

A Comparison of the Properties of Diluted Bitumen Crudes with other Oils

POLARIS Applied Sciences, Inc. (2013)

Abstract

Diluted bitumen (dilbit) crude oil represents a range of oils produced from bitumen extracted from oil sands in Western, Canada. As these reserves are increasingly in demand, more transportation options are being sought to deliver the product to refineries both in North America and abroad. Concerns over potential spills have been the point of discussion with questions raised about applicable countermeasures and limitations, the possible fate and behavior of these oils, and environmental effects. Limited related research has been conducted on these oils over the past 30 years although recent testing was completed in 2013. Laboratory and mesoscale weathering experiments show dilbits have physical properties very much aligned with a range of intermediate fuel oils and other heavy crude oils and generally, depending the initial blend and the state of weathering, and are not characterized as nonfloating oils. This paper provides a review of dilbit oil properties, applicable countermeasures, and potential fate and behavior for spills to land, freshwater, and marine settings and compares these oils to other oil commodities transported and used over the past decades.

Contents

| | |
|--|----|
| Introduction | 3 |
| Oil Classifications | 3 |
| Floating and Non-floating Oils | 4 |
| Comparison of Physical Properties | 5 |
| Comparison of Chemical Properties | 7 |
| Comparison of Spilled Oil Behavior | 8 |
| Behavior for Spills to Ground or Shore | 11 |
| Behavior for Spills to Water | 13 |
| Comparison of Spill Countermeasures, Effectiveness and Limitations | 14 |
| Mechanical Containment and Recovery | 14 |
| Dispersant Application | 17 |
| In-Situ Burning (ISB) | 18 |
| Shoreline Cleanup | 19 |
| Wildlife Treatment | 20 |
| Conclusions | 21 |
| References | 23 |

Introduction

The oil properties and behavior of diluted 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 diluted Alberta oil sands crude oils to export destinations. 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 (Brown and Nicholson, 1991; Brown et al., 1992; SLRoss 2010a,b; WPW, 2013). Oil fate, behavior and spill response issues associated with heavy oils in general have been the focus of numerous reports (Ansell et al., 2001; BMT Cordah, 2009; Brown et al., 1997; Lee et al., 1992; Michel et al., 1995; NRC, 1999). This review and compilation of dilbit properties and comparison to other crude oils and refined products provides perspective to their behavior, effects, and potential oil spill countermeasures in context of the range of hydrocarbons commonly transported today.

The bitumen contained in the Alberta oil sands is naturally occurring petroleum that exists in the semi-solid or solid phase in natural deposits. The extracted bitumen is extremely viscous and will not flow unless heated or diluted with lighter hydrocarbons used as a diluent. At room temperature, it is much like cold molasses. The World Energy Council (WEC) defines natural bitumen as "oil having a viscosity greater than 10,000 centipoise under reservoir conditions and an API gravity of less than 10° API". In order to transport it through pipelines, a diluent is added to the bitumen. The combination of bitumen with diluent produces a homogeneous blend that has considerably lower density and viscosity with good pumping and flow properties. This product is often referred to as Diluted Bitumen or Dilbit. The diluent used could be lighter crude oils, synthetic crude oils, or natural gas condensates. The dilbit product must meet quality specifications that are posted with the National Energy Board in Canada and the Federal Energy Regulatory Commission in the U.S. To ensure pipeline transportability, NEB tariffs specify that the density of crude oil shipments not exceed 940 kg/m³ at a reference temperature of 15°C and that viscosity not exceed 350 cSt, when measured at the posted pipeline operating temperature. Given the range of temperatures throughout the year in which pipelines operate, the posting temperatures vary and blending must be adjusted to ensure viscosity is not exceeded.

Oil Classifications

Petroleum-based oils range from naturally occurring materials, such as condensate, crude oil, bitumen, and tar, to refined processed products such as aviation fuels, gasoline, and lube oils. Whether naturally occurring or processed, petroleum-based oils encompass a wide range of physical and chemical properties. The oil spill response community has developed different classifications to pool types of oil. Classifications include:

- persistent and non-persistent (see examples of used in Alaska Dep. Of Environmental Conservation regulations, OPRC Conventions, and International Tanker Owners Pollution Federation),
- Groups 1 through 5 (or I through V)

In the US, the EPA and USCG define petroleum-based oil groups as follows:

Group 1 oils include:

Petroleum-based oil that, at the time of shipment, consists of hydrocarbon fractions:

- at least 50 percent of which by volume, distill at a temperature of 340 degrees C (645 degrees F); and
- at least 95 percent of which by volume, distill at a temperature of 370 degrees C (700 degrees F); and

Group 2 - specific gravity less than 0.85;

Group 3 - specific gravity equal to or greater than 0.85 and less than 0.95;

Group 4 - specific gravity equal to or greater than 0.95 and less than 1.0; or

Group 5 - specific gravity equal to or greater than 1.0.

Group 1 oils (non-persistent) tend to dissipate completely through evaporation within a few hours and do not normally form emulsions (Table 1). Group 2 and 3 oils can lose up to 40% by volume through evaporation but, because of their tendency to form viscous emulsions, there may be an initial volume increase as well as limited natural dispersion, particularly in the case of Group 3 oils. Group 4 oils are very persistent due to the minimal content of volatile hydrocarbons and their high viscosity, which preclude both evaporation and dispersion. Group 5 is meant to collectively classify oils whose density is higher than that of freshwater.

Table 1 Oil groups and examples

| Group | Density | API | Examples |
|---------|-----------------------------------|--------------------|---|
| Group 1 | Less than 0.8 | >45.2 | Gasoline, Kerosene |
| Group 2 | 0.8 - 0.85 | 45.2-34.8 | Gas Oil, Alberta light crude |
| Group 3 | 0.85 - 0.95 | 34.8-17.3 | Alberta medium to heavy crude oils; dilbits |
| Group 4 | Greater than 0.95 and less than 1 | <17.3 to ≥ 10 | Intermediate Fuel Oil (IFO) 180 (Bunker B), IFO ≥ 380 (Bunker C) |
| Group 5 | Greater than 1 | <10 | Orimulsion®, Boscan crude |

Floating and Non-floating Oils

Group 5 oils are by definition more dense than freshwater and, as such, would sink if spilled into water with a density of 1. There have been a number of Group 5 spills attended to by response organizations, some of which showed that even Group 5 oils can float depending on their composition and the characteristics of the receiving waters (salinity, temperature, suspended sediment content) (Michel et al., 1995; Michel, 2008). Oils in Groups 3 and 4 can become neutrally or negatively buoyant in freshwater or saltwater, as can Group 5 oils in saltwater, through several mechanisms (Michel and Galt, 1995). Burns et al. (1995) reported two factors as the major causes for the formation of non-floating oil during the discharge of over 3,000 m³ of low API gravity oil in San Juan, Puerto Rico in 1994: (1) the oil properties (Group 5 with an API gravity of 9.5) and (2) a high likelihood of sand being rapidly mixed with

oil into the high energy surf zone. These same mechanisms are recognized as the primary factors causing heavy oils to submerge or sink (NRC, 1999).

Whether a dilbit sinks after losing its light fractions due to evaporation was one of the main questions that triggered tank tests to investigate the behavior of diluted bitumen when spilled into a freshwater (SL Ross 2010) or brackish marine environment (WPW, 2013). Both Cold Lake and Access Western Blend dilbits are lighter than freshwater, as required for pipeline specifications (i.e., absolute density less than or equal to 940 at reference temperature). Mesoscale weathering experiments done in Gainford, Alberta (WPW 2013) showed that Cold Lake (CL) and Access Western Blend (AWB) dilbits exhibited properties typical of a heavy, “conventional” crude oil as they weathered but in no instance was any oil observed to have sunk after 10 days of weathering on 20 ppt brackish water under varied physical conditions. The physical properties of weathering oil measured during those tests showed that dilbit spilled into fresh, brackish, or saltwater will stay on the water surface for days unless another mechanism mixes it into the water column, as would be the case for most Group 3 and 4 oils. Only after extensive weathering, or mixing with suspended particulate material, may some portion of weathered dilbit become submerged or sink.

Comparison of Physical Properties

Typical physical properties for a broad range of oil types are summarized in Table 2.

Table 2 Ranges of physical properties for example oil types.

| Property | Units | Oil Types | | | | | | | |
|---------------------|---------------------------|-----------|-----------|-------------|---|--------------|-----------------------|------------------|--------------------|
| | | Gasoline | Diesel | Light Crude | Dilbit ¹ | Heavy Crude | Intermediate Fuel Oil | Bunker C | Crude Oil Emulsion |
| Density | Kg/m ³ at 15°C | 720 | 840 | 780 to 880 | 824 to 941 | 880 to 1000 | 940 to 990 | 960 to 1040 | 950 to 1000 |
| API Gravity | | 65 | 35 | 30 to 50 | 18 to 39 | 10 to 30 | 10 to 20 | 5 to 15 | 10 to 15 |
| Viscosity | mPas at 15°C | 0.5 | 2 | 5 to 50 | 270.5* to 265,263** | 50 to 50,000 | 1,000 to 15,000 | 10,000 to 50,000 | 20,000 to 100,000 |
| Flash point | 15°C | -35 | 45 | -30 to 30 | <-35** ^m to 58* ^m | -30 to 60 | 80 to 100 | >100 | >80 |
| Solubility in Water | ppm | 200 | 40 | 10 to 50 | - | 5 to 30 | 10 to 30 | 1 to 5 | - |
| Pour Point | °C | NR | -35 TO -1 | -40 to 30 | -30** ^m to 15** ^m | -40 to 30 | -10 to 10 | 5 to 20 | >50 |
| Interfacial Tension | mN/m at 15°C | 27 | 27 | 10 to 30 | 27* ^m to 150* ^m | 15 to 30 | 25 to 30 | 25 to 35 | - |

Modified from Fingas (2001); ¹Values provided include weathered dilbit from tests; NA= not relevant; * Calculated for AWB; ** Calculated value for CL; *^m Measured value of AWB; **^m Measured value of CL

Crude oils produced in Alberta have similar physical characteristics that encompass the light to heavy crude oil properties (Table 3) and overlap with intermediate fuel oil and bunker fuel listed in Table 2. The Access Western Blend (AWB) and Cold Lake (CL) dilbits tested at Gainford (WPW, 2013), were slightly less dense (922 and 928 Kg/m³, respectively) than 5 other common oil products from Alberta and within 3% of the average density of the listed Alberta crude oil blends in Table 3.

Table 3 Ranges of physical properties for example Alberta crude oil blends and ANS crude

| Properties | Mixed Sweet Blend (MSW) | Husky Synthetic Blend (HSB) | Premium Albian Synthetic (PAS) | Lloyd Kerrobert (LLK) | Wabasca Heavy (WH) | Western Canadian Blend (WCB) | Access Western Blend (AWB) | Cold Lake (CL) | Western Canadian Select (WCS) | Albian Heavy Synthetic (AHS) | ANS Crude ² |
|---|-------------------------|-----------------------------|--------------------------------|-------------------------|--------------------|------------------------------|----------------------------|----------------|-------------------------------|------------------------------|------------------------|
| Type crude | Light sweet | Light synthetic | | Heavy sour conventional | | | Dilbit | | | Dilsynbit | Medium |
| Density ¹ (kg/m ³) | 827.2 ± 3.3 | 863.8 ± 3.8 | 860.4 ± 5.4 | 929.8 ± 4.6 | 932.2 ± 4.8 | 929.5 ± 4.7 | 922.2 ± 5.4 | 928.0 ± 5.1 | 929.3 ± 4.9 | 938.8 ± 2.4 | 866 - 894 |
| Gravity ¹ (°API) | 39.4 ± 0.7 | 32.2 ± 0.7 | 32.8 ± 1.0 | 20.6 ± 0.7 | 20.2 ± 0.8 | 20.6 ± 0.8 | 21.8 ± 0.9 | 20.9 ± 0.8 | 20.6 ± 0.8 | 19.1 ± 0.4 | 31.8 - 26.6 |
| 10% Mass Recovered ¹ | 87.4 ± 9.26 | 175.1 ± 11.07 | 174.1 ± 5.90 | 141.8 ± 44.55 | 142.6 ± 20.54 | 162.9 ± 28.69 | 83.0 ± 17.27 | 105.3 ± 25.76 | 127.8 ± 34.17 | 106.4 ± 25.45 | 99 - 127 |
| 20% Mass Recovered ¹ | 130.9 ± 8.50 | 240.1 ± 9.60 | 212.8 ± 7.08 | 271.1 ± 19.59 | 249.6 ± 15.61 | 265.8 ± 13.40 | 234.3 ± 44.40 | 255.3 ± 20.62 | 261.4 ± 19.36 | 256.8 ± 47.21 | 159 - 197 |
| 30% Mass Recovered ¹ | 183.6 ± 10.86 | 277.4 ± 9.50 | 240.7 ± 8.70 | 343.0 ± 15.07 | 324.1 ± 13.11 | 331.6 ± 11.67 | 348.7 ± 21.50 | 340.2 ± 13.90 | 336.9 ± 13.29 | 377.0 ± 17.89 | 216 - 262 |
| 40% Mass Recovered ¹ | 240.1 ± 12.26 | 307.0 ± 8.78 | 265.0 ± 9.79 | 408.6 ± 13.54 | 394.9 ± 12.57 | 394.2 ± 12.01 | 424.1 ± 17.81 | 411.4 ± 13.30 | 403.6 ± 13.12 | 433.8 ± 12.07 | 236 - 316 |

Notes: 1) from CrudeMonitor (2013) - 5-yr average and range; 2) Range obtained from ETC Oil Database

Comparison of Chemical Properties

The principal compounds in petroleum are paraffins (alkanes), naphthenes (cyclohexanes), and aromatic hydrocarbons, with lesser amounts of asphaltic materials. Paraffins are alkanes consisting only of hydrogen and carbon atoms forming an open chain by single bonds (not joined in cyclic structures). The simplest possible alkane (the parent molecule) is methane, CH₄. Saturated oils and waxes are examples of larger alkanes where the number of carbon atoms-in chain is greater than 10, with a hydrogen atom in every possible location (saturated). Crude oils have a wide range of alkanes from as low as 20% to over 60% by composition. Diluted bitumen blends contain between 20 to over 30% alkanes below C10 (Table 4), the most common being pentanes and hexanes as is typical in other crude oils. C11 through C30 (saturated oils and waxes) represented another approximately 20% by weight of the dilbits tested at Gainford (WPW, 2013). The overall composition of paraffins in dilbit blends of 40 to 50% found during the Gainford tests (WPW, 2013) is within the range of other crude oils.

Monocyclic and polycyclic aromatic hydrocarbons are commonly associated with the majority of acute and chronic oil toxicity and are more commonly evaluated analytically following oil spills. Crude oils contain lower percentages of aromatics than refined oils that have both higher aromatic and residual concentrations from the refining process. The AWB and CL dilbit tested at Gainford contained approximately 5% (AWB) to 11% (CL) total PAH by weight prior to weathering, with approximately 1% by weight comprised of monocyclic compounds (BTEX) (WPW, 2013). The aromatic composition is similar to other crude oils and much less than intermediate fuel oils with aromatics of 30% or more. An overall comparison of BTEX and alkane content of example dilbit blends is provided in Table 4.

Cyclohexanes are commonly called naphthenes in the oil industry and consist of saturated hydrocarbon structures linked in a ring. Naphthenes comprise the remainder of the composition of crude oils at 30 to 60%.

Table 4 Ranges of select chemical properties (volume percent) for example Alberta crude oil blends

| Component | Mixed Sweet Blend | Husky Synthetic Blend | Premium Albion Synthetic | Lloyd Kerrobert | Wabasca Heavy | Western Canadian Blend | Access Western Blend | Cold Lake | Western Canadian Select | Albian Heavy Synthetic |
|---------------|-------------------|-----------------------|--------------------------|-----------------|---------------|------------------------|----------------------|-------------|-------------------------|------------------------|
| | (MSW) | (HSB) | (PAS) | (LLK) | (WH) | (WCB) | (AWB) | (CL) | (WCS) | (AHS) |
| Benzene | 0.27 ± 0.05 | 0.04 ± 0.01 | 0.03 ± 0.01 | 0.14 ± 0.05 | 0.12 ± 0.02 | 0.10 ± 0.03 | 0.29 ± 0.03 | 0.23 ± 0.03 | 0.16 ± 0.03 | 0.15 ± 0.03 |
| Toluene | 0.81 ± 0.13 | 0.15 ± 0.03 | 0.21 ± 0.07 | 0.21 ± 0.08 | 0.29 ± 0.07 | 0.18 ± 0.04 | 0.50 ± 0.08 | 0.39 ± 0.07 | 0.30 ± 0.06 | 0.37 ± 0.09 |
| Ethyl Benzene | 0.24 ± 0.03 | 0.10 ± 0.02 | 0.16 ± 0.03 | 0.04 ± 0.01 | 0.13 ± 0.02 | 0.06 ± 0.01 | 0.06 ± 0.01 | 0.06 ± 0.01 | 0.06 ± 0.01 | 0.12 ± 0.03 |
| Xylenes | 1.06 ± 0.13 | 0.33 ± 0.05 | 0.54 ± 0.16 | 0.19 ± 0.06 | 0.47 ± 0.10 | 0.25 ± 0.04 | 0.39 ± 0.08 | 0.33 ± 0.07 | 0.29 ± 0.06 | 0.43 ± 0.12 |
| Butanes | 3.86 ± 0.62 | 2.32 ± 0.74 | 0.24 ± 0.45 | 1.75 ± 0.36 | 1.73 ± 0.34 | 0.62 ± 0.12 | 0.68 ± 0.15 | 1.02 ± 0.25 | 2.02 ± 0.39 | 1.50 ± 0.33 |
| Pentanes | 3.35 ± 0.58 | 1.61 ± 0.34 | 0.41 ± 0.27 | 5.57 ± 0.92 | 2.70 ± 0.79 | 3.72 ± 0.76 | 8.42 ± 1.21 | 6.18 ± 0.99 | 4.36 ± 0.81 | 4.66 ± 1.19 |
| Hexanes | 5.68 ± 0.55 | 2.02 ± 0.31 | 1.04 ± 0.29 | 3.19 ± 0.84 | 3.07 ± 0.37 | 3.11 ± 0.47 | 6.81 ± 0.67 | 5.31 ± 0.64 | 3.90 ± 0.54 | 5.10 ± 0.66 |
| Heptanes | 7.05 ± 0.57 | 2.03 ± 0.27 | 1.75 ± 0.34 | 2.07 ± 0.51 | 2.95 ± 0.40 | 2.51 ± 0.29 | 4.35 ± 0.49 | 3.36 ± 0.47 | 2.80 ± 0.43 | 3.81 ± 0.55 |
| Octanes | 7.10 ± 0.60 | 2.73 ± 0.34 | 3.31 ± 0.55 | 1.48 ± 0.35 | 3.01 ± 0.54 | 2.13 ± 0.22 | 2.57 ± 0.44 | 2.23 ± 0.43 | 2.11 ± 0.37 | 3.30 ± 0.64 |
| Nonanes | 5.51 ± 0.46 | 2.43 ± 0.31 | 3.96 ± 0.62 | 1.20 ± 0.29 | 2.50 ± 0.49 | 1.84 ± 0.31 | 1.25 ± 0.24 | 1.35 ± 0.31 | 1.49 ± 0.31 | 2.08 ± 0.51 |
| Decanes | 2.49 ± 0.26 | 1.29 ± 0.17 | 2.35 ± 0.40 | 0.59 ± 0.19 | 1.13 ± 0.28 | 0.88 ± 0.25 | 0.54 ± 0.12 | 0.63 ± 0.18 | 0.71 ± 0.16 | 0.93 ± 0.24 |

Source: CrudeMonitor (2013) - 5-yr average and range

Comparison of Spilled Oil Behavior

The main properties that affect the fate of spilled oil at sea are: specific gravity or density; distillation characteristics (its volatility); viscosity (its resistance to flow); and pour point (the temperature below which it will not flow). In addition, the wax and asphaltene content influence the likelihood that the oil will mix with water to form a water-in-oil emulsion. Oils that form stable oil-in-water emulsions persist longer at the water surface. The resin and asphaltene content determine the likelihood of tar-ball formation. These properties will change through time as spilled oil weathers. The behavior and character of the weathering oil are important considerations for spill response strategies and tactics.

Table 5 provides a summary comparison of the *changes* in key physical properties of representative oils through evaporative loss of lighter-end hydrocarbons. Table 6 summarizes example changes in oil chemistry.

Table 5 Changes in oil physical properties as a function of evaporative loss of light-ends

| | Weathering (weight %) | API | Sulphur Content (weight %) | Water (vol %) | Flash Point (C) | Density (g/mL) @ 0/15 | | Pour Point (C) | Dynamic Viscosity (cP) @ 0/15 | | Chemical Dispersability (%) | Adhesion (g/m ²) | Surface Tension (mN/m) @ 0/15 | | Oil/Brine(33ppt) Interfacial Tension (mN/m) @ 0/15 | | Oil Freshwater Interfacial Tension (mN/m) @ 0/15 | | Emulsion Formation | | | | | |
|--------------------------|-----------------------|-------------------|----------------------------|---------------|-----------------|-----------------------|--------|----------------|-------------------------------|--------|-----------------------------|------------------------------|-------------------------------|------|--|------|--|------|-------------------------|------------------|----------------------|----------------------------|-----------|---|
| | | | | | | 0 C/1 C* | 15 C | | 0 C/1 C* | 15 C | | | 0 C | 15 C | 0 C | 15 C | 0 C | 15 C | 15 C/14 C* | Visual Stability | Complex Modulus (Pa) | Emulsion Water Content (%) | Reference | |
| ANS Crude Oil | 0 | 30.89 | 1.1 | <0.1 | <-8 | 0.877 | 0.8663 | -32 | 23.2 | 11.5 | 47 | 20 | 27.3 | 26.4 | 22.5 | 20.2 | 26.7 | 23.6 | Unstable | | | 1 | | |
| | 10 | | 1.2 | <0.1 | 19 | 0.9054 | 0.894 | -20 | 76.7 | 31.8 | 45 | 35 | 29.8 | 28.4 | 25.3 | 23.1 | 28.1 | 25.5 | Unstable | | | 1 | | |
| | 22.5 | | 1.38 | <0.1 | 75 | 0.9303 | 0.9189 | -9 | 614 | 152 | 34 | 38 | 31.2 | 30.4 | 26.8 | 24.2 | 30.8 | 27.7 | Unstable | | | 1 | | |
| | 30.5 | | 1.5 | <0.1 | 115 | 0.9457 | 0.934 | -6 | 4230 | 614.7 | 15 | 40 | 33.1 | 31.8 | 30.1 | 25.6 | 33.2 | 30.2 | Mesostable | 155 | 72.9 | 1 | | |
| Albert Sweet Mixed Blend | 0 | 35.72 | 0.63 | <0.1 | -4.3 | 0.8536 | 0.8404 | -18 | 23.6 | 6.1 | 28.1 | 4.8 | 28.3 | 25.5 | 19.2 | 23.1 | 30.7 | 14.3 | Mesostable | 133 | 89.6 | 1 | | |
| | 12.6 | | 0.7 | <0.1 | 27.8 | 0.8805 | 0.8676 | -12 | 45.3 | 13.8 | 26.6 | 25 | 29.1 | 27.2 | 29 | 23.1 | 33.9 | 16 | Mesostable | 409 | 92.9 | 1 | | |
| | 24.3 | | 0.78 | <0.1 | 67.8 | 0.8987 | 0.8852 | -12 | | 31.5 | 17.2 | 33.6 | 30.1 | 28 | 21.1 | 24.1 | 31.1 | 15.3 | Stable | 630 | 87.7 | 1 | | |
| | 36.8 | | 0.89 | <0.1 | >110 | 0.9151 | 0.9017 | 9 | | 123.2 | 10.9 | 43.7 | 31.1 | 29.9 | 20.1 | 23.2 | 32.7 | 14.3 | Stable | 1025 | 86 | 1 | | |
| Arabian Light | 0 | 31.3 | 1.93 | <0.1 | <-10 | 0.8776 | 0.8641 | -21 | 32.6 | 13 | 19 | 17 | 27.2 | 26 | 21.3 | 21.6 | 23.5 | 23.8 | Mesostable | 92.7 | 91.1 | 1 | | |
| | 9.2 | | 2.17 | <0.1 | 36.5 | 0.8994 | 0.866 | -15 | 77.6 | 27.4 | 13.8 | 28 | 29.2 | 27.9 | 22.2 | 22.8 | 22.4 | 22 | Mesostable | 212 | 88.6 | 1 | | |
| | 17.6 | | 2.36 | <0.1 | 71.7 | 0.9154 | 0.9028 | -8 | | 59.9 | 10 | 30 | 30.6 | 28.4 | 16.4 | 24.6 | 28.3 | 25.7 | Stable | 274 | 83.8 | 1 | | |
| | 26 | | 2.6 | <0.1 | >110 | 0.9321 | 0.9193 | -9 | | 173.7 | 7.9 | 35 | 30.9 | 30.2 | 26.8 | 20.4 | 30.1 | 22.4 | Stable | 503 | 83.8 | 1 | | |
| Sockeye | 0 | 19.32 | 4.51 | 0.8 | -4 | 0.9465 | 0.9354 | -25 | 3220 | 761 | 11.8 | 70 | 30.1 | 28.8 | 23 | 21.9 | 23.7 | 21.4 | Mesostable | 183 | 75.6 | 1 | | |
| | 6.9 | | 4.95 | 0.1 | 35 | 0.9642 | 0.9537 | -18 | 13600 | 2720 | 9.6 | 70 | NM | 31.3 | NM | 23.1 | NM | 24.9 | Mesostable | 251 | 73.3 | 1 | | |
| | 13 | | 5.19 | 0.1 | 72 | 0.9798 | 0.9692 | 2 | 143000 | 15100 | 10.1 | 90 | NM | 32.2 | NM | NM | NM | NM | Entrained Water | 391 | 53.4 | 1 | | |
| | 19.8 | | 5.47 | <0.1 | >110 | 0.9951 | 0.9839 | 13 | 5300000 | 274000 | 8.9 | 350 | NM | NM | NM | NM | NM | NM | Entrained Water | 1298 | 17.7 | 1 | | |
| South Louisiana | 0 | 32.72 | 0.49 | <0.1 | <-10 | 0.8668 | 0.8562 | -41 | 18.5 | 10.1 | 26.5 | 24 | 28.3 | 26.1 | 20.9 | 16.8 | 20.8 | 15.5 | Unstable | | | 1 | | |
| | 10.9 | | 0.71 | <0.1 | 42.3 | 0.8888 | 0.877 | -19 | 54.8 | 23.7 | 23.5 | 34 | 29.3 | 28.1 | 22 | 19.4 | 25.2 | 15.8 | Unstable | | | 1 | | |
| | 19.7 | | 0.79 | <0.1 | 80.7 | 0.9025 | 0.8906 | -14 | 217.3 | 48.9 | 15.8 | 50 | 30.4 | 29.4 | 22 | 22.2 | 25.3 | 22.3 | Unstable | | | 1 | | |
| | 27.7 | | 0.88 | <0.1 | >110 | 0.9135 | 0.9018 | -11 | 515.9 | 141 | 10.3 | 28 | 31.1 | 29.8 | 20.6 | 18.4 | 24.7 | 21.9 | Unstable | | | 1 | | |
| West Texas Intermediate | 0 | 34.38 | 0.86 | <0.1 | <-10 | 0.8594 | 0.8474 | -22 | 19.2 | 8.6 | 27.7 | 12.4 | 27.4 | 26 | 18.8 | 15.6 | 19.3 | 15.8 | Unstable | | | 1 | | |
| | 10.1 | | 1.01 | <0.1 | 32.8 | 0.8792 | 0.8665 | -12 | 42.1 | 16.4 | 23.6 | 16.8 | 28.7 | 27.6 | 19.4 | 14.6 | 19.9 | 18.1 | Unstable | | | 1 | | |
| | 21 | | 1.11 | <0.1 | 66 | 0.8956 | 0.8827 | 1 | 253.6 | 37.5 | 13.3 | 27.6 | 29.7 | 28.7 | 19.2 | 12.6 | 21 | 17.2 | Mesostable | 19.1 | 82.7 | 1 | | |
| | 31.7 | | 1.24 | <0.1 | >110 | 0.9103 | 0.8973 | 7 | 853.6 | 112.3 | 12.8 | 33.2 | 31.4 | 29.2 | 19.9 | 17.3 | 22.7 | 17.1 | Mesostable | 81.9 | 83.6 | 1 | | |
| Fuel Oil #2/Diesel | 0 | 37.52 | 0.09 | <0.1 | 54 | 0.8423 | 0.831 | -50 | 4.08 | 2.76 | 72 | 2 | 28.7 | 27.5 | 21.5 | 18.1 | 25 | 21.6 | Unstable | | | 1 | | |
| | 7.2 | | 0.1 | <0.1 | 65 | 0.8468 | 0.835 | -49 | 4.55 | 3.27 | 71 | 12 | 28.8 | 27.7 | 24.8 | 19.5 | 28.1 | 23.9 | Unstable | | | 1 | | |
| | 14.2 | | 0.1 | <0.1 | 76 | 0.8493 | 0.8383 | -43 | 5.16 | 3.42 | 64 | 13 | 28.6 | 28.1 | 26.6 | 20.7 | 28.5 | 24.3 | Unstable | | | 1 | | |
| | 22 | | 0.1 | <0.1 | 85 | 0.8524 | 0.8416 | -41 | 5.59 | 4.18 | 66 | 8 | 29.3 | 28.3 | 28.5 | 21.9 | 29.1 | 25.7 | Unstable | | | 1 | | |
| Fuel Oil #5 | 0 | 11.5 | 1 | 3.1 | 94 | 1.0034 | 0.9883 | -19 | 18600 | 1410 | 15 | 34 | NM | NM | NM | NM | NM | NM | Stable | 1590 | 78.3 | 1 | | |
| | 7.2 | | 1.08 | <0.1 | 136 | 1.016 | 1.0032 | -3 | 72000 | 4530 | 7 | 47 | NM | NM | NM | NM | NM | NM | Stable | 2490 | 72.8 | 1 | | |
| | | | | | | | | | | | | | | | | | | | | | | | 1 | |
| | | | | | | | | | | | | | | | | | | | | | | | | 1 |
| Heavy Fuel Oil | 0 | 11.47 | 1.48 | 0.1 | 111 | 1.0015 | 0.9888 | -1 | 241000 | 22800 | 9 | 100 | NM | NM | NM | NM | NM | NM | Entrained | 752 | 57.7 | 1 | | |
| | 2.5 | | 1.5 | <0.1 | 133 | 1.0101 | 0.9988 | 11 | 3600000 | 149000 | 6 | 240 | NM | NM | NM | NM | NM | NM | Entrained | 984 | 24.1 | 1 | | |
| | | | | | | | | | | | | | | | | | | | | | | | | 1 |
| | | | | | | | | | | | | | | | | | | | | | | | | 1 |
| CL | 0 | 21.4 ⁺ | | 0.9 | -4.5 | 0.0948 [*] | 0.936 | <-24 | 1363 [*] | 368 | | | | | | | | | Mesostable [*] | | 53 | 2/3 | | |
| | 14.3 | 14.3 ⁺ | | | 4 | 0.987 [*] | 0.977 | -15 | 57548 [*] | 9227 | | | | | | | | | Unstable [*] | | 0 | 2/3 | | |
| | 17 | 12.1 ⁺ | | | 4 | 0.990 [*] | 0.981 | -12 | 98625 [*] | 14486 | | | | | | | | | Unstable [*] | | 0 | 2/3 | | |
| | 23 ⁺ | 10.2 | | 33.4 | 56 | | 0.9986 | 9 | | | | | | | | | | | | | | | 3 | |

References: 1) Wang et al 2003, 2) Values are calculated based on data from WPW (2013) and fit to the evaporation vs. density chart from SL Ross (2010a)

Table 6 Changes in key oil chemical properties as a function of evaporative loss of light-ends

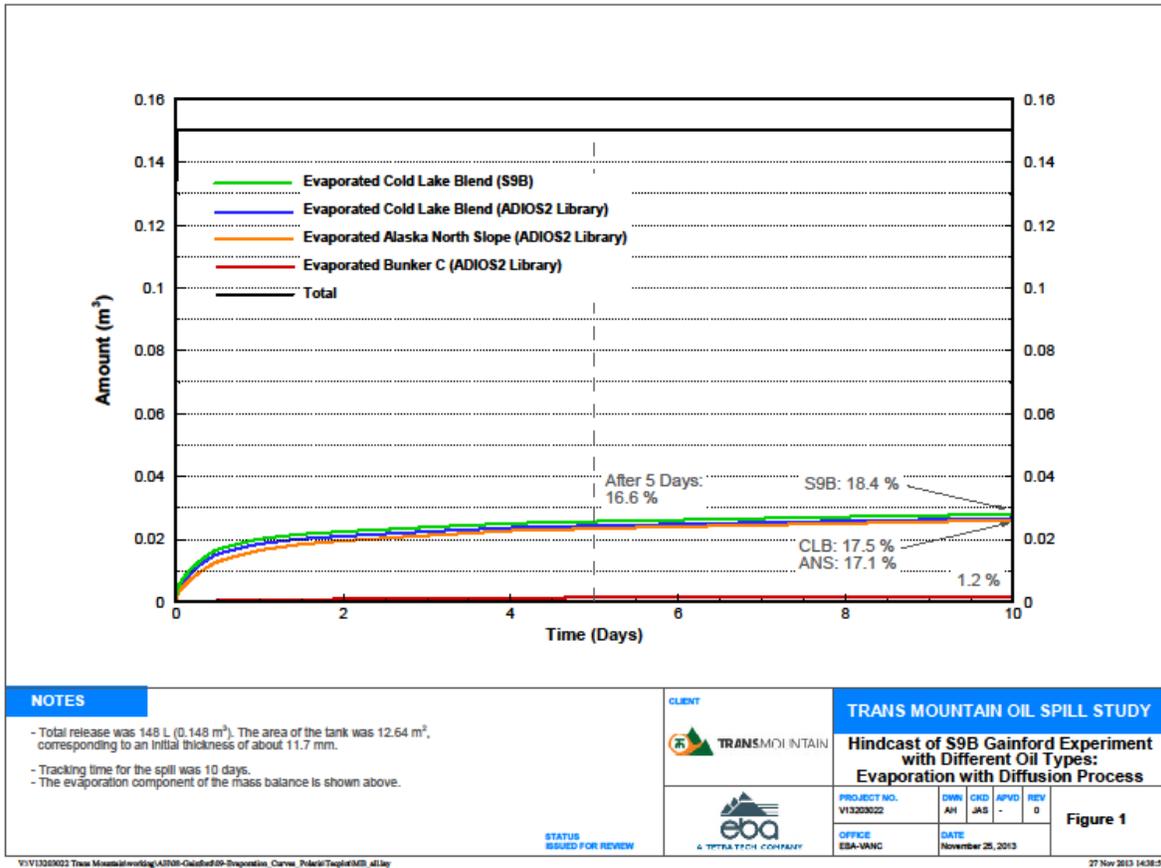
| | Weathering (weight %) | Benzene | | Toluene | | Ethylbenzene | | Xylenes | | BTEX | | Reference |
|---------------------------|-----------------------|---------|------|---------|------|--------------|------|---------|------|-------|-------|-----------|
| | | % vol | ug/g | % vol | ug/g | % vol | ug/g | % vol | ug/g | % vol | ug/g | |
| ANS Crude Oil | 0 | 0.283 | 2866 | 0.592 | 5928 | 0.132 | 1319 | 0.616 | 6187 | 1.624 | 16300 | 1 |
| | 30.5 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 |
| Alberta Sweet Mixed Blend | 0 | 0.217 | 2261 | 0.515 | 5308 | 0.160 | 1646 | 0.865 | 8954 | 1.756 | 18170 | 1 |
| | 36.8 | 0 | 0 | 0.001 | 10 | 0 | 0 | 0.865 | 0 | 1.756 | 10 | 1 |
| Arabian Light | 0 | 0.097 | 979 | 0.304 | 3050 | 0.199 | 1995 | 0.489 | 4927 | 1.089 | 10950 | 1 |
| | 26 | 0.001 | 11 | 0.007 | 74 | 0.043 | 434 | 0.150 | 1508 | 0.202 | 2030 | 1 |
| Sockeye | 0 | 0.143 | 1343 | 0.219 | 2031 | 0.105 | 974 | 0.417 | 3880 | 0.885 | 8230 | 1 |
| | 19.8 | 0.001 | 9 | 0.001 | 12 | 0 | 0 | 0.000 | 1 | 0.002 | 20 | 1 |
| South Louisiana | 0 | 0.156 | 1598 | 0.351 | 3552 | 0.088 | 891 | 0.607 | 6164 | 1.202 | 12210 | 1 |
| | 27.7 | 0 | 0 | 0.001 | 10 | 0 | 0 | 0.000 | 2 | 0.001 | 12 | 1 |
| West Texas Intermediate | 0 | 0.389 | 4026 | 0.723 | 7395 | 0.474 | 4845 | 0.692 | 7105 | 2.278 | 23370 | 1 |
| | 31.7 | 0 | 0 | 0.001 | 13 | 0.000 | 0 | 0.000 | 1 | 0.001 | 14 | 1 |
| Fuel Oil #2/Diesel | 0 | 0.013 | 136 | 0.098 | 1024 | 0.059 | 619 | 0.360 | 3774 | 0.531 | 5550 | 1 |
| | 22 | 0 | 0 | 0 | 0 | 0 | 0 | 0.001 | 7 | 0.001 | 7 | 1 |
| Fuel Oil #5 | 0 | 0 | 0 | 0.017 | 149 | 0.014 | 124 | 0.070 | 612 | 0.101 | 890 | 1 |
| | 7.2 | 0 | 0 | 0 | 0 | 0.000 | 1 | 0.000 | 2 | 0.000 | 0 | 1 |
| Heavy Fuel Oil | 0 | 0.005 | 40 | 0.016 | 136 | 0.007 | 58 | 0.045 | 396 | 0.072 | 630 | 1 |
| | 2.5 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 |
| Orimulsion-400 | 0 | 0.002 | 16 | 0.003 | 29 | 0.003 | 22 | 0.003 | 29 | 0.011 | 100 | 1 |
| Lloyd Kerrobert | 0 | 0.13 | 1226 | 0.19 | 1772 | 0.05 | 466 | 0.17 | 1592 | 0.54 | 5056 | 2 |
| AWB | 0 | 0.3 | 2849 | 0.51 | 4791 | 0.06 | 563 | 0.38 | 3583 | 1.25 | 11787 | 3 |
| | | | | | | | | | | | | |
| CL | 0 | 0.24 | 2247 | 0.43 | 3983 | 0.06 | 555 | 0.36 | 3346 | 1.25 | 10132 | 3 |
| | | | | | | | | | | | | |
| Albian Heavy Synthetic | 0 | 0.2 | 1879 | 0.37 | 3438 | 0.08 | 743 | 0.35 | 3264 | 1.25 | 9324 | 2 |
| | | | | | | | | | | | | |

Reference: 1) Wang et al 2003; 2) CrudeMonitor; 3) WPW, 2013

Evaporation studies of CL (Brown and Nicholson, 1991; SLRoss 2010a) showed that the first hours of exposure to air results in rapid loss of portions of the diluent with resulting increases in density and viscosity. Evaporative loss is partly a function of air temperature, oil surface area and thickness, and wind. Figure 1 compares the predicted evaporative loss for CL, ANS and Bunker C oil under conditions assumed to be similar to those prevailing at Gainford for CL weathering under static conditions. The comparison shows a faster loss of light ends from dilbit with respect to ANS crude; however, the final evaporative loss for the two oils is similar. The heavier Bunker C has minimal light ends and negligible evaporative loss. The Gainford tests (WPW, 2013) showed that the absolute densities and viscosities (at 15°C) for CL increased from the fresh dilbit values of approximately 925 and 220 cSt, respectively, to over 960 and 4500 cSt within 6 to 24 hours of weathering, depending on the degree of physical energy applied to the oil on water, and corresponding to near 8% volume loss through evaporation (inferred from SLRoss (2010a) evaporation curves). These weathered properties are comparable to ANS crude at

only at colder temperatures (near 1°C) and after 30% volume loss (Table 5). Slower evaporation rates for dilbit would be expected for colder winter conditions (Brown and Nicholson, 1991).

Figure 1 Comparison of evaporative loss versus time for example oils



Behavior for Spills to Ground or Shore

Oil spilled to soil, ground or on shorelines (including river/stream banks) will tend to spread, evaporate, move downslope, and penetrate into the substrate. Key factors in oil behavior over substrates include ambient temperature, substrate grain sizes, substrate saturation (water), and additional components on or in substrate such as organic matter, vegetation, roots, and snow. Oil penetration into substrate is a function of oil viscosity (affected by temperature and emulsion, if stranded after being on water) and effective permeability (measured relative to the viscosity of the stranded oil).

Tsapralis, et al., 2013 reported the results of a study comparing the vertical penetration of a representative light, medium-heavy, heavy conventional crude oil, and dilbit in a sand-column. The conventional heavy crude (oil type not specified but initial viscosity of 177 cSt) penetrated the sand column more quickly than the diluted bitumen (180 cSt). The study concluded that the dilbit will spread and penetrate less into sand than the comparable crudes in the event of a spill.

Examples of measured oil retention in sediment are provided for Bunker C and IFO in Table 7. Coastal and Ocean Resources (2013) estimated dilbit penetration and retention on different substrates, assuming that weathered dilbit will: (1) have <1 cm of penetration in sands, < 5 cm in pebbles and < 10 cm in cobbles (Harper and Kory 1995); (2) retention of 300 L/m³ for sand, 200 L/m³ for pebble and 100 L/m³ for cobbles (Harper and Kory 1995); and (3) a layer of weathered oil above the sediments of 1 cm for rock, sand, pebbles and cobbles. These assumptions are derived from extrapolating the Bunker C results, which may reasonably reflect weathered dilbit behavior but are not representative of fresh dilbit.

Table 7 Comparison of measured and estimated oil retention in sediments

| Oil Type (% Evap, Temp) | Viscosity (cP) | Oil Retention (L/m ³) | | |
|----------------------------|-------------------|-----------------------------------|------------------|---------------------|
| | | Medium Pebbles | Large Pebbles | V. Large Pebbles |
| Bunker-6%, 2° | 160,000 | 288 | 157 | 85 |
| Bunker-0%, 2° | 80,000 | 197 | 94 | 77 |
| Bunker-0%, 5° | 50,000 | 213 | 130 | 51 |
| Bunker-0%, 10° | 30,000 | 155 | 47 | 24 |
| Bunker-0%, 15° | 15,000 | 52 | 68 | 5 |
| IFO-2.5%, 2° | 13,000 | 60 | 30 | 5 |
| IFO-2.5%, 15° | 3,000 | 18 | 5 | 0.1 |

Data from SOCSEX II (Harper and Kory 1995)

The range of viscosities associated with dilbits, depending on original blending and state of weathering, has implicit implications on the degree of potential penetration into soils or shoreline and retention. As with all crude oils, relatively fresh dilbit may penetrate into more porous and permeable materials but is less likely to be retained. As the degree of oil weathering, and viscosity, increases there is less penetration and a higher retention for oil that does enter into substrate pore space.

Table 8 documents oil penetration and the evaporative loss of CL that had been artificially weathered for 24 hours from four types of shoreline material at 10°C. Evaporative loss for stranded dilbit was highest on mixed sediment in low energy conditions, reaching 9.5% by the end of 48 hours after application.

Table 8 Summary of CL evaporation and penetration in Burrard Inlet sediments (derived from Brown et al., 1992)

| | Sediment characteristics | | | Percent Evaporation | | Penetration |
|----------------------------------|--------------------------|--|--|---------------------------|-------------------------------|--|
| | % Shell fragments | Sorting | Sand | hr | % | |
| Low energy mixed sediment | 10 - 60 | Wide variation; all sizes up to 4 cm | Top 3" of shore at mid tide point | 8 15 24 36 48 | 2.5 5 7.2 8.8 9.5 | Low water retention, resulted in high oil permeability |
| High energy mixed sediment | 10% | Wide variation of well-rounded rock sizes: 10 cm to 5 mm | Small amount | 8 15 24 36 48 | 2 3 3.8 4.5 4.7 | |
| Low energy sand sediment | - | Well sorted sandy shore | Tidal flat sandy beach | 8 15 24 36 48 | 1 2 3.4 4 4.6 | High penetration at top 1 mm; below 1 mm wet sediment has low oil permeability |
| Low energy estuary sand sediment | - | Well sorted sandy shore | Fine sediment, sand from estuary beach | 8 15 24 36 48 | 0.8 1 1.8 2.1 2.2 | |

Behavior for Spills to Water

Major factors influencing the behavior of spilled oil to water include size of spill relative to receiving waterbody (e.g., limited vs. unlimited spreading), ambient temperature (water and air), salinity, flow (turbulent, laminar, static), wind and wave energy, and materials in the waterbody such as vegetation, suspended sediment loads, organic matter, and snow/ice. Spreading and evaporation are more significant processes in the early stages of oil fate on water.

Understanding of the behavior of dilbit spilled to water is available from lab to mesoscale testing in tanks and from observations made following actual spills, such as the Westridge 2007 (Stantec, 2012) and Marshall 2010 (Enbridge, 2013; NTSB, 2012) spills. The most significant observations are that the behavior of dilbits tested or spilled are consistent with Group 3 and 4 crude oils: they float on water until oil densities change through weathering and/or sediment uptake. As with most crude oils, dilbits may gradually overwash, become suspended in the water column, or sink depending on the degree of weathering and formation of oil-mineral aggregates. The Marshall spill into Talmadge Creek and the Kalamazoo River resulted in oil transport down river with most oil remaining on the water surface. A portion of oil, mixed with river bank and/or suspended sediment, and submerged or in places sank. The Westridge spill resulted in a portion of dilbit on the surface waters of Burrard Inlet. No submerged or sunken oil was noted during that incident (Stantec, 2012). NRC (2012) noted that from 1991 to 1996, approximately 23% of the petroleum products spilled in U.S. waters were heavy oils. In only 20% of

those spills did a significant portion of the spilled products sink or become suspended in the water column. Most of the time, spills of heavy oil remained on the surface, as would be the case for most dilbit spills to non-turbulent water.

Comparison of Spill Countermeasures, Effectiveness and Limitations

Oil spill countermeasures include the more widely used mechanical systems for containment and collection as well as non-mechanical options. Response methodologies in these two general categories are applicable to most oils although the lightest and heaviest ends of the oil spectrum typically limit effective applicability of either.

Mechanical Containment and Recovery

Barriers commonly are used to mechanically impede oil spreading and movement. On land these may consist of berms, walls, and trenches. Booms, dams, and weirs are used to contain and concentrate oil on water. Containment challenges with booms include flow relative to the boom (current or towing speeds), turbulence, wave action, oil load in boom, and oil density relative to water. Heavy floating oil can be contained with conventional boom but boom efficiency may decrease as oil weathers to densities near those of the water body.

As oils are entrained into the water column, either through turbulence or combination of flow and densities near those of the receiving water body, conventional surface booming becomes less effective. Conventional booms might help to contain oils that are only slightly submerged and references that trawl nets specifically designed to recover heavy oils have proved effective in some incidents (BMT, 2009). Brown et al., (1992) performed containment tests on 24-hr weathered dilbit, bitumen, and emulsified dilbits using three barrier systems: conventional boom, fine mesh net, and bubble barrier. Only the boom and net barriers proved to be partially successful. Boom with mesh skirts provided moderately improved containment but were limited to approximately 0.48 m/s. Boom losses were greater for bitumen and emulsified dilbit relative to the 24-hr weathered dilbit. As would be expected for any heavy oil (natural or through weathering and/or emulsification), increased current speed and oil density result in less effective containment. The fine mesh tested successfully trapped floating and submerged oil, though some of that oil gradually extruded from the net.

Boom containment for dilbits and heavy oils is most effective prior to significant weathering and before any sediment uptake, hence the need to contain the relatively fresh oil. Once oil is easily overwashed or near neutral density, alternative forms of containment must be considered (Figure 2).

Figure 2 Containment options for submerged oil

| Oil has: | Depth (m) is: | |
|--|---|---|
| Near Neutral Buoyancy (oil suspended in water column) → | 0-2 ± → | • Physical Barrier |
| | 0-3 ± → | • Silt Curtain |
| | Maximum working depth not established → | • Pneumatic Curtain • Contain Onshore |
| Negative Buoyancy (sinks to bottom) → | 0-2 ± → | • Physical Barrier |
| | No depth restriction → | • Allow to collect in natural or artificial depression • Contain Onshore |
| SOURCE: Castle <i>et al.</i> 1995 | | |

Practical experience with containing dilbit was gained during response to the Marshall spill (Enbridge 2010). Containment on land encompassed berms and sorbent barriers. On water containment entailed multiple boom lines. These barriers helped to minimize oil movement and to concentrate oil for collection. As oil weathered and interacted with sediment, a portion became neutrally to negatively buoyant. Containment of the submerged to sunken portions of the oil included natural collection points (pools, basins) for sunken oil and geotextile barriers for submerged oil.

Skimming or collection of spilled dilbit can, and has been, achieved through conventional mechanical spill skimmer and pump systems. Pumps and skimmers that can recovery medium oils are well suited to collecting dilbits (Figure 3). Skimming systems are used to collect oil from the water surface and work best if oil is contained and preferably concentrated (hence booms) at the skimmer. Pumps are used in conjunction with skimmers to transfer oil to tanks but pumps also can be used directly on pooled oil, either on land or from sumps or collection/concentration areas in the case of sunken oil (BMT, 2009; Burns et.al., 1995; Ploen, 1995).

Figure 3 Skimmer selection guide (from ExxonMobil, 2008)

| | | Skimmer Type | | | | | | | | | | | | | | | |
|---|----------------------------------|---------------|--------------------|--------------------------------|----------------|-----------|---------------------|------|----------|---------------------------------|----------------------|------------------------|-----------|-----------------------|---------------|-------------|---|
| | | Weir Skimmers | | | | | Oleophilic Skimmers | | | | | Hydro-dynamic Skimmers | | | * | | |
| | | Simple Weir | Self-Leveling Weir | Weir with Integral Screw Auger | Advancing Weir | Weir Boom | Drum | Disc | Rope Mop | Zero Relative Velocity Rope Mop | Sorbent Lifting Belt | Brush | Water Jet | Submersion Plane/Belt | Rotating Vane | Paddle Belt | |
| Operating Environment | Open Water | ● | ● | ● | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ |
| | Protected Water | ○ | ● | ● | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ |
| | Calm Water | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ |
| | High Current >1 knot (> 0.5 m/s) | ● | ● | ○ | ○ | ○ | ● | ● | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ |
| | Shallow Water <1 foot (< 0.3 m) | ○ | ○ | ● | ● | ● | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ |
| | Debris (Including ice) | ● | ● | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ |
| Oil Viscosity | High Viscosity | ● | ● | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ |
| | Medium Viscosity | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ |
| | Low Viscosity | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ |
| Skimmer Characteristics | Oil/Water Pickup % ** | ● | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ |
| | Recovery Rate | ○ | ● | ● | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ |
| | Ease of Deployment | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ |
| Available as VOSS (Vessel of Opportunity Skimming System) | | ✓ | ✓ | ✓ | | ✓ | ✓ | ✓ | | ✓ | ✓ | | | | ✓ | ✓ | |
| Available as Advancing Skimmer | | | | | ✓ | ✓ | | | ✓ | ✓ | ✓ | ✓ | ✓ | | | ✓ | |
| Available with Storage | | | | | ✓ | ✓ | ✓ | ✓ | | ✓ | ✓ | ✓ | ✓ | ✓ | | ✓ | |

Legend ○ Good ● Fair ● Poor ✓ = Yes

* Other Devices

** Oil/Water Pickup % = % Oil in Recovered Product

The Gainford trials (WPW, 2013) revealed effective skimming capacity for three brush-style skimmers on CL and AWS dilbits throughout the 10-day weathering study. The skimmers tested were:

1. Aquaguard RBS Triton 60 DI3
2. Desmi DBD-5
3. Lamor MultiMax LAM 50/3C

Test results showed that all skimmers effectively recovered dilbit from the water surface for up to 8 days of weathering in open tanks. Weathered oil densities reaching 0.99 g/cm^3 and viscosities of over 30,000 cSt (both expressed at 15°C). Skimmer efficiencies (i.e., oil collected, some partially emulsified or with entrained water but not free water) generally ranged from near 70% to over 95% with weathered oil recovery rates ranging from approximately 1 to $3 \text{ m}^3/\text{hr}$. Skimmer manufacturers at the Gainford trials noted that the equipment, oleophilic brush systems set up for heavy oil collection, may have benefited from a different approach initially, such as using oleophilic disks and even weir skimmers with suitable pumps during the first days of the trials.

As oil weathers and attains high viscosity, enhanced skimming and pumping systems are required to maintain effective recovery. Numerous systems have been developed and tested to handle viscous oils (Hansen, 2010; Hvidbak, 2005). Three brush adapters used with weir skimmers and a screw pump were successfully tested with a GT-185 skimmer in highly viscous oil by SAIC Canada at Environment Canada's Environmental Technology Centre in February 2006 (Cooper, 2006). Three other skimmers tested by Cooper (2006) successfully picked up and processed refloated bitumen:

1. The ERE Skimmer (Dynamic Inclined Plane; Western Canada)- a small stationary skimmer that features a mesh honey-comb structure steel belt
2. The KLK 602 Skimmer- a small stationary device with two counter-rotating nonsymmetrical drums that lift, or scoop, viscous oil.
3. The larger Hobs rotating belt skimmer that lifts oil to a scraper and deposits it into a sump.

Western Canada Spill Services (WCSS) continues to work on a smaller version of the ERE Oriliminator 30 heavy oil skimmer with applicability to bitumen and dilbit oil recovery.

If a portion of a dilbit or even moderate to heavy oil achieves higher densities through weathering and/or material incorporated into the oil mass, then its location in the water column or on the bottom is more challenging to define relative to oil on the water surface. The underwater environment poses major complications for oil containment and recovery including poor visibility, difficulty in tracking oil spill movement, and colder temperatures (Hansen et al., 2009). Effective tracking and recovery methods and technologies suitable for these conditions are major challenges. Review of techniques applicable for tracking, containment, and recovery of submerged and sunken oils are provided in Castle et al. (1995), CRCC (2007), BMT Cordah (2009), and Hansen (2010).

Dispersant Application

Chemical dispersants cause a physical interaction between oil and water that help with oil droplet formation and stability within the water column. The increased surface area of oil droplets relative to undispersed oil aids natural weathering rates of the oil. Dispersants can be used in conjunction with mechanical recovery and other countermeasures to reduce the overall impact of a spill, although not on the same portion of a slick.

The effectiveness of dispersants is a function of the density, pour point, and viscosity of the oil (Figure 4). Some oils will not disperse, as their viscosity is too high. As oils emulsify, the viscosity increases significantly. For most crude oils, dispersants begin to lose their effectiveness after twenty-four (24)

hours and most oils will no longer disperse after four to five (4-5) days. General guidelines for dispersant use note that the technique may be effective for oil viscosities up to approximately 5,000 cSt (IMO, 2005) and that limited effectiveness shown may be extended to *in-situ* viscosities of up to 10,000 cSt (Daling and Lewis, 2001; ITOPF, 2011). Gainford trials (WPW, 2013) with AWS and CL dilbits showed that chemical dispersant may be an option during the first 6 hours of weathering but given the significant increase in viscosity of dilbits as they weather, the available window of opportunity for dispersant is limited. Many spills are not instantaneous but occur over a prolonged time frame, which can extend the window of opportunity for dispersant use. In this regard, the option and limitations for use of dispersant on dilbit spills is similar to that of intermediate to heavy fuel oils, other heavy crude oils, and even lighter but emulsified crude oils.

Figure 4 General guide for dispersant applicability to spilled oil on marine waters

| | | | | |
|----------------|--|---|---|--|
| POUR POINT (F) | 41 | Medium weight material. Fairly persistent. Probably difficult to disperse if water temperature is below pour point of material. | Light weight material relatively non-persistent. Probably difficult to disperse if water temperature is below pour point of material. | No need to disperse. Very light weight material. Oil will dissipate rapidly. |
| | Probably difficult or impossible to disperse | Medium weight material. Fairly persistent. Easily dispersed if treated promptly. | Light weight material. Relatively non-persistent. Easily dispersed. | |
| | API 17 | 34.5 | 45 | |
| | GRAVITY.953 | .852 | .802 | |

Derived from information published by the International Tanker Owners Pollution Federation, Ltd., London (API 1986)

In-Situ Burning (ISB)

Controlled on-water burning is a viable response option under appropriate conditions for dilbit spills. Mitchell and Moir (1992) reported on successful burns of dilbit floating on water in tanks and positive results of using an additive (RMS 9757) to reduce smoke emissions. The Gainford tests (WPW, 2013) proved that CL ignited easily after 6 and 12 hours of weathering. Although not as easy to ignite as lighter

oils, the Gainford trials showed that CL is similar to other medium and heavy crude oils with respect to the potential applicability of ISB (Table 9).

Table 9 Comparison of burn characteristics of different oils (from WCCS, 2012)

| Fuel | Burnability | Ease of Ignition | Flame Spread | Burning Rate* (mm/min) | Sootiness of Flame | Efficiency Range (%) |
|--------------------|-------------|-----------------------|-----------------------------|---------------------------|--------------------|----------------------|
| Gasoline | Very high | Very easy | Very rapid – through vapors | 4 | Medium | 95-99 |
| Diesel Fuel | High | Easy | Moderate | 3.5 | Very high | 90-98 |
| Light Crude | High | Easy | Moderate | 3.5 | High | 85-98 |
| Medium Crude | Moderate | Easy | Moderate | 3.5 | Medium | 80-95 |
| Heavy Crude | Moderate | Easy | Moderate | 3 | Medium | 75-90 |
| Weathered Crude | Low | Difficult, add primer | Slow | 2.8 | Low | 50-90 |
| Crude oil with ice | Low | Difficult, add primer | Slow | 2 | Medium | 50-90 |
| Heavy Fuel Oil | Very low | Difficult, add primer | Slow | 2.2 | Low | 40-70 |
| Waste Oil | low | Difficult, add primer | slow | 2 | Medium | 30-60 |

*Typical rates only – to get the rate in L/m²/hour multiply by 60

Shoreline Cleanup

Guidelines such as those presented in the Waste Management Calculator (PAS and TOSTC, 2008), NOAA (1992), Owens et al (1992), and Environment Canada (2010) provide an indication of treatment options for distinct shoreline types and as a function of oil type (Figure 5). As spilled oil properties change with weathering, treatment options may also need to be adjusted. For instance, low pressure flushing is an applicable treatment technique for medium oils, including relatively fresh dilbit, on coarse and mixed substrates; however, the technique may be ineffective for a heavy oil or weathered dilbit. The Gainford trials showed that low pressure washing to remove weathered dilbit from tiles was ineffective until combined with a surface washing agent (WPW, 2013). The mesoscale tests showed that oil that had weathered for five days on water and then had remained on tiles exposed to air for four days was effectively removed when washing the substrate treated with Corexit 9580. The Gainford washing tests, like those completed for Orimulsion and Bunker C (Gu nette et al., 1998) and IFO 380 (J z quel et al., 2009), emphasize the need for an expedited approval process for use of tested surface treating agents as part of spill response planning and readiness.

| Substrate Type | Treatment Tactic - Medium Oil | | | | | | |
|------------------|-------------------------------|------------------|----------------|--------------------|---------------------------|-----------------|-----------------|
| | Natural Recovery | Washing Recovery | Manual Removal | Mechanical Removal | In-situ Mixing Relocation | In-situ Burning | Bio-remediation |
| sand-mixed | Y | Y | YS | Y | Y | N | YS |
| course sediment | Y | Y | YS | Y | Y | N | YS |
| cobble / boulder | Y | Y | YS | Y | Y | N | YS |
| bedrock - solid | Y | Y | YS | N | N | N | YS |
| vegetation | Y | Y | YS | N | N | Y | N |
| oiled debris | Y | N | YS | Y | N | Y | N |
| snow | YS | Y | YS | Y | Y | Y | N |

| Substrate Type | Treatment Tactic - Heavy Oil | | | | | | |
|------------------|------------------------------|------------------|----------------|--------------------|---------------------------|-----------------|-----------------|
| | Natural Recovery | Washing Recovery | Manual Removal | Mechanical Removal | In-situ Mixing Relocation | In-situ Burning | Bio-remediation |
| sand-mixed | N | N | YS | Y | Y | N | YS |
| course sediment | N | N | YS | Y | Y | N | YS |
| cobble / boulder | N | N | YS | Y | N | N | YS |
| bedrock - solid | YS | Y | YS | N | N | N | YS |
| vegetation | YS | N | YS | N | N | Y | N |
| oiled debris | Y | N | YS | Y | N | Y | N |
| snow | N | N | YS | Y | N | N | N |

Figure 5 Guidelines for shoreline treatment options for medium and heavy oils (from PAS and TOSTC, 2008)

Experience from shoreline cleanup of the AHS dilbit following the 2007 Westridge spill showed that techniques used on the mixed sediment shorelines of Burrard Inlet (flushing, manual cleanup, shore cleaning agents, and tilling) worked effectively as applied for appropriate shore types and oiling conditions (Stantec, 2012). Techniques used on land and along stream/river banks following the Marshall (2010) spill included manual and mechanical removal and flushing.

Wildlife Treatment

Wildlife may be exposed to spilled oil through several pathways: inhalation, ingestion, and direct contact. The latter may entail smothering and/or thermal impairment due to oil coating on fur or feathers. Due to the relatively rapid loss, or lower concentration, of light-end volatile hydrocarbons, most wildlife treatment is for stabilization, cleaning, and rehabilitating oiled animals. Wildlife treatment following the 2010 Marshall spill response entailed cleaning and rehabilitation of birds and many turtles using protocols and procedures common to spills of medium to heavy oils. Focus Wildlife, contracted by Enbridge for the response, reported successful use of mineral oil as a cleaning agent for turtles and Dawn™ soap for feathers (birds).

Conclusions

Dilbits are not a new commodity on the oil market; however, the increased production of crude oil from the Alberta oil sands and its transport to refineries and markets has heightened awareness about dilbits and some of the differences between these oils and other crude oils. Dilbits have a range of properties similar to other medium to heavy oils and, like most oils, these properties depend on temperature and local environmental conditions. Furthermore, oil properties change as oil weathers and interacts with other media.

Spill response countermeasures applicable and appropriate for response to a medium crude are also applicable to the CL and AWS dilbits tested at Gainford. As the medium crude weathers and increases in density, viscosity, and pour point, spill countermeasures should be reassessed and adjusted for those changes and for differences in the environmental setting. Similarly, adjustments must be made for response to a dilbit release. The key difference between a CL dilbit, for example, and a medium crude oil, such as ANS, is a shorter weathering timeframe for a dilbit. The ANS crude may weather and/or emulsify to achieve the characteristics of a heavy oil generally over the course of many days to weeks whereas a dilbit may weather to a heavy oil state within one to a few days, depending on its original formulation and the active weathering processes.

Knowledge of the behavior of dilbit spilled to water is available from lab to mesoscale testing in tanks and from observations made following actual spills (Westridge and Marshall). Most significantly, the behavior of dilbits tested or spilled are consistent with Group 3 and 4 crude oils: they float on water until oil densities change through weathering and/or sediment uptake. As with most crude oils, dilbits gradually may overwash, become suspended in the water column, or sink depending on the degree of weathering and uptake of particulate matter.

A concluding comparison and potential challenges of dilbit spills in context of other oils is provided in (Table 10).

Table 10 Summary of oil type physical/chemical properties adverse effects on environment

| Oil Type | Physical/Chemical Properties | Adverse Effects on Environment |
|--|--|--|
| Light to volatile oils | <ul style="list-style-type: none"> • Spread rapidly • Tend to form unstable emulsions • High evaporation and solubility • May penetrate substrate • Removed from surfaces by agitation and low-pressure flushing | <ul style="list-style-type: none"> • Toxicity is related to the type and concentration of aromatic fractions: 1) naphthalene, 2) benzene • Toxicity of aromatic fractions depends on their biological half- lives in different species • Toxic to biota when fresh • Marsh plants may be chronically affected due to penetration and persistence of aromatic compounds in sediments |
| Moderate to heavy oils (with notes re dilbits) | <ul style="list-style-type: none"> • Moderate to high viscosity • Tend to form stable emulsions under high energy marine environments (dependent on type of dilbit) • Penetration depends on substrate particle size (CL appears to have less penetration than comparable viscosity crude) • Weathered residue may sink and be absorbed by sediment (may become neutrally buoyant to sink, depending on degree of weathering, type of dilbit, and receiving water) • Immiscibility assists in separation from water • Weather to tar balls | <ul style="list-style-type: none"> • Adverse effects in marine organisms result from chemical toxicity and smothering • Toxicity depends on size of light fraction (dilbit formulation dependent but typically very light end diluents are rapidly lost through evaporation) • Low toxicity residue tends to smother plants or animals • Light fractions contaminate interstitial waters |
| Asphalt, #6 fuel-oil, Bunker C, waste oil | <ul style="list-style-type: none"> • Form tar balls at ambient temperatures • Resist spreading and may sink • May soften and flow when exposed to sunlight • Very difficult to recover from the water • Easy to remove manually from beach surface with conventional equipment | <ul style="list-style-type: none"> • Immediate and delayed adverse effects due to small aromatic fractions and smothering • Most toxic effects due to incorporation in sediment • Absorption of radiated heat places thermal stress on the environment • Lower toxicity on marine plants than mobile animals |

(modified from ExxonMobil, 2008)

References

- Ansell, D.V., Dicks, B., Guenette, C.C., Moller, T.H., Santner, R.S., and White, I.C., 2001. A review of the problems posed by spills of heavy oils. *In* International Oil Spill Conference, Vol. 2001, p. 591-596, American Petroleum Institute, Washington DC.
- BMT Cordah, 2009. Sunken and Submerged Oils – Behavior and Response. A report for the Maritime and Coastguard Agency –UK.(Feb, 2009)
- Brown, H.M. and Nicholson, P., 1991. The physical-chemical properties of bitumen in relation to oil spill response. In: Proceedings of the 14th Arctic and Marine Oil Spill Program, Technical Seminar. Ottawa, Ontario: Environment Canada. pp. 107-117.
- Brown, H.M., Goodman, R.H., and Nicholson, P., 1992. The containment of heavy oil in flowing water. In: Proceedings of the 15th Arctic and Marine Oil Spill Program, Technical Seminar. Ottawa, Ontario: Environment Canada. pp. 457-465.
- Brown H., E.H. Owens, M. Green, 1997. Submerged and sunken oil: behavior, response options, feasibility, and expectations. In: Proceedings of the 21st Arctic and Marine Oil Spill Program, Technical Seminar. Ottawa, Ontario: Environment Canada. pp. 135-146.
- Burns III, G. H., Benson, C. B., Eason, T., Michel, J., Kelly, S., Benggio, B., & Ploen, M., 1995. Recovery of submerged oil at San Juan, Puerto Rico 1994. *In* International Oil Spill Conference, Vol. 1995, No. 1, pp. 551-557. American Petroleum Institute, Washington DC.
- Castle, R.W., Wehrenberg, F., Bartlett, J. and Nuckols, J., 1995. Heavy oil spills: out of sight, out of mind. *In* International Oil Spill Conference, American Petroleum Institute, Pub. No. 4620, p. 565–571. American Petroleum Institute, Washington DC.
- Coastal and Ocean Resources, 2013. Procedures for Estimating Oil Retention in Spill Modeling. Report prepared for Trans Mountain Pipeline.
- Cooper, D. 2006. Floating heavy oil recovery: Current state analysis. U.S. Coast Guard Research & Development Center, Groton, CT. 23 pp.
- CRRC (Coastal Response Research Center), 2007. Submerged Oil – State of the Practice and Research Needs. Prepared by the Coastal Response Research Center, Durham, New Hampshire, 29 pp +appendix.
- CrudeMonitor, 2013. <http://www.crudemonitor.ca/> (accessed Sept 2013)
- Daling, P.S. and A. Lewis, 2001. Oil Spill Dispersants. Guidelines on the planning and effective use of oil spill dispersant to minimize the effect of oil spills”. SINTEF report: STF6601018. 113pp.
- Enbridge, 2013. Enbridge Line 6B Response, <http://response.enbridgeus.com/response/main.aspx?id=12783> (accessed Nov. 2013)

- Environment Canada, 2010. A field guide to oil spill response on marine shorelines. Prepare by Polaris Applied Sciences, Inc. and S3 Environmental Inc., Ottawa, ON, 223 pp.
- ETC (Environmental Technology Centre), 2013. Oil properties database. <http://www.etc-cte.ec.gc.ca/databases/oilproperties/> (accessed Oct 2013)
- ExxonMobil, 2008. Oil Spill Response Field Manual. ExxonMobil Research and Engineering Co., USA.
- Fingas, M., 2001. The Basics of oil Spill Cleanup. Lewis Publishers, Washington DC. 233 pp.
- Hansen, K. A., 2010. Research efforts for detection and recovery of submerged oil. *In*: Proceedings of the 33rd Arctic and Marine Oil Spill Program, Technical Seminar. Ottawa, Ontario: Environment Canada. pp. 1055-1069.
- Guénette, C.C., G.A. Sergy, and B. Fieldhouse. 1998. Removal of Stranded Bitumen from Intertidal Sediments Using Chemical Agents. Phase I: Screening of Chemical Agents. Manuscript Report EE-162. Environment Canada, Ottawa, Ontario, Canada. 18pp.
- Harper, J.R., and M. Kory. 1995. Stranded Oil in Coarse Sediment Experiments (SOCSEX II). Manuscript Report EE-155, Emergencies Science Division, Environment Canada, Ottawa, Ontario, Canada.
- Hvidbak, F., 2005. Preparedness for heavy oil spills: More focus on mechanical feeder skimmers. *In* International Oil Spill Conference, Vol. 2005, p. 551-557. American Petroleum Institute, Washington DC.
- IMO (International Maritime Organization), 2005. Manual on Oil Pollution, Section IV, Combating oil spills. London. 211pp.
- ITOPF 2011. The use of dispersants to treat oil spill. Technical Information Paper 4, London. 12pp.
- Jézéquel, R., J. Lebastard, and F.X. Merlin, 2009. Influence of weathering of heavy fuel oil on high pressure washing efficiency with and without cleaning agent. *In*: Proceedings of the 32nd Arctic and Marine Oil Spill Program, Technical Seminar. Ottawa, Ontario: Environment Canada. pp. 177-193.
- Keystone Supplemental EIS (2012), at <http://keystonepipeline-xl.state.gov/documents/organization/205638.pdf> (accessed Sept 2013)
- Lee, S.C., Shui, W. Y., and Mackay, D., 1992. A study of the long-term fate and behavior of heavy oils. EE-128. Ottawa, Ontario. Environment Canada.
- Michel, J. 2006. Assessment and recovery of submerged oil: Current state analysis. U.S. Coast Guard Research & Development Center, Groton, CT. 34 pp. + appendices.
- Michel, J., 2008. Spills of nonfloating oil: evaluation of response technologies. *In* International Oil Spill Conference, Vol. 2008, No. 1, p. 261-267. American Petroleum Institute, Washington DC.

- Michel, J., and Galt, J.A., 1995. Conditions under which floating slicks can sink in marine settings. Proc. International Oil Spill Conference, American Petroleum Institute Pub. No. 4620, p. 573–576. American Petroleum Institute, Washington DC.
- Michel, J., Scholz, D., Henry, C. B., & Benggio, B. L., 1995. Group V fuel oils: source, behavior, and response issues. *In* International Oil Spill Conference, Vol. 1995, No. 1, p. 559-564. American Petroleum Institute, Washington DC.
- Mitchell, J.B. and Moir, M.E., 1992. Mesoscale testing of smoke reduction from dilbit combustion. In: Proceedings of the 15th Arctic and Marine Oil Spill Program, Technical Seminar. Ottawa, Ontario: Environment Canada. pp. 681-686.
- NOAA, 1992. Shoreline Countermeasures Manual – Temperate Coastal Environments. Hazardous Materials Response & Assessment Division. Seattle, USA. 95 pp.
- NRC (National Research Council), 1999. Spills of Nonfloating Oils: Risk and Response. Committee on Marine Transportation of Heavy Oils. The National Academies, Washington, D.C. 75pp.
- NTSB (National Transportation Safety Board), 2012. Enbridge Incorporated Hazardous Liquid Pipeline Rupture and Release, Marshall, Michigan, July 25, 2010. Accident Report NTSB/PAR-12/01, PB2012-916501. 164 pp.
- Owens, E.H., Cramer, M.A. and Howes, D.E., 1992. British Columbia Marine Oil Spill Shoreline Protection and Cleanup Manual. B.C. Ministry of Environment, Victoria, BC, 104 pp. plus appendices.
- PAS and TOSTC (Polaris Applied Sciences and The Oil Spill Training Company), 2008. Waste Management Calculator. Prepared for the Emergency Prevention, Preparedness and Response (EPPR) Working Group of the Arctic Council.
- Ploen, M., 1995. Submerged oil recovery. Proceedings of the 2nd International Oil Spill R&D Forum, International Maritime Organization, London, UK. p 165-173.
- SL Ross, 2010a. Properties and Fate of Hydrocarbons Associated with Hypothetical Spill at the Marine Terminal and in the Confined Channel Assessment Area. Technical Data Report prepared for Enbridge Northern Gateway. 132 pp.
- SL Ross, 2010b. Mesoscale weathering of Cold Lake bitumen/condensate blend. 27 pp.
- Stantec, 2012.. Summary of Clean-up and Effects of the 2007 Spill of Oil from Trans Mountain Pipeline to Burrard Inlet. Project report 1231-10505.
- Tsaprailis, H., 2013. Properties of Dilbit and Conventional Crude Oils. Report prepared by Alberta Innovates Technology Futures (“AITF”) on behalf of Alberta Innovates Energy and Environment Solutions (“AIEES”). At http://ai-ees.ca/media/10927/properties_of_dilbit_and_conventional_crude_oils_-_aitf_-_final_report.pdf (accessed Nov 2013)

Wang, Z. Zhendi Wang, B.P. Hollebone, M. Fingas, B. Fieldhouse, L. Sigouin, M. Landriault, P. Smith, J. Noonan, and G. Thouin. 2003. Characteristics of Spilled Oils, Fuels, and Petroleum Products: 1. Composition and Properties of Selected Oils. EPA/600/R-03/072

WPW (Witt O'Briens, Polaris Applied Sciences, and Western Canada Marine Response Corporation), 2013. A study of fate and behavior of diluted bitumen oils on marine waters. Report prepared for Trans Mountain Pipeline, 163 pp.