

Article

Estimating the Usefulness of Chemical Dispersant to Treat Surface Spills of Oil Sands Products

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Abstract: This study examines the use of chemical dispersant to treat an oil spill after the initial release. The natural and chemically enhanced dispersion of four oil products (dilbit, dilynbit, synbit and conventional crude) were investigated in a wave tank. Experiments were conducted in spring and summer to capture the impact of temperature, and the conditions in the tank were of breaking waves with a wave height of 0.4 m. The results showed that natural dispersion effectiveness (DE) was less than 10%. But the application of dispersant increased the DE by an order of magnitude with a statistically significant level ($p < 0.05$). Season (spring versus summer) had an effect on chemical DE of all oils, except for the conventional oil. Thus, the DE of dilbit products is highly dependent on the season/temperature. A model was fitted to the DE as a function of oil viscosity for the chemically dispersed oil, and the correlation was found to be very good. The model was then combined with a previous model compiled by the author predicting oil viscosity as a function of time, to produce a model that predicts the DE as function of time. Such a relation could be used for responders tackling oil spills.

Keywords: Access Western Blend (condensate/bitumen-dilbit); Western Canadian Select (condensate mixed with synthetic crude/bitumen-dilsynbit); Synthetic Bitumen (synthetic crude/bitumen-Synbit); Heidrun; dispersant; wave tank; dispersion effectiveness (DE)

1. Introduction

Crude bitumen, produced in Alberta, Canada, is a highly viscous crude oil and semi-solid at room temperature. The majority of the oil produced is shipped via pipeline and railcars outside the province for refinement or export. In order to meet conventional oil pipeline specifications, the crude bitumen is diluted with a lighter hydrocarbon oil to reduce its viscosity and subsequently improve flow. The blending process for crude bitumen is at the discretion of the oil producer, so a wide variety of products of varying chemical composition is produced [1]. Heavy oil sands (blended bitumen) represent ca. two million barrels per day (b/d) of the four million b/d of crude oil produced and transported in Canada [2]. From pipelines, oil products may be transferred to tankers for shipment to global markets. Canada's production, transport, and sale of these products are expected to increase by a million barrels per day in the next decade [2]. The anticipated growth in oil production and transport increases the risk of oil spills in aquatic areas, and places greater demands on oil spill transport routes and capabilities to respond to spills.

In July of 2016, Environment Canada released new regulations and a list of approved oil spill treating agents that included COREXIT[®]EC9500A as an alternative measure, to recovery, to mitigate oil spills that occur in waters offshore Canada [3]. The use of a spill treating agent in offshore areas, by the responding parties, is to reduce damage to shoreline areas that are highly productive and sensitive, and also costly to clean. The application of conventional techniques, such as spill treating agents, are limited to studies showing significant, but incomplete effectiveness of COREXIT[®]EC9500A on a Cold Lake bitumen blend (e.g., Cold Lake crude bitumen blend with 30% condensate, dilbit) spilled under different environmental conditions [4,5]. However, there is no information in the literature to support the use of chemical dispersant to treat surface spills of various other oil sands products (e.g., Access Western Blend (AWB) or dilbit, Western Canadian Select (WCS) of dilsynbit and synthetic bitumen or synbit) that have weathered at sea, post spill. In addition, a science-based tool to estimate the window of opportunity to treat such spills is highly desirable. According to a Royal Society of Canada report on the behaviour and environmental impacts of crude oil released into aquatic environments [6], more research is required on the natural and chemically enhanced dispersion of bitumen blends under a variety of oceanographic conditions.

Chemical dispersants have been shown to be effective in treating heavy fuel oil, but water temperature can be a limiting factor [7,8]. Therefore, seasonal temperature variations are considered in this study, since the blended bitumen products are classified as heavy oils. Also, weathering of oil can increase its viscosity, which reduces the effectiveness of chemical dispersant to treat spills [9]. The chemical dispersant, COREXIT[®]EC9500A (as the only listed dispersant for offshore use in Canada), is tested at a dispersant-to-oil ratio (DOR) of 1:20 (manufacturer's recommended dose) to determine its effectiveness at treating surface spills of bitumen blends and readily dispersible conventional oil spilled on seawater in a flow-through wave tank during spring and summer of 2016 and 2017 in Atlantic Canada.

Attempts are made to address these gaps in knowledge by evaluating (1) dispersant effectiveness by oil type, including fresh and weathered products and seasonal effects (i.e., water temperature) to generate a new dispersant model based on empirical data; and (2) a previously generated viscosity weathering model [9] integrated with the newly generated dispersion effectiveness model to provide a means to estimate the effectiveness of dispersant to treat weathered oil. The information generated will aid oil spill responders and decision-makers on the appropriate conditions, where dispersant might be applicable to treat oil spills that have weathered at sea.

2. Materials and Methods

2.1. Oil Types and Characterizing the Chemical Composition and Physical Properties of the Oil Products

Access Western Blend (a dilbit comprised of crude bitumen blended at 30% with condensate), synthetic bitumen (a synbit made up of 50% synthetic crude oil blended with crude bitumen) and Western Canadian Select (a dilsynbit consisting of 50% synthetic crude oil/condensate blended with crude bitumen) were selected, because they represent the highest volume of oil sands products transported throughout Canada. Heidrun was also selected as the reference conventional crude, since its physical properties are reasonably close to the blended bitumen products. Similar to the technique used by Li et al. [10], the bitumen oil products were artificially weathered by purging them with nitrogen for 48 h at ~20 °C. Weathering the products prior to placing the oil in the tank for dispersion effectiveness testing is a key step as weathering generally increases oil viscosity and is likely to limit chemical dispersant effectiveness.

Samples of the unweathered oils were evaluated for saturates, aromatics, resins and asphaltenes (SARAs) using thin-layer chromatography coupled with flame ionization detection (TLC-FID) [1,11]. To monitor changes in the physical properties of the oil at various seawater temperatures; recovered oil samples were analyzed by an Anton Paar SVM 3000 Analyzer to quantify viscosity [12] and density [13].

2.2. Wave Tank Facility

The wave tank facility is located at the Bedford Institute of Oceanography (BIO) in Dartmouth, Nova Scotia. The tank dimensions are 30 m long, 0.6 m wide and 2.0 m high, with a typical water level of 1.5 m (Figure 1). The tank is equipped with a series of manifolds to generate a more or less uniform current along the wave propagation direction; hence, the label flow-through system has been used to evaluate dispersant effectiveness of fresh and weathered crude oils [4,5,8,14–16].

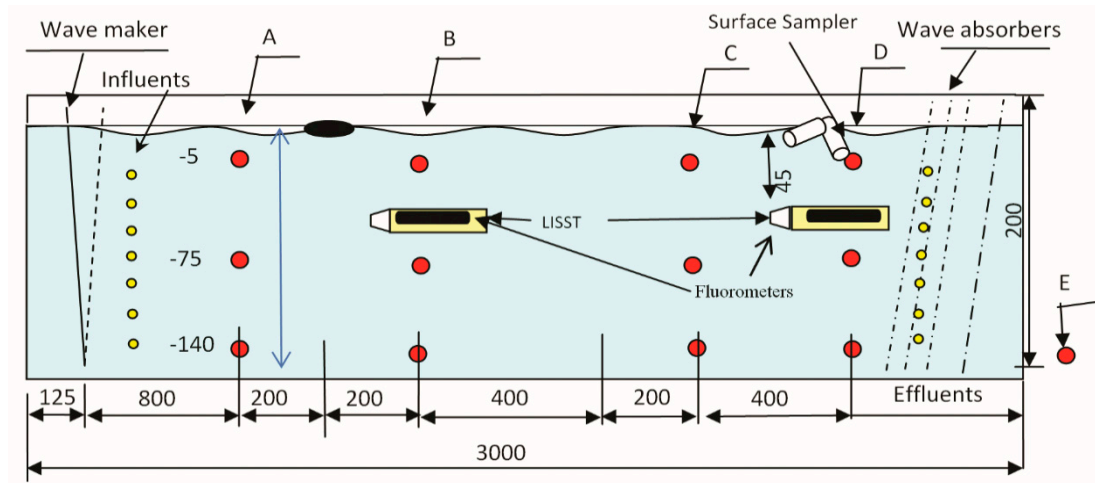


Figure 1. Schematic diagram (not to scale, all units in cm) illustrating the location of the oil source (black ellipse between A and B), Laser In-situ Scattering and Transmissometry (LISST) particle counters, sampling locations at A, B, C, D (3 depths), the effluent port E (1 port) and surface (near sample location D). LISST#1 is at location B (ca. 1.2 m downstream at a 0.45 m depth) and LISST#2 is at location D (ca. 12 m downstream at a 0.45 m depth) of oil release.

The hydrodynamics of the various wave types generated in the wave tank facility has been characterized in prior works [17,18]. Each experiment was conducted for one hour during which each wave cycle (four breakers) lasts for 15 s followed by a quiescence period that lasts for 25 s.

2.3. Oil and Dispersant Application during Wave Tank Tests

The experimental factorial design involves testing of four oils with two treatments (without and with dispersant) in triplicate over two seasons. Therefore, the total number of runs was 24, conducted in random order for spring and summer experiments. Briefly, for each experiment, quiescent conditions were achieved in the tank (i.e., no waves). Next, ca. 240 g of oil product was gently poured onto the filtered seawater surface within a 40 cm diameter ring located 10 m downstream from the wave-maker and ~12 g of the dispersant COREXIT® EC9500A (Nalco, active surfactant is dioctyl sodium sulfosuccinate; U.S. Patent No. 614285) was sprayed gently onto the oil slick through a pressurized nozzle (60 psi, 0.635 mm i.d.). This resulted in a DOR of 1:20. The wave-maker was started, and produced a sequence of waves. The ring was promptly lifted prior to the arrival of the first breaking wave on the location of the ring. The sequence of waves; generated a 0.4 m high plunging breaker (where the water curls and re-enters the water surface downstream) every 40 s at the same location using the dispersive focusing technique [19]. In this study, only breaking waves were investigated with the use of chemical dispersant to treat oil spills, since an earlier study [20] revealed that spill treating agents were ineffective in the dispersion of condensate bitumen blends when no wave breaking occurs.

2.4. Wave Tank In Situ Measuring Devices

Two particle size counters (Laser In-situ Scattering Transmissometry (LISST)-100X, Sequoia Scientific, Inc., Bellevue, WA, USA) were employed during the experiments, one at 1.2 m and another at 12 m downstream of the oil release point and both at a depth of 0.45 m (Figure 1). Particle size (2 to 500 μm) distributions were recorded at 2.0 s intervals for 1 h per experiment as in previous studies [4,8,10,14–16].

The Sauter mean diameter D_{Sauter} was estimated based on the LISST measurement [21]. It is obtained as:

$$D_{Sauter} = D_{32} = \frac{\sum_i^M c_i D_i^3}{\sum_i^M c_i D_i^2} \quad (1)$$

where c_i is the concentration of particles, calculated from the volume concentration as obtained from the LISST measurements ($c_i = \frac{V_i}{(\frac{\pi}{6})D_i^3}$); D is the particle diameter; the subscript i refers to the size class, and M is the total size bins (32 intervals herein).

2.5. Laboratory Analysis of Seawater Samples from Wave Tank Studies

The experimental and sampling procedures were consistent with the crude oil dispersant efficacy testing in the flow-through wave tank reported previously [4]. Four water sampling devices were deployed, one at 2.0 m upstream from the oil release point and the other three downstream at 2.0 m, 8.0 m and 12 m from the oil release point (Figure 1). Each of the four samplers, collect water (~100 mL) at three depths (0.05, 0.75 and 1.4 m) in the tank at the time points: 5, 15, 30, 45, and 60 min. In addition, effluent samples (from the side opposite the wave-maker) were taken (Figure 1). Four time-zero samples (prior to oil release, to check background levels) were selected at arbitrary sampling locations (Figure 1).

The collected water samples were extracted and analysed for total petroleum hydrocarbons (TPH) using a gas chromatograph equipped with flame ionization detection (GC-FID) [4,22]. The method is a modified version of EPA 3500C, whereby the sample container is the extraction vessel. Briefly, 12 mLs of dichloromethane (DCM) were added to a 125 mL amber glass sample bottle containing ~80 mLs of seawater collected during the experiments. Next, the sample was placed on a Wheaton R₂P roller (VWR, Canada) for 18 h. The roller has been modified to accommodate a 3-inch (internal diameter) PVC pipe into each roller slot. This modification permits sample containers of different sizes to be used in the apparatus. Once extraction was complete, the sample bottles were removed and the DCM was recovered. The recovered DCM was placed in a pre-weighed 15 mL centrifuge tube, and the solvent was removed using a nitrogen evaporator until the final volume reached 1.0 mL graduation on the centrifuge tube. The extracts were then analysed by GC-FID. Calibration standards prepared from the test oils were used to develop calibration curves for evaluating the oil concentration in the seawater extracts. The method detection limit is <0.5 mg/L. The benefit of this procedure is that 240 samples can be extracted simultaneously; thus increasing productivity with acceptable accuracy and precision.

3. Results and Discussion

3.1. Composition and Physical Properties of Test Oils

In their unweathered state, bitumen blends have viscosities >200 cSt @ 15 °C and are classified as heavy oils (Table 1). The bitumen blends contain a greater percentage of resin and asphaltenes compared to Heidrun crude oil, which is the medium conventional crude. Depending on the rate of diluent released and seawater temperatures during a spill, these high molecular weight (>500 atomic mass units) chemicals can greatly affect the physical properties (e.g., density and viscosity) of the oils that are relevant to responding to spills. The source of these chemicals in blended bitumen

products is most likely from the crude bitumen. Oil sands products are expected to significantly weather within a few hours post-spill, thus significantly altering their viscosities, which would limit dispersant effectiveness [9]. Heidrun is not expected to weather to the extent that limits its treatment with chemical dispersant after a spill. The viscosities and densities of the four oils, at the recorded experimental seawater temperatures are found in Table S1 (Supplementary Materials) where one notes a viscosity range varying from 60 up to 10,000 cSt.

Table 1. Saturates, aromatics, resins and asphaltenes (SARAs) contribution and physical properties for the three oils (unweathered).

Oil Type	Chemical Composition				Physical Properties			Oil Class
	Sat	Aro	Resin	Asph	Viscosity	Density	API°	
	%Contribution				(cSt)	(g/cm ³)		
Access Western Blend (AWB)	14	23	46	17	244	0.9189	22.3	Heavy
Heidrun	38	40	27	4	68.9	0.9132	23.3	Medium
Synbit	20	10	52	18	205	0.9304	20.4	Heavy
Western Canadian Select (WCS)	20	10	57	13	211	0.9214	21.9	Heavy

3.2. Test Conditions during Wave Tank Studies

To capture the effect of water temperature on the chemical dispersion of the test oil products, experiments were conducted consecutively during the spring and summer of 2016 and 2017 in Atlantic Canada and the physical measurements of the seawater obtained are recorded in Table S1 (Supplementary Materials). The water was obtained directly from the Bedford Basin, Dartmouth Nova Scotia, Canada and its temperature ranged from 3.7 °C to 19.7 °C for the entire study. Water temperature can affect dispersant effectiveness when treating heavy conventional oils such as Intermediate Fuel Oil (IFO) 180 [8]. Salinity is also an important factor to consider, since it can affect the efficacy of dispersants, such as COREXITEC[®]9500A, that are formulated for saltwater environments [23]. In our experiments, the salinity, over spring and summer months, ranged from 25.5 to 30.4 parts-per-thousand (ppt). The small difference between these values suggests that salinity variation would not make a measureable impact on the behavior of the test oils during the experiment.

3.3. Laser In-Situ Scattering Transmissometry (LISST)-100x

Since natural dispersion was very poor and due to transport and dilution, information collected from the first LISST (1.2 m from oil release) was placed in the Supplementary Materials (Figures S1, S3 and S5). Figure 2 reports contour plots of oil droplet volume concentration ($\mu\text{L}/\text{L}$) obtained from the second LISST-100x (12 m from the oil application) for the natural dispersion case as a function of time. The vertical axis (y -axis) represents particle or oil droplet size (μm). Additional information on particle sizes, volume concentrations and Sauter values can be found in the Supplementary Materials (Figures S1–S4). Without any treatment, the four oils showed poor natural dispersion under spring and summer conditions, where very little oil (in dispersed form or as small droplets) was in the water column; only the largest size (i.e., $>100 \mu\text{m}$) droplets had a non-negligible concentration, but still low. The findings in Figure 2 are consistent with the literature of conventional oils; oil droplets that have been produced by breaking waves in the absence of dispersant are typically larger than $100 \mu\text{m}$, have a unimodal distribution, and tend to rise to the surface where they are likely to coalesce [8,10,14]. The Sauter mean diameter values of Figure 2 varied between 150 to $350 \mu\text{m}$, which is in agreement with prior studies on heavy oil dispersion.

Figure 3 reports contour plots of oil droplet volume concentrations ($\mu\text{L}/\text{L}$) obtained from the LISST-100x (12 m from the oil application) for the chemical dispersion case as a function of time. The vertical axis (y -axis) represents particle or oil droplet size (μm). The oil detected by the first LISST (1.2 m from oil release, Supplementary Materials) remained dispersed in the water.

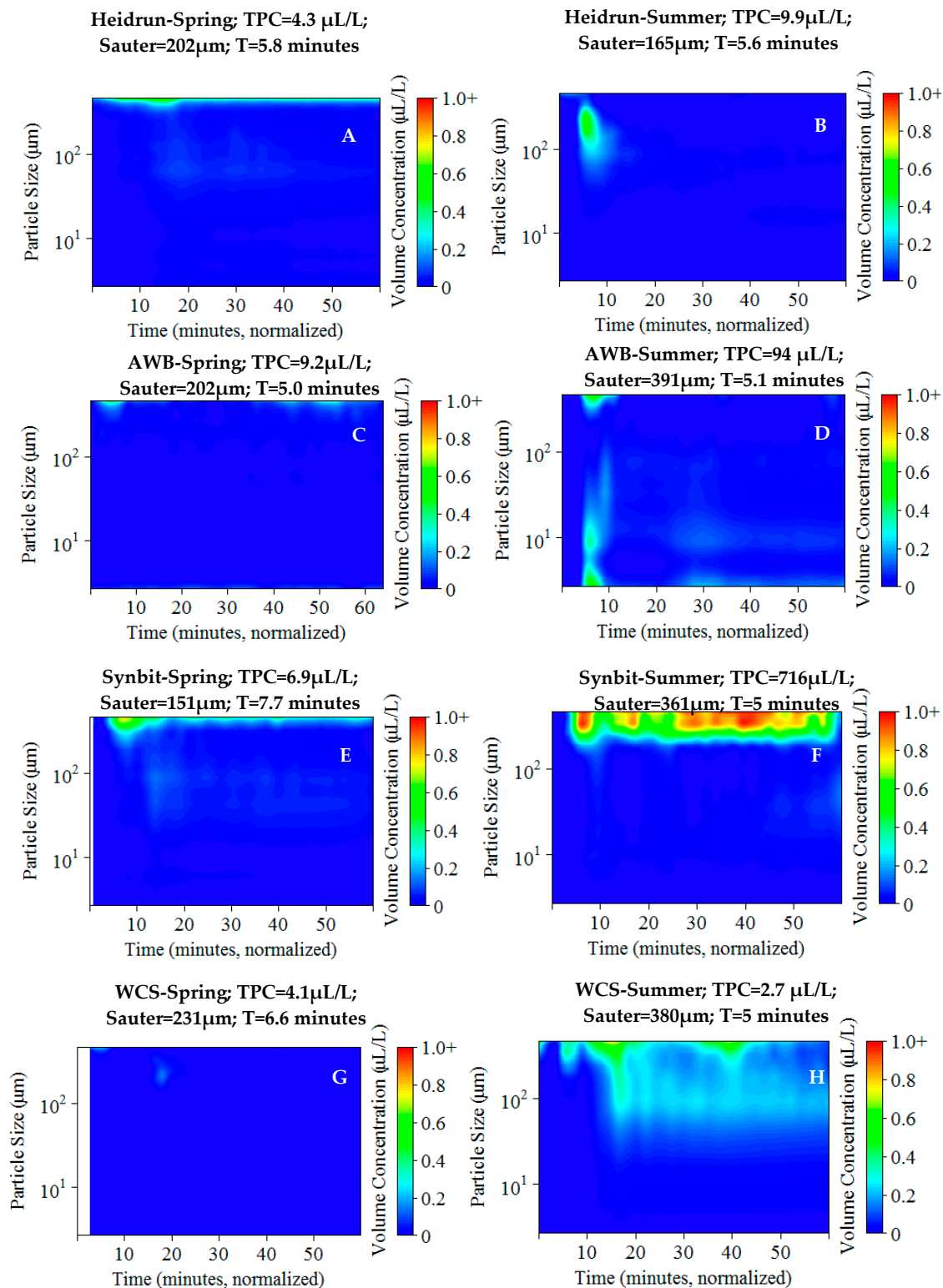


Figure 2. Contour plots (LISST data, 12 m from oil release) showing seasonal effects on the concentration of oil particle size simulated in the wave tank for the natural dispersion of: (A) Heidrun-spring, (B) Heidrun-Summer, (C) AWB-Spring, (D) AWB-Summer, (E) Synbit-Spring, (F) Synbit-Summer, (G) WCS-Spring, and (H) WCS-summer. The Sauter mean diameter values varied between 150 to 350 μm and low concentration of small particles ($<100 \mu\text{m}$) were detected in all cases.

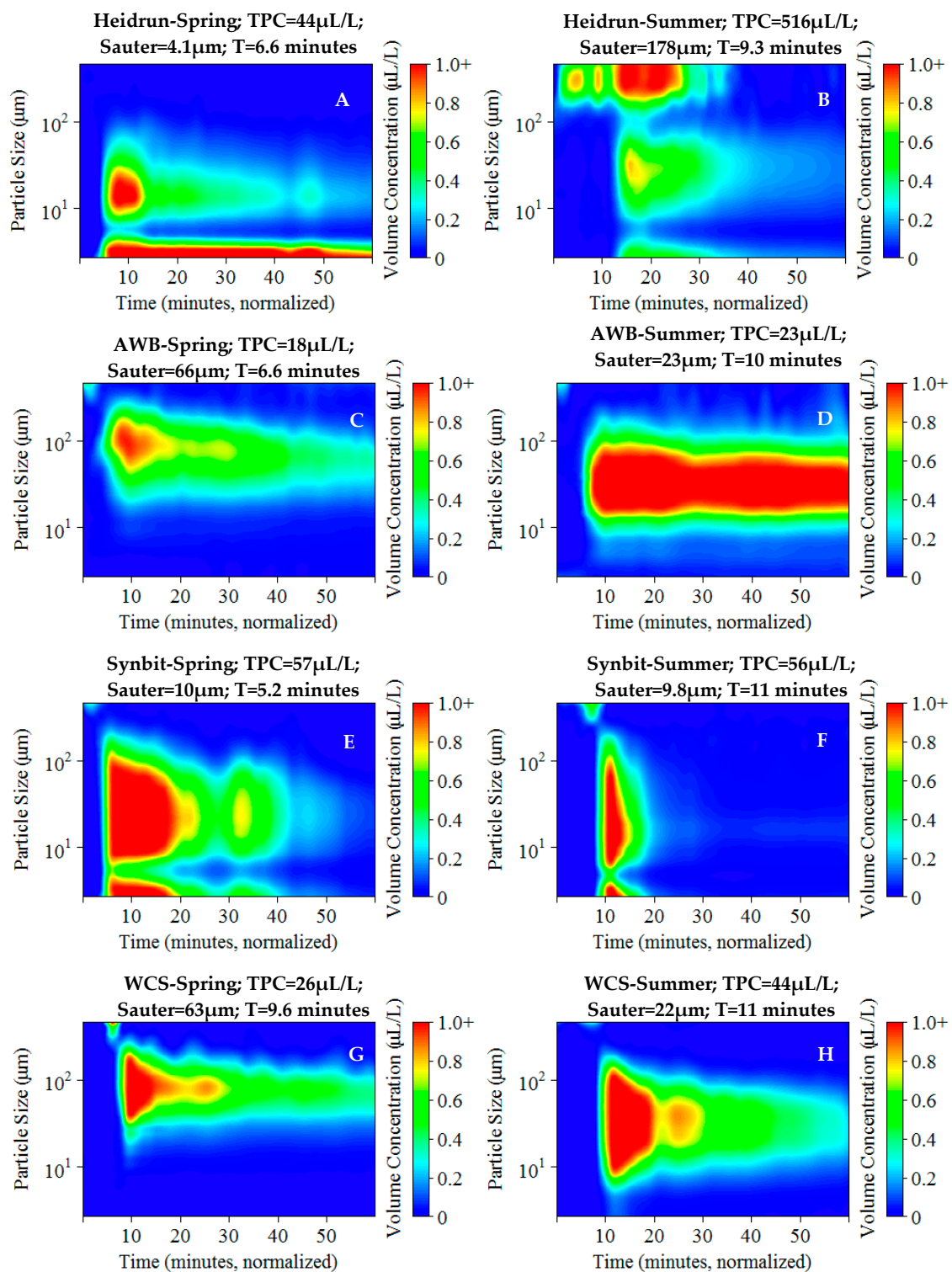


Figure 3. Contour plots (data from LISST, 12 m from oil release) illustrating seasonal effects on the concentration of oil particle size for chemically enhanced dispersion of: (A) Heidrun-spring, (B) Heidrun-Summer, (C) AWB-Spring, (D) AWB-Summer, (E) Synbit-Spring, (F) Synbit-Summer, (G) WCS-Spring, and (H) WCS-summer. The Sauter mean diameter values varied between 4 to 170 µm and high concentration of small particles (<100 µm) were detected in all cases.

Figure 3 displayed higher volume concentrations and smaller particle sizes (<50 µm) in the water column compared to natural dispersion (without dispersant) of all oil types for spring and summer

conditions. In general, higher concentrations of small particles (<50 µm) were detected in summer conditions. The chemical dispersion of Heidrun and synbit (both in spring and summer) produced large concentrations of very small droplets (<10 µm). This occurred also for the chemical dispersion of WCS, but only in summer conditions.

Our recent investigation [21] elucidated two major aspects of the LISST that should be considered when evaluating the droplet size distribution. The first is the impact of high concentrations, and it was found that if the optical transmission drops below 30%, the measured peak value of the LISST tended to underestimate the true peak by up to 50%, and the instrument accuracy decreased by up to ~30%. Fortunately, all LISST measurements in this study had an optical transmission that was larger than 45%. The out-of-range sizes of particles affected the LISST measurements especially near the limits of the range (but also slightly within the mid-range) when very high concentrations were detected. However, the impact of the out-of-range values decreases sharply as the size associated with that concentration is farther from the limit. In Zhao et al. [21], concentrations of 1.0 micron droplets increased the readings of the 2.3 micron concentrations by 20% of the 1.0 micron concentration. Thus, unless the out of range concentrations are 10 times or larger than those within range, the LISST should be viewed as capturing the totality of the mass of the droplets within range.

3.4. Total Petroleum Hydrocarbons (TPH) in the Water Column

Averaged TPH concentrations at all depths (0.05, 0.75, and 1.4 m) for location D (10 m from oil release point; Figure 1) are plotted in Figure 4 as function of time for the four oils under natural and chemically enhanced dispersion conditions in spring and summer. Each curve represents the average of a triplicate. Low TPH concentrations were observed under natural dispersion conditions, which have been reported by others [8,10]. The concentration during the summer was slightly higher than spring (warmer temperatures decrease the viscosity thus affecting dispersion), but remained an order of magnitude smaller than the chemically dispersed TPH for both seasons. For all four oil types, TPH concentrations reached at maximum and gradually declined with dilution and transport by waves and currents in the tank. These trends were similar for the natural and chemically enhanced dispersion of other oils in spring and summer from previous studies [4,8].

During dispersant application, the increased oil concentration in the water column creates controversy from a policy point of view, since it makes the oil more bioavailable to aquatic species, but reduces the amount of oil reaching the sensitive habitats in shoreline areas. Through natural dilution and transport the TPH concentrations in the water column dropped to near background levels for each of the four oil types. Sufficient mixing and water currents to transport dispersed oil are critical components when assessing not only dispersant effectiveness to treat oil products, but also the rate of dilution and transport to ensure minimal impacts to aquatic species and their habitats.

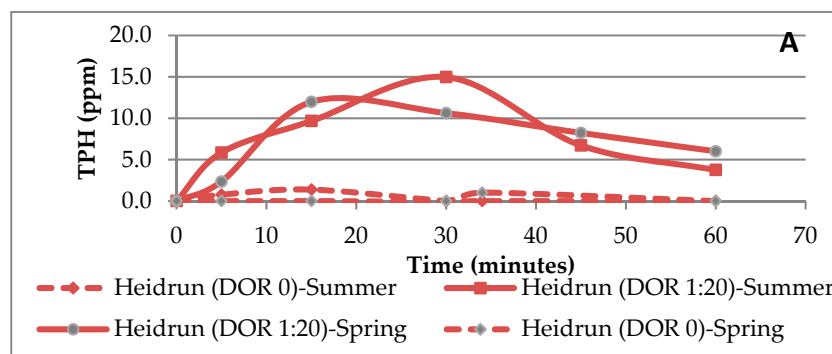


Figure 4. Cont.

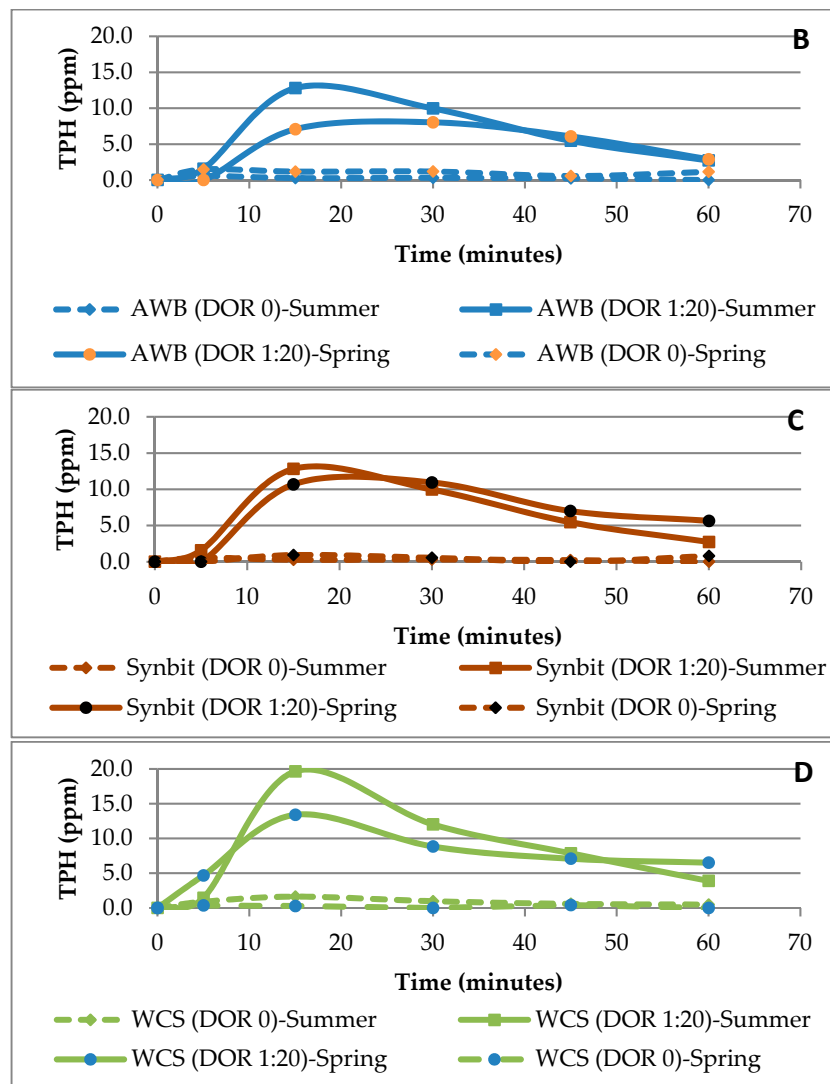


Figure 4. Average total petroleum hydrocarbon (TPH) concentrations in the water column over a depth of 0.05 to 1.4 m located 12 m downstream from the oil release point for treated and untreated oils: (A) Heidrun, (B) AWB, (C) Synbit and (D) WCS under spring and summer conditions. TPH concentrations were an order magnitude higher for oils treated with dispersant.

3.5. Dispersant Effectiveness (DE)

The averaged TPH concentrations for all depths at each sampling location (A, B, C, D, and E) were used to generate DE (%) values, which was obtained over the duration of the entire experiment by computing the fraction of dispersed oil in the effluent from the wave tank and the residual dispersed oil in the water column at the end of each experiment. Details on calculating DE (%) values during wave tank studies can be found in King et al. [4,5,8].

Table 2 (analysis of variance [ANOVA] single factor, Excel) shows the natural and chemically enhanced dispersion of the four oils under breaking waves and spring and summer environmental conditions. For each untreated and treated oil type, DE testing was performed in triplicate covering a range of seawater temperatures over two seasons and the experiments were conducted in random order. Natural dispersion effectiveness ranged from 0 to 7% for all four oils (Table S1). The application of a chemical dispersant had a significant ($p < 0.05$) effect on dispersion of all oil types. In the discussions to follow reference is made to viscosities in units of centipoise (cP) when taken from the literature. To get viscosity in cSt, divide cP by the density of the oil. In this case, cSt values would be approximately 10% higher than cP. Oil viscosity is critical in studying dispersants, because thin, medium-viscosity oils

(<2000 cP) are readily dispersible, but heavy, highly-viscous oils (>10,000 cP) are not [24,25]. Lewis [26] reported that a 2000 cP oil treated with COREXIT®EC9500A dispersed quickly and completely, but a more viscous 7000 cP fuel oil did not. This implies that viscosity has an effect on dispersion of oil; however in that study the time window of opportunity to treat weathered oil is not considered. Since, Heidrun’s viscosity is <2000 cSt even with seasonal temperature factored in, the performance of the chemical dispersant was not affected when treating it. For the bitumen blends (e.g., AWB, synbit and WCS), DE was notably lower (~20 to 30% less) most likely due to the fact that these products are more viscous, in their pre-weathered state, than the fresh Heidrun crude oil. Also, the dispersant had an effectiveness of 40 to 50% and low as 30% for bitumen blends with viscosities of 4000 and near 10,000 cSt, respectively.

Table 2. Analysis of variance of the randomization tests showing the dispersion effectiveness of dispersant to the natural dispersion of four oils under breaking waves. The value of “*p*” provides information on the probability of the observation (i.e., difference) to be due to randomness. The smaller the value of “*p*” the less likely the difference is due to randomness. Average ± Standard Deviation (Ave ± std).

Treatment	<i>n</i> *	Spring			Summer		
		Value (%) (Ave ± std)	Difference (%)	<i>p</i>	Value (%) (Ave ± std)	Difference (%)	<i>p</i>
No Treatment	6	1.7 ± 1.6	-	-	1.8 ± 1.1	-	-
Corexit/AWB	6	30.6 ± 2.8	-28.9	1.0 × 10 ⁻⁴	53.2 ± 3.3	-51.4	1.0 × 10 ⁻⁵
No Treatment	6	2.7 ± 1.2	-	-	1.8 ± 1.1	-	-
COREXIT/Heidrun	6	70.6 ± 1.7	-67.9	5.0 × 10 ⁻⁷	76.0 ± 7.4	-74.2	7.9 × 10 ⁻⁵
No Treatment	6	4.2 ± 3.0	-	-	4.0 ± 1.6	-	-
COREXIT/Synbit	6	48.4 ± 4.8	-44.2	1.7 × 10 ⁻⁴	59.2 ± 2.9	-55.2	9.0 × 10 ⁻⁶
No Treatment	6	2.7 ± 1.6	-	-	3.5 ± 1.0	-	-
COREXIT/WCS	6	41.3 ± 4.2	-38.6	1.2 × 10 ⁻⁴	53.5 ± 4.0	-50.0	3.1 × 10 ⁻⁵

* *n* = *n*₁ + *n*₂ observations.

Significantly (*p* < 0.05) higher DE values were recorded during summer than spring conditions, since seasonal temperature affects the viscosity of these heavy oil products (Table 3). This is consistent with a study on heavy conventional oil products such as IFO 180, which was effectively dispersed with a DE of 90% at high temperature (16 °C) and had low DE (<10%) at low temperatures (<10 °C) using the same test facility [8]. Also, laboratory studies showed a 20% difference in DE of heavy oils between 16 and 5 °C [7]. The seasonal effects (% difference) on DE for the bitumen blends were greatest (22.3%) for AWB (dilbit) and the least (10.8%) for synbit (Table 3). This is most likely due to the fact that synthetic crude as the diluent portion of synbit is less volatile than the condensate in AWB (dilbit). Its composition contains a greater portion of chemicals including saturates in the range of C₁₇ to C₃₅ and alkylated polycyclic aromatics [27] that are less susceptible to natural attenuation by evaporation than condensate (primarily of low molecular weight aromatics and aliphatics in the range of *n*-C₅ to C₁₀) [28] when dispensed in a dynamic state in spring and summer. Both diluents (condensate and synthetic crude) are present in WCS (dilsynbit), so the seasonal effect (% difference) on DE falls between the other two blends. Also, one can note that the bitumen blends prior to treatment have different viscosities, since they were pre-weathered (7% *w/w*) under similar conditions. Heidrun crude oil was readily dispersible when treated with chemical dispersant over the entire temperature range with DE values >70% for both spring (7.1 ± 0.8 °C) and summer (16.8 ± 1.6 °C) conditions. With this medium crude oil, the reported seawater temperature range did not have a significant (*p* = 0.28) influence on the effectiveness of the chemical dispersant (Table 3).

Table 3. Analysis of Variance of the randomization tests show the DE of oils affected by seasonal water temperatures under breaking waves. The value of “*p*” provides information on the probability of the observation (i.e., difference) to be due to randomness. The smaller the value of “*p*” the less likely the difference is due to randomness. Average ± standard deviation (Ave ± std).

The Effect of Seasonal Water Temperature on DE				
Treatment	<i>n</i> *	Value (%) (Ave ± std)	Difference (%)	<i>p</i>
COREXIT/AWB-Spring	6	30.6 ± 2.8	-	-
COREXIT/AWB-Summer	6	53.2 ± 3.3	−22.6	0.00088
COREXIT/Heidrun-Spring	6	70.6 ± 1.7	-	-
COREXIT/Heidrun-Summer	6	76.0 ± 7.4	−5.4	0.28
COREXIT/Synbit-Spring	6	48.4 ± 4.8	-	-
COREXIT/Synbit-Summer	6	59.2 ± 2.9	−10.8	0.029
COREXIT/WCS-Spring	6	41.3 ± 4.2	-	-
COREXIT/WCS-Summer	6	53.5 ± 4.0	−12.2	0.023

3.6. Modelling Dispersion Effectiveness

The four different oil types, consisting of fresh and artificial weathered products, selected for this study cover a board range of viscosities, over two seasons, with measured DE values (Table S1). The untreated (naturally dispersed) oil DE values were plotted as a function of oil viscosity (Figure 5). The plot revealed that natural DE was very similar or changes were minimal for all four oils dispersed under spring and summer conditions. Figure 6 reports the DE as function of the viscosity for the chemically enhanced dispersion of the four oils. A linear model was fitted to the plot of chemical DE as a function of oil viscosity (Figure 6). Therefore one would write the equation:

$$DE = m \ln(v) + b \tag{2}$$

where *m* is slope, *v* is the viscosity of the oil and *b* is the y-intercept.

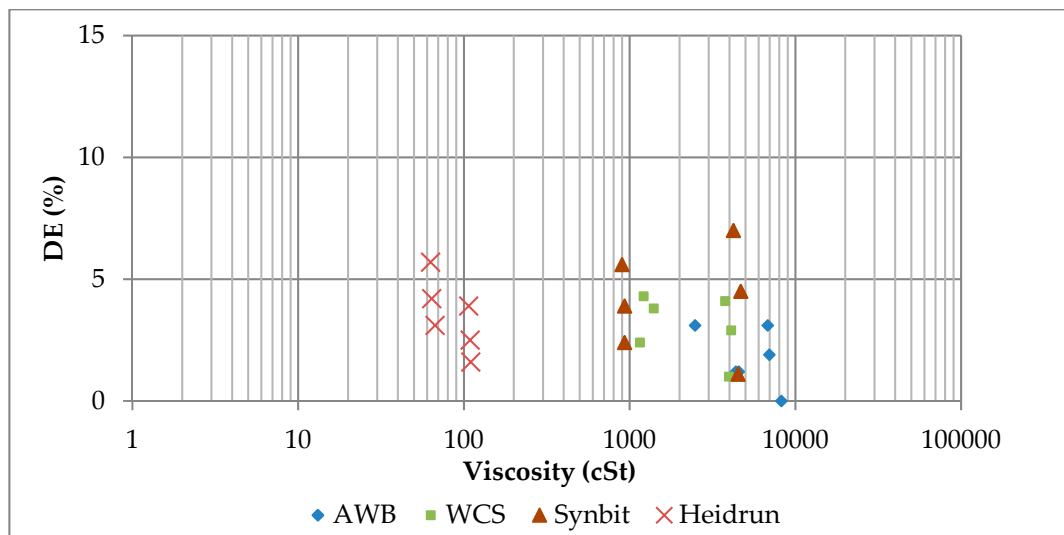


Figure 5. A plot of effectiveness of natural dispersion (DE %) as a function of oil viscosity. Experiments were conducted in spring and summer (Table S1). DE is <10% for all oils tested.

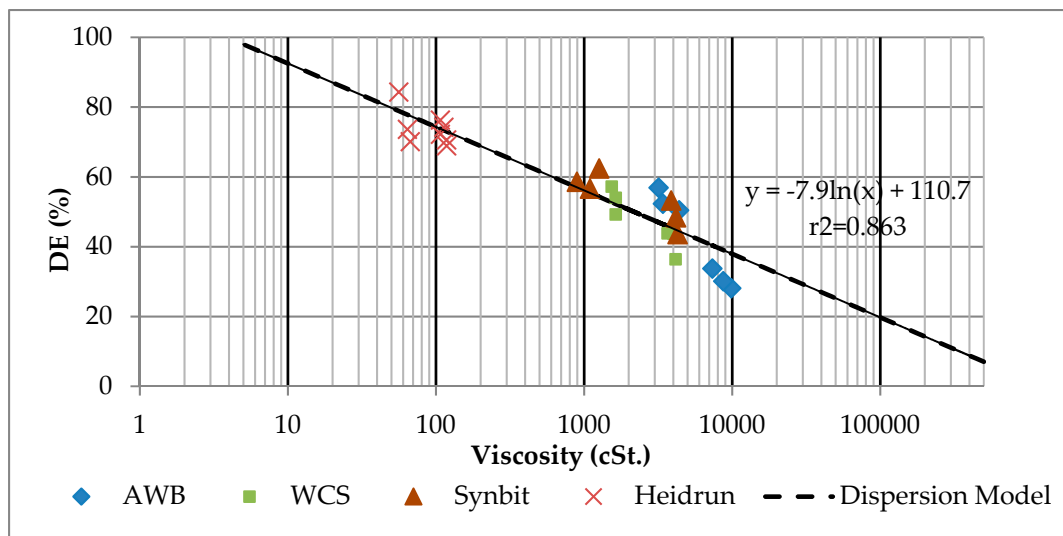


Figure 6. A plot of the effectiveness of chemically enhanced dispersion (DE %) as a function of oil viscosity. Experiments were conducted in spring and summer with fresh and weathered oils (Table S1). A dispersion model was fitted to the data points that represent four different oil types. DE (%) decreases with the increasing viscosities of oils, but effectiveness better than natural dispersion.

The fit was generally good, as one notes visually through the absence of any systematic bias (undershooting or overshooting), and the large coefficient of determination, $R^2 > 0.86$ and ANOVA showed a significant ($p < 0.001$) curve fit. If the viscosity of oil, at a specific temperature is known, then the model can be used to predict the chemically enhanced DE (%) of spilled oil at sea.

3.7. Combining Dispersant Effectiveness (DE) and Viscosity Functions to Estimate the Window of Opportunity to Treat Surface Spills of Oil after the Initial Release

King et al. [9] developed a model for the temporal evolution of viscosity due to weathering:

$$v = (v_0 + (v_f - v_0) \left(\frac{t}{T + t} \right)^n) \tag{3}$$

where v represents the viscosity (cSt) of weathered oil, v_0 and v_f are the initial and final oil viscosities, respectively, and t represents time in hours. The parameter “ T ” represents the “half-weathering rate constant”; the value of t when $v/v_{max} = 0.5$, and the parameter “ n ” reflects the slope of the curve to reach the maximum value. The advantage of Equation (3) is that it allows for the rapid increase in the early hours, and then for the plateaus in the data.

Equation (3) can be substituted for v into Equation (4) to determine DE as function of time for various oils:

$$DE = a \ln((v_0 + (v_f - v_0) \left(\frac{t}{T + t} \right)^n) + b) \tag{4}$$

Table S2 (Supplementary Materials) shows DE values generated using Equation (4) for the four oil products considered herein that were weathered under different conditions. Thus, assuming weathering conditions similar to those reported in King et al. [9], calm seas in either spring or summer, one can predict the DE based simply on time, if conditions change to a more energetic state where dispersants are applicable. The predicted data presented (Table S2) shows changes in oil viscosity with time of weathering and the DE to treat a spill on water after the initial release in spring (ca. 6 °C) and summer (ca. 15 °C) conditions. In this case, the bitumen blends’ viscosities exceeded 2000 cSt in 24 h for spring and summer, thus having a great effect on the predicted DE to treat these weathered oil products. For the conventional crude (Heidrun), changes in its viscosity were <500 cSt in 360 h after weathering on water and the predicted DE to treat the weathered oil was good. However, similar to

King et al. [9] the data was based on an oil slick thickness of 4 mm and the effect of slick thickness on the rate of weathering of oil is considered in the discussion to follow.

A previous report [29] suggested that temperature and time were greater factors in oil evaporation than surface wind speed or oil slick thickness for a wide range of crude oils. In contrast, Gros et al. [30] determined that wind speed strongly affected the thickness of the oil slick and thus evaporation very early in an experimental spill of Norwegian crude in the North Sea. So one would assume that the thickness of the oil slick can affect the rate of weathering of condensate bitumen blends (where 30% of the product is gas condensate). This was substantiated by King et al. [9], where the thickness of the oil slick affected the rate of weathering of condensate bitumen blends. However, the results of that study showed that for a 4 mm thick slick of AWB, the viscosity exceeded 10,000 cSt within three hours of weathering on temperate (22 °C) water. Under such conditions there was a rapid change in the viscosity of the oil regardless of oil slick thickness, where the time window for dispersant use would be closed, as indicated from studies by others [24–26]. Temperature and the thickness of the oil slick affects the rate of weathering of oil [27], so these factors could affect the use of Equation (4) to estimate DE. The effects of temperature on DE have been substantiated by Li et al. [8], but not the weathering of oil at different temperatures and its inherent effect on DE to treat a spill at various points in time after the initial release as shown in Table S2. The function (Equation (4)) proposed here may be applicable to other oil types with the limitations mentioned above.

4. Conclusions

The natural and chemically enhanced dispersion of four oil products were investigated in the wave tank of the Center for Offshore Oil and Gas Research (COOGER), placed outdoor in Halifax Nova Scotia, Canada. The products were: Access Western Blend, Heidrun (conventional heavy crude), synbit, and Western Canadian Select, and the dispersant was COREXIT9500A. Experiments were conducted in spring and summer to capture the impact of temperature, and the hydrodynamic conditions in the tank were of breaking waves with a wave height of 0.4 m. The results showed that the natural (or physical) dispersion of these oils was less than 10%, and there was essentially no difference in behavior between seasons. The application of dispersant increased the DE by an order of magnitude within a significant statistical level ($p < 0.05$). Also, temperature (summer versus spring) resulted in larger chemical DE for all oils, except for the conventional oil (Heidrun). For this study, oil type, fresh and weathered oil, and seasonal effect data produced a broad range of oil viscosities with measured DE values that were fitted to a linear regression model. The approach could, therefore, be readily used to estimate the chemical DE values of released oil.

Equation (4) has the potential to predict the DE based simply on the time of weathering of oil. For this study it was applied to various bitumen blends and the conventional crude, Heidrun, but may be applicable to other oils as well. However, some limitations of the function to consider are the oil type, thickness of the oil slick, temperature, and the fact that the weathering of oil initially occurs in calm waters prior to more energetic sea states where dispersant is applicable. Although the dispersion model has only been considered in its application to oil spills in Canadian waters, it may be applicable to predict the use of dispersant to treat spills in international waters as well.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2077-1312/6/4/128/s1>; Table S1: Summary of test conditions, physical properties of test oils, and dispersion effectiveness measurements; Table S2: Predicted viscosity data generated from oil weathering (Equation (2)) and dispersion effectiveness (Equation (3)) models; Figure S1: The plot represents the seasonal effect on particle size distribution data (LISST 100X-#1; 1.2 m from oil release) obtained at the point in time of maximum total particle concentration during the natural dispersion of four oils; Figure S2: The plot represents the seasonal effect on particle size distribution data (LISST 100X-#2; 12 m from oil release) obtained at the point in time of maximum total particle concentration during the natural dispersion of four oils; Figure S3: The plot represents the seasonal effect on particle size distribution data (LISST 100X-#1; 1.2 m from oil release) obtained at the point in time of maximum total particle concentration during the chemically enhanced dispersion of four oils; Figure S4: The plot represents the seasonal effect on particle size distribution data (LISST 100X-#2; 12 m from oil release) obtained at the point in time of maximum total particle concentration during the chemically enhanced dispersion of four oils; Figure S5: Contour plots (LISST 100X-#1; 1.2 m from oil release) illustrating seasonal effect on the concentration of oil particle sizes simulated in the wave tank for the natural dispersion of four oil types.

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