Acquisition Directorate

Research & Development Center

Report No. CG-D-03-21

Literature Review of Diluted Bitumen (Dilbit)

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June 2021

N O T I C E

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Technical Report Documentation Page

1. Report No.
CG-D-03-21

2. Government Accession Number

3. Recipient's Catalog No.

4. Title and Subtitle
Literature Review of Diluted Bitumen (dilbit)

5. Report Date
June 2021

6. Performing Organization Code
Project No. 4204

7. Author(s)
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8. Performing Report No.
RDC UDI # 1952

9. Performing Organization Name and Address
U.S. Coast Guard
Research and Development Center
1 Chelsea Street
New London, CT 06320

10. Work Unit No. (TRAIS)

11. Contract or Grant No.

12. Sponsoring Organization Name and Address
COMMANDER, NINTH COAST GUARD DISTRICT (dr)
1240 EAST NINTH STREET
CLEVELAND, OH 44199

COMMANDANT (CG-MER)
US COAST GUARD STOP 7516
2703 MARTIN LUTHER KING JR AVE SE
WASHINGTON, DC 20593

13. Type of Report & Period Covered
Final

14. Sponsoring Agency Code
CGD9 (dr)

COMDT (CG-MER)

15. Supplementary Notes
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16. Abstract (MAXIMUM 200 WORDS)

The growth in oil production in North America is due primarily to the increase in production and distribution of Canadian oil sands products. Several recent spills of oil sands products (e.g., diluted bitumen (dilbit)) have demonstrated that they behave differently than conventional crude oil when spilled. In order to better understand next steps in response, an in-depth literature review of dilbit research was performed to determine gaps and identify needed research.

There have been many studies on oil research. Twelve studies from 1992 to 2020 were selected and reviewed. These studies were chosen because they either provide the latest understanding of dilbit gained from actual spill recovery (EPA, 2013; Brown, 1992); are the most in-depth studies of research on dilbit (Ortmann, 2020; Stoyanovich, 2019; RDC, 2018; Yang, 2016; King, 2014; Canada, 2013; SL Ross, 2013) or include innovative development or testing (RDC, 2019; RDC, 2017; Zhou, 2015). Five of the studies covered dilbit interaction in salt water, six studies involved fresh water, and one study performed testing in both salt and fresh water.

17. Key Words
diluted bitumen spill, dilbit, diluents, oil, hydrocarbon, oil-particle aggregates, weathering, unconventional oil, fresh water, oil spill, oil-sediment interaction, oil buoyancy, salt water

18. Distribution Statement
Distribution Statement A: Approved for public release; distribution is unlimited.

19. Security Class (This Report)
UNCLAS// Public

20. Security Class (This Page)
UNCLAS// Public

21. No of Pages
60

22. Price

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EXECUTIVE SUMMARY

The growth in oil production in North America is due primarily to the increase in the production and distribution of Canadian oil sands products. Several recent spills of oil sands products (e.g., diluted bitumen (dilbit)) have demonstrated different behavior than conventional crude oil spills. The environmental factors, the type of dilbit, and nature of the spill, all play a role in knowing how best to respond to a dilbit spill. In order to better understand next steps in response, an in-depth literature review of dilbit research was performed to determine gaps and identify needed research.

There have been many studies on dilbit research. Twelve studies from 1992 to 2020 were selected and reviewed. These studies were chosen because they either provide the latest understanding of dilbit gained from actual spill recovery (EPA, 2013; Brown, 1992); are the most in-depth studies of dilbit research (Ortmann, 2020; Stoyanovich, 2019; RDC, 2018; Yang, 2016; King, 2014; Canada, 2013; SL Ross, 2013) or include innovative development or testing (RDC, 2019; RDC, 2017; Zhou, 2015). Five studies covered dilbit interaction in salt water, six studies involved fresh water, and one study involved testing in both salt and fresh water.

Understanding the chemical composition and physical properties of bitumen, diluents, and the interaction of these products with air and water (i.e., weathering) is necessary to properly understand dilbit behavior when spilled.

The literature review determined on initial release into fresh and salt water, dilbit (e.g., Access Western Blend, Cold Lake Blend, Western Canadian Select) generally floats. Dilbit weathers rapidly in fresh and salt water, as compared to traditional crude oil. As the diluent evaporates in fresh and salt water, the density and viscosity increases, and the remaining oil behaves similar to a heavy oil. When conditions are calm with no agitation or sediment in the water, dilbit will stay afloat for 6-10 days in both fresh and salt water. The same containment and recovery tools used for crude oil can be used on dilbit when floating. With the presence of suspended particles in a high-energy mixing environment, dilbit will sink after several days in salt water.

This literature review identified several knowledge gaps. The exact conditions at the water surface and sub-surface that cause dilbit to submerge (e.g., type of sediment, sediment/oil interaction, high energy vs low energy conditions, seasonal temperature changes) in fresh water need further research. The precise length of time that dilbit stays afloat before sinking in fresh water is unpredictable. Weathering of synthetic bitumen and diluted synthetic bitumen in salt and fresh water was not found in the studies reviewed. More work on the effects of nutrients to speed up or slow down biodegradation, and on each type of pure bitumen and dilbit (e.g., rates of anaerobic biodegradation, what factors effect long term and short-term biodegradation) is needed. Precise rates of photo-oxidation of dilbit are needed. The development and testing of containment and recovery tools for detection, mapping and mitigation of submerged and sunken oil is needed. The effects of weathered bitumen on aquatic organisms are not well understood.

Based on these knowledge gaps the Coast Guard Research and Development Center (RDC) intends to develop and execute controlled tests of various dilbit products with and without sediment (i.e., different types of sediment) in fresh water. These studies will help to better understand how long it will take for dilbit to sink. The information gained from this research will provide first responders and Federal On-Scene Coordinators with knowledge to better manage a dilbit spill.

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TABLE OF CONTENTS

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LIST OF FIGURES

LIST OF TABLES

LIST OF ACRONYMS, ABBREVIATIONS, AND SYMBOLS

°C	Degrees Centigrade
°F	Degrees Fahrenheit
AER	Alberta Energy Regulator
APACs	Alkylated Polycyclic Aromatic Compounds
API	American Petroleum Institute
ASMB	Alberta Sweet Mixed Blend
ASTM	American Society for Testing and Materials
AWB	Access Western Blend
BP	Boiling Point
BTEX	Benzene, Toulene, Ethyl Benzene and Xylenes
C4	Four Carbon Chain Compound
C5	Five Carbon Chain Compound
CC	Conventional Crude
CCME	Canadian Council of Ministries of the Environment
CG	Coast Guard
CLB	Cold Lake Blend
CLWB	Cold Lake Winter Blend
CM	Centimeter
Dilbit	Diluted Bitumen
DSD	Droplet Size Distribution
EPA	Environmental Protection Agency
FLUO	Fluorene
FOSC	Federal On-Scene Coordinator
G	Grams
G/ML	Grams per milliliter
HWM	High Molecular Weight
IFO	Intermediate Fuel Oil
KM	Kilometer
LMW	Low Molecular Weight
M	Meter
MSB	Medium Sour Blend
NC	Carbon Number
NAP	Naphthalene
NAS	National Academies of Sciences
NOAA	National Oceanic and Atmospheric Administration
NTSB	National Transportation Safety Board
OPA	Oil-particle Aggregates
OSP	Oil Sands Product
PAC	Polycyclic Aromatic Compounds
PAH	Polycyclic Aromatic Hydrocarbons
PHE	Phenanthrene
R&D	Research and Development
SYNBIT	Synthetic Dilbit

LIST OF ACRONYMS, ABBREVIATIONS, AND SYMBOLS (Continued)

µg/L	Micrograms per Liter
TPH	Total Petroleum Hydrocarbon
TRO	Total Recovered Oil
UC	Unconventional Crudes
USCG	United States Coast Guard
WCS	Western Canadian Select
WT	Weight

1 INTRODUCTION

Bitumen is an unconventional oil that does not easily flow or pour (Dew et al., 2015). It is a semi-solid form of petroleum that is sticky and contains highly viscous liquid. Bitumen is produced or extracted from natural oil sands (Government of Canada, 2013; Read and Whiteoak, 2003) (see Figure 1). As a result of bitumen's high viscosity and its abundance in landlocked Alberta, Canada (i.e., approximately 97% of Canada's total crude oil reserve), the future of this oil sands product (OSP) as a reliable energy source is dependent on how it can be transported to distant refineries.

Figure 1. Natural bitumen (left) and a handful of Canadian oil sands/Source: Suncor (right).

Oil sands can be transported if heated, or if diluted with lighter hydrocarbons or natural gas condensates known as diluents (Crosby et al., 2013) (see Figure 2). Diluted bitumen (dilbit), one type of OSP, is typically comprised of 70 percent bitumen and 30 percent diluent. Producers normally transport dilbit by rail or pipeline, although they may also use marine vessels such as barges and coastal tankers. Every transportation method carries with it an inherent risk of spillage. Spills of OSP have occurred in the past, and real-world experience demonstrates that OSPs behave differently than conventional crude oil during an incident. Scientists and researchers continue to study dilbit's properties as well as its fate and behavior if spilled into the environment (Fitzpatrick, 2020).

Figure 2. Dilbit.

The increase of oil sands production in Canada has been a major contributing factor to the overall growth of crude oil production in North America. There have been both small and large spills containing dilbit products that have occurred in the U.S. and Canada in both fresh and marine environments. Two of these major spills are described in Section 4.3. These real-world events demonstrate that OSPs behave differently than conventional crude oil during an incident. The environmental factors, the type of dilbit, and nature of the spill all play a role in knowing how best to respond to a dilbit spill. In order to better understand next steps in response, the United States Coast Guard (USCG) Research and Development Center (RDC) conducted an in-depth literature review of dilbit research to determine gaps and identify needed research.

1.1 Scope

This report begins with the breakdown of the physical, chemical, and complex aspects of dilbit compared with conventional crude oil. It then provides a review of 12 dilbit research studies performed by a variety of sources including, the RDC, Government of Canada, the US Environmental Protection Agency, and others. The report identifies gaps in research and testing and recommends needed testing to improve the body of knowledge for a dilbit oil spill.

2 DILBIT CHARACTERISTICS

2.1 Dilbit Composition

Dilbit typically is comprised of 70−80% bitumen and 20−30% diluent or condensates or lighter hydrocarbons (Yang et al., 2018; Crosby et al., 2013; Government of Canada, 2013). There are four classes of dilbit:

- Standard dilbit (bitumen diluted with gas condensates),
- Synbit (bitumen diluted with synthetic crude),
- Lightened dilbit (gas condensates with added C4 and/or C5 diluents), and
- Dilbit diluted with a synthetic naphtha.

Modified synbit (dilsynbit) is not considered a class on its own, but it is important to understand the differences in dilbit products. It is diluted bitumen with synthetic crude and condensates (Fingas, 2015).

Dilbit contains a number of volatile organic compounds:

- Benzene, toluene, ethylbenzene and xylene (BTEX). BTEX makes up 0.8-1.2% of dilbit by volume (Government of Canada, 2013).
- Parent and alkylated polycyclic aromatic hydrocarbons (PAHs)
- Representative alkanes and petroleum biomarkers (e.g., hopanes, terpanes and steranes),

Upon the release of dilbit, the light ends and BTEX undergo evaporation leaving behind only bitumen, a heavy oil. The properties of the starting bitumens vary widely, as do the diluents, resulting in highly variable products with highly variable behaviors (Fingas, 2015b). Table 1 shows the summary properties of 12 different bitumen blends organized by class.

Table 1. Summary of physical properties and chemistry data of selected diluted bitumen products.

Name	Product	Diluent/Source	Density (kg/m^3)	Sediment (ppmw)	Light Ends* (vol%)	BTEX (vol%)
Standard Dilbit - (gas condensates)						
Access Western Blend	(AWB)	Condensate	918 - 928	80 - 98	22 - 26	1.1- 1.4
Christina Dilbit Blend	(CDB)	Condensate	920 - 930	47 - 129	21 - 25	1.0 - 1.3
Cold Lake Blend	(CLB)	Condensate	923 - 933	52 - 136	19 - 22	0.9 - 1.2
Western Canadian Select	(WCS)	Condensate	924 - 932	261 - 307	17 - 20	0.7 – 1.0
Synbit – (synthetic crude)						
Statoil Cheecham Blend	(SCB)	North East AB	924 - 933	70 - 268	22 - 26	0.9 - 1.2
Long Lake Heavy	(PSH)	North East AB	929 - 936	18	15 - 17	0.8 - 1.0
Statoil Cheecham Synbit	(SCS)	North East AB	926 - 935	60 - 82	12 - 15	0.7 - 0.9
Surmont Heavy Blend	(SHB)	North East AB	932 - 940	59 - 143	10 - 12	0.5 - 0.7
Suncor Synthetic H	(OSH)	North East AB	934 - 939	39	9 - 11	0.4 - 0.5
Lightened dilbit - (gas condensates with added 4 and/or 5 Carbon-chain (C4 and/or C5) diluents)						
Peace River Heavy	(PH)	Condensate(+C_4)	926 - 935	67 - 127	21 - 24	0.9 - 1.1
Dilbit with a synthetic **naphtha**						
Borealis Heavy Blend	(BHB)	Hydro-treated naphtha	922 - 933	67 - 121	22 - 26	0.9 - 1.1
DilSynbit - modified synbit (synthetic crude and a condensates)						
Albian Heavy Synthetic	(AHS)	Edmonton area	935 - 942	555 - 1018	22 - 25	0.8 - 1.1

*Light Ends compromise the sum of all butanes through decanes, inclusive.
Source: Government of Canada, 2013; Fingas 2015.

2.2 Physical Properties of Dilbit

Table 2 compares the physical properties of dilbit to a broad range of oil types. The properties listed are the main properties that affect the fate of spilled oil. Each of these properties is defined below the table.

Table 2. Ranges of physical properties for different oil types.

Property	Units	Gasoline	Diesel	Light Crude	Dilbit	Heavy Crude
Density	Kg/m3 at 15°C	720	840	780 - 880	824 -941	880 - 1000
API Gravity	Degrees on Hydrometer	65	35	30 - 50	18 -39	10 - 30
Viscosity	mPa.s at 15°C	0.5	2	5 - 50	270.5* - 265,263 **	50 - 50,000
Flash-point	°C	(-35)	45	(-30) - 30	<(-35)** - 58*	(-30) - 60
Solubility in Water	ppm	200	40	10 - 50	-	5 - 30
Pour-point	°C	NA	(-35) – (-1)	(-40) - 30	(-30)** -15**	(-40) - 30
Interfacial Tension	mN/m at 15°C	27	27	10 - 30	27* - 150*	15 - 30

Modified from Fingas (2001); Values provided include weathered dilbit from tests; NA= not applicable; * Calculated for AWB; ** Calculated value for CLB

- **Density** is the ratio of mass and volume of oil with a unit expressed in grams per cubic centimeter (kg/m^3) and is used to determine if a certain oil will float or sink in the water column.
- **American Petroleum Institute (API) Gravity** is a measure of density that describes the density of oil at 60^{o}F relative to that of water. It is based on the standard point of reference of pure water, which is 10^o (10 degrees). Any material with an API gravity less than 10^o will sink in pure water and an API gravity greater than 10 ^{o} will float in pure water (Crosby et al., 2013).
- **Viscosity** is the rate of spreading and resistance to being dispersed into droplets. Viscosity of dilbit is >300 milli Pa•s. During oil cleanup, viscosity can affect the behavior of oil due to the fact that viscous oil does not have the ability to spread or penetrate soil or sediment.
- **Flash-point** is the minimum temperature at which a volatile liquid evaporates to support ignition when exposed to an open flame (Government of Canada, 2013; Fingas, 2015). Any liquid with a flash point less than 60^{o}C is categorized as flammable.
- **Solubility** is a measure in parts per million of the amount of oil in the water column on a molecular level with the decreased solubility for most bitumen in the water column (Fingas, 2015).
- **Pour-point** is the minimum temperature in degrees centigrade at which oil flows. Although it has been used in past studies to predict the behavior of oil in the environment, it is not the best method in predicting the behavior of oil (Fingas 2015).
- **Interfacial Surface Tension** is the force of attraction in milli-Newton/meter at 15 degrees centigrade between the molecules at the interface of two fluids**.** This is one of the significant factors of understanding the behavior of oil as it controls the size of the oil droplet and thickness of the oil film (Government of Canada, 2013).

3 GENERAL BEHAVIOR OF DILBIT IN WATER

After any oil, including dilbit, is released and has been exposed to the atmosphere, it immediately starts to undergo physical and chemical changes, or weathering. These changes can occur on land or in water. Figure 3 illustrates the most common weathering processes affecting the behavior of dilbit.

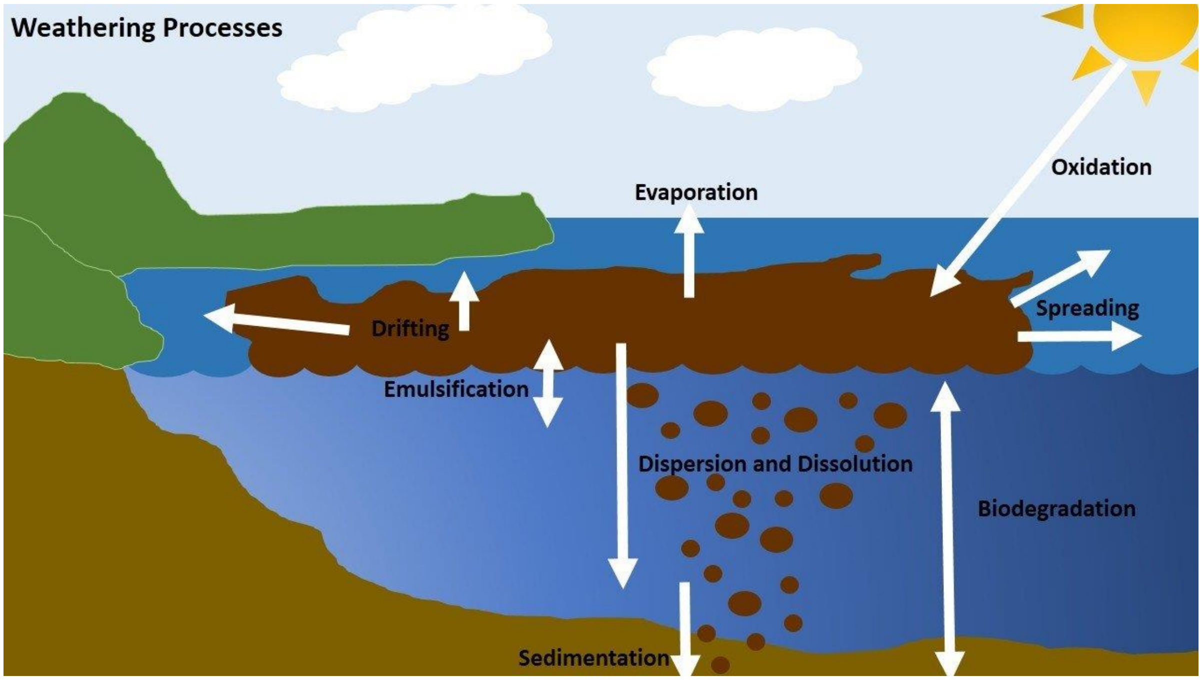


Figure 3. Oil weathering processes (Independent Petroleum Laboratory).

Physical weathering changes the bitumen's physical properties while chemical weathering alters the chemical make-up of the dilbit (Government of Canada, 2013). Weathering processes include evaporation, emulsification, spreading, dispersion, dissolution, photo-oxidation, and biodegradation (Garett et al., 1998; Stoyanovich et al., 2019). These processes happen at different rates when exposed to the natural elements (Fingas, 2012; Stoyanovich et al., 2019). Below is a brief overview of these processes. A more in-depth discussion of physical and chemical weathering can be found in Appendix A.

- **Evaporation:** A weathering process where volatile compounds vaporize, leaving behind heavier hydrocarbons. Evaporation accounts for the greatest amount of loss from all other weathering processes (National Research Council, 2003).

- **Emulsification:** Emulsification occurs when oil droplets are suspended in water or when water droplets are suspended in oil. Emulsions play an important role in oil spills. Emulsification increases the volume of an oil spill (typical emulsions contain 50% to 70% water).

- **Spreading:** Spreading occurs when oil encounters the surface of water; oil spreads out across the surface of the water and continues to spread out until the oil forms a thin film, or "sheen" (Fay, 1969).

- **Dispersion:** Oil dispersion refers to droplets of oil suspended in the water column (National Academies of Sciences, Engineering, and Medicine, 2016). When a dispersant is added to oil, the tension between the oil and water is reduced by 10 to 200 fold (Johansen et al., 2013).

- **Dissolution:** Dissolution is a chemical weathering process that removes soluble particles in water during an oil spill (Tarr et al., 2016). It is dependent on the oil/water surface. The diluent in bitumen is easily vaporized and solvent is lost by evaporation.

- **Photo-oxidation:** Photo-oxidation is a form of chemical weathering and occurs when spilled oil is exposed to large amounts of solar radiation and oxygen. It creates a dense crust on the surface of the exposed oil (Hollebone et al., 2011). Photochemical oxidation causes the viscosity, density, and adhesion properties of the oil to increase.

- **Biodegradation:** Biodegradation is a form of chemical weathering that occurs when living organisms, typically bacteria, break down compounds (Prince, 1993).

- **Sedimentation:** Sedimentation can lead to sinking after the attachment of sediment particles onto the oil, forming oil-particle aggregates (OPA).

4 LITERATURE REVIEW ON DILBIT

Research has been conducted on dilbit over the past 30 years including experiments on oil weathering, oil containment, diversion tools and techniques, and chemical analysis for salt and fresh water. The following section briefly describes the historical studies reviewed, their key findings, and is divided into studies performed in salt and fresh water. These studies were chosen because they either provide the latest understanding of dilbit gained from actual spill recovery or are the most in-depth studies of research on dilbit. Table 3 lists the research reviewed in reverse chronological order, provides short names for each study for easy reference, and indicates if the study was done in fresh or salt water. Two studies were performed in both fresh and salt and are listed twice. A more detailed analysis of each of these studies can be found in Appendix B.

Table 3. Fresh and salt water research.

Marine Water/Coastal/ Salt Water	Study Short Name	Fresh Water	Study Short Name
Ortmann et al., 2020 (AWB, WCS and Synbit)	Ortmann	RDC 2019 - Containment and Recovery (CLB)	RDC 2019
RDC 2017 – Sediment Sampling	RDC 2017	Stoyanovich at al., 2019 (CLB)	Stoyanovich
Yang et al., 2016 (CLB, AWBl)	Yang	RDC 2018 – Oil Sands Recovery	RDC 2018
King et al., 2014 (AWB, CLB)	King	Zhou et al., 2015 (CLB)	Zhou
Government of Canada 2013 (AWB and CLB)	CAN	EPA 2013 (CLB and WCS)	EPA
Brown et al., 1992 (heavy oil)	Brown	SL Ross Environmental Research 2013 (CLB)	SL Ross
		Brown et al., 1992 (Heavy oil)	Brown
Note: RDC 2020 report, *Oil Sands Spill Response,* was also reviewed. It summarizes the three RDC reports listed above (in both fresh and salt water) and is not summarized separately in this section.			

4.1 Dilbit in Salt Water

4.1.1 Physical Weathering (in salt water)

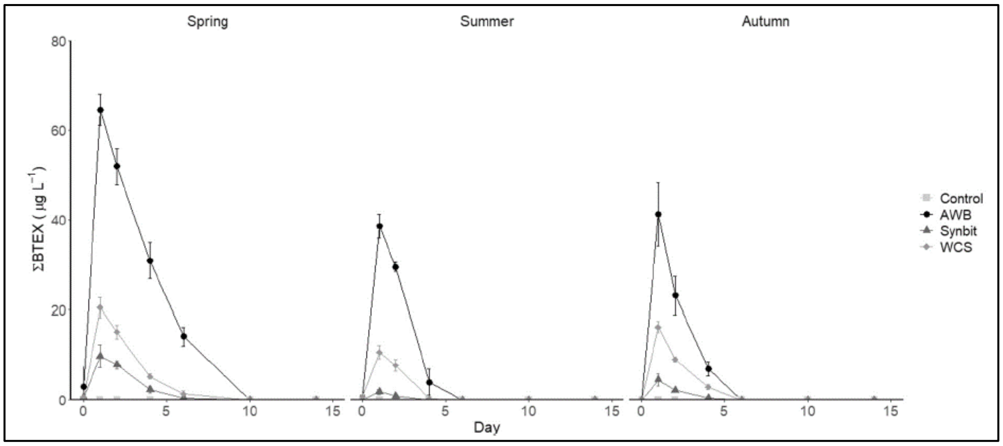
- Government of Canada, 2013 researched the effects of evaporation on two types of dilbit, Access Western Blend (AWB) and Cold Lake Blend (CLB) compared to intermediate fuel oil (IFO). The results of the study found that both bitumen products floated on salt water (free of sediment), even after evaporation. Density, pour-point, flash-point and viscosity all increased with increasing evaporation. Both dilbit products exceeded more than 20% mass loss due to evaporation (in 55 hours for AWB and 147 hours for CLB). The IFO 180 was not found to exceed 5% mass loss in a test of 200 hours.

- King, 2014 investigated the environmental condition under which AWB and CLB dilbit would sink in salt water. A 13-day weathering study was conducted using filtered salt water (to remove particles greater than 5µm) and natural conditions (i.e., waves, currents, sunlight, wind, and salinity). This study demonstrated that dilbit product can sink (after 6 days) in the presence of natural weathering conditions without suspended particles with a low energy environment in salt water.

- Yang, 2016 investigated the effects of temperature and solar intensity during different seasons (e.g., summer and winter) on the photolytic behavior of dilbits (CLB, AWB) in salt water. Results showed that seasons (i.e., air and water temperature changes) affect the efficiencies of the chemical structure of petroleum hydrocarbon in CLB and AWB.

4.1.2 Chemical Weathering (in salt water)

- Ortmann, 2020 measured concentrations of BTEX and PAHs before and after weathering of AWB, WCS and synbit during different environmental conditions. The dilbit with the highest amount of condensate (AWB) produced the highest concentrations of BTEX in the water column. Cooler water and air temperature during spring were associated with higher concentrations of BTEX and PAHs in the water column (Figure 4).



Source: Ortmann, et al, 2020, 2010.

Figure 4. Average and standard deviation for measured BTEX in the water column.

- RDC, 2017 (Underwater Sediment Sampling) developed a bench top system to determine, in situ, the amount of total petroleum hydrocarbons (TPH) in an oil/sediment mixture (Figure 5). Results showed that the concentration of TPH in oil impacted sediments was found to be directly related to the concentration of oil detected in the sediment pore waters.[1]

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[1] Pore waters is the water contained in the interstices/pore spaces of sediments.

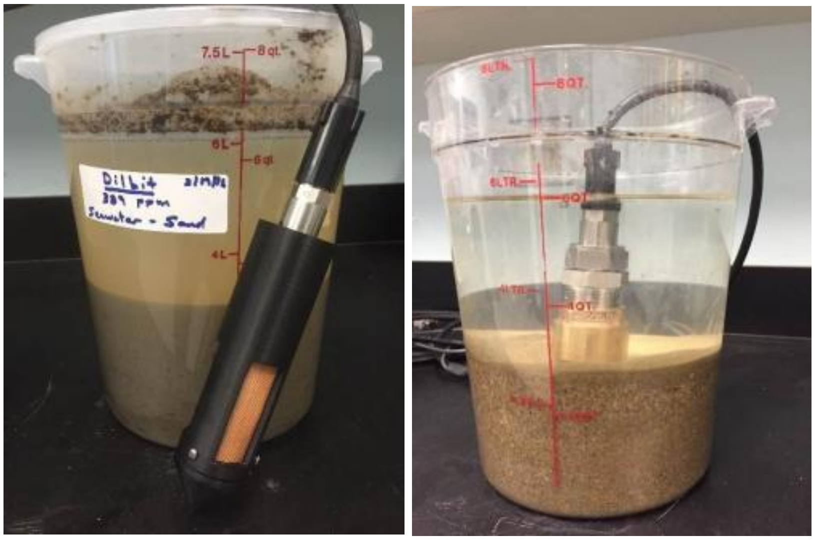


Figure 5. Prototype crude dilbit sensor shown housed in a probe to be inserted in oil-impacted sediments.

- Yang et al., 2016 measures the PAHs, TPH, petroleum biomarkers and PAHs alkylated homologous for CLB and AWB. A faster photo-oxidation rate can be observed with aromatic hydrocarbons and alkanes while the least photo-oxidation tendency can be observed with biomarkers, steranes and terpanes. Hydrocarbons and n-alkanes do not photolyze in winter but have a higher photolysis in n-alkanes due to radiation intensity and temperature. Photolysis behavior affects the chemical structure of petroleum hydrocarbon.

4.1.3 Containment and Recovery (in salt water)

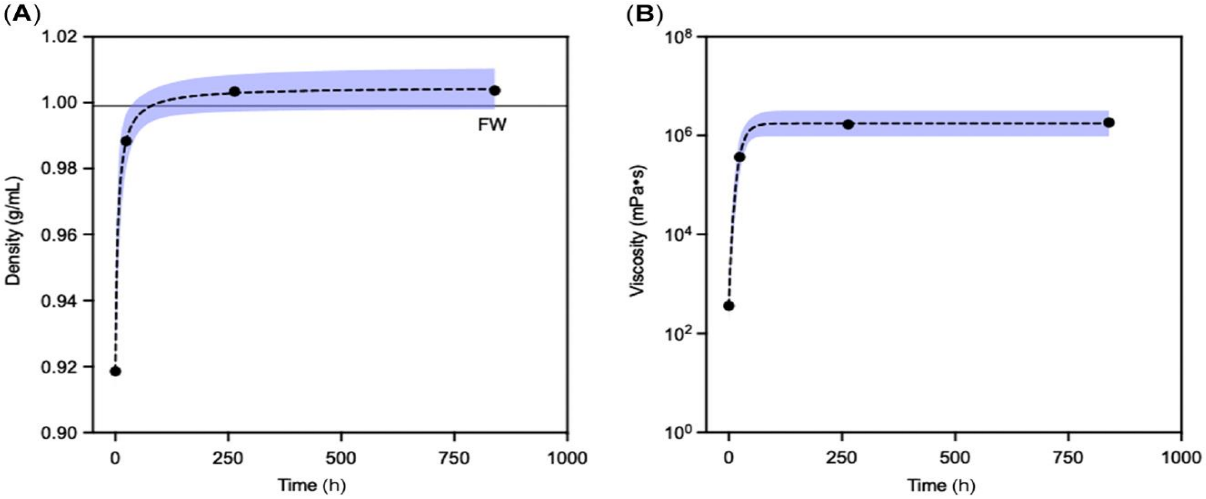
- Brown et al, 1992 tested the efficiency of different oil diversion techniques used in the cleanup of spilled oil in salt and fresh water. Three different types of diversion techniques were tested in a flowing channel to divert the weathered dilbit: river boom, mesh net, and a bubble net. Results showed that as the velocity of the water increased, the effectiveness of the boom and nets decreased.

4.2 Dilbit in Fresh Water

4.2.1 Physical Weathering (in fresh water)

- SL Ross Environmental Research Limited, 2013 (SL Ross) researched the effects of photo-oxidation on weathered CLB dilbit in freshwater for 11 days under constant wind and current conditions. In the presence of ultraviolet light (UV) light, oil droplets were formed which was a result of the breakdown of oil. The oil remained buoyant in the tank in the absence of UV light.

- Stoyanovich et al, 2019 researched weathered dilbit (CLB) in low energy for 11 days. In the first 24 hours of the experiment, evaporation caused the dilbit to increase in both viscosity and density. The dilbit eventually sank after 8 days due to the density exceeding that of fresh water (Figure 6).



Source: Stoyanovich et al, 2019.

Figure 6. Change in density (A) and viscosity (B) over a 840-hour test period.

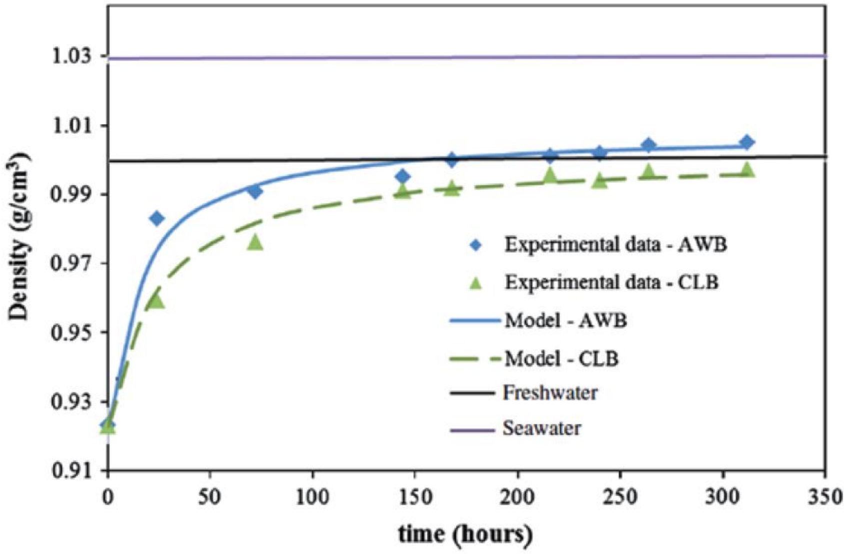
- Zhou, 2015 researched how WCS blend and CLB dilbit and crude reacted to agitation during an 8-day weathering study (Figure 7). Results showed that dilbit did disperse when there was no wave activity. The dilbit did not disperse into the water column when waves were present. Results from Zhou's experiments indicate that dilbit can stay afloat for ten days when there is no contact with sediments (Table 4).

Figure 7. Wave test tank.

Table 4. Weathering results.

	High Energy - 0-6 days	Still - 2-4 days	Still - 6-8 days
Cold Lake Dilbit	Most oil floating at beach	Thick layer of oil covering water surface	Thick layer of bubbly oil covering water surface
Crude	Oil dispersed/ submerged (none floating)	Thick layer of bubbly oil covering water surface	No oil on surface, all oil submerged

- EPA, 2013 researched short-term biodegradation using the dilbit from the Kalamazoo River spill. Over a period of 28 days dilbit (blends included CLB and WCS) was exposed to an aerobic environment and various inorganic nutrients. Twenty five percent of the hydrocarbons degraded over the 28 days; however, most biodegradation happened in the first 14 days. Figure 8 shows the changes in density due to biodegradation.



Source: National Academies of Sciences, Engineering, and Medicine, 2016.

Figure 8. Observed increases in density for two dilbit products due to biodegradation.

4.2.2 Chemical Weathering (in fresh water)

- Stoyanovich, 2019 researched weathered dilbit (CLB) and examined the behavior of polycyclic aromatic compounds (PACs). Samples were taken from the water column (dissolved and particulates) to determine possible concentrations of the biota that could have been exposed. Results showed an increase in the concentration of 2- and 3-ring phenanthrenes, dibenzothiophenes, and fluorenes. The concentrations of PACs increased for the first 96 hours and then began to decrease until the end of the study.

4.2.3 Containment and Recovery (in fresh water)

- The Brown study from 1992 looked at the efficiency of the types of diversion techniques used in the cleanup of spilled oil (Brown et al., 1992). Three different types of diversion techniques were tested to divert weathered and emulsified dilbit: river boom, mesh net, and a bubble net. Results showed that as the velocity of the water increased, the effectiveness of the devices in trapping, and diverting the oil decreased.

- The RDC 2018 study (Testing of Oil Sands Products Recovery in Fresh Water) evaluated the recovery of CLWB dilbit in fresh water to determine if there were any significant differences compared to the traditional recovery of floating, heavy oil in salt water (Balsley and Hansen, 2018). Results showed that standard skimmers do not need special modifications to recover dilbit in fresh water, especially in the early stages of a spill while the oil is on the surface. More powerful pumps may be needed during the later stages of a spill involving dilbit as the viscosity increases.

- The RDC 2019 study (Mitigation of Oil Sands Recovery in Fresh Water) developed and tested three oil spill response prototypes designed to effectively contain submerged oil in offshore and inshore environments. This study describes the potential capability of each design and the effectiveness of deploying and recovering each prototype.

4.3 Historical Spills

There have been different small and large spills of dilbit products in U.S. and Canada in the past 6 years in both fresh and marine environments (see Table 5). While responding to these spills, responders learned, mostly through trial and error, how best to manage the dilbit. These spills have been documented in several of the studies reviewed. Lessons learned from these spills adds to the body of knowledge and understanding of the fate of dilbit in a spill. While some of these dilbit spills were small and a short timeframe, others were major dilbit spills. Two dilbit spills in particular stand out and are detailed below.

- The Kinder Morgan spill, which occurred in the marine environment, and
- The pipeline rupture in Talmadge creek which then flowing into the Kalamazoo river (Dew et al., 2015).

Table 5. Historical dilbit oil spills.

Dilbit Oil Spill	Year	Pipeline	Size (bbl)	Crude Type
Exxon Mobil Pegasus pipeline near Mayflower, Arkansas	March 29, 2013	Exxon Mobile Pegasus pipeline	2000 to 5000	Wabasca Heavy, a heavy sour dilbit product
Kinder Morgan, Burnaby British Columbia	July 24, 2007	Excavator bucket striking the Westridge Transfer line in Burnaby, British Columbia	1,400	Synthetic crude oil
Kalamazoo River (Marshall, Michigan Enbridge)	July 25,2010	Enbridge's Line 6B pipeline	20,082	CLB
Romeoville, Illinois Enbridge spill	September 9, 2010	Enbridge Lakehead system on Line 6A pipeline	6,095	Dilbit product

Source: Crosby et al, 2013.

The Kinder Morgan, Burnaby British Columbia spill that occurred in July 2007 spilled 1,409 barrels of Albian Heavy, a blend of synthetic crude oil and heavier oil sand product (Government of Canada, 2013). The dilbit was released from a ruptured pipeline operated by Kinder Morgan, and it travelled through the storm drain system into the inlet, and it spread on the water (Hua et al., 2018). The oil from the spill did not sink and was recovered by treating it as a conventional spill using skimming and booming. The cleanup took several months, with 1,302 barrels of oil recovered (Crosby et al., 2013)

On the other hand, the Kalamazoo river dilbit spill flowed into the wetlands and traveled into a stream before entering into the river, where it interacted with sediment particles. The dilbit product was reported to have weathered before entering the river. The interaction with the sediment must have resulted in the sinking of the weathered dilbit, making the cleanup of the spill challenging. The amount of oil recovered was greater than the amount of spilled oil that was reported (Crosby et al., 2013). Approximately, 20%-30% of dilbit product still remain in the river three years after the spill (Dew et al., 2015).

While both real world spill experiences were pipeline ruptures, it revealed that spilled dilbit product required a different response based on the environmental factors and nature of the spill.

5 SUMMARY OF LITERATURE REVIEW

Tables 6, 7, and 8 provide a summary of all the past research reviewed for the three most common/transported dilbit products (i.e. AWB, CLB, and WCS (all diluted with condensate)) and synbit. These tables divide the literature reviewed into those tests performed in salt water and fresh water. Some studies overlap with testing in multiple areas. Some studies were extensive and others less rigorous. The purpose of these tables is to provide a general sense of the state of dilbit research which can then help to guide the recommendations for future research.

5.1 Properties of Dilbit

Table 6 summarizes studies that evaluated and tested the physical and chemical properties of dilbit. The information presented in Table 6 indicates that dilbit behavior in salt water has been well researched. Synbit behavior in freshwater is not well studied. Viscosity testing of AWB in fresh water was not found in this review, neither was physical and chemical analysis of synbit in fresh water.

Table 6. Literature review summary of the physical and chemical properties studies of dilbit.

	SALT water					**FRESH Water**			
The three most transported Dilbit products in the Great Lakes and Synbit	**AWB**	**CLB**	**WCS**	**Synbit**		**AWB**	**CLB**	**WCS**	**Synbit**
	PHYSICAL PROPERTIES ANALYSIS OF DILBIT								
Density of Dilbit - Changes due to weathering @15^0C	CAN, Yang	CAN, Yang	Ortmann	Ortmann		SL Ross	SL Ross, Stoyanovich	SL Ross	🟥
Viscosity of Dilbit - Changes due to Weathering @15^0C	CAN, Yang	CAN, Yang	Ortmann	Ortmann		🟥	Stoyanovtch	SL Ross	🟥
	CHEMICAL ANALYSIS OF DILBIT								
% BTEX, PAHS, and Alkanes Oil sediment (hydrocarbons)	Yang, Ortmann	Yang	Ortmann	Ortmann		EPA	Stoyanovich	EPA	🟥

5.2 Weathering of Dilbit

Table 7 summarizes weathering studies that are divided into surface and subsurface processes. The studies reviewed indicate that physical and chemical weathering of dilbit is well researched. However, the significant number of weathering processes that act upon the oil as well as the interaction with the water and any particles in it is very complex and not well researched. The variations of oil type, water type, temperature, wind, current, etc., all play a part in understanding how dilbit will react when spilled.

Table 7. Literature review summary of physical and chemical weathering of dilbit.

	Salt water				FRESH Water			
The three most transported Dilbit products in the Great Lakes and newer synbit	**AWB**	**CLB**	**WCS**	**Synbit**	**AWB**	**CLB**	**WCS**	**Synbit**
	PHYSICAL AND CHEMICAL WEATHERING PROCESSES							
SURFACE of Water								
Evaporation	CAN	EPA, CAN, KIng	EPA	🟥	EPA	Stoyanovich	EPA	🟥
Spreading/Drifting/Sheen	🟥	EPA	🟥	🟥	EPA	EPA	EPA	🟥
Photo-oxidation (photo-degradation)	CAN	EPA, CAN, King	🟥	🟥	EPA	SL Ross	EPA	🟥
Oil-particle Aggregates (OPA)	CAN	EPA, CAN,	🟥	🟥	EPA	EPA	EPA	🟥
SUB-SURFACE of Water								
Suspension/Emulsification	CAN	EPA, CAN	🟥	🟥	EPA	EPA	EPA	🟥
Natural Dispersion		EPA	🟥	🟥	EPA	EPA	EPA	🟥
Biodegradation	EPA	EPA	EPA	🟥	EPA	EPA	EPA	🟥
Dissolution (water breaking down oil)	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥
Sinking (Particle Mixing)	🟥	EPA	🟥	🟥	🟥	🟥	🟥	🟥
Sinking (no particle mixing)	🟥	🟥	🟥	🟥	🟥	Stoyanovich	🟥	🟥
Seasonal - Temperature/Currents	Yang, Ortmann	Yang	Ortmann	Ortmann	🟥	🟥	🟥	🟥

Table 7 shows that there are gaps in knowledge on physical and chemical weathering, specifically:

- Dissolution for all oil types for salt and fresh water
- Weathering on synbit for both salt and fresh water
- Spreading, photo-oxidation, OPA, suspension, and natural dispersion of WCS in salt water
- Understanding of the exact time before dilbit sinks for AWB, WCS and synbit in fresh and salt water
- Seasonal impacts on AWB, CLB, WCS and synbit in fresh water

5.3 Containment and Recovery of Dilbit

Table 8 reviews containment and recovery studies. Lab testing is limited for thorough evaluation of physical and mechanical systems. Testing in the real world is most often done without oil unless dealing with an actual spill or using very small amounts in a controlled lab environment.

Table 8 shows that there are significant gaps in knowledge concerning in situ burning, dispersants, surface cleaning agents and containment and recovery of dilbit in both salt and fresh water. The "no oil" column indicates research that did not include actual oil in the water.

Table 8. Literature review summary of containment and recovery of dilbit.

CONTAINMENT & RECOVERY											
	SALT water						FRESH Water				
	No Oil	AWB	CLB	WCS	Synbit		No Oil	AWB	CLB	WCS	Synbit
Mechanical Recovery Device	RDC 2017	🟥	🟥	🟥	🟥		RDC 2019	Brown	🟥	🟥	🟥
In Situ Burning	🟥	🟥	🟥	🟥	🟥		🟥	🟥	🟥	🟥	🟥
Dispersants	🟥	🟥	🟥	🟥	🟥		RDC 2018	🟥	🟥	🟥	🟥
Surface Cleaning Agents	🟥	🟥	🟥	🟥	🟥		RDC 2018	🟥	🟥	🟥	🟥
Submerged/Sunken Oil Detection/Recovery	🟥	🟥	🟥	🟥	🟥		RDC 2019	🟥	🟥	🟥	🟥

6 CONCLUSION OF LITERATURE REVIEW

Below is a summary of the key findings from the twelve historical literature reports reviewed. These conclusions summarize what is known about dilbit. They build upon the results from the 2020 RDC Oil Sands Products Spill Response report. CWB and AWB dilbit are the predominant dilbit transported/used, therefore are found in the majority of studies reviewed.

6.1 Identification of Knowledge

- When initially released into fresh and salt water, dilbit generally floats.
- In fresh and salt water, as diluent evaporates, the density and viscosity of dilbit increases and the *remaining oil behaves similar to a heavy oil.*
- Dilbit will stay afloat between 6-10 days in both fresh and salt water, when conditions are calm with no agitation or sediment in the water.
- Dilbit will sink after several days in salt water, but only with the presence of suspended particles and under high-energy mixing environment.
- Dilbit weathers rapidly in fresh and salt water, as compared to traditional crude oil.
- The same containment and recovery tools that are used with crude oil can be used on dilbit when floating.

6.2 Identification of Knowledge Gaps

The knowledge gaps identified below are derived from the twelve research studies reviewed.

- Exact conditions on the water surface and sub-surface that cause dilbit to submerge (e.g., type of sediment, sediment/oil interaction, high energy vs low energy conditions) in fresh water.
- Length of time that dilbit stays afloat before sinking in fresh water in different conditions.

- Further understanding of the behavior (i.e., weathering) of synthetics (e.g., synbit and dilsynbit) in salt and fresh water.
- The effects of nutrients to speed up or slow down biodegradation, and on each type of pure bitumen and dilbit (e.g., rates of anaerobic biodegradation, what factors effect long term and short-term biodegradation).
- Understanding precise rates of photo-oxidation of dilbit.
- The effects of weathered bitumen on aquatic organisms.
- The effects of various temperatures (seasonal changes) on the weathering of dilbit in fresh water.

6.3 Future Research Initiatives

Understanding the primary need for containment and recovery tools, including those for detection, mapping, and mitigation of sunken oil, RDC intends to conduct field experiments on weathering of various dilbit products (i.e., including synbit) with agitation, and with and without sediment (i.e., including different types of sediments) in fresh water. The influence of suspended sediment will be analyzed to determine how dilbit sinks in fresh water.

The original fresh oil and weathered dilbit oil will be characterized for physical properties (e.g., viscosity, density, pour point, flash point) and chemical properties (e.g., alkanes and selected PAHs). This study will help to better understand how long it will take for dilbit to sink.

The results of these dilbit-weathering studies will be summarized in a report. Based on findings of the fate and transport of dilbit, RDC intends to provide a basis for functional characteristics of tools to detect, map, and recover oil sands products. The information gained from this research will also provide first responders and Federal On-Scene Coordinators with knowledge to better manage a dilbit spill.

RDC recommends that this literature review be updated periodically to include additional past studies and new future studies. This should be a working document of dilbit research summaries which can be used as reference and to assist with the development of plans for future research efforts.

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APPENDIX A. INDEPTH ANALYSIS OF LITERATURE REVIEWED

A.1 Weathering - Physical and Chemical

Understanding the chemical composition and physical properties of bitumen products is necessary to study dilbit behavior when spilled in the freshwater environment (Government of Canada, 2013). In addition, this knowledge helps to predict the fate and transport of diluted bitumen (dilbit) if spilled in the environment. For this reason, it is important to develop safety measures and response planning (Ortmann et al., 2020). The pollution risks that can result from transport of dilbit across the Great Lakes region present challenges for response personnel. These risks are underscored by the lessons learned from a major spill of dilbit in the 2010 Marshall Michigan spill in the Kalamazoo River, where significant quantities of dilbit were submerged after weathering changed or altered the physical and chemical properties of the oil (Tarr et al., 2016; Stoyanovich et al., 2019; Ortmann et al., 2020). A challenge was encountered in spill response and cleaning when a significant amount of the dilbit oil sank (Dollhopf et al., 2014).

One major unknown question with dilbit spills in a fresh water environment is when dilbit will sink once the spilled dilbit is exposed to the environment. The density of dilbit is lower than the density of freshwater (Crude Quality Inc, 2015; Hua et al., 2018). Due to this difference, a freshly spilled dilbit will initially float on a water column until acted upon by weathering and suspended sediment (Environmental Protection Agency (EPA) 2013; Crosby et al., 2013; Dew et al., 2015; Hua et al., 2018; Stoyanovich et al., 2019). When dilbit is released or spilled into the environment, it undergoes a processes of weathering (e.g., evaporation, photo-oxidation, biodegradation, and emulsification) and sediment uptake (Government of Canada, 2013, Yang et al., 2018). All these weathering processes in a dilbit spill affects the physical properties of dilbit. This weathering process is observed with conventional oils, but it occurs at a faster rate with dilbit. Yang et al., (2016) demonstrated that rate difference with photo-oxidation (Yang et al., 2016).

A.1.1 Evaporation

Of all weathering processes, evaporation is the most important affecting physical properties (Fingas, 2012; Hua et al., 2018; Brown & Nicholson, 1991; Fieldhouse et al., 2014; Government of Canada, 2013) as it accounts for the greatest amount of substance loss. (National Research Council, 2003). Once dilbit comes into contact with the atmosphere, the lighter and more volatile compounds of dilbit are vaporized leaving behind heavier hydrocarbons. Lighter hydrocarbons, such as natural gas and gasoline, can completely evaporate in just a few days (National Academies of Sciences, Engineering, and Medicine, 2016). The density and viscosity increase as the lighter ends of the dilbit are removed. As the lighter compounds are removed, the dilbit's physical properties become more like pure bitumen, since the diluents are lighter and more volatile. The warmer the weather, the faster the lighter compounds will evaporate (Crosby et al., 2013). Wind speed is one of the most important factors in evaporation since the oil-atmosphere boundary is the limiting step in evaporation (Fingas, 2013).

After evaporation has removed the more volatile hydrocarbons, the adhesive nature of the dilbit increases. Increased adhesion permits the dilbit to efficiently cling to various surfaces, such as plants, rocks, and animals. Adhesion allows the dilbit to incorporate various material; the addition of this extra material increases the density and can cause submersion (National Academies of Sciences, Engineering, and Medicine, 2016).

The sinking of dilbit makes response cleaning difficult due to contaminated sediment and risk of toxicity to wild life (Dew et al., 2015 and Hua et al., 2018). Due to the sinking of dilbit product, the Kalamazoo River cleanup extended to three years after spill impacting the environment (Winter and Haddad 2014; Stoyanovich et al., 2019).

SL Ross Environmental Research Limited conducted mesoscale weathering studies AWB and CLB dilbit products. These studies have shown that behavior of dilbit when spilled in the environment is dependent on the type of oil, water and environment. This still leaves many questions about the fate and impact of dilbit in the environment (SL Ross, 2013 and Government of Canada 2013).

A study by Hua et al., used the dilbit product CLB-Winter, demonstrated how the weathering processes influenced the spill and the interaction of dilbit-sediment forming oil-particle aggregates (OPA) have an effect on its ability to sink or float in the water column (Hua et al., 2018).

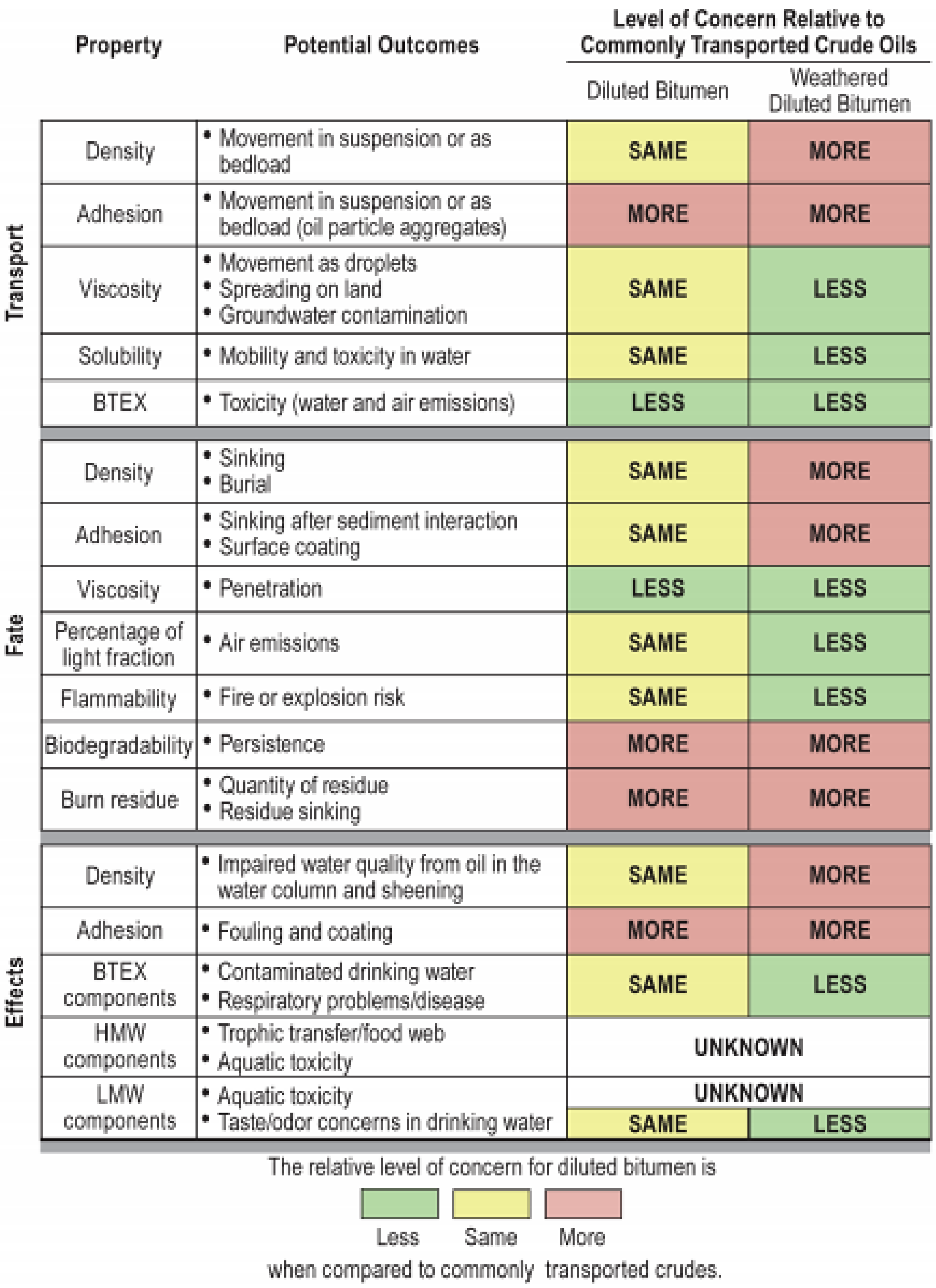
A.1.2 Oil Particle Aggregates

OPA is the interaction between floating oil and sediments in marine environments (Yu et al., 2019). There are two major types of OPA: oil droplets coated by small particles and oil trapped within large particles (Frelichowska et al, 2010). OPA formations allow for researchers to develop a better understanding of the nature of oil-sediment interaction (Hua et al., 2018). Previous studies on OPA have been conducted in marine and aquatic environments (Hua et al., 2018). Salinity has a large role in the formation of OPA, which can also form in salinities that are as low as 1/200 of salt water (Le Floch et al., 2002).

OPA have unique physical characteristics and develop from oil dispersion within an open water body (Johnson et al, 2018). OPAs tend to break away from the oil mass within which they form.

OPA with smaller sizes tend to sink while larger OPA are more buoyant and tend to float (Zhao et al., 2014). The density, size, and shape of the OPA determines whether it sinks to the bottom or floats to the surface; in still water larger OPA are less prone to be displaced by turbulence than smaller ones. Typically, the more viscous the oil, the larger the OPA (Wang & Calabrese, 1986).

Weathering processes are what control the behavior of dilbit. These processes happen at different rates to different substances that are exposed to the natural elements (Fingas, 2012; Stoyanovich et al., 2019). During the duration of a dilbit spill, weathering rates are inconsistent with a high rate of occurrence immediately after a spill (Fingas, 2015). The density of bitumen depends on the reservoir and temperature of the source material (Crosby et al., 2013). Figure A-1 compares general level of concerns of fresh dilbit and weathered dilbit to conventional crude (CC) on possible physical weathering scenarios and effects of the physical weathering.



	Property	Potential Outcomes	Level of Concern Relative to Commonly Transported Crude Oils: Diluted Bitumen	Level of Concern Relative to Commonly Transported Crude Oils: Weathered Diluted Bitumen
Transport	Density	Movement in suspension or as bedload	SAME	MORE
	Adhesion	Movement in suspension or as bedload (oil particle aggregates)	MORE	MORE
	Viscosity	Movement as droplets Spreading on land Groundwater contamination	SAME	LESS
	Solubility	Mobility and toxicity in water	SAME	LESS
	BTEX	Toxicity (water and air emissions)	LESS	LESS
Fate	Density	Sinking Burial	SAME	MORE
	Adhesion	Sinking after sediment interaction Surface coating	SAME	MORE
	Viscosity	Penetration	LESS	LESS
	Percentage of light fraction	Air emissions	SAME	LESS
	Flammability	Fire or explosion risk	SAME	LESS
	Biodegradability	Persistence	MORE	MORE
	Burn residue	Quantity of residue Residue sinking	MORE	MORE
Effects	Density	Impaired water quality from oil in the water column and sheening	SAME	MORE
	Adhesion	Fouling and coating	MORE	MORE
	BTEX components	Contaminated drinking water Respiratory problems/disease	SAME	LESS
	HMW components	Trophic transfer/food web Aquatic toxicity	UNKNOWN	
	LMW components	Aquatic toxicity Taste/odor concerns in drinking water	UNKNOWN SAME	 LESS

The relative level of concern for diluted bitumen is

🟩 Less 🟨 Same 🟥 More

when compared to commonly transported crudes.

HMW: high molecular weight; LMW: low molecular weight.
Source: National Academies of Sciences, Engineering, and Medicine 2016.National Academies of Sciences, Engineering, and Medicine, 2016.

Figure A-1. Transportation, date, and effects of dilbit relative to conventional crudes (CC).

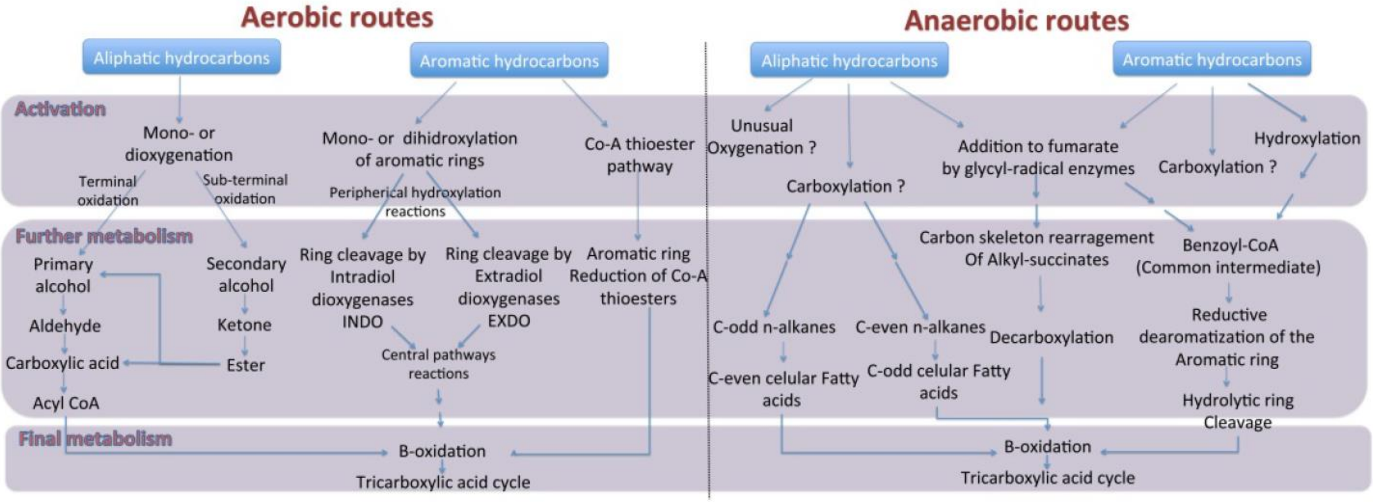
A.1.3 Photo-oxidation

Photo-oxidation, also referred to as photochemical oxidation, occurs when spilled CC is exposed to large amounts of solar radiation and oxygen. It creates a dense crust on the surface of the exposed oil (Hollebone et al., 2011). During photochemical oxidation, covalent bonds form with oxygen or oxygenated compounds. Photochemical oxidation causes the viscosity, density, and adhesion properties of the oil to increase (Collin et al., 2018). It is also known to be the key process driving oil oxidation (Bacosa et al., 2015). As the oil oxidizes, the effectiveness of dispersants decreases (Collin et al., 2018). Aromatic hydrocarbons oxidize at a faster rate than alkane hydrocarbons (Garrett et al., 1998). The photochemical oxidation rate of CC under ultraviolet radiation is 5% for branched alkanes, 9% for linear alkanes, and 37% for aromatic hydrocarbons (D’Auria et al., 2009). The molecules created by photochemical oxidation can remain in the environment for an extended period of time (Aeppli et al., 2012).

Toxicity for polycyclic aromatic hydrocarbons (PAHs) can increase as photochemical oxidation occurs. PAHs are created by the incomplete combustion of fossil fuels (Cerniglia, 1993). Organisms that have been exposed to PAHs can experience increased toxicity (up to 48 times) when illuminated by natural light (Barron et al., 2003).

A.1.4 Biodegradation

Biodegradation occurs when living organisms, typically bacteria, break down compounds (Prince, 1993). This process happens quickest in an aerobic environment, but can also occur in an anaerobic environment. The rate of biodegradation for oil is dependent on environmental factors, such as oxygen concentration, nutrients, temperature, and type of oil. The rate of biodegradation increases with abundant oxygen and nutrients (Torlapati & Boufadel, 2014). Figure shows the break down for hydrocarbon biodegradation in aerobic and anaerobic environments. Bacteria metabolizes the hydrocarbons until they reach the beta oxidation (The step in the metabolic process where fatty acids are broken down to produce energy.) and the tricarboxylic acid cycle (A stage of cellular respiration where organic molecules are broken down for the cell to grow.) (Sierra-Garcia & Oliveira, 2013).



Source: Sierra-Garcia & Oliveira, 2013.

Figure A-2. Breakdown of bacterial biodegradation on hydrocarbons.

Biodegradation of bitumen can lead to an increased concentration of sulfur, resins, asphaltenes, and metals (Shuqing et al., 2008). As biodegradation occurs there is a reduction of mass that occurs; as the lighter hydrocarbons are removed, the viscosity and density increases. Bitumen is extracted from oil deposits that have already experienced extensive anaerobic biodegradation and thus can be resistant to additional biodegradation. Further studies are required for dilbit biodegradation with aerobic bacteria and nutrients

(Wang & Fingas, 1996). There is also no quantitative field studies on the effects of biodegradation on dilbit; however, it is expected that it would take weeks to years for biodegradation to occur (National Academies of Sciences, Engineering, and Medicine, 2016).

A.1.5 Emulsification

Emulsification occurs when oil droplets are suspended in water or when water droplets are suspended in oil. In order to be classified as an emulsion, the compound must be physically stable. Emulsified oil (oil droplets suspended in water) has the appearance of chocolate mousse and has very different properties from the parent oil.

Water can be present in oil in five various ways.

1) Some oils contain about 1% soluble water. The water does not significantly change the properties of the oil (National Academies of Sciences, Engineering, and Medicine, 2016).
2) Emulsions formed when water droplets are incorporated into the oil by wave action and the emulsified oil is not viscous enough to prevent droplets from separating (National Academies of Sciences, Engineering, and Medicine, 2016).
3) Mesostable emulsion is formed when small droplets of water are stabilized by a combination of viscosity of the oil and interfacial action of asphaltenes and resins. Viscosities of the mesostable emulsion are between 20 to 80 times higher than the starting oil (National Academies of Sciences, Engineering, and Medicine, 2016). This form of emulsification typically breaks down in a few days (Fingas & Fieldhouse, 2009). Mesostable emulsions have a reddish brown color and are viscous compounds.
4) High viscous mesostable emulsions are between 800 to 1000 times more viscous than the starting oil. The emulsion will remain stable weeks to months after formation. These highly viscous compounds tend not to spread and instead remain in mats or lumps (National Academies of Sciences, Engineering, and Medicine, 2016).
5) Viscosity entrainment occurs when the viscosity of the oil is low enough that the oil can penetrate the water column. The oil contains 30% to 40% water in a turbulent body of water. Once the water calms down, the entrained water slowly drains and will dissipate within two days (National Academies of Sciences, Engineering, and Medicine, 2016).

Emulsions play an important role in oil spills. Emulsification increases the volume of an oil spill (typical emulsions contain 50% to 70% water); this volume increase can cause the oil spill to triple in volume (National Academies of Sciences, Engineering, and Medicine, 2016). Once dilbit becomes emulsified, evaporation and biodegradation slow down considerably.

A.1.6 Spreading

Spreading occurs when oil encounters the surface of water; oil spreads out across the surface of the water and continues to spread out until the oil forms a thin film, or “sheen” (Fay, 1969). As the sheen increases in size, the rate of evaporation and photo-oxidation also increases. Small amounts of oil can cover a very large area, thus accessing a spill’s severity can be very difficult (National Academies of Sciences, Engineering, and Medicine, 2016). These sheens impair water quality and can exist for long periods of time.

Submerged or sunken oil can also serve as a source of a sheen. An example of a submerged oil source are natural oil seeps located in the Gulf of Mexico and off the shore of California. These oil seeps are quite slow, yet leave a fairly large sheen on the surface of the water.

A.1.7 Dispersion

Oil dispersion refers to droplets of oil suspended in the water column (National Academies of Sciences, Engineering, and Medicine, 2016). When a dispersant is added to oil, the tension between the oil and water is reduced by 10 to 200 fold (Johansen et al., 2013). The reduction of the tension between the oil and water increases the rate of dispersion. The rate of dispersion depends on several factors, such as oil viscosity, agitation of wind/currents, and the tension between the oil and water (National Research Council, 2005). Droplet size distribution (DSD) of oil determines the behavior of the dispersed oil. Larger droplets are more buoyant and tend to float towards the surface; smaller droplets will remain in the water column (National Academies of Sciences, Engineering, and Medicine, 2016).

During the Deepwater Horizon oil spill, larger oil droplets (>1 mm) rose at a vertical angle and reached the surface quite quickly (in a few hours) (Boufadel et al., 2014). The smaller droplets rose at a slower rate or remained suspended in the water (Valentine et al., 2014). DSD also plays an important role in the toxicity of dispersed oil. Toxicity increases as the DSD decreases; the smaller the droplet size results in a larger overall surface area for the oil mass (Reddy et al., 2012). Evaporation losses are typically expected to be larger than dispersion losses but take longer to achieve (National Academies of Sciences, Engineering, and Medicine, 2016).

A.1.8 Dissolution

Dissolution is a chemical weathering process that removes soluble particles in water during an oil spill (Tarr et al., 2016). It is dependent on the oil/water surface. The diluent in bitumen is easily vaporized and solvent is lost by evaporation. This loss by evaporation is anticipated to be more than the loss by dissolution (National Academies of Sciences, Engineering, and Medicine, 2016). Dissolution is more significant after sinking of the dilbit in a spill (Tarr et al., 2016).

APPENDIX B. INDEPTH SUMMARY OF STUDIES

B.1 Ortmann et al., 2020

Three different dilbit products (Access Western Blend (AWB), Surmont Synbit (Synbit), and Western Canadian Select (WCS)) (Table B-1) were added in a flume tank study with filtered salt water under controlled temperature. The experiments were conducted in spring (May), summer (July), and autumn (November), to determine effect of environmental timing and conditions on an oil/dilbit spill. All seasons were exposed to a light source. Each experiment was allowed to weather for 14 days. Four treatments (in triplicates) were included in each experiment.

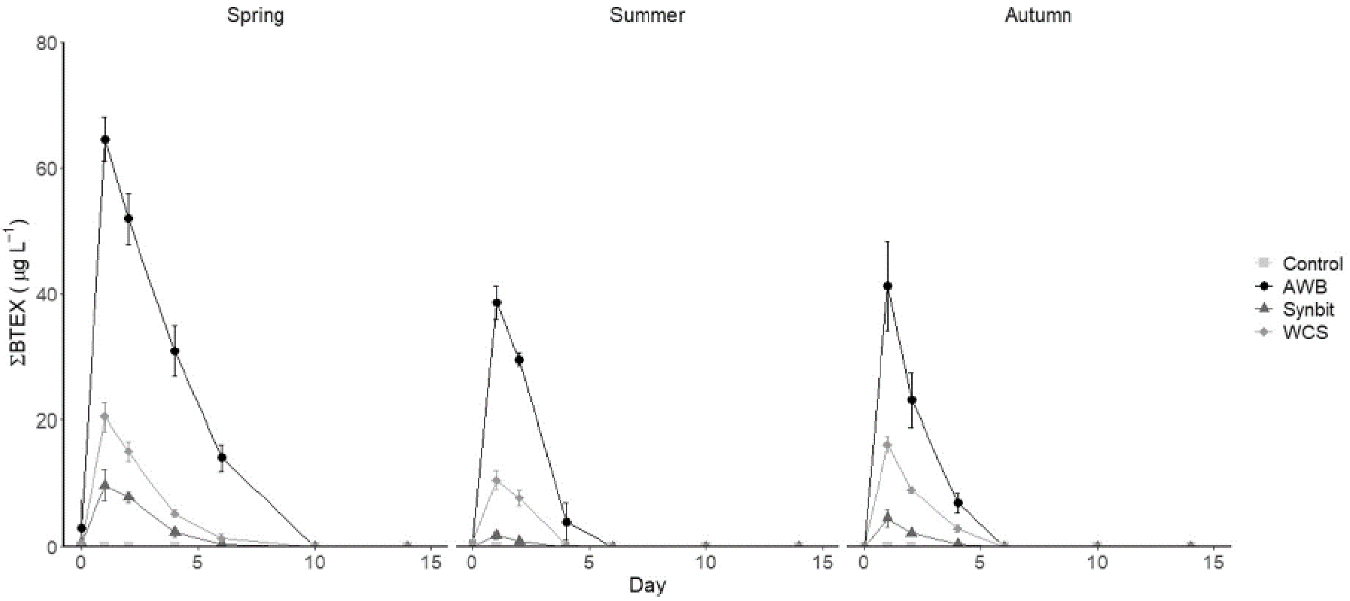
Table B-1. Physical and chemical properties of the three different fresh dilbit used in this study.

Property	**AWB**	**Synbit**	**WCS**
Diluent	Condensate	Synthetic Crude	Condensate + Synthetic crude + other petroleum products
Class	Heavy	Heavy	Heavy
API°	22.3	20.4	21.9
Density (g mL^{-1}, @ 15°C)	0.9189	0.9304	0.9214
Viscosity (cSt, @ 15°C)	243.89	204.65	211.29
% BTEX[a]	1.96	0.56	0.87
% Saturates	14	20	20
% Aromatics	23	10	10
% Resins	46	57	52
% Asphaltenes	17	13	18
Σ Alkanes (ng g^{-1})	6.8×10^6	11.3×10^6	8.0×10^6
Σ PAHs (ng g^{-1})	1.3×10^5	2.8×10^5	3.4×10^5
Σ Alkylated PAHs (ng g^{-1})	3.0×10^6	3.3×10^6	5.2×10^6

Source: Ortmann et al., 2020.

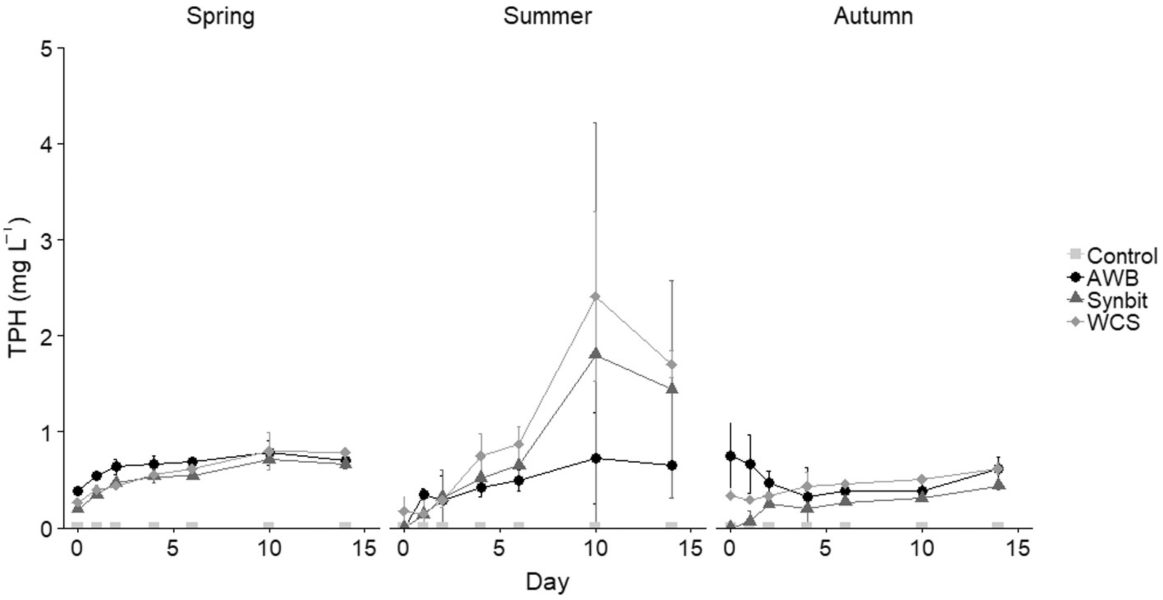
BTEX and TPHs (measures specific alkanes, PAHs, and alkylated PAHs) were determined for the samples before and during weathering. BTEX showed a different pattern than TPH. As shown in Figure B-1, concentrations increased for AWB, with highest peak concentration in spring and lower in summer and autumn. BTEX concentration was detected until day 10 in spring and less days for summer and autumn.

For the dilbit products in all the three experiments, hydrocarbons were detected for the duration of the 14 days. Over time, some of the hydrocarbons evaporated or degraded in the water column. Droplets are released in the water column by these dilbit types. AWB contained more condensates among the three dilbit products, therefore producing the highest BTEX concentration in the water column. TPH concentration during the experiment increased in the spring and summer but stayed constant during autumn (Figure B-2). TPH concentration was highest in summer, with warmer water having higher variability. The concentration of VOC and TPH varied with seasons and type of dilbit product.



Source: Ortmann, et al, 2020, 2010.

Figure B-1. Average and standard deviation for measured BTEX in the water column.



Source: Ortmann, et al, 2020.

Figure B-2. Average and standard deviation for TPH measured in the water column.

This study shows that under low energy, sinking does not immediately occur after a dilbit is spilled in the temperate coastal water when the density of salt water is higher than the density of the dilbit weathered product (Ortmann et al., 2020). This demonstrates that the oil can be removed from the surface slick by a rapid conventional clean up response before it weathers and sinks. This study also shows that in the event of a dilbit spill, the fate of the spill depends on the dilbit type and environmental conditions. The presence of hydrocarbon in the water over time will impact aquatic organisms. While this study demonstrated the potential fate and behavior of three dilbit products in different seasons in a salt water environment for 14 days weathering, it did not consider the effect of suspended particles in the water column, which have been reported in past studies to influence weathering of dilbit (Hua et al., 2018). In addition, it did not consider the effect of UV light or photo-oxidation and the light source did not provide sufficient data.

B.2 USCG RDC 2019, Containment and Recovery

The U.S. Coast Guard Research and Development Center (RDC) developed and tested three prototype devices (Figure B-3) designed to effectively contain submerged oil in the inland and offshore environments. This effort was in response to dealing with a difficult non-floating oil spill in the Kalamazoo River. The RDC OSP Assessment Report (Hansen et al., 2015) noted barriers for this application should function effectively in a range of bottom current conditions, be flexible, possess the ability to be rapidly deployed, and be appropriately adjustable to meet the dimensional requirements of the deployment site. Procedures and capabilities should be in place to enable the responders to track the location and efficiency of the barrier.

Figure B-3. Two inland and one offshore prototypes being deployed (Balsley, 2019).

B.2.1 RDC's First Inland Mitigation System Prototype (Boom Type)

RDC's first inland mitigation system prototype consisted of three separate 25-foot boom-like sections linked together with slide connectors for a total length of 75 feet. Each 25-foot section weighed approximately 500 pounds with the flotation and weights covered with polyvinyl chloride (PVC) material. The system's primary purpose is to divert moving, sunken oil from a faster part of the river towards the shoreline where current velocity is less (Balsley, 2019).

- Conclusion and Recommendation on device (Fitzpatrick, et. al., 2020):
    - With limited access for barge platforms or large vessels on smaller tributaries, boom-type systems might need shore deployment and towing to the desired position to overcome a smaller vessel's deck footprint.
    - Cleaning a system after use may be challenging with limited deck space, especially if decks become oiled during recovery.
    - A sectional boom-type system requires connecting features that prevent oil from flowing past. Irregular bottom features (rocks, obstructions) can impede effective use of a bottom-hugging system.

B.2.2 RDC's Second Inland Mitigation System (CLAMShell)

DC's second inland mitigation system called the CLAMShell system was designed to be deployed as part of a long-term cleanup strategy instead of a first response option. The prototype consisted of four sections (27 feet each) for a total length of 108 feet. The purpose of this mitigation system is to promote deposition of moving, sunken oil along the length of the system (Balsley, 2019).

- Conclusion and Recommendation on device (Fitzpatrick, et. al., 2020):
    - Deploying and recovering a relatively-light system from the bow of a modified 24-ft deck boat can be quick and effective. However, side thruster capability to maximize maneuverability and keeping station for an extended amount of time might enhance operations.
    - Key to a successful system is deployment and retrieval with at most three people, two to work directly with the system and one to operate the vessel.
    - To maintain position in river currents up to two knots, proper anchor line configuration is paramount, and can allow submerged systems conform to natural features on the river bottom.

B.2.3 RDC's Third Prototype, For Offshore Mitigation

RDC's third prototype, for offshore mitigation, was made of semi-rigid high-density polyethylene (HDPE) panels covered with PVC. The system was approximately 3 feet high and was 200 feet in total length. Its primary objective was to collect sunken oil rather than diverting it to a specific location (Balsley, 2019).

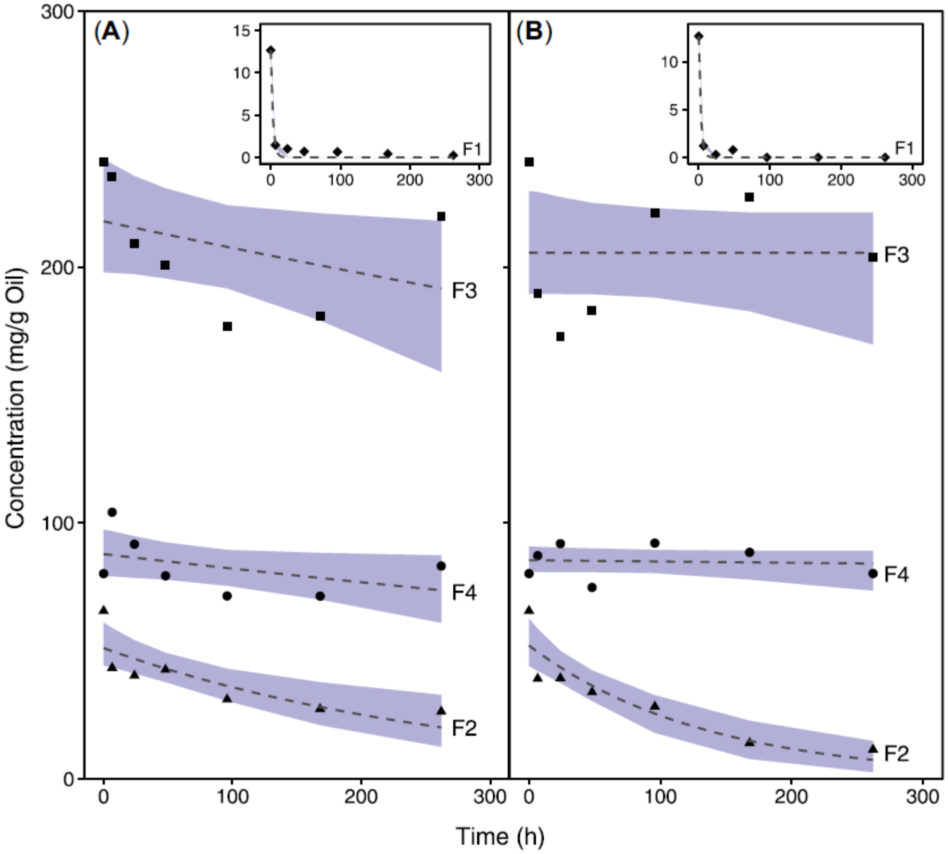
- Conclusion and Recommendation on device (Fitzpatrick, et. al, 2020):
    - If a mitigation system requires the use of divers to complete installation, dive platforms should be stable.
    - Coast Guard buoy tenders are capable of deploying a submerged-boom system "sideways". However, it would be difficult to do the same from a vessel of opportunity lacking side thruster capability. For other vessels with ample deck space aft, a stern deployment (and recovery) method would likely work best.
    - Using a crane to recover a submerged-boom system may be a practical approach in very low-wind conditions, but alternative methods such as the use of cross-deck winches or boom reels keep the boom sections lower to the deck and out of the wind, for safer recovery.
    - Operators need to carefully consider anchor and anchor line arrangements to prevent entanglement and improper setting during deployment. Anchoring options must account for multiple conditions, i.e., heavier anchors for open water, different anchors for different bottom types, different anchor-line scope, etc. Additionally, varied anchoring options might allow use by a wider range of vessels of opportunity.
    - The RDC prototype required diver deployment. Any adaptation of this concept should develop deployment and recovery techniques, possibly with remotely operated vehicles to eliminate the need for divers.

B.2.4 Overall Conclusions and Recommendations

RDC sought to advance the science of response technologies for moving sunken oil with the development and testing of three mitigation systems. After reviewing results and lessons learned, RDC recommends further developmental efforts and testing with oil to determine actual effectiveness for all three mitigation systems before they can be used as response tools for real world oil spill incidents that involve moving sunken oil.

B.3 Stoyanovich and Colleagues 2019 Studies

The Stoyanovich study from 2019 looked at how dilbit (CWB) weathered in a simulated ecosystem with low energy for 11 days (Stoyanovich et al, 2019). The researchers observed that in the first 24 hours of the experiment the volatile hydrocarbons—hydrocarbons with low boiling point—evaporated causing the dilbit to increase in both viscosity and density. The changes in these two physical properties caused the dilbit to sink after eight days. The carbon number (nC) is the number of carbon atoms in each molecule; the property of the hydrocarbon is directly correlated to the carbon number. The hydrocarbons with the lower carbon number (<nC16) quickly evaporated, leaving behind the hydrocarbons with the larger carbon number (>nC16). After the third day, the hydrocarbons with a carbon number greater than 16 did not experience significant change in composition (Lee et al., 2015) (Figure B-4).

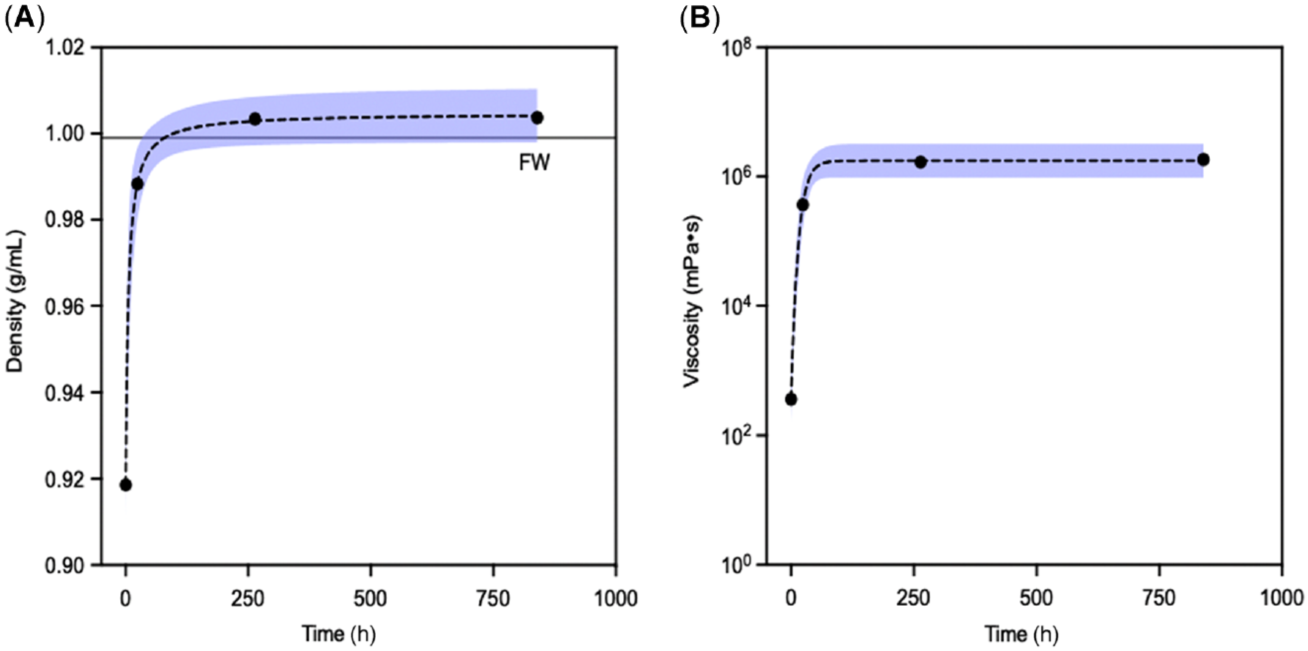


Source: Stoyanovich, 2019.

Figure B-4. Changes in concentration over time of the 4 major petroleum fractions of dilbit.

Over the course of the experiment, the physical characteristics of the dilbit altered by forming a crust over the surface and the color changing from dark black or light brown. In freshwater the composition of dilbit can change quickly causing an increase in density and a decrease in buoyancy. In Figure 8, F1 (<nC10), F2 (nC10-nC16), F3 (nC16-nC34), and F4 (>nC34). Samples were collected from the surface slick of the low-treatment (A) and high-treatment (B) microcosms. Line of best fit (dashed) and 95% confidence intervals (purple) are indicated.

In another experiment, Stoyanovich weathered dilbit in a fresh water tank for 840 hours; during the experiment the density and viscosity was closely monitored. In the first 24 hours the density increased from .945 g/mL to .998 g/mL (Stoyanovich et al, 2019) (Figure). At the end of the 840th hour the density of the dilbit had increased to 1.0037 g/mL. The viscosity of the dilbit increased from 362 to 367,000 mPa s^{-1} during the first 24 hours, then increased to 1,837,000 mPa s^{-1} over the 840-hour timeframe (Stoyanovich et al, 2019) Table B-2). At the start of the study water concentration of the oil slick started at .41% and after 24 hours had reached 18.66%, but never passed 20%. This viscosity of the dilbit prevents further penetration of the water (Fingas, 2015).



Source: Stoyanovich et al, 2019.

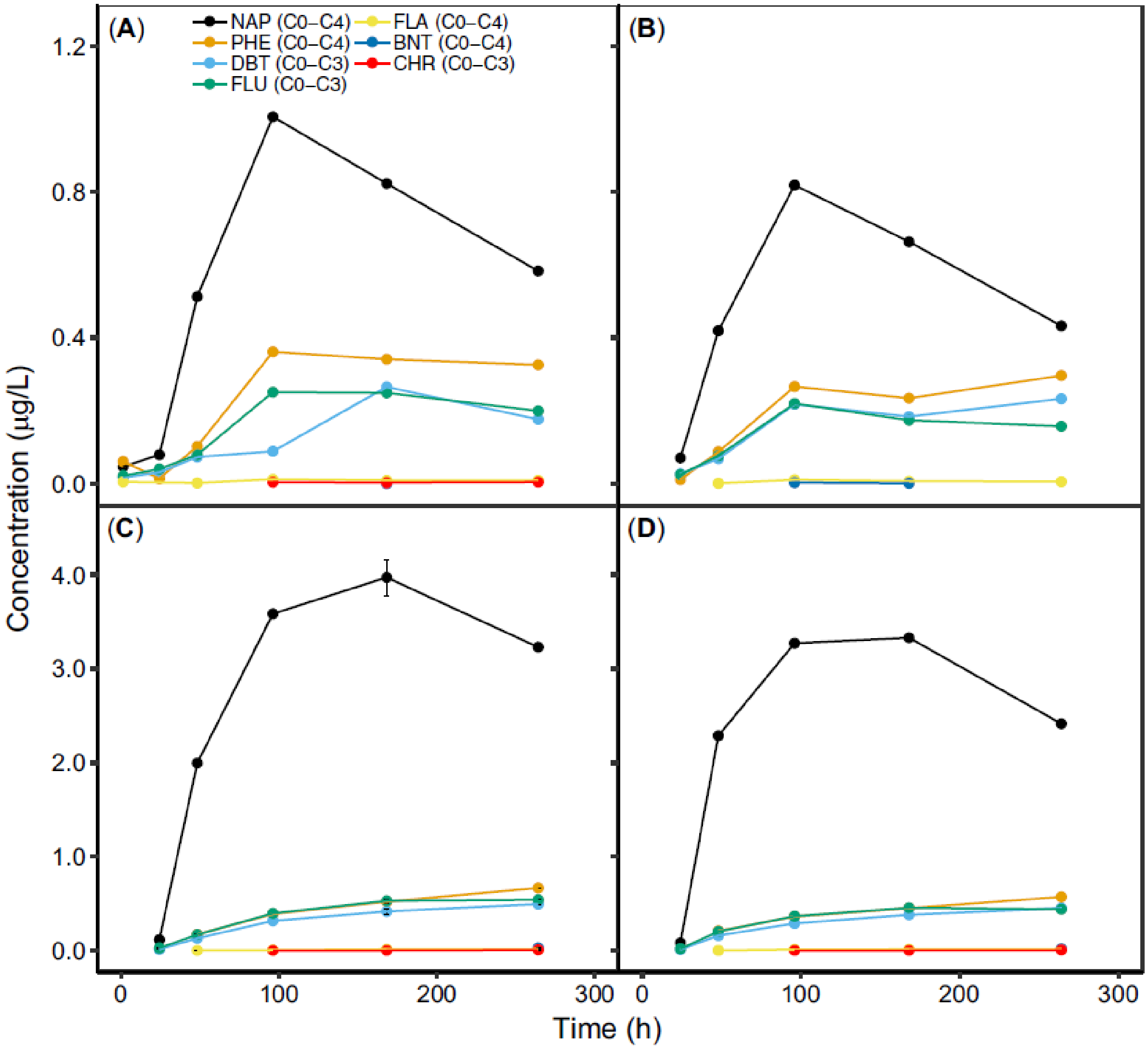
Figure B-5. Change in density (A) and viscosity (B) over an 840-hour test period.

Table B-2. Dilbit properties over life of study.

	Start	**24th Hour**	**264th hour**	**840th Hour**
Density	0.945 g/mL	0.998 g/mL	1.0034 g/mL	1.0037 g/mL
Viscosity	362 mPa s^{-1}	367,000 mPa s^{-1}	1,670,000 mPa s^{-1}	1,837,000 mPa s^{-1}

Source: Stoyanovich, 2019.

The team examined the behavior of PACs (parent and alkylated) from the slick. Samples were taken from the water column (dissolved and particulates) to determine possible concentrations of the biota that could have been exposed. The experiment was broken into two tanks; one tank had a ratio of oil to water 1:8000 (low treatment) and the other tank had a ratio of oil to water 1:800 (high treatment). Over the course of the experiment, there was an increase of concentration of 2- and 3-ring phenanthrenes, dibenzothiophenes, and fluorenes (Figure B-6). The concentrations of PACs increased for the first 96 hours and then began to decrease until the end of the study. The increasing viscosity of the dilbit could be the reason that the PACs dissolved at a decreasing rate (Stoyanovich et al, 2019). Naphthalene increased in both microcosms showing a dependence on dosage; it reached max concentrations on the 4th day (1.0 µg/L) in low treatment and max concentration on the 7th day (4.0 µg/L) in the high treatment. Afterwards, the naphthalene began to decrease over time, most likely due to evaporation to air.



Source: Stoyanovich, 2019.

Figure B-6. Water column concentrations of 7 major polycyclic aromatic compound groups in the low-treatment microcosm at 10-cm (A) and 40-cm (B) depths and the high-treatment microcosm at 10-cm (C) and 40-cm (D) depths.

B.4 USCG RDC 2018, Testing of Oil Sands Products Recovery in Fresh Water with Skimmers

In the past, researchers performed limited recovery tests for response to dilbit in salt and brackish water, but did not perform these tests in fresh water, which may have different outcomes due to the lower density of fresh water. For example, brackish water (20 ppt salinity) skimmer test results on CLWB dilbit from Witt|O'Brian's et al. (2013) included:

- No performance shortcomings observed in the current inventory of recovery equipment available to the participating company.
- Even the more viscous oil did not cause skimmer malfunctions.
- Operational adjustments to compensate for increased dilbit viscosity were no different than field adjustments made to equipment during actual spill events for most types of oils.
- This particular dilbit behaved similarly to any other crude oil that the participating spill response professionals had experienced in the past.

RDC evaluated the recovery of weathered dilbit in fresh water to determine if there were any differences compared to the traditional recovery of floating, heavy oil in salt water (Balsley and Hansen, 2018). The research team collaborated with a transportation company to acquire the appropriate oil (CLWB) and identified a drum skimmer and a brush skimmer to represent the two classes of skimmer commonly found in responders' inventories. The Bureau of Safety and Environmental Enforcement's National Oil Spill Response Research and Renewable Energy Test Facility (Ohmsett) installed a separate test tank adjacent to the main test tank and filled it with fresh water (Figure B-7). Ohmsett conducted the test using the American Society of Testing and Materials (ASTM) standard F2709, Standard Test Method for Determining Nameplate Recovery Rate of Stationary Oil Skimmer Systems. Ohmsett personnel weathered the oil to simulate a spill lasting over eight days. The recovery efficiency was never below 70 percent for either skimmer, although the recovery rates varied somewhat due to the skimmer configuration.

The data collected during that evaluation indicated that with care, standard skimmers do not need special modifications to recover dilbit in fresh water, especially in the early stages of a spill while the oil is on the surface. Skimmers need to be monitored closely for rotational speed during the early stages to ensure efficiency. A lower recovery rate may be acceptable for increased efficiency. Responders may need more powerful pumps during the later stages of a spill involving this type of product as the viscosity increases.

Figure B-7. Skimmer test with dilbit in Ohmsett's fresh water tank.

B.5 USCG RDC 2017, Underwater Sediment Sampling Research

Underwater Sediment Sampling: The goal was to develop a bench top system to determine, in situ, the amount of total petroleum hydrocarbons (TPH) in underwater bottom sediment. This situation can occur whenever oil is weathered and mixed with silt or sand. The result is that the oil sticks to the silt and sinks to the bottom. Poles were used to agitate the bottom during the Kalamazoo River spill in 2010 and the measure of the oil locations was whether sheening did or did not occur. Currently, the only reliable method to determine the exact concentration is to obtain a full sample and perform an analysis in a laboratory. During the Deepwater Horizon spill response, a large amount of samples were needed because oil only comprised about 10-20 percent of the tar mats and can be very scattered.

The approach here is to sample the interstitial water between the grains of sand and attempt to determine the amount of oil in and on the surrounding particles. This effort focused on locating dilbit, due to limited response experience with dilbit spills; however, this study sought a system that could also be applied to the other types of crude oil and environments. This report describes the equipment and processes followed for the demonstration and includes recommendations for further efforts needed to develop a field able system for use in subsequent testing. This system would need to function at depth of up to 100 feet, in currents of up to 0.5 knots, and perform at least five (5) samples per hour during a 12-hour operating window without bringing a sample to the surface, based on the experiences during the Deepwater Horizon and Kalamazoo River Spills.

A bench top system was successfully demonstrated in the laboratory, measuring TPH concentrations in sediments containing Dilbit and Texas Raw Crude oil, based on a mathematical relationship for each type of oil. This relationship does not provide the exact concentration of oil in the sediment but could provide decision-makers with better information on the location of potential oil patches. Due to the unusual hydrophobic nature (Stickiness) of Dilbit, significantly, difficulty was experienced in preparing the oil/sediment/water mixtures in the laboratory, and innovative procedures were developed to resolve the issue. More work needs to be done before this can be an operational system. A process needs to be developed that can address the calibrations needed and how this might be done in the field.

B.6 Yang et al., 2016: The photolytic behavior of diluted bitumen in simulated seawater by exposed to the natural sunlight

Two dilbit, Cold Lake Blend (CLB), Accessed Western Blend (AWB), and Alberta Sweet Mixed Blend #5 crude oil (ASMB#5), were spiked into 3.3% NaCl aqueous solution, then exposed to natural sunlight for 90 days in the winter and summer in the Northern Hemisphere (Ottawa, Canada). The effects of temperature and solar intensity on the photolytic behavior of dilbit were evaluated. Simultaneously, the photolytic similarities and differences between dilbit and crude oil were compared. It was found that, in all test oils, the decrease of all total petroleum hydrocarbons followed a pseudo-first-order reaction kinetic with the exposure time regardless of seasons. Aromatic fractions had the highest apparent rate constants. Similarly, the chemical fingerprinting analysis of test oils demonstrated that polycyclic aromatic hydrocarbons (PAHs) and their alkylated homologues (APAHs) were the most photosensitive compounds among the identified targets, followed by n-alkanes, then terpanes, and steranes. The photolytic efficiencies of the target petroleum hydrocarbons in ASMB#5 were generally higher than the two dilbit. Photolysis of APAHs occurred faster in summer than in winter; however, APAHs with different number of rings and degree of alkylation did not have obvious photolytic differences. These phenomena suggest that the photolytic similarities between dilbits and conventional crude oil depend on their similar chemical structure of petroleum hydrocarbons; their differences depend on the specific oil properties. The accumulated solar irradiation intensity and temperature are the main factors contributing to their photolytic differences for winter and summer exposed oils.

In the test samples, two dilbit (CLB and AWB) and a representative crude oil, aromatic hydrocarbons, followed by n-alkanes, were observed to be the fastest photo-oxidized compounds studied. The weathering resistant biomarkers, steranes and terpanes, were the least photo-oxidized. Results indicated that chemical structure of petroleum hydrocarbons was the main parameter affecting their photolysis behavior. Of the oils tested, the crude oil was the fastest photolyzed, followed by the two dilbit samples, suggesting that photolysis efficiency was dependent upon oil. The decreased photolysis efficiencies of petroleum hydrocarbons in winter demonstrated that temperature and/or radiation intensity were the other control factors affecting the photolysis of petroleum hydrocarbons. This study demonstrates that photo-oxidation is one of the important weathering processes for both conventional and non-conventional petroleum products, especially in the environments with intense solar radiation and high temperature. The purpose of comparing winter and summer solar exposure is to evaluate the importance of photo-oxidation process under specific environmental conditions. This study supplies scientific support for appropriate remediation technologies in the event of oil spill in the marine environment.

B.7 Zhou 2015

Zhou's research looked into how dilbit and CC reacted physically to agitation. Table summarizes the results of an 8-day weathering study (at 15°C.) (Zhou et al, 2015). When the tank had dilbit in the water and experienced wave activity, the dilbit migrated to the beach and did not disperse into the water column. When there was no wave activity the dilbit spread out over the surface of the water. During the experiment the dilbit did not adhere to the window or sides of the tank. As dilbit weathers, the density increases due to the evaporation of lighter more volatile components. The densest dilbit came from the beach; this is most likely because of more exposure to weathering. Table B-3 and Table B-4 compare physical properties of dilbit (weathered and fresh) against CC (weathered and fresh). The CC had a lower viscosity than the dilbit and both weathered oils had higher viscosities than the fresh oils (Table B-5). When the boiling point (bp) of the hydrocarbon increases, the loss percentage decreases showing a direct correlation between bp and total recoverable amount. The hydrocarbons with the lowest bp (<204°C) experienced the largest amount of mass loss. Table B-5 represents a scenario where more dilbit was collected than bp calculations predicted (percentage of sediment and water in oil was 46%). The reason for this difference is due to the high levels of adhesion to sediments and percentage of water in the dilbit. As the dilbit becomes more viscous, the rate of dispersion decreases, thus displaying the negative correlation between the two forces. Results from Zhou's laboratory experiments indicate that dilbit can stay afloat for ten days when there is no contact with sediments.

Table B-3. Summary of weathering tests in wave tank.

		Time Periods			
Oil	**Tank Location**	**Days 0–2: High Energy**	**Days 2–4: Still**	**Days 4–6: High Energy**	**Days 6–8: Still**
Cold Lake Dilbit	Water	*Most oil floating at beach*	*Thick layer of oil covering water surface*	*Most oil floating at beach*	*Thick layer of oil covering water surface*
	Beach	*Some oil stuck at beach*	*Some oil stuck at beach*	*Some oil stuck at beach*	*Some oil stuck at beach*
	Window	*Oil line on window, otherwise clear*	*Oil line on window, otherwise clear*	*Oil line on window, otherwise clear*	*Oil line on window, otherwise clear*
MSB CC	Water	*Oil dispersed / Submerged (none floating)*	*Thick layer of bubbly oil covering water surface*	*Oil dispersed / Submerged (none floating)*	*No oil on surface; all oil submerged*
	Beach	*Some oil stuck to beach*	*Some oil stuck to beach*	*Oil removed from beach*	*No oil on beach*
	Window	*Window covered in oil*	*Top 25% of window cleared of oil*	*Window covered in oil*	*Top 25% of window cleared of oil*

Source: Zhou et al, 2015.

Table B-4. Densities (g/mL) of fresh and weathered oils.

Temperature (C°)	**Dilbit (Cold Lake)**			**CC (MSB)**	
	Fresh	**Floating**[a]	**Beached**[b]	**Fresh**	**Submerged**[c]
4	0.9365	0.9977		0.8331	0.8999
15	**0.9284**	**0.9935**		**0.8249**	**0.8929**
25	0.9247	0.9916		0.8212	0.8897
30	0.9213	0.9900	0.9940	0.8176	0.8865
35	0.9174	0.9873		0.8138	0.8833

[a] Contains 32vol%; [b] Contains 10vol%; [c] Contains 1vol%

Source: Zhou et al, 2015.

Table B-5. Contents of distillation fractions of dilbit before and after weathering and losses calculations.

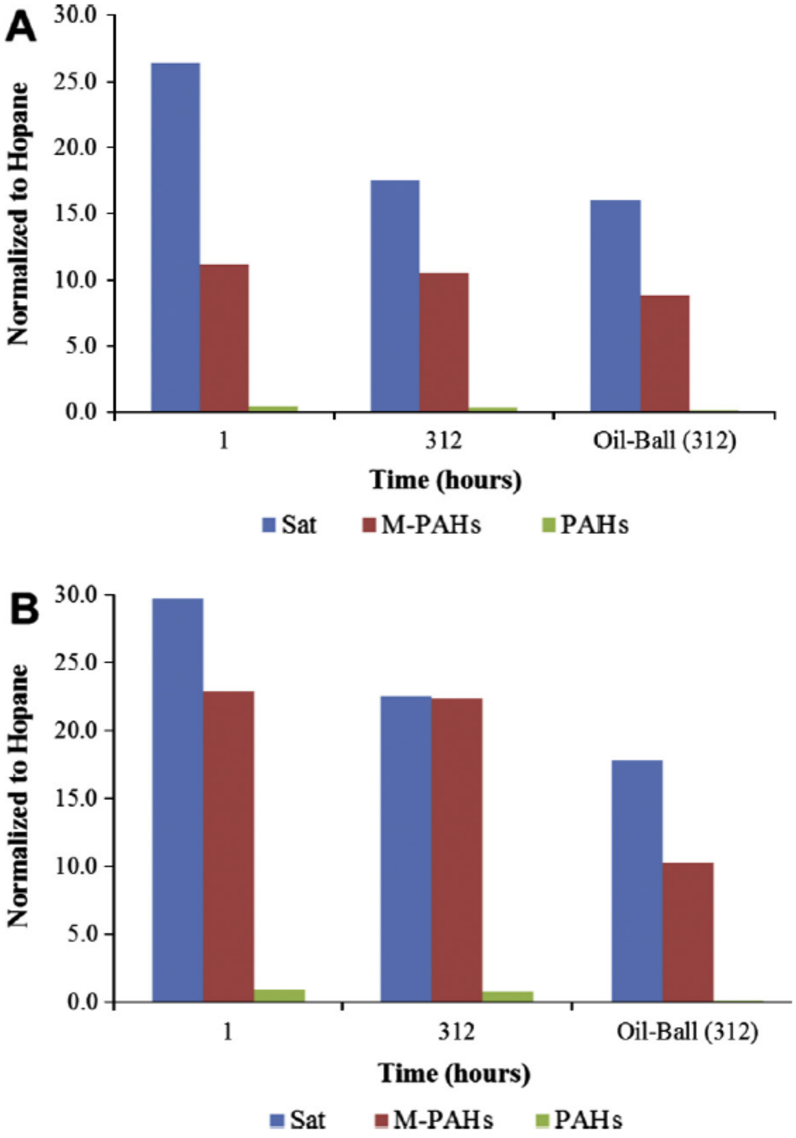
Boiling Point Fraction	**Content (wt%)**				**Oil Loss (g) per 100g Fresh**	**Wt % Loss of Fraction**
	Fresh	**Floating**	**Beach**	**Total Recovered Oil (TRO)***	**By BP**	
<204° C	13.3	2.2	1.2	2.2	11.3	85.3
204° to 343° C	14.9	15.6	11.4	15.6	1.2	8.3
343° to 524° C	26.0	29.8	23.4	29.7	0.0	0.0
>524° C	45.9	52.3	64.1	52.5	0.1	0.1

Source: Zhou et al, 2015.

B.8 King 2014

The flume tank study by King et al. investigated the environmental condition under which AWB and CLB dilbit would sink following a spill in marine environment. A weathering study was conducted in a 13-day (312 hours) experiment, using salt water and natural conditions (i.e., waves, currents, sunlight, wind, and salinity). The salt water was filtered to remove particles greater than 5µm. Four rings full of AWB and CLB, two each, were placed in the tank. Samples of each type of oil were collected at different times for the duration of the experiment. The duplicate oil containment ring was left untouched for mass balance calculations, which was estimated as ~15%–18% of the starting dilbit product when weathered under natural conditions. The conditions reported for this study were an average wind speed of ~9.0 km/h and rainfall totaling 56. 6mm (King et al., 2014).

Droplet detachment from AWB was observed on day 6, which was sufficient for sinking. AWB was dense (> 1.0 kg/m^3) forming oil-balls. After day 7, sinking was observed. An increase in density was also observed in CLB but AWB showed a faster rate when compared to CLB, this is due to the concentration of the chemical composition (alkylated PAHs). CLB has an increase concentration of alkylated PAHs, which slowly degrades (Figure B-8) (King et al., 2014). The presence of higher concentration of alkylated PAHs compared with alkanes and PAHs identified in AWB and CLB may be indications of the sinking.



Source: King et al., 2014.

Figure B-8. Chemical composition of oil samples collected for AWB (A) and CLB (B) at 1 h, 312 h and oil-ball (312 h).

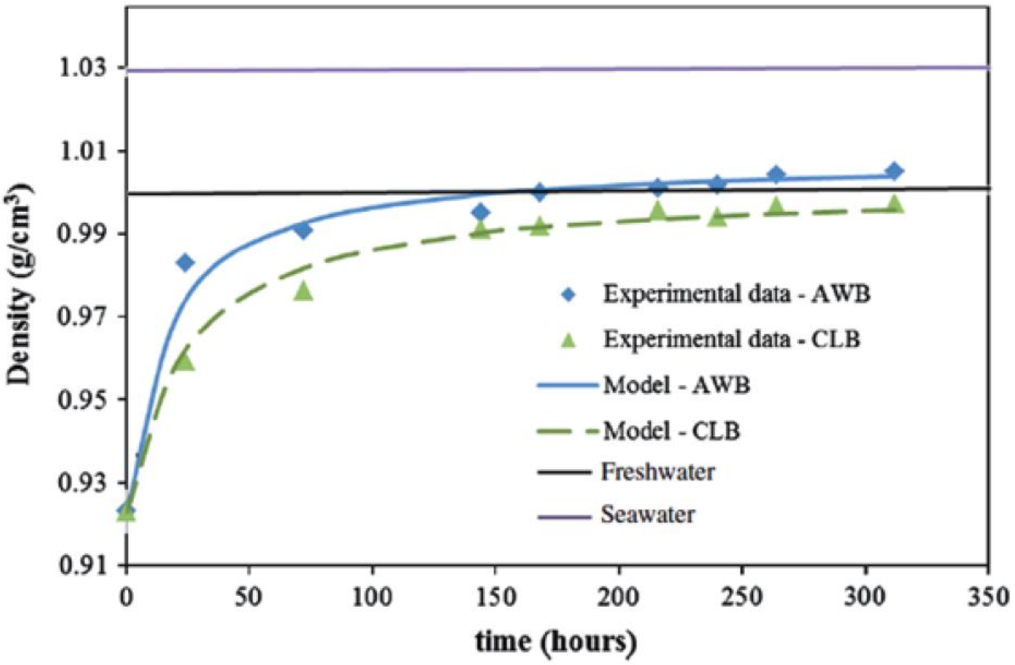
This study demonstrated that dilbit product can sink in the presence of natural weathering conditions without suspended particles with a low energy environment in salt water. In addition, chemical composition of the dilbit products may influence its behavior, which includes sinking.

B.9 Environmental Potential Agency (EPA) 2013 Studies

The EPA conducted a study in 2013 that examined short-term biodegradation using the dilbit from the Kalamazoo River spill; at the time of the study the Kalamazoo River spill occurred 19-20 months prior (EPA, 2013). Over a period of 28 days the dilbit (blends included CLB and WCS) was exposed to an aerobic environment and various inorganic nutrients. Twenty five percent of the hydrocarbons degraded over the 28 days; however, most biodegradation happened in the first 14 days (Figure B-9). Settling rates for the two dilbit blends were measured to be about 2 mm/s.

The largest spill of dilbit into freshwater happened at the Kalamazoo River located in Marshall, Michigan. The spill included both Cold Lake Blend (CLB) and Western Canadian Select (WCS) in dilbit mixtures. There have been difficulties in isolating the exact physical properties that determined the fate of both CLB and WCS. Responders from Environmental Protection Agency (EPA), National Oceanic and Atmospheric Administration (NOAA), and the National Transportation Safety Board (NTSB) reported that the oil was a combination of floating, submerged, and sunken dilbit in the river system (National Transportation Safety Board (NTSB), 2010).

The responders stated that there were masses of oil moving through the water columns, as well as sunken dilbit that rested at the bottom of the river (J. Winter, personal communication, 2012). Factors that could impact the behavior of the dilbit include: floods, strong turbidity, the velocity of the river, density of dilbit, and weathering time period (NTSB, 2010).



Source: National Academies of Sciences, Engineering, and Medicine, 2016.

Figure B-9. Observed increases in density for two dilbit.

B.10 Government of Canada 2013 Studies

Emergencies Science and Technology of Environment Canada conducted a mesoscale studies on the effects of weathering (evaporation and photo-oxidation) and buoyancy of the dilbit product. The two types of dilbit used are AWB and CLB; the selection was due to the transportation increase. An intermediate fuel oil (IFO 180) and a medium crude oil was used for comparison (Government of Canada, 2013).

A rotary evaporation was used for environmental weathering with a speed of 135 revolutions per minute (rpm) and air flow of 13L/min. Each oil sample held at 80°C and each sample had three weathered fractions

(W1, W2 and W3) with a weathering period of 48 hours on an open water exposure. An additional weathering fraction (W2) was prepared for 96 hours. The measurement temperatures were between 0ºC and 15ºC and the working temperature was selected as 15ºC. The factors considered in this study simulates natural environment. These factors are high mixing energy, high sediment load, extended evaporation, and photo-oxidation. This was simulated for 120 hours and resulted in a change of surface temperature. Diatomaceous earth (DE) and mineral fines (kaolin) were added to compare with sediment (Government of Canada 2013). In the event of a spill, the presence of suspended particles and bottom sediment will impact the behavior of the dilbit.

The physical characteristics (density, viscosity, and surface tension) (Table B-6 and Table B-7) of weathered AWB and CLB were affected in the water column (Table B-6 and Table B-7). The viscosity of weathered AWB and CLB was observed to increased, when compared to the starting oil. The density for AWB dilbit increased with evaporation, while temperature decreased with oil density (Government of Canada, 2013).

Table B-6. Physical properties of AWB.

		Degree of Evaporation (Mass Loss w/w%)				
		Fresh (0%)	**W1 (8.5%)**	**W2 (16.9%)**	**W3 (25.3%)**	**W4 (26.5%)**
Sulphur Content (% w/w)		3.0	4.1	4.5	4.9	4.8
Water Content (% w/w)		1.5	0.9	0.2	0.0	0.0
Flash Point (°C)		< -5	< -5	29	159	173
Pour Point (°C)		< -25	< -25	-6	24	33
Density (g/mL)	0°C	0.9399	0.9646	0.9949	1.0214	1.0211
	15°C	0.9253	0.9531	0.9846	1.0127	1.014
	20°C	0.9148	0.9547*			
API Gravity		20.9	16.6	12.0	8.2	8.0
Dynamic Viscosity	0°C	1.30E+03	9.82E+03	2.04E+05	9.35E+07	>1.00E+08
(mPa•s)	15°C	3.47E+02	1.72E+03	2.97E+04	2.52E+05	7.91E+06
	40°C	59.8	348*			
Emulsion Formation	Stability Class	Entrained	Entrained	Entrained	Entrained	DNF
Tendency and Stability	Complex Modulus (Pa)	4.46	8.97	4.67	1.26E+04	N/A
	Water Content (%w/w)	40	35	33	6	N/A
Surface Tension	0°C	31.2	31.9	NM	NM	NM
(Air/Oil, mN/m)	15°C	30.2	31.1	31.2	NM	NM
	20°C	27.5				
Interfacial Tension	0°C	24.8	NM	NM	NM	NM
(Oil/Water, mN/m)	15°C	24.2	28.0	NM	NM	NM
Interfacial Tension	0°C	25.0	NM	NM	NM	NM
(Oil/33‰ Brine, mN/m)	15°C	23.8	26.0	NM	NM	NM

NM – Not Measurable, too viscous;
DNF – Did not Form, too viscous;
N/A – Not applicable;
*Measured at 8.8% evaporated via sparging.
Source: Government of Canada, 2013.

Table B-7. Physical properties of CLB.

		Fresh (0%)	**W1 (8.5%)**	**W2 (16.9%)**	**W3 (25.3%)**	**W4 (26.5%)**
Sulphur Content (% w/w)		3.7	4	4.2	4.5	4.6
Water Content (% w/w)		0.6	0.2	0	0	0
Flash Point (°C)		< -5	-1	66	155	169
Pour Point (°C)		< -25	< -25	-12	21	27
Density (g/mL)	0°C	0.9376	0.9665	0.9909	1.013	1.0176
	15°C	0.9249	0.9537	0.9816	1.0034	1.0085
	20°C	0.9216	0.9471*			
API Gravity		21	16.5	12.5	9.5	8.8
Dynamic Viscosity	0°C	803	6.98E+03	1.29E+05	1.85E+07	5.71E+07
(mPa•s)	15°C	285	1.33E+03	1.83E+04	3.91E+05	3.21E+05
40°C		59	175*			
Emulsion Formation	Stability Class	Meso	Entrained	Entrained	Entrained	Entrained
Tendency and Stability	Complex Modulus (Pa)	90.5	64	267	3.60E+03	9.24E+03
	Water Content (%w/w)	72	46	38	9	10
Surface Tension	0°C	30	30.8	NM	NM	NM
(Air/Oil, mN/m)	15°C	28.8	30.1	30.2	NM	NM
	20°C	28				
Interfacial Tension	0°C	30.6	NM	NM	NM	NM
(Oil/Water, mN/m)	15°C	27.7	28.9	NM	NM	NM
Interfacial Tension	0°C	30.4	NM	NM	NM	NM
(Oil/33‰ Brine, mN/m)	15°C	26.3	27.6	NM	NM	NM

NM – Not Measurable, too viscous
*Measured at 8.8% evaporated via sparging.
Source: Government of Canada, 2013.

This study reported that the starting and weathered dilbit product (AWB and CLB) initially floated in the water column, but with the interaction of dilbit product with suspended particles under high-energy mixing environment contributed to its sinking in the marine environment.

B.11 SL Ross Environmental Research Limited 2013 Studies

This study was performed in a freshwater test tank at 15ºC to measure the weathering density of CLB dilbit for 11 days under constant wind and current conditions. Samples were taken for the duration of the experiment. There were two tests; in the presence and absence of ultraviolet (UV) light. CLB was observed to form an oil in water mixture with an initial density of 0.945 g/mL, the maximum density with UV light is 0.995 g/mL and the density in the absence of UV light reached 0.998g/mL. In the presence of UV light, oil droplets were formed which was a result of the breakdown of oil. This was not observed in the absence of UV light; rather the oil remained buoyant in the tank for the duration of the experiment.

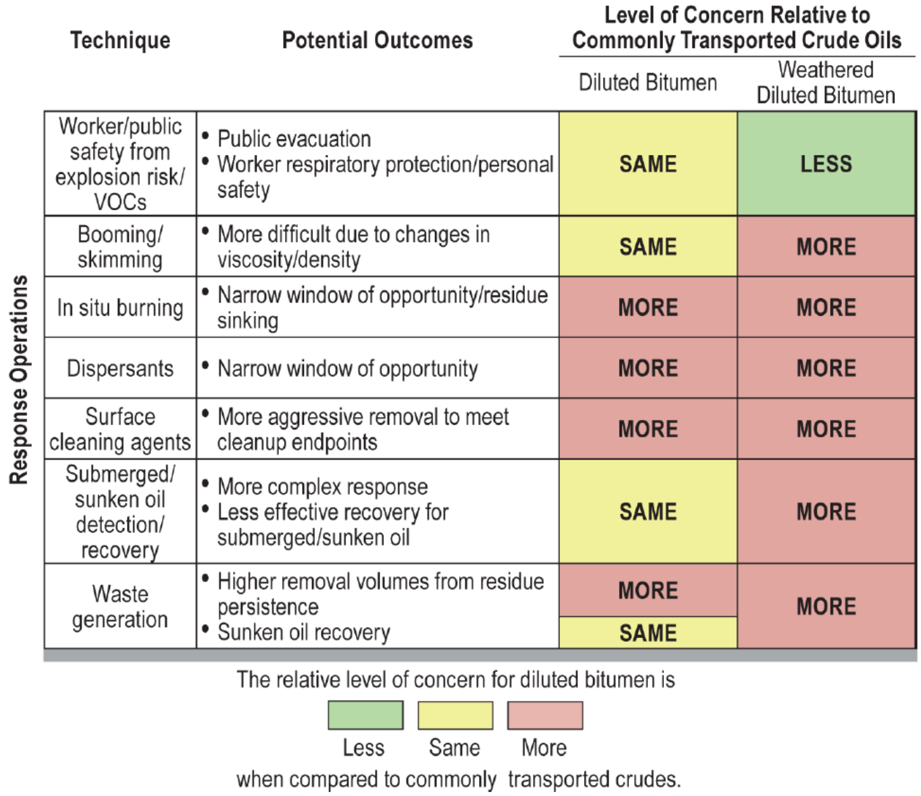
At the end of the experiment, oil was recovered both at the test tank wall and the surface of the water. Approximately 15% of oil was recovered on the tank wall, 10cm below the water level and the remaining in the water column. CLB dilbit was not observed to sink in this experiment. The oil measured at the end of the test was reported to be more than the oil at the beginning of this test, this was due to the viscosity of the oil (Dew et al., 2015).

While this study did a great job in reporting the changes in weathering density of CLB dilbit over time in the water column, it did not examine the influence of the dilbit product (CLB) and its interaction with sediment in the test tank. Past studies have reported the impact of sediment affecting the tendency to float or sink in the water column (Government of Canada, 2013; Hua et al., 2018).

B.12 Brown et al., 1992 Studies

The Brown study from 1992 looked at the efficiency of the types of diversion techniques used in the cleanup of spilled oil (Brown et al., 1992). Figure B-10 shows how fresh and weathered dilbit differ from CC with various clean up techniques. Bitumen spilled into river systems can be difficult to cleanup because current oil barriers do not collect weathered bitumen efficiently. In this experiment three types of dilbit were used:

- Dilbit emulsified with fresh water and weathered for 24 hours.
- Dilbit emulsified with salt water and weathered for 24 hours.
- Dilbit that was weathered for 24 hours on calm waters.



	Technique	Potential Outcomes	Level of Concern Relative to Commonly Transported Crude Oils	
			Diluted Bitumen	Weathered Diluted Bitumen
Response Operations	Worker/public safety from explosion risk/ VOCs	• Public evacuation • Worker respiratory protection/personal safety	SAME	LESS
	Booming/ skimming	• More difficult due to changes in viscosity/density	SAME	MORE
	In situ burning	• Narrow window of opportunity/residue sinking	MORE	MORE
	Dispersants	• Narrow window of opportunity	MORE	MORE
	Surface cleaning agents	• More aggressive removal to meet cleanup endpoints	MORE	MORE
	Submerged/ sunken oil detection/ recovery	• More complex response • Less effective recovery for submerged/sunken oil	SAME	MORE
	Waste generation	• Higher removal volumes from residue persistence	MORE	MORE
		• Sunken oil recovery	SAME	

The relative level of concern for diluted bitumen is

🟩 Less 🟨 Same 🟥 More

when compared to commonly transported crudes.

Source: National Academies of Sciences, Engineering, and Medicine, 2016.

Figure B-10. Clean up difficulty of dilbit compared to CC.

With each type of dilbit, three different types of diversion techniques were tested to divert the weathered dilbit: river boom, mesh net, and a bubble net. The river boom (3m x 15cm x 15cm) was a small conventional river boom with cylindrical Styrofoam floats attached to the ends with a 15cm deep skirt. Steel cables provided tension by running though the floats and along the bottom of the skirt. The nylon mesh weave net was a 5m long by 0.5m deep nylon braided net with holes that were 1mm by 1mm to allow water to flow through. The bubble barrier was created by running a 5m long hose across the bottom of the river and supplying 73 liters/second of air to the hose to create a uniformed curtain of fine bubbles (Brown et al., 1992).

The river boom failed to hold oil after the waters reached a velocity of 0.25 m/sec (Brown et al., 1992). Table B-8 shows the overall efficiency of the river boom on weathered dilbit in a river system. At higher velocities and densities the dilbit was only momentarily stopped by the boom (Brown et al., 1992).

Table B-8. River boom diversion.

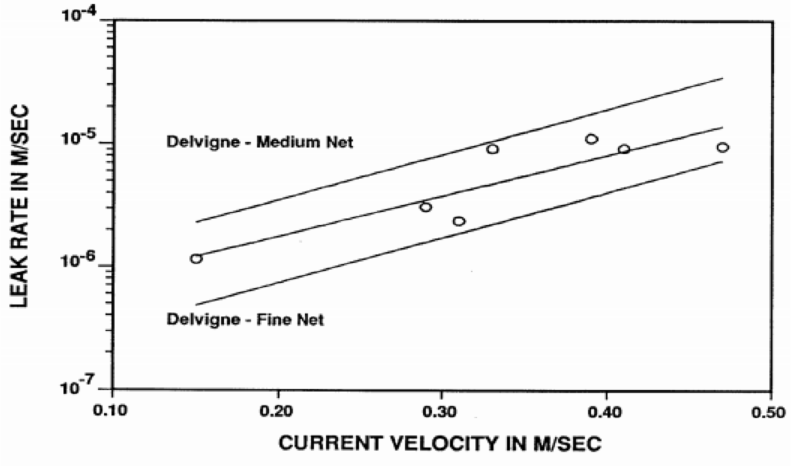
Velocity (m/sec)	**Material**	**Density**	**Boom Angle**	**Comments of Failure**
0.25	Emulsified with Fresh Water	0.989	90	Oil retained indefinitely
	Emulsified with Salt water	0.999	90	Oil retained indefinitely
	Weathered	0.983	90	Vortex shedding loss after 250 seconds
	Weathered	0.983	90	Oil retained – but end loss
0.29	Weathered	0.983	90	Vortex shedding loss after 150 seconds
	Weathered	0.983	90	No retention
	Emulsified with Salt water	0.999	90	Oil retained – but end loss
	Emulsified with Salt water	0.999	90	Oil retained
	Emulsified with Fresh Water	0.989	90	Oil retained – but end loss
0.33	Emulsified with Salt water	0.983	90	No retention
	Emulsified with Fresh Water	0.989	90	No retention
0.36	Weathered	0.983	45	Some diverted
	Weathered	0.978	45	All of sample diverted
0.42	Weathered	0.983	45	No diversion
	Weathered	0.978	45	All diverted
0.48	Weathered	0.978	45	Sample partially diverted

Source: Brown et al., 1992.

In each of the trapping experiments using the fine mesh net, results showed that the weathered and emulsified dilbit were trapped and adhered to the net. The mesh net trapped floating and submerged oil, but the retention depended on the velocity of the oil (Brown et al., 1992). The leak rate of the net represents the working efficiency of the mesh net. The lower the leak rate, the more the oil is restrained by the net. Figure demonstrates the theoretical (marked as solid lines) and observed (marked as circles) leak rate in comparison to the oil's velocity. The equation used to determine the theoretical leak rate is as follows (Delvigne, 1987):

$$L\left(\frac{m}{s}\right) = (.5)(10^{10})ASv^{-1.83}e^{8.5U}$$

Where: A = mesh area (m2)
S = ratio of mesh area to total area of the net
v = oil viscosity (cs, at shear rate = 1/s)
U = relative current velocity (m/s) perpendicular to the net
L = leak rate



Source: Brown et al., 1992.

Figure B-11. Observed vs computed fine mesh net leak rate.

As the velocity of the oil increased, the effectiveness of the mesh net decreased (Brown et al., 1992), and over time mesh nets can lose effectiveness (Morris, 1986). The leak rate for the net depends on the leak rate per area and total area of net covered by oil (Delvigne, 1987).

Experiments using the bubble barrier demonstrated that this technique was ineffective once the oil reached velocities greater than 0.15 m/sec. Table B-9 shows the results from the bubble barrier tests and how the bubble affected the velocity of floating dilbit product. The bubble barrier was not effective in trapping floating or submerged oil. During times of low velocities, the bubble net could divert some oil, but this was inconsistent (Brown et al., 1992).

Table B-9. Bubble barrier results.

Velocity m/sec)	**Sample Position**	**Barrier Behavior**
0.33	Bottom of water column	No diversion of sample
0.28	Mid- column	Barrier 60° to flow; oil not diverted
0.28	Bottom of water column	Barrier 30° in following tests/oil not diverted
0.28	Mid- column	Oil diverted twice
0.28	Bottom of water column	Oil diverted
0.24	Surface of water column	Oil broken but diverted
0.24	Bottom of water column	Oil diverted then surfaces and crosses barrier
0.24	Mid- column	Oil successfully diverted

Source: Brown et al., 1992.

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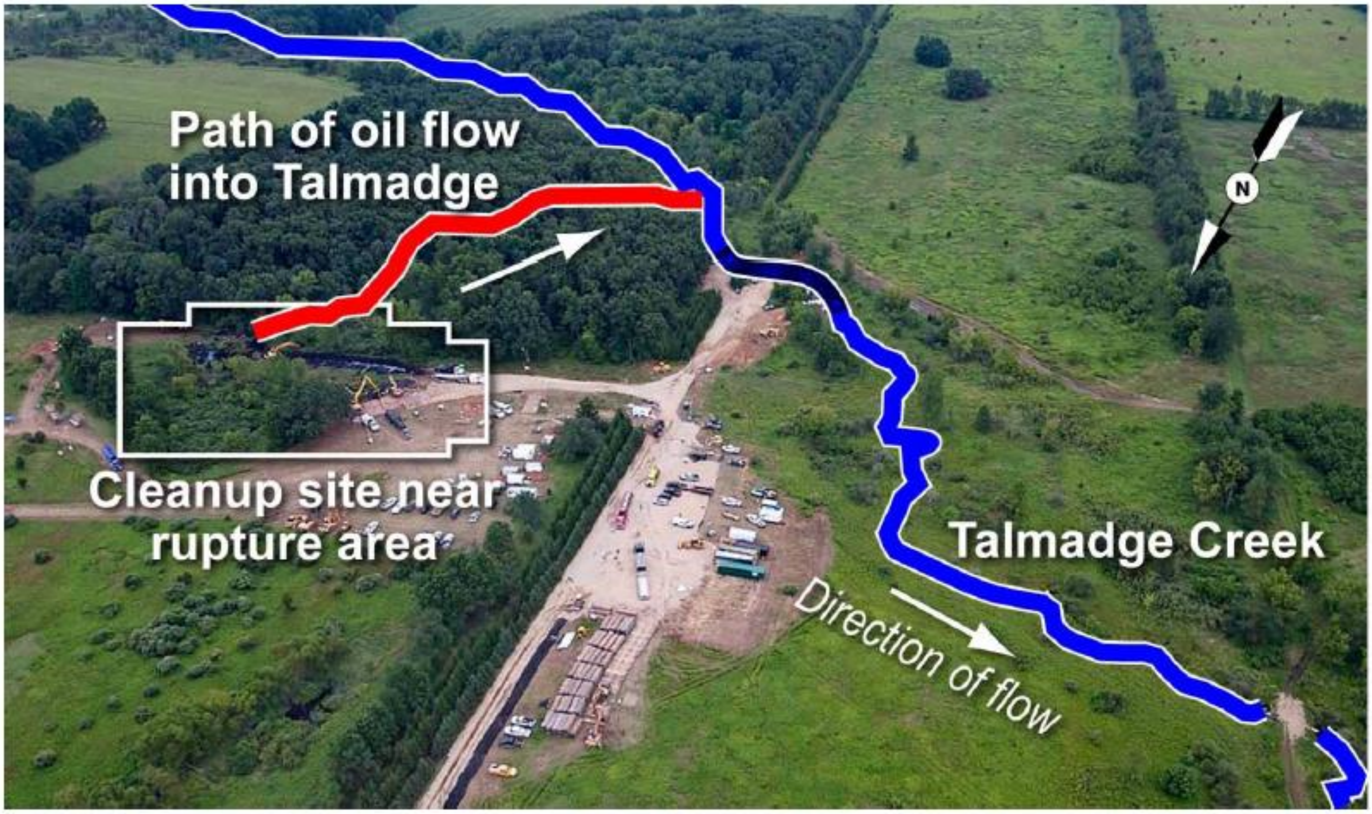
APPENDIX C. CASE STUDY

C.1 Marshall, Michigan (2010) and Sundre, Alberta (2012)

The 2010 Kalamazoo River in Marshall, Michigan experienced the largest inland bitumen spill in recorded U.S. history (Crosby et al., 2013). The spill was released from the Enbridge Line 6B pipeline into a wetland then flowed into Talmadge Creek and ultimately into the Kalamazoo River (Figure C-1) (Dollhopf et al., 2014). An estimated 20,082 barrels of dilbit were spilled after the pipeline ruptured, with an estimated 8,033 barrels leaked into the Talmadge Creek and Kalamazoo River (Crosby et al., 2013). The dilbit product contained the Cold Lake Blend and the Western Canadian Select Crude oil condensates mixture with a specific gravity of 0.65 to 0.75 (NTSB, 2010).



Source: NTSB, 2010.

Figure C-1. The view of the Kalamazoo spill incident located with the ruptured site on the left and dilbit flowing to the Talmadge Creek and eventually into the river.

In 2012, Sundre, Alberta experienced a leak from a pipeline that released 3,200 barrels of light sour crude into the Red Deer River system. Table C-1 provides a general comparison of the two spills.

Table C-1. General comparison of the spill at Marshall, Michigan and Sundre, Alberta.

	Marshall, Michigan (Kalamazoo River)	**Sundre, Alberta (Red Deer River)**
Date of Spill	July 25, 2010	June 7, 2012
Oil Type	Diluted Bitumen	Light Crude
Duration of breach	17.3 hours	2.5 hours
Spill Volume	3,800 m^3	463 m^3
Recovered oil from the surface	>85%	None
Distance travelled by oil	56 km	38 km
Spill location relative to rivers	Spilled on land, seeped through soil	Oil released under red river

Source: Zhou et al., 2015.

In both oil spills experts worried about Benzene, Toluene, Ethyl Benzene, and Xyenes (BTEX) exposure to the local population. During the spill, at the Red Deer River fumes were strong enough to force people to seek medical attention for several hours late Thursday (June 7th, 2012) night (Alberta Energy Regulator (AER), 2014). Residents in the surrounding area made phone calls to the local oil and gas operators reporting a strong rotten egg smell earlier that day. The source of the spill was identified 38 km away at Jackson Creek. On July 26th, 2010, EPA received a report about a leak in a 30-inch pipeline that had already released 20,071 barrels of oil into the Kalamazoo River. Voluntary evacuation notices were issued for 50 houses along the Kalamazoo River due to the strong odors (EPA, 2015). According to the Canadian government, the first nine days the levels of BTEX exceeded the safety levels in the local waters (Canadian Council of Ministries of the Environment (CCME), 2001). For the first ten days, Marshall, Michigan experienced lower concentrations of BTEX than the spill at Red Deer River; however, the BTEX concentrations persisted in the local waters of Marshall much longer than Red Deer (Zhou, 2015). Dilbit has lower concentrations of BTEX then light sour crude, but it does have higher concentrations of metals and sulfur. The BTEX levels were lower at Marshall, Michigan, but lasted at a heightened level for a month before returning to normal (EPA, 2015).

NTSB reported that cleanup efforts in Michigan included floating and sunken bitumen (NTSB, 2010). During the start of the clean-up there was visible oil slicks on the surface, but as the clean-up continued responders found masses of free floating oil moving inside the water column and some dilbit that had settled on the bottom (NTSB, 2010).