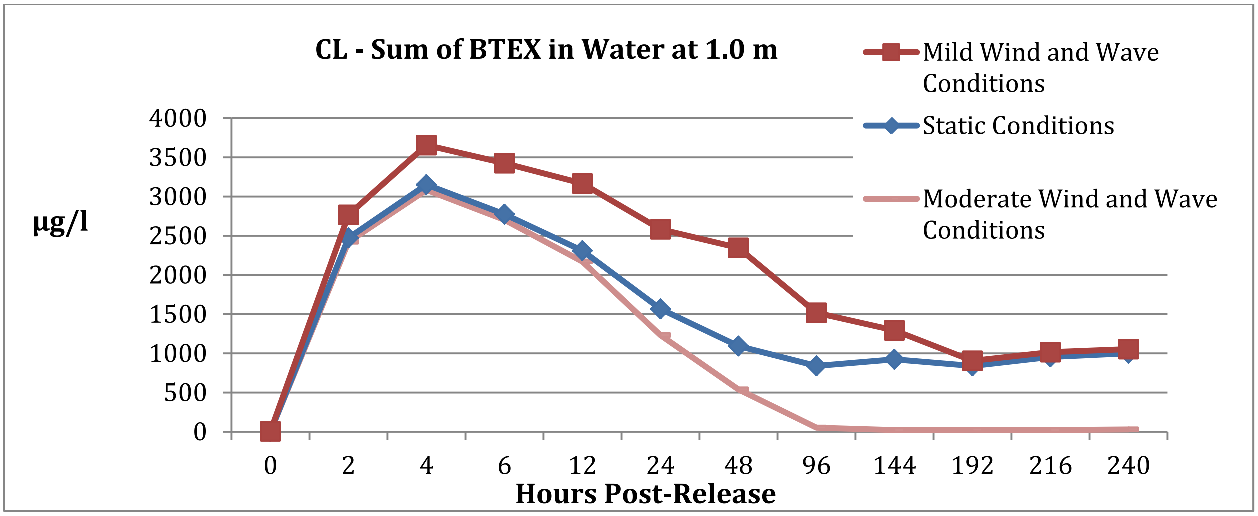

Figure 9. *BTEX concentrations in water at 1 m depth below CLWB dilbit*

C1-C30 analysis of the original and weathered oils shows rapid depletion of lower molecular weight compounds in all instances and maximum depletion in the tanks with moderate weathering conditions (Figures 10 and 11). The percent of compounds present by weight decreases rapidly for the lighter compounds and can consequently increase in heavier molecular weight compounds in light or low weathering conditions. Moderate agitation resulted in greatest reduction in percent by weight among all compounds.

Fresh oil samples of CLWB and AWB dilbits contained 1.1 and 0.45 percent PAH by weight, respectively. The National Research Council (2003) reports an average PAH content of 1.39 for 25 crude oils (heavy and light) using data from numerous sources.

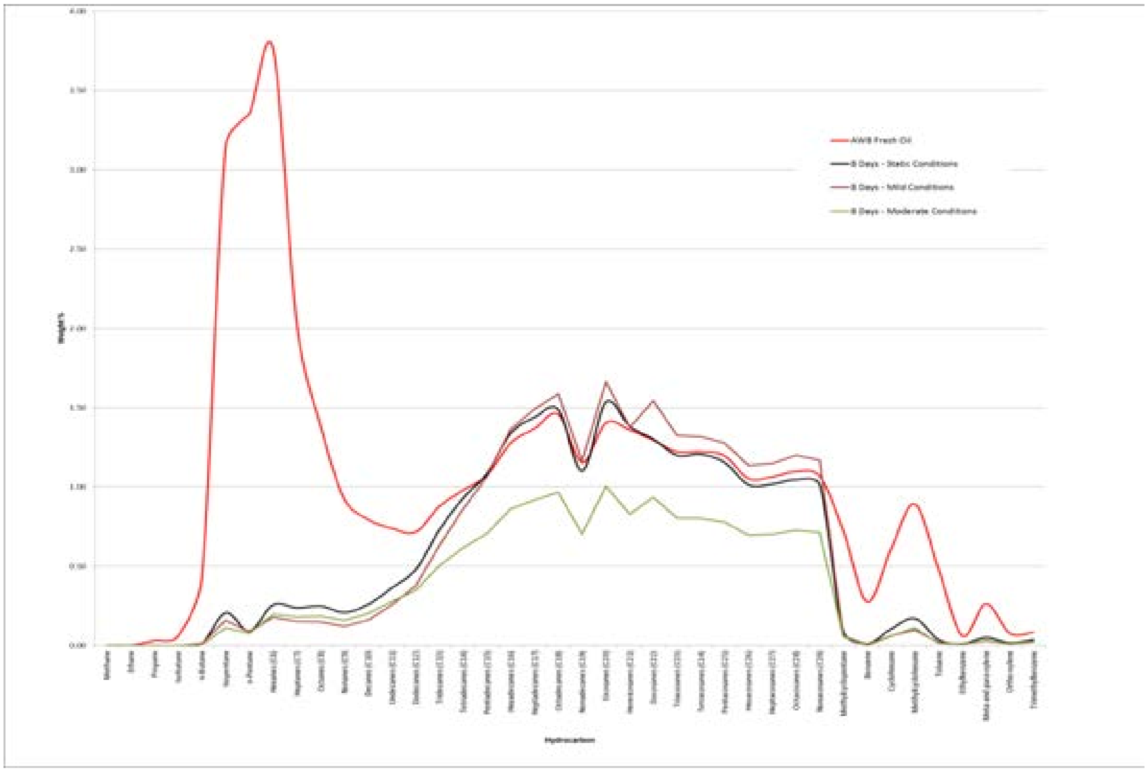

Figure 10. *Light ends (C1 – C30) AWB*

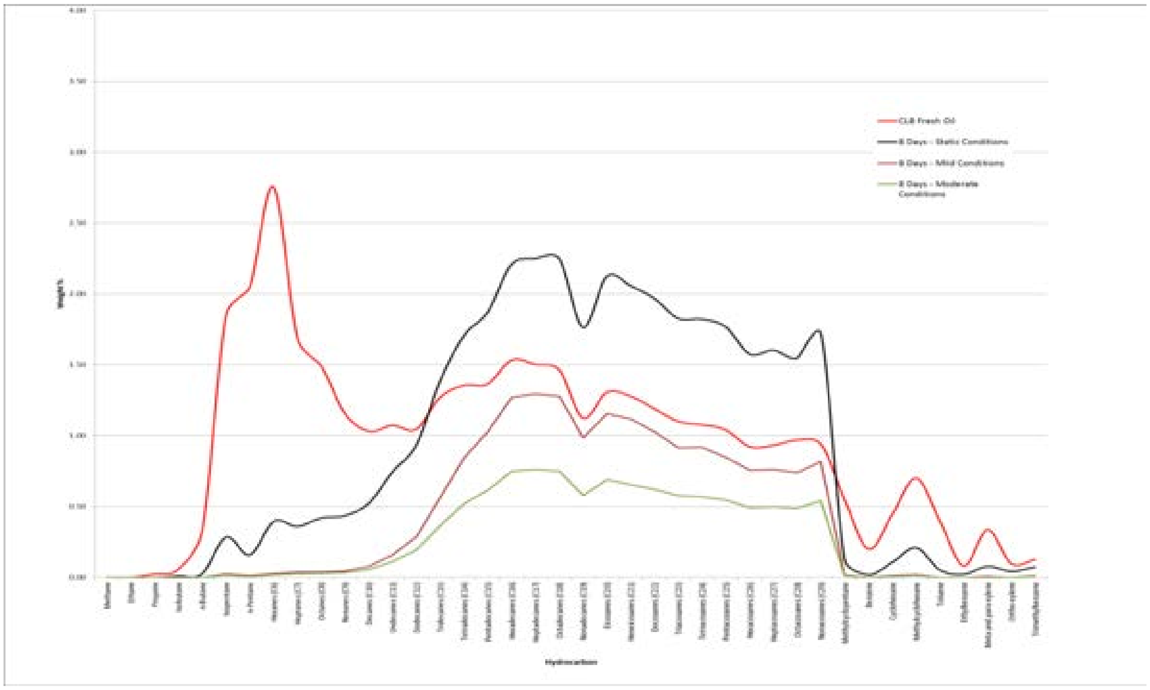

Figure 11. *Light ends (C1-C30) CLWB dilbit*

4.3 Chemical Dispersant Application

Visual observations suggested that the dispersant was marginally effective on the relatively fresh oil (6-hour weathered CLWB) but not effective on the 1-day weathered CLWB. The 1-day weathered CLWB was affected by the dispersant as application produced oil globules/droplets in the centimeter-scale size range; however, substantially more oil remained on, or returned to, the surface following the test than the 6-hour weathered oil sample. Comparisons of the weights of applied oil and oil recovered on sorbent pads corroborate the visual assessment of dispersant action (Table 6). Measures of the TPH content in the water column prior to oil placement, following oil placement and prior to dispersing, and post-dispersant application (Table 7) corroborate the visual observations.

Table 6. Calculated weights of CLWB tested and recovered during dispersant trials

Oil Sample (Weathering Time)	Weight Applied (g)	Weight Recovered (g)	% Dispersed (Not Recovered on Sorbent)
SD-6HR	871	422	52
SD-1 Day	895	929	-4

Table 7. TPH / Alkanes (mg/L) measured in water samples during dispersant trials

Oil Sample ID	Description (Weathering Time)	TPH / Alkanes (mg/L)
SD-0H-W500	Water sample taken prior to spill (6 hours weathered CLWB)	<2.0
SD-6H-W500-1	Water sample taken 20 min after spill (6 hours weathered CLWB)	<2.0
SD-6H-W500-2	Water sample taken 20 min after using Corexit 9500 on oil (6 hours weathered CLWB)	360 (1)
SD-1D-W500	Water sample taken prior to spill (1 day weathered CLWB)	<2.0
SD-1D-W500-1	Water sample taken 20 min after spill (1 day weathered CLWB)	<2.0
SD-1D-W500-2	Water sample taken 20 min after using Corexit 9500 on oil (1 day weathered CLWB)	80 (1)

4.4 Controlled Burning

Tests revealed that CLWB can be successfully ignited and burned provided weathering is limited to less than three days (i.e., the 1-day weathered oil had an equivalent density of less than 984.2 kg/m^3 and viscosity of approximately 25,000 cSt at 15 °C). The first burn test (6-hour weathered CLWB) ignited relatively easily and burned well for a period of approximately 2 minutes and extinguished on its own. The second test (24-hour weathered CLWB) was difficult to ignite and took two attempts. The second attempt, using more accelerant than 6 hour weathered CLWB (200 mL more diesel) and higher torch-temperature, burned for approximately 2 minutes once started. A sustained burn was not achieved for the 72-hour weathered oil sample, despite added diesel as an accelerant and repeated direct attempts with the propane torch. Comparisons of the weights of applied oil and oil recovered on sorbent pads provide approximate oil removal efficiency from the test burns (Table 8). Burn residue from the successful tests was sticky and formed cohesive residue that remained floating on the fresh water surface, though easily submerged. Burn residue on the steel ring was only partially removed between burns two and three and likely contributed to the higher amount of oil recovered on sorbents following the S4-3 day post-burn attempt.

Table 8. Calculated weights of CLWB dilbit tested and recovered during burn trials

Oil Sample (Weathering Time)	Weight Applied (g)	Weight Recovered^ (g)	% Burned (Not Recovered on Sorbent)
S4-6HR	1735	447	74
S4-1 Day	1803	856	53
S4-3 Day	1657	1912	0

4.5 Substrate Washing

Flushing alone was ineffective at removing the majority of bulk oil and black stain in all instances. Increasing pressure removed bulk oil throughout the experiment but black stain persisted. Only increasing the pressure and temperature to >60 psi (0.41 MPa) and >60 °C, a point known to be more harmful to biota than the benefit of the treatment (Mauseth et al., 1997), removed all but a black stain during the test period without the use of a shoreline cleaning agent.

As expected, oil exposure to sunlight made a difference in cleaner effectiveness. Oiled tiles that remained in shade were effectively cleaned with Corexit 9580 after up to 5 days (120 hours) of air exposure. The time oil spent weathering on water had little noticeable effect given that Corexit 9580 effectively removed oil from the tiles for all three on-water weathering periods tested – 1 day (24 hours), 3 days (72 hours), and 5 days (120 hours) –when oil was allowed to sit on the tiles for 96 hours (sunlight) to 120 hours (shade). The thickness of the oil on tiles after 24 hours, however, varied from 0.5 mm (24 hours in water) to up to 2 mm (5 days in water) (Figure 4). Despite slightly thicker oil on tiles after the oil from the tanks had weathered for 3 and 5 days on water, Corexit 9580 appeared to be similarly effective on these tiles after equivalent drying times. Oil thickness may also be affected by slope and temperature, although there was no observed difference in oil thickness on several tiles that were flat. Colder temperatures or prolonged weathering may result in greater oil thickness, which could lead to variations in shoreline cleaning agent effectiveness.

4.6 Equipment Testing

The average density of the oil in the equipment test tanks was initially 925.2 kg/m^3 (absolute density at 15 °C/API 21.3) on May 13 and steadily increased to 988.8 kg/m^3 (API 11.5) by May 21. These density numbers represent an average value for the oil contained in each of the three equipment test tanks over that time period. This oil was not only weathering but was also being agitated and emulsified by the skimmers. Oil densities for the undisturbed oil in tank E7 (the static tank) ranged from 925.2 kg/m^3 (API 21.3) to 975.1 kg/m^3 (API 13.5). Viscosities calculated (per ASTM 341) to 15°C, based on laboratory tests of oil samples collected from the tanks before skimming, ranged from a starting value of 220 to over 30,000 cSt (Table 9).

In evaluating the equipment test results it was noted that oil recovery efficiencies (oil collected vs. water) ranged from a low of 19% to a high of 98%, with the lower efficiencies corresponding to the skimmer tests on the freshest oil. In retrospect, skimmer operators stated that to improve their early recovery performance they would have initially started the test using oleophilic discs on the fresher, less viscous oil, before switching to brush skimmers for use on weathered oil. Over the 9-day test period, oil recovery rates ranged from 0.12-0.86 l/s (0.43-3.1 m^3/hr) for all skimmers and all stages of oil weathering. Maximum recovery rates for oil weathered for up to 8 days ranged from of 0.59-0.86 l/s (2.12-3.1 m^3/hr) before notably dropping to 0.26 l/s (0.94 m^3/hr) on Day 9 (Table 9).

Table 9. Equipment Test Table

Date of Test	Approx. Elapsed Time from Oil Release that Test was Conducted (Hrs.)	Duration of Peak Test	Density of Oil Sample (lab result; Absolute; kg/m3 @ 15 °C)	Viscosity of Oil Sample (lab result: cSt extrapolated to 15 °C)*	Number of Skimmers Tested	Range of Water Content in Oil Sample from Cal. Cubes (lab result; %)		Range in Rate of Oil Recovery (liters/sec.)		Range of % of Oil Content in Cal. Cube	
						High	Low	High	Low	High	Low
13-May	4	2 min	925.2^	220	3	22.0	5.7	0.86	0.21	33	19
15-May	46	4 min	952.4^	1252	3	11.8[#]	8.2	0.59	0.58	95	81
17-May	96	4 min	970.1 - 985.1	6603 - 15523	3	50.4	24.1	0.70	0.31	98	79
19-May	144	4 min	982.5 - 989.9	7982 – 17234*	3	47.5	20.0	0.71	0.40	94	28
21-May	192	4 min	986.2 - 993.0	15903 – 30304	3	49.0	26.2	0.82	0.25	95	79
22-May	216	4 min	975.1^^	9642	2	17.0	13.2	0.26	0.12	97	73

^ Values were for the oil at the beginning of the test and the oil from the common discharge tank. After the modification of the test, such that skimmers were discharging into their own tanks, there was a high and low value from those three tanks.

^^ Value is from one tank (E7) which had been left for 10 days undisturbed.

*Tank E5 extrapolated values for May 18 not included in range as curve was outlier.

[#] Following laboratory analysis, the initial subject sample jar returned an anomalous 91.1% water content. As such, the results from a second sample jar are presented here with confidence that this alternate is more representative of the product recovered in the test.

5. Conclusions

The overall study objective was to obtain an expanded understanding and assessment of dilbit behavior, weathering, and OSR countermeasures performance under controlled simulated conditions similar to the potential receiving environment of Burrard Inlet. This objective was achieved through the Gainford meso-scale tests.

Based mostly on visual observation alone, both dilbits exhibited properties that one would expect of a heavy, “conventional” crude oil. There was no two-phase separation into bitumen and diluent. In no instance was any oil observed to have sunk. Densities increased as oil weathered approaching, and in some cases exceeding, values of 1000 kg/m^3. Viscosities increased rapidly with weathering reaching in excess of 10,000cP within 24 hours for both dilbits exposed to moderate agitation.

Chemical analyses of the weathered oils and of the water column showed that concentrations of BTEX diminished rapidly within 48 hours and that TPH in the water column only exceeded the detection limit (2 mg/L) during the first 48 hours in tanks with moderate surface agitation, despite the artificial confinement imposed by tanks relative to what may be expected in an open, natural setting. Depletion of BTEX compounds in the water column and in mid-range PAHs in the weathered oil reflected the imposed energy during weathering. As expected, higher depletion rates were documented for higher agitation.

Three non-mechanical countermeasures were investigated for their ability to mitigate spilled CLB dilbit under specific conditions. The chemical dispersant Corexit 9500 was marginally effective on 6-hour weathered oil and not particularly effective for more weathered CLWB dilbit. Similar results were noted in the Environment Canada et al., (2013) tests. The early test burn (6-hour weathered CLWB dilbit) was effective with a sustained burn of 2 L of oil lasting for more than 2 minutes with approximately 70 percent of oil removed through burning. Additional burn testing showed approximately 50 percent of 24 hour weathered oil was removed, but only after sustained effort to ignite. The 72-hour weathered oil was not successfully ignited. Tests with the substrate cleaning agent Corexit 9580 found it to be effective on oils weathered up to five days. Test observations noted that the time oil weathers on water before being placed on the tile was less important than the time the weathered oil was exposed to air.

For the equipment portion of the study, each recovery device was uniformly tested and analyzed for its ability to recover fresh and weathered CLB, and the efficiency with which that task was accomplished. All skimming devices were able to recover the spilled dilbits at all stages of the 10-day weathering cycle. The oil floated throughout the 10 day period. No instances were observed of the oil’s buoyancy being compromised either neutrally downward in the water column or sunken to the bottom of the tank. Visual observations of the tanks during final decontamination further affirmed the absence of sunken oil. Vendors and contractors both agreed that under the test conditions used, this dilbit behaved no differently than other crude oils and proved to be mechanically recoverable by the skimming units tested. The starting dilbit was less viscous than anticipated, prompting the vendors to indicate they would have preferred to have used oleophilic discs or drums at the outset of the test and then to have switched to brushes later as the oil became more viscous.

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