

Integrating physical, chemical and biological data to understand fate, behaviour and effects of diluted bitumen in coastal waters

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Production of bitumen from oil sands is predicted to rise over the next decade. Some of this increased production will be transported to coastal areas for export. While some product will be transported via rail, the majority is likely to be transported through pipelines as diluted bitumen. This unconventional oil product is a mixture of the highly viscous bitumen with differing amounts of diluent, which can include condensates, synthetic crudes or conventional crudes. As a mixture of products, the behaviour of diluted bitumen may differ from conventional heavy crude oils following a spill. This is of concern in Canada as the main transportation route for exporting diluted bitumen will go through the Salish Sea, home to endangered southern resident killer whales, economically important commercial and traditional fisheries including Pacific salmon, and millions of people. Knowing how diluted bitumen products will behave and their potential impacts if a spill occurs in these coastal waters is important in developing an effective response plan.

The Centre for Offshore Oil, Gas and Energy Research (COOGER) within Fisheries and Oceans Canada (DFO) has been carrying out research to characterize and predict the fate and behaviour of diluted bitumen products in marine environments over the last seven years. Using a combination of small-scale microcosms, medium-scale mesocosms, large-scale weathering and

wave tank studies as well as field experiments, we have collected a broad range of data providing insights into how diluted bitumen might behave following a spill.

Our research suggests that diluted bitumen will weather rapidly, with density and viscosity increasing significantly over the first 48 h. Low concentrations of hydrocarbons are typically detected in the water column, even in the presence of high energy breaking waves. The amount of weathering and water column hydrocarbons vary with season, but overall the microbial community shows a small response to the presence of diluted bitumen. Conventional spill response technologies may be used within the first 48 h of a spill, but extensive weathering will further limit their effectiveness. While the studies provide a more complete understanding of the fate and behaviour of diluted bitumen in coastal waters, there are important questions yet to be answered, some of which are presented here.

INTRODUCTION

Oil sand or tar sand deposits are found in northwestern Canada where they are mined to extract the bitumen. Bitumen is a semi-solid unconventional oil product produced by microbial

Table 1 Properties of raw bitumen from the Canadian oil sands measured at 15°C (Fingas, 2015).

Source	Density (g cm ³)	Viscosity (cSt.)
Athabasca	1.006 – 1.016	90,000 – 900,000
Cold Lake	0.977 – 1.006	100,000 – 450,000
Peace River	1.001 – 1.006	90,000 – 900,000

degradation of lighter oil products over time. Bitumen is dense and viscous with relatively more resins and asphaltenes compared to conventional

crude oils (Table 1). Within Canada, there are three main reservoirs of bitumen: Peace River, Cold Lake and the largest deposit, Athabasca. The source bitumen varies slightly among these reservoirs, but the majority of the variation in properties for diluted bitumen products is due to the diluents.

Because of its density and viscosity, bitumen must be diluted for transportation through pipelines by mixing with lighter hydrocarbons to create a product that meets the pipeline specifications; hence, diluted bitumen. The amount of diluent (~30%), which can vary seasonally, and the type of diluent gives each diluted bitumen product its specific physical and chemical properties (Table 2). Diluted bitumen includes products diluted with natural gas condensates (dilbit), synthetic crudes produced through partial processing of bitumen (synbit) or a mixture of condensates, synthetic crude and other conventional or unconventional oil. Western Canadian Select (WCS), is the benchmark product that sets the prices of diluted bitumen products.

Table 2 Properties of the fresh diluted bitumen products used by COOGER in experiments.

Property	AWB ^b	CLB ^c (winter)	CLB (summer)	Synbit	WCS
Diluent	Condensate	Condensate	Condensate	Synthetic Crude	Condensate + Synthetic crude + other petroleum products
Class	Heavy	Heavy	Heavy	Heavy	Heavy
API ^o	22.3	21.5	19.3	20.4	21.9
Density (g cm ⁻³) ^a	0.9189	0.9242	0.9375	0.9304	0.9214
Viscosity (cSt) ^a	244	237	575	205	211
% BTEX	1.96	0.89	0.59	0.56	0.87
% Saturates	14	13	12	20	20
% Aromatics	23	35	14	10	10
% Resins	46	38	60	57	52
% Asphaltenes	17	14	14	13	18
Σ Alkanes (μg g ⁻¹)	7,447	7,899	3,557	11,133	7,793
Σ PAHs (μg g ⁻¹)	217	302	312	326	352
Σ Alkylated PAHs (μg g ⁻¹)	2,611	5,228	4,791	3,349	4,904
^a Measured at 15°C ^b Access Western Blend ^c Cold Lake Blend					

With increasing interest in shipping diluted bitumen to overseas customers through ports in British Columbia (BC), concerns have been raised regarding the behaviour of diluted bitumen

in the event of a spill (reviewed in Johannessen et al., 2019). The Trans Mountain Pipeline is currently under construction and will twin an existing pipeline from Edmonton, AB, CA to a terminal in Burnaby, BC, CA where the diluted bitumen will be loaded onto tankers. The number of tankers is predicted to increase ~ five-fold due to the new pipeline. Tankers will transit through Burrard Inlet and Vancouver Harbour before entering the Strait of Georgia and the Strait of Juan de Fuca (the Salish Sea) and eventually the Pacific Ocean. The main concerns are the impacts of increased shipping vessel noise and potential diluted bitumen spills on the endemic and endangered southern resident killer whales, Pacific salmon populations and the overall ecology of the Salish Sea.

Most of what we know about the behaviour of diluted bitumen following a spill comes from the 2010 Kalamazoo River, MI, USA spill (Lee et al., 2015), in which 3,200 m³ of diluted bitumen leaked from the Enbridge Line 6B pipeline, flowed through a wetland and entered Talmadge Creek and eventually the Kalamazoo River during a period of high water flow. Due to the combination of high mixing energy and high sediment loading, much of the released diluted bitumen eventually sank after seven days. The ensuing clean-up was costly both in terms of money as well as impact to the habitat of the Kalamazoo River. How well the observed fate and behaviour of diluted bitumen in the Kalamazoo River predicts what could happen in the Salish Sea is an open question. In 2007, a small spill (< 250 m³) of diluted heavy synthetic crude oil occurred from a ruptured pipe near the Burnaby, BC transshipment facility (Lee et al., 2015). The oil flowed through the sewer system into Burrard Inlet. Most of the oil was recovered, but there was some oiling of intertidal habits. The response to this spill was immediate, with time to deploy booms prior to the oil reaching the inlet, the sea-state was calm and the volume was small. The same may not be the case in the event of a tanker spill.

Understanding the fate and behaviour of diluted bitumen in the marine environment has been a focus of study by COOGER over the last seven years. Research has been conducted on physical weathering, chemical changes and potential for natural attenuation (biodegradation) in marine waters to better predict what might happen in the event of a diluted bitumen spill in the Salish Sea or other coastal regions. This paper summarizes research in which COOGER has been involved, but does not present an exhaustive summary of all recent research on diluted bitumen.

EXPERIMENTAL APPROACHES

A range of different approaches were employed by COOGER to capture physical, chemical and biological processes that drive the fate and behaviour of diluted bitumen. In all cases, natural seawater has been used, with larger organisms ($> 5 \mu\text{m}$) removed through filtration for some experiments. Natural microbial communities, either from the west coast (British Columbia) or eastern Canada (Nova Scotia) have been used when measuring rates of biodegradation or characterizing microbial responses. The design and data collection for the experiments have varied depending on the specific questions being addressed, with scale, time frames and measured parameters changing accordingly.

Experiments have ranged from small-scale, with 100 mL seawater in baffle flasks, to larger-scale experiments using 215 L mesocosms, 1,300 L circular flume tank, 28,000 L wave tank or a 30,000 L flume tank. Wave tank studies tended to be of short duration, lasting for an hour, while weathering studies and mesocosm studies lasted for approximately two weeks. Biodegradation studies covered weeks to months (Table 3).

Depending on the experimental design and purpose, subsamples from experiments were collected and processed to measure physical, chemical and biological properties of the oil or seawater. Physical measurements of viscosity and density were taken to quantify the degree of

weathering from time series experiments. Chemical analysis of water collected from wave tank, weathering tank, mesocosm and microcosm experiments were analyzed to determine the concentrations of different chemicals including volatile compounds (BTEX – benzene, toluene, ethyl benzene and xylene), total petroleum hydrocarbons (TPH) or for specific analytes (*n*-alkanes, polycyclic aromatic hydrocarbons (PAHs) or alkylated homologs of PAHs). Biological studies focused on changes in the abundance or diversity of the microbial community including viruses, prokaryotes (Bacteria and Archaea), phytoplankton and microzooplankton.

Table 3 Summary of experimental goals and approaches used by COOGER to study the fate and behaviour of diluted bitumen products.

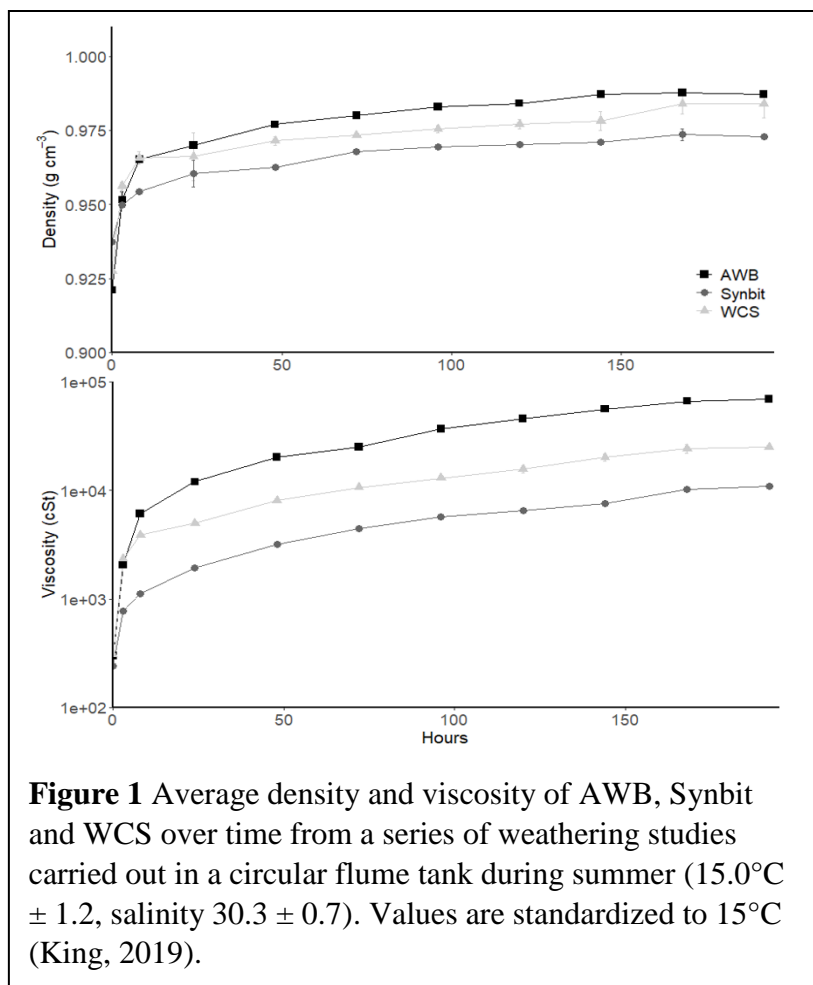
Approach	Experimental Goals	Length	References
Microcosm	<ul style="list-style-type: none"> • Measure biodegradation • Quantify seasonal effects on rates and community composition 	5-42 d	Ortmann et al., 2019 Schreiber et al., 2019
Mesocosm	<ul style="list-style-type: none"> • Quantify seasonal effects on distribution of hydrocarbons in water column and microbial responses 	14 d	Ortmann et al., 2020 Unpublished data
Circular Flume Tank	<ul style="list-style-type: none"> • Quantify changes in density and viscosity and water column BTEX • Measure impacts of slick thicknesses • Quantify effects of season and salinity 	8-14 d	King et al., 2017 King et al., 2019 King et al., 2019
Flume Tank	<ul style="list-style-type: none"> • Measure physical and chemical changes to a slick with natural weathering 	13 d	King et al., 2014
Wave Tank	<ul style="list-style-type: none"> • Measure natural dispersion and chemical dispersants with breaking waves including droplet size and hydrocarbon concentrations • Quantify OPA formation 	1-4 h	King et al., 2018 King et al., 2019 King et al., 2015 O'Laughlin et al., 2017
Model	<ul style="list-style-type: none"> • Predict droplet distribution with and without chemical dispersants • Predict likelihood of OPA formation • Trajectory modelling • Site specific predictions for sinking 		Zhao et al., 2014 Wu et al., 2016 Niu et al., 2017 Johannessen et al., 2019

PHYSICAL WEATHERING OF DILUTED BITUMENS

One of the main concerns with a diluted bitumen spill is that weathering will lead to sinking as the density of the diluted bitumen increases towards that of fresh bitumen (Table 1).

Density and viscosity are also important variables in determining an appropriate spill response. During weathering studies, rapid increases in density and viscosity have been measured for several diluted bitumen products. The rapid increases occur in the first 24 to 48 h, followed by a longer period of minimal change (King et al., 2019c; King et al., 2014; King et al., 2017b). Diluted bitumens, such as AWB, CLB and WCS, which contain condensates tend to weather faster and to a greater extent than products like Synbit or conventional crudes and heavy refined products (King et al., 2019d). Based on a number of studies, AWB has the potential to weather sufficiently to sink in fresh to brackish water, while Synbit is unlikely to become dense enough to sink, even in freshwater (Figure 1). These studies were carried out without additional sediment, which may play an important role in sinking as observed during the Kalamazoo spill (Lee et al., 2015).

Several factors have been tested to determine what might control the rate of weathering. Generally, higher air and water temperatures lead to faster increases in density, indicating a summer spill may have a shorter response window compared to a spill in spring or autumn (King et al., 2019c; King et al., 2019d). Warmer water temperatures may facilitate more dissolution of oil into the water column, and warmer air temperatures can also lead to more evaporation. Both scenarios can increase weathering in summer and have potential impacts on the biological effects (water column concentrations) and spill response (selection of response and risks to human health). One factor that appears to have little impact on the rate and extent of weathering is salinity. Weathering of diluted bitumen on saltwater was not significantly different from weathering on freshwater (King et al., 2019b; King et al., 2019d). However, the threshold for sinking in freshwater is lower than in higher density saltwater, so decreased salinity due to



freshwater input from rivers or heavy rain events could lead to sinking of weathered diluted bitumen. The weathered material may sink to the bottom if the density of the water allows, or it could become neutrally buoyant and suspended within the water column.

The remaining hydrocarbons stay as a slick on the surface of the water under low energy conditions.

Although the density of floating diluted bitumen increases as it weathers, it is often not enough to sink in coastal environments. Analysis of the materials remaining in the slick confirm the removal of saturates and aromatics resulting in a general increase in the proportion of resins and asphaltenes (King et al., 2019c). Weathering is not consistent, with slicks after 14 d ranging from having no remaining saturates to being almost indistinguishable from a fresh slick (Ortmann et al., 2020). This could be due to variable environmental conditions including differences in wind, air and water temperature, light or slick thickness. A more complete understanding of how each of these parameters will affect weathering of diluted bitumen will aid in predicting fate and behaviour following a spill.

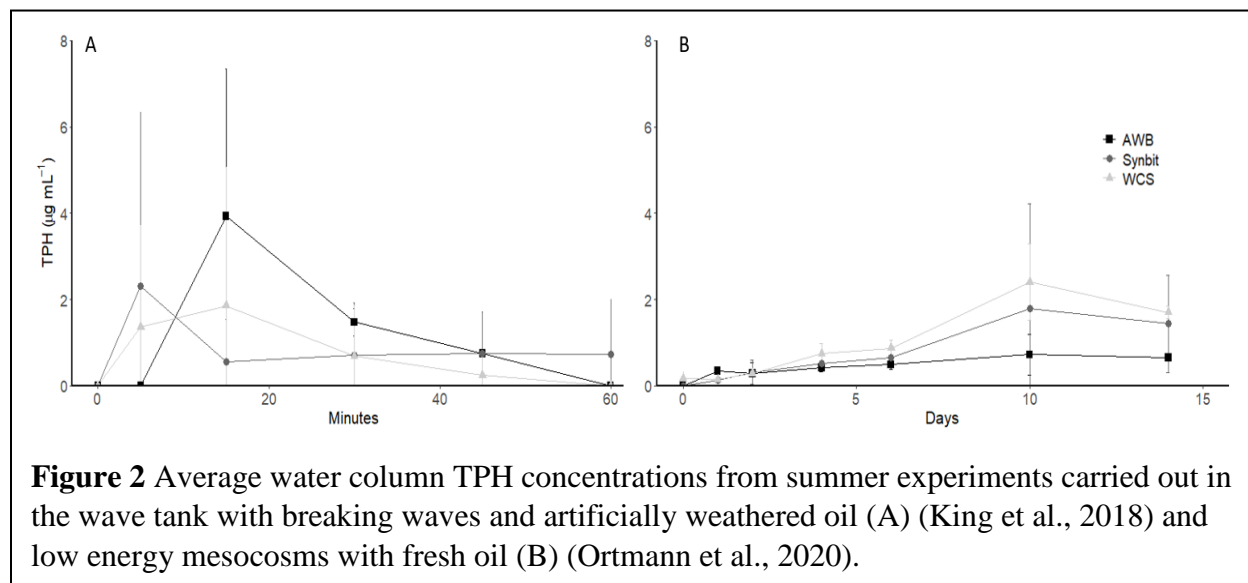
HYDROCARBONS IN THE WATER COLUMN

Hydrocarbons from a surface spill can enter the water column through dissolution and dispersion. The hydrocarbons found in diluted bitumen range in their water solubility, which changes as a function of temperature and salinity, affecting the amount of oil that dissolves into the water column. Dispersion of droplets due to wave action varies depending on the mixing energy and degree of weathering, but may also vary with the type of diluted bitumen. Regardless of the mechanisms, once oil enters the water column, it can interact with organisms as well as organic and inorganic particles.

Most quantification of hydrocarbons in the water is done without filtering and thus represents both the dissolved and dispersed fractions of the oil. Low energy environments result in low hydrocarbon concentrations in the water column. Only 2-4% of the BTEX in AWB, WCS and Synbit were found to enter the water column in a series of experiments (King et al., 2019a) (Ortmann et al., 2020). This is higher than for Heidrun, a crude oil, where only 0.3% of the BTEX was found to enter the water column (King et al., 2019a). The amount of BTEX entering the water column varied among seasons, with higher peak concentrations and longer peaks during cooler weather and more rapid increases and decreases in warmer weather. Higher water column concentrations in cooler weather is likely due to reduced evaporation of volatile compounds. Diluted bitumen products containing condensates resulted in higher water column BTEX concentrations, although absolute concentrations were low ($2-110 \mu\text{g L}^{-1}$) relative to concentrations known to cause harm to organisms ($> 500 \mu\text{g L}^{-1}$) (Barron et al., 2018).

Across a range of diluted bitumen products, water column hydrocarbon concentrations were consistently low, regardless of mixing energy. Essentially no dispersion was measured in wave tank experiments using low energy, non-breaking waves with artificially weathered diluted

bitumen. To weather products, fresh oils were bubbled with air or nitrogen for 24 – 48 h resulting in ~7% loss of mass (King et al., 2017a). Weathered CLB resulted in maximum TPH concentrations of 0.8 – 1.2 mg L⁻¹, with slightly higher concentrations in summer compared to spring (King et al., 2015). Experiments using weathered Synbit, AWB and WCS in the wave tank with high energy, breaking waves found slightly higher, but variable, maximum TPH concentrations (Figure 2A) (King et al., 2018). In mesocosm experiments with low-energy mixing over 14 d and no dilution, TPH concentrations increased gradually to a peak of 1 mg L⁻¹ in enclosures with fresh AWB in all seasons and Synbit and WCS in spring and autumn (Ortmann et al., 2020). In enclosures with fresh Synbit and WCS in summer, TPH concentrations peaked at 2 mg L⁻¹ after 10 d (Figure 2B). Visible oil droplets were observed on filters used to process water from those enclosures indicating increased dispersion had occurred relative to other enclosures.



Few studies have looked at concentrations of specific PAHs in the water column. In a series of mesocosm experiments, naphthalene and its alkylated homologs were found to have the highest concentrations in the water column, regardless of the type of diluted bitumen spilled or

the season in which the experiment was conducted (Ortmann et al., 2020). Absolute concentrations of PAHs and alkylated PAHs varied among the diluted bitumens, with the highest concentrations associated with WCS, a diluted bitumen containing a wide range of different diluents (Table 2). PAHs and alkylated PAHs may be derived from both the diluent and the bitumen. As was observed for TPH, concentrations of PAHs and alkylated PAHs ($0-8 \mu\text{g L}^{-1}$) were at the lower end of concentrations shown to have biological effects ($> 6 \mu\text{g L}^{-1}$ for chronic effects and $> 16 \mu\text{g L}^{-1}$ for acute effects) (Barron et al., 2018). Under natural conditions where dilution would occur, these concentrations would likely be even lower.

Dispersion of diluted bitumen by breaking waves results in low concentrations of oil in the water column, but produces large droplets. Large droplets tend to resurface and may coalesce rather than staying in the water column. Natural dispersion by breaking waves resulted in a small number of droplets $> 100 \mu\text{m}$, with many $> 300 \mu\text{m}$ for four different weathered diluted bitumen products (King et al., 2018; King et al., 2015). Modeling using the VDROD model suggests that droplets larger than $500 \mu\text{m}$ may occur; however, the instruments used in the wave tank to measure droplets cannot detect these larger particles (Zhao et al., 2014). Testing of natural dispersion of weathered Synbit in fresh and brackish water did not identify any effects of salinity (King et al., 2019d), suggesting that natural dispersion will be low for all water bodies in the absence of very high mixing energy and that much of the dispersed oil may be expected to resurface due to the buoyancy of large droplets.

In coastal marine environments, there can be a large number of suspended particles in the water column, but the concentrations will vary significantly due to location and season (Johannessen et al., 2019). These particles include organic material, microorganisms and inorganic particles. Interactions of oil droplets with inorganic particles are of particular interest

because these particles tend to have high densities and may contribute to sinking of oil. The formation of oil mineral aggregates (OMA, or oil particle aggregates, OPA) are thought to have contributed to the rapid sinking of oil during the diluted bitumen spill in the Kalamazoo River (Lee et al., 2015). Modelling suggests that droplet size, sediment composition (size) and concentration, mixing energy and mixing time are important in determining OPA formation (Wu et al., 2016). Temperature and salinity are also important as they determine the density of seawater and ultimately whether any single OPA will sink and to what depth. In lab experiments, with high mixing energy and relatively high concentrations of fine sediment (10 and 50 mg L⁻¹), OPA formation was observed with weathered CLB and AWB (O'Laughlin et al., 2017). Larger OPA with higher settling velocities were formed at the higher sediment concentrations. On a larger scale, wave tank experiments failed to show significant OPA formation (O'Laughlin et al., 2017). Wave tank experiments used shorter mixing times, 2 h vs 16 h, and lower mixing energy with sediment concentrations (15-20 mg L⁻¹) similar to the lower concentrations used in the lab experiments. Higher organic matter in the wave tank experiments compared to the lab experiments may also have affected OPA formation. Together these experiments indicate that, while OPA formation in coastal environments is possible, the likelihood of formation is strongly dependant on local sediment loads and mixing energy. Once formed, sinking of OPA will depend on the local seawater density profile where the spill occurs (Johannessen et al., 2019).

MICROBIAL COMMUNITY RESPONSES

Regardless of the response activities that may be undertaken following an oil spill, natural attenuation will occur as hydrocarbon degrading microorganisms increase in abundance in response to oil. Generally, *n*-alkanes are biodegraded faster than PAHs. In a 13-day flume tank experiment, degradation rates for *n*-alkanes and PAHs from AWB and CLB could be calculated

(Figure 3), although rates were low (King et al., 2014). Degradation rates for alkylated PAHs could not be calculated. In microcosm experiments with the addition of nitrogen and phosphorous, degradation of *n*-alkanes was determined to be 10-fold higher for AWB compared to the flume tank experiment (Figure 3); however, no degradation was observed for PAHs or alkylated PAHs (Ortmann et al., 2019). Over 28 d in a series of microcosms using weathered AWB or CLB supplemented with inorganic nutrients, >84% of the *n*-alkanes were removed in both summer and winter experiments (Schreiber et al., 2019). Removal of PAHs was higher for 2-ring compounds and those with fewer alkyl groups, with differences due to season and type of diluted bitumen used, but the majority of the PAHs were still present after 28 d. *n*-alkanes and PAHs make up a relatively small proportion of the total hydrocarbons in diluted bitumen (Table 2), so removal of these compounds by microorganisms still leaves a significant amount of hydrocarbons in the environment, including alkylated PAHs, resins and asphaltenes.

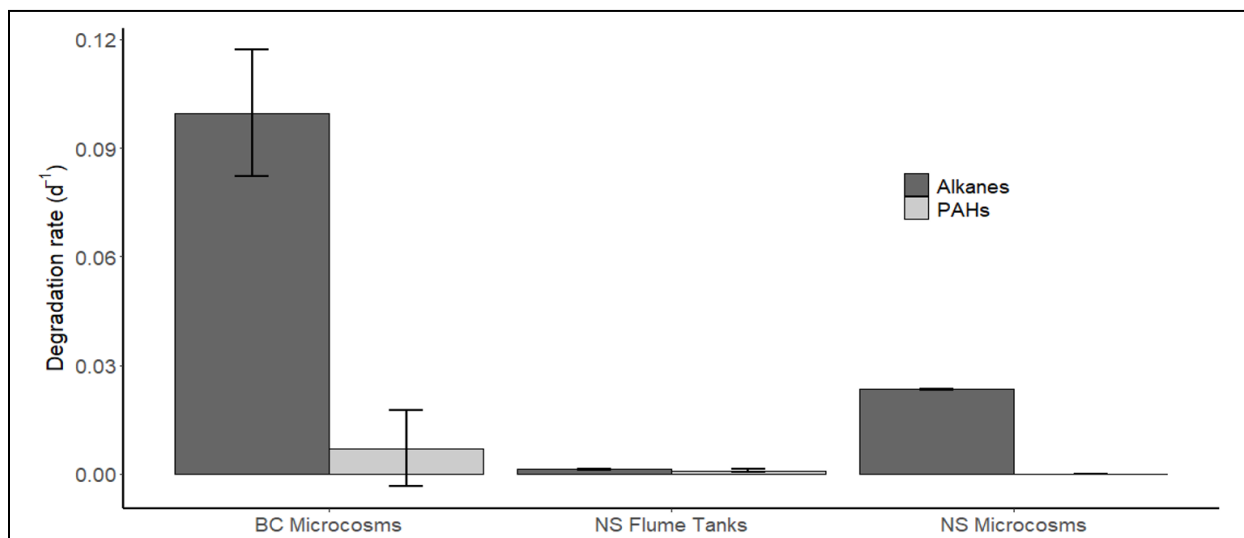


Figure 3 Comparison of degradation rates in three different experiments. BC Microcosms = AWB, CLB-winter and CLB-summer, 28 d incubations in summer, northern BC with Bushnell Haas broth (Schreiber et al., 2019). NS Flume Tank = AWB and CLB, 13 d weathering in summer, Bedford Basin, NS (King et al., 2014). NS Microcosms = AWB, 5 d incubation in winter, Bedford Basin, NS with phosphate and nitrate or ammonium (Ortmann et al., 2019).

While degradation rates show little differences among seasons, the microbial communities that respond to the presence of diluted bitumen are strongly driven by location and season. The initial community structure will drive the overall community response. In the Douglas Channel experiments, summer *n*-alkane degraders were different from those detected in winter (Schreiber et al., 2019). Some similarities in the communities that responded in winter were observed in experiments conducted on opposite coasts, with Colwelliaceae and Rhodobacteriaceae detected in both (Ortmann et al., 2019; Schreiber et al., 2019). Within experiments conducted in different seasons in Nova Scotia, hydrocarbon degraders were found to respond positively to diluted bitumen in spring, summer and autumn, but the specific organism varied with season (Unpublished data).

SPILL RESPONSE

The rapid increases in density and viscosity of the floating material can have significant impacts on the choice and effectiveness of response measures (Kin et al., 2017). As long as the diluted bitumen remains on the surface, traditional oil spill response measures remain an option. In the Salish Sea, response organizations are close by with the materials necessary to respond to a spill within hours to a few days (wcmrc.com). This time frame is well within the period when diluted bitumen would be expected to remain on the surface. For all of the experiments discussed above, the earliest that naturally dispersed oil was observed was 7 d post-spill, after a large rain event (King et al., 2014). Without rain, small droplets were observed after 10 d (Ortmann et al., 2020), but in all studies, the majority of the spilled product remained floating.

All response options have limitations and need to be considered based on spill-specific conditions (reviewed in Lee et al., 2015). The most common response measure is booming and skimming to remove the oil from the water's surface. Booming requires the oil to be floating, but

also calm sea states for the booms to be effective. Skimming is affected by the viscosity of the oil, as highly viscous products cannot easily be recovered. A second response measure is dispersion, either using chemicals or the application of mineral fines. Both of these processes are also dependant on the viscosity of the oil and the sea state, although dispersion requires a higher sea state to effectively mix the material with the oil compared to booming and skimming.

The rapid change in viscosity of diluted bitumen following a spill indicates that there is a short window for effective recovery of material by skimming. Most skimmers require the oil to be able to flow, but after only 48 h, AWB can reach a viscosity of 100,000 cSt, while Synbit may only reach 10,000 cSt (King et al., 2019c). This suggests that different diluted bitumens may allow for different response options.

High viscosity also reduces the effectiveness of chemical dispersants. Several experiments, including lab-scale and the wave tank have measured the effectiveness of chemical dispersants, including COREXIT®EC9500A and SPC 1000. Using weathered (~7% loss w/w) diluted bitumen (AWB, CLB, Synbit, WCS) in wave tank experiments in spring and summer, chemical dispersants were found to significantly decrease droplet size and increase TPH concentrations (King et al., 2018; King et al., 2017b; King et al., 2015). Droplet sizes decreased from > 100 µm with breaking waves to 2.5 -70 µm with breaking waves and COREXIT®EC9500A. At the same time, TPH concentrations increased from 1 ppm under natural dispersion to 10-15 ppm. Dispersant effectiveness varied from 30 – 60%, depending on the season and type of diluted bitumen. This is still lower than the dispersant effectiveness of 70 – 75% for Heidrun, a medium crude (King et al., 2018). Based on natural weathering rates and changes in viscosity, King *et al.* (2017b) suggest that for condensate-type diluted bitumen products (e.g. AWB and CLB), chemical dispersants may only be 50 – 60% effective if applied

within 3 h of a spill. Even in the Salish Sea where the response would likely to be rapid, this is an unlikely scenario. For Synbit, chemical dispersants may be 90% effective if applied within the first 24 h.

The rapid weathering of diluted bitumens, particularly those diluted with condensate, suggests that novel response measures are needed. The oil is likely to stay on the surface, simplifying tracking and monitoring, but further development of skimming or retrieval systems for highly viscous products may be needed. *In situ* burning may be an option in some locations for some diluted bitumen products (King et al., 2017b), but the high population density around the Salish Sea likely precludes use where a ship-based diluted bitumen spill may occur.

SUMMARY AND FUTURE DIRECTIONS

Over the past several years, COOGER has used a range of different approaches to better understand and predict the fate and behaviour of diluted bitumen if spilled in coastal waters. The research has highlighted the very rapid weathering for diluted bitumens, with significant changes in viscosity and density when the diluent is condensate. As fast as the products weather, they are unlikely to reach densities that will cause sinking in brackish to saline water. Most are unlikely to sink in freshwater without extensive weathering over weeks. Interactions with sediment can lead to the formation of OPA, but only under conditions where sediment loading and mixing energy are both high. This could be in areas of significant freshwater inflow (river mouths, deltas), where lower water density along with higher sediment loading may contribute to sinking. Regardless of whether the diluted bitumen sinks or floats, some of the hydrocarbons will be available to the microbial community for biodegradation. This process will quickly remove the *n*-alkanes and some of the PAHs, but larger PAHs, alkylated PAHs, resins and asphaltenes will persist.

Using much of the data on diluted bitumen fate and behaviour generated by COOGER, along with environmental data from the Salish Sea and northern British Columbia, Johannessen *et al.* (2019) evaluated the likelihood that diluted bitumen would sink following a spill. The analysis included oil weathering, density, OPA formation, site specific details about suspended particle concentrations, water densities and water residence times. The authors concluded that Synbit would be less likely to sink than AWB or CLB, but that any significant sinking would be unlikely. Low residence times, low sediment loads and relatively low mixing energy would preclude formation of OPA in most cases. They did suggest that potential sinking or stranding was highest along freshwater river banks and the shallow banks at the mouth of the Fraser River.

Stranding and contamination of shorelines was the main fate of diluted bitumen when stochastic models for the Salish Sea were applied to model possible oil spills (Niu *et al.*, 2017). Little of the diluted bitumen was predicted to enter the water column or reach the bottom sediments, although concentrations in both increased when chemical dispersant was added to the model. However, dispersants were modelled as if they were applied at the time of the spill, which is unlikely to happen, so these impacts would be reduced due to weathering of the diluted bitumen before dispersant is applied. Little research has been carried out on the best methods for removing diluted bitumen from shorelines. After weathering, stranded diluted bitumen will likely pose many of the same challenges as other persistent oils.

While we have learned a significant amount about the fate and behaviour of diluted bitumen in marine environments, there are still some outstanding areas for future study. None of the studies have specifically addressed the impact of photo-oxidation on weathering of diluted bitumen. While some studies have included natural sunlight, the specific degradation products and pathways remain unknown. Some of the studies found that salinity did not influence physical

and chemical changes in diluted bitumen, but the potential interactions with the biological community were not studied. Recent experiments at the Experimental Lakes Area in Ontario will help to address this knowledge gap (Cederwall et al., 2020; Stoyanovich et al., 2019).

As well as developing novel approaches to respond to and clean up a diluted bitumen spill, further research into the effects of its persistent components would be helpful. Another important area of study would be to understand the trade-offs between continued clean-up of hard to remove weathered diluted bitumen, and simply leaving the material in the environment. For example, if bitumen does sink into the sediments, it would be important to understand how it changes, and how it impacts the environment over time, and contrast that with the impacts of extensive clean up activities. Defining an end point to a response and understanding what ecosystem recovery looks like ecologically and economically is as important as predicting the fate and behaviour of diluted bitumen at the beginning of a spill.

REFERENCES

- Barron, M.G., Conmy, R.N., Holder, E.L., Meyer, P., Wilson, G.J., Principe, V.E., Willming, M.M., 2018. Toxicity of Cold Lake Blend and Western Canadian Select dilbits to standard aquatic test species. *Chemosphere* 191, 1-6. <https://doi.org/10.1016/j.chemosphere.2017.10.014>
- Cederwall, J., Black T.A., Blais, J.M., Hanson, M.L., Lollebone, B.P., Palace, V.P., Rodriguez-Gil, J.L., Greer, C.W., Maynard, C., Ortmann, A.C., Rooney, R.C., Orihel, D.M., 2020. Life under an oil slick: Response of a freshwater food web to simulated spills of diluted bitumen in field mesocosms. *Can J Fish Aquat Sci*, 99:1. <https://doi.org/10.1139/cjfas-2019-0224>
- Fingas, M., 2015. Review of the properties and behaviour of diluted bitumens, 38th AMOP Technical Seminar, Vancouver, British Columbia, pp. 470-494.
- Johannessen, S.C., Greer, C.W., Hannah, C.G., King, T.L., Lee, K., Pawlowicz, R., Wright, C.A., 2019. Fate of diluted bitumen spilled in the coastal waters of British Columbia, Canada. *Mar Pollut Bull*, 50:110691. <https://doi.org/10.1016/j.marpolbul.2019.110691>
- King T.L., 2019. Physical properties dynamics of oil sands products and their influence on spill response. PhD Thesis, <http://library2.smu.ca/handle/01/28226#.XjBzib5KiUI>

King, T., Mason, J., Thamer, P., Wohlgeschaffen, G., Lee, K., Clyburne, J., 2017a. Composition of bitumen blends relevant to ecological impacts and spill response, 40th AMOP Technical Seminar, Calgary, AB, pp. 463-475.

King, T., Robinson, B., Lee, K., Li, H., Boufadel, M., Clyburne, J., 2019a. Seasonal climatic factors influence on monocyclic aromatics rates of release and decay in water from surface spills of oil sands products, 42nd AMOP Technical Seminar, Halifax, NS, pp. 773-790.

King, T., Robinson, B., Ryan, S., Lee, K., Boufadel, M., Clyburne, J., 2018. Estimating the usefulness of chemical dispersant to treat surface spills of oil sands products. *J Mar Sci Eng* 6: 128. <https://doi.org/10.3390/jmse6040128>

King, T., Robinson, B., Toole, P., Clyburne, J., 2019b. Access Western Blend (dilbit) weathered on cold fresh and marine salt waters, 42nd AMOP Technical Seminar, Halifax, NS, pp. 847-858.

King, T., Toole, P., Robinson, B., Ryan, S., Lee, K., Boufadel, M., Li, H., Clyburne, J., 2019c. Influence of climatic parameters on changes in the density and viscosity of diluted bitumen after a spill. *J Environ Sci Poll Res* 5, 373-382. <https://doi.org/10.30799/jespr.176.19050305>

King, T.L., Robinson, B., Boufadel, M., Lee, K., 2014. Flume tank studies to elucidate the fate and behavior of diluted bitumen spilled at sea. *Mar Pollut Bull* 83, 32-37. <https://doi.org/10.1016/j.marpolbul.2014.04.042>

King, T.L., Robinson, B., Cui, F., Boufadel, M., Lee, K., Clyburne, J.A.C., 2017b. An oil spill decision matrix in response to surface spills of various bitumen blends. *Environ Sci-Proc Imp* 19, 928-938. <https://doi.org/10.1039/C7EM00118E>

King, T.L., Robinson, B., McIntyre, C., Toole, P., Ryan, S., Saleh, F., Boufadel, M.C., Lee, K., 2015. Fate of surface spills of Cold Lake Blend diluted bitumen treated with dispersant and mineral fines in a wave tank. *Environ Eng Sci* 32, 250-261. <https://doi.org/10.1089/ees.2014.0459>

King, T.L., Robinson, B., Ryan, S.A., Mason, J., Soper, G., Toole, P., Clyburne, J., 2019d. Physical and chemically enhanced dispersion of synthetic bitumen in fresh and brackish waters, 42nd AMOP Technical Seminar, Halifax, NS, pp. 859-869.

Lee, K., Boufadel, M.C., Chen, B., Foght, J., Hodson, P., Swanson, S., Venosa, A., 2015. Expert panel report on the behaviour and environmental impacts of crude oil released into aqueous environments. Royal Society of Canada, Ottawa, ON, Canada, p. 489.

Niu, H., Li, S., Li, P., King, T., Lee, K., 2017. Stochastic modeling of the fate and behaviors of an oil spill in the Salish Sea. *Int J Offshore Polar* 27, 337-345.

O'Laughlin, C.M., Law, B.A., Zions, V.S., King, T.L., Robinson, B., Wu, Y., 2017. Settling of dilbit-derived oil-mineral aggregates (OMAs) & transport parameters for oil spill modelling. *Mar Pollut Bull* 124, 292-302. <https://doi.org/10.1016/j.marpolbul.2017.07.042>

Ortmann, A.C., Cobanli, S.E., Wohlgeschaffen, G., MacDonald, J., Gladwell, A., Davis, A., Robinson, B., Mason, J., King, T.L., Measuring the fate of different diluted bitumen products in coastal surface waters. *Mar Pollut Bull*, 153:111003.

<https://doi.org/10.1016/j.marpolbul.2020.111003>

Ortmann, A.C., Cobanli, S.E., Wohlgeschaffen, G., Thamer, P., McIntyre, C., Mason, J., King, T.L., 2019. Inorganic nutrients have a significant, but minimal, impact on a coastal microbial community's response to fresh diluted bitumen. *Mar Pollut Bull* 139, 381-389.

<https://doi.org/10.1016/j.marpolbul.2019.01.012>

Schreiber, L., Fortin, N., Tremblay, J., Wassercheid, J., Elias, M., Mason, J., Sanschagrín, S., Cobanli, S., King, T., Lee, K., Greer, C.W., 2019. Potential for microbially mediated natural attenuation of diluted bitumen on the coast of British Columbia (Canada). *Appl Environ Microb* 85, e00086-00019. <https://doi.org/10.1128/AEM.00086-19>

Stoyanovich, S.S., Yang, Z., Hanson, M., Hollebhone, B.P., Orihel, D.M., Palace, V., Rodriguez-Gil, J.L., Faragher, R., Mirnaghi, F.S., Shah, K. and Blais, J.M., 2019. Simulating a spill of diluted bitumen: Environmental weathering and submergence in a model freshwater system. *Environ Toxicol Chem*, 38(12), pp.2621-2628. <https://doi.org/10.1002/etc.4600>

Wu, Y., Hanna, C.G., Law, B.A., King, T.L., Robinson, B., 2016. An estimate of the sinking rate of spilled diluted bitumen in sediment laden coastal waters, 39th AMOP Technical Seminar, Halifax, NS, pp. 331-347.

Zhao, L., Torlapati, J., King, T., Robinson, B., Boufadel, M.C., Lee, K., 2014. A numerical model to simulate the droplet formation process resulting from the release of diluted bitumen products in marine environment, International Oil Spill Conference, pp. 449-462.

<https://doi.org/10.7901/2169-3358-2014.1.449>